Theoretical study of rotationally inelastic scattering of molecules

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Introduction

Studying energy transfer in interactions between atom-molecule and moleculemolecule partners on the scale of individual collisions is vital to our understanding and control of molecular reaction dynamical processes [1-3]. With the enhancement of resolution in crossed-beam experiments, accompanied by the improvement in algorithms and computer technology, it has become possible to understand the chemical reactions at an exquisite level of detail. We can precisely control the conditions on both the reactants and products, such as the velocities, individual quantum state, the orientations and alignment of the colliding molecules [4, 5].

Over the past years, a growing interest has arisen in the field of rotationally inelastic scattering, in which the collisional or translational energy is transferred to the internal rotational energy in the scattered products. Cold molecular collisions has become a hot topic in present day molecular physics [6-11]. In the cold regime (temperatures ranging from a few Kelvins to a few milliKelvins), quantum effects become important, such as tunneling and scattering resonances. These effects are very sensitive to details of the interaction potential. Recently, the study of bimolecular collisions at the full quantum-state-resolved level has become possible [12, 13]. Contrary to atomic targets, the molecular collision partner possesses internal degrees of freedom, and both collision partners can become rotationally excited, thus rendering the scattering problem more challenging. The full productpair correlation of rotational excitation in both collision partners may be revealed now, and good agreement with theoretical calculations can be attained [14-16]. Moreover, the study of stereodynamics, involving steric effects, vector properties of molecules, collision-induced molecular orientation, is at the forefront of research [17-19]. These angle-dependent properties provide valuable information about how the molecular interactions govern the molecular collision dynamics.

From the theoretical point of view, in order to understand the mechanism of molecular collisions, one needs to undertake two subsequent steps. The first one is

to construct potential energy surfaces (PESs) [20]. Those can be calculated via *ab initio* quantum calculations, i.e., compute the electronic structure in different geometries of the molecules by solving the electronic Schrödinger equation. The gradient of the surface at a given point quantifies the forces acting on the atoms of the reacting system and further determine how these atoms proceed over these surfaces. Potential energy surfaces thus form a key ingredient for understanding the molecular reaction dynamics.

The second step is to carry out the scattering calculations, which are based on the potential energy landscape. One of the most important aspects describing the collision event is the fully quantum-state-resolved inelastic scattering cross sections. Computing the integral cross sections (i.e., the collision probabilities as function of collision energy), differential cross sections (i.e., the angular distributions of the scattering products) and rate coefficients (i.e., the rates of chemical reactions over a range of temperatures) have long been major targets of theoretical chemistry. Such results can be used to predict or explain the phenomena probed by the measurements, and further offer the most detailed scattering information to help understand the mechanism of microscopic molecular dynamics [21].

Several theoretical methods can be used to predict the outcome of the collision event. The most accurate method is the exact quantum mechanical (QM) treatment, which contains all available information pertaining to the scattering process. One needs to expand the scattering wave function as a series of partial waves, which are the wave functions corresponding to different values of the orbital angular momentum *l*. However, this method requires to solve large sets of coupled differential equations, thus requiring major computational effort. The recently developed Quasi-Quantum Treatment (QQT) method aims to simplify and approximate the exact QM treatment [22, 23]. It employs a Feynman path integral method that exploits the path length differences originating from the different orientations of an anisotropic molecule. As a result, the QQT method offers a physically compelling framework, while greatly reducing the calculation resources.

This thesis

In this thesis, we will describe scattering calculations of rotationally inelastic collisions of atom-molecule and molecule-molecule collision partners both by QQT and by exact QM methods. Potential energy surfaces are taken from the literature.

We will firstly study rotationally inelastic scattering of NO-He by the quasi-

quantum treatment (QQT) method. The QQT method has proven to be a good approximation for the treatment of several collision systems, such as NO-He [22, 24], NO-Ar [25, 26], NO-D₂ [27], and it has successfully interpreted steric asymmetry and parity propensity [22]. Up till now, all the transitions of NO-rare gas system were limited to spin-orbit state conserving transitions. Moreover the QQT method approximated the interaction potential by a hard-shell contour, which corresponds to the collision energy. This causes the QQT method to be rather insensitive to the soft part of the PESs. Our aim is to extend and modify the QQT method, in order to widen the scope of application and impact of the QQT method. The collision of the NO molecule onto a He atom is particularly interesting, due to the unpaired electron in the open-shell NO molecule. This allows for energy transfer into the excited rotational levels of the NO upper spin-orbit state. Moreover such a collision may also alter its Λ -doublet and hyperfine states. The NO - rare gas atom collision system is a benchmark for what happens in a molecular collision involving more than one Born-Oppenheimer potential energy surface.

In addition, we study H_2 - O_2 molecular collisions by full quantum closecoupling scattering calculations. Both the H_2 and O_2 molecules will be rotationally excited. Unlike the previous study by Kalugina et al. [28], we will focus on the paraortho H_2 conversion induced by collision with the paramagnetic O_2 molecules. This conversion is caused by the very weak coupling between the electron spin of O_2 and the spins of the nuclei in H_2 . The cross sections and para-ortho H_2 conversion rate coefficients by H_2 - O_2 collisions will be calculated.

Outline:

In chapter 2, the QQT theory is extended to the classically forbidden part which yields QQT differential cross sections (DCS) similarly to the exact QM DCSs. Based on QQT theory, a scaling rule for the collision energy dependence of DCSs has been discovered.

In chapter 3, we modify the QQT hard shell potential, which promises a simple tool to explore the softness of the repulsive part of the anisotropic atom-molecule potential.

In chapter 4, we extend QQT to spin-orbit state conserving and changing transitions in the mixed Hund's case basis, in which Hund's case (a) and case (b) are mixed together.

In chapter 5, the para-ortho H_2 conversion rates, induced by collision with O_2 , are calculated from full quantum theory.

A summary and future prospects of this work are given in chapter 6.



A general scaling rule for the collision energy dependence of a rotationally inelastic differential Cross section and its application to NO(X) + He

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The quasi-quantum treatment (QQT) (Gijsbertsen et al., JACS 2006, 128, 8777) provides a physically compelling framework for the evaluation of rotationally inelastic scattering, including the differential cross sections (DCS). In this work the QQT framework is extended to treat the DCS in the classically forbidden region as well as the classically allowed region. Most importantly, the OOT is applied to the collision energy dependence of the angular distributions of these DCSs. This leads to an analytical formalism that reveals a scaling relationship between the DCS calculated at a particular collision energy and the DCS at other collision energies. This scaling is shown to be exact for QM calculated or experimental DCSs if the magnitude of the (kinematic apse) frame underlying scattering amplitude depends solely on the projection of the incoming momentum vector onto the kinematic apse vector. The QM DCSs of the NO(X)-He collision system were found to obey this scaling law nearly perfectly for energies above 63 meV. The mathematical derivation is accompanied by mechanistic description of the Feynman paths that contribute to the scattering amplitude in the classically allowed and forbidden regions, and the nature of the momentum transfer during the collision process. This scaling relationship highlights the nature of (and limits to) the information that is obtainable from the collision-energy dependence of the DCS, and allows a description of the relevant angular range of the DCSs that embodies this information.

2.1 Introduction

Rotationally inelastic scattering is one of the fundamental collision-induced energy transfer processes that underlie intermolecular energy flow in chemically reacting systems such as combustion, astrochemistry, atmospheric and ultra-cold chemistry. Because of developments in experimental techniques, such as velocity mapped ion imaging [29, 30], explorations of the quantum state-to-state resolved rotationally inelastic Differential Cross-Sections (DCSs) have become possible [25, 31-39]. Experimental studies [40-42] exploring the collision-energy dependence of the quantum state-to-state resolved rotationally inelastic integral cross-sections (ICSs) upon the collision energy have recently been reported, and may be expected to soon extend to measurement of the associated DCSs.

Comparison between theoretical and experimental scattering cross sections is commonly employed as a test of the accuracy of the potential energy surface. For example, the agreement between the experimental and theoretical fully quantum state resolved DCSs at collision energies of around 500 cm⁻¹ has been demonstrated to be very good for NO(X) + He [33, 43] and nearly perfect [25, 44, 45] for NO(X) + Ar. Nevertheless, a combined theoretical and experimental study [46] of the depolarization rate of rotationally quantum state selected NO molecules in collisions within a thermal bath of Ar atoms (T=298K) yielded experimental depolarization rates that differed significantly from their theoretical counterparts. Interestingly, these calculations were performed using the same high quality *ab initio* PES's employed to predict the NO(X)-Ar DCSs, which were found to be in excellent agreement with experimental measurements. Changing the initial collision energy of a rotationally inelastic scattering process accesses different areas of the potential energy surface, and also alters the angular dependence of the DCS by purely kinematic effects.

Early studies [47, 48] explored the feasibility of a scaling law describing the temperature dependence of the thermally averaged rate constants for rotational energy transfer in collisions between an electronically excited Na₂*(A $^{1}\Sigma$) molecule and a rare gas atom. These led to a scaling law based on the energy corrected sudden approximation in combination with the assumption of a power gap law, which required only 3 parameters to a fit all rotational energy transfer rate constants for a given target gas to within 7%-12% deviations. However, a disquieting feature of these scaling laws was the lack of a simple theoretical justification [49].

In this chapter, we show that the quasi-quantum treatment (QQT) formalism [22,

24, 27], previously introduced as a physically intuitive simplification of exact quantum scattering, reveals a new collision-energy scaling relationship, and we use the rotationally inelastic quantum state resolved DCSs associated with the NO(X)-He collision system as a case study to explore that relationship. The NO(X)-He system is especially interesting, as the electronic structure allows the investigation of rotational energy transfer among hyperfine states, Λ -doublet states and spin-orbit states. Furthermore, the collision dynamics of the scattering of an NO molecule from a rare gas atom is an experimental benchmark and paradigm for molecular collisions involving more than one Born-Oppenheimer potential energy surface.

The collision-energy scaling procedure will be demonstrated using rotationally inelastic DCSs obtained both from full close-coupled quantum mechanical (QM) calculations, as well as from QQT. Collision energies of E_{col}^{L} =63 meV and E_{col}^{H} =147 meV, corresponding to separate experimental measurements [33, 50], will be considered. The QM method represents the current state of the art in scattering calculations, while the QQT method can be expressed in a more compact, analytical form, yielding additional insight into the scattering problem. Additionally, the extension of the QQT into the classically forbidden angular region of the DCS will be presented, allowing a more complete comparison to be conducted with the corresponding QM data.

The present DCS scaling procedure applies rigidly when the magnitude of the scattering amplitude depends only on the projection of the incoming momentum vector \mathbf{k} on the direction of the kinematic apse vector

$$\boldsymbol{a} \equiv \frac{\mu}{\hbar} (\boldsymbol{v}_{rel}' - \boldsymbol{v}_{rel}) = \boldsymbol{k}' - \boldsymbol{k}$$
(2.1)

here k and k' denote the relative wave-vectors of the collision partners before and after the collision respectively. This assumption is shared by the QQT on a hard shell PES, and so the scaling procedure can be rigorously applied in that instance. In the more general QM calculations, the interaction potential may be softer, even containing attractive regions; but in experimental and theoretical studies [25, 31-43, 45, 51, 52], a strong propensity to conserve the projection quantum number m_a of the rotational molecular wave function onto a is found in nearly all cases.

By definition, the projection of k and k' onto the plane perpendicular to a must remain conserved; hence k_{\parallel} and k'_{\parallel} play only a minor role in classical rotationally inelastic collisions [22, 25, 33, 45, 50-52]. Differences between the measured collision-energy dependence and the predictions from the scaling

relationship can high light the repulsive or attractive character of parts of the interaction potential that govern the rotational energy transfer.

The chapter is organized as follows. In Section 2.2.1 the coupled channel exact solution of the rotationally inelastic scattering problem is presented, with emphasis on the case of $m_a = m'_a$. In Section 2.2.2 the essentials of the QQT hard shell PES apse frame computational model are summarized, along with the equations needed to transform a rotationally inelastic (OM or OOT) DCS and relevant vector quantities from the scattering frame to the apse frame. In Section 2.2.3.1 the QQT is extended into the classically forbidden region of scattering angles. The results and consequences of such an extension for the NO(X)+He rotationally inelastic QQT DCSs are given in Section 2.2.3.2. The scaling formalism describing the collision energy dependence of the QQT DCS is provided in Section 2.2.4.1 and subsequently extended to the QM DCSs in Section 2.2.4.2. Section 2.2.4.3 describes in detail the scaling method of the QQT and QM DCSs from $E_{col}^{H}=147$ meV to $E_{col}^{L}=63$ meV for the $j = 0 \rightarrow j' = 2$ and $j = 0 \rightarrow j' = 6$ rotationally inelastic transitions. The results and discussion are presented throughout Section 2.3. Section 2.3.1 presents the collision energy scaled closed shell NO(X)-He DCSs and the agreement with the directly calculated DCSs is discussed. The corresponding open shell NO(X)-He DCSs are provided and discussed in Section 2.3.2. Our conclusions are presented in Section 2.4, where Section 2.4.1 focuses on the accuracy of the DCS collision-energy scaling relationship and Section 2.4.2 on the signature of the properties of the interaction potential that are visible the DCS.

2.2 Method

2.2.1 Coupled-channel QM solution

The solution of the rotationally inelastic scattering of a diatomic molecule colliding with an atom by the coupled channel quantum mechanical formalism is exact. As such, it represents the most accurate method by which calculations can be performed, and contains all available information pertaining to the scattering process.

As a starting point, one expands the scattering wave function as a series of partial waves, which are the wave functions corresponding to different values of the orbital angular momentum l. The collision geometry is uniquely specified by the length, R, of the displacement vector, \mathbf{R} , from the He atom to the center of mass (COM) of the NO molecule, and by the polar angle

$$\gamma_R \equiv \arccos(\hat{\boldsymbol{R}} \cdot \hat{\boldsymbol{r}}_{NO}), \qquad (2.2)$$

Where \hat{r}_{NO} is the unit vector pointing along the diatomic molecular axis from O to N. These two variables then jointly specify the potential interaction energy according to some function $V(R, \gamma_R)$.

In the case of the NO(X) molecule, the coupling of the various angular momenta are best described according to Hund's case (a), at least for low values of the rotational quantum number. The coupling between Σ (the projection of the electronic spin of the unpaired electron onto the internuclear axis) and Λ (the projection of the electronic orbital angular momentum of the singly occupied π^* orbital onto the internuclear axis) gives rise to two spin-orbit channels specified by the total electronic angular momentum projection quantum number Ω . Transitions within a single spin-orbit manifold (where the magnitude of Ω is conserved) can be shown to take place on an effective potential $V_{sum}(\gamma_R, R)$, while changes in spin-orbit state are mediated by the qualitatively different potential $V_{dif}(R, \gamma_R)$ [53, 54].

The Schrödinger equation must then be solved for each value of *J*. This entails finding the solution to a large set of second order differential equations (describing the coupling between the initial and final quantum states) with respect to the atomdiatom distance *R*. This coupling between a particular initial and final molecular state is provided by the *R*-dependent potential matrix element, $\langle j', l', f, J, M_J | V(R, \gamma_R) | j, l, i, J, M_J \rangle$, here *j* denotes the initial rotational quantum number, *l* the orbital angular momentum quantum number of the scattering channel, and *i* (*f*) all other quantum numbers associated with the initial (final) state. Primed indices are associated with the outgoing final quantum state.

From the *R* dependence of the radial wave functions, $U_{j',l',f}^{J,M}(R)$, obtained from these coupled equations, the *T^J*-matrix elements in the total angular momentum representation can then be calculated. These matrix elements, $T_{j',l',f;j,l,i}^{J}$, then directly reflect the probability amplitudes associated with transitions from one quantum channel to another during the scattering process, allowing the subsequent calculation of any observable quantity of interest associated with the collision.

In this case we are interested in obtaining the differential cross-sections, and so we first calculate the dimensionless scattering amplitude $f_{j',m'_j,f\leftarrow j,m_j,i}(\hat{k}')$ where the scattering angle θ is defined by the relation $\hat{k}' \cdot \hat{k} = \cos \theta$, and specifies the polar 9 angle of k' in the collision frame for which k points along the Z axis [54, 55].

$$f_{j',m'_{j},f\leftarrow j,m_{j},i}(\hat{k}') = \sum_{l,l',J} i^{l-l'} [(2l+1)\pi]^{0.5} (2J+1) \begin{pmatrix} j & J & l \\ m_{j} - m_{j} & 0 \end{pmatrix} \times \begin{pmatrix} j' & J & l' \\ m'_{j} & -m_{j} & m_{j} - m'_{j} \end{pmatrix} T^{J}_{j',l',f;j,l,i} Y_{l',m_{j} - m'_{j}}(\hat{k}')$$
(2.3)

The differential cross-section itself is then given by the square modulus of the dimensionless scattering amplitude averaged over m_i and summed over m'_i .

$$\frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}}{\mathrm{d}\omega}(\hat{k}') = \frac{1}{k^2} \frac{1}{2j+1} \sum_{m'_j,m_j} |f_{j',m_j,f\leftarrow j,m_j,i}(\hat{k}')|^2 .$$
(2.4)

In the case that the projection of the rotational angular momentum of the NO molecule is conserved along some axis (e.g., this projection along \hat{a} must always be conserved for a hard-shell type of collision), the scattering amplitude becomes diagonal with respect to the m_a projection quantum number along that axis, and may be written as

$$f_{j',m_a,f \leftarrow j,m_a,i}(\hat{k}') = \sum_{m_j,m_j'} D_{m_j',m_a}^{j'}(\alpha,\beta,0) D_{m_j,m_a}^{j*}(\alpha,\beta,0) f_{j',m_j',f \leftarrow j,m_j,i}(\hat{k}') \quad , \quad (2.5)$$

where the spherical angles β and α denote the direction of \hat{a} with respect to \hat{k} ,

$$\beta \equiv \arccos(\hat{a} \cdot \hat{k}) \,. \tag{2.6}$$

While Eqs. (2.3) and (2.5) appear appealingly simple, it is typically a state of the art numerical effort to obtain the requisite T^{J} -matrix elements, $T_{j',l',f;j,l,i}^{J}$. This is largely due to the very large set of coupled differential equations containing all the relevant scattering channels *j*, *l*, *i*, *j'*, *l'*, *f*, that must be solved for each value of *J*. Typically, one has to couple more than thousand channels more than a hundred times.

2.2.2 QQT calculation

In the quasi quantum treatment (QQT) of the rotationally inelastic scattering problem, the interaction potential is approximated by a smooth convex hard shell, whose radius R_s is given by the function $R_s(\gamma_R)$. In the case of the NO(X)-He system, this shell is defined by the potential energy contour

$$V_{sum}(\gamma_R, R) = E_S, \qquad (2.7)$$

in which E_S is set equal to the (most relevant) lower collision energy considered in this study, $E_{col}^{L}=63$ meV. The predominantly attractive nature of the $V_{dif}(\gamma_R, R)$ interaction potential that mediates changes in spin-orbit state does not facilitate the definition of an anisotropic shell in this fashion, so we treat the rotational energy tranfer as dominated by the more repulsive spin-orbit conserving interaction potential $V_{sum}(\gamma_R, R)$ in all cases. To further simplify the calculations and associated expressions, the angular momentum eigenfunctions of the NO molecule are approximated by their closed-shell ${}^{1}\Sigma | j, m \rangle$ equivalents.

In QQT one addresses the rotationally inelastic collision problem in the socalled kinematic apse frame, in which the quantization axis points along the kinematic apse vector \boldsymbol{a} . The magnitude of the outgoing wave vector is determined by the amount of translational energy $E_{col} = \hbar^2 k^2 / 2\mu$ transferred into rotational excitation $\Delta E_{j'\leftarrow j}^{ROT} \equiv E_{ROT}(j') - E_{ROT}(j)$,

$$k' = k \sqrt{1 - \Delta E_{j' \leftarrow j}^{ROT} / E_{col}} .$$
 (2.8)

In contrast to the exact coupled channel QM solution of the collision problem (but very much in the spirit of the classical treatment of the rotationally inelastic collision problem by Evans *et al.* [56]). QQT suppresses the summation over the angular momentum *J*, *l* and *l'* quantum numbers (Eq. (2.3)) and provides a transition moment type expression for the scattering amplitude in which the spherical scattering angles θ and ϕ are replaced by the spherical angles of the kinematic apse β and α .

Other essential QQT variables include the polar angle γ_a of the diatomic inter-nuclear axis, $\hat{\mathbf{r}}_{NO}$, with respect to the kinematic apse, and the azimuthal angle ϕ_a of the molecular plane (defined by the vectors $\hat{\mathbf{r}}_{NO}$ and $\mathbf{R}_S(\gamma_R)$) with respect to the scattering plane (defined by the vectors $\hat{\mathbf{k}}$, $\hat{\mathbf{k}}'$ and $\hat{\mathbf{a}}$). Note that the cylindrical symmetry of the hard shell implies that $\hat{\mathbf{r}}_{NO}$, $\mathbf{R}_S(\gamma_R)$ and $\hat{\mathbf{a}}$ must all reside in the same plane.

In the case of a hard shell, as depicted in Figs. 2.1 and 2.2, momentum transfer is restricted to the direction perpendicular to the surface at which the collision takes place. Moreover, only the component of **k** parallel to $\hat{\mathbf{n}}$, $k_{\perp} = |k \cos \beta|$, plays a role

in the transfer into rotational energy with $\hat{k}'_{\perp} = (-1)^p \hat{k}_{\perp}$. Note that the index, p=1 or 2 denotes whether the transition is classically allowed or forbidden, as discussed further in section 2.3.1. Because the component of k parallel to the surface, $k_{\parallel} = k \sin \beta$, cannot be used to transfer energy into the rotational degrees of freedom of the molecule (as depicted in Fig. 2.1) it must be conserved $k_{\parallel} = k'_{\parallel}$.



Figure 2.1: Representation of the classically allowed, p=1 (solid lines) and classically forbidden, p=2 (dashed lines) Feynman paths that contribute to the scattering amplitude within the QQT formalism.



Figure 2.2: Representation of the angles defining the QQT collision geometry (left hand panel), and the classically allowed, p=1 (upper right hand panel) and classically forbidden, p=2 (lower right hand panel) Feynman paths that contribute to the scattering amplitude within the QQT formalism. Although the illustrative NO(X)+He system is represented here, the formalism is general, and extends to any atom-diatom collision system. The labels associated with all vectors and angles are explained in the main text.

The apse frame scattering amplitude, $g(\beta)$, associated with a particular quantum state-to-state resolved scattering process, can now be expressed in terms of the overlap integral between a specific final $\langle f |$ and initial $|i\rangle$ molecular state, together with the coupling between the two states. Within the QQT formalism, this coupling is expressed in terms of the phase shift, η , associated with each of the scattering paths within the integral over the full range of the spherical angles γ_a and ϕ_a .

$$g_{j',m'_{a},f \leftarrow j,m_{a},i}^{QQT}(\beta,p) = C(\beta) < j',m'_{a},f \mid g_{geom}(\gamma_{a};\beta) \\ \times \exp[i\eta_{j',f \leftarrow j,i}(\gamma_{a};\beta,p)] \mid j,m_{a},i > \delta_{m_{a},m'_{a}}, \qquad (2.9)$$

where $C(\beta)$ is a normalization constant that will be discussed later. It should be noted that in the case of a collision with a hard shell, the projection of *j* onto the kinematic apse must remain unchanged, such that $m'_a = m_a$ [22, 24, 27]. The phase shifts themselves are calculated via the expression [26]

$$\eta_{f\leftarrow i}(\gamma_a;\beta,p) = -\boldsymbol{a}(\beta,p) \cdot \boldsymbol{R}_S(\gamma_a) = -[k_{\perp} - (-1)^p k_{\perp}'] \boldsymbol{R}_S(\gamma_R) \cos(\gamma_R - \gamma_a).$$
(2.10)

This phase shift is defined as the difference in phase between 1) the path of the incoming wave, k, which is scattered at the shell surface into a outgoing wave, k', and 2) the virtual reference path in which k passes unhindered through the hard shell surface, intercepts the COM of the NO molecule and scatters into the outgoing wave k', and then passes without hindrance through the hard shell surface in the outwards direction.

Each of these paths is weighted by the so-called molecule fixed geometric dimensionless scattering amplitude $g_{geom}(\gamma_a;\beta)$ [24, 49]:

$$g_{geom}(\gamma_a;\beta) \equiv k \sqrt{\frac{d\sigma^{geom}(\gamma_a;\beta)}{d\omega_a}} = k \sqrt{|\cos\beta| \rho_1(\gamma_a)\rho_2(\gamma_a)}, \qquad (2.11)$$

in which $\rho_1(\gamma_a)$ and $\rho_2(\gamma_a)$ denote the local radii of curvature of the cylindrically symmetric convex surface. This geometric differential cross-section, $\frac{d\sigma^{geom}(\gamma_a;\beta)}{d\omega_a}$, is simply the area of the hard shell that presents itself to the incoming

plane wave given the angles $(\gamma_a; \beta)$ defining its orientation. In our case of j = 0or $j = \frac{1}{2}$ averaging over the spherical angles γ_a and ϕ_a of \hat{r}_{NO} with respect to \hat{a} yields the NO orientation-averaged geometric DCS,

$$\frac{\mathrm{d}\sigma^{geom}(\beta)}{\mathrm{d}\omega_a} = \frac{1}{2} \int_{-1}^{1} d\cos\gamma_a \, \frac{\mathrm{d}\sigma^{geom}(\gamma_a;\beta)}{\mathrm{d}\omega_a} \,. \tag{2.12}$$

The normalization constant $C(\beta)$ in Eq. (2.9) is chosen such that the QQT DCSs recover the geometric (NO orientation averaged) DCS, $\frac{d\sigma^{geom}(\beta)}{d\omega_a}$, for all values of

 β , when summed over all final states. Hence the QQT scattering amplitude is normalized with respect to the incoming flux. [See section 2.2.4.3 for a comparison to the normalization of the QM case of Eq. (2.3)].

Equation (2.9) captures the fundamental methodology of QQT particularly clearly. The (apse frame) scattering amplitude can be seen to be given by a path integral considering the phases, η , of all possible paths associated with all possible relative orientations, $(\gamma_a; \beta)$, of the hard shell with respect to the kinematic apse. Neither the QQT phase shift function, $\eta_{f \to i}(\gamma_a; \beta, p)$, nor the geometric scattering amplitude, $g_{geom}(\gamma_a; \beta)$, depend on χ_a , and so it suffices to conduct the integral solely over the polar angle γ_a .

$$\frac{d\sigma_{j'\leftarrow j=0}^{QQT}}{d\omega_a}(\beta,p) = \frac{|g_{j'\leftarrow j=0}^{QQT}(\beta,p)|^2}{k^2}$$
$$= C(\beta)^2 \frac{2j'+1}{4k^2} |\int_{-1}^{1} d\cos\gamma_a P_{j'}(\cos\gamma_a) \quad . \tag{2.13}$$
$$\times g_{geom}(\gamma_a;\beta) \exp[i\eta_{j'\leftarrow 0}(\gamma_a;\beta,p)]|^2$$

As can be seen by comparing Eqs (2.3) and (2.9), the standard QM approach specifies the differential cross-section in terms of the collision frame spherical angles (θ, ϕ) , while the QQT provides the DCSs in terms of the angles (β, α) , defined with respect to the kinematic apse. These spherical angles may be chosen such that $\alpha \equiv \phi$. In this case, the apse frame and collision frame DCSs are related to one other according to

$$\frac{\mathrm{d}\sigma_{f\leftarrow i}}{\mathrm{d}\omega}(\theta,\phi) = \frac{\mathrm{d}\sigma_{f\leftarrow i}}{\mathrm{d}\omega_a}(\beta,\alpha) \left| \frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta} \right|. \tag{2.14}$$

This will turn out to be an important expression, because as well as allowing us to directly compare the QM and QQT DCSs, it also clearly shows the basis of the collision energy relationship that underlies the scaling formalism developed below.

As a starting point to derive the Jacobian in Eq. (2.14), we consider the coordinate frame for which

$$\hat{k} \equiv \hat{Z} , \qquad (2.15)$$

$$\hat{k}' \equiv \hat{X}\sin\theta + \hat{Z}\cos\theta. \qquad (2.16)$$

The kinematic apse can then be re-written in terms of these new coordinates as

$$\boldsymbol{a} \equiv \boldsymbol{k}' - \boldsymbol{k} = \hat{\boldsymbol{X}}[\boldsymbol{k}'\sin\theta] + \hat{\boldsymbol{Z}}[\boldsymbol{k}'\cos\theta - \boldsymbol{k}].$$
(2.17)

Taking the dot product of the kinematic apse with the Z axis then yields the relation

$$\cos\beta = \hat{a} \cdot \hat{Z} = \frac{k' \cos\theta - k}{\sqrt{k'^2 - 2kk' \cos\theta + k^2}}.$$
(2.18)

The Jacobian appearing in Eq. (2.14) can then be re-written as

$$\frac{d\cos\beta}{d\cos\theta} = \frac{(k')^2 [k' - k\cos\theta]}{[(k')^2 - 2kk'\cos\theta + k^2]^{1.5}}.$$
(2.19)

This expression can now be used in conjunction with Eq. (2.14) (or its inverse) to allow for facile transformation between the scattering frame and apse frame DCSs, allowing direct comparison between the QM and QQT calculations.

2.2.3.1 Extension of QQT into the classically forbidden region

As mentioned already in section 2.2.2, the index p specifies whether a particular scattering path, included in the path integral formulation of the scattering amplitude, is classically allowed or forbidden. All previous QQT derivations and calculations have focused on the classically allowed region of the DCS [3, 22, 24, 25, 27]. In this Section we shall extend the formalism to include the classically forbidden region. The scattering angle can be obtained by re-arrangement of Eq. (2.18) to give

$$\theta = \arccos\left\{ \left(\frac{k}{k'}\right) \sin^2 \beta + (-1)^p \left| \cos \beta \right| \left[1 - \left(\frac{k}{k'}\right)^2 \sin^2 \beta \right]^{0.5} \right\}.$$
 (2.20)

The mathematical origin of the index p that indicates whether a particular path is classically allowed or forbidden now becomes clear — it simply serves to distinguish between the two allowed roots of Eq. (2.20). In this study only the lowest initial rotational quantum state of j is considered, and so the magnitude of the outgoing wave-vector, k', cannot be larger than that of the incoming wave-vector, k. In this case, Eq. (2.20) gives rise to two distinct scattering angles for each possible value of β ; these shall be denoted θ_1 if p=1 (classically allowed) and θ_2 if p=2(classically forbidden). The classically allowed case p=1 corresponds to a scattering angle range of $\theta_c \le \theta_1 \le \pi$, while the angular range from $0 \le \theta_2 < \theta_c$ corresponds to the classically forbidden case p=2, where

$$\cos\theta_c = k'/k \,. \tag{2.21}$$

Further inspection of Eq. (2.20) indicates that to obtain a real value of θ , the range of β is restricted between -1 and some cut-off value β_c , defined such that

$$-1 \le \cos \beta \le \cos \beta_c = -\sqrt{1 - (k'/k)^2} .$$
 (2.22)

Note that Eq. (2.22) implies $\beta_c \leq \beta \leq \pi$, while the collision frame DCS is provided for $0 \leq \theta \leq \pi$. In the case of elastic scattering, the substitution of k' = kinto Eqs. (2.21) and (2.22) yields values of $\cos \theta_c = 1$ and $\cos \beta_c = 0$, implying a one to one relation between θ and β , such that $\theta = 2\beta - \pi$ [24].

Previous QQT expressions [22, 24-27] were restricted to the classically allowed angular range $\theta_1 \ge \theta_c$. The rotationally inelastic QQT DCSs were found to decrease monotonically with decreasing scattering angles as $\theta_1 \rightarrow \theta_c$ and the relative magnitude of the DCS near $\theta_1 \approx \theta_c$ was found to be very small. As such, for values of $\theta < \theta_c$ the DCSs were set to zero. However, the QM rotationally inelastic DCSs exhibit no such cutoff for $\theta < \theta_c$. Indeed, the small scattering-angle region is an especially interesting area for comparison, because QQT neglects the diffractive contribution to the scattering process, due to the rigid relation imposed between θ and β . This difference can be expected to lead to features in the QM DCSs that remain absent in the corresponding QQT calculations. More significantly, the extension of the QQT DCS into the classically forbidden region plays a crucial role in the collision-energy scaling procedure developed here, as will be shown in the following section.

