Inelastic semiclassical collisions in cold dipolar gases

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Abstract. Two elementary models of molecular structure are used to investigate inelastic collisions in cold trapped dipolar gases. A two-state model of a polar molecule (such as one with a $\Lambda$-doublet) permits analytic description of the inelastic collision process at energies considerably higher than the gap energy, predicting rate constants and cross sections given by elementary formulae. Alternatively, a three-state model of a rotor molecule in an electric field is investigated, with resultant rate constants and cross sections scaling simply with molecular mass, rotational constant, dipole moment and polarizing field strength. Semiclassical inelastic collision cross sections and rate constants are demonstrated to depend strongly on the model used, especially as regards their dependence on the polarizing field. Inelastic cross sections among doublet dipoles decrease with increasing field strength, while they increase in proportion to the square of the field strength for collisions between rotor dipoles.
1. Introduction

Recent theoretical studies of elastic dipole–dipole scattering have identified universal cross sections [1] and rate coefficients in a semiclassical regime pertinent to many experimental efforts to trap and cool polar molecules [2, 3]. As summarized in the preceding article in this issue [4], the elastic scattering of two polarized molecules is dominated by a single-length scale, \( D = M \mu^2 / \hbar^2 \), and by a single energy scale, \( E_D = \hbar^6 / M^3 \mu^4 \), where \( \mu \) is the induced dipole moment of the molecule and \( M \) is the reduced mass of the pair of dipoles. A collision is regarded as semiclassical if the deBroglie wavelength \( \frac{2 \pi}{k} < D \), where \( k \) is the collision wavenumber, or alternatively where \( E > \frac{2 \pi^2}{E_D} \). Because molecular masses are large, \( E_D \) is typically measured in tens or hundreds of nanokelvin, so that semiclassical collisions occur even in the microkelvin regime for many molecules.

Semiclassical collisions tend to be impulsive [5]. Semiclassical elastic dipole–dipole cross sections, for example, are understood ([6] and references therein) from the Massey criterion [7], \( \Delta E \Delta t \sim \hbar \). In scaled units, the dipole–dipole energy is \( \sim (D/b)^3 \), where \( b \) is the optimal impact parameter, while the collision time is \( \sim (b/D)/\sqrt{2E/E_D} \), so that the Massey criterion yields the cross section \( b^2 \sim D^2 / \sqrt{2E/E_D} = D/K \). The more elaborate derivation presented in the preceding article, using Glauber’s eikonal approximation [8, 9], yielded the universal result \( \sigma_{\text{ei}} = 8 \pi D/3K \) upon averaging over the polarization direction. It follows that the elastic rate coefficient, \( v\sigma = 8 \pi \hbar D/3M = 8 \pi \mu^2 / 3 \hbar \) is a constant for dipole–dipole scattering in the semiclassical regime, independent of the mass of the collision partners, and tunable to the extent that the induced moment \( \mu \) varies with the applied field (see section 2).

When one considers the wide range of parameters that can affect collisions of heteronuclear molecules, including the mass, rotational and other spectroscopic constants, intrinsic moments of the molecules, and the strength of the polarizing field, (not to mention complex short-ranged
interactions!), the existence of a temperature regime of practical import in which collision cross sections have such elementary scaling properties is a welcome simplification.

The purpose of this paper is to survey how such elementary considerations can be extended to inelastic collisions of polar molecules. Inelastic dipole–dipole collisions are, of course, a primary mechanism of instability in a trap: most traps [10] are designed to confine dipoles of a specific orientation (in low-field seeking states, for example), and inelastic processes typically reverse this orientation for one or both of the collision partners. On a more positive note, inelastic processes may eventually provide important diagnostics of ultracold trapped ensembles through studies of the interaction of such ensembles with a velocity-tuned molecular beam [11]. In any event, it seems remarkable—given the wide energy and temperature ranges of semiclassical collisions—that very few ‘rules-of-thumb’ apply for these elementary and fundamental processes. As the vast majority of molecules are heteronuclear, possess intrinsic dipole moments, and have high mass, the considerations in this paper should apply rather broadly and in contexts far from the cooling and trapping of degenerate gases.

The myriad spectroscopic details associated with heteronuclear molecules, including hyperfine, nuclear, rotational, vibrational and electronic couplings, made even more complex through Stark alignment in an external field, render the theoretical description of even single isolated molecules severely challenging. To then consider collisions of two such molecules, with multiple potential surfaces and associated channels for realignment and/or reactivity, seems a truly daunting task [12]. Our goal, instead, is to seek those simplifying elements that arise solely from the long-range dipole–dipole interactions of the aligned molecules and from the short deBroglie wavelength attendant to the semiclassical energy (or temperature) regime. This basic premise follows the early work of Rogovin [13], who recognized the applicability of Glauber’s eikonal approximation to molecular rotational excitation.

To identify such simplifying elements, we consider here only the two most elementary models of molecular structure, with wanton disregard for all other considerations. Section 2 utilizes a two-state molecule [14], relevant perhaps to a \( \Lambda \)-doublet in a molecule whose electronic angular momentum has a nonzero component along the molecular symmetry axis. Section 3 considers a three-state rotor [15, 16], as might describe weak-field seeking molecules in \( \Sigma \) molecular states. Each section presents the elementary model of the molecule, and then turns to collision dynamics in the semiclassical regime. We conclude with a general discussion in section 4.

2. The simplest model

2.1. Two-state dipoles

The simplest model of a polarizable molecule of intrinsic dipole-moment \( d \) is one with only two states of opposite parity in a field-free region, separated by an energy gap, \( \delta \). For simplicity, consider the lowest state \( |e\rangle \) to have even parity and energy \(-\delta/2\) and the excited state \( |o\rangle \) to have odd parity and energy \(+\delta/2\). Within this representation of parity eigenstates, the molecular Hamiltonian \( H_0 = -d \cdot \vec{E} \) in the presence of a polarizing field \( \vec{E} = E \hat{E} \) is

\[
H = \begin{pmatrix}
-\delta/2 & -dE \\
-dE & +\delta/2
\end{pmatrix} = -\Delta \begin{pmatrix}
\cos \gamma & \sin \gamma \\
\sin \gamma & -\cos \gamma
\end{pmatrix},
\]

\[1\]
where we have introduced a pair of parameters \( \Delta = +\sqrt{\delta/2 + d^2} \) and \( \gamma = \tan^{-1}(2dE/\delta) \). The dipole operator in the parity basis is

\[
\vec{d} = d \hat{\vec{E}} = \begin{pmatrix} 0 & d \\ d & 0 \end{pmatrix} \hat{\vec{E}}.
\] (2)

An example of such a two-state dipole [14] is a molecule whose ground state has nonzero electronic angular momentum along the symmetry axis, \( \Lambda = \hat{\vec{r}} \cdot \vec{L} \). Absent rotations, two states of such a molecule (\( \Lambda \) and \( -\Lambda \)) are degenerate in energy. However, the degeneracy is broken by rotations of the molecular axis \( \hat{\vec{r}} \) either into, or perpendicular to, the electronic charge distribution, producing an energy splitting (i.e. a \( \Lambda \)-doublet) much smaller than the rotational constant of the molecule.

