An Examination of Elastic Collision Dynamics in Strong Infrared Laser Fields

by

Daniel Robert Matusek

B.Sc. (Hon.), Queen's University Kingston (1994)

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctorate of Philosophy.

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submitted by

Daniel Robert Matusek, B.Sc. (Hon.), Queen's University Kingston (1994)

in partial fulfillment of the requirements

for the degree of Doctor of Philosophy

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Abstract

It is hypothesised that the dynamics of elastic collisions in the presence of a homogeneous, linearly polarised, infrared frequency laser will be altered significantly; this should lead to laser-induced dynamical effects which can be correlated with the changes induced in the collision potential. To test the hypotheses, the classical dynamics of binary collisions between atoms are examined under the conditions appropriate to a crossed molecular beam experiment. The Hamiltonian used to represent the laser-molecule interaction is based on the quasi-static approximation and assumes the laser is non-resonant with any electronic transitions; field terms of up to second order are included in the potential. The diatom + interaction potential is modelled by simple functions of the exchange-dispersion type which describe rare-gas dimers.

The classical collision dynamics of the rare-gas dimers HeAr and He₂ are examined both numerically and analytically using impulse approximation models over a large range of laser and collision parameters. Examination of system trajectories leads to the identification of four novel classes of collision, or collision mechanisms, which are brought about by three main features of the laser-diatom potential surface. These collision mechanisms are shown to give rise to characteristic, although not always unambiguous, behaviour in the classical deflection function. The characteristics of the deflection function can be traced through to specific features of the collision cross sections. Thus a qualitative link is established between the laser-induced changes to the potential energy surface and experimental observables (the cross sections) via the collision mechanisms.

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While I do not wish to brag, this thesis has taken over eight years to complete; so while it may have appeared to those around me to have been a task which I have only trifled with occasionally throughout that time, my interest in this work has been one which I can say, without any hint of exaggeration, was all-consuming. Yet I am not the only interested party in this endeavour; there have been many people who have influenced the course of my work and whose role should be acknowledged. I cannot do a adequate job of this of course as there have been many. To those I do not make mention of here: your contribution may not be noted herein but this does not diminish my appreciation.

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Chapter 1

Introductory Considerations

1.1 Molecular Dynamics and Lasers

Molecular Dynamics is a sub-discipline of physical chemistry devoted to the study of the molecular mechanisms of elementary physical and chemical processes [1]. Specifically, it deals with the relationship between the interaction potential of both intra- and intermolecular motions and the observed bulk properties of a system via statistical mechanics. Its historical development can be traced back to the kinetic theory of gases at the end of the nineteenth century, where the notion of intermolecular collisions being the underlying “cause” of observed properties of simple gases and liquids, was accepted [1, 2]. This concept has been generalised fruitfully to problems concerning the determination of reaction rates from first principles, energy disposal in reactive and non-reactive collisions and surface-molecule processes to name some examples [3–11]. Through the study of effects of features of the interaction potential on the motion of the constituent species in a chemical system, more knowledge is acquired for the purposes of both providing an explanation of existing concepts in chemistry and influencing the outcome of chemical events.

Over the last two decades, advances in laser technology have produced devices which attain much higher power per unit area than was possible initially. This means that, within a given volume, a very large amount of energy can be delivered to a system per unit time [12–16]. While these developments are interesting in their own right, there have been a number of exciting consequences for the study of atoms and molecules [17–28]. Traditionally, weaker intensity lasers (less than a Megawatt per square centimeter, or $I < 10^6$ W/cm²) have been used to probe molecular systems via spectroscopy and spectrometry [5, 29–41]. However, as laser intensities have increased, the electric and magnetic fields produced by them have become of sufficient strength as to become active participants in the chemical process under observation. The current state of technology has attained laser fields of up to $I \sim 10^{19}$ W/cm² [12, 13], producing electric fields, $\vec{E}$, which exert forces on molecules comparable to, or even exceeding, those forces which bind nuclei and electrons together [17–19, 23, 24]. Advances in laser pulse shaping have also allowed a significant degree of control of the temporal behaviour of $\vec{E}$ to be possible [14, 42–44]. This has led to the proposal of the control of chemical events using lasers. Some examples of strong-field lasers in molecular dynamics are femtochemistry [45–48], analytical laser-mass spectrometry [49], Coulomb explosion imaging [24, 50–52], coherent- and optimal control of chemistry [26, 27, 53–63]. The last example holds particular promise as it is possible to construct a laser pulse which optimally obtains the desired experimental outcome without a detailed understanding of the system dynamics.

Of the above applications of lasers to chemistry, optimal control methods are the most relevant to the present work as it is based on developments in infrared strong fields [15, 16, 43]; in the infrared laser frequency regime (frequencies of 10 to 10000 cm⁻¹), fields of up to $I \approx 10^{16}$ W/cm² can be generated. Since this frequency region is typically that

of vibrational motion of atoms within molecules, strong field lasers of this type can be expected to have significant influence on the molecular dynamics of a system. Although initially only studied with respect to ionisation dynamics [18, 24, 64–68], strong infrared fields have been studied in connection with atomic and molecular trapping [69–72], alignment [73–78], and enhancement of both uni- and bimolecular reactions [79–89]. Most of this work has focussed on the intramolecular motion of molecules with little emphasis on the effects of strong fields on the intermolecular motion; since both types of motion are equally important in molecular dynamics, it is therefore the general purpose of the present work to fill this gap and study the effects of strong infrared fields on intermolecular motion.

1.2 Theoretical Framework for Strong, Infrared Field Interaction

In order to carry out a study of the effects of strong infrared fields on the intermolecular motion of chemical systems, it is necessary to establish that there will indeed be a significant modification to the intermolecular interaction potential in the presence of such a field. If any alterations to the potential are possible, it follows that some change in the dynamics should be observed. To establish the context of what a “significant modification to the potential” is, an outline of the basic formalisms of laser-molecule interaction is required. As will become apparent, a number of approximations must be made to obtain a Hamiltonian which can be analysed. The approximations outlined below are regarded as axiomatic in the sense that their validity is not tested and the Hamiltonian which results from their application is taken as the starting point of the investigation.

As far as atomic and molecular systems are concerned, the most comprehensive the-

ory of the interaction of light and matter is given by relativistic Quantum Electrodynamics (QED) theory [90, 91], with other more complex gauge theories being the relevant only to elementary particle interactions [92]. Relativistic QED theory treats both matter and light as quantum mechanical objects with interactions that are invariant to Lorentz transformations. For chemical systems, the effects of special relativity are generally small, consisting mainly of spin-orbit corrections to the intermolecular potential energy surface which are small except for the heavy elements [93, 94]. In the case of interaction with photons, relativistic effects are important for electronic motion in strong fields; this is because the interaction energy of a strong field with an electron is comparable to the rest energy of the particle. Thus, even though the speeds of the electrons in a system are not relativistic necessarily, the resulting interaction with the photons accelerates them to such a point¹ [12, 13, 18]. In the case of molecular systems, the increased rest energy (due to the larger mass) indicates that the interaction energy will not accelerate the nuclei to speeds near that of light [14, 18]. Thus, even though relativistic corrections to the interaction potential may be pertinent, there is no need to consider relativity in the nuclear motion.

The other main feature of the “exact” description afforded by QED theory is that of the quantised light field, or photons. Non-relativistic QED theory has been applied to the study of molecular systems successfully [29, 95–98]. However increased laser intensity implies that a greater number of photons per unit volume are present. In the limit of high photon density, the light can be approximated to be a classical electro-magnetic field (governed by Maxwell’s equations) rather than a quantum oscillator. This semi-classical description of light-matter interaction is thus appropriate for a molecule in a strong infrared field ($I \gtrsim 10^{12}$ W/cm²)².

---

¹N.B.: this fact has been used to create relativistic experiments using strong fields.

²The time-independent equations of motion for the QED Hamiltonian can be shown to be equivalent to

The interaction of matter with a classical electro-magnetic field is described by the time-dependent Schrödinger equation with scalar- and vector-field interaction terms for all charged particles, both electrons and nuclei [29, 99]. For convenience it is assumed that the laser field is homogeneous (in space) and linearly polarised. The equation for the interacting system is not uniquely defined without a choice of gauge; in the present work the length gauge is employed although identical results can be obtained in the Coulomb gauge [18, 29, 96, 100].

In infrared fields, the wavelength of the laser is much larger than the molecular dimensions so the dipole approximation may be employed in the field-matter Hamiltonian obtained thus far [18, 29, 96, 98, 101]. By making this approximation, higher order electric and magnetic multipole interaction terms are neglected. Such an approximation has been shown to be valid for linearly polarised strong fields in the case of ionisation of atoms [18–20]. If it is further assumed that nuclear contributions to the dipole operator are small (since these are inversely proportional to the nuclear mass) and that the magnetic field interaction is negligible (typically by orders of magnitude) the Hamiltonian contains only interaction terms which are of the form $-\vec{\mu} \cdot \vec{\mathcal{E}}(t)$, where $\vec{\mathcal{E}}(t)$ is the time-dependent electric field vector and $\vec{\mu}$ is the quantum mechanical electric dipole operator (summed over all electrons). This equation is the starting point for theoretical descriptions of most spectroscopies and the DC-Stark effect [29, 96, 102–104].

At this point, the time-dependent Schrödinger equation for the nuclear degrees of freedom is obtained using the Born-Oppenheimer solutions to the electronic part of the Hamiltonian as an expansion basis [105, 106]. The resulting Hamiltonian matrix for the nuclear motion contains both radiative and non-radiative terms in the off-diagonal coupling ele-

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the time-dependent results for a classical field via S -matrix theory and a transformation of the Hamiltonian to the interaction picture and taking the limit of large average photon number [96].

ments [96, 98]. Since the non-radiative (i.e. non-adiabatic) coupling terms are independent of the field they do not contribute to laser-induced processes directly. Indeed, for strong fields the radiative contributions should dominate the off-diagonal contributions to the Hamiltonian matrix and non-radiative couplings can be regarded as a secondary effect; when this situation will occur is independent of the relative magnitude of the non-radiative coupling to the Born-Oppenheimer energy level separations, which is the usual condition of validity of the approximation [93]. Thus, even for a system where the Born-Oppenheimer approximation is not valid in the absence of a field, it can be justifiably invoked for a sufficiently large field³.

With the separation of the nuclear and electronic degrees of freedom in the laser-molecule Hamiltonian, the motion of the nuclei takes place on a potential energy surface which includes all interactions with the field. The solutions to the electronic Schrödinger equation must now be sought and this is where most approaches to laser-molecule interactions differ. In weak fields, time-dependent perturbation theory of the Fermi “golden rule”-type are applicable: this includes theories for most spectroscopies [5, 29, 99] (e.g. Raman, microwave, etc.) and early work on multi-photon processes [19, 22, 107–116]. For intermediate intensities, $I \sim 10^9$ W/cm², Floquet theory is useful [104, 117–122]. These methods are most appropriate in describing the effects of resonance with an electronic transition between field-free Born-Oppenheimer surfaces and both reintroduce the concept of photons in the results. When there is significant non-resonant coupling with the field, these approaches become computationally difficult. In general, a Hamiltonian matrix with time-dependent elements is obtained with expansion of the electronic wave function using the field-free basis and approximations of some sort must be made in order to obtain a so-

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³N.B.: There is also an explicitly time-dependent form of the approximation which is useful for a derivation starting from semi-classical radiation theory [99].

lution. In the present work, the quasi-static approximation is employed, which is a form of adiabatic perturbation theory [20, 24]. The approximation assumes that the electrons can instantaneously adjust to the variation of the field over time; this is valid when the frequency of the laser is much smaller than the energy level separation of the field-free Born-Oppenheimer surfaces. While this is not true for highly excited states, if only the ground electronic state is considered then the validity is assured for infrared fields since electronic transitions occur in the UV-range. Therefore, only fields that are non-resonant with electronic transitions can be considered presently.

The advantage of the use of the quasi-static approximation is that the field-molecule electronic Schrödinger equation can be solved at any instant in time as if the field was static. The solution to the electronic problem in a static field is well known from the study of the Stark effect [102, 123]. Formally, the Hamiltonian matrix must be diagonalised to obtain the Stark-shifted surfaces. Equivalently, an infinite perturbation series in the orders of the field can be obtained which collects interaction terms of the transition matrix elements into the electric moments of the system, i.e. dipole moment, polarisability and hyperpolarisabilities [103, 124, 125]. The latter approach is adopted in the present work since $\vec{\mathcal{E}}$ is assumed to be non-resonant. If the system is excited electronically, then motion on these excited states must be included in which case the explicit diagonalisation of the Hamiltonian would be necessary.

For a description of the electronic states beyond the quasi-static approximation, frequency-dependent electric moments can be used [103, 124, 125]. These moments formally diverge at electronic resonances and hence, are only useful for non-resonant fields. If it is assumed that the laser frequency is much less than the transition energy between the ground and first excited electronic state, then static field moments can be used since the frequency de-

pendence is small far from resonance. This is valid for infrared laser frequencies since electronic transitions are typically in the UV-range. Therefore, the model presently employed is only applicable to ground-state molecular systems that have no resonances with the first electronic excited state for a given laser frequency; this must hold for all nuclear configurations which are accessed in the dynamical process of interest.

While the convergence of the perturbation series is not guaranteed for strong fields, only terms up to second order, namely the permanent dipole moment and polarisability, are retained for the present work. Higher order terms have been shown to be important for fields of larger intensity than will be considered here [126]. Regardless of the particular radius of convergence of this series, which is generally unknown [102], the description is qualitatively correct using only two terms since the dipole and polarisability contain the correct even-odd field dependence of the interaction terms. Neglect of higher order terms could be incorporated into the magnitude of these moments but the overall behaviour of the interaction potential is unchanged.

Finally, the nuclear motion on the quasi-static potential surface, which varies parametrically with time, can be solved for. This could be done quantum-mechanically using numerical methods to solve the nuclear time-dependent Schrödinger equation [96, 127–129]. However, in this work the nuclear motion will be treated classically (thus the Hamiltonian is “de-quantised”). This approximation is motivated primarily by the desire to determine the qualitative nature of the system dynamics; classical mechanics offers a simpler means of interpreting the motion. Furthermore, a great deal of work has shown that classical mechanics does indeed provide a useful quantitative description of collision processes as a first approximation with additional refinements being possible through semi-classical correction formulae [93, 130–134].

The Hamiltonian described above, using either classical or quantum mechanical nuclear motion, has been used to study a number of strong-field molecular phenomena, such as multi-photon dissociation [58, 80, 81, 135–146] and exchange reactions [85–88, 147]. Qualitatively, the nuclei move on a Born-Oppenheimer potential surface which is modified by a Stark shift which oscillates in time with the laser frequency. A “significant” interaction with the field is thus determined by the magnitude of the Stark shift relative to the field-free potential. Since the primary interest of the present work is intermolecular motion, chemical processes where such motion is important must be examined in order to propose an experimental situation where laser-induced effects can be studied.

1.3 Elastic Collisions in Chemistry

The simplest system that exhibits intermolecular motion is an elastic collision between two atoms. Elastic scattering, where the total energy or internal state is unchanged by the collision, is the most basic event in chemistry; any other collision process (i.e. inelastic or reactive) which involves more than one molecule will always occur concurrently with an analogous elastic process [1, 131]. It follows that the areas where elastic collisions play a role are also areas for possible control by laser-induced interactions. The bulk properties of liquids and gases (e.g. viscosity, diffusion, thermal conductivity, virial coefficients etc ...) are determined largely by the elastic collisions between pairs (or higher number) of molecules [2, 5, 7]. These properties involve averaging over thermal distributions of collision pairs and hence only retain broad features of the interaction potential, although they have been used to obtain interaction potentials in the past [148].

A somewhat more sensitive way of observing the interactions of binary collisions is through spectral line-shape studies. Collision induced absorption [33, 149–151] and collision-

induced light scattering [31, 33, 152–154] are well-established methods for the determination of the interaction-induced dipole moments and polarisabilities, respectively, of weakly interacting systems. The methods are based on the fact that the dipole or polarisability of the binary system changes over the course of a collision, with a corresponding change in the intensity of the absorbed or scattered light, in analogy with traditional infrared and Raman spectroscopy [155–164]. Thus, the dynamics of the collision and behaviour of the dipole or polarisability (as a function of internuclear separation) become important in the shape of the spectral line (which occurs in the far infrared region). By calculating the time-correlation function of a given system using either classical or quantum dynamics to describe the collision, a theoretical line-shape can be compared with that of experiment [5, 165–168]. In this case, models of the potential and pertinent optical property as a function of internuclear separation are required a priori. Alternatively, it is possible to determine the dipole or polarisability by inversion of the spectra if the potential is known [31, 33, 150, 151, 153]. This procedure has been used with a great deal of success in obtaining the qualitative form of the optical properties of the system [161, 169–175]. The possibility of examining collision induced absorption spectra for bimolecular reactions in a strong field has been examined previously [87].

In addition to the change in the spectra due to collisions, the spectra of any dimers which form are also studied with the above method. Dimers produce discrete rotational and vibrational spectra as in the case of the infrared and Raman spectroscopy of strongly bound molecules, which contribute to the overall line-shape. This fact has been used to determine the probability and rates of forming dimers in gases and gas mixtures of weakly interacting species [150, 153, 169, 174–178]. Thus the method of collision induced spectroscopy has the ability, in principle, to obtain the potential through inversion in a system where the

interaction with the laser is non-negligible. However, the ensemble averaging inherent in the line-shape may obscure laser-induced effects.

It would appear that the influence of the potential on elastic collision dynamics is not a directly observable quantity and hence, any laser-induced effects will be hard to identify. Fortunately, a more direct way to observe elastic collisions exists through the technique of molecular beam scattering [1, 131, 179]. Historically, the technique was an important breakthrough for just this reason; the use of molecular beams allows experimental control of the initial velocity in the centre of mass frame and of the initial chemical state of the collision species. Thus, much of the averaging which is required for the determination of the above-mentioned experimental observables is not inherent in a beam experiment, increasing the sensitivity to the potential. The principal observable in scattering experiments is the differential collision cross section [180–182]. In fact, many of the bulk properties of systems mentioned above can be determined from knowledge of the differential cross section and this was used initially in applications of the beam technique [1, 7, 131, 183–185]. Further work has shown that specific features of the differential cross section can be used to determine molecular potential parameters indirectly [186–191]. Additionally, in the case of elastic scattering the differential cross section is amenable to inversion allowing an accurate determination of the potential [131, 180, 188, 192–195].

The differential cross section can be determined theoretically using either classical [192, 193, 196–205] or quantum mechanics [131, 180, 190, 191]. In the former case, given a potential, the classical equations of motion are solved to yield the angle of deflection, which measures the rotation of the final velocity vector relative to its initial direction [180, 206]. From this, a differential cross section can be determined. In the case of quantum mechanics, it is not possible to define a deflection angle due to the uncertainty principle but

the differential cross section is evaluated directly by considering the differences between the initial and final state continuum wave functions [131, 180, 181, 190]. The classical deflection function displays characteristic features which can be related to the interaction potential. These features do in fact manifest themselves in the differential cross section determined by both theories. Thus classical mechanics has been shown to be useful in the interpretation of experimental (i.e. quantum mechanical) measurements [186–191, 193].

The features of the classical differential cross section (or equivalently the deflection angle function) which can be related to potential parameters are: small angle/high energy scattering, glory scattering, orbiting and rainbow scattering. In the limit of large collision energy (initial relative velocity), much of the scattering is confined to small angles (i.e. very little scattering of the system) [191, 192, 200, 206]; this produces a singularity in the differential cross section at zero scattering angle. The slope of the scattering intensity as the scattering angle is varied can be related to the asymptotic portion of the interaction potential, yielding information regarding the long-range attraction or repulsion experienced by the system.

If the potential has both attractive and repulsive components (the latter being short range), then glory scattering may be observed; this manifests itself as an additional singularity at zero scattering angle [191]. The glory effect can be shown to arise from the net balance of forces in the collision system such that no scattering is experienced. The effect is therefore related to the ratio of the long-range attractive and short-range repulsive terms in the potential [186, 187].

For low collisional energies, there exists the possibility that a collision can result in the formation of a “stable” complex. That is, the two collision partners orbit each other at a constant separation. This is possible if the classical trajectory lands exactly on a local

maximum in the potential surface (a stable point⁴) [180, 186, 187, 191]. The presence of orbiting is exhibited as a singularity in the classical deflection function and as a background term in the differential cross section⁵ [131, 180]. The presence of orbiting is determined by the attractive part of the potential (which is necessary for the existence of a stable point) while the maximum collisional energy that exhibits orbiting is related to the potential well depth. Thus this effect gives some information about the short range part of the potential [180, 183, 191].

Finally, at higher collisional energies (specifically beyond which no orbiting is observed) the differential cross section exhibits another singularity due to rainbow scattering. This is caused by the existence of a deflection angle that is insensitive to variation of initial conditions (i.e. its first derivative with respect to the initial conditions is zero) [180, 186, 187, 189–191, 203, 205, 208]. The position of the rainbow singularity in the differential cross section is related to the ratio of the collisional energy and the well depth of the potential.

All the above mentioned features of the differential cross sections can be examined numerically and through the use of analytic models which approximate the dynamics [191]. It follows that study of the differential cross section (or the classical deflection function) as a function of laser parameters can lead to information regarding the same parts of the laser-induced potential and the concomitant changes to the intermolecular dynamics. Since the interests of the present work are mostly qualitative, it is desirable to find the simplest system that exhibits the dynamical features possible in an elastic collision system; exper-

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⁴This is by definition an unstable point since any perturbation will result in the decay of the orbit [207]. However, such terminology does not lend itself to the description of the phenomena.

⁵In this case it is preferable to examine the deflection function since the effect is more easily observed. Quantum mechanics shows classical orbiting through scattering resonances in the total cross section [190, 191].

iments have shown that diatomic systems contain such features and additionally simple mathematical models of their potentials can be used successfully to qualitatively analyse their dynamics.

1.4 Modelling Binary Systems

From section 1.3, it is clear that a diatomic elastic collision system is sufficiently complex as to produce good qualitative information on intermolecular dynamics. A simple mathematical model of the diatomic potential and its electric moments (relevant to the present description of laser-molecule interaction of section 1.2) is desirable since any results are transferable to different molecular systems with similar model parameters. It remains to discuss which simple model is best suited to the study of diatomic elastic collisions in a strong infrared field.

The choice of the particular form of the model used to represent the molecular system implicitly limits the type of chemistry that can be studied; this is due to the fact that no simple functional form can represent the interaction potential, dipole moment and polarisability of an arbitrary diatomic system. Functions with only a few parameters are not flexible enough for this task. Thus for the present work, only models that describe the comparatively weak interactions of intermolecular forces will be considered. The reason for this is simply that if the field-free interaction is small then observation of a laser-induced effect which is comparatively large is more easily accomplished. Qualitatively, any conclusions that result should be applicable to more strongly bound systems. As the field-dependence in the potential is limited to second order, models are required for the permanent dipole moment and polarisability as functions of internuclear separation, in addition to the field-free interaction potential.

In the case of the interaction potential, perturbation theory gives the long-range form in terms of a multipole expansion in R^{-1} , where R is the internuclear separation between the two atoms. The coefficients of the expansion are evaluated from the electric moments of the separated atoms, producing Coulomb's law, charge-dipole, dipole-dipole terms, etc [148, 209–212]. This multipole expansion has been very successful in describing the long range form of molecular interaction potentials and almost all simple models make use of it [148, 191, 212]. Typically, interactions between neutral atoms are described by the dispersion term, which is always attractive. The major difference in the form of model potentials lies with the description of the short range part of the interaction. Short-range perturbation theories show that the repulsive behaviour arises from the exchange energy which can be related to the overlap integral between the two centres. The exchange-dispersion model is the simplest form of interaction potential that is analytically correct at the two separation limits [191, 213]⁶. Other more complicated potential forms exist and have been used with different degrees of success in reproducing the experimental properties of weakly interacting systems, such as the rare gases [210, 212, 214, 215] while more strongly bound systems require different models [148, 191, 216–221]. The Lennard-Jones (6,12) potential is the simplest and most well-known function which qualitatively describes the interaction of van der Waals dimers [148]. Quantitatively, the function has been shown to be insufficiently flexible for the purpose of reproducing high-accuracy experiments [7, 183, 212, 222]. In spite of this deficiency, the Lennard-Jones function is an appropriate choice of model potential due to its simplicity and (see appendix B) reasonable quantitative accuracy which is sufficient for the purposes of the present work.

There have been comparatively few simple model functions proposed to describe the

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⁶This particular model is referred to as the Buckingham-Slater potential [148].

permanent dipole moment of a diatomic bond [219, 220, 223–226]. For weakly bound systems, the formalism of perturbation theory can also be used to predict the analytic form of the permanent dipole moment [227–231]. The formalism can be expressed in terms of the separated atomic properties but there is no classical correspondence with electrostatics as in the case of the interaction potential. The theory yields an exchange-dispersion form of the permanent dipole moment as the basic model. This model has been used previously with some success in describing the collision induced absorption spectra of the rare-gas mixtures [150, 151, 175, 230, 231]. Ab initio calculations of the dipole moment of these species have also been fit well by this functional form [232–234].

There seems to be some evidence for a corresponding states form of the polarisability as a function of internuclear separation. However, very few model forms have been proposed to describe it [235–238]. The polarisability can be determined from long- and short range perturbation theory [212, 231, 239, 240]. The long-range result is also a multipole expansion form and, like the interaction potential, its coefficients (which are determined from atomic polarisabilities) have a correspondence with classical electrostatics. The leading term corresponds to the dipole induced-dipole (DID) term which can be derived from electrostatics [153]. Short range theory again predicts an exchange form; thus the basic model of exchange-dispersion is used for the polarisability. This model has been used extensively to describe the polarisabilities of rare gases and molecular dimers in collision induced light scattering experiments [153, 231, 239–241].

It appears from the above considerations that if investigation is limited to weakly interacting species, a model based on the Lennard-Jones (6,12) potential with exchange-dispersion forms for dipoles and polarisabilities will be sufficiently accurate. Such a model offers a simple interpretation of contributions to the laser-induced potential surface and few

parameters to consider.

1.5 Field-Induced Effects in Elastic Collisions

In spite of the large amount of work dedicated to the Stark effect in vibrational-rotational spectroscopy of diatomics [102, 123, 242–248], little has been done toward the study of the scattering of binary systems (intermolecular motion) under the same conditions. This is due in part to the historical perspective of the Stark effect as being a perturbation to the system, i.e. strong fields which can be generated now were not available when the effect was discovered. Nonetheless, Stark spectroscopy essentially predicts what should be observed in a strong field (within the quasi-static approximation) for the bound states of a diatomic system. Specifically, these are: an increase in the well depth and harmonic frequency and a shortening of the equilibrium bond length (the position of the minimum of the potential well) [102]. However, the magnitude of these effects in strong fields has not been studied explicitly and hence the overall change in the potential remains uncharacterised.

One effect on bound systems which has been noted for the case of quasi-static fields is the creation of pendular states [69–71, 73, 75, 77, 78, 119, 249–256]. This effect can be observed in the rotational spectra of diatomic molecules and is characterised by the creation of a rotational potential well. Since the molecular polarisability is anisotropic (i.e. different when measured parallel or perpendicular to the molecular axis) an angular-dependent term arises in the field-molecule potential. The result is a potential minimum when the molecular axis is aligned with the field axis. For strong fields, this causes a potential well along the coordinate of rotation which is deep enough to support bound states where none existed previously. Theoretically, this is found from considering a rigid rotor model in the presence of a strong field interacting via the polarisability [69, 70, 73], however the permanent dipole

moment should also induce a similar effect [71]. Experimentally, this has been shown in a number of molecules [75]. Measurement of the field-dependent rotational spectra can, at least in principle, be used to obtain the polarisability anisotropy of the molecule [69, 70]. The effect is also important in its own right as it can be used to control the alignment and orientation of molecules. This work shows that the potential of a binary system in the field is no longer centrosymmetric, a fact which should be observable in the collision dynamics of such a system.

As noted previously, much work has been done on the effect of resonant strong fields and its application to elastic collisions. Within the Dressed-State model, laser-induced avoided crossings modify the collision potential [23, 96, 107, 109–112, 114, 115, 257–260]. The resulting potential can have a well which is stronger or weaker than the field-free potential through the mechanisms of bond-hardening and softening, respectively [119, 121, 259–261]. However, this has mostly been applied to the study of electronic excitation between dressed states. Resonant multi-photon dissociation occurs on a single dressed surface [119, 260–262] but this work has necessarily focused on intramolecular dynamics. In the present work, the lack of resonance allows for the possibility of elastic collisions on a single surface. Since the field intensities of previous work were too weak to induce large non-resonant effects, the non-resonant field effects on the dynamics of a system are largely unexplored. Diatomic dissociation via infrared multi-photon absorption [80, 135–141] is an exception to this statement but again attention has paid only to the non-resonant effects on intramolecular dynamics (i.e. bound states).

Atoms in strong fields exhibit tunnelling ionisation [18, 20, 24, 64, 263]. This is also true of molecules when the field is in the infrared region (i.e. well below any electronic resonance). Ionisation lifetimes are predicted reasonably well by the atomic tunnelling

formulae [24, 66, 67, 80, 264]. Thus any chance to observe the dynamics of the neutral system in the field requires that the collision (or spectroscopic observations) must occur on a time-scale which is much shorter than the ionisation lifetime in the strong field. This places a fundamental limit on the strength of field that may be applied to the system and to the species involved since the tunnelling rate is sensitive to the ionisation potential of the system.

1.6 Purpose of Present Work and Outline of Subsequent Chapters

It is clear from sections 1.2 and 1.5 that application of a homogeneous, non-resonant infrared laser field will alter the potential energy surface of a molecular system in a non-trivial manner. A number of questions naturally arise from this conclusion: what are the detailed natures of these changes and are they significantly dependent on the chemical identity of the system? How might the differences be observed? Can this be used to control the outcome of chemical events? A reasonable route to answering the first of these questions is to examine a simple model system, such as two atoms, where the chemical identity of the species involved is introduced through model parameters. The exchange-dispersion models for diatomic systems of the type discussed in section 1.4 are thus suitable for this purpose.

The question of observation of laser-induced effects may be answered by using the two-atom model to predict observables of experiments where the interaction potential has a well-understood role and is sensitive to its features. From the observables of the chosen experiment, the form of the laser-induced potential can be determined indirectly by exam-

ining the functional dependence on laser parameters and directly if an inversion procedure exists. In the case of diatomic systems, section 1.3 shows that elastic collision experiments provide a relatively direct route to the potential surface through known features of the collision cross sections and their inversion.

Based on the arguments of this chapter, it is clear that the study of elastic collisions of a model diatomic system in a strong infrared field will provide a simple means for studying the laser-induced effects on the potential energy surface. A schematic of the experimental arrangement necessary to study the elastic collision dynamics⁷ is shown in figure 1.1; the two crossed molecular beams (at a fixed angle) together determine the plane of collision and fix the direction of the initial relative momentum $\vec{P}_{AB}$ of the two collision partners in the centre of mass frame, as is typical of molecular beam experiments [1]. If the strong field laser is propagated in the direction normal to the collision plane, then the electric field vector $\vec{E}$ is also coplanar with $\vec{P}_{AB}$. The direction of $\vec{E}$ can be controlled experimentally, thus fixing the relative orientation of $\vec{E}$ and $\vec{P}_{AB}$. The volume where A, B and $\vec{E}$ all interact is shown by the shaded area of figure 1.1; this volume must be large compared with the range of the potential in order for the field to be considered homogeneous. This is easily seen to be true for an interaction volume of $1 \mu\text{m}^3$, a common order of magnitude for laser focal dimensions, since the range of the (laser-induced) potential ($\sim 10 \text{ \AA}$) is much smaller than this.

The hypothetical laser + molecular beam experiment described above will be used to study the rare-gas pairs RgRg' ($\text{Rg, Rg}' = \text{He, Ne, Ar}$) since model potential parameters of the exchange-dispersion type can be found with a comparatively high degree of accuracy

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⁷N.B.: A similar experimental scheme has been proposed to study the laser-assisted collisional ionisation of atoms by protons [264, 265]. The experiment envisioned in the present work is simpler since there is no ionised electron to detect and correlate with collision events.

Figure 1.1: A schematic of a molecular beam experiment to measure laser-induced elastic scattering. Beams of molecules A and B are crossed to define the initial relative momentum in the centre of mass frame $\vec{P}_{AB}$. The laser beam is propagated in the direction normal to the collision plane. The direction of the field $\vec{\epsilon}$ is fixed experimentally relative to $\vec{P}_{AB}$. The volume of interaction with A, B and $\vec{\epsilon}$ is shown as shaded.

for these systems. The rare gas dimers are also desirable for study since they generally possess essentially isolated electronic ground states with large ionisation potentials; thus, they fulfill the requirements of non-resonance and long ionisation lifetime necessary for the observation of the dynamics associated with the Hamiltonian discussed section 1.2.

With the above in mind, the purpose of the present work may now be stated in two simple hypotheses:

1. The effect of a strong, infrared laser field can be observed in the elastic collision dynamics of the rare gas dimers as studied under the conditions of a molecular beam experiment.
2. The origin of laser-induced effects in the dynamical observables can be traced back to various features of the potential energy surface. In particular, the contributions of the iso- and anisotropic parts of the potential can be determined.

A number of concomitant tasks result from these two hypotheses. Namely:

1. Identify any characteristic features unique to laser-induced motion, give qualitative explanation of their origin in terms of the potential and show how these are to be observed experimentally.
2. Determine categories of laser and/or collision parameters where the dynamics are similar.
3. Derive and test approximate models that can be used to simplify the analysis of the system.
4. Determine a corresponding states form of the laser-molecule potential surface and thus test the similarity of different molecular systems.

The remainder of this work is organised as follows: chapter 2 presents the general theory, defines observables and develops approximate analytical models; chapter 3 gives computational details for the numerical calculations performed; chapter 4 presents numerical calculations of the $RgRg'$ systems ($RgRg' = He_2, HeAr$) and evaluates the accuracy of analytic models while chapter 5 summarises the conclusions of the present work. A number of appendices are also present for the reader interested in some of the mathematical details pertaining to the present work, including two derivations (appendices D and E) for formulae not found in the literature. Additional appendices, B and C, contain the details of the determination of molecular model parameters and the range of laser parameters where the quasi-static Hamiltonian is expected to be valid. Finally, the contents of the supplementary compact disk are given in appendix I.

Chapter 2

Theory of Binary Collisions in Strong IR Fields

This chapter develops theoretical models for the proposed elastic scattering of two atoms within an infrared laser field. The laser-molecule Hamiltonian is given for a diatomic system with either time-dependent fields or fields in the limit of high laser carrier frequency. Features of the potential energy surface that are deemed important are introduced. The initial conditions required for the molecular beam-type experiment proposed in section 1.6 are given and the classical observables which might be extracted from such an experiment (e.g. the deflection function, differential cross section, etc.) are defined.

From section 1.4, it was concluded that a simple analytic model of the diatomic potential, dipole moment and polarisability would be sufficient for the description of the main features of the laser-molecule potential. Presently, such model functions are given along with a scaling of units which puts the potential into a simple, dimensionless form. Partitions of the potential are identified which separate spherical and non-spherical terms from the Hamiltonian in order to quantify the different contributions to the dynamics. A similar

partitioning of the time-dependence of the Hamiltonian is also performed.

With the simple model form of the laser-molecule Hamiltonian, it becomes possible to obtain approximate expressions for some of the potential features and dynamic observables of the system. This allows estimation of the behaviour of the system as a function of laser and molecular parameters. In particular, special features of the classical deflection function which arise from characteristic trajectories are discussed. The overall goal of this chapter is thus to identify the variables pertinent to the proposed strong field molecular-beam experiment and develop the procedures which are used to predict (both computationally and analytically) and analyse its results.

2.1 The Quasi-Static Hamiltonian

As explained in section 1.2, a number of approximations must be made to the description of the laser-matter interaction in order to be able to contemplate a tractable problem. The “derivation” of the quasi-static classical Hamiltonian presented here considers as its starting point a system of two atoms interacting in a manner prescribed by these approximations; i.e. the potential is identical to that of a system in a classical DC electric field $\vec{\mathcal{E}}$ with the time-dependence introduced parametrically (vis a vis the quasi-static approximation) [20],

$$\vec{\mathcal{E}} \rightarrow \vec{\mathcal{E}}(t) . \quad (2.1)$$

The component of $\vec{\mathcal{E}}(t)$ along any coordinate, $\mathcal{E}(t)$, is composed of three parts

$$\mathcal{E}(t) = |\mathcal{E}_0| \cos(\omega_c t) f(t) , \quad (2.2)$$

where the first term is the field amplitude, $|\mathcal{E}_0|$, the second variation due to the carrier wave, $\cos(\omega_c t)$, where ω_c is the carrier frequency and the third term is the pulse function $f(t)$ which attenuates the field over a time scale which is in general different from that of the carrier wave. The particular choice of (2.2) fixes the laser field to be linearly polarised. The amplitude and pulse functions can be varied freely. Since $\vec{\mathcal{E}}(t)$ is considered homogeneous, the centre of mass motion may be neglected in the Hamiltonian [266, 267]. The relative motion is thus equivalent to that of a single particle moving with respect the centre of mass origin with reduced mass μ .

With the above remarks in mind, the Hamiltonian of a system with two atoms interacting with a homogeneous infrared field is given as ¹,

$$\begin{aligned} H &= T + V \\ &= \frac{1}{2\mu} (p_1^2 + p_2^2 + p_3^2) + V(q_1, q_2, q_3; t), \end{aligned} \quad (2.3)$$

where the Cartesian coordinates for the particle are $\{q_1, q_2, q_3\}$ with conjugate momenta $\{p_1, p_2, p_3\}$ (defining T) and t denotes time. In this description of the field-matter interaction, the interaction terms are contained within the potential energy term only.

The potential energy of the system in the absence of an external field is only a function of the relative separation of the two atoms, and hence in the centre of mass frame, only a function of the distance of the coordinates from the origin (the scattering centre). The appropriate choice of coordinate system is therefore spherical polar coordinates [266, 268]. Using the definitions

$$q_1 = R \sin \theta \cos \phi \quad (2.4a)$$

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¹Unless stated otherwise, all results are expressed in atomic units.

$$q_2 = R \sin \theta \sin \phi \quad (2.4b)$$

$$q_3 = R \cos \theta \quad (2.4c)$$

and deriving the corresponding relations between the velocities, the Hamiltonian becomes,

$$H = \frac{1}{2\mu} \left(p_R^2 + \left(\frac{p_\theta}{R} \right)^2 + \left(\frac{p_\phi}{R \sin \theta} \right)^2 \right) + V(R, \theta, \phi; t) \quad (2.5)$$

where R is the distance from the origin, θ is the angle formed by the position vector $\vec{R}$ and the q_3 axis and ϕ is the angle between the q_2 axis and the projection of $\vec{R}$ onto the (q_1, q_2) plane. The kinetic energy is now expressed in terms of the radial (p_R) and two angular (p_θ, p_ϕ) momentum components.

By virtue of the quasi-static approximation and the assumed absence of electronic resonances, the potential function $V(\vec{R}; t)$ may be obtained from the static field potential, which may be written as a summation over orders of the electric field magnitude $|\mathcal{E}_0|$ with the time-dependence introduced by (2.1) and (2.2). The field-perturbation expansion diverges for extremely large fields, but it is assumed presently that $|\mathcal{E}_0|$ is small enough that the series expansion may be truncated at second order. Thus, $V(\vec{R}; t)$ reduces to a field-independent contribution, $V_0(R)$ and two interactions with the components of $\vec{\mathcal{E}}(t)$ [103, 125],

$$V(\vec{R}; t) \approx V_0(R) - \sum_{i=1}^3 \mathcal{E}_i(t) d_i(\vec{R}) - \frac{1}{2} \sum_{i,j=1}^3 \mathcal{E}_i(t) \mathcal{E}_j(t) \alpha_{ij}(\vec{R}) \quad (2.6)$$

where the indices (i, j) denote the vector or tensor components of the the field (2.2) ($|\mathcal{E}_0|$ can be different for each component), molecular dipole moment d and molecular polarisability α along the q_i -axes. The interaction energy of the field with the system is thus dependent on the orientation of the field and position vectors of the system (via the dipole

and polarisability components). Without any loss of generality, the field orientation may be fixed with the positive q_3 axis (i.e. all other components are zero) giving

$$V(\vec{R};t) \approx V_0(R) - \mathcal{E}(t)d_3(\vec{R}) - \frac{1}{2}\mathcal{E}^2(t)\alpha_{33}(\vec{R}) . \quad (2.7)$$

This can be related to the dipole and polarisability in the molecular frame by noting that, for axially symmetric molecules [124, 125],

$$d_3 = d(R) \cos \theta \quad (2.8a)$$

$$\alpha_{33} = \alpha_{\perp}(R) + (\alpha_{\parallel}(R) - \alpha_{\perp}(R)) \cos^2 \theta . \quad (2.8b)$$

Here, $d(R)$ is the dipole moment along the interatomic axis while $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ denote the polarisability tensor components which are parallel and perpendicular to the axis, respectively. Equivalently, the polarisability interaction can be expressed in terms of the invariants of the tensor; its trace α and anisotropy β , which is a convenient form for spectroscopic measurement [125, 153],

$$\alpha(R) = \frac{1}{3}(\alpha_{\parallel}(R) + 2\alpha_{\perp}(R)) \quad (2.9a)$$

$$\beta(R) = \alpha_{\parallel}(R) - \alpha_{\perp}(R) . \quad (2.9b)$$

From the above argument, the potential for a diatomic system in a quasi-static field can be expressed completely in terms of the polar coordinates (R, θ) :

$$V(R, \theta; t) = V_0(R) - \mathcal{E}(t)d(R) \cos \theta - \frac{1}{2}\mathcal{E}^2(t) \left(2\alpha(R) + \beta(R) \left(\frac{1}{3} + \cos 2\theta \right) \right) . \quad (2.10)$$

The form of the potential (2.10) shows that the Hamiltonian is invariant with respect to rotation of the molecular axis about the field axis (variation of ϕ). By Noether's theorem [269] a conservation law must exist for p_ϕ and this term of the kinetic energy can be regarded as an additional potential term. The motion is thus confined to the (R, θ) plane while this plane precesses about the field axis with a fixed momentum p_ϕ . In the laser + molecular beam arrangement of figure 1.1, the initial momentum $\vec{P}$ and $\vec{\mathcal{E}}$ are coplanar by construction; since there is no force acting on the system which will move $\vec{P}$ out of the plane, the motion remains with $p_\phi = 0$ throughout the collision. Thus the p_ϕ term in the Hamiltonian can be neglected altogether and only the dynamics of the two-dimensional system of R and θ need be studied.

Using the results for (2.10), (2.2) and (2.5), the Hamiltonian of the system becomes

$$H^{(AC)} = \overbrace{\frac{1}{2\mu} \left(p_R^2 + \left(\frac{p_\theta}{R} \right)^2 \right)}^T + V_0(R) - |\mathcal{E}_0| \cos(\omega_c t) f(t) d(R) \cos \theta - \frac{1}{4} (|\mathcal{E}_0| \cos(\omega_c t) f(t))^2 \left(2\alpha(R) + \beta(R) \left(\frac{1}{3} + \cos 2\theta \right) \right), \quad (2.11)$$

where the superscript (AC) denotes the time dependence of the field². Note that the parts of $\mathcal{E}(t)$ are shown explicitly for comparison with the limit obtained for large carrier frequency ω_c .

2.1.1 High Frequency Limit

In the case where there is no laser pulse ($f(t) = 1$), known as the continuous wave (c.w.)-case, the forced oscillations of the field can be averaged in the limit of high carrier

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²N.B.: AC stands for alternating current in contrast to a DC, or direct current field where there is no time-dependence.

frequency. This is done using the Kapitza-Dirac separation of fast and slow motions (see appendix H) and results in a time independent Hamiltonian. For the diatom-laser system (2.11), averaging over the laser oscillation period gives the result (see equation (H.25))

$$\begin{aligned}
 H^{(\text{HFL})} &= T + V^{(\text{HFL})}(R, \theta) \\
 &\approx T + V_0(R) - \frac{1}{8}|\mathcal{E}_0|^2 \left[2\alpha(R) + \beta(R) \left(\frac{1}{3} + \cos 2\theta \right) \right. \\
 &\quad \left. - \frac{1}{\mu\omega_c^2} \left((d'(R))^2 (1 + \cos 2\theta) + \left(\frac{d(R)}{R} \right)^2 (1 - \cos 2\theta) \right) \right], \tag{2.12}
 \end{aligned}$$

where d' denotes the derivative of the dipole with respect to R .

The result of (2.12) represents a great simplification of the dynamics of the system since it is time-independent; this constitutes an entirely separate regime for dynamical study. Physically, it is clear that the averaged potential is applicable when the nuclei cannot respond instantaneously to the rapid oscillations of the field. Since the average values of $\cos\omega_c t$ and $\cos^2\omega_c t$ are 0 and 1/2, respectively, it follows that the contribution of the dipole term to the averaged potential is zero while that of the polarisability is non-zero. The frequency-dependent dipole term in $H^{(\text{HFL})}$ is a result of including perturbations of the field up to second order in ω_c . In (2.12), the ponderomotive-type terms due to the polarisability have not been retained since these are $O(|\mathcal{E}_0|^4)$. These terms should be included when higher-order electric moments (hyperpolarisabilities [124]) are introduced to the Hamiltonian since they are of comparable magnitude. Note that (2.12) is equivalent to the result of a static field ($\omega_c = 0$) with $|\mathcal{E}_0|$ being replaced by $|\mathcal{E}_0|/\sqrt{2}$ when the system has no dipole. The conditions for the validity of (2.12) are given for the general case in appendix H; their specific restrictions on $|\mathcal{E}_0|$, ω_c and other parameters of this system are discussed in appendix C.

2.1.2 Model Hamiltonian

The Hamiltonians (2.11) and (2.12) are general for any diatom collision in a linearly polarised, homogeneous infrared field. In order to simplify the analysis, simple functional forms of the potential and electric moments are used; this allows the detailed behaviour of these molecular properties to be described using a small number of parameters. The model system is expressed in terms of dimensionless variables: this makes apparent the mechanical similarity between different diatomic systems in addition to simplifying the mathematical description.

Based on the arguments in chapter 1, only weakly interacting systems are considered in this model. Thus the Lennard-Jones (6,12) potential [148, 191] lends itself to the description of $V_0(R)$:

$$\begin{aligned} V_0(R) &= D \left(\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right) \\ &\equiv DU_0(R/R_0) , \end{aligned} \tag{2.13}$$

where D is the well depth of the diatom system and R_0 is the internuclear separation at the potential minimum. The dimensionless potential U_0 is thus

$$U_0(X) = X^{-12} - 2X^{-6} \tag{2.14}$$

if the length R is scaled by a factor of R_0 . Similarly, time should be scaled by some fraction of the harmonic frequency of the bound system to reduce the time scale to a similar order of magnitude for systems of different reduced masses. Therefore, the following reduced

variables are defined,

$$X = \frac{R}{R_0} \quad (2.15a)$$

$$\tau = \sqrt{\frac{D}{\mu R_0^2}} t \quad (2.15b)$$

$$P_X = \frac{pR}{\sqrt{\mu D}} \quad (2.15c)$$

$$P_\theta = \frac{p_\theta}{\sqrt{\mu D R_0^2}}. \quad (2.15d)$$

Note that the time scale factor is derived from the harmonic frequency of the field-free potential (the harmonic frequency of (2.13) is $\sqrt{72D/\mu R_0^2}$ in a.u.).

The interaction terms are scaled by considering specific model functions which describe the interaction. All the interaction functions are represented by functions of the exchange-dispersion form (see chapter 1). The appropriate dipole function thus takes the form [150]

$$d(R) = \lambda_d e^{-R/R_d} - \frac{D_7}{R^7}, \quad (2.16)$$

where D_7 is the dispersion contribution derived from perturbation theory and (λ_d, R_d) describe the short-range, exchange contributions to the dipole³. Similarly, the polarisability trace and anisotropy terms are modelled by [153]

$$\alpha(R) = \frac{A_6}{R^6} - \lambda_\alpha e^{-R/R_\alpha} \quad (2.17a)$$

$$\beta(R) = \frac{B_3}{R^3} + \frac{B_6}{R^6} - \lambda_\beta e^{-R/R_\beta}. \quad (2.17b)$$

---

³This form, has the correct long- (to leading order) and short-range behaviour for weakly bound systems. However, the behaviour at $R = 0$ is incorrect (which is true also for the polarisability) since the dispersion term is undamped. This should not present any difficulties since the region of the potential affected is not dynamically significant.

The inverse polynomial terms of (2.17) can also be derived classically from the Dipole-Induced-Dipole (DID) model of the polarisability [153]. While A_6 , B_3 and B_6 are considered adjustable parameters presently, the DID model yields analytic expressions for them in terms of the separated atom polarisabilities, $\alpha_{(a,b)}$,

$$B_3 = 6\alpha_a\alpha_b \quad (2.18a)$$

$$B_6 = 3\alpha_a\alpha_b(\alpha_a + \alpha_b) \quad (2.18b)$$

$$A_6 = 2\alpha_a\alpha_b(\alpha_a + \alpha_b) . \quad (2.18c)$$

The results of the DID model (2.18) provide useful estimates of the magnitude of the interaction terms in the Hamiltonian.

Substitution of (2.15) into (2.16) and (2.17) yields reduced trace and anisotropy polarisability functions $(\bar{\alpha}, \bar{\beta})$:

$$\begin{aligned} \alpha(R) &= \frac{B_3}{R_0^3} \bar{\alpha}(X) \\ &= \frac{B_3}{R_0^3} \left(\frac{\Lambda_{\alpha_1}}{X^6} - \Lambda_{\alpha_2} e^{-\gamma_\alpha X} \right) \end{aligned} \quad (2.19a)$$

$$\begin{aligned} \beta(R) &= \frac{B_3}{R_0^3} \bar{\beta}(X) , \\ &= \frac{B_3}{R_0^3} \left(\frac{1}{X^3} + \frac{\Lambda_{\beta_1}}{X^6} - \Lambda_{\beta_2} e^{-\gamma_\beta X} \right) , \end{aligned} \quad (2.19b)$$

where

$$\Lambda_{\alpha_1} = A_6 B_3^{-1} R_0^{-3} , \quad \Lambda_{\alpha_2} = \lambda_\alpha B_3^{-1} R_0^3 , \quad \gamma_\alpha = \frac{R_0}{R_\alpha} , \quad (2.20a)$$

$$\Lambda_{\beta_1} = B_6 B_3^{-1} R_0^{-3} , \quad \Lambda_{\beta_2} = \lambda_\beta B_3^{-1} R_0^3 , \quad \gamma_\beta = \frac{R_0}{R_\beta} , \quad (2.20b)$$

are the scaled versions of the parameters in (2.17). The scaling is done with respect to B_3 since it should be the dominant term in the polarisability. Estimates of Λ_{α_1} and Λ_{β_1} are found from (2.18) to be

$$\Lambda_{\alpha_1} = (1/3)(\bar{\alpha}_a + \bar{\alpha}_b) \quad (2.21a)$$

$$\Lambda_{\beta_1} = (1/2)(\bar{\alpha}_a + \bar{\alpha}_b) , \quad (2.21b)$$

where $\bar{\alpha}_{(a,b)} = \alpha_{(a,b)}/R_0^3$ are the scaled atomic polarisabilities.

The dipole model (2.16) is scaled similarly relative to the leading anisotropy term by introducing

$$Q = \frac{D_7}{\sqrt{DB_3R_0^{11}}} , \quad \gamma_d = \frac{R_0}{R_d} , \quad \Lambda_d = \frac{\lambda_d R_0^7}{D_7} . \quad (2.22)$$

Thus,

$$\begin{aligned} d(R) &= \sqrt{\frac{DB_3}{R_0^3}} \bar{d}(X) \\ &= \sqrt{\frac{DB_3}{R_0^3}} Q (\Lambda_d e^{-\gamma_d X} - X^{-7}) . \end{aligned} \quad (2.23)$$

The laser field parameters are scaled by the frequency factor of time in (2.15) and the Stark shift due to the leading term in the polarisability B_3 . The pulse function is by definition a normalised, dimensionless function; thus, $f(t) = f(\tau)$. The scaled field amplitude and frequency are F and Ω , respectively,

$$F = |\mathcal{E}_0| \sqrt{\frac{B_3}{DR_0^3}} , \quad \Omega = \omega_c \sqrt{\frac{\mu R_0^2}{D}} , \quad (2.24a)$$

and for brevity

$$F(\tau) = Ff(\tau) \cos \Omega \tau . \quad (2.24b)$$

Using (2.19)–(2.24) in (2.11) with the scaling of the dynamical variables (2.15) gives the form of the Hamiltonian with energy scaled by a factor of D ,

$$H = D\bar{H} , \quad (2.25)$$

where the reduced Hamiltonian $\bar{H}^{(AC)}$ is

$$\begin{aligned} \bar{H}^{(AC)} = \frac{1}{2} \left(P_X^2 + \frac{P_\theta^2}{X^2} \right) + U_0(X) - F(\tau) \bar{d}(X) \cos \theta \\ - \frac{1}{4} F^2(\tau) \left[2\bar{\alpha}(X) + \bar{\beta}(X) \left(\frac{1}{3} + \cos 2\theta \right) \right] . \end{aligned} \quad (2.26)$$

Similarly, in the high-frequency limit, (2.12) becomes

$$\begin{aligned} \bar{H}^{(HFL)} = \frac{1}{2} \left(P_X^2 + \frac{P_\theta^2}{X^2} \right) + U_0(X) - \frac{1}{8} F^2 \left[2\bar{\alpha}(X) + \bar{\beta}(X) \left(\frac{1}{3} + \cos 2\theta \right) \right. \\ \left. - \frac{1}{\Omega^2} \left(\left(\bar{d}'(X) \right)^2 (1 + \cos 2\theta) + \left(\frac{\bar{d}(X)}{X} \right)^2 (1 - \cos 2\theta) \right) \right] . \end{aligned} \quad (2.27)$$

The Hamiltonians of (2.26) and (2.27) using the model potential, dipole and polarisability functions ((2.14), (2.23) and (2.19), respectively) are hereafter used exclusively in the analysis of the two-atom collision system. The over-line notation is accordingly dispensed with.

2.1.3 Partitions of the Hamiltonians

At this point it is necessary to identify and separate as much as possible the different effects present in $H^{(AC)}$ and $H^{(HFL)}$. The qualitative categories of the forces present are: isotropic (spherically symmetric), anisotropic (spherically asymmetric), time-independent and time-dependent. The first two are applicable to both Hamiltonians while the last are only relevant to $H^{(AC)}$.

2.1.3.1 Isotropic and Anisotropic Partitions

As in previous studies of anisotropic scattering [206, 270–275], an approximate separation of the laser-induced effects on the dynamics is made in order to assess the contribution of the anisotropic forces in both (2.26) and (2.27) vs. those which are isotropic. To accomplish this, the isotropic potential is defined by an average over $\cos\theta^4$. The difference between this and the full potential is the anisotropic contribution to the potential.

The time-dependent potential of (2.26) is partitioned according to

$$U^{(AC)}(X, \theta; F, \Omega, \tau) \equiv U_{\text{iso}}^{(AC)}(X; F, \Omega, \tau) + U_{\text{aniso}}^{(AC)}(X, \theta; F, \Omega, \tau) , \quad (2.28)$$

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⁴N.B.: This procedure identifies the components of the potential as obtained by a Legendre polynomial expansion.

where the isotropic potential is defined by [206]

$$\begin{aligned}
 U_{\text{iso}}^{(\text{AC})}(X; F, \Omega, \tau) &= \left\langle U^{(\text{AC})}(X, \theta; F, \Omega, \tau) \right\rangle_{\theta} \\
 &= \frac{1}{2} \int_0^\pi U^{(\text{AC})}(X, \theta; F, \Omega, \tau) \sin \theta d\theta \\
 &= U_0 - \frac{1}{2} F^2(\tau) \alpha \\
 &\equiv U_0 + U_{\text{iso}, \alpha}^{(\text{AC})},
 \end{aligned} \tag{2.29}$$

where the results of $\langle \cos \theta \rangle_{\theta} = 0$ and $\langle \cos 2\theta \rangle_{\theta} = -1/3$ have been used. The equation is further divided into the contributions from the field free potential $U_0(X)$ and the polarisability term $U_{\text{iso}, \alpha}^{(\text{AC})}$. The anisotropic part of $U^{(\text{AC})}(X, \theta; F, \Omega, \tau)$ is therefore,

$$\begin{aligned}
 U_{\text{aniso}}^{(\text{AC})}(X, \theta; F, \Omega, \tau) &\equiv U^{(\text{AC})}(X, \theta; F, \Omega, \tau) - U_{\text{iso}}^{(\text{AC})}(X; F, \Omega, \tau) \\
 &= - \left(F(\tau) d \cos \theta + \frac{1}{4} F^2(\tau) \beta \left(\frac{1}{3} + \cos 2\theta \right) \right) \\
 &\equiv U_{\text{aniso}, d}^{(\text{AC})} + U_{\text{aniso}, \alpha}^{(\text{AC})}.
 \end{aligned} \tag{2.30}$$

The last line defines the sub-partitions containing the permanent dipole and polarisability contributions, respectively.

Similarly the high-frequency limit potential (2.27) is partitioned into

$$U^{(\text{HFL})}(X, \theta; F, \Omega) \equiv U_{\text{iso}}^{(\text{HFL})}(X; F, \Omega) + U_{\text{aniso}}^{(\text{HFL})}(X, \theta; F, \Omega), \tag{2.31}$$

where

$$\begin{aligned}
 U_{\text{iso}}^{(\text{HFL})}(X; F, \Omega) &\equiv U_0 + U_{\text{iso}, d}^{(\text{HFL})} + U_{\text{iso}, \alpha}^{(\text{HFL})} \\
 &= U_0 + \frac{F^2}{12\Omega^2} \left(d'^2 + 2 \left(\frac{d}{X} \right)^2 \right) - \frac{F^2}{4} \alpha,
 \end{aligned} \tag{2.32}$$

and the anisotropic part is

$$\begin{aligned}
 U_{\text{aniso}}^{(\text{HFL})}(X, \theta; F, \Omega) &\equiv U_{\text{aniso},d}^{(\text{HFL})} + U_{\text{aniso},\alpha}^{(\text{HFL})} \\
 &= \frac{F^2}{8\Omega^2} \left(\frac{1}{3} + \cos 2\theta \right) \left(d'^2 - \left(\frac{d}{X} \right)^2 \right) - \frac{F^2}{8} \left(\frac{1}{3} + \cos 2\theta \right) \beta. \quad (2.33)
 \end{aligned}$$

The results of (2.29)–(2.33) are not specific to the scaling of their respective Hamiltonians; similar results are obtained for the unscaled systems (2.11) and (2.12).

2.1.3.2 Time-Dependent and Time-Independent Partitions

The basic separation between the time-independent parts of $U^{(\text{AC})}$ and the parts solely dependent on τ is accomplished by considering the cycle-averaged potential, $\langle U^{(\text{AC})} \rangle_{\phi_c}$. This is done by replacing $\Omega\tau$ in $U^{(\text{AC})}$ with ϕ_c , an arbitrary phase angle, and averaging over all angles⁵:

$$\begin{aligned}
 \left\langle U^{(\text{AC})}(X, \theta; F, \phi_c) \right\rangle_{\phi_c} &\equiv \frac{1}{2\pi} \int_0^{2\pi} U^{(\text{AC})}(X, \theta; F, \phi_c) d\phi_c \\
 &= U_0 - \frac{F^2}{8} \left(2\alpha + \beta \left(\frac{1}{3} + \cos 2\theta \right) \right) \\
 &= U_0 + U_{\text{iso},\alpha}^{(\text{HFL})} + U_{\text{aniso},\alpha}^{(\text{HFL})}. \quad (2.34)
 \end{aligned}$$

---

⁵N.B.: These results apply only to the c.w. case.

The potential $\langle U^{(AC)} \rangle_{\phi_c}$ defines the basic structure of the surface which the system experiences. Time-dependence is contained in the result of $U_{\tau}^{(AC)}$:

$$\begin{aligned}
 U_{\tau}^{(AC)} &\equiv U^{(AC)} - \langle U^{(AC)} \rangle_{\phi_c} \\
 &= -(F \cos \Omega \tau) d \cos \theta - \frac{F^2}{8} \cos 2\Omega \tau \left(2\alpha + \beta \left(\frac{1}{3} + \cos 2\theta \right) \right) \\
 &= U_{\text{aniso},d}^{(AC)} + (U_{\text{iso},\alpha}^{(AC)} - U_{\text{iso},\alpha}^{(\text{HFL})}) + (U_{\text{aniso},\alpha}^{(AC)} - U_{\text{aniso},\alpha}^{(\text{HFL})}) .
 \end{aligned} \tag{2.35}$$

The polarisability term in (2.35) depends on $2\Omega\tau$; thus fluctuations about $\langle U^{(AC)} \rangle_{\phi_c}$ in $U^{(AC)}$ due to the polarisability are inherently faster than those of the dipole. Again, the definitions of $\langle U^{(AC)} \rangle_{\phi_c}$ and $U_{\tau}^{(AC)}$ are independent of the scaling of the coordinate system.

2.1.4 Initial conditions and equations of motion

Initial conditions required to describe the dynamics are dependent on the type of experiment envisioned for the system. From chapter 1, a molecular beam scattering experiment was determined to be the most appropriate. Since the relative orientation of the field and initial momentum vector can be fixed experimentally, the initial conditions of the system can be chosen to be identical to those used normally to describe the field-free system [266]⁶. The initial conditions are shown in figure 2.1 The traditional scattering parameters are the impact parameter and collisional energy. The impact parameter b is the offset along the Cartesian coordinate perpendicular to the field ($\theta = 0$, also the field axis) axis and is scaled relative to R_0 . The collisional energy K is the initial kinetic energy of the separated atoms (i.e. when the potential is zero); it is scaled relative to D . Since the field is homogeneous, it is only meaningful to speak of initial collision conditions if the potential, including the

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⁶If the orientation of the two vectors are not under experimental control, an average over all such orientations would be required in the calculation of any observable (e.g. the differential cross section).

Figure 2.1: A schematic diagram of the collision system. The collision plane is shown along with definitions of the polar coordinate system in terms of the Cartesian axes. Distances identifying the initial conditions pertinent to the Hamiltonians (2.26) and (2.27) are shown. Since the field vector $\vec{\epsilon}$ and initial momentum vector $\vec{P}_i$ can be fixed as anti-parallel, the initial conditions are identical to those of the field-free system. See text and (2.36) for definitions. Note that the initial momentum $\vec{P}_i$ is found from $|\vec{P}_i| = \sqrt{2K}$.

interaction, goes to zero asymptotically⁷. For a three-dimensional system, b is defined on the interval $[0, +\infty)$ while $K \in (0, +\infty)$. Negative impact parameters are equivalent to a rotation in the azimuthal angle while values of $K \leq 0$ correspond to motion of bound states and do not describe scattering.

The initial conditions (K, b) refer to a state when the atoms are infinitely separated (denoted $\tau = -\infty$). For the trajectory calculations performed in the present work, the initial condition $(X_i, \theta_i, P_{X,i}, P_{\theta,i}, \tau = \tau_i)$ must be finite but correspond to (K, b) . This is accomplished by assuming that the trajectory from $\tau = -\infty$ to τ_i takes place in the absence of a potential. In this case, the motion is rectilinear and anti-parallel to the field axis. The initial conditions of a trajectory are then found from conversion of the Cartesian components of the momenta at $\tau = -\infty$ to polar ones:

$$X_i = \sqrt{X_{\text{dist}}^2 + b^2} \quad (2.36a)$$

$$\theta_i = \arctan\left(\frac{b}{X_{\text{dist}}}\right) \quad (2.36b)$$

$$P_{X,i} = -\sqrt{2K} \frac{X_{\text{dist}}}{\sqrt{X_{\text{dist}}^2 + b^2}} \quad (2.36c)$$

$$P_{\theta,i} = \sqrt{2K} b. \quad (2.36d)$$

In (2.36), the distance along the Cartesian coordinate parallel to the field axis is denoted X_{dist} . This is defined as the minimum distance from the scattering centre for which the potential is approximately zero. The appropriate value of X_{dist} is dependent on the specific nature of the potential used. In the present model, it must be a function of the parameters

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⁷Thus, collision dynamics between asymmetrically charged systems cannot be studied with (2.26) since $d(X) \sim QX$ and the interaction energy goes to infinity for the separated atoms. Charged systems are therefore required to be studied either in inhomogeneous fields, finite pulses, or in the momentum gauge of the field interaction [260].

Parameter type	Symbol
Dipole	Q, Λ_d, γ_d
Trace	$\Lambda_{\alpha_1}, \Lambda_{\alpha_2}, \gamma_\alpha$
Anisotropy	$\Lambda_{\beta_1}, \Lambda_{\beta_2}, \gamma_\beta$
Dynamical	X_{dist}, b, K
Laser	F, Ω, ϕ_c

Table 2.1: A summary and categorisation of the different parameters needed to specify a classical trajectory for the model Hamiltonians (2.26) and (2.27).

which describe the interaction (see table 2.1) and larger than the range of the potential ($X_{\text{dist}} \gg 1$). The numerical determination of X_{dist} is discussed in appendix C.1.

In the limit of high carrier frequency when (2.27) is valid, the laser is specified completely by F and Ω . For the c.w. case of (2.26), an additional initial condition is required to describe the phase of the laser field at the start of the collision. The carrier phase is thus $\phi_c \in [0, 2\pi]$; this initial condition is not under experimental control since is not possible to control at what point in time the two colliding atoms reach a distance where their interaction is non-negligible. Such a situation is equivalent to starting a trajectory at a fixed distance but with the laser at some arbitrary point in its cycle. The value of ϕ_c is completely random and hence any observables must be averaged over all (equally probable) values⁸.

The equations of motion for (2.26) are

$$\dot{X} = P_X \tag{2.37a}$$

$$\dot{\theta} = \frac{P_\theta}{X^2} \tag{2.37b}$$

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⁸N.B.: Although not considered presently, the case of a pulsed field requires the addition of an initial condition to the system. When the system reaches a point of non-negligible interaction, the pulse envelope may be at any point in its evolution. This point in time is some fraction of the total pulse period and thus defines a “pulse phase” ϕ_p . Isolated pulses are problematic in that they have an infinite period. In the calculation of the observables of the system, averaging the “pulse phase” ϕ_p must be performed in addition to that of ϕ_c .

$$\dot{P}_X = \frac{P_\theta^2}{X^3} - U'_0 + F(\tau)d' \cos \theta + \frac{1}{4}F^2(\tau) \left(2\alpha' + \beta' \left(\frac{1}{3} + \cos 2\theta \right) \right) \quad (2.37c)$$

$$\dot{P}_\theta = - \left(F(\tau)d \sin \theta + \frac{1}{2}F^2(\tau)\beta \sin 2\theta \right). \quad (2.37d)$$

The equations of motion for the subsystems of $U^{(AC)}$ are identical for the coordinates (2.37)(a) and (b); for $U_{\text{iso}}^{(AC)}$, the remaining equations are

$$\dot{P}_X = \frac{P_\theta^2}{X^3} - U'_0 + \frac{1}{2}F^2(\tau)\alpha' \quad (2.38a)$$

$$\dot{P}_\theta = 0, \quad (2.38b)$$

while for $U_{\text{aniso}}^{(AC)}$ they become

$$\dot{P}_X = \frac{P_\theta^2}{X^3} + F(\tau)d' \cos \theta + \frac{1}{4}F^2(\tau)\beta' \left(\frac{1}{3} + \cos 2\theta \right) \quad (2.39a)$$

$$\dot{P}_\theta = - \left(F(\tau)d \sin \theta + \frac{1}{2}F^2(\tau)\beta \sin 2\theta \right). \quad (2.39b)$$

In the case of the high frequency limit (2.27), the equations for the full potential $U^{(\text{HFL})}$ are

$$\dot{X} = P_X \quad (2.40a)$$

$$\dot{\theta} = \frac{P_\theta}{X^2} \quad (2.40b)$$

$$\begin{aligned} \dot{P}_X = & \frac{P_\theta^2}{X^3} - U'_0 + \frac{F^2}{8} \left[2\alpha' + \beta' \left(\frac{1}{3} + \cos 2\theta \right) \right. \\ & \left. - \frac{2}{\Omega^2} \left(d'd''(1 + \cos 2\theta) + \frac{d}{X^2} \left(d' - \frac{d}{X} \right) (1 - \cos 2\theta) \right) \right] \end{aligned} \quad (2.40c)$$

$$\dot{P}_\theta = \frac{F^2}{4} \left[\frac{1}{\Omega^2} \left(d'^2 - \left(\frac{d}{X} \right)^2 \right) - \beta \right] \sin 2\theta. \quad (2.40d)$$

As before the momentum equations are different for each partition; for $U_{\text{iso}}^{(\text{HFL})}$ these are given by

$$\dot{P}_X = \frac{P_\theta^2}{X^3} - U'_0 + \frac{F^2}{4} \left[\alpha' - \frac{2}{3\Omega^2} \left(d' d'' + 2 \frac{d}{X^2} \left(d' - \frac{d}{X} \right) \right) \right] \quad (2.41a)$$

$$\dot{P}_\theta = 0, \quad (2.41b)$$

and for $U_{\text{aniso}}^{(\text{HFL})}$ they are

$$\dot{P}_X = \frac{P_\theta^2}{X^3} - \frac{F^2}{4} \left(\frac{1}{3} + \cos 2\theta \right) \left[\frac{2}{\Omega^2} \left(d' d'' - \frac{d}{X^2} \left(d' - \frac{d}{X} \right) \right) - \beta' \right] \quad (2.42a)$$

$$\dot{P}_\theta = \frac{F^2}{4} \left[\frac{1}{\Omega^2} \left(d'^2 - \left(\frac{d}{X} \right)^2 \right) - \beta \right] \sin 2\theta. \quad (2.42b)$$

For the model potential and interaction functions used, the derivatives in (2.37) and (2.40) are defined as:

$$U'_0 = -12X^{-6}(X^{-6} - 1) \quad (2.43a)$$

$$d' = Q \left(\frac{7}{X^8} - \gamma_d \Lambda_d e^{-\gamma_d X} \right) \quad (2.43b)$$

$$d'' = Q \left(\gamma_d^2 \Lambda_d e^{-\gamma_d X} - \frac{56}{X^9} \right) \quad (2.43c)$$

$$\alpha' = \gamma_\alpha \Lambda_{\alpha_2} e^{-\gamma_\alpha X} - \frac{6\Lambda_{\alpha_1}}{X^7} \quad (2.43d)$$

$$\beta' = \gamma_\beta \Lambda_{\beta_2} e^{-\gamma_\beta X} - \frac{3}{X^4} \left(1 + \frac{2\Lambda_{\beta_1}}{X^3} \right). \quad (2.43e)$$

2.2 Features of the Potential Surface

While the dynamics of a collision are in general sensitive to the detailed shape of the potential surface, it is possible to define some simple quantities which provide a measure

of the features of the potential which will dominate the dynamics. Often these can be determined by the rotational and vibrational spectroscopy of bound systems [30] but additional quantities unique to the laser-modified system are given here. The $\cos 2\theta$ term in $U^{(\text{AC})}$ and $U^{(\text{HFL})}$ indicates that there will be local minima in the potential at $\theta = \{0, \pi\}$ while local maxima exist at $\theta = \{\pi/2, 3\pi/2\}$. Thus, quantities which characterise the potential parallel and perpendicular to the field axis are of particular interest.

The main features of the laser-diatom potential are described by: the equilibrium bond length, barrier position, radial dissociation energy, rotational well depth and rotational barrier height. The first two of these observables are defined by the condition:

$$\left(\frac{\partial U}{\partial X}\right) = 0, \quad (2.44)$$

where $U(X, \theta)$ is the potential energy function for the system, either $U^{(\text{AC})}$ or $U^{(\text{HFL})}$, the former at a fixed point in the laser cycle. The geometry at which the above is true gives the equilibrium bond length, $X_{\min}$, when the point corresponds to a local or global minimum in U ⁹. In general (2.44) has multiple solutions for any fixed θ ; those which correspond to a local or global maximum in U are denoted by $X_{\max}$.

Since U_0 possesses one minimum, the laser-modified potential will also have one at $\theta = 0$; the minimum at $\theta = \pi$ is identical for $U^{(\text{HFL})}$ or $U^{(\text{AC})}$ when there is no dipole. The radial dissociation energy Δ_e is defined by the minimum at $\theta = 0$,

$$\Delta_e = U(+\infty, 0) - U(X_{\min}, 0), \quad (2.45)$$

where the separated products are denoted by $X = +\infty$. Note that for $F = 0$, Δ_e corresponds

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⁹The condition (2.44) is identical for an unscaled system.

to the diatomic dissociation energy.