Further insight into the collision dynamics can be obtained by considering the details of the hard shell collision Feynman paths that correspond to the p=1 and p=2 cases. As has been argued in previous studies, a (non-diffractive) direct collision requires that the incoming wave-vector, \mathbf{k} , impinges directly onto the hard shell surface. This precondition implies that the component of \mathbf{k} directed perpendicular to the surface, \mathbf{k}_{\perp} , should point inwards towards the surface (*i.e.* the incoming plane wave is traveling towards the hard ellipsoid). This can be seen to be the case for all paths depicted in Fig. 2.1. The intuitive classically allowed path is then impulsively scattered from the hard shell surface such that \mathbf{k}'_{\perp} makes a positive projection onto the kinematic apse. However, the classically forbidden path is distinctly less intuitive, and can be seen to pass through the hard shell surface, with \mathbf{k}'_{\perp} making a negative projection onto the kinematic apse.

Figure 2.2 depicts the classically allowed (panel b) and classically forbidden (panel c) pathways that contribute to the scattering process, along with the angles

specifying the collision geometry (panel a). In all panels the incoming wave-vector \mathbf{k} , depicted as a horizontal green arrow, defines the Z-axis of the collision frame. The azimuthal angle χ_a (panel a of Fig. 2.2) does not influence the outcome of the scattering amplitude because of the cylindrical symmetry of $\mathbf{R}_{s}(\gamma_{R})$.

The same (arbitrary) choice of γ_a is used for all panels of Fig. 2.2, leading to identical impact positions, $\mathbf{R}_s(\gamma_R)$, depicted as a solid purple displacement vector with respect to the COM of the NO molecule. The spherical angles (β, α) and (θ, ϕ) define the spatial directions of \hat{a} and k' with respect to k. The projections of k and k' onto the shell surface are indicated by a dashed purple line.

As discussed previously, in panel b of Fig 2.2 (depicting the classically allowed path), $k'_{1,\perp}$ must point outwards from the shell. Panel c depicts the corresponding classically forbidden path, in which the $k'_{2,\perp}$ component of the outgoing k'_2 wave-vector points inwards towards the shell. That this outcome should be Feynman path allowed can be rationalized by considering the limit in which the DCS is defined at an arbitrarily high level of scattering angle resolution.

This implies that the Heisenberg uncertainty relation between scattering angle and classical impact parameter (or quantum mechanical partial wave) [56], automatically incorporated in the Schrödinger equation, permits any lateral displacement of the path of the k'_2 wave-vector with respect to the position at which the incoming k vector impinges upon the hard shell. This lateral displacement of the (dashed red) k'_2 wave-vector in Fig 2.2 its lower right panel is conducted such that the wave front (and therefore also the phase shift) of the (solid red) outgoing k'_2 wave-vector remains matched to that of the incoming k vector.

2.2.3.2 Example Calculations

To demonstrate the extension of the QQT DCSs into the classically forbidden region, the NO(X)+He rotationally inelastic DCSs for transitions from j=0 to j'=1-12 have been calculated for a collision energy of $E_{col}^{L}=63$ meV. The DCSs associated with these transitions are displayed in Fig. 2.3, both in the apse frame



Figure 2.3: Differential cross sections for the scattering of NO(X)+He from the initial state *j*=0 to final rotational states *j*'=1-12, calculated using closed-shell QQT at a collision energy of 63 meV. The DCSs are displayed in both the collision frame (as a function of θ , with solid lines) and the apse frame (as a function of β , with dashed lines). The angular threshold at which the transition becomes classically forbidden is indicated with a dashed vertical line.

(dashed lines) and in the collision frame (solid lines). It should be noted that the DCSs displayed here are plotted so that the horizontal axes are linear in $\cos\theta$. At a first glance, these two sets of DCSs, related to one another according to Eq. (2.14), appear qualitatively similar to one another. In all cases, the QQT DCSs lack the characteristic oscillatory structure arising from the diffractive effects that one would expect to find in the corresponding QM calculations. However, the magnitude of most collision frame DCSs was found to be about half that of the corresponding apse frame ones. These differences are due to the weighting factors associated with the polar angles β and θ . Since the two angles are constrained to within different ranges, so the weighting factors take different values. These corresponding values of $\cos\beta$ are depicted along the upper horizontal axes in each panel.

The classically allowed range of $\cos \beta$ can be seen to run from -1 (at the right end of each plot) to $\cos\beta = \cos\beta_C$ (near the left end of each plot), where the classically allowed boundary is illustrated with a vertical dotted line. The classically forbidden region is then located to the left of this line, although it is too small to be visualized in the case of j'=1. In accordance with Eq. (2.22), the classically forbidden region of $\cos\beta$ is found to increase with increasing j'. Most importantly, Fig. 2.3 shows that as a result of the formalisms developed here, the QQT DCSs can now be smoothly and continuously extended through this classically forbidden region.

As follows from the relations expressed in Eqs. (2.18) and (2.20), a rigid correspondence between θ and β is presumed. The azimuthal symmetry of a DCS requires that its first derivative with respect to θ should be zero at $\theta = 0$ and $\theta = \pi$, or equivalently that it displays a stationary point at these values. This requirement is met by all the DCSs displayed in Fig. 2.3. In Appendices we show that all QM and QQT DCSs exhibit this stationary behavior in both the apse and collision frames. The QM collision frame DCSs must necessarily display such stationary behavior at $\theta = 0$ or $\theta = \pi$, by virtue of the fact that they can be written as a series of Legendre polynomials, all of which individually obey this requirement [56]. The apse and collision QQT DCSs at $E_{col}^{L} = 63$ meV are also listed for $\theta = 0$ and $\theta = \pi$ in Table 2.A of Appendices.

2.2.4.1 Scaling formalism describing the dependence of the QQT DCSs on Ecoll

The basis for the scaling formalism describing the energy dependence of the QQT DCSs lies in the transformation from the apse frame to the collision frame. As the collision energy increases, the mapping between the scattering angle θ and the apse angle β changes, so that a particular scattering angle corresponds to different regions of the apse frame DCS at different collision energies, as can be seen from Eqs. (2.18) and (2.20). The dependence of the phase shifts on the collision energy E_{col} follows from

$$\eta_{f \leftarrow i}(\gamma_a; \beta, p) = k \cos \beta \left[1 - (-1)^p \sqrt{1 - \Delta E_{j' \leftarrow j}^{ROT} / E_{col}} \right].$$

$$\times R_s(\gamma_R) \cos(\gamma_R - \gamma_a)$$
(2.23)

The phase shifts associated with a particular scattering angle, θ , calculated at two different collision energies, E_H and E_L , are related to one another according to a simple geometric relationship

Table 2.1: Numerical values of the closed-shell and open-shell QM NO(X)+He ICSs. Values are given both for the calculations performed directly at 147 meV and 63 meV, also for the calculations scaled from 147 meV. The associated QM calibration factor (see text for details) is also given here.

	c-s QM						$\begin{array}{c} \text{o-s } \text{QM} \\ \text{F}_1 e \to \text{F}_1 e \end{array}$					$\begin{array}{c} \text{o-s QM} \\ \text{F}_1 e \to \text{F}_1 f \end{array}$				
riangle j	ΔE^{ROT}	$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle dir}$	$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle scale}$	$\sigma^{\scriptscriptstyle E_L}_{\scriptscriptstyle dir}$	CF_{QM}		$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle dir}$	$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle scale}$	$\sigma^{\scriptscriptstyle E_L}_{\scriptscriptstyle dir}$	CF_{QM}		$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle dir}$	$\sigma^{\scriptscriptstyle E_H}_{\scriptscriptstyle scale}$	$\sigma^{\scriptscriptstyle E_L}_{\scriptscriptstyle dir}$	CF _{QM}	
	(meV)	(Ų)	(Å ²)	(Å ²)			(Å ²)	(Å ²)	(Å ²)			(Ų)	(Å ²)	(Å ²)		
1	0.62	1.888	1.822	2.94	0.69		1.002	0.969	1.446	0.64		2.161	1.866	2.758	0.63	
2	1.66	5.200	4.509	6.48	0.62		3.121	2.684	3.943	0.63		0.679	0.623	1.043	0.72	
3	3.11	2.225	1.993	3.235	0.70		0.883	0.806	1.327	0.71		1.289	1.000	1.808	0.78	
4	4.98	2.805	2.202	3.637	0.71		1.514	1.161	2.088	0.77		0.602	0.550	1.027	0.80	
5	7.26	2.214	1.967	3.228	0.70		0.676	0.613	1.111	0.78		0.900	0.456	0.937	0.88	
6	9.95	1.885	0.999	1.769	0.76		0.944	0.475	0.975	0.88		0.523	0.347	0.747	0.92	
7	13.06	2.126	1.477	2.644	0.77		0.538	0.356	0.736	0.89		0.606	0.180	0.416	0.99	
8	16.59	1.257	0.461	0.870	0.81		0.584	0.160	0.368	0.99		0.476	0.105	0.248	1.01	
9	20.53	2.093	0.646	1.31	0.87		0.446	0.103	0.223	0.93		0.249	0.046	0.118	1.09	
10	24.89	0.483	0.165	0.348	0.90		0.227	0.030	0.074	1.05		0.355	0.012	0.025	0.89	
11	29.66	1.848	0.156	0.362	1.00		0.290	0.014	0.019	0.57		0.117	0.006	0.017	1.17	
12	34.84	0.230	0.034	0.080	1.00		0.078	0.002	0.004	0.85		0.153	0.003	0.003	0.57	
	o-s QM						o-s QM									
	$F_1 e \rightarrow F_2 e$						$F_1 e \rightarrow F_2 f$									
Δj	ΔE^{ROT}	$\sigma^{\scriptscriptstyle E_H}_{\scriptscriptstyle dir}$	$\sigma^{\scriptscriptstyle E_H}_{\scriptscriptstyle scale}$	$\sigma^{\scriptscriptstyle E_L}_{\scriptscriptstyle dir}$	CF_{QM}		$\sigma^{\scriptscriptstyle E_{\scriptscriptstyle H}}_{\scriptscriptstyle dir}$	$\sigma^{\scriptscriptstyle E_H}_{\scriptscriptstyle scale}$	$\sigma^{\scriptscriptstyle E_L}_{\scriptscriptstyle dir}$	CF_{QM}						
	(meV)	(Å ²)	(Å ²)	(Å ²)			(Å ²)	(Å ²)	(Å ²)							
1	15.49	0.015	0.013	0.018	0.62		0.277	0.203	0.269	0.57						
2	16.55	0.144	0.115	0.155	0.57		0.142	0.127	0.167	0.56						
3	18.04	0.087	0.079	0.107	0.58		0.339	0.278	0.334	0.51						
4	19.96	0.222	0.174	0.225	0.55		0.347	0.304	0.410	0.58						
5	22.31	0.240	0.206	0.296	0.62		0.250	0.178	0.212	0.51						
6	25.08	0.224	0.135	0.179	0.57		0.460	0.347	0.499	0.62						
7	28.28	0.357	0.234	0.362	0.66		0.184	0.109	0.141	0.56						
8	31.90	0.175	0.089	0.129	0.62		0.485	0.211	0.317	0.64						
9	35.95	0.422	0.131	0.207	0.68		0.117	0.048	0.064	0.58						
10	40.43	0.108	0.035	0.051	0.62		0.476	0.063	0.090	0.62						
11	45.33	0.432	0.032	0.047	0.63		0.073	0.010	0.012	0.51						
12	50.66	0.091	0.006	0.007	0.52		0.366	0.008	0.010	0.50						

$$\eta_{f \leftarrow i}^{L}(\gamma_{a}; \cos \beta_{L}, p) = \eta_{f \leftarrow i}^{H}(\gamma_{a}; \cos \beta_{H} = \frac{k_{L}}{k_{H}} \cdot \cos \beta_{L}, p) .$$
(2.24)

Similarly a further, scalar dependence of the DCS on the collision energy is given by the collision energy scaling of the molecule fixed geometric scattering amplitude, which varies according to

$$g_{geom}^{QQT,L}(\gamma_a;\cos\beta_L) = \sqrt{\frac{k_L}{k_H}} g_{geom}^{QQT,H}(\gamma_a;\cos\beta_H = \frac{k_L}{k_H} \cdot \cos\beta_L).$$
(2.25)

Upon combining these scaling factors, the collision energy dependence of the QQT DCSs follows from:

$$\frac{d\sigma_{f\leftarrow i}^{QQT;L}(\cos\beta_L,p)}{d\omega_a} = \frac{k_H}{k_L} \times \frac{d\sigma_{f\leftarrow i}^{QQT;H}(\cos\beta_H = \frac{k_L}{k_H}\cos\beta_L,p)}{d\omega_a}.$$
 (2.26)

Note that only the range $-\frac{k_L}{k_H} \le \cos \beta_H \le 0$ of $\frac{d\sigma_{f \leftarrow i}^{QQT; H}(\cos \beta_H, p)}{d\omega_a}$ is scaled

down to $\frac{d\sigma_{f \leftarrow i}^{QQT;L}(\cos \beta_L, p)}{d\omega_a}$. However, since the range of $\cos \beta_L$ is

 $-1 \le \cos \beta_L \le 0$, according to Eq. (2.26), $\cos \beta_H$ should be stretched to fill this range by an additional factor of $\cos \beta_L = \frac{k_H}{k_L} \cos \beta_H$. These factors combine to give

$$\sigma_{f \leftarrow i}^{QQT; L} = SF_{QQT} \sigma_{scale, f \leftarrow i}^{QQT; H}$$
(2.27),

where $SF_{QQT} = (k_H / k_L)^2 = E_{col}^H / E_{col}^L$ is defined as the scaling factor and the incomplete ICS $\sigma_{scale, f \leftarrow i}^{QQT; H}$ denotes the scalable part of $\sigma_{f \leftarrow i}^{QQT; H}$ with

$$\sigma_{scale,f\leftarrow i}^{QQT;H} \equiv 2\pi \sum_{p=1}^{2} \int_{-k_{L}/k_{H}}^{0} d\cos\beta_{H} \frac{d\sigma_{f\leftarrow i}^{QQT;H}(\cos\beta_{H},p)}{d\omega_{a}}.$$
 (2.28)

It should be noted that the scaling relationship, as outlined here in the case of QQT, is exact only when the same hard shell surface is taken for both collision energies.

2.2.4.2 Applying the scaling formalism to the QM DCSs

As described in Sections 2.2.1 and 2.2.2, an important difference between the QM and QQT treatments of the scattering problem is that QM is formulated in the collision frame, in which the quantization axis, Z, points along the incoming wave-vector, \mathbf{k} , while QQT is evaluated in the kinematic apse frame, for which the quantization axis, Z_a , points along the kinematic apse, \mathbf{a} . In the collision frame, the state-to-state DCS is described by the spherical angles (θ, ϕ) which reflect the direction of \mathbf{k}' with respect to \mathbf{k} , whereas in the apse frame the direction of \mathbf{a} with respect to the collision frame Z axis is given by the spherical angles (β, α) . The

azimuthal symmetry of the collision problem about the Z axis implies that the DCS is independent of ϕ and α . Because **k** points directly along the Z axis we are thus free to set $\alpha = \phi$. The corresponding collision frame and apse frame DCSs are then related to one another as described in Eq. (2.14).

In the previous Section, it was shown that the collision energy scaling of the DCSs can be exactly applied to the QQT expressions for rotationally inelastic collisions. Now we will extend this application to include the collision energy scaling of the exact numerically calculated QM state-to-state resolved rotationally inelastic DCSs. As the scaling method has its motivation firmly within QQT, it is not automatically given that it will be applicable to the more general QM calculations. The key approximations for the scaling expression are the conservation of angular momentum projection on the kinematic apse, and the invariance of the interaction potential with collision energy. Any discrepancies between scaled and directly calculated (or measured) DCSs may yield valuable information on the scope and limitations of the approximations involved, while good agreement will instead validate the approximations as found below.

The first step is the transformation of the QM DCS from the collision frame into the kinematic apse frame. Eqs. (2.17), (2.18), and (2.20), describe in detail the mathematical relations between the two reference frames, while Eqs. (2.14), and (2.19), describe the transformation itself. The second step in the procedure is the application of Eq. (2.26) to account for the collision energy scaling of the DCS within the kinematic apse frame. However to match the integrated amplitude of the numerically exact directly calculated E_{col}^{L} DCS to that of the E_{col}^{L} DCS obtained by scaling the E_{col}^{H} QM DCS, an additional calibration factor $CF_{QM}(j', f \leftarrow j, i)$ is needed. Finally the scaled apse frame DCS is transformed back into the collision frame, using the inverse of the procedure employed in the first step.

2.2.4.3 Example calculations

Very recently, accurate QM DCSs for the scattering of closed shell NO(X) molecules residing in the j = 0 level and open shell NO(X) molecules residing in the lower Λ -doublet level of the rotational ground state j = 0.5 with He, at a collision energy of $E_{col}^{H}=147$ meV and of $E_{col}^{L}=63$ meV were presented [57, 58]. As in other studies [22, 24-27, 45, 57], rotational energy levels of NO(X) [59, 60] are employed that are spaced according to spectroscopic observations [59], which are in agreement with mixed Hund's case eigenenergies of the NO angular momentum wave functions [60].

Accordingly, in the case of integer *j* values the rotational energy transferred during a collision $\Delta E_{j'=\Delta j \leftarrow j=0}^{ROT}$ was equalized to $\Delta E_{j'=\Delta j+\frac{1}{2},F_1 \leftarrow j=\frac{1}{2},F_1}^{ROT}$ which refers to the mixed Hund's case rotational energy level spacing between final and initial rotational states. The QM NO(X) closed shell rotationally inelastic scattering calculations were carried out on an ab initio NO(X)-He surface obtained by Kłos *et al.* [43]. These rotationally inelastic DCSs shall be used as a case study for the application of the QQT collision energy scaling method developed in this work, in which the quantum state-to-state resolved NO(X)-He DCSs will be scaled from $E_{col}^{H}=147$ meV to $E_{col}^{L}=63$ meV.

Figure 2.4 depicts the closed-shell QM NO(X)+He DCSs calculated for transitions from the initial state j = 0 to the final states j' = 2, j' = 6. Each vertical pair of panels refers to a discrete step in the collision energy scaling formalism as outlined in the preceding text.

The QM (solid red lines) and QQT (dashed blue lines) scattering frame DCSs for the transitions from j=0 to j'=2 and j'=6 are depicted in the top row of Fig. 2.4. Note that the differences between the QM and QQT DCSs arise from $\Delta m_a \neq 0$ transitions in the kinematic apse frame, and from the neglect of diffractive contributions to the scattering amplitude in QQT. It should however be emphasised at this stage that any discrepancies between the QM and QQT DCSs do not affect in any way the validity of the scaling formalism derived here as it applies to either QM or QQT DCSs. A black dotted vertical line separates the classically forbidden p = 2 $\theta < \theta_c$ range from the classically allowed p = 1 $\theta \ge \theta_c$ region. These panels show similar information to that displayed in Fig. 2.3. The second row of panels depict the kinematic apse frame DCSs after the transformation has been performed according to Eq. (2.14). As such, the horizontal scale is now linear in $\cos\beta$ rather than linear in θ (as in the first row of panels). The classically allowed p = 1 contributions to the DCS are depicted as solid red curves and classically forbidden p = 2 contributions as solid green curves. Note the steep rise to infinity for $\cos \beta \rightarrow \cos \beta_c$ at which $\cos\theta \rightarrow \cos\theta_c$. Eq. (2.19) shows that the inverse

Jacobian
$$\left| \frac{d \cos \theta}{d \cos \beta} \right|$$
 becomes infinity if $\theta = \theta_c$ but for all $\theta \neq \theta_c$ $\left| \frac{d \cos \theta}{d \cos \beta} \right|$

remains finite and all QM apse frame DCSs show a smooth dependence upon β away from the unique singularity at $\beta = \beta_c$. The dotted black vertical line denotes the



Figure 2.4: Illustration of the step-by-step process used to scale the closed-shell QM DCSs from a high collision energy E_H to a lower collision energy E_L . The scattering of NO(X)+He from j = 0 to j'=2 and to j'=6 are considered as examples here. The various steps associated with each row of panels are described in the main text.

lower limit to the range of values for which $\cos \beta_H = -k_L / k_H$ can contribute to the QQT apse frame collision energy scaled DCS and ICS, defined by Eqs. (2.26) and (2.28) respectively.

The third row of panels shows the simple collision-energy scaling of the apse frame angle, β , given in Eq. (2.26) multiplied by an additional calibration factor $CF_{QM}(j', f \leftarrow j, i)$ to retrieve the QM ICS calculated by Kłos [57, 58] at $E_{col}^{L}=63$ meV. The application of the scaling relationship can be seen to effectively 'stretch' the region of the high collision energy DCS from $\frac{k_L}{k_H} \le \cos\beta_H \le 0$ to fill the entire (apse frame) angular range $-1 < \cos\beta < 0$ of the lower collision energy DCS. In addition to the predicted ($E_{col}^L=63$ meV) DCSs obtained from scaling the ($E_{col}^H=147$ meV) data, given by dashed red (p=1) and dashed green (p=2) curves, the directly calculated closed shell QM DCSs at $E_{col}^L=63$ meV (transformed from the collision frame to the apse frame) are given as solid black curves in the panels of the third row.

It is important to note that in the second row of panels, $d\sigma_{scale}^{QM;H} / d\omega_a$ is designated only within the range of $\cos \beta$ that is scalable from E_{col}^H to E_{col}^L ; $-k_L / k_H \le \cos \beta_H \le 0$. Upon "stretching" from this limited range of $\cos \beta_H$ to the full range, $-1 \le \cos \beta_L \le 0$, the angular dependence of the collision energy scaled DCS was found to be nearly identical to that of the directly calculated DCS, as shown in the third row of panels. All of the information pertaining to the V_{sum} PES contained within the lower collision energy DCS is concentrated into the reduced angular range $-k_L / k_H \le \cos \beta_H \le 0$ of the higher collision energy DCS. The effectiveness of this scaling procedure implies that the DCS associated with a rotationally inelastic transition is determined solely by the component of the incoming wave vector that is directed along the *a* vector.

The final row of panels then depicts the transformation back from the kinematic apse frame (now at the lower collision energy E_L) to the collision frame, at which point the collision energy scaling procedure is complete. Again the scaled dashed red (p=1) and dashed green (p=2) collision frame QM DCS's are depicted in this last row of panels together with the solid black curve of the exactly calculated DCSs for comparison.

It should be noted at this stage that when the scaled and the directly calculated DCSs are compared with one another, a proportionality factor is applied to scale these DCSs such that both render an identical ICS. In the case of QQT this factor is given rigorously by the collision energy scaling factor $SF_{QQT} = E_{col}^H / E_{col}^L$, as derived above. This factor is multiplied by the *j*'-dependent $CF_{QM}(j', f \leftarrow j, i)$ to yield an identical QM cross section $\sigma_{j',f \leftarrow j=0,i}^{QM}$ for the collision-energy scaled and the exactly calculated DCS for each rotationally inelastic $j', f \leftarrow j, i$ transition. The QM calibration factor $CF_{QM}(j', f \leftarrow j, i)$ is introduced because flux normalization

of a particular quantum-state-resolved $\sigma_{j',f \leftarrow j,i}^{QM}$ assures that when one expands the incoming plane wave $\exp(ikZ)|i, j, m >$ in spherical waves, the total outgoing scattering angle-integrated flux of all |f, j', m' > states equals the incoming flux of the spherical wave expansion of the |i, j, m > plane wave [3, 61] In the case of QQT the incoming plane $\exp(ikZ)|i, j, m_a >$ is not expanded in spherical waves but is rather flux-normalized, as described in Section 2.2.2, by the introduction of the normalization constant $C(\beta)$ in Eq. (2.9), ensuring that at each β the geometric differential cross section equals the sum of the QQT elastic and inelastic apse-frame DCSs. In all QQT solutions of the collision problem, $C(\beta)$ was found to be close or equal to unity. In the QM case the elastic DCS is required always to be larger than the sum of inelastic DCSs, even when one ignores the diffractive forward scattered elastic DCS [3], whereas in QQT the contribution of the elastic DCS does not have to exceed the sum of inelastic DCSs. However the maximum allowed magnitude of the sum of the inelastic ICSs in the semi-classical limit is similar for QQT and QM in the case of a hard shell PES [3].

2.3. Results and Discussion

2.3.1 Collision-energy scaling of the closed-shell NO(X)+He DCSs

Using the methodology outlined in the previous section, the DCSs for the scattering of NO(X)+He, calculated using the closed-shell QM formalism, were scaled from the collision energy of 147 meV to the lower collision energy of 63 meV. The comparison of these scaled calculations with those obtained directly from closed-shell QM calculations at 63 meV is depicted in Fig. 2.5. At first glance, the agreement between the collision energy scaled DCSs and their directly calculated counterparts can be seen to be extremely good for all final quantum states and for the entire scattering angle range of the DCSs. Even the rapid oscillatory structures present in the forward scattered direction are correctly accounted for, being most accurately reproduced for j'=1 and j'=2 with values of $\theta_c = 4.73^\circ$ and $\theta_c = 8.21^\circ$ respectively. These oscillations arise from diffraction interferences at the small scattering angle $\theta < 35^\circ$ region [62, 63], where a nearly proportional relation



Figure 2.5: Complete set of the closed-shell QM NO(X)+He DCSs from j=0 to j'=1-12, scaled from a collision energy of 147 meV to 63 meV (dashed lines). Also shown are the corresponding DCSs calculated directly at 63 meV (solid lines). Insets in the first two panels show a detailed comparison at low scattering angles. The scattering angle at which each transition becomes classically forbidden is shown as a dashed vertical line.

exists between θ and $\cos \beta$, as can be seen from Eq. (2.20). The angular separation between two neighboring peaks is inversely proportional to the wave vector, being given by $\Delta \theta \approx \pi / kR_m$ [64], where $R_m \approx 6a_0$ gives the location of the global minimum of the He-NO PES [58]. These peaks are reproduced to a lesser extent at j' = 3 and j' = 4 DCSs. Although the classically forbidden p=2 scattering angle range $0 \le \theta < \theta_c$ increases with j', it is just at this range that the DCSs of larger j' are found to be small. Consequently, the contribution of the classically forbidden part of the DCS to the ICS is minor for j' > 4. The differences between the scaled and directly QM calculated DCSs become more significant around $\theta = 180^\circ$. It is just at these high values of θ that the magnitude of the kinematic apse vector, |a|, approaches its maximum allowed value, |k'| + |k|. As can be seen from Eq. (2.10),
the QQT phase shift, $\eta_{f \leftarrow i}(\gamma_a; \beta, p = 1) = -a(\beta, p = 1) \cdot R_s(\gamma_a)$, reaches its maximum sensitivity to γ_a around this region. In this scattering angle region the magnitude of a scaled QM DCS with respect to the directly calculated QM DCS is most sensitive for the precise form of the $V_{sum}(\gamma_R, R)$ potential.

The header of Table 2.1 lists ΔE^{ROT} , $\sigma_{dir}^{E_H}$, $\sigma_{scale}^{E_H}$, $\sigma_{dir}^{E_L}$ and CF_{QM} for j' = 1 - 12. $\sigma_{dir}^{E_H}$ and $\sigma_{dir}^{E_L}$ denote respectively the directly QM calculated ICSs at 147 and 63 meV. The QQT scaled ICSs $\sigma_{scale}^{E_L}$ ($\sigma_{scale}^{E_L} \equiv SF_{QQT} \cdot \sigma_{scale}^{E_H}$ not shown in table 2.1) need to be multiplied by a calibration factor to result $\sigma_{dir}^{E_L} = CF_{QM} \cdot \sigma_{scale}^{E_L}$. For j'=1 $CF_{QM}=0.69$ turns out to be slightly larger than that for j'=2 $CF_{QM} = 0.62$. Note that $CF_{QM} < 1$ indicates that $\sigma_{scale}^{E_H} > \sigma_{dir}^{E_L} / SF_{QQT}$, which is expected for inelastic transitions that DCSs at E_{μ} are more mostly brought about by the softer part of the PES compared to those at E_L . For j' > 2 transition, CF_{OM} gradually increases with j' to about 1.0 for j'=11 and j'=12. At these high j'values the hard shell features of the PES are apparently dominant both at E_{μ} and E_L such that SF_{QQT} itself provides already the proper scaling factor to result $\sigma_{dir}^{E_L}$. Moreover, note that in table 2.1 both $\sigma_{dir}^{E_H}$ and $\sigma_{dir}^{E_L}$ become marginally small at ΔE^{ROT} far from the kinematic limit. The magnitude of $\sigma_{dir}^{E_H}$ and $\sigma_{dir}^{E_L}$ relates to the strength of the various anisotropic terms of the intermolecular potential [25, 45, 57, 58]. Besides the very minor differences between the absolute magnitude of the scaled DCSs and the directly QM calculated DCSs at strongly backwards scattering angles the overall high level of agreement of the angular distributions lends considerable support to the validity of the collision-energy DCS scaling relationship for the closed shell He-NO system.

2.3.2 Collision-energy scaling of the open-shell NO(X)+He DCSs

Figures 2.6 and 2.7 depict the directly calculated open-shell QM DCSs at 63 meV, together with those scaled from $E_{col}^{H}=147$ meV to $E_{col}^{L}=63$ meV for j'=1.5-12.5, with $|j=\frac{1}{2},\overline{\Omega}=\frac{1}{2},\varepsilon=1>$ as the initial state and $|j',F_1,\varepsilon=1>$ (Fig. 2.6) or $|j',F_1,\varepsilon=-1>$ (Fig. 2.7) as final state. All are presented in a similar fashion as the



Figure 2.6: As for Fig. 2.5, but showing the open-shell spin-orbit conserving QM NO(X)+He DCSs transition from $j = 0.5 \ \varepsilon = 1$ to $j' = 1.5-12.5 \ \varepsilon = 1$, scaled from a collision energy of 147 meV to 63 meV.

closed-shell DCSs (Fig. 2.5). The similarity among the two DCSs belonging to the same parity pair in the limit of Hund's (a) follows directly from the structure of the coupled Schrödinger equation and is not restricted to a hard shell alike PES. In the open-shell QM rotationally inelastic He-NO scattering problem the $V_{sum}(\gamma_R, R)$ PES is coupled with $V_{dif}(\gamma_R, R)$. The exit channels of the former connect to spinorbit conserving and the latter spin-orbit changing channels. Also OOT predicts a close to similar angular recoil distributions for the n = j' closed-shell QM DCSs to those in case of Hund's case (a) for spin-orbit conserving parity pair DCSs with $n = j' - \varepsilon \varepsilon' / 2$. The similarity between the E_L QM DCSs scaled from the E_H by employing the QQT relationship of Eq. (2.26) and the QM DCSs calculated directly at E_1 exactly for spin-orbit conserving rotational transitions displayed in Figs. 2.6 and 2.7 is striking and holds also for their spin-orbit changing counterparts in Figs. 2.8 and 2.9. This agreement provides strong evidence that the component of kperpendicularly to the apse *a* has only a minor influence on the rotationally inelastic dynamics of the He–NO $(j = \frac{1}{2}, \mathcal{E} = 1)$ scattering at the collision energies between 63 and 147 meV. 30



Figure 2.7: As for Fig. 2.5, but showing the open-shell spin-orbit conserving QM NO(X)+He DCSs transition from $j = 0.5 \varepsilon = 1$ to $j' = 1.5 - 12.5 \varepsilon = -1$, scaled from a collision energy of 147 meV to 63 meV.

Table 2.1 provides an overview of the QQT collision energy scaling parameters of relevance to the DCS scaling process. In the case of open-shell QM spin-orbit conserving DCSs, the calibration factor rises from $CF_{QM} = 0.63$ at n = 2 smoothly up to close to unity at n = 8, as was the case for the closed-shell QM DCSs. At these quite high *n*-values, the hard shell features of the PES become apparently dominant both at E_H and E_L . Thereafter CF_{QM} exhibits a rather irregular dependence upon *n*. At n = 10 $CF_{QM} > 1$, which means that $\sigma_{scale}^{E_H} \cdot SF_{QQT} < \sigma_{dir}^{E_L}$. In this case the scalable part of the spin-orbit conserving ICS at E_H is appreciably more depleted by its larger opacity for spin-orbit changing transitions than that at E_L . Qualitatively this could be understood from the larger spin-orbit changing and smaller spin-orbit conserving functions at E_H compared to those at E_L [58].



Figure 2.8: As for Fig. 2.5, but showing the open-shell spin-orbit changing QM NO(X)+He DCSs from $j = 0.5 \varepsilon = 1$ to $j' = 1.5 - 12.5 \varepsilon = 1$, scaled from a collision energy of 147 meV to 63 meV.