Diagonalization of the Hamiltonian is elementary and yields a pair of states of energy

\[
H' = \begin{pmatrix} -\Delta & 0 \\ 0 & +\Delta \end{pmatrix}.
\] (3)

according to the prescription

\[
(| -\Delta \rangle | +\Delta \rangle) = |e\rangle |o\rangle \begin{pmatrix} \cos(\gamma/2) & -\sin(\gamma/2) \\ \sin(\gamma/2) & \cos(\gamma/2) \end{pmatrix}.
\] (4)

These states have induced dipole moments of

\[
\mu' = -\frac{dH'}{dE} = \begin{pmatrix} \mu & 0 \\ 0 & -\mu \end{pmatrix},
\] (5)

where \( \mu = d^2E/\Delta \) (which tends to \( d \) at high-field strengths). The moment of the lower energy state is aligned with the field axis so that, in an inhomogeneous field, the molecule would seek high fields; conversely, the moment of the high-energy state is anti-aligned with the field and the molecule is a 'low-field seeker'.

For completeness, we also cite the dipole operator (2) in the energy basis

\[
d' = d \begin{pmatrix} \sin \gamma & \cos \gamma \\ \cos \gamma & -\sin \gamma \end{pmatrix} = \mu \begin{pmatrix} 1 & \delta/2dE \\ \delta/2dE & -1 \end{pmatrix}.
\] (6)

We emphasize that \( d'/\mu \) is dependent on both the field and the gap in this model, a characteristic not shared by the more complex model presented in section 3.

Finally, it will prove useful to introduce a third representation—the eigen-dipole basis [17], in which the field–dipole interaction alone is diagonal (as if the splitting of the alternate parity states were zero). In the eigen-dipole basis

\[
(| +d\rangle | -d\rangle) = \frac{1}{\sqrt{2}}(|e\rangle |o\rangle) \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}
\]

\[
= (| -\Delta\rangle | +\Delta \rangle) \begin{pmatrix} \cos[\frac{1}{2}(\gamma - \pi/2)] & \sin[\frac{1}{2}(\gamma - \pi/2)] \\ -\sin[\frac{1}{2}(\gamma - \pi/2)] & \cos[\frac{1}{2}(\gamma - \pi/2)] \end{pmatrix},
\] (7)

the dipole operator is diagonal

\[
d'' = \begin{pmatrix} d & 0 \\ 0 & -d \end{pmatrix}.
\] (8)
Figure 1. The two-state molecule, in which even $|e\rangle$ and odd $|o\rangle$ parity states are coupled by an applied electric field $E$. Two alternative base pairs, the energy eigenstates $|\pm \Delta\rangle$ (blue) and the eigen-dipole states $|\pm d\rangle$ (dashed) are also displayed.

while the energy is not

$$ H'' = \begin{pmatrix} -dE & \delta/2 \\ \delta/2 & dE \end{pmatrix}. $$

(9)

We will see below how these alternative representations produce distinct dynamical equations leading to useful approximation methods for collisional processes. The three different basis sets and their diagonal energies are displayed in figure 1.

2.2. Two-dipole states

We introduced in the previous section the simplest possible model of a polar molecule; that is, a molecule with two energy states of opposite parity in the absence of a polarizing field. We now wish to introduce three different representations of two-molecule states. The convention introduced in the previous section—namely, using un-primed operators for the parity basis, primed operators for the energy basis, and double-primed operators for the eigen-dipole basis—will be retained in this section.

No matter which basis we choose, we should recognize that the dipole–dipole interaction

$$ V(\vec{R}) = \frac{1}{R^3} \left( \vec{d}_1 \cdot \vec{d}_2 - 3(\vec{d}_1 \cdot \vec{R})(\vec{d}_2 \cdot \vec{R}) \right) $$

(10)

with $\vec{R}$ the relative displacement of the center-of-mass of the two dipoles, is invariant under interchange of the dipoles (assumed indistinguishable). Accordingly, of the four possible states

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of a pair of two-state dipoles, we can choose three which are even and one which is odd under dipole interchange. The odd state is not coupled to the others, and so does not contribute to inelastic processes; we will ignore it here.

We will form our three-remaining states from direct products of independent-dipole states, and order them in terms of increasing energy: for the parity basis, we have

\[
|1\rangle = |e, e\rangle,
\]

\[
|2\rangle = \frac{1}{\sqrt{2}} (|e, o\rangle + |o, e\rangle),
\]

\[
|3\rangle = |o, o\rangle,
\]

where, for example, \(|e, o\rangle = |e\rangle|o\rangle\). Likewise, in the energy basis, we have

\[
|1\rangle' = |-\Delta, -\Delta\rangle,
\]

\[
|2\rangle' = \frac{1}{\sqrt{2}} (|-\Delta, +\Delta\rangle + |+\Delta, -\Delta\rangle),
\]

\[
|3\rangle' = |+\Delta, +\Delta\rangle,
\]

and in the eigen-dipole basis

\[
|1\rangle'' = |+d, +d\rangle,
\]

\[
|2\rangle'' = \frac{1}{\sqrt{2}} (|+d, -d\rangle + |-d, +d\rangle),
\]

\[
|3\rangle'' = |-d, -d\rangle.
\]

The Hamiltonian for our system of two dipoles consists of a kinetic energy of relative motion, \(T_{\vec{R}}\), the internal energies of the field-fixed dipoles, and the dipole–dipole interaction (10):

\[
H = T_{\vec{R}} + H^{(0)} + V(\vec{R}),
\]

where the ‘internal’ energy of the dipoles is

\[
H^{(0)} = (H_1^{(1)} - \vec{d}_1 \cdot \vec{E}) + (H_2^{(2)} - \vec{d}_2 \cdot \vec{E}),
\]

while

\[
T_{\vec{R}} = \frac{-\hbar^2}{2M} \nabla^2_{\vec{R}}
\]

and \(M\) is the reduced mass of the pair. Interactions associated with close approach of the molecules are explicitly disregarded since we seek only to evaluate the contribution to scattering processes from high partial waves at semiclassical energies.

It is an elementary (but instructive) exercise to construct these operators in the alternative representations (11–13). In the parity basis, we have

\[
H^{(0)} = \begin{pmatrix}
-\delta & -\sqrt{2}d\epsilon & 0 \\
-\sqrt{2}d\epsilon & 0 & -\sqrt{2}d\epsilon \\
0 & -\sqrt{2}d\epsilon & \delta
\end{pmatrix},
\]

\[
V(\vec{R}) = \frac{\hbar^2}{R^3} \left(1 - 3(\vec{R} \cdot \hat{\vec{E}})^2\right) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}.
\]
while in the energy basis

\[
H^{(0)\nu} = \begin{pmatrix}
-2\Delta & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & +2\Delta
\end{pmatrix}
\]

\[
V(\vec{R})' = \frac{d^2}{R^3} \sin^2 \gamma \left(1 - 3(\vec{R} \cdot \hat{E})^2\right) \begin{pmatrix}
1 & \sqrt{2} \cot \gamma & \cot^2 \gamma \\
\sqrt{2} \cot \gamma & \cot^2 \gamma - 1 & -\sqrt{2} \cot \gamma \\
\cot^2 \gamma & -\sqrt{2} \cot \gamma & 1
\end{pmatrix}
\]

and in the eigen-dipole basis

\[
H^{(0)\nu}'' = \begin{pmatrix}
-2dE & \delta/\sqrt{2} & 0 \\
\delta/\sqrt{2} & 0 & \delta/\sqrt{2} \\
0 & \delta/\sqrt{2} & 2dE
\end{pmatrix}
\]

\[
V(\vec{R})'' = \frac{d^2}{R^3} \left(1 - 3(\vec{R} \cdot \hat{E})^2\right) \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

In the limit of small zero-field splittings, \( \delta \to 0 \), the channels uncouple and are explicitly diagonal in both the energy and the eigen-dipole bases (which become identical). A curious feature of the eigen-dipole representation is that the extreme states \( |1\rangle'' \) and \( |3\rangle'' \) are not directly coupled, but interact only through the intermediate state \( |2\rangle'' \).