Both $U^{(\text{AC})}$ and $U^{(\text{HFL})}$ are symmetric perpendicular to the field axis, hence only the case $\theta = \pi/2$ is considered. Since any minima at $\theta = \pi/2$ must be higher in energy than at $\theta = 0$ (for $F > 0$), this implies the creation of a potential well along θ which hinders rotation. The rotational well is characterised by its well-depth, $\Delta_{\theta,-}$,

$$\Delta_{\theta,-} = U(X_{\min}, \pi/2) - U(X_{\min}, 0) . \quad (2.46)$$

If there are any local maxima in U perpendicular to the field, this implies the creation of a barrier to rotation at $\theta = \pi/2$. The barrier to rotation is associated with a positive potential energy ($U > U(+\infty)$) and is therefore not necessarily related to the rotational well. The barrier to rotation is characterised by its barrier height,

$$\Delta_{\theta,+} = U(X_{\max}, \pi/2) - U(+\infty, \pi/2) . \quad (2.47)$$

It should be noted that for $U^{(\text{AC})}$, the above properties become parametric functions of the laser phase $\phi_c \in [0, 2\pi]$. The values of $X_{\min}^{(\text{AC})}(\phi_c)$, $X_{\max}^{(\text{AC})}(\phi_c)$, $\Delta_e^{(\text{AC})}(\phi_c)$, $\Delta_{\theta,-}^{(\text{AC})}(\phi_c)$ and $\Delta_{\theta,+}^{(\text{AC})}(\phi_c)$ can either be averaged ($\langle X_{\min}^{(\text{AC})} \rangle_{\phi_c}$, $\sigma_{\text{RMS}, X_{\min}^{(\text{AC})}}$, etc ...) to obtain a measure of the features of $U^{(\text{AC})}$ or the features of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ can be examined. It is also of use when comparing $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ features to recall that $U^{(\text{AC})}$ experiences effectively larger values of F than $U^{(\text{HFL})}$ at the peak of the laser cycle. Thus, a $U^{(\text{AC})}$ feature may correspond to a $U^{(\text{HFL})}$ feature with a field of $\sqrt{2}F$.

2.3 Comparing Isotropic vs. Anisotropic and Time Independent vs. Time Dependent Effects

Given the partitions of the Hamiltonians of section 2.1.3, the initial conditions of section 2.1.4 and the potential features defined in 2.2, it is now possible to estimate the conditions under which the different effects in $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ will dominate the dynamics. As shown in 2.1.3, these are based on θ -dependence and τ -dependence and the two categories may be examined separately. The dynamical conditions are defined by the impact parameter and collision energy, b and K , respectively; each has three regimes, small ($\ll 1$), medium (~ 1) and large ($\gg 1$)¹⁰.

A general condition of a potential U having an influence on the motion of a system is $|U| \gtrsim K$, where $|U|$ is evaluated over the trajectory. Thus, if $K \gg |U|$ over the course of the collision, the potential energy has only a perturbative role. The estimate of $|U|$ is thus dependent on the impact parameter b since this generally determines which part of the potential is sampled by the trajectory. Examination of the potentials (vide infra) show that $|U|$ is best estimated by the potential features of section 2.2:

$$|U| \sim \begin{cases} \{\Delta_e, \Delta_{\theta,-}\} & , \text{ small or mid-range } b , \\ \{0.1\Delta_e, \Delta_{\theta,+}\} & , \text{ large } b . \end{cases} \quad (2.48)$$

In (2.48) each impact parameter region has one isotropic and one anisotropic potential feature associated with it, providing a measure of the energy scale of the corresponding potential partition. Note that the energy scale of the long-range isotropic part of U used for large b is obtained from the estimate $|U| \ll \Delta_e \approx 0.1\Delta_e$; this places an upper bound on the

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¹⁰N.B.: These are specific to the scaled coordinate system.

isotropic feature of the potential.

To estimate the conditions for the dominance of the isotropy vs. the anisotropy in $U^{(\text{HFL})}$, for example, the quantities K , $|U_{\text{iso}}^{(\text{HFL})}|$ and $|U_{\text{aniso}}^{(\text{HFL})}|$ are compared. This yields four basic regimes of the potential function:

$$K \gg \{|U_{\text{iso}}^{(\text{HFL})}|, |U_{\text{aniso}}^{(\text{HFL})}|\} \quad (\text{perturbative potential}), \quad (2.49a)$$

$$|U_{\text{iso}}^{(\text{HFL})}| \gtrsim K \gg |U_{\text{aniso}}^{(\text{HFL})}| \quad (\text{isotropic potential}), \quad (2.49b)$$

$$|U_{\text{aniso}}^{(\text{HFL})}| \gtrsim K \gg |U_{\text{iso}}^{(\text{HFL})}| \quad (\text{anisotropic potential}), \quad (2.49c)$$

$$\{|U_{\text{iso}}^{(\text{HFL})}|, |U_{\text{aniso}}^{(\text{HFL})}|\} \gtrsim K \quad (\text{coupled potential}). \quad (2.49d)$$

Conditions similar to (2.49) apply to $U^{(\text{AC})}$ by replacing $\{U_{\text{iso}}^{(\text{HFL})}, U_{\text{aniso}}^{(\text{HFL})}\}$ with $\{\langle U_{\text{iso}}^{(\text{AC})} \rangle_{\phi_c}, \langle U_{\text{aniso}}^{(\text{AC})} \rangle_{\phi_c}\}$. Use of these conditions for either potential requires the substitution of the relevant quantities of equation (2.48) in (2.49). For example, in the small b range for $U^{(\text{HFL})}$, $|U_{\text{iso}}^{(\text{HFL})}| \sim \Delta_e^{(\text{HFL})}$ and $|U_{\text{aniso}}^{(\text{HFL})}| \sim \Delta_{\theta,-}^{(\text{HFL})}$. Therefore, once $\{\Delta_e^{(\text{HFL})}, \Delta_{\theta,-}^{(\text{HFL})}\}$ are known for the pertinent value of F , the potential regime can be determined for a given K . In the case of $U^{(\text{AC})}$, the relevant properties are of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ and hence the corresponding $U^{(\text{HFL})}$ features can be used provided $(U_{\text{iso},d}^{(\text{HFL})}, U_{\text{aniso},d}^{(\text{HFL})}) \approx 0$.

The different potential regimes of equation (2.49) are indicative of what will determine the form of the motion of the system. In the perturbative potential regime, motion is approximately that of a $U = 0$ system since K is larger than any feature of U . In either the isotropic or anisotropic regimes, the dynamics is determined by U_{iso} or U_{aniso} , respectively, with the remaining partition contributing in a perturbative role. The coupled regime is the case where the motion is sensitive to all features of the potential.

In the case of $U^{(\text{AC})}$, the additional time-dependence raises the question of whether

$\langle U^{(AC)} \rangle_{\phi_c}$ or the fluctuations due to $U_{\tau}^{(AC)}$ have a more significant influence on the motion; this can be estimated by considering both the amplitude of the potential fluctuations and their relative time scale compared to the motion of the system. The energy scale of $\langle U^{(AC)} \rangle_{\phi_c}$ is established for a given impact parameter range (via (2.48)) by use of $\langle U^{(AC)} \rangle_{\phi_c} = U^{(HFL)}$ (homonuclear) and determining the properties of $\{\Delta_e^{(HFL)}, \Delta_{\theta,-}^{(HFL)}, \Delta_{\theta,+}^{(HFL)}\}$ for the appropriate field. The energy scale of the fluctuations in $U_{\tau}^{(AC)}$ can be estimated by the variance of $U^{(AC)}$ over the laser cycle [276]:

$$\begin{aligned} \sigma_{\text{RMS},U^{(AC)}} &\equiv \left[\langle U^{(AC)2} \rangle_{\phi_c} - \langle U^{(AC)} \rangle_{\phi_c}^2 \right]^{1/2} \\ &= \frac{1}{2\sqrt{2}} \left[4U_{\text{aniso},d}^{(AC)2} \sec^2 \phi_c + \left(U_{\text{iso},\alpha}^{(AC)} + U_{\text{aniso},\alpha}^{(AC)} \right)^2 \sec^4 \phi_c \right]^{1/2} \\ &= \frac{1}{\sqrt{2}} \left[U_{\text{aniso},d}^{(AC)2} \sec^2 \phi_c + \left(U_{\text{iso},\alpha}^{(HFL)} + U_{\text{aniso},\alpha}^{(HFL)} \right)^2 \right]^{1/2}. \end{aligned} \quad (2.50)$$

Note that in (2.50) there is no ϕ_c -dependence due to the definitions of the partitions given in section 2.1.3.1.

An estimate of $\sigma_{\text{RMS},U^{(AC)}}$ in a given b -range is obtained by approximately evaluating the variance of a potential feature of $U^{(AC)}$. Let $u^{(AC)}$ be one of $\{\Delta_e^{(AC)}, \Delta_{\theta,-}^{(AC)}, \Delta_{\theta,+}^{(AC)}\}$:

$$\begin{aligned} \sigma_{\text{RMS},U^{(AC)}}^2 &\approx \sigma_{\text{RMS},u^{(AC)}}^2 \\ &= \langle u^{(AC)2} \rangle_{\phi_c} - \langle u^{(AC)} \rangle_{\phi_c}^2 \\ &\leq \max\{u^{(AC)2}(\phi_c)\} - \langle u^{(AC)} \rangle_{\phi_c}^2 \\ &\approx \max\{u^{(AC)2}(\phi_c)\} - u^{(HFL)2}. \end{aligned} \quad (2.51)$$

The above result is an approximate upper bound on the amplitude. Note that $u^{(HFL)}$ refers to the corresponding potential feature evaluated with $\langle U^{(AC)} \rangle_{\phi_c} \approx U^{(HFL)}$ as in (2.49).

In analogy with (2.49), there are four regimes which classify the amplitudes,

$$\{|\langle U^{(AC)} \rangle_{\phi_c}|, \sigma_{\text{RMS}, U^{(AC)}}\} \ll K \quad (\text{perturbative amplitude}), \quad (2.52a)$$

$$|\langle U^{(AC)} \rangle_{\phi_c}| \gtrsim K \gg \sigma_{\text{RMS}, U^{(AC)}} \quad (\text{small amplitude}), \quad (2.52b)$$

$$\sigma_{\text{RMS}, U^{(AC)}} \gtrsim K \gg |\langle U^{(AC)} \rangle_{\phi_c}| \quad (\text{large amplitude}), \quad (2.52c)$$

$$\{|\langle U^{(AC)} \rangle_{\phi_c}|, \sigma_{\text{RMS}, U^{(AC)}}\} \gtrsim K \quad (\text{coupled amplitude}). \quad (2.52d)$$

The potential features used to estimate $|\langle U^{(AC)} \rangle_{\phi_c}|$ and $\sigma_{\text{RMS}, U^{(AC)}}$ (via (2.51)) are given in (2.48) for a specified b -range. As in the potential regimes of (2.49), the perturbative amplitude regime predicts that the dynamics will be only perturbed by the presence of $U^{(AC)}$. The small amplitude regime indicates that the variation of the relevant potential features of the laser cycle is small enough that the qualitative nature of the potential is effectively that of $\langle U^{(AC)} \rangle_{\phi_c}$. In contrast, the large amplitude regime predicts that $\langle U^{(AC)} \rangle_{\phi_c}$ has little contribution to the motion since the fluctuations of $U_{\tau}^{(AC)}$ are large. Finally, the coupled amplitude regime expresses the case where the motion will be sensitive to all the details of the potential for any given part of the laser cycle.

The conditions of (2.52) establish the importance of the amplitude of fluctuations in $U^{(AC)}$. However, these are not only considerations; it is well known that even small amplitude forced oscillations can greatly affect the dynamics of a system when they are in or near resonance [266]. Resonance requires a matching of the time scales of both the system motion and the oscillation period. In the present case, the laser period $2\pi/\Omega$ must be similar to the time scale of the motion on $U^{(AC)}$. For unbound ($K > 0$) states the time scale is measured by the time required for the system to travel in a straight line across a circle of radius X_i , $\tau_{\text{coll}} = \sqrt{2/K} X_i \cos \theta_i$, where $\cos \theta_i$ is the initial angle (see (2.36)). As an order of

magnitude estimate, let $X_i \cos \theta_i = b\pi$, where b is the impact parameter (see section 2.1.4).

The ratio of τ_{coll} to the laser period is thus

$$w = \frac{\Omega b}{\sqrt{2K}}. \quad (2.53)$$

The quantity w thus gives the number of laser periods over the time scale of the collision. There are three cases of time scale based on (2.53):

$$w \ll 1, \text{ static field limit} \quad (2.54a)$$

$$w \sim 1, \text{ resonance} \quad (2.54b)$$

$$w \gg 1, \text{ high frequency limit.} \quad (2.54c)$$

The high frequency limit has been noted previously and is time-independent since the system cannot respond to the laser oscillations fast enough. The system dynamics will be very sensitive to the fluctuations in $U^{(\text{AC})}$ when $w \sim 1$ in the resonance regime; in this regime it is possible that the perturbative- and small amplitude regimes of (2.52) will exhibit significant departures from the effectively time-independent behaviour of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ -dynamics predicted. Finally, as $w \rightarrow 0$, the system approaches the static field limit where the oscillations in $U^{(\text{AC})}$ are negligible compared to the limited time of the collision. Thus time-dependence in this limit is also negligible and only the conditions of (2.52) are relevant.

2.4 Dynamical Observables

Since the elastic collision system (2.27) is effectively two dimensional the trajectories of the classical collisions generated by integrating the equations of motion (2.37) are suffi-

ciently described by the rotation of the momentum vector $\vec{P}_f$ relative to its initial direction $\vec{P}_i$ in the plane of fixed azimuthal angle¹¹. The absence of time-dependence in (2.12) implies the total energy is conserved in the collision and thus only the partitioning of the momentum between the two components can change as a result of the collision. Therefore the dynamics are completely described by measuring the change in direction of the total momentum vector and the magnitude of its components relative to their values at the start of the trajectory. The dynamical observables of the system which measure these are the deflection angle, scattering angle, angular- and radial momentum difference, and the differential and integrated cross sections. In the case of the time-dependent system (2.26), the lack of energy conservation permits gain or loss of energy by the molecule in addition to the repartitioning of the final momentum.

2.4.1 The Deflection and Scattering Angles

The change in the direction of $\vec{P}$ as a result of collision is described by an angle of deflection χ and a scattering angle Θ in the centre of mass frame [131, 180, 277]. The relationship between them is given by

$$\Theta = (-1)^n(|\chi| - 2m\pi), \quad (2.55)$$

where

$$n = \left\lfloor \frac{|\chi|}{\pi} \right\rfloor, \quad m = \left\lfloor \frac{n+1}{2} \right\rfloor \quad (2.56)$$

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¹¹For three-dimensional systems, the rotation of the momentum vector must be described by a vector with in-plane and out-of-plane rotation angles [199, 206].

and the brackets $\lfloor \rfloor$ denote the integer of the expression. From (2.55), it is clear that $\Theta \in [0, \pi]$.

The deflection angle χ yields more information regarding the path of the collision as it can take values of $\chi \in [-\infty, +\infty]$. In a central potential, such as U_0 , χ is given by the integral¹² [131]

$$\chi = \pi - 2b \int_{X_c}^{\infty} \frac{dX}{X^2 \sqrt{1 - (b^2/X^2) - (U_0/K)}} . \quad (2.57)$$

Here, X_c denotes the distance of closest approach. Specifically, it is the largest root of the radical in (2.57):

$$X_c \equiv \max\{X | 1 - (b/X)^2 - (U_0/K) = 0\} . \quad (2.58)$$

Both energy and angular momentum conservation are used in the derivation of (2.57); it is therefore inappropriate for the case of $F \neq 0$. Even in the case of a field-free system, it is not useful when the dynamics are solved by integrating equations of motion since the exact value of X_c is not easily determined with arbitrary accuracy. However, X_c is conceptually useful in the qualitative analysis of dynamics since, from (2.57), χ is very sensitive to it and such sensitivity should persist in the $F \neq 0$ case for trajectories which behave like those of a central potential.

The interpretation of χ in a field-free system relates its value to the orbiting of the system about the scattering centre [131, 180, 266, 277]. Thus, rotation of the momentum vector is related to the rotation of the position vector of the system. This relationship can be

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¹²This formula is identical in to the result in an unscaled coordinate system provided the impact parameter outside the integral is multiplied by R_0 .

proven for a non-central potential. The result, which is derived in appendix D, is expressed in terms of the initial and final values of the polar position angle, thus removing any need for the determination of X_c :

$$\begin{aligned}\chi &= \pi - \theta_{+\infty} \\ &\approx \pi - (\theta_i + \theta_f) ,\end{aligned}\tag{2.59}$$

where $\theta_{(i,f)}$ are the polar angles at the initial and final (finite) trajectory times. In the limit of infinite collision time, the value of $\theta_i = \theta_{-\infty} = 0$ and it follows that the exact deflection angle is only a function of the final position angle $\theta_{+\infty}$. The approximation which allows the use of finite integration time is valid when $\tau_{(i,f)}$ are very large (i.e. well outside the region of interaction) and $X_i = X_f$. Thus the condition, $X_i = X_f \gg 1 |U(X_{(i,f)}, \theta; \tau) \approx 0$ defines a “shell” beyond which the collision is effectively “over.” In the case of $U^{(AC)}$, the deflection angle is parametrically dependent on the carrier phase ϕ_c and thus averaged quantities $\langle \chi^{(AC)} \rangle_{\phi_c}$ and $\langle \Theta^{(AC)} \rangle_{\phi_c}$ and their standard deviation may be of interest.

2.4.2 The Collision Cross Sections

Once the scattering function $\Theta^{(HFL)}(b, K)$ or $\Theta^{(AC)}(b, K, \phi_c)$ is obtained from integration of the equations of motion (2.37) and (2.55), a classical differential and integrated cross section can be calculated for comparison with experiment and more sophisticated calculations. The definition of a collision cross section in the literature [131, 191, 199, 205, 266, 278] is valid for the systems of (2.26) and (2.27) since the differential cross section is not dependent on the azimuthal angle. The differential cross section of the number of

particles scattered per unit solid angle into an angle ζ per unit time is given by (for $H^{(\text{AC})}$)¹³

$$\frac{d\sigma^{(\text{AC})}}{d\Omega}(\zeta; K, F, \Omega) = \frac{1}{2\pi} \int_0^{2\pi} \sum_{k=1}^N b_k \csc \zeta \left| \left(\frac{\partial \Theta^{(\text{AC})}}{\partial b} \right) \right|_{b=b_k}^{-1} d\phi_c \quad (2.60)$$

where the scattering function $\Theta^{(\text{AC})}(b; K, F, \Omega, \phi_c)$ and its inverse $b(\Theta^{(\text{AC})}; K, F, \Omega, \phi_c)$ are defined in (2.55) over the domain of laser and collision parameters. For $H^{(\text{HFL})}$, $d\sigma^{(\text{HFL})}/d\Omega$ is calculated according to (2.60) with the simplification that no ϕ_c -dependence is present. Note that $\zeta \in [0, \pi]$ and that the averaging over ϕ_c is required for both $U^{(\text{AC})}$ and $U^{(\text{HFL})}$ since it is not a spatial variable [199]¹⁴. In general, there will be $N(\zeta; K, F, \Omega, \phi_c)$ impact parameters which give rise to a given scattering angle, and hence the summation over all b_k contributions to the differential cross section is required; this can range from zero to infinity in the case of an orbiting singularity [131, 180]. Although there are a number of ways to numerically evaluate (2.60) [198, 200–204], presently the $\{b_k\}$ are found from the roots of the equation $\Theta^{(\text{AC})}(b; K, F, \Omega, \phi_c) - \zeta = 0$ and the derivative term in (2.60) is evaluated directly using either finite differences or the analytical derivatives found from fitting to a spline [279]. Note that the ϕ_c -averaged cross section is only related to $\langle \Theta^{(\text{AC})} \rangle_{\phi_c}$ through an expansion in the distribution moments of $\Theta^{(\text{AC})}$ so averaging must be the last operation [276, 279].

The integrated cross section σ is defined by integration of (2.60) over solid angles larger than ζ ¹⁵. The result, while known, is derived in appendix E (equation (E.15)) since it is

¹³The common symbol for the solid angle $d\Omega$ element should not be confused with that of the laser frequency.

¹⁴N.B.: The result of (2.60) is multiplied by a factor of R_0^2 to obtain the result of an unscaled coordinate system.

¹⁵N.B.: This is also known as the incomplete integrated cross section. The total cross section is defined when the integration extends over all solid angles.

not forthcoming¹⁶ in the literature [184, 199, 200]¹⁷. For $H^{(AC)}$, $\sigma^{(AC)}(\zeta; K, F, \Omega)$ is found from

$$\begin{aligned}\sigma^{(AC)}(\zeta; K, F, \Omega) &= \left\langle \int_{\sigma(\zeta)}^{\sigma(\pi)} d\sigma \right\rangle_{\phi_c} \\ &= - \left\langle \int_{\zeta}^{\pi} \int_0^{2\pi} \frac{d\sigma^{(AC)}}{d\Omega} \sin \Theta d\Theta d\phi \right\rangle_{\phi_c} \\ &= \pi \left\langle \sum_{k=0}^N s'_k b_k^2 \right\rangle_{\phi_c}.\end{aligned}\tag{2.61}$$

In the case of $\sigma^{(HFL)}$, (2.61) is used with the understanding that there is no ϕ_c dependence in $d\sigma^{(HFL)}/d\Omega$. The integration in (2.61) extends over all azimuthal angles ϕ and scattering angles $\Theta \geq \zeta$. Thus $\sigma(\zeta)$ denotes the collisional cross section for all angles greater than or equal to ζ . The sum in (2.61) is over all $N(\zeta; K, F, \Omega, \phi_c)$ roots of $\Theta^{(AC)}(b; K, F, \Omega, \phi_c) - \zeta = 0$ as in (2.60) and s'_k (see equation (E.13)) is zero for roots where $\partial\Theta/\partial b$ is zero and the negative sign of the derivative otherwise. The result of (2.61) is valid for the deflection functions encountered in atom-atom collisions; the more general case is discussed in appendix E.

2.4.3 Special Features of the Differential Cross Section

While the relationship between U and the differential cross section of (2.60) is in general complex, there exist characteristic features which, when present, can be related to the behaviour of the deflection function $\chi(b)$. The deflection function possesses these characteristic features because there are classes of collisions which are generic to atom-atom

¹⁶Of the literature cited, only [200] reports results which are valid for arbitrary molecular potentials. Others simply give the special case which is valid for inverse deflection functions with only three branches.

¹⁷As for the differential cross section, the unscaled form of (2.61) is obtained by multiplying by R_0^2 .

scattering potentials. The deflection function can then be used, through approximate treatments, to relate potential surface features with those of the differential cross section. The types of collisions which are common diagnostic tools in isotropic collisions are: glory-, rainbow-, small angle- and orbital scattering.

Since no quantitative use is made of the formulae presented here and their derivation follows essentially that of the literature, only a brief outline of the method is given. However, the results presented here are of great use in interpreting the contributions to the scattering intensity (i.e. the differential cross section) of various laser-induced features of the deflection functions of $\chi^{(\text{AC})}$ and $\chi^{(\text{HFL})}$.

2.4.3.1 Small-Angle Scattering

The most prominent feature of the differential cross section is due to small-angle scattering [131, 191–193]. To illustrate its contribution, consider a deflection function $\chi(b)$ which asymptotically approaches zero from either positive or negative values:

$$\chi(b) \sim cb^{-s}, \quad (2.62)$$

where c and s are constants dependent on the potential function and other collision conditions. Since $\Theta \sim 0$, it follows that only the branches of $\chi \in (-\pi, +\pi)$ need be considered and hence, by (2.55), $\Theta = |\chi|$. Thus, inversion of the scattering function is straightforward and substitution into (2.60) yields

$$\sin \Theta \frac{d\sigma}{d\Omega} \sim \frac{|c|^{2/s}}{s} \Theta^{-(s+2)/s}. \quad (2.63)$$

Thus the small-angle scattering, related to the large b portion of $\chi(b)$, produces an infinity in the differential cross section at $\Theta = 0$. The exponent and proportionality constant of this singularity can be related to the potential function parameters by considering models of $\chi(b)$ such as that obtained by the impulse approximation. In general a broad (narrow) singularity, characterised by small (large) s and large (small) $|c|$, indicates a weak (strong) long-range potential. Note that the singularity is independent of the sign of c and hence attractive ($c < 0$) long-range scattering is indistinguishable from repulsive ($c > 0$).

Since small-angle scattering is due to large impact parameters, it is also the primary contribution to the integrated cross section (see equation (2.61)). Using the above model for $\chi(b)$, a simple calculation yields

$$\sigma(\zeta) \sim \pi \left(\frac{|c|}{\zeta} \right)^{2/s}. \quad (2.64)$$

Thus a stronger long-range potential will increase the integrated cross section for a given angle $\zeta \ll 1$.

2.4.3.2 Glory Scattering

For molecular potentials, glory scattering occurs when the attractive and repulsive forces of the potential balance and the resulting deflection angle is $\chi = n\pi$ with $n \in \mathbb{Z}$ for a finite impact parameter [180, 186, 191]; forward glories have n even and map to $\Theta = 0$ while backward glories are of odd n and map to $\Theta = \pi$. Forward glory scattering causes an additional singularity at $\Theta = 0$ in the differential cross section which is superimposed with that of small angle scattering (see section 2.4.3.1).

To examine the contribution of glory scattering to the differential cross section, the

deflection function $\chi(b)$ is expanded in a Taylor series to first order,

$$\chi(b) \approx n\pi + \chi'_g(b - b_g), \quad (2.65)$$

where the glory impact parameter b_g and the corresponding slope χ'_g are determined by the details of the dynamics. Inversion of the above equation using the scattering angle definition (2.55) and substitution into (2.60) yields two branches of $b(\Theta)$ contributing to the differential cross section; this is because $\chi(b)$ changes branches at b_g . The result is independent of the particular value of n , only on the glory being forward or backward¹⁸:

$$\frac{d\sigma}{d\Omega} \sim \begin{cases} 2b_g/|\chi'_g\Theta| & , \text{ forward glory,} \\ 2b_g/|\chi'_g(\pi - \Theta)| & , \text{ backward glory.} \end{cases} \quad (2.66)$$

Note that the factor of $\sin\Theta$ has been expanded about the glory angle.

The result of (2.66) shows that the divergence of the differential cross section at $\Theta = 0$ or π is much slower than that of (2.63). The forward glory scattering is thus always obscured by small-angle scattering intensity contribution. However, backward glory scattering can be identified using (2.66) or noting that $\sin\Theta d\sigma/d\Omega$ has a non-zero limit at $\Theta = \pi$. The intensity contribution is large when b_g is large and $|\chi'_g|$ is small. If there are more than one b_g then the intensity contribution is the sum over all such glories as determined by (2.66).

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¹⁸Note the error in the corresponding result found in [191].

2.4.3.3 Rainbow Scattering

An additional prominent feature of classical scattering which can be related to the potential parameters is rainbow scattering [131, 180, 184]. This type of scattering occurs when the deflection angle becomes stationary with respect to variations in impact parameter. Thus $\chi(b)$ must pass through a local extremum. The scattering angle contains a local extremum and consequently there is a singularity in the differential cross section. Additional types of rainbow singularities in scattering can occur due to multiple collisions in many-body systems [203, 205, 208, 270, 272, 275]. The rainbow singularity is important in the interpretation of quantum mechanical cross sections [186, 187, 189, 190] and can be used to obtain the potential parameters.

The contribution to the differential cross section from rainbow scattering is found from an expansion of $\chi(b)$ to second order:

$$\chi(b) \approx \chi_r + \frac{1}{2} \chi_r'' (b - b_r)^2, \quad (2.67)$$

where b_r is the impact parameter where the extremum occurs, χ_r is the rainbow deflection angle and χ_r'' is the curvature at this point. Using (2.55) yields an inverse scattering function which has two branches,

$$b_{\pm}(\Theta) = b_r \pm \sqrt{(2/\chi_r'') \text{sgn}(\chi_r) (-1)^{n_r} (\Theta - \Theta_r)}. \quad (2.68)$$

Here, n_r is given by (2.55) with $\chi = \chi_r$ and Θ_r is the corresponding rainbow scattering angle.

Use of the above inverse scattering function in (2.60) yields an approximate form of the

differential cross section near the rainbow angle:

$$\sin \Theta \frac{d\sigma}{d\Omega} \sim \begin{cases} |2b_r/\chi_r''(\Theta - \Theta_r)|^{1/2} & , \text{bright side,} \\ 0 & , \text{dark side.} \end{cases} \quad (2.69)$$

Note the singularity at $\Theta = \Theta_r$. The bright, or non-zero intensity, side of a rainbow is determined from the condition $\text{sgn}(\chi_r)\text{sgn}(\chi_r'')(-1)^{n_r}(\Theta - \Theta_r) > 0$. Thus, a forward rainbow is defined such that the bright side lies on the interval $0 < \Theta < \Theta_r$ while a backward rainbow has a bright side on $\Theta_r < \Theta < \pi$; the two types of rainbows are distinguished by the condition

$$\text{sgn}(\chi_r)\text{sgn}(\chi_r'')(-1)^{n_r} = \begin{cases} -1 & , \text{forward rainbow,} \\ +1 & , \text{backward rainbow.} \end{cases} \quad (2.70)$$

The singularity in the differential cross section due to rainbow scattering is seen from (2.69) to be completely characterised by the parameters of b_r , χ_r and χ_r'' ; these can be found numerically and are dependent on the potential function. The position of the singularity is Θ_r and the intensity depends on $b_r/|\chi_r''|$, yielding the broadness of the singularity, a small value indicating a narrow spike and vice versa.

2.4.3.4 Orbital Scattering

For a binary system with a central potential containing an attractive component, it is possible for the system to become “trapped” in a periodic orbit [131, 180]. This corresponds physically to the situation when the two collision partners rotate about the centre of mass with a constant separation. The deflection angle in this case goes to $\pm\infty$ depending on

the sense of rotation about the scattering centre. Since the orbit is unstable, the deflection function $\chi(b, K)$ in the vicinity of the singularity is characterised by large deflection angles and fast oscillations in the scattering function $\Theta(b, K)$.

The orbiting phenomenon is the result of a balance of forces in a trajectory and consequently the quantification of the impact parameter where it occurs, $b_{orb,(\pm)}$ and the maximum collision energy for which it is allowed, $K_{orb,(\pm)}$ (the $\pm$ label refers to the sign of the infinity) can be related to the potential parameters, which includes the laser parameters in the present case¹⁹. The conditions for orbiting are defined for an arbitrary central potential [191, 194]. Briefly, there must be a maximum in the centrifugally modified potential

$$U'(X) - \frac{P_\theta^2}{X^3} = 0, \quad (2.71)$$

where the prime denotes the derivative with respect to X . This specifies the orbiting radius $X_{orb,(\pm)}$ in terms of the angular momentum. The trajectory must arrive exactly at the maximum in order to remain at the orbiting radius. Thus $U(X_{orb,(\pm)}) = K$ and it follows from (2.71) that

$$K = U(X_{orb,(\pm)}) + \frac{X_{orb,(\pm)}}{2} U'(X_{orb,(\pm)}). \quad (2.72)$$

The collision energy and impact parameter where orbiting can occur are thus completely specified by (2.71) and (2.72), noting that, by (2.36) $P_\theta = \pm b\sqrt{2K}$ for a central potential. Maximisation of (2.72) gives the largest collision energy which allows orbiting

$$3U'(X_{orb,(\pm)}) + X_{orb,(\pm)} U''(X_{orb,(\pm)}) = 0, \quad (2.73)$$

---

¹⁹Above the maximum orbiting energy, rainbow scattering is observed [131, 191].

where the resulting $X_{orb,(\pm)}$ is substituted into (2.72) to obtain $K_{orb,(\pm)}$. The sign of the infinity for an isotropic potential is determined by the sign of the initial angular momentum; positive (negative) P_θ yields $b_{orb,(-)}$ and $K_{orb,(-)}$ ($b_{orb,(+)}$ and $K_{orb,(+)}$).

From the above results, a given collision energy $K \leq K_{orb,(\pm)}$ will have exactly one trajectory $b = b_{orb,(\pm)}$ which exhibits orbiting. In general, the value of $b_{orb,(\pm)}$ increases as K decreases, making this a function of the long-range attractive part of the potential. The value of $K_{orb,(\pm)}$, in contrast, is defined by the presence of a short range repulsion in the potential (in order for it to be finite). The behaviour of the deflection function near an orbiting singularity is described by a logarithmically divergent function [180, 186]:

$$\chi(b) \approx \begin{cases} \chi_+ + k_+ \ln(\xi - 1) & , \xi > 1, \\ \chi_- + k_- \ln(1 - \xi) & , \xi < 1, \end{cases} \quad (2.74)$$

where $\xi = b/b_{orb,(\pm)}$ and $\{\chi_\pm, k_\pm\}$ are arbitrary constants²⁰.

The inverse scattering function is now an infinitely-valued function, each branch of which contributes to the differential cross section. Substitution of the value of each branch term into (2.60) yields

$$\begin{aligned} \sin \Theta \frac{d\sigma}{d\Omega} \approx & b_{orb,(\pm)}^2 \sum_{n=0}^{\infty} \frac{1}{|k_+|} \left[\exp \left(-\frac{(-1)^n \Theta + 2m\pi - \chi_+}{|k_+|} \right) \right. \\ & \left. + \exp \left(-2 \left(\frac{(-1)^n \Theta + 2m\pi - \chi_+}{|k_+|} \right) \right) \right] + \frac{1}{|k_-|} \left[\exp \left(-\frac{(-1)^n \Theta + 2m\pi - \chi_-}{|k_-|} \right) \right. \\ & \left. + \exp \left(-2 \left(\frac{(-1)^n \Theta + 2m\pi - \chi_-}{|k_-|} \right) \right) \right]. \quad (2.75) \end{aligned}$$

---

²⁰N.B.: For a central potential, these constants are determined by the behaviour of the potential near the barrier; this is also the origin of the logarithmic form of the deflection function. However, the form is also applicable to anisotropic potentials but the constants no longer have the same significance.

Here, $m = \lfloor (n+1)/2 \rfloor$.

The above equation may be simplified by rearranging some of the series terms and use of the binomial series [280] giving the final form of the orbiting contribution to be

$$\begin{aligned} \sin \Theta \frac{d\sigma}{d\Omega} \approx & \frac{b_{orb,(\pm)}^2}{|k_+| e^{\chi_+/k_+} (1 - e^{-\pi/|k_+|})} \left\{ e^{-\Theta/|k_+|} + e^{-(\pi-\Theta)/|k_+|} \right. \\ & \left. + \frac{1}{1 + e^{-\pi/|k_+|}} \left[e^{-2\Theta/|k_+|} + e^{-2(\pi-\Theta)/|k_+|} \right] \right\} \\ & + \frac{b_{orb,(\pm)}^2}{|k_-| e^{\chi_-/k_-} (1 - e^{-\pi/|k_-|})} \left\{ e^{-\Theta/|k_-|} + e^{-(\pi-\Theta)/|k_-|} \right. \\ & \left. + \frac{1}{1 + e^{-\pi/|k_-|}} \left[e^{-2\Theta/|k_-|} + e^{-2(\pi-\Theta)/|k_-|} \right] \right\}. \quad (2.76) \end{aligned}$$

Note that, in (2.76), the orbital contribution to the differential cross section is independent of the sign of $k_{\pm}$, indicating that it is impossible to distinguish the sign of the orbiting singularity from this. The intensity contribution is generally small compared to other contributions due to the exponential form but is symmetric about $\Theta = \pi/2$ and is proportional to $b_{orb,(\pm)}^2$.

2.5 Approximate Models

In order to anticipate the effect of the laser parameters on the system, simplifications are applied to $U^{(HFL)}$ which yield analytic expressions for the system observables described in section 2.4.

2.5.1 The Static Field Limit

The static field limit defined in section 2.3 also represents a useful quantitative tool for evaluating the approximate dynamics. Since the potential is effectively one with a field of $F(\tau) = F \cos \phi_c$ in $U^{(AC)}$. If the system has no dipole terms,

$$U^{(AC)} \xrightarrow{w \ll 1} \langle U^{(AC)} \rangle_{\phi_c} \quad (2.77a)$$

in the static field limit where the substitution

$$F \rightarrow F \sqrt{2} \cos \phi_c \quad (2.77b)$$

is made into $\langle U^{(AC)} \rangle_{\phi_c}$. Since $U^{(HFL)} = \langle U^{(AC)} \rangle_{\phi_c}$, (2.77) demonstrates that any approximate result obtained for $U^{(HFL)}$ can be related to $U^{(AC)}$ in the static field limit if the appropriate range of fields are used.

2.5.2 Potential Features of the HDID Model

The properties sought are those of $U^{(HFL)}$ defined in section 2.2: $X_{\min}^{(HFL)}$, $\Delta_e^{(HFL)}$, $X_{\max}^{(HFL)}$, $\Delta_{\theta,-}^{(HFL)}$ and $\Delta_{\theta,+}^{(HFL)}$ (if the last three exist). The main effort in obtaining expressions for these quantities is in finding an approximate model which yields an exact solution to (2.44). This is possible for $U^{(HFL)}$ or $\langle U^{(AC)} \rangle_{\phi_c}$ provided two assumptions are made: (a) for $U^{(HFL)}$, the system is homonuclear ($Q = 0$ in (2.23)); (b) the short-range exchange terms in the polarisability are neglected ($\Lambda_{\alpha_2} = \Lambda_{\beta_2} = 0$ in (2.19)). The resulting homonuclear,

dipole-induced dipole (HDID) model of the potential gives (from (2.27)),

$$U^{(\text{HFL})} \approx X^{-12} - 2X^{-6} - \frac{F^2}{8} \left(2\Lambda_{\alpha_1} X^{-6} + \left(X^{-3} + \Lambda_{\beta_1} X^{-6} \right) \left(\frac{1}{3} + \cos 2\theta \right) \right). \quad (2.78)$$

The potential (2.78) retains the asymptotically correct interaction terms in addition to the exact angular dependence of $U^{(\text{HFL})}$. If it is noted that

$$\frac{d^n (X^{-m})}{dX^n} = (-1)^n \frac{(m-1+n)!}{(m-1)!} X^{-(m+n)}, \quad (2.79)$$

then the n th-order derivative of the approximate potential (2.78) is given by

$$\frac{d^n U^{(\text{HFL})}}{dX^n} = (-1)^n \frac{(n+11)!}{11!} Z^{(n+3)/3} \left(Z^3 - C_2 \frac{(n+5)!11!}{(n+11)!5!} Z - C_1 \frac{(n+2)!11!}{(n+11)!2!} \right). \quad (2.80)$$

Here $Z = X^{-3}$ and

$$C_1 = \frac{F^2}{8} \left(\frac{1}{3} + \cos 2\theta \right) \quad (2.81a)$$

$$C_2 = 2 + \frac{F^2}{4} \Lambda_{\alpha_1} + \Lambda_{\beta_1} C_1 \quad (2.81b)$$

which are obtained from (2.78) by collecting like powers of X . The restrictions on the parameters in (2.78) are that (from (2.21)) $(\Lambda_{\alpha_1}, \Lambda_{\beta_1}) \geq 0$; no constraint on F is necessary²¹. The positions of the extrema of the potential along X will depend on the values of $C_{(1,2)}$, and hence parametrically on θ . From (2.81), the condition that $C_2 \geq 0$ is satisfied when

---

²¹If the dipole contributions are included in the model, this is unchanged since they also depend on the square of the field.

$C_1 \geq 0$. The latter result is only satisfied for values of $\theta \leq \theta_*$ where²²

$$\begin{aligned}\theta_* &= (1/2) \arccos(-1/3) \\ &\approx 0.304\pi \text{ (54.7°)} .\end{aligned}\tag{2.82}$$

Note θ_* is the angle at which $U^{(\text{HFL})}(\theta_*) = U_0$.

The condition for a local extremum given by (2.44) is equivalent to (2.80) set to zero with $n = 1$,

$$Z_m^3 - \frac{C_2}{2}Z_m - \frac{C_1}{4} = 0 ,\tag{2.83}$$

where Z_m is either $(X_{\min}^{(\text{HFL})})^{-3}$ or $(X_{\max}^{(\text{HFL})})^{-3}$. Using (2.83), substitution into the definitions of other potential features yields simple expressions for them in terms of Z_m . The value of $U^{(\text{HFL})}(+\infty, \theta)$ from (2.78) is zero. Thus the radial dissociation energy is given by substitution of (2.83) ($Z_m = Z_{\min}$) into (2.45) gives

$$\begin{aligned}\Delta_e^{(\text{HFL})} &= -\frac{d^0 U}{dX^0}(X = X_{\min}^{(\text{HFL})}) \\ &\approx \frac{Z_{\min}}{2} \left(C_2 Z_{\min} + \frac{3}{2} C_1 \right) ,\end{aligned}\tag{2.84}$$

where it is understood that (2.84) is evaluated at $\theta = 0$. Similarly the rotational well depth is found from (2.46) to be

$$\Delta_{\theta,-}^{(\text{HFL})} \approx \frac{Z_{\min}(0)}{2} \left(C_2(0)Z_{\min}(0) + \frac{3}{2}C_1(0) \right)$$

---

²²The value of θ_* is a function of X for the exact potential $U^{(\text{HFL})}$:

$$\theta_* = (1/2) \arccos \left(-1 + (2/3)(\Omega^2 X^2 (\beta - 3\alpha)) / (X^2 (\beta \Omega^2 - d'^2) + d^2) \right) .$$

$$-\frac{Z_{\min}(\pi/2)}{2} \left(C_2(\pi/2)Z_{\min}(\pi/2) + \frac{3}{2}C_1(\pi/2) \right) . \quad (2.85)$$

Here the values in brackets indicate the angle at which each is evaluated. Finally, the barrier to rotation (at $\theta = \pi/2$) in this approximation becomes (from (2.47))

$$\Delta_{\theta,+}^{(\text{HFL})} \approx -\frac{Z_{\max}}{2} \left(C_2Z_{\max} + \frac{3}{2}C_1 \right) . \quad (2.86)$$

The values of the local extrema of (2.78) are found from the roots of the cubic equation (2.83). These can be obtained in closed form from the general expression for the roots of a cubic [276, 279]. For the particular case of (2.83), the roots are

$$Z_1 = -\sqrt{2C_2/3} \cos(\eta/3) , \quad S < 0 \quad (2.87a)$$

$$Z_2 = -\sqrt{2C_2/3} \cos \frac{1}{3}(\eta + 2\pi) , \quad S < 0 \quad (2.87b)$$

$$Z_3 = -\sqrt{2C_2/3} \cos \frac{1}{3}(\eta - 2\pi) , \quad S < 0 \quad (2.87c)$$

$$Z_1 = \sqrt[3]{C_1} , \quad S = 0 \quad (2.87d)$$

$$Z_2 = -(1/2)\sqrt[3]{C_1} , \quad S = 0 \quad (2.87e)$$

$$Z_3 = -(1/2)\sqrt[3]{C_1} , \quad S = 0 \quad (2.87f)$$

$$\begin{aligned} Z_1 = (1/2) \left(C_1 + \sqrt{C_1^2 - (2C_2/3)^3} \right)^{1/3} \\ + (C_2/3) \left(C_1 + \sqrt{C_1^2 - (2C_2/3)^3} \right)^{-1/3} , \quad S > 0 \end{aligned} \quad (2.87g)$$

$$Z_2 \in \mathbb{C} , \quad S > 0 \quad (2.87h)$$

$$Z_3 \in \mathbb{C} , \quad S > 0 , \quad (2.87i)$$

i	$\text{sgn}(Z_i)$ and $\text{sgn}(U^{(\text{HFL})''}(Z_i))$									
	$S < 0$				$S = 0$				$S > 0$	
	$\theta \leq \theta_*$	$\theta > \theta_*$	$\theta \leq \theta_*$	$\theta > \theta_*$	$\theta \leq \theta_*$	$\theta > \theta_*$	$\theta \leq \theta_*$	$\theta > \theta_*$	$\theta \leq \theta_*$	$\theta > \theta_*$
1	–	–	–	+	+	+	–	+	+	–
2	+	+	+	+	–	0	+	0	$\in \mathbb{C}$	
3	–	–	+	–	–	0	+	0	$\in \mathbb{C}$	

Table 2.2: Properties of the solutions to equation (2.83) over all possible ranges of S and θ . The entries contain the signs of the solutions Z_i and the second derivative of $U^{(\text{HFL})}$ at Z_i (equation (2.80) with $n = 2$). Zeroes denote solutions which are identically zero and solutions which are complex are denoted $\in \mathbb{C}$.

where

$$S = \frac{1}{8} \left(\frac{C_1^2}{8} - \frac{C_2^3}{27} \right) \quad (2.88)$$

and

$$\eta = \arccos \left(-(3/2C_2)^{3/2} C_1 \right) . \quad (2.89)$$

It now remains to identify which of the above roots correspond to physical solutions; this means that the root must be real and positive (hence the solutions (2.87h) and (2.87i) are omitted since they are known to be complex [276]). In what follows, each case of the quantity S is examined with the additional consideration of whether $\theta \gtrless \theta_*$ as this changes the signs of $C_{(1,2)}$. The second derivative test of a root [281] characterises it as either a maximum or minimum; the expression for this is equivalent to evaluating equation (2.80) with $n = 2$ at $Z = Z_i$ ($i \in \{1, 2, 3\}$). The resulting signs are given in table 2.2. The table shows that the HDID surface has two basic regions: one region where only a single minimum exists and a second where a minimum and a maximum are present. At a critical value of F and θ where $S = 0$, the maximum and minimum merge into an inflection point.

This confirms that the field does indeed induce a barrier to rotation for a sufficiently large value of F .

Within the HDID model of $U^{(\text{HFL})}$, the above analysis shows that the minimum $X_{\min}^{(\text{HFL})}$ is given by

$$X_{\min}^{(\text{HFL})} = \begin{cases} (3/2C_2)^{1/6} \left(\sec \frac{1}{3}(\eta - \pi) \right)^{1/3} & , S < 0, \\ (C_1)^{-1/9} & , S = 0, \theta < \theta_*, \\ \left[(1/2) \left(C_1 + \sqrt{C_1^2 - (2C_2/3)^3} \right)^{1/3} \right. \\ \left. + (C_2/3) \left(C_1 + \sqrt{C_1^2 - (2C_2/3)^3} \right)^{-1/3} \right]^{-1/3} & , S > 0, \theta < \theta_*, \end{cases} \quad (2.90)$$

where S is given by (2.88), η by (2.89), θ_* by (2.82) and $C_{(1,2)}$ by (2.81). If $S = 0$ and $\theta \geq \theta_*$, the position of the inflection point in U is given by

$$X_{\text{infl}}^{(\text{HFL})} = (2/\sqrt[3]{|C_1|})^{1/3}. \quad (2.91)$$

The local maximum and its conditions for existence are given by,

$$X_{\max}^{(\text{HFL})} = (3/2C_2)^{1/6} \left(\sec \frac{1}{3}(\eta + \pi) \right)^{1/3}, \quad S < 0, \theta \geq \theta_*. \quad (2.92)$$

With the appropriate solutions to the local extrema, the closed forms of $\Delta_e^{(\text{HFL})}$, $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{HFL})}$ are given implicitly by equations (2.84), (2.85) and (2.86), respectively. For heteronuclear systems, additional contributions to these properties from the dipole potential terms are expected but the model results presented here should be accurate provided these

are small compared to the effect of the polarisability²³. It should also be noted that the results apply equally to $\langle U^{(AC)} \rangle_{\phi_c}$.

2.5.3 Dynamical Models

Most information about the dynamics of a system is contained in the deflection function $\chi(b;K)$ (2.59). In the study of chemical dynamics, the deflection function is not an observable due to its violation of the uncertainty principle (i.e. the trajectory cannot be measured over the entire collision) and therefore the differential (2.60) and integrated (2.61) cross sections are the principal measures of scattering [1, 193].

2.5.3.1 Scattering within the Impulse Approximation (IA model)

An analytic expression can be obtained for the deflection angle $\chi^{(AC)}$ or $\chi^{(HFL)}$ in the limit of high impact parameter/collision energy; this approach is based on the impulse approximation (the IA model)²⁴, which treats the potential as a perturbation to the rectilinear motion of the unperturbed system [131, 191, 192, 200, 203, 266]. The impulse approximation has a range of validity which is related to $K \gg |U|$, the perturbative potential regime of $U^{(HFL)}$ and $U^{(AC)}$ of section 2.1.3; it is thus not necessarily limited to small deflection angles [191, 192] and can be used to obtain analytic expressions for the differential and integrated cross sections [200, 202, 203, 206]. The results presented here thus serve as a basis for the analysis of other dynamical features in this potential regime (discussed in subsequent sections) and may provide some insight into the other dynamical regimes of section 2.1.3.

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²³This is always the case in the limit of very high frequency ($\Omega \gg 1$).

²⁴This is alternatively known as the momentum- or impact approximation and classical perturbation scattering theory [191, 203].

The formulation of the impulse approximation expression for the deflection angle in the case of an anisotropic potential is given by [200, 206]

$$\begin{aligned}\chi &\approx \chi_{\text{IA}} \\ &= -\frac{1}{\sqrt{2K}} \int_{-\infty}^{+\infty} \left\{ \left(\frac{\partial U}{\partial X} \right) \sin \theta + \left(\frac{\partial U}{\partial \theta} \right) \frac{\cos \theta}{X} \right\} d\tau.\end{aligned}\quad (2.93)$$

This expression is derived from considering the first order corrections to the deflection angle due to changes in the Cartesian momentum components. The change in the momentum is expressed as a time-integral over the force perpendicular to the unperturbed path. The integrand is implicitly a function of time by the unperturbed solutions:

$$X(\tau) = \sqrt{2K\tau^2 + b^2} \quad (2.94a)$$

$$\theta(\tau) = \arctan \left(-b/\tau\sqrt{2K} \right) \quad (2.94b)$$

$$P_X(\tau) = 2K\tau/\sqrt{2K\tau^2 + b^2} \quad (2.94c)$$

$$P_\theta(\tau) = b\sqrt{2K}. \quad (2.94d)$$

The point of closest approach (X_c, θ_c) in (2.94) occurs at $\tau = 0$.

Using (2.94) allows the deflection angle to be expressed in terms of the polar angle θ

$$\chi_{\text{IA}} = -\frac{1}{2K} \int_0^\pi \left\{ \left(\frac{\partial U}{\partial X} \right) b \csc \theta + \left(\frac{\partial U}{\partial \theta} \right) \cot \theta \right\} d\theta, \quad (2.95)$$

where it is understood that the integrand is expressed as a function of θ using (2.94).

For the laser-diatom system in the limit of high frequency, the potential defined by (2.27) yields contributions to the scattering by the isotropic and anisotropic portions of the potential, $U_{\text{iso}}^{(\text{HFL})}$ and $U_{\text{aniso}}^{(\text{HFL})}$ (given by (2.32) and (2.33), respectively). The calculation

can be broken down into the individual contributions to (2.95),

$$\begin{aligned}
 K\chi_{\text{IA}}^{(\text{HFL})} &= K \sum_{k \in \mathcal{U}^{(\text{HFL})}} \chi_{k,\text{IA}}^{(\text{HFL})} \\
 &= - \sum_{k \in \mathcal{U}^{(\text{HFL})}} \frac{1}{2} \int_0^\pi \left\{ b \left(\frac{\partial U_k}{\partial X} \right) \csc \theta + \left(\frac{\partial U_k}{\partial \theta} \right) \cot \theta \right\} d\theta.
 \end{aligned} \tag{2.96}$$

Here the sum runs over all components of the potential in (2.27),

$$\mathcal{U}^{(\text{HFL})} \equiv \{U_0, U_{\text{iso},d}^{(\text{HFL})}, U_{\text{iso},\alpha}^{(\text{HFL})}, U_{\text{aniso},d}^{(\text{HFL})}, U_{\text{aniso},\alpha}^{(\text{HFL})}\}.$$

The potential terms are defined in (2.32) and (2.33).

To solve (2.96), the model forms for U_0 , d , α and β are used (see (2.14), (2.23), (2.19), respectively) along with their derivatives (2.43) to obtain the pertinent derivatives of the potential terms $\mathcal{U}^{(\text{HFL})}$. Using some trigonometric identities and $X = b \csc \theta$ from (2.94) and substituting the results into (2.96) yields $K\chi_{\text{IA}}^{(\text{HFL})}$ in terms of three integrals over θ :

$$K\chi_{0,\text{IA}} = 6\mathfrak{M}_{\{0,12\}}^{(1)} b^{-12} - 6\mathfrak{M}_{\{0,6\}}^{(1)} b^{-6}, \tag{2.97a}$$

$$\begin{aligned}
 K\chi_{\text{iso},d,\text{IA}}^{(\text{HFL})} &= \frac{1}{3} \left(\frac{FQ}{2\Omega} \right)^2 \left\{ 408\mathfrak{M}_{\{0,16\}}^{(1)} b^{-16} + \Lambda_d^2 b^{-2} \left[(\gamma_d b)^3 \mathfrak{M}_{\{0,-1,2\gamma_d b\}}^{(2)} \right. \right. \\
 &\quad \left. \left. + 2\gamma_d b \mathfrak{M}_{\{0,1,2\gamma_d b\}}^{(2)} + 2\mathfrak{M}_{\{0,2,2\gamma_d b\}}^{(2)} \right] - \Lambda_d b^{-9} \left[7(\gamma_d b)^2 \mathfrak{M}_{\{0,7,\gamma_d b\}}^{(2)} \right. \right. \\
 &\quad \left. \left. + 58\gamma_d b \mathfrak{M}_{\{0,8,\gamma_d b\}}^{(2)} + 18\mathfrak{M}_{\{0,9,\gamma_d b\}}^{(2)} \right] \right\},
 \end{aligned} \tag{2.97b}$$

$$K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{HFL})} = \frac{F^2}{4} \left\{ \frac{\Lambda_{\alpha_2}}{2} \gamma_\alpha b \mathfrak{M}_{\{0,-1,\gamma_\alpha b\}}^{(2)} - 3\Lambda_{\alpha_1} \mathfrak{M}_{\{0,6\}}^{(1)} b^{-6} \right\}, \tag{2.97c}$$

$$\begin{aligned}
 K\chi_{\text{aniso},d,\text{IA}}^{(\text{HFL})} &= \left(\frac{FQ}{2\Omega} \right)^2 \left\{ \left[352\mathfrak{M}_{\{0,16\}}^{(1)} - 480\mathfrak{M}_{\{0,18\}}^{(1)} \right] b^{-16} \right. \\
 &\quad \left. + \Lambda_d^2 b^{-2} \left[\frac{2}{3} (\gamma_d b)^3 \mathfrak{M}_{\{0,-1,2\gamma_d b\}}^{(2)} + 2(\gamma_d b)^2 \mathfrak{M}_{\{0,0,2\gamma_d b\}}^{(2)} \right. \right. \\
 &\quad \left. \left. - (\gamma_d b) \left((\gamma_d b)^2 + \frac{2}{3} \right) \mathfrak{M}_{\{0,1,2\gamma_d b\}}^{(2)} - 2 \left((\gamma_d b)^2 + \frac{4}{3} \right) \mathfrak{M}_{\{0,2,2\gamma_d b\}}^{(2)} \right] \right\}
 \end{aligned}$$

$$\begin{aligned}
& + (\gamma_d b) \mathfrak{M}_{\{0,3,2\gamma_d b\}}^{(2)} + 3 \mathfrak{M}_{\{0,4,2\gamma_d b\}}^{(2)} \Big] - \Lambda_d b^{-9} \Big[\frac{14}{3} (\gamma_d b)^2 \mathfrak{M}_{\{0,7,\gamma_d b\}}^{(2)} \\
& + \frac{194}{3} \gamma_d b \mathfrak{M}_{\{0,8,\gamma_d b\}}^{(2)} - (7(\gamma_d b)^2 + 10) \mathfrak{M}_{\{0,9,\gamma_d b\}}^{(2)} - 83 \gamma_d b \mathfrak{M}_{\{0,10,\gamma_d b\}}^{(2)} \\
& + 13 \mathfrak{M}_{\{0,11,\gamma_d b\}}^{(2)} \Big] \Big\} , \tag{2.97d}
\end{aligned}$$

$$\begin{aligned}
K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{HFL})} = & \frac{F^2}{4} \left\{ \left[\frac{5}{2} \mathfrak{M}_{\{0,5\}}^{(1)} - 2 \mathfrak{M}_{\{0,3\}}^{(1)} \right] b^{-3} + \Lambda_{\beta_1} \left[4 \mathfrak{M}_{\{0,8\}}^{(1)} - 3 \mathfrak{M}_{\{0,6\}}^{(1)} \right] b^{-6} \right. \\
& \left. + \Lambda_{\beta_2} \left[\frac{\gamma_\beta b}{3} \mathfrak{M}_{\{0,-1,\gamma_\beta b\}}^{(2)} + \mathfrak{M}_{\{0,0,\gamma_\beta b\}}^{(2)} - \frac{\gamma_\beta b}{2} \mathfrak{M}_{\{0,1,\gamma_\beta b\}}^{(2)} - \mathfrak{M}_{\{0,2,\gamma_\beta b\}}^{(2)} \right] \right\} . \tag{2.97e}
\end{aligned}$$

The integrals $\mathfrak{M}_{\{m,n,z\}}^{(1,2)}$ which occur in (2.97) are defined and evaluated exactly in appendix F (see also appendix G).

Substituting the values from tables F.1 and G.1 into (2.97) yields, after some algebra,

$$K\chi_{0,\text{IA}} = \frac{3\pi}{8} \left\{ \frac{231}{64} b^{-12} - 5b^{-6} \right\} \tag{2.98a}$$

$$\begin{aligned}
K\chi_{\text{iso},d,\text{IA}}^{(\text{HFL})} = & \frac{2}{3} \left(\frac{FQ}{2\Omega} \right)^2 \left\{ \Lambda_d^2 b^{-2} \left[((\gamma_d b)^3 + 2\gamma_d b) K_0(2\gamma_d b) + \mathbf{Ki}_1(2\gamma_d b) \right] \right. \\
& + \frac{\Lambda_d b^{-9}}{5040} \left[(47(\gamma_d b)^7 + 2126(\gamma_d b)^5 + 32427(\gamma_d b)^3 - 36864\gamma_d b) K_1(\gamma_d b) \right. \\
& - (47(\gamma_d b)^6 + 2220(\gamma_d b)^4 + 73557(\gamma_d b)^2) K_0(\gamma_d b) - (47(\gamma_d b)^7 \\
& + 2079(\gamma_d b)^5 + 29925(\gamma_d b)^3 + 5125\gamma_d b) \mathbf{Ki}_1(\gamma_d b) \Big] \\
& \left. + \frac{328185}{4096} \pi b^{-16} \right\} \tag{2.98b}
\end{aligned}$$

$$K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{HFL})} = -\frac{F^2}{4} \left\{ \frac{15\pi}{16} \Lambda_{\alpha_1} b^{-6} - \Lambda_{\alpha_2} \gamma_\alpha b K_0(\gamma_\alpha b) \right\} \tag{2.98c}$$

$$\begin{aligned}
K\chi_{\text{aniso},d,\text{IA}}^{(\text{HFL})} = & \left(\frac{FQ}{2\Omega} \right)^2 \left\{ \frac{\Lambda_d^2 b^{-2}}{12} \left[(32(\gamma_d b)^4 + 44(\gamma_d b)^2) K_1(2\gamma_d b) - (40(\gamma_d b)^3 \right. \right. \\
& \left. \left. - 6\gamma_d b) K_0(2\gamma_d b) - (32(\gamma_d b)^4 + 24(\gamma_d b)^2 + 5) \mathbf{Ki}_1(2\gamma_d b) \right] \right\}
\end{aligned}$$

$$\begin{aligned}
& - \frac{\Lambda_d b^{-9}}{4989600} \left[(39(\gamma_d b)^{11} - 3481(\gamma_d b)^9 - 44419(\gamma_d b)^7 - 64155(\gamma_d b)^5 \right. \\
& + 7842600(\gamma_d b)^3 + 7372800\gamma_d b) K_1(\gamma_d b) - (39(\gamma_d b)^{10} - 3403(\gamma_d b)^8 \\
& - 50055(\gamma_d b)^6 - 220725(\gamma_d b)^4 + 28330200(\gamma_d b)^2) K_0(\gamma_d b) \\
& - (39(\gamma_d b)^{11} - 3520(\gamma_d b)^9 - 41250(\gamma_d b)^7 + 8575875(\gamma_d b)^3 \\
& \left. + 32016600\gamma_d b) \mathbf{Ki}_1(\gamma_d b) \right] - \frac{40755}{2048} \pi b^{-16} \Big\} \quad (2.98d)
\end{aligned}$$

$$K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{HFL})} = -\frac{F^2}{4} \left\{ \frac{\Lambda_{\beta_2}}{3} \gamma_{\beta} b K_0(\gamma_{\beta} b) - \Lambda_{\beta_2} \mathbf{Ki}_1(\gamma_{\beta} b) - \frac{5\pi}{32} \Lambda_{\beta_1} b^{-6} \right\}. \quad (2.98e)$$

Here, $K_v(z)$ denotes the modified Bessel function of the second kind, order v with argument z while $\mathbf{Ki}_1(z)$ symbolises the first incomplete integral of $K_0(z)$; these higher transcendental functions are discussed in appendix G. The results of (2.98), in combination with (2.96) provides the contributions of each part of the potential to the scattering as an explicit function of impact parameter. Note that the collision energy K is not contained in the right side of (2.98), verifying a correspondence principle noted previously for central potentials [192].

In the case of a c.w. laser field, it is possible to obtain a similar result for $U^{(\text{AC})}$ (equation (2.26)). The only additional complication is the appearance of the terms $F(\tau) = F \cos(\Omega\tau + \phi_c)$, where the phase is retained explicitly in the calculation as it is an initial condition of the collision. Trigonometric identities give

$$\cos(\Omega\tau + \phi_c) = \cos\Omega\tau \cos\phi_c - \sin\Omega\tau \sin\phi_c$$

and

$$2 \cos^2(\Omega\tau + \phi_c) = 1 + \cos 2\Omega\tau \cos 2\phi_c - \sin 2\Omega\tau \sin 2\phi_c ,$$

which increase the number of integrals for a given potential term. In transforming the resulting integrands to ones over θ , the solutions of (2.94) give

$$\cos(n\Omega\tau) = \cos(nw \cot \theta) \quad (2.99a)$$

$$\sin(n\Omega\tau) = -\sin(nw \cot \theta) , \quad (2.99b)$$

where n is a positive integer and $w = \Omega b / \sqrt{2K}$ is given in (2.53).

Using (2.95), the definitions of the partitions of $U^{(AC)}$ in (2.29) and (2.30), along with (2.99) yield expressions for the components of the deflection angle, $\chi_{IA}^{(AC)}$, in terms of a particular integral

$$K\chi_{iso,\alpha,IA}^{(AC)} = K\chi_{iso,\alpha,IA}^{(HFL)} + \frac{F^2}{8} \left\{ \Lambda_{\alpha_2} \gamma_{\alpha} b \mathfrak{G}_{\{0,-1,2w,\gamma_{\alpha}b\}}^{(2)} - 6\Lambda_{\alpha_1} b^{-6} \mathfrak{G}_{\{0,6,2w,0\}}^{(2)} \right\} \quad (2.100a)$$

$$K\chi_{aniso,d,IA}^{(AC)} = \frac{FQ}{2} \left\{ 8b^{-7} \mathfrak{G}_{\{1,7,w,0\}}^{(1)} - \Lambda_d \left[\gamma_d b \mathfrak{G}_{\{1,-1,w,\gamma_d b\}}^{(1)} + \mathfrak{G}_{\{1,0,w,\gamma_d b\}}^{(1)} \right] \right\} \quad (2.100b)$$

$$\begin{aligned} K\chi_{aniso,\alpha,IA}^{(AC)} = & K\chi_{aniso,\alpha,IA}^{(HFL)} + \frac{F^2}{8} \left\{ b^{-3} \left[5\mathfrak{G}_{\{0,5,2w,0\}}^{(2)} - 4\mathfrak{G}_{\{0,3,2w,0\}}^{(2)} \right] \right. \\ & + 2\Lambda_{\beta_1} b^{-6} \left[4\mathfrak{G}_{\{0,8,2w,0\}}^{(2)} - 3\mathfrak{G}_{\{0,6,2w,0\}}^{(2)} \right] \\ & + 2\Lambda_{\beta_2} \left[\mathfrak{G}_{\{0,0,2w,\gamma_{\beta}b\}}^{(2)} - \mathfrak{G}_{\{0,2,2w,\gamma_{\beta}b\}}^{(2)} \right] \\ & \left. + \Lambda_{\beta_2} \gamma_{\beta} b \left[\frac{2}{3} \mathfrak{G}_{\{0,-1,2w,\gamma_{\beta}b\}}^{(2)} - \mathfrak{G}_{\{0,1,2w,\gamma_{\beta}b\}}^{(2)} \right] \right\} \end{aligned} \quad (2.100c)$$

$$(2.100d)$$

The deflection angle for the full Hamiltonian is thus

$$K\chi_{IA}^{(AC)} = K \sum_{k \in \mathcal{U}^{(AC)}} \chi_{k,IA}^{(AC)} , \quad (2.101)$$

where

$$\mathcal{U}^{(AC)} \equiv \{U_0, U_{\text{iso},\alpha}^{(AC)}, U_{\text{aniso},d}^{(AC)}, U_{\text{aniso},\alpha}^{(AC)}\}$$

and $K\chi_{0,IA}$ is given by (2.98a).

The integral in (2.100) is defined as²⁵

$$\mathfrak{G}_{\{m,n,p,z\}}^{(k)} = \begin{cases} \cos k\phi_c \operatorname{Re}(\mathfrak{M}_{\{m,n,p\}}^{(3)}) + \sin k\phi_c \operatorname{Im}(\mathfrak{M}_{\{m,n,p\}}^{(3)}) & , z = 0 \\ \cos k\phi_c \operatorname{Re}(\mathfrak{M}_{\{m,n,p,z\}}^{(4)}) + \sin k\phi_c \operatorname{Im}(\mathfrak{M}_{\{m,n,p,z\}}^{(4)}) & , z \neq 0 . \end{cases} \quad (2.102)$$

The integrals $\mathfrak{M}_{\{m,n,p\}}^{(3)}$ and $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ are evaluated in appendix F; in the case of $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ an exact form is not possible for arbitrary arguments but an approximate solution can be obtained to any desired degree of accuracy. Using the results of appendix F,

$$\mathfrak{G}_{\{0,-1,2w,\gamma_\alpha b\}}^{(2)} = 2 \cos 2\phi_c K_0 \left(\sqrt{(\gamma_\alpha b)^2 + 4w^2} \right) , \quad (2.103a)$$

$$\mathfrak{G}_{\{0,6,2w,0\}}^{(2)} = \frac{\pi^{3/2}}{3} \cos 2\phi_c w^{7/2} K_{7/2}(2w) , \quad (2.103b)$$

$$\mathfrak{G}_{\{1,7,w,0\}}^{(1)} = -\sin \phi_c \frac{\pi^{3/2}}{12} (w/2)^{9/2} K_{7/2}(w) , \quad (2.103c)$$

$$\begin{aligned} \gamma_d b \mathfrak{G}_{\{1,-1,w,\gamma_d b\}}^{(1)} + \mathfrak{G}_{\{1,0,w,\gamma_d b\}}^{(1)} \\ = -2 \sin \phi_c w K_0 \left(\sqrt{(\gamma_d b)^2 + w^2} \right) , \end{aligned} \quad (2.103d)$$

---

²⁵N.B.: $\operatorname{Re} z$ and $\operatorname{Im} z$ denote the real and imaginary components of z , respectively.

$$\begin{aligned}
5\mathfrak{G}_{\{0,5,2w,0\}}^{(2)} - 4\mathfrak{G}_{\{0,3,2w,0\}}^{(2)} \\
= \frac{16}{3}\pi \cos 2\phi_c w^3 K_1(2w) , \quad (2.103e)
\end{aligned}$$

$$\begin{aligned}
4\mathfrak{G}_{\{0,8,2w,0\}}^{(2)} - 3\mathfrak{G}_{\{0,6,2w,0\}}^{(2)} \\
= \frac{\pi^{3/2}}{3} \cos 2\phi_c w^{7/2} [wK_{5/2}(2w) + (1/2)K_{7/2}(2w)] , \quad (2.103f)
\end{aligned}$$

and (see appendix F for notation definitions)

$$\begin{aligned}
2\mathfrak{G}_{\{0,0,2w,\gamma_\beta b\}}^{(2)} - 2\mathfrak{G}_{\{0,2,2w,\gamma_\beta b\}}^{(2)} + \frac{2}{3}\gamma_\beta b \mathfrak{G}_{\{0,-1,2w,\gamma_\beta b\}}^{(2)} - \gamma_\beta b \mathfrak{G}_{\{0,1,2w,\gamma_\beta b\}}^{(2)} \\
\approx 2 \cos 2\phi_c \left\{ \mathbf{Ki}_1(\gamma_\beta b) - \gamma_\beta b K_0(\gamma_\beta b) + \frac{2}{3}\gamma_\beta b K_0\left(\sqrt{(\gamma_\beta b)^2 + 4w^2}\right) \right. \\
+ \sqrt{\frac{2\pi}{j_{1,1}'^2 - 1}} \left(\frac{2wj_{1,1}' J_1(j_{1,1}')}{j_{1,1}'^2 + 4w^2} \right) \left[2w\gamma_\beta b K_0\left((\gamma_\beta b/2w)\sqrt{j_{1,1}'^2 + 4w^2}\right) \right. \\
\left. \left. - \frac{(2j_{1,1}'^2 + 4w^2)}{\sqrt{j_{1,1}'^2 + 4w^2}} \mathbf{Ki}_1\left((\gamma_\beta b/2w)\sqrt{j_{1,1}'^2 + 4w^2}\right) \right] \right\} . \quad (2.103g)
\end{aligned}$$

Substitution of (2.103) into (2.100) gives

$$\begin{aligned}
K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{AC})} = K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{HFL})} + \frac{F^2}{4}b \cos 2\phi_c \left\{ \Lambda_{\alpha_2} \gamma_\alpha K_0 \left(b \sqrt{\gamma_\alpha^2 + \frac{2}{K}\Omega^2} \right) \right. \\
\left. - \Lambda_{\alpha_1} \pi^{3/2} \left(\frac{\Omega}{b\sqrt{2K}} \right)^{7/2} K_{7/2} \left(\sqrt{\frac{2}{K}} \Omega b \right) \right\} , \quad (2.104a)
\end{aligned}$$

$$\begin{aligned}
K\chi_{\text{aniso},d,\text{IA}}^{(\text{AC})} = -FQ \sin \phi_c \frac{\Omega b}{\sqrt{2K}} \left\{ \frac{\pi^{3/2}}{6} \left(\frac{\Omega}{2b\sqrt{2K}} \right)^{7/2} K_{7/2} \left(\frac{\Omega b}{\sqrt{2K}} \right) \right. \\
\left. - \Lambda_d K_0 \left(b \sqrt{\gamma_d^2 + \frac{\Omega^2}{2K}} \right) \right\} \quad (2.104b)
\end{aligned}$$

$$\begin{aligned}
K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{AC})} \approx & K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{HFL})} + \frac{F^2}{4} \cos 2\phi_c \left\{ \frac{\pi}{3} \left(\sqrt{\frac{2}{K}} \Omega \right)^3 \left[\text{K}_1 \left(\sqrt{\frac{2}{K}} \Omega b \right) \right. \right. \\
& + \frac{\Lambda_{\beta_1}}{16} \left(\frac{\pi \Omega}{\sqrt{2K} b^5} \right)^{1/2} \left(\sqrt{\frac{2}{K}} \Omega b \text{K}_{5/2} \left(\sqrt{\frac{2}{K}} \Omega b \right) + \text{K}_{7/2} \left(\sqrt{\frac{2}{K}} \Omega b \right) \right) \left. \right] \\
& + \Lambda_{\beta_2} \left[\text{Ki}_1(\gamma_{\beta} b) - \gamma_{\beta} b \text{K}_0(\gamma_{\beta} b) + \frac{2}{3} \gamma_{\beta} b \text{K}_0 \left(b \sqrt{\gamma_{\beta}^2 + \frac{2}{K} \Omega^2} \right) \right. \\
& + \sqrt{\frac{2\pi}{j'_{1,1}{}^2 - 1}} \left(\frac{2j'_{1,1} \text{J}_1(j'_{1,1}) \Omega b}{K j'_{1,1}{}^2 + 2\Omega^2 b^2} \right) \left(\Omega \gamma_{\beta} b^2 \text{K}_0 \left(\frac{\gamma_{\beta}}{\Omega} \sqrt{\frac{K}{2} j'_{1,1}{}^2 + \Omega^2 b^2} \right) \right. \\
& \left. \left. - \sqrt{\frac{2}{K j'_{1,1}{}^2 + 2\Omega^2 b^2}} (K j'_{1,1}{}^2 + \Omega^2 b^2) \text{Ki}_1 \left(\frac{\gamma_{\beta}}{\Omega} \sqrt{\frac{K}{2} j'_{1,1}{}^2 + \Omega^2 b^2} \right) \right) \right] \left. \right\}. \quad (2.104\text{c})
\end{aligned}$$

Here (2.53) has been employed to express $\chi_{\text{IA}}^{(\text{AC})}$ explicitly in terms of the initial conditions of the system and its laser parameters. Note that the K -dependence in $\chi_{\text{IA}}^{(\text{AC})}$ is more complicated than of $\chi_{\text{IA}}^{(\text{HFL})}$ (2.98), indicating a possible means of separating the contributions of the time-dependent field.