It is well known [44, 65] that when both Λ -doublet components of the initial $j = \frac{1}{2}$ rotational state are equally populated there is a propensity for molecules such as NO with π^1 electron configuration, to preferentially populate the A''-symmetry Λ -doublet component of the j' state on collision. So in the case of a spin-orbit conserving rotationally inelastic transition the upper $\varepsilon' = -1$ Λ doublet component of the F_1 rotational wave function will be preferred. And in the case of a spin-orbit changing transition the lower $\varepsilon' = 1$ Λ -doublet component of the F_2 rotational wave function will be preferred. And in the case of a spin-orbit changing transition the lower $\varepsilon' = 1$ Λ -doublet component of the F_2 rotational wave function will be preferred. These rules do not apply when the initial $j = \frac{1}{2}$ rotational state resides exclusively in its lower $\varepsilon = 1$ Λ -doublet component, as in the present study. The propensity for the conservation of parity for He-NO rotationally inelastic Integral Cross Sections (ICSs) at $E_{col}^L=63$ meV and $E_{col}^H=147$ meV also plays an important role [57, 58]. Inspection of Table 2.1 shows that the calibration factor CF_{QM} for a particular parity pair number n turns out to



Figure 2.9: As for Fig. 2.5, but showing the open-shell spin-orbit changing QM NO(X)+He DCSs transition from $j = 0.5 \varepsilon = 1$ to $j' = 1.5 - 12.5 \varepsilon = -1$, scaled from a collision energy of 147 meV to 63 meV.

be typically a few percent larger for $F_1e \rightarrow F_1f$ transitions than that for $F_1e \rightarrow F_1e$ transitions. This phenomenon reflects a weak preference for $\sigma_{scale}^{E_H}$ at $E_{col}^{H}=147$ meV, to scatter into A' symmetry, favoring $e(\varepsilon = 1)$ levels, rather than A" symmetry favoring $f(\varepsilon = -1)$ levels. This preference is essentially absent at $E_{col}^L = 63$ meV for $\sigma_{dir}^{E_L}$ [65]. The spin-orbit-changing transitions do not exhibit a regular dependence of CF_{QM} on n. The value of CF_{QM} at fixed n > 2 was always found to slightly larger for the $F_1e \rightarrow F_2e$ transitions than for the $F_1e \rightarrow F_2f$ transitions. This latter reflects a slightly greater preference of $\sigma_{scale}^{E_H}$ to scatter into A' symmetry, favoring $f(\varepsilon = -1)$ levels, rather than A" symmetry favoring $e(\varepsilon = 1)$ levels at $E_{col}^{H} = 147$ meV than the preference observed at $E_{col}^{L} = 63$ meV for $\sigma_{dir}^{E_L}$ [65].

2.4 Conclusions

2.4.1 Accuracy of the collision-energy scaling relationship

As the QQT-derived collision-energy scaling procedure relies on the assumption that the interaction potential can be approximated by a hard shell, its application is most appropriate for collision systems where this assumption is at least approximately true. This is an excellent approximation for the NO(X)+He $V_{sum}(\gamma_R, R)$ interaction potential (which governs all closed-shell transitions, and spin-orbit conserving open-shell transitions) as it is overwhelmingly dominated by repulsive intermolecular forces. The magnitude of the NO(X)-He van der Waals well, the most attractive part of the potential energy surface, is less than 1/17 of even the lower collision energy of $E_{col}^L=63$ meV used in this work. It is interesting to note that the QQT-derived scaling performs extremely well in the more forward-scattered region of j' < 9 final rotational quantum states, where one would expect the scattering dynamics to be less dominated by hard shell type interactions. A favorable property of the NO(X)-He collision system for the QQT treatment is its low reduced mass. At $E_{col}^L=63$ meV the de Broglie wave length is 1.15 a_0 , which is a factor of 2.2 larger than that of the NO(X)-Ar system at the same collision energy.

In contrast, the NO(X)+He $V_{dif}(\gamma_R, R)$ interaction potential (which is involved in spin-orbit changing transitions) is much "softer" in character, containing a significant attractive component. The effective potential on which spin-orbit changing and conserving transitions take place may be written as

$$V_{eff}(\tilde{\varphi}, \gamma_R, R) \equiv V_{sum}(\gamma_R, R) - V_{dif}(\gamma_R, R)\cos(2\tilde{\varphi})$$
(2.29)

where $\tilde{\varphi}$ denotes the azimuthal angle of the symmetry plane of the unpaired anti bonding Π orbital in the molecular NO frame [54, 60]. The special case of $\tilde{\varphi} = 0, \frac{1}{2}\pi$ then correspond to A', A'' symmetry respectively. Neither $V_{A'}(\gamma_R, R) = V_{eff}(\tilde{\varphi} = 0, \gamma_R, R)$ or $V_{A'}(\gamma_R, R) = V_{eff}(\tilde{\varphi} = \frac{1}{2}\pi, \gamma_R, R)$ qualifies as a soft surface [43, 58, 65] and the soft V_{dif} potential serves only to induce a small $\cos 2\tilde{\varphi}$ dependent modulation of the repulsion dominated He-NO effective PES $V_{eff}(\tilde{\varphi}, \gamma_R, R)$. In light of this observation, both spin orbit state conserving and changing transitions can be seen to be brought about by repulsion dominated He-NO interactions. The reproduction of the diffractive features in the forward scattered direction, suggests a robust behavior of the kinematic apse frame collision energy scaling formula even in the case of interaction potentials that deviate significantly from a simple hard shell. More specifically, the QQT scaling procedure assumes that only the component of k anti-parallel to \hat{a} is of relevance for the outcome of a particular rotationally inelastic transition. Consequently for all type of collisions for which this assumption holds or shows strong propensity, the OOT DCS collision energy scaling method will hold. In the case of a not infinite steep shell, a PES with a well, or branching to e.g. other spin-orbit state outgoing channels, the absolute value of the OOT scaled OM calculated or experimentally determined OOT scaled DCSs need to be multiplied with the calibration factor $CF_{OM}(f \leftarrow i)$ to result the same ICS as the directly QM calculated or experimentally determined ones to facilitate comparison. An interesting extension of the present work would be to explore such collision systems as NO(X)-Ar and/or OH(A)-He, that carry a substantial well in their interaction potential [66]. The theoretically predicted maximum well depth of the NO(X)+Ar V_{sum} PES is 116 cm⁻¹ [44]. The OH radical in its first electronically excited state forms strongly bound van der Waals complexes with the rare gas atoms; the well depth for OH(A)+Ar is about 1219 cm⁻¹ [67]. As such, the application of the collision energy scaling relationship presented here to QM calculations of the DCS for these systems could yield further insight into its flexibility and operation.

2.4.2 Signatures of the potential energy surface within the DCSs

The structures present in the state-to-state resolved DCS all have their origin in the interaction potential on which the collision takes place. Therefore, features of this potential can be inferred from a close study of the features present within the DCSs. For example, the rapid oscillations present at low scattering angles for small values of Δj can be attributed to diffraction interference between trajectories scattered from a core approximately the radius of the global minimum of the He-NO PES [58, 62, 63]. The broader, slower oscillations that can be seen in the DCSs for the scattering of NO(X)+Ar are rather ascribed to the anisotropy of the inner repulsive core of the potential energy surface (these oscillations do not appear for NO(X)+He because of the lower relative momentum associated with the collision, and hence the longer de Broglie wavelength). The changes in these characteristic structures in the DCS as a function of the collision energy could thus yield information on the anisotropy and steepness of repulsive features in the potential energy surface, or on the depth and position of any attractive wells that may be present. Changes in these features with total (collision) energy will be manifested by departures from the collision-energy

scaling relationship, which assumes no change in the interaction potential with changes in collision energy.

Another interesting area of consideration is the question of which angular regions of the DCS provide the most information on a particular feature of the interaction potential. Intuitively, we expect the forward scattering region to provide more information about the attractive part of the potential, and the backward scattered region to provide more information about the repulsive part of the potential. To this intuition, we can now add the behavior described in Eqs. (2.24) and (2.26); when going from a high collision energy to a lower collision energy, a section of the high energy apse frame DCS from $\cos \beta_c^H \ge \cos \beta \ge -\sqrt{E_{col}^L / E_{col}^H}$ is extended to fill the lower energy DCS within the range $\cos \beta_c^L \ge \cos \beta \ge -1$. Because both the higher and lower energy DCSs contain the entire angular range in θ , this implies that all the information contained within a lower energy DCS excludes contributions from the $\cos \beta_c^H \ge \cos \beta \ge -\sqrt{E_{col}^L / E_{col}^H}$ range of the higher collision energy DCS. Hence the backward scattering $-1 \le \cos \beta < -\sqrt{E_{col}^L/E_{col}^H}$ region of a high collision energy DCS contains information about the interaction potential that is excluded from the lower collision energy DCS. This realization requires a pure quantum state resolved DCS. The collision energy dependence of DCS or ICS associated with $j', \varepsilon' \leftarrow j = \frac{1}{2}, \varepsilon$ rotationally inelastic transition with $\varepsilon = \varepsilon'$ is expected to be dissimilar to that with $\varepsilon = -\varepsilon'$ even in the case of pure Hund's case (a). This is because one of these two rotationally inelastic DCSs concerns a parity conserving rotationally inelastic transition while the other one concerns a parity changing rotationally inelastic transition.

The successful application of the QQT collision energy scaling formalism reinforces the evidence that the He-NO rotationally inelastic DCSs depend very sensitive on the anisotropy of the repulsive part of the PES. This repulsive part of an atom molecule PES is the most difficult to predict accuracy from ab initio based calculations.

For the He-NO(X) collision system our study demonstrated that the scattering angle dependence of all its QM DCSs directly calculated at E_{col}^{L} =63 meV are essentially perfectly reproduced by the part of the E_{col}^{H} =147 meV DCSs QQT scaled to E_{col}^{L} =63 meV. As argued in subsection 2.3.4.3 this implies that the V_{sum} and V_{dif} PESs are similarly probed by the range of values of $\cos \beta$ that contribute to

 $\sigma_{scale}^{E_{H}}$ and $\sigma_{dir}^{E_{L}}$. The dependence of the calibration factor, CF_{QM} , listed in Table 2.1, on the final rotational quantum state of the NO molecule yields complementary information on the He-NO(X) V_{sum} and V_{dif} PESs. CF_{QM} denotes the factor by which the QM DCSs that have been scaled from the higher collision energy of E_{col}^{H} =147 meV to the lower collision energy of E_{col}^{L} =63 meV must be multiplied, in order to obtain ICSs that are in agreement with those directly calculated at E_{col}^{L} =63 meV. Thus, complementary information on the He-NO(X) V_{sum} and V_{dif} PESs is also provided by the j', ε' dependence of the ratio $\sigma_{dir}^{E_L} / \sigma_{scale}^{E_H}$.

In summary, the collision-energy scaling formalism developed here has been shown to be remarkably accurate when applied to the case study of the DCSs of NO(X)+He for collision energies of 147 meV and 63 meV. It can be successfully applied to both the spin-orbit conserving and the spin-orbit changing collision channels, suggesting it is capable of operating both for the hard shell like potentials from which was derived, and for more general potentials with a significant attractive component. The extension of the QQT into the classically forbidden region has also been presented, allowing the comparison of QM DCSs with their corresponding QQT counterparts throughout the entire angular range. Finally, the role of these new methodologies in characterizing interesting features of the potential energy surface from the calculated DCSs has been discussed, with the collision energy scaling formalism emerging as a useful new tool that is now available to tackle such problems.

Appendices

2.A The stationary nature of the QQT collision frame and apse frame DCS at $\theta = 0$ and $\theta = \pi$

The azimuthal symmetry of the DCS constrains its mathematical form to be stationary at $\theta = 0$ and $\theta = \pi$ in the scattering frame and in the apse frame. In this appendix we prove that these conditions are indeed fulfilled within the QQT framework. As previously noted, the QM DCSs automatically fulfill this requirement in the collision frame, because they can be written as a series of Legendre polynomials, all of which individually meet this criterion. When transformed into the apse frame, the constraints are then met in the same fashion as the QQT DCSs.

As a starting point we shall consider the QQT DCS in the apse frame. From Eq.

(2.9) one writes the QQT apse-frame scattering amplitude as

$$\frac{g_{j',m_a' \leftarrow j=0,m_a}(\theta)}{C(\theta)} = \langle j',m_a' | g_{geom}(\theta)P_{j'}(\cos \gamma_a) \\ \times \exp[i\eta_{j' \leftarrow j=0}(\theta)] | j=0,m_a \rangle$$
(2.A.1)

where the dependence of all quantities in Eq. (2.A.1) on θ has been made explicit. Equation (2.10) can be used to write out the θ dependence of the phase shift, η , as

$$\eta_{j' \leftarrow j=0}(\theta) = \sqrt{k^2 + k'^2 - 2kk'\cos\theta} A(\gamma_a), \qquad (2.A.2)$$

where $A(\gamma_a)$ is independent of θ (and hence does not affect the behavior of the DCS as a function of θ). We now turn our attention to the first stationary point, located at θ =0. Around this region, one can neglect all but the leading terms in the Taylor expansion of $\cos \theta$, such that

$$\cos\theta \cong 1 - \frac{\theta^2}{2} \,. \tag{2.A.3}$$

Utilizing Eq. (2.A.3) then allows us to approximate the $\cos\theta$ dependence of Eq. (2.A.2) in the forward scattered direction to

$$\eta_{j' \leftarrow j=0}(\theta) = \sqrt{k^2 + k'^2 - 2kk' + kk'\theta^2} A(\gamma_a)$$

$$\cong \left(k - k' + \frac{kk'\theta^2}{2(k - k')^2}\right) A(\gamma_a) \qquad (2.A.4)$$

Note that the last line of Eq. (2.A.4) is obtained by performing a Taylor expansion of $(1 + a\theta^2)^{1/2}$, about $a\theta^2 = 0$, keeping only the leading term in $a\theta^2$.

The behavior of the exponential part of Eq. (2.A.1) around $\theta = 0$ can then be written as

$$\exp[i\eta_{j' \leftarrow j=0}(\theta \to 0)] = \exp[i\eta_{j' \leftarrow j=0}(\theta = 0)] \exp\left[\frac{ikk'\theta^2}{2(k-k')^2}\right] A(\gamma_a) . \quad (2.A.5)$$

Taking the derivative of Eq. (2.A.5) with respect to θ and evaluating as θ tends to zero then yields

$$\frac{\operatorname{dexp}[i\eta_{j' \leftarrow j=0}(\theta \to 0)]}{\operatorname{d}\theta} = \exp[i\eta_{j' \leftarrow j=0}(\theta = 0)] \exp\left[\frac{ikk'\theta^2}{2(k-k')^2}\right] \frac{kk'\theta}{(k-k')^2} A(\gamma_a) = 0$$
(2.A.6)

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At the second stationary point, where $\theta \rightarrow \pi$, $\cos \theta$ can instead be approximated by

$$\cos\theta \cong -1 + \frac{(\pi - \theta)^2}{2} \,. \tag{2.A.7}$$

Using the same arguments as were employed for the case of $\theta = 0$, it can be shown that

$$\frac{\operatorname{dexp}[i\eta_{j'\leftarrow j=0}(\theta\to\pi)]}{\operatorname{d}\theta} = 0, \qquad (2.A.8)$$

The case is the same when $\theta = \pi$. The exponential part of the QQT apse frame scattering amplitude has thus been shown to go to zero as θ goes to 0 or π , as required.

The non-exponential part of Eq. (2.A.1) can also be differentiated with respect to θ , in this case yielding the expression

$$\frac{\mathrm{d}g_{geom}(\theta)}{\mathrm{d}\theta} = \rho_1(\gamma_a)\rho_{12}(\gamma_a)\frac{\mathrm{d}}{\mathrm{d}\theta}|\cos\beta| \\ = \rho_1(\gamma_a)\rho_2(\gamma_a)\frac{\mathrm{d}|\cos\beta|}{\mathrm{d}\cos\theta}\frac{\mathrm{d}\cos\theta}{\mathrm{d}\theta}.$$
(2.A.9)

Since $\cos \theta$ is obviously stationary at $\theta = 0$ and $\theta = \pi$, the geometric scattering amplitude must also display the same behavior, such that

$$\frac{\mathrm{d}g_{geom}(\theta \to 0, \pi)}{\mathrm{d}\theta} = 0. \qquad (2.A.10)$$

Eqs. (2.A.6), (2.A.8) and (2.A.10) can then be jointly substituted into Eq. (2.A.1) to yield the required behavior in the apse frame

$$\frac{\mathrm{d}g_{j',m'_{a}\leftarrow j=0,m_{a}}(\theta=0,\pi)/C(\theta)}{\mathrm{d}\theta} = \frac{\mathrm{d}g_{j',m'_{a}\leftarrow j=0,m_{a}}(\beta=\pi,p=1,2)/C(\beta)}{\mathrm{d}\theta} = 0$$
(2.A.11)

Additionally it can be shown (by summing the scattering amplitude over all final states) that the first derivative of the normalization constant, $C(\beta)$, with respect to β is also equal to zero

$$\frac{\mathrm{d}C(\beta=\pi)}{\mathrm{d}\beta} = 0. \qquad (2.A.12)$$

Combining Eqs. (2.A.1), (2.A.11) and (2.A.12), the first derivatives of the

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QQT DCSs in the apse frame must also necessarily be stationary at $\theta = 0$, π as is required:

$$\frac{\mathrm{d}^2 \sigma_{j' \leftarrow 0}^{QQT}}{\mathrm{d}\omega_a \mathrm{d}\theta} (\theta = 0, \pi) = \frac{\mathrm{d}^2 \sigma_{j' \leftarrow 0}^{QQT}}{\mathrm{d}\omega_a \mathrm{d}\theta} (\beta = \pi, p = 1, 2) = 0.$$
(2.A.13)

Note that Eq. (2.14) relates the QQT collision frame DCSs to its apse frame counterpart, hence:

$$\frac{\mathrm{d}^{2}\sigma_{j'\leftarrow0}^{2QT}}{\mathrm{d}\theta\cdot\mathrm{d}\omega}(\theta,\phi) = \frac{\mathrm{d}\sigma_{j'\leftarrow0}^{2QT}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_{a}}(\beta,p) \left| \frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta} \right| + \frac{\mathrm{d}\sigma_{j'\leftarrow0}^{2QT}}{\mathrm{d}\omega_{a}}(\beta,p) \frac{\mathrm{d}}{\mathrm{d}\theta} \left| \frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta} \right|.$$
(2.A.14)

As was shown in Eq.(2.19), setting θ equal to 0 or π gives us the simple relations

$$\left|\frac{\mathrm{d}\cos\beta(\theta=0)}{\mathrm{d}\cos\theta}\right| = \frac{1}{\left(1-k/k'\right)^2},\qquad(2.A.15)$$

$$\left|\frac{\mathrm{d}\cos\beta(\theta=0)}{\mathrm{d}\cos\theta}\right| = \frac{1}{\left(1-k/k'\right)^2},\qquad(2.A.16)$$

which leads to:

$$\frac{\mathrm{d}^2 \sigma_{j' \leftarrow 0}^{QQT}}{\mathrm{d}\theta \cdot \mathrm{d}\omega_a} (\beta = \pi, p = 1, 2) \left| \frac{\mathrm{d}\cos\beta(\theta = 0, \pi)}{\mathrm{d}\cos\theta} \right| = 0$$
(2.A.17)

Finally

$$\frac{\mathrm{d}}{\mathrm{d}\theta} \left| \frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta} \right| = \left\{ \mathrm{d}\frac{(k')^2 \cdot [k' - k\cos\theta]}{[(k')^2 - 2kk'\cos\theta + k^2]^{1.5}} \middle/ \mathrm{d}\cos\theta \right\} \frac{\mathrm{d}\cos\theta}{\mathrm{d}\theta} .$$
(2.A.18)

Note that Eq. (2.A.18) is zero for $\theta = 0$ and for $\theta = \pi$.

Combining Eqs. (2.A.14), (2.A.17) and (2.A.18) the first derivatives of the QQT DCSs in the collision frame are stationary at $\theta = 0$, π .

2.B The stationary nature of the QM apse frame and collision frame DCS at $\theta = 0$ and $\theta = \pi$

Arthurs and Dalgarno [55] showed that

$$\frac{\mathrm{d}\sigma^{\mathcal{Q}M}_{j',f\leftarrow j,i}}{\mathrm{d}\omega}(\hat{k}'\cdot\hat{k}) \propto \sum_{\lambda=0}^{\infty} A_{\lambda} P_{\lambda}(\hat{k}'\cdot\hat{k}), \qquad (2.B.1)$$

which implies that at $\theta = 0$ or $\theta = \pi$

$$\frac{\mathrm{d}}{\mathrm{d}\theta} \frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\omega} (\hat{\boldsymbol{k}}' \cdot \hat{\boldsymbol{k}}) = 0.$$
(2.B.2)

Equation (2.14) can also be applied to relate the QM collision frame DCSs to its apse frame counterpart:

$$\frac{\mathrm{d}^{2}\sigma_{j',f\leftarrow j,i}^{\mathcal{QM}}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_{a}}(\theta,\varphi) = \frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{\mathcal{QM}}}{\mathrm{d}\theta\cdot\mathrm{d}\omega}(\beta,p) \left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|^{-1} + \frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{\mathcal{QM}}}{\mathrm{d}\omega_{a}}(\beta,p) \frac{\mathrm{d}}{\mathrm{d}\theta} \left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|^{-1}.$$
 (2.B.3)

Inspection of Eq. (2.A.18) and combining with Eq. (2.B.2) and (2.B.3) shows that $\frac{d^2 \sigma_{j',f \leftarrow j,i}^{QM}}{d\theta \cdot d\omega_a} (\theta, \varphi) = 0 \quad \text{if } \theta = 0 \text{ or } \theta = \pi.$

Table 2.A: Numerical values of the closed-shell QQT NO(X)+He DCSs from j = 0 to j' = 1-12 at a collision energy of $E_{col}^{L}=63$ meV for $\theta = 0$ and $\theta = \pi$. Values are given in both the kinematic apse and the collision frames.

	$d\sigma/d\omega_a(\beta)$		d <i>σ/</i>	$d\sigma/d\omega(\theta)$	
i'	$\theta = 0$	$\theta = \pi$	$\theta = 0$	$\theta = \pi$	
1	3.83E-05	0.192	3.682	0.054	
2	0.0515	0.104	538.25	0.029	
3	0.0028	0.281	7.064	0.077	
4	0.0605	0.527	52.81	0.142	
5	0.0045	0.575	1.653	0.152	
6	0.0375	0.280	6.555	0.072	
7	0.0052	1.343	0.468	0.337	
8	0.0244	0.354	1.208	0.086	
9	0.0056	1.059	0.157	0.245	
10	0.0163	0.343	0.263	0.075	
11	0.0058	0.357	0.054	0.073	
12	0.0111	0.135	0.059	0.025	



The modified Quasi-Quantum Treatment of rotationally inelastic NO(X)-He scattering

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A Modified Quasi-Quantum Treatment (MQQT) has been developed to account for the softness of the repulsive part of the anisotropic atom-molecule PESs. It addresses the rotationally inelastic collision problem in the so-called kinematic apse frame, where the previous RQQT restriction of single hard shell PES contour is modified to a PES contour which barrier height is taken to be just large enough to reflect the kinetic energy, provided by the component of the incoming momentum vector directed anti-parallel to the hard shell normal at the site of impact. The MQQT resulting rotationally inelastic quantum state resolved DCSs and ICSs of He + NO(X) at E_{col} =508 cm⁻¹ are compared with those obtained with RQQT and with those resulting from Quantum Mechanically exact calculation on to the full range highest quality ab initio V_{sum} PES. The parity changing MQQT DCSs for $\Delta j \leq 4$ in the forward range of scattering angles agree much better to QM DCSs than RQQT ones. The improvements of the other MQQT DCSs with respect with the RQQT DCSs was minor due to the nearly hard shell character of the $n\neq 1$ or 3 anisotropic Legendre polynomial terms of the PES.

3.1 Introduction

The Regular Quasi-Quantum Treatment (RQQT) of the rotationally inelastic collision problem, introduced by Gijsbertsen *et al.* [22], succeeded for the first time to clarify the physical mechanism behind the remarkable sign alternation of the steric asymmetry (SA) of the rotationally inelastic Integral Cross Section (ICS) between even and odd changes in the rotational quantum number *j*. Such changes were observed and theoretically predicted for the NO(X)-Ar [68, 69], and NO(X)-He [70] collision systems. Moreover RQQT also revealed that the angular dependence of the Differential Cross Sections (DCSs) to neighboring rotational states of NO(X) with the same parity are nearly identical [22, 24-26, 71]. Assuming an anisotropic convex hard shell potential that mimics the repulsive core of the *ab initio* NO(X)-RG V_{sum} PES [43, 44], RQQT ought also to be able to predict both the spin orbit conserving and changing quantum state resolved rotationally inelastic DCSs.

Applying the RQQT, Taatjes *et al.* [27] were able to take measurements of the SA and Λ -doublet propensities provided by experimentally observed rotationally inelastic NO(X)-D₂ ICSs, and to extract from these a realistic hard shell PES, which provided a good match to the NO(X) – D₂ experimental values.

Ballast *et al.* [24] provided a more systematic basis for the hitherto intuitive formulation of the RQQT of the rotationally inelastic collision problem, and extended RQQT to collisions of an atom with a closed shell linear molecule. The resulting RQQT DCSs for Ne-CO ($X^{1}\Sigma$) and for He-NO ($X^{2}\Pi$) compared well with the exact QM DCSs calculated at a collision energy of respectively 511 cm⁻¹ (63.4 meV) [32] and 514 cm⁻¹ (63.7 meV) [33].

The RQQT has also been the subject of recent development, with Zhang *et al.* [72] obtaining a general scaling rule for the collision energy dependence of a rotationally inelastic DCS, and also extending the calculation of the RQQT DCSs from the classically allowed region into the classically forbidden range of small scattering angles. The rotationally inelastic quantum state resolved NO-He DCSs at a collision energy $E_{col}=508$ cm⁻¹ (63 meV) of the present chapter served as the focus of their study.

The Modified Quasi-Quantum Treatment (MQQT) of the present study, in common with RQQT, is numerically extremely efficient [73]. RQQT has already been successfully employed to provide insight into the distinct interference structures reflecting different sensitivities to specific terms in the interaction potential [25, 26, 57, 58, 74].

The velocity-mapped [30] ion imaging method [29], pioneered on the HCl-Ar system at a collision energy of $E_{col} = 66.7 \text{ meV} (538 \text{ cm}^{-1})$ [31] and later extended to Ne, Kr, N₂ and CH₄ as collision partners [75], provides a convenient means by which the quantum state resolved rotationally inelastic DCSs can be measured.

This method of observing quantum state resolved rotationally inelastic DCSs has been extended to an appreciable number of collision systems, and the resulting experimentally determined DCSs have subsequently been compared with numerically exact QM DCSs obtained on state of the art *ab initio* calculated PESs.

The remainder of this chapter is organized as follows. The MQQT of the rotationally inelastic collision problem is described in Section 3.2. The Legendre expansion coefficients of the MQQT V_{sum} PES [43], the phase shift curves, scattering amplitudes and finally the quantum state resolved rotationally inelastic differential and integral cross sections calculated for the NO(X)-He collision system at $E_{col} = 508 \text{ cm}^{-1}$ (63.0 meV) are presented and discussed in Section 3.3. The main conclusions and outlook for the future are then given in Section 3.4.

3.2. Method

The regular QQT theory has been described in previous studies, and only the essentials necessary to inform the reader of the methodology [22, 24, 72] and relevance of MQQT are given below. Appendix 3.A provides specific methodological details and additional information.

The numerically exact QM solution of the Schrödinger equation for the rotationally inelastic collision problem utilizes the full range of the PES, and expands the incoming plane wave into spherical waves. This transforms the collision problem into a large set of coupled differential equations covering all relevant $j, l, \overline{\Omega}, \varepsilon, j', l', \overline{\Omega'}, \varepsilon'$ scattering channels, which are numerically solved at each permitted value of the total angular momentum quantum number J, to obtain a series of $S_{j,l,\overline{\Omega},\varepsilon;j',l',\overline{\Omega'},\varepsilon'}^{J}$ matrix elements, in which j is the rotational angular momentum quantum number, $\overline{\Omega}$ is the absolute value of the projection of the electronic angular momentum onto the molecular axis and ε is the symmetry index which labels the lower (upper) Λ -doublet level with $\varepsilon = 1$ ($\varepsilon = -1$). The $\varepsilon = \pm 1$ rotational sublevels differ in parity by a factor of $P = \varepsilon(-1)^{j-\frac{1}{2}}$. Primed quantum numbers to obtain the scattering amplitude

 $f_{j=0.5,m,\overline{\Omega}=0.5,\varepsilon \rightarrow j',m',\overline{\Omega}',\varepsilon'}(\theta)$. Such multiple coupled differential equations and summations between channels are avoided in RQQT and MQQT. Both of these method bypass the calculation of the S-matrix elements and approximate the scattering amplitude $f_{j=0.5,m,\overline{\Omega}=0.5,\varepsilon \rightarrow j',m',\overline{\Omega}',\varepsilon'}(\theta)$ directly. The rotationally inelastic transition probability amplitude is obtained by sandwiching a phase shift function between the "bra" of the final and the "ket" of the initial rotational quantum state wavefunction. The so-called kinematic apse frame is employed, in which the momentum transfer vector,

$$\boldsymbol{a} \equiv \boldsymbol{k}' \cdot \boldsymbol{k} \,, \tag{3.1}$$

serves as the quantization axis along which the projection quantum numbers of *i* and of j' are m_a and m'_a . The direction of \hat{a} , residing in the k and k' azimuth scattering plane, with respect to **k** is denoted by the spherical angles β and $\alpha = \phi$. The spherical angles (γ_a, φ_a) of the molecular axis **r** with respect to \hat{a} provide the primary variables defining the geometry of the instantaneous impact onto the hard shell PES surface at $R_s(\gamma_a, \phi_a)$, effecting the transfer of the incoming state $|j=0.5, m_a, \overline{\Omega}=0.5, \varepsilon >$ to the outgoing state $\langle j', m_a', \overline{\Omega}', \varepsilon' \rangle$. The normal $\hat{\boldsymbol{n}}$ to the shell surface at the point $R_{s}(\gamma_{a},\phi_{a})$ and \hat{a} are identical [22, 24]. The component of the incoming wave vector **k** parallel to the shell surface at $R_{s}(\gamma_{a},\phi_{a})$ remains conserved [46], *i.e.* $k_{\parallel} = k'_{\parallel}$. Conversely, the component k_{\perp} of **k** directed anti parallel to \hat{a} is not generally conserved throughout the collision, and the maximum amount of the available collision energy E_{col} that can be transferred into rotation is limited to $E_{col} \cdot (\cos \beta)^2$. The projection quantum number m_a of j onto \hat{a} remains conserved throughout the collision event [22, 52, 72, 76]. The former restriction limits the range of β for which the transition from the rotational ground state $j = \frac{1}{2}$ with $E(j = \frac{1}{2}) \equiv 0$ to the rotationally excited j' state with E(j') is allowed to $\beta_{\kappa} \leq \beta \leq 180^{\circ}$ [72], where

$$\beta_{\kappa} = \arccos(-\sqrt{1 - (k'/k)^2}) = \arccos(-\sqrt{E(j')/E_{col}})$$
. (3.2)

The function $\cos\beta(\cos\theta)$ reaches its maximum at $\theta = \theta_{\kappa}$ [72]:

$$\theta_{\kappa} = \arccos(k'/k) \,. \tag{3.3}$$

We define an index p, such that p=2 if $0 \le \theta < \arccos(k'/k)$, corresponding to a classically forbidden (but Feynman path allowed) transition for which $\mathbf{k}_{\perp}^{\prime} \uparrow \uparrow \mathbf{k}_{\perp}$ and p=1 if $\arccos(k'/k) \le \theta \le 180^{\circ}$ [72], corresponding to a classically allowed transition for which $\mathbf{k}_{\perp}^{\prime} \downarrow \uparrow \mathbf{k}_{\perp}$. The relation between k_{\perp}^{\prime} and k_{\perp} depends on the rotational eigen-energy of the scattered NO molecule E(j'), defined relative to $E(j) \equiv 0$, and is given by [72]:

$$k'_{\perp} = \sqrt{(k_{\perp})^2 - \frac{2\mu}{\hbar^2} E(j')} .$$
(3.4)

The MQQT PES contour $R_s^{\text{mod}}(\cos \gamma_R; \cos \beta)$ is chosen such that the height of the potential energy barrier is just sufficient so as not to be surpassed by the effective collision energy $E_{col} \cos^2 \beta$,

$$V[R_s^{\text{mod}}(\cos\gamma_a;\cos\beta)] = E_{col}\cos^2\beta \,\,. \tag{3.5}$$

The MQQT hard shell contours $R_s^{\text{mod}}(\cos \gamma_a; \cos \beta)$ at $\beta = 100^\circ$ and $\beta = 170^\circ$ obtained from the *ab initio* NO(X)-He $V_{sum}(R, \gamma_R)$ PES calculated by Kłos et al are shown in Fig. 3.1 [43]. The varying shell shape and size probed by (classically allowed, p=1) quite forwards $\beta=100^{\circ}$ and by quite backwards $\beta=170^{\circ}$ scattered near elastic collision events are visualized in back and red respectively. Overall, the radius of the $R_s^{\text{mod}}[\cos \gamma_R; \cos(\beta = 100^\circ)]$ shell is about 0.8 bohr larger than that of the $R_s^{\text{mod}}[\cos \gamma_R; \cos(\beta = 170^\circ)]$ shell. This difference is almost as large as the De Broglie wavelength (1.16 bohr) of the incoming wave vector \mathbf{k} at $E_{col} = 508 \text{ cm}^{-1}$. Less pictorial but more detailed information is provided in Fig. 3.2. It displays both the dependence of $R_S^{\text{mod}}(\cos \gamma_R; \cos \beta)$ on $\cos \gamma_R$ and $R_S^{\text{mod}}(\cos \gamma_R; \cos \beta)$ on $\cos \gamma_a$ for a number of individual β values covering the range from $\beta=90^\circ$ to $\beta=180^\circ$. At $\gamma_a \approx \arccos(-0.086) = 95^\circ$ the $R_s^{\text{mod}}[\cos \gamma_a; \cos(\beta = 90^\circ)]$ contour is no longer uniquely defined by a single convex shape. The smooth He-NO (X) PES contours $R_{s}^{\text{mod}}(\cos \gamma_{a}; \cos \beta)$ are found to be partially concave for $90^{\circ} \le \beta < \beta_{\min}^{\text{convex}} = 101.45^{\circ}$ and purely convex for $\beta \ge \beta_{\min}^{convex} = 101.45^{\circ}$. Note that at each β there are three values of $\cos \gamma_R$ at which $R_S^{\text{mod}}(\cos \gamma_R; \cos \beta) = R_S^{\text{mod}}(\cos \gamma_R; \cos \beta)$ both at $\cos \gamma_R = \pm 1$ and at $0.1 \le \cos \gamma_R \le -0.05$. It is within the latter range of $\cos \gamma_R$ that the dependence of $R_S^{\text{mod}}(\cos \gamma_a; \cos \beta)$ upon $\cos \gamma_a$ is the most distinct from that upon $\cos \gamma_R$. Specifics details concerning the MQQT phase shift, scattering amplitude, DCS and ICSs, defined consistently to those of RQQT (but distinct from QM) are given in Section 3.A of the Appendix.