In a field-free region, using the representation (11) of parity eigenstates, state \( |2\rangle \) decouples from \( |1\rangle \) and \( |3\rangle \) as a consequence of parity conservation. As the latter two states remain coupled by \( V(\vec{R}) \), inelastic collisions should be expected even in the absence of an aligning field, and will require the ‘flipping’ of both dipoles (with energy defect \( 2\delta \)). Accordingly, using this simple molecular model, we should expect that for very low fields ‘double-flip’ processes will dominate ‘single-flip’ processes in spite of their lower energy defect (i.e. \( \delta \)).

Since we will assume that the highest energy state, in which both molecules are weak-field seekers, is the initial state of our collision complex, it will be convenient to shift all energies by \( E_3 = +2\Delta \), and so to remove it from the equations of motion.

### 2.3. Dimensional analysis

Consider now the full Schrödinger equation associated with the Hamiltonian (14), expressed here in the energy basis

\[
\left[ -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 - (E' + 2\Delta A') \right] \Psi(\vec{R})' = -\frac{\mu^2}{R^3} \left(1 - 3(\vec{R} \cdot \hat{E})^2\right) B' \Psi(\vec{R})',
\]

where \( E' = E - 2\Delta \), \( \Psi \) is a three-component column vector

\[
A' = \begin{pmatrix}
2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

and

\[
B' = \begin{pmatrix}
1 & \sqrt{2} \cot \gamma & \cot^2 \gamma \\
\sqrt{2} \cot \gamma & \cot^2 \gamma - 1 & -\sqrt{2} \cot \gamma \\
\cot^2 \gamma & -\sqrt{2} \cot \gamma & 1
\end{pmatrix}
\]
As in the previous paper in this volume [4], we now introduce dipole units by rescaling both the displacement $\vec{R} = D\vec{r}$ and the energy $E' = \epsilon E_D$, where $D = M\mu^2/\hbar^2$ and $E_D = \hbar^6/M^3\mu^4$, to render (20) in the dimensionless form

$$\left[ -\frac{1}{2}\nabla^2 - \left( \epsilon + 2\frac{\Delta}{E_D}\frac{\Delta'}{\Delta} \right) \right] \Psi'(\vec{r})' = -\frac{1}{r^3} \left( 1 - 3\hat{\vec{r}} \cdot \hat{\vec{E}} \right)^2 B'\Psi'(\vec{r})'.$$

(23)

Measured in dipole units, and neglecting any contributions from close approach of the molecules, collision dynamics is independent of $M$ and depends only on the scale of figure 1 (i.e. $\Delta/E_D$) and on its aspect ratio $\delta/2d\epsilon$ (i.e. cot $\gamma$).

2.4. Semiclassics

It is apparent from (21) and the left-hand side of (23) that three wavenumbers apply far from the scattering region, namely

$$k_1 = \sqrt{2 \left( \epsilon + 4\frac{\Delta}{E_D} \right)};$$

$$k_2 = \sqrt{2 \left( \epsilon + 2\frac{\Delta}{E_D} \right)};$$

$$k_3 = \sqrt{2\epsilon}.$$  

(24)

A minimal requirement for semiclassical analysis to be relevant is that the corresponding wavelengths be less than the intrinsic length scale $D$ of the dipole–dipole interaction. The onset of the semiclassical region can then be expected when (in any units)

$$E' > 2\pi^2 E_D$$

identical to the constraint on elastic semiclassical scattering given in [4]. We mentioned earlier that $E_D$ can lie in the microkelvin regime for some molecules. Energy defects $\Delta$ differ greatly among the polar species, but are typically measured in millikelvin for molecules with small $\Lambda$-doublets.

While (23) appears harmless enough, its severe complexity lies in the anisotropy of the dipole–dipole interaction, which sequentially couples all partial waves of the same parity. Accordingly, in a partial wave analysis with polar axis along $\vec{E}$, (23) consists of approximately $3L_{\text{max}}/2$ coupled second-order differential equations, where $L_{\text{max}}$ is the maximum angular momentum quantum number required for convergence of the cross sections: furthermore, this set of equations must be solved for approximately $L_{\text{max}}$ alternative conserved magnetic quantum numbers $m = \hat{\vec{E}} \cdot \hat{\vec{L}}$, although this number decreases for particular collision geometries. Finally, the entire procedure must be repeated for alternative collision geometries (i.e. $\vec{k}_{\text{inc}} \cdot \vec{E}$) and for each energy of interest. To estimate $L_{\text{max}}$, we note that partial wave contributions to elastic scattering peak at $L \sim \sqrt{k}$ in units of $\hbar$ [4, 18, 19], with the onset of semiclassics at $k \sim 2\pi$. This suggests a minimal requirement of $L_{\text{max}} \sim 6$ at the onset of semiclassics, and increasing by a factor of three for every 10-fold increase in the collision energy or temperature. Progress has been made in performing such calculations, even with more realistic molecular models, though most emphasis has been on energies far colder than suggested by (25), and including only a few partial waves [20]–[23].
In contrast, our approach will be to identify the limiting behavior of inelastic cross sections and rate constants at energies considerably higher than the semiclassical onset (25), where differences in the three wavenumbers (24) are small

\[
k_1 = k + \frac{4\Delta}{kE_D} + \cdots,
\]

\[
k_2 = k + \frac{2\Delta}{kE_D} + \cdots,
\]

\[
k_3 = \sqrt{2\epsilon} = k,
\]

(26)
a requirement satisfied providing \(E' \gg 2\Delta\).