In the static field limit introduced in section 2.1.3.2, (2.104) yields a simplified expression for $\chi_{\text{IA}}^{(\text{AC})}$ as $w \rightarrow 0$:

$$K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{AC})} \sim K\chi_{\text{iso},\alpha,\text{IA}}^{(\text{HFL})} (1 + \cos 2\phi_c), \quad (2.105\text{a})$$

$$K\chi_{\text{aniso},d,\text{IA}}^{(\text{AC})} \sim 0, \quad (2.105\text{b})$$

$$K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{AC})} \sim K\chi_{\text{aniso},\alpha,\text{IA}}^{(\text{HFL})} (1 + \cos 2\phi_c). \quad (2.105\text{c})$$

Again, the special cases of $\mathfrak{G}_{\{m,n,p,z\}}^{(k)}$ which occur in the evaluation of (2.105) are discussed in appendix F. The important point to be made with (2.105) is that in the limit of large collision energy, the dynamics approach those of a static field with the effective field strength determined by ϕ_c .

The results obtained for $\chi_{IA}^{(AC)}$ show a very simple dependence on ϕ_c . From (2.104),

$$\langle \chi_{IA}^{(AC)} \rangle_{\phi_c} = \chi_{IA}^{(HFL)}, \quad (2.106)$$

for any frequency. The standard deviation of (2.104) is found to be

$$\sigma_{\text{RMS}, \chi_{IA}^{(AC)}} = \frac{1}{\sqrt{2}} \left| \chi_{\text{aniso}, d, IA}^{(AC)2} \csc^2 \phi_c + \left(\chi_{\text{iso}, \alpha, IA}^{(AC)} - \chi_{\text{iso}, \alpha, IA}^{(HFL)} + \chi_{\text{aniso}, \alpha, IA}^{(AC)} - \chi_{\text{aniso}, \alpha, IA}^{(HFL)} \right)^2 \sec^2 2\phi_c \right|^{1/2}, \quad (2.107)$$

where it is stressed that the result is indeed independent of ϕ_c from (2.104). From the form of the equations, the only terms which contribute to $\sigma_{\text{RMS}, \chi_{IA}^{(AC)}}$ are those present in $U_{\tau}^{(AC)}$. In the case of the static-field limit, (2.105) yields a simpler result

$$\sigma_{\text{RMS}, \chi_{IA}^{(AC)}} \sim \frac{1}{\sqrt{2}} \left| \chi_{IA}^{(HFL)} - \left(\chi_{0, IA} + \chi_{\text{iso}, d, IA}^{(HFL)} + \chi_{\text{aniso}, d, IA}^{(HFL)} \right) \right|^{1/2}, \quad (2.108)$$

where the variation with ϕ_c is due exclusively to the polarisability-induced scattering terms of $\chi_{IA}^{(HFL)}$, or equivalently $\langle U^{(AC)} \rangle_{\phi_c}$.

While the results of (2.106) and (2.108) are derived under the assumption of $b > 1$, it is reasonable to expect that these results will be valid for all impact parameters provided the collision energy is large enough: i.e. the system is still in the so-called perturbative, or possibly the large amplitude, regime of equation (2.52) provided the static field limit is valid. It follows that (2.108) may be applied to predict the exact $\chi^{(AC)}$ by using numerically determined $\chi^{(HFL)}$ (or χ determined from $\langle U^{(AC)} \rangle_{\phi_c}$).

2.5.3.2 Scattering within the HDID and Impulse Approximations (HDID-IA model)

Using the HDID model of the potential surface of $U^{(\text{HFL})}$ in conjunction with the IA model for $\chi^{(\text{HFL})}$ from section 2.5.3.1 yields a simplified form of the deflection angle which can be used to estimate all the collision cross sections and parameters for the special features of $d\sigma^{(\text{HFL})}/d\Omega$ given in section 2.4.3. The starting point is (2.98) which reduces to a quadratic in b^{-6} once the dipole terms and non-DID terms are neglected (the HDID model),

$$K\chi_{\text{IA}}^{(\text{HFL})} = C_{12}b^{-12} - C_6b^{-6} \quad (\text{HDID-IA model}), \quad (2.109)$$

where

$$C_{12} = \frac{693}{512}\pi, \quad C_6 = \frac{5\pi}{8} \left(3 + \left(\frac{F}{4} \right)^2 (6\Lambda_{\alpha_1} - \Lambda_{\beta_1}) \right). \quad (2.110)$$

Note that (2.109) is valid for $K > |U^{(\text{HFL})}|$ and hence cannot describe orbiting. However, glory and rainbow scattering are contained within the expression. In what follows, all the results can be generalised to the case of an AC field within the static field limit by making the substitution of $F \rightarrow F\sqrt{2}\cos\phi_c$ and averaging the results.

Glory Scattering From the roots of (2.109), an estimate of the first forward glory impact parameter ($n = 0$) is found to be

$$\begin{aligned} b_g^{(\text{HFL})} &\approx \left(\frac{C_{12}}{C_6} \right)^{1/6} \\ &= \frac{1}{2} \left(\frac{693}{5} \right)^{1/6} \left(3 + \frac{F^2}{16} (6\Lambda_{\alpha_1} - \Lambda_{\beta_1}) \right)^{-1/6}. \end{aligned} \quad (2.111)$$

Other glories exist within this approximation, i.e. those with $n \in [1, \infty)$. However, these glories are associated with the portion of $\chi_{IA}^{(HFL)}$ where the impulse approximation is invalid and (2.109) diverges. The corresponding glories are therefore unphysical and are not considered.

The contribution of the glory singularity to $d\sigma^{(HFL)}/d\Omega$ within the HDID-IA model is given by (2.66) and the parameters $b_g^{(HFL)}$ and $\chi_g^{(HFL)'}:$

$$\begin{aligned} K\chi_g^{(HFL)'} &\approx -6C_6 \left(\frac{C_6}{C_{12}} \right)^{7/6} \\ &= -\frac{400\pi}{231} \left(\frac{320}{693} \right)^{1/6} \left(3 + \frac{F^2}{16} (6\Lambda_{\alpha_1} - \Lambda_{\beta_1}) \right)^{13/6}. \end{aligned} \quad (2.112)$$

The behaviour of (2.111) and (2.112) shows that $b_g^{(HFL)}/|\chi_g^{(HFL)' }|$ decreases²⁶ with F as both are monotonically decreasing. The above estimate of the glory parameters is not expected to be quantitative for systems which have large non-DID polarisability terms since the distance of closest approach is approximately $b_g^{(HFL)}$ which is small ($b_g \approx 0.94$ for $F = 0$). Additionally, the impulse approximation is not valid for low energies and no energy dependence is predicted from (2.111). However, the qualitative behaviour of $b_g^{(HFL)}$ with respect to F and K for real systems may be similar to that of the HDID-IA model.

Rainbow Scattering Using the deflection function (2.109), there is only one minimum in $\chi_{IA}^{(HFL)}$ within the HDID-IA model:

$$\begin{aligned} b_r^{(HFL)} &\approx \left(\frac{2C_{12}}{C_6} \right)^{1/6} \\ &= 2^{1/6} b_g^{(HFL)}, \end{aligned} \quad (2.113)$$

---

²⁶N.B.: the intensity factor of (2.66) within the HDID-IA model is $(K/6)C_{12}^{4/3}/C_6^{7/3}$.

where $b_g^{(\text{HFL})}$ is the glory impact parameter given by (2.111). Back-substitution into (2.109) gives the rainbow deflection angle,

$$\begin{aligned} K\chi_r^{(\text{HFL})} &= -\frac{C_6^2}{4C_{12}} \\ &= -\frac{50\pi}{693} \left(3 + \frac{F^2}{16} (6\Lambda_{\alpha_1} - \Lambda_{\beta_1}) \right)^2. \end{aligned} \quad (2.114)$$

The second derivative of the rainbow deflection angle within the HDID-IA model is found from (2.109):

$$K\chi_r^{(\text{HFL})''} = \frac{800}{77} \pi \left(\frac{20}{693} \right)^{1/3} \left(3 + \frac{F^2}{16} (6\Lambda_{\alpha_1} - \Lambda_{\beta_1}) \right)^{7/3}. \quad (2.115)$$

The scattering angle $\Theta_r^{(\text{HFL})}$ can be found from (2.55) in conjunction with (2.114). The rainbow is thus completely characterised by the HDID-IA model. The rainbow angle $\chi_r^{(\text{HFL})}$ is always negative for $F \geq 0$; this means that $\Theta_r^{(\text{HFL})}$ will oscillate between 0 and π as F is increased. In fact, the rainbow angle of (2.114) will be indistinguishable from a glory singularity (i.e. $\chi_r^{(\text{HFL})}(F_k) = -k\pi$) when $F = F_k$, where²⁷

$$F_k = \frac{4}{5} \sqrt{\frac{693k^{1/2} - 150}{2(6\Lambda_{\alpha_1} - \Lambda_{\beta_1})}}. \quad (2.116)$$

The rainbow conditions of (2.70) show, in conjunction with the HDID-IA results of above, that for $F < F_1$ the rainbow is of a forward type while $F_1 < F < F_2$ is backwards, etc. The behaviour of the HDID-IA rainbow parameters with F all indicate that the singularity in $d\sigma^{(\text{HFL})}/d\Omega$ narrows²⁸ with F .

²⁷N.B.: It is implicit that the polarisability coefficient term is positive such as would be suggested by the DID estimates of Λ_{α_1} and Λ_{β_1} given in (2.21).

²⁸N.B.: the intensity factor is $\sqrt{K}(\sqrt[3]{2}/3)C_{12}^{5/6}/C_6^{4/3}$.

The HDID-IA model rainbow parameters are expected to be qualitatively correct for systems where the impulse approximation is valid. The neglect of the non-DID polarisability terms will have an effect only if the distance of closest approach of the trajectory has a strong non-DID polarisability value at that point. From the form of the non-DID terms and the fact that within the impulse approximation, the distance of closest approach would be $\sim b_r$ as predicted by (2.113), the condition

$$(\gamma_\alpha b_r, \gamma_\beta b_r) \gg 1, \quad (2.117)$$

ensures the validity for neglecting the non-DID terms in the polarisability. For heteronuclear systems, the limit of large K yields $\chi_{\text{aniso},d}^{(\text{AC})} \approx 0$ by (2.105). Similarly, for higher frequencies $\chi_{\text{iso},d}^{(\text{HFL})}$ and $\chi_{\text{aniso},d}^{(\text{HFL})}$ are of order Ω^{-2} . Thus it is only expected that the neglect of the permanent dipole terms in the scattering will have an effect on $\Theta_r^{(\text{AC})}$ when $w \sim 1$ (see (2.53)).

Cross Sections and Small-Angle Scattering A simple closed form for $d\sigma^{(\text{HFL})}/d\Omega$ (or $d\sigma^{(\text{AC})}/d\Omega$ in the static field limit) can be obtained from the HDID-IA model. The scattering function derived from (2.109) can be inverted exactly to give all the branches which contribute to the differential cross section²⁹. For simplicity, it has been assumed that $F < F_1$ of (2.116), and hence $\Theta_r = |\chi_r^{(\text{HFL})}|$, but similar results can be derived for other cases. Using

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²⁹N.B.: There are other branches which contribute but these occur in regions where the impulse approximation result diverges. The branches included in the calculation are limited to $\chi \in [-\pi, \pi]$.

(2.109),

$$b(\Theta) = \begin{cases} b_r^{(\text{HFL})} (1 \pm f_+)^{-1/6} & , b > b_g^{(\text{HFL})} , \\ b_r^{(\text{HFL})} (1 \pm f_-)^{-1/6} & , b \leq b_g^{(\text{HFL})} , \end{cases} \quad (2.118)$$

where $b_g^{(\text{HFL})}$ and $b_r^{(\text{HFL})}$ are the HDID-IA estimates of (2.111) and (2.113), respectively; furthermore,

$$f_{\pm}(\Theta) = \sqrt{1 \pm \frac{\Theta}{\Theta_r^{(\text{HFL})}}} , \quad (2.119)$$

with $\Theta_r^{(\text{HFL})} = |\chi_r^{(\text{HFL})}|$ similarly given by (2.114). Only three of the four possible branches are physically acceptable for any Θ and only one is so when $f_- \notin \mathbb{R}$ or $\Theta > \Theta_r^{(\text{HFL})}$.

Using (2.118), the derivative of each branch is

$$\frac{db}{d\Theta} = \begin{cases} \mp (b_r^{(\text{HFL})}/12\Theta_r^{(\text{HFL})}) (1 \pm f_+)^{-7/6}/f_+ & , b > b_g^{(\text{HFL})} , \\ \pm (b_r^{(\text{HFL})}/12\Theta_r^{(\text{HFL})}) (1 \pm f_-)^{-7/6}/f_- & , b \leq b_g^{(\text{HFL})} . \end{cases} \quad (2.120)$$

Substitution of the above results into (2.60) gives the differential cross section for $\Theta =$

ζ :

$$\zeta \sin \zeta \frac{d\sigma^{(\text{HFL})}}{d\Omega}(\zeta, K) = \begin{cases} (b_r^{(\text{HFL})} 2\zeta/12\Theta_r^{(\text{HFL})}) \left(f_-^{-1} |1 + f_-|^{-4/3} \right. \\ \left. + f_-^{-1} |1 - f_-|^{-4/3} + f_+^{-1} |1 + f_+|^{-4/3} \right) & , \zeta < \Theta_r^{(\text{HFL})} . \\ (b_r^{(\text{HFL})} 2\zeta/12\Theta_r^{(\text{HFL})}) f_+^{-1} |1 + f_+|^{-4/3} & , \zeta \geq \Theta_r^{(\text{HFL})} \end{cases} \quad (2.121)$$

Note that this expression only depends on the product $K\zeta$ [192].

The integrated cross section is obtained from (2.118) and (2.61); for an integration angle ζ ,

$$\sigma^{(\text{HFL})}(\zeta; K) = \begin{cases} \pi b_r^{(\text{HFL})2} \left(|1 + \mathbf{f}_+|^{-1/3} \right. \\ \left. - |1 + \mathbf{f}_-|^{-1/3} + |1 - \mathbf{f}_-|^{-1/3} \right) & , \zeta \leq \Theta_r^{(\text{HFL})} \\ \pi b_r^{(\text{HFL})2} |1 + \mathbf{f}_+|^{-1/3} & , \zeta > \Theta_r^{(\text{HFL})} . \end{cases} \quad (2.122)$$

The small angle scattering contribution can be found from (2.109) and compared with (2.63) and (2.64), respectively; this shows that $s = 6$ and $c = -C_6/K$, yielding

$$\zeta \sin \zeta \frac{d\sigma^{(\text{HFL})}}{d\Omega} \sim \frac{1}{6} \left(\frac{C_6}{K\zeta} \right)^{1/3} \quad (2.123a)$$

and

$$\sigma^{(\text{HFL})}(\zeta) \sim \pi \left(\frac{C_6}{K\zeta} \right)^{1/3} . \quad (2.123b)$$

Thus the slope of the small angle scattering singularity and the integrated cross section will increase with F . Note that for use with the static-field limit of $d\sigma^{(\text{AC})}/d\Omega$, the above results must be averaged over ϕ_c .

While (2.121) and (2.122) are not expected to be quantitative for smaller impact parameters or low energies due to the neglect of the short-range polarisability terms and the impulse approximation, the behaviour for small $K\Theta$ (large b) should be accurate. Within the HDID-IA model, the collision cross section is dominated by $U_{\text{iso}}^{(\text{HFL})}$; the model is therefore of use in extracting quantitative information about the potential in this limit. In the case

of $F = 0$, the above results reduce to those of the literature [191].

2.5.3.3 Orbital Scattering within the Isotropic Model

An estimate of $b_{orb,(-)}^{(HFL)}$ and $K_{orb,(-)}^{(HFL)}$ can be obtained by considering the isotropic potential (2.32) within the HDID potential model. By evaluating the orbiting conditions (2.71)–(2.73) within this set of approximations, the effect of the field on $b_{orb,(-)}^{(HFL)}(K, F)$ and $K_{orb,(-)}^{(HFL)}(F)$ can be quantified. Using the HDID form of $U_{iso}^{(HFL)}$ (2.32) gives

$$\begin{aligned} U^{(HFL)} &\approx U_0 + U_{iso,\alpha}^{(HFL)} \\ &\approx X^{-12} - \frac{1}{4}(8 + \Lambda_{\alpha_1} F^2)X^{-6}. \end{aligned} \quad (2.124)$$

The radius of orbiting for this potential is given from (2.72) as

$$X_{orb,(-)}^{(HFL)} \approx \left(\frac{20}{8 + \Lambda_{\alpha_1} F^2} \right)^{1/6} \left(1 - \sqrt{1 - \frac{80K}{(8 + \Lambda_{\alpha_1} F^2)^2}} \right)^{-1/6}. \quad (2.125)$$

From (2.71) the impact parameter where orbiting occurs is

$$\begin{aligned} b_{orb,(-)}^{(HFL)} &\approx \left(\frac{3}{K} \right)^{1/2} \left(\frac{8 + \Lambda_{\alpha_1} F^2}{20} \right)^{5/6} \left(1 - \sqrt{1 - \frac{80K}{(8 + \Lambda_{\alpha_1} F^2)^2}} \right)^{1/3} \\ &\times \left(3 + 2\sqrt{1 - \frac{80K}{(8 + \Lambda_{\alpha_1} F^2)^2}} \right)^{1/2}. \end{aligned} \quad (2.126)$$

The maximum orbiting energy is found from (2.73) and (2.72):

$$K_{orb,(-)}^{(HFL)} \approx \frac{(8 + \Lambda_{\alpha_1} F^2)^2}{80}. \quad (2.127)$$

Note that these results reduce to the correct ones for a Lennard-Jones (6,12) potential in the case of $F = 0$ [183].

The field dependence of $b_{orb,(-)}^{(HFL)}$ and $K_{orb,(-)}^{(HFL)}$ shows that these are both monotonically increasing functions $\Lambda_{\alpha_1} F^2$. In particular, (2.127) shows that the field dependence of $K_{orb,(-)}^{(HFL)}$ can demonstrate the increased attractive forces of the potential and possibly be used as a direct measure of Λ_{α} . The assumptions of the HDID model are valid if the non-DID terms are negligible at the orbiting radius. From (2.72) and (2.19), the condition becomes

$$\left[\left(\frac{8 + \Lambda_{\alpha_1} F^2}{20} \right) \left(1 - \sqrt{1 - \frac{80K}{(8 + \Lambda_{\alpha_1} F^2)^2}} \right) \right]^{1/6} \ll \gamma_{\alpha}. \quad (2.128)$$

The approximation of $U^{(HFL)} \approx U_{iso}^{(HFL)}$ is acceptable for either $F \ll 1$ or $\Lambda_{\alpha_1} \gg 1$. For systems with moderate anisotropy the qualitative behaviour of the above model is still expected to hold for weak fields ($F \ll 1$).

Chapter 3

Details of the Calculations

This chapter contains details of the computational methods used to generate the results presented in chapter 4. For all the calculations in this work, computer code has been written to evaluate the necessary observables using the theory developed in chapter 2. Additional details of the programs identified here are found in appendix I, which describes the contents of the supplementary compact disk; the source code given is also commented extensively and should complete the description of the methods given here. For reference, all calculations were performed on a Pentium II, 266 MHz processor with 64 MB RAM and 8 GB hard disk space. The most demanding calculation was the determination of $K_{orb,(\pm)}^{(AC)}(F, \Omega)$ (see section 3.4) which required 117614904 trajectories or approximately 13.6 days to complete (at 0.01 s per trajectory).

3.1 Laser-Induced Potential Features

The functions used to examine $U^{(HFL)}$, $U_{iso}^{(HFL)}$ and $U^{(AC)}$ are defined within the binary program for a given set of molecular, laser and spatial parameters. Thus, energy contour

data sets were obtained by creating a potential grid with the program which can be used with the gnuplot for contouring. A similar approach was taken for all the contour plots presented in this work.

The potential features of the He_2 and HeAr systems were determined by numerical solutions to (2.44) using $U^{(\text{HFL})}(X)$ generated by the binary program for a fixed F , Ω and θ . The numerical roots, their ordinate values, and first- and second derivatives were computed with the nonlin program using the option of interpolation of the data set and its derivative with an improved Akima spline [282–285]; the root-finding method used was that of Ridder [279]. Analytic estimates of the potential features observables were furnished from (2.84)–(2.86), (2.90) and (2.92) as found in the binarymod program.

3.2 Classical Trajectory Calculations

All trajectories were generated using the binary program which solved the equations of motion appropriate to any partitions of $U^{(\text{HFL})}$ or $U^{(\text{AC})}$ as given in equations (2.37)–(2.42). The integration of the equations is accomplished using the variable time-step method of Bulirsch and Stoer [279]; the source code for the cited reference was modified to force an integration time step for the case of an underflow error in the routine which estimates the appropriate time step. The integration of a trajectory is specified for a starting and finishing time with the variable time-step routine controlling the sub-intervals chosen. It was found after some numerical experimentation that the performance of the integrator could be optimised by sub-dividing the trajectory integration time: this prevents the variable-time step algorithm from excessive “failed” integration sub-intervals (integrations where the time step was too large to maintain error tolerances, eps , in the solution values [279]). Too large a number of sub-divisions effectively eliminates the variable time-step algorithm from the

Name	Symbol	Exact	Apprx.	Name	Symbol	Exact	Apprx.
n	N	∞	20	m	See [279]	∞	10
isafe	I_{safe}	∞	2000	eps	See [279]	0	$0.1(-5)$
vtol	ε	0	$0.1(-3)$	xscal		≥ 1	2
ttol	ε'	0	0.1	npc	N_{ϕ_c}	∞	101

Table 3.1: The internal parameters necessary for the numerical solution of the equations of motion for $U^{(\text{HFL})}$ or $U^{(\text{AC})}$ using the binary program. Columns show: parameter name used in the code; symbol used in the text, if applicable; the “exact” and “approximate” values. Exact refers to parameter values for which, in theory, the true solutions to the equations of motion are achieved. The parameter values which achieve convergence to three digits is shown in the approximate column. Parentheses show the appropriate power of ten. See the comments of the binary source code for more details.

integration (i.e. the integrator has the limiting behaviour of a fixed time-step method) and is less efficient.

The trajectory initial conditions were found using the approach described in section C.1.1 with the input condition being $\varepsilon \equiv \text{vtol} \leq 1$; the integration lasts from a minimum time based on τ_{coll} of (C.13) sub-divided into N intervals as noted above. A trajectory is continued for a minimum of N intervals with additional ones added until one of two conditions is met: i) the maximum number of intervals of $N + I_{\text{safe}}$ is exceeded; ii) the current radial separation exceeds the value of $X_i \sqrt{|P_{\theta,i}/\varepsilon' P_{\theta,i}|}$, where $\varepsilon' \equiv \text{ttol} \leq 1$. Once the final values of the trajectory have been calculated, the observables may be calculated using the formulae given in section 2.4.

A summary of the internal parameters of the binary program and the values used in the calculations of the present work is given in table 3.1. The variable names are consistent with that of the source code. Further explanation may be found in the extensive comments of the program. The specific values of the parameters chosen were the result of numerical convergence studies; all parameters shown in table 3.1 have “exact” limits such that the trajectory approaches the true solution to the equations of motion. These exact values are

given in the table. Convergence of the trajectory to its exact value can be measured by its stability as one or all the parameters approach their exact limits. The parameters reported in the table yield χ to three stable figures, i.e. digits which do not change with the further variation of parameters. The accuracy of the results with these parameters is probably higher than stated since variations are not much larger than the order of magnitude of the next significant figure. More convergence is possible but this was found to be computationally prohibitive (i.e. more than 1s for a trajectory).

In the case of $U^{(AC)}$, the addition of ϕ_c -averaging makes the choice of the number of equally distributed phases from 0 to 2π important. A convergence study was performed for the phase-averaged dynamical observables at several impact parameters and collisional energies. It was found that $N_{\phi_c} = 101$ was sufficient to obtain three converged digits for high collision energies and strong fields but not at low collision energies; here the convergence is only about two digits. The latter effect is due to pendular scattering of the system at low collision energies (vide infra) so convergence, if at all possible, is extremely slow.

Trajectories which were integrated for the purposes of displaying the path of the system were computed with the same parameters as in table 3.1. The only difference was that the trajectory path was stored at every sub-division step. The actual time-step size used depended on the length of the trajectory but once this was determined, the number of stored points was chosen such that the step size was about one reduced time unit. Obtaining the averages and the higher-order central moments of the ϕ_c -distribution was done by numerical integration of $\chi^{(AC)}(\phi_c)$ data sets of equally spaced abscissae using the extended Simpson's rule [276, 279, 286]. All averaging was performed with the xavg program. The accuracy of the calculations of $\chi(b)$ using the binary program was checked against tabulated values [183, 287] for the field-free case.

3.3 Impulse Approximation Calculations

The deflection angle functions $\chi^{(\text{HFL})}(b; K, F, \Omega)$, $\chi^{(\text{AC})}(b; K, F, \Omega, \phi_c)$ and any single potential partition as well as the sums of the iso- and anisotropic terms were calculated within the impulse approximation formulae of (2.98) and (2.104). The source code which performs this function evaluation is given in the impulse program. The evaluation of the equations is straightforward with the exception of the required Bessel functions. The values of $K_n(x)$ were obtained from available code extended to double precision arithmetic [279]. The evaluation of $\text{Ki}_1(x)$ was accomplished by the klint program (written as an external function); the numerical formulae required for this function are given in appendix G (see also figure G.1). The values of $j'_{1,1}$ and $J_1(j'_{1,1})$, which are required for the steepest descent approximation of one integral, are tabulated [276] but to obtain more significant digits these were determined independently. The value of $j'_{1,1}$ was found from numerical evaluation of the equation

$$j'_{1,1} J_0(j'_{1,1}) - J_1(j'_{1,1}) = 0 ,$$

using Ridder's method [279]. The value of $J_1(j'_{1,1})$ was also found from numerical evaluation.

3.4 Special Features of the Deflection Function

The special features of the deflection function to be studied are those associated with glory, rainbow and orbiting scattering. Specifically: $\{b_g^{(\text{HFL})}, \chi_g^{(\text{HFL})}\}$, $\{b_r^{(\text{HFL})}, \chi_r^{(\text{HFL})}, \chi_r^{(\text{HFL})''}\}$ and $\{b_{orb,(\pm)}^{(\text{HFL})}, K_{orb,(\pm)}^{(\text{HFL})}\}$. The analogous quantities for $U^{(\text{AC})}$ are: $\{b_g^{(\text{AC})}, \chi_g^{(\text{HFL})}\}$,

$\{b_r^{(\text{AC})}, \chi_r^{(\text{HFL})}, \chi_r^{(\text{HFL})''}\}$ and $\{b_{\text{orb},(\pm)}^{(\text{AC})}, K_{\text{orb},(\pm)}^{(\text{AC})}\}$. In the case of $U^{(\text{AC})}$, some averaged values of the glory and rainbow properties with their concomitant standard deviations, e.g. $\langle b_g^{(\text{AC})} \rangle_{\phi_c}$ and $\sigma_{\text{RMS}, b_g^{(\text{AC})}}$ etc ... were also determined. Numerically, the glory parameters are determined from the solutions to the equation

$$(\chi^{(\text{HFL})}(b), \chi^{(\text{AC})}(b)) = n\pi ,$$

where $n \in \mathbb{Z}$. The rainbow and orbiting parameters are determined from the solutions to

$$(\chi^{(\text{AC})'}(b), \chi^{(\text{HFL})'}(b)) = 0 ,$$

where the derivatives are with respect to the impact parameter. In the case of the orbiting threshold $K_{\text{orb},(\pm)}^{(\text{AC})}$, the result is determined by the highest collision energy where orbiting exists and hence it is not appropriate to average the result over ϕ_c .

To obtain the special features of the deflection functions over a range of laser parameters (F, Ω) and K , the numerical solutions to the above non-linear equations and the corresponding first and second derivatives (i.e. a set of (x, y, y', y'')) were collected as a function of (F, Ω, ϕ_c, K) for both HeAr and He₂ using the nonlin program for the analysis. The program provides interpolation of a data set with Akima splines [282–285] and numerical roots of either equation using Ridder's method [279]. The basic data sets were $\chi^{(\text{HFL})}$ or $\chi^{(\text{AC})}$ as a function of b for fixed (F, Ω, ϕ_c, K) ; details of the trajectory calculations are given in section 3.2. The range of parameters examined for the glory and rainbow/orbiting scattering were: $U^{(\text{HFL})}$ — $b \in [0, 5]$, with a resolution of 0.01, $K \in \{0.1, 1.0, 10\}$, $\Omega = \Omega_{\text{CO}_2}$ (see table C.1), and $F \in [0, 3]$ with resolution of 0.01; $U^{(\text{AC})}$ — the same b and K ranges were used but $\Omega \in [0, 20]$ with resolution of 2 and $F \in [0, 3]$ with resolution of 0.5. The carrier

phase in the latter case was $\phi_c \in [0, 2\pi]$ with a resolution of $2\pi/100$ ($N_{\phi_c} = 101$).

The properties of each deflection function data set were calculated and stored with the aid of the shell script `prp.dynm.csh`. In the case of the glory scattering for both $U^{(\text{HFL})}$ and $U^{(\text{AC})}$, the values of n chosen were $n \in \{-1, 0, 1\}$. In the case of $U^{(\text{AC})}$ the results were averaged over ϕ_c using the `xavg` program when required (see section 3.2).

In the case of local extrema of $\chi^{(\text{HFL})}$ and $\chi^{(\text{AC})}$, a distinction must be made between the orbital scattering, where the deflection function goes to $\pm\infty$ and rainbow scattering where the maximum/minimum is finite but possibly large. Due to the method of calculation of the deflection angle, an integration of the equations of motion for a finite time interval, true infinities of the deflection angle cannot be obtained as this requires an infinite time interval. Since an orbiting trajectory, or one near orbiting, will result in a large value of χ , both the orbiting and rainbow scattering manifest themselves as finite local extrema in the deflection function. Thus, some method must be employed to distinguish between orbiting singularities and true rainbow extrema. A proper determination of orbiting can be obtained via the methods of non-linear mechanics [269, 288]. However, a simple ad hoc definition of orbiting is found from examination of the deflection function for the case of $F = 0$ where $b_{\text{orb},(\pm)}$ and $K_{\text{orb},(\pm)}$ are known analytically (see section 2.4.3.4). From this data it was determined that orbiting singularities are characterised by finite maxima/minima of $|\chi| > 1.75 \times \pi$, $|\chi''| > 10^5$ and $\text{sgn}(\chi\chi'') < 0$. The first two conditions ensure that any extrema labelled as an orbiting singularity is a sufficiently large and narrow “spike” in $\chi(b)$, as would be required by the assumption that orbiting singularities are logarithmically divergent [131, 180, 186, 187]; the last condition excludes local extrema of χ which are sufficiently large and narrow but must cross $\chi = 0$ in order to diverge to $\pm\infty$. These criteria for orbiting are in effect an estimate of the location of a true singularity. The particular

choice of the lower bounds on the angle and its second derivative are empirical and chosen to reproduce the exact results for the field-free case.

The set of local extrema of the deflection function for a given (F, Ω, K) were separated in likely orbiting and rainbow sets using the above method in conjunction with the shell script rnb.sep.csh with further distinction of $\pm\infty$ orbiting being possible from the examination of the sign of the deflection angle at $b_{orb,(\pm)}$.

For the determination of $K_{orb,(\pm)}^{(HFL)}$ and $K_{orb,(\pm)}^{(AC)}$, separate sets of deflection function data were generated with the binary program with $b \in [1, 3]$ and a resolution of 0.005. Many collision energies were used to bracket the thresholds with increasing resolution in K ; i.e. an initial sweep of $K \in [0.1, 10]$ in steps of 1.0 determines a bracketing range in K of $K_{orb,(\pm)}$. Another sweep of K is performed between these two bracketing energies in steps of 0.1 to obtain a narrower bracket for the next sweep, etc. For the final determination of both $K_{orb,(\pm)}$, a resolution of 0.001 in K was used. The ranges of F and Ω were chosen to be identical with the previous set of calculations for the special properties of the deflection functions. The rainbow/orbiting data was generated from the deflection functions using the prp.dynm.csh script and separated using the rnb.sep.csh script. The highest collision energy where $+\infty$ and $-\infty$ orbiting was observed for a given F, Ω and/or ϕ_c was extracted from this data using the korb.csh script. The parameters used for the separation of orbiting/rainbow scattering extrema were slightly different than those used for finding $b_{orb,(\pm)}^{(HFL)}$ for a fixed K ; it was found that $|\chi| < 2\pi$ and $|\chi''| < 6 \times 10^5$ were required for a reasonably accurate determination of $K_{orb,(-)}^{(HFL)}$ for $F = 0.0$.

For all of the special properties of the deflection function, comparison was made with the results of the impulse approximation values of $\chi_{IA}^{(HFL)}$ and $\chi_{IA}^{(AC)}$ as given by (2.98) and (2.104), respectively. The deflection function data sets were generated using the impulse

program described in section 3.3 and the results were analysed using the same scripts as for the trajectory calculations. The HDID-IA model results for the glory and rainbow parameters in addition to the isotropic orbiting model as given by (2.111)–(2.127) were coded in the impprp program as functions of (F, Ω, K) for $U^{(\text{HFL})}$ only. The static field limit results using these models were accomplished by generating results with different effective F according to (2.77) with a resolution in ϕ_c of $2\pi/100$. The individual effective field results were then averaged with the xavg program.

3.5 Differential and Integrated Cross Sections

The differential cross sections of $d\sigma^{(\text{HFL})}/d\Omega$ and $d\sigma^{(\text{AC})}/d\Omega$ were determined from the trajectory calculations described in section 3.2. Use of equation (2.60) requires that the input of the deflection function $\chi(b)$ and its first derivative $\chi'(b)$ are interpolated using Akima splines [282–285]. The scattering function $\Theta(b)$ is then found from the spline of the deflection function using (2.55). For a fixed scattering angle ζ , the roots of the equation $\Theta(b) = \zeta$ are found using Ridder's method [279] with root bracketing every two data points; thus, the bracketing interval was 0.01 units of b for these calculations which ensured no root was missed. With the set of roots, equation (2.60) was used to sum each contribution at a fixed ζ . The derivatives of χ were evaluated using the analytic derivative of the Akima spline. By varying ζ , $d\sigma^{(\text{HFL})}/d\Omega$ or $d\sigma^{(\text{AC})}/d\Omega(\phi_c)$ was obtained. In the case of $U^{(\text{AC})}$, the cross section was determined for each laser carrier phase ϕ_c and the results subsequently averaged for each value of ζ , yielding $d\sigma^{(\text{AC})}/d\Omega$. Results for the present work used 1800 values of ζ for a resolution of 0.1° in the differential cross section. The algorithm for obtaining differential cross sections was coded in the cross program. Parsing of the main data files for generating the differential cross section was performed with the

prp.xscn.csh script. Averaging for $d\sigma^{(AC)}/d\Omega$ was done with the extended Simpson's rule program xavg.

The integrated cross sections $\sigma^{(HFL)}$ and $\sigma^{(AC)}$ were calculated from (2.61), derived in appendix E. For a fixed lower integration limit ζ , the roots of $\Theta(b) = \zeta$ were determined using the same procedure as described for the differential cross section. The derivatives of $\Theta(b)$ were evaluated using the splined χ data and the analytic Akima spline derivative in order to determine the appropriate s'_k . All contributions were then summed according to (2.61). In the case of $\chi^{(AC)}$, the cross section was obtained for each ϕ_c and then averaged to obtain $\sigma^{(AC)}$. The algorithm for obtaining the integrated cross section was coded in the cross program. Parsing of the main data files for generating the integrated cross section was performed with the prp.xscn.csh script. Averaging for $\sigma^{(AC)}$ was done with the extended Simpson's rule program xavg. In all cross sections reported, the lower integration angle used was $\zeta = 4.5^\circ$. Both differential and integrated cross sections calculated for the field-free case were checked against available literature data for the Lennard-Jones (6,12) potential [191].

Since the cross program takes arbitrary deflection function data as its input, the impulse approximation expressions of (2.98) and (2.104) were used to generate cross sections. The impulse program was used to generate $\chi_{IA}^{(HFL)}$ and $\chi_{IA}^{(AC)}$ in a range of $b \in [0.8, 5]$ with a resolution of 0.01. The differential and integrated cross sections of these calculations were determined using the methods described above.

Finally, the HDID-IA model expressions of $d\sigma^{(HFL)}/d\Omega$ and $\sigma^{(HFL)}$ of section 2.5.3.2 were calculated. The results of equations (2.121) and (2.122) were coded in the impprp program. The model was derived explicitly for $U^{(HFL)}$ but results for $U^{(AC)}$ were obtained in the static field limit by weighting the input field strength F by a factor of $\sqrt{2} \cos \phi_c$.

according to (2.77). The results for each fixed ϕ_c (101 in total, equidistant over $[0, 2\pi]$) were then averaged to estimate $d\sigma^{(AC)}/d\Omega$ and $\sigma^{(AC)}$ using the model. Averaging was performed with the xavg program. The impprp.drv.csh script performed the model static-field limit calculations.

Chapter 4

Discussion of Results for HeAr and He₂

The present chapter is devoted to presenting the results of dynamical calculations on the strong-field Hamiltonians. A number of the simple models developed in chapter 2 are also tested quantitatively. The main emphasis of these results is to establish a link between the laser-induced potential features and those of the observables (the collision cross section) of the molecular beam experiment proposed in chapter 1. To this end, the properties of $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ are examined in section 4.1. A link between the laser-induced potential features and the dynamics is established in section 4.2, via examination of classical trajectories, resulting in the identification of classes of similar dynamical behaviour; these “collision mechanisms” are shown to arise from specific laser-induced features of $U^{(\text{AC})}$ and/or $U^{(\text{HFL})}$ and result in characteristic behaviours in the deflection function. In section 4.3, the special features of the classical deflection function are examined over a wide range of laser parameters and collision energies, characterising the conditions where the collision mechanisms exist and their signatures in the collision cross sections. Finally, section 4.4 examines the collision cross sections over a range of conditions and their behaviour is interpreted in terms of contributions from different collision mechanisms. Thus a qual-

itative link between laser-induced potential features and the observables of the molecular beam experiment is established.

In the subsequent calculations, molecular parameters for HeAr are used predominantly although some discussion of results for He₂ is also given. These parameters were determined empirically from literature results and showed that the reduced parameter set are similar for all rare-gas dimers RgRg' (Rg, Rg' = He, Ne, Ar). Hence, only two representatives are taken from this family. Details of the determination and the resulting parameters are given in appendix B. In addition, the range of laser parameters (F, Ω) and dynamical initial conditions (K, b) were determined for HeAr and He₂ such that they correspond to realistic experimental conditions; the details of these considerations are given in appendix C.

4.1 Features of the Laser-Induced Potentials

The particular behaviour of the RgRg' systems (see appendix B) shows that $U^{(\text{HFL})}$ is dominated by $U_{\text{aniso},\alpha}^{(\text{HFL})}$. In figure 4.1, $U_{\text{iso}}^{(\text{HFL})}$ is shown as a function of distance X for $F \in \{0, 3\}$ and $\Omega \in \{1, \Omega_{\text{CO}_2}\}$ for HeAr using the parameters of table B.9. The solid line shows $F = 0$ or U_0 as a reference curve. When the field is increased, two competing effects emerge: repulsion due to $U_{\text{iso},d}^{(\text{HFL})}$ and attraction from $U_{\text{iso},\alpha}^{(\text{HFL})}$. From the trace polarisabilities of the Rg-dimers (shown in figure B.3), it is expected that $U_{\text{iso}}^{(\text{HFL})} \approx U_0$ except perhaps at $X \ll 1$ where there may be some additional repulsion. This is shown in figure 4.1 by the dashed line for $U_{\text{iso}}^{(\text{HFL})}$ with $F = 3$ and $\Omega = \Omega_{\text{CO}_2}$ (value given in table C.1). The dipole term $U_{\text{iso},d}^{(\text{HFL})} \approx 0$ in this case since the frequency factor for $\Omega_{\text{CO}_2}^{-2}$ is approximately $1/90000$. The net effect of $U_{\text{iso},\alpha}^{(\text{HFL})}$ is therefore seen to consist of a small increase in long-range attraction (cf. dashed and solid lines in figure 4.1) and an equally small decrease in the radial well depth near $X \approx 1$.

Figure 4.1: The potential $U_{\text{iso}}^{(\text{HFL})}$ vs. X for HeAr. Model parameters are taken from table B.9 with Ω_{CO_2} taken from table C.1. All quantities are in reduced units. Solid line — $F = 0$; dotted line — $F = 3$, $\Omega = 1$; dashed line — $F = 3$, $\Omega = \Omega_{\text{CO}_2}$. Note that the high frequency limit is not valid at $\Omega = 1$.

The contribution of $U_{\text{iso},d}^{(\text{HFL})}$ to $U_{\text{iso}}^{(\text{HFL})}$ will be non-negligible for $\Omega \ll \Omega_{\text{CO}_2}$; this is demonstrated by the unrealistic case of $\Omega = 1$ (where the high-frequency limit is not valid), shown as the dotted line in figure 4.1. Here, in spite of the small value of Q (table B.9), there is a strong short-range repulsion which is required by the form of $U_{\text{iso},d}^{(\text{HFL})}$, the magnitude of which is determined by Λ_d . However, for realistic frequencies $U_{\text{iso}}^{(\text{HFL})} \approx U_0$ for the RgRg' systems considered here; it follows that in the isotropic potential regime of equation (2.49) will only occur for $U^{(\text{HFL})}$ in weak fields ($F \ll 1$) since $U_{\text{iso}}^{(\text{HFL})}$ is independent of F .

The effect of $U_{\text{aniso}}^{(\text{HFL})}$ is demonstrated for HeAr and He₂ in figures 4.2 and 4.3, respectively. In both these figures, $F = 3$ and $\Omega = \Omega_{\text{CO}_2}$ (see table C.1 for values) to provide a more dramatic example of the field-induced effects. The figures show polar contour plots of $U^{(\text{HFL})}(X, \theta)$ with contour values given in reduced units in the figures. A number of things are evident from consideration of the figures: first, that the two molecular systems are almost quantitatively identical (cf. values in table B.9), implying $U_{\text{aniso},d}^{(\text{HFL})} \approx 0$ for HeAr. Second, there are two potential wells located at $\theta \in \{0, \pi\}$ and these are significantly deeper than the field-free well. The minimum is now less than -2.0, over double that of the field-free radial well depth. This is a consequence of the large attractive force induced by the polarisability anisotropy in $U_{\text{aniso},\alpha}^{(\text{HFL})}$. As θ is increased from 0, $U_{\text{aniso},\alpha}^{(\text{HFL})}$ passes from an attractive to a repulsive contribution at $\pi/2$. This results in two new potential features, a “rotational well” and a “barrier to rotation” (see section 2.2 for definitions). For the particular systems shown in figures 4.2 and 4.3, the rotational well depth is such that higher energy bound states can sample both potential wells along the field axis; however, the potential minimum is ca. -0.3 perpendicular to the field, thus the rotational well should have a significant influence on the dynamics for all but the perturbative potential regime. The barrier to rotation is seen for $X \gtrsim 0.5$ (zero contours in the figures), going through a small

Figure 4.2: A polar contour plot of $U^{(\text{HFL})}(X, \theta)$ for HeAr with $F = 3$ and $\Omega = \Omega_{\text{CO}_2}$. The radial coordinate shows $X \in [0, 3]$ (rings mark every 1.0 of X) while the polar coordinate denotes $\theta \in [0, 2\pi]$ radians (axis marks at 0 and $\pi/2$). The solid dark contours shown potential energy values indicated in the figure. Lighter contour lines denote minor increments of 0.2 units. The dashed contours label positive energy values of 0.02 and 0.04. Molecular parameters are taken from table B.9 with Ω_{CO_2} from table C.1. The potential function is given in (2.27).

Figure 4.3: A polar contour plot of $U^{(\text{HFL})}(X, \theta)$ for He_2 with $F = 3$ and $\Omega = \Omega_{\text{CO}_2}$. The radial coordinate shows $X \in [0, 3]$ (rings mark every 1.0 of X) while the polar coordinate denotes $\theta \in [0, 2\pi]$ radians (axis marks at 0 and $\pi/2$). The solid dark contours shown potential energy values indicated in the figure. Lighter contour lines denote minor increments of 0.2 units. The dashed contours label positive energy values of 0.02 and 0.04. Molecular parameters are taken from table B.9 with Ω_{CO_2} from table C.1. The potential function is given in (2.27). Note the similarity to figure 4.2.

(ca. 0.04) maximum near $X = 1$. Since the value of the local maximum is not large, it is anticipated that the system will be sensitive to it only for small kinetic energies, i.e. in the anisotropic or coupled potential regimes of equation (2.49).

The cycle-averaged potential for the time-dependent c.w. field, $\langle U^{(AC)} \rangle_{\phi_c}$ will have similar features to those of $U^{(HFL)}$ since the dipole contributions to the latter are negligible. However, in $U^{(AC)}$ a larger interaction at the peak of the field is possible than in $U^{(HFL)}$. This is demonstrated in figure 4.4: here the potential surface is shown for a fixed value of θ and $F = 3$ for both HeAr and He₂. In all figures 4.4(a)–(d), the progression of the surface through the laser cycle is shown with curves of fixed ϕ_c ($\Omega\tau$ is set to zero in (2.26); phases which are redundant due to symmetry are not shown). In figure 4.4(a) He₂ with $\theta = 0$ is shown. The symmetry of the $\cos^2 \phi_c$ term in $U^{(AC)}$ produces potential curves which are symmetric about $\phi_c = \pi/2$. The potential thus oscillates between its field-free value at $\phi_c = \pi/2$ (green line in figure) and a Stark-shift twice that of $\langle U^{(AC)} \rangle_{\phi_c}$ at $\phi_c = 0$ (black line). For comparison, the $U^{(HFL)}$ curve is identical to that of $\phi_c = \pi/4$ (blue curve in figure 4.4(a)). There is no large shift $X_{\min}^{(AC)}$ with ϕ_c but the radial well depth at the peak of the cycle appears to be substantially larger than the field-free value (ca. $\times 4$ at $\phi_c = 0$) and the $U^{(HFL)}$ value (ca. $\times 2$).

The presence of a permanent dipole moment gives a symmetry over the cycle about $\phi_c = \pi$; this is shown in figure 4.4(b) for HeAr with $\theta = 0$. The radial well is deepened by a much larger amount at the peak of the cycle ($\phi_c = 0$, black curve in (b)) in comparison to that of $\langle U^{(AC)} \rangle_{\phi_c}$ (approximated by the $\phi_c = \pi/4$ (red) curve). Comparison of phases where the only difference is the sign of the dipole term, i.e. ϕ_c vs. $\pi - \phi_c$ show that in $U^{(AC)}$ the dipole has an effect on the potential surface. As an example, the $\phi_c = 0$ and $\phi_c = \pi$ curves (black and green lines in figure 4.4(b), respectively) have radial well depths

Figure 4.4: A plot of the potential energy curves of $U^{(AC)}$ vs. X for HeAr and He₂ over a laser cycle. Values of the laser phase ϕ_c are given in the legends. For clarity, phases which are redundant due to symmetry are not displayed. In all cases (2.26) is used with $F = 3$ and molecular parameters taken from table B.9. Figure (a) — He₂, $\theta = 0$; (b) — HeAr, $\theta = 0$; (c) — He₂, $\theta = \pi/2$; (d) — HeAr, $\theta = \pi/2$.

of approximately 6 and 3 times the field-free value and minimum geometries of 0.9 and 1.0, respectively. This large difference in the properties of the potential well is due entirely to the repulsive interaction of the permanent dipole moment when $\phi_c = \pi$. That the dipole effect only short-range is evident from the fact that the two curves are identical for $X \gtrsim 1.3$. Similar behaviour is noted for the other phases of the figure. From comparison with the homonuclear case of figure 4.4(a), the effects of the permanent dipole should be discernible for any observable which is sensitive to the position and depth of the well in the limit of low carrier frequency. It should be noted that the behaviour of the potential well at $\theta = \pi$ is identical to that shown in figure 4.4(b) with $\pi - \phi_c$ phase dependence.

Figures 4.4(c) and (d) show He_2 and HeAr at $\theta = \pi/2$, respectively. Since the dipole term is identically zero perpendicular to the field, the two systems have essentially the same potential curve over the laser cycle. The polarisability interaction is repulsive at this angle due to the $\cos 2\theta$ term in $U^{(\text{AC})}$. Consequently, the potential oscillates from its field-free value ($\phi_c = \pi/2$) to a completely repulsive state ($\phi_c = 0$). The greater interaction with the field in $U^{(\text{AC})}$ is shown from comparison with the $\langle U^{(\text{AC})} \rangle_{\phi_c}$ curve ($\phi_c = \pi/4$ in both figures) which still contains a metastable radial well (cf. with figures 4.2 and 4.3). The prohibition of rotation (for all bound states) in the case of $U^{(\text{AC})}$ at the peak of the cycle (black curve) should cause some significant qualitative differences from the dynamics of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ (or $U^{(\text{HFL})}$).

The above statements can be quantified by examining the pertinent features of the potential surface given in section 2.2: $X_{\min}$, $X_{\max}$, Δ_e , $\Delta_{\theta,-}$ and $\Delta_{\theta,+}$ for $U^{(\text{AC})}$ and $U^{(\text{HFL})}$. Figure 4.5 shows the behaviour of these properties as a function of F for HeAr and He_2 . In the case of $U^{(\text{HFL})}$, the symmetry of the system requires only the potential well at $\theta = 0$ be analysed while for $U^{(\text{AC})}$, the dipole of HeAr requires the additional results of $\theta = \pi$ to

Figure 4.5: Plots of the laser-induced features of $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ as functions of F for HeAr and He₂. Figure (a) shows $X_{\min}$; (b) — $X_{\max}$; (c) — Δ_e ; (d) — $\Delta_{\theta,-}$ (inset $\Delta_{\theta,+}$). In all figures, black denotes $U^{(\text{AC})}$, He₂; red — $U^{(\text{AC})}$, HeAr; blue — $U^{(\text{HFL})}$, He₂; green — $U^{(\text{HFL})}$, HeAr. Line styles denote results for $\theta = 0$ (solid), $\theta = \pi/2$ (dotted) and $\theta = \pi$ (dashed) in all figures. In all calculations for $U^{(\text{AC})}$, $\phi_c = 0$ was used. All data was generated from numerical solutions to (2.44)–(2.47). See section 3.1 for numerical details.

also be shown. For completeness $X_{\min}$ at $\theta = \pi/2$ is also shown in figure (a). Details of the calculations, the numerical solutions to (2.44)–(2.47), are presented in section 3.1.

In figure 4.5(a), $X_{\min}^{(\text{HFL})}$ for He_2 (blue lines) and HeAr (green lines) shows that the potential well geometry decreases with F at $\theta = 0$ (solid lines) but increases for $\theta = \pi/2$ (dotted lines). The behaviour can be explained in terms of the laser-induced interactions of $U^{(\text{HFL})}$: for $\theta = 0$, the net polarisability interaction of $U_{\text{aniso},\alpha}^{(\text{HFL})}$ is stabilising (i.e. negative). Since the interaction is largest at $X < 1$, the effect of the stabilisation is to shift the minimum of the potential well to shorter X . For He_2 , this results in a shortening of $X_{\min}^{(\text{HFL})}$ to ca. 0.98 for ($F = 3, \theta = 0$) which, though small in relative terms, is of an experimentally observable magnitude (approximately 0.1 a.u. given the value of R_0 in table B.1). In contradistinction to the latter behaviour, the Stark shift is destabilising for $\theta = \pi/2$ and the added repulsive term to the potential results in shift of $X_{\min}^{(\text{HFL})}$ to larger X ; the effect is larger in this case, with $X_{\min}^{(\text{HFL})} \approx 1.03$ for $F = 3$ near $\theta = \pi/2$. Note that there is no significant quantitative difference between HeAr and He_2 results.

The results of $X_{\min}^{(\text{AC})}$ for He_2 (black lines) and HeAr (red lines) shown in figure 4.5(a) can be used to find the behaviour of $X_{\min}^{(\text{AC})}$ over the whole laser cycle by letting $F \cos \phi_c \rightarrow F$ and using the results of the figure for $\theta = 0$ ($\phi_c \in [0, \pi/2]$ and $\phi_c \in [3\pi/2, 2\pi]$) and $\theta = \pi$ ($\phi_c \in (\pi/2, 3\pi/2)$)¹. The qualitative effect is the same as that of $X_{\min}^{(\text{HFL})}$: thus, the attractive field-interaction at $\theta = 0$ (solid lines) decrease $X_{\min}^{(\text{AC})}$ and increases it along $\theta = \pi/2$. For HeAr , the dipole introduces an additional attraction (repulsion) when the field is parallel (anti-parallel); thus, $X_{\min}^{(\text{AC})}$ for $\theta = \pi$ (dashed red line) increases with F until the

¹For example, when $F = 2.0$ and $\phi_c \in [0, \pi/2]$ for HeAr , $X_{\min}^{(\text{AC})}$ is initially ca. 0.92 and follows the solid red curve to 1.0 at $\phi_c = \pi/2$. For $\phi \in (\pi/2, \pi]$, $X_{\min}^{(\text{AC})}$ follows the dashed red line from $F = 0.0$ to $F = 2.0$ at $\phi_c = \pi$; the value of $X_{\min}^{(\text{AC})}$ then retraces this path as ϕ_c goes to 2π . For a homonuclear system, the path is confined to values on the $\theta = 0$ curve. This procedure can also be used to obtain the remaining features of $U^{(\text{AC})}$ over the course of the laser cycle.

polarisability interaction begins to dominate at $F \gtrsim 1$. Since no dipole is present at $\theta = \pi/2$, the results for $X_{\min}^{(\text{AC})}$ of HeAr and He₂ (dotted lines) are quantitatively similar.

The analysis of $X_{\max}^{(\text{AC})}$ and $X_{\max}^{(\text{HFL})}$ in figure 4.5(b) follows in a manner similar to $X_{\min}$. No dipole contributes at $\theta = \pi/2$ and hence the $X_{\max}^{(\text{AC})}$ for He₂ and HeAr are identical (black and red lines, respectively), with a similar agreement observed for $X_{\max}^{(\text{HFL})}$ (blue and green lines). Comparison between $X_{\max}^{(\text{AC})}$ and $X_{\max}^{(\text{HFL})}$ shows that the $U^{(\text{AC})}$ barrier position is at smaller X due to the higher effective field at the peak of the laser cycle. For both potentials, the position of the barrier is comparable to $X_{\min}$ for $F \gtrsim 1$. Hence, the barrier to rotation generally influences dynamics of the long-range part of $U^{(\text{HFL})}$ or $U^{(\text{AC})}$.

The behaviour of the radial well-depths $\Delta_e^{(\text{HFL})}$ and $\Delta_e^{(\text{AC})}$ of figure 4.5(c) demonstrate the dramatic strengthening of the bond in the laser field. Both He₂ and HeAr (blue and green lines, respectively) show an increase in $\Delta_e^{(\text{HFL})}$ to ca. twice the field-free well depth as F is increased to 3.0. The attractive Stark shift is increased in $U^{(\text{AC})}$ as shown by $\Delta_e^{(\text{AC})}$ of He₂ (black line) going to a maximum of approximately 4.0 over the same range. As might be expected the effect of the dipole on $\Delta_e^{(\text{AC})}$ in HeAr reduces the well depth considerably from $\theta = 0$ (solid red line) to $\theta = \pi$ (red dashed line); in fact, for $F \lesssim 1$, the value of $\Delta_e^{(\text{AC})}$ at $\theta = \pi$ is less than the field-free value, indicating that the polarisability dominates $U^{(\text{AC})}$ only at larger fields. The effect of the dipole leads to a maximum value of $\Delta_e^{(\text{AC})}$ of ca. 6 at $F = 3.0$, showing that the laser can significantly stabilise the system.

Figure 4.5(d) shows $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,-}^{(\text{AC})}$ for HeAr and He₂. The rotational well depth of $U^{(\text{HFL})}$ shows similar qualitative behaviour to that of $\Delta_e^{(\text{HFL})}$ and can be approximated by $\Delta_{\theta,-}^{(\text{HFL})} \approx \Delta_e^{(\text{HFL})} - 1$ for larger values of F . Thus the rotational well depth of $U^{(\text{HFL})}$ is comparable in energy to $\Delta_e^{(\text{HFL})}$ for larger fields and its dynamic effects cannot be neglected except perhaps in the perturbative potential regime of (2.49). For $\Delta_{\theta,-}^{(\text{AC})}$, figure 4.5(d) shows

that $\Delta_{\theta,-}^{(\text{AC})} \sim \Delta_e^{(\text{AC})}$ for larger F and is even larger than the radial well depth for $F \approx 3$. Thus for large F the potential along $\theta = \pi/2$ is completely repulsive and no rotation is possible; this implies that dynamics will be significantly different for $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ when F is large.

The inset of figure 4.5(d) shows $\Delta_{\theta,+}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{AC})}$ as a function of F for HeAr and He₂. For all but the highest fields considered, the barrier to rotation is negligibly small. For $F \gtrsim 2$, $\Delta_{\theta,+}^{(\text{AC})}$ is larger than 0.1; thus, the effects of the barrier to rotation may be observable in the dynamics of $U^{(\text{AC})}$ when the collision energy is comparable to this value. In the case of $U^{(\text{HFL})}$, $\Delta_{\theta,+}^{(\text{HFL})}$ has a maximum value at $F = 3.0$ of less than 0.1, implying the effects of the barrier to rotation will not be significant except for very low- K dynamics.

The quantitative accuracy of the HDID model of section 2.5.2 is examined in figure 4.6. The figure shows $X_{\min}^{(\text{HFL})}$, $X_{\max}^{(\text{HFL})}$, $\Delta_e^{(\text{HFL})}$, $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{HFL})}$ as functions of F for both He₂ (red symbols) and HeAr (blue symbols). The symbols in the figure are exact results (cf. figure 4.5) while the solid and dashed lines represent the HDID model predictions for each of the features for He₂ and HeAr, respectively. Circles identify features evaluated at $\theta = 0$ and squares correspond to $\theta = \pi/2$. Figure 4.6(a) shows $X_{\min}^{(\text{HFL})}$ vs. F : that (2.90) is only qualitatively correct for high fields is evident. The HDID model overestimates the contraction of the minimum geometry at $\theta = 0$ and predicts a larger difference between He₂ and HeAr than is actually observed for the numerical results. For $\theta = \pi/2$, agreement with the model persists to larger field strengths but the model progressively underestimates the lengthening of the bond as F increases. This effect must be due to the neglect of the exchange terms from the polarisability in (2.90) since the dipole is negligible; since $X_{\min}^{(\text{HFL})} \sim 1$, the exchange terms in α and β influence the minimum geometry due to their non-negligible contribution to $U^{(\text{HFL})}$ at this distance. The disagreement is most likely

Figure 4.6: Plots of the features of $U^{(\text{HFL})}$ vs. F for He₂ and HeAr with $\Omega = \Omega_{\text{CO}_2}$. In all figures, blue symbols indicate exact results for He₂ (cf. with the corresponding result of figure 4.5) while red denote HeAr; circles denote properties evaluated at $\theta = 0$ and squares $\theta = \pi/2$. Lines show the corresponding HDID model predictions (equations (2.84), (2.85), (2.86), (2.90) and (2.92)): solid — HeAr, dashed — He₂. Figure (a) — $X_{\min}^{(\text{HFL})}$; (b) — $X_{\max}^{(\text{HFL})}$; (c) — $\Delta_e^{(\text{HFL})}$; (d) — $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{HFL})}$ (inset). See section 3.1 for numerical details.

due to the neglect of the exchange term in the polarisability trace since the DID model is qualitatively inaccurate for this property.

Figure 4.6(b) shows $X_{\max}^{(\text{HFL})}$ vs. F for the two systems. Agreement between the HDID model (2.92) and the numerical results is excellent. Additionally, there is no discernible difference between He_2 and HeAr . The agreement of the model with the results for the actual surface can be attributed to the fact that, for the range of F examined, $X_{\max}^{(\text{HFL})} > 1$; for these distances, the exchange terms of both the trace and anisotropy are negligible and the approximations used in the derivation of (2.92) are therefore valid.

The radial well depth, $\Delta_e^{(\text{HFL})}$, of He_2 and HeAr are shown in figure 4.6(c). The HDID model result of (2.84) appears to overestimate the binding for $F \gtrsim 1$. The quantitative inaccuracy of the model of $\Delta_e^{(\text{HFL})}$ is simply a consequence of the propagation of the initial error in $X_{\min}^{(\text{HFL})}$ by (2.90) through equation (2.84).

Finally, figure 4.6(d) shows the rotational well depth $\Delta_{\theta,-}^{(\text{HFL})}$ and barrier to rotation $\Delta_{\theta,+}^{(\text{HFL})}$ (inset) as functions of F ; the HDID model predictions using equations (2.85) and (2.86), respectively are shown to be more accurate at large F than for the corresponding $\Delta_e^{(\text{HFL})}$. The agreement is much better for $\Delta_{\theta,+}^{(\text{HFL})}$ than for $\Delta_{\theta,-}^{(\text{HFL})}$ due to the inclusion of $\theta = 0$ energies in the latter. The barrier to rotation occurs at larger X and thus exchange terms do not contribute to this feature of $U^{(\text{HFL})}$.

The totality of the effects of laser interaction as evidenced by the results presented above is to increase the radial potential well depth, induce a rotational well and a barrier to rotation as F is increased; in terms of energetic importance, the radial potential well is largest and the rotational well only becomes comparable at high fields. The barrier to rotation is generally an order of magnitude less than the other features for both $U^{(\text{HFL})}$ and $U^{(\text{AC})}$. With the exception of the potential well at $\theta = \pi$ in a heteronuclear system, all the

above properties vary monotonically with F . It is also clear that the time-dependence of $U^{(AC)}$ endows the potential with features that are comparable to those of $U^{(HFL)}$ for a higher effective field; this relationship is quantitative for homonuclear systems since $\langle U^{(AC)} \rangle_{\phi_c} = U^{(HFL)}$. Thus, $U^{(AC)}$ dynamics will exhibit features of $U^{(HFL)}$ dynamics at stronger fields provided $w \lesssim 1$ (see equation (2.53)). Finally, the HDID model of $U^{(HFL)}$ is shown to be qualitatively correct for the potential features, indicating that the dynamics should show similar agreement.

4.2 Analysis of Laser-Induced Dynamics

The following section considers the detailed behaviour of the scattering in the potentials of $U^{(HFL)}$ and $U^{(AC)}$; in particular, correlations are established between features of the potential surface identified in section 4.1, and the observed deflection functions. The field dependence and, in the case of $U^{(AC)}$, the phase and frequency dependence of the dynamics are also examined. The analysis proceeds through different regimes of collision energy K and carrier frequency Ω in the order of increasing complexity and decreasing amount of analytical information. Study of the trajectories leads to identification of collision mechanisms which correlate groups of trajectories with potential features and any signatures evident in the deflection functions. Details of the classical trajectory calculations and the numerical averaging methods are given in section 3.2 while those of the impulse approximation calculations are given in section 3.3.

4.2.1 Collisions in the High Frequency Limit

In the limit of high laser carrier frequency, such as is obtained for $\Omega = \Omega_{\text{CO}_2}$ (see table C.1) in the case of the Rg-dimers, the time-independence of $U^{(\text{HFL})}$ and its implicit energy conservation dictate that the only parameters of interest are the collision energy K and the field strength F . The carrier frequency Ω is not relevant since at values required for $U^{(\text{HFL})}$ to be valid, $U_{\text{iso},d}^{(\text{HFL})}$ and $U_{\text{aniso},d}^{(\text{HFL})}$ are negligible, making $U^{(\text{HFL})}$ effectively independent of Ω . Thus, only results for HeAr need be obtained since those of other Rg-dimers will be identical².

4.2.1.1 High Energy Regime

In the regime of high kinetic energy collisions, where e.g. $K = 10$, examination of (2.49) shows that $K \gg |U^{(\text{HFL})}|$ is valid over all impact parameter and F -ranges; thus, the system is uniformly in the perturbative potential regime. This implies that the dynamics will be qualitatively similar to that of the field-free case overall. In addition, the impulse approximations to the deflection angles of $\chi^{(\text{HFL})}$ given by (2.98) will yield accurate predictions of the dynamics. Furthermore, calculations of the dynamic observables using the partitioned potentials $\{U_{\text{iso}}^{(\text{HFL})}, U_{\text{aniso}}^{(\text{HFL})}\}$ of (2.32) and (2.33) may be used to determine the origin of their specific features.

The qualitative similarity between $\chi^{(\text{HFL})}(b; F = 0)$ and $\chi^{(\text{HFL})}(b; F \neq 0)$ in the perturbative regime is examined in figure 4.7; shown are some sample trajectories of HeAr from the $F = 0.0$ (dashed lines) and $F = 3.0$ (solid lines) deflection functions (calculation details are given in section 3.2). Lines with the same colour correspond to the same initial conditions, differing only in the field strength used. The trajectories are plotted over top of

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²N.B.: This has been verified numerically.

Figure 4.7: Some sample trajectories for HeAr, $F \in \{0.0, 3.0\}$, $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. Trajectories are shown over top of a contour plot of the $F = 3.0$ surface of $U^{(\text{HFL})}$; contour values shown are those of figure 4.2. Solid lines show trajectories for $F = 3.0$ while dashed lines of the same colour are $F = 0.0$ trajectories. Glory and rainbow trajectories on the $F = 3.0$ surface are indicated by $b_g^{(\text{HFL})}$ and $b_r^{(\text{HFL})}$, respectively. Impact parameters used are: violet line — $b = 0.20$; dark green — $b = 0.60$; light green — $b = 0.80$; blue — $b = 1.00$; turquoise — $b_g^{(\text{HFL})} \approx 1.03$; maroon — $b_r^{(\text{HFL})} \approx 1.13$; red — $b = 1.50$; magenta — $b = 2.00$. Arrows indicate the time-flow of the trajectories. Details of the calculations are described in section 3.2.

the contour surface of $U^{(\text{HFL})}$, $F = 3.0$ given in figure 4.2 for HeAr (see figure for contour values). Impact parameters selected cover the small- and mid-range, including the glory and rainbow impact parameters $b_g^{(\text{HFL})}$ and $b_r^{(\text{HFL})}$, respectively. The figure shows the origin of the field-induced differences in the scattering: up to the distance of closest approach, the $F = 3.0$ trajectories are essentially identical to those of $F = 0.0$ for all impact parameters. At the distance of closest approach X_c , angular momentum is changed due to $U_{\text{aniso},\alpha}^{(\text{HFL})}$, specifically due to the rotational well feature. The magnitude of $\Delta P_\theta^{(\text{HFL})}$ is determined by F and X_c since $U_{\text{aniso},\alpha}^{(\text{HFL})}$ is larger at smaller X while the sign of $\Delta P_\theta^{(\text{HFL})}$ is determined by $\sin 2\theta_c$, where θ_c is the angle of closest approach. From the definition of the deflection angle (2.59), $\Delta P_\theta^{(\text{HFL})}$ alters $\dot{\theta}$ which in turn changes $\theta_{+\infty}$ and hence $\chi^{(\text{HFL})}$. Thus, small b trajectories have larger $\chi^{(\text{HFL})}$ for $F = 3$ since X_c is small and $\theta_c \leq \pi/2$; for the mid-range impact parameters ($b > 1.03$ in figure 4.7), the difference in $\chi^{(\text{HFL})}$ is small and negative.

Selected HeAr deflection functions $\chi^{(\text{HFL})}(b)$ for the fields $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$, $K = 10$ and $\Omega = \Omega_{\text{CO}_2}$ are shown in figure 4.8; all angles are reported in units of π -radians. The results illustrate the effect of the field more clearly; for small impact parameters where $\chi^{(\text{HFL})}(b)$ is large, the deflection function is monotonically increasing with F for a fixed b as is expected from considering the effect of increasing $U_{\text{aniso},\alpha}^{(\text{HFL})}$. The small degree of sensitivity to the field appears to have a maximum in this region near $b \approx 0.6$, decreasing as b approaches either a head-on collision ($b = 0$) or the rainbow impact parameter $b_r^{(\text{HFL})}$; the first effect is due to the decrease in initial angular momentum which limits the loss $\Delta P_\theta^{(\text{HFL})}$. For $b > b_r^{(\text{HFL})}$, $\Delta P_\theta^{(\text{HFL})}$ and $\chi^{(\text{HFL})}$ are determined as discussed above and the deflection function is monotonically decreasing with F at fixed b . While the rainbow impact parameter $b_r^{(\text{HFL})}$ shifts to higher b with increasing F , there appears to be little variation in the value of the rainbow angle $\chi_r^{(\text{HFL})}$, where the deflection function passes through a local

Figure 4.8: Sample deflection functions $\chi^{(\text{HFL})}$ vs. b using $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. The data is identical to that used in figure 4.9. Angles reported are in units of π -radians. Indicated in the figure are the regions of the forward glory $\chi^{(\text{HFL})} = 0$ and rainbow $\chi_r^{(\text{HFL})}$ deflection angles. Black line — $F = 0.0$; red line — $F = 1.0$; blue line — $F = 2.0$; orange line — $F = 2.5$; green line — $F = 3.0$. Details of the calculations are described in section 3.2.

minimum.

Figure 4.9 confirms the assertion that the dynamics lie in the perturbative potential regime. The figure shows a contour plot of $\chi^{(\text{HFL})}(b, F)$ for $K = 10$ and $\Omega = \Omega_{\text{CO}_2}$ for HeAr. All contours are reported in units of π -radians. The forward glory contour ($\chi^{(\text{HFL})} = 0$) is shown as a thick dashed line. The rainbow angle contour, while not identified explicitly in the figure, lies between the -0.0625π contours (green lines) centred around the impact parameter of $b_r^{(\text{HFL})} \approx 1.1$. Numerical details of the trajectory calculations are given in section 3.2. Note that all contours shift to higher impact parameters as F is increased, in keeping with the interpretation of the field-induced effects on $\chi^{(\text{HFL})}$ in terms of $\Delta P_\theta^{(\text{HFL})}$. However, only the small impact parameter region exhibits a great degree of sensitivity to F , and the whole system resides in the perturbative potential regime.

Further examination of the dominant potential contributions to $\chi^{(\text{HFL})}$ in the high- K regime is performed in figure 4.10; here $\chi_{\text{iso}}^{(\text{HFL})}$ and $\chi_{\text{aniso}}^{(\text{HFL})}$ are calculated using the partition equations of motion defined in (2.32) and (2.33), respectively. Both exact trajectories (black lines) and the impulse approximation formulae $\chi_{\text{IA}}^{(\text{HFL})}$, $\chi_{\text{iso,IA}}^{(\text{HFL})}$ and $\chi_{\text{aniso,IA}}^{(\text{HFL})}$ (red lines) given in equations (2.98) (numerical details are given in sections 3.2 and 3.3) are shown. While the anisotropy is essential to the mechanism which causes an increase in $\chi^{(\text{HFL})}$ at small impact parameter, it is clear from the figure that the $\chi_{\text{aniso}}^{(\text{HFL})}$ trajectories (black, dashed line) do not give even qualitative agreement with those of $\chi^{(\text{HFL})}$ (black, solid line). The isotropic $\chi_{\text{iso}}^{(\text{HFL})}$ is in much better agreement (black, dotted line). However, the $U_{\text{iso}}^{(\text{HFL})}$ calculation underestimates the exact deflection angle in this region since no loss of angular momentum is possible. In the large-impact parameter region (inset of figure 4.10), it is shown that $\chi_{\text{aniso}}^{(\text{HFL})} > 0$ which is in qualitative disagreement with $\chi^{(\text{HFL})}$. Similar results are obtained from the impulse approximation formulae, with $\chi_{\text{aniso,IA}}^{(\text{HFL})} > 0$ (red dashed line) for all impact

Figure 4.9: A contour plot of $\chi^{(\text{HFL})}(b, F)$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. Contour values shown are given labelled with units of π -radians. The forward glory angle contour ($\chi^{(\text{HFL})} = 0$) is shown as a thick dashed line. Details of the calculations are described in section 3.2.