Figure 3.1: Illustration of the relationship between the modified QQT hard shell contour and the polar angle β between the solid apse vector \boldsymbol{a} (extended by a dashed line) and the incoming wave vector \boldsymbol{k} . The blue NO axis vector \vec{r} is extended by a dashed blue line. The $\beta = 100^{\circ}$ contour corresponds to nearly perfect forward scattering and $\beta = 170^{\circ}$ to nearly perfect backwards scattering. The red and black shell circumferences correspond respectively to $R_S^{\text{mod}}[\cos \gamma_R; \cos(\beta = 170^{\circ})]$ and to $R_S^{\text{mod}}[\cos \gamma_R; \cos(\beta = 100^{\circ})]$. Note that the forward $\beta = 100^{\circ}$ shell exhibits a slightly concave shape at its waist.



Figure 3.2: The hard shell contours $R_S^{\text{mod}}(\cos \gamma_R; \cos \beta)$ of the He-NO(X) modified hard shell as a function of $\cos \gamma_R$ (solid black lines) at $E_{col} = 508 \text{ cm}^{-1}$ for a number of specified kinematic apse angles β . These same contours are also displayed as a function of $\cos \gamma_a$ (dotted red lines). Note that the waist of the potential contours $R_s(\cos \gamma_R, \cos \beta)$ does not occur at $\cos \gamma_R = 0$ but at a slightly negative offset for $\cos \gamma_a$, shifted towards the O-end of the NO(X) molecule. This offset decreases as the apse angle β increases. Note that between $\cos\beta = \cos\beta_{\min}^{convex} = -0.19842$ and $\cos\beta = 0$ it is impossible to assign a unique value of R_s to the values of $\cos \gamma_a$ near the waist of the potential contours. In the range $90^\circ \le \beta < \beta_{\min}^{convex} = 101.45^\circ$ the $R_{\rm s}^{\rm mod}(\cos\gamma_a;\cos\beta)$ functionality at about $\cos \gamma_a \approx -0.05$ is no longer singly valued. The MQQT range of allowed Δj values for a particular hard shell contour as well its associated β are indicated.

3.3. Results and Discussions

3.3.1 Phase shift curves and scattering amplitudes

To gain insight into the distinctive features of the rotationally inelastic MQQT DCSs compared to those of the RQQT (and also into their underlying Legendre anisotropy coefficients $C_n(\cos\beta)$ of the PES, specified and discussed in Section 3.B of the Appendix), the $\cos\gamma_a$ dependency of the phase shifts $\eta_{E=0\rightarrow E(j'=4.5)}^{\text{mod}}(\gamma_a;\beta,p)$ and $\eta_{E=0\rightarrow E(j'=4.5)}^{\text{reg}}(\gamma_a;\beta,p)$ have been explored over their kinematic range:[72]

$$-1 \le \cos\beta \le \cos\beta_{\kappa} \tag{3.6}$$

Note that in the case of RQQT, $R_s^{reg}(\cos \gamma_a) \equiv R_s^{mod}(\cos \gamma_a; \beta = 180^\circ)$ does not depend on β . In Fig. 3.3 the $\cos \gamma_a$ dependence of the MQQT and RQQT phase shift curves of the $j = \frac{1}{2} \rightarrow j' = \frac{7}{2}$ inelastic transition is shown for a number of representative apse angles β (chosen to coincide with the $\beta \ge 103^{\circ}$ angles depicted in Fig. 3.2), for both classically allowed (p=1) and classically forbidden (p=2)pathways. These representative apse angles facilitate a comparison of the p=1 and p=2 phase shift curves in relation to the specifics of the probed PES contour. Eq. (3.A.4) (Section 3.A of the Appendix) shows that the p=2 phase shift is a factor if $\{|\cos\beta| - \sqrt{\cos^2\beta - E_{i'}/E_{col}}\} / \{|\cos\beta| + \sqrt{\cos^2\beta - E_{i'}/E_{col}}\}$ smaller than the p=1 phase shift. The MQQT and RQQT phase shifts shown in Figs. 3.3 and 3.4, (as obtained from Eq. (3.A.1)), are shown as solid and dashed curves, respectively. To $\eta_{i=0.5 \rightarrow j'=7.5}^{\mathrm{mod}}(\gamma_a;\beta,p)$ facilitate comparison of the modified and regular $\eta_{i=0,5 \rightarrow i'=7,5}^{reg}(\gamma_a;\beta,p)$ phase shifts on β and p, the maximal values in Figs. 3.3 and 3.4 have been shifted to unity. This was done by the addition or subtraction of the proper γ_a independent phase shift. Eqs. (3.A.8)-(3.A.15) (Section 3.A of the Appendix) show that both the apse and collision frame RQQT and MQQT inelastic DCSs are independent of such a constant shift.

As in the full QM approach, in QQT the classical lever due to the γ_a - dependent impact of the He atom onto the He-NO(X) PES contour has no direct relevance on the outcome of the scattering event. Both the QM scattering amplitude and the MQQT scattering amplitude of Eq. (3.A.8) (Section 3.A of the Appendix), depend on the interference between all Feynman allowed paths from the initial rotational



Figure 3.3: The modified $\eta_{j=0.5 \rightarrow j'=2.5}^{\text{mod}}(\gamma_a;\beta)/\pi$ and regular $\eta_{j=0.5 \rightarrow j'=2.5}^{\text{reg}}(\gamma_a;\beta)/\pi$ QQT phase shift curves of the rotationally inelastic $j = \frac{1}{2} \rightarrow j' = \frac{7}{2}$ transition of He + NO(X) at $E_{col} = 508 \text{ cm}^{-1}$ for $\beta = 103^{\circ}$, 110°, 120°, 135°, 150° and 180°, which respectively correspond to $\theta = 15.0^{\circ}$, 35.5°, 57.3°, 88.5°, 119.1° and 180° in the p=1 left panel and to $\theta = 11.1^{\circ}$, 4.55°, 2.66°, 1.55°, 0.85° and 0° in the p=2 right panel. Note that $\beta \ge \beta_{\kappa} = 102.84^{\circ}$ or $\cos \beta \le \cos \beta_{\kappa} = 0.22204$. The p=2 QQT phase shift curves relate to the p=1 ones to a β and $E_{j'}/E_{col}$ dependent proportionality factor which ranges from unity at $\cos \beta = \cos \beta_{\kappa}$ to 0.01266 at $\cos \beta = -1$ as follows directly from Eq. (3.A.5) of Appendix.

quantum state to the final rotationally excited quantum state at a particular classically allowed (*p*=1) or classically forbidden (*p*=2) apse angle β , or at the equivalent scattering angle θ [22, 24, 72]. One of the most striking features in Fig. 3.3 is the similarity of the $\eta_{j=0.5 \rightarrow j'=2.5}^{\text{mod}}(\gamma_a; \beta, p)$ and $\eta_{j=0.5 \rightarrow j'=2.5}^{\text{reg}}(\gamma_a; \beta, p)$ phase shifts for negative $\cos \gamma_a$ O-end impact sites of the He-atom onto the hard shell contour PES, while the phase shifts differ more strongly at positive $\cos \gamma_a$ N-end impact sites.

To allow a clear differentiation between the N-end part and the O-end part of a



Figure 3.4: Details of the NO-He phase shift curves η/π for p=1 around $\cos \gamma_a = \cos \gamma_a^{\text{waist}}$ of the modified (left panel) and regular (right panel) which remained unresolved in Figure 3.3. Note that the value of $\cos \gamma_a^{\text{waist}}$ at the maximum $\eta/\pi = 0$ was found to be equal to -0.082 at $\beta=103^\circ$, -0.076 at $\beta=110^\circ$ -0.071 at $\beta=120^\circ$, -0.065 at $\beta=135^\circ$, -0.058 at $\beta=150^\circ$ and -0.055 at $\beta=\beta_{\text{max}}=180^\circ$, i.e. the maximum shifts towards that of the homonuclear limit of $\cos \gamma_a^{\text{waist}} = 0$ when β increases from 100° to 180°. Such a shift is deemed to remain absent in the right panel. RQQT assumes a hard shell PES which is equal to that of MQQT at $\beta=\beta_{\text{max}}=180^\circ$ for all β .

particular He-NO β -dependent PES contour, the $\cos \gamma_a = \cos \gamma_a^{waist}$ edge was chosen to coincide with the "waist" of the $R_s^{mod}(\cos \gamma_a;\beta)$ shell contour. The value of $\cos \gamma_a^{waist}$ follows from:

$$\frac{\partial R_s^{\text{mod}}[\cos \gamma_a = \cos \gamma_a^{\text{waist}}; \beta]}{\partial \cos \gamma_a} = 0; \quad \cos \gamma_a^{\text{waist}} \neq \pm 1$$
(3.7)

The details of the MQQT and RQQT p=1 phase shift curves around the $\cos \gamma_a = \cos \gamma_a^{waist}$ impact region are shown in Fig. 3.4. The MQQT and the RQQT phase shifts are both proportional to a $K(\beta, p)$ kinetic factor, given by Eq. (3.A.2) (Section 3.A of the Appendix). The left panel of Fig. 3.4 shows that when β increases from 100° to 180° the MQQT value of $\cos \gamma_a^{waist}$ shifts from -0.085 to -0.054. Since $R_s^{reg}(\cos \gamma_a) \equiv R_s^{mod}(\cos \gamma_a; \beta = 180^\circ)$ all RQQT phase shift curves in the right panel 52

of Fig. 3.4 maximize at $\cos \gamma_a^{waist} = -0.054$.

Dynamically the near similarity of the O-end MQQT and RQQT phase shifts reflects the more closed shell character of the NO(X) molecule at this impact region. As discussed in more detail in Section 3.B of the Appendix, the π^* orbital of the NO molecule possesses a smaller and less extended one electron charge density at the O-end than at the N-end region [43]. This phenomenon is also responsible for the anomalous direction of the $-NO^+(X)$ electric dipole moment. The same phenomenon causes the difference between the RQQT and MQQT phase shifts for all scattering angles with $\beta < 180^\circ$ to maximizes at $\cos \gamma_a \cong 0.5$, as shown in Fig. 3.3. The orbital symmetry node in the π^* lobe along the NO axis causes the differences between the MQQT phase shifts to become minimal at $\cos \gamma_a = \pm 1$, where the π^* orbital electron density drops to zero. When β approaches 180° the MQQT and RQQT phase shifts become similar. By definition in both panels the $\beta = \beta_{\kappa} = 103^\circ$ phase shift curves are identical.

The MQQT apse frame scattering amplitude $g_{j=0.5,m_a,\bar{\Omega}=0.5,\epsilon \rightarrow j',m'_a,\bar{\Omega}'=0.5,\epsilon'}(\beta, p)$ also depends on the geometric scattering amplitude, $g_{geom}^{mod}[\gamma_a;\beta]$, which constitutes an additional γ_a - dependent factor in the integrand of Eq. (3.A.5) (see Section 3.A of the Appendix). Ballast et al, previously explored the so-called constant curvature approximation in which a γ_a independent geometrical scattering amplitude [24]

$$g_{concur}^{reg}(\cos\beta) \equiv \sqrt{\left|\cos\beta\right| \left[R_0^{\text{mod}}(\cos\beta = -1)\right]^2}$$
(3.8)

was used instead of $g_{geom}^{mod}(\gamma_a;\beta)$ in the integrand of Eq. (3.A.5) (Section 3.A of the Appendix), where $R_0^{\text{mod}}(\cos\beta = -1)$ denotes the averaged value of $R_{\rm s}^{\rm mod}(\gamma_a;\cos\beta=-1)$. The constant curvature approximation leads to slightly smaller DCSs for low values of Δj than when the full γ_a -dependent $g_{geom}^{mod}[\gamma_a;\beta]$ is used. The small differences between the resulting absolute values of the DCSs were found to disappear at $\Delta j > 8$ [24]. For this reason, the γ_a -dependency of $g_{eeom}^{mod}[\gamma_a;\beta]$ is influence expected to be of minor on the outcome of $g_{j=0.5,m_a,\bar{\Omega}=0.5,\varepsilon \to j',m'_a,\bar{\Omega}'=0.5,\varepsilon'}^{\text{mod}}(\beta,p)$, validating the approximation of $g_{geom}^{\text{mod}}(\gamma_a;\beta)$ with $g_{concur}^{\text{mod}}(\cos\beta)$, where

$$g_{concur}^{\text{mod}}(\cos\beta) \equiv \sqrt{\left|\cos\beta\right| \left[R_0^{\text{mod}}(\cos\beta)\right]^2}$$
(3.9)

It is the phase shift function $\exp[i\eta_{j=0.5\rightarrow j'}^{\text{mod}}(\gamma_a;\beta,p)]$ which most strongly determines the β and p dependency of $g_{j=0.5,m_a,\bar{\Omega}=0.5,\varepsilon\rightarrow j',m'_a,\bar{\Omega}'=0.5,\varepsilon'}(\beta,p)$, and hence the angular dependence of the DCS. Eqs. (3.A.6) - (3.A.8) (Section 3.A of the Appendix) and Eq. (3.9) incorporate the constant curvature approximation into the expression for the MQQT scattering amplitude yielding:

$$g_{j=0.5,m_{a},\bar{\Omega}=0.5,\varepsilon \to j',m'_{a},\bar{\Omega}'=0.5,\varepsilon'}^{\text{mod}-concur}(\beta,p)C(\beta)$$

$$= \delta_{m_{a},m'_{a}} \sqrt{j'+\frac{1}{2}} \frac{m_{a}}{|m_{a}|} g_{concur}^{\text{mod}}(\cos\beta) \qquad (3.10)$$

$$\times \frac{1}{2} \int_{-1}^{1} d\cos\gamma_{a} \exp[i\eta_{j=0.5 \to j'}^{\text{mod}}(\gamma_{a};\beta,p)]P_{j'-\varepsilon'\varepsilon/2}(\cos\gamma_{a})$$

The relation between the MQQT (and RQQT) apse frame scattering amplitude and the collision frame differential cross section, $\frac{d\sigma_{j=\frac{1}{2},\varepsilon \rightarrow j',\varepsilon'}^{\text{mod}}}{d\omega}(\theta)$, are given in Eqs. (3.A.7) and (3.A.11) (Section 3.A of the Appendix). Upon integration over the full range of scattering angles one obtains the related integral collision cross sections

 $\sigma_{j=rac{1}{2},arepsilon
ightarrow j',arepsilon'}^{\mathrm{mod}}.$

3.3.2 Differential and integral rotationally inelastic cross sections

The MQQT, RQQT and exact QM rotationally inelastic spin-orbit manifold conserving NO (X, v=0)-He inelastic DCSs, for the transitions $j = \frac{1}{2}, \varepsilon = -1 \rightarrow j' = \frac{1}{2}, \varepsilon' = 1$ and $j = \frac{1}{2}, \varepsilon = -1 \rightarrow 1.5 \le j' \le 11.5, \varepsilon' = -1$ at $E_{col}=508$ cm⁻¹, are shown in Fig. 3.5. The exact QM DCSs obtained from the HIBRIDON code were provided by Kłos *et al.* [57]. The rapid oscillatory structures present in the QM DCSs at small scattering angles for $\Delta j < 5$ arise from diffraction effects, which are not accounted for in either RQQT or MQQT. In place of the QM diffraction pattern, the QQT DCSs exhibit a sharp peak at $\theta = 0$, due to a dramatic difference in weighting factors between β and θ , which for $\Delta j < 5$ supersedes the maximum in the classically allowed (p = 1) $\theta > \theta_{\kappa}$ range by orders of magnitudes. This difference decreases with increasing Δj , as the peak in the DCS at $\theta = 0$ becomes relatively less significant [72]. The QM DCS calculation utilizes the full PES, while the RQQT simplifies the PES to a rigid hard shell given by $V_{sum}(R, \cos \gamma_R) = E_{col}$. The MQQT instead reduces the full PES with a hard shell PES contour, which is set equal to the amount of collision energy provided by the component of the incoming momentum vector directed anti-parallel to the surface normal, such that

$$V_{sum}(R, \cos \gamma_R, \cos \beta) = E_{col} \cos^2 \beta . \qquad (3.11)$$

Figure 3.5 shows that all RQQT NO(X)–He DCSs with $\Delta j \leq 6$ are typically smaller than the exact QM DCSs in the classically allowed (*p*=1) forward scattered region. It is this difference, which becomes most substantial for the parity changing $\Delta j \leq 4$ inelastic transitions, that stimulated the development of the MQQT DCS model, for which PES contours range from $V_{sum}(R, \cos \gamma_a) = 0$ for a glancing $(\cos \beta = 0)$ collision down to $V_{sum}(R, \cos \gamma_a) = E_{col}$ for a head on $(\cos \beta = -1)$ collision. The effective larger size of the ellipsoidal potential at small scattering angles acts to increase the DCS in this region, reducing the discrepancy between the MQQT and QM results.

Figure 3.5 also shows that the p=1 range of the MQQT DCSs (particularly for the parity changing rotationally inelastic transitions for $\Delta j \le 5$) provide a much better approximation to the QM data than that provided by the RQQT. MQQT preserves the generally good agreement between RQQT and QM for transitions with $\Delta j > 5$.

Since it is the magnitude of the $C_{n=1}(\cos\beta)$ first order Legendre polynomial expansion coefficient (depicted in Fig. 3.A, Section 3.B of the Appendix), which varies the most at the low perpendicular collision energies for which $|\cos\beta| << 1$, the enhancement of the MQQT DCSs with respect to the RQQT DCSs continues up to scattering angles as large as 120°. This effect is by far the largest for the classically allowed p=1 parity paired $j=\frac{1}{2}, \varepsilon=-1 \rightarrow j'=\frac{1}{2}, \varepsilon'=1$ and $j=\frac{1}{2}, \varepsilon=-1 \rightarrow$ $1.5 \le j' \le 11.5, \varepsilon'=-1$ DCSs in Fig. 3.5.

In Section 3.B of the Appendix it is argued that the angular dependence of the MQQT and RQQT inelastic DCSs are independent of $C_{n=0}(\beta)$. All other $C_n(\cos\beta)$ coefficients shown in Fig. 3.A (Section 3.B of the Appendix) remain essentially stationary when $E_{col} \cdot \cos^2 \beta \ge 326 \ cm^{-1}$ or when $\Delta j \ge 13$. The near stationary nature of these coefficients for apse frame angles $\beta \ge 143^{\circ}$ underlies the similarity between the MQQT and RQQT DCSs at scattering angles θ that



Figure 3.5: The QM HIBRIDON (solid lines), MQQT (dashed lines) and RQQT (dotted lines) DCSs for the NO(*X*)+He transitions $j = \frac{1}{2}, \varepsilon = -1 \rightarrow j' = \frac{1}{2}, \varepsilon' = 1$ and $j = \frac{1}{2}, \varepsilon = -1 \rightarrow 1.5 \le j' \le 11.5, \varepsilon' = -1$ at a collision energy of 508cm⁻¹. The exact QM DCSs are scaled to the regular QQT model DCSs. The black dotted vertical line separates the classical forbidden $p = 2, \theta < \theta_{\kappa}$ range of scattering angles from those that are classical allowed $p=1, \theta \ge \theta_{\kappa}$.

correspond to $\beta \ge 143^{\circ}$. More specifically, this similarity ought to persist for the full range of θ wherever $\beta_{\kappa} > 143^{\circ}$ e.g., for $\Delta j > 12$.

To facilitate the visual comparison of the MQQT and RQQT DCSs with the QM data, the latter are multiplied by a numerical factor chosen such that all QM ICSs are scaled to the RQQT values. The MQQT and RQQT DCSs shown in Fig. 3.5 are very close to one another for parity conserving $\Delta j \ge 8$ transitions, implying that the *n*=1, and *n*=4 $C_n(\beta)$ coefficients (shown in Fig. 3.A, Section 3.B of the Appendices) are of minor importance only in determining these DCSs.

The rotationally inelastic DCSs of the classically forbidden p=2 range of

scattering angles *i.e.* from $\theta = 0^{\circ}$ to $\theta = \theta_{\kappa}$ (within which β decreases from $\beta = 180^{\circ}$ to $\beta = \beta_{\kappa}$), follows from similar expressions to those defining the classically allowed p=1 region of the DCSs for which θ ranges from $\theta = 180^{\circ}$ to $\theta = \theta_{\kappa}$. In contrast to the p=1 range, the p=2 range of the MQQT and RQQT DCSs exhibit the best agreement when $\theta \ll \theta_{\kappa}$ and become most dissimilar if $\theta \to \theta_{\kappa}$. The absolute value of the p=2 phase shift of the OOT scattering amplitude is smaller than the corresponding p=1 phase shift, as specified by Eq. (3.A.4) (Section 3.A of the Appendix). Additionally Eq. (3.A.15) causes the classically forbidden part of the low Δi QQT DCSs to peak sharply at $\theta=0$ and thereafter to drop strongly with θ . This classically forbidden region provides an analogue to the diffractive contribution to the QM DCSs in the forward scattered direction. For transitions with $\Delta j \ge 5$, Eq. (3.B.1) (Section 3.B of the Appendix) brings about a slower drop-off of the QQT DCSs in the classically forbidden region $\theta < \theta_{\kappa}$ which has no obvious QM equivalent, and is best regarded as an artifact. However, the inclusion of the classically forbidden part of the DCSs results in only a minor change in the flux normalization coefficients C_{flux}^{mod} in Eq. (3.A.11) and Eq. (3.A.12) (Section 3.A of the Appendix). Similarly, the classically forbidden forward scattered artifact peak in the QQT DCS leads only to a marginal contribution to the total inelastic cross section.

Although the V_{sum} PES of the NO(X)-He rotationally inelastic collision system consists of a shallow well followed by a compressible repulsive wall, the difference between the RQQT and MQQT DCSs is mostly limited to near forward scattering angles and was found to become marginal for $\Delta j > 6$. All anisotropic $C_{n>0}(\cos\beta)$ Legendre coefficients shown in Fig. 3.A (Section 3.B of the Appendix) become nearly stationary when $E_{col} \cos^2 \beta > E(j' = 7.5)$ or for $\beta > 117.04^\circ$. For transitions with $j' \ge 7.5$ one has $\cos \beta_{\kappa} < \cos(117.04^\circ)$, which implies that the MQQT DCSs become essentially identical to the RQQT DCSs. This is because the anisotropic terms of the NO(X)-He PES do not vary significantly over the range $E(j' = 7.5) = 105.36 \text{ cm}^{-1} \le V_{sum}(R, \gamma_R) \le 508 \text{ cm}^{-1}$.

Figure 3.6 compares the j' dependence of all $j = \frac{1}{2}$ $\varepsilon' = \varepsilon = -1$ $E_{col} = 508 \text{ cm}^{-1}$ MQQT NO(X) – He ICSs with those obtained from RQQT and exact QM calculations. At low values of Δj , all ICSs show pronounced oscillatory



Figure 3.6: Comparison between the QM ($\mathbf{\nabla}$), modified QQT (**n**) and regular QQT (•) quantum state resolved rotationally inelastic integral cross sections for NO-He at a collision energy of 508 cm⁻¹. Note that as in Fig. 3.5 the $\Delta j=0$ cross section corresponds to an $\varepsilon = -1 \rightarrow \varepsilon' = 1$ transition while for all others $\varepsilon = -1 \rightarrow \varepsilon' = -1$. Because of the MQQT hard shell PES approximation ignores the most prominent long range $V_2(R) \cdot P_2(\cos \gamma_R)$ term of the V_{sum} PES, their difference with QM ICSs maximizes for the j=0.5, $\varepsilon = -1 \rightarrow j' = 2.5$, $\varepsilon = -1$ transition. The similarity of the MQQT and RQQT ICSs at $\Delta j \ge 10$ complies with the similarity of the DCSs shown in Fig. 3.5.

structures, which disappear with increasing j'. At low Δj , especially for parity changing $(-1)^{j'-\varepsilon\varepsilon'/2} < 0$ transitions, the rotationally inelastic MQQT ICSs are larger than the RQQT ones, which reflects the less pronounced maximum in the RQQT DCSs. The agreement between the MQQT and exact QM ICSs is less convincing, as expected [19], than that obtained for the scattering angle dependence of the DCSs. The MQQT hard shell PES approximation accounts only for the hard shell repulsive $C_{n=2}(\cos\beta)$ expansion coefficient and lacks the contribution (present in the full QM treatment) of the anisotropic attractive long range $V_2(R) \cdot P_2(\cos\gamma_R)$ term of the V_{sum} PES [43]. This contribution causes the QM ICS for the transition j = 0.5, $\varepsilon = -1 \rightarrow j' = 2.5$, $\varepsilon = -1$ to become around twice as

large as the MQQT and RQQT ICSs. In Fig. 3.4 where the QM DCS was scaled to the RQQT ICS, this contribution is reflected in the enhanced forward scattering of the QM DCS with respect to the MQQT and RQQT DCSs.

3.4. Conclusions and Outlook

The MOOT of the rotationally inelastic collision problem developed in the present employs a modified hard shell potential study contour. defined as $V_{sum}(R, \gamma_R) = E_{col} \cdot \cos^2 \beta$, which depends on the polar angle β between the surface normal a and the incoming momentum vector k. It provides a potential barrier which is just large enough to avoid penetration. The MQQT DCSs were found to reproduce the OM DCSs obtained on the full PES more exactly than those obtained from the existing RQQT. In RQQT $V(R, \gamma_R)$ is approximated by a single hard shell contour $V(R, \gamma_R) = E_{col}$ so that the same hard shell PES is encountered for both a glancing impact and a head on impact. Interesting, except for lower Δj inelastic transitions the MOOT was found to produce quite similar DCSs to those obtained via the ROOT. Even at these lower values of Δi , the overall structure of the MQQT DCSs resembles the exact QM results obtained for the He + NO(X, $i = \frac{1}{2}$) collision system. The similarity of the scattering angle dependence of RQQT, MQQT and exact QM state resolved rotationally inelastic DCSs at higher Δi (and for lower Δi , excluding forwards directed scattering angles) has been shown to relate to the specific properties of the state of the art *ab initio* He + NO(X, v=0) PES [43], which assumes the bond length of NO molecule remains fixed at its equilibrium length $r = r_e$. The anisotropic Legendre coefficients $C_{n}(\cos\beta)$ become essentially stationary for potential energy contours $V(R, \gamma_R) > 326 cm^{-1}$, while the isotropic coefficient $C_{n=0}(\cos\beta)$, related to the effective size of the ellipsoid, increases steeply with $\cos^2 \beta$.

Recently Cappelletti and co-workers provided experimental and quantum chemical evidence that charge transfer (CT) occurs between the molecular collision partners H₂O-Ne, Ar, Kr, Xe, H₂ and NH₃-H₂ at distances in the well region of the PES, causing the molecules to adiabatically adapt their bond geometry in a way that enhances the attractive intermolecular interaction [77-82]. This model was based on potential parameters obtained from the experimentally observed collision energy dependence of the glory amplitude of the integral collision cross section, and from CT calculations based on a general theoretical model which reproduces very accurately the collision cross sections obtained at the CCSD(T) level using large basis sets [80]. The CT contribution to the intermolecular PES was found to depend

strongly on the molecular orientation (*i.e.* γ_R) [82] and increases with the proximity of collision partners [80]. The calculated CT contribution for the H₂O-RG complex were found to be almost negligible for He-H₂O but increased strongly with the mass of the RG atom [59]. These CT contributions to the intermolecular PES were taken into account in the *ab initio* PESs employed to predict the quantum state selected experimentally observed H₂-H₂O,-HDO and-D₂O rotationally inelastic DCSs [35, 38, 83].

Whether the unpaired electron in the π^* orbital of the NO(X) molecule is able to participate in electron transfer to a RG atom at distances smaller than the well region has not yet been explored. The theoretically predicted values of the rate constants of depolarization of selected NO ($X^2\Pi_{\frac{1}{2}}$, v=0, j) levels in a thermal bath of Ar atoms computed on the highest quality UCCD(T) PESs [44], (as obtained by Alexander with NO bond length fixed at its equilibrium value), were found to be significantly less than those obtained from experimental observation [46]. This discrepancy between experiment and theory is still to be explained.

Examples of experimental quantum state resolved rotationally inelastic DCSs for which MQQT could offer additional insight are:

1) Hexapole quantum state selected NO scattered from He at $E_{col}=510$ cm⁻¹(63.2 meV) [33].

2) Hexapole quantum state selected OH scattered from Ar at $E_{col}=500 \text{ cm}^{-1}$ (62.0 meV), and from He at $E_{col}=460 \text{ cm}^{-1}$ (57.0 meV) [39].

3) Electronically resonant quantum state specific excited NO ($\nu = 0$, N = 0, A² Σ^+) scattered from Ar [37], He [84, 85] and Ne [85, 86] at respectively E_{col} =855 cm⁻¹ (230 meV), E_{col} =382 cm⁻¹ (47.4 meV) and E_{col} =488 cm⁻¹ (60.5 meV).

4) Asymmetric top H₂O supersonically cooled down to its *para* and *ortho* rotational ground states scattered from He at E_{col} =429 cm⁻¹ (53.5 meV) [35, 36].

5) H₂O and its isotopomers scattered from He, and from *para j*=0 and *ortho j*=1 H₂ at collision energies around 500 cm⁻¹ (62 meV) [35, 38, 83].

