On the energy dependence of the steric effect in atom–molecule reactive scattering. I. A quasiclassical approach

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Experimental studies have shown that the steric effect in chemical reactions can decrease (e.g., for Ba+N2O→BaO*+N2) or increase [e.g., for Ca(1D2)+CH3F→CaF*+CH4] with increasing translational energy. Decreasing (negative) energy dependences have successfully been modeled with the angle dependent line of centers model. We present a classical model in which a positive energy dependence of the steric effect is explained by an isotropic, attractive long range potential. In this “trapping” model we assume the reaction—apart from a cone of nonreaction at one side of the molecule—to be barrierless. This model shows that a positive energy dependence of the steric effect is not indicative of reorientation of the molecule, as has been suggested in the literature. Rather, the positive or negative energy dependence of the steric effect is shown to correlate with the absence or presence of a barrier to reaction and an attractive or repulsive long range potential. For the reorientation effects which occur in the case of anisotropic potentials, we consider the application of the standard quasiclassical trajectory (QCT) method and we introduce a modified QCT method. We argue that the latter is more suitable for the computation of the orientation dependent reactive cross section.

I. INTRODUCTION

The dependence of the reactivity on the orientation of the reagents is a key issue in dynamical stereochemistry.\(^{1,2}\) Experimentally, a symmetric top molecule with nonzero dipole moment (or a symmetric top like molecule such as N2O) can be oriented using a hexapole state selector\(^3\) followed by a homogeneous electric field. This technique allows the control of the (average) orientation \((\bar{\theta})\) of the molecular symmetry axis with respect to the initial relative velocity of the reagents in a crossed beam experiment. The first experiments of this type were done by Brooks et al.\(^4\) and Beuhler et al.\(^5\) for the reactions of K and Rb with partially oriented CH3I. Recently, Janssen, Parker, and Stolte\(^6\) performed experiments with well defined initial states for the reaction of Ca(1D2)+CH3F(JKM). They report the steric effect, i.e., the difference between the reactive cross sections for favorably and unfavorably oriented molecules relative to the reactive cross section for unoriented molecules, as a function of the angle of attack \((\gamma)\) between the symmetry axis of the molecule and the line of centers (i.e., the line connecting the centers of mass of the two reactants). Usually, \(\gamma=0^\circ\) corresponds to the relative orientation most favorable for reaction. Furthermore, the barrier is often taken to be infinite between a certain cutoff angle \((\gamma=\gamma_c)\) and \(\gamma=180^\circ\). This region is called “cone of nonreaction.”

The reason for the current study is the surprising positive energy dependence of the steric effect measured for the Ca(1D2)+CH3F reaction. With the ADLC model in mind this is counterintuitive; one would expect that at higher energies the trajectories will have enough energy to cross the angle-dependent barrier over a wider range of angles of attack \(\gamma\), thus opening up the “cone of reaction” and lowering the steric effect. The ADLC model has successfully been used to account for the negative energy dependence of the steric effect in the reaction of Ba+N2O.\(^6\)

It has been suggested\(^6,11\) that the decrease of the steric effect at lower energies for the Ca(1D2)+CH3F reaction might be caused by reorientation of the CH3F molecule due to anisotropic long range interactions between CH3F and the electronically excited Ca(1D2). Supposedly, the “F end” of the CH3F molecule would rotate towards the approaching Ca(1D2), thus washing out the effect of the initial orientation of the molecule. At higher translational energies there would not be enough time for this reorientation to occur and the steric effect would increase.

However, in a series of trajectory calculations, employing several potential energy surfaces (PESs) (both ad hoc potentials and potentials based on computed electrostatic long range interactions) we found that the anisotropy in the potential, even though it can cause some reorientation, contributes little to the decrease of the steric effect.\(^12\) Under certain conditions, it might even increase the steric effect. At the same time, however, we find that it is possible to reproduce the experimentally found positive energy dependence of the steric effect with a model employing a purely isotropic long-range potential in combination with an angle dependent barrier that is zero between \(\gamma=0^\circ\) and the cutoff angle \(\gamma=\gamma_c\).
between $\gamma$ and $\theta$ is less important, on the other hand, for
have relatively small impact parameters and the distinction
be reactive. Hence, in that case, reactive trajectories will
is usually focused on $\gamma$. For example, an orientational opac-
literature several times. However, most of the attention
a certain range of $\gamma$. In Sec. II we define the orientation dependent cross section in terms of $\theta$. This definition was first introduced by
have an appealing physical interpretation: $\sigma_0$ is the
total cross section, $\sigma_1/\sigma_0$ is the orientation or steric effect and
In Sec. III we work out the theory for the computation of the orientation dependent cross section for isotropic potentials of the form
$V(R) = e R^{-n}$, \hspace{1cm} (1)
with $n=1...6$. We include both the attractive ($c<0$) and
the repulsive ($c>0$) case, where the former corresponds to a bar-
rierless reaction and the latter to a reaction with a barrier. We
will show the energy dependence of the first three Legendre moments ($\sigma_0$, $\sigma_1/\sigma_0$, and $\sigma_2/\sigma_0$) for several values of the
cutoff angle $\gamma_c$. This is possible because the result turns out
not to depend on $R_f$, $c$, and $E$ separately, but rather on one
dimensionless parameter, the reduced energy $\alpha = ER_f/c$. We
only give results for $n=4$ since this corresponds to the lead-
ting term in the long range potential for Ca$^+(D_2)+\text{CH}_2\text{F}$. The
dependence of the leading term in the Ca$^+(D_2)+\text{CH}_2\text{F}$ long range potential arises from the electrostatic interaction
between the dipole moment of $\text{CH}_2\text{F}$ and the quadrupole moments of the
substates of Ca$^+(D_2)$. For more details see Ref. 12.
In Sec. IV we discuss the case of a general anisotropic potential. In this case the rotation of the symmetric top molecule must be explicitly included in the model. One way to compute the orientation dependent cross section is by a standard quasiclassical trajectory (QCT) simulation of the
experiment. We will show, however, that with this method the
equations to obtain the Legendre moments $\sigma_0/\sigma_0$ for $i>1$
must be adapted in order to be consistent with the isotropic
model. We present an alternative method which we call the
modified quasiclassical trajectory (MQCT) method. This
method yields again the same results for isotropic potentials,
but we will argue that it is better for arbitrary anisotropic
potentials. Furthermore, the MQCT method has numerical
advantages.
We do not give numerical results for the anisotropic case. Rather, we will show the application of this theory to Ca$^+(D_2)+\text{CH}_2\text{F}$ in a separate paper. The reason for this is
that the application to this system involves several issues,
such as the choice of the potential and its asymptotic
spectrum, which are beyond the scope of the present paper.
II. THE ORIENTATION DEPENDENT CROSS SECTION