Figure 4.10: A comparison of the deflection functions of the partitions of $U^{(\text{HFL})}$ for HeAr with $K = 10$, $\Omega = \Omega_{\text{CO}_2}$ and $F = 3.0$. The deflection functions are given in units of π -radians. Black lines show numerical trajectory results with: solid line — $\chi^{(\text{HFL})}$; dotted line — $\chi_{\text{iso}}^{(\text{HFL})}$; dashed line — $\chi_{\text{aniso}}^{(\text{HFL})}$. Red lines show the results of the impulse approximation of equation (2.98): solid line — $\chi_{\text{IA}}^{(\text{HFL})}$; dotted line — $\chi_{\text{iso,IA}}^{(\text{HFL})}$; dashed line — $\chi_{\text{aniso,IA}}^{(\text{HFL})}$. The inset shows a detail of the large-impact parameter portion of the deflection function. Details of the calculations are described in sections 3.2 and 3.3.

parameters and better agreement being obtained, both qualitative and quantitative, between $\chi_{\text{iso,IA}}^{(\text{HFL})}$ (dotted red line) and $\chi_{\text{IA}}^{(\text{HFL})}$ (solid red line).

From figure 4.10, it is seen that $\chi_{\text{IA}}^{(\text{HFL})} \approx \chi^{(\text{HFL})}$ for impact parameters larger than $b_g^{(\text{HFL})}$, below which the approximation breaks down. A more detailed comparison is made in figure 4.11, where the difference of $\chi_{\text{IA}}^{(\text{HFL})} - \chi^{(\text{HFL})}$ is plotted as a function of b for HeAr with $\Omega = \Omega_{\text{CO}_2}$, $K = 10$ and $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$. For very small b , the disagreement becomes large although it appears to be independent of F . For impact parameters between $b_g^{(\text{HFL})}$ and $b_r^{(\text{HFL})}$ (indicated in the figure), the impulse approximation alternately over- and underestimates the actual deflection angle by an amount which increases in absolute magnitude with F (with a maximum of ca. 0.05π or 9°). For $b > b_r^{(\text{HFL})}$, $\chi_{\text{IA}}^{(\text{HFL})}$ consistently predicts more positive (i.e. closer to zero) deflection than is observed; this is vanishingly small (ca. 0.08°) for impact parameters larger than $b \approx 2$ although the disagreement does increase with F but at a rate which is much smaller than at intermediate impact parameters. The approximations of (2.98) therefore appear to be valid for $b > b_r^{(\text{HFL})}$ in the range of laser parameters studied.

It follows from the above results that the dynamics of $U^{(\text{HFL})}$ in the perturbative potential regime is almost identical to that of the field-free dynamics even for a strong field. The deflection function is only appreciably sensitive to F for small impact parameter trajectories which sample the region of the potential well which is of a comparable energy scale to K . Furthermore $\chi_{\text{IA}}^{(\text{HFL})}$ appears accurate for the perturbative potential regime but breaks down for small b .

Figure 4.11: The difference $\chi_{IA}^{(HFL)} - \chi^{(HFL)}$ vs. b for HeAr, $\Omega = \Omega_{CO_2}$, $K = 10$ and $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$. Differences are reported in units of π -radians. The regions of the forward glory $\chi^{(HFL)} = 0$ and rainbow angle $\chi_r^{(HFL)}$ are indicated. The inset shows the behaviour in the large-impact parameter region. Black line — $F = 0.0$; red line — $F = 1.0$; blue line — $F = 2.0$; orange line — $F = 2.5$; green line — $F = 3.0$. Details of the calculations are described in sections 3.2 and 3.3.

4.2.1.2 Mid-Energy Regime

Medium kinetic energy collisions with weak fields, for example $K = 1.0$ and $F \leq 1$, fulfill the conditions of the isotropic potential regime for small- ($b < 1$) and mid-range ($1 \lesssim b \lesssim 3$) impact parameters while for large b ($b > 3$), the system is in the perturbative potential regime; this was determined by the potential features of figure 4.5 and (2.49). For stronger fields, the energetic scale of $U_{\text{aniso}}^{(\text{HFL})}$ is comparable to K and the system is in the coupled potential regime for small- and mid-range b ; for large b , the perturbative potential regime is again valid. Thus the system is expected to be more sensitive to the details of the potential at this K , and hence to variations in F . While the impulse approximation is not expected to be valid, partition calculations of the dynamics should yield useful information regarding the role of $U_{\text{aniso}}^{(\text{HFL})}$ in determining the origin of features of $\chi^{(\text{HFL})}$.

Figure 4.12 shows a contour plot of $\chi^{(\text{HFL})}(b, F)$ for $(b, F) \in [0, 3]$ using the molecular parameters of HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 1$. The contour labels denote $\chi^{(\text{HFL})}$ in units of π -radians. The continuity of the contours with variation in F shows that $\chi^{(\text{HFL})}$ is qualitatively similar to the high- K regime in its field dependence. The surface of $\chi^{(\text{HFL})}(b, F)$ possesses one forward glory and rainbow angle contour, located at $b_g^{(\text{HFL})} \approx 1.15$ (thick dashed line in figure 4.12) and $b_r^{(\text{HFL})} \approx 1.50$ (red and black contours in figure), respectively for $F = 0$. All contours shift to larger impact parameters with increasing field. Thus, for $b < b_r^{(\text{HFL})}$, $\chi^{(\text{HFL})}$ is monotonically increasing with F while for $b > b_r^{(\text{HFL})}$, it is a monotonically decreasing function. The value of $\chi_r^{(\text{HFL})}$ appears to be decreasing with F . Note that there is greater sensitivity to F for the contours than observed in the high- K case.

Figure 4.13 confirms the trends noted above, showing selected deflection functions from figure 4.12. The F -dependence of $\chi^{(\text{HFL})}$ is identical to that of the high- K regime, implying that the rotational well plays the same role determining $\Delta P_\theta^{(\text{HFL})}$. The laser interaction

Figure 4.12: A contour plot of $\chi^{(\text{HFL})}(b, F)$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 1$. Contour values shown are given labelled with units of π -radians. The forward glory angle contour ($\chi^{(\text{HFL})} = 0$) is shown as a thick dashed line. Details of the calculations are described in section 3.2.

Figure 4.13: Sample deflection functions $\chi^{(\text{HFL})}$ vs. b using $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 1$. The data is identical to that used in figure 4.12. Angles reported are in units of π -radians. Indicated in the figure are the regions of the forward glory $\chi^{(\text{HFL})} = 0$ and rainbow $\chi_r^{(\text{HFL})}$ deflection angles. Black line — $F = 0.0$; red line — $F = 1.0$; blue line — $F = 2.0$; orange line — $F = 2.5$; green line — $F = 3.0$. Details of the calculations are described in section 3.2.

has more of a dramatic effect in this collisional energy regime: $b_g^{(\text{HFL})}$, $b_r^{(\text{HFL})}$ and $\chi_r^{(\text{HFL})}$ have larger field-induced shifts than in the $K = 10$ results (all features are indicated in the figure). No orbiting is expected for this value of K in the field-free case ($K_{orb,(-)} = 0.8$, see section 2.5.3.3). No orbiting is observed for the higher field results; this was verified numerically for $F = 3.0$ using a higher resolution in impact parameter ($\Delta b = 10^{-4}$). The absence of orbiting implies that the laser interaction terms in $U^{(\text{HFL})}$ do not dominate over U_0 even though the potential well is approximately 2.5 times deeper at $F = 3.0$ (cf. figure 4.5(c)).

Examination of the dynamics of the partitions of $U^{(\text{HFL})}$ provides further support for the role of the rotational well in the collisions. The results for HeAr with $K = 1$, $F = 3.0$ and $\Omega = \Omega_{\text{CO}_2}$ are shown in figure 4.14. The deflection functions $\chi^{(\text{HFL})}$, $\chi_{\text{iso}}^{(\text{HFL})}$ and $\chi_{\text{aniso}}^{(\text{HFL})}$ were found from trajectory calculations (see section 3.2) as functions of impact parameter. For $b < b_g^{(\text{HFL})}$, $U_{\text{iso}}^{(\text{HFL})}$ is the dominant term in the potential although the results of $\chi_{\text{aniso}}^{(\text{HFL})}$ are markedly improved over the analogous calculation for $K = 10$ (cf. results of figure 4.10). In the rainbow region, the isotropic potential again dominates since $\chi_{\text{aniso}}^{(\text{HFL})}$ is in qualitative disagreement with $\chi^{(\text{HFL})}$. For $b > b_r^{(\text{HFL})}$, shown in the inset of the figure, the system displays perturbative potential regime dynamics. The $\chi_{\text{iso}}^{(\text{HFL})}$ contribution to $\chi^{(\text{HFL})}$ is dominant with $\chi_{\text{aniso}}^{(\text{HFL})}$ providing a small repulsive correction to the deflection angle.

Qualitatively, the effect of reducing the collision energy K to a “medium” value such that $K \sim 1$ does not alter the dynamics of the collision system a great deal even in the presence of a strong field such that the coupled potential regime is valid; the system still exhibits only dynamics of the perturbative or isotropic regimes for large and small impact parameter ranges, respectively just as in the high- K case. Quantitatively, the F dependence of all the features of $\chi^{(\text{HFL})}$ are more pronounced; hence, this collision energy regime may be

Figure 4.14: A comparison of the deflection functions of the partitions of $U^{(\text{HFL})}$ for HeAr with $K = 1.0$, $\Omega = \Omega_{\text{CO}_2}$ and $F = 3.0$. The deflection functions are given in units of π -radians. Lines show numerical trajectory results with: solid line — $\chi^{(\text{HFL})}$; dotted line — $\chi_{\text{iso}}^{(\text{HFL})}$; dashed line — $\chi_{\text{aniso}}^{(\text{HFL})}$. The inset shows a detail of the large-impact parameter portion of the deflection function. Details of the calculations are described in sections 3.2.

useful in that observation of field-induced effects may be possible while the corresponding interpretation is relatively simple.

4.2.1.3 Low Energy Regime

In the regime of low collision energy, exemplified by $K = 0.1$, the conditions of (2.49) show that the system is only in the isotropic potential regime for large impact parameters ($b \gtrsim 3$). For mid-range b , $\Delta_e^{(\text{HFL})} \gg K$ for all F while $\Delta_{\theta,-}^{(\text{HFL})} \gg K$ for $F \gtrsim 1$. The barrier to rotation is even comparable to K for $F \gtrsim 3$. Thus, the dynamics for these impact parameter range should be in the isotropic potential regime for small to moderate F and in the coupled potential regime for large F . It follows that this collision energy regime should exhibit new laser-induced dynamical features, in contradistinction to those of the mid- and high- K cases.

Figure 4.15 shows sample trajectories of HeAr with $K = 0.1$, $F = 2.5$ and $\Omega = \Omega_{\text{CO}_2}$ in the small impact parameter region. The contours of the $U^{(\text{HFL})}$ potential with $F = 2.5$ are shown (black/gray lines denoting the same contour values as in figure 4.2) with trajectories (coloured lines with arrows indicating time-flow) plotted over top. Numerical details of the trajectory calculations are given in section 3.2. The impact parameters chosen are representative of the small b range with $F > 1$ (the coupled potential regime).

Figure 4.15 shows that the interpretation of $\chi^{(\text{HFL})}$ for small impact parameters employed in the high- and mid- K regimes can be extended to the low K case. The interaction with the rotational well causes a loss in angular momentum near the distance of closest approach. However, unlike the higher K cases, the interaction with the rotational well is much stronger and results in an angular turning point, i.e. P_θ changes sign, before the distance of closest approach. As a consequence, the exit part of the trajectory goes to below the field

Figure 4.15: Some sample trajectories for HeAr, $F = 2.5$, $\Omega = \Omega_{\text{CO}_2}$ and $K = 0.1$. Trajectories are shown over top of a contour plot of the $F = 2.5$ surface of $U^{(\text{HFL})}$; contour values shown are those of figure 4.2. Solid lines show trajectories for $F = 2.5$ (figure 4.17). Glory and rainbow trajectories on the $F = 2.5$ surface are indicated by $b_g^{(\text{HFL})}$ and $b_r^{(\text{HFL})}$, respectively. Impact parameters used are: red line — $b = 0.50$; green line — $b = 1.00$; blue line — $b = 2.00$; yellow line — $b_r^{(\text{HFL})} \approx 2.04$; violet line — $b = 2.08$; cyan line — $b = 2.20$; dark green line — $b_g^{(\text{HFL})} \approx 2.29$; magenta line — $b = 2.36$; orange line — $b_g^{(\text{HFL})} \approx 2.38$. Arrows indicate the time-flow of the trajectories. Details of the calculations are described in section 3.2.

($\theta = 0$) axis and thus $\theta_{+\infty} < 0$; this leads to $\chi^{(\text{HFL})} \in [\pi, 2\pi]$. Such trajectories are common and hence they constitute the first new collision mechanism:

Collision Mechanism 1 (Reflex Scattering) Any trajectory which executes one angular turning point due to the rotational well and exits the region of significant interaction below the field axis is a reflex scattering trajectory. Such trajectories lead to deflection angles between π and 2π radians.

Reflex scattering³ is controlled by $\Delta_{\theta,-}^{(\text{HFL})}$ since a strong aligning force is required to cause an angular turning point. The range of $\chi^{(\text{HFL})}$ associated with reflex scattering is limited to 2π radians since these trajectories only sample the one potential well at $\theta = 0$; sampling of the anti-parallel well at $\theta = \pi$ leads to more complex behaviour. For a fixed b , $\chi^{(\text{HFL})}$ increases with F in the reflex scattering region. As impact parameter is varied, figure 4.15 shows that $\chi^{(\text{HFL})}$ is non-monotonic and passes through a maximum at $b_r^{(\text{HFL})} \approx 2.04$, followed by a backwards glory at $b_g^{(\text{HFL})} \approx 2.29$. These reflex rainbows and backwards glories are clear signatures in $\chi^{(\text{HFL})}$ of the presence of the rotational well. At larger impact parameters the trajectory still interacts with the rotational well but since $\theta_c \approx \pi/2$, the interaction is weak and leads to forward scattering.

Unique laser-induced dynamics are also present in mid-range impact parameters. Figure 4.16 shows trajectories for HeAr, $K = 0.1$, $F = 3.0$ and $\Omega = \Omega_{\text{CO}_2}$ with the corresponding $U^{(\text{HFL})}$ contour surface (contour values of figure 4.2) shown in black/gray. The increased anisotropy of the potential relative to the $F = 2.5$ surface shown previously has an effect; in the figure, the majority of the trajectories experience more than one radial turning point, i.e. where P_χ changes sign, in the region of the potential well. In an isotropic

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³N.B.: The name of this collision mechanism is derived from the nomenclature of angles between 180 and 360 degrees.

Figure 4.16: Some sample trajectories for HeAr, $F = 3.0$, $\Omega = \Omega_{\text{CO}_2}$ and $K = 0.1$. Trajectories are shown over top of a contour plot of the $F = 3.0$ surface of $U^{(\text{HFL})}$; contour values shown are those of figure 4.2. Solid lines show trajectories for $F = 3.0$ (figure 4.17). Glory, rainbow and orbiting trajectories on the $F = 3.0$ surface are indicated by $b_g^{(\text{HFL})}$, $b_r^{(\text{HFL})}$ and $b_{\text{orb},(\pm)}^{(\text{HFL})}$, respectively. Impact parameters used are: dark green line — $b = 2.00$; orange line — $b_{\text{orb},(+)}^{(\text{HFL})} \approx 2.22$; blue line — $b_r^{(\text{HFL})} \approx 2.29$; light blue line — $b_g^{(\text{HFL})} \approx 2.44$; maroon line — $b_r^{(\text{HFL})} \approx 2.59$; red line — $b_{\text{orb},(-)}^{(\text{HFL})} \approx 2.69$; magenta line — $b = 2.75$. Arrows indicate the time-flow of the trajectories. Details of the calculations are described in section 3.2.

potential, only one radial turning point is possible, i.e. at X_c ; such a turning point is due to interaction with the repulsive core and also occurs in an anisotropic potential. Turning points which push the system back towards the core can only occur in an anisotropic potential; these occur when a metastable barrier is created along the radial coordinate, either from an increase in P_θ (centrifugal barrier) or due to the radial component of $U_{\text{aniso},\alpha}^{(\text{HFL})}$ directly (recall $U^{(\text{HFL})}$ is metastable along $\pi/2$). This mechanism is akin to the bobsled effect noted for collinear exchange reactions where θ is analogous to the reaction coordinate and X the coordinate orthogonal to it.

The presence of multiple radial turning points in the mid-range impact parameter region of the system leads to a number of effects in the deflection function. In particular, the trajectories of figure 4.16 show that more than one impact parameter leads to orbiting about the scattering centre and that the orbiting may be of either rotational sense about the centre; the trajectories of $b_{\text{orb},(+)}^{(\text{HFL})} \approx 2.22$ and $b_{\text{orb},(-)}^{(\text{HFL})} \approx 2.69$ are examples of positive and negative orbiting, respectively. Since the wide variety of trajectories originate from a single dynamical phenomenon (multiple radial turning points), they are collected under one collision mechanism:

Collision Mechanism 2 (Multi-Orbital Scattering) Any trajectory which experiences multiple radial turning points due to the interaction with the anisotropy in a potential well is a multi-orbiting trajectory. The exit and resulting deflection angle is dependent on the number of radial turning points which occur and thus $\chi \in [-\infty, +\infty]$.

Multi-orbiting trajectories sample at least one of the potential wells of the system, either parallel or anti-parallel to the field axis. Thus, this class of trajectories is not exclusive to bona fide orbiting ones, e.g. $b = 2.00$ of figure 4.16. Since the system is in the coupled potential regime at this collisional energy, it is clear that multi-orbital scattering is a result

of the interplay between radial- and angular parts of $U^{(\text{HFL})}$. Hence, $\Delta_e^{(\text{HFL})}$, $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{HFL})}$ all govern the dynamics in this collision mechanism. Collisions of this type can lead to any deflection angle in $[-\infty, +\infty]$ since the point where a trajectory exits the region of significant interaction is dependent upon the number of radial turning points which occur, i.e. more turning points imply more revolutions about the scattering centre with a concomitant increase in $|\chi|$. Multi-orbital scattering leads to a number of glories, rainbows and orbiting trajectories in $\chi^{(\text{HFL})}$ which are required by the continuity of the deflection function with variation in b . However, which features are present is sensitive to F .

The ubiquity of the mechanisms of reflex and multi-orbital scattering described above can be demonstrated with figure 4.17. The deflection functions of HeAr shown for a fixed fields $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$ with $K = 0.1$ and $\Omega = \Omega_{\text{CO}_2}$. Special features of glory, rainbow and orbital scattering are indicated in the figure. The $F = 0.0$ result (black line) shows the isotropic features of the scattering: a single forward glory at $b_g^{(\text{HFL})} \approx 1.7$ and an orbiting singularity at $b_{\text{orb},(-)}^{(\text{HFL})} \approx 2.25$. A typical weak field is shown by $F = 1.0$ (red line); here $b_g^{(\text{HFL})}$ and $b_{\text{orb},(-)}^{(\text{HFL})}$ are shifted to larger impact parameters and a rainbow angle appears at $b_r^{(\text{HFL})} \approx 2.2$. For weak fields, the system is in the coupled potential regime for small- and mid-range b : for $F = 1.0$, $\Delta_{\theta,-}^{(\text{HFL})} \approx 0.25$, $\Delta_e^{(\text{HFL})} \approx 1.25$ compared to $K = 0.1$. It is surprising that no reflex scattering is observed at small b . However, some multi-orbital scattering is observed for mid-range b by the presence of a rainbow minimum in $\chi^{(\text{HFL})}$ near the orbiting singularity. The lack of coupled potential dynamics from the weak field may be due to the fact that $|U_{\text{aniso},\alpha}^{(\text{HFL})}| \ll |U_0|$, implying that isotropic dynamics are dominant even though $K \sim |U_{\text{aniso},\alpha}^{(\text{HFL})}|$.

Typical stronger fields of $F = 2.0$ and $F = 2.5$ are shown in figure 4.17 as blue and orange lines, respectively. For these fields the system is in the coupled potential regime of

Figure 4.17: Sample deflection functions $\chi^{(\text{HFL})}$ vs. b using $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 0.1$. The data is identical to that used in figure 4.18. Angles reported are in units of π -radians. Indicated in the figure are the regions of the forward/backward glory- ($\chi_g^{(\text{HFL})} \in \{0, \pi\}$), rainbow- ($\chi_r^{(\text{HFL})}$) and orbital ($\chi_{orb,(\pm)}^{(\text{HFL})}$) deflection angles. Black line — $F = 0.0$; red line — $F = 1.0$; blue line — $F = 2.0$; orange line — $F = 2.5$; green line — $F = 3.0$. Details of the calculations are described in section 3.2.

equation (2.49) but now $\Delta_{\theta,-}^{(\text{HFL})} \sim \Delta_e^{(\text{HFL})}$. Hence, $\chi^{(\text{HFL})}$ exhibits reflex scattering regions with rainbow angles (both denoted $\chi_r^{(\text{HFL})}$ in figure 4.17) at a local maximum, followed by the backward glory at $\chi^{(\text{HFL})} = \pi$. Medium impact parameters are also classified as coupled potential dynamics and there are a number of (negative) orbiting singularities which result from the multi-orbital scattering collision mechanism.

The highest field given in figure 4.17 ($F = 3.0$, green line) shows different behaviour than the weak- and medium-field deflection functions. The reflex scattering region of small impact parameters extends up to the orbiting singularity $b_{\text{orb},(+)}^{(\text{HFL})} \approx 2.2$ which is a positive singularity (i.e. $\chi^{(\text{HFL})} = +\infty$). The mid-range impact parameter region contains a number of orbiting singularities, forward/backward glories and rainbow extrema (labelled in the figure) which arise from multi-orbital scattering. The behaviour of $\chi^{(\text{HFL})}$ demonstrates that the multi-orbital collision mechanism can lead to many features in the deflection function; their only commonality, besides the underlying mechanism, is the impact parameter range in which they occur.

The general features of the dynamics and their field-dependent trends can be assessed from figure 4.18, which shows the deflection function $\chi^{(\text{HFL})}$ as a contour plot with $b \in [0, 3]$ and $F \in [0, 3]$. The contour values of the deflection angle are in units of π -radians. For smaller fields ($F \lesssim 1.0$), the behaviour is similar to that encountered in the high collisional energy regimes; contours are continuously shifted to larger b for $b < b_g^{(\text{HFL})}$ and $b > b_{\text{orb},(-)}^{(\text{HFL})}$ with increasing F . The forward glory $b_g^{(\text{HFL})}$ is shown as a thick dashed (violet) line in the figure while the orbiting impact parameter is shown as a black contour ($\chi^{(\text{HFL})} = -2\pi$) starting at $b \approx 2.25$ at $F = 0.0$. The region in between the forward glory and the orbiting singularity is contrasted by a shift of the contours to smaller impact parameter with the field. Thus, for $b < b_g^{(\text{HFL})}$, $\chi^{(\text{HFL})}$ is monotonically increasing with the field while for

Figure 4.18: A contour plot of $\chi^{(\text{HFL})}(b, F)$ for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K = 0.1$. Contour values shown are labelled with units of π -radians. The forward/backward glory angle contours ($\chi^{(\text{HFL})} \in \{0, \pi\}$) are shown as thick dashed lines. Details of the calculations are described in section 3.2.

$b > b_g^{(\text{HFL})}$ it is decreasing. These field-induced shifts result in a deflection function which still resembles qualitatively that of the field-free function. This behaviour is anticipated by (2.49) since $K \sim \Delta_e^{(\text{HFL})} \gg \Delta_{\theta,-}^{(\text{HFL})}$ is satisfied, the system is in the isotropic potential regime.

Multi-orbital scattering is the first non-perturbative, anisotropic phenomenon to emerge for fields larger than unity. This is shown by the bifurcation of the $\chi^{(\text{HFL})} = -\pi$ (red) contour in figure 4.18 for $F \approx 0.8$. The mid-range impact parameter region continues to have new extrema emerge as F increases; this is observed by the emergence and bifurcation of $\chi^{(\text{HFL})} \in \{-2\pi, -\pi\}$ and higher contours. At $F \gtrapprox 2.7$, the appearance of a $\chi^{(\text{HFL})} = +2\pi$ contour (green line in figure) marks the emergence of positive orbiting singularities, indicating a strong anisotropic effect (and large $\Delta_{\theta,-}^{(\text{HFL})}$). That multi-orbital scattering emerges for lower fields is anticipated by the passing of the system from the isotropic to coupled potential regime as $\Delta_{\theta,-}^{(\text{HFL})}$ increases sharply with F over the range of $F \in [1, 3]$ (see figure 4.5(d)), becoming comparable to $\Delta_e^{(\text{HFL})}$.

For $F \gtrapprox 1.7$, reflex scattering emerges at small impact parameters; this is observed from the appearance of a $\chi^{(\text{HFL})} = +\pi$ (backward glory) contour followed by successively larger positive contours. The impact parameter range given to reflex scattering also increases with F . Reflex scattering is not as sensitive to F as multi-orbital scattering due to the fact that $\Delta_{\theta,-}^{(\text{HFL})}$ must be very large in order to induce an angular turning point. Thus, the system must be well within the coupled potential regime for the phenomenon to occur.

The influence of the barrier to rotation, $\Delta_{\theta,+}^{(\text{HFL})}$, can be seen in the behaviour of the small angle contours, e.g. $\chi^{(\text{HFL})} = -0.0625\pi$ (brown), in figure 4.18. As F increases, these contours shift first to higher impact parameter but for $F \gtrapprox 2.5$ they shift back to smaller b ; this behaviour implies a transition of the large- b portion of $\chi^{(\text{HFL})}$ from one of

net attraction ($\chi^{(\text{HFL})} < 0$) to repulsive scattering ($\chi^{(\text{HFL})} > 0$). The field-induced transition is a result of the increased repulsive contribution of $U_{\text{aniso},\alpha}^{(\text{HFL})}$ to $U^{(\text{HFL})}$ and is characterised by the value of $\Delta_{\theta,+}^{(\text{HFL})}$. For weak fields, $K \gg \Delta_{\theta,+}^{(\text{HFL})}$, the system is in the isotropic potential regime for large b , and hence the overall effect of $U^{(\text{HFL})}$ is to induce attractive scattering since the long-range part of $U_{\text{iso}}^{(\text{HFL})}$ is net attractive. As F is increased the system enters the coupled potential regime, $X_{\text{max}}^{(\text{HFL})}$ decreases to a value where the barrier position can influence $b \sim 3$ trajectories. Furthermore, the value of $\Delta_{\theta,+}^{(\text{HFL})} \sim K$ for $F \sim 3$, implying the barrier has an effect on the trajectories. Thus, coefficient c of the large- b portion of $\chi^{(\text{HFL})}$ (see equation (2.62)) first decreases with F and then increases, reducing $|c|$, as the effect of the barrier to rotation becomes non-negligible. For $F \gg 3$ (not shown), $c > 0$ since $\Delta_{\theta,+}^{(\text{HFL})} > K$.

The classification of reflex and multi-orbital scattering in $\chi^{(\text{HFL})}$ discussed above is determined by analysis of the partitioned potentials $U_{\text{iso}}^{(\text{HFL})}$ and $U_{\text{aniso}}^{(\text{HFL})}$. Figures 4.19 shows calculated deflection functions for HeAr with $K = 0.1$, $\Omega = \Omega_{\text{CO}_2}$ and $F = 3.0$. The functions of $\chi^{(\text{HFL})}$, $\chi_{\text{iso}}^{(\text{HFL})}$ and $\chi_{\text{aniso}}^{(\text{HFL})}$ are shown as solid, dotted and dashed lines in the figures, respectively.

For small impact parameters, figure 4.19 shows the typical results of a partition calculation in the region of reflex scattering; agreement of $\chi_{\text{aniso}}^{(\text{HFL})}$ with $\chi^{(\text{HFL})}$ is quantitative for very small impact parameters but the deviation increases as $b_{\text{orb},(+)}^{(\text{HFL})}$ is approached. The overall agreement is qualitative in that $\chi_{\text{aniso}}^{(\text{HFL})}$ reproduces the general reflex behaviour although the oscillations in $\chi_{\text{aniso}}^{(\text{HFL})}$ are not present in $\chi^{(\text{HFL})}$. In contrast, $\chi_{\text{iso}}^{(\text{HFL})}$ yields obtuse scattering in this impact parameter region. Thus, the dynamics, which from comparison of K , $\Delta_e^{(\text{HFL})}$ and $\Delta_{\theta,-}^{(\text{HFL})}$ are classified by (2.49) as coupled, are dominated by $U_{\text{aniso}}^{(\text{HFL})}$.

In the case of mid-range impact parameters, (2.49) again shows that the dynamics are

Figure 4.19: A comparison of the deflection functions of the partitions of $U^{(\text{HFL})}$ for HeAr with $K = 0.1$, $\Omega = \Omega_{\text{CO}_2}$ and $F = 3.0$. The deflection angles are given in units of π -radians. Lines show numerical trajectory results with: solid line — $\chi^{(\text{HFL})}$; dotted line — $\chi_{\text{iso}}^{(\text{HFL})}$; dashed line — $\chi_{\text{aniso}}^{(\text{HFL})}$. The inset shows a detail of the large-impact parameter portion of the deflection function. Numerical details are given in section 3.2.

of the coupled potential regime. However, the dynamics are not dominated by $U_{\text{aniso}}^{(\text{HFL})}$ alone since neither $\chi_{\text{iso}}^{(\text{HFL})}$ nor $\chi_{\text{aniso}}^{(\text{HFL})}$ reproduces the multi-orbital scattering of $\chi^{(\text{HFL})}$ in figure 4.19; this is expected since multi-orbital scattering requires coupled rotational and vibrational motion. The isotropic calculation $\chi_{\text{iso}}^{(\text{HFL})}$ does reproduce one negative orbiting singularity of $\chi^{(\text{HFL})}$, although $b_{\text{orb},(-)}^{(\text{HFL})}$ is shifted considerably. This orbiting singularity correlates with the $F = 0.0$ case and is thus isotropic in origin (cf. figure 4.18).

The large impact parameter region, shown in the insets of figure 4.19, are not additive for $\chi_{\text{iso}}^{(\text{HFL})}$ and $\chi_{\text{aniso}}^{(\text{HFL})}$ except perhaps for $b \gtrsim 4$. The anisotropic potential $U_{\text{aniso}}^{(\text{HFL})}$ yields positive scattering for large impact parameters at both fields. The converse is observed for $\chi_{\text{iso}}^{(\text{HFL})}$: agreement with $\chi^{(\text{HFL})}$ is quantitative over the range shown in both figures. It follows that the large impact parameter scattering, as in all other collisional energy regimes of $U^{(\text{HFL})}$, corresponds to perturbative or isotropic potential regimes. The dynamics are not affected by $\Delta_{\theta,+}^{(\text{HFL})}$ until the system is well into the coupled potential regime, i.e. $K \ll \Delta_{\theta,+}^{(\text{HFL})}$, which is not realised for $F \in [0, 3]$.

4.2.2 Collisions in the Mid-to-Low Frequency Limit

For lower carrier frequencies ($\Omega \ll \Omega_{\text{CO}_2}$), $U^{(\text{HFL})}$ is not an appropriate description of the system and $U^{(\text{AC})}$ must be employed. It is expected that the potential regime is determined by $\langle U^{(\text{AC})} \rangle_{\phi_c}$ and the conditions of (2.49), hence the collision mechanisms of reflex and multi-orbital scattering will be relevant. The presence of $U_{\tau}^{(\text{AC})}$ requires that the amplitude and time scale of the laser-induced fluctuations also be taken into consideration as described in section 2.3 by (2.52) and (2.54), respectively.

4.2.2.1 High Energy Regime

In the regime of high kinetic energy collisions ($K = 10$), comparison of the quantities of figure 4.5 according to section 2.3 shows that the system is in the perturbative potential and amplitude regimes over all $F \in [0, 3]$. It is therefore expected that the potential will have little influence on $\chi^{(AC)}$ and only small field-induced effects will be observed, even for large F . The amplitude condition implies that, excluding any resonance effects, $\chi^{(AC)}$ will only have a weak dependence on Ω and ϕ_c . The impulse approximation to $\chi^{(AC)}$ given by (2.104) is expected to yield reasonable results in this regime.

Figure 4.20 shows $\chi^{(AC)}(b, \phi_c)$ for HeAr with $K = 10$, $F \in \{1.0, 2.0, 3.0\}$ (figures (a,b), (c,d), (e,f), respectively) and $\Omega \in \{2.0, 10.0\}$ (figures (a,c,e) and (b,d,f), respectively). The polar contour plots are for $b \in [0, 3]$ (radial coordinate) and $\phi_c \in [0, 2\pi]$ (polar coordinate). Contour values of $\chi^{(AC)}$ are given in units of π -radians in the figure legends. The figure shows as predicted by the potential and amplitude regimes that there is little dependence on any of ϕ_c , Ω or F . The slight ellipticity of the contours demonstrates the small ϕ_c -dependence of $\chi^{(AC)}$: the degree of ellipticity increases with F and decreases with Ω but the shifts are small. As in the high- K regime of $U^{(HFL)}$, $\chi^{(AC)}$ resembles the field-free deflection function, having a small rainbow minimum $b_r^{(AC)}(\phi_c)$ bracketed by the -0.05π contours (dark green in figure 4.20). The behaviour of $\chi^{(AC)}$ with F is identical to that of $\chi^{(HFL)}$ in the same regime (cf. results of figure 4.8): the perturbative limit of reflex scattering, due to $\Delta_{\theta,-}^{(AC)}$ results in angular momentum exchange which increases $\chi^{(AC)}$ for $b < b_r^{(AC)}$ and decreases $\chi^{(AC)}$ for $b > b_r^{(AC)}$.

The effects of time-dependence can be seen in the $\chi^{(AC)}$ of figure 4.20(b) and (c); for these fields ($F = 2.0$ and 3.0 , respectively) and $\Omega = 2.0$, there are regions of $b > b_r^{(AC)}$ where the scattering goes from attractive to repulsive as is evidenced from the presence

Figure 4.20: Polar contour plots of $\chi^{(\text{AC})}(b, \phi_c)$ with $b \in [0, 3]$ (radial-) and $\phi_c \in [0, 2\pi]$ (polar coordinate). Contour values (legends) are given in π -radians. Calculations are for HeAr with $K = 10$ and: (a) $\Omega = 2.0, F = 1.0$; (b) $\Omega = 10.0, F = 1.0$; (c) $\Omega = 2.0, F = 2.0$; (d) $\Omega = 10.0, F = 2.0$; (e) $\Omega = 2.0, F = 3.0$; (f) $\Omega = 10.0, F = 3.0$. Numerical details are given in section 3.2.

of a $\chi^{(\text{AC})} = 0$ contour (red line) at $b \sim 3$. Examination of the trajectories (not shown) reveals that the repulsive scattering is due to the deflection of the system off the barrier to rotation away from the field axis. This effect persists for impact parameter that can pass near the barrier to rotation. Such a transition was discussed in the low- K regime of $U^{(\text{HFL})}$ (see section 4.2.1.3); in that situation $\Delta_{\theta,+}^{(\text{HFL})}$ was too small to do more than reduce the net attractive scattering in the large- b limit. In the case of $\chi^{(\text{AC})}$, $\Delta_{\theta,+}^{(\text{AC})}$ is an order of magnitude larger (ca. 0.3 for HeAr) than the corresponding $\Delta_{\theta,+}^{(\text{HFL})}$ at the peak of the laser cycle. Thus, the barrier to rotation can have an effect on a trajectory provided $\Delta_{\theta,+}^{(\text{AC})}$ remains at its peak value on a time scale which is long compared to the time it takes to traverse the barrier. For $\Omega = 2.0$ and $K = 10$, $w \sim 1$ for impact parameters near ca. 2.23; the transition to repulsive scattering at large impact parameters occurs in figure 4.20(b) and (c) for $b \gtrsim 2$, verifying the importance of resonance for this mechanism:

Collision Mechanism 3 (Barrier Scattering) Any trajectory which is repelled by interaction with the barrier to rotation to a path away from the field axis is said to undergo barrier scattering. The resulting deflection angle is therefore always greater than zero.

From the collision mechanism, the controlling feature of the potential is $\Delta_{\theta,+}^{(\text{AC})}$ or $\Delta_{\theta,+}^{(\text{HFL})}$; time-dependence is not a necessary condition for barrier scattering but since it allows the effective barrier to rotation to be much larger, its presence permits barrier scattering to occur for lower fields. It follows from the finite range of the barrier to rotation, both in θ and in X , that $\chi^{(\text{AC})}$ must decrease for impact parameters which sample the potential well. Therefore, a forward glory ($\chi^{(\text{AC})} = 0$) must occur at mid- to large impact parameters which marks the onset of barrier scattering. In addition, the requirement that $\lim_{b \rightarrow +\infty} \chi = 0$ implies that there must be a rainbow maximum in $\chi^{(\text{AC})}$ at some impact parameter $b_r^{(\text{AC})} > b_g^{(\text{AC})}$.

The different time-dependence regimes are illustrated by considering the behaviour

of $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ for the two different frequencies. Figure 4.21 shows the $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ curves of $F = 3.0$ for $\Omega \in \{2.0, 10.0\}$ (blue and orange lines, respectively). The estimates of $w \ll 1$ indicate that the system is described the static field limit when $b \lesssim 3$ for $\Omega = 2.0$ and $b \lesssim 0.5$ for $\Omega = 10.0$. For large b , $w \sim 1$ for $\Omega = 2.0$ while $w \gg 1$ for $\Omega = 10.0$. Since $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ is the same for both limits by (2.106), $\chi^{(\text{HFL})}$ for $\Omega = \Omega_{\text{CO}_2}$ under the same conditions (cf. figure 4.8) is shown by red data in the figure. The error bars of the static field limit $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ are estimated via equation (2.108); this was done by finding $\chi^{(\text{HFL})}(b; F) - \chi_0(b)$ from the exact results of section 4.2.1.1. Comparison with $\Omega = 2.0$ shows that the static field limit approximation is valid for $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ for $b < \langle b_r^{(\text{AC})} \rangle_{\phi_c}$; the standard deviation $\sigma_{\text{RMS}, \chi^{(\text{AC})}}(b)$ (error bars in figure) is underestimated by the static-field limit expressions. This is due to the fact that $U^{(\text{AC})}$ samples higher effective F over the cycle and has ϕ_c where the laser-induced effects are greater than in $\chi^{(\text{HFL})}$. Hence, while $\langle \chi^{(\text{AC})} \rangle_{\phi_c} \approx \chi^{(\text{HFL})}$, $\sigma_{\text{RMS}, \chi^{(\text{AC})}} > 1/\sqrt{2}(\chi^{(\text{HFL})} - \chi_0)$. For the large impact parameter region (inset of figure 4.21), the presence of barrier scattering is responsible for the deviation of $\sigma_{\text{RMS}, \chi^{(\text{AC})}}$ from the static field limit estimate. For $\Omega = 10.0$, agreement between the static field limit and $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ is also good over the whole range of b . Agreement for $\sigma_{\text{RMS}, \chi^{(\text{AC})}}$ is good for $b > \langle b_r^{(\text{AC})} \rangle_{\phi_c}$ but is underestimated by (2.108) for the same reason as the $\Omega = 2.0$ results. The large impact parameter region (inset) shows very small $\sigma_{\text{RMS}, \chi^{(\text{AC})}}$, indicating no barrier scattering is present at $\Omega = 10.0$.

The above results show that the perturbative potential regime of $U^{(\text{AC})}$ and $U^{(\text{HFL})}$ are essentially the same, with the exception of barrier scattering in the former. It follows that the origin of the features of the deflection function $\chi^{(\text{AC})}$ should be similar to that of $\chi^{(\text{HFL})}$. To examine this $\chi^{(\text{AC})}$, $\chi_{\text{iso}}^{(\text{AC})}$ and $\chi_{\text{aniso}}^{(\text{AC})}$ were calculated for HeAr with $K = 10$, $\Omega = 2.0$, $F = 3.0$ and $\phi_c = 0.0$, the results of which are shown in figure 4.22(a). Here, the black

Figure 4.21: The deflection function $\langle \chi^{(AC)} \rangle_{\phi_c}$ vs. b for HeAr, $K = 10$, $\Omega \in \{2.0, 10.0\}$ and $F = 3.0$. Error bars are $\sigma_{\text{RMS}, \chi^{(AC)}}$. Also shown is the average obtained in the static field limit (see (2.106)) with $\sigma_{\text{RMS}, \chi^{(AC)}}$ estimated from (2.108). For clarity not all error bars are shown. Red line — static field limit; blue line — $\chi^{(AC)}$, $\Omega = 2.0$; orange line — $\chi^{(AC)}$, $\Omega = 10.0$. Inset shows the large impact parameter region. Numerical details are given in section 3.2.

lines in the figure show numerical deflection functions while red lines show impulse approximation results of (2.104). Over small- and mid-range impact parameters, the $\chi_{\text{iso}}^{(\text{AC})}$ results are qualitatively in agreement with $\chi^{(\text{AC})}$. For large b (inset), $\chi_{\text{aniso}}^{(\text{AC})} \sim \chi^{(\text{AC})}$ as might be expected due to the necessity of $\Delta_{\theta,+}^{(\text{AC})}$ for barrier scattering to occur. The impulse approximation result ($\chi_{\text{IA}}^{(\text{AC})}$, solid red line in figure 4.22(a)) does reproduce barrier scattering but only qualitatively; the parameters $b_r^{(\text{AC})}$ and $\chi_r^{(\text{AC})}$ due to the barrier scattering rainbow are under- and overestimated, respectively by $\chi_{\text{IA}}^{(\text{AC})}$. The glory scattering position $b_g^{(\text{AC})}$ produced by the barrier scattering mechanism is also underestimated by the impulse approximation results. The dominance of the different partitions are also reflected in $\chi_{\text{IA}}^{(\text{AC})}$: $\chi_{\text{iso,IA}}^{(\text{AC})}$ reproduces the short- and mid- b behaviour while $\chi_{\text{aniso,IA}}^{(\text{AC})}$ dominates large impact parameters.

Results similar to those above are obtained for the higher frequency partition calculations shown ($\Omega = 10.0$) in figure 4.22(b). The qualitative difference resulting from the increased frequency is $\chi^{(\text{AC})} \approx \chi_{\text{iso}}^{(\text{AC})}$ (black solid and dashed lines, respectively) for the whole range of b ; the same approximation holds for $\chi_{\text{IA}}^{(\text{AC})}$ and $\chi_{\text{iso,IA}}^{(\text{AC})}$ (red solid and dotted lines). Since $w \gg 1$ for large impact parameters, $\chi_{\text{aniso,IA}}^{(\text{AC})}$ makes little contribution to $\chi_{\text{IA}}^{(\text{AC})}$. Such behaviour is indicative of the role of the time-dependence in the barrier scattering effect; by increasing the frequency, the w -dependent terms of $\chi_{\text{aniso,IA}}^{(\text{AC})}$ are decreased and approach the $\chi_{\text{IA}}^{(\text{HFL})}$ values. This is completely independent of $\Delta_{\theta,+}^{(\text{AC})}$ at the peak of the field. However, as the frequency increases, the oscillations of the barrier become faster relative to the time it takes for the system to cross it. Thus, the peak value of $\Delta_{\theta,+}^{(\text{AC})}$ is replaced by the average $\Delta_{\theta,+}^{(\text{HFL})}$ and the concomitant influence on the dynamics is reduced. Thus, from considering the impulse approximation partitions, the effect of barrier scattering is seen to be achieved through either resonance ($w \lesssim 1$) effects for $\Delta_{\theta,+}^{(\text{AC})} \ll K$ or by increasing F

Figure 4.22: A comparison of the deflection functions of the partitions of $U^{(AC)}$ for HeAr with $K = 10$, $\Omega \in \{2.0, 10.0\}$, $F = 3.0$ and $\phi_c = 0$. Figure (a) — $\Omega = 2.0$; figure (b) — $\Omega = 10.0$. All deflection angles are in units of π -radians. Black lines show numerical trajectory results with: solid line — $\chi^{(AC)}$; dotted line — $\chi_{iso}^{(AC)}$; dashed line — $\chi_{aniso}^{(AC)}$. Red lines show the results of the impulse approximation of equation (2.104): solid line — $\chi_{IA}^{(AC)}$; dotted line — $\chi_{iso,IA}^{(AC)}$; dashed line — $\chi_{aniso,IA}^{(AC)}$. The insets show details of large-impact parameters. Numerical details are given in sections 3.2 and 3.3.

such that $\Delta_{\theta,+}^{(\text{HFL})} \gtrsim K$ in the case of $w \gg 1$.

The impulse approximation calculations using (2.104) have been shown to be less accurate than in the case of $U^{(\text{HFL})}$. A quantitative comparison is shown in figure 4.23 for HeAr with $K = 10$, $F = 3$ and $\Omega \in \{2.0, 10.0\}$ (red and blue lines, respectively). The averaged difference of $\chi_{\text{IA}}^{(\text{AC})} - \chi^{(\text{AC})}$ is shown as a function of impact parameter with error bars denoting the calculated standard deviations (all in π -radians). At large impact parameters (inset), the average is zero with small standard deviation for $\Omega = 10.0$. The higher standard deviation for $\Omega = 2.0$ is indicative of the inability of $\chi_{\text{IA}}^{(\text{AC})}$ to reproduce the rainbow present at large b . Both the average and standard deviation of the discrepancies rise near the isotropic rainbow ($b \approx 1.2$), indicating that the predicted values of the impulse approximation tend to be more positive. The average agreement near the forward glory angle is good but the large standard deviation indicates that there is poor agreement with the approximation for a fixed value of ϕ_c .

4.2.2.2 Mid-Energy Regime

Medium kinetic energy collisions (e.g. $K = 1$) fulfill the condition $K \gg |\langle U^{(\text{AC})} \rangle_{\phi_c}|$ (perturbative potential regime) for large impact parameters only (all $F \in [0, 3]$). Further examination of equation (2.49) with the parameters of figure 4.5 show that weak fields ($F < 1$) are in the isotropic potential regime for small and mid-range b ; for $F > 1$, this range of impact parameter passes into the coupled regime of the potential partitions. Thus, weak fields should exhibit only small effects from the anisotropy and generally resemble the field-free dynamics. For stronger fields, the dynamics will be sensitive to both $\Delta_e^{(\text{AC})}$ and $\Delta_{\theta,-}^{(\text{AC})}$ for $b \lesssim 3$. The role of the fluctuations of $U_{\tau}^{(\text{AC})}$ is determined from (2.52) to be strong for all but large impact parameters over the range of $F \in [0, 3]$; comparison of $\sigma_{\text{RMS}, \Delta_e^{(\text{AC})}}$

Figure 4.23: The difference $\langle \chi_{IA}^{(AC)} - \chi^{(AC)} \rangle_{\phi_c}$ vs. b for HeAr, $F = 3.0$, $K = 10$ and $\Omega \in \{2.0, 10.0\}$. Differences are reported in units of π -radians. Error bars of selected points show the standards deviations of $\chi_{IA}^{(AC)} - \chi^{(AC)}$. The regions of the forward glory $\chi_g^{(AC)} = 0$ and rainbow angle $\chi_r^{(AC)}$ are indicated. The inset shows the behaviour in the large-impact parameter region. Red line — $\Omega = 2.0$; blue line — $\Omega = 10.0$. Numerical details are given in sections 3.2 and 3.3.

with $\Delta_e^{(\text{HFL})}$, etc. shows that the system is in the coupled amplitude regime for small- and mid-range b while for large b it is in the perturbative amplitude regime. Thus, $U_\tau^{(\text{AC})}$ will play an important role in the dynamics for all but large impact parameters. Evaluation of w shows that for higher frequencies ($\Omega \gtrsim 10$), there are a large number of laser cycles over the course of the collision for all impact parameters; this is true also for lower frequencies ($\Omega \sim 2$) in the large- b range. However, the system makes the transition from the static field limit to resonance near mid-range b for these frequencies. It is evident that this collision energy regime will be very sensitive to F and (Ω, ϕ_c) in the sense that their variation will cause transitions between different dynamical regimes.

In the coupled potential regime, the sensitivity to both $\Delta_e^{(\text{AC})}$ and $\Delta_{\theta,-}^{(\text{AC})}$ is expected to give rise to both reflex- and multi-orbital scattering as in the case of $U^{(\text{HFL})}$. Barrier scattering is not expected to be present since in the large- b range, the role of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ and $U_\tau^{(\text{AC})}$ are completely perturbative and $w \gg 1$; thus barrier scattering should only occur if $\Delta_{\theta,+}^{(\text{HFL})} \gtrsim K$, which is not the case (see figure 4.5(d)). Examination of the trajectories for a number of combinations of laser parameters has confirmed this and an additional class of trajectories has also been noted. Figure 4.24 shows some examples of this new type of scattering which occurs in the coupled potential/coupled amplitude regimes; trajectories of HeAr with $F = 3.0$, $\Omega = 10.0$, $K = 1.0$ and $\phi_c = 0$ are given for different $b < 1$. For small impact parameters, the trajectories sample the potential well. The system then undergoes a number of radial and angular turning points before exiting either above or below the field axis. The motion is akin to that of multi-orbital scattering except that there are multiple angular turning points. It follows that the mechanism for inducing these turning points is essentially the same: creation of a radial barrier via either the centrifugal potential or $U_{\text{aniso}}^{(\text{AC})}$ produces the “bobsled-like” effect noted earlier. Angular turning points are induced by the

Figure 4.24: Some sample trajectories for HeAr, $F = 3.0$, $\Omega = 10.0$, $K = 1.0$ and $\phi_c = 0$. Trajectories are shown over top a contour plot of the $F = 3.0$, $\Omega = \Omega_{\text{CO}_2}$ surface of $U^{(\text{HFL})}$; contour values shown are those of figure 4.2. Solid lines show trajectories for $F = 3.0$ (figure 4.25). Impact parameters used are: maroon line — $b = 0.30$; indigo line — $b = 0.34$; violet line — $b = 0.38$; magenta line — $b = 0.42$; blue line — $b = 0.46$; red line — $b = 0.50$. Inset shows a detail of the region in the potential well ($X < 2$). Arrows indicate the time-flow of the trajectories. Details of the calculations are described in section 3.2.

fluctuations of $\Delta_{\theta,-}^{(AC)}$ over the laser cycle. It is also possible, due to $U_{\tau}^{(AC)}$, for the system to exchange kinetic energy directly with the laser field and this may also cause turning points in either coordinate. The overall effect of the interaction with the potential well is to induce pendular motion as this part of the potential corresponds to the pendular states of the bound system [69, 70, 73]. The new collision mechanism is thus named after the type of motion:

Collision Mechanism 4 (Pendular Scattering) Any trajectory which enters one potential well and undergoes multiple radial and angular oscillations before exiting either above or below the field axis belongs to the class of pendular scattering trajectories. Pendular scattering results in a deflection angle $\chi \sim \pi$ with only small deviations from this value.

That pendular scattering produces a deflection angle near π -radians is a result of the fact that the system interacts only with the parallel⁴ potential wells. Sampling only the parallel well implies the system never crosses the axis perpendicular to the field. Thus $|\theta(\tau)| < \pi/2$ and the resulting deflection angle is bounded by $\chi \in (\pi/2, 3\pi/2)$. From the trajectories of figure 4.24, it appears that the resulting $\chi^{(AC)}$ is very sensitive to impact parameter; this is because b determines the amount of time the system spends as a “pendular complex” and hence, whether the exit will be above or below the field axis. Therefore a feature of pendular scattering is that $\chi(b)$ oscillates rapidly about π when b is varied. It should be noted that pendular scattering will give rise to backward glories from where the oscillations in $\chi^{(AC)}(b)$ cross π and where the deflection function leaves the region of pendular scattering. The oscillations in the deflection function due to pendular scattering also give rise to additional rainbows at the multiple extrema of these oscillations.

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⁴N.B.: It is possible that pendular scattering can occur using the anti-parallel well. However, this requires a rotation of the field axis relative to the initial momentum vector; such a situation is not considered in the present work.

The transitions between the different dynamical regimes available to $U^{(\text{AC})}$ in the medium- K case are demonstrated in figure 4.25: the figure shows polar contour plots of $\chi^{(\text{AC})}(b, \phi_c)$ where $b \in [0, 2]$ is the radial coordinate and $\phi_c \in [0, 2\pi]$ is the angular coordinate. Contours of the deflection angles are in units of π -radians (values given in legends). Six plots are shown for calculations of HeAr with $K = 1.0$: (a) $F = 1.0, \Omega = 2.0$; (b) $F = 1.0, \Omega = 10.0$; (c) $F = 2.0, \Omega = 2.0$; (d) $F = 2.0, \Omega = 10.0$; (e) $F = 3.0, \Omega = 2.0$; (f) $F = 3.0, \Omega = 10.0$. The first thing to note about the calculations presented is the large number of laser phases where $\chi^{(\text{AC})}(b)$ resembles the equivalent deflection function of $\chi^{(\text{HFL})}$ (cf. results of figure 4.13). This is most prevalent in the $F = 1.0$ results (figures 4.25(a) and (b)) where the system is in either the isotropic or perturbative potential regime; the amplitudes of the field-induced oscillations, while comparable to K , are either on time scales too low or too high for any significant effect at $\Omega = 2.0$ or 10.0 , respectively. For these phases, the effect on $\chi^{(\text{AC})}$ is identical to the perturbative effects seen in $\chi^{(\text{HFL})}$ (section 4.2.1.2); this can be seen in the case of small b by the shifting of the $\pi/2$ -contour (cyan line in the figure) to higher impact parameters as F is increased. In particular, there is net attractive scattering in the large- b range for all laser parameters surveyed; this is expected due to the system always being in perturbative regimes over this range of impact parameter. No barrier scattering is observed.

As the system enters the coupled potential regime ($F > 2.0$, figures 4.25(c) and (d)), there is an onset of multi-orbital dynamics. This is seen for mid-range b where the contours which identify the rainbow angle (black, maroon, indigo, violet and blue in the figure) lose their simple ϕ_c -dependence. The values of the contours indicate that the rainbow angle $\chi_r^{(\text{AC})}$ varies between -2π (black) and -0.325π (blue), often with more than one minimum. Where $\chi^{(\text{AC})} < -2\pi$ may correspond to orbiting singularities in the deflection

Figure 4.25: Polar contour plots of $\chi^{(\text{AC})}(b, \phi_c)$ with $b \in [0, 2]$ (radial-) and $\phi_c \in [0, 2\pi]$ (polar coordinate). Contour values (legends) are given in π -radians. Calculations are for HeAr with $K = 1.0$ and: (a) $\Omega = 2.0, F = 1.0$; (b) $\Omega = 10.0, F = 1.0$; (c) $\Omega = 2.0, F = 2.0$; (d) $\Omega = 10.0, F = 2.0$; (e) $\Omega = 2.0, F = 3.0$; (f) $\Omega = 10.0, F = 3.0$. Numerical details are given in section 3.2.

function, a feature not observed in $\chi^{(\text{HFL})}$ (see figure 4.12). The regions of multi-orbital scattering increase both in the range of b and ϕ_c as F is increased. The time scale estimates of w show that the $\Omega = 2.0$ results (figure 4.25(a), (c) and (e)) are near resonance for this impact parameter region while $w \gg 1$ for $\Omega = 10.0$ (figures (b), (d) and (f)). The effect of time scale on the multi-orbital scattering is shown by comparison of these two frequencies; results for $w \gg 1$ show much smoother (i.e. elliptic) behaviour with ϕ_c while the $\Omega = 2.0$ results are very sensitive to ϕ_c in the mid- b range.

For small impact parameters, the system is also expected to exhibit sensitivity to the details of the potential well when $F > 2.0$. Such behaviour is seen with the emergence of “lobes” and “swirls” of regions where $\chi^{(\text{AC})} > \pi$. These regions of (b, ϕ_c) exhibit pendular scattering noted earlier, as evidenced by the rapid oscillations of $\chi^{(\text{AC})}$ with b (close spacing of the π and 1.250π contours in figure 4.25). Reflex scattering is also present in the regions where the contours of $\chi^{(\text{AC})} > \pi$ are not closely spaced. In general, the (b, ϕ_c) region of pendular scattering is enlarged by increasing F and Ω . The F -dependence is due to the necessity of $\Delta_{\theta,-}^{(\text{AC})}$ being large enough to induce an angular turning point. The Ω -dependence of pendular scattering arises from the possibility that the system can exit the rotational well if the axis perpendicular to the field is crossed when the barrier is at the low point in the laser cycle⁵.

The presence of multi-orbital, reflex and pendular scattering causes larger variation in $\chi^{(\text{AC})}$ beyond what might be expected from the static field limit expressions of (2.108) for $\sigma_{\text{RMS},\chi^{(\text{AC})}}$. Figure 4.26 tests the veracity of (2.108) against the results for HeAr, $K = 1$, $F = 3.0$ and $\Omega \in \{2.0, 10.0\}$. The result of (2.106) appears to hold, since $\chi^{(\text{HFL})}$ of $F = 3.0$, $K = 1$ (red line, also given in figure 4.13) compares quantitatively with both

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⁵Such an effect has been observed in laser-induced collinear exchange reactions [89].

Figure 4.26: The deflection function $\langle \chi^{(AC)} \rangle_{\phi_c}$ vs. b for HeAr, $K = 1.0$, $\Omega \in \{2.0, 10.0\}$ and $F = 3.0$. Error bars are $\sigma_{\text{RMS}, \chi^{(AC)}}$. Also shown is the average obtained in the static field limit (identical to $\chi^{(\text{HFL})}$ of the same field by (2.106); cf. figure 4.13) with $\sigma_{\text{RMS}, \chi^{(AC)}}$ estimated from (2.108). For clarity not all error bars are shown. Red line — static field limit; blue line — $\chi^{(AC)}$, $\Omega = 2.0$; orange line — $\chi^{(AC)}$, $\Omega = 10.0$. Inset shows the large impact parameter range. Numerical details are given in section 3.2.

frequencies. In contrast to the high- K regime, there are more distinct differences between the two frequencies; the $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ function of $\Omega = 2.0$ (blue line in figure) is smaller than that of $\Omega = 10.0$ (orange line) for impact parameters less than the rainbow position due to the greater presence of pendular scattering in the latter. Thus the $\Omega = 2.0$ results are in better agreement with the static field limit for this impact parameters range as might be expected from w . However, for the rainbow region, the $\Omega = 10.0$ results are in better agreement with the static field limit, those of $\Omega = 2.0$ being larger; this behaviour is due to the presence of pendular scattering at $b \sim \langle b_r^{(\text{AC})} \rangle_{\phi_c}$ near $\phi_c \approx \pi/4$ and $5\pi/4$. For $\Omega = 10.0$, $\sigma_{\text{RMS},\chi^{(\text{AC})}}$ (error bars in figure) are also increased due to the oscillations of the pendular scattering regions and thus $\sigma_{\text{RMS},\chi^{(\text{AC})}}(\Omega = 10.0) > \sigma_{\text{RMS},\chi^{(\text{AC})}}(\Omega = 2.0)$ for small b but the converse is true for $b \sim \langle b_r^{(\text{AC})} \rangle_{\phi_c}$. The $\sigma_{\text{RMS},\chi^{(\text{AC})}}$ estimated from (2.108) is too small for impact parameters less than the rainbow position (red error bars in figure 4.26) due to the presence of the non-perturbative collision mechanisms. Agreement in the large- b range (inset of figure) is improved since the system is effectively time-independent at both frequencies.

The role of the different partitions of $U^{(\text{AC})}$ in the dynamics is straightforward in the case of weaker fields ($F < 1$) or large impact parameters, the latter being completely perturbative. For weak fields at small- and mid-range b , the dynamics are dominated by $\langle U_{\text{iso}}^{(\text{AC})} \rangle_{\phi_c}$, hence no reflex scattering is observed; both the magnitude of the fluctuations and the time scale of $U_{\text{iso}}^{(\text{AC})}$ have an effect at mid-range b and this leads to the multi-orbital scattering seen in figure 4.25(a) and (b). However, the small magnitude of $\langle U_{\text{aniso}}^{(\text{AC})} \rangle_{\phi_c}$ indicates that the time-dependent effects are introduced via $U_{\text{iso}}^{(\text{AC})}$ rather than $U_{\text{aniso}}^{(\text{AC})}$. For stronger fields, the system is in the coupled potential and amplitude regimes, hence the dominant partitions must be assessed by direct calculation; an example of this is shown

in figure 4.27 for HeAr with $K = 1$, $F = 3.0$, $\phi_c = 0$ and $\Omega \in \{2.0, 10.0\}$ (figures (a) and (b), respectively). Trajectory calculations with the individual partitions compare $\chi^{(AC)}$ (solid lines) with $\chi_{iso}^{(AC)}$ (dotted lines) and $\chi_{aniso}^{(AC)}$ (dashed lines). Results show examples of both the perturbative and non-perturbative dynamics which are observed for different laser phases at either frequency. The $\Omega = 2.0$ results are an example of the former, showing that $\chi_{iso}^{(AC)} \approx \chi^{(AC)}$ over the entire impact parameter range; the oscillations in $\chi_{aniso}^{(AC)}$ preclude $U_{aniso}^{(AC)}$ being taken as the origin of the behaviour of $\chi^{(AC)}$. Thus, although the system is in the coupled regime of potential and amplitude, the isotropic partition $\langle U_{iso}^{(AC)} \rangle_{\phi_c}$ can dominate the dynamics for this particular phase; such ϕ_c dependence has its origin in the details of the trajectory and cannot be ascribed to a simple feature.

Figure 4.27(b) shows an example of non-perturbative dynamics for $\Omega = 10.0$. Here $\chi^{(AC)}$ (solid line) shows reflex and pendular scattering at small impact parameters where there are a few regions of monotonic behaviour and oscillations, respectively. Multi-orbital scattering yields two additional rainbows, one minimum and one maximum at mid-range b . The origin of the reflex scattering has been shown in $U^{(HFL)}$ to be $\Delta_{\theta,-}^{(HFL)}$ in the coupled potential regime. Such conditions apply to $\langle U^{(AC)} \rangle_{\phi_c}$ and hence some impact parameters should exhibit reflex scattering. Pendular scattering requires multiple angular turning points and hence the amplitude and time scale of $U_{\tau}^{(AC)}$ is important. In support of these points, it is observed that $\chi_{iso}^{(AC)} \not\approx \chi^{(AC)}$ at small b . The $\chi_{aniso}^{(AC)}$ calculation (dashed line) does produce some oscillatory behaviour which is $\sim \pi$ but the monotonic regions are not reproduced. Thus, the time-dependence of $U_{aniso}^{(AC)}$ leads to pendular scattering but not reflex scattering and hence the mechanisms are time-dependent and independent in nature, respectively. For mid-range b , $\chi_{iso}^{(AC)}$ does reproduce the isotropic orbiting singularity but the full potential is required to create the multi-orbital rainbows; neither single partition

Figure 4.27: A comparison of the deflection functions of the partitions of $U^{(AC)}$ for HeAr with $K = 1$, $\Omega = 2.0$ (figure (a)) and $\Omega = 10.0$ (figure (b)), $F = 3.0$ and $\phi_c = 0$. Deflection angles are given in units of π -radians. Lines show numerical trajectory results with: solid line — $\chi^{(AC)}$; dotted line — $\chi_{iso}^{(AC)}$; dashed line — $\chi_{aniso}^{(AC)}$. The insets show details of the large-impact parameter portion of the deflection function. Numerical details are given in section 3.2.

is qualitatively responsible for the multi-orbital region. At large impact parameters, the perturbative behaviour is seen from $\chi^{(AC)} \approx \chi_{\text{iso}}^{(AC)}$ with a small, essentially additive, effect resulting from $\chi_{\text{aniso}}^{(AC)}$.

4.2.2.3 Low Energy Regime

In the regime of low collision energy, e.g. $K = 0.1$, comparison of the potential features with K shows via equation (2.49) that the system is in the coupled potential regime for all fields and impact parameter ranges with the exception of weak fields ($F < 1$) and large impact parameter ($b > 3$), where it is in the isotropic potential regime. Examination of the amplitudes in (2.52) shows that the fluctuations of $U_{\tau}^{(AC)}$ are large enough that the system is in the coupled amplitude regime for all F and b . Due to the low collision energy, $w \gg 1$ for all b and $\Omega \gtrsim 2$; however, for lower frequencies and small impact parameters $w \sim 1$. Thus, the dynamics of the system will be such that all details of $U^{(AC)}$ are important over the laser cycle; however, the size of the amplitudes indicates that the potential features at the peak of the cycle can dominate the dynamics. The effects of time dependence will be uniform since the number of laser cycles over the course of the collision is large for most conditions; thus little sensitivity to ϕ_c and Ω is expected.

The general features of $\chi^{(AC)}$ are shown in figures 4.28(a) and 4.28(b) which contain $\langle \chi^{(AC)} \rangle_{\phi_c}$ vs. b for HeAr, $K = 0.1$, $F \in \{0.0, 1.0, 2.0, 3.0\}$ and $\Omega = 2.0$ and 10.0, respectively. Numerical details of the trajectory calculations are given in section 3.2. The field free deflection function is shown as the black line in each figure for reference. For small impact parameters, $\langle \chi^{(AC)} \rangle_{\phi_c} > \pi$ in general for both frequencies; however, the large values of $\sigma_{\text{RMS}, \chi^{(AC)}}$ and oscillations in the averages for these impact parameters indicate that the behaviour of $\langle \chi^{(AC)} \rangle_{\phi_c}$ is not indicative of $\chi^{(AC)}(b, \phi_c)$ and both reflex and pendular

Figure 4.28: A plot of the phase-averaged deflection function $\langle \chi^{(AC)} \rangle_{\phi_c}$ vs. b for HeAr with $K = 0.1$. Figure (a) — $\Omega = 2.0$, (b) — $\Omega = 10.0$. Error bars are $\sigma_{\text{RMS}, \chi^{(AC)}}$. All angles are in units of π -radians. For clarity, not all data points have their standard deviations displayed. Black line — $F = 0.0$; red line — $F = 1.0$, blue line — $F = 2.0$; orange line — $F = 3.0$. Insets show corresponding details of the large impact parameter region. Numerical details are given in section 3.2.

scattering mechanisms may be present. For $\Omega = 10.0$, the standard deviations are smaller than $\Omega = 2.0$ in this impact parameter region (cf. error bars in figures). As a function of F , the region of scattering into reflex angles extends to larger impact parameters for both frequencies. For large impact parameters ($b \gtrsim 3$, insets of figures (a) and (b)) show that $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ is net attractive, indicating dynamics of the perturbative type; only the $F = 3.0$, $\Omega = 10.0$ (orange line in figure 4.28(b)) calculation appears to have $\sigma_{\text{RMS}, \chi^{(\text{AC})}}$ large enough to extend into net repulsive scattering. Hence this is the only field which contains possible barrier scattering. For mid-range b , the transition from reflex/pendular scattering to perturbative/barrier scattering is characterised by large $\sigma_{\text{RMS}, \chi^{(\text{AC})}}$ with the exception of the $F = 3.0$ results where the transition is abrupt. For the lower fields, $\langle \chi^{(\text{AC})} \rangle_{\phi_c}$ resembles the $F = 0.0$ result near the isotropic orbiting singularity; this indicates that there is a multi-orbital scattering region for all but the strongest fields.

The detailed behaviour of $\chi^{(\text{AC})}(b, \phi_c)$ can be determined from figure 4.29; the figure shows polar contour plots (cf. figure 4.20 and 4.25) for HeAr with $K = 0.1$. The radial coordinate corresponds to $b \in [0, 3]$ while the angular coordinate shows $\phi_c \in [0, 2\pi]$ (rings mark $b \in \{1, 2, 3\}$, axes mark $\phi_c \in \{(0, \pi), (\pi/2, 3\pi/2)\}$). The six plots show the $\chi^{(\text{AC})}$ surface for: a) $F = 1.0, \Omega = 2.0$; b) $F = 1.0, \Omega = 10.0$; c) $F = 2.0, \Omega = 2.0$; d) $F = 2.0, \Omega = 10.0$; e) $F = 3.0, \Omega = 2.0$; f) $F = 3.0, \Omega = 10.0$. Contour values (given in legends) give $\chi^{(\text{AC})}$ in units of π -radians. Of particular note are the turquoise and green contours which indicate $\chi^{(\text{AC})} \geq \pi$. As in the mid- K regime, these regions correspond to oscillations of $\chi^{(\text{AC})}$ about π , the closely spaced contours demonstrate pendular scattering (e.g. those of figure 4.29(f)) while the more widely spaced regions demonstrate reflex scattering (figure 4.29(c)). The multi-orbital scattering region (dark contours) is seen for all laser parameter but the range of b where this occurs decreases with increasing F (figure (f) has almost none). For $F = 1.0$

Figure 4.29: Polar contour plots of $\chi^{(AC)}(b, \phi_c)$ with $b \in [0, 3]$ (radial-) and $\phi_c \in [0, 2\pi]$ (polar coordinate). Contour values (legends) are given in π -radians. Calculations are for HeAr with $K = 0.1$ and: (a) $\Omega = 2.0, F = 1.0$; (b) $\Omega = 10.0, F = 1.0$; (c) $\Omega = 2.0, F = 2.0$; (d) $\Omega = 10.0, F = 2.0$; (e) $\Omega = 2.0, F = 3.0$; (f) $\Omega = 10.0, F = 3.0$. Numerical details are given in section 3.2.

(figures (a) and (b)), there is at least one $b_{orb,(-)}^{(AC)}$ for every ϕ_c (black contours) while this is not observed for higher fields. The overall increase of pendular/reflex scattering with F is easily understood to be related to the magnitude of $\Delta_{\theta,-}^{(AC)}$, which becomes very large for $F = 3.0$ (cf. figure 4.5(d)). Multi-orbital scattering, which requires $\Delta_e^{(AC)}$ and $\Delta_{\theta,-}^{(AC)}$ to be comparable becomes less common for higher F as $\Delta_{\theta,-}^{(AC)}$ enters the range where $\Delta_{\theta,-}^{(AC)} \gtrsim \Delta_e^{(AC)}$ at the peak of the cycle.

Estimates of w for the low- K regime predict that the dynamics will be largely insensitive to (Ω, ϕ_c) in spite of the comparable role of $\langle U^{(AC)} \rangle_{\phi_c}$ and $U_{\tau}^{(AC)}$. Comparison between frequencies for the same field (4.29(a) vs. (b), etc ...) shows that the $\Omega = 10.0$ results are less sensitive to ϕ_c as the contours resemble concentric circles more so than those of $\Omega = 2.0$, particularly outside the region of reflex/pendular scattering. As Ω is increased, it is observed that pendular scattering predominates small impact parameters over reflex scattering (density of green contours); this is due to the efficiency of inducing multiple angular turning points which is the main distinction between pendular and reflex scattering. For $\Omega = 2.0$, $w \sim 1$, implying that the oscillations in $\Delta_{\theta,-}^{(AC)}$ and $\Delta_e^{(AC)}$ are too slow to trap the system in the potential well, resulting in reflex scattering. For $\Omega = 10.0$, $w \gg 1$ which implies the system experiences the average potential. However, the system is in the coupled amplitude regime and hence the peak field values of $\Delta_e^{(AC)}$ and $\Delta_{\theta,-}^{(AC)}$ cannot be discounted dynamically. For larger F at the peak of the field, $\Delta_e^{(AC)} \sim \Delta_{\theta,-}^{(AC)}$ which implies that the system is confined to $\theta \in [-\pi/2, +\pi/2]$. Hence the system must undergo multiple angular turning points and the resultant pendular scattering.

The collision dynamics of the low- K regime of $U^{(AC)}$ appear to be dominated by pendular scattering which has been shown to be controlled by $\Delta_{\theta,-}^{(AC)}$ and $\Delta_e^{(AC)}$ (cf. results of figure 4.27). Figures 4.30(a) and 4.30(b) show the results of trajectory calculations for

Figure 4.30: A comparison of the deflection functions of the partitions of $U^{(AC)}$ for HeAr with $K = 0.1$, $\Omega \in \{2.0, 10.0\}$, $F = 3.0$ and $\phi_c = 0$. Deflection angles are given in units of π -radians. Figure (a) — $\Omega = 2.0$; (b) — $\Omega = 10.0$. Lines show numerical trajectory results with: solid line — $\chi^{(AC)}$; dotted line — $\chi_{iso}^{(AC)}$; dashed line — $\chi_{aniso}^{(AC)}$. The insets show details of the large-impact parameter portion of the deflection function. Numerical details are given in section 3.2.

HeAr, $K = 0.1$, $F = 3.0$, $\phi_c = 0.0$ and $\Omega = 2.0$ and 10.0 , respectively. Deflection functions of the partitions $\chi^{(AC)}$, $\chi_{iso}^{(AC)}$ and $\chi_{aniso}^{(AC)}$ are shown respectively as solid, dotted and dashed lines. For small impact parameters where pendular scattering causes oscillations in $\chi^{(AC)}$, the function $\chi_{aniso}^{(AC)}$ reproduces the full calculation very well at both frequencies. There are more oscillations in $\chi_{aniso}^{(AC)}$ with the variation of b than are observed in $\chi^{(AC)}$ but the basic result of oscillations between obtuse and reflex angles is correct. In contrast, $\chi_{iso}^{(AC)}$ produces strictly obtuse scattering in this impact parameter range for both frequencies; this is a consequence of angular momentum conservation in $U_{iso}^{(AC)}$ which prevents the occurrence of angular turning points and hence, pendular scattering. In contrast to the mid- K pendular scattering (section 4.2.2.2), where it was shown that pendular scattering was the result of strong sensitivity of the trajectory to both $U_{iso}^{(AC)}$ and $U_{aniso}^{(AC)}$, the calculations of figure 4.30 show that the large amplitude fluctuations of the time-dependent part of $U_{aniso}^{(AC)}$ are sufficient to produce pendular scattering. This implies that pendular scattering possibly exists in regimes other than that of coupled potential/coupled amplitude.

In the intermediate impact parameter range, $\chi_{aniso}^{(AC)}$ is also a qualitative approximation to $\chi^{(AC)}$ but the agreement is less than that observed at small b . In particular, both figures 4.30(a) and 4.30(b) show that $\chi_{aniso}^{(AC)}$ lacks the positive orbiting singularities of $\chi^{(AC)}$ (where $\chi^{(AC)} > 2\pi$). The results of $\chi_{iso}^{(AC)}$ are similarly unrelated to those of the exact deflection function. Thus, multi-orbital scattering, as determined in other collision energy regimes of $U^{(AC)}$ and $U^{(HFL)}$, requires coupled potential conditions.

In agreement with the estimates of $w \gg 1$, the large impact parameter range of $\chi^{(AC)}$ is approximated by $\chi_{iso}^{(AC)}$ for both $\Omega = 2.0$ and $\Omega = 10.0$. This implies that the system experiences effectively the averaged potential $\langle U^{(AC)} \rangle_{\phi_c}$. However, the amplitudes are sufficiently large as to invalidate this approximate picture as is evidenced by the appearance

of barrier scattering at some ϕ_c (see section 4.3).

4.3 Special Features of the Deflection Function

In this section features of the deflection function $\chi^{(\text{HFL})}$ or $\chi^{(\text{AC})}$ are examined over a broader range of laser parameters to assess their influence on real observables. The deflection function is not experimentally observable but special features, e.g. glory-, rainbow- and orbital scattering, all have specific effects on the differential and integrated cross sections and thus can be related to experiment. From section 4.2, the dynamical origins and the influence of the potential on the features of χ are understood in terms of the identified collision mechanisms; this is to say that all collision mechanisms give rise to glory- and rainbow scattering. Thus, by mapping the regions of (F, Ω, K) where different collision mechanism exist, the conditions for the mechanisms and the dynamical regimes (section 2.3) can be established. Additionally, difficulties in observing unambiguous signatures of the collision mechanisms within the collision cross sections can be assessed.

4.3.1 Glory Scattering

From section 2.4.3.2, glory scattering is known to be characterised by n , the magnitude of the glory (i.e. $\chi = n\pi$ and n is an integer), the impact parameter b_g and the slope of the deflection function at b_g , χ'_g ; this feature leads to a singularity in the differential scattering cross section at $\Theta = 0$ or π , depending on n being even or odd. The intensity contribution to the differential cross section (weighted by $\sin \Theta$) is independent of the scattering angle near 0 or π and is proportional to $2b_g/|\chi'_g|$ by (2.66). In the field-free dynamics, only forward glory scattering ($\chi = 0$) is significant since the backscattering at $b = 0$ does not contribute to

the cross section. From section 4.2, reflex and pendular scattering lead to $n = +1$ backward glories, barrier scattering leads to $n = 0$ forward glories and multi-orbital scattering can give rise to $n \in \{0, \pm 1\}$ features. Higher $|n|$ -glories are not examined presently since their contributions to the scattering intensity are often associated with orbital scattering.

4.3.1.1 High Carrier Frequency

For the high-frequency limit potential $U^{(\text{HFL})}$, glory scattering occurs generally when there is a transition from one range of impact parameter to another, the detailed behaviour of which is governed by the complexity of the features contained in each region. From section 4.2, it is clear that only low collisional energies give rise to non-perturbative/anisotropic dynamics, i.e. reflex and multi-orbital scattering. Thus there will not be a great deal of sensitivity to F for the glory scattering in the mid- to high- K regimes.

The set of glory scattering parameters $\{b_g^{(\text{HFL})}\}$ and $\{\chi_g^{(\text{HFL})'}\}$ are shown as functions of F in figures 4.31(a) and (b), respectively. The results shown are for HeAr with $\Omega = \Omega_{\text{CO}_2}$ and $K \in \{0.1, 1.0, 10\}$. The different values of the glory angles, $n\pi$, are shown for the range $n \in [-1, +1]$ at all values of K . The details of these calculations are given in section 3.4. Although the results are shown only for HeAr, quantitatively similar results are obtained with the He₂ model parameters (see table B.9) and consequently these results are not shown. In figure 4.31(a), the values of $b_g^{(\text{HFL})}$ follow the contours of the deflection functions $\chi^{(\text{HFL})}(b; K, F)$ given in figures 4.9, 4.12 and 4.18. For high K , only forward glories are observed ($n = 0$, black data in figure) with a small, monotonic increase with F . Similarly, figure 4.31(b) shows the $\chi_g^{(\text{HFL})'}$ to be small and insensitive to F . The glory scattering at high K passes to the field-free limit in a continuous manner; thus the feature is clearly isotropic in origin which explains its comparative insensitivity to F . Similar

Figure 4.31: Glory scattering for $U^{(\text{HFL})}$ of HeAr with $\Omega = \Omega_{\text{CO}_2}$ and $K \in \{0.1, 1.0, 10\}$. Figure (a) shows $\{b_g^{(\text{HFL})}\}$ vs. F for a number of collision energies and glory angles of $n\pi$; figure (b) shows the corresponding values of $\{\chi_g^{(\text{HFL})'}\}$ in units of π -radians. In both figures data sets are labelled: black — $K = 10, n = 0$; red — $K = 1.0, n = -1$; blue — $K = 1.0, n = 0$; cyan — $K = 0.1, n = -1$; magenta — $K = 0.1, n = 0$; yellow — $K = 0.1, n = 1$. Data shown as circles in figure (a) have $\chi_g^{(\text{HFL})'} < 0$ and $\chi_g^{(\text{HFL})'} > 0$ for squares. Details of the calculations are given in 3.4.

behaviour is observed for the $n = 0$ forward glory of $K = 1.0$ and $K = 0.1$ (blue and magenta data, respectively). However, as the collision energy is decreased, there is an increased sensitivity to the value of F as might be anticipated from the system entering the coupled potential regime. In all cases the effect of F is to increase both $b_g^{(\text{HFL})}$ and $|\chi_g^{(\text{HFL})}|$ of the isotropic forward glory. Qualitatively, the increase in the slope at the glory impact parameter is larger than that of $b_g^{(\text{HFL})}$ and thus the overall intensity contributions should decrease with F .

Another feature which is isotropic in origin is that of the backward $n = -1$ glory for $K = 1.0$ (red data in figure 4.31). The two glories surround the minimum in the deflection function, as confirmed by figure 4.12, which persists for all field strengths. The gradual increase of both the $b_g^{(\text{HFL})}$ with F is offset on one hand by the large increase in positive branch of the $\chi_g^{(\text{HFL})}$ (corresponding to red squares in figure (a)), making the contribution to the cross section negligible. On the other hand, $b_g^{(\text{HFL})}$ with $\chi_g^{(\text{HFL})} < 0$ (red circles in figure (a)) decrease in absolute value of $\chi_g^{(\text{HFL})}$ with F ; thus the contribution to the differential cross section near $\Theta = \pi$ should increase.

For $K = 0.1$, the $n = -1$ results (cyan data in figure 4.31) show the emergence of the coupled potential regime dynamics as F is increased. Two isotropic glories exist at $F = 0$ which surround the orbiting singularity; as F is increased, these $b_g^{(\text{HFL})}$ are monotonically increasing until $F \approx 0.8$ where the negative sloped branch (circle data) of $b_g^{(\text{HFL})}$ bifurcates and two new glory branches emerge. The bifurcation is also observed in figure 4.31(b) for the negative isotropic glory branch, the other branches being off the scale of the graph. Bifurcation of the $b_g^{(\text{HFL})}$ branches is indicative of the onset of the multi-orbital scattering shown to occur in the mid-range impact parameter region in section 4.2. The increasing number of glory branches as a function of F demonstrates the increasing dominance of

$U_{\text{aniso}}^{(\text{HFL})}$ on the dynamics. In contradistinction to this increasing anisotropic dominance is the observation that the isotropic branches of $b_g^{(\text{HFL})}$ are seen to persist at all field strengths (from the continuity of the cyan data in figure 4.31(a), although $\chi_g^{(\text{HFL})'}$ changes sign); this illustrates the utility of the analysis of special features of the deflection function in determining specific influences of the potential on the dynamics via the continuity over the variation in F .

The forward glory $n = 0$ of $K = 0.1$ (magenta data in figure 4.31) varies continuously with F from the field free results. The value of $b_g^{(\text{HFL})}$ increases sharply with F while $\chi_g^{(\text{HFL})'}$ decreases; comparison of the relative magnitudes of the two parameters show that this contribution to the forward scattering intensity should decrease strongly with F . At very high fields ($F \gtrsim 2.7$), the presence of the multi-orbital scattering region (cf. figure 4.18) in the low- K $\chi^{(\text{HFL})}$ causes another multi-orbital forward glory to emerge (upper right corner of figure 4.31(a)). The glory is the result of the narrow obtuse/reflex scattering shoulder which occurs at very large impact parameters (see $F = 3.0$ results of figure 4.17 near $b \approx 2.7$). However, the large values of $\chi_g^{(\text{HFL})'}$ associated with this feature make its contribution to the differential cross section negligible.

The contributions to the scattering intensity from backward $n = +1$ glories of $K = 0.1$ (yellow data in figure 4.31) for large $F \gtrsim 2.5$ are completely laser-induced since none correlate with the $F = 0.0$ limit; however, the different branches arise from two distinct collision mechanisms. First the isolated branch of $b_g^{(\text{HFL})}$ of $n = +1$ in figure 4.31(a) originates at moderate fields ($F \approx 1.7$). From section 4.2, this glory is shown to indicate the onset of reflex scattering. The size of the reflex scattering region is thus shown to increase with F , along with $b_g^{(\text{HFL})}$. The reflex scattering glory singularity is a backward singularity which initially has a decreasing $|\chi_g^{(\text{HFL})}'|$ until $F \approx 2.0$ (where it changes sign); this region does

not contain a maxima in $\chi^{(\text{HFL})}$ and hence, the reflex contribution to the backward scattering intensity should be most prominent for fields less than this value. For larger fields, a rainbow singularity (vide infra) will obscure this feature.

The second set of $K = 0.1$, $n = +1$ glory singularities occur at mid-range impact parameters and only emerge with large F (figure 4.31(a), $F \gtrsim 2.7$). These glory scattering singularities arise from the presence of local maxima in the deflection function which, at large F , produce positive orbiting singularities ($\chi^{(\text{HFL})} = +\infty$); such features are produced by multi-orbital scattering. In general, these glories have a large $|\chi_g^{(\text{HFL})}|$ (figure 4.31(b)) after the bifurcation point so their contribution to the cross section intensity decreases with F .

In the high- K regime of perturbative potential dynamics, it was shown in section 4.2 that the deflection function $\chi^{(\text{HFL})}$ was at least qualitatively described by the impulse approximation calculations (2.98). In addition, the HDID-IA model of section 2.5.3.2 estimates glory parameters in this regime. Figure 4.32 tests these models for HeAr and He₂ at $K = 10$, $\Omega = \Omega_{\text{CO}_2}$ (details of the calculations are given in section 3.4). Figure 4.32(a) shows the forward glory impact parameter $n = 0$ $\{b_g^{(\text{HFL})}\}$ vs. F while figure (b) shows the corresponding $\chi_g^{(\text{HFL})}$ vs. F . Results for HeAr and He₂ are shown as red and black data, respectively. The glory parameters calculated from different models are shown as different line-styles in the figure: solid — numerical roots of $\chi^{(\text{HFL})}$ (cf. results of figure 4.31); dashed — numerical roots of $\chi_{\text{IA}}^{(\text{HFL})}$, given by (2.98); dotted — the HDID-IA model of (2.111) and (2.112). The results show first that the glory parameters of HeAr and He₂ do not differ significantly except when calculated from $\chi_{\text{IA}}^{(\text{HFL})}$ ⁶. Such similarity is expected

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⁶N.B.: This is due to the difference in the parameter Λ_{β_2} , which is the only significant difference in table B.9. Similarity of other parameters allows a cancellation of terms in (2.98) which result in the difference between the deflection functions being dominated by terms with Λ_{β_2} . The difference thus increases with F . Since the sensitivity to the exchange terms in α and β is not exhibited in the exact calculations, the observation

Figure 4.32: Models of glory scattering for $U^{(\text{HFL})}$ of HeAr and He₂ with $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. Figure (a) shows $\{b_g^{(\text{HFL})}\}$ vs. F for the forward ($n = 0$) glory; figure (b) shows the corresponding values of $\{\chi_g^{(\text{HFL})'}\}$ vs. F in units of π -radians. In both figures, black and red data denote He₂ and HeAr, respectively. Line styles correspond to: solid — numerical roots of $\chi^{(\text{HFL})}$ (cf. figure 4.31); dotted — HDID-IA model of (2.111) and (2.112); dashed — numerical roots of $\chi_{\text{IA}}^{(\text{HFL})}$ as given by (2.98). Details of the calculations are given in section 3.4.

from the $U^{(\text{HFL})}$ dynamics since the potential surfaces are almost identical (cf. figures 4.2 and 4.3). Neither of the model calculations shown in figure 4.32 are quantitatively accurate nor consistent in their qualitative accuracy. The numerical results for $\chi_{\text{IA}}^{(\text{HFL})}$ show qualitatively correct field dependence for $b_g^{(\text{HFL})}$ but not for $\chi_g^{(\text{HFL})}$, and a significant difference between the two molecular systems at high F .

The poor predictive ability of the model calculations shown in figure 4.32 can be ascribed to the failure of the impulse approximation at small impact parameters. Near $b_g^{(\text{HFL})}$, both $\chi_{\text{IA}}^{(\text{HFL})}$ from (2.98) and (2.109) diverge rapidly from $\chi^{(\text{HFL})}$ (cf. results of figure 4.11); hence there will necessarily be a discrepancy which grows with F . The difference between the two model calculations is solely due to the inclusion of the short-range (exchange) terms of the polarisability since the dipole terms of (2.98) are small in comparison. Inclusion of the exchange terms in $\chi_{\text{IA}}^{(\text{HFL})}$ adds a net repulsive term to the deflection function which grows with F compared to that of (2.109); this has the effect of shifting $b_g^{(\text{HFL})}$ to larger impact parameters as F increases (dashed lines in figure 4.32(a)). As the net attractive DID polarisability potential contributions to $\chi_{\text{IA}}^{(\text{HFL})}$ also increase with F , their effect is to shift $b_g^{(\text{HFL})}$ to smaller b . Thus, the absence of the exchange terms in the HDID-IA model of (2.111) results in $b_g^{(\text{HFL})}$ decreasing with F (dotted lines in figure 4.32(a)). Therefore, it appears that the full impulse approximation results of (2.98) are more predictive than the HDID-IA model; this is emphasised by the approximately constant difference between the exact and $\chi_{\text{IA}}^{(\text{HFL})}$ calculations for HeAr over the range of F shown in the figure.

The situation for the quantity $\chi_g^{(\text{HFL})}$ is reversed from that of $b_g^{(\text{HFL})}$ above. Here, figure 4.32(b) shows that the HDID-IA model of (2.112) is qualitatively correct while the calculations of $\chi_{\text{IA}}^{(\text{HFL})}$ using (2.98) increase the value of the derivative at the glory angle.

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is not pertinent to the present work.

The inclusion of the net repulsive exchange terms in (2.98) necessarily introduces a positive correction to the slope in order to increase $b_g^{(\text{HFL})}$. Thus (2.112) yields correct qualitative behaviour coincidentally. The failure of either model to yield consistent qualitatively correct behaviour is due to the fact that it is not possible to increase $b_g^{(\text{HFL})}$ and decrease $\chi_g^{(\text{HFL})}$, using additive terms in the deflection function as prescribed by the impulse approximation.

4.3.1.2 Low-to-Medium Carrier Frequency

From examination of the deflection functions produced by $U^{(\text{AC})}$ in section 4.2, it was determined that $\chi^{(\text{AC})}$ contains most of the same features of $\chi^{(\text{HFL})}$ in addition to the mechanisms of pendular and barrier scattering. Pendular scattering was shown in section 4.2 to lead to multiple backwards ($n = 1$) glories at small impact parameters while barrier scattering is characterised by a $n = 0$ forward glory at large impact parameters. In the cases where the glory parameters $\{b_g^{(\text{AC})}, \chi_g^{(\text{AC})'}\}$ are single-valued over the domain of ϕ_c , the averaged quantities $\{\langle b_g^{(\text{AC})} \rangle_{\phi_c}, \langle \chi_g^{(\text{AC})'} \rangle_{\phi_c}\}$ can be analysed.

Figures 4.33, 4.34 and 4.35 show $\{b_g^{(\text{AC})}\}$ and $\{\chi_g^{(\text{AC})'}\}$ of HeAr as a function of Ω for two field strengths ($F \in \{1.0, 3.0\}$) and three collision energies ($K = 10, 1.0$ and 0.1 , respectively). Details of the calculation methods are given in section 3.4. Glory parameters are shown for both forward ($n = 0$: yellow data in all figures) and backward ($n \in \{-1, +1\}$: red and blue data, respectively) scattering. In all three figures, (a) and (c) contain results for $F = 1.0$ while (b) and (d) contain those of $F = 3.0$. The figures (a) and (b) plot $\{b_g^{(\text{AC})}\}$, (c) and (d) display the corresponding $\{\chi_g^{(\text{AC})'}\}$. In order to better follow the individual features within the three figures, data shown as circles in (a) and (b) have negative $\chi_g^{(\text{AC})}'$ while those shown as squares possess positive $\chi_g^{(\text{AC})}'$.

Figure 4.33 shows the glory parameters for $K = 10$. Only $n = 0$ forward glories are

Figure 4.33: Glory scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 10$. Figures (a) and (b) show $b_g^{(AC)}$ vs. Ω for $F = 1.0$ and $F = 3.0$, respectively. Corresponding $\{\chi_g^{(AC)}\}$ vs. Ω are shown in figures (c) and (d) (units of π -rad.) All figures show $n = 0$ glories. In figures (a) and (b), circles denote glories with negative $\chi^{(AC)}$ while squares show positive $\chi_g^{(AC)}$. Details of the calculations are given in section 3.4.

Figure 4.34: Glory scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 1.0$. Figures (a) and (b) show $b_g^{(AC)}$ vs. Ω for $F = 1.0$ and $F = 3.0$, respectively. Corresponding $\{\chi_g^{(AC)}\}$ vs. Ω are shown in figures (c) and (d) (units of π -rad.) All figures show $n\pi$ glories as different colours: red — $n = -1$; yellow — $n = 0$; blue — $n = +1$. In figures (a) and (b), circles denote glories with negative $\chi_g^{(AC)}$ while squares show positive $\chi_g^{(AC)}$. Details of the calculations are given in section 3.4.

Figure 4.35: Glory scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 0.1$. Figures (a) and (b) show $b_g^{(AC)}$ vs. Ω for $F = 1.0$ and $F = 3.0$, respectively. Corresponding $\{\chi_g^{(AC)}\}$ vs. Ω are shown in figures (c) and (d) (units of π -rad.) All figures show $n\pi$ glories as different colours: red — $n = -1$; yellow — $n = 0$; blue — $n = +1$. In figures (a) and (b), circles denote glories with negative $\chi_g^{(AC)}$ while squares show positive $\chi_g^{(AC)}$. Details of the calculations are given in section 3.4.

present at this collision energy with a single isotropic glory at $b_g^{(AC)} \sim 1$ which is insensitive to Ω . As noted in section 4.2.2.1, barrier scattering is observed for $F = 3.0$ and $\Omega = 2.0$; this is confirmed in figure 4.33(b) where a second set of $b_g^{(AC)}$ appears at large impact parameters ($b \gtrsim 2$). Barrier scattering glories are also observed at $\Omega = 4.0$ and $\Omega = 2.0$ with $F = 1.0$ (figure (a)). The absence of barrier scattering at other frequencies indicates that the mechanism is sensitive to w when $\Delta_{\theta,+}^{(AC)} \ll K$. The glory slopes $|\chi_g^{(AC)}|'$ are seen to increase in absolute value as F is increased (cf. figure 4.33(c) vs. (d)) while remaining insensitive to Ω as a group; this implies that the contribution to the scattering intensity will decrease with increasing F by equation (2.66). From section 4.2.2.1 the glory at $b_g^{(AC)} \sim 1$ was shown to be isotropic in origin, i.e. arising from $U_{iso}^{(AC)}$. Such features should exhibit little Ω dependence since $U_{iso}^{(AC)} \approx U_0$ for HeAr.

The glory parameters shown in figure 4.34 correspond to $K = 1.0$. Figures (a) and (c) show $\{b_g^{(AC)}\}$ and $\{\chi_g^{(AC)}\}'$ respectively for $F = 1.0$. For $n = -1$ glories (red data), $b_g^{(AC)}$ is centred about 1.5 with little variation over ϕ_c or Ω . The corresponding $\chi_g^{(AC)}'$ have a wider variation with ϕ_c at lower Ω but converge to $|\chi_g^{(AC)}'| \sim 50\pi$ for higher frequencies. The $n = 0$ forward glories (yellow data) have $b_g^{(AC)} \sim 1$ and $|\chi_g^{(AC)}'| \sim 50\pi$ which appear to be independent of Ω and have little dependence on ϕ_c (the spread of the data points). Backward ($n = +1$) glories are also observed over a range of $b_g^{(AC)} \lesssim 0.4$ for $\Omega > 10.0$; the corresponding values of $|\chi_g^{(AC)}'|$ are large, ca. 150π with some variation with Ω . Overall, the contributions to the scattering intensity is largest from the $n = 0$ glories by (2.66) since $|\chi_g^{(AC)}'|$ is smallest.

For stronger fields ($F = 3.0$), figure 4.34(b) and (d) show that the $\{b_g^{(AC)}\}$ of $n = -1$ has increased relative to the $F = 1.0$ results but is still insensitive to Ω ; however, the number of such glories is larger for $\Omega \lesssim 10.0$. The $\chi_g^{(AC)}'$ of $n = -1$ glories a wide range of values

($|\chi_g^{(AC)}| \lesssim 250\pi$) until $\Omega \geq 10.0$, where $|\chi_g^{(AC)}| \sim 50\pi$. Similarly, forward $n = 0$ glories have $b_g^{(AC)}$ insensitive to Ω and are also shifted relative to the $F = 1.0$ results by ca. 0.4. The related $|\chi_g^{(AC)}|$ are $\sim 250\pi$ for $\Omega \leq 10.0$ and $\leq 50\pi$ for higher frequencies. Finally, the $n = +1$ glories are present at all frequencies, spanning a range of $b_g^{(AC)} \lesssim 1.2$ in an almost continuous fashion; the $|\chi_g^{(AC)}|$ are similarly $\lesssim 250\pi$ for all Ω .

The results of section 4.2.2.2 showed that multi-orbital scattering can give rise to $n = -1$ glories in addition to those that arise from an isotropic rainbow singularity. The frequency independent $\{b_g^{(AC)}, \chi_g^{(AC)}\}$ for $n = -1$ correspond to those ϕ_c where the system exhibits perturbative/isotropic potential dynamics: this is seen from the glories of figure 4.34(a) and (b) which correlate with $\{b_g^{(HFL)}, \chi_g^{(HFL)}\}$ of figure 4.31. This implies that such dynamics are determined by $\langle U^{(AC)} \rangle_{\phi_c}$. The remaining $n = -1$ glories are due to multi-orbital scattering and are concentrated near the isotropic glory since both are mid-range b phenomena. The field-induced glories are sensitive to Ω , predominating at lower frequencies ($\Omega \lesssim 10.0$), where $w \sim 1$. The isotropic $n = 0$ glory also shows the same correspondence with $b_g^{(HFL)}$ for both fields (ca. 1.2 and 1.4, for $F = 1.0$ and 3.0, respectively). Multi-orbital scattering does give rise to some $n = 0$ in the coupled potential/coupled amplitude regime ($F = 3.0$) which disappear for frequencies where $w > 1$ ($\Omega \gtrsim 10.0$).

Pendular scattering was also noted for mid- K dynamics in the isotropic or coupled potential regimes in conjunction with the coupled amplitude regime; this generates multiple $n = +1$ glories at small impact parameters. The Ω dependence of this mechanism appears to be large for the isotropic potential regime (figure 4.34(a)) where there is a threshold of ($\Omega \approx 10.0, b_g^{(AC)} \lesssim 0.4$), or $w \sim 1$. For the coupled potential regime (figure 4.34(b)), pendular scattering is observed at $b_g^{(AC)} \lesssim 1.2$ and is independent of Ω ; this corresponds to $w \gg 1$ and hence the degree of sensitivity to w is determined by the potential regime. From

(2.66), the isotropic glories should yield the largest contributions to the scattering intensity.

Figure 4.35 shows HeAr glory parameters for $F = 1.0$ and 3.0 at $K = 0.1$. The results reflect the behaviour of $\chi^{(AC)}(b; \phi_c)$ shown in figure 4.29. For weak fields (figures 4.35(a) and (c)), bands of glory scattering are observed at $1.0 \lesssim b_g^{(AC)} \lesssim 2.4$ for $n = -1$ (some of these are obscured in the figure), $1.0 \lesssim b_g^{(AC)} \lesssim 2.0$ and $b_g^{(AC)} \lesssim 1.0$ for $n = +1$. For strong fields (figures 4.35(b) and (d)), $b_g^{(AC)} \approx 2.7$ for $n = -1$, $b_g^{(AC)} \gtrsim 3.0$ for $n = 0$ and $b_g^{(AC)} \lesssim 2.7$ for $n = +1$. In the case of $\{\chi_g^{(AC)'}\}$, the $F = 1.0$ results span a wider range while for $F = 3.0$ (figure (d)), $|\chi_g^{(AC)'}| \lesssim 500\pi$.

As in the mid- K case, $n = -1$ glories arise from multi-orbital scattering, a number of which correspond to the isotropic glories of the field-free system. From figure 4.31, $2.1 \lesssim b_g^{(HFL)} \lesssim 2.3$ for $F = 1.0$ and $b_g^{(HFL)} \sim 2.6$ for $F = 3.0$; glories occur at these impact parameters in figure 4.35(a) and (b) over all Ω ; these glories, while not all isotropic, do arise from $\langle U^{(AC)} \rangle_{\phi_c}$ and are hence independent of w . The remainder of the multi-orbital scattering $n = -1$ glories are sensitive to w but due to their large number, the range of impact parameters spanned is approximately constant over Ω . In contrast, figure 4.35(b) shows that only the $n = -1$ glories induced by $\langle U^{(AC)} \rangle_{\phi_c}$ persist in $F = 3.0$. This narrowing of the multi-orbital impact parameter region is due to the presence of high-amplitude fluctuations in $U^{(AC)}$ which cause the peak field value of $\Delta_{\theta,-}^{(AC)}$ to dominate the dynamics; for this field, $\Delta_{\theta,-}^{(AC)} \approx \Delta_e^{(AC)}$ and multi-orbital scattering is difficult since the system cannot pass between wells at the peak of the field. Multi-orbital scattering also gives rise to the band of $n = 0$ glories seen in figure 4.35(a) ($F = 1.0$, yellow data); those not centred about $b_g^{(AC)} \approx 2.8$ do not correspond to any $\langle U^{(AC)} \rangle_{\phi_c}$ -induced forward glory. The apparent insensitivity to Ω of these features is due to their large numbers.

Barrier scattering is seen in figure 4.35(b) where a number of $n = 0$ glories occur for

large impact parameters; the range of b covered extends to lower impact parameters as Ω is increased. Even though $w \gg 1$ over all Ω examined, the system is in the coupled potential/coupled amplitude regime and the magnitude of the fluctuations in $U^{(AC)}$ make the peak field potential dominate the dynamics. In this case $\Delta_{\theta,+}^{(AC)} > K$ (ca. 0.3) and hence, the barrier to rotation can have an influence on impact parameters larger than $X_{\max}^{(AC)}$ (ca. 1.5). From figure 4.35(d), the barrier scattering glories have comparable $|\chi_g^{(AC)}|'$ to other glories; hence the contributions to the scattering intensity should be large due to the large values of $b_g^{(AC)}$.

Pendular scattering is seen to give rise to $n = +1$ glories for all frequencies at both fields in figure 4.35 (blue data). As noted in section 4.2.2.3, an increase in F results in an increase in the upper bound on $b_g^{(AC)}$. As with the $n = 0$ multi-orbital glories, the apparent lack of frequency dependence in the $n = +1$ pendular glories is a result of intermixing between a large number of such features. For strong fields (figure 4.35(d)), the values of $|\chi_g^{(AC)}|'$ are small and hence the scattering intensity contribution should be large.

The high- K glory feature is useful for the observation of the perturbative effect of the laser-induced potential. Figure 4.36 shows $\langle b_g^{(AC)} \rangle_{\phi_c}$ (figure (a)) and $\langle \chi_g^{(AC)} \rangle_{\phi_c}$ (figure (b)) of the $n = 0$ glory as a function of Ω for He₂ (black data) and HeAr (red data) with $K = 10$ and $F = 3.0$. Error bars shown in the figure correspond to the values of $\sigma_{\text{RMS},b_g^{(AC)}}$ and $\sigma_{\text{RMS},\chi_g^{(AC)'}}$. The blue (maroon) data shows the resulting glory parameters for He₂ (HeAr) calculated from $\chi_{\text{IA}}^{(AC)}$ (equation (2.104)). The first thing to note about figure 4.36 is that, while the average values are the same, the variance of the exact glory parameters is larger in the HeAr (red) results than in those of He₂ (black). The behaviour of the results for $\chi_{\text{IA}}^{(AC)}$ is similar to that of $\chi_{\text{IA}}^{(\text{HFL})}$ (cf. results of figure 4.32); the breakdown of the impulse approximation occurs at the relevant impact parameters. Thus, additive terms for the repulsive

Figure 4.36: Models of glory scattering for $U^{(AC)}$ of HeAr and He₂ with $F = 3.0$ and $K = 10$. Figure (a) shows $\{\langle b_g^{(AC)} \rangle_{\phi_c}\}$ vs. Ω for the forward ($n = 0$) glory; figure (b) shows the corresponding values of $\{\langle \chi_g^{(HFL)} \rangle_{\phi_c}\}$ vs. Ω in units of π -radians. Error bars show $\sigma_{\text{RMS}, b_g^{(AC)}}$ and $\sigma_{\text{RMS}, \chi_g^{(AC)}}$, in (a) and (b), respectively. Black data — He₂, numerical roots of $\chi^{(AC)}$; red data — HeAr, numerical roots of $\chi^{(AC)}$ (cf. figure 4.33); blue data — He₂, numerical roots of $\chi_{\text{IA}}^{(AC)}$ (equation (2.104)); maroon data — HeAr, numerical roots of $\chi_{\text{IA}}^{(AC)}$. Details of the calculations are given in section 3.4.

potential contributions may yield a reasonable result for $\langle b_g^{(AC)} \rangle_{\phi_c}$, qualitatively incorrect behaviour is obtained for $\langle \chi_g^{(AC)} \rangle_{\phi_c}$. The ϕ_c -dependence of the impulse approximation results is also apparent since both $\sigma_{\text{RMS}, b_g^{(AC)}}$ and $\sigma_{\text{RMS}, \chi_g^{(AC)}}$ are overestimated⁷.

4.3.2 Rainbow Scattering

The phenomenon of rainbow scattering, described in section 2.4.3.3, is characterised by the parameters $\{b_r, \chi_r, \chi_r''\}$; forward rainbows are defined as having a bright side on $\Theta \leq \Theta_r$ and backward rainbows on $\Theta \geq \Theta_r$ (determined via equation (2.70)). Reflex-, barrier-, pendular- and multi-orbital scattering all give rise to rainbows in various different parts of the deflection function. In contrast, the perturbative potential regime of the field-free dynamics gives rise to a single forward rainbow for $K \gtrsim 1$. Therefore a significant test for the presence of laser-induced dynamics is the appearance of other rainbows as laser parameters are varied.

4.3.2.1 High Carrier Frequency

In the high-frequency limit, $U^{(\text{HFL})}$ gives rise to both reflex- and multi-orbital scattering in non-perturbative potential regimes. The former occur at small impact parameter and the latter at mid-range b . From section 4.2, low- K collision dynamics are more sensitive to the details of the potential and hence the corresponding rainbow parameters should exhibit a stronger dependence on the laser field.

Figure 4.37 shows the resulting rainbow parameters $\{b_r^{(\text{HFL})}\}$ (figure (a)), $\{\chi_r^{(\text{HFL})}\}$

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⁷N.B.: The drastic difference between the $\langle b_g^{(AC)} \rangle_{\phi_c}$ impulse approximation results of He₂ and HeAr can be ascribed, as in $\chi_{\text{IA}}^{(\text{HFL})}$ (see footnote, page 174) to small differences in Λ_{β_r} . The enhanced repulsive effect in He₂ leads to values of ϕ_c where no glory is present; this sparseness of $b_g^{(AC)}$ is manifested in a decrease in $\langle b_g^{(AC)} \rangle_{\phi_c}$. Since the discrepancy is not seen in the exact dynamics, it is not relevant to the present discussion.

(figure (b)) and $\{\chi_r^{(\text{HFL})''}\}$ (figure (c)) vs. F for HeAr, $\Omega = \Omega_{\text{CO}_2}$ and $K \in \{0.1, 1.0, 10\}$ (blue and cyan, red and black data, respectively, in order of increasing K). Details of the calculations are given in section 3.4. For high- and mid- K scattering, the results may be compared to the original deflection functions of figures 4.9 and 4.12. As surmised in sections 4.2.1.1 and 4.2.1.2, the dynamics of these collision energies are in the perturbative potential regime; this conclusion supports the observed correlation of the rainbow parameters with the $F = 0.0$ limit in figure 4.37 (black and red data). The isotropic rainbows identified are important since they are isolated features of the deflection function and can follow the perturbative influence of $U_{\text{aniso}}^{(\text{HFL})}$ on the dynamics. The rainbow parameter of these collisional energies yield only forward rainbows via (2.70) and this does not change with increasing F . The field-dependence shows both $b_r^{(\text{HFL})}$ and $\chi_r^{(\text{HFL})''}$ monotonically increasing while $\chi_r^{(\text{HFL})}$ is decreasing; this sensitivity to F is more pronounced for the $K = 1.0$ results (red) than those of $K = 10$ (black). The intensity factor of the rainbow singularity in the differential cross section (2.69) should thus be approximately constant while the position of the rainbow shifts towards $\Theta = 0$ with increasing F . Since the overall variations in the parameters are small, such a shift may be difficult to observe.

The low- K results (blue and cyan data in figure 4.37 denote forward and backward rainbows, respectively) reflect the increased sensitivity of the deflection function (figure 4.18) in the coupled potential regime for small- and mid-range b . At the particular collision energy of $K = 0.1$, no isotropic rainbow is possible at $F = 0$; thus no rainbow is observed which correlates with the field-free limit. Rainbows which appear at the weakest fields are dubious since they occur in the region of isotropic orbiting (vide infra) and are more likely a numerical artefact of the method used to separate orbiting from rainbow collisions (see section 3.4). The rainbows seen in figure 4.37 emerge from either multi-orbiting dynamics

Figure 4.37: Rainbow scattering for $U^{(\text{HFL})}$ of HeAr with $\Omega = \Omega_{\text{CO}_2}$ and $K \in \{0.1, 1.0, 10\}$. Figure (a) shows $\{b_r^{(\text{HFL})}\}$ vs. F with corresponding values of $\{\chi_r^{(\text{HFL})}\}$ and $\{\chi_r^{(\text{HFL})''}\}$ (units of π -radians) shown in figures (b) and (c), respectively. In all figures data sets are: black — $K = 10$, forward rainbows; red — $K = 1.0$, forward rainbows; blue — $K = 0.1$, forward rainbows; cyan — $K = 0.1$, backward rainbows. Details of the calculations are given in 3.4.

or reflex scattering. Multi-orbiting rainbows emerge at mid-range impact parameters (for $F \gtrsim 0.8$) and are characterised by a bifurcation structure with increasing F (cf. results of glory scattering in section 4.3.1.1). Both branches of the bifurcation increase $b_r^{(\text{HFL})}$ with F . These rainbows emerge as a result of the regions of $\chi^{(\text{HFL})}(b)$ in between two orbiting singularities or are “satellites” of the isotropic orbiting singularity. In any case, the complex dynamics of this impact parameter region prohibit following a single feature as a function of F . In general rainbow singularities resulting from the multi-orbiting region are of both types (forward and backward) with possibly non-monotonic field dependence of their intensity. In general, figure 4.37(c) shows $|\chi_r^{(\text{HFL})''}| \gg 1$ which indicates that the corresponding rainbows do not have a large intensity contribution on their bright sides (i.e. the singularities are narrow in the differential cross section).

A distinct feature arises from the reflex scattering region for low K . Figure 4.37(a) shows that for $F \gtrsim 1.8$, the reflex rainbow impact parameter emerges and shifts from small to very large impact parameters with F . The concomitant $\chi_r^{(\text{HFL})}$ shifts from π to 2π over the same field range in a continuous manner. For very high fields, the feature disappears since it becomes a positive orbiting singularity in $\chi^{(\text{HFL})}(b)$ (see figure 4.17). Since the reflex rainbow is a maximum in $\chi^{(\text{HFL})}$ with small curvature, the feature is seen as a backwards rainbow in the differential cross section. From figure 4.37(c), it is difficult to identify a distinct trend in the curvature which might correspond to the reflex rainbow. However, there is a continuous branch of $\chi_r^{(\text{HFL})''}$ (cyan data) which is near zero and relatively constant with F . Taken with the strong $b_r^{(\text{HFL})}$ dependence, it appears that the reflex rainbow should be observed as a “wide” backwards rainbow singularity which migrates from $\Theta = \pi$ to zero with increasing F . Such a feature should be a clear indication of the laser-induced effects on $U^{(\text{HFL})}$.

In the high- K limit, the impulse approximation deflection functions of either (2.98) or its simplified HDID-IA counterpart can be used to predict the rainbow parameters. Figure 4.38 shows the isotropic $b_r^{(\text{HFL})}$, $\chi_r^{(\text{HFL})}$ and $\chi_r^{(\text{HFL})''}$ vs. F for $K = 10$, $\Omega = \Omega_{\text{CO}_2}$ in figures (a)–(c), respectively. Black and red data show results for He_2 and HeAr , respectively. Numerical calculations of the rainbow parameters using $\chi_{\text{IA}}^{(\text{HFL})}$ of (2.98) are given by dashed lines while the HDID-IA models of $b_r^{(\text{HFL})}$, $\chi_r^{(\text{HFL})}$ and $\chi_r^{(\text{HFL})''}$ (corresponding to equations (2.113)–(2.115)) are shown by dotted lines. As in the glory results of section 4.3.1.1 (cf. those of figure 4.32), neither model produces qualitatively correct results for the field-dependence of all parameters consistently. The validity of the impulse approximation in the region of the isotropic rainbow is thus questionable. Additive terms describing the short-range repulsive scattering of $U^{(\text{HFL})}$ in $\chi_{\text{IA}}^{(\text{HFL})}$ yield an increase in $b_r^{(\text{HFL})}$ with F for both molecules in agreement with the exact results. Thus, the exclusion of these terms in (2.113) is clearly incorrect. Figure 4.38(b) shows the additive nature of the short-range terms in $\chi_{\text{IA}}^{(\text{HFL})}$ can only increase the value of $\chi_r^{(\text{HFL})}$ with F , contradicting the observed behaviour of the exact calculation. Hence, the HDID-IA model of (2.114) gives correct F dependence by accident. Both models overestimate the field-dependence of $\chi_r^{(\text{HFL})}$ considerably.

The curvature at the rainbow impact parameter $\chi_r^{(\text{HFL})''}$, shown in figure 4.38(c) increases with F for the exact calculation⁸. Again, the additive short-range terms cannot yield the correct behaviour and the numerical results of $\chi_{\text{IA}}^{(\text{HFL})}$ exhibit the opposite field dependence and their absence in HDID-IA model of (2.115) gives coincidentally correct results. Typically, the impulse approximation is regarded as qualitatively correct for field-

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⁸N.B.: The “noise” in the exact results of figure 4.38 arises from the low accuracy of the Akima spline second derivative. Possible improvement of the spline might be obtained from using a higher degree interpolation polynomial; currently this is cubic.

Figure 4.38: Models of rainbow scattering for $U^{(\text{HFL})}$ of HeAr and He₂ with $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. Figure (a) shows $\{b_r^{(\text{HFL})}\}$ vs. F while figures (b) and (c) show the corresponding values of $\{\chi_r^{(\text{HFL})}\}$ and $\{\chi_r^{(\text{HFL})''}\}$ vs. F in units of π -radians. In all figures, black and red data denote He₂ and HeAr, respectively. Line styles correspond to: solid — numerical extrema of $\chi^{(\text{HFL})}$ (cf. figure 4.37); dotted — HDID-IA model of (2.113)–(2.115); dashed — numerical extrema of $\chi_{\text{IA}}^{(\text{HFL})}$ as given by (2.98). Details of the calculations are given in 3.4.

free dynamics (see section 1.3) but the results here show that the additive behaviour of the approximation does not yield the correct shape-dependence of the potential.

4.3.2.2 Low-to-Medium Carrier Frequency

In analogy to the glory parameter results of section 4.3.1.2, the rainbow parameters should exhibit a greater degree of sensitivity to ϕ_c and Ω when $w \sim 1$; independence of w is achieved in either the static field or high frequency limits provided the potential amplitudes are large. The sensitivity to $U_{\tau}^{(AC)}$ is dependent on the dynamical origin of the feature in question. However, the basic regions of dynamical behaviour are defined by $\langle U^{(AC)} \rangle_{\phi_c}$, barring resonance effects.

The rainbow parameters $\{b_r^{(AC)}, \chi_r^{(AC)}, \chi_r^{(AC)''}\}$ of HeAr are shown as functions of carrier frequency Ω with $F \in \{1.0, 3.0\}$ in figures 4.39, 4.40 and 4.41 for $K = 10, 1.0$ and 0.1 , respectively; in each figure (a), (b) and (c) show parameters for $F = 1.0$ while those of (d) through (f) correspond to $F = 3.0$. The rainbow parameters of $\{b_r^{(AC)}\}$, $\{\chi_r^{(AC)}\}$ and $\{\chi_r^{(AC)''}\}$ are shown in the pairs (a,d), (b,e) and (c,f), respectively. In all figures, yellow data correspond to forward rainbows while red data are backwards rainbows. Details of the calculations are given in 3.4.

The perturbative potential/perturbative amplitude dynamics exhibited in section 4.2.2.1 for high- K collisions translate to a single, isotropic forward rainbow for $K = 10$ (yellow data in figure 4.39) that is insensitive to Ω . For $F = 1.0$, figure 4.39(a) shows that $b_r^{(AC)} \approx 1$; figures (b) and (c) show $\chi_r^{(AC)}$ and $\chi_r^{(AC)''}$ are centred about $\chi_r^{(AC)} \approx -0.07\pi$ and $\chi_r^{(AC)''} \approx 5\pi$ with more variation with ϕ_c than in the case of $b_r^{(AC)}$. These results are consistent with the system being in the static field limit ($w \ll 1$) for most impact parameter ranges and frequencies. From the data shown, this is a forward rainbow with a large slope.

Figure 4.39: Rainbow scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 10$. Figures (a–c) show results for $F = 1.0$ while (d–f) show $F = 3.0$. Figures (a) and (d) are of $\{b_r^{(AC)}\}$ vs. Ω , (b) and (e) $\{\chi_r^{(AC)}\}$ vs. Ω (π -radians), while (c) and (f) show $\{\chi_r^{(AC)''}\}$ vs. Ω (π -radians). In all figures colours denote different types of rainbows: yellow — forward; red — backward. Details of the calculations are given in 3.4.

Figure 4.40: Rainbow scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 1.0$. Figures (a–c) show results for $F = 1.0$ while (d–f) show $F = 3.0$. Figures (a) and (d) are of $\{b_r^{(AC)}\}$ vs. Ω , (b) and (e) $\{\chi_r^{(AC)}\}$ vs. Ω (π -radians), while (c) and (f) show $\{\chi_r^{(AC)''}\}$ vs. Ω ($\pi \times 10^4$ -radians). In all figures colours denote different types of rainbows: yellow — forward; red — backward. Details of the calculations are given in 3.4.

Figure 4.41: Rainbow scattering for $U^{(AC)}$ of HeAr with $F \in \{1.0, 3.0\}$ and $K = 0.1$. Figures (a–c) show results for $F = 1.0$ while (d–f) show $F = 3.0$. Figures (a) and (d) are of $\{b_r^{(AC)}\}$ vs. Ω , (b) and (e) $\{\chi_r^{(AC)}\}$ vs. Ω (π -radians), while (c) and (f) show $\{\chi_r^{(AC)'''}\}$ vs. Ω ($\pi \times 10^4$ -radians). In all figures colours denote different types of rainbows: yellow — forward; red — backward. Details of the calculations are given in 3.4.

However, the actual appearance in the differential cross section will be a superposition of rainbows, one for each ϕ_c , over the range of covered by $\chi_r^{(AC)}$; this will have the net effect of broadening the rainbow region and is a clear signature of laser-induced effects. In figure 4.33(a), $n = 0$ glories at $\Omega = 2.0$ were observed, indicating the presence of barrier scattering at very large impact parameters. No corresponding forward rainbows are observed with large $b_r^{(AC)}$ in figure 4.39(a), indicating that these barrier scattering rainbows occur at $b_r^{(AC)} > 5$.

At stronger fields, e.g. figure 4.39(d), the isotropic rainbow is still independent of Ω and $b_r^{(AC)} \approx b_r^{(HFL)}$ (cf. results of figure 4.37(a)) as is expected for such features. Additional forward rainbows are observed at $\Omega \in \{2.0, 4.0\}$ with corresponding $\chi_r^{(AC)} > 0$ and $\chi_r^{(AC)''} < 0$ in figures 4.39(e) and (f), respectively. These are signatures of the barrier scattering noted for the case of $w \sim 1$ which also give rise to the $n = 0$ glories in figure 4.33(b) at large impact parameters. The rainbow parameters of these features show using (2.69) that they have large intensity factors. Note that some backwards rainbows are seen in figure 4.39(d) (red data) at large impact parameters but examination of the corresponding deflection function shows that they are artefacts of the spline used in the identification of the extrema of $\chi^{(AC)}$ ⁹.

As the system makes the transition from high- to mid- K , new dynamical regimes are entered at small and mid-range impact parameters which give rise to additional collision mechanisms. Figure 4.40 shows rainbow parameters for $K = 1.0$. The perturbative rainbows correlating with the field free case are seen in both $F \in \{1.0, 3.0\}$ (figure 4.40(a) and (d), respectively) to be at $b_r^{(AC)} \approx b_r^{(HFL)}$ (1.5 and 1.6 from figure 4.37(a)), being forward

⁹ This is to say the the oscillations in the deflection function data points are smaller than the significant figures obtained in section 3.2. Splining such data leads to exaggeration of the oscillations, causing extrema in $\chi(b)$ at large b that are unphysical and do not demonstrate barrier scattering. This is also demonstrated by the lack of $n = 0$ glories in figure 4.33.

or backward depending on $\chi^{(\text{AC})} \lesseqgtr -\pi$, respectively; this is confirmed in figures 4.40(b) and (e) where many $\chi_r^{(\text{AC})}$ are clustered about $-\pi$. Multi-orbital scattering induces rainbows in mid-range b (compare glory structure of figure 4.34) where $\chi_r^{(\text{AC})} \in [-\pi, 0]$ for this K , also confirmed by figures 4.40(b) and (e). The multi-orbital scattering rainbows may be both forward and backward types, depending on the detailed behaviour of $\chi^{(\text{AC})}$ in the mid-range impact parameter region. Pendular scattering has been shown to give rise to forward/backward rainbows at small b , with $\chi_r^{(\text{AC})} \sim \pi$ and curvatures $\chi_r^{(\text{AC})''}$ which are large due to the rapid oscillations in $\chi^{(\text{AC})}$ as b is varied. The signatures of this mechanism are confirmed in the $w \sim 1$ region of $F = 1.0$ and the $w \gtrsim 1$ regions of $F = 3.0$, in keeping with the idea that large anisotropic potential features and amplitudes have an effect which is important even when $w \gg 1$. The intensity factors of the pendular scattering rainbows are small due to their large $|\chi_r^{(\text{AC})''}|$, indicating that pendular scattering will be observed in the differential cross section as a dense set of narrow forward and backward rainbows in the region of $\Theta \sim \pi$.

A number of rainbows of both forward and backward types occur at large impact parameters in both figure 4.40(a) and (d). Examination of the deflection functions show that these are again numerical artefacts associated with the method of determining rainbow extrema (see footnote, page 196). This is also indicated by examination of the glories in figures 4.34(a) and (b) where no corresponding $n = 0$ glories exist at large impact parameters which would indicate the presence of barrier scattering.

The data in figure 4.41 show the rainbow parameters for $K = 0.1$. For $F = 1.0$ (figures (a)–(c)), the number of small- and mid-range impact parameter rainbows appears to be independent of Ω . In contrast, the large impact parameter rainbows do not emerge until $\Omega \gtrsim 6$; these rainbows are not physically relevant since they are the result of poor

spline interpolation of $\chi^{(\text{AC})}(b)$ (see footnote, page 196). Multi-orbital scattering does result in rainbows at mid-range b (figure 4.41(a)) and these correspond to the rainbows at $\chi_r^{(\text{AC})} \in [-\pi, 0]$ in figure 4.41(b). The multi-orbital scattering rainbows do not appear to be affected by Ω as a group although individual features are. For strong fields, shown in figures 4.41(d)–(f), the multi-orbital scattering rainbows disappear; this is not evident from figure 4.41(d) but comparison with figure 4.35(b) shows that the $b_r^{(\text{AC})}$ are surrounded by $n = +1$ $b_g^{(\text{AC})}$ and hence do not arise from multi-orbital scattering (see also figure 4.29). Pendular and reflex scattering are also observed at small b for both field strengths. Reflex scattering does not necessarily give rise to a rainbow but pendular scattering must. Thus, the large number of forward and backward rainbows observed in figure 4.41(a) and (d) at $b_r^{(\text{AC})} \lesssim 2$ and 3, respectively, correspond to the $\chi_r^{(\text{AC})} \sim \pi$ in figures 4.41(b) and (e). As in the mid- K results, these rainbows are narrow and correspond to the large $|\chi_r^{(\text{AC})}'''|$ seen in figures 4.41(c) and (f). Finally, a large number of forward rainbows emerge at $F = 3.0$ for $\Omega > 2.0$ at large impact parameters; these are related to the large number of $n = 0$ glories seen in figure 4.35(b) and are due to barrier scattering, giving rise to rainbows with $\chi_r^{(\text{AC})} \gtrsim 0$. There are also a number of forward rainbows in the same region of b which correspond to local minima in $\chi^{(\text{AC})}$; however, the majority of these are spline-artefacts and are unphysical. The overall behaviour of the rainbows is independent of Ω due to the fact that they span the range of b and χ with high density; thus it is difficult to follow individual mechanism signatures over a range of Ω .

Tests of the impulse approximation and its ability to reproduce the rainbow parameters in the limit of high collision energy are shown in figure 4.42 for $K = 10$ and $F = 3.0$. Results are obtained from the exact data (numerical extrema of $\chi^{(\text{AC})}$) for He₂ (black) and HeAr (red). Calculations using $\chi_{\text{IA}}^{(\text{AC})}$ for He₂ (blue) and HeAr (maroon) are also shown.

Figure 4.42: Models of rainbow scattering for $U^{(AC)}$ of HeAr and He₂ with $F = 3.0$ and $K = 10$. Figure (a) shows $\{\langle b_r^{(AC)} \rangle_{\phi_c}\}$ vs. Ω ; figures (b) and (c) show the corresponding values of $\{\langle \chi_r^{(AC)} \rangle_{\phi_c}\}$ and $\{\langle \chi_r^{(AC)''} \rangle_{\phi_c}\}$ (π -radians) vs. Ω , respectively. Error bars shown are $\sigma_{\text{RMS}, b_r^{(AC)}}$, $\sigma_{\text{RMS}, \chi_r^{(AC)}}$ and $\sigma_{\text{RMS}, \chi_r^{(AC)''}}$ in (a)–(c), respectively. In all figures: black data — He₂, numerical extrema of $\chi^{(AC)}$; red data — HeAr, numerical extrema of $\chi^{(AC)}$ (cf. figure 4.39); blue data — He₂, numerical extrema of $\chi_{IA}^{(AC)}$ (equation (2.104)); maroon data — HeAr, numerical extrema of $\chi_{IA}^{(AC)}$. Details of the calculations are given in 3.4.

Figures 4.42(a), (b) and (c) give results for $\langle b_r^{(AC)} \rangle_{\phi_c} \pm \sigma_{\text{RMS}, b_r^{(AC)}}$, $\langle \chi_r^{(AC)} \rangle_{\phi_c} \pm \sigma_{\text{RMS}, \chi_r^{(AC)}}$ and $\langle \chi_r^{(AC)'''} \rangle_{\phi_c} \pm \sigma_{\text{RMS}, \chi_r^{(AC)'}}$, respectively. The data show the deficiencies of the impulse approximation (2.104) noted previously for the glory parameters. The discrepancies between the model and the exact calculations are due to three factors: the break-down of the impulse approximation at small impact parameters; the approximate treatment of the anisotropic polarisability contribution to $\chi_{\text{IA}}^{(AC)}$ (equation (2.104)(c)) via the steepest descents value of the integral (F.22); the numerical form of the Bessel functions $K_\nu(z)$ (see appendix G) which diverge for small argument. The first of these should be seen as a systematic error for fixed F and K . For the cases where $\langle b_r^{(AC)} \rangle_{\phi_c} \Omega \gg \sqrt{2K}$, the numerical evaluation of the Bessel functions is not an issue and from figure 4.42 it is seen that the Ω -dependence is improved for higher frequencies ($\Omega \gtrsim 10$). Thus the second source of error (the steepest descent approximation) is seen to result in an overestimation of $\langle \chi_r^{(AC)} \rangle_{\phi_c}$ (figure 4.42(b)) and $|\langle \chi_r^{(AC)'''} \rangle_{\phi_c}|$ (figure 4.42(c)). For lower frequencies, the results show that the divergence of the numerical evaluation of $\chi_{\text{IA}}^{(AC)}$ results in over-sensitivity to Ω in $\langle \chi_r^{(AC)} \rangle_{\phi_c}$ and $\langle \chi_r^{(AC)'''} \rangle_{\phi_c}$. The model value of $\langle b_r^{(AC)} \rangle_{\phi_c}$ is not dependent on Ω to a great extent; this is due to the fact that the dominant contribution to $\chi_{\text{IA}}^{(AC)}$ is that of $\chi_{\text{IA}}^{(\text{HFL})}$, which is independent of Ω . This also explains the fact that the impulse approximation calculations obtain the correct order of magnitude for the rainbow parameters.

4.3.3 Orbital Scattering

The phenomenon of orbital scattering is a significant feature in the deflection function of the system. Classically, this does not represent a strong feature of the differential cross section since the contribution is shown to be an exponentially decaying term in equation

(2.76)¹⁰. The observables of orbiting are the impact parameter $b_{orb,(\pm)}$ and collision energy threshold $K_{orb,(\pm)}$ defined in section 2.4.3.4; estimate of these parameters are given by the isotropic model of section 2.5.3.3. In particular, the orbiting threshold $K_{orb,(\pm)}$ defines the boundary between perturbative and non-perturbative dynamical regimes. Multi-orbital scattering is, by definition the only collision mechanism which gives rise to orbiting. Since this mechanism is very sensitive to the potential features Δ_e and $\Delta_{\theta,-}$, measurement of $\{b_{orb,(\pm)}, K_{orb,(\pm)}\}$ can lead to information on the potential.

4.3.3.1 High Carrier Frequency

For $U^{(HFL)}$ the parameters which characterise orbiting are $\{b_{orb,(\pm)}^{(HFL)}\}$ and $K_{orb,(\pm)}^{(HFL)}$ as defined in section 2.4.3.4, there being little Ω -dependence. In the isotropic potential regime, where $|U_{iso}^{(HFL)}| \gtrsim K \gg |U_{aniso}^{(HFL)}|$, the isotropic model of (2.126) and (2.127) can be used to approximate the values of $b_{orb,(-)}^{(HFL)}$ and $K_{orb,(-)}^{(HFL)}$, respectively. This regime exists for weak fields, low collision energies and small- to mid-range impact parameters.

The orbital scattering impact parameters $\{b_{orb,(\pm)}^{(HFL)}\}$ are shown in figure 4.43 for HeAr, $K = 0.1$ and $\Omega = \Omega_{CO_2}$ as a function of F . The isotropic orbiting singularity is shown as the negative orbiting singularity (open circles in the figure) which correlates to the $F = 0.0$ limit. The isotropic $b_{orb,(-)}^{(HFL)}$ is not continuous with F : this is most likely due to the imperfections in the numerical method for identifying orbiting singularities and not due to any physical effect (see section 3.4 for details). Until values of F are attained where $\Delta_{\theta,-}^{(HFL)} > \Delta_e^{(HFL)}$, i.e. where no there is minimum along $\theta = \pi/2$, trajectories can pass over the metastable point and orbit about the scattering centre. For larger fields, the isotropic

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¹⁰However, in quantum mechanical cross sections, orbiting is seen as a singularity in the integrated cross section due to bound state resonances; thus analysis of the phenomenon is important for more comprehensive studies of the laser-molecule system.

Figure 4.43: Orbital scattering for $U^{(HFL)}$ of HeAr with $\Omega = \Omega_{CO_2}$ and $K = 0.1$. Open circles show $\{b_{orb,(-)}^{(HFL)}\}$ vs. F ; filled circles correspond to $b_{orb,(+)}^{(HFL)}$ orbiting impact parameters. Details of the calculations are given in 3.4.

orbiting singularity may therefore disappear.

The multi-orbiting region of mid-range impact parameters is seen in figure 4.43 to emerge at $F \gtrsim 1.0$. The bifurcation structure seen is consistent with the observed rainbows in this region (section 4.3.2.1). There are multiple bifurcation points seen in the figure; this is an indication that increased $|U_{\text{aniso}}^{(\text{HFL})}|$, as measured by $\Delta_{\theta,-}^{(\text{HFL})}$, allows the creation of larger radial barriers which induce the necessary turning points, hence trajectories with higher $P_{\theta,i}$ (or b) can lead to orbiting.

At very high fields ($F \gtrsim 2.7$), positive orbiting occurs ($b_{\text{orb},(+)}^{(\text{HFL})}$ are shown by the filled circles in figure 4.43). The feature shows that while $\Delta_{\theta,-}^{(\text{HFL})} < \Delta_e^{(\text{HFL})}$ for these fields, some trajectories are deflected through an angular turning point. Thus, positive orbiting can occur when $\Delta_e^{(\text{HFL})} \approx \Delta_{\theta,-}^{(\text{HFL})}$ (cf. results of figure 4.5). As in the case of the multi-orbital $\{b_{\text{orb},(-)}^{(\text{HFL})}\}$, there are bifurcation structures associated with $\{b_{\text{orb},(+)}^{(\text{HFL})}\}$. Note that positive orbiting first appears at the value of F where the reflex rainbow scattering singularity disappears (see section 4.3.2.1 and figure 4.37). This is consistent with the dynamical origin of both features and shows that even though there is no global mutual exclusion of rainbow and orbital scattering for $F \neq 0$, there may be some such rule for a given feature: i.e. any given rainbow extremum will transform to an orbiting singularity in a continuous fashion as F is increased and vice versa.

The degree of dominance of $\Delta_e^{(\text{HFL})}$ over $\Delta_{\theta,-}^{(\text{HFL})}$ can be assessed from the results of figure 4.44. Shown in the figure are the $\{b_{\text{orb},(-)}^{(\text{HFL})}\}$ vs. F for both HeAr (red circles) and He₂ (black circles). Also shown are the values of $b_{\text{orb},(-)}^{(\text{HFL})}$ predicted from the isotropic model (2.126) as a function of F (solid lines in figure 4.44). It should be first noted that no significant difference is observed between HeAr and He₂; this is in keeping with the observations of other properties of $\chi^{(\text{HFL})}$ but the present results confirm that the similarity

Figure 4.44: Orbital scattering for $U^{(HFL)}$ of HeAr and He₂ with $\Omega = \Omega_{CO_2}$ and $K = 0.1$. In all data, black denotes He₂ results while red denotes HeAr. Circles show $\{b_{orb,(-)}^{(HFL)}\}$ vs. F determined from numerical analysis of $\chi^{(HFL)}$. Lines show results of the isotropic model of (2.126). Details of the calculations are given in 3.4.

of the dynamics persists in the limit of low K . The isotropic model of (2.126) predicts the existence and position of only one orbiting singularity. The model is exact for $F = 0.0$ and agreement with the numerical results for $F \lesssim 0.5$ is acceptable; from figure 4.5, $\Delta_e^{(\text{HFL})} \approx 1.04$ and $\Delta_{\theta,-}^{(\text{HFL})} \approx 0.05$ at this field. Since the isotropic model includes only trace polarisability terms which have a relatively small effect, it is expected that the model and numerical results should diverge for larger values of F . However, the model is qualitatively correct in predicting the field dependence of the isotropic orbiting singularity over the entire range of F examined.

The threshold collisional energy $K_{orb,(\pm)}^{(\text{HFL})}$ is also related to the well depth of the system. The isotropic model of (2.127) predicts that $K_{orb,(-)}^{(\text{HFL})}$ should increase with F as the potential well is deepened. Figure 4.45 shows $\{K_{orb,(\pm)}^{(\text{HFL})}\}$ for both He_2 (black data) and HeAr (red data) for $\Omega = \Omega_{\text{CO}_2}$ as a function of F . The dashed lines (inset of the figure) show $K_{orb,(+)}^{(\text{HFL})}$ while solid lines show $K_{orb,(-)}^{(\text{HFL})}$ determined numerically from trajectory calculations. The predictions of $K_{orb,(-)}^{(\text{HFL})}$ by the isotropic model of (2.127) are shown by dotted lines. As observed for $\{b_{orb,(\pm)}^{(\text{HFL})}\}$, no difference is discernible between HeAr and He_2 . The numerical data for $K_{orb,(-)}^{(\text{HFL})}$ shows a systematic error in the method used to determine the threshold. The exact value of $K_{orb,(-)}^{(\text{HFL})} = 0.8$ for the $F = 0.0$ limit is not obtained (cf. the dotted and solid lines in the figure). The oscillations in the numerical $K_{orb,(-)}^{(\text{HFL})}$ are also indicative of the imperfections of the method (see section 3.4 for details) since it is more likely that the threshold is a smooth function of F .

The oscillations of figure 4.45 notwithstanding, the qualitative trend in $K_{orb,(-)}^{(\text{HFL})}$ is evident: after an initial increase, there is a decrease in the orbiting collisional energy threshold to below its field-free value. Such behaviour has not been anticipated but can be understood in terms of multi-orbital scattering (see section 4.2.1.3). As the field is increased,

Figure 4.45: Orbital scattering thresholds $K_{orb,(\pm)}^{(HFL)}$ vs. F of HeAr and He₂ with $\Omega = \Omega_{CO_2}$. In all data, red denotes HeAr results while black denotes He₂. Solid lines show $\{K_{orb,(-)}^{(HFL)}\}$ vs. F determined from numerical analysis of $\chi^{(HFL)}$. Dashed lines (inset) show similar calculation results for $K_{orb,(+)}^{(HFL)}$. The results of the isotropic model of (2.127) (for $K_{orb,(-)}^{(HFL)}$ only) are shown as dotted lines. All numerical thresholds shown are known to within ± 0.001 in reduced units of K . Details of the calculations are given in section 3.4.

both $\Delta_e^{(\text{HFL})}$ and $K_{orb,(\pm)}^{(\text{HFL})}$ increase in an approximately isotropic potential. However, $\Delta_{\theta,-}^{(\text{HFL})}$ also increases and this causes $b_{orb,(\pm)}^{(\text{HFL})}$ to increase (generally) beyond what is required by an isotropic model; higher angular momentum at the outer radial turning point which follows circumvention of the rotational well (or barrier) implies that K must be reduced for P_X to remain below the critical level required for trapping. These two competing trends prevent $K_{orb,(-)}^{(\text{HFL})}$ from having a monotonic behaviour and it follows that after the potential leaves the isotropic regime of weak fields, $K_{orb,(-)}^{(\text{HFL})}$ should decrease as $\Delta_e^{(\text{HFL})} \sim \Delta_{\theta,-}^{(\text{HFL})}$.

In contrast to $K_{orb,(-)}^{(\text{HFL})}$, the threshold $K_{orb,(+)}^{(\text{HFL})}$ is a monotonically increasing function of F (inset of figure 4.45, dashed lines). No orbiting of this type is observed for $F \leq 2.66 \pm 0.01$ for HeAr (2.71 ± 0.01 for He₂). The thresholds found are very low, $K_{orb,(+)}^{(\text{HFL})} \sim 0.1$ for all F where it exists. It is not known if the apparently linear increase with F persists for higher fields but this initial behaviour correlates well with both $\Delta_{\theta,-}^{(\text{HFL})}$ and $\Delta_{\theta,+}^{(\text{HFL})}$.

The isotropic model was shown to approximate $b_{orb,(-)}^{(\text{HFL})}$ up to ca. $F = 0.5$ (figure 4.44). The concomitant results of the model for $K_{orb,(-)}^{(\text{HFL})}$ are shown in figure 4.45 as dotted lines. Equation (2.127) is exact for $F = 0.0$ and shows a quartic dependence on F . Once the difference between the field-free values is accounted for, the model compares well with the numerical results for both HeAr and He₂ provided $F \lesssim 0.5$. At this point, the anisotropy has an effect on $K_{orb,(-)}^{(\text{HFL})}$ which causes it to increase at a smaller rate. The maximum in $K_{orb,(-)}^{(\text{HFL})} \approx 0.828 \pm 0.001$ occurs at $F \approx 1.89$ while the minimum threshold at $F = 3.0$ is $K_{orb,(-)}^{(\text{HFL})} \approx 0.803 \pm 0.001$.

4.3.3.2 Low-to-Medium Carrier Frequency

For low-to-medium carrier frequencies, the orbiting parameters examined are $\{b_{orb,(\pm)}^{(\text{AC})}\}$ and $K_{orb,(\pm)}^{(\text{AC})}$. As seen in section 4.3.1.2 and 4.3.2.2, the impact parameter ranges observed

orbiting in $U^{(AC)}$ are defined by $\langle U^{(AC)} \rangle_{\phi_c}$ and require minimally the isotropic potential regime. However, as with other effects in $U^{(AC)}$, the details will be sensitive to the amplitude regime and w . From the analysis of $U^{(AC)}$ glories and rainbows, pendular scattering occurs at large F in the same region of b where orbiting of $\langle U^{(AC)} \rangle_{\phi_c}$ occurs. Thus orbiting is expected to be less common in $U^{(AC)}$ at strong fields due to the competition between the two collision mechanisms.

Figure 4.46 shows $\{b_{orb,(\pm)}^{(AC)}\}$ as a function of Ω for HeAr at $K \in \{0.1, 1.0\}$ and $F \in \{1.0, 3.0\}$. Figure 4.46(a) shows results for $F = 1.0$ and (b) correspondingly shows $F = 3.0$. In both figures, blue data denotes $\{b_{orb,(-)}^{(AC)}\}$ of $K = 0.1$; cyan — $\{b_{orb,(+)}^{(AC)}\}$ of $K = 0.1$; red — $\{b_{orb,(-)}^{(AC)}\}$ of $K = 1.0$; magenta — $\{b_{orb,(+)}^{(AC)}\}$ of $K = 1.0$. Details of the calculations are to be found in section 3.4.

For $F = 1.0$, the mid- K results (red data in figure 4.46(a)) show no orbiting except at $\Omega = 2.0$; while $U^{(HFL)}$ does not permit orbiting at this K , $U^{(AC)}$ is in the coupled amplitude regime and hence the amplitudes are sufficiently large that the restrictions of the potential regime can be overcome for some trajectories. For $K = 0.1$, $\{b_{orb,(\pm)}^{(AC)}\}$ are dense in the region of $1.0 \lesssim b \lesssim 2.5$ for all Ω . Here $w \gg 1$ for all Ω in the mid- b region but both the potential and amplitudes are in the coupled regimes. As a result the motion of the system is sensitive to the details of the potential over the whole laser cycle. There does not appear to be any convergence to the high frequency limit at this K . Note that the $\{b_{orb,(+)}^{(AC)}\}$ occur at smaller impact parameters on the boundary of the pendular scattering region, in agreement with the $\chi^{(AC)}(b, \phi_c)$ of figure 4.29.

When the field is increased to $F = 3.0$ (in figure 4.46(b)), orbiting is still not observed for $K = 1.0$ in $\chi^{(HFL)}$. In the case of $U^{(AC)}$, both positive and negative orbiting is seen for $\Omega \lesssim 10.0$. As in the weak field case, $\{b_{orb,(+)}^{(AC)}\}$ occurs in the pendular scattering region

Figure 4.46: Orbital scattering for $U^{(AC)}$ of HeAr with $F = 3.0$ and $K \in \{0.1, 1.0\}$. Data sets are coloured according to: blue — $K = 0.1$, $b_{orb,(-)}^{(AC)}$; cyan — $K = 0.1$, $b_{orb,(+)}^{(AC)}$; red — $K = 1.0$, $b_{orb,(-)}^{(AC)}$; magenta — $K = 1.0$, $b_{orb,(+)}^{(AC)}$. Figure (a) — $F = 1.0$; figure (b) — $F = 3.0$. Details of the calculations are given in 3.4.

while $\{b_{orb,(-)}^{(AC)}\}$ tend to be in the mid- b range. The disappearance of orbiting occurs when $w \gg 1$, implying some convergence to the high frequency limit. For $K = 0.1$ (blue and cyan data in figure 4.46(b)), both positive and negative orbiting are present in the high frequency limit. For low frequencies the pendular scattering region is seen to contain more $b_{orb,(+)}^{(AC)}$ than at high frequencies. The range covered by $\{b_{orb,(\pm)}^{(AC)}\}$ is $0 \lesssim b \lesssim 2.5$ for $\Omega \lesssim 4.0$ and $1.0 \lesssim b \lesssim 2.5$ for $\Omega \gtrsim 4.0$. Note that $\{b_{orb,(-)}^{(AC)}\}$ is particularly sparse in this region, implying that the mechanism for inducing angular turning points is efficient.

The threshold collisional energy surfaces $K_{orb,(\pm)}^{(AC)}(F, \Omega)$ are shown in figure 4.47. Results for both HeAr (figures (a) and (b)) and He₂ (figures (c) and (d)) are given to within ± 0.001 reduced units of collisional energy. Figures (a) and (c) show $K_{orb,(-)}^{(AC)}$ while (b) and (d) show $K_{orb,(+)}^{(AC)}$ for the two molecular systems. In each figure, the data points calculated are indicated with symbols with the accompanying value of $K_{orb,(\pm)}^{(AC)}$ in red text. The splined contours (black lines) are in increments of 0.1. Further details of the calculations can be found in 3.4. The contours given figure 4.47 are an approximate picture of the true $K_{orb,(\pm)}^{(AC)}(F, \Omega)$ surface since the calculated points are clearly too sparse. As in the results of $K_{orb,(\pm)}^{(HFL)}$, the calculation methodology for $K_{orb,(\pm)}^{(AC)}$ yields “noisy” data which further distort the contour values and hence only the general features of the orbiting thresholds can be discerned.