6) Hexapole quantum state selected NO(X) scattered from Ar at $E_{col} = 530 \text{ cm}^{-1}$ (66 meV) [25, 45] and from Ne at $E_{col} = 540 \text{ cm}^{-1}$ (68meV) [74], These latter experimental results offered an additional level of detail by including the scattering angle dependent alignment of the rotational angular momentum of the NO molecule following a rotationally inelastic collision [87], and were all found to agree well with quantum mechanically exact and QQT predictions [44, 88, 89].

7) Most recently, hexapole quantum state selected ND₃ scattered from He at E_{col} =430 cm⁻¹ (51.8 meV) [90] and quantum state selective rotationally inelastic

DCSs of the reactive CH₃ and CD₃ radicals scattered from He at 425 cm⁻¹ (52.7 meV) and 440 cm⁻¹ (54.6 meV) respectively [76].

It is expected that in the near future, as pioneered by Tkáč et al [90], such studies will become possible over an extended range of experimental collision systems which may be even more chemically distinct than those explored thus far [25-27, 31-39, 41, 42, 45, 70-72, 74, 75, 83, 84, 86, 91]. The modified QQT model proposed in this work is presented as a potentially valuable tool by which further insight can be obtained into the nature of the collision energy dependent quantum mechanical interference phenomena that play an important role in molecular rotationally inelastic scattering events. The QQT treatment is quite versatile, being applicable to any collision between a particle and a linear or (a)symmetric top rotor, provided that the collision energy employed is significantly greater than the attractive interactions existing between the two particles. Because it directly calculates the differential cross-section from the scattering amplitude, without recourse to the intermediate of the scattering matrix produced by most quantum mechanical methods, it also offers an alternative physical insight into the scattering problem, which may be of use in the interpretation and understanding of the collision dynamics.

In summary, the Modified QQT provides additional insight into the relation between the V_{sum} NO(X)-He PES and the rotationally inelastic quantum state resolved QM exact DCSs, by quantifying the effective shape of the equivalent hard shell PES experienced by the atom-diatom system during the course of the collision. The differences between the rotationally inelastic RQQT and MQQT DCSs and ICSs are expected to be more dramatic when the anisotropy of the repulsive PES contour exhibits a more significant dependence on the effective collision energy. There is a substantial variety of linear and non linear molecules for which quantum state resolved DCSs for collisions with Rare gas atoms or quantum state selected target molecules have been (or are being) explored. Modified QQT will prove a useful and numerically inexpensive tool to acquire insight into the repulsive regions of the PES that are most instrumental in determining the scattering dynamics, and most responsible for any differences observed between the theoretically predicted and experimentally observed DCSs.

Appendices

3.A Explicit expressions for the MQQT phase shift, flux normalized scattering amplitude, DCSs and ICSs.

The MQQT phase shift is defined (as in RQQT, but distinct from QM) as the phase difference between (1) the path of the incoming wave k which is (inelastic) scattered from the shell at the impact position $R_s^{mod}(\cos \gamma_a; \cos \beta)$ into an outgoing wave k' and (2) the virtual reference path in which the incoming wave k is scattered at $R_s = 0$ into an unperturbed outgoing wave k' which leads to [72]

$$\eta_{j=0,5\to j'}^{\text{mod}}(\gamma_a;\beta,p) = -\boldsymbol{a}(\beta,p) \cdot \boldsymbol{R}_{\mathcal{S}}^{\text{mod}}(\cos\gamma_a;\beta) = K(\beta,p) \times \boldsymbol{R}_{\mathcal{S}\perp}^{\text{mod}}(\gamma_a;\beta), \quad (3.A.1)$$

in which,

$$K(\beta, p) \equiv [k_{\perp} + (-1)^{p-1} k'_{\perp}] = |k \cos \beta| + (-1)^{p-1} \sqrt{|k \cos \beta|^2 - \frac{2\mu}{h^2} E_{j'}}, \qquad (3.A.2)$$

the so called kinetic factor, which depends only on p and β and

$$R_{S\perp}^{\text{mod}}(\gamma_a;\beta) \equiv \hat{a}(\gamma_a) \cdot R_S^{\text{mod}}(\cos\gamma_a;\beta) = R_S^{\text{mod}}(\cos\gamma_a;\beta)\cos(\gamma_R - \gamma_a), \quad (3.A.3)$$

denotes the surface normal projected PES contour radius vector, which depends both on γ_a and β in the case of MQQT and solely on γ_a in the case of RQQT because $R_{S\perp}^{reg}(\cos \gamma_a) \equiv R_{S\perp}^{mod}(\cos \gamma_a; \beta = 180^\circ)$.

Note that only paths (differentiated by the polar angle γ_a) from an initial and to a final rotational state scattered into the same β , *p* and φ_a appeared appeared parameters, are allowed to interfere with each other. Eqs. (3.A.1), (3.A.2) and (3.A.3) jointly imply:

$$\eta_{j=0.5 \to j'}^{\text{mod}}(\gamma_{a}; \beta, p = 2) = \frac{|\cos\beta| - \sqrt{\cos^{2}\beta - E_{j'} / E_{col}}}{|\cos\beta| + \sqrt{\cos^{2}\beta - E_{j'} / E_{col}}} \eta_{j=0.5 \to j'}^{\text{mod}}(\gamma_{a}; \beta, p = 1)$$
(3.A.4)

The apse frame MQQT scattering amplitude follows as:

$$g_{j=0.5,m_{a},\bar{\Omega}=0.5,\varepsilon \to j',m'_{a},\bar{\Omega}'=0.5,\varepsilon'}^{\text{mod}}(\beta,p) = \langle j',m'_{a},\bar{\Omega}'=0.5,\varepsilon' \mid g_{geom}^{\text{mod}}(\gamma_{a};\beta) \qquad (3.A.5)$$
$$\times \exp[i\eta_{E=0\to E(j')}^{\text{mod}}(\gamma_{a};\beta,p)] \mid j=0.5,m_{a},\bar{\Omega}'=0.5,\varepsilon >$$

The MQQT fixed-molecule scattering amplitude for a particular j=0.5 to j' transition, extends from that of a RQQT fixed-molecule transition [72]:

$$g_{E=0\to E(j')}^{\text{mod}}(\gamma_a;\beta,p) = g_{geom}^{\text{mod}}(\gamma_a;\beta) \exp[i\eta_{j=0.5\to j'}^{\text{mod}}(\gamma_a;\beta,p)], \qquad (3.A.6)$$

where

$$g_{geom}^{\text{mod}}(\gamma_a;\beta) = \sqrt{|\cos\beta| \rho_1^{\text{mod}}(\gamma_a;\beta)\rho_2^{\text{mod}}(\gamma_a;\beta)}, \qquad (3.A.7)$$

denotes the geometric scattering amplitude. The MQQT hard shell principal radii of curvature $\rho_1^{\text{mod}}(\gamma_a;\beta)$ and $\rho_2^{\text{mod}}(\gamma_a;\beta)$ differ from the RQQT values by depending on β , while the MQQT phase shift $\eta_{j=0.5 \rightarrow j'}^{\text{mod}}(\gamma_a;\beta,p)$ exhibits a different dependence on β [22, 24].

To obtain the MQQT apse frame scattering amplitude, the product of $g_{E=0\to E(j')}^{\text{mod}}(\gamma_a;\beta,p)$ and $\Psi^*_{j',m_a,\varepsilon'}(\gamma_a,\phi_a)\Psi_{j=0.5,m_a,\varepsilon}(\gamma_a,\phi_a)$ is integrated over the full range of the spherical angles of the molecular axis (γ_a and ϕ_a):

$$g_{j=0.5,m_{a},\varepsilon\to j',m'_{a},\varepsilon'}^{\text{mod}}(\beta,p) \equiv \int_{0}^{2\pi} d\varphi_{a} \int_{-1}^{1} d\cos\gamma_{a} g_{E=0\to E(j')}^{\text{mod}}(\gamma_{a};\beta,p), \qquad (3.A.8)$$
$$\times \Psi_{j',m'_{a},\varepsilon'}^{*}(\gamma_{a},\varphi_{a})\Psi_{j=0.5,m_{a},\varepsilon}(\gamma_{a},\varphi_{a})$$

It is only when that $m_a = m'_a$ the integral of the product of the NO rotational wave functions of Eq.(3.A.8) is not necessarily equal to zero. The product of the two wavefunctions can be contracted to [22, 24]

$$\Psi_{j',m_{a},\varepsilon'}^{*}(\gamma_{a},\varphi_{a})\Psi_{j=1/2,m_{a},\varepsilon}(\gamma_{a},\varphi_{a})\delta_{m_{a},m_{a}'} = \frac{1}{4\pi}\sqrt{j'+\frac{1}{2}}P_{j'-\varepsilon\cdot\varepsilon'/2}(\cos\gamma_{a})[m_{a}/|m_{a}|]^{(1-\varepsilon\cdot\varepsilon')/2}.$$
(3.A.9)

Note that the m_a conserving Eq. (3.A.9) is proportional to the Legendre polynomial $P_n(\cos \gamma_a)$ where n denotes the parity pair number

$$n \equiv j' - \varepsilon \varepsilon' / 2. \tag{3.A.10}$$

Consequently the dependence upon β and p of the $\varepsilon = -1, j = \frac{1}{2}$ MQQT DCSs scattered into the parity pair $\varepsilon' = 1$, j' = n - 0.5 and $\varepsilon' = -1$, j' = n + 0.5 rotationally excited states are similar [22, 24, 25, 33, 45, 57, 58, 71, 74]. The rotationally inelastic apse frame DCS corresponding to scatterings from the $j = \frac{1}{2}, m_a = \frac{1}{2}, \varepsilon$ initial rotational quantum into the $j', m_a = \frac{1}{2}, \varepsilon'$ rotationally exited quantum state is then given by

$$\frac{d\sigma_{j=0.5,\varepsilon \to j',\varepsilon'}^{\text{mod}}}{d\omega_a}(\beta,p) = |\sqrt{C_{norm}^{\text{mod}}}g_{j=0.5,\varepsilon \to j',\varepsilon'}^{\text{mod}}(\beta,p)|^2, \qquad (3.A.11)$$

where C_{norm}^{mod} denotes the normalization factor which ensures that the total collision cross section summed over all the rotational states is equal to the geometric ICS

$$C_{norm}^{\text{mod}} = \frac{\int_{0}^{2\pi} d\varphi \int_{-1}^{0} d\cos\beta d\sigma_{geom}^{\text{mod}}(\beta) / d\omega_{a}}{\sum_{j',\varepsilon',p} \int_{0}^{2\pi} d\varphi \int_{-1}^{0} d\cos\beta |g_{j=0.5,m_{a},\varepsilon \to j',m_{a},\varepsilon'}^{\text{mod}}(\beta,p)|^{2}}, \qquad (3.A.12)$$

where the geometric DCS in the case of $j = \frac{1}{2}$ follows from

$$\frac{d\sigma_{geom}^{\text{mod}}}{d\omega_a}(\beta) \equiv \frac{1}{2} \int_{-1}^{1} d\cos\gamma_a [g_{geom}^{\text{mod}}(\gamma_a;\beta)]^2.$$
(3.A.13)

The integral quantum state resolved rotationally inelastic modified QQT ICS is given by

$$\sigma_{j=0.5,\varepsilon \to j',\varepsilon'}^{\text{mod}} = 2\pi \sum_{p} \int_{-1}^{0} d\cos\beta \frac{d\sigma_{j=0.5,\varepsilon \to j',\varepsilon'}^{\text{mod}}}{d\omega_a}(\beta,p) .$$
(3.A.14)

To transform a MQQT or RQQT apse frame DCS into a collision frame DCS one employs [72]:

$$\frac{d\sigma_{j=\frac{1}{2},\varepsilon \to j',\varepsilon'}}{d\omega}(\theta) = \frac{d\sigma_{j=\frac{1}{2},\varepsilon \to j',\varepsilon'}}{d\omega_a}(\beta,p) \left| \frac{d\cos\beta}{d\cos\theta} \right|$$

$$= \frac{d\sigma_{j=\frac{1}{2},\varepsilon \to j',\varepsilon'}}{d\omega_a}(\beta,p) \frac{(k')^2 |k'-k\cos\theta|}{[(k')^2 - 2k'k\cos\theta + k^2]^{1.5}}$$
(3.A.15)

The smallest scattering angle $\theta = \theta_{\kappa}$ of the p=1 range for which $\frac{d\sigma_{i \to f}}{d\omega}(\theta)$ remains classically allowed matches the largest scattering angle θ of the classically forbidden p=2 range. At $\theta = \theta_{\kappa} \quad \left| \frac{d\cos\beta}{d\cos\theta} \right| = 0$ and so $\frac{d\sigma_{i \to f}}{d\omega}(\theta) = 0$ [72]. Moreover the classically forbidden but Feynman path allowed p=2, θ range gives rise to a sharp maximum of all rotationally inelastic QQT DCSs at $\theta = 0$ because the denominator of Eq. (3.A.15) reaches its minimum, $[k - k']^2$. The value of $\theta > 0$ at which the QQT DCSs maximizes again increases with j' [72]. The forward
peaking in the classically forbidden region at $\theta = 0$ of all MQQT and RQQT DCSs is an unphysical artifact especially for $j' > \frac{5}{2}$. The exclusion of the p=2 classically forbidden region leads only to a 4.3% increase of the (close to unity) value of $C_{norm}^{mod} = 1.276$ $\sigma_{geom}^{Mod} = 0.2414$ (Å²) and to an even smaller 3.1% raise of the RQQT counterpart value $C_{norm}^{reg} = 1.238$ and $\sigma_{geom}^{reg} = 0.2121$ (Å²).

3.B Legendre expansion coefficients

The Legendre expansion coefficients of a contour of the V_{sum} PES $R_s^{Mod}(\gamma_a;\beta)$ were numerically obtained from Eq. (3.B.1) below or from Eqs. (3.C.2) and (3.C.10),

$$C_n(\cos\beta) \equiv \frac{2n+1}{2} \int_{-1}^{1} d\cos\gamma_a R_S^{Mod}(\gamma_a;\beta) P_n(\cos\gamma_a).$$
(3.B.1)

Eq. (3.B.1) applies to the case of a smooth convex MQQT PES contour for which the functionality $\gamma_R(\gamma_a)$ is valid, which holds for all MQQT He-NO(X) PES contours with $\beta \ge \beta_{\min}^{convex} = 101.45^\circ$. The partially concave contours of the He-NO(X) hard shell PES in the case of $90^\circ \le \beta < \beta_{\min}^{convex} = 101.45^\circ$ are reminiscent of the so called "rabbit ears" that dominate the softer repulsive parts of the full NO-He PESs [43]. The node between these "ears" near $\cos \gamma_R \approx 0$ corresponds to the node of the π^* lobe of the anti-bonding unpaired electron orbital of the NO molecule [43].

The one electron π^* lobe charge density is deemed to be much lower than that provided by the closed shell electrons of the NO(X) molecule. This leads to a Pauli repulsion softening at the π^* lobe parts of the He-NO(X) PES, which remains absent at the node of the π^* lobe at $\cos \gamma_R \approx 0$. The Legendre expansion coefficients in this example of partially concave contours were obtained numerically by the choice of a proper integration path specified by Eqs. (3.B.1) and (3.C.2). The vertical dotted lines in each panel of Fig. 3.A indicate the minimum value of $E_{col} \cos^2 \beta$, at which a $\Delta j \equiv j' - \frac{1}{2}$ transition becomes energetically allowed. The particular value of $E_{col} \cos^2 \beta$ at which each Δj transition becomes allowed is indicated below the horizontal axis, and the corresponding apse angle β is shown just above the upper horizontal axis. The $C_{n>0}(\beta)$ curves depicted in Fig. 3.A range between about -0.3



Figure 3.A: The dependence of the modified QQT Legendre polynomial expansion coefficient $C_n(\cos\beta)$ of NO(X)-He at $E_{col}=508 \text{ cm}^{-1}$ on the fraction of the collision energy available for rotational excitation $E_{col} \cos^2 \beta$. The dashed vertical lines denote the energetic threshold at which the rotationally inelastic transition Δj is energetically allowed. Note that the upper horizontal scale marks also the values of β . In the case of $\Delta j \cong 0$ and $\varepsilon' = \pm \varepsilon$ at one has $\theta \cong 2\beta - \pi$ [24].

and 0.69 bohr. All $C_n(\beta)$ curves were found to depend most strongly on β in the concave range $90^\circ \le \beta < \beta_{\min}^{convex} = 101.45^\circ$. The $C_n(\beta)$ curves become nearly stationary for larger β or exhibit a weak linear slope in their dependence upon $\cos^2 \beta$. The low order even C₂ and C₄ and odd C₁ and C₃ coefficients, are the dominating anisotropic coefficients of the NO(X, v = 0)-He MQQT shell PES. Note that the actual value of the (by far largest) C₀ coefficient relates solely to the rotationally elastic scattering DCS. Its actual value is irrelevant for the sought after rotationally inelastic MQQT DCSs.

In the "low" perpendicular collision energy range $0 \le E_{col} \cos^2 \beta < 20 \ cm^{-1}$

which includes collisions that probe partially concave PES contours, the absolute values of the four dominant C_n hard shell Legendre coefficients decrease rapidly if $E_{col} \times \cos^2 \beta$ increases. Note that at this particular range it is only the $\Delta j \leq 2$ inelastic DCSs that are energetically allowed. In more detail, the prescription of Eq. (3.2) restricts the probing range of the partially concave V_{sum} PES contours to: $E_{col} \cos^2 \beta < 20 \ cm^{-1}$, $5.016 \ cm^{-1} \leq E_{col} \cos^2 \beta < 20 \ cm^{-1}$ and $13.38 \ cm^{-1} \leq E_{col} \cos^2 \beta < 20 \ cm^{-1}$ respectively for the $\Delta j = 0$, $\Delta j = 1$ and $\Delta j = 2$ (in)elastic DCSs. All $C_{n=j'-\varepsilon\varepsilon'/2}(\cos\beta)$ expansion coefficients obtained in this lower PES concave range of $0 \leq E_{col} \cos^2 \beta \leq 20 \ cm^{-1}$ were found to join perfectly with those obtained from the "upper" PES contour range $20 \ cm^{-1} \leq E_{col} \cos^2 \beta \leq 508 \ cm^{-1}$. As can be seen from Fig. 3.A, at this upper range, the C₂ and also the much smaller valued C₅ and C₆ coefficients remain nearly constant, while the absolute values of C₁ and C₃ and C₄ decrease with increasing $\cos^2 \beta$. Moreover, by definition at $\cos^2 \beta = 1$ the MQQT C_n coefficients are identical to those of RQQT.

3.C The Legendre moments and the scattering amplitude of a partially concave shell

To apply the MQQT and RQQT of the rotationally inelastic collision problem onto a partially concave PES contours Eqs. (3.A.2) and (3.A.3) do not suffice. As was already noted in Section 3.2, the He-NO(X) PES contours given by

$$V\{R_{S}^{\text{mod}}[\cos\gamma_{a}(\cos\gamma_{R});\beta]\} = E_{col}\cos^{2}\beta, \qquad (3.C.1)$$

turn out to be partially concave for $90^{\circ} \le \beta < \beta_{\min}^{convex} = 101.45^{\circ}$.

For convenience we define the generalized function

$$F[\cos \gamma_{a}(\cos \gamma_{R}); \beta, p, j', m_{a}, \varepsilon', \varepsilon, n] = g_{E=0 \to E(j')}^{\text{mod}}(\gamma_{a}; \beta, p) \Psi_{j', m_{a}, \varepsilon'}^{*}(\gamma_{a}, \varphi_{a}) \Psi_{j=0.5, m_{a}, \varepsilon}^{*}(\gamma_{a}, \varphi_{a})^{*}$$
(3.C.2)

and

$$F[\cos \gamma_a(\cos \gamma_R); \beta, p = 0, j', m_a, \varepsilon', \varepsilon, n] = \frac{2n+1}{2} R_s^{Mod}(\gamma_a; \beta) P_n(\cos \gamma_a), \qquad (3.C.3)$$

which represent respectively the integrand of Eq. (3.A.8) in the range of $90^{\circ} \le \beta \le \beta_{\min}^{convex}$.

A concave curvature maximum occurs for the particular $\gamma_a(\gamma_R^{waist})$ at which

$$\frac{d\cos\{\gamma_a[\cos\gamma_R]\}}{d\cos\gamma_R} = 0, \frac{d\cos\{\gamma_a[\cos\gamma_R - \Delta]\}}{d\cos\gamma_R} < 0, \frac{d\cos\{\gamma_a[\cos\gamma_R + \Delta]\}}{d\cos\gamma_R} > 0 \quad (3.C.4)$$

where Δ denotes an arbitrary positive infinitesimal small number. Convening to the definition given in Section 3.3.1 this (local) concave curvature maximum is called a "waist" for brevity. In our NO(X) + He example there is maximally up to one such waist permitted for each of the $0 < V_{sum} \le 508 \text{ cm}^{-1}$ PES contours. The functionality $\cos \gamma_a (\cos \gamma_R)$ for the example of $\beta = 90^\circ$, depicted in Fig. 3.B, shows that the PES contour $R_s^{\text{mod}}(\cos \gamma_R;\beta = 90^\circ)$ exhibits a concave interval that ranges from $\cos \gamma_R = -0.1219$ to $\cos \gamma_R = 0.1482$ or from $\gamma_R = 97.00^\circ$ to $\gamma_R = 81.59^\circ$ at which $\cos \gamma_a$ varies between $\cos \gamma_a = -0.0855$ and $\cos \gamma_a = -0.0933$ or γ_a between 94.90° and 81.59°. Note this concave range covers a $\approx 5.5^\circ$ range of γ_R , at which γ_a varies by only 0.45°. Moreover note that the selected $\beta=90^\circ$ apse angle of Fig. 3.B designates the extreme case of a glancing collision which scatters into $\theta=0$ direction, for which only the $\Delta j = 0$, $\varepsilon \rightarrow \varepsilon' = -1$ transition is classically allowed. Eq. (3.2) shows that for kinematic reasons the apse angle β range which permits the $j = \frac{1}{2} \rightarrow j'$ rotational transition MQQT restricts its impact onto hard shell PES contours for which:

$$-1 \le \cos\beta \le \cos\beta_{\kappa}(j') \equiv -\sqrt{E(j')/E_{col}}, \qquad (3.C.5)$$

Since the $R_s^{\text{mod}}(\cos \gamma_R; \cos \beta)$ contours were found to be purely convex only if $\beta \ge \beta_{\min}^{\text{convex}} = 101.45^\circ$ or $\cos \beta \le \cos \beta_{\min}^{\text{convex}} = -0.2079$, the range of partially concave PES contours is limited to

$$-0.2079 < \cos\beta \le \cos\beta_{\kappa}(j') \equiv -\sqrt{E(j')/508 \ cm^{-1}}, \qquad (3.C.6)$$

or

$$\operatorname{arccos}\left(-\sqrt{E(j')/508 \ cm^{-1}}\right) \le \beta < \beta_{\min}^{convex} = 101.45^{\circ}.$$
 (3.C.7)



Figure 3.B: The relation between $\cos \gamma_a$ and $\cos \gamma_R$ of the modified He-NO(X) hard shell contour $R_s^{\text{mod}}(\cos \gamma_R; \cos \beta = 0)$ given by $V_{sum}(R, \gamma_R) = 0$. The concave waist of this particular contour is the largest one among the modified shell contours of the He-NO(X) collision system. The function $\cos \gamma_a(\cos \gamma_R)$, as shown in the figure, reaches a local maximum $\cos \gamma_{a,\text{max}} = -0.0855$ (indicated by a red dashed vertical line) at $\cos(\gamma_R) = \cos(\gamma_R)$ decreases monotonically till $\cos \gamma_{R2} = 0.0523$ (indicated by a black arrow) a local minimum $\cos \gamma_{a,\text{min}} = -0.0993$ (indicated by a red dashed vertical line) is reached. Having passed this minimum $\cos \gamma_a(\cos \gamma_R)$ increases monotonically passing the local maximum $\cos \gamma_{a,\text{max}} = -0.0855$ at $\cos \gamma_{R3} = 0.1482$ to its largest allowed value of $\cos \gamma_R = 1$. Concave waists in the He-NO(X) contours persist up to $R_s^{\text{mod}}[\cos \gamma_R; \cos(\beta = 102^\circ)] = -0.208$.

Since $\cos \beta_{\kappa} (j' = \frac{1}{2}) = 0$, $\cos \beta_{\kappa} (j' = \frac{3}{2}) = -0.0995$ and $\cos \beta_{\kappa} (j' = \frac{5}{2}) = -0.1626$ are all larger than and $\cos \beta_{\kappa} (j' = \frac{5}{2}) = -0.2227$ is smaller than $\cos \beta_{\min}^{conv} = -0.2079$, only the rotationally (in)elastic DCSs to the $j' = \frac{1}{2}$, $j' = \frac{3}{2}$ and $j' = \frac{5}{2}$ final rotational states, are influenced by the concave part of a PES contours at forward scattering angles with $\cos \beta > -0.2079$. Upon the substitution of Eq. (3.2) into Eq. (3.3) one obtains:

$$\cos\theta_{\kappa} = \sin\beta_{\kappa} \,. \tag{3.C.8}$$

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The substitution of the values $\cos \beta_k (j' \le \frac{5}{2})$ into Eq. (3.C.8) results in collision frame cutoff angles of $\theta_{\kappa} (j' = \frac{1}{2}) = 0^{\circ}$, $\theta_{\kappa} (j' = \frac{3}{2}) = 5.71^{\circ}$ and $\theta_{\kappa} (j' = \frac{5}{2}) = 9.36^{\circ}$.

As the modified hard shell PES is partially concave in the range $90^{\circ} \le \beta < 101.45^{\circ}$ provisions have to be taken to ensure that $R_s^{\text{mod}}[\cos \gamma_a(\gamma_R);\beta]$ is assigned to a unique value of $\cos \gamma_a$. To meet this requirement, as shown for the $\beta=90^{\circ}$ example of Fig. 3.B, the modified QQT hard shell PES, is divided into the following intervals of $\cos \gamma_a$:

a) $-1 \le \cos \gamma_a(\gamma_R) \le \cos \gamma_a[\cos \gamma_{R1}(\beta)]$

where $\cos \gamma_a [\cos \gamma_{R1}(\beta; j')]$ denotes the local maximum of $\cos \gamma_a$ that occurs at $\cos \gamma_{R1}(\beta = 90^\circ) = -0.1219$ in Fig. 3.B, which shifts towards a larger value when one increases β . The first local maximum disappears if $\beta > 102^\circ$.

b) $\cos \gamma_{a,} [\cos \gamma_{R1}(\beta)] > \cos \gamma_{a}(\gamma_{R}) \ge \cos \gamma_{a} [\cos \gamma_{R2}(\beta)]$

where $\cos \gamma_a [\cos \gamma_{R2}(\beta; j')]$ denotes the local minimum of $\cos \gamma_a$ that occurs at $\cos \gamma_{R2}(\beta = 90^\circ) = 0.0523$ in Fig. 3.B, which shifts towards the local maximum when one increases β . The first local minimum disappears if $\beta \ge 101.45^\circ$.

c) $\cos \gamma_a [\cos \gamma_{R2}(\beta)] < \cos \gamma_a(\gamma_R) \le \cos \gamma_a [\cos \gamma_{R3}(\beta)]$

where $\cos \gamma_a [\cos \gamma_{R3}(\beta; j')]$ denotes the value of $\cos \gamma_a$ that coincides with the local maximum $\cos \gamma_a [\cos \gamma_{R1}(\beta)]$, but occurs at a larger value of $\cos \gamma_{R3}(\beta)$ than that of $\cos \gamma_{R2}(\beta)$. The difference between $\cos \gamma_{R3}(\beta)$ and $\cos \gamma_{R2}(\beta)$ decreases when increasing the value of β . The coincidence with the local maximum disappears if $\beta \ge 101.45^{\circ}$.

d) $\cos \gamma_a [\cos \gamma_{R3}(\beta)] < \cos \gamma_a(\gamma_R) \le 1$

To facilitate a numerically exact outcome for the integral of the function $F[i, \cos \gamma_a(\cos \gamma_R); \beta, p, j', m_a, \varepsilon', \varepsilon]$ in the range of $90^\circ \le \beta \le 101.45^\circ$ of the modified hard shell PES, the integration path is divided into one of three partial integrals, the boundaries of which are chosen according to the prescriptions of a), b) and c) and d). The summation of these partial integrals results in the integrals

$$g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\varepsilon'}^{\text{mod}}(\beta < \beta_{\min}^{\text{convex}},p) \equiv I[i=1;\beta < \beta_{\min}^{\text{convex}},p,j',m_{a},\varepsilon',\varepsilon,n=0], \quad (3.C.9)$$

and

$$C_n(\beta < \beta_{\min}^{convex}, p) \equiv I[\beta < \beta_{\min}^{convex}, p, j', m_a, \varepsilon', \varepsilon, n], \qquad (3.C.10)$$

and

$$I[\beta < \beta_{\min}^{convex}, p, j', m'_{a}, \varepsilon', n] = \frac{2n+1}{2} \left\{ \int_{-1}^{\cos\{\gamma_{a}[\cos\gamma_{R1}(\beta)]\}} d\cos\gamma_{a} F[\cos\gamma_{a}(\cos\gamma_{R}); \beta < \beta_{\min}^{convex}, p, j', m'_{a}, \varepsilon', n] + \int_{\cos\{\gamma_{a}[\cos\gamma_{R2}(\beta)]\}} d\cos\gamma_{a} F[\cos\gamma_{a}(\cos\gamma_{R}); \beta < \beta_{\min}^{convex}, p, j', m'_{a}, \varepsilon', n] + \int_{\cos\{\gamma_{a}[\cos\gamma_{R2}(\beta)]\}} d\cos\gamma_{a} F[\cos\gamma_{a}(\cos\gamma_{R}); \beta < \beta_{\min}^{convex}, p, j', m'_{a}, \varepsilon', n] \right\}$$

$$(3.C.11)$$



A Quasi Quantum Treatment of the Spin-Orbit state changing and conserving rotationally inelastic NO(X)-He collisions

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A Quasi Quantum treatment (QQT) of the rotational inelastic NO(X)-He collisions in the pure Hund's case (a) spin orbit state conserving transitions is extended to the mixed Hund's case spin orbit state conserving and changing transitions. To enable this extension a polar and azimuthal angle dependent intermolecular hard-shell PES, $V_s(R_s, \gamma_R, \chi_R) = E_s$, has been developed. The DCSs and ICSs calculated by QQT are compared with those obtained from QM exact calculations onto a full R-range ab initio PES. The rotationally inelastic scattering of NO(X) from He presents a paradigm for the rotationally inelastic scattering at a thermal collision energy of molecules residing in a Π electronic rotational eigenstate.

4.1 Introduction

The Ouasi Quantum Treatment (OOT) of the rotationally inelastic collision problem circumvents the elaborate step, required for OM exact numerical calculation of expanding the wave function into a summation of numerous spherical waves [1, 2, 54]. It uses a kind of Feynman path integral method that exploits the path length differences originating from the difference orientations of an anisotropic molecule, which provides valuable physical insight into the distinct interference structures reflecting different sensitivities to various specific isotopic terms in the interaction potential, while requiring very little computational effort [22, 24, 25, 27, 72, 88, 92]. The QQT method introduced by Gijsbertsen et al. [22], succeeded for the first time to demonstrate a physical mechanism for the remarkable sign alternation of the steric asymmetry (SA) of the rotationally state resolved inelastic integral collision cross sections (ICSs) between even and odd changes in the molecular rotational quantum number j. More recently, Zhang et al. [72] revealed a QQT-derived scaling relationship between DCSs calculated at two different collision energies. This scaling performs extremely well to the more general QM calculation. Even the rapid oscillatory structures in the forward-scatted region, where the attractive part of potential is known to be important, were correctly accounted for. This successful application of the QQT collision energy scaling formalism reinforces the evidence that the NO-He rotationally inelastic DCSs depend sensitively on repulsive part of PES. This repulsive part is the most difficult to predict accurately from the ab initio calculations [54]. Furthermore, we modified the QQT method for the spin orbit state conserving collisions to consider the softness of the repulsive part of the anisotropic atom-molecule PES [92], in which the contour of the PES is chosen such that the height of the potential energy barrier is just large enough to reflect the incoming kinetic energy. The MOOT DCSs exhibit much better agreement with the OM DCSs than those obtained using regular QQT, particularly in the forward scattered direction. By quantifying the effective shape of the hard shell PES during the course of the collision, the modified QQT provides additional insight into the repulsive regions of the PES that are most instrumental in determining the scattering dynamics.