Accordingly, we extract from the wavefunction its dominant phase

\[
\Psi'(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \psi'(\vec{r}),
\]

(27)

where the magnitude of \(\vec{k}\) is simply \(\sqrt{2\epsilon}\), and its direction, \(\hat{k}\), can be chosen at our discretion. Early in the history of semiclassical theory, \(\hat{k}\) was selected to be the direction of incidence of a beam. However, Glauber \[8\] later showed that differential cross sections are improved by choosing \(\hat{k}\) along the direction of the average of the initial and final wavevectors, \((\vec{k}_i + \vec{k}_f)/2\), as this choice better simulates the wavefronts in the vicinity of the scattering center, and better accommodates the manifest symmetries of quantum scattering amplitudes. We need not distinguish these cases here, since semiclassical dipole–dipole scattering is strongly peaked in the forward direction, and since we will only be concerned with total cross sections. Schrödinger’s equation (23) is then

\[
\left[-\frac{1}{2} \nabla^2 - i\vec{k} \cdot \nabla\right] \psi'(\vec{r}) = \left[+2\frac{\Delta}{E_D} A' - \frac{1}{r^3} \left(1 - 3(\hat{r} \cdot \hat{\mathcal{E}})^2\right) B'\right] \psi'(\vec{r}).
\]

(28)

With the dominant phase extracted, the remaining wave amplitude \(\psi'(\vec{r})\) should vary slowly on the scale of the wavelength \(2\pi/k\), in which case its second derivative is negligible

\[
i\vec{k} \cdot \nabla \psi'(\vec{r})' = \left[-2\frac{\Delta}{E_D} A' + \frac{1}{r^3} \left(1 - 3(\hat{r} \cdot \hat{\mathcal{E}})^2\right) B'\right] \psi'(\vec{r})'.
\]

(29)

Choosing cylindrical coordinates aligned with the \(\hat{k}\) axis, \(\vec{r} = \hat{\rho} + z\hat{k}\), and expressing the dipole–dipole potential in more symmetric form gives

\[
i k \frac{\partial}{\partial z} \psi(\hat{\rho}, z)' = \left[-2\frac{\Delta}{E_D} A' + \frac{T\hat{\rho}^2 - 3C\hat{z}\hat{\rho} + Lz^2}{(\hat{\rho}^2 + z^2)^{5/2}} B'\right] \psi(\hat{\rho}, z)',
\]

(30)

where \(T, C\) and \(L\) are geometric constants defined by

\[
T = 1 - 3(\hat{\rho} \cdot \hat{\mathcal{E}})^2,
\]

\[
C = 2(\hat{\rho} \cdot \hat{\mathcal{E}})(\hat{k} \cdot \hat{\mathcal{E}}),
\]

\[
L = 1 - 3(\hat{k} \cdot \hat{\mathcal{E}})^2
\]

(31)

and named to suggest transverse, cross-term and longitudinal parts of the interaction.

Since the partial derivative with respect to \(z\) on the left-hand side of (30) is taken with \(\hat{\rho}\) held fixed, \(\psi\) varies with \(\hat{\rho}\) only parametrically: it may be regarded as the classical impact parameter.
of a rectilinear trajectory (see, for example [24]). A simple change of variables, \(z = \kappa t\), then reduces (30) to the familiar time-dependent Schrödinger equation

\[
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = \left[ -2 \frac{\Delta}{E_D} + \frac{T \tau^2 - 3 C t \tau + L t^2}{k^3 (\tau^2 + t^2)^{5/2}} \right] \psi(\vec{k}, \hat{\rho}, \tau, t)',
\]

where we have replaced \(\rho\) by the collision time \(\tau = \rho / k\), a measure of the width of the collision pulse. It is amusing to note that this time-dependent Schrödinger equation emerges from the time-independent one in the semiclassical limit, a circumstance that belies many textbook presentations on the fundamentals of quantum mechanics and continues to spark interest [25].

The time-dependent form of Schrödinger’s equation emphasizes the impulsive nature of the collision process. The pulse has a width \(\tau\) and a height \(1/(k \tau)^3\). The Massey criterion suggests that the integrated contribution of the potential to the phase will peak when their product is unity (in scaled units), or when \(\tau \sim 1/k^3/2\). In contrast, the phase contribution of the diagonal energy term in (32) will be of order \(2 \Delta \tau / E_D \sim (2 \Delta / k E_d) / \sqrt{k}\). Comparing this with (26), it is clear that the assumption of a common wavenumber in all channels is consistent with neglecting the diagonal energy splittings in (32) during the collision process. We now obtain

\[
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = + \frac{T \tau^2 - 3 C t \tau + L t^2}{k^3 (\tau^2 + t^2)^{5/2}} B' \psi(\vec{k}, \hat{\rho}, \tau, t)' \),
\]

Because the interaction in our simple model is separable into spatial and internal factors, this equation is solved precisely by diagonalizing \(B'\); that is, by transforming to the eigen-dipole basis, where it takes the diagonal form

\[
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = + \frac{T \tau^2 - 3 C t \tau + L t^2}{k^3 \sin^2 \gamma (\tau^2 + t^2)^{5/2}} B'' \psi(\vec{k}, \hat{\rho}, \tau, t)''
\]

with

\[
B'' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]

Schrödinger’s equation can now be integrated, component by component,

\[
\ln \left[ \frac{\psi_i(t)}{\psi_i(-\infty)} \right]'' = -i B'' \int_{-\infty}^{t} ds \frac{T \tau^2 - 3 C s \tau + L s^2}{k^3 \sin^2 \gamma (\tau^2 + s^2)^{5/2}}
\]

with the result

\[
\psi''(+\infty) = U''(+\infty, -\infty) \psi''(-\infty),
\]

where the time-evolution operator has the diagonal form

\[
U''(+\infty, -\infty) = \exp \left[ -i \frac{2 B''}{\tau^2 k^3 \sin^2 \gamma} \left( 1 - (\hat{k} \cdot \hat{\rho})^2 - 2 (\hat{\rho} \cdot \hat{E})^2 \right) \right].
\]

The geometric factors simplify upon introducing spherical-polar coordinates for the polarizing-field direction

\[
\hat{E} = \cos \theta \hat{k} + \sin \theta \cos \phi \hat{\rho} + \sin \theta \sin \phi (\hat{k} \times \hat{\rho}),
\]

so that

\[
U''(+\infty, -\infty) = e^{i B'' x},
\]
where $\chi$ is simply the elastic eikonal phase (see [4]) in the eigen-dipole representation
\[
\chi = \frac{2 \sin^2 \theta \cos \phi}{k \rho^2 \sin^2 \gamma}.
\] (41)

Note that it differs from the eikonal phase for elastic scattering [4] by the factor of $1/\sin^2 \gamma$, an effect that can be traced to the occurrence of the intrinsic dipole moment, as opposed to the induced dipole moment, in (19): recall that $d = \mu/\sin \gamma$. Experimentalists do not prepare and detect eigen-dipole states, but energy states, so (40) must be transformed back into the energy basis, with the result
\[
U'(+\infty, -\infty) = \begin{pmatrix}
\cos \chi + i \sin \chi \sin^2 \gamma & \frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & i \sin \chi \cos^2 \gamma \\
\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & \cos \chi + i \sin \chi \cos 2\gamma & -\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma \\
i \sin \chi \cos^2 \gamma & -\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & \cos \chi + i \sin \chi \sin^2 \gamma
\end{pmatrix}.
\] (42)

Semiclassical analysis has simply resolved the collision into a quantum beat [26] resulting from the mismatch between the creation and detection of energy eigenstates and the quasi-free evolution of eigen-dipole states.