For $K_{orb,(-)}^{(AC)}$, the general effect of increasing the field strength appears to be an increase in the threshold when the carrier frequency is low; this is in contrast to the behaviour of $K_{orb,(-)}^{(HFL)}$ (see figure 4.45). It follows that there must be a time-dependent effect which permits orbiting in spite of an increased $\Delta_{0,-}^{(AC)}$: the node in the laser cycle causes the barrier to disappear (i.e. there is no field effect) which creates a “window” through which the trajectory can pass to the anti-parallel potential well. The removal of $\Delta_{0,-}^{(AC)}$ via this mecha-

Figure 4.47: Orbital scattering thresholds $K_{orb,(\pm)}^{(AC)}$ of HeAr and He₂ as a function of F and Ω . Threshold energies at points marked by symbols are shown in red text (accurate to ± 0.001 reduced units). The contours shown (black lines) are in increments of 0.1 in K . Contours were generated from cubic splines. Figure (a) shows $K_{orb,(-)}^{(AC)}$ for HeAr; (b) — $K_{orb,(+)}^{(AC)}$, HeAr; (c) — $K_{orb,(-)}^{(AC)}$, He₂; (d) — $K_{orb,(+)}^{(AC)}$, He₂. Details of the calculations are given in 3.4.

nism is necessarily sensitive to ϕ_c , Ω and K since this determines if the trajectory can pass over the barrier during this portion of the laser cycle. Thus, the maximum of $K_{orb,(-)}^{(AC)}$ in figures 4.47(a) and (c) near $\Omega = 2$ is seen to meet these criteria since both static- and high-frequency fields yield static $\Delta_{\theta,-}$. The value of $K_{orb,(-)}^{(AC)}$ at the maximum increases with F . This is consistent with an isotropic model but, as in the case of $K_{orb,(-)}^{(HFL)}$, the anisotropic should induce a decrease in $K_{orb,(-)}^{(AC)}$. However, as $\Delta_{\theta,-}^{(AC)} = 0$ for part of the laser cycle, it is possible for a trajectory to orbit by this mechanism even for a large F ; this is all that is required to increase $K_{orb,(-)}^{(AC)}$ since it is a threshold property. The result is a large increase in $K_{orb,(-)}^{(AC)}$ up to ca. 2.3, far above the field-free threshold of 0.8. Both HeAr and He₂ have a maximum near $\Omega = 2$. However, the behaviour of the surface of $K_{orb,(-)}^{(AC)}$ at higher frequencies distinguishes between the two systems in that the convergence to the high-frequency limit for HeAr is more gradual than He₂.

The results of $K_{orb,(+)}^{(AC)}(F, \Omega)$ are shown in figures 4.47(b) and (d) for HeAr and He₂, respectively. As in $K_{orb,(-)}^{(AC)}$, both molecular systems exhibit a maximum near $\Omega = 2$; this is due to the oscillating barrier mechanism above having the same effect on positive orbiting. The threshold maximum is much larger than the field free result of zero (no orbiting possible), approximately 2.2 for HeAr and 1.2 for He₂. Convergence to the high-frequency limit thresholds occurs at lower Ω for He₂ than for HeAr due to the effective 2Ω -time dependence of the latter system. In general, $K_{orb,(+)}^{(AC)}$ is a monotonically increasing function of F at any frequency; this is due to the necessity of the presence of a barrier to rotation in order for positive orbital scattering to occur (i.e. by an initial angular turning point).

4.4 Differential and Integrated Cross Sections

The differential cross sections $d\sigma^{(\text{HFL})}/d\Omega$ and $d\sigma^{(\text{AC})}/d\Omega$ are the principal observables in a crossed molecular beam experiment as discussed in section 2.4. These provide information on the scattering intensity as a function of observed scattering angle. For both $U^{(\text{HFL})}$ and $U^{(\text{AC})}$ these cross sections can be evaluated and information regarding the dynamics can be extracted. The integrated cross sections of the two potentials $\sigma^{(\text{HFL})}$ and $\sigma^{(\text{AC})}$, respectively, also contain dynamical information, though of a less detailed nature. The studies of sections 4.2 and 4.3 are now used in that the behaviour of the special features of the deflection function give rise to signatures in both cross sections, and these have been analysed over a range of F , Ω and K in terms of the dynamical mechanisms encountered in trajectory analysis. It is therefore possible now to make a connection between dynamics (trajectories) and experimental observables (cross sections) for the laser-molecule system.

4.4.1 Differential Cross Sections

The features of $d\sigma^{(\text{HFL})}/d\Omega$ and $d\sigma^{(\text{AC})}/d\Omega$ which are most often used in the analysis of dynamics are those of small angle-, glory-, rainbow- and orbital scattering; their contributions to the differential cross section are discussed in section 2.4.3. The analysis of section 4.3 showed that each type of collision mechanism has distinct signatures in the differential cross section. Note that the calculation of $d\sigma^{(\text{AC})}/d\Omega$ and $\sigma^{(\text{AC})}$ imply an averaging over ϕ_c ; thus the results of section 2.4.3 must be averaged in order to obtain the form applicable to the $U^{(\text{AC})}$ observables.

4.4.1.1 High Carrier Frequency

The behaviour of $d\sigma^{(\text{HFL})}/d\Omega$ in the perturbative potential regime is exemplified in figure 4.48 where sample differential cross sections are shown as functions of scattering angle for HeAr, $\Omega = \Omega_{\text{CO}_2}$, and $K = 10$. The field strengths used correspond to the deflection functions $\chi^{(\text{HFL})}$ shown in figure 4.8. Details of the cross section calculations are given in section 3.5. As shown in section 4.2.1.1, the laser field induces only a small response in the dynamics. Hence the $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ vs. Θ shown are all very similar to the $F = 0.0$ result (black line in the figure). The long-range part of $\chi^{(\text{HFL})}$ results in the singularity as Θ approaches zero. The steepness of the singularity does not appear to be affected by variation in F as is anticipated from the impulse approximation formulae (2.98) (see also (2.63)); the equations show that the strongest part of the field-induced interaction, that of the leading term in the DID-polarisability anisotropy, has no effect on the deflection function. Results of section 4.3.2.1 (figure 4.37) show that the rainbow parameters are comparatively insensitive to the field and hence the singularity noted at $\Theta \approx 0.06\pi$ is unchanged in both position and width for fields up to $F = 3.0$ (green line in figure). It should be noted that the rainbow singularity does not appear as an infinite singularity due to the finite resolution in Θ for calculations of $d\sigma^{(\text{HFL})}/d\Omega$. The isotropic rainbow is shown to be a forward rainbow as predicted by equation (2.69).

The small field effect observed in the $d\sigma^{(\text{HFL})}/d\Omega$ shown in figure 4.48 for $\Theta < \Theta_r^{(\text{HFL})}$ is consistent with the dynamics perturbed by the presence of $U^{(\text{HFL})}$ at high- K . From section 4.2.1.1, increasing F was shown to increase $\chi^{(\text{HFL})}$ for $b < b_r^{(\text{HFL})}$; this leads to an increase in $b(\Theta)$ and a decrease in $db/d\Theta$ and hence an increase in the cross section for large angles. The effect is demonstrated in the variation of $d\sigma^{(\text{HFL})}/d\Omega$ with F for $\Theta \gtrsim 0.35\pi$ in figure 4.48. The scattering intensity increases monotonically in this region with

Figure 4.48: The differential cross section $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ vs. Θ for $U^{(\text{HFL})}$ of HeAr with $\Omega = \Omega_{\text{CO}_2}$, $K = 10$ and $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$. The scattering angle is shown in units of π -radians. Black line — $F = 0.0$; red — $F = 1.0$; blue — $F = 2.0$; orange — $F = 2.5$; green — $F = 3.0$. Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

F . Between the rainbow angle and 0.35π there is a slight decrease in scattering intensity with F . Therefore $d\sigma^{(\text{HFL})}/d\Omega$ in the large angle scattering region can be used to probe $|U_{\text{aniso}}^{(\text{HFL})}|$, and possibly $\Delta_{\theta,-}^{(\text{HFL})}$, in comparison to K . Note that no backward glory is observed for $U^{(\text{HFL})}$ in the high- K limit and hence $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ falls to zero at $\Theta = \pi$.

Conditions identical to those above were examined in the mid- K regime for HeAr^{11} and are shown in figure 4.49. The corresponding $\chi^{(\text{HFL})}$ are given in figure 4.13. The dynamics are similar to those of the high- K regime (perturbative) as discussed in section 4.2.1.2: the isotropic potential regime dynamics dominate at all impact parameters and F . However as K is lower, a greater field-induced effect is observed. For small angle (large- b) scattering, this is manifested by a visible variation of the slope of the singularity at $\Theta = 0$, monotonically decreasing with F . From equation (2.63) this corresponds to a decrease in the range parameter s , indicating a gradual contribution from the leading term in β to the dynamics. There is a single forward rainbow which is not evident in the figure: this is due to the particular rainbow parameters at $K = 1.0$. The rainbow impact parameter is $b_r^{(\text{HFL})} \sim 1.5$ and $\chi_r^{(\text{HFL})} \sim 20000\pi$, making the singularity very narrow. The $\Theta_r^{(\text{HFL})}$ is ca. π at $F = 0.0$ and shifts to approximately 0.8π for $F = 3.0$ (see figure 4.37). Thus, although the isotropic rainbow is present, by (2.69), it is such a narrow spike that more resolution in Θ is required for it to be unambiguous in $d\sigma^{(\text{HFL})}/d\Omega$. Presently, the rainbow is indirectly evident from the discontinuities of $d\sigma^{(\text{HFL})}/d\Omega$ in the region of $\Theta \gtrsim 0.8\pi$. As in the high- K case, the dynamics of the small impact parameter region are sensitive to F . Consequently, figure 4.49 shows an increase in $d\sigma^{(\text{HFL})}/d\Omega$ with F for $\Theta > 0.5\pi$, implying a correlation with $\Delta_{\theta,-}^{(\text{HFL})}$. Isotropic backward ($n = -1$) glories are observed for this system at all values of F (see figure 4.31). Hence the differential cross sections are observed to approach a finite limit at

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¹¹N.B.: results for He_2 were identical.

Figure 4.49: The differential cross section $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ vs. Θ for $U^{(\text{HFL})}$ of HeAr with $\Omega = \Omega_{\text{CO}_2}$, $K = 1.0$ and $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$. The scattering angle is shown in units of π -radians. Black line — $F = 0.0$; red — $F = 1.0$; blue — $F = 2.0$; orange — $F = 2.5$; green — $F = 3.0$. Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

$$\Theta = \pi.$$

From section 4.2.1.3, the dynamics of low collisional energies were shown to be much more complex since the system is in the coupled potential regime of equation (2.49). The effects of reflex- and multi-orbital scattering were noted in section 4.3. The signatures of the collision mechanisms are shown in figure 4.50; the $d\sigma^{(\text{HFL})}/d\Omega$ vs. Θ are shown for the deflection functions given in figure 4.17 (HeAr, $K = 0.1$, $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$, $\Omega = \Omega_{\text{CO}_2}$). The field-free results (black line in figure 4.50) show the small-angle scattering singularity with a smooth decrease to a finite and equal limit at $\Theta = \pi$. The latter feature is the result of the isotropic orbiting singularity, which has finite contributions at scattering angles of 0 and π radians (see (2.76)). This differential cross section is thus the starting point for examining the changes induced by the laser field.

For weaker fields ($F = 1.0$, red line in figure 4.50), the increased scattering of the large impact parameter part of $\chi^{(\text{HFL})}$ (red line in figure 4.17) causes the decrease in the slope of the small-angle scattering singularity relative to the $F = 0.0$ result. As in the case of mid- and high- K scattering, the presence of the $U_{\text{aniso}}^{(\text{HFL})}$ terms in the potential cause an increase in $d\sigma^{(\text{HFL})}/d\Omega$ at large angles. However, the $F = 1.0$ cross section shows that its limit at $\Theta = \pi$ is much larger than that of $F = 0.0$. At this field strength, figure 4.31 shows that multi-orbital scattering has the effect of introducing two backwards glory singularities which manifest themselves as finite contributions to $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ at $\Theta = \pi$ over and above the contribution from the isotropic orbiting singularity; hence, the differential cross section of $F = 1.0$ is larger than $F = 0.0$ at this angle. Multi-orbiting dynamics also has the effect of inducing two backward rainbow singularities (figure 4.37) near $\Theta \approx 0.80\pi$ and $\Theta \approx 0.96\pi$. These singularities are of moderate intensity ($b_r^{(\text{HFL})} \sim 2$ and $|\chi_r^{(\text{HFL})''}| < 1000\pi$) and therefore show up in $d\sigma^{(\text{HFL})}/d\Omega$ of $F = 1.0$ further increasing the large-angle

Figure 4.50: The differential cross section $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ vs. Θ for $U^{(\text{HFL})}$ of HeAr with $\Omega = \Omega_{\text{CO}_2}$, $K = 0.1$ and $F \in \{0.0, 1.0, 2.0, 2.5, 3.0\}$. The scattering angle is shown in units of π -radians. Black line — $F = 0.0$; red — $F = 1.0$; blue — $F = 2.0$; orange — $F = 2.5$; green — $F = 3.0$. Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

scattering intensity. Thus, even for weak fields, there exist clear signatures of laser-induced dynamics in the system.

For the stronger fields, i.e. $F = 2.0$ and 2.5 , (blue and orange lines in figure 4.50, respectively) the basic structure of the multi-orbiting region of $\chi^{(\text{HFL})}$ is unchanged but shifts to larger impact parameters with F (cf. results of figure 4.17). This results in some complicated behaviour in $d\sigma^{(\text{HFL})}/d\Omega$ characterised by a number of small rainbow singularities at angles of ca. $\pi/2$ radians. The slope of the small-angle singularity is seen to monotonically decrease with F as it has for all other cross sections examined. The most dramatic feature which emerges in $d\sigma^{(\text{HFL})}/d\Omega$ for these two field strengths is the rainbow singularity associated with reflex scattering. As shown in section 4.3.2.1, the backward rainbow starts at $\Theta = \pi$ (cf. results of $F = 2.0$) and shifts to smaller angles. The increase in the slope of the rainbow up to $F \approx 2.5$ is due to the increase in $b_r^{(\text{HFL})}$ (see figure 4.37). The presence of the reflex rainbow is a clear signature of $U_{\text{aniso}}^{(\text{HFL})}$ (as characterised by $\Delta_{\theta,-}^{(\text{HFL})}$) since backward rainbows are not the norm.

Finally, the green line in figure 4.50 shows the differential cross section for $F = 3.0$. The dynamical features which differ from those discussed previously are in the large-angle range; a significant increase is observed for $\Theta > \pi/2$ as are a number of backwards rainbow singularities and a large finite value of $\sin\Theta d\sigma^{(\text{HFL})}/d\Omega$ at $\Theta = \pi$. These features are caused by the change in the basic structure of the multi-orbiting region of $\chi^{(\text{HFL})}$ (figure 4.17) which now contains a positive anisotropic orbiting singularity in addition to the isotropic orbiting singularity. There are a number of additional backwards glories and two multi-orbiting rainbow structures in $\chi^{(\text{HFL})}$. The origin of the broad hump is due to the large reflex region of $\chi^{(\text{HFL})}$ which terminates at $b_{\text{orb},(+)}^{(\text{HFL})} \approx 2.2^{12}$. The slope of the deflec-

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¹²This is due to the mutual exclusion of orbital and rainbow scattering which apparently exists for a given

tion function in the reflex region is nearly constant and hence $d\sigma^{(\text{HFL})}/d\Omega$ should increase linearly with the impact parameter along this branch of $b(\Theta)$ for large scattering angles, with the smallest contribution at $\Theta = \pi$. The contributions from the positive orbiting singularity and the backward glories lead to a larger contribution at $\Theta = \pi$. The multi-orbiting rainbows are both backwards and near $\Theta = \pi$. Since these features are necessitated (from the continuity of $\chi^{(\text{HFL})}(b)$) by the presence of a positive orbiting singularity, they are strong (but indirect) evidence for a high rotational well.

The high- K regime yielded a number of models for $\chi^{(\text{HFL})}$. The resulting differential cross sections for HeAr with $K = 10$, $F = 3.0$ and $\Omega = \Omega_{\text{CO}_2}$ are shown in figure 4.51. The exact results (cf. figure 4.48) are shown by the solid black line in the figure. The numerical $d\sigma^{(\text{HFL})}/d\Omega$ obtained from $\chi_{\text{iso}}^{(\text{HFL})}$ (cf. results of figure 4.10) are shown with the dashed black line. The impulse approximation model results are shown in red: the solid line corresponds to numerical cross sections from $\chi_{\text{IA}}^{(\text{HFL})}$ of (2.98) while the dashed line shows the HDID-IA model of $d\sigma^{(\text{HFL})}/d\Omega$ (2.121). The log-log form of the plot emphasises the differences between the $d\sigma^{(\text{HFL})}/d\Omega$ obtained from $\chi^{(\text{HFL})}$ vs. that of $\chi_{\text{iso}}^{(\text{HFL})}$; only the large-angle scattering is significantly different (i.e. for $K\Theta \gtrsim 10$). The position and intensity of the rainbow are reproduced well by $\chi_{\text{iso}}^{(\text{HFL})}$, quantitatively reinforcing the conclusion that the rainbow is isotropic in origin. All three approximate calculations appear to essentially reproduce the correct slope for the small-angle singularity which implies that the impulse approximation is valid for $K\Theta \lesssim 0.5$. Of the two impulse approximation models, the numerical calculation of $d\sigma^{(\text{HFL})}/d\Omega$ using $\chi_{\text{IA}}^{(\text{HFL})}$ of (2.98) is the least accurate. The position of the rainbow angle is underestimated by a small amount; from section 4.3.2.1, it is known that this discrepancy increases with F due to the inaccuracies of the short-range exchange

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feature, though not globally as in $U_{\text{iso}}^{(\text{HFL})}$.

Figure 4.51: A log-log plot of $\Theta \sin \Theta d\sigma^{(HFL)} / d\Omega$ vs. $K\Theta$ of HeAr with $\Omega = \Omega_{CO_2}$, $K = 10$ and $F = 3.0$ using different approximate models. Cross sections derived from different approximations to the deflection function are shown as: solid black line — exact $\chi^{(HFL)}$ (cf. with figure 4.48); dashed black line — exact $\chi_{iso}^{(HFL)}$ (equation (2.32)); solid red line — numerical cross sections from $\chi_{IA}^{(HFL)}$ (2.98); dashed red line — HDID-IA model (2.121). Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

terms. The slope of the rainbow is reproduced well by both approximate calculations while in contrast, neither yield accurate results for large-angle scattering. This last discrepancy is to be expected from the invalidity of the impulse approximation at small impact parameters. Overall, the HDID-IA model (dashed red line) yields very good agreement with the exact calculation in spite of the fact that it is a less refined approximation than (2.98).

4.4.1.2 Low-to-Medium Carrier Frequency

From section 4.2.2.1, it was demonstrated that the dynamics of $U^{(AC)}$ in the limit of high collision energy were perturbative and indeed exhibited static-field behaviour for most values of Ω such that $w \ll 1$. The effects of this kind of dynamics on $d\sigma^{(AC)}/d\Omega$ can be seen in figure 4.52 which shows $\sin\Theta d\sigma^{(AC)}/d\Omega$ vs. Θ for HeAr with $K = 10$. Figure 4.52(a) shows results for $F = 1.0$ while those of $F = 3.0$ are shown in figure (b). In both, the black line corresponds to $\Omega = 2$; red line, $\Omega = 8$; blue line, $\Omega = 18$ and the green line shows $d\sigma^{(HFL)}/d\Omega$, labelled $\Omega = \Omega_{CO_2}$ (cf. figure 4.48). From the figure, it is clear that the only significant deviation from the high-frequency limit cross section occurs in the rainbow region for either field. That for small- and large-angle scattering $d\sigma^{(AC)}/d\Omega \approx d\sigma^{(HFL)}/d\Omega$ is easily anticipated from the result of $\langle \chi^{(AC)} \rangle_{\phi_c} \approx \chi^{(HFL)}$ shown in section 4.2.2.1; the smooth behaviour of $\chi^{(AC)}$ with ϕ_c implies that the cross section for each phase is smoothly varying with ϕ_c and hence their average will compare well with $d\sigma^{(HFL)}/d\Omega$. The smooth ϕ_c dependence of $\chi^{(AC)}$ in this regime has a different effect near the rainbow region: each ϕ_c has a rainbow singularity near $\chi_r^{(HFL)}$ and consequently there is a range of Θ where rainbow singularities occur. The boundaries of the region are given by the bright side of the rainbow for which $\Theta_r^{(AC)}(\phi_c)$ is smallest and the dark side of the rainbow for which it is largest. Within these boundaries $d\sigma^{(AC)}/d\Omega$ is infinite. Thus the rainbow for $U^{(AC)}$

Figure 4.52: The differential cross section $\sin\Theta d\sigma^{(AC)}/d\Omega$ vs. Θ of HeAr with $\epsilon \in \{2, 10, 18, \Omega_{\text{CO}_2}\}$, $K = 10$ and $F \in \{1.0, 3.0\}$. The scattering angle is shown in units of π -radians. Figure (a) shows results for $F = 1.0$ while (b) shows those of $F = 3.0$. In both figures: black line — $\Omega = 2$; red — $\Omega = 10$; blue — $\Omega = 18$; green — $d\sigma^{(\text{HFL})}/d\Omega$, $\Omega = \Omega_{\text{CO}_2}$ (cf. with figure 4.48). Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

is characterised by an infinity of non-zero width in Θ , in contrast to the $U^{(\text{HFL})}$ situation where the rainbow occurs for a single scattering angle.

The width of the rainbow infinity in the high- K limit of $U^{(\text{AC})}$ is defined by $\{\chi_r^{(\text{AC})}\}$ which in turn depends on F and Ω . In figure 4.52(a), the width of the rainbow is not much larger than that of $U^{(\text{HFL})}$ (green line, denoted $\Omega = \Omega_{\text{CO}_2}$) for $F = 1.0$ at any frequency. It should be noted that the “infinities” of the rainbows occurring at different ϕ_c are in fact finite due to the finite resolution of Θ in the calculation of the differential cross section (see section 3.5). Numerical averaging over ϕ_c also reduces the maximum of the rainbow spike for a given phase. Hence, the presence of multiple rainbows manifests itself in figure 4.52 as a set of irregular peaks¹³. In spite of these numerical difficulties, the behaviour for weak fields is clear: there is very little ϕ_c -dependence on $\chi_r^{(\text{AC})}$ and thus little or no spread in the width of the rainbow region. For $F = 3.0$, shown in figure 4.52(b), the width of the rainbow region is noticeably larger with a maximum for $\Omega = 10.0$ (red line in figure). These results are consistent with the system being in the static-field limit, and hence insensitive to ϕ_c , for low Ω ($w \ll 1$) while for larger Ω , convergence to the high frequency limit ($w \gg 1$) also requires an insensitivity to ϕ_c . When the frequency is such that $w \sim 1$, which occurs at $\Omega = 10.0$ in the mid- b range, the larger variation of $\chi_r^{(\text{AC})}$ with ϕ_c is observed (cf. results of figure 4.39).

Similar effect to those described for high- K are expected to be seen for mid-range collision energies. An analogous plot of the differential cross sections for HeAr with $K = 1.0$ are given in figure 4.53. The figure shows values of F and Ω identical to those used in figure 4.52. The cross sections of $F = 1.0$ (figure 4.53(a)) are independent of Ω for $\Theta \lesssim 0.3\pi$. In the large-angle scattering region of $d\sigma^{(\text{AC})}/d\Omega$, the presence of the isotropic rainbow

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¹³Increased resolution in the scattering angle sampled does correct this but convergence is slow. The problem is exacerbated for the case of rainbows with small intensity factors.

Figure 4.53: The differential cross section $\sin\Theta d\sigma^{(AC)}/d\Omega$ vs. Θ of HeAr with $\epsilon \in \{2, 10, 18, \Omega_{\text{CO}_2}\}$, $K = 1.0$ and $F \in \{1.0, 3.0\}$. The scattering angle is shown in units of π -radians. Figure (a) shows results for $F = 1.0$ while (b) shows those of $F = 3.0$. In both figures: black line — $\Omega = 2$; red — $\Omega = 10$; blue — $\Omega = 18$; green — $d\sigma^{(\text{HFL})}/d\Omega$, $\Omega = \Omega_{\text{CO}_2}$ (cf. with figure 4.49). Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

is seen to be roughly independent of Ω , as discussed in section 4.3.2.2. Since there is no strong frequency dependence to the backward glory scattering intensity (since such glories are weak to begin with, see section 4.3.1.2) at $F = 1.0$, figure 4.53(a) shows no significant change in the limiting behaviour of $\sin\Theta d\sigma^{(AC)}/d\Omega$ near $\Theta = \pi$. The rainbow region discussed in section 4.3.2.2, is composed of multi-orbital and possible pendular scattering rainbows; these are indicated by the “noise” in $d\sigma^{(AC)}/d\Omega$ in the approximate region of $\Theta \in [0.3\pi, 0.7\pi]$. Proper singularities are not observed for the same numerical reasons outlined for the high- K results. Note that the results of $\Omega = 18.0$ (blue line) contain the largest number of rainbows, in agreement with pendular scattering contributing strongly to higher frequencies (see figure 4.40). The sparseness of the rainbows is reflected by the seemingly random pattern of spikes in $d\sigma^{(AC)}/d\Omega$ of figure 4.53(a) in contrast to the band-structure observed for the isotropic rainbow at high- K (figure 4.52(a)); this results from the rainbow parameters not being smooth functions of, or existing only for isolated values of ϕ_c . The results of figure 4.34 show that the backwards glory scattering intensity is small, in agreement with figure 4.53(a).

Figure 4.53(b) shows the differential cross sections for HeAr with $K = 1.0$, $F = 3.0$ and $\Omega \in \{2, 10, 18, \Omega_{CO_2}\}$ where Ω_{CO_2} denotes the results for $d\sigma^{(HFL)}/d\Omega$. As in the weak field example, the small-angle scattering contribution to the differential cross section is unaffected by Ω , which is rationalised by $w \gg 1$ for this impact parameter region. The pendular- and multi-orbiting regions of $\chi^{(AC)}$ contribute rainbow singularities in the range of $\Theta \gtrsim 0.3\pi$ to $\Theta \lesssim 0.7\pi$; the lower limit of the rainbow regions appears to be sensitive to Ω with the $\Omega = 10$ results (red line in figure) achieving the smallest lower bound ($\Theta \approx 0.1\pi$). At large scattering angles ($\Theta \gtrsim 0.8\pi$) the rainbows solely due to pendular scattering are observed. Since pendular scattering requires a rotational well, rainbows in the region of

0.8π to π are a signature of large $\Delta_{\theta,-}^{(AC)}$. The frequency dependence of the large-angle region of the differential cross section is small for $\Omega \gtrsim 10$. This is mainly due to the change in the isotropic rainbow and backwards ($n = -1$) glories since the contribution to $d\sigma^{(AC)}/d\Omega$ from the pendular scattering (figure 4.34 and 4.40) is essentially constant over the range of Ω examined. The parameters associated with $n = \pm 1$ glories of this system (figure 4.34) do not lead to large contributions but the sharp increase in their number over the weak field results leads to a large contribution to $d\sigma^{(AC)}/d\Omega$ at $\Theta = \pi$.

The main feature of $\chi^{(AC)}$ noted for the low- K limit was the increasing extent of the pendular scattering region of the deflection function as F was increased (see figure 4.29). Figure 4.54 shows $\sin\Theta d\sigma^{(AC)}/d\Omega$ vs. Θ for HeAr with $K = 0.1$, $\Omega \in \{2, 10, 18, \Omega_{CO_2}\}$, $F = 1.0$ (figure (a)) and $F = 3.0$ (figure (b)). In comparing the deflection functions shown in figure 4.29 with the cross sections shown in figure 4.54(a), the majority of the rainbows observed over the range of $\Theta \in [0, \pi/2]$ are due to the multi-orbital scattering region of $\chi^{(AC)}$; the rainbows, observed noise in $d\sigma^{(AC)}/d\Omega$ (see discussion of figure 4.52), near $\Theta \sim 0$ may also be due in part to barrier-type scattering for $\Omega > 4$. The multi-orbital rainbows of $U^{(AC)}$ must converge to those of $U^{(HFL)}$ (green line in figure 4.54(a), labelled Ω_{CO_2}) which are isolated near $\Theta \sim \pi$. Thus, a strong frequency dependence exists in the region of $\Theta > \pi/2$. The glory parameters of section 4.3.1.2 were shown to be independent of Ω with only a moderate contribution from pendular scattering and hence, $d\sigma^{(AC)}/d\Omega$ for all $\Omega < \Omega_{CO_2}$ are shown to have the same limiting value for $\Theta = \pi$. The rainbow singularities arising from pendular scattering do not have large individual contributions to $d\sigma^{(AC)}/d\Omega$ as shown in section 4.3.2.2; however, the large number of them lead to a clear signature of pendular scattering (much noise) in figure 4.54(a).

In figure 4.54(b), the $F = 3.0$ results show similar features as those of $F = 1.0$: rain-

Figure 4.54: The differential cross section $\sin\Theta d\sigma^{(AC)}/d\Omega$ vs. Θ for $U^{(AC)}$ of HeAr with $\Omega \in \{2, 10, 18, \Omega_{CO_2}\}$, $K = 0.1$ and $F \in \{1.0, 3.0\}$. The scattering angle is shown in units of π -radians. Figure (a) shows results for $F = 1.0$ while (b) shows those of $F = 3.0$. In both figures: black line — $\Omega = 2$; red — $\Omega = 10$; blue — $\Omega = 18$; green — $d\sigma^{(HFL)}/d\Omega$, $\Omega = \Omega_{CO_2}$ (cf. with figure 4.50). Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

bows due to barrier- and multi-orbital scattering are seen at small- and mid- Θ , verifying the results of figure 4.41. There is a strong contribution from pendular scattering which gives rise to the increase in $d\sigma^{(AC)}/d\Omega$ near $\Theta = \pi$; in particular there is a large number of rainbow singularities occurring in this region. The main frequency dependence of $d\sigma^{(AC)}/d\Omega$ is seen to occur in the range of $\Theta \in [0.3\pi, 0.9\pi]$ where multi-orbital and pendular scattering give rise to the features of the cross section. Low frequencies ($\Omega = 2$, black line in the figure) are in close agreement with the high-frequency limit cross section (green line) while the scattering intensity falls off in this region as Ω is increased. Obviously, the cross section in this region of Θ must increase again to converge to $d\sigma^{(HFL)}/d\Omega$. The variation can be ascribed to the increase of pendular scattering over reflex scattering seen at lower Ω and in $\chi^{(HFL)}$ (cf. figure 4.29). Oscillations in $\chi^{(AC)}$ due to pendular scattering lead to multiple branches contributing to $d\sigma^{(AC)}/d\Omega$ at a given Θ ; however, the increased values of $|db/d\Theta|$ that result from rapid oscillations tend to reduce the contribution to the cross section at a given angle. This is in contrast to the behaviour of reflex scattering described in section 4.4.1.1. It follows that the frequency dependence of $d\sigma^{(AC)}/d\Omega$ in the coupled potential/coupled amplitude regime can be used to investigate the transition from reflex- to pendular scattering dynamics.

Figure 4.55 shows a log-log plot of $\Theta \sin \Theta d\sigma^{(AC)}/d\Omega$ vs. $K\Theta$ for HeAr with $F = 3.0$, $K = 10$ and $\Omega = 2.0$ for different approximate calculation methods (details given in section 3.5). Shown are the numerical cross sections calculated from $\chi^{(AC)}$ (solid black line, cf. that of figure 4.52(b)), $\chi_{iso}^{(AC)}$ or the isotropic Hamiltonian of (2.29) (dashed black line), and $\chi_{IA}^{(AC)}$ using the impulse approximation equations of (2.104). The red dashed line shows the results of the HDID-IA model for $d\sigma^{(HFL)}/d\Omega$ of (2.105) averaged (numerically) over ϕ_c using the static-field limit approximation of (2.77). Comparison of the $\chi_{iso}^{(AC)}$ results

Figure 4.55: A log-log plot of $\Theta \sin \Theta d\sigma^{(AC)}/d\Omega$ vs. $K\Theta$ for $U^{(AC)}$ of HeAr with $\Omega = 2$, $K = 10$ and $F = 3.0$ using different approximate models. Cross sections derived from different approximations to the deflection function are shown as: solid black line — exact $\chi^{(AC)}$ (cf. with figure 4.52); dashed black line — exact $\chi_{iso}^{(AC)}$ (equation (2.29)); solid red line — numerical cross sections from $\chi_{IA}^{(AC)}$ (2.104); dashed red line — HDID-IA model of (2.121) averaged over ϕ_c using the static-field limit of (2.77). Resolution in Θ is 0.1° in all cases. Details of the calculations are described in section 3.5.

shows that while the small- and large-angle portions of the scattering cross section are qualitatively in agreement, $d\sigma^{(AC)}/d\Omega$ in the rainbow region is incorrect. This is due to the laser phase dependence on the position of the isotropic rainbow which causes the infinity to extend over a range of scattering angles, the lower limit of which is roughly that of $\chi_{iso}^{(AC)}$. Since $U_{iso}^{(AC)}$ does not contain a significant amount of field dependence, only inclusion of the anisotropic terms allows $\chi_r^{(AC)}$ to vary with ϕ_c . The full impulse approximation results of $\chi_{IA}^{(AC)}$ have been shown previously to be in disagreement with exact results for the rainbow parameters. These errors are translated into the shift of the rainbow region to higher angles, although the width and intensity of the region appears to be reasonable. Finally, the static-field limit HDID-IA model of $d\sigma^{(AC)}/d\Omega$ (red dashed line) is shown to be quite accurate for $\Theta < \Theta_r^{(AC)}$. The width of the rainbow region is also reproduced well by this model. As noted previously, the agreement is somewhat coincidental since the exclusion of short-range terms in $\chi_{IA}^{(AC)}$ should make the model less accurate.

4.4.2 Integrated Cross Sections

The integrated collision cross sections (the “total” cross sections) $\sigma^{(HFL)}$ and $\sigma^{(AC)}$ do not contain as much detailed dynamical information as the differential cross sections of the collision system. From (2.61)¹⁴ it is seen that the principal contribution to σ is due to small-angle scattering since this will produce the largest impact parameter for a fixed integration angle ζ . Thus any laser-induced changes in the large-impact parameter region of the deflection function will be seen in σ ; these are estimated by (2.64). Other dynamical features do contribute to σ but these are secondary effects since the corresponding impact parameters are paired with one of similar magnitude but opposite sign.

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¹⁴See also appendix E for a more generalised treatment.

4.4.2.1 High Carrier Frequency

In the case of $U^{(\text{HFL})}$, the only relevant parameters for analysis are F and K . Figure 4.56 shows the integrated collision cross section $\sigma^{(\text{HFL})}$ vs. F for HeAr with $\Omega = \Omega_{\text{CO}_2}$ and $K \in \{0.1, 1.0, 10\}$. Numerical details of the calculations are given in section 3.5. Similar calculations for He₂ (not shown) yield quantitatively identical results. In all calculations of $\sigma^{(\text{HFL})}$, the lower integration angle chosen was $\zeta = 4.5^\circ$ (0.025π radians) since this yielded finite cross sections which were sensitive to variations in K for the $F = 0.0$ case over the range of collision energies studied (see also reference [191]).

In the high- K limit, the perturbative potential regime of (2.49) was shown to yield small field-induced effects. Figure 4.56 shows $\sigma^{(\text{HFL})}$ for $K = 10$ (dashed line) increases monotonically with F by about 5%. From the form of the $\chi^{(\text{HFL})}$ (figure 4.9), only three branches contribute to $\sigma^{(\text{HFL})}$ for any F . The small angle scattering branch of $\chi^{(\text{HFL})}$ is seen to decrease with F for a fixed impact parameter, i.e. fixed contours of $\chi^{(\text{HFL})}$ all shift to higher b with increasing F . From (2.64), an increase in $\sigma^{(\text{HFL})}$ can arise from either a variation in the parameters c or s ; the latter is not likely since terms greater than order b^{-6} do not contribute significantly to $\chi_{\text{IA}}^{(\text{HFL})}$, hence the behaviour observed is most likely due to an increase in $|c|$ with F . An increase in attractive scattering can be correlated with the increase of $\Delta_e^{(\text{HFL})}$ with F . A similar interpretation can be applied to the mid- K results of $K = 1.0$ (dotted line in figure 4.56); the only difference is in this case the $F = 0.0$ cross section has increased since collisions are more sensitive to small variations in $U^{(\text{HFL})}$ at lower K . The relative increase of $\sigma^{(\text{HFL})}$ over the range of F is also slightly larger, ca. 6%.

The cross section $\sigma^{(\text{HFL})}$ for $K = 0.1$ is shown to be a non-monotonic function of F in figure 4.56 (solid line), with a maximum value of approximately 31.9 for $F \approx 2.14$. Thereafter, $\sigma^{(\text{HFL})}$ decreases below the field-free value at $F = 3.0$. The overall cross section is

Figure 4.56: The integrated cross section $\sigma^{(HFL)}$ vs. F of HeAr with $\Omega = \Omega_{CO_2}$, $K \in \{0.1, 1.0, 10\}$. Solid line — $K = 0.1$; dotted — $K = 1.0$; dashed — $K = 10$. In all cases the integration angle used is $\zeta = 4.5^\circ$. Further details of the calculations are described in section 3.5.

higher than at the other two collision energies since $\sigma^{(\text{HFL})}$ must increase with decreasing K . The low- K system is in a different potential regime than the other results and in section 4.2.1.3 it was noted that the large- b range of $\chi^{(\text{HFL})}$ is sensitive to the presence of $\Delta_{\theta,+}^{(\text{HFL})}$. At $F \gtrsim 1.9$, $\Delta_{\theta,+}^{(\text{HFL})} \sim K$ and $\chi^{(\text{HFL})}$ has a reduced attractive scattering contribution to the small-angle branch. The net effect for the range of F examined is to decrease $|c|$ of equation (2.64); the range parameter s cannot change since the barrier to rotation is a result of the leading (X^{-3}) term of β and hence would effectively decrease s . Such a variation in s would lead to a larger $\sigma^{(\text{HFL})}$. Thus, $|c|$ is varied by F in (2.64). The result of an increase in $\Delta_{\theta,+}^{(\text{HFL})}$ can thus be observed by the decrease in $\sigma^{(\text{HFL})}$ via equation (2.64).

Figure 4.57 shows the results of $\sigma^{(\text{HFL})}$ vs. F for both HeAr and He₂ using the different dynamical models for $K = 10$ and $\Omega = \Omega_{\text{CO}_2}$. Numerical details are also given in section 3.5. The exact $\sigma^{(\text{HFL})}$ are shown with solid lines while numerical cross sections calculated from $\chi_{\text{IA}}^{(\text{HFL})}$ of equation (2.98), are shown as dashed lines. The results of the HDID-IA model of $\sigma^{(\text{HFL})}$ given in equation (2.122) are shown as dotted lines. Black and red data denote HeAr and He₂, respectively. While both impulse approximation models have been shown to yield a quantitative description of the large impact parameter region of $\chi^{(\text{HFL})}$, the inclusion of the short-range polarisability terms in (2.98) has been shown to increase the disagreement between $\chi_{\text{IA}}^{(\text{HFL})}$ and $\chi^{(\text{HFL})}$ (cf. the results of figure 4.11). Thus the branches of $\chi_{\text{IA}}^{(\text{HFL})}$ that are $b < b_r^{(\text{HFL})}$ where the impulse approximation breaks down lead to this cross section decreasing with F . Since the HDID-IA model of (2.122) does not contain the short-range polarisability terms, the divergence of the deflection function in the small impact parameter region is less dependent on F . The accuracy of the small-angle scattering leads to a qualitatively correct behaviour of increasing $\sigma^{(\text{HFL})}$ with F . A small systematic error exists for the $F = 0.0$ result (ca. 0.073), which when corrected, shows that

Figure 4.57: The integrated cross section $\sigma^{(\text{HFL})}$ vs. F of HeAr (black lines) and He₂ (red lines) with $\Omega = \Omega_{\text{CO}_2}$ and $K = 10$. For both molecules, cross sections derived from different approximations to the deflection function are shown as: solid line — exact $\sigma^{(\text{HFL})}$ (cf. with figure 4.56); dashed — numerical cross sections of $\chi_{\text{IA}}^{(\text{HFL})}$ (2.98); dotted — HDID-IA model of $\sigma^{(\text{HFL})}$ (2.122). In all cases the integration angle used is $\zeta = 4.5^\circ$. Further details of the calculations are described in section 3.5.

the HDID-IA model is in good quantitative agreement with the cross section of $\chi^{(\text{HFL})}$ for fields up to $F \approx 0.5$. For larger fields the model result does not increase as much as the exact with respect to F .

4.4.2.2 Low-to-Medium Carrier Frequency

The parameters to be explored in the case of $\sigma^{(\text{AC})}$ are F , K and Ω . In particular, the Ω -dependence of $\sigma^{(\text{AC})}$ should yield some information about the effect of the time-dependence of $U^{(\text{AC})}$ on the dynamics. The integrated cross sections $\sigma^{(\text{AC})}$ are shown in figure 4.58 as functions of Ω for HeAr at various collision energies and field strengths. Each value of K is given a different line-style: solid — $K = 0.1$; dotted — $K = 1.0$ and dashed — $K = 10$. Similarly, symbol types distinguish the different values of field used (see figure caption, $F \in \{0.5, 1.0, 1.5, 2.0, 2.5, 3.0\}$). The results show a great similarity to those of the high-frequency limit (figure 4.56): $\sigma^{(\text{AC})}$ depends on both K and F in the same way as $\sigma^{(\text{HFL})}$, decreasing monotonically with K and monotonically increasing with F for higher collision energies. In the case of low K , $\sigma^{(\text{AC})}$ also shows the same non-monotonic behaviour with respect to variations in F as $\sigma^{(\text{HFL})}$ (higher fields yield cross sections less than the $F = 0.0$ case). Quantitatively, the $U^{(\text{AC})}$ cross sections cover the same range as $\sigma^{(\text{HFL})}$ (note the two figures have the same scales). The only exception to this correspondence is seen in the $K = 0.1$ results for $\Omega = 0.0$; this might be attributed to the fact that $\sigma^{(\text{AC})}$ of a DC-field, when averaged over ϕ_c , contains contributions from much higher effective fields (by $\sqrt{2}$) than in the high-frequency limit. Thus $\sigma^{(\text{AC})}$ may exhibit F -dependence of higher fields than were examined for $\sigma^{(\text{HFL})}$.

Only very small variations in Ω are observed in figure 4.58 for a fixed K and F . For high K (dashed lines), sensitivity to Ω increases with F and is confined to $\Omega \lesssim 10$. There appears

Figure 4.58: The integrated cross section $\sigma^{(AC)}$ vs. Ω for $U^{(AC)}$ of HeAr with $K \in \{0.1, 1.0, 10\}$ and $F \in \{0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0\}$. Solid lines show $K = 0.1$; dotted — $K = 1.0$; dashed — $K = 10$. Circle symbols show $F = 0.0$; squares — $F = 0.5$; diamonds — $F = 1.0$; triangle up — $F = 1.5$; triangle left — $F = 2.0$; triangle down — $F = 2.5$; triangle right — $F = 3.0$. In all cases the integration angle used is $\zeta = 4.5^\circ$. Further details of the calculations are described in section 3.5.

to be a small local maximum near $\Omega = 2$ and minima at $\Omega = 6$. The behaviour can be explained by the effect of barrier scattering upon the small-angle portion of $\chi^{(AC)}$. Barrier scattering is only observed at $\Omega = 2.0$ for this collision energy. In addition, the $\{\chi_r^{(AC)}\}$ associated with the mechanism do not contribute to $\sigma^{(AC)}$ directly since $|\chi_r^{(AC)}| \ll \zeta$. Thus the major contribution to $\sigma^{(AC)}$ at this K is the isotropic rainbow region of $\chi^{(AC)}$. The presence of a barrier scattering maximum in $\chi^{(AC)}$ will affect indirectly the shape of the deflection function in the vicinity of the isotropic rainbow minimum since the presence of the former must, by the continuity of $\chi^{(AC)}$, alter the curvature at the latter. Such variations could result in either an increase or decrease in $\sigma^{(AC)}$, depending on the detailed behaviour of $\chi^{(AC)}$ as Ω is changed. However, barrier scattering is the only variation observed in the large b region of $\chi^{(AC)}$ for the perturbative potential regime and must therefore account for the observed variation in $\sigma^{(AC)}$.

While the differential cross section of $U^{(AC)}$ in the mid- K regime has more complexities, the results for the integrated cross section (dotted lines in figure 4.58) show a simple behaviour akin to that of the high- K results. The interpretation is based on the $\chi^{(AC)}$ shown in figure 4.25 from section 4.2.2.2: the figure shows the large- b contours (magenta line in figure 4.25) are more elliptic with variation of ϕ_c for low Ω . Such ellipticity is due to the barrier to rotation being essentially static over the course of the collision and thus variation of ϕ_c is equivalent to varying F . Thus phases where $\chi^{(AC)}$ is less attractive at large- b contribute to $\sigma^{(AC)}$ and reduce its value. As Ω increases, convergence to the high frequency limit implies that the average barrier to rotation is the relevant parameter and, since $\Delta_{\theta,+}^{(HFL)} < \Delta_{\theta,+}^{(AC)}$ at the peak of the cycle, $\sigma^{(AC)}$ increases with Ω to the limit of $\sigma^{(HFL)}$. Estimates of w show that $w \gg 1$ for $K = 1.0$ in the large b range when $\Omega \approx 4.7$, in basic agreement with the results of figure 4.58. For $K = 0.1$ (solid lines), $\sigma^{(AC)}$ is non-monotonic

with Ω .

The evaluation of the quantitative accuracy of the impulse approximation models for both the field- and frequency dependence of $\sigma^{(AC)}$ is shown in figure 4.59. In figure 4.59(a), $\sigma^{(AC)}$ vs. F is shown for HeAr (black lines) and He₂ (red lines) with $K = 10$ and $\Omega = 2.0$. Solid lines label the exact numerical cross sections $\sigma^{(AC)}$ (cf. results of figure 4.58), dashed lines show the numerical cross section evaluated from $\chi_{IA}^{(AC)}$ of equation (2.104) while the dotted lines show the results of using the HDID-IA model of (2.122) averaged over ϕ_c using the static-field limit approximation of (2.77). As was shown in the case of $\sigma^{(HFL)}$ (figure 4.57), the exclusion of the short-range terms in the impulse approximation model of (2.122) yields the qualitative field-dependence of $\sigma^{(AC)}$ once averaged. If the results are shifted to agreement at $F = 0.0$, the model is quantitatively accurate for $F \lesssim 0.5$. In contrast, use of $\chi_{IA}^{(AC)}$ to obtain $\sigma^{(AC)}$ yields qualitatively incorrect results. Since $\chi^{(AC)} \approx \chi_{IA}^{(AC)}$ for large b , the disagreement must lie in the contributions from the impact parameters around the glory impact parameter where the impulse approximation has been shown to break down.

The frequency dependence of $\sigma^{(AC)}$ is shown in figure 4.59(b) for HeAr and He₂ with $F = 3.0$ and $K = 10$. The exact $\sigma^{(AC)}$ for HeAr is identical to that of He₂, demonstrating that no discernible difference between the two systems is evident in the limit of large K for a wide range of Ω . The behaviour the $\chi_{IA}^{(AC)}$ cross section with Ω is complex but qualitatively reproduces the non-monotonic behaviour of $\sigma^{(AC)}$ with a local maximum at $\Omega \approx 3.0$ and minimum at $\Omega \approx 9.0$; for $\Omega \gtrsim 16$, there is little Ω dependence exhibited. Quantitatively, the behaviour of the $\chi_{IA}^{(AC)}$ cross section is incorrect, exaggerating the variation with Ω even when the systematic error at high frequencies is corrected. Such behaviour has been noted in the results of other observables derived from $\chi_{IA}^{(AC)}$; in figure 4.22, the ability of $\chi_{IA}^{(AC)}$

Figure 4.59: The integrated cross section $\sigma^{(AC)}$ of HeAr and He₂ for $K = 10$. Figure (a) shows $\sigma^{(AC)}$ vs. F for $\Omega = 2$ and figure (b) shows $\sigma^{(AC)}$ vs. Ω for $F = 3.0$. In both figures black and red lines denote HeAr and He₂, respectively. For both molecules, cross sections derived from different approximations to the deflection function are shown as: solid line — exact $\sigma^{(AC)}$ (cf. with figure 4.58); dashed — numerical cross sections of $\chi_{IA}^{(AC)}$ (2.104); dotted — HDID-IA model of $\sigma^{(HFL)}$ (2.122) averaged according to the static-field limit (2.77). In all cases the integration angle used is $\zeta = 4.5^\circ$. Further details of the calculations are described in section 3.5.

to reproduce the effects of barrier scattering was noted to be poor. Thus, the discrepancies shown at lower frequencies may be due to numerical evaluation of Bessel functions which diverge near zero (see appendix G) as these contribute to the repulsive terms required for barrier scattering. It is also possible that the approximate evaluation of some of the integrals (see appendix F) may introduce this error.

Chapter 5

Discussion and Conclusions

The overall goal of the present work has been to investigate the effect of a strong infrared (homogeneous) laser field upon the dynamics of intermolecular collisions. To that end it was determined in chapter 1 that the study of elastic collisions between two atoms within a strong IR field was a system of sufficient complexity as to yield important laser-induced dynamical effects. Furthermore, it was argued that a simple model which invoked the quasi-static approximation and treated the collisions classically would be sufficient and useful for the analysis; this approach was also favoured since it led to a more generalised model which could describe weakly interacting systems qualitatively, and quantitatively describe those of the rare-gas dimers. It now remains to summarise the main results of the present investigation.

5.1 A Brief Discussion of the Hypotheses

In section 1.6 two hypotheses were stated which encapsulated the aims of the present work. The first postulated that the study of the laser + elastic collision system under con-

ditions of a crossed molecular beam experiment would yield evidence of laser-induced effects. This hypothesis is trivially shown to be correct by making reference to the differential and integrated cross sections calculated in section 4.4 which do vary with laser parameters F and Ω under a wide variety of conditions. While this hypothesis may appear to be of no consequence, its veracity is of importance in that if it did turn out to be false, some new set of experimental conditions would have to be devised which could examine the effects of the laser on the system. Additionally, any laser-induced effects that were present would necessarily be small since the molecular beam technique is a very sensitive probe of the shape of the potential energy surface. As the results of the investigation were conducted in a system cast in its corresponding states form, the variations of the observables of chapter 4 are thus shown to be due to changes in the shape of the potential and are therefore non-trivial.

The second hypothesis of section 1.6 concerned the detailed analysis of the shape-changes induced in the potential energy surface of the diatomic system by the laser and the correlation between these and the observables of the system. This hypothesis has been tested through the bulk of the work of chapter 4 which established firstly what fundamental features of the potential would be important in the dynamics of the system (section 4.1). The features identified were: the radial potential well of depth Δ_e , the rotational well of depth $\Delta_{\theta,-}$ and the barrier to rotation of a height $\Delta_{\theta,+}$; the first of these exists in a purely isotropic potential while the other two are laser-induced in origin. Time-dependence manifests itself in the oscillation of these features about an average value related to the features obtained in the limit of high carrier frequency. These potential features, their average values and standard deviations were used in conjunction with the laser parameters and dynamical initial conditions to define dynamic regimes (section 2.3) which allowed a measure of

prediction of dynamic effects.

In section 4.2 the connection between the potential features described above and the collision system trajectories was made. Four “collision mechanisms” were identified and categorised in terms of the potential features within different dynamical regimes. In section 4.3 the observables of a molecular beam experiment were examined as a function of laser parameters and the results were used to establish that each collision mechanism had a visible effect on the dynamical observables. Therefore the second hypothesis of 1.6 has been verified by making a qualitative connection between the main features of the potential and the collision cross sections of section 4.4 by way of the collision mechanisms discovered. The second hypothesis is thus of more importance and its testing non-trivial since both the potential features and the collision mechanisms determined have not been noted previously in the literature. A more detailed summary of the results of this work follows in the next section which also addresses some of the corollaries of the main hypotheses given in section 1.6.

5.2 Summary of Main Conclusions

The main results of the present investigation are categorised according to the order of their presentation. The first summary therefore deals with the properties of the laser-induced potential energy surface for two atoms in a linearly-polarised, homogeneous, infrared laser field. Second, the dynamical consequences of the potential features are reiterated in condensed form with particular attention paid to the collision mechanisms identified. Third, the manifestation of the collision mechanisms in the observables defined for a molecular beam experiment are summarised. Finally, the results pertaining to the approximate models used throughout the present work are commented upon.

5.2.1 Laser-Induced Potential Features

The laser-molecule Hamiltonian defined in chapter 2 contains terms which are categorised according to: isotropic, anisotropic, time-independent and time-dependent. It is also noted that terms which are combinations of these categories are contained within the laser-molecule potential. The field-free potential energy function is both isotropic and time-independent. The separation of time-dependence is first seen by examination of the high-frequency limit potential $U^{(\text{HFL})}$ which has terms that are analogous to those of the time-dependent potential $U^{(\text{AC})}$ when averaged over the laser cycle ($\langle U^{(\text{AC})} \rangle_{\phi_c}$) and hence its features are also present in $U^{(\text{AC})}$ before the time-dependence of the latter is taken into account. From section 4.1, the dominant features of $U^{(\text{HFL})}$ were found to be:

1. An increased radial well depth. This laser-induced effect is due to both isotropic and anisotropic parts of $U^{(\text{HFL})}$. However, for the particular systems examined (HeAr and He₂), $U_{\text{iso}}^{(\text{HFL})}$ was found to have little field dependence due to the small variation in the polarisability trace in $U_{\text{iso},\alpha}^{(\text{HFL})}$ and the isotropic dipole terms $U_{\text{iso},d}^{(\text{HFL})}$. The radial potential well, characterised by its depth $\Delta_e^{(\text{HFL})}$, exists in the field-free potential and is thus isotropic.
2. The appearance of a rotational well. The potential was shown to have a minimum when aligned with the field axis. Thus the increasing potential as θ moves away from the field axis causes this degree of freedom to be confined by a potential well characterised by its depth $\Delta_{\theta,-}^{(\text{HFL})}$. This feature is anisotropic since it cannot exist without $U_{\text{aniso},d}^{(\text{HFL})}$ or $U_{\text{aniso},\alpha}^{(\text{HFL})}$ being non-zero. In $U^{(\text{HFL})}$ two potential wells are created parallel and anti-parallel to the field axis which are identical; this symmetry is broken in the case of $U^{(\text{AC})}$.

3. The appearance of a barrier to rotation. This feature is related to the rotational well but refers to a region of the potential which lies outside of the typical equilibrium geometry. When the molecular axis is perpendicular to the field, the laser-induced anisotropic terms are repulsive. Thus for sufficient field strength, not only is the local minimum in the potential higher than that of the aligned system (the rotational well) but a local maximum appears on the potential at a larger internuclear separation, $X_{\max}^{(\text{HFL})}$. The energy of the local maximum increases with F until the potential is positive within its vicinity, with a barrier height given by $\Delta_{\theta,+}^{(\text{HFL})}$. For higher fields, it is possible for $U^{(\text{HFL})}$ to become everywhere repulsive perpendicular to the field. Since the feature does not exist except for highly anisotropic potentials, it is a feature of anisotropic origin.

The dynamics of $U^{(\text{HFL})}$ are thus determined by the energetics of the above potential features in comparison with the collision energy K , leading to the classification of the potential regime in (2.49). The regimes, perturbative, isotropic, anisotropic and coupled, can be used to anticipate the relative influence of the isotropic and anisotropic parts of $U^{(\text{HFL})}$. The only pertinent laser parameter which influences the magnitude $\{\Delta_e^{(\text{HFL})}, \Delta_{\theta,-}^{(\text{HFL})}, \Delta_{\theta,+}^{(\text{HFL})}\}$ is the field strength F . The laser carrier frequency Ω does enter into $U^{(\text{HFL})}$ but in the region of the latter's validity, say Ω_{CO_2} , the contribution of Ω -dependent terms $U_{\text{iso},d}^{(\text{HFL})}$ and $U_{\text{aniso},d}^{(\text{HFL})}$ are negligible.

For the time dependent Hamiltonian whose potential is denoted $U^{(\text{AC})}$, the effect of the time-dependence introduces both Ω and ϕ_c as active laser parameters. The potential is partitioned into the phase-averaged potential $\langle U^{(\text{AC})} \rangle_{\phi_c}$ which is time-independent and its remaining time-dependent partition $U_{\tau}^{(\text{AC})}$. For a homonuclear system $\langle U^{(\text{AC})} \rangle_{\phi_c} = U^{(\text{HFL})}$ thus the potential features of $\{\Delta_e^{(\text{AC})}, \Delta_{\theta,-}^{(\text{AC})}, \Delta_{\theta,+}^{(\text{AC})}\}$ are time-dependent quantities which

oscillate about the corresponding $U^{(\text{HFL})}$ values. Thus the basic potential regime of $U^{(\text{AC})}$ is therefore the same as that of $U^{(\text{HFL})}$ by (2.49) and $U_{\tau}^{(\text{AC})}$ has simply the effect of introducing fluctuations of the features about the average value. The energetic magnitude of these fluctuations is characterised by the standard deviation of $U^{(\text{AC})}$, $\sigma_{\text{RMS},U^{(\text{AC})}}$. To gauge the effect of fluctuations on a particular feature, the corresponding standard deviations are calculated. This leads to a comparison of K , $|\langle U^{(\text{AC})} \rangle_{\phi_c}|$ and $\sigma_{\text{RMS},U^{(\text{AC})}}$ in equation (2.52) which identifies the amplitude regime of the system. The regimes, perturbative, small, large and coupled, describe the relative dominance of $\langle U^{(\text{AC})} \rangle_{\phi_c}$ vs. $\sigma_{\text{RMS},U^{(\text{AC})}}$ in the dynamics.

The time-dependence of $U^{(\text{AC})}$ has another component besides the magnitude of the fluctuations. The number of laser cycles over the course of the collision determines if the time scales of the laser and the system motion are comparable. The parameter w was used to define three frequency regimes: the static field limit ($w \ll 1$); resonance $w \sim 1$; the high frequency limit ($w \gg 1$). Only resonance has a significant effect on the motion, even when the $U^{(\text{AC})}$ fluctuations are small in magnitude. However, the two effectively time-independent limits can also be affected by $U_{\tau}^{(\text{AC})}$ if $\sigma_{\text{RMS},U^{(\text{AC})}}$ is very large; in such a case the properties of $\{\Delta_e^{(\text{AC})}, \Delta_{\theta,-}^{(\text{AC})}, \Delta_{\theta,+}^{(\text{AC})}\}$ at their maximum values are a more accurate estimate of the laser-induced potential effects.

5.2.2 Collision Mechanisms and Dynamics

The consequences of the potential features and different dynamical regimes outlined above is seen by the changes induced by the laser field to the system trajectories. Examination of the classical deflection functions of both the time-independent and time-dependent potentials, $\chi^{(\text{HFL})}$ and $\chi^{(\text{AC})}$, respectively, showed that a large number of trajectories over different ranges of impact parameter b followed similar paths. These paths were the re-

sult of the influence of different parts of the potential and hence the following “collision mechanisms” were identified (see sections 4.2.1.3, 4.2.2.1 and 4.2.2.2):

1. **Reflex Scattering.** This type of collision occurs when the trajectory undergoes one angular turning point, i.e. P_θ changes sign, due to the interaction with the short-range part of $U_{\text{aniso}}^{(\text{HFL})}$, specifically the rotational well. The exit path of the trajectory then crosses the field axis ($\theta = 0$). The resulting effect on the deflection angle is that it takes on values in the range of π to 2π radians. The mechanism has been observed in $U^{(\text{HFL})}$ in the coupled potential regime while in $U^{(\text{AC})}$ it has been observed in the isotropic potential/coupled amplitude and coupled potential/coupled amplitude regimes with $w \sim 1$ in both cases. The mechanism is not sensitive to small variations in $\{\Delta_{\theta,-}^{(\text{AC})}, \Delta_{\theta,-}^{(\text{HFL})}\}$ since it is observed only at moderately high fields ($F > 1$). This is due to the fact that a large rotational well is required to induce an angular turning point.
2. **Multi-Orbital Scattering.** Any trajectory which experiences multiple radial turning points due to the interaction with the anisotropy in a potential well is a multi-orbital trajectory. Radial turning points are caused by the creation of barriers to dissociation along the radial coordinate via either the centrifugal- or anisotropic potential contributions. In the case of $U^{(\text{AC})}$ kinetic energy exchange with the field is another possible cause. The mechanism encompasses a broad class of trajectories, the resulting deflection angles of which depend on the number of radial turning points which occur; thus multi-orbital scattering can lead to $\chi \in [-\infty, +\infty]$. The mechanism has been observed for $U^{(\text{HFL})}$ in the isotropic- and coupled potential regimes. In the case of $U^{(\text{AC})}$, the mechanism occurs in either the isotropic- or coupled potential regimes in conjunction with the coupled amplitude regime for a range of w in resonance or the

high-frequency limit. The mechanism is sensitive to all parameters $\{\Delta_e, \Delta_{\theta,-}, \Delta_{\theta,+}\}$. The collision energy threshold where multi-orbital scattering can occur is K less than the orbiting collisional energy $K_{orb,(\pm)}^{(HFL)}$ or $K_{orb,(\pm)}^{(AC)}$, where the $\pm$ denotes the sign of the orbiting singularity (i.e. $\chi = \pm\infty$); the collision energy of $K_{orb,(-)}$ is of particular note since it defines the exact boundary between perturbative and non-perturbative dynamics.

3. Barrier Scattering. As the name implies, this mechanism arises when the trajectory interacts with the barrier to rotation located at larger internuclear separations. Since the barrier is a repulsive feature, the trajectory is made to follow a path away from the scattering centre and not towards it as is normally found in the isotropic case. The resulting deflection angle is thus $\chi \gtrsim 0$. The potential feature which governs the existence of this type of collision is $\Delta_{\theta,+}$. The mechanism has been observed directly only in $U^{(AC)}$ for the perturbative potential/perturbative amplitude regime with $w \sim 1$ and the coupled potential/coupled amplitude regime with $w \gg 1$.
4. Pendular Scattering. Trajectories which enter one potential well and undergo multiple radial- and angular turning points before exiting either above or below the field axis belong to this collision mechanism. Pendular scattering results in a deflection angle $\chi \sim \pi$. The exit path is very sensitive to impact parameter and hence $\chi(b)$ oscillates about π where the collision mechanism occurs. The mechanism has only been observed for $U^{(AC)}$ when the system is in the isotropic potential regime and the coupled amplitude regime with $w \sim 1$ and in the coupled potential/coupled amplitude regime with $w \sim 1$ or $w \gg 1$.

The classification, dominant potential terms, approximate parameter ranges of occurrence and the resulting effect on the deflection function of the above collision mechanisms can be determined from the definitions of the dynamic regimes of section 2.3 but are summarised explicitly in table 5.1. The results of section 4.2 leading to the above mechanisms have also yielded some other useful conclusions. First, the dynamical behaviour of the system when it is in the perturbative potential regime is governed by K ; laser-induced effects are simply perturbations on the qualitative form of χ derived from an isotropic potential. Thus, χ increases with F for $b < b_r$ and decreases for $b \geq b_r$. Even for very high fields ($F \sim 3$), the dynamics are perturbative for a sufficient value of K . Similarly, there is little sensitivity to Ω in the high- K regime. In particular the concept of the static field limit ($w \ll 1$) was shown to be qualitatively and quantitatively useful in describing $\chi^{(AC)}$ when $K \gg 1$.

Second, the effects of time-dependence and hence sensitivity to Ω and ϕ_c are reasonably well predicted by w , although large amplitudes in $U_\tau^{(AC)}$ do yield exceptions to this rule. Thus, high- K dynamics take place essentially in a static field while low K has resonance features. Mid- K dynamics of $U^{(AC)}$ are characterised by a mix of the two types of behaviour with more laser-induced effects than comparable $U^{(HFL)}$ results.

Finally, it was found that the regions of impact parameter where different collision mechanisms were operative in $U^{(AC)}$ was the same as in $U^{(HFL)}$. Thus the form of $\langle U^{(AC)} \rangle_{\phi_c}$ determines the basic behaviour of the system. For example, the high-frequency limit results for low- K showed that the region of reflex scattering corresponded to the region of pendular scattering, for the same F , in $U^{(AC)}$. Similar connections were found for the other collision mechanisms which predominated the low- K dynamics. In general, low K dynamics were the most sensitive to F and exhibited the largest departure from field-free dynamics.

Collision Mechanism	Classification [†]	U-Features [‡]	Conditions [§]	Effect on χ			
	$\langle U_{\text{(AC)}} \rangle_{\phi_c}$ or $U_{\text{(HFL)}}$	$U_{\text{(HFL)}}^{\text{iso}}$ or $U_{\text{(AC)}}^{\text{iso}}$	$U_{\text{(HFL)}}^{\text{aniso}}$ or $U_{\text{(AC)}}^{\text{aniso}}$				
		Radial Well					
		Rotational Well					
		Barrier to Rotation					
	$U_{\text{(AC)}}^r$		b	K			
			F	Ω			
Reflex Scattering	n	y	n	s	m,l	N/A	$\chi \in [\pi, 2\pi]$
Barrier Scattering	y	n	y	l	s,m	m,l	$0 < \chi \ll 1$
Pendular Scattering	y	n	y	s	s,m	m,l	Oscillations about $\chi \sim \pi$
Multi-Orbital Scattering	y	y	y	m	s,m	m,l	N/A
							$\chi \rightarrow \pm\infty$ at multiple b otherwise $ \chi < 2\pi$

[†]. Refers to the terms in U minimally required for the mechanism to occur.

[‡]. If the mechanism requires $U_{\text{AC}}^{(1)}$ then the fluctuation of the pertinent feature of the laser-induced potential is implied. See 2.2 for definitions.

[§]. Ranges of parameters required for the mechanism to be observed: s — small; m — medium; l — large. For b these are $\{< 1, \sim 1, > 3\}$, respectively; K — $\{0.1, 1, 10\}$; F — $\{< 1, \sim 1, > 3\}$; Ω — $\{< 2, \sim 10, > 20\}$. Note that “N/A” implies an insensitivity to the parameter.

Table 5.1: A summary of the properties for the collision mechanisms identified in the laser-induced dynamics. The mechanisms are classified according to: terms of the potential which must be present; the laser-induced potential features which govern the mechanism; the ranges of the parameters $\{b, K, F, \Omega\}$ where the mechanism has been observed; the resulting effect on the deflection angle at a single impact parameter or the behaviour of the deflection function in the range of b where the mechanism is operative.

5.2.3 Signatures of the Collision Mechanisms

Sections 4.3 and 4.4 are devoted to following the behaviour of the dynamical observables over a range of laser parameters to establish distinct signatures of the collision mechanisms of table 5.1 in experimental observables. Signatures of the mechanisms, such as they are, are summarised below:

1. Reflex Scattering. Since $\lim_{b \rightarrow +\infty} \chi = 0$, the presence of reflex scattering requires by continuity that a backwards $n = +1$ glory and a backwards rainbow must be present in $\chi^{(\text{HFL})}$; note that both occur at smaller impact parameters and $b_g^{(\text{HFL})} > b_r^{(\text{HFL})}$. The rainbow is broad in general and shifts to smaller angles with F while the glory tends to decrease in intensity with F . The differential cross section has a higher intensity in the backscattering (large Θ) region as a result of this type of scattering. The features emerge at $F \gtrsim 1$ and persist until the rainbow transforms into a positive orbiting singularity at $F \gtrsim 3$.
2. Barrier Scattering. For this collision mechanism, the condition that $\chi^{(\text{AC})} \rightarrow 0^+$ and the onset of net attractive scattering at mid-range b implies that a maximum in $\chi^{(\text{AC})}$ must occur at large b . Thus a $n = 0$ forward glory and a forward rainbow occur in $\chi^{(\text{AC})}$; these are long-range effects and hence $1 \ll b_g^{(\text{AC})} < b_r^{(\text{AC})}$. The forward barrier scattering rainbow singularity appears near $\Theta = 0$ in the differential cross section and shifts to higher Θ with F .
3. Pendular Scattering. The oscillations induced by this mechanism in $\chi^{(\text{AC})}$ are generally less than $\pm\pi/2$ -radians in amplitude. Thus the alternating maxima and minima in this region form a set of multiple backwards rainbow singularities in the region of $\Theta \in (\pi/2, \pi]$. There is also, by continuity, a number of backwards $n = \pm 1$ glo-

ries which arise from this type of scattering. The $\{b_r^{(AC)}\}$ and $\{\chi_r^{(AC)''}\}$ were shown to be small and large, respectively; hence the rainbow singularities are narrow in general. However, the range of impact parameter where pendular scattering occurs increases with F and it follows that the rainbows will become more numerous and less narrow. Overall, $d\sigma^{(AC)}/d\Omega$ becomes larger in the backscattering region due to this mechanism.

4. Multi-Orbital Scattering. The mechanism gives rise to complex dynamics, particularly in the time-dependent case. The most dramatic effect is the presence of more than one orbiting singularity in $\chi(b)$ (negative and positive orbiting) and the existence of a range of collision energy $K < K_{orb,(\pm)}^{(HFL)}$, or $K < K_{orb,(\pm)}^{(AC)}$, where orbiting and rainbows coexist. Due to continuity, a number of $n = 0$ glories and forward/backward rainbows occur due to this mechanism. Since orbiting does not have a unambiguous signature in the differential cross section, multi-orbital scattering is noted by the presence of rainbows which emerge at a non-zero field in the region of $\Theta \sim \pi/2$.

Of all the mechanisms given above, only barrier scattering actually affects the long-range part of the potential and hence is the only mechanism which has any influence on the small-angle scattering region of the deflection function. In general, the effect of the field is to increase the long-range attraction of the potential, except near the barrier, and thus large- b deflection functions have a negative slope which increases in absolute value with F . This effect is shown to increase the slope of the singularity at $\Theta = 0$ in the differential cross section and to increase the integrated cross section. When $\Delta_{0,+} \sim K$, the transition from long-range attractive- to repulsive scattering results in a decrease in the total cross section.

In the analysis of section 4.3 it was found that almost always the dynamical signatures of the isotropic, field-free potential persisted even in very strong fields. The field-free $n = 0$ forward glory, rainbow and orbiting singularity simply have their parameters shifted by the effects of the anisotropic potential. The effects of time-dependence on these isotropic features is to introduce a ϕ_c dependence which tends to augment their presence in the differential and integrated cross sections, e.g. the continuous spread of the isotropic rainbow observed for high- K $\chi^{(AC)}$. However, when F is very large, K is low or $w \sim 1$, the deflection function does not appear to possess any isotropic features.

5.3 Approximate Models Used in the Present Work

A number of approximations were tested throughout the investigation, for the potential features and dynamic observables. The fundamental approximations made in most models were the neglect of the dipole- and any short-range polarisability terms in the potential (the HDID model). Dynamics were treated within the impulse approximation (IA) and approximate results for $d\sigma^{(HFL)}/d\Omega$ and $\sigma^{(HFL)}$ within the HDID-IA model were also determined; HDID-IA results for $U^{(AC)}$ were obtained within the static field limit. The neglect of potential terms was shown to yield reasonable results for potential features for either the case of weak fields or $\theta = \pi/2$. Thus, the HDID model of section 2.5.2 more accurately describes the barrier to rotation than any other potential feature.

In comparison of the IA and HDID-IA models of glory and rainbow parameters in addition to collision cross sections, the resulting dynamical observables showed that neither model is consistently accurate, either qualitatively or quantitatively. Overall, the HDID-IA model fared better, producing qualitatively correct field dependence in most of the special features of the deflection function and collision cross sections. Inclusion of the short-range

polarisability terms were determined to be introducing most of the error since these are non-negligible only at small impact parameter where the impulse approximation breaks down; thus, their inclusion can only introduce more error. The $U^{(AC)}$ impulse approximation results of (2.104) for $\chi_{IA}^{(AC)}$ were shown to yield the poorest agreement of all, possibly due to the numerical evaluation of Bessel functions near their divergence. In predicting the collision cross sections, the static-field limit combined with the HDID-IA model provided far better agreement with the exact $d\sigma^{(AC)}/d\Omega$ and $\sigma^{(AC)}$ as functions of F . Overall, the impulse approximation is best suited to the analysis of small-angle scattering where it was shown for some select calculations to be accurate. Since the laser field F influences the order of magnitude of the potential energy relative to K , the validity of the impulse approximation breaks down as F is increased for a fixed K .

In contrast to the above, the use of the static field limit approximation, $F \rightarrow \sqrt{2} \cos \phi_c$, in conjunction with the IA model of $U^{(HFL)}$ was useful in predicting the qualitative behaviour of $U^{(AC)}$ for low frequencies. The values of $\langle \chi^{(AC)} \rangle_{\phi_c}$ and $\sigma_{RMS, \chi^{(AC)}}$ agree well with their static field limit values; this agreement persists through the special features of the deflection function to the collision cross sections (the HDID-IA model) given above; the fact of its success recommends it for use in further work.

5.4 Problems, Perspectives and Prognostications

The deficiencies of the present work are essentially diagnostic in nature. However, there are two methodological problems: in the analysis of orbital scattering and the evaluation of the differential cross sections. The latter arises in the calculation of $d\sigma^{(AC)}/d\Omega$ where there are many narrow rainbow singularities. The uniform sampling of scattering angles used in the present investigation is not sufficiently high in resolution to reveal the singularities. A

larger sample size (smaller spacing in between sample points) does improve this but at the cost of computational effort¹. A more efficient method to accurately evaluate $d\sigma^{(AC)}/d\Omega$ is necessary which might involve non-uniform sampling with increased resolution around rainbow singularities, the zeros of $\chi^{(AC)}(b)'$. An altogether different method for evaluating the cross section might be more efficient; for example direct determination of the Fourier coefficients of $d\sigma^{(AC)}/d\Omega$ as described in [200–202]. A more accurate quadrature method for averaging over ϕ_c , as is required in $d\sigma^{(AC)}/d\Omega$, may also improve results.

The problem of orbital scattering is more complex. The accurate determination of an orbiting singularity in the deflection function requires the tools of non-linear dynamical analysis. In particular a means of identifying efficiently the regular and irregular hyperbolic fixed points in the phase space of the collision system is required in order to characterise orbiting [269, 288]. Within the limitations of the method used in the present work, some improvement in identifying orbiting singularities might be obtained by increasing the sampling of impact parameters in the evaluation of the deflection function; this would prevent “passing over” the narrow spike in χ near the orbiting impact parameter. A more stringent set of parameters for distinguishing orbiting could then be used (see section 3.4).

The present work has demonstrated a number of qualitative relationships between the laser-induced potential features and the observables of a molecular beam experiment. However, the quantification of these novel relationships remains to be done; thus this work may be regarded as a first step in establishing a standard interpretation of features in the collision cross sections such as the one which exists for isotropic potentials. While determining the behaviour of system observables as a function of laser parameter provides an indirect correlation between the potential features and experiment, a quantitative relationship must

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¹More specifically, 1800 sample points, used in the present calculations, requires ~ 1 s while 180000 sample points leads to a cross section calculation of ~ 1 hr. See chapter 3.

be established before this work can be regarded as complete. This could be accomplished in a number of ways: first, the functional behaviour of the signatures of the collision mechanisms with respect to the magnitude of potential features can be determined numerically and subsequently codified through empirical fitting laws. Alternatively, a slightly simplified model would allow for the scaling of the Hamiltonians to reflect the corresponding states within the laser field, e.g. internuclear separation and energy scaled by the equilibrium geometry and radial well depth of the laser-diatom system, respectively. With this scaling, shape-differences of different molecular systems would also be better defined.

The analytic models employed in the present work have only a limited applicability. With regard to the potential features/observables correlations discussed above, it is also necessary to further develop approximation methods in order to quantify the conditions of validity for the different collision mechanisms in addition to the quantitative prediction of collision cross sections. The impulse approximation used in the present work should be sufficient to describe barrier scattering since it is a large impact parameter phenomenon. However, a higher order of perturbation to χ_{IA} is required to reproduce the exact behaviour. In particular, it was shown that the leading term in the long-range potential, the R^{-3} polarisability anisotropy, does not contribute in the impulse approximation; higher perturbation orders (i.e. those larger than $O(K^{-2})$) would correct this. The remaining collision mechanisms are not predicted by the impulse approximation and hence a new approximation scheme must be developed. Such analysis would involve the generalisation of the series method of Smith et al. [192] to anisotropic potentials. Additionally, the conditions for orbiting in such potentials must be derived, if possible.

While only systems of the type $RgRg'$ have been studied, particularly HeAr, it is felt that the potential features and their dynamical consequences (the collision mechanisms) are

generic to diatomic systems. This can be argued on the basis of the general nature of the potential and polarisability models used. However, it is reasonable to test the transferability of the collision mechanisms to qualitatively different classes of molecular systems. These classes would include: systems with covalent bonds which have a different long-range behaviour than the van der Waals-type potential studied here; diatoms with non-negligible dipole moments, particularly the effects in $U^{(AC)}$; molecules which also had stronger field-dependence in the isotropic part of the potential would also be of interest.

Accomplishment of the above tasks would complement the present investigation and allow some general, yet quite fully quantified, statements to be made regarding two-atom scattering within strong IR fields. As it stands, the qualitative conclusions drawn make a strong argument for IR fields having a significant impact on intermolecular motion. For instance in considering atom-diatom collisions, a zeroth-order picture which neglects the internal structure of the diatom naturally leads to identical dynamics as those studied here. The implications for such a system would be that pre-exponential factors of collision-related rates, which generally depend on σ , would be increased by the application of the field. Knowledge of the intermolecular dynamics might also allow a reduction in the initial condition phase space when examining these more complex systems.

Further work which might also enlarge the relevance of the type of collision system studied presently, both fundamentally and in its applications, is the examination of laser pulse effects. Calculations of the simple fluid properties of the laser-molecule system, e.g. viscosity using the Chapman-Cowling method, could also provide alternative experimental methods for characterising the system. A system parameter not explored in this work was the relative orientation of the field polarisation vector with the initial momentum vector, fixed to be anti-parallel here. Variation of this parameter could be used to establish

new correlations. A complementary study of this system using semi-classical and fully quantum mechanical methods should be undertaken to make direct predictions of experimental results. However, the qualitative conclusions obtained from the present work will serve as the basis for any such analysis.

The choice to investigate theoretically/computationally the conditions of a molecular beam + laser experiment was made on the basis of the method being sensitive to laser-induced potential features. However, it is also important to note that the addition of the laser to such an experimental apparatus does not present a significant alteration of the molecular beam experiment. Since the RgRg' examined in appendix B show that the rare-gas dimers all have essentially the same laser-modified potential (in scaled form), all are equally useful for exhibiting the effects outlined in section 5.2. Thus the only basis for choice of a molecular system is that it should not have collision conditions (K, F, Ω) which present technical obstacles. The results of table A.2 (appendix A) show that experimental conditions for Ar₂ fit these requirements best. The lower limit of the collision energy range $K \in [.1, 10]$ corresponds to a beam temperature of $T = 15.319$ K which is accessible using liquid Helium (ca. 4 K), implying that mid- to low- K dynamics could be investigated with standard molecular beam techniques. Table A.2 shows that a CO₂ laser intensity of $I = 7.16 \times 10^{13}$ W/cm² corresponds to $F = 3$, which yields an ionisation lifetime of approximately 2.3 ns; this peak laser intensity is well below the limits of CO₂ laser capabilities while the ionisation lifetime estimate of the Ar₂ molecule implies that all collisions will occur between the neutral species except in the case where an orbiting complex forms (i.e. with an infinite collision lifetime).

From the above considerations the $d\sigma^{(\text{HFL})}/d\Omega$ of figures 4.48–4.50 “predict”² the re-

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²Neglecting quantum effects and the symmetry of the differential cross section for identical particle scattering; the latter complicates the interpretation of the cross section but can be avoided by isotopic labelling.

sults for Ar₂ with centre of mass collision energies of 1258, -119.9 and -257.8 °C, respectively (after scaling the scattering intensities by a factor of 14.1 Å²). Similarly, the integrated cross sections of figure 4.56 reproduce $\sigma^{(\text{HFL})}$ for Ar₂ at these collision energies: scaling shows that at -257.8 °C the integrated cross section rises from ca. 409 Å² at $I = 0$ to a maximum of 451 Å² at $I = 3.68 \times 10^{13}$ W/cm²; the minimum cross section occurs at $I = 7.16 \times 10^{13}$ W/cm², where $\sigma^{(\text{HFL})} \approx 388$ Å². The total variation of 63 Å² is well within the detection limits of experiment. Thus the proposed experiment allows the observation of many new laser-induced dynamic effects with only a small extension of existing techniques; hence the possibilities of this area of research can be explored today and need not be confined only to theoretical examinations.

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Appendix A

Physical Constants and Conversion Factors

The present appendix contains physical constants used in the calculations. Although all numerical work was conducted using either the reduced units of chapter 2 or atomic units, as in appendix B, the values of the fundamental constants shown in table A.1 were used to derive the conversion factors between the two and are thus shown for the reader's convenience. Conversion between the reduced units for the quantities of τ , b , K , Ω and F to more common measures is accomplished with the help of table A.2; these factors were derived from the formulae of chapter 2 using the data for $R_g R_{g'}$ ($R_g, R_{g'} = \text{He, Ne, Ar}$) given in appendix B in atomic units. The subsequent conversion to SI, etc. made use of the data in table A.1. Note that F may be expressed as an intensity (TW/cm^2 in the table) and this factor applies to F^2 .

Constants [†]	Conversion Factors
$\pi \approx 3.141592653589793238462643^{\ddagger}$	E_h to J: $4.359748226 \times 10^{-18}$
Planck's constant, $h = 6.626075540 \times 10^{-34}$ J·s	E_h to eV: 27.211396181
a.m.u. = $1.660540210 \times 10^{-27}$ kg	E_h to cm^{-1} : 219474.6306726
Avogadro's number, $N_A = 6.022136736 \times 10^{23}$	E_h to kcal/mol: 627.5095
Boltzmann constant, $k_b = 1.38065812 \times 10^{-23}$ J/K	E_h to K: 3.15773327×10^5
Speed of light, $c = 2.99792458 \times 10^8$ m/s	eV to cm^{-1} : 8065.541024
Fine structure constant, $\alpha^{-1} = 4\pi\epsilon_0\hbar c/e^2 = 137.035989561$	eV to kcal/mol: 23.06035
Permittivity of a vacuum, $\epsilon_0 = 1/(4\pi \times 10^{-7} c^2) = 8.854187817 \times 10^{-12}$ C/Vm	kJ/mol to eV: 1.0364272×10^{-2}
Bohr radius, $a_0 = 0.52917724924$ Å	cal to J: 4.184
Electron charge, $e = 1.6021773349 \times 10^{-19}$ C	a.m.u to m_e : 1822.888530
Electron mass, $m_e = 9.109389754 \times 10^{-31}$ kg	
Proton mass/electron mass, $m_p/m_e = 1836.15270137$	
Neutron mass/electron mass, $m_n/m_e = 1838.68366240$	
Conversion Factors for Atomic Units to SI.	
a.u. to fs: $2.41888435 \times 10^{-2}$	
a.u. to ms^{-1} : 2.1876914×10^6	
a.u. to kgms^{-1} : 1.992853×10^{-24}	
a.u. to kgms^{-2} : 8.2387295×10^{-8}	
a.u. to C m: $8.478357919 \times 10^{-30}$	
a.u. to Debye: 2.541745	
a.u. to V m^{-1} : $5.142208246 \times 10^{11}$	
a.u. of intensity to W cm^{-2} : 3.5094476×10^{16}	

[†] Constants taken from [289].

[‡] From [276].

Table A.1: The fundamental physical constants and a number of conversion factors between SI and atomic units. Also given are a number of conversion factors between different energy units. All conversion factors are multiplicative. $E_h = e^2/4\pi\epsilon_0 a_0$ denotes a Hartree. All values calculated directly from fundamental constants. Note that intensity is related to field strength by $I = (1/2)c\epsilon_0|\mathcal{E}_0|^2$ (SI) and $I = (\alpha^{-1}/8\pi)|\mathcal{E}_0|^2$ (a.u.).

RgRg'	$\tau(\text{ps})^\dagger$	$b(\text{\AA})^\ddagger$	$K^\S$		$\Omega(\text{cm}^{-1})^\P$	(a.u./100)	(MV/cm)	$F^\P$
			(meV)	(K)				
He ₂	1.404	2.959	0.926	11.97	3.77	2.281	117.3	18.25
HeNe	1.476	3.091	1.524	19.71	3.59	2.258	116.1	17.89
HeAr	1.512	3.563	2.106	27.23	3.51	1.634	84.0	9.36
Ne ₂	1.811	3.136	3.129	40.45	2.93	2.390	122.9	20.03
NeAr	1.749	3.491	5.540	71.62	3.03	1.857	95.5	12.09
Ar ₂	1.576	3.755	11.850	153.19	3.37	1.507	77.5	7.96

[†] See equation (2.15).

[‡] See equation (2.15) and discussion of page 39.

[§] See discussion of page 39.

[¶] See equation (2.24).

Table A.2: Conversion factors from the reduced units of chapter 2 (column headings) to more common measures. All conversion formulae and symbols are defined in chapter 2 and the factors given are multiplicative. Model parameter data for the RgRg' dimers are given in appendix B. Conversion factors between atomic and SI units are given in table A.1. Note that the last column shows the corresponding intensity factor for F^2 in TW/cm².

Appendix B

Determination of Molecular Parameters

This appendix contains material on the process of determining the values of the parameters used in the molecular model of the present work. The models are reviewed, numerical methods described and the results of the non-linear, least-squares fit are given. The final result of a set of scaled molecular parameters for the rare gas dimers $RgRg'$ ($Rg, Rg' = \text{He, Ne, Ar}$) are presented and it is shown that the degree of similarity is such that only HeAr and He_2 are necessary for detailed study.

B.1 Diatom Models

As described in section 2.1.2, the pertinent functions are the field-free diatom potential $V_0(R)$, the permanent dipole moment function $d(R)$, the polarisability trace $\alpha(R)$ and anisotropy $\beta(R)$. The model functions and their parameters are given by

$$V_0(R) = D \left(\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right) \quad (\text{B.1a})$$

$$d(R) = \lambda_d e^{-R/R_d} - \frac{D_7}{R^7} \quad (\text{B.1b})$$

$$\alpha(R) = \frac{A_6}{R^6} - \lambda_\alpha e^{-R/R_\alpha} \quad (\text{B.1c})$$

$$\beta(R) = \frac{B_3}{R^3} + \frac{B_6}{R^6} - \lambda_\beta e^{-R/R_\beta} . \quad (\text{B.1d})$$

Thus the set of parameters which define the molecular system are D , R_0 , D_7 , R_d , A_6 , λ_α , R_α , B_3 , B_6 , λ_β and R_β .

According to the scaling of the parameters described in section 2.1.2, the dimensionless analogues of the parameters of (B.1) are

$$Q = \frac{D_7}{\sqrt{DB_3R_0^{11}}} , \quad \gamma_d = \frac{R_0}{R_d} , \quad \Lambda_d = \frac{\lambda_d R_0^7}{D_7} , \quad (\text{B.2a})$$

$$\Lambda_{\alpha_1} = A_6 B_3^{-1} R_0^{-3} , \quad \Lambda_{\alpha_2} = \lambda_\alpha B_3^{-1} R_0^3 , \quad \gamma_\alpha = \frac{R_0}{R_\alpha} , \quad (\text{B.2b})$$

$$\Lambda_{\beta_1} = B_6 B_3^{-1} R_0^{-3} , \quad \Lambda_{\beta_2} = \lambda_\beta B_3^{-1} R_0^3 , \quad \gamma_\beta = \frac{R_0}{R_\beta} . \quad (\text{B.2c})$$

It remains to find the parameters of (B.1) for RgRg' and by (B.2) the reduced set of molecular parameters for these systems.

B.2 Numerical Methods

The model parameters of section B.1 are obtained from fitting data sets derived from available literature; in the case of the field-free potentials $V_0(R)$, elaborate semi-empirical functions are available [214, 290–293], while permanent dipole [232, 234] and polarisability [241, 294, 295] data are obtained from tabulated ab initio values. For $V_0(R)$, the highly accurate semi-empirical functions were coded and used to generate large sets of data ($N=101, 101, 101, 69, 101, 101$ for He_2 , HeNe , HeAr , Ne_2 , NeAr and Ar_2 , respectively) as input for the fitting procedure. The uniformly sampled range in all cases was approximately

$R \in [5, 10]$ bohr; the exact range used was determined by experiment based on the well depth obtained. In all cases, fewer points were used on the inner repulsive wall in order to obtain an accurate well depth.

In fitting the permanent dipole moments of HeNe, HeAr and NeAr, the tabulated ab initio data were fit to (2.16) with the values of D_7 fixed according to the recommended literature value [229]; this was done to account for the presence of the long-range term in the fit even though the data contained no points in this range. Such a procedure is in keeping with previous modelling of the dipoles of the rare-gas dimers [234].

For the polarisability functions $\alpha(R)$ and $\beta(R)$, the tabulated ab initio data for the homonuclear dimers was fit to (2.17) directly. Initial estimates of the parameters were obtained from inspection of the data sets and use of the DID values for the coefficients in the model (2.18). No data for the polarisability of heteronuclear dimers was found. Consequently, the values of A_6 , B_3 and B_6 were estimated using the DID model formulae with “atomic” polarisabilities determined from (2.18) using the polarisability parameters obtained from the constituent homonuclear dimers¹. The exchange term parameters were estimated from the mean values of the corresponding scaled parameters (2.20) of the homonuclear dimers.

The determination of all parameters was done using the Marquardt-Levenberg iterative method for non-linear, least-squares fitting; the source code for this is given in the nonlin program (see appendix I). The basic algorithm is described elsewhere [279] but the relevant details of the nonlin program are that analytic derivatives were used for every model function fit and the convergence criterion was defined as minimum 200 iterations followed

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¹The actual values of the atomic polarisabilities were not used since these do not produce accurate values of the long-range coefficients in the homonuclear dimers.

by the first iteration where the change in χ^2 is zero². Variation of the minimum number of iterations was found to have no effect on the results.

In all the parameters determined from the non-linear, least squares method, unweighted data sets were used. In some cases statistical weighting was tried but did not consistently improve the quality of the fit. For unweighted data, the uncertainties of the resulting parameters were derived from the diagonal elements of the covariance matrix and weighted with an additional factor of $\sqrt{\chi^2/v}$, where χ^2 is the final chi-squared value and v is the number of statistical degrees of freedom in the fit. This tends to reduce the reported uncertainties but assumes that the chi-squared probability is unity, making an independent assessment of this impossible. This correction is standard practice for non-linear fitting of data [279]. The resulting deviations of the model from the data points were used to calculate the central moments of the errors: the mean absolute deviation and standard deviation of the errors were determined from these results using standard methods [279]. In calculating the scaled parameters of the system, standard error propagation methods were used to determine the uncertainties of the scaled parameters from those of the unscaled ones.

B.3 Numerical Results

In presenting and discussing the fit results for each diatomic property, the quantities used to evaluate the accuracy of the fit are (for a property $f(x)$): absolute deviation of the errors $A\text{Dev}(\Delta f)$, root mean square deviation (standard deviation) $\sigma_{\text{RMS}, \Delta f}$ and the data point of maximum deviation $(x, f, \Delta f)_{\text{max}}$.

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²N.B.: The value of χ^2 is defined as the merit function of the fit, which is minimised [279], and should not be confused with the deflection angle χ .

RgRg'	Parameters (a.u.)		Ref.
	D	R_0	
He ₂	$0.3404(-4) \pm 0.1445(-6)$	$0.5591(+1) \pm 0.2922(-2)$	[293]
HeNe	$0.5602(-4) \pm 0.3386(-6)$	$0.5841(+1) \pm 0.1715(-2)$	[214]
HeAr	$0.7741(-4) \pm 0.4681(-6)$	$0.6733(+1) \pm 0.2419(-2)$	[214]
Ne ₂	$0.1150(-3) \pm 0.9341(-6)$	$0.5927(+1) \pm 0.4756(-2)$	[292]
NeAr	$0.2036(-3) \pm 0.1638(-5)$	$0.6597(+1) \pm 0.4134(-2)$	[290]
Ar ₂	$0.4355(-3) \pm 0.2584(-5)$	$0.7096(+1) \pm 0.2310(-2)$	[291]

Table B.1: Parameters for the potentials RgRg' (Rg,Rg' = He, Ne, Ar) using a Lennard-Jones (6,12) model (2.14). The results for the well depth D and minimum geometry R_0 are reported in atomic units. The parameters were obtained from fitting highly accurate semi-empirical potential functions from the reference indicated. Details of the procedure are described in B.2. Numbers in parentheses denote the appropriate powers of ten.

RgRg'	ADev(ΔV)	$\sigma_{\text{RMS},\Delta V}$	R_{max}	V_{max}	ΔV_{max}
He ₂	0.4934(-6)	0.6180(-6)	0.570(+1)	-0.3466(-4)	-0.1025(-5)
HeNe	0.8296(-6)	0.1204(-5)	0.482(+1)	0.2084(-3)	-0.3845(-5)
HeAr	0.1117(-5)	0.1515(-5)	0.660(+1)	-0.7936(-4)	-0.3196(-5)
Ne ₂	0.2865(-5)	0.3506(-5)	0.524(+1)	0.2971(-4)	0.7245(-5)
NeAr	0.3893(-5)	0.5203(-5)	0.660(+1)	-0.2140(-3)	-0.1044(-4)
Ar ₂	0.1244(-4)	0.1403(-4)	0.950(+1)	-0.1175(-3)	-0.2064(-4)

Table B.2: Analysis of fitting RgRg' potentials to (2.14). Parameters are given in tables B.1. The average absolute deviation ADev(ΔV), root mean square deviation $\sigma_{\text{RMS},\Delta V}$ and the data point of maximum deviation $(R, V, \Delta V)_{\text{max}}$ are reported in atomic units.

B.3.1 Field-Free Potential Parameters

For the rare gas dimers, a number of highly accurate potential functions are available in the literature which are based on empirical fits to a large set of experimental and theoretical data [214, 290–293]. For the six rare gas dimers, the results of non-linear fitting of (2.14) to these higher quality functions are shown in table B.1. Details of the procedure are described in section B.2. In spite of the simplicity of the fitting function, the overall quality of the results appears to be high; this is established by examination of some of the indicators shown in table B.2. The table shows ADev(ΔV), $\sigma_{\text{RMS},\Delta V}$ and the point

$(R, V(R), \Delta V)_{\max}$. From the data, it appears that Ar_2 has the poorest overall fit since both $\text{ADev}(\Delta V)$ and $\sigma_{\text{RMS}, \Delta V}$ are largest. However, these are still an order of magnitude lower than the corresponding value of D in table B.1. The point of maximum deviation is very close to the minimum in all cases, indicating that the problems with the fit are in this region³. This is confirmed by inspection of figure B.1 which shows the data sets scaled by the R_0 and D values of table B.1 appropriate to each system. The scaled model potential, U_0 , is generated from (2.14) and shown as a solid line. In all systems, the position of the minima are reproduced well by the model (all are approximately unity). The well depths for these potentials appear to be underestimated by the model; in addition, the outer walls of the potentials rise more quickly than allowed by the fitting function, indicating that there are stronger repulsive forces in the true potential at this range. However, in all cases these deviations are small enough (less than 10%) that (2.14) sufficiently describes (both qualitatively and quantitatively) the potentials of these systems for the purposes of the present work.

B.3.2 Diatom Permanent Dipole Parameters

The permanent dipole moments of the heteronuclear rare gas dimers, HeNe , HeAr and NeAr were fit to (2.16) from ab initio data that describes the short-range part of the dipoles [232, 234] (details are given in B.2). Thus, λ_d and R_d were obtained from this data while the values of D_7 were fixed to their values as given from perturbation theory [229]. The results of the fitting are given in table B.3. The results are in agreement with previous determinations of similar models of these systems [232, 234]. The analysis of the fit is given in

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³If more points were included from the inner wall of the potentials, the largest deviations occur in this region.

Figure B.1: Comparison of the fit of (2.14) to the potential functions of $R_g R_{g'}$ ($R_g, R_{g'} = \text{He, Ne, Ar}$). Symbols indicate data points of the actual potentials scaled by the appropriate R_0 and D values found from table B.1: circles — He_2 ; squares — HeNe ; diamonds — HeAr ; up-triangles — Ne_2 ; left-triangles — NeAr ; down-triangles — Ar_2 . Solid line shows (2.14). All results are in dimensionless units with the separated atom limit taken as zero. Numerical details are given section B.2.

RgRg'	Parameters (a.u.)		
	λ_d	R_d^{-1}	D_7^a
HeNe ^b	0.3608(+2) $\pm$ 0.8120	0.2429(+1) $\pm$ 0.1101(-1)	0.8840(+1)
HeAr ^c	0.2101(+2) $\pm$ 0.4036(+1)	0.1430(+1) $\pm$ 0.4115(-1)	0.1250(+3)
NeAr ^c	0.4771(+2) $\pm$ 0.2944(+1)	0.1460(+1) $\pm$ 0.1482(-1)	0.2000(+3)

^a From reference [229].

^b Data from reference [232].

^c Data from reference [234].

Table B.3: Results of non-linear, least-squares fitting of the permanent dipole moments of HeNe, HeAr, NeAr to (2.16). The values of the parameters λ_d , R_d and D_7 are reported in atomic units. References for the data sets are given in the table. Note that the values of D_7 were constrained in the fit to those of [229]. The polarity of the dipoles is such that the heavier atoms correspond to the positive end of the dipole. Details of the fit are given in B.2.

RgRg'	ADev(Δd)	$\sigma_{\text{RMS}, \Delta d}$	R_{max}	d_{max}	Δd_{max}
HeNe	0.1761(-3)	0.2974(-3)	0.300(+1)	0.2125(-1)	0.5607(-3)
HeAr	0.2294(-3)	0.2983(-3)	0.500(+1)	0.1530(-1)	0.4161(-3)
NeAr	0.3550(-3)	0.4603(-3)	0.600(+1)	0.6100(-2)	-0.6514(-3)

Table B.4: Analysis of fitting RgRg' dipoles to (2.16). Parameters are given in tables B.3. The average absolute deviation ADev(Δd), root mean square deviation $\sigma_{\text{RMS}, \Delta d}$ and the data point of maximum deviation $(R, d, \Delta d)_{\text{max}}$ are reported in atomic units.

table B.4 and the results are displayed in figure B.2. The values of the absolute mean and standard deviations are both much lower than typical values of the dipole for all three systems. The maximum deviations occur for values of R where the dispersion term becomes large. This is a result of constraining the values of D_7 and the lack of damping of the dispersion term in (2.16). It would appear that the inclusion of the dispersion term reduces the accuracy of the dipole; however, work in collision-induced absorption experiments shows that the D_7 term is necessary in order to reproduce the spectrum [150, 234].

From figure B.2, it is interesting to note that the scaled form of the dipole moment function shows a difference between the results for HeNe and the remaining two dimers, the latter being larger. In general, the dipole does not take on very large values until $X \lesssim 0.7$,

Figure B.2: Comparison of the fit of (2.16) to the dipole moment functions of $RgRg'$ ($Rg, Rg' = \text{He, Ne, Ar}$). Symbols indicate ab initio data points scaled according to (2.23) with the appropriate R_0 and B_3 values from tables B.1 and B.7. Lines show the scaled model function $d(X)$ with the parameters of table B.3 scaled according to (2.22). Symbol/line-style pairs show: circles/solid — HeNe; squares/dashed — HeAr; diamonds/dotted-dashed — NeAr. The inset shows the long-range portion of the dipoles as determined from perturbation theory [229]. Numerical details are given section B.2.

	Parameter value for RgRg' (a.u.)		
	He ₂ ^a	Ne ₂ ^b	Ar ₂ ^c
A_6	0.1291(+3)±0.4046(+1)	0.5069(+3)±0.2337(+2)	0.2528(+5)±0.1477(+4)
λ_α	0.3277(+2)±0.9010	0.6803(+2)±0.3706(+1)	0.4196(+3)±0.1913(+2)
R_α^{-1}	0.1558(+1)±0.3564(-2)	0.1401(+1)±0.7894(-2)	0.1061(+1)±0.3692(-2)
	HeNe ^d	HeAr ^d	NeAr ^d
A_6	0.2625(+3)±0.7535(+1)	0.2552(+4)±0.9703(+2)	0.4367(+4)±0.1724(+3)
λ_α	0.4607(+2)±0.1373(+1)	0.1044(+3)±0.2743(+1)	0.1643(+3)±0.6413(+1)
R_α^{-1}	0.1456(+1)±0.4428(-2)	0.1206(+1)±0.2512(-2)	0.1200(+1)±0.4168(-2)

^a Data from [241].

^b Data from [294].

^c Data from [295].

^d Estimated from (2.18) and (2.20) using homonuclear values.

Table B.5: Parameters for fitting RgRg' polarisability traces (Rg,Rg' = He, Ne, Ar) using (2.17). All parameter values given in atomic units. In all fits, the separated atom limit is set to zero. Numbers in parentheses denote appropriate powers of ten. Details of the fitting and estimation of the parameters for the heteronuclear dimers are given in B.2.

where the U_0 potential is large (cf. figure B.1); however, the variation in the region of $X \in [0.7, 1.0]$ may still be of significance. The inset of the figure shows that the minimum in the dipole moment caused by the dispersion term is larger for HeNe but is not of a sufficiently high magnitude to be significant.

B.3.3 Diatom Polarisability Parameters

The results of fitting (2.17) to the trace polarisability data of the homonuclear rare gas dimers are shown in table B.5. The $\{A_6, \lambda_\alpha, R_\alpha^{-1}\}$ are reported in atomic units with the appropriate reference to the original data set. The data sets have been zeroed against the separated atom limit since this plays no role in the field-induced effects on the potential. Immediately it is evident that the dispersion term A_6 is at least one order of magnitude greater than the exchange term λ_α , implying that the former term contributes at smaller internuclear separations. The values of A_6 for the heteronuclear dimers are estimated from

Rg_2	$A\text{Dev}(\Delta\alpha)$	$\sigma_{\text{RMS},\Delta\alpha}$	R_{max}	α_{max}	$\Delta\alpha_{\text{max}}$
He ₂	0.1314(−3)	0.1587(−3)	0.700(+1)	0.1890(−3)	−0.3090(−3)
Ne ₂	0.3044(−3)	0.3872(−3)	0.800(+1)	0.2000(−3)	−0.8088(−3)
Ar ₂	0.2820(−2)	0.3516(−2)	0.100(+2)	0.8070(−2)	−0.6834(−2)

Table B.6: Analysis of fitting Rg_2 ($Rg = \text{He, Ne, Ar}$) polarisability traces to (2.17). Parameters are given in tables B.5. The average absolute deviation $A\text{Dev}(\Delta\alpha)$, root mean square deviation $\sigma_{\text{RMS},\Delta\alpha}$ and the data point of maximum deviation $(R, \alpha, \Delta\alpha)_{\text{max}}$ are reported in atomic units. Numbers in parentheses denote appropriate powers of ten.

combining the homonuclear A_6 values of the table using (2.18)(c) (see section B.2).

The quantitative accuracy of the parameters of table B.5 is summarised in table B.6 which shows the same indicators as table B.2 for the potential fitting. Here, the model (2.17) tends to overestimate the value of $\alpha(R)$ for large R as is evidenced by the negative values of the maximum deviation $\Delta\alpha_{\text{max}}$ which occur at $R > R_0$ for all systems. This is demonstrated in figure B.3, which shows the results of the fit compared to the ab initio data of the Rg_2 systems as a function of internuclear separation. All the data (given by symbols) are scaled by the appropriate value of R_0 and B_3 from tables B.1 and B.7 according to (2.19) with the separated atom values of $\alpha(X)$ taken as zero. Lines in the figure show the model fitting function (2.17) with the parameters of table B.5 scaled with the same values of R_0 and B_3 according to (2.20). The figure shows that the trace functions of the three different systems are all of the same order of magnitude. The other main feature is that the trace does not take on large values until $X \lesssim 0.8$, where U_0 is very large (cf. figure B.1). The quality of the fit appears to be least accurate at $R > R_0$, or $X > 1$, as shown in the inset of the figure; this is confirmed by the values of R_{max} in table B.6. However, given the small magnitude of the trace at these distances, the overall fit is sufficiently accurate for the present work.

Using the same ab initio data sets, the polarisability anisotropies $\beta(R)$ were fit to (2.17) for He₂, Ne₂, and Ar₂. The results, shown in table B.7 have large exchange terms in

Figure B.3: Results of fitting polarisability traces of Rg_2 ($\text{Rg} = \text{He}, \text{Ne}, \text{Ar}$) to the model function of (2.17) as a function of internuclear distance. All results are reported in dimensionless units zeroed against the separated atom limit; the ab initio data points (symbols) were scaled according to (2.19) with appropriate values of R_0 and B_3 from tables B.1 and B.7. The model functions $\alpha(X)$ (lines) were found from scaling the parameters of table B.5 according to (2.20). Symbol/line-style pairs show: circles/solid — He; squares/dashed — Ne; triangles/dotted-dashed — Ar. The inset shows the long-range portion of $\alpha(X)$. Numerical details are given section B.2.

	Parameter value for RgRg' (a.u.)		
	He ₂ ^a	Ne ₂ ^b	Ar ₂ ^c
B_3	0.1143(+2)±0.1358	0.4191(+2)±0.4559	0.6848(+3)±0.5979(+1)
B_6	0.1797(+3)±0.1655(+2)	0.1269(+4)±0.7202(+2)	0.8583(+5)±0.4543(+4)
λ_β	0.4394(+2)±0.4084(+1)	0.2408(+3)±0.1487(+2)	0.2018(+4)±0.1035(+3)
R_β^{-1}	0.1498(+1)±0.1915(-1)	0.1456(+1)±0.1166(-1)	0.1124(+1)±0.4195(-2)
	HeNe ^d	HeAr ^d	NeAr ^d
B_3	0.2188(+2)±0.1763	0.8846(+2)±0.6523	0.1694(+3)±0.1182(+1)
B_6	0.5032(+3)±0.2605(+2)	0.6192(+4)±0.2954(+3)	0.1312(+5)±0.5122(+3)
λ_β	0.1026(+3)±0.5442(+1)	0.2500(+3)±0.1224(+2)	0.6635(+3)±0.2782(+2)
R_β^{-1}	0.1456(+1)±0.1094(-1)	0.1214(+1)±0.8272(-2)	0.1258(+1)±0.5783(-2)

^a Data from [241].

^b Data from [294].

^c Data from [295].

^d Estimated from (2.18) and (2.20) using homonuclear values.

Table B.7: Parameters for fitting RgRg' polarisability anisotropies (Rg,Rg' = He, Ne, Ar) using (2.17). All parameter values given in atomic units. Parameters for the heteronuclear dimers are estimated from (2.18)(a) and (b), and (2.20) by combining the homonuclear coefficients. Numbers in parentheses denote appropriate powers of ten. Details of the fitting and estimation procedure are given in section B.2.

analogy with the results for the trace (cf. values in table B.5). The large uncertainty in B_6 is due to a correlation between B_3 and B_6 , demonstrated by the large correlation matrix element between the two (not shown). The usual indicators of the fit quality are given in table B.8. Here the larger deviations of the model from the data occur at $R \approx R_0$ (seen from the $(R, \beta, \Delta\beta)_{\max}$ results). At these distances, the R^{-6} DID-term becomes large and uncertainties in B_6 have an effect. Since both the mean absolute deviation and the standard

Rg	ADev($\Delta\beta$)	$\sigma_{\text{RMS}, \Delta\beta}$	$R_{\max}$	$\beta_{\max}$	$\Delta\beta_{\max}$
He	0.2609(-3)	0.3330(-3)	0.400(+1)	0.1120	-0.6177(-3)
Ne	0.3368(-3)	0.4788(-3)	0.600(+1)	0.1834	0.8636(-3)
Ar	0.2879(-2)	0.3606(-2)	0.150(+2)	0.2176	0.7269(-2)

Table B.8: Analysis of fitting Rg₂ polarisability anisotropies to (2.17). Parameters are given in tables B.7. The average absolute deviation ADev($\Delta\beta$), root mean square deviation $\sigma_{\text{RMS}, \Delta\beta}$ and the data point of maximum deviation $(R, \beta, \Delta\beta)_{\max}$ are reported in atomic units. Numbers in parentheses denote appropriate powers of ten.

deviation of the errors are both many orders of magnitude smaller than the value of $\beta(R)$, the results in the table indicate a good fit by (2.17).

The ab initio data sets used are shown in figure B.4 (symbols in figure). The corresponding model anisotropies of (2.17) using the parameters of table B.7 are shown as lines. In the figure, all results have been scaled to the dimensionless units; in the case of the ab initio data, the scaling is described in (2.19) using R_0 values of table B.1 and B_3 values of table B.7. The model functions $\beta(X)$ were obtained by scaling the parameters of table B.7 using the same R_0 values according to (2.20).

Qualitatively, the fit of (2.17) to the anisotropies seems accurate with no obvious deviations being apparent. The results for Ne_2 are qualitatively different from the other two rare gas dimers in the presence of the dip at short X . While the dip may be an artefact of the fitting, the ab initio data used do show that the anisotropy of the neon dimer does not increase at short R . The scaling of the $\beta(R)$ functions to dimensionless units again demonstrates the similarity between the dimer systems. The long-range portion of the anisotropy is larger than any other interaction term for these systems (cf. figure B.2 and B.3) while the short-range portion $X \sim 1$ takes on significant values (i.e. unity).

Using the parameters from tables B.1, B.5 and B.7, and the parameter scalings defined in (2.20), the scaled parameters for the model Hamiltonian (2.27) are shown in table B.9. Note that all the uncertainties of the parameters reported are less than 10%. Once scaled, all parameters are on the same order of magnitude for all the systems except for Λ_{β_2} , where Ne_2 and Ar_2 are larger than that of He_2 . The Rg_2 systems should thus exhibit very similar behaviour with respect to field dependence as their parameters are very similar. In comparison of the relative magnitude of the permanent dipoles and polarisabilities, it is clear from the values of Q in the table that the dipoles are quite small and should have little influence

Figure B.4: Results of fitting polarisability anisotropies of Rg_2 ($Rg = \text{He, Ne, Ar}$) to the model function of (2.17). All results are reported in dimensionless units zeroed against the separated atom limit; the ab initio data points (symbols) were scaled according to (2.19) with appropriate values of R_0 and B_3 from tables B.1 and B.7. The model functions $\beta(X)$ (lines) were found from scaling the parameters of table B.7 according to (2.20). Symbol/line-style pairs show: circles/solid — He_2 ; squares/dashed — Ne_2 ; triangles/dotted-dashed — Ar_2 . Numerical details are given section B.2.

	Parameter Value for RgRg' (dimensionless)			
	He ₂		Ne ₂	Ar ₂
Λ_{α_1}	0.6466(-1) $\pm$ 0.2169(-2)	0.5810(-1) $\pm$ 0.2756(-2)	0.1033	$\pm$ 0.6103(-2)
Λ_{α_2}	0.5014(+3) $\pm$ 0.1504(+2)	0.3379(+3) $\pm$ 0.1879(+2)	0.2189(+3) $\pm$ 0.1017(+2)	
γ_{α}	0.8713(+1) $\pm$ 0.2044(-1)	0.8302(+1) $\pm$ 0.4726(-1)	0.7527(+1) $\pm$ 0.2632(-1)	
Λ_{β_1}	0.8997(-1) $\pm$ 0.8355(-2)	0.1455 $\pm$ 0.8414(-2)	0.3507 $\pm$ 0.1882(-1)	
Λ_{β_2}	0.6723(+3) $\pm$ 0.6299(+2)	0.1196(+4) $\pm$ 0.7505(+2)	0.1053(+4) $\pm$ 0.5477(+2)	
γ_{β}	0.8375(+1) $\pm$ 0.1071	0.8629(+1) $\pm$ 0.6943(-1)	0.7973(+1) $\pm$ 0.2988(-1)	
	HeNe		HeAr	NeAr
Λ_{α_1}	0.6019(-1) $\pm$ 0.1795(-2)	0.9452(-1) $\pm$ 0.3662(-2)	0.8978(-1) $\pm$ 0.3602(-2)	
Λ_{α_2}	0.4197(+3) $\pm$ 0.1203(+2)	0.3602(+3) $\pm$ 0.9076(+1)	0.2784(+3) $\pm$ 0.1068(+2)	
γ_{α}	0.8507(+1) $\pm$ 0.2574(-1)	0.8120(+1) $\pm$ 0.1666(-1)	0.7914(+1) $\pm$ 0.2705(-1)	
Λ_{β_1}	0.1154 $\pm$ 0.6046(-2)	0.2294 $\pm$ 0.1107(-1)	0.2697 $\pm$ 0.1071(-1)	
Λ_{β_2}	0.9343(+3) $\pm$ 0.4899(+2)	0.8625(+3) $\pm$ 0.4174(+2)	0.1124(+4) $\pm$ 0.4645(+2)	
γ_{β}	0.8502(+1) $\pm$ 0.6384(-1)	0.8174(+1) $\pm$ 0.5562(-1)	0.8301(+1) $\pm$ 0.3779(-1)	
Q	0.1536(-1) $\pm$ 0.8123(-4)	0.4208(-1) $\pm$ 0.2172(-3)	0.3355(-1) $\pm$ 0.2128(-3)	
Λ_d	0.9473(+6) $\pm$ 0.2141(+5)	0.1054(+6) $\pm$ 0.2026(+5)	0.1297(+6) $\pm$ 0.8026(+4)	
γ_d	0.1419(+2) $\pm$ 0.6445(-1)	0.9629(+1) $\pm$ 0.2771	0.9635(+1) $\pm$ 0.9797(-1)	

Table B.9: Scaled parameters for the dipole and polarisability models of the RgRg' systems (Rg,Rg' = He, Ne, Ar). The values used were taken from tables B.1, B.3, B.5 and B.7. All data reported here are dimensionless, with the scalings defined in (2.20) and (2.22). Numbers in parentheses denote powers of ten.

on the laser-induced potentials of these systems. In particular, there should be virtually no effect in the limit of high laser frequency since the dipole term in (2.27) is proportional to $(FQ/\Omega)^2$. However, in a time-dependent system, the large short-range part of the dipole (given by Λ_d) may produce a dynamical effect.

The marked similarity between the parameters of table B.9 suggests that it is redundant to analyse each of the six systems (see also figures B.1–B.4). The essential features of the laser-induced potential surfaces and dynamics of the $RgRg'$ dimers can be studied effectively by considering only two representative systems, one homonuclear and one heteronuclear dimer. While some differences in the relative magnitude of the short-range dipoles and polarisabilities of the systems are neglected in doing this, there is not a sufficient difference in the orders of magnitude of these terms to warrant a more comprehensive study. Therefore only He_2 and $HeAr$ need be retained as quantitative examples; the latter is chosen as the representative heterodimer since it possesses the largest scaled dipole moment as shown in figure B.2.

Appendix C

Limits for Parameters in Calculations

This appendix describes the theoretical considerations, numerical methods and results used to determine the appropriate limits on the dynamical and laser parameters required for the calculations of the present work. The basic aim of this appendix is to arrive at a reasonable range of parameters such that they lie within the realm of experimental possibility. See chapters 1 and 2 for further details.

C.1 Estimation Methods

The parameters which specify the laser-diatom system within the quasi-static approximation and the present model are given in table 2.1. While the parameters connected with the molecular properties are derived from comparison with real systems, those which specify the laser and the initial conditions of the collision are constrained to lie in ranges determined by the requirement that conditions resemble those of a molecular beam experiment in conjunction with a CO₂ laser. For the present model, F , Ω and K are the parameters which are restricted. In this section, expressions are derived for the appropriate upper

and/or lower bounds on each of these parameters which incorporate the experimental constraints. The results are also useful in that they provide an appropriate order-of-magnitude estimate for the dimensionless (and unfamiliar) units used presently.

C.1.1 Dynamic Initial Conditions

The initial conditions of the collision system (X_{dist}, b, K) are defined in section 2.1.4. There is no restriction on the impact parameter except that it is positive. The value of X_{dist} is required for trajectory calculations: not only as an estimate of where to start the system but also to obtain an idea of the time of a collision. Since the collision system is assumed to be prepared initially at infinite separation with energy K , the value of X_{dist} must be such that the potential at that point is approximately zero. The value of the potential can be evaluated using the leading asymptotic term of (2.27). This depends on the field and the molecular parameters. If $F = 0$, $U = U_0 \sim -2X^{-6}$ and the requirement that $U \leq U_T$, where U_T is some tolerance energy (set as a fraction of the collision energy K), gives

$$X_{\text{dist}} \geq X_0 = |2/U_T|^{1/6}. \quad (\text{C.1})$$

The value of X_0 defines the equality of $U \leq U_T$. The potential term in the high frequency limit arising from the dipole is largest along $\theta = 0$. In order to obtain a simple expression for the asymptotic form, it is noted that $U_{\text{iso},d}^{(\text{HFL})} + U_{\text{aniso},d}^{(\text{HFL})} \sim 49(FQ/2\Lambda_d\Omega)^2 X^{-16}$ which is always bounded from above by FQX^{-7} (for $X \gg 1$)¹. Thus the potential condition gives

$$X_{\text{dist}} \geq X_d = |FQ/U_T|^{1/7}. \quad (\text{C.2})$$

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¹N.B.: Thus the estimate is also correct for the c.w.-field case.

The leading term in the polarisability is that of the anisotropy, $U_{\text{aniso},\alpha}^{(\text{HFL})} \sim -F^2/6X^3$. Rearranging this gives

$$X_{\text{dist}} \geq X_{\alpha} = |F^2/6U_T|^{1/3}. \quad (\text{C.3})$$

The value of X_{dist} is therefore the largest of these possible values

$$X_{\text{dist}} \gg \max\{X_0, X_d, X_{\alpha}\}. \quad (\text{C.4})$$

Note that this solution has both F - and K dependence implicitly in the $\{X_0, X_d, X_{\alpha}\}$ (the latter via $U_T \equiv \epsilon K$ with $\epsilon \ll 1$).

The collision energy K must be greater than zero for a scattering system. An upper bound on K is established from the validity of the high-frequency limiting form of the Hamiltonian as stated in appendix H in equation (H.27). The kinetic energy is limited such that the change in the potential over the period of the laser is small compared to a characteristic energy scale. This means that high energy systems cannot be regarded as time-independent because the time scale of “significant” motion is the same as that of the laser. The upper bound on K can be estimated from finding the energy change per laser period $2\pi/\Omega$ as a function of K .

The characteristic energy scale from section 2.1.1 is $E_0 = D$ (D is the well depth of the field-free potential) and hence is unity once scaled. An expression that relates Ω and K is found from expanding the potential U as a Taylor series in τ ; this should be valid since $\Omega \gg 1$ by assumption. The variation of U should be largest when the motion goes through a turning point since the forces are large in magnitude there. Thus a second order expansion

is required and the left side of equation (H.27) becomes

$$\begin{aligned}\Delta U &= U(\tau_0 + 2\pi/\Omega) - U(\tau_0) \\ &\approx \frac{1}{2} \left. \frac{d^2 U}{d\tau^2} \right|_{\tau=\tau_0} (2\pi/\Omega)^2.\end{aligned}\tag{C.5}$$

Here τ_0 indicates a turning point in the motion (i.e. where the kinetic energy is zero). The second derivative is evaluated using Poisson brackets and noting that both components of the momenta are zero, giving [266]

$$\left. \frac{d^2 U}{d\tau^2} \right|_{\tau=\tau_0} = - \left[\left(\frac{\partial U}{\partial X} \right)^2 + \frac{1}{X^2} \left(\frac{\partial U}{\partial \theta} \right)^2 \right].\tag{C.6}$$

The possible turning points are defined by $U(X, \theta) = K$ and the ones where the gradients are largest for the diatomic system are at the inner repulsive wall. At this short range, the potential is dominated by the repulsive term in U_0 and is thus independent of the field and θ . Thus, at the turning point, $U \approx X^{-12} = K$ and

$$\left. \frac{d^2 U}{d\tau^2} \right|_{\tau=\tau_0} \approx -144K^{13/6}.\tag{C.7}$$

This yields an estimate of ΔU and the condition of validity of $H^{(\text{HFL})}$ becomes, via (H.27)

$$K \ll \left(\frac{\Omega}{12\sqrt{2}\pi} \right)^{12/13}.\tag{C.8}$$

The result (C.8) imposes an upper bound on K in terms of the laser frequency Ω . This result is conservative since not all collisions sample the repulsive part of the potential and hence the forces encountered are smaller in magnitude. For very large F , (C.8) is probably not valid since variations in the potential may occur which are larger than that experienced

at an inner turning point. However, in such a case limitations imposed on F due to the amplitude size and tunnelling ionisation prevent the collision system from entering the regime in which the field dependence in (C.8) manifests itself.

C.1.2 Laser Parameters

The laser parameters F and Ω are restricted by three conditions: non-resonance, the amplitude of the field-induced oscillations and tunnelling ionisation. For non-resonance, the laser frequency must not match any electronic transition from the ground state over the portion of the potential surface sampled by the motion. Since the systems considered here are assumed to be in their ground electronic state, the approximation is satisfied if Ω is much less than the transition frequency to the first excited state. Thus

$$\omega_c \ll \omega_{if} ,$$

or in scaled units,

$$\Omega \ll \Omega_{if} . \tag{C.9}$$

Here Ω_{if} is the electronic transition frequency between the field-free ground and first electronic excited states. This provides an upper bound on Ω which is independent of F or K . In general Ω_{if} is a function of X for a diatomic system but its order of magnitude is found from the transition frequency of the separated atoms². Thus Ω_{if} for $X = \infty$ is sufficient to establish an estimated upper bound on Ω .

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²N.B.: This assumes that the molecular electronic states considered are not degenerate at the separated atom limit. Only systems where this is valid will be considered.

The validity of the high frequency Hamiltonian (2.27) is dependent on the amplitudes of the laser-induced oscillations in (X, θ) being small in comparison with their characteristic scales (see appendix H). The amplitudes are given by expressing (H.26) in terms of scaled units:

$$\xi_{X,d} = -\frac{F}{\Omega^2} d' \cos \theta \quad (\text{C.10a})$$

$$\xi_{X,\alpha} = -\frac{F^2}{32\Omega^2} \left(2\alpha' + \beta' \left(\frac{1}{3} + \cos 2\theta \right) \right) \quad (\text{C.10b})$$

$$\xi_{\theta,d} = \frac{F}{\Omega^2 X^2} d \sin \theta \quad (\text{C.10c})$$

$$\xi_{\theta,\alpha} = \frac{F^2}{16\Omega^2 X^2} \beta \sin 2\theta \quad (\text{C.10d})$$

An estimate is now required of the value of each amplitude over the motion of the system.

Each of the amplitudes in (C.10) is a function of the coordinates. The (X, θ) which maximises the absolute value of each amplitude is required to obtain an upper bound. In the case of θ , the optimum angle sets the trigonometric terms in (C.10) to unity. For X , the model functions used in (2.27) have large values at $X \sim 1$. In all the model interaction functions, there is an unphysical singularity at $X = 0$. Since in the real interaction functions the dispersion term is not present at short distances, these maxima at the origin are ignored. Hence, an upper bound on the amplitudes of the strong-field induced oscillations can be found in terms of the molecular parameters using $X = 1$. Thus, for $|\xi_{X,d}|$,

$$\begin{aligned} |\xi_{X,d}| &\leq \frac{F}{\Omega^2} |d'| \\ &\approx \frac{F}{\Omega^2} |d'(1)| \\ &= \left| \frac{F}{\Omega^2} Q(7 - \gamma_d \Lambda_d e^{-\gamma_d}) \right|, \end{aligned} \quad (\text{C.11a})$$

and similarly,

$$|\xi_{X,\alpha}| \leq \left| \left(\frac{F}{4\Omega} \right)^2 \left(\Lambda_{\alpha_2} \gamma_{\alpha} e^{-\gamma_{\alpha}} + \frac{2}{3} (\Lambda_{\beta_2} \gamma_{\beta} e^{-\gamma_{\beta}} - 3(1 + 2\Lambda_{\beta_1})) \right) \right|, \quad (\text{C.11b})$$

$$|\xi_{\theta,d}| \leq \left| \frac{F}{\Omega^2} Q(\Lambda_d e^{-\gamma_d} - 1) \right|, \quad (\text{C.11c})$$

$$|\xi_{\theta,\alpha}| \leq \left| \left(\frac{F}{4\Omega} \right)^2 (1 + \Lambda_{\beta_1} - \Lambda_{\beta_2} e^{-\gamma_{\beta}}) \right|. \quad (\text{C.11d})$$

The characteristic length scales of X and θ are both unity in this particular choice of units³. Thus, all amplitudes ξ must be much less than unity for $H^{(\text{HFL})}$ to be valid. Rearranging this result using (C.11a)–(C.11d) yields a condition for both F and Ω in terms of the molecular parameters:

$$\begin{aligned} \frac{F}{\Omega} \ll \min \bigg\{ & \Omega |Q(7 - \gamma_d \Lambda_d e^{-\gamma_d})|^{-1}, \Omega |Q(\Lambda_d e^{-\gamma_d} - 1)|^{-1}, \\ & 4 \left| \left(\Lambda_{\alpha_2} \gamma_{\alpha} e^{-\gamma_{\alpha}} + \frac{2}{3} (\Lambda_{\beta_2} \gamma_{\beta} e^{-\gamma_{\beta}} - 3(1 + 2\Lambda_{\beta_1})) \right) \right|^{-1/2}, \\ & 4 |(1 + \Lambda_{\beta_1} - \Lambda_{\beta_2} e^{-\gamma_{\beta}})|^{-1/2} \bigg\}. \end{aligned} \quad (\text{C.12})$$

From (C.12), an upper bound on F can be obtained as a function of Ω . This does not represent a serious restriction on F since Ω may be adjusted to ensure the validity of the approximation.

An upper limit to the field strength which is independent of the laser frequency is found from considering tunnelling ionisation. Since the laser field is a continuous wave, the system will eventually ionise given enough time in any non-zero field. However, the dynamics of the neutral system can be examined if the collision is over and the two atoms are es-

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³See section 2.1.1. Note that θ is in radians.

entially isolated. The condition which permits this is $\tau_{\text{coll}} < \tau_{\text{ion}}$, where τ_{coll} is the time of collision and τ_{ion} is the ionisation lifetime of the system. The time of collision can be infinite in the case of an orbiting collision but a mean estimate can be obtained from the time required for the system to travel a distance $2X_{\text{dist}}$ when $U = 0$:

$$\tau_{\text{coll}} \approx \sqrt{\frac{2}{K}} X_{\text{dist}}, \quad (\text{C.13})$$

where X_{dist} is given by (C.4). Thus the collision time increases with F .

A simple estimate of the tunnelling ionisation lifetime is obtained from using only the exponential portion of the Delone formula [20, 263] (see also chapter 1). In dimensionless units, $\tau_{\text{ion}} \propto \tau_1 \exp((2/3)(2\Xi)^{3/2}/F)$, where $\tau_1 = \sqrt{D/\mu R_0^2}$ is an atomic unit of time scaled according to (2.15) and Ξ is the scaled atomic field of the system,

$$\Xi = \sqrt[3]{\frac{B_3}{D}} \left(\frac{I_p}{R_0} \right). \quad (\text{C.14})$$

Here I_p is the ionisation potential of the system and the remaining constants are defined in (2.17)). Using this result and the estimate of τ_{coll} gives the condition on the ionisation limit to F :

$$F \ll \frac{2}{3} (2\Xi)^{3/2} \left[\ln \left(\frac{X_{\text{dist}}}{\tau_1} \sqrt{\frac{2}{K}} \right) \right]^{-1}. \quad (\text{C.15})$$

The condition of (C.15) only defines F implicitly since X_{dist} is also a function of F and K from (C.4). It should be noted that (C.15) is applicable to either $H^{(\text{AC})}$ or $H^{(\text{HFL})}$ since the tunnelling ionisation lifetime is independent of the laser frequency.

It can be seen from the forms of the limits on the initial conditions and laser parameters

of the system (equations (C.4), (C.8), (C.9), (C.12) and (C.15)) that the appropriate ranges of F , Ω and K are interrelated. While it may be possible to simplify these relationships to obtain an expression for the appropriate volume of parameter space (Ω, F, K) , it is more straightforward to examine their behaviour numerically for the systems to be studied. In the case of $H^{(AC)}$, the only limitations are (C.4), (C.9) and (C.15).

C.2 Numerical Methods

The determination of the limits of Ω , K and F were done by evaluation of the relevant expressions (C.9), (C.8), (C.8) and (C.15). The only expression which requires more than a simple function evaluation is that of the ionisation limit (C.15); the corresponding upper bound of F was found from the numerical roots of the equality of the condition (C.15). Root-finding was performed using Ridder's method [279] with the root being bracketed (approximately) first; further details of this are described in the `fionlim` program (see appendix I). The calculation requires an estimate of X_{dist} which was determined from (C.4) with a value of $U_T = K/1000$, a typical value at which dynamical calculations (see section 3.2) are performed.

C.3 Numerical Results

Details of the subsequent calculations are given in section C.2. The values of the parameters required and their corresponding scaled values are given in table C.1. For τ_1 (defined on page 314), the values of table B.1 may be used in conjunction with the appropriate reduced masses (4, 20, 40 a.m.u. for He, Ne and Ar, respectively⁴). While only He₂ and

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⁴It is assumed that the proton and neutron mass is approximately 1 a.m.u.

RgRg'	$\tau_1/10^{-4}$	$\Omega_{if}/10^5$	Ξ	$\Omega_{\text{CO}_2}/10^3$
He ₂	0.172201	0.447393	0.112303(+2)	0.264891
HeNe	0.163775	0.374075	0.991714(+1)	0.278207
HeAr	0.159921	0.271805	0.899301(+1)	0.284912
Ne ₂	0.133547	0.458746	0.955041(+1)	0.341178
NeAr	0.138230	0.314457	0.825703(+1)	0.329620
Ar ₂	0.153461	0.283247	0.949090(+1)	0.296905

Table C.1: Parameters required for the estimation of the limits to K , F , and Ω in order to ensure the validity of the Hamiltonian (2.27) for the systems RgRg' (Rg, Rg' = He, Ne, Ar). All values are dimensionless quantities: τ_1 , Ω_{if} and Ξ are defined in (2.15) (see also page 314), (C.9) and (C.14), respectively. See section C.2 for further details.

HeAr are pertinent to the present work, the parameters of the remaining systems are given for completeness.

The value of Ω_{if} is obtained from the lowest excitation energy of the constituent atoms. This corresponds to the molecular excitation energy at the separated atom limit and provides the correct order of magnitude of the real adiabatic transition. The atomic wavelengths are 591.412, 743.720, 1048.22 Å for He, Ne and Ar, respectively [289]. Similarly, the value of Ξ is obtained from the atomic ionisation potentials I_p ; the values used for the Rg systems are 24.58741, 21.56454 and 15.75962 eV for He, Ne and Ar. The values of B_3 needed are taken from table B.7. The value of Ω_{CO_2} is the carrier frequency of the CO₂ laser in scaled units for each system ($\sim 1000 \text{ cm}^{-1}$ [289]).

The restrictions on the validity of $H^{(\text{HFL})}$ provide an upper bound on the collision energy through (C.8). This is shown in figure C.1, where the maximum K is given as a function of laser frequency Ω . For a CO₂ laser, $\Omega \sim 300$ for all the RgRg' systems (see table C.1). This gives an upper bound on K of approximately 10 from figure C.1 (squares denote Ω_{CO_2}). While this is not a very large collision energy, it is accessible experimentally for these systems, corresponding to approximately 107 K and 244 K for He₂ and

Figure C.1: Upper bound on the collisional energy K as a function of laser frequency Ω based on (C.8) (solid line). Circles shown are the values of Ω_{if} while squares show Ω_{CO_2} from table C.1 for all $RgRg'$ systems.

HeAr, respectively.

An upper bound for the laser frequency Ω is present due to the condition of non-resonance; for the RgRg' systems, table C.1 gives the estimated excitation frequency for the lowest electronic state. The table shows that the values are very high compared to the frequency of nuclear motion and thus a wide range of Ω is possible for these systems. In particular, the values of Ω_{CO_2} are much less than Ω_{if} (cf. circles vs. squares in figure C.1); this implies that the condition of non-resonance is satisfied for Ω_{CO_2} . In order to make use of $H^{(\text{HFL})}$, a lower bound on Ω is required from the condition that the laser frequency be much larger than the harmonic frequency of the field-free potential⁵. The harmonic frequency of U_0 is found to be $6\sqrt{2} \approx 8.5$. Thus the choice of $\Omega = \Omega_{\text{CO}_2}$ also satisfies the conditions of validity of the high-frequency limit.

Tunnelling ionisation places an upper bound on the field strength which is parametrically dependent on the collision energy K through the implicit equation of (C.15). Figure C.2 shows the results of (C.15) (using (C.4) to obtain X_{dist}) for all six rare gas dimers. The roots of the non-linear equation are found using the model parameters for the dimers from tables B.9 and C.1. The value of U_T chosen was $K/1000$ with further numerical details described in section C.2 of chapter 3. The figure shows a strong dependence on K . For a value of $K = 10$, the maximum field allowed is $F \approx 4$ for HeAr while He₂ has a corresponding maximum of $F \approx 5.5$. For lower collision energies, this limit falls to $F \approx 3$. Thus, the upper bound due to ionisation is estimated to be $F \lesssim 3$ in order to be conservative (i.e. to allow collision times to be larger than estimated by (C.13)). This also allows the same range of collision energies to be studied for all field strengths. It should be noted that the limit of F due to ionisation is required for both $H^{(\text{AC})}$ or $H^{(\text{HFL})}$ calculations but in the

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⁵This is the “characteristic frequency of motion” of appendix H.

Figure C.2: The upper bound on the field strength F as a function of collision energy K to account for tunnelling ionisation as estimated from (C.15). The roots of (C.15) are found using (C.4) with a value of $U_T = K/1000$. Parameters for the RgRg' systems are taken from tables B.9 and C.1. Further numerical details are found in C.2. Solid line — He₂; dotted — HeNe; short dashed — HeAr; long dashed — Ne₂; dash-dotted — NeAr; dash-multiple-dotted — Ar₂.

latter case, additional restrictions on F also exist.

The size of the laser-induced amplitudes (C.12) create an upper bound on the ratio of F/Ω , which furnishes an additional lower bound on Ω and an upper bound on F . For He_2 and HeAr , use of the parameters of table B.9 and (C.12) give,

$$\frac{F}{\Omega} \ll 3.707, \quad (\text{C.16a})$$

for He_2 while for HeAr ,

$$\frac{F}{\Omega} \ll \begin{cases} 0.398\Omega & , \Omega \lesssim 8.894 \\ 3.536 & , \Omega \gtrsim 8.894 \end{cases}. \quad (\text{C.16b})$$

For a maximum field of $F = 3$, the lower bound on Ω obtained from (C.16) is generally smaller than the harmonic frequency. For $\Omega = \Omega_{\text{CO}_2}$, the maximum field obtained from this restriction is much larger than the value set by tunnelling ionisation. Thus for the RgRg' systems considered here, the amplitudes do not restrict the parameters K , Ω and F .

From the above results, in order to study the dynamics of He_2 and HeAr in the high-frequency limit of (2.27), the field is limited to the range of $F \in [0, 3]$ to prevent ionisation during the collision. The laser carrier frequency should be restricted to $\Omega \in (6\sqrt{2}, \Omega_{\text{CO}_2}]$ to ensure that the amplitudes of the field-induced oscillations are small and that there are no electronic resonances along the collision path. The collisional energy K is limited to the interval $K \in [0.10, 10]$, the lower limit being determined by ionisation and the upper limit by (C.8). In the case of dynamics outside the high-frequency limit, there is no restriction on K (except indirectly through ionisation) or Ω . The field strength should be in the same range as the high-frequency limit but $\Omega \lesssim 6\sqrt{2}$ since higher frequencies in $U^{(\text{AC})}$ produce

the same results as $U^{(\text{HFL})}$.

Appendix D

The Geometric Relationship Between χ and the Dynamical Variables

The relationship between the deflection angle χ and the dynamical variables of the trajectory position (X, θ) ¹ for two-body scattering (see chapter 2) has been presented in the literature [206] but its derivation and limitations of validity are not available². The relationship is derived from the construction shown in figure D.1. The path of the system is shown as the dashed line in the figure. The scattering centre is located at the origin of the coordinate system O. The restriction on the nature of the potential is that there is only one scattering centre located at the origin O. In the case where the coordinate system origin is not taken to be coincident with the scattering centre, additional correction formulae are required to obtain agreement with the results derived presently.

The relationship between the trajectory path and the construction of figure D.1 is a requirement of the line segments $\overline{BC}$ and $\overline{AB}$ being coincident with the lines describing

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¹The following results are identical for scaled or unscaled coordinate systems. Presently, the scaled system is used in keeping with the notation developed in chapter 2.

²To the best of the author's knowledge.

Figure D.1: Geometric construction describing a trajectory in a single-centre scattering potential. Pertinent angles are labelled as in the text. The dashed line shows a trajectory with the scattering centre at O.

the asymptotic paths at $\tau = +\infty$ and $\tau = -\infty$, respectively. Their point of intersection, B, is arbitrary aside from the assumption that it exists. The points A and C are chosen such that they are arbitrarily close to the asymptotic paths of the trajectory, viz for some initial (X_i, θ_i) and final (X_f, θ_f) points on the trajectory, $|\overline{OC}| \approx X_i$ and $|\overline{OA}| \approx X_f$. The coordinate system is completely defined by constructing $\overline{OR} \parallel \overline{BC}$; thus $\angle COR = \theta_i$ and $\angle AOR = \theta_f$. Finally, the line $\overline{OS}$ is constructed to be parallel to $\overline{AB}$ and by definition $\angle SOA = \delta$.

The deflection angle χ of the trajectory is defined as $\pi - \angle ABC$. It is trivial to show, using the parallel line theorem [296], that

$$\chi = \pi - (\theta_f + \delta) . \quad (D.1)$$

The value of δ can be expressed in terms of θ_i which is assumed to be known (as are $X_{i,f}$ and θ_f). As $\overline{OS} \parallel \overline{AB}$ and $\overline{OR} \parallel \overline{BC}$, δ and θ_i are given by $\angle OAB$ and $\angle OCB$, respectively. Using the cosine law on $\triangle AOB$ and $\triangle COB$ and the fact that these triangles share $\overline{OB}$ gives

$$\begin{aligned} \cos \delta = & \frac{|\overline{OA}|^2 + |\overline{AB}|^2 - |\overline{OC}|^2 - |\overline{BC}|^2}{2|\overline{OA}||\overline{AB}|} \\ & + \frac{|\overline{OC}||\overline{BC}|}{|\overline{OA}||\overline{AB}|} \cos \theta_i . \end{aligned} \quad (D.2)$$

This results is valid for any triangle, including the case where $|\overline{OB}| = 0$.

In the case of a central potential, the trajectory is symmetric around the distance of closest approach and this reflection symmetry line is coincident with $\overline{OB}$ [266]. Thus, if A and C are chosen such that they are related by reflection, $\triangle AOB \cong \triangle COB$ [296] and (D.2) reduces to $\cos \delta = \cos \theta_i$. Substitution into (D.1) gives

$$\chi = \pi - (\theta_f + \theta_i) \text{ (central potential, } X_i = X_f\text{)}. \quad (D.3)$$

Here, the reflection symmetry relation requires that the initial and final points be such that $X_i = X_f$ but are otherwise arbitrary. In fact, if $\theta_i = \theta_f$ then this is the angle of closest approach which is the basis of the standard formulation of χ [266].

When the potential is anisotropic, no symmetry relation exists between A and C. The exact definition of the deflection angle is found from allowing the point A to be extended along the line of final asymptotic path. Thus

$$\lim_{\{|\overline{AB}|, |\overline{OA}|\} \rightarrow \infty} \cos \delta = 1, \quad (\text{D.4})$$

giving the value of χ to be

$$\chi = \pi - \theta_{+\infty}. \quad (\text{D.5})$$

This equation (identical to (2.59)) is valid also for a central potential. The only restriction is that θ_f be evaluated at $\tau_f = +\infty$. While (D.5) is formally correct, a numerically more useful approximation is derived by considering the limit as both A and C are extended. If the points are chosen such that $X_i = X_f$ then by the construction, $|\overline{OA}| \approx |\overline{OC}|$ and (D.2) becomes

$$\cos \delta \approx \frac{|\overline{AB}|}{2|\overline{OA}|} - \frac{|\overline{BC}|^2}{2|\overline{OA}||\overline{AB}|} + \frac{|\overline{BC}|}{|\overline{AB}|} \cos \theta_i. \quad (\text{D.6})$$

Taking the limit of (D.6) gives

$$\lim_{\{|\overline{OA}|, |\overline{AB}|, |\overline{BC}|\} \rightarrow \infty} \cos \delta = \cos \theta_i, \quad (\text{D.7})$$

since the length of the line segments must increase proportionally in accord with the restric-

tion that $X_i = X_f$. Substitution of this result gives an approximate form of the deflection angle for finite time-points:

$$\chi \approx \pi - (\theta_f + \theta_i) \quad (\text{non-central potential, } X_i = X_f), \quad (\text{D.8})$$

where it is required that $X_i = X_f$ and both initial and final points are in the asymptotic regions of the trajectory (i.e. $X_{i,f}$ are both very large).

The results (D.3), (D.5) and (D.8) show that the deflection angle can be derived from knowledge of the polar angle θ . Since θ can take any value, a deflection angle calculated in this way can reflect orbiting around the scattering centre O.

Appendix E

Derivation of the Integrated Collision Cross Section

The integrated cross section $\sigma(\zeta)$ is commonly given for the case of a central potentials typical to stable diatomic molecules and it is known a priori that the deflection function gives rise to three impact parameter terms [131, 184, 191, 199]. Metastable potentials can give rise to more than three terms and this more generalised result has been presented [200]. The derivation of these expressions for $\sigma(\zeta)$ is not forthcoming in the literature and no expression has been presented for an arbitrary deflection/scattering function. Direct numerical integration of the differential cross section (see section 2.4.2, equation (2.60)) is not always advisable since the presence of rainbow singularities make quadrature difficult [198, 200–204]. This appendix therefore derives an expression for $\sigma(\zeta)$ in terms of the impact parameter for the general case and shows that this reduces to the special case of the results presented in the literature¹.

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¹N.B.: Presently, the dependence of the differential cross section on ϕ_c does not affect the results since the averaging over any initial conditions which are not spatial coordinates can be done after any manipulations [199]. Hence the inclusion of ϕ_c in the notation is dispensed with and the observed cross section is actually

The generalised form of the integrated cross section is obtained from integration over all the branches of the differential cross section. In the following derivation, it is assumed that the scattering function $\Theta(b)$ (see (2.55) of section 2.4.1) is continuous (but not piecewise continuous) and independent of the azimuthal angle since this changes the definition of the differential cross section [199]. In this case, the differential cross section is given by (2.60)²

$$\frac{d\sigma}{d\Omega} = \sum_{k=1}^{N(\zeta)} b_k(\zeta) \csc \zeta \left| \left(\frac{\partial \Theta}{\partial b} \right) \right|_{b=b_k(\zeta)}^{-1} \quad (\text{E.1})$$

where the scattering function $\Theta(b)$ is defined in (2.55) for the domain of b and fixed values of other parameters. The angle of scattering is $\zeta \in [0, \pi]^3$. In general, there will be $N(\zeta)$ impact parameters which give rise to a given scattering angle, and hence the summation over all $b_k(\zeta)$ contributions to the differential cross section.

The integrated cross section $\sigma(\zeta)$ is defined by

$$- \int_{\zeta}^{\pi} d\sigma = \int_{\Omega} \left(\frac{d\sigma}{d\Omega} \right) d\Omega, \quad (\text{E.2})$$

where it is implicit that the collision energy K and other system variables are constant. The minus sign is introduced in order to obtain a positive value of the cross sectional area. Since the value of $\sigma(\pi) = 0$,

$$\sigma(\zeta) = 2\pi \int_{\zeta}^{\pi} \sum_{k=1}^{N(\Theta)} b_k(\Theta) \left| \left(\frac{\partial \Theta}{\partial b} \right) \right|_{b=b_k(\Theta)}^{-1} d\Theta \quad (\text{E.3})$$

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the phase average of the result derived here.

²See section 2.4.2 for notation definitions.

³N.B.: The use of scaled or unscaled coordinates does not change the following results except for a scale factor of R_0^2 . This arises from the choice of expressing the impact parameter as a dimensionless quantity or not.

where the number of contributing branches is explicitly made a function of Θ . The value of $\sigma(\zeta)$ corresponds to the total scattering intensity for all angles greater than ζ .