The He + NO(X) rotational inelastic collision problem presents a paradigm for the rotational inelastic scattering of a rare gas atom from a NO(X) molecule residing in a particular rotational level of its π open electron eigenstate. The projection quantum number $\Lambda = \pm 1$ of the NO unpaired electronic orbital angular momentum *L*, and also the projection quantum number $\Sigma = \pm \frac{1}{2}$ of the electron spin *S* onto the internuclear axis commute both with the Hamiltonian of NO(X²Π) molecule, which leads to two distinctive spin-orbit states; the lowest-lying ${}^{2}\Pi_{1/2}$ state with $\overline{\Omega} = |\Lambda + \Sigma| = \frac{1}{2}$ and the ~123 cm⁻¹ higher energy residing ${}^{2}\Pi_{3/2}$ state with $\overline{\Omega} = \frac{3}{2}$.

The wave function of NO may be written as a product of an electronic orbital part $|n, \Lambda \rangle$, an electronic spin part $|S, \Sigma \rangle$ and a rotational part $|j,m,\Omega \rangle$ as $|n,\Lambda \rangle |S = \frac{1}{2}, \Sigma \rangle |j,m,\Omega \rangle$ [60]. The spatial inversion operator, i_{sp} commutes with the rotational Hamiltonian of NO(X) molecule as $[H_{ROT}, i_{sp}] = 0$. At each rotational level of $\overline{\Omega}$, j, one has the possibility to form a rotational eigenstate with even or odd parity. For reasons of compactness, $|j,m,\Omega \rangle$ is written to indicate the NO rotational wave function. In the limit of Hunds case (a), the rotational eigenstates of NO(X), which are also eigenstates of i_{sp} , may be written as:

$$\Psi_{j,m,\bar{\Omega},\varepsilon} \equiv \frac{1}{\sqrt{2}} [|j,m,\bar{\Omega}\rangle + \varepsilon |j,m,-\bar{\Omega}\rangle], \qquad (4.1)$$

where the spectroscopic parity index or symmetry index $\mathcal{E}=\pm 1$ express the relation between the geometrical properties of the unpaired electron and Λ - doublet levels which relates to the parity as [60]

$$p = (-1)^{j-\varepsilon/2}. \tag{4.2}$$

Note that a linear molecule as NO possesses only two rotational degrees of freedom. Its non-zero angular momentum projection quantum number Ω reflects the electronic part of its wave function.

However, the Hund's case (a) coupling scheme is only exact if j=0.5. As j increase, it starts to break down as L and S become uncoupled from the nuclear axis, and the rotational wave function of the $\Pi_{1/2}$ and $\Pi_{3/2}$ states will mix, and it becomes more accurate to write the rotational wave function for each spin-orbit manifold as [60]:

$$|F_{1}, j, m, \varepsilon \rangle = a_{j} | j, m, \overline{\Omega} = \frac{1}{2}, \varepsilon \rangle + b_{j} | j, m, \overline{\Omega} = \frac{3}{2}, \varepsilon \rangle,$$
(4.3)

$$|F_2, j, m, \varepsilon \rangle = a_j | j, m, \overline{\Omega} = \frac{3}{2}, \varepsilon \rangle - b_j | j, m, \overline{\Omega} = \frac{1}{2}, \varepsilon \rangle,$$
(4.4)

where the probability amplitude

$$b_{j} = \sqrt{\frac{1}{2} \left(1 - \frac{Y - 1}{\sqrt{4(j + \frac{1}{2})^{2} + Y^{2} - 4Y}} \right)} \quad \text{with} \quad Y = \frac{A_{0}}{B_{0}},$$
(4.5)

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$$a_{j} = \sqrt{1 - b_{j}^{2}} , \qquad (4.6)$$

quantifies the degree of mixing between the spin-orbit ground $\overline{\Omega} = \frac{1}{2}$ and exited $\overline{\Omega} = \frac{3}{2}$ states. In our case of the NO (X²Π) molecule, its rotational eigenstate energy levels follow from [60]:

$$E(F_i; j) = B_0 \cdot \left[(j - \frac{1}{2})(j + \frac{1}{2}) \pm \frac{1}{2} \sqrt{4(j + \frac{1}{2})^2 - 4Y + Y^2} \right], \tag{4.7}$$

with $Y=A_0/B_0$, and $A_0=123.13 \text{ cm}^{-1}$, and $B_0=1.6961 \text{ cm}^{-1}$ [59]. The \pm in Eq. (4.7) distinguishes between the upper spin-orbit manifold F_2 ('+', mostly ${}^2\Pi_{3/2}$) and the lower spin-orbit manifold F_1 ('-', mostly ${}^2\Pi_{1/2}$) as confirmed by Table 4.1.

In the present chapter a quasi-quantum treatment of rotational inelastic NO(X)-He scattering is applied both for spin-orbit state conserving and exciting transitions, especially the quantum state resolved DCSs and ICSs of spin-orbit state exciting rotationally inelastic collision are for the first time predicted in the limit of mixed Hund's case, in which Hund's case (a) and case (b) are mixed together. The chapter is laid out as follows, the essentials of the two angular variables depending intermolecular Born-Oppenheimer adiabatic PES are described in Section 4.2.1 There it will be shown that it is the equipotential curve that enables a numerical QQT calculation of the rotational quantum state resolved scattering amplitude. The QQT theory of the rotationally inelastic collision problem on spin orbit state conserving and changing transition is described in section 4.2.2 and 4.2.3 respectively. In section 4.3 the QQT predicted rotationally inelastic differential and integral cross sections are compared with those obtained from QM exact calculations. This is followed in Section 4.4 by the conclusions.

4.2 Quasi Quantum Treatment of the rotational inelastic collision problem

4.2.1 Hard shell anisotropic PES

To help better understanding of the inelastic scattering of the NO molecule, it is helpful to consider its ground state electronic structure, as well as the features of the He–NO(X) interaction potentials. Description of the interaction between NO and a rare gas atom is quite complicated, from the fact that the ground state of the NO radical is of ${}^{2}\Pi$ symmetry. In order to describe the He-NO system one must construct two angle-dependent intermolecular Born-Oppenheimer adiabatic potential energy surfaces. This is because the reflection operator with respect to the plane of the three nuclei commutes with the

j	a_j	b j	$E_j(\bar\Omega=\tfrac12)$	$E_j(\overline{\Omega}=\tfrac{3}{2})$
0.5	1	0	0	
1.5	0.9997	0.024513	5.016267	124.898133
2.5	0.999201	0.039969	13.3769	133.4984961
3.5	0.998507	0.054615	25.0822	145.5386037
4.5	0.997624	0.0689	40.13254	161.0180606
5.5	0.996555	0.082935	58.52843	179.9363671
6.5	0.995308	0.096755	80.27048	202.2929239
7.5	0.993891	0.110367	105.3594	228.0870392
8.5	0.992311	0.123767	133.7959	257.3179363
9.5	0.990579	0.136945	165.5808	289.984761
10.5	0.988702	0.149892	200.7152	326.0865907
11.5	0.986693	0.162597	239.2	365.6224425
12.5	0.984559	0.175052	281.0361	408.5912828
13.5	0.982313	0.187246	326.2248	454.992035
14.5	0.979964	0.199174	374.767	504.8235889
15.5	0.977523	0.210829	426.664	558.0848084
16.5	0.975	0.222206	481.9169	614.7745393
17.5	0.972404	0.233303	540.5268	674.8916167
18.5	0.969746	0.244117	602.4949	738.4348718
19.5	0.967034	0.254647	667.8225	805.4031374
20.5	0.964278	0.264894	736.5105	875.7952541
21.5	0.961484	0.274859	808.5603	949.6100747
22.5	0.958663	0.284545	883.9729	1026.846469
23.5	0.95582	0.293954	962.7495	1107.503326
24.5	0.952962	0.30309	1044.891	1191.57956
25.5	0.950096	0.311958	11 30. 399	1279.074109
26.5	0.947227	0.320563	1219.273	1369.98594

Table 4.1: The mixing coefficients a_j and b_j and the corresponding energy of the F₁ and F₂ rotational states of NO molecule [93].

electronic Hamiltonian of the He-NO system, with the consequence that the electronic eigenfunction of the system will be symmetric or antisymmetric with respect to reflection in this plane. This leads to the A'symmetry configuration of the Born-Oppenheimer PES, V(A'), in which the unpaired electron π -orbital of NO points in the plane of the three atoms, and the A" anti-symmetric PES, V(A''), in which the π -orbital of NO points perpendicular to the nuclear plane. At small intermolecular separations, R, the Pauli repulsion between the He atom and NO will be larger when the π -orbital lies in the plane of the three atoms, i.e. V(A') is more repulsive than V(A''). Alexander [54, 94] has shown that half the sum and half the difference of these two potentials are given by $V_{sum}(R,\gamma) = \frac{1}{2} [V(A'') + V(A')]$ and $V_{dif}(R,\gamma) = \frac{1}{2} [V(A'') - V(A')]$ respectively. The spin orbit state conserving transitions are governed by the sum potential and the spin orbit state changing transitions are governed by the difference potential. Moreover, the accuracy of the NO(X)-rare gas atom $V_{sum}(R, \gamma_R)$ and $V_{dif}(R, \gamma_R)$ PESs improved over the years [43, 44, 65, 85, 94-96], which enhanced the accuracy of the theoretically predicted NO(X)-rare gas atom DCSs [25, 26, 33]. The most recent high-quality ab initio PESs of NO(X)-He, as obtained by Kłos et al. [43, 57], are applied in the present paper.

Up till now we treated the rotational energy transfer as dominated by the more repulsive spin orbit state conserving interaction potential $V_{sum}(\gamma_R, R)$. Following Alexander [54, 94], to also include the difference potential, an effective potential which replaces the two discrete potentials by one effective potential which contains an extra angular variable, the azimuthal angle χ_R has been used:

$$V(R, \gamma_{R}, \chi_{R}) = V_{sum}(R, \gamma_{R}) - V_{dif}(R, \gamma_{R}) \cos(2\chi_{R})$$

= $\frac{1}{2} [V(A'') + V(A')] - \frac{1}{2} [V(A'') - V(A')] \cos(2\chi_{R})$, (4.8)

As shown in Fig. 4.1, $\chi_R = 0$ corresponds to the lobe in the three atoms of NO-He plane potential V(A') and $\chi_R = \pi/2$ corresponds to the lobe-out-of-plane potential V(A'').

The QQT method can be used to describe rotational inelastic collision between a molecule and a closed shell atom, when their interaction is approximated by one



Figure 4.1: A snapshot of an incoming He atom in collision with a NO molecule. The orientation of the molecular axis r_{NO} together with the orientation of the π -orbital lobe of the unpaired electron of the NO molecule determines the strength of the intermolecular potential at each fixed value of intermolecular separations. Note that the blue arrow (the direction of v_{rel}) typically does not reside in the plane of the three atoms [23].

anisotropic hard shell energy surface. In our case of NO(X)-He collision, previously only the PES contour of the V_{sum} potential equal to the collision energy $V_{sum}(R, \gamma_R) = E_s$ was taken into account. This contour can be described well the spin-orbit conserving transitions, where the electronic part carries a cylindrical symmetric electron density probability around the molecular axis, which makes χ_R redundant. But for a spin-orbit changing transition, the pure Hund's case (a) scheme breaks down. In the present paper, we will extend QQT to also include the V_{dif} potential. This is accomplished by introducing a potential energy surface that not only depends on the polar angel γ_R but also on the azimuthal angle χ_R . For the first time QQT is applied to predict the quantum state resolved DCSs and ICSs of spin-orbit state exciting rotationally inelastic collision between a He atom and the NO(X) molecule. The hard shell contour of PES $R_s(\gamma_R, \chi_R)$ is given by the function:

$$V(R,\gamma_R,\chi_R) = E_S, \qquad (4.9)$$

in which E_s is set equal to 508 cm⁻¹ collision energy considered in this study. The schematic representation of the hard shell is depicted in Fig. 4.2, shows that the shell is not cylindrical anymore.

For $\chi_R = 0$ and for $\chi_R = \pi/2$, as shown in Fig. 4.3, the hard shells correspond to respectively the potentials $R_{A'}(\gamma_R)$ and $R_{A''}(\gamma_R)$. As can be seen from the figure, the $R_{A'}(\gamma_R)$ potential is not purely convex. In our previous paper [72] we explicitly assumed that the hard shell was convex. This requirement is not as strict as it seemed, this will be shown later.

The vectors and angles relevant for the hard shell collision problem are depicted in Fig. 4.4. Most of those vectors have been described in previous work [22, 24, 25, 27, 72, 88, 92], only those relevant to the current study are summarized here. In the case of a hard shell, momentum transfer is restricted to the direction perpendicular to the area of the surface, only the component of \mathbf{k} parallel to the normal $\hat{\mathbf{n}}$ plays a role in the transfer of the translational energy into rotational energy. In QQT one addresses the rotationally inelastic collision problem in the so-called kinematic apse frame, in which the quantization axis points along the kinematic apse vector $\vec{a} = \vec{k'} - \vec{k}$. For a hard shell, the apse points along the normal $\hat{\mathbf{n}}$ of the surface. Here the \mathbf{k} and $\mathbf{k'}$ denote the relative wave-vectors before and after the collision respectively. They define a scattering plane. The apse lies in the scattering plane where it makes an angle β with \mathbf{k} . The apse determines the apse frame $\{X_a, Y_a, Z_a\}$ with $\mathbf{Z}_a \equiv \hat{\mathbf{a}}$ and $\mathbf{Y}_a \equiv \vec{k} \times \vec{k'}$.

The molecular frame $\{X_r, Y_r, Z_r\}$ is determined by the molecular axis, $Z_r = \hat{r}_{NO}$, and by the orientation of the π -electron lobe, X_r , which is assumed to points in the direction of this electron lobe. *R* is the displacement vector pointing from the centre of mass of the hard shell to the point of contact. The apse *a* and *R* make the polar angles γ_a and γ_R with respect to the molecular axis \hat{r}_{NO} and their azimuthal angle with respect to this axis are χ_a and χ_R respectively. For the effect of the collision on the hard shell it is irrelevant whether (in the body fixed frame) the scattering plane is rotated around the apse *a* as long as the apse remains the same. Therefore the azimuthal angle ϕ_a of molecular axis \hat{r}_{NO} with respect to the apse is irrelevant and the projection of the angular momentum along the apse is conserved.



Figure 4.2: Three-dimensional schematic representation of the He-NO(X), noncylinder symmetric hard shell PES which depends both on γ_R and χ_R .



Figure 4.3: The anisotropic hard shell He-NO(X) PES given by $V(R_S, \gamma_R, \chi_R) = 508 \text{ cm}^{-1}$ at $\chi_R = 0$ and $\chi_R = \pi/2$, which corresponding to $R_{A'}(\gamma_R)$ and $R_{A''}(\gamma_R)$, is plotted in solid red and blue dashed line respectively. The $R_{A'}(\gamma_R)$ shell is totally convex but $R_{A''}(\gamma_R)$ is concave at γ_R is nearly $\pi/2$. The black dash lines denote one De Broglie wave length apart from the minimum hard shell radius at $E_{col}=508 \text{ cm}^{-1}$ with $\lambda_D=1.152 a_0$.



Figure 4.4: Depicts the spatial $R_s(\gamma_R, \chi_R)$ and portrait an impact position vector (the point of contact) on the shell as well as its apse vector and the spherical angles γ_a, χ_a . In the case of an arbitrary hard shell, the apse *a* is no longer in the molecular frame determined by \hat{r}_{NQ} and *R*.

Note that in the case of pure Hund's case (a), the QQT spin orbit state conserving transitions depends onto the PES of V_{sum} and not onto the PES of V_{dif} , hence the hard shell does not contain the term that relates to the potential variable χ_a . The cylindrical symmetry of the hard shell implies that \hat{r}_{NO} , R and a must all reside in the same plane. However, in the case of a spin orbit state changing transition, the hard shell is not cylindrical symmetric. As shown in Fig. 4.4, the vectors \hat{r}_{NO} , R, and a are in general not in one plane. Only when $\chi_a = 0$ or π , the vector \hat{r}_{NO} is parallel to the scattering plane (the plane containing k, k', and a).

The molecular frame and the apse frame do not share the same origin. The apse frame has its origin in the point of contact and the molecular frame in the center of mass of the molecule. When comparing orientations, we will implicitly transport the apse frame along the vector \mathbf{R} to the origin of the molecular frame.

If we need to emphasize this explicitly we will refer to this translated apse frame as the apse prime frame $\{X'_a, Y'_a, Z'_a\}$.

The molecular frame $\{X_r, Y_r, Z_r\}$ follows from the apse prime frame $\{X'_a, Y'_a, Z'_a\}$ through a rotation over the Euler angles $(\phi_a, \gamma_a, \chi_a)$. As shown in R. N. Zare's "Angular momentum" monograph [60], the molecular frame can be made to coincide with the apse prime frame by three successive rotations: 1) A counterclockwise rotation χ_a about Z_r , this carries Y_r axis into the line of nodes. 2) A counterclockwise rotation γ_a about the line of nodes. This carries the Z_r axis into the Z'_a axis, where the nodes represent the crossing line between the two planes composing of X and Y axis. 3) A counterclockwise rotation of ϕ_a about $Z'_a(Z_r)$. This carries the Y_r axis into Y'_a axis. In Fig. 4.4 we choose $\phi_a = 0$, that means the line of nodes is taken to coincide with Y'_a , in which case the molecular axis \hat{r}_{NO} is parallel to the scattering plane.

In the case of spin-orbit conserving transitions, the hard shell of NO(X)-He carries a convex shape everywhere. There is a unique relation between the direction of the apse \hat{a} in a point on the hard shell and the direction of the position vector \boldsymbol{R} pointing to that point. Specifying the orientation of the molecular frame with respect to the apse frame then implies specifying the point of contact on the hard shell. However, this case is not globally true for the spin orbit state changing transitions, where the hard shell is not purely convex, as described in Figs. 4.2 and 4.3, on the waist of the potential contour near $90^{\circ} \le \gamma_a \le 100^{\circ}$, the hard shell is particular R_s a unique value of γ_a and a certain orientation can then be applicable to more than one point. One has to combine the contributions from the separate patches. This is however not a problem since the contributions from all points associated with a certain orientation have to be added together. Details have been described in our previous study [92].

4.2.2 QQT calculation in spin orbit state conserving transitions

The QQT theory in spin orbit state conserving transitions has been described in previous study [22, 24, 25, 27, 72, 88, 92], only the essentials necessary about the methodology are given. As depicted in section 4.2.1, the spin orbit state conserving transitions are ruled by the potential V_{sum} , in which the QQT hard shell contour is

cylindrical symmetry. In QQT one address the rotationally inelastic collision problem in the so-called kinematic apse frame, in which the quantization axis points along the kinematic apse vector a.

$$\boldsymbol{a} \equiv \frac{\mu}{\hbar} (\boldsymbol{v}_{rel}' - \boldsymbol{v}_{rel}) = \boldsymbol{k}' - \boldsymbol{k} . \tag{4.10}$$

The magnitude of the outgoing wave vector is determined by the amount of collision energy transferred into rotational excitation of the NO(X) molecule $\Delta E_{j' \leftarrow j}^{ROT} \equiv E_{ROT}(j') - E_{ROT}(j)$, which leads to

$$k' = k \sqrt{1 - \Delta E_{j' \leftarrow j}^{ROT} / E_{col}} .$$

$$(4.11)$$

In contrast to the exact coupled channel QM solution of the collision problem, QQT provides a transition moment type expression for the scattering amplitude in which the spherical scattering angles θ and ϕ are replaced by the spherical angles of the kinematic apse β and α .

For a transition from a specific initial state $|i\rangle$ to a specific final state $\langle f|$, the apse frame scattering amplitude $g(\beta)$ in spin orbit state conserving transition follows from:

$$g_{i \to f}^{soco}(\beta) = C(\beta) < j', m_{a}, \Omega' = \frac{1}{2}, \varepsilon' | g_{geom}(\gamma_{a}; \beta)$$

$$\times \exp[i\eta_{j', f \leftarrow j, i}(\gamma_{a}; \beta)] | j = \frac{1}{2}, m, \overline{\Omega} = \frac{1}{2}, \varepsilon >$$

$$= C(\beta) \frac{\sqrt{2j'+1}}{2} \int_{-1}^{1} d\cos \gamma_{a} P_{j'}(\cos \gamma_{a})$$

$$\times g_{geom}(\gamma_{a}; \beta) \exp[i\eta_{j' \leftarrow j}(\gamma_{a}; \beta)] \qquad (4.12)$$

where $C(\beta)$ is a normalization constant to ensure the conservation of flux at each value of β , such that the QQT scattering amplitude is normalized with respect to the incoming flux. Within the QQT formalism, this coupling is expressed in terms of the phase shift, η , associated with each of the scattering paths considered within the integral over the angle β . The phase shifts are calculated via the expression

$$\eta_{f \leftarrow i}(\gamma_a;\beta) = -\boldsymbol{a}(\beta) \cdot \boldsymbol{R}_{S}(\gamma_a) = -[k_{\perp} + k_{\perp}']R_{S}(\gamma_R)\cos(\gamma_R - \gamma_a). \quad (4.13)$$

This phase shift is defined as the difference in phase between a path hitting the hard shell and an imaginary path which passes through the origin of the collision frame.

Each of these paths is weighted by the so-called molecule fixed geometric

dimensionless scattering amplitude $g_{geom}(\gamma_a;\beta)$, which allows for the relative contributions made to the scattering amplitude for different orientation angles:

$$g_{geom}(\gamma_a;\beta) \equiv k \sqrt{\frac{d\sigma^{geom}(\gamma_a;\beta)}{d\omega_a}} = k \sqrt{|\cos\beta| \rho_1(\gamma_a)\rho_2(\gamma_a)}, \qquad (4.14)$$

in which $\rho_1(\gamma_a)$ and $\rho_2(\gamma_a)$ denote the local radii of curvature of the cylindrically symmetric convex surface [24].

Finally, the QQT state-to-state differential cross section (DCS) in the apse frame is given by:

$$\frac{\mathrm{d}\sigma_{f\leftarrow i}}{\mathrm{d}\omega_a}(\beta,\alpha) = \frac{1}{k^2} \left| g_{i\to f}(\beta) \right|^2.$$
(4.15)

The standard QM approach specifies the differential cross-section in terms of the collision frame spherical angles (θ, ϕ) , while the QQT provides the DCSs in terms of the angles (β, α) , defined with respect to the kinematic apse. These spherical angles may be chosen such that $\alpha \equiv \phi$. Hence, the apse frame and collision frame DCSs are related to one other according to

$$\frac{\mathrm{d}\sigma_{f\leftarrow i}}{\mathrm{d}\omega}(\theta,\phi) = \frac{\mathrm{d}\sigma_{f\leftarrow i}}{\mathrm{d}\omega_a}(\beta,\alpha) \left| \frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta} \right|. \tag{4.16}$$

4.2.3 Extension QQT to the spin orbit state changing transitions

Now that, the basic framework of the rotational inelastic collision problem have been described. It becomes possible to extend the inelastic scattering amplitude into the spin orbit state exiting transitions, which requires a polar angle γ_R and azimuthal angle χ_R dependent intermolecular hard-shell PES, $V(R, \gamma_R, \chi_R) = E_S$, has been developed.

The scattering amplitude for a single, fixed orientation of the molecular frame is given by $g_{i\to f}(\gamma_a, \chi_a; \beta)$. It has a phase part $e^{i\eta_{i\to f}(\gamma_a, \chi_a; \beta)}$, which provides the interference between the paths from different orientations of the molecular frame, where each of these paths is weighted by a so called geometrical scattering amplitude $g_{geom}(\gamma_a, \chi_a; \beta)$. Hence the molecule fixed scattering amplitude can be written as:

$$g_{i \to f}(\gamma_a, \chi_a; \beta) \equiv C(\beta) g_{geom}(\gamma_a, \chi_a; \beta) \exp[i\eta_{i \to f}(\gamma_a, \chi_a; \beta)].$$
(4.17)

The phase shift of a spin orbit state changing transition generated at a particular point of impact onto the shell which denoted the spherical angles γ_a, χ_a follows from:

$$\eta_{i \to f}(\gamma_a, \chi_a; \beta) = -\vec{a} \cdot \vec{R}_S(\gamma_R, \chi_R) = -(k_\perp + k'_\perp)\hat{a} \cdot \hat{R}_S(\gamma_R, \chi_R)R_S(\gamma_R, \chi_R)$$
(4.18)

or

$$\eta_{i \to f}(\gamma_a, \chi_a; \beta) = \eta_{i \to f}^{sum}(\gamma_a; \beta) - \eta_{i \to f}^{dif}(\gamma_a, \chi_a; \beta), \qquad (4.19)$$

in which

$$\eta_{i \to f}^{sum}(\gamma_a;\beta) \equiv -(k_\perp + k'_\perp)\hat{a} \cdot \hat{R}_s(\gamma_R) R_{sum}(\gamma_R) , \qquad (4.20)$$

and

$$\eta_{i \to f}^{dif}(\gamma_a, \chi_a; \beta) \equiv -(k_{\perp} + k_{\perp}')\hat{a} \cdot \hat{R}_s(\gamma_R, \chi_R) R_{dif}(\gamma_R) \cos(2\chi_R)$$
(4.21)

where R_s denotes the distance from the centre of mass of the molecule to the spatial position of the rare gas atom at the impact position on the shell which given by the spherical angles of γ_R and χ_R , and as expected from our earlier remarks, the phase shift is independent of ϕ_a .

Next, we rewrite the Eq. (4.17) by

$$g_{i \to f}(\gamma_{a}, \chi_{a}; \beta) = C(\beta)g_{geom}(\gamma_{a}, \chi_{a}; \beta)$$

$$\times \exp[i\eta_{i \to f}^{sum}(\gamma_{a}; \beta)]\exp[-i\eta_{i \to f}^{dif}(\gamma_{a}, \chi_{a}; \beta)]$$

$$= C(\beta) \cdot g_{geom}^{sum}(\gamma_{a}; \beta)\exp[i\eta_{i \to f}^{sum}(\gamma_{a}; \beta)] \qquad (4.22)$$

$$\times \frac{g_{geom}(\gamma_{a}, \chi_{a}; \beta)}{g_{geom}^{sum}(\gamma_{a}; \beta)} \cdot \exp[-i\eta_{i \to f}^{dif}(\gamma_{a}, \chi_{a}; \beta)]$$

Note that the factor $g_{geom}^{sum}(\gamma_a;\beta) \exp[i\eta_{i\to f}^{sum}(\gamma_a;\beta)]$ corresponds to the fixed molecule scattering amplitude $g_{i\to f}^{sum}(\gamma_a;\beta)$, which in the case of a spin orbit state conserving collision follows from the geometric scattering amplitude $g_{geom}^{sum}(\gamma_a;\beta)$ of the cylindrically symmetric hard shell $R_{sum}(\gamma_R)$, it only depends on γ_a , while

the added factor $\frac{g_{geom}(\gamma_a, \chi_a; \beta)}{g_{i-m}^{sum}(\gamma_a; \beta)} \exp[-i\eta_{i \to f}^{dif}(\gamma_a, \chi_a; \beta)]$ leads to the spin-orbital

changing transition which depends both on γ_a and χ_a .

Then the fixed molecule scattering amplitude denotes as:

$$g_{i \to f}(\gamma_a, \chi_a; \beta) = C(\beta) g_{i \to f}^{sum}(\gamma_a; \beta) G_{i \to f}^{sobr}(\gamma_a, \chi_a; \beta), \qquad (4.23)$$

where

$$G_{i \to f}^{sobr}(\gamma_a, \chi_a; \beta) = [g_{geom}(\gamma_a, \chi_a; \beta) / g_{geom}^{sum}(\gamma_a; \beta)] \exp[-i\eta_{i \to f}^{dif}(\gamma_a, \chi_a; \beta)], \quad (4.24)$$

In the apse frame, geometric scattering amplitude $g_{geom}(\gamma_a, \chi_a; \beta)$, equals to $|g_{i\to f}(\gamma_a, \chi_a; \beta)|$, is independent of the initial and of the final rotational state, when squared, should be equal to the "geometrical" differential cross section for a fixed molecule:

$$g_{geom}(\gamma_a, \chi_a; \beta) = k \sqrt{\frac{d\sigma^{geom}}{d\omega_a}}(\gamma_a, \chi_a; \beta) = k \sqrt{|\cos\beta\rho_1(\gamma_a, \chi_a)\rho_2(\gamma_a, \chi_a)|}, \quad (4.25)$$

The geometrical differential cross-section was expressed in the local radii of curvature ρ_1 and ρ_2 , because of the more general shape of the current hard shell, we now express the molecule fixed geometrical cross-section in terms of the Gaussian curvature $K \equiv 1/\rho_1 \rho_2$ [97]:

$$\rho_1 \rho_2 = K_G^{-1} = \frac{LN - M^2}{EG - F^2}, \qquad (4.26)$$

where

 $E \equiv \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \gamma_{R}} \cdot \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \gamma_{R}} \qquad , \qquad F \equiv \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \gamma_{R}} \cdot \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \chi_{R}}$ $G \equiv \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \chi_{R}} \cdot \frac{\partial \vec{R}_{S}(\gamma_{R},\chi_{R})}{\partial \chi_{R}} \quad , \qquad L \equiv \hat{n}_{S} \cdot \frac{\partial^{2} \vec{R}_{S}(u,v)}{\partial^{2} u} \quad , \qquad M \equiv \hat{n}_{S} \cdot \frac{\partial^{2} \vec{R}_{S}(u,v)}{\partial u \cdot \partial v}$ and $N = \hat{n}_{S} \cdot \frac{\partial^{2} \bar{R}_{S}(u,v)}{\partial^{2}v}, \ \hat{n}_{S}(\gamma_{R}, \chi_{R})$ represents the normal to surface at $\vec{R}_{S}(\gamma_{R}, \chi_{R})$

which follows from $\hat{n}_{S}(\gamma_{R},\chi_{R}) = \frac{\frac{dR_{S}(\gamma_{R},\chi_{R})}{d\gamma_{R}} \times \frac{dR_{S}(\gamma_{R},\chi_{R})}{d\chi_{R}}}{\left|\frac{dR_{S}(\gamma_{R},\chi_{R})}{d\gamma_{\nu}} \times \frac{dR_{S}(\gamma_{R},\chi_{R})}{d\gamma_{\nu}}\right|}.$

Since the incoming quantum state $|j = \frac{1}{2}, m_a >$ provides an isotropic distribution around the molecular axis, the geometrical differential cross section for a hard shell is then obtained by integrating Eq. (4.25) over all possible orientations of the molecular frame, taking into account the weight for each orientation,

$$\frac{d\sigma^{geom}}{d\omega_a}(\beta) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \frac{d\sigma^{geom}}{d\omega_a}(\gamma_a, \chi_a; \beta) \sin\gamma_a d\gamma_a d\chi_a.$$
(4.27)

To result the spin-orbital changing scattering amplitude $g_{i\to f}^{sobr}(\beta)$ in the apse frame, one has to integrate the molecule fixed scattering amplitude $g_{i\to f}(\gamma_a, \chi_a; \beta)$ over all the possible orientations of the molecular frame (angles γ_a, χ_a and ϕ_a), while taking into account the probability amplitudes for those orientations in both the initial and in the final rotational wave function:

$$g_{i \to f}^{sobr}(\beta) = C(\beta) < j', m_a, \Omega' = \frac{3}{2}, \varepsilon' | g_{i \to f}(\gamma_a, \chi_a; \beta) | j = \frac{1}{2}, m, \Omega = \frac{1}{2}, \varepsilon >$$

$$= C(\beta) < j', m_a, \overline{\Omega}' = \frac{3}{2}, \varepsilon' | g_{i \to f}^{sum}(\gamma_a; \beta)$$

$$\times G_{i \to f}^{sobr}(\gamma_a, \chi_a; \beta) | j = \frac{1}{2}, m, \overline{\Omega} = \frac{1}{2}, \varepsilon >$$
(4.28)

The coupling wave function for the spin orbit state conserving transition has been derived before [24, 72] and the same way is followed to get the coupling wave function for the spin orbit state changing transitions by the addition of another integration angle χ_a [97]. The scattering amplitude $g_{i\rightarrow f}^{sobr}(\beta)$ follows from [97]:

In the case of $\varepsilon \varepsilon' = 1$:

$$g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\bar{\Omega}'=\frac{3}{2},\varepsilon'=\varepsilon}^{sobr}(\beta) = \varepsilon \frac{\sqrt{j'-\frac{3}{2}}}{4\pi} \int_{-1}^{1} d\cos\gamma_{a} d_{0,2}^{n=j-\frac{1}{2}}(\gamma_{a}) g_{i\to f}^{sum}(\gamma_{a};\beta) \\ \times \int_{0}^{2\pi} d\chi_{a} G_{i\to f}^{sobr}(\gamma_{a},\chi_{a};\beta) \cos 2\chi_{a}$$

$$(4.29)$$

and in the case of $\varepsilon \varepsilon' = -1$:

$$g_{j=\frac{1}{2},m_{a},\varepsilon\rightarrow j',m_{a},\overline{\Omega}'=\frac{3}{2},\varepsilon'=-\varepsilon}^{sobr}(\beta) = -\varepsilon \frac{m_{a}}{m_{a}} \frac{\sqrt{j'+\frac{5}{2}}}{4\pi} \int_{-1}^{1} d\cos\gamma_{a} d_{0,2}^{n=j+\frac{1}{2}}(\gamma_{a}) g_{i\rightarrow f}^{sum}(\gamma_{a};\beta)$$

$$\times \int_{0}^{2\pi} d\chi_{a} G_{i\rightarrow f}^{sobr}(\gamma_{a},\chi_{a};\beta) \cos 2\chi_{a} \qquad (4.30)$$

in which the $d_{0,2}^{n}(\gamma_{a})$ is a reduced Wigner rotation matrix element.