Assuming that our molecules are polarized and trapped in the low-field seeking state $|3\rangle'$, the probability for a single-flip transition, as a function of impact parameter $\rho$, is then
\[
P_{3 \rightarrow 2}(\rho) = \left| \frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma \right|^2 = 2 \sin^2 \gamma \cos^2 \gamma \sin^2 \left[ \frac{2 \sin^2 \theta \cos 2\phi}{k \rho^2 \sin^2 \gamma} \right],
\] (43)

while for a double-flip transition
\[
P_{3 \rightarrow 1}(\rho) = |i \sin \chi \cos^2 \gamma|^2 = \cos^4 \gamma \sin^2 \left[ \frac{2 \sin^2 \theta \cos 2\phi}{k \rho^2 \sin^2 \gamma} \right].
\] (44)

The ratio of single- to double-flip cross sections is therefore
\[
\frac{\sigma_{3 \rightarrow 2}}{\sigma_{3 \rightarrow 1}} = 2 \tan^2 \gamma = \frac{8 d^2 E^2}{\delta^2},
\] (45)

which indicates the propensity for double-flip transitions in weak fields, owing to parity conservation, as discussed earlier.

Explicit estimation of the cross sections follows from an incoherent sum of probabilities over distinct classical paths, i.e.
\[
\frac{\sigma_{3 \rightarrow 2}}{D^2} = \int d\rho P_{3 \rightarrow 2}(\rho) = \frac{2\pi}{k} \cos^2 \gamma \left( 1 - (\hat{k} \cdot \hat{E})^2 \right)
\] (46)

and
\[
\frac{\sigma_{3 \rightarrow 1}}{D^2} = \int d\rho P_{3 \rightarrow 1}(\rho) = \frac{\pi}{k} \cos^2 \gamma \cot^2 \gamma \left( 1 - (\hat{k} \cdot \hat{E})^2 \right).
\] (47)

As with the eikonal elastic scattering cross section [4], and with the eikonal phase (41), our inelastic cross sections vanish when the incident axis is aligned with the polarizing field.
However, as discussed in [4], the semiclassical ansatz is weakest for this collision geometry because of the dominance of low-magnetic quantum number states about the field axis, resulting in severe diffraction of the \( m = 0 \) component of the incident wave.

It is also of interest to extract from (42) a formula for the elastic scattering cross section, and to see whether it deviates from the eikonal result in [4] due to the incorporation of inelastic channels. The amplitude can be rewritten

\[
U_{3\rightarrow 3} = e^{i\chi} - i \sin \chi \cos^2 \gamma
\]  

(48)

and reduces to \( e^{i\chi_{\text{EI}}} \) when \( \gamma \rightarrow \pi/2 \) (or \( \delta \rightarrow 0 \)). However, the elastic cross section cannot be calculated from an incoherent sum of probabilities, as there is no way to distinguish scattered from unscattered trajectories in the beam. Accordingly, some analysis of the diffraction of the beam is required. This is accomplished by substituting our \( \Psi(\vec{r}) \) into the integral equation for the scattering amplitude; the analysis proceeds precisely as indicated in [8], with the result

\[
f_{\text{el}}(\vec{k}_i, \vec{k}_f) = \frac{k}{2\pi i} \int d\vec{\rho} e^{i\vec{q} \cdot \vec{\rho}} \left[ e^{i\chi} - 1 - i \sin \chi \cos^2 \gamma \right],
\]  

(49)

which differs from the eikonal expression in two ways: the replacement of the eikonal phase with the eigen-dipole phase, and the addition of the last term.

The total cross section is then obtained from the optical theorem, to which the last term—which is real—does not contribute

\[
\frac{\sigma_{3\rightarrow 3}}{D^2} = \frac{4\pi}{k} \Im f_{\text{el}}(\vec{k}_i, \vec{k}_f) = 2\pi \int d\vec{\rho} \left[ 1 - e^{i\chi} \right]
\]

\[
= \frac{4\pi}{k \sin^2 \gamma} \left[ 1 - \left( \hat{k}_i \cdot \hat{E} \right)^2 \right] = \frac{\sigma_{\text{EI}}}{D^2 \sin^2 \gamma}.
\]  

(50)

Comparing with (46) and (47), the ratio of inelastic to elastic cross sections is independent of the direction of incidence, with \( \sigma_{3\rightarrow 2}/\sigma_{3\rightarrow 3} = \sin^2 (2\gamma)/8 \) and \( \sigma_{3\rightarrow 1}/\sigma_{3\rightarrow 3} = \cos^4 (\gamma)/4 \). In the limit of zero applied field, \( \gamma \rightarrow 0 \), and the double-flip cross section is one-fourth of the elastic cross section.

Averaging the above results over the direction of the polarizing field, and expressing them as collision rates \( (K = v\sigma) \) in conventional units, we find

\[
K_{3\rightarrow 2} = v\sigma_{3\rightarrow 2} = \frac{4\pi}{3} \frac{d^2}{\hbar} \sin^2 \gamma \cos^2 \gamma,
\]

\[
K_{3\rightarrow 1} = v\sigma_{3\rightarrow 1} = \frac{2\pi}{3} \frac{d^2}{\hbar} \cos^4 \gamma,
\]

\[
K_{3\rightarrow 3} = v\sigma_{3\rightarrow 3} = \frac{8\pi}{3} \frac{d^2}{\hbar},
\]  

(51)

where \( v \) is the incident velocity. To set the scale, note that for a dipole moment of 1 Debye = 0.39 au, \( K_{3\rightarrow 3} = 7.8 \times 10^{-9} \text{cm}^3 \text{s}^{-1} \). This corresponds to quite large cross sections: for example, for a zero-field energy splitting of \( \delta = 4 \text{mK} \), at an impact energy of \( E' = 108 \text{a} \), a molecule of mass 20 amu has a velocity of 3000 cm s\(^{-1}\), corresponding to a cross section of \( 2.6 \times 10^{-4} (\mu \text{m})^2 \). Results with similar scaling, but different magnitudes, were obtained earlier by applying a unitarized version of perturbation theory [27].

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The beauty of dimensional analysis and dipole scaling is illustrated by comparing these results with another manifestation of dipolar interactions in atomic collision physics. For example, opposite parity Na\((n, s)\) and Na\((n-1, p)\) Rydberg states are coupled through a resonant interaction of intrinsic moment \(d = \langle n-1, p | z | n, s \rangle \propto n^2\text{au}\). Cross sections for resonant excitation at thermal velocities \(v = 10^{-4}\text{au}\) therefore have collision cross sections of \(n^4/v\), which, for \(n = 20\) corresponds to \(10^9\alpha_0^2\), as discussed in a series of articles by Gallagher and co-workers [6, 28].

Importantly, the elastic rate \(K_{3\to3}\) differs from the eikonal result, in that it depends on the intrinsic rather than the induced dipole moment. At high collision speeds, it is the intrinsic dipole moment that matters, and therefore the elastic rate is independent of the applied field. It is also curious that, in this simple model, even in the absence of a polarizing field, the dipole–dipole interaction results in significant rate constants for both elastic and inelastic scattering over a broad temperature range, with the inelastic constant equal to 1/4 of the elastic constant.

Other seminal characteristics of the model are displayed in figure 2, including (a) the suppression of single-flip transitions at zero field due to parity conservation, (b) the dominance of single-flip transitions at high-field strengths due to their smaller energy defect, (c) the rapid decline of inelastic processes with increasing field strength, and (4) a total inelastic rate constant which peaks at one-fourth of the elastic collision rate. For an electric field of 300 V cm\(^{-1}\) and a dipole moment of 1 Debye, a molecule with a gap of \(4 \times 10^{-3}\text{K}\), would have an aspect ratio of \(2dE/\delta = 3.6\).