The inverse of the scattering function, $b(\Theta)$, can have an arbitrary number of branches. Let each branch be denoted $b_k(\Theta)$ which is a function defined on the domain $[\Theta_{k,L}, \Theta_{k,U}] \subseteq [0, \pi]$. For any ζ , $M(\zeta)$ branches contribute to the cross section, i.e. if $[\Theta_{k,L}, \Theta_{k,U}] \cap [\zeta, \pi] \neq \emptyset$ then $b_k(\Theta)$ contributes. The total number of branches in $b(\Theta)$ is given by $M(0) \equiv M \geq 1$. The integrated cross section can now be written in terms of the contributions from each branch of $b(\Theta)$:

$$\sigma(\zeta) = 2\pi \sum_{k=1}^M \int_{\zeta}^{\pi} b_k(\Theta) \left| \left(\frac{\partial \Theta}{\partial b} \right) \right|_{b=b_k(\Theta)}^{-1} \times h(\Theta - \Theta_{k,L}) h(\Theta_{k,U} - \Theta) d\Theta, \quad (\text{E.4})$$

where $h(x)$ denotes the Heaviside function [276].

For an arbitrary scattering function $\Theta(b)$, (E.4) is the simplest form that can be used in the calculation of $\sigma(\zeta)$. In what follows, it is assumed that the scattering function $\Theta(b)$ is continuous⁴ and single-valued⁵ on $b \in [0, \infty)$. It follows from these two assumptions that the inverse scattering function $b(\Theta)$ must have the following properties:

1. Each branch $b_k(\Theta)$ is monotonic on its domain (single-valued Θ).
2. The branch k meets the branch $k+1$ ($k < M$) at a single point; similarly the k branch meets the $k-1$ ($k > 1$) branch at a single scattering angle. The $k=1$ branch meets

⁴The scattering function is continuous and its first derivative is minimally piecewise continuous. Cusps will exist due to the formal b -dependence of n in (2.55). The formal treatment of (E.4) is not affected by this since the principal value of the integral can always be taken. However, the numerical determination of $\sigma(\zeta)$ requires the sign of the derivative, which is undefined at these points. Thus, it is necessary to define the derivative as zero at these points.

⁵For three-dimensional systems, this assumption is not necessarily true since the scattering function is implicitly dependent on a number of dynamical parameters other than b [199, 278].

$b = 0$ and the $k = M$ branch meets $b = +\infty$ (Θ is continuous)⁶.

3. The continuity of $\Theta(b)$ requires that the signs of $d\Theta/db$ for each branch alternate.

The assumed properties of $\Theta(b)$ and the corollaries 1–3 result in inverse functions $b(\Theta)$ of the forms shown in figure E.1. These functions are typical of the type encountered in molecular scattering. Figure E.1(a) shows the case when the initial branch $b_1(\Theta)$ is monotonically increasing while E.1(b) shows the case where $b_1(\Theta)$ is monotonically decreasing.

The integration over scattering angle in (E.4) can be transformed one over impact parameter by noting that $|x| = x \operatorname{sgn}(x)$. From the assumed single-valued form of $\Theta(b)$ and corollary 1, the sign of the derivative of $d\Theta/db$ is constant over the k -th branch of $b(\Theta)$ and can be taken outside the integral. Without the absolute value, the derivative term in (E.4) defines a transformation between b and Θ . With this accomplished, the integral over each branch of $b(\Theta)$ can be done analytically and hence

$$\sigma(\zeta) = \pi \sum_{k=1}^{M(\zeta)} s_k (b_{k,U}^2 - b_{k,L}^2) . \quad (\text{E.5})$$

Here,

$$s_k = \operatorname{sgn} \left(\left(\frac{\partial \Theta}{\partial b} \right) \bigg|_{b=b_k(\Theta)} \right) \quad (\text{E.6a})$$

$$b_{k,U} = b_k(\min\{\Theta_{k,U}, \pi\}) \quad (\text{E.6b})$$

$$b_{k,L} = b_k(\max\{\Theta_{k,L}, \zeta\}) . \quad (\text{E.6c})$$

The result of (E.5) can be simplified even further (to a point amenable to numerical computations) by use of the properties 1–3 as these define recurrence relations for (E.6)

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⁶It is implied that the ordering of the branches is such that the range of $b_k(\Theta)$ is less than that of $b_{k+1}(\Theta)$.

Figure E.1: Schematic inverse functions of the scattering angle $\Theta(b)$ where it is assumed that the scattering functions are continuous (piecewise up to the first derivative) and single-valued, typical of molecular scattering. The branches of $b_k(\Theta)$ of the inverse are defined on the intervals $[\Theta_{k,L}, \Theta_{k,U}] \subseteq [0, \pi]$ (shown for b_1) are monotonic and alternately increasing and decreasing. Note that continuity of $\Theta(b)$ ensures that at least one of the recurrence relations (E.6) holds for each branch. Figure (a) shows the case when $s_1 = 1$ while (b) shows that of $s_1 = -1$.

which are illustrated in figure E.1. From 3, $s_k = -s_{k+1}$ or equivalently

$$s_k = (-1)^{k-1} s_1 . \quad (\text{E.7})$$

From corollary 2, a recurrence relation exists between $\Theta_{k,(U,L)}$ and $\Theta_{k+1,(U,L)}$. The conditions are determined by the value of s_1 and hence the cases illustrated in figure E.1(a) and (b) must be distinguished:

$$\Theta_{k,L} = \Theta_{k+1,L} \begin{cases} s_1 = +1 & , (k \bmod 2 = 0, k \in [2, 2\lfloor (M-1)/2 \rfloor]) \\ s_1 = -1 & , (k \bmod 2 \neq 0, k \in [1, 2\lfloor M/2 \rfloor - 1]) \end{cases} \quad (\text{E.8a})$$

$$\Theta_{k,U} = \Theta_{k+1,U} \begin{cases} s_1 = +1 & , (k \bmod 2 \neq 0, k \in [1, 2\lfloor M/2 \rfloor - 1]) \\ s_1 = -1 & , (k \bmod 2 = 0, k \in [2, 2\lfloor (M-1)/2 \rfloor]) \end{cases} \quad (\text{E.8b})$$

where $\lfloor x \rfloor$ denotes the integer value of x . The significance of (E.8) is that if $\Theta_{k,(U,L)}$ satisfies one of the recursion relations, then $b_{k,(U,L)} = b_{k+1,(U,L)}$ and the contribution to the integrated cross section by these two branch limits can be zero by (due to (E.7)). The cancellation of terms is dependent on whether $\Theta_{k,(U,L)} \in [\zeta, \pi]$.

In order to demonstrate the cancellation of terms, let

$$S_L = \sum_{k=1}^{M(\zeta)} (-1)^{k-1} b_{k,L}^2 \quad (\text{E.9})$$

$$S_U = \sum_{k=1}^{M(\zeta)} (-1)^{k-1} b_{k,U}^2 \quad (\text{E.10})$$

and $\sigma(\zeta) = s_1 \pi (S_U - S_L)$ by (E.5). In either sum, if two branches are such that $b_k(\Theta) = b_{k+1}(\Theta)$ then the alternating signs in $S_{(U,L)}$ ensure that there is no contribution from those

impact parameters. From (E.8), the recurrence relation holds between branches which are neither first nor last in $b(\Theta)$; this does hold for the first and last branches depending on $M(\zeta)$ being even or odd. For $b_{k,U}$, $\min\{\Theta_{k,U}, \pi\} = \Theta_{k,U}$. Thus $b_{k,U} = b_{k+1,U}$ for all k which satisfy (E.8). In the case of $b_{k,L}$, branches can contribute to S_L if they do not satisfy the recurrence relation (E.8) or $\max\{\Theta_{k,L}, \zeta\} = \zeta$, i.e. $\Theta_{k,L} \notin [\zeta, \pi]$. Therefore, the only non-zero terms in $S_{(U,L)}$ are:

$$S_U = \begin{cases} fb_{M,U}^2 & , s_1 = +1 \\ b_{1,U}^2 - (1-f)b_{M,U}^2 & , s_1 = -1 \end{cases} \quad (\text{E.11a})$$

$$S_L = \begin{cases} b_{1,L}^2 - (1-f)b_{M,L}^2 - \sum_{k \in \mathcal{A}^+} b_{k,L}^2 - b_{k+1,L}^2 & , s_1 = +1 \\ fb_{M,L}^2 + \sum_{k \in \mathcal{A}^-} b_{k,L}^2 - b_{k+1,L}^2 & , s_1 = -1 \end{cases} \quad (\text{E.11b})$$

where $f = M(\zeta) \bmod 2$, and the pairs of branch indices $(k, k+1)$ denote scattering angles $\Theta_{k,(U,L)} \in \mathcal{A}^\pm$. The sets are defined by:

$$\mathcal{A}^+ = \left\{ \Theta_{k,L} \left| \Theta_{k,L} = \Theta_{k+1,L}, s_1 = +1, k \bmod 2 = 0, \right. \right. \\ \left. \left. k \in \left[2, 2 \left\lfloor \frac{M-1}{2} \right\rfloor \right], \Theta_{k,L} < \zeta \right\}, \quad (\text{E.12a})$$

and

$$\mathcal{A}^- = \left\{ \Theta_{k,L} \left| \Theta_{k,L} = \Theta_{k+1,L}, s_1 = -1, k \bmod 2 \neq 0, \right. \right. \\ \left. \left. k \in \left[1, 2 \left\lfloor \frac{M}{2} \right\rfloor - 1 \right], \Theta_{k,L} < \zeta \right\}. \quad (\text{E.12b})$$

The results of $S_{(U,L)}$ show the form of the integrated cross section for a continuous,

single-valued scattering function. Numerically, the sets $\mathcal{A}^\pm$ are difficult to identify since the set $\{\Theta_{k,L}\}$ is not known a priori. However, it is possible to find the roots of $\Theta(b) = \zeta$ numerically; the results of which can contain roots which are not part of $\mathcal{A}^\pm$. These are degenerate roots which occur when $\zeta = \Theta_{k,L}$ where k satisfies (E.8). Since the two roots are equal, their contribution to S_L is zero. Additionally, roots of $\Theta(b) = \zeta$ which do not correspond to elements of $\mathcal{A}^\pm$ can arise for the $k = 1$ or $k = M$ branch. These cases can be distinguished from those roots in $\mathcal{A}^\pm$ by the value of $d\Theta/db$: if the root is degenerate, then the derivative will be zero at that point. By letting

$$s'_k = \begin{cases} -s_k & , (\partial\Theta/\partial b)|_{b=b_k(\zeta)} \neq 0 \\ 0 & , (\partial\Theta/\partial b)|_{b=b_k(\zeta)} = 0 \end{cases} \quad (\text{E.13})$$

the integrated cross section can be written in terms of the $N(\zeta)$ numerical roots of $\Theta(b) = \zeta$:

$$\begin{aligned} \sigma(\zeta)/\pi &= s_1 (S_U - S_L) \\ &= \begin{cases} fb_{M,U}^2 + (1-f)h(\Theta_{M,L} - \zeta)b_{M,L}^2 - h(\Theta_{1,L} - \zeta)b_{1,L}^2 \\ + \sum_{k=1}^{N(\zeta)} s'_k b_k^2(\zeta) & , s_1 = +1 \\ (1-f)b_{M,U}^2 - b_{1,U}^2 + fh(\Theta_{M,L} - \zeta)b_{M,L}^2 \\ + \sum_{k=1}^{N(\zeta)} s'_k b_k^2(\zeta) & , s_1 = -1 \end{cases} \quad (\text{E.14}) \end{aligned}$$

Here, the sum in each case runs over all the numerical roots of $\Theta(b_k) = \zeta$ ($N(\zeta) \leq M(\zeta)$, $f = M(\zeta) \bmod 2$). The Heaviside functions $h(x)$ have been introduced to (E.14) in order to prevent the double counting of the end branch terms.

The result of (E.14) still requires the knowledge of the branch structure of $b(\Theta)$ since

the end branch terms do not necessarily show up as roots of the equation $\Theta(b_k) = \zeta$. If the first and last branches of the function can be identified, then (E.14) furnishes the integrated cross section for any continuous, single-valued scattering function $\Theta(b)$. For the special case of scattering with molecular potentials, the end branch terms do not contribute due to the general form of the scattering function. For any potential with a short-range repulsive core, $\lim_{b \rightarrow 0} \Theta(b) = \pi$ while its asymptotic behaviour ensures that $\lim_{b \rightarrow \infty} \Theta(b) = 0$. From the former, it follows that $s_1 = -1$ while from the latter, $M(0)$ is odd. Thus $\zeta \geq \Theta_{M,L}$ and $b_{1,U} = 0$; the form of (E.14) which results contains the commonly quoted form of $\sigma(\zeta)$ as a special case:

$$\sigma(\zeta) = \pi \sum_{k=1}^{N(\zeta)} s'_k b_k^2(\zeta). \quad (\text{E.15})$$

Since M is odd, $N(\zeta)$ must also be an odd number never larger than M . This is identical with the $N(\zeta)$ used in (E.1). Equation (E.15) is identical with literature results [200]. For the case of a central potential which is not metastable (e.g. one that is a sum of attractive and repulsive forces), $N(\zeta) = 3$ for K above the orbiting energy limit and $\zeta < \Theta_r$; thus, (E.15) reduced to the commonly quoted expression for $\sigma(\zeta)$ (see e.g. [184]).

Appendix F

Evaluation of Integrals Occurring in the Impulse Approximation

The integrals evaluated in this chapter are used in the calculation of the deflection angle of the binary scattering of atoms in a strong laser field¹. However, they are of general interest since they contain forms of trigonometric functions which are not found in standard tables. Therefore, the derivation of their solutions are given in some detail. Although a general solution for arbitrary argument is too complex to develop for all integrals and is unnecessary for the present application, the methods applied for the relevant cases should suffice for determining any desired integral of the same type. Where possible, the general case is given or some remarks are made as to how such a solution would be obtained. Finally, some tables of results are presented for integrals which are required for the present application.

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¹The total energy and angular momentum changes within the impulse approximation can also be evaluated using the integrals of this appendix.

The integrals which occur in chapter 2 are defined as

$$\mathfrak{M}_{\{m,n\}}^{(1)} = \int_0^\pi \cos^m \theta \sin^n \theta d\theta \quad (\text{F.1a})$$

$$\mathfrak{M}_{\{m,n,z\}}^{(2)} = \int_0^\pi \cos^m \theta \sin^n \theta \exp(-z \csc \theta) d\theta \quad (\text{F.1b})$$

$$\mathfrak{M}_{\{m,n,p\}}^{(3)} = \int_0^\pi \cos^m \theta \sin^n \theta \exp(ip \cot \theta) d\theta \quad (\text{F.1c})$$

$$\mathfrak{M}_{\{m,n,p,z\}}^{(4)} = \int_0^\pi \cos^m \theta \sin^n \theta \exp(ip \cot \theta - z \csc \theta) d\theta . \quad (\text{F.1d})$$

As can be seen from (F.1), all integrals are special cases of $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ where one or both of $(z, p) = 0$. Each case is now discussed.

F.1 Case 1: $z = p = 0$

The first integral (F.1a), $\mathfrak{M}_{\{m,n\}}^{(1)} = \mathfrak{M}_{\{m,n,0,0\}}^{(4)}$, reduces to

$$\mathfrak{M}_{\{m,n\}}^{(1)} = (1 + (-1)^m) \int_0^{\pi/2} \cos^m \theta \sin^n \theta d\theta \quad (\text{F.2})$$

once the periodic properties of the trigonometric functions have been used. Thus, the integral is zero identically for all m odd.

The above integral defines an integral representation of the Beta function [276]

$$\begin{aligned} B(x, y) &\equiv 2 \int_0^{\pi/2} \cos^{2y-1} \theta \sin^{2x-1} \theta d\theta , \\ &= B(y, x) \\ &= \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)} \end{aligned} \quad (\text{F.3})$$

n	$\mathfrak{M}_{\{0,n\}}^{(1)}$	n	$\mathfrak{M}_{\{0,n\}}^{(1)}$
3	4/3	12	231 π /1024
5	16/15	16	6435 π /32768
6	5 π /16	18	12155 π /65536
8	35 π /128		

Table F.1: Values of the integral $\mathfrak{M}_{\{0,n\}}^{(1)}$ pertinent to the determination of the deflection angle in the impulse approximation. The integral is defined in (F.1a). The integrals are evaluated using (F.4).

where $\text{Re}(x,y) > 0$ and Γ denotes the Gamma function². By substitution, the integral is evaluated for any argument

$$\mathfrak{M}_{\{m,n\}}^{(1)} = \begin{cases} \Gamma((m+1)/2)\Gamma((n+1)/2)/\Gamma((m+n+2)/2) & , m \bmod 2 = 0 \\ 0 & , m \bmod 2 \neq 0 \end{cases} \quad (\text{F.4})$$

with the restriction $\text{Re}(m,n) > -1$. Note that this result reduces to Wallis' formula for the case of $m = 0$ [276]. The values of $\mathfrak{M}_{\{m,n\}}^{(1)}$ which occur in the impulse approximation calculations are given in table F.1.

F.2 Case 2: $p = 0$

As in the case of $\mathfrak{M}_{\{m,n\}}^{(1)}$, the symmetry of the cosine term forces all m -odd values of $\mathfrak{M}_{\{m,n,z\}}^{(2)} = \mathfrak{M}_{\{m,n,0,z\}}^{(4)}$ to be identically zero. Making the substitution $u = \csc \theta$ into (F.1b) yields

$$\mathfrak{M}_{\{m,n,z\}}^{(2)} = (1 + (-1)^m) \mathfrak{L} \left\{ u^{-k} (\sqrt{u^2 - 1})^{m-1} h(u-1) \middle| z \right\} \quad (\text{F.5})$$

²N.B: In the present case the following properties of the Gamma function are of use; $\Gamma(k+1) = k!$ and $\Gamma(k+1/2) = \pi^{1/2} (2k-1)!! / 2^k$, where $k \in \mathbb{N}$.

where $h(s)$ is a Heaviside step function, $k = m + n + 1$ and $\mathfrak{L}\{f(u)|z\}$ is the Laplace transform of the function $f(u)$ [276, 297] with argument z . For the case $k = 0$, the integral reduces to a known integral representation of the modified Bessel function of the second kind, order m (denoted $K_m(z)$):

$$\mathfrak{L}\left\{(\sqrt{u^2 - 1})^{m-1} h(u-1) \middle| z\right\} = \frac{\Gamma(m+1/2)}{\pi^{1/2}} \left(\frac{z}{2}\right)^{-m} K_m(z) . \quad (\text{F.6})$$

Use of the properties of Laplace transforms yields the general solution

$$\begin{aligned} \mathfrak{M}_{\{m,n,z\}}^{(2)} &= (1 + (-1)^m) \frac{2^m \Gamma(m+1/2)}{\pi^{1/2}} \\ &\times \begin{cases} (-1)^{|k|} \frac{d^{|k|}}{dz^{|k|}} (z^{-m} K_m(z)) & , k \leq 0 \\ \int_z^\infty \int_{z_{k-1}}^\infty \cdots \int_{z_2}^\infty \int_{z_1}^\infty z_0^{-m} K_m(z_0) dz_0 dz_1 \cdots dz_{k-1} & , k > 0 \end{cases} \quad (\text{F.7}) \end{aligned}$$

The only relevant cases of (F.7) are for $m = 0$ and 1. The latter is zero while the former reduces to the repeated indefinite integral of $K_0(z)$ (see appendix G for details, note that $k = n + 1 > 0$),

$$\mathfrak{M}_{\{0,n,z\}}^{(2)} = 2\mathbf{Ki}_{n+1}(z) \quad (n > -1) . \quad (\text{F.8})$$

The functions $\mathbf{Ki}_{n+1}(z)$ require further manipulation to be reduced to a form amenable to computation. These expressions are given in table G.1 for all the $\mathbf{Ki}_{n+1}(z)$ pertinent to the impulse calculations.

The case of $m \neq 0$ can be solved in terms of the $\mathbf{Ki}_n(z)$. For the case of $k \leq 0$, simple application of the chain rule followed by the use of the derivative expression for the modified Bessel functions (see (G.2)) yields a double sum over terms of the form $z^{-\mu} K_\nu(z)$.

Similarly, the $k > 0$ case can be reduced by first expressing the integrand as a sum of the form $z^{-\mu} \mathbf{Ki}_{-\nu}(z)$ which is obtained from the derivative relations of the $\mathbf{K}_{\nu}(z)$ [276]. This sum can be simplified to linear combinations of the $\mathbf{Ki}_{-\nu}(z)$ through use of their recursion relations (G.2). Hence all integrals of this case may be expressed as linear combinations of the $\mathbf{Ki}_n(z)$.

F.3 Case 3: $z = 0$

In this case the integral $\mathfrak{M}_{\{m,n,p\}}^{(3)} = \mathfrak{M}_{\{m,n,p,0\}}^{(4)}$ can be expressed as a Fourier transform. Letting $u = \cot \theta$ in (F.1c) yields

$$\mathfrak{M}_{\{m,n,p\}}^{(3)} = i^m \left(\frac{\partial^m}{\partial p^m} \right) \mathfrak{F}_e \left\{ (1 - iu)^{-2k} (1 + iu)^{-2k} \middle| -p \right\}, \quad (\text{F.9})$$

where $\mathfrak{F}_e \left\{ f(u) \middle| p \right\}$ is the exponential Fourier transform of the function $f(u)$ with argument p ($p > 0$)³ [298] and $k = (m + n + 2)/4$. The above result assumes that $m \geq 0$, which is the only relevant condition in the present work. The Fourier integral given for the $m = 0$ case is a specific integral representation of Whittaker's Confluent Hypergeometric function⁴ [298], denoted $W_{\mu,\nu}(z)$,

$$\mathfrak{F}_e \left\{ (1 - iu)^{-2k} (1 + iu)^{-2k} \middle| p \right\} = \text{sgn}(p) \frac{\pi}{\Gamma(2k)} \left(\frac{|p|}{2} \right)^{2k-1} W_{0,-2k+1/2}(2|p|). \quad (\text{F.10})$$

The Whittaker function reduces to a modified Bessel function in the case of the first

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³N.B.: Some texts give slightly different definitions. In the present case, the definition used is that of the cited text.

⁴N.B.: This is also known as a Whittaker function.

m	n	p	$\mathfrak{M}_{\{m,n,p\}}^{(3)}$
0	1	$2w$	$4\pi w K_1(2w)$
0	3	$2w$	$(8/3)\pi w^2 K_2(2w)$
0	4	$2w$	$\pi^{3/2} w^{5/2} K_{5/2}(2w)$
0	5	$2w$	$(16/15)\pi w^3 K_3(2w)$
0	6	w	$(\pi^{3/2}/24\sqrt{2})w^{7/2} K_{7/2}(w)$
0	6	$2w$	$(\pi^{3/2}/3)w^{7/2} K_{7/2}(2w)$
0	8	$2w$	$(\pi^{3/2}/12)w^{9/2} K_{9/2}(2w)$
1	2	$2w$	$-(8\pi/3)iw^2 K_1(2w)$
1	5	w	$-(\pi^{3/2}/24\sqrt{2})iw^{7/2} K_{5/2}(w)$
1	5	$2w$	$-(\pi^{3/2}/3)iw^{7/2} K_{5/2}(2w)$
1	7	w	$-(\pi^{3/2}/12)i(w/2)^{9/2} K_{7/2}(w)$
2	1	$2w$	$(4\pi/3)w(K_1(2w) - 2wK_0(2w))$
2	4	$2w$	$(\pi^{3/2}/6)w^{5/2}(K_{5/2}(2w) - 2wK_{3/2}(2w))$

Table F.2: Values of the integral $\mathfrak{M}_{\{m,n,p\}}^{(3)}$ pertinent to the determination of the deflection angle in the impulse approximation. The integral is defined in (F.1). The integrals are evaluated using (F.11). The argument, w , is defined in (2.53). The modified Bessel functions of the second kind $K_\nu(z)$ are discussed in appendix G.

index being zero [276, 299]. Using this property produces the final result in terms of $K_\nu(p)$,

$$\mathfrak{M}_{\{m,n,p\}}^{(3)} = i^m \left(\frac{\partial^m}{\partial p^m} \right) \frac{2\pi^{3/2}}{\Gamma(1 + (m+n)/2)} \left(\sqrt{\frac{p}{2}} \right)^{m+n+1} K_{(m+n+1)/2}(p), \quad (\text{F.11})$$

which is valid for $n > -1$, $m \geq 0$ and $p > 0$. Explicit expressions for the (m, n, p) relevant to the calculations of chapter 2 are given in table F.2.

F.4 Case 4: $z, p \neq 0$

Integrals of the type (F.1d) do not have exact solutions in most cases and a general solution for arbitrary (m, n) is too cumbersome to develop. However, the general technique used to obtain expressions for (m, n) of interest can be used for any (m, n) . By the change

of variables $u = \cot\theta$, a Fourier-type integral is obtained and the properties of the Fourier transform yield

$$\begin{aligned}\mathfrak{M}_{\{m,n,p,z\}}^{(4)} &= \int_{-\infty}^{+\infty} u^m (\sqrt{u^2-1})^{-k} \exp(ipu - z\sqrt{u^2-1}) du \\ &= 2i^m \left(\frac{\partial^m}{\partial p^m} \right) \int_z^\infty \int_{z_{k-1}}^\infty \\ &\quad \cdots \int_{z_2}^\infty \int_{z_1}^\infty \mathfrak{F}_c \left\{ e^{-z_0\sqrt{u^2-1}} \middle| -p \right\} dz_0 dz_1 \cdots dz_{k-1}\end{aligned}\quad (\text{F.12})$$

where $m \geq 0$ and $k = m + n + 2 \geq 0$. The identity $\mathfrak{F}_c\{f(u)|p\} = 2\mathfrak{F}_c\{f(u)|p\}$ has been employed where $\mathfrak{F}_c$ is the Fourier cosine transform [298] and $f(u)$ is an even function. The cosine transform is known and tabulated [298], thus

$$\begin{aligned}\mathfrak{M}_{\{0,-2,p,z\}}^{(4)} &\equiv \mathfrak{F}_c \left\{ e^{-z_0\sqrt{u^2-1}} \middle| -p \right\} \\ &= \frac{z}{\sqrt{z^2+p^2}} K_1 \left(\sqrt{z^2+p^2} \right),\end{aligned}\quad (\text{F.13})$$

where $z > 0$ and $K_1(z)$ is the modified Bessel function of the second kind, order 1.

The only cases of interest in the present work are $\{m=0; k \in \{0,1,2,3,4\}\}$, $\{m=1; k \in \{1,2,3\}\}$ and $\{m=2, k=2\}$. Thus, finding expressions for the former set is sufficient determination of the remaining integrals (by (F.12)). The first integral of (F.13) is trivial and thus

$$\mathfrak{M}_{\{0,-1,p,z\}}^{(4)} = 2K_0 \left(\sqrt{z^2+p^2} \right). \quad (\text{F.14})$$

The remaining integrals are obtained by repeated integration of (F.14).

To obtain an expression for the repeated integrals of (F.14), it is necessary to separate z and p in the argument to the Bessel function. This is accomplished by making use of a

Hankel transform⁵ [300],

$$\frac{p^n}{z^m} \left(\frac{\sqrt{z^2 + p^2}}{y} \right)^{m-n-1} K_{m-n-1} \left(y \sqrt{z^2 + p^2} \right) = \int_0^\infty \frac{K_m \left(z \sqrt{x^2 + y^2} \right)}{(x^2 + y^2)^{m/2}} x^{n+1} J_n(px) dx, \quad (\text{F.15})$$

where $(z, y, p) > 0$ and $n > -1$. The function $J_\nu(z)$ is a Bessel function of the first kind, order ν [276]. Further integration by parts of (F.15) yields a similar expression

$$\begin{aligned} \int_0^\infty \frac{K_{m-1} \left(z \sqrt{x^2 + y^2} \right)}{(x^2 + y^2)^{(m-1)/2}} x^n J_{n-1}(px) dx = \\ \frac{p^{n-1}}{z^{m-1}} \left(\frac{\sqrt{z^2 + p^2}}{y} \right)^{m-n-1} K_{m-n-1} \left(y \sqrt{z^2 + p^2} \right) \\ - (py^{m-1})^{-1} K_{m-1}(zy) \delta_{n,0}, \quad (\text{F.16}) \end{aligned}$$

where $(m, n) \geq 0$ ⁶.

Using (F.16) with $m = 1$ and $n = 0$, noting that $J_{-1}(z) = -J_1(z)$, yields a general expression for the repeated integration with respect to z in (F.14):

$$\begin{aligned} \int_z^\infty \int_{z_{k-1}}^\infty \cdots \int_{z_2}^\infty \int_{z_1}^\infty K_0 \left(y \sqrt{z_0^2 + p^2} \right) dz_0 dz_1 \cdots dz_{k-1} = \\ y^{-k} \mathbf{Ki}_k(zy) - p \int_0^\infty \frac{\mathbf{Ki}_k \left(z \sqrt{x^2 + y^2} \right)}{(x^2 + y^2)^{k/2}} J_1(px) dx. \quad (\text{F.17}) \end{aligned}$$

Here, the $\mathbf{Ki}_k(z)$ are described in appendix G. The values of k which are of interest are

⁵N.B.: The additional variable y is introduced for the purposes of calculation. In all final results it is set to unity.

⁶N.B.: The Kronecker delta term arises from the limit $J_n(z) \sim z^n$ for small z [276].

$k \in \{0, 1, 2, 3\}$. For $k = 0$, it is easy to show

$$\begin{aligned}\mathfrak{M}_{\{1,-2,p,z\}}^{(4)} &= i \left(\frac{\partial \mathfrak{M}_{\{0,-1,p,z\}}^{(4)}}{\partial p} \right) \\ &= -\frac{2ip}{\sqrt{z^2+p^2}} K_1 \left(\sqrt{z^2+p^2} \right).\end{aligned}\quad (\text{F.18})$$

The case of $k = 1$ cannot be evaluated in a closed form and its approximation will be deferred to later in the section.

For $k > 1$ in (F.17), the recurrence properties of the $\mathbf{Ki}_k(z)$ show that all functions of this type can be expressed in terms of $\mathbf{Ki}_1(z)$, $K_0(z)$ and $K_1(z)$ weighted by polynomials in z . Since the last two of these often have known inverse Hankel transforms (i.e. (F.15) and (F.16)), using the recurrence relation (G.2) in (F.17) reduces the integral to terms which cannot be evaluated analytically. Thus,

$$\begin{aligned}\int_0^\infty \frac{\mathbf{Ki}_2(z\sqrt{x^2+y^2})}{x^2+y^2} J_1(px) dx &= z \left[\frac{1}{py} K_1(zy) - \frac{\sqrt{z^2+p^2}}{pzy} K_1(y\sqrt{z^2+p^2}) \right. \\ &\quad \left. - \int_0^\infty \frac{\mathbf{Ki}_1(z\sqrt{x^2+y^2})}{(x^2+y^2)^{1/2}} J_1(px) dx \right]\end{aligned}\quad (\text{F.19a})$$

$$\begin{aligned}\int_0^\infty \frac{\mathbf{Ki}_3(z\sqrt{x^2+y^2})}{(x^2+y^2)^{3/2}} J_1(px) dx &= \frac{1}{2} \left[\frac{z\sqrt{z^2+p^2}}{py} K_1(y\sqrt{z^2+p^2}) - \frac{z^2}{py} K_1(zy) \right. \\ &\quad + z^2 \int_0^\infty \frac{\mathbf{Ki}_1(z\sqrt{x^2+y^2})}{(x^2+y^2)^{1/2}} J_1(px) dx \\ &\quad \left. - \frac{1}{y} \left(\frac{\partial}{\partial y} \right) \int_0^\infty \frac{\mathbf{Ki}_1(z\sqrt{x^2+y^2})}{(x^2+y^2)^{1/2}} J_1(px) dx \right].\end{aligned}\quad (\text{F.19b})$$

Substitution of (F.19) into (F.17) gives the $k \in \{2, 3\}$ cases

$$\int_z^\infty \int_{z_1}^\infty K_0\left(y\sqrt{z_0^2+p^2}\right) dz_0 dz_1 = \frac{\sqrt{z^2+p^2}}{y} K_1\left(y\sqrt{z^2+p^2}\right) - z \int_z^\infty K_0\left(y\sqrt{z_0^2+p^2}\right) dz_0 \quad (\text{F.20a})$$

$$\int_z^\infty \int_{z_2}^\infty \int_{z_1}^\infty K_0\left(y\sqrt{z_0^2+p^2}\right) dz_0 dz_1 dz_2 = \frac{1}{2} \left[\frac{z}{y^2} K_0(zy) + \frac{1}{y^3} \mathbf{Ki}_1(zy) + \frac{p}{y} \left(\frac{\partial}{\partial y} \right) \int_0^\infty \frac{\mathbf{Ki}_1\left(z\sqrt{x^2+y^2}\right)}{(x^2+y^2)^{1/2}} J_1(px) dx - z \int_z^\infty \int_{z_1}^\infty K_0\left(y\sqrt{z_0^2+p^2}\right) dz_0 dz_1 \right]. \quad (\text{F.20b})$$

From (F.20), it is clear that all $k > 1$ expressions contain one component which cannot be evaluated exactly⁷. An approximate solution to the integral can be obtained from the method of Steepest Descent [268, 297]. Initially the integral is broken down into sub-intervals with zero end-points:

$$\int_0^\infty \frac{\mathbf{Ki}_1\left(z\sqrt{x^2+y^2}\right)}{\sqrt{x^2+y^2}} J_1(px) dx = \sum_{s=1}^\infty \text{sgn}(J_1(px)) \int_{j_{1,s}/p}^{j_{1,s+1}/p} \frac{\mathbf{Ki}_1\left(z\sqrt{x^2+y^2}\right)}{\sqrt{x^2+y^2}} |J_1(px)| dx, \quad (\text{F.21})$$

where $j_{1,s}$ is the s -th zero of the Bessel function $J_1(z)$ [276]. Between each pair of zeroes, $J_1(z)$ has a constant sign and a single extremum at the point $j'_{1,s}$. The remaining part of the integrand is monotonically decreasing (exponentially from the $\mathbf{Ki}_1(z)$). Thus the dominant contribution to the integral over each segment $[j_{1,s}/p, j_{1,s+1}/p]$ is at the local maximum of $|J_1(px)|$. This statement is quantified by using the method of steepest descent to evaluate

⁷N.B.: It is possible that this integral could be evaluated in terms of definite integrals of Struve and modified Bessel functions.

each sub-interval. Thus, approximating (F.21) to second order,

$$\sum_{s=1}^{\infty} \text{sgn}(J_1(px)) \int_{j_{1,s}/p}^{j_{1,s+1}/p} \frac{\mathbf{Ki}_1(z\sqrt{x^2+y^2})}{\sqrt{x^2+y^2}} |J_1(px)| dx \approx \sum_{s=1}^{\infty} \sqrt{\frac{2\pi}{j_{1,s}'^2 - 1}} \frac{j_{1,s}' J_1(j_{1,s}')}{\sqrt{j_{1,s}'^2 + (py)^2}} \mathbf{Ki}_1\left((z/p) \sqrt{j_{1,s}'^2 + (py)^2}\right). \quad (\text{F.22})$$

The series of (F.22) converges since $j_{1,s}' < j_{1,s+1}'$ and both $J_1(j_{1,s}')$ and $\mathbf{Ki}_1(z)$ are monotonically decreasing, the latter exponentially. Additionally, the signs of $J_1(j_{1,s}')$ alternate, implying cancellation between higher terms. The method of steepest descents also admits higher order terms for each sub-interval by retaining higher degree terms in the Taylor expansion of the integrand about the maximum [297]. Therefore, it is possible to evaluate the integral of (F.21) to any desired accuracy. It is sufficient for the present purposes to retain only the $s = 1$ term in (F.22) since this is the dominant term. The values of $j_{1,s}$, $j_{1,s}'$ and $J_1(j_{1,s}')$ are known and tabulated [276]; thus the integral can be evaluated strictly in terms of z , p and $\mathbf{Ki}_1(z)$ (see appendix G). Using the result of (F.22) gives the partial derivative of the integral with respect to y ,

$$-\frac{1}{y} \left(\frac{\partial}{\partial y} \right) \int_0^{\infty} \frac{\mathbf{Ki}_1(z\sqrt{x^2+y^2})}{\sqrt{x^2+y^2}} J_1(px) dx \approx p^2 \sqrt{\frac{2\pi}{j_{1,1}'^2 - 1}} \frac{j_{1,1}' J_1(j_{1,1}')}{j_{1,1}'^2 + p^2} \left\{ \frac{\mathbf{Ki}_1\left((z/p) \sqrt{j_{1,1}'^2 + p^2}\right)}{\sqrt{j_{1,1}'^2 + p^2}} + \frac{z}{p} \mathbf{K}_0\left((z/p) \sqrt{j_{1,1}'^2 + p^2}\right) \right\}, \quad (\text{F.23})$$

when $y = 1$.

Substitution of the result of (F.22) and (F.23) using only the first term of the series into

(F.20) yields the final expressions for the remaining integrals $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ (letting $y = 1$):

$$\mathfrak{M}_{\{0,0,p,z\}}^{(4)} \approx 2\mathbf{Ki}_1(z) - 2p \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} \frac{j'_{1,1} J_1(j'_{1,1})}{\sqrt{j'_{1,1}{}^2 + p^2}} \mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right), \quad (\text{F.24a})$$

$$\begin{aligned} \mathfrak{M}_{\{0,1,p,z\}}^{(4)} \approx & 2 \left\{ \sqrt{z^2 + p^2} K_1\left(\sqrt{z^2 + p^2}\right) - z \mathbf{Ki}_1(z) \right. \\ & \left. + zp \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} \frac{j'_{1,1} J_1(j'_{1,1})}{\sqrt{j'_{1,1}{}^2 + p^2}} \mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) \right\}, \end{aligned} \quad (\text{F.24b})$$

$$\begin{aligned} \mathfrak{M}_{\{0,2,p,z\}}^{(4)} \approx & z K_0(z) + (z^2 + 1) \mathbf{Ki}_1(z) - z \sqrt{z^2 + p^2} K_1\left(\sqrt{z^2 + p^2}\right) \\ & - p \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} j'_{1,1} J_1(j'_{1,1}) \left\{ \left(z^2 + \frac{p^2}{j'_{1,1}{}^2 + p^2} \right) \right. \\ & \left. \times \frac{\mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right)}{\sqrt{j'_{1,1}{}^2 + p^2}} + \frac{z}{j'_{1,1}{}^2 + p^2} K_0\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) \right\}, \end{aligned} \quad (\text{F.24c})$$

$$\begin{aligned} \mathfrak{M}_{\{1,-1,p,z\}}^{(4)} \approx & -2i \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} \frac{j'_{1,1}{}^3 J_1(j'_{1,1})}{(j'_{1,1}{}^2 + p^2)^{3/2}} \left\{ \mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) \right. \\ & \left. + \frac{z}{p} \sqrt{j'_{1,1}{}^2 + p^2} K_0\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) \right\}, \end{aligned} \quad (\text{F.24d})$$

$$\begin{aligned} \mathfrak{M}_{\{1,0,p,z\}}^{(4)} \approx & -2ip K_0\left(\sqrt{z^2 + p^2}\right) + 2i \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} \frac{j'_{1,1}{}^3 J_1(j'_{1,1})}{(j'_{1,1}{}^2 + p^2)^{3/2}} \\ & \times \left\{ \mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) + \frac{z}{p} \sqrt{j'_{1,1}{}^2 + p^2} \right. \\ & \left. \times K_0\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) \right\}, \end{aligned} \quad (\text{F.24e})$$

$$\begin{aligned} \mathfrak{M}_{\{2,-2,p,z\}}^{(4)} \approx & 2 \sqrt{\frac{2\pi}{j'_{1,s}{}^2 - 1}} \frac{j'_{1,1}{}^3 J_1(j'_{1,1})}{(j'_{1,1}{}^2 + p^2)^{5/2}} \\ & \times \left\{ 3p \mathbf{Ki}_1\left((z/p) \sqrt{j'_{1,1}{}^2 + p^2}\right) + 3z \sqrt{j'_{1,1}{}^2 + p^2} \right. \end{aligned}$$

$$\begin{aligned}
& \times K_0 \left((z/p) \sqrt{j_{1,1}'^2 + p^2} \right) - \frac{z^2}{p^3} j_{1,1}'^2 (j_{1,1}'^2 + p^2) \\
& \times K_1 \left((z/p) \sqrt{j_{1,1}'^2 + p^2} \right) \Big\} \quad (F.24f)
\end{aligned}$$

The last three of these integrals were evaluated by finding the partial derivative with respect to p of $\mathfrak{M}_{\{0,0,p,z\}}^{(4)}$, $\mathfrak{M}_{\{0,1,p,z\}}^{(4)}$ and $\mathfrak{M}_{\{1,-1,p,z\}}^{(4)}$, respectively.

With (F.24) and (F.14), all the integrals required in the impulse calculation of chapter 2 are evaluated approximately, with higher accuracy expressions being possible. In their application in chapter 2, some combinations of $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ produce a cancellation of the terms which cannot be evaluated exactly. The cancellation is derived from (F.20) and is not simply a coincidence for the zeroth order terms in the series of (F.22).

The resulting solutions for $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ pertinent to the calculations in chapter 2 are summarised in table F.3 for various m and n . The necessary expressions for the calculations of

m	n	$\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$
0	-2	$(z/\sqrt{z^2+p^2})K_1(\sqrt{z^2+p^2})$
0	-1	$2K_0(\sqrt{z^2+p^2})$
0	0	$2\mathbf{Ki}_1(z) - 2Ap\mathbf{Ki}_1(\varpi)$
0	1	$2\sqrt{z^2+p^2}K_1(\sqrt{z^2+p^2}) - \mathfrak{M}_{\{0,0,p,z\}}^{(4)}$
0	2	$zK_0(z) + (z^2+1)\mathbf{Ki}_1(z) - z\sqrt{z^2+p^2}K_1(\sqrt{z^2+p^2})$ $- (Az^2/\varpi)[(\varpi+1/\varpi)p\mathbf{Ki}_1(\varpi) + zK_0(\varpi)]$
1	-2	$-(2ip/\sqrt{z^2+p^2})K_1(\sqrt{z^2+p^2})$
1	-1	$-2i(1-(z/\varpi)^2)[\mathbf{Ki}_1(\varpi) - \varpi K_0(\varpi)]$
1	0	$-(ip\mathfrak{M}_{\{0,-1,p,z\}}^{(4)} + z\mathfrak{M}_{\{1,-1,p,z\}}^{(4)})$
2	-2	$2A(\varpi^2-z^2)(z/p\varpi^2)^2[3p\mathbf{Ki}_1(\varpi) + 3p\varpi K_0(\varpi)$ $-(\varpi^2-z^2)p(\varpi/z)^2K_1(\varpi)]$

Table F.3: Summary of results for the evaluation of the integral $\mathfrak{M}_{\{m,n,p,z\}}^{(4)}$ for various arguments (m,n) . The entries in the table correspond to equations (F.13), (F.14) and (F.24). The auxiliary variables $A(p)$ and $\varpi(z,p)$ are defined in (F.25).

the present work can be obtained from the table using appropriate substitutions for z , p and the auxiliary variables defined below:

$$A(p) \equiv \sqrt{\frac{2\pi}{j_{1,1}'^2 - 1}} \frac{j_{1,1}' J_1(j_{1,1}')}{\sqrt{j_{1,1}'^2 + p^2}} \quad (\text{F.25a})$$

and

$$\varpi(z, p) \equiv \frac{z}{p} \sqrt{j_{1,1}'^2 + p^2} . \quad (\text{F.25b})$$

Appendix G

Properties and Numerical Evaluation of $\mathbf{Ki}_n(x)$

The functions $\mathbf{Ki}_n(x)$ are defined in terms of repeated, indefinite integration or differentiation of the modified Bessel functions of the second kind, order zero, $K_0(x)$. The definition of $\mathbf{Ki}_n(x)$ is given as [276]:

$$\mathbf{Ki}_n(x) = \begin{cases} (-1)^n \frac{d^{|n|}}{dx^{|n|}} K_0(x) & , n \leq 0 \\ \int_x^\infty \int_{x_{(n-1)}}^\infty \cdots \int_{x_2}^\infty \int_{x_1}^\infty K_0(x_0) dx_0 dx_1 \cdots dx_{n-1} & , n > 0 . \end{cases} \quad (\text{G.1})$$

From the recursion relations of the modified Bessel functions, $\mathbf{Ki}_n(x)$ may be expressed as combinations of lower order integrals when $n > 0$. In the case of $n < 0$, the properties of the derivatives of $K_0(x)$ allow the integral to be expressed in terms of higher order $K_n(x)$. Thus,

$$n\mathbf{Ki}_{n+1}(x) = -x\mathbf{Ki}_n(x) + (n-1)\mathbf{Ki}_{n-1}(x) + x\mathbf{Ki}_{n-2}(x) \quad (\text{G.2a})$$

$$\frac{d^m}{dx^m} K_n(x) = \left(-\frac{1}{2}\right)^m \sum_{k=0}^m \binom{m}{k} K_{n-m+2k}(x) \quad (G.2b)$$

$$K_{-n}(x) = K_n(x) . \quad (G.2c)$$

It should also be noted that $\mathbf{Ki}_n(x)$ is finite for all x when $n \geq 0$; the $K_n(x)$ diverge logarithmically at $x = 0$. For any n , $\mathbf{Ki}_n(x)$ decays exponentially with $x \gg 1$ [276].

The properties (G.2) show that any $\mathbf{Ki}_n(x)$ may be evaluated numerically if the $K_n(x)$ and $\mathbf{Ki}_1(x)$ are known. In the particular case of $n > 0$, (G.2a) shows that any $\mathbf{Ki}_n(x)$ can be expressed as a combination of $\mathbf{Ki}_{-1}(x) = K_1(x)$, $\mathbf{Ki}_0(x) = K_0(x)$ and $\mathbf{Ki}_1(x)$ (the last of which does not have a less complex form). Thus,

$$\mathbf{Ki}_n(x) = M_n \sum_{k=-1}^{+1} P_{k,n}(x) \mathbf{Ki}_k(x) \quad (n > 1) \quad (G.3)$$

where M_n is a constant and $P_{k,n}(x)$ are polynomials in x of degree $n - 1$. From the recursion relation of (G.2a), the M_n and $P_{k,n}(x)$ may be obtained through

$$M_{n+1} = nM_n \quad (G.4a)$$

$$P_{k,n+1}(x) = x \left((n-1)(n-2)P_{k,n-2}(x) - P_{k,n}(x) \right) + (n-1)^2 P_{k,n-1}(x) , \quad (G.4b)$$

which facilitates the tabulation of $\mathbf{Ki}_n(x)$. Using (G.2) and (G.4), the forms of $\mathbf{Ki}_n(x)$ ($-2 \leq n \leq 12$) are tabulated (see table G.1). In the case of $n \geq 0$, only the values of $P_{k,n}(x)$ are tabulated, the function being obtained from (G.3).

From the above results, the problem of the numerical evaluation of $\mathbf{Ki}_n(x)$ is reduced to evaluation of the Bessel functions and $\mathbf{Ki}_1(x)$. In the case of $K_n(x)$, standard numerical methods are readily available [279]. Numerical evaluation of $\mathbf{Ki}_1(x)$ is accomplished by

n	$\mathbf{Ki}_n(x)$
-2	$(1/2)(K_0(x) + K_2(x))$
-1	$K_1(x)$
0	$K_0(x)$
1	$\mathbf{Ki}_1(x)$
M_n	$\{P_{-1,n}(x), P_{0,n}(x), P_{1,n}(x)\}$
2	1 $\{x, 0, -x\}$
3	2 $\{-x^2, x, x^2 + 1\}$
4	6 $\{x^3 + 4x, -x^2, -(x^3 + 3x)\}$
5	24 $\{-(x^4 + 7x^2), x^3 + 9x, x^4 + 6x^2 + 9\}$
6	120 $\{x^5 + 11x^3 + 64x, -(x^4 + 13x^2), -(x^5 + 10x^3 + 45x)\}$
7	720 $\{-(x^6 + 16x^4 + 159x^2), x^5 + 18x^3 + 225x, x^6 + 15x^4 + 135x^2 + 225\}$
8	5040 $\{x^7 + 22x^5 + 345x^3 + 2304x, -(x^6 + 24x^4 + 423x^2), -(x^7 + 21x^5 + 315x^3 + 1575x)\}$
9	40320 $\{-(x^8 + 29x^6 + 667x^4 + 7407x^2), x^7 + 31x^5 + 759x^3 + 11025x, x^8 + 28x^6 + 6300x^2 + 11025\}$
10	362880 $\{x^9 + 37x^7 + 1179x^5 + 20583x^3 + 147456x, -(x^8 + 39x^6 + 1287x^4 + 25497x^2), -(x^9 + 36x^7 + 1134x^5 + 18900x^3 + 99225x)\}$
11	3628800 $\{-(x^{10} + 46x^8 + 1944x^6 + 49770x^4 + 581535x^2), x^9 + 48x^7 + 2070x^5 + 56520x^3 + 893025x, x^{10} + 45x^8 + 1890x^6 + 47250x^4 + 496125x^2 + 893025\}$
12	39916800 $\{x^{11} + 56x^9 + 3034x^7 + 107640x^5 + 1973205x^3 + 14745600x, -(x^{10} + 58x^8 + 3180x^6 + 116910x^4 + 2450475x^2), -(x^{11} + 55x^9 + 2970x^7 + 103950x^5 + 1819125x^3 + 9828275x)\}$

Table G.1: The functions $\mathbf{Ki}_n(x)$ (defined in (G.1)) for integer $n \in [-2, 12]$. For $n < 0$, the functions are given explicitly in terms of the modified Bessel functions of integer order $K_n(x)$. For $n \geq 2$, only the values of the polynomials $P_{k,n}(x)$ are given for use with (G.3).

making use of its exact ascending series representation¹ [276]

$$\mathbf{Ki}_1(x) = \frac{\pi}{2} + x(\gamma + \ln(x/2)) \sum_{k=0}^{\infty} \frac{(x/2)^{2k}}{(k!)^2(2k+1)} \times \left[1 - x \left(\frac{1}{2k+1} + \left(\sum_{m=1}^k m^{-1} \right) \right) \right] . \quad (\text{G.5})$$

Here, γ denotes Euler's number. The series of (G.5) is convergent for all $x > 0$ but is numerically unstable for $x > 1$. For $x \gg 1$, asymptotic expansions exist for $\mathbf{Ki}_1(x)$ but these have also been found to be unstable, or at best slowly convergent. Fortunately, Chebyshev polynomial approximations have been computed for the asymptotic expansion of $\mathbf{Ki}_1(x)$ [301]. Thus, for $x \geq 1$,

$$\mathbf{Ki}_1(x) \approx e^{-x} \sqrt{\frac{\pi}{2x}} \sum_{k=0}^{13} a_k (-x)^{-k} \quad (\text{G.6})$$

where the a_k are taken from [301]. A graphical representation of $\mathbf{Ki}_1(x)$ is shown in figure G.1. Using (G.5) for $x < 1$ and (G.6) for $x \geq 1$, $\mathbf{Ki}_1(x)$ is uniformly defined over all x . Comparison of the function (given in the `k1int.f` routine in appendix I) with tabulated values of $\mathbf{Ki}_1(x)$ [276] are in agreement to eight significant figures. The Chebyshev approximation coefficients used $\{a_k\}$ are expected to yield an accuracy of $\pm 2 \times 10^{-10}$ in $\mathbf{Ki}_1(x)$ [301].

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¹N.B.: The function can actually be expressed in terms of modified Struve functions but this is not useful in the present case.

Figure G.1: A log-log plot of $(2/\pi)e^x \text{Ki}_1(x)$ vs. x . Numerical evaluation is made with (G.5) for $x < 1$ and (G.6) for $x \geq 1$.

Appendix H

Derivation of the Kapitza-Dirac Lagrangian for Fast Oscillations

The following is a proof of the Kapitza-Dirac separation of fast and slow motions, formula (30.10) of Landau [266], for the most general case: many degrees of freedom with an arbitrary coordinate system. Only the case of one-dimensional motion for a Cartesian coordinate is given explicitly in [266] and the proof for generalised coordinates and many dimensions is “a somewhat more lengthy calculation” left as an exercise for the reader. The result describes the change in the equations of motion for a system undergoing forced oscillations which are a perturbation to the “evolution” of the system. An example of a system would be the path of a simple pendulum when its base is being moved quickly back and forth. This also describes the motion of particles in a c.w. electric field when the oscillations of the field are much faster than the time-scale of the particle motion.

The outline of the approach, which is a form of classical perturbation theory [302], is to obtain the Lagrangian equations of motion for the system, expand the dynamical variables in terms of two variables, the small oscillations and the slow evolution of the system. The

small oscillations are determined from the solution to set of first order equations, which are approximately separable. These are then substituted back into the equations of motion and an average of one period of the oscillation is performed to obtain the equations of motion for the slow variables. The equations are inverted to obtain an effective Lagrangian which will reproduce them.

Using the same notation as Landau [266], the Lagrangian of a many-dimensional system with N coordinates $\mathbf{q} \equiv \{q_i\}$ and corresponding velocities $\{\dot{q}_i\}$ is given as

$$\begin{aligned} L &= T - U \\ L &= \frac{1}{2} \sum_{i,j} a_{ij}(\mathbf{q}) \dot{q}_i \dot{q}_j - U(\mathbf{q}; t), \end{aligned} \quad (\text{H.1})$$

where the kinetic energy coefficients a_{ij} are implicitly functions of the coordinates $\{q_i\}$ and the implicit double sum in i and j runs over all N degrees of freedom. The potential is given by

$$\begin{aligned} U(\mathbf{q}; t) &= U_0(\mathbf{q}) + U_1(\mathbf{q}; t) \\ &= U_0(\mathbf{q}) + V_1(\mathbf{q}) \cos \omega t + V_2(\mathbf{q}) \sin \omega t. \end{aligned} \quad (\text{H.2})$$

The Euler-Lagrange equation for q_k is given by [266],

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_k} \right) - \left(\frac{\partial L}{\partial q_k} \right) = 0,$$

where

$$\left(\frac{\partial T}{\partial \dot{q}_k} \right) = \frac{1}{2} \sum_{i,j} a_{ij} \left(\frac{\partial \dot{q}_i}{\partial \dot{q}_k} \right) \dot{q}_j + a_{ij} \left(\frac{\partial \dot{q}_j}{\partial \dot{q}_k} \right) \dot{q}_i$$

$$\begin{aligned}
&= \frac{1}{2} \sum_{i,j} a_{ij} (\delta_{ik} \dot{q}_j + \delta_{jk} \dot{q}_i) \\
&= \frac{1}{2} \left(\sum_{j \neq k} a_{kj} \dot{q}_j + \sum_{i \neq k} a_{ik} \dot{q}_i + 2a_{kk} \dot{q}_k \right),
\end{aligned}$$

and using the symmetry of the kinetic energy coefficients $\{a_{ij}\}$,

$$= \sum_j a_{kj} \dot{q}_j.$$

Substitution gives the explicit form of the equations of motion:

$$\sum_j \dot{a}_{kj} \dot{q}_j + a_{kj} \ddot{q}_j - \frac{1}{2} \sum_{i,j} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \dot{q}_i \dot{q}_j + \left(\frac{\partial U_0}{\partial q_k} \right) + \left(\frac{\partial U_1}{\partial q_k} \right) = 0. \quad (\text{H.3})$$

However

$$\dot{a}_{kj} = \sum_i \left(\frac{\partial a_{kj}}{\partial q_i} \right) \dot{q}_i,$$

which gives on substitution into (H.3)

$$\sum_j a_{kj} \ddot{q}_j + \sum_{i,j} \left\{ \left(\frac{\partial a_{kj}}{\partial q_i} \right) - \frac{1}{2} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \right\} \dot{q}_i \dot{q}_j + \left(\frac{\partial U_0}{\partial q_k} \right) + \left(\frac{\partial U_1}{\partial q_k} \right) = 0. \quad (\text{H.4})$$

Thus far no assumptions have been made regarding the magnitude of the time dependent term, U_1 . If the presence of the time-dependent term induces a fast oscillation on the motion of each coordinate which is small in amplitude then these motions are essentially independent. It is therefore possible to make the approximation

$$q_i \approx Q_i + \xi_i, \quad \forall i \in \{q_i\}, \quad (\text{H.5})$$

where $\{\xi_i\}$ are the fast oscillations in $\{q_i\}$, and the slower "evolution" of the coordinates are denoted $\{Q_i\}$. Substitution of (H.5) into (H.4) and expanding all terms to first order in $\{\xi_i\}$ gives:

$$\begin{aligned} \sum_j \left\{ a_{kj} + \sum_i \left(\frac{\partial a_{kj}}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \xi_i \right\} (\ddot{Q}_j + \ddot{\xi}_j) + \sum_{i,j} \left\{ \left(\frac{\partial a_{kj}}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} - \frac{1}{2} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right. \\ \left. + \sum_m \left[\left(\frac{\partial^2 a_{kj}}{\partial q_i \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} - \frac{1}{2} \left(\frac{\partial^2 a_{ij}}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right] \xi_m \right\} (\dot{Q}_j + \dot{\xi}_j)(\dot{Q}_i + \dot{\xi}_i) \\ + \left(\frac{\partial U_0}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} + \left(\frac{\partial U_1}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} + \sum_m \left\{ \left(\frac{\partial^2 U_0}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} + \left(\frac{\partial^2 U_1}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right\} \xi_m \\ = 0. \quad (\text{H.6}) \end{aligned}$$

This gives the equation for ξ_i implicitly by collecting the terms for $\ddot{\xi}_i$, and other terms which are of second order in ω ¹. Thus,

$$\sum_j a_{kj} \ddot{\xi}_j = - \left(\frac{\partial U_1}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}}, \quad (\text{H.7})$$

Equation (H.7) implies the matrix equation $\mathbf{A} \ddot{\boldsymbol{\xi}} = -\nabla_{\mathbf{q}} U_1$, or more explicitly,

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1N} \\ a_{21} & a_{22} & \dots & a_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ a_{N1} & a_{N2} & \dots & a_{NN} \end{bmatrix} \begin{bmatrix} \ddot{\xi}_1 \\ \ddot{\xi}_2 \\ \vdots \\ \ddot{\xi}_N \end{bmatrix} = - \begin{bmatrix} \left(\frac{\partial U_1}{\partial q_1} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \\ \left(\frac{\partial U_1}{\partial q_2} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \\ \vdots \\ \left(\frac{\partial U_1}{\partial q_N} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \end{bmatrix}. \quad (\text{H.8})$$

Let $\mathbf{A}^{-1} \equiv \mathbf{B}$; the elements of the inverse matrix are denoted $b_{ij}(\mathbf{Q})$. From (H.8), the

¹Note that the $\ddot{\xi}^2$ terms are not included even though they are on the order of ω^2 since they are not the result of a first order expansion, *i.e.* $x^2 \approx a^2 + 2a(x-a)$ to first order.

form of $\ddot{\xi}_i$ is given by

$$\ddot{\xi}_i = - \sum_j b_{ij} \left(\frac{\partial U_1}{\partial q_j} \right) \Big|_{\mathbf{q}=\mathbf{Q}}, \quad (\text{H.9})$$

the solution of which is obtained by integration using equation (H.2),

$$\xi_i = \frac{1}{\omega^2} \sum_j b_{ij} \left(\frac{\partial U_1}{\partial q_j} \right) \Big|_{\mathbf{q}=\mathbf{Q}}. \quad (\text{H.10})$$

Substitution of (H.10) into (H.6) and use of (H.7) removes the $\ddot{\xi}_j$ terms. If the resulting expression is time-averaged over a period of ω , the $\mathbf{Q}$ will be approximately constant and terms which are not proportional to $\langle \cos^2 \omega t \rangle$ or $\langle \sin^2 \omega t \rangle$ will go to zero (from (H.10) and (H.2)). This leaves as the equation of motion for Q_k ,

$$\begin{aligned} \sum_j a_{kj} \ddot{Q}_j + \sum_{i,j} \left\{ \left(\frac{\partial a_{kj}}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \langle \xi_i \ddot{\xi}_j \rangle + \left[\left(\frac{\partial a_{kj}}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} - \frac{1}{2} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right] \right. \\ \left. \times \left(\dot{Q}_i \dot{Q}_j + \langle \dot{\xi}_i \dot{\xi}_j \rangle \right) \right\} + \left(\frac{\partial U_0}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} + \sum_m \left\langle \left(\frac{\partial^2 U_1}{\partial q_m \partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \xi_m \right\rangle = 0. \quad (\text{H.11}) \end{aligned}$$

The values of the averaged terms are given by

$$\begin{aligned} \langle \xi_i \ddot{\xi}_j \rangle &= \left\langle \left(\frac{1}{\omega^2} \sum_m b_{im} \left(\frac{\partial U_1}{\partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right) \left(- \sum_n b_{jn} \left(\frac{\partial U_1}{\partial q_n} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right) \right\rangle \\ &= - \frac{1}{2\omega^2} \sum_{m,n} b_{im} b_{jn} \left\{ \left(\frac{\partial V_1}{\partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \left(\frac{\partial V_1}{\partial q_n} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right. \\ &\quad \left. + \left(\frac{\partial V_2}{\partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \left(\frac{\partial V_2}{\partial q_n} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right\} \\ &\equiv - \frac{1}{2\omega^2} \sum_{m,n} b_{im} b_{jn} V_{mn} \end{aligned} \quad (\text{H.12})$$

where the coordinate dependent elements of U_1 are written explicitly using (H.2) and symbolised by $\mathcal{V}_{mn}$. Similarly, it can be shown that

$$\langle \dot{\xi}_i \dot{\xi}_j \rangle = \frac{1}{2\omega^2} \sum_{m,n} b_{im} b_{jn} \mathcal{V}_{mn} . \quad (\text{H.13})$$

The last term in (H.11) is found to be

$$\begin{aligned} \sum_m \left\langle \left(\frac{\partial^2 U_1}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \xi_m \right\rangle &= \frac{1}{2\omega^2} \sum_{m,n} b_{mn} \left\{ \left(\frac{\partial V_1}{\partial q_n} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \left(\frac{\partial^2 V_1}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right. \\ &\quad \left. + \left(\frac{\partial V_2}{\partial q_n} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \left(\frac{\partial^2 V_2}{\partial q_k \partial q_m} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right\} \\ &= \frac{1}{4\omega^2} \sum_{m,n} b_{mn} \left(\frac{\partial \mathcal{V}_{mn}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \quad (\text{H.14}) \end{aligned}$$

If (H.12), (H.13) and (H.14) are substituted back into (H.11) and it is noted that

$$\sum_{i,j} \left(\frac{\partial a_{kj}}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \dot{Q}_i \dot{Q}_j = \sum_j \dot{a}_{kj} \dot{Q}_j \quad (\text{H.15})$$

then it follows that

$$\begin{aligned} \sum_j a_{kj} \ddot{Q}_j + \dot{a}_{kj} \dot{Q}_j - \frac{1}{2} \sum_{i,j} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \dot{Q}_i \dot{Q}_j + \left(\frac{\partial U_0}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \\ + \frac{1}{4\omega^2} \sum_{m,n} b_{mn} \left(\frac{\partial \mathcal{V}_{mn}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} - \frac{1}{4\omega^2} \sum_{i,j,m,n} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} b_{im} b_{jn} \mathcal{V}_{mn} \\ = 0 . \quad (\text{H.16}) \end{aligned}$$

The equations of motion described by (H.16) may be inverted to obtain the effective

Lagrangian for the slow variables $\mathbf{Q}$. The equation can be represented as

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_k} \right) - \left(\frac{\partial T}{\partial q_k} \right) + \left(\frac{\partial U_{\text{eff}}}{\partial q_k} \right) = 0, \quad (\text{H.17})$$

where the kinetic term is as before,

$$T = \frac{1}{2} \sum_{i,j} a_{ij}(\mathbf{Q}) \dot{Q}_i \dot{Q}_j, \quad (\text{H.18})$$

and this gives the first two terms of (H.16). The effective potential, U_{eff} , accounts for the remaining three terms in (H.16):

$$\left(\frac{\partial U_{\text{eff}}}{\partial q_k} \right) = \left(\frac{\partial U_0}{\partial q_k} \right) + \frac{1}{4\omega^2} \sum_{m,n} \left\{ b_{mn} \left(\frac{\partial \mathcal{V}_{mn}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} - \mathcal{V}_{mn} \left[\sum_{i,j} \left(\frac{\partial a_{ij}}{\partial q_k} \right) \Big|_{\mathbf{q}=\mathbf{Q}} b_{mi} b_{jn} \right] \right\}. \quad (\text{H.19})$$

From the matrix identity $\mathbf{B} = \mathbf{B}\mathbf{A}\mathbf{B}$, it can be shown that

$$b_{mn} = \sum_{i,j} b_{mi} a_{ij} b_{jn}. \quad (\text{H.20})$$

Differentiation of this expression yields

$$\left(\frac{\partial b_{mn}}{\partial q_k} \right) = \sum_{i,j} \left(\frac{\partial b_{mi}}{\partial q_k} \right) a_{ij} b_{jn} + \left(\frac{\partial b_{jn}}{\partial q_k} \right) a_{ij} b_{mi} + \left(\frac{\partial a_{ij}}{\partial q_k} \right) b_{mi} b_{jn}, \quad (\text{H.21})$$

but

$$\sum_i b_{mi} a_{in} = \delta_{mn}, \quad (\text{H.22})$$

which gives

$$\begin{aligned} \left(\frac{\partial b_{mn}}{\partial q_k} \right) &= \sum_i \left(\frac{\partial b_{mi}}{\partial q_k} \right) \delta_{in} + \sum_j \left(\frac{\partial b_{jn}}{\partial q_k} \right) \delta_{mj} + \sum_{i,j} \left(\frac{\partial a_{ij}}{\partial q_k} \right) b_{mi} b_{jn} \\ &= 2 \left(\frac{\partial b_{mn}}{\partial q_k} \right) + \sum_{i,j} \left(\frac{\partial a_{ij}}{\partial q_k} \right) b_{mi} b_{jn} . \end{aligned} \quad (\text{H.23})$$

Upon substitution into (H.19) the form of the effective potential which reproduces the averaged equations of motion for $\mathbf{Q}$ is found:

$$\left(\frac{\partial U_{\text{eff}}}{\partial q_k} \right) = \left(\frac{\partial}{\partial q_k} \right) \left\{ U_0 + \frac{1}{4\omega^2} \sum_{i,j} b_{ij} \mathcal{V}_{ij} \right\} . \quad (\text{H.24})$$

Returning to the original definition of the time dependent part of the potential (H.2), yields

$$U_{\text{eff}}(\mathbf{Q}) = U_0(\mathbf{Q}) + \frac{1}{2\omega^2} \sum_{i,j} b_{ij} \left\langle \left(\frac{\partial U_1}{\partial q_i} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \left(\frac{\partial U_1}{\partial q_j} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right\rangle , \quad (\text{H.25})$$

which is identical to equation (30.10) of Landau [266]. Thus the effect of separation of fast and slow motions in the system is to produce a potential which contains the time average of U and a perturbation term of order $O(\omega^{-2})$ which represents the time-average of the forces induced by U_1 ; these forces must be small in order for the resulting effective potential to be valid.

The conditions for the validity of (H.25) are that:

1. The amplitude of the oscillations in ξ remain small compared to the characteristic values of the slow variables $\{Q_i^*\}$

$$|\xi_i| \ll Q_i^* , \quad \forall i \in \{Q_i\}$$

or

$$\left| \frac{1}{\omega^2} \sum_j b_{ij} \left\{ \left(\frac{\partial V_1}{\partial q_j} \right) \Big|_{\mathbf{q}=\mathbf{Q}} + \left(\frac{\partial V_2}{\partial q_j} \right) \Big|_{\mathbf{q}=\mathbf{Q}} \right\} \right| \ll \mathcal{Q}_i^* . \quad (\text{H.26})$$

2. The motion of $\mathbf{Q}$ is such that the potential does not change significantly over a period of $2\pi/\omega$ for a trajectory

$$U_{\text{eff}}(\mathbf{Q}(t + 2\pi/\omega)) - U_{\text{eff}}(\mathbf{Q}(t)) \ll E^* , \quad (\text{H.27})$$

where E^* is the characteristic energy of the system.

Appendix I

Supplementary Material

The CD-ROM accompanying this thesis contains a number of computer programs useful for producing the dynamical data and its subsequent analysis. The basic procedures are given in chapter 3 so only a brief description of each piece of code is given while more detailed comments may be found in the programs themselves. The programs have been written in FORTRAN 77 mostly but some FORTRAN 90 syntax is used; however, the code complies on both GNU g77 (egcs-2.91.66) and SUN f77 (5.0) compilers. Only completely original source code is given. Unfortunately, subroutines which make use of the code of W. Press et. al [279] are not given here for copyright reasons. In each main program, a list of the names of these missing routines are provided which can be used as given in [279] once converted to double precision. Scripts which are included here are written for the (t)C-shell (Linux 4.4BSD-compatible). Some renaming of the paths in these scripts may be required. The FORTRAN source code included is:

1. akimaddv.f, akimadv.f, akimafit.f, akimaint.f — a set of numerical subroutines used for fitting, interpolation and evaluating the derivative of an improved Akima spline.

2. binary.f — solves Hamilton's equations of motion for $H^{(AC)}$ or $H^{(HFL)}$ with paths, deflections functions or potential energy surfaces as output. All subroutines used are named in this file.
3. binarymod.f — evaluates the HDID model potential features as a function of laser parameters.
4. cross.f — evaluates the classical collision cross sections from deflection function data.
5. estmdprm.f — estimates the polarisability parameters of a heteronuclear diatom system from those of the constituent homonuclear systems.
6. fionlim.f — evaluates the non-linear equation (C.15) to determine the maximum F allowed by tunnelling ionisation.
7. impprp.f — evaluates glory and rainbow parameters associated with the HDID-IA model as a function of laser parameters.
8. impulse.f — evaluates $\chi_{IA}^{(AC)}$, $\chi_{IA}^{(HFL)}$ and any partition thereof as a function of b and laser parameters.
9. k1int.f — a function which evaluates $Ki_1(x)$.
10. mdsclprm.f — converts diatomic potential, dipole and polarisability model parameters to scaled units.
11. mlimit.f — a function, used in a number of programs, which evaluates numerical “machine precision.”

12. nonlin.f — performs (Marquardt-Levenberg) non-linear, least-squares fitting, location of roots and local extrema for a given data set. Uses a pre-defined set of model functions. Necessary subroutines are given in separate files.
13. splinddv.f, splindrv.f — subroutines which evaluate the derivatives of data set using natural cubic splines.
14. xavg.f — a program which performs averaging via the extended Simpson's rule on a given data set. Necessary subroutines are given in separate files.

The shell scripts used in data analysis are:

1. acavg.csh — creates an averaged deflection function from a block of $\chi^{(AC)}$ data.
2. bfchi.csh — generates a set of contour table output files (using gnuplot) for polar or Cartesian contour plots.
3. cntrgen.csh — creates a potential energy surface contour plot (using gnuplot).
4. g4.dt.gen.csh — a driver for g4.prs.csh.
5. g4.prs.csh — parses glory or rainbow data files to generate property data sets.
6. grp4.csh — main driver script for generating and parsing special deflection function properties.
7. impdrv.csh — a driver for the impulse program.
8. impprdrv.csh — generates static field limit collision cross sections using the HDID-IA results of the impprp program.

9. jobscript — collects run statistics, error messages and file management for executables.
10. korb.csh — parses a orbiting data set for the highest collision energy.
11. korb.drv.csh — a driver script for all programs necessary for evaluating $K_{orb,(\pm)}^{(HFL)}$ and $K_{orb,(\pm)}^{(AC)}$.
12. plt.gn.csh — generates a gnuplot input file for a contour table output with arguments from the input.
13. prp.dynm.csh — extracts the special features from a deflection function data set.
14. prp.spec.csh — determines the values of the potential features of a potential surface.
15. prp.xscn.csh — generates averaged cross sections for $d\sigma^{(AC)}/d\Omega$ and $\sigma^{(AC)}$.
16. mb.sep.csh — separates orbiting singularities from a data set of local deflection function extrema.
17. trajplot.csh — generates trajectory plots.

Sample input files are:

1. [he2,hear]_[hflscn,tdscn][",a,i].[1,2,3].in — a set of binary input files which correspond to He₂ or HeAr (first bracket), $U^{(HFL)}$ or $U^{(AC)}$ (second bracket), the full- or (an)isotropic partitions (third bracket) at three collision energies (fourth bracket).
2. [he2,hear].bmod.in — input files for binarymod for either He₂ or HeAr.
3. [ar2,he2,ne2,hene,hear,near].[in,data] — nonlin input files and data sets.
4. fionlim.in — input file for fionlim.

5. hear_estmdprm.in — HeAr input file for estmdprm.
6. hear_mdprm.in — HeAr input file for mdscprm.