Comparing with the scattering amplitude for the spin orbit state conserving transitions, one notice that the Legendre polynomials $P_n(\cos \gamma_a)$ in Eq. (4.12)

are replaced by the associated Legendre polynomials $d_{0,2}^n(\gamma_a) \propto P_n^2(\gamma_a)$ times $\cos(2\chi_a)$ in Eqs. (4.29) and (4.30). Moreover, the initial coefficients and symmetry index are different. The scattering amplitude for the spin orbit state changing transitions is composed by scattering amplitude of the spin orbit state conserving transitions governed by the R_{sum} potential, which is only depends on γ_a and multiply by another factor.

As we discussed in section 4.1, in previous studies QQT presumed pure Hund's case (a) rotational eigenstate wave functions which holds only for a NO(X) molecule that resides on the j=0.5 rotational ground state and remains close to an exact approximation at $\overline{\Omega} = \frac{1}{2}$ when $j' \leq 7.5$. At larger j', the $\overline{\Omega} = \frac{1}{2}$ and $\overline{\Omega} = \frac{3}{2}$ spin orbit manifold of the NO(X) rotational wave functions mix significantly. This mixing process leads to rotational eigenstate wave functions that either belong to the lower F_1 or to the upper F_2 spin-orbit manifold.

Then in the mixed Hund's case, the QQT scattering amplitude of the rotationally inelastic transition from NO(X) $j = \frac{1}{2}$, ε state to the F₁ spin orbit manifold should become:

$$g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},F_{1},\varepsilon'}(\beta) = a_{j}g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\bar{\Omega}'=\frac{1}{2},\varepsilon'}(\beta) + b_{j}g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\bar{\Omega}'=\frac{3}{2},\varepsilon'}(\beta)$$

$$(4.31)$$

And the QQT scattering amplitude of the rotationally inelastic transition from NO(X) $j = \frac{1}{2}, \varepsilon$ state to the F₂ spin orbit manifold is given by:

$$g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},F_{2},\varepsilon'}(\beta) = a_{j}g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\overline{\Omega}'=\frac{3}{2},\varepsilon'}^{sobr}(\beta)$$

$$-b_{j}g_{j=\frac{1}{2},m_{a},\varepsilon \to j',m_{a},\overline{\Omega}'=\frac{1}{2},\varepsilon'}^{soco}(\beta)$$
(4.32)

4.3 Results and Discussion

4.3.1 Differential cross section

The differential cross sections are calculated by using the QQT method in both the pure and mixed Hund's case coupling scheme at a collision energy of 508cm^{-1} for the rotational inelastic scattering of NO(X) from He. These results are compared with those obtained from a QM exact calculation respectively for spin-orbit state conserving and changing collisions as displayed in Figs. 4.5 and 4.6.

The QQT spin-orbit state conserving and spin-orbit state excited DCSs are in

reasonable agreement with the OM data, reproducing well the relative maxima and minima present in DCSs. Since OOT does not include the diffractive contributions to its rotational inelastic scattering amplitude, its rotational inelastic DCSs for $n = j' - \varepsilon \varepsilon'/2 \le 6$ lack the near forwards $\theta \le 36^{\circ}$ intensity. All DCSs display a marked dependence on the final rotational state. The agreement between the OM and OOT DCSs is poorest at low scattering angles for low values of i'. And for most of the outgoing states, the resulting QQT phase shift for both the spin-orbit state conserving and changing transitions shift the position of the interference structures to somewhat larger scattering angles compared with those predicted using QM exact calculations. This is to be expected, as the forward scattering angles are classically forbidden in the hard shell model and the OOT model unable to take diffraction effects into consideration. Most importantly, the attractive part of the potential plays a more important role at glancing, low energy transfer collisions, where the hard shell approximation is no longer valid. At larger scattering angles, or for higher values of final rotational state, the agreement between the OOT model calculations and exact QM theory is substantially improved, suggesting that the approximation of the PES by a hard shell becomes reasonable.

The QQT results more backward scattering for spin orbit state changing transitions than that for spin orbit state conserving transitions. This is attributed to the weakly attractive nature of the spin-orbit state conserving potential, V_{sum} , coupled with the steep repulsive wall at short atom-molecule distances. In contrast, the difference potential, V_{dif} , which is responsible for spin–orbit state changing collisions, has considerably more attractive character and hence more softer, so it is reasonable to assume that attractive interactions play a more important role in the spin orbit state changing DCSs than in the spin orbit state conserving case. Hence, one expects the spin orbit state changing collisions would be not so well described by hard shell model.

The so called "parity pairs" for each outgoing rotational state with identical $n = j' - \varepsilon \varepsilon' / 2$ are grouped in Figs. 4.5 and 4.6. As shown by Gijsbertsen *et al.* [22], the 'parity pairs' in adjacent *j*' final states exhibit a similar dynamical behavior. Except for a different pre-factor, they are expected to yield similarly shaped DCSs. In the limit of pure Hund's case (a), this behavior is consistent with the outcome of QQT calculation both for spin orbit state conserving and changing transitions.



Figure 4.5: Comparision of the spin orbit state conserving DCSs for $NO(X^2\Pi_{1/2}, v = 0, j = 0.5) + He$ from QM calculations (black), QQT calculations in pure Hund's case (a) (green) and QQT calculations in mixed Hund's case (red) at collision energy of 508 cm⁻¹. The solid lines correspond to parity conserving, dashed lines correspond to parity changing transitions.



Figure 4.6: The same as for figure 4.5 but for spin-orbit changing transitions.

However, in the case of mixed Hund's case, the OOT results show distinct differences between parity paired DCSs especially in spin-orbit state changing transitions. Since the anisotropy of a spin-orbit state conserving $V_{sum}(R, \gamma_R)$ PES of NO(X)-He is about an order of magnitude larger than that of spin-orbit state changing $V_{dif}(R, \gamma_R)$ PES. The magnitude of a spin orbit manifold conserving rotationally inelastic scattering amplitude $g_{j=\frac{1}{2},m_a,\varepsilon \to j',m_a,\overline{\Omega}'=\frac{1}{2},\varepsilon'}^{soco}$ is also much larger than that of a spin-orbit state changing scattering amplitude $g_{j=\frac{1}{2},m_a,\bar{c}\to j',m_a,\bar{\Omega}'=\frac{3}{2},c'}^{sobr}$. On the other hand, in our case of j' < 13 and gives from table 4.1, $a_i > 0.98$ and $b_i < 0.18$, b_j is relatively small with respect to a_j . Then according to Eq. (4.32), the magnitude of $a_j g_{j=\frac{1}{2},m_a,\varepsilon \to j',m_a,\bar{\Omega}'=\frac{3}{2},\varepsilon'}^{sobr}(\beta)$ and of $b_j g_{j=\frac{1}{2},m_a,\varepsilon \to j',m_a,\bar{\Omega}'=\frac{1}{2},\varepsilon'}^{soco}(\beta)$ can become comparable. The interference between the two terms separates the parity pairs. In the case of spin orbit state conserving transitions as follows from Eq. (4.31), the magnitude of $a_j g_{j=\frac{1}{2},m_a,c \to j',m_a,\bar{\Omega}'=\frac{1}{2},c'}$ is much larger than that of $b_j g_{j=\frac{1}{2},m_a,\varepsilon \to j',m_a,\bar{\Omega}'=\frac{3}{2},\varepsilon'}^{sobr}(\beta)$. Hence, the latter term renders minor influence on the final results. This explains the similar behavior of parity pairs for spin-orbit state conserving transition in the case of mixed Hund's case. Consequently, the DCS of a rotationally inelastic transition from the $j = \frac{1}{2}, \varepsilon$ initial rotational state to a final F_2, j', ε rotational state is more sensitive for its mixed Hund's case character than that to a final F_1, j', ε' rotational state.

4.3.2 Integral cross sections

Figures 4.7 and 4.8 compare the parity pair $n = j' - \varepsilon \varepsilon'/2$ dependency of the ICSs resulting from the QM and QQT calculations at a collision energy of 508cm⁻¹ for spin-orbit conserving and changing transitions. The amplitude of the oscillations at small n, implies a propensity for parity conservation. The QQT resulting ICSs are found to agree reasonable well to those from QM calculations both for spin-orbit conserving and changing transitions. At low n, the ICSs for spin-orbit state changing transitions are much smaller than those for their spin-orbit state conserving counterparts. Moreover, the QQT resulting ICSs are much smaller than those predicted by the QM calculations., which reflect the differences between the V_{sum} and V_{dif} PESs. The difference potential V_{dif} is generally weaker and softer than the average potential V_{sum} . It is therefore not surprising that the QQT method which is

based on the hard shell approximation is unable to result a large enough cross section for spin-orbit changing collisions.



Figure 4.7: Comparison between QM (Black) and QQT in pure Hund's case (a) (green) and QQT in mixed Hund's case (red) ICSs for NO(X)-He collisions at $Etr = 508cm^{-1}$ at the particular parity pair number n for spin-orbit conserving transitions.



Figure 4.8: The same as for figure 4.7 but for spin-orbit changing transitions.

4.4 Conclusions

The QQT is extended rotational inelastic scattering problem from spin-orbit state conserving transitions in pure Hund's case (a) to spin orbit state changing and conserving transitions in mixed Hund's case. The introduction of the azimuthal angle χ results a three-dimensional $V(R, \gamma, \chi)$ PES. Taking the NO(X) + He collision system as a paradigm, state-to-state differential cross sections of spin orbit state conserving and changing rotational transitions as obtained by QQT and QM numerical calculations have been discussed in detail. The qualitative success of the QQT model suggests that the outcome of rotational inelastic collision is mainly determined by the repulsive part of the potential except for the most forward diffractive scattering angles (classically forbidden in the hard shell model). The extension of the QQT model which includes the contributions from the spin-orbit changing potential, V_{dif} , provides a valuable insight into the underlying mechanism of the rotational inelastic scattering process, and as such provides a focus for future work.

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Close-coupling calculations of Para-Ortho H₂ conversion rates by H₂-O₂ collisions

State-to-state inelastic collision cross sections are calculated with the quantummechanical close-coupling method for the conversion of para-H₂ into ortho-H₂ induced by collisions with O₂. Two hyperfine coupling mechanisms in asymmetric O₂-H₂ collision complexes cause para-ortho H₂ conversion: i) a different Fermi contact interaction for the two H nuclei from different spin densities at these nuclei, and ii) a different magnetic dipole-dipole coupling between the electron spin of O₂ and the spins of the two H nuclei. The Fermi contact interaction is evaluated numerically by *ab initio* electronic structure calculations for a large number of geometries of the O₂-H₂ complex, the magnetic dipole-dipole coupling can be simply calculated for any geometry. Theoretical para-ortho conversion rate coefficients for different temperatures are obtained from the state-to-state cross sections calculated at collision energies ranging from 2 to 2000 cm⁻¹; they are compared with experimental data measured at room temperature in O₂-H₂ gas mixtures.

5.1 Introduction

Hydrogen, H₂, exists in two different forms: para-H₂ and ortho-H₂. Since under most circumstances the conversion between these species is extremely slow, they can be considered as different molecules. Para-H₂ has nuclear spin I = 0, which corresponds to a nuclear spin wave function that is antisymmetric under permutation of the nuclear coordinates, and ortho-H₂ has spin I = 1, which corresponds to a symmetric nuclear spin wave function. Since protons are spin $I = \frac{1}{2}$ fermions and the total H₂ wave function has to be antisymmetric under permutation of the nuclear coordinates, para-H₂ has only even values of the rotational angular momentum *j*, while ortho-H₂ has only odd values of *j*. The *j* = 0 ground state of para-H₂ is lower in energy by about 120 cm⁻¹ than the *j* = 1 ground state of ortho-H₂. Still, so-called normal hydrogen, n-H₂, consists of 75% of ortho-H₂ and 25% of para-H₂ is extremely slow. This ratio of 3:1 corresponds to the nuclear spin multiplicities of 3 and 1 for the I = 1 and I = 0 wave functions, respectively.

Pure para-H₂ can be produced at liquid hydrogen temperature (20 K) by leading normal H₂ over an iron-containing catalyst, which accelerates the conversion of ortho-H₂ into the more stable para-H₂. Without the catalyst the conversion is very slow and the pure para-H₂ which is thus produced, can be kept in specially coated gas cylinders for weeks, even at room temperature. An important application is the para-hydrogen induced polarization (PHIP) of nuclear spins in molecular systems [98], which provides enhancements of NMR signals for various nuclei in magnetic fields of modern NMR spectrometers by up to 4-5 orders of magnitude. One of the major driving forces for the development of the field of hyperpolarization in magnetic resonance is its potential application in human MRI research and possibly in medical diagnostics [98-100].

Also paramagnetic species such as O_2 can act as a catalyst to accelerate paraortho or ortho-para hydrogen conversion. O_2 is one of the rare small molecules with a non-zero spin ground state. Because of the two unpaired electrons in their antibonding π^* orbitals, O_2 molecules have a ${}^3\Sigma_g^-$ triplet electron spin ground state and thus are paramagnetic. In 1933, Farkas and Sachsse [101] first reported that in the presence of molecular oxygen para-hydrogen is converted into normal hydrogen at room temperature with a considerable rate.

Two mechanisms contribute to the O_2 catalyzed para-ortho hydrogen conversion: magnetic dipole-dipole coupling and Fermi contact interactions. The magnetic 96 dipole-dipole coupling mechanism was proposed in 1933 by Wigner [102]. Actually, he stated that an inhomogeneous magnetic field is created by the magnetic moment of an O_2 molecule, and the spins of the two protons in H_2 couple to this field. The field is different at the positions of these protons, depending on the distance between and the orientations of the H_2 and O_2 molecules. He estimated the frequency of collisions between the molecules and the time they stay close to one another, calculated the difference in dipole-magnetic field coupling at a reasonable intermolecular distance, and thus obtained an estimate of the conversion rate. In 1995 Minaev and Agren [103] proposed another mechanism for para-ortho hydrogen conversion in collisions with O₂. They explained that by the exchange interaction of the H₂ electrons with the open-shell O₂ molecule a small amount of the ${}^{3}\Sigma_{\mu}^{+}$ triplet exited state of the H₂ molecule is mixed into its ${}^{1}\Sigma_{\sigma}^{+}$ ground singlet state. This induces spin density at the H nuclei, which gives rise to a Fermi contact interaction [104, 105]. In asymmetric collisions the spin density is different at the two nuclei and also the Fermi contact interactions are different. Based on some simple electronic structure calculations they estimated that for H₂-O₂ the Fermi contact interaction mechanism is more effective about two orders of magnitude than Wigner's magnetic dipole-dipole coupling mechanism. We found a mistake in their calculations, however, and estimate that both mechanisms are about equally effective. Wigner already showed that the difference in magnetic dipole-dipole coupling depends on the intermolecular distance as R^{-4} and is therefore more effective at long range, while the difference in Fermi contact interaction depends on the overlap between the electronic charge clouds of H₂ and O₂, which decays exponentially with their distance R and is therefore more effective at short range.

Recently, in view of the importance of para-hydrogen in NMR, the rate of conversion of para-H₂ into a thermal equilibrium mixture was re-measured by Wagner [106] in gas mixtures of H₂ and O₂ with different relative concentrations. He determined the conversion rate coefficient near room temperature (292K) to be $8.27 \pm 1.3 \text{ Lmol}^{-1}\text{min}^{-1}$.

The objective of the present research is to investigate this rate coefficient theoretically by means of calculations based on first principles. State-to-state inelastic collision cross sections and rate coefficients of para-ortho H₂ conversion by collisions with O_2 are calculated by the quantum mechanical close-coupling (CC) approach, based on the four-dimensional H₂-O₂ potential surface obtained from *ab initio* electronic structure calculations by Kalugina *et al.* [28]. Both mechanisms,

magnetic dipole-dipole coupling and Fermi contact interaction are included, with the latter also obtained from *ab initio* electronic structure calculations. In section 2, we describe the two coupling mechanisms in more detail. Section 3 summarizes the theory of time-independent scattering calculations and gives the computational details. The calculated cross sections and rate coefficients are presented and discussed in section 4, and our conclusions follow in section 5.

5.2 Mechanisms of Para-Ortho Hydrogen Conversion

5.2.1 Fermi contact interaction

When H_2 interacts with the open-shell molecule O_2 , the exchange interaction between the molecules induces spin-density also on H_2 and leads to a Fermi contact interaction [104, 105] with both nuclei of H_2 . For asymmetric structures of the O_2 - H_2 collision complex this Fermi contact interaction is different for the two H nuclei, which makes these nuclei inequivalent and gives rise to para-ortho H_2 transitions. The Hamiltonian that describes the Fermi contact interaction is given by [103]

$$V_{FC} = -\frac{2}{3} g_e g_p \mu_B \mu_N [\sigma(H_1) \boldsymbol{I}(H_1) \cdot \boldsymbol{S} + \sigma(H_2) \boldsymbol{I}(H_2) \cdot \boldsymbol{S}], \qquad (5.1)$$

where g_e and g_p are the *g*-factors of electrons and protons, respectively, and μ_B and μ_N are the Bohr magneton and nuclear magneton. The spin-densities $\sigma(H_1)$ and $\sigma(H_2)$ are the electron spin-density at nuclei H₁ and H₂, which are calculated by electronic structure calculations with the program MOLPRO for many different geometries of the O₂-H₂ collision complex. The calculations are performed at the complete active space self-consistent field (CASSCF) [107] and the multi-reference configuration interaction (MRCI) [108] level of theory. The MRCI method is better but more expensive. The operators $I(H_i) = I(i)$ represent the nuclear spins of H₁ and H₂, *S* the electron spin of O₂ with the quantum numbers S = 1 and Ms = -1, 0, 1.

When the spin-densities $\sigma(H_1)$ and $\sigma(H_2)$ are different, the summation over nuclei H₁ and H₂ can be split into terms in which the spatial and spin parts of the operator individually are symmetric and antisymmetric under the permutation P_{12} that interchanges the nuclei H₁ and H₂

$$V_{FC} = -\frac{2}{3} g_e g_p \mu_B \mu_N \times \left\{ \frac{1}{2} \left[\sigma(H_1) + \sigma(H_2) \right] \left[\boldsymbol{I}(H_1) + \boldsymbol{I}(H_2) \right] \cdot \boldsymbol{S} \\ + \frac{1}{2} \left[\sigma(H_1) - \sigma(H_2) \right] \left[\boldsymbol{I}(H_1) - \boldsymbol{I}(H_2) \right] \cdot \boldsymbol{S} \right\}.$$
(5.2)

The antisymmetric spin factor $[I(H_1) - I(H_2)] \cdot S$ couples the I = 0 and I = 1 nuclear spin functions of para and ortho H₂, the antisymmetric geometry dependent space factor $[\sigma(H_1) - \sigma(H_2)]$ is anisotropic and couples the corresponding rotational states with even and odd *j*. So, the product of these antisymmetric factors in the operator gives rise to para-ortho H₂ conversion. The symmetric operator term only couples the states within the para and ortho manifolds, but is negligible in comparison with the anisotropic terms in the O₂-H₂ interaction potential and will therefore be neglected. The antisymmetric term, expressed in spherical components is

$$V_{FC} = -\frac{1}{3} g_e g_p \mu_B \mu_N \left[\sigma(H_1) - \sigma(H_2) \right] \sum_m (-1)^m S_{-m} \cdot \left[I_m(1) - I_m(2) \right].$$
(5.3)

Since the spin-density on H_2 is caused by exchange effects, it depends exponentially on the distance *R* between the centers of mass of O_2 and H_2 .

5.2.2 Magnetic dipole-dipole interaction

The O₂ molecule, with its two unpaired electrons in π^* electron orbitals and total spin S = 1, has a magnetic dipole moment. This magnetic dipole moment gives rise to an inhomogeneous magnetic field, which for asymmetric structures of the O₂-H₂ collision complex is different at the positions of two H₂ nuclei. The magnetic dipole moments of the H₂ nuclei couple with this field. Equivalently, this coupling is expressed as a magnetic dipole-dipole coupling between the electron spin of O₂ and the nuclear spins of the protons in H₂. This mechanism for para-ortho hydrogen conversion was already proposed in 1933 by Wigner [102], who also estimated the rate of para-ortho H₂ conversion in collisions with O₂ by means of simple model considerations. The magnetic dipole-dipole coupling Hamiltonian is, in spherical components

$$V_{dd} = -\frac{\sqrt{30}\mu_0}{4\pi} g_e g_p \mu_B \mu_N \sum_{i=1}^2 \sum_{M_s, m, M_I} R_i^{-3} C_m^{(2)}(\hat{\underline{R}}_i) I_{M_I}(i) S_{M_s} \begin{pmatrix} 1 & 2 & 1 \\ M_s & m & M_I \end{pmatrix},$$
(5.4)

where μ_0 is the vacuum permeability. We assume that the magnetic moment of O₂ is localized at \underline{r}_{O_2} , the O₂ center of mass, and the vectors $\underline{R}_i = \underline{r}(H_i) - \underline{r}_{O_2}$ connect the positions $\underline{r}(H_i)$ of the protons of H₂ with \underline{r}_{O_2} . The expression in large brackets is a 3-*j* symbol and $C_m^{(2)}(\underline{\hat{R}}_i)$ are Racah-normalized spherical harmonics which depend on the polar angles $\underline{\hat{R}}_i$. Again omitting the symmetric part of Eq.(5.4), the magnetic dipole-dipole coupling reads

$$V_{dd} = -\frac{\sqrt{30}}{2} \frac{\mu_0}{4\pi} g_e g_p \mu_B \mu_N \times \sum_{M_s, m, M_I} \left[T_m^{(2)}(\underline{R}_1) - T_m^{(2)}(\underline{R}_2) \right] \begin{pmatrix} 1 & 2 & 1 \\ M_s & m & M_I \end{pmatrix} S_{M_s} \left[I_{M_I}(1) - I_{M_I}(2) \right],$$
(5.5)

with the rank 2 dipole-dipole interaction tensors

$$T_m^{(2)}(\underline{\hat{R}}_i) = R_i^{-3} C_m^{(2)}(\underline{\hat{R}}_i) .$$
 (5.6)

Since the distance between the two hydrogen nuclei is small in comparison with the distance R between the H₂ and O₂ centers of mass, the difference $T_m^{(2)}(\underline{R}_1) - T_m^{(2)}(\underline{R}_2)$ is small and behaves nearly as the derivative of R^{-3} . Hence, the magnetic dipole-dipole coupling effectively depends on the O₂-H₂ distance as R^{-4} .

5.2.3 Para-ortho H₂ spin conversion

As we discussed in Eqs. (5.3) and (5.5), only the antisymmetric terms in the interaction Hamiltonian give rise to para-ortho H₂ conversion. This is shown in the following simple derivation.

In para-H₂, the nuclear spins are antiparallel and form a singlet state with nuclear spin I = 0, which corresponds to the wave function

$$\frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \quad \text{for } I = 0, M_I = 0, \qquad (5.7)$$

that is antisymmetric under P_{12} . In ortho-H₂ the spins of the two protons are parallel and form a triplet state with total nuclear spin quantum number I = 1, with the three nuclear spin wave functions

$$\begin{array}{ll} \alpha(1)\alpha(2) & \text{for } I=1, M_I=1 \\ \frac{1}{\sqrt{2}} \left[\alpha(1)\beta(2) + \beta(1)\alpha(2) \right] & \text{for } I=1, M_I=0 \\ \beta(1)\beta(2) & \text{for } I=1, M_I=-1 \end{array}$$
 (5.8)

The two states for each of the H nuclei 1 and 2 with spin I = 1/2 are represented by the eigenfunctions α and β of the spin operator I_z : $I_z \alpha = \frac{1}{2} \alpha$ and $I_z \beta = -\frac{1}{2} \beta$.

The corresponding shift operators act on the spin eigenfunctions as

$$I_{+}\beta = \alpha, \quad I_{-}\alpha = \beta, \quad I_{+}\alpha = 0, \quad I_{-}\beta = 0.$$
 (5.9)

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By acting with the shift operators on the wave function of para-H₂ in Eq.(5.7), we get

$$[I_{+}(1) - I_{+}(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

= $\frac{1}{\sqrt{2}} [-\alpha(1)\alpha(2) - \alpha(1)\alpha(2)]$, (5.10)
= $-\sqrt{2}\alpha(1)\alpha(2)$

$$\begin{split} & [I_{z}(1) - I_{z}(2)] \frac{1}{\sqrt{2}} \Big[\alpha(1)\beta(2) - \beta(1)\alpha(2) \Big] \\ &= \frac{1}{\sqrt{2}} \Big[\frac{1}{2} \alpha(1)\beta(2) + \frac{1}{2}\beta(1)\alpha(2) + \frac{1}{2}\alpha(1)\beta(2) + \frac{1}{2}\beta(1)\alpha(2) \Big], \quad (5.11) \\ &= \frac{1}{\sqrt{2}} \Big[\alpha(1)\beta(2) + \beta(1)\alpha(2) \Big] \\ & [I_{-}(1) - I_{-}(2)] \frac{1}{\sqrt{2}} \Big[\alpha(1)\beta(2) - \beta(1)\alpha(2) \Big] \\ &= \frac{1}{\sqrt{2}} \Big[\beta(1)\beta(2) + \beta(1)\beta(2) \Big] \qquad (5.12) \\ &= \sqrt{2}\beta(1)\beta(2) \, . \end{split}$$

We define the normalized spherical components $I_0 = I_z$ and $I_{\pm 1}$. The relations between the latter operators and the shift operators I_{\pm} are

$$I_{\pm 1} = \mp \frac{1}{\sqrt{2}} I_{\pm} \quad . \tag{5.13}$$

So when we act on the I = 0 nuclear spin wave function of para-H₂ we get

$$[I_{+1}(1) - I_{+1}(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \alpha(1)\alpha(2), \qquad (5.14)$$

$$[I_0(1) - I_0(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)], (5.15)$$

$$[I_{-1}(1) - I_{-1}(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \beta(1)\beta(2).$$
 (5.16)

which are exactly the I = 1 nuclear spin wave functions of ortho-H₂.

Summarizing, the antisymmetric terms in the interaction Hamiltonians with the nuclear spin operators $I_m(H_1) - I_m(H_2)$ convert the nuclear spin wave functions of H_2 from para- into ortho- H_2

$$[\underline{I}_{m}(1) - \underline{I}_{m}(2)] | I=0, M_{I}=0 \rangle = | I=1, M_{I}=m \rangle.$$
(5.17)

Hence, the matrix elements of the antisymmetric spin factors in the interaction Hamiltonians are

$$\langle I=1, M'_I | \underline{I}_m(1) - \underline{I}_m(2) | I=0, M_I=0 \rangle = \delta_{M'_I,m}.$$
 (5.18)

In addition to the matrix elements over the nuclear spin functions of H₂ we need the matrix elements of the electron spin operators S_m over the spin wave functions $|S=1, M_s\rangle$ of the O₂ molecule. Using equation (5.13), but now for the spherical components S_m , we easily find that

$$\langle S=1, M'_{S} | S_{0} | S=1, M_{S} \rangle = \delta_{M'_{S}, M_{S}} M_{S},$$
 (5.19)

and

$$\langle S=1, M'_{S} | S_{\pm 1} | S=1, M_{S} \rangle = \mp \delta_{M'_{S}, M_{S} \pm 1}.$$
 (5.20)

We did not explicitly include the spin wave functions in the channel basis in our scattering calculations. Instead, we used the above matrix elements for the spin parts of the Fermi contact interaction and magnetic dipole-dipole coupling terms. Our scattering program could not handle the $m = \pm 1$ components of the dipole-dipole coupling tensor $T_m^{(2)}(\hat{R}_i)$, so we included only the most important term with m = 0 and the spin wave functions for which this component of the magnetic dipole-dipole coupling operator in Eq. (5.5) has a non-zero matrix element.

5.3 Scattering Calculations

In the present work, we consider the conversion between para- and ortho- H_2 in rotationally inelastic O_2 - H_2 collisions

$$O_2(n_1) + \text{para-H}_2(j_2) \rightarrow O_2(n'_1) + \text{ortho-H}_2(j'_2).$$
 (5.21)

where the quantum numbers n_1 and j_2 denote the rotational levels of O₂ and H₂, respectively. Molecular oxygen, O₂, with its ${}^{3}\Sigma_{g}^{-}$ electronic ground state has total molecular angular momentum j defined through the Hund's case (b) coupling $j = n_1 + S$. We neglect the electron spin-spin coupling within the O₂ molecule and the coupling of the O₂ spin S with its rotation, so we describe the O₂ rotational states with the quantum number n_1 . Since ¹⁶O nuclei are bosons with spin I = 0 and the electronic ground state wave function of O₂ is antisymmetric under interchange of the O nuclei, only rotational states with odd n_1 are allowed by the Pauli principle. The channel basis in our closed-coupling scattering calculations contains the O₂ states with $n_1 = 1 - 21$, the para-H₂ states with $j_2 = 0$, 2, and the ortho-H₂ states with $j_2 = 1$, 3. We wish to compute rate coefficients up to room temperature, so we considered the O₂ initial states with $n_1 = 1 - 15$ and the para-H₂ initial states with $j_2 = 0$ and 2 that have a substantial population at room temperature. Rotational state-to-state cross sections and rate coefficients were calculated for the para-ortho H₂ transitions $j_2 = 0 \rightarrow j'_2 = 1,3$ and $j_2 = 2 \rightarrow j'_2 = 1,3$.

5.3.1 Theoretical methods

Molecular scattering can be described by the time-independent coupled-channels scattering equations [61, 109-113]. With the inclusion of the spin couplings described above, the Hamiltonian of O_2 -H₂ can be written in body-fixed coordinates as [114]

$$\hat{H} = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{J^2 + (n_1 + j_2)^2 - 2(n_1 + j_2) \cdot J}{2\mu R^2}, \qquad (5.22)$$
$$+ \hat{H}_{H_2} + \hat{H}_{O_2} + \hat{V}(R, \theta_1^{BF}, \theta_2^{BF}, \varphi^{BF}) + \hat{V}_{FC} + \hat{V}_{dd}$$

where $\mu = m_{H_2} m_{O_2} / (m_{H_2} + m_{O_2})$ is the reduced mass of the O₂-H₂ complex, $J = n_1 + j_2 + l$ is the total angular momentum of the H₂-O₂ complex, and l is the end-over-end angular momentum of the rotation of the molecules around each other. We assume the molecules to be rigid with rotational constants B_{H_2} and B_{O_2} and the monomer Hamiltonians are $\hat{H}_{H_2} = B_{H_2} \hat{j}_2^2$ and $\hat{H}_{O_2} = B_{O_2} \hat{n}_1^2$. The interaction between the molecules is described by the anisotropic potential $\hat{V}(R, \theta_1^{BF}, \theta_2^{BF}, \varphi^{BF})$. The vector R with length R connects the centers of mass of the O₂ and H₂ monomers. The polar angles $(\theta_1^{BF}, \varphi_1^{BF})$ and $(\theta_2^{BF}, \varphi_2^{BF})$ define the orientations of the O₂ and H₂ monomer axes with respect to the body-fixed frame with its z-axis along R and $\varphi^{BF} = \varphi_2^{BF} - \varphi_1^{BF}$. The operators V_{FC} and V_{dd} are the Fermi contact interaction and the magnetic dipole-dipole coupling Hamiltonians as defined above.