Finally, note that the decline of the inelastic rates with increasing field contrasts with the low-energy results of [23], in which inelastic hyperfine transitions increase and saturate with applied field at collision energies far below the semiclassical onset. However, at higher energies,
the coupled-channel calculations in [23] do suggest both the 1/k scaling of all cross sections and the preponderance of elastic over inelastic collisions as follows from the analysis presented above.

3. Rotor dipoles

3.1. Three-state dipoles

A very different, yet still quite simple, model of a polar molecule is formed by the states of a rigid rotor in a polarizing field [15, 16], with Hamiltonian

\[ H = B \vec{L}^2 - d \hat{r} \cdot \vec{E}, \]  

(52)

where \( \vec{L}^2 \) is the squared angular momentum operator of the rotor with eigenvalues \( L(L+1) \) (L integral), \( B \) is the rotational constant in units of energy, \( d \) is the intrinsic dipole moment of the molecule, and \( \hat{r} \) is the direction of orientation of the rotor axis. This Hamiltonian is invariant under rotations about the field axis, so that \( \hat{E} \cdot \vec{L} \) is conserved, with integer eigenvalues \( m \).

The energy spectrum of (52) is readily constructed to second order in the polarizing field by elementary perturbative methods. The three states of interest correlate to the odd-parity \( L = 1 \) states as \( \hat{E} \rightarrow 0 \). In the representation \( |L, m\rangle \), the upper (low-field seeking) state is

\[ |0\rangle = \left[ |1, 0\rangle - \frac{dE}{2B\sqrt{3}} \left( |0, 0\rangle - \frac{1}{\sqrt{5}} |2, 0\rangle \right) + \cdots \right] \]  

(53)

with energy

\[ E_0 = 2B + \frac{d^2E^2}{10B} + \cdots. \]  

(54)

There are also two degenerate (high-field seeking) states

\[ |\pm 1\rangle = \left[ |1, \pm 1\rangle + \frac{dE}{4B\sqrt{5}} |2, \pm 1\rangle + \cdots \right], \]  

(55)

of energy

\[ E_{\pm 1} = 2B - \frac{d^2E^2}{20B} + \cdots. \]  

(56)

We have chosen to label the states by their conserved magnetic quantum number, \( m \). In the presence of a field, the three-odd parity states accordingly form a polar multiplet, with an energy gap of

\[ \Delta = \frac{3d^2E^2}{20B}, \]  

(57)

as displayed in figure 3. For illustration, the physical attributes of a few molecules are listed in table 1 at a presumed electric field strength of 1 kV cm\(^{-1}\).

The dipole operator in the basis of our three states (ordered \( |1\rangle, |0\rangle, |−1\rangle \)) is

\[ \vec{d}' = d\vec{r}' = \mu \left[ \hat{z} \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1/2 \end{pmatrix} + \hat{e}_- \begin{pmatrix} 0 & 5/4 & 0 \\ 0 & 0 & -5/4 \\ 0 & 0 & 0 \end{pmatrix} + \hat{e}_+ \begin{pmatrix} 0 & 0 & 0 \\ 5/4 & 0 & 0 \\ 0 & -5/4 & 0 \end{pmatrix} \right], \]  

(58)

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**Figure 3.** A model three-state dipole constructed to second order in the polarizing field $\mathcal{E}$, for a rigid rotor of rotational constant $B$. Three odd-parity states ($L = 1; m = 0, \pm 1$) form a polar multiplet of energy defect $\Delta$: the splitting is produced by electric field coupling to even parity states which are energetically far removed.

**Table 1.** Physical parameters of some molecules with rotor-like spectra. The last six entries for each molecule are field-dependent; values are given assuming a field of strength $\mathcal{E} = 1$ kV cm$^{-1}$.

| Molecule | Mass (amu) | $d$ (Debye) | $B$ (K) | $\mu$ (Debye) | $\Delta$ (K) | $D$ (µm) | $E_D$ (K) | $\Delta / E_D$ | $d\mathcal{E} / B$ |
|----------|------------|-------------|--------|---------------|-------------|---------|---------|-------------|----------------|
| NaF      | 42         | 8.16        | 0.625  | 0.516         | 9.38(-3)    | 8.35(-2) | 3.31(-6) | 2.83(+3)    | 0.316          |
| KF       | 58         | 8.59        | 0.401  | 0.891         | 1.62(-2)    | 3.44(-1) | 1.41(-7) | 1.15(+5)    | 0.519          |

where we use standard polarization unit vectors $\hat{\epsilon}_\pm = (\hat{x} \pm i\hat{y}) / \sqrt{2}$, and where

$$\mu \equiv \frac{d^2 \mathcal{E}}{5B}$$

is the magnitude of the induced dipole moment of the weak-field seeking state $|0\rangle$. Note that

$$\mu' = -\frac{dH'}{d\mathcal{E}} = \begin{pmatrix} \mu/2 & 0 & 0 \\ 0 & -\mu & 0 \\ 0 & 0 & \mu/2 \end{pmatrix}.$$  

These results indicate that rotor dipoles are both far more complex and far simpler than the two-state dipoles of section 2! They are more complex because the component matrices $d_\pm, d_x$ and $d_z$ do not commute with one another: accordingly, it is not possible to construct eigen-dipole states, and we should expect non-Abelian time-evolution in the semiclassical theory. To see why
Figure 4. The energy spectrum of two non-interacting rotor dipoles. The initial state, in which both dipoles are weak-field seekers, is labeled $E_1$. Only symmetric states are coupled to it by dipole–dipole interactions.

...they are simpler, compare the energy-representations of the dipole operators, (6) and (58). Since $\vec{d}/\mu$ is entirely independent of the polarizing field for rotor dipoles, they will display a much higher degree of universality than two-state dipoles. There is no analogue to the aspect ratio $\cot \gamma$ for rotor dipoles.

3.2. Two-rotor states

Nine direct-product states can be formed from a system of two rotor dipoles. The eigenenergies of the non-interacting Hamiltonian

$$ H^{(0)} = \left( B \vec{L}_1^2 - \vec{d}_1 \cdot \vec{E} \right) + \left( B \vec{L}_2^2 - \vec{d}_2 \cdot \vec{E} \right) $$

are displayed in figure 4. The spectrum separates into states, which are either even or odd under dipole interchange. The even states are

$$ |1\rangle = |0, 0\rangle, \quad E_1 = 4B + 4\Delta/3, $$
$$ |2\rangle = (1/\sqrt{2}) (|1, 0\rangle + |0, 1\rangle), \quad E_2 = E_1 - \Delta, $$
$$ |3\rangle = (1/\sqrt{2}) (| - 1, 0\rangle + |0, -1\rangle), \quad E_3 = E_1 - \Delta, $$
$$ |4\rangle = |1, 1\rangle, \quad E_4 = E_1 - 2\Delta, $$
$$ |5\rangle = (1/\sqrt{2}) (|1, -1\rangle + | - 1, 1\rangle), \quad E_5 = E_1 - 2\Delta, $$
$$ |6\rangle = | - 1, -1\rangle, \quad E_6 = E_1 - 2\Delta, $$

while for the odd states

$$ |7\rangle = (1/\sqrt{2}) (|1, 0\rangle - |0, 1\rangle), \quad E_7 = E_1 - \Delta, $$
$$ |8\rangle = (1/\sqrt{2}) (| - 1, 0\rangle - |0, -1\rangle), \quad E_8 = E_1 - \Delta, $$
$$ |9\rangle = (1/\sqrt{2}) (|1, -1\rangle - | - 1, 1\rangle), \quad E_9 = E_1 - 2\Delta. $$
While inelastic collisions can now occur among the odd states, they are nevertheless not coupled to state $|1\rangle$, which we choose as the initial state of the collision process. We therefore consider transitions among the six even states, with energy gaps of $\Delta$ and $2\Delta$, and with one, two and threefold degeneracy, respectively.

Since we will neglect transitions to states outside of the dipole multiplets, it will be convenient to shift all energies by $E_1$, and so to remove it from the equations of motion which follow.

3.3. Dimensional analysis

The full wave Shrödinger equation for our system of two rotor dipoles can now be written (in the energy representation)

$$
-\frac{\hbar^2}{2M} \nabla^2_{\vec{R}} - \left( E' + \Delta A' \right) \Psi(\vec{R})' = - \frac{\mu^2}{R^3} B'(\vec{R}) \Psi(\vec{R})',
$$

where $E' = E - 4B - 4\Delta/3$,

$$
A' = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & 0 \\
0 & 0 & 0 & 0 & 2 & 0 \\
0 & 0 & 0 & 0 & 0 & 2
\end{pmatrix}
$$

and where $B'$ is a rather cumbersome $6 \times 6$ matrix, which we will not specify explicitly. A key feature of the model, however, is that, having extracted $\mu^2$ from the dipole–dipole interaction, $B'$ depends only on $\hat{R}$ and on the orientation unit vectors $(\hat{z}, \hat{\epsilon}_\pm)$ of the dipole states, where $\hat{z}$ is the direction of the polarizing field.

Transforming to dipole units, $\vec{R} = D\vec{r}$ and $E' = E_D\epsilon$, precisely as specified in section 2, leaves the dimensionless form

$$
-\frac{1}{2} \nabla^2_{\vec{r}} - \left( \epsilon + \frac{\Delta}{E_D} A' \right) \Psi(\vec{r})' = - \frac{1}{R^3} B'(\vec{r}) \Psi(\vec{r})'.
$$

Measured in dipole units, and neglecting contributions from close approach of the molecules, collision dynamics of a pair of rotor dipoles is independent of $M$, and depends solely on the dimensionless ratio $\Delta/E_D$.

3.4. Semiclassics

Free relative motion of the rotors, far from the interaction region, is characterized by three distinct wavenumbers

$$
k_1 = k_k = \sqrt{2\epsilon},
$$

$$
k_2 = k_3 = \sqrt{2 \left( \epsilon + \frac{\Delta}{E_D} \right)} \approx k_1 + \frac{\Delta}{k_1 E_D} + \cdots,
$$

$$
k_4 = k_5 = k_6 = \sqrt{2 \left( \epsilon + \frac{2\Delta}{E_D} \right)} \approx k_1 + \frac{2\Delta}{k_1 E_D} + \cdots,
$$

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so that the minimal requirement for the onset of semiclassical physics is that the kinetic energy of relative motion in the initial state (assumed to be the uppermost state with two weak-field seekers, \(|0, 0\rangle\)) is

\[ E' > 2\pi^2 E_D. \]  \tag{68} 

To extract a common wavenumber in all channels, however, we make the more stringent requirement \(E' \gg \Delta\).

These assumptions lead, according to the prescription given in section 2, to the time-dependent Schrödinger equation

\[ i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = \left[ -\frac{\Delta}{E_D} A' + \frac{T' \tau^2 - 3C't\tau + L't^2}{k^3(\tau^2 + t^2)^{3/2}} \right] \psi(\vec{k}, \hat{\rho}, \tau, t)', \]  \tag{69} 

where \(T', C'\) and \(L'\) are now matrices of the operators

\[ T = \frac{1}{\mu^2} \left[ \vec{d}_1 \cdot \vec{d}_2 - 3(\hat{\rho} \cdot \vec{d}_1)(\hat{\rho} \cdot \vec{d}_2) \right], \]

\[ C = \frac{1}{\mu^2} \left[ (\hat{\rho} \cdot \vec{d}_1)(\hat{k} \cdot \vec{d}_2) + (\hat{k} \cdot \vec{d}_1)(\hat{\rho} \cdot \vec{d}_2) \right], \]  \tag{70} 

\[ L = \frac{1}{\mu^2} \left[ \vec{d}_1 \cdot \vec{d}_2 - 3(\hat{k} \cdot \vec{d}_1)(\hat{k} \cdot \vec{d}_2) \right], \]

which, upon explicit evaluation, are independent of \(d, \mu\) and \(E\) and depend only on geometric factors: recall the values of \(\vec{d}/\mu\) from (58).

The \(\Delta/E_D\) term is negligible at sufficiently high energies, at which point collisions of rotor dipoles become truly universal; that is, (69) has no remaining parameters. To illustrate this transition to the high-energy limit, we integrated (69) numerically for the specific collision geometry in which the angle of incidence relative to the polarizing field is 45°. For each impact parameter \(\hat{\rho}\), starting in state \(|1\rangle\), probabilities for transitions among the six states of the model were calculated using Runge–Kutta propagation. These were then integrated over all impact parameters to obtain inelastic cross sections and collision rates. Results for single-flip transitions are shown in figure 5, where they are compared with similar calculations that neglect the \(\Delta/E_D\) term in (69). Note that at incident kinetic energies greater than 10 times the energy gap, the \(\Delta/E_D\) term in (69) becomes negligible, and

\[ i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = + \frac{T' \tau^2 - 3C't\tau + L't^2}{k^3(\tau^2 + t^2)^{3/2}} \psi(\vec{k}, \hat{\rho}, \tau, t)' \equiv V'(t)\psi(\vec{k}, \hat{\rho}, \tau, t)', \]  \tag{71} 

which is parameter-free within the three-state rotor model.

As anticipated, with rotor dipoles, the time dependence of the interaction does not separate from geometric factors, and the matrix on the right-hand side of (71) cannot be rendered in diagonal form at all times. The absence of an eigen-dipole representation in this case implies a richer dynamics than in the case of two-state dipoles. Results of a complete numerical solution of this equation are presented below: however, an approximate solution which closely approaches the exact numerical results is first detailed to illustrate the impulsive nature of the collision process.
3.5. Sudden limit

One approach to the solution of (71) is to construct the Magnus [12] expansion to the time-evolution operator

$$U'(t,t_0) = \exp M'(t,t_0),$$

(72)

in which $M'$ is a matrix that is expressed as a series

$$M'(t,t_0) = -i \int_{t_0}^{t} dt_1 V'(t_1) - \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 [V'(t_1), V'(t_2)] + \cdots$$

(73)

and where higher order terms in the series involve higher order commutators of the potential matrix with itself at different times. The expansion is predicated upon the notion that, for interactions that are strongly pulsed—or for short periods of propagation $(t - t_0)$—successive terms in the expansion are of one higher order in the pulse width, so that the expansion may be terminated at a specified order without compromising the unitarity of $U'$.

Consider now evaluating the Magnus series over the entire duration of the collision process, from $t = -\infty$ to $t = +\infty$. The scaling of successive terms is elementary: the $N$th term contains $N$ powers of the potential, and $N$ factors $dt$. Setting $t = \tau \sigma$ for each time variable, and extracting all powers of $\tau$ and $k$ from the various integrals, one finds that the $N$th term is proportional to $(1/k \rho^2)^N$. Since we are interested here only in the high-energy limit, this suggests retaining only the first term in the series, which is known as the infinite-order sudden approximation,
given by

\[ U'(-\infty, \infty) = \exp \left\{ -i \int_{-\infty}^{\infty} dt V'(t) \right\} = \exp \left\{ -i \frac{2(2T'(\theta, \phi) + L'(\theta, \phi))}{3k\rho^2} \right\} , \tag{74} \]

where we note explicitly the dependence on the direction of the polarizing field (39).

Within the sudden approximation, the collision process has again been reduced to a quantum beat: energy eigenstates are prepared and detected in experiments, but it is the sudden eigenstates of \( 2T' + L' \) that evolve freely in time. Accordingly, a diagonal \( U S \) is first evaluated by diagonalizing and exponentiating the \( 2T' + L' \) operator for each orientation of the field. The eigenvectors of the diagonalization are then used to transform back to the energy representation for the calculation of transition amplitudes, precisely as indicated in section 2.

Results of these sudden approximation calculations are discussed below, where they are compared with exact results obtained by direct numerical integration of (71) for each impact parameter and collision geometry.

3.6. Results

The universal characteristics of collisions of rotor dipoles emerge, not from semiclassical analysis, but directly from the dimensionless form of (64), which indicates that our calculated cross sections depend only on the ratio \( \Delta / E_D \). Furthermore, even this dependence vanishes in the high-energy limit. Let us consider what this high-energy universality implies for our calculated cross sections and collision rates. By changing variables to \( t = \tau \sigma \), one can see directly that (71) depends only on the combination \( k\rho^2 \). Since cross sections are obtained by integrating dimensionless probabilities over \( d\rho d\varphi \), a change of variables \( s = k\rho^2 \) yields \( (1/2k) \int ds P(s) \). Accordingly, all cross sections must scale as \( 1/k \) at sufficiently high velocities, either in the exact solutions of (69) or in the sudden approximation; i.e. for \( E' \gg \Delta \)

\[ \frac{\sigma_{1 \rightarrow j}}{D^2} = \frac{C_{1 \rightarrow j}(\cos \theta)}{k} \],

where \( C \) is a dimensionless function of the angle between the polarizing field and the beam, \( \cos \theta = \hat{k} \cdot \hat{z} \). This implies rate constants (for final states \( j \neq 1 \)) in conventional units (with dimensions \( [L^3/T] \))

\[ K_{1 \rightarrow j} = \frac{\hbar K}{M} \sigma_{1 \rightarrow j} = \frac{\mu^2}{\hbar} C_{1 \rightarrow j}(\cos \theta) = \frac{d^2}{25\hbar} \left[ \frac{dE}{B} \right]^2 \]

\[ C_{1 \rightarrow j}(\cos \theta) \].

Note that the rate constants all vanish in the absence of a polarizing field, in contrast to the two-state dipoles of section 2. For the molecules listed in table 1, assuming a polarizing field of 1 kV cm\(^{-1} \), \( \mu^2/\hbar \) in (76) is \( 2.6 \times 10^{-10} \) cm\(^3\) s\(^{-1} \) for NaF and \( 2.75 \times 10^{-10} \) cm\(^3\) s\(^{-1} \) for KF.

The variation of inelastic rates with angle of incidence relative to the field, embodied by universal dimensionless coefficients \( C_{1 \rightarrow j}(\cos \theta) \), is shown in figure 6. The sum of the coefficients for single-flip and double-flip transitions is plotted versus the angle of incidence, revealing a preponderance of double-flip processes for all geometries. Note that the sudden approximation agrees qualitatively with the exact numerical results, and agrees quantitatively within 10% when averaged over the angle of incidence; thereby illustrating the impulsive nature of these inelastic processes.
Figure 6. Universal dimensionless angular distributions of inelastic collision rates of rotor dipoles, plotted as a function of the angle of incidence relative to the field axis. The dashed curves were calculated in sudden approximation, whereas the solid curves are exact numerical results. Collision rates are obtained by multiplication of these curves by $\mu^2/\hbar$ for the dipole of interest.

Figure 6 also reveals another qualitative difference with the two-state dipoles discussed in section 2. While all cross sections (elastic and inelastic) vanish when $\hat{k}_i \cdot \hat{E} = 1$ for two-state dipoles, the two-flip cross section for rotor dipoles actually peaks for this collision geometry.

4. Discussion

It is striking that the two simplest models of a dipole yield dramatically different results for elastic and inelastic collision rates. Inelastic scattering of two-state dipoles peaks at zero field, whereas all scattering cross sections vanish in this limit for rotor dipoles. In some sense, the ‘intrinsic’ dipole moment of a rotor molecule should probably be called a ‘virtual’ moment instead; it exists only due to the indirect influence of far-distant even-parity spectator states of the molecule, and so becomes observable at zero field only at energies larger than the rotational constant of the molecule (which are not explored here). Furthermore, the angular distributions of the collision rates could hardly be more different in the two models.

Since even the two simplest models yield qualitatively different results, one might expect plenty of subtleties as models become richer and more realistic.

Most real molecules have more complex spectra than do our models, and so the results presented herein should be used with caution. We have made estimates where it seemed that they would assist in orienting the reader, but these should also be viewed skeptically. In particular, the $\Lambda$-doubling of many real molecules is not well represented by our two-state analogy [14],

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and often involves a complex mix of hyperfine levels. As with all good ‘rules-of-thumb’, the most interesting cases may be where the formulae do not apply.

However, the techniques of dimensional analysis and semiclassical estimation, developed early in the history of quantum mechanics and applied here in the context of cold and ultracold molecular gases, are more reliable than the model-dipoles themselves, and, hopefully, can be developed and extended to more realistic models and toward the interpretation of ongoing experiments. Accordingly, we have attempted to clarify both the reasoning behind and the limitations of semiclassical theory as it applies to these systems.

Even our simple models are not yet complete. It would be nice to see, for example, the dependence of collision rates on $\Delta / E_D$ down to energies approaching $\Delta$ within the semiclassical analysis; i.e. using (32) and (69). Furthermore, the models could be extended to ultracold temperatures using the full wave Schrödinger equations, (23) and (66), which retain universal characteristics, albeit with the additional complexity of differentiating Bose from Fermi molecules: but these analyses remain beyond the scope of this article.

Finally, as was the case with elastic scattering [4], the semiclassical formulae presented herein present high energy limits that can be used to test fully quantum mechanical close-coupling codes, and so provide a useful constraint to other theoretical analyses.

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