Information about the energy dependence of the steric effect is obtained by measuring the energy dependent, initial state selected, reactive cross sections $\sigma^{RM}(E)$. The symmetric top quantum numbers are $J$, the total angular momentum, $M$, the projection of $J$ onto the space fixed $z$ axis (which is

![FIG. 1. High impact parameter (b) trajectories can be trapped by an isotropic long-range potential at low translational energy, thus washing out possible steric effects. In this figure, $r$, $r_f$, and $r_f^*$ are reduced quantities, i.e., $\hat{b}=b/b_{\text{max}}$, and $r_f=r_f/b_{\text{max}}$, where $b_{\text{max}}$ is the largest impact parameter that can lead to reaction. The subscript $f$ means at the harpooning radius and $R$ and $\chi$ are the space-fixed polar coordinates of the line of centers.](image)
defined parallel to the homogeneous electric field) and \( K \), the projection of \( J \) on the molecular symmetry axis (\( z' \)). Different \( M \) states (for given \( J \) and \( K \)) have different average orientations

\[
\langle \cos \theta \rangle_{JKM} = \frac{KM}{J(J+1)},
\]

where \( \theta \) is the angle between \( z \) and \( z' \). The experimental setup is such that the relative velocity of the reagents is (approximately) parallel to the homogeneous electric field. Thus measuring \( \sigma^{كم}(E) \) for a set of \( M \) values gives information about the orientation dependence of the reactive cross section. Since a given \( M \) state does not correspond to a sharp value of \( \rho = \cos \theta \), but to a distribution of \( \rho \) values \( \varphi^{كم}(\rho) \) (see Appendix A), we define the orientation dependent cross section \( \sigma^{JK}(\rho, E) \) implicitly by

\[
\sigma^{كم}(E) = \int \sigma^{JK}(\rho, E) \varphi^{كم}(\rho) d\rho.
\]

Usually, the orientation dependent cross section is defined in the context of a classical model in which the rotation of the molecule is decoupled from the motion of the approaching atom. In such a model, \( \sigma^{JK}(\rho, E) \) arises as the reactive cross section for a nonrotating molecule with a fixed orientation \( \rho = \cos \theta \). In that case, the initial distribution \( \varphi^{كم}(\rho) \) remains unchanged during the approach of atom and Eq. (3) can be used to compute \( \sigma^{كم}(E) \) as a weighted average of \( \sigma^{JK}(\rho, E) \). In our definition \( \sigma^{JK}(\rho, E) \) does not arise from any specific model, but is defined as a function that satisfies Eq. (3) for known \( \sigma^{كم}(E) \) and \( \varphi^{كم}(\rho) \). For given values of \( J \) and \( K \) there are only \( 2J+1 \) possible \( M \) values (\( M = -J, -J+1, \ldots, J \)) and there could still be an infinite number of functions \( \varphi^{كم}(\rho) \) satisfying Eq. (3). We fix \( \sigma^{JK}(\rho, E) \) by the additional requirement that it is a linear combination of \( 2J+1 \) Legendre polynomials,

\[
\sigma^{JK}(\rho, E) = \sum_{l=0}^{2J} \sigma^{JK}_l(E) P_l(\rho).
\]

The probability distribution function \( \varphi^{كم}(\rho) \) can also be expanded in Legendre polynomials

\[
\varphi^{كم}(\rho) = \sum_{l=0}^{2J} c^{كم}_l P_l(\rho).
\]

The expansion coefficients \( c^{كم}_l \) are known analytically (see Appendix A). By substituting Eqs. (4) and (5) into Eq. (3) and integrating over \( \rho \), we obtain the following set of \( 2J+1 \) linear equations relating the Legendre moments \( \{ \sigma^{JK}_l(E) \}_{l=0, 1, \ldots, 2J} \) to the reactive cross sections \( \{ \sigma^{كم}(E) \}_{M = -J, -J+1, \ldots, J} \):

\[
\sigma^{كم}(E) = \sum_{l=0}^{2J} \sigma^{JK}_l(E) c^{كم}_l \frac{2l+1}{2l+1}.
\]

Inversion of these linear equations for \( J = K = 1 \) leads to the well known expressions for the Legendre moments in terms of the reactive cross sections

\[
\begin{align*}
\sigma^{كم,1}_0(E) &= \sigma^{كم,1}_0(E), \\
\sigma^{كم,1}_1(E) &= \frac{\sigma^{كم,1,1}(E) - \sigma^{كم,1,-1}(E)}{\sigma^{كم,1}_0(E)}, \\
\sigma^{كم,1}_2(E) &= \frac{\sigma^{كم,1,1}(E) + \sigma^{كم,1,-1}(E)}{\sigma^{كم,1}_0(E)} - \frac{1}{2}.
\end{align*}
\]

Here, \( \sigma^{كم}(E) = \sigma^{كم}_0(E) \) denotes the cross section for the unoriented molecules, which is equal to

\[
\sigma^{JK}_0(E) = \frac{1}{2J+1} \sum_{M=-J}^{J} \sigma^{كم}(E).
\]

Thus the zeroth Legendre moment is equal to \( \sigma^{كم,1}_0(E) \) and we use it to normalize the other Legendre moments. It is advantageous to use \( \sigma^{JK}(E) \) rather than \( \sigma^{كم}(E) \) with \( M=0 \), because the former is more easily accessible experimentally.

In Sec. III we consider an isotropic interaction potential, which decouples the rotation of the molecule from the motion of the atom. As a result, the ADLC type model described in Sec. I leads to an expression for the cross sections \( \sigma^{كم}(E) \) which has the form of Eq. (3) and we obtain an expression for \( \sigma^{JK}(\rho, E) \) in a straightforward manner. The results from this Section could also have been obtained if \( \sigma^{JK}(\rho, E) \) had been defined as the reactive cross section for a nonrotating molecule.

By contrast, in Sec. IV we consider an anisotropic interaction potential that can reorient the molecule. Computing \( \sigma^{JK}(\rho, E) \) from trajectories that have initially nonrotating molecules would not give meaningful results, since the response of a nonrotating molecule to a torque is different from the response of a rotating molecule. One way to proceed would be to replace the reactive cross sections \( \sigma^{كم}(E) \) in Eqs. (7)–(9) by their standard quasiclassical approximations \( \tilde{\sigma}^{كم}(E) \) (where \( j, k, \) and \( m \) are the classical analogs of \( J, K, \) and \( M \)–see Sec. IV A). However, in the model for reaction we made the assumption that the angle of attack \( \gamma \) and therefore indirectly the orientation of the molecule \( \varphi \) determines whether reaction occurs or not. Thus, we think that instead of using \( m \) (the moment conjugate to \( 4 \)) to make the connection between classical and quantum mechanics, we should use the orientation dependent cross section \( \sigma^{JK}(\rho, E) \) to make this connection. In other words: if we would make the correspondence \( \sigma^{كم}(E) \approx \tilde{\sigma}^{كم}(E) \) we would ignore the fact that the classical distribution of orientations \( \varphi^{كم}(\rho) \) differs considerably from the quantum mechanical distribution \( \varphi^{كم}(E) \). Therefore, we propose to compute a quasiclassical approximation \( \tilde{\sigma}^{JK}(\rho, E) \) to the orientation dependent cross section by solving the classical analog of Eq. (3)

\[
\tilde{\sigma}^{كم}(E) = \int_{-1}^{1} \tilde{\sigma}^{jk}(\rho, E) \varphi^{كم}(\rho) d\rho.
\]

In Sec. IV we present two methods to solve \( \tilde{\sigma}^{jk}(\rho, E) \) from this equation. In the first method we only use trajectories that start with \( m \) values that correspond to the quantum mechanical values \( M \). Since we do not make the connection \( \sigma^{كم}(E) \approx \tilde{\sigma}^{كم}(E) \) but instead \( \sigma^{JK}(\rho, E) \approx \tilde{\sigma}^{JK}(\rho, E) \), we
FIG. 2. The atom hits the imaginary sphere at the point determined by the polar angle $\chi$ and the azimuthal angle $\phi$. The polar angle of the symmetry axis of the molecule is $\theta$. The reaction probability is a function of the angle of attack $\chi$. In Eq. (19) the integration over $\theta$ and $\phi$ is replaced by the integration over $\gamma$ and $\xi$.

have complete freedom in the choice of $m$ and in the second method, which we will refer to as the modified quasiclassical trajectory (MQCT) method, we use all classically allowed $m$ values. The MQCT method can be viewed as an alternative method to quantize $m$: we compute $g_{jk}(p,E)$ from Eq. (11) using all possible $m$ values, and substitute it back into Eq. (3) to obtain approximations to $dKM(E)$ for quantum mechanical $M$ values.

III. THE ISOTROPIC CASE

In the case of an isotropic interaction potential between the symmetric top molecule and the atom, the motion of the centers of mass of the molecule and the atom decouple from the rotation of the molecule. Therefore, we can describe this rotation quantum mechanically, using the probability function $\mathcal{G}_{JKM}(\phi,\theta,\psi)$ defined in Eq. (A3) and treat the centers of mass motion classically. We choose a space-fixed coordinate system with its origin in the center of mass of the atom–molecule system. The $z$ axis is chosen parallel to the initial relative velocity. The vector connecting the centers of mass will be described using the Euler angles $(\phi,\theta,\psi)$ in the space-fixed frame. The molecular symmetry axis is

$$z' = \begin{bmatrix} 
\sin \theta \cos \phi \\
\sin \theta \sin \phi \\
\cos \theta
\end{bmatrix}. \tag{12}
$$

We propagate $(R,\chi)$ until $R$ reaches some fixed final value $R_f$. The final angle $\chi_f$ depends on the impact parameter and on the translational energy $E$: $\chi_f = \chi_f(b,E)$. Reaction is assumed to occur if the angle of attack $\chi$ between $R_f$ and the molecular symmetry axis $z'$ is less than a critical value $\chi_c$ (the angles are shown in Fig. 2). Introducing the reaction probability

$$W(\chi) = \begin{cases} 
1; & 0 \leq \chi \leq \chi_c \\
0; & \chi_c < \chi \leq \pi
\end{cases} \tag{13}
$$

we can write the reactive cross section as

$$\sigma_{JKM}(E) = 2\pi \int_0^{b_{\text{max}}(E)} b \, db \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi \int_{-1}^{1} d \cos \theta \times \mathcal{G}_{JKM}(\phi,\theta,\psi) W(\chi_f(b,E),\phi,\theta). \tag{14}
$$

where $b_{\text{max}}(E)$ must be equal to or larger than the largest impact parameter that can lead to reaction. Using Eqs. (A3)–(A5) we can perform the integration over $\psi$, which gives

$$\sigma_{JKM}(E) = \int_0^{b_{\text{max}}(E)} b \, db \int_0^{2\pi} d\phi \int_{-1}^{1} d \cos \theta \times \mathcal{G}_{JKM}(\cos \theta) W(\chi_f(b,E),\phi,\theta). \tag{15}
$$

Comparing this equation to Eq. (3) we find for the orientation dependent reactive cross section

$$\sigma_{JK}(E) = \frac{2l+1}{2} \int_0^{b_{\text{max}}(E)} b \, db \int_0^{2\pi} d\phi \int_{-1}^{1} d \cos \theta \times \mathcal{G}_{JK}(\cos \theta) W(\chi_f(b,E),\phi,\theta) \tag{17}
$$

and for its Legendre moments [using Eqs. (A7) and (4)]

$$\sigma_{JK}(E) = \frac{2l+1}{2} \int_0^{b_{\text{max}}(E)} b \, db \int_0^{2\pi} d\phi \int_{-1}^{1} d \cos \theta \times \mathcal{G}_{JK}(\cos \theta) W(\chi_f(b,E),\phi,\theta). \tag{18}
$$

The discontinuity in $W(\chi)$ makes it difficult to evaluate the integral. This problem can be removed by the following change of variables $(\theta,\phi) \rightarrow (\gamma,\xi)$. Here $\gamma$ is the angle between the $(x,z)$ plane and the plane through $R_f$ and $z'$ [see Fig. 2]. Thus $\gamma$ and $\xi$ are the polar angles of the $z'$ axis in a frame which arises from rotating the space fixed frame around the $y$ axis over an angle $\chi_f$. Hence, we can replace

$$\int_{-1}^{1} d \cos \theta \int_0^{2\pi} d\phi \int_{-1}^{1} d \cos \gamma \int_0^{2\pi} d\xi. \tag{19}
$$

We now eliminate $W$ from Eq. (18) by limiting the range of integration for $\gamma$

$$\sigma_{JK}(E) = \frac{2l+1}{2} \int_0^{b_{\text{max}}(E)} b \, db \int_0^{2\pi} d\phi \int_{-1}^{1} d \cos \gamma \int_0^{2\pi} d\xi \times \mathcal{G}_{JK}(\cos \theta) W(\chi_f(b,E),\gamma,\xi). \tag{20}
$$

The expression for $\cos \theta$ is

$$\cos \theta = \sin \chi_f \cos \xi + \cos \chi_f \cos \gamma. \tag{21}
$$

All that remains to be done before we can evaluate this integral is to derive formulas for $\chi_f(b,E)$ and $b_{\text{max}}(E)$. Of course, these functions depend on the shape of the potential. However, we will first draw a few conclusions that are independent of $V(R)$.

A. Special cases

First, we note that in the current model the Legendre moments [Eq. (20)] are independent of $J$ and $K$ and in the
remainder of this section, we will drop those labels [N.B. the reactive cross sections $\sigma_{\text{KM}}^{J,K}(E)$ still depend on $J$ and $K$ because the probability density functions $\rho_J^\text{KM}(p)$ are $J,K$ dependent, see Eq. (3)].

For $l=0$ we can evaluate the integral analytically and we obtain the following simple expression for the total reactive cross section:

$$\sigma_0(E) = \pi b_{\text{max}}^2(E) \left(1 - \cos \gamma_c \right).$$  \hspace{1cm} (22)

In the limit of large energy [$E \gg V(R)$] we have $b_{\text{max}} = R_f$ and find the completely intuitive result that the reactive cross section is equal to a collisional cross section multiplied by a factor between zero and one that depends on the size of the cone of reaction.

For $l=1$ we derive [without approximations]

$$\frac{\sigma_1(E)}{\sigma_0(E)} = 3(1 + \cos \gamma_c) \frac{1}{b_{\text{max}}^2} \int_0^{b_{\text{max}}(E)} \cos \chi_f(b,E) b \, db.$$ \hspace{1cm} (23)

Again we can take the limit for large $E$, in which case $\cos \chi_f$ can be determined by the geometric relation

$$\cos \chi_f(b) = \sqrt{1 - (b/b_{\text{max}})^2} \hspace{1cm} \text{(24)}$$

and we obtain

$$\lim_{E \to \infty} \frac{\sigma_1(E)}{\sigma_0(E)} = 1 + \cos \gamma_c.$$ \hspace{1cm} (25)

Hence, in the limit of high energy the steric effect must be positive and have a maximum of 2. Note that the high energy limit actually applies to any potential, even to anisotropic ones.

Before we proceed to derive the general formulas we will give a lower and upper bound for the steric effect valid for arbitrary energies. These values are obtained by setting $\chi_f$ to $\pi$ and 0 in Eq. (23), respectively. The upper limit can actually be approached in the case of a repulsive potential at low energies, in which case only small impact parameter trajectories are reactive. One expects always to stay clear of the lower limit

$$-\frac{3}{2} (1 + \cos \gamma_c) < \frac{\sigma_1(E)}{\sigma_0(E)} \leq \frac{3}{2} (1 + \cos \gamma_c).$$ \hspace{1cm} (26)

Note that these limits rely on the assumption of an isotropic potential.

**B. General solution**

The general expressions for $\chi_f(b,E)$ and $b_{\text{max}}(E)$ are found by solving the classical equations of motion of the centers of mass of the atom–molecule system. The solution of this effective central force problem is well known. \cite{13,19} For the deflection angle at $R_f$ we find

$$\chi_f(b,E) = \int_0^{R_f} \frac{b}{\sqrt{R^4 - b^2 R^2 - R^4 V(R)E^{-1}}} \, dR.$$ \hspace{1cm} (27)

We derive the expression for $b_{\text{max}}(E)$ in the usual way by considering the effective potential \cite{13} [see Eq. (1)]

\begin{align*}
V_{\text{eff}}(R,b,E) & = \frac{b^2 E}{R^2} + \frac{c}{R^a}.
\end{align*}  \hspace{1cm} (28)

We find $b_{\text{max}}$ from condition (I)

$$V_{\text{eff}}(R_f,b_{\text{max}},E) = E.$$  \hspace{1cm} \text{(29)}$$

However, we must be aware that for $c < 0$ and $n \geq 3$ the effective potential has a maximum at

$$R_c(b,E) = \frac{-nc}{2b^2E}.$$  \hspace{1cm} \text{(30)}$$

as shown in Fig. (3). Hence, if $R_f < R_c(b,E)$, then $b_{\text{max}}$ is found from condition (II)

$$V_{\text{eff}}\left[R_c(b_{\text{max}},E),b_{\text{max}},E\right] = E.$$  \hspace{1cm} \text{(31)}$$

Condition (I) gives

$$b_{\text{max}}^{(I)} = R_f \sqrt{1 - \frac{c}{E R_f^a}}.$$ \hspace{1cm} \text{(32)}$$

and condition (II) leads to

$$b_{\text{max}}^{(II)} = \left(\frac{-c}{E}\right)^{\frac{1}{n}}\left(\frac{n}{2}\right)^{\frac{1}{n}} \left(\frac{n-1}{2}\right)^{\frac{1}{n}} E^{\frac{1}{n}}.$$ \hspace{1cm} \text{(33)}$$

and also

$$R_c(E,n,c) = \left(\frac{-c}{E}\right)^{\frac{1}{n}}\left(\frac{n}{2}\right)^{\frac{1}{n}} \left(\frac{n-1}{2}\right)^{\frac{1}{n}}$$ \hspace{1cm} \text{(34)}$$

Note that this last result is identical to the Langevin model. \cite{13}

Thus we are in regime (II) if all of the following three conditions are satisfied:

(1) $c < 0$;
(2) $n \geq 3$;
(3) $R_f < R_c(E,n,c),$

and otherwise we are in regime (I).

We now have presented all the formulas needed to compute the Legendre moments $\alpha_l$ of Eq. (20) for a given $E$, $R_f$, $c$, $n$, and $\gamma_c$. It turns out, however, that by introducing the reduced energy

$$\alpha = E R_f^a/c.$$ \hspace{1cm} \text{(35)}$$

the Legendre moments can be written as
\[ \sigma_{f}(E,n,c,R_f,\gamma_c) = \pi b_{\text{max}}^2(\alpha,n,R_f)s_{f}(\alpha,n,\gamma_c), \]

(36)

and as a result, \( \sigma_{f}/\sigma_0 \) depends on three parameters only \((\alpha,n,\gamma_c)\). This is an extremely important result, since it allows us to easily examine the behavior of our model for the entire parameter space. For \( \sigma_0(E) \) we actually have a simple closed formula (see below) which depends on three parameters \((\alpha, R_f, \gamma_c)\) in regime (I) and on four parameters \((\alpha, R_f, \gamma_c, n)\) in regime (II).

First, using the equations for \( R_c \) and \( \alpha \) [Eqs. (34) and (35)] we rewrite the three conditions that determine when we are in regime (II) in the compact form

\[ 1 - \frac{n}{2} \leq \alpha < 0. \]

(37)

For \( b_{\text{max}} \) we find the expressions

\[ b_{\text{max}}^{(I)}(\alpha,R_f) = R_f \left( 1 - \frac{1}{\alpha} \right)^{1/2}, \]

(38)

\[ b_{\text{max}}^{(II)}(\alpha,R_f,n) = R_f (-\alpha)^{-1/n} \left( \frac{n}{2} \right)^{1/2} \left( \frac{n}{2} - 1 \right)^{-1/n}. \]

(39)

Introducing the reduced impact parameter

\[ \bar{b} = b / b_{\text{max}}, \]

(40)

we find for the last factor in Eq. (36), using Eq. (20)

\[ s_{f}(\alpha,n,\gamma_c) = \frac{2\ell + 1}{2} \int_{0}^{\pi} \int_{0}^{\xi} d\xi d\gamma_c \int_{\cos \gamma_c}^{1} d \cos \gamma \]

\[ \times \chi_{f}(\cos \theta(\bar{b},E),\xi,\gamma), \]

(41)

where \( \chi_{f}(\bar{b},E) \) is given by

\[ \chi_{f}(\bar{b},E) = \int_{r_{f}}^{\infty} \frac{\bar{b}}{\sqrt{r_f^2 - b^2 - \bar{b}^2 - r_f^4 - \bar{b}^4 - n^2 r_f^4}} dr. \]

(42)

Here, \( r_f \) is the reduced final radius

\[ r_f = R_f / b_{\text{max}} \]

(43)

which is expressed as a function of \( \alpha \) (in regime I) or \( \alpha \) and \( n \) (in regime II) using Eqs. (38) and (39), respectively. For numerical evaluation of this integral it is convenient to map the infinite range \([r_{f}, \infty]\) onto \([0,1/r_{f}]\) by the substitution \( y = 1/r_{f} \). This gives our final formula for \( \chi_{f} \)

\[ \chi_{f}(\bar{b},E) = \int_{0}^{r_f^{-1}} \frac{\bar{b}}{\sqrt{1 - \bar{b}^2 y^2 - \bar{b}^4} - \alpha^{-1} r_f^{4} \bar{b}^2} dy. \]

(44)

Summarizing, Eqs. (21) and (35)–(44) are all we need to compute \( \sigma_{f}(E) / \sigma_{0}(E) \). We wrote a small Fortran program to compute the integrals of Eqs. (41) and (44), using the NAG library routines D01AJF for the integral over \( b \), D01DAF for the integrals over \( \xi \) and \( \cos(\gamma) \) and D01ATF for the integral over \( y \). In addition, we made one more substitution to facilitate the numerical evaluation of the integral; in Eq. (41) we substitute \( g = \bar{b}^2 \) giving

\[ \int_{0}^{1} \bar{b} d\bar{b} = \frac{1}{2} \int_{0}^{1} dg. \]

(45)

Because of all the transformations the integrands are well behaved and the required computer time is negligible.

To compute \( \sigma_{0}(E) \) no integrals have to be evaluated, Eqs. (22), (38), and (39) suffice.

C. Results

In Fig. 4 we show the energy dependence of the total reactive cross section, the steric effect and the alignment effect for a \( c R^{-n}, n = 4 \) potential. The solid curves correspond to an attractive potential \([\alpha < 0, c < 0]\), see Eq. (35)] and the dashed curves to a repulsive potential \([\alpha > 0]\). We give results for cutoff angles \( \gamma_c \) of 60, 90, and 120 degrees.

Panel (a) gives the total reactive cross section normalized to the high energy collisional cross section \((\pi R_f^2)\). At high energy we have \( b_{\text{max}} = R_f \), thus from Eq. (22) we know that the curves, independently of the sign of \( \alpha \), should converge to \( 1/4, 1/2, \) and \( 3/4 \) for \( \gamma_c = 60, 90, \) and 120 degrees,
respectively. For repulsive potentials, the reactive cross section is zero for $\alpha<1$, since the total energy is less than the potential at the harpooning radius $R_f$ in that case [see Eq. (35)]. We see that in all cases an attractive potential results in a negative energy dependence of the total reactive cross section and a repulsive potential in a positive energy dependence.

In panel (b) we show the steric effect $\sigma_{\gamma}/\sigma_0$. The most important conclusion is that the energy dependence is exactly opposite to the energy dependence of $\sigma_0$: It is positive for attractive potentials and negative for repulsive potentials. Furthermore, the larger the cutoff angle ($\gamma_c$), the smaller the steric effect. In agreement with Eq. (25) the high energy limits are $3/2$, $1$, and $1/2$ for $\gamma_c=60^\circ$, $90^\circ$, and $120^\circ$, respectively. We reach the upper limit given in Eq. (26) for repulsive potentials near $\gamma_c=1$. The lower limit given in the same equation is not reached, but low energies ($|\varepsilon|<0.11$, approximately) we actually get a negative steric effect: because of the trapping, as shown in Fig. 1, trajectories are more likely to hit tails than heads.

Finally, panel (c) shows the alignment effect $\sigma_{\gamma}/\sigma_0$. For attractive potentials it is small and nearly energy independent. For $\gamma_c=90^\circ$ it is identically zero at all energies for both the repulsive and the attractive potentials. For repulsive potentials the alignment effect is much more sensitive to the cutoff angle than for attractive potentials, but in any case it is positive for $\gamma_c>90^\circ$ and negative for $\gamma_c<90^\circ$.

IV. THE ANISOTROPIC CASE

We present two methods to obtain the quasiclassical orientation dependent cross section $\tilde{\sigma}^{jk}(E)$ from Eq. (11). Both methods have the desirable property that they yield the same result as the method described in Sec. II in the case of an isotropic potential. For a general potential they might give different results, and below we will argue why we prefer the second method. Before we describe the two methods we must give a brief introduction into the classical description of a symmetric top.

A. Classical description of a symmetric top

The orientation of the symmetric top is given by the three Euler angles $(\phi, \theta, \psi)$. The moments conjugate to these angles are $p_\phi$, $p_\theta$, and $p_\psi$. The symmetric top classical Hamiltonian is given by

$$H_{\text{rot}} = A \frac{(p_\phi - p_\theta)^2}{1 - \rho^2} + C p_\theta^2 + C p_\phi^2 + B p_\phi^2,$$  

where $A$ and $C$ are the rotational constants. From Hamilton’s classical equations of motion we have

$$p_\phi = -\frac{\partial H}{\partial \phi} = 0,$$  

$$p_\theta = -\frac{\partial H}{\partial \theta} = 0,$$  

and thus $p_\phi$ and $p_\theta$ are constants of the motion and we define $p_\phi = m$ and $p_\theta = k$. For a total angular momentum $j$ the energy is

$$E_{\text{rot}} = J^2 + (C - A)k^2.$$  

Solving $H = E$ for $p_\theta$ gives

$$p_\theta^2 = \frac{J^2 - k^2}{m^2} - \frac{(m^2 k^2 - k^2)}{1 - \rho^2},$$

and we derive the classical distribution

$$\tilde{\sigma}^{jk}(p) \sim \frac{1}{|p|} \frac{1}{|p_\theta \sin \theta|}.$$  

With the appropriate normalization we have

$$\tilde{\sigma}^{jk}(p) = \begin{cases} \frac{1}{\pi} \left( p^2 + 2 \frac{m k}{J^2} \rho + 1 - \frac{m^2}{J^2} \frac{k^2}{J^2} \right)^{-1/2}, & \text{for } p_1 < \rho < p_2, \\ 0, & \text{otherwise,} \end{cases}$$

where

$$p_1,2^2 = \frac{m k}{J^2} \pm \sqrt{1 - \frac{k^2}{J^2} \left(1 - \frac{m^2}{J^2}\right)}.$$  

This distribution function has been obtained by Choi et al.\textsuperscript{21} from geometrical arguments. The quasiclassical approximation of the state $|JKM\rangle$ is obtained by setting

$$j = \hbar \sqrt{J(J+1)},$$  

$$m = \hbar M,$$  

$$k = \hbar K.$$  

If we follow the derivation in Sec. III using Eq. (11) to define $\tilde{\sigma}^{jk}(E)$ we obtain an expression for $\tilde{\sigma}^{jk}(E)$ identical to Eq. (17). In other words, we have $\tilde{\sigma}^{jk}(E) = \tilde{\sigma}^{jk}(E)$ for isotropic potentials. We may now define the two methods that apply to the anisotropic case.

B. Quasiclassical trajectory (QCT) method

The quasiclassical reactive cross sections $\tilde{\sigma}^{jk}(E)$ are obtained by trajectory calculations. We have the following initial conditions: $\phi$ and $\psi$ are sampled uniformly, cos $\theta$ is sampled according to distribution Eq. (52) and for the impact parameter we have $p(b) \sim b$, $0 < b < b_{\text{max}}$. The conjugate momenta are given by Eqs. (50), (55), and (56). For each trajectory the classical equations of motion are integrated numerically and we determine the final angle $\gamma$. The reaction probability $W(\gamma)$ as defined in Eq. (13) determines whether a trajectory is reactive or not. The reactive cross section is approximated by

$$\tilde{\sigma}^{jk}(E) = \frac{N_r(E)}{N_t} \pi b_{\text{max}}^2,$$  

where $N_r(E)$ is the number of reactive trajectories and $N_t$ the total number of trajectories. $b_{\text{max}}$ must be chosen large enough not to miss any reactive trajectories, $N_t$ must be increased to improve the accuracy.

We expand the classical distribution in Legendre polynomials

$$\tilde{\sigma}^{jk}(E) = \sum_{\ell=0}^{\infty} \sum_{\ell=0}^{\infty} \sigma^{jk}_{\ell} \frac{1}{\ell!} \frac{1}{\ell!} \left( E - E_{\text{rot}} \right)^{\ell} \left( E_{\text{rot}} - E \left( C - A \right) k^2 \right)^{\ell}.$$  

For the expansion coefficients we have an analytic expression (see Appendix B)
\[
\tilde{\mathcal{J}}_{l}^{\ell,m}(\rho) = \sum_{l=0}^{\infty} \tilde{c}_{l}^{\ell,m} \mathcal{P}_{l}(\rho).
\]

For the expansion coefficients we have an analytic expression (see Appendix B)
\[
\tilde{c}_{l}^{\ell,m} = \frac{2l+1}{2} P_{l}(m) P_{l}(m).
\]

We can now compute the Legendre moments of the orientation dependent reactive cross section \(\tilde{\sigma}^{\ell}(\rho, E)\) from the classical analog of Eq. (6).

Just as in Sec. II we can replace the equation with \(m=0\) by the equation for the unoriented reactive cross section. For this purpose we must generate trajectories with random \(m\) values \(m \in [-j,j]\). The corresponding distribution in \(\rho\) is indeed uniform
\[
\tilde{\mathcal{J}}_{l}^{\ell,m}(\rho) = \frac{1}{2j} \int_{-j}^{j} \tilde{\mathcal{J}}_{l}^{\ell,m}(\rho) d\rho = \frac{1}{2}.
\]

For the example \(J=K=1\) we now find
\[
\tilde{\sigma}_{0,0}^{1,1}(E) = \tilde{\sigma}_{1,0}^{1,1}(E),
\]
\[
\tilde{\sigma}_{1,0}^{1,1}(E) = \frac{\tilde{\sigma}_{1,1}^{1,0}(E) + \tilde{\sigma}_{1,1}^{1,1}(E)}{\tilde{\sigma}_{0,0}^{1,1}(E)},
\]
\[
\tilde{\sigma}_{2,0}^{1,1}(E) = \frac{\tilde{\sigma}_{1,1}^{1,1}(E) + \tilde{\sigma}_{1,1}^{1,1}(E)}{\tilde{\sigma}_{0,0}^{1,1}(E)} - 2.
\]

Comparing this to Eqs. (7)–(9) we find that only the expression for the alignment effect is different from the quantum version.

### C. Modified quasiclassical trajectory (MQCT) method

This method only requires the computation of trajectories with random \(m\) [which are also required for the computation of \(\sigma_{0}(E)\) in the QCT method]. We introduce the expansion
\[
\tilde{\sigma}_{l}^{\ell}(E) = \sum_{l=0}^{\infty} \tilde{c}_{l}^{\ell}(E) P_{l}(m/j).
\]

which gives
\[
\tilde{c}_{l}^{\ell}(E) = \frac{\int_{-1}^{1} d(m/j) P_{l}(m/j) \tilde{\sigma}_{l}^{\ell}(E)}{\int_{-1}^{1} d(m/j) P_{l}(m/j)}.
\]

Using the Monte Carlo approximation to the integral
\[
\int_{a}^{b} f(x) dx = \frac{b-a}{N} \sum_{i=1}^{N} f(x_{i}),
\]

we find
\[
\tilde{c}_{l}^{\ell}(E) = \frac{2l+1}{2} \frac{2}{N} \sum_{l=0}^{\infty} \frac{1}{l} \frac{1}{l} P_{l}(m/j),
\]

where the summation is only over the reactive trajectories. If we substitute expansion (64) together with
\[
\tilde{\sigma}_{l}^{\ell}(E) = \sum_{l=0}^{\infty} \tilde{c}_{l}^{\ell}(E) P_{l}(m/j),
\]

into Eq. (11), we find
\[
\sum_{l=0}^{\infty} \tilde{c}_{l}^{\ell}(E) P_{l}(m/j) = \int_{-1}^{1} \int_{-1}^{1} d\rho P_{l}(m/j) \tilde{\sigma}_{l}^{\ell}(E) \tilde{\sigma}_{l}^{\ell}(E) \tilde{\sigma}_{l}^{\ell}(E) d\rho.
\]

Multiplying this equation with \(P_{l}(m/j)\) and integrating over \(m/j\) gives
\[
\tilde{c}_{l}^{\ell}(E) = \sum_{l=0}^{\infty} A_{ll'}(j,k) \tilde{\sigma}_{l}^{\ell}(E),
\]

where
\[
A_{ll'}(j,k) = \frac{2l'+1}{2} \frac{2}{N} \sum_{l=0}^{\infty} \frac{1}{l} \frac{1}{l} P_{l}(m/j) \tilde{\sigma}_{l}^{\ell}(E) \tilde{\sigma}_{l}^{\ell}(E) \tilde{\sigma}_{l}^{\ell}(E) d\rho.
\]

Comparing the two methods we see that in the QCT method the steric effect is computed from the difference of the reactive cross section for two values of \(m\) [Eq. (62)], whereas the MQCT method relies on all classically allowed \(m\) values [Eqs. (67) and (73)]. The classical probability density function corresponding to a specific \(m\) value is sharply peaked and very different from the smooth quantum mechanical probability density function (see, e.g., Fig. 1 in the accompanying paper2 or Fig. 4 in Ref. 21). Therefore, we expect the MQCT to sample the potential energy surface much more realistically than the QCT method. Numerically, the MQCT has the advantage that it only requires trajectories for random \(m\) values, which are needed anyway to compute \(\sigma_{0}(E)\).

Note that one cannot generate the quantum mechanical probability distribution by simply taking the initial \(\rho\) values of the trajectories according to \(\mathcal{J}_{l}^{\ell,km}(\rho)\). First of all, with \(m\) fixed by the quantization condition Eq. (55), some trajectories would have to start in a classically forbidden region. Second, the resulting distribution of trajectories would not be stationary and the fraction of reactive trajectories would depend on \(R(0)\). Lifting the quantization condition form makes it possible to generate stationary distributions of \(\rho\) that differ from the classical distribution. Continuing along this line of thought led us to the development of the MQCT method.

Note, incidentally, that with the QCT method one computes at most \(2J+1\) Legendre moments, as in the quantum mechanical case, whereas with the MQCT method one can...
formally compute as many Legendre moments as desired. In practice, this has little relevance, since both methods are expected to be very sensitive to statistical errors for the higher Legendre moments.

V. CONCLUSION

It has been shown that a positive energy dependence of the steric effect does not require reorientation. We have presented a model with three elements, an imaginary shell (with radius $R_f$) surrounding the molecule at which reaction is assumed to occur, a critical angle $\gamma_c$ which determines which part of the shell is reactive, and an isotropic long range potential of the form $c R^{-n}$. This model predicts a positive energy dependence of the steric effect for attractive potentials and a negative one for repulsive potentials. For $\sigma_0(E)$ the energy dependence is reversed. For attractive potentials our model predicts a small, almost energy independent alignment effect. The computation of $\sigma_0/\sigma_0$ for isotropic potentials is numerically easy, since most of the work can be done analytically.

We also present two methods for the computation of $\sigma_0/\sigma_0$ for arbitrary (anisotropic) potentials. The first method is based on the standard quasiclassical trajectory (QCT) method for the computation of state selected reactive cross sections $\sigma^{Jk}(E)$. The most important conclusion with respect to this method is that the relation between $\sigma_0/\sigma_0$ for $i \gg 2$ and the reactive cross sections from QCT differ from the quantum mechanical version, because all but the zeroth and first Legendre moments of the classical distribution function $\psi^{Jk}(p)$ are different from the quantum mechanical ones.

The second method, which we refer to as the modified quasiclassical trajectory method (MQCT), is based on the computation of $\sigma^{Jk}(E)$ for all classically allowed $m$ values, and not just from the discrete set used in the QCT. The coefficients of the expansion of $\sigma^{Jk}(E)$ in Legendre polynomials in $(m/j)$ are directly related to the Legendre moments $g^{Jk}(E)$ of the orientation dependent reactive cross section. We favor this MQCT method over the QCT method because we expect the MQCT method to sample the potential energy surface more evenly and thus give a better orientation dependent reactive cross section. For isotropic potentials both methods give the same result.

In the accompanying paper we will show that the parameters in the isotropic model needed to reproduce the experimental results for the energy dependence of the steric and alignment effects in the Ca($^2D_3$)+CH$_3$F reaction are physically reasonable. We will also study the effects of anisotropy in the potential using the MQCT method and we will compare the MQCT and QCT numerically.

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APPENDIX A

The orientation of a symmetric top molecule with respect to the space-fixed frame is specified by the three Euler angles $(\phi, \theta, \psi)$. We use the $zyz$ parametrization, the domain of the angles is $[0, 2\pi]$ for $\phi$ and $\psi$ and $[0, \pi]$ for $\theta$, the volume element is $d\tau = d\phi d\psi d\cos \theta$. Using active rotations, the wave function is given by

$$\psi^{Jk}(\phi, \theta, \psi) = \left( \frac{2J+1}{8\pi} \right)^{1/2} D_{MK}^J(\phi, \theta, \psi)^*,$$

using notational conventions.

The probability function, i.e., the square modulus of the wave function

$$P^{Jk}(\phi, \theta, \psi) = \frac{2J+1}{8\pi^2} |d_{MK}^J(\theta)|^2,$$

thus only depends on $\theta$ and we define

$$P^{Jk}(\rho) = \int_0^{2\pi} \int_0^\pi \psi^{Jk}(\phi, \theta, \psi) d\phi d\psi,$$

with $\rho = \cos \theta$. This $\rho$-dependent probability function can be expanded as a finite sum of Legendre polynomials\textsuperscript{21}

$$P^{Jk}(\rho) = \sum_{|m/j|} c^{Jk}_{m/j} P_j(\rho).$$

We use unnormalized Legendre polynomials, i.e., $P_0(\rho) = 1$, $P_1(\rho) = \rho$, $P_2(\rho) = \frac{1}{2}(3\rho^2-1)$, etc., and

$$\int_{-1}^{1} P_\ell(\rho) P_{\ell'}(\rho) d\rho = \frac{2}{2\ell+1} \delta_{\ell\ell'}.$$

The expansion coefficients expressed in $3jm$ symbols are

$$c^{Jk}_{m/j} = \frac{2J+1}{2} (-1)^{M-K}(2J+1)(J J I)_{M-M-K0} \times \begin{pmatrix} J & J & I \\ K & -K & 0 \end{pmatrix}. $$

APPENDIX B

In this Appendix we will give the proofs for Eqs. (59) and (72) from Sec. IV. We first prove the following theorem.

Theorem 1: For $-1 \leq m/j \leq 1$ and $-1 \leq k/l \leq 1$, we have
where \( p_1 \) and \( p_2 \) denote the zero points of the second degree polynomial in \( \rho \) under the square root sign, given by

\[
P_{1,2}(\rho) = P_1\left(\frac{m}{j}\right), \quad \rho_1, 2 = \frac{mk}{j^2} \pm \sqrt{\left(1 - \left(\frac{m}{j}\right)^2\right)\left(1 - \left(\frac{k}{j}\right)^2\right)}.
\]

Substituting,

\[
y = \frac{2\rho - p_1 - p_2}{p_2 - p_1}
\]

into Eq. (B1) and using definitions Eqs. (B2), gives

\[
I = \frac{1}{\pi} \int_{-1}^{1} P_1\left(\frac{mk}{j^2} + y \sqrt{1 - \left(\frac{m}{j}\right)^2\left(1 - \left(\frac{k}{j}\right)^2\right)}\right) dy.
\]

Substituting \(-\cos u\) for \(y\) gives

\[
I = \frac{1}{\pi} \int_{0}^{\pi} P_1\left(\frac{mk}{j^2} - \cos u \sqrt{1 - \left(\frac{m}{j}\right)^2\left(1 - \left(\frac{k}{j}\right)^2\right)}\right) du.
\]

We now substitute \(mlj = \cos \eta\) and \(klj = \cos \zeta\), thus we can write the argument of the Legendre polynomial in Eq. (B5) as

\[
\frac{mk}{j^2} - \cos u \sqrt{1 - \left(\frac{m}{j}\right)^2\left(1 - \left(\frac{k}{j}\right)^2\right)} = \cos \eta \cos \zeta - \sin \eta \sin \zeta \cos u = \cos \omega.
\]

Physically, we can interpret \(\omega\) as the angle between the total angular momentum vector \(j\) and the space-fixed (SF) \(z\) axis, \(\zeta\) as the angle between \(j\) and the body-fixed (BF) \(z\) axis \(=z')\) in Eq. (12), and \(\omega\) as the angle between the SF \(z\) axis and the BF \(z\) axis. The angle \(\omega\) can be conceived as the dihedral angle between the plane through \(j\) and the SF \(z\) axis and the plane through \(j\) and the BF \(z\) axis. We now use the spherical addition theorem,

\[
P_j(\cos \omega) = \sum_{\ell} C_{j\ell}^p(\xi, \theta) C_{\ell q}(\eta, \phi),
\]

where \(C_{j\ell}^p(\eta, \phi)\) is a spherical harmonic function in the Racah normalization, to rewrite Eq. (B5). Subsequent integration over \(u\) only leaves the terms with \(q = 0\), which themselves are Legendre polynomials, proving Theorem (1).

Using Eqs. (71) and (52) and Theorem (1) and the orthogonality of the Legendre polynomials we can prove Eq. (72). To prove Eq. (59) we multiply Eq. (58) by \(P_1'(\rho)\) and integrate over \(\rho\) using, again, Theorem (1) and the orthogonality of the Legendre polynomials.

As an interesting aside we note that one can also derive the expansion coefficients for the classical probability density function (PDF) of Eq. (59) by starting with the quantum mechanical expression of Eq. (A8) and using the correspondence principle, i.e.,

\[
c_{km}^j = \lim_{h \to 0} c_{km}^j (kM).
\]

When taking this limit \((jkm)\) and \(l\) are fixed and \((jkm)\) is related to \((km)\) through Eqs. (54)–(56). Thus taking the limit of \(h \to 0\) corresponds to taking \(J \to \infty\). For \(J \geq 1\) we have the asymptotic expression for the Clebsch–Gordan (CG) coefficients\(^{22-24}\)

\[
C_{jM}^{jM0} = P_{1/2}^{M/2}.
\]

The \(3jm\) symbols in Eq. (A8) are related to the CG coefficients by

\[
(-1)^{l+M+2j} \frac{1}{\sqrt{2l+1}} C_{jkm}^j = (-1)^{l+M+2j} \frac{1}{\sqrt{2l+1}} C_{jkm}^j
\]

with, of course, a similar expression for the \(3jm\) symbol with \(K\) instead of \(M\) (note that we used the fact that cyclic permutations of the columns leave \(3jm\) symbols unchanged). Furthermore, for large \(J\) we have \(M/(J+1/2) \sim mlj\) and we find

\[
\lim_{h \to 0} c_{km}^j = \frac{2l+1}{2} P_{1/2}^{M/2} \left(\frac{m}{M}\right) \left(\frac{k}{M}\right),
\]

which again is a proof of Eq. (59).

Note, incidentally, that although the Legendre moments of the quantum mechanical PDF converge to the classical Legendre moments for large \(J\), there is no pointwise convergence of the quantum mechanical PDF and the classical PDF. In particular, for larger and larger \(J\)s the quantum mechanical PDF has an increasing number of zeros. Mathematically, this lack of pointwise convergence is caused by the fact that Eq. (B9) no longer holds when \(l\) approaches \(J\).

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