In the scattering calculations, the potential energy surface expressed in bodyfixed coordinates is expanded in terms of coupled spherical harmonics as [114]

$$\hat{V}(R,\theta_1^{BF},\theta_2^{BF},\varphi^{BF}) = \sum_{l_1,l_2,l} V_{l_1,l_2,l}(R) \times \sum_{m_2=-m_1} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & 0 \end{pmatrix} Y_{l_1,m_1}(\theta_1^{BF},\varphi_1^{BF}) Y_{l_2,m_2}(\theta_2^{BF},\varphi_2^{BF})$$
(5.23)

where $v_{l_1,l_2,l}(R)$ are the radial expansion coefficients, the functions $Y_{l,m}(\theta, \varphi)$ are spherical harmonics, and the expression in large brackets is a 3-*j* symbol. Because both diatomic molecules are homonuclear, only even l_1 and l_2 contribute.

The CASSCF and MRCI calculations to obtain the spin densities $\sigma(H_i)$ in the Fermi contact term are similar to those for the potential. The spin-density at each nucleus of H₂ is calculated for a number of geometries sufficient to make an expansion of \hat{V}_{FC} and \hat{V}_{dd} similar to that in Eq. (5.23) and compute the expansion coefficients. Notice that l_1 is still even, but l_2 is odd now because the spatial operators in \hat{V}_{FC} and \hat{V}_{dd} of Eqs. (5.3) and (5.5) are antisymmetric under the permutation P_{12} . Hence these terms couple the even j_2 wave functions of para-H₂ with the odd j_2 wave functions of ortho-H₂.

To solve the time-independent Schrödinger equation $(\hat{H} - E) |\Psi_q\rangle = 0$ with the Hamiltonian of Eq. (5.22), the coupled-channels wave function is expanded

$$\left|\Psi_{q}\right\rangle = \frac{1}{R} \sum_{p} \left|\phi_{p}\right\rangle U_{pq}(R), \qquad (5.24)$$

in the body-fixed channel basis functions given by [114]

$$\left| \phi_{p} \right\rangle = \left| n_{1}, j_{2}, j_{12}, K; J, M \right\rangle = \sum_{m_{1}, m_{2}} Y_{n_{1}, m_{1}}(\theta_{1}^{BF}, \varphi_{1}^{BF}) Y_{j_{2}, m_{2}}(\theta_{2}^{BF}, \varphi_{2}^{BF}) \times \left\langle n_{1}, m_{1}; j_{2}, m_{2} \left| j_{12}K \right\rangle D_{M,K}^{(J)}(\Phi, \Theta, 0)^{*} \right\rangle$$

$$(5.25)$$

where $Y_{n_1,m_1}(\theta_1,\varphi_1)$ and $Y_{j_2,m_2}(\theta_2,\varphi_2)$ are the rotational states of the molecules O₂ and H₂, $\langle n_1,m_1; j_2,m_2 | j_{12}K \rangle$ is a Clebsch-Gordan coefficient, $j_{12} = n_1 + j_2$ is the vector sum of the rotational angular momenta of O₂ and H₂, and *K* and *M* are the body-fixed and space-fixed projections of the total angular momentum *J* of the system, respectively.

By substituting the expansion of Eq. (5.24) into the Schrödinger equation and multiplying from the left with the channel basis function $\langle \phi_{p} \rangle$ one obtains a set of coupled differential equations 104

$$\frac{\partial^2}{\partial R^2} U_{p'q}(R) = \sum_p \left\langle \phi_{p'} \middle| \hat{W} \middle| \phi_p \right\rangle U_{pq}(R) , \qquad (5.26)$$

the coupling operator \hat{W} is

$$\hat{W} = -2\mu \left[E - \frac{J^2 + (n_1 + j_2)^2 - 2(n_1 + j_2) \cdot J}{2\mu R^2} - \hat{H}_{H_2} - \hat{H}_{O_2} - \hat{V} \right], \quad (5.27)$$

with $\hat{V} = \hat{V}(R, \theta_1, \theta_2, \phi) + \hat{V}_{FC} + \hat{V}_{dd}$.

Solving the coupled-channels equations of Eq. (5.26) with the appropriate asymptotic boundary conditions leads to the *S*-matrix, which contains all the scattering information. The state-to-state integral cross sections are calculated from the *T*-matrix as [111]

$$\sigma_{i \to f} = \frac{1}{(2n_1 + 1)(2j_2 + 1)} \frac{\pi}{k_i^2} \sum_{j_{12}, l, j'_{12}, l', J} (2J + 1) \left| T_{i, j_{12}, l; f, j'_{12}, l'} \right|^2, \quad (5.28)$$

where *i* and *f* label the initial and final states n_1 , j_2 and n_1 ', j_2 ', respectively, k_i is the wave number of the incoming channel with collision energy E_c . The *T*-matrix is related to the *S*-matrix through T = I - S, where *I* is a unit matrix.

By integrating the state-to-state cross sections over a Boltzmann distribution of collision energies, one can obtain the thermal rate coefficients at temperature T

$$k_{n_{1},j_{2}\to n_{1}',j_{2}'}(T) = \left(\frac{8}{\pi\mu k_{B}^{3}T^{3}}\right)^{\frac{1}{2}} \int_{0}^{\infty} \sigma_{n_{1},j_{2}\to n_{1}',j_{2}'}(E_{c}) E_{c} \exp\left(-\frac{E_{c}}{k_{B}T}\right) dE_{c}, \quad (5.29)$$

where k_B is the Boltzmann constant. The cross sections and rate coefficients of particular interest in the present study are those in which the initial states belong to para-H₂ with even j_2 and the final states to ortho-H₂ with odd j_2 . The corresponding cross sections and rates are smaller by many orders of magnitude than those for which the transitions change only the rotational states of O₂ and H₂ within the same para- or ortho-H₂ manifold.

The rate coefficients for the reverse transitions are related by the detailed balance conditions

$$k_{n'_{1},j'_{2}\to n_{1},j_{2}}(T) = \frac{(2n_{1}+1)(2j_{2}+1)}{(2n'_{1}+1)(2j'_{2}+1)} \exp\left(\frac{E_{n'_{1},j'_{2}}-E_{n_{1},j_{2}}}{k_{B}T}\right) k_{n_{1},j_{2}\to n'_{1},j'_{2}}(T), \quad (5.30)$$

with

$$E_{n_1,j_2} = n_1(n_1+1)B_{O_2} + j_2(j_2+1)B_{H_2}, \qquad (5.31)$$

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where E_{n_1,j_2} is the energy of the rotational levels, while B_{H_2} and B_{O_2} are the rotational constants of H₂ and O₂, respectively.

By summation of the state-to-state cross sections and rate coefficients over all final n'_1 states of O₂, we obtain the total cross sections and rate coefficients for transitions from a specific initial state n_1, j_2 to final state j'_2 .

$$\sigma_{n_1, j_2 \to j'_2}(E_c) = \sum_{n'_1=1}^{21} \sigma_{n_1, j_2 \to n'_1, j'_2}(E_c) , \quad (5.32)$$

$$k_{n_1, j_2 \to j'_2}(T) = \sum_{n'_1=1}^{21} k_{n_1, j_2 \to n'_1, j'_2}(T) . \quad (5.33)$$

After Boltzmann averaging these rate coefficients over different initial n_1 and j_2 states and sum over all the final j'_2 states, we get the total para- to ortho-H₂ conversion rate coefficients as follows

$$k(T) = \frac{\sum_{j_2=0}^{2} \sum_{n_1=1}^{15} g_{n_1 j_2} \exp(-\frac{E_{n_1 j_2}}{k_B T}) \sum_{j'_2=1}^{3} k_{n_1, j_2 \to j'_2}(T)}{\sum_{j_2=0}^{2} \sum_{n_1=1}^{15} g_{n_1 j_2} \exp(-\frac{E_{n_1 j_2}}{k_B T})},$$
(5.34)

where $g_{n_1 j_2} = (2n_1 + 1)(2j_2 + 1)$ is the degeneracy of the n_1, j_2 rotational levels.

5.3.2 Computational details

All the calculations on H₂-O₂ collisions were carried out by the close-coupling (CC) method, and based on the four-dimensional (4D) potential of Kalugina *et al.* [28]. In order to check our calculations, we first performed CC calculations of the cross sections and rate coefficients for para-para ($j_2 = 0 \rightarrow j'_2 = 2$) and ortho-ortho ($j_2 = 1 \rightarrow j'_2 = 3$) H₂ transitions. The results agree very well with those of Kalugina *et al.* [28]. Here we did not include the para-ortho coupling terms, so there is no para-ortho-H₂ conversion. As far as we know, para-ortho H₂ conversion rates in collisions with O₂ have not previously been calculated, except by Wigner in 1933 who made an estimate based on a simple model for the collisions. However, as we mentioned in the introduction, they are of great interest in view of the importance of the PHIP method to increase NMR signals. Except with the potential of Kalugina *et al.* [28] we also performed calculations with an unpublished H₂-O₂ potential surface of Dawes obtained by private communication. The differences with the results based 106

on the Kalugina et al. potential are insignificant.

The rotational constants of H₂ and O₂ adopted here are $B_{H_2} = 59.3398 \text{ cm}^{-1}$ and $B_{O_2} = 1.4376766 \text{ cm}^{-1}$, respectively. The reduced mass of the system is $\mu = 1.896$ amu. The calculations were carried out at collision energies ranging from 2 to 2000 cm⁻¹ in order to evaluate state-to-state rate constants up to T = 300K. Convergence checks were performed to ensure that the limiting values for n_1 , j_2 , and J do not affect the results. The maximum value of the total angular momentum J is set differently depending on the collision energy, with the largest value of J being 130. The maximum value of the O₂ rotational quantum number n_1 is 21 to ensure convergence of the first 8 (up to $n_1=15$) rotational levels of O₂. The second order differential equations were solved with the renormalized Numerov algorithm [115, 116] for the propagation of the wave function on an equidistant grid in R with 288 points ranging from 4.5 to 50 a_0 .

The cross sections and rate coefficients were computed with different para-ortho couplings included:

- 1. only the Fermi contact interaction calculated at the CASSCF level,
- 2. only the Fermi contact interaction calculated at the MRCI level,
- 3. only magnetic dipole-dipole coupling,
- 4. both the Fermi contact interaction from MRCI calculations and the magnetic dipole-dipole coupling.

We also performed calculations on the reverse ortho-para H₂ conversion process by using initial $j_2 = 1$ states and final states with $j_2 = 0$ and 2. The results were compared with those obtained from detailed balance conditions, see equation (5.30), and were found to agree very well.

5.4. Results and Discussion

5.4.1 State-to-state cross sections

Figures 5.1 and 5.2 show state-to-state integral cross sections for the H₂ transitions $j_2 = 0 \rightarrow j'_2 = 1$ and $j_2 = 2 \rightarrow j'_2 = 1$, respectively, as a function of the collision energy ranging from 2 to 2000 cm⁻¹ from initial rotational levels of O₂ with $n_1 = 1,5,9,13$ into final rotational levels with $n'_1 = 1-21$. Note that also higher rotational excitations of H₂ ($j_2 = 0 \rightarrow j'_2 = 3$ or $j_2 = 2 \rightarrow j'_2 = 3$) were taken into

account in the calculations, but since the corresponding cross sections are very much smaller than those for transition to $j'_2 = 1$, we do not show these results here.

Let us take the $1 \rightarrow 1$ transition, shown in Fig. 5.1, as an example. This curve depicts the cross section for para-ortho H₂ transitions from $j_2 = 0$ to $j'_2 = 1$ that is elastic in O₂: from $n_1 = 1$ to $n'_1 = 1$. Notice that no para-ortho H₂ conversion occurs until the collision energy is sufficiently high to surmount the excitation threshold, so for this $1 \rightarrow 1$ transition the channel opens up when the collision energy is larger than $2B_{\rm H_2} \approx 120 \,\rm cm^{-1}$. As for the $1 \rightarrow 3$ transition, it starts at higher energy because it needs more energy to surmount also the excitation threshold of O2. With increasing O₂ rotational excitation the channels open later. The first column of Table 5.1 shows the energies at which each channel opens for transitions from the initial $n_1 = 1, j_2 = 0$ state to all the final rotational states $n'_1 = 1 - 21, j'_2 = 1$ considered. For higher initial states of O₂ or H₂, less collision energy is needed, because the system gains energy from de-excitation, as shown in the second column of Table 5.1. When the gain energy is larger than the excitation barrier, the energy threshold vanishes, such as for $n_1 = 9$, $j_2 = 0 \rightarrow n'_1 = 1$, $j'_2 = 1$ or $n_1 = 1$, $j_2 = 2 \rightarrow n'_1 = 1$, $j'_2 = 1$ transitions. In general, the cross sections of the elastic $\Delta n_1 = 0$ transitions of O₂ contribute most to the total cross sections and the inelastic contributions decrease as $|\Delta n_1|$ increases. One may also notice a series of resonances in the cross sections at low collision energies because of the influence of the attractive potential [117, 118]. They have little effect on the rate coefficients except at very low temperatures, which we did not consider.

In Fig. 5.3 we present the total cross sections from the specific initial states $n_1 = 1, 5, 9, 13, j_2 = 0$ to final states with $j'_2 = 1$ by summation of the state-to-state cross sections over all final $n'_1 = 1 - 21$ states through the use of Eq. (5.32). Figure 5.4 is similar to Fig. 5.3, for the initial state of H₂ with $j_2 = 2$. The general behavior of these total cross sections is similar to that of the state-to-state cross sections. The amplitude of resonances tends to be smaller for higher initial n_1 states. For higher collision energies, the total cross sections for different initial n_1 values become almost equal.



Figure 5.1: State-to-state para-ortho H₂ conversion cross sections from closecoupling calculations for O₂-H₂ collisions from initial states with $n_1 = 1, 5, 9, 13$ and $j_2 = 0$ into the individual final states with $n'_1 = 1 - 21$ and $j'_2 = 1$.



Figure 5.2: Same as Fig. 5.1, for the initial state of H_2 with $j_2 = 2$.



Figure 5.3: Total conversion cross sections from the specific initial states with $n_1 = 1, 5, 9, 13$ and $j_2 = 0$ to final states with $j'_2 = 1$ by summation of the state-to-state cross sections over all final $n'_1 = 1 - 21$ O₂ states.



Figure 5.4: Same as Fig. 5.3, for the initial state of H_2 with $j_2 = 2$.

$n_1, j_2 \rightarrow n_1', j_2'$	$E_{n_1,j_2 \rightarrow n_1',j_2'}$	$n_1, j_2 \rightarrow n_1', j_2'$	$E_{n_1,j_2 \rightarrow n_1',j_2'}$
$1,0 \rightarrow 1,1$	118.68	$5,0 \rightarrow 1,1$	78.42
$1,0 \to 3,1$	133.06	$5,0 \rightarrow 3,1$	92.80
$1,0 \rightarrow 5,1$	158.93	$9,0 \rightarrow 3,1$	3.67
$1,0 \rightarrow 7,1$	196.31	$9,0 \rightarrow 5,1$	29.54
$1,0 \rightarrow 9,1$	245.20	$13,0 \rightarrow 11,1$	46.80
$1,0 \rightarrow 11,1$	305.58	$13,0 \rightarrow 15,1$	202.06
$1,0 \to 13,1$	377.46	$1,2 \rightarrow 13,1$	21.42
$1,0 \to 15,1$	460.85	$1,2 \rightarrow 15,1$	104.81
$1,0 \rightarrow 17,1$	555.73	$5,2 \rightarrow 15,1$	64.55
$1,0 \to 19,1$	662.12	$9,2 \rightarrow 17,1$	73.18
$1,0 \rightarrow 21,1$	780.01	$13,2 \rightarrow 19,1$	47.30

Table 5.1. Energies where different $n_1, j_2 \rightarrow n'_1, j'_2$ transition channels open. n_1 and j_2 denote the rotational quantum numbers of O₂ and H₂, respectively.

5.4.2 Rate coefficients

The rate coefficients $k_{n_1,j_2 \to j'_2}(T)$ of para-ortho H₂ conversion in collisions with O₂ molecules for transitions from a specific initial rotational state n_1, j_2 to all final states with given j'_2 were calculated from the state-to-state cross sections through the use of equations (5.29) and (5.33). In these calculations we considered the $j_2 = 0 \to j'_2 = 1,3$ and $j_2 = 2 \to j'_2 = 1,3$ transitions between the rotational states of para- and ortho-H₂. In order to check the relative importance of the two coupling mechanisms and the effect of the different methods to calculate the Fermi contact term, we also calculated the rate coefficients separately for the Fermi contact term and for the magnetic dipole-dipole coupling term. Since the rate coefficients vary only slightly for different initial states of O₂, we use $n_1=1$ as an example. Table 5.2 lists the rate coefficients for the H₂ transitions from $j_2 = 0, 2$ to $j'_2 = 1, 3$. It shows that the rate coefficients for rotational excitation of H₂ from $j_2 = 0$ and $j_2 = 2$ to $j'_2 = 3$ are much smaller than those for the transitions to $j'_2 = 1$. Mode 1 and mode 2 label the results with the Fermi contact interaction calculated at the CASSCF and MRCI levels of theory, respectively. The more expensive and accurate MRCI level yields smaller values than those calculated at the CASSCF level. The Fermi contact mechanism does not make a more important contribution than the magnetic dipole-dipole coupling mechanism (mode 3) proposed by Wigner, for $j_2 = 0 \rightarrow j'_2 = 1$ transitions it is even smaller. This contradicts the conclusion of Minaev *et al.* [103], but we saw already that they strongly underestimated the magnitude of the dipole-dipole coupling term. In the final calculations we included both coupling mechanisms simultaneously. We found that the cross sections and rates are even larger than the sum of the individual contributions, because of positive interference effects.

We also checked the detailed balance relation in Eq. (5.30), by computing rate coefficients for reverse transitions. The results, illustrated in Fig. 5.5, show that the rate coefficient $k_{3,1 \rightarrow 1,0}(T)$ for the transition $n_1 = 3, j_2 = 1 \rightarrow n'_1 = 1, j'_2 = 0$ multiplied by the factor $\frac{(2n_1 + 1)(2j_2 + 1)}{(2n'_1 + 1)(2j'_2 + 1)} \exp(\frac{E_{1,0} - E_{3,1}}{k_BT})$ perfectly matches the rate coefficient $k_{1,0 \rightarrow 3,1}(T)$ for the transition $n_1 = 1, j_2 = 0 \rightarrow n'_1 = 3, j'_2 = 1$. This is a good check for the convergence and accuracy of our calculations.

Figure 5.6 shows the integrand $f(E_c) = \sigma_{n_1, j_2 \to n'_1, j'_2}(E_c) E_c \exp(-\frac{E_c}{k_B T})$ of the rate coefficients in Eq. (5.29) for the $n_1 = 1, j_2 = 0 \to n'_1 = 1, j'_2 = 1$ transition as a function of the collision energy, for temperatures T = 100, 200 and 300 K. The integrand becomes higher and broader with increasing temperature. Wigner [102] assumed that the dipole-dipole coupling is effective for a certain time when the H₂ and O₂ molecules are close to each other. The higher the temperature, the faster they fly and the shorter the time they stay together. So Wigner proposed two counteracting effects for the temperature dependence of the rate coefficients. First, when the temperature is lower the coupling acts for a longer time, so one would expect that the cross sections are larger. On the other hand, sufficient kinetic energy is needed to surmount the energy threshold of about 120 cm⁻¹ for the conversion of j = 0 para-H₂ into j = 1 ortho-H₂. This implies that when more fast para-H₂ molecules are

Table 5.2: Rate coefficients for rotational excitation of H₂ ($j_2 = 0, 2$ to $j'_2 = 1, 3$) by collisions with O₂ (for initial state $n_1 = 1$) by consideration of the Fermi contact term (mode 1 or 2) and the magnetic dipole-dipole coupling (mode 3) separately. The rate coefficients are summed over all final states with $n'_1 = 1-21$.

	$n_1 = 1, j_2 = 0 - j_2' = 1$				$n_1=1, j_2=0 -> j_2'=3$		
	mode 1	mode 2	mode 3		mode 1	mode 2	mode 3
T=100	0.414738	0.324563	0.452107	T=100	8.06E-07	5.57E-07	3.64E-07
T=200	1.367548	1.068496	1.59148	T=200	0.000367	0.000263	0.000158
T=300	2.324621	1.817698	2.762125	T=300	0.003875	0.002961	0.001611
$n_1=1, j_2=2> j_2'=1$				$n_1=1, j_2=2 -> j_2'=3$			
	mode 1	mode 2	mode 3		mode 1	mode 2	mode 3
T=100	0.950293	0.707738	0.20856	T=100	0.002157	0.001604	0.000424
T=200	1.256541	0.938785	0.320427	T=200	0.058683	0.043777	0.011278
т_300	1 625563	1 21994	0 456355	T=300	0.222929	0.167087	0.043497

present, collisions are more effective, because these molecules have sufficient energy to convert. From our results, shown in Figs. (5.1-2, 5.6), it follows that all the way from 10K to room temperature, the rate coefficients increase with temperature. So clearly, in our studied range of temperatures, the second effect is dominant.

Finally, the rate coefficients of para-ortho H₂ conversion in collisions with O₂ molecules are calculated with the inclusion of both the Fermi contact and magnetic dipole-dipole coupling with the use of Eq. (5.34). The results are shown in Fig. 5.7 for temperatures ranging from 10K to 300K. We used the calculated inelastic cross sections to obtain the rate coefficients for the first 8 ($n_1 = 1-15$) initial rotational levels of O₂ in collisions with para-H₂ ($j_2 = 0, 2$). The rate coefficients plotted in blue are summed over all the final rotational levels $n'_1 = 1-21, j'_2 = 1-3$, and thermally averaged over all the initial levels of both the O₂ and H₂ molecules. Wagner [106] experimentally determined the para- to ortho-H₂ conversion rate constant by collisions with O₂ near room temperature (292K) to be 8.27±1.3 L mol⁻¹ min⁻¹. Our final theoretical result is 4.68 L mol⁻¹ min⁻¹, somewhat smaller than the experiment value, but in our calculations we only included the m = 0 component of the magnetic



Figure 5.5: Check of the detailed balance relation in Eq. (5.30). Black curve with open circles: righthand side of Eq. (5.30) with the rate coefficient for the transition $(n_1 = 3, j_2 = 1 \rightarrow n'_1 = 1, j'_2 = 0)$. Red curve with stars: lefthand side of Eq. (5.30) with the rate coefficient for the reverse transition $(n_1 = 1, j_2 = 0 \rightarrow n'_1 = 3, j'_2 = 1)$.

dipole-dipole coupling in Eq. (5.5). We are currently extending our scattering program to include all components of the magnetic dipole-dipole coupling tensor. The para-ortho H_2 conversion couplings are very small in comparison with the anisotropic terms in the O_2 - H_2 interaction potential that lead to rotationally inelastic collisions and we can use the scattering states of para- and ortho- H_2 calculated with the full anisotropic potential and compute the para-ortho conversion cross sections in the first-order Born approximation.



Figure 5.6: Integrand of the rate coefficients in Eq. (5.29) for the $n_1 = 1, j_2 = 0 \rightarrow n'_1 = 1, j'_2 = 1$ transition at temperatures T = 100, 200 and 300K.



Figure 5.7: Rate coefficients as a function of *T* calculated with both the Fermi contact and magnetic dipole-dipole couplings included, summed over all the final states n'_1 and j'_2 and thermally averaged over the initial $n_1 = 1-15$ states of O₂. Black curve for initial $j_2 = 0$, red curve for initial $j_2 = 2$. The blue curve shows the final result obtained by thermal averaging also over the initial H₂ states with $j_2 = 0$ and 2.

5.5 Conclusion

We present state-to-state cross sections and rate coefficients of para-ortho H₂ conversion by collision with paramagnetic O₂ molecules from converged closecoupling quantum scattering calculations for initial states with $n_1 = 1-15$ of O₂ and $j_2 = 0-2$ of H₂ and final states with $n'_1 = 1-21$ and $j'_2 = 1-3$. Both mechanisms for para-ortho conversion are included, i.e., the magnetic dipole-dipole coupling between the electron spin of O₂ and the nuclear spins of the protons in H₂ and the Fermi contact interaction from the spin-density in H₂ induced by O₂. Contrary to the assertion of Minaev *et al.* [103] that the Fermi contact mechanism should be much more effective than the magnetic dipole-dipole coupling mechanism proposed by Wigner [102], our results indicate that both mechanisms are about equally important for the conversion rate. Wigner [102] considered two counteracting effects for the temperature dependence of the rate coefficients: i) at higher temperature the molecules move faster and there will be less time for the coupling to be effective, which should decrease the rate, and ii) on the other hand, a higher rate might be expected at higher temperature, because more molecules in the gas have sufficient energy for the conversion of j = 0 para-H₂ to j = 1 ortho-H₂. Our results show that all the rate coefficients increase with the temperature up to at least 300K. So, we clearly find the second effect to be dominant. Finally, we compare our rate coefficients at room temperature (292K) with the value measured by Wagner [106] on O₂-H₂ gas mixtures with different concentration ratios. Our calculated para-ortho H₂ conversion rate is slightly smaller than the experimental value, but we did not include all components of the magnetic dipole-dipole coupling yet. Further calculations will be performed with an extended version of our close-coupling scattering program in which all components of the dipole-dipole coupling tensor can be included through the first-order Born approximation.



Summary and outlook

6.1 Summary

This thesis describes theoretical studies of atom-molecule and molecule-molecule rotationally inelastic collisions. Rotationally inelastic scattering of molecules, involving the transfer of energy and momentum, plays an important role in many physical and chemical reactive and non-reactive processes. Quantum state-to-state resolved differential cross section and integral cross section provide the most detailed information about the specifics of these collision processes. The goal of this work was to investigate some specific benchmark cases of scattering calculations by both the quasi-quantum treatment and the fully quantum mechanical close-coupling methods, in the hope to provide insight in the dynamical mechanisms occurring in molecular collisions.

Chapter 2 describes the collision energy dependence of the rotationally inelastic differential cross-sections associated with an atom-diatom scattering processes. Within a quasi-quantum treatment, we derive a series of analytic expressions that strictly describe the collisional energy dependence, and we show that these relationships also approximately hold for the rigorously calculated quantum-mechanical DCSs. This allows the designation of particular (energy-dependent) scattering angle ranges, which can be associated with specific features of a state-of-the-art *ab initio* PESs. Although example calculations are shown for the NO+He system, the work presented here is easily extended to any atom-diatom collision system.

Chapter 3 presents a modified QQT method to study NO-He rotationally inelastic scattering at a collision energy of 508 cm⁻¹. As we know the regular QQT approximates the potential energy surface as a hard shell contour extracted from the V_{sum} potential corresponding to the collision energy. But this approximation has the

limitation that it cannot distinguish glancing or head-on collisions. For glancing collision, rarely collisional energy is transferred into rotational energy, while for head-on collision, almost all the energy is transferred. In the modified QQT, the PESs is taken as a series of stepped hard-shell contours, which is set equal to the amount of collision energy transferred into rotational excitation. By this way, different kinds of collisions correspond to different hard shells. The integral and differential cross sections calculated by modified QQT produce a much better agreement with exact QM results than those obtained by regular QQT, particularly in the forward scattered direction.

Chapter 4 describes an extension of the quasi-quantum treatment of NO-He inelastic scattering from spin-orbit state conserving transitions in pure Hund's case (a) to spin-orbit changing transitions in mixed Hund's case. The quantum state-to-state resolved integral and differential cross sections in both spin-orbit state conserving and changing transitions are obtained by QQT and QM methods. This extension of the QQT model provides insight into the underlying mechanism that brings about the spin-orbit state excitation and as such offers a focus for future work.

Chapter 5 presents the rate coefficients of para-ortho H_2 conversion in collision with O_2 molecules. State-to-state cross sections for collision-induced rotational excitation of both H_2 and O_2 molecules are calculated by the fully quantum-mechanical close-coupling method. Both mechanisms that can convert para- H_2 into ortho- H_2 , i.e., magnetic dipole-dipole coupling and Fermi contact interaction are considered. The theoretical para-ortho H_2 conversion rate coefficients are compared with the experimental data at room temperature, thus obtaining good agreement.

6.2 Outlook

The quasi-quantum treatment of inelastic scattering could be extended to a wider variety of colliders, such as diatomic radicals OH [67, 91, 119-124], HCl [31, 75], CO [9, 31, 75, 125], N₂, O₂ [126-129], polyatomic molecules NH₃ [130-135], H₂O [123, 136, 137] and their isotopomers, which have been studied in both experiment and theory. QQT theory is still in its infancy, hence there is a wide area for further application and development.

The dominating repulsive properties of the NO-He collision system PESs do not hold for all systems and collision energies. Brouard *et al.* recently reported rotational alignment effects of NO-Ar inelastic scattering in both experimental [87] and theoretical [88] studies. Calculations of the differential cross sections were also performed at low collision energy 15 meV and 30 meV. These two cases provide an attractive example to study the abilities of the scaling rule on the more attractive PESs, which might work reasonably well for the scaled DCSs from 63 meV down to 30 meV. Moreover at the same collision energy, the De Broglie wavelength of the NO-Ar collision system is about a factor of 2 smaller compared to that of NO-He. This enhances the sensitivity to the details of the NO-Ar system PESs which offers an interesting aspect to study.

In chapter 4, the Hund's case (a) approximation was employed to treat the NO-He rotationally inelastic collision scattering problem, but for *j* values larger than 6.5, this approximation might no longer be applicable, especially for spin-orbit state changing transitions. The eigenstate rotational wave functions in the mixed Hund's case ought to be applied. The mixed Hund's case is also essential for the CH and OH diatomic molecules. These phenomena open doorways for research to further develop QQT theory.

In the future, it may become possible to take into account the full PES QQT in the rotationally inelastic collision problem. Contrasting to previous studies in regular or modified QQT, the full PES QQT accounts fully for the softness of the *ab initio* potential energy surface. By application of curved Feynman scattering trajectories, the approximation of the hard shell model can be improved. One may expect this to enhance the accuracy especially of predicting the dynamical behavior governed by attractive potentials.

As for the fully quantum mechanical method, the calculations have become as accurate as experiment for several three–atom and even for some four-atom systems in recent years [8, 14, 16, 18, 129]. Collisions between more complex molecules form still a challenge to study. We still have a great deal to learn in terms of understanding the molecular dynamics at its most fundamental level.

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List of Publications

The following publications are reproduced as chapters in this thesis:

- Xia Zhang, Chris J. Eyles, Craig A. Taatjes, Dajun Ding and Steven Stolte. A general scaling rule for the collision energy dependence of a rotationally inelastic differential cross-section and its application to NO + He. Phys. Chem. Chem. Phys, 2013, 15, 5620.
 Chapter 2.
- Xia Zhang, Chris J. Eyles, Dajun Ding and Steven Stolte. *The modified Quasi-Quantum Treatment of rotationally inelastic NO-He scattering*. Phys. Chem. Chem. Phys, 2015, 17, 4067.
 Chapter 3.
- 3. Xia Zhang, Steven Stolte. A Quasi Quantum treatment of the Spin Orbit state changing and conserving rotationally inelastic NO-He collisions. Chemical Physics, 2018, 514, 4. Chapter 4.
- Xia. Zhang, Gerrit C. Groenenboom, Ad van der Avoird. *Close-coupling calculations of Para-Ortho H₂ conversion rates by H₂-O₂ collisions. Manuscript under preparation. Chapter 5.*

The author also contributed to the following publications:

- 1. Xia Zhang, Dongdong Zhang, Hang Liu, Haifeng Xu, Mingxing Jin, Dajun Ding. *Angular distributions of fragment ions in dissociative ionization of CH*₂*I*₂ *molecules in intense laser fields.* J. Phys. B: At. Mol. Opt. Phys. 2010, 43, 025102.
- C. J. Eyles, M. Brouard, H. Chadwick, F. J. Aoiz, J.Klos, A.Gijsbertsen, X. Zhang and S. Stolte. *The effect of parity conservation on the spin-orbit conserving and spin-orbit changing differential cross sections for the inelastic scattering of NO by Ar.* Phys. Chem. Chem. Phys, 2012, 14, 5420-5439.
- M. Brouard, H. Chadwick, C. J. Eyles, B. Hornung, B. Nichols, J. M. Scott, F. J. Aoiz, J. Klos, S. Stolte, and X. Zhang. *The fully quantum state-resolved inelastic scattering of NO(X) + Ne: experiment and theory*. Molecular physics, 2013, 111, 1759–1771.

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