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Approximations for the rotational excitation of molecules by atoms

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The applicability of the effective close-coupling approximation of Rabitz and the centrifugal decoupling approximation of McGuire and Kouri is examined for a system which models the rotational excitation of molecular nitrogen in collisions with helium atoms. For small values of the rotational quantum number both methods are more accurate for total elastic scattering cross sections than for inelastic and neither is capable of providing reliable inelastic cross sections close to the rotational threshold. Agreement with the close-coupling cross sections improves with increasing impact energy. The accuracy of the centrifugal decoupling approximation appears to be stable with respect to the magnitude of the repulsive anisotropy whereas the effective close-coupling method is sensitive to it and the approximation becomes inaccurate when the anisotropy is large. The detailed-balancing relationship is not satisfied by the effective close-coupling method and modifications that depend upon energy and upon the magnitude of the anisotropy are needed.

I. INTRODUCTION

Several quantal approximations have been proposed recently for the description of collisions involving rotational excitation of molecules, which seek to reduce the large number of coupled equations that enter the conventional close-coupling formulation.[1] The methods include the fixed-nuclei (FN) approximation, based upon the adiabatic theory of electron–molecule scattering,[2] the effective close-coupling (ECC) approximation of Rabitz,[3] and the centrifugal decoupling (CD) approximation of Pack and of McGuire and Kouri.[4] In a study of collisions between hydrogen atoms and carbon monoxide,[5] we found that the FN method is unreliable at low energies and impractical at high energies, but the ECC and CD methods are capable of providing results of acceptable accuracy. However, calculations for other systems using the ECC and CD approximations[6] have met with varying success, and in this paper we present a systematic study of the range of applicability of the two approximations as the impact energy is varied and as the potential anisotropy is varied.

II. THE INTERACTION POTENTIAL

As a model interaction, we adopted a Lennard-Jones (12, 6) potential with a short-range repulsive anisotropy α in the form

$$V(\mathbf{R}) = v_0(R) + \alpha v_2(R) P_2(\cos\theta)\,, \tag{1}$$

where

$$v_0(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R^6)]\,,$$

$$v_2(R) = 4\epsilon(\sigma/R)^{12}\,,$$

R is the vector joining the atom to the center of mass of the rigid rotator, and θ is the angle between R and the rotator axis. The representation (1) was used recently by Tsien and Pack.[7]

We chose the parameters σ and ϵ so that (1) simulated the interaction potential between He and N_2. The values are $\sigma = 3.164$ Å and $\epsilon/k = 25.11$ °K. We varied the anisotropy parameter α between 0.1 and 2.0.

III. SCATTERING CALCULATIONS

The coupled differential equations resulting from the close-coupling, the effective close-coupling, and the centrifugal decoupling approximations were solved using the Numerov algorithm.[8] In the calculations, we included all open channels in the basis set, and the scattering S-matrix elements were calculated to an accuracy within 0.5%.

TABLE I. Total elastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=0)$, calculated using the close-coupling (CC), effective close-coupling (ECC), and centrifugal decoupling (CD) methods at $E = 1.8\times10^{-3}$ eV.[a] α measures the repulsive anisotropy. The cross sections are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(\text{ECC})}{\sigma(\text{CC})}$	$\frac{\sigma(\text{CD})}{\sigma(\text{CC})}$
0.10	124.4	124.3	124.2	1.000	0.999
0.25	124.2	123.8	123.3	0.996	0.993
0.50	123.8	121.5	120.4	0.981	0.973
0.75	123.1	116.2	116.2	0.944	0.944
1.00	122.6	105.8	111.0	0.863	0.906
1.50	124.5	77.8	102.8	0.625	0.826
2.00	145.3	663.2	140.2	4.566	0.965

[a]This energy is near the $j=0 \rightarrow j'=2$ rotational threshold.

TABLE II. Total inelastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=2)$, calculated from the CC, ECC, and CD methods, at $E = 1.8\times10^{-3}$ eV.[a] α is the repulsive anisotropy and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(\text{ECC})}{\sigma(\text{CC})}$	$\frac{\sigma(\text{CD})}{\sigma(\text{CC})}$
0.10	0.0085	0.016	0.031	1.896	3.663
0.25	0.051	0.11	0.18	2.202	3.470
0.50	0.20	0.58	0.64	2.905	3.221
0.75	0.45	1.79	1.35	3.987	3.014
1.00	0.83	4.86	2.35	5.870	2.845
1.50	2.25	34.84	5.63	15.484	2.504
2.00	6.18	19.02	11.42	3.078	1.856

[a]This energy is near the $j=0 \rightarrow j'=2$ rotational threshold.

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TABLE III. Total elastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=0)$ calculated from the CC, ECC, and CD methods at $E = 5\times10^{-3}$ eV. α is the repulsive anisotropy, and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.10	150.3	150.4	150.3	1.000	1.000
0.25	149.7	149.9	149.4	1.001	0.998
0.50	147.7	148.1	146.4	1.002	0.991
0.75	144.6	144.6	141.9	1.000	0.982
1.00	140.4	139.1	136.1	0.991	0.970
1.50	129.1	122.3	122.7	0.948	0.950
2.00	117.3	145.7	117.4	1.243	1.001

TABLE V. Total elastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=0)$ calculated from the CC, ECC, and CD methods at $E = 5\times10^{-2}$ eV. α is the repulsive anisotropy, and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.1	167.1	167.0	166.9	1.000	0.999
0.5	159.9	163.0	159.8	1.020	1.000
0.75	152.1	157.1	151.2	1.033	0.994
1.0	141.7	147.8	139.4	1.043	0.984
1.5	112.9	126.5	107.7	1.120	0.954
2.0	81.0	136.0	81.6	1.679	1.008

The results for total energies E from near the 0–2 rotational threshold to 0.05 eV are summarized in Tables I–VIII, which present the calculated values of the ECC, the CD, and the CC cross sections.

Table I gives the elastic cross sections near threshold. The elastic σ(ECC) and σ(CC) cross sections agree to within 6% for $\alpha < 0.75$, but a large discrepancy occurs as α increases above unity, and at $\alpha = 2.0$, the ratio of σ(ECC) to σ(CC) is 4.6. The CD elastic cross sections are less sensitive to α, and σ(CD) agrees with σ(CC) to within 20% over the whole range of α. Thus, both the ECC and the CD methods appear to give accurate elastic cross sections near the inelastic threshold provided that the anisotropy is not large. When α becomes large, the ECC method becomes unreliable but the CD method remains useful.

Table II lists the inelastic cross sections near threshold. Neither the ECC nor the CD method gives accurate inelastic cross sections over the entire range of α. The ECC method is sensitive to α, and it rapidly loses accuracy as α increases. There is some improvement at $\alpha = 2.0$, which is associated with an overestimate of the elastic cross section. The CD method is less sensitive to the magnitude of α, and the ratio σ(CD)/σ(CC) decreases from 3.7 to 1.9 as α increases from 0.1 to 2.0. The CD method shows a tendency to predict more accurate inelastic and less accurate elastic cross sections as the repulsive anisotropy becomes stronger, and Walker and Light[9] have suggested that errors in the phases of the elastic S-matrix elements are responsible.

The elastic cross sections at higher energies of 0.005 eV, 0.01 eV and 0.05 eV are presented in Tables III, IV, and V, respectively, and the inelastic cross sections in Tables VI, VII, and VIII respectively. The pattern that occurs near threshold is repeated, though the accuracy of both approximations is much improved. The insensitivity of the accuracy of the CD cross sections to α persists, and the ECC cross sections are inaccurate for strong anisotropies. Figure 1 is a qualitative illustration of the behavior of the ECC and CD cross sections with energy for several values of α. The inelastic ratios, σ(ECC)/σ(CC), are larger than unity near threshold but smaller than unity at high energies. This behavior is associated with the detailed-balance requirement, and the accuracy of the ECC approximation at intermediate energies is fortuitous.

IV. DISCUSSION

The relative insensitivity to the anisotropy parameter α of the ECC and CD approximations to the elastic cross sections occurs because the elastic scattering is largely controlled by the diagonal interaction or distortion term which is independent of α for the $j = 0$ state. The behavior may differ for higher rotational levels.[9] The assumption in the CD method that the effect of rotation on the body-oriented wavefunctions is negligible is strictly correct only for $j = j' = 0$.

The increasing inaccuracy of the ECC approximation to the inelastic cross sections as the anisotropy becomes stronger and the energy approaches threshold is expected. Rabitz[3] has shown that the ECC approximation

TABLE IV. Total elastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=0)$ calculated from the CC, ECC, and CD methods at $E = 1.0\times10^{-2}$ eV. α is the repulsive anisotropy and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.10	160.2	160.3	160.2	1.001	1.000
0.25	159.4	159.8	159.2	1.003	0.999
0.50	156.6	157.6	155.6	1.007	0.994
0.75	151.9	153.4	149.7	1.010	0.986
1.00	145.3	146.0	141.5	1.005	0.973
1.50	124.7	128.3	117.8	1.029	0.944
2.00	96.5	161.2	101.3	1.672	1.050

TABLE VI. Total inelastic cross sections for the process He + $N_2(j=0) \rightarrow$ He + $N_2(j'=2)$ calculated from the CC, ECC, and CD methods at $E = 5\times10^{-3}$ eV. α is the repulsive anisotropy, and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.10	0.11	0.08	0.17	0.767	1.596
0.25	0.66	0.55	1.03	0.843	1.572
0.50	2.48	2.47	3.89	0.996	1.571
0.75	5.38	6.31	8.38	1.173	1.564
1.00	9.40	13.10	14.56	1.394	1.553
1.50	21.65	44.37	32.99	2.049	1.522
2.00	42.88	127.86	63.14	2.982	1.472

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TABLE VII. Total inelastic cross sections for the process $He + N_2(j=0) \rightarrow He + N_2(j'=2)$ calculated from the CC, ECC, and CD methods at $E = 1.0 \times 10^{-2}$ eV. α is the repulsive anisotropy, and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.10	0.14	0.09	0.19	0.632	1.326
0.25	0.87	0.60	1.15	0.689	1.322
0.50	3.34	2.67	4.41	0.798	1.320
0.75	7.43	6.89	9.79	0.927	1.317
1.00	13.39	14.61	17.56	1.091	1.311
1.50	33.46	50.76	43.06	1.517	1.287
2.00	73.82	38.04	88.04	0.515	1.203

TABLE VIII. Total inelastic cross sections for the process $He + N_2(j=0) \rightarrow He + N_2(j'=2)$ calculated from the CC, ECC, and CD methods at $E = 5 \times 10^{-2}$ eV. α is the repulsive anisotropy, and σ are in units of a_0^2.

α	σ(CC)	σ(ECC)	σ(CD)	$\frac{\sigma(ECC)}{\sigma(CC)}$	$\frac{\sigma(CD)}{\sigma(CC)}$
0.1	0.26	0.14	0.29	0.527	1.117
0.5	5.82	3.74	6.48	0.643	1.113
0.75	12.47	8.94	13.78	0.717	1.105
1.0	21.17	16.61	23.16	0.785	1.094
1.5	43.32	30.44	45.12	0.703	1.042
2.0	65.44	18.62	58.88	0.285	0.900

is accurate to first order in the ratio $(E - H_0)^{-1}V$, where $H_0 + V$ is the system Hamiltonian, but differences appear in second order.

The ECC approximation also has the property that states are labeled by j and not by j, m_j, with the consequence that the cross sections satisfy[3]

$$k_j^2 \sigma(j \rightarrow j') = k_{j'}^2 \sigma(j' \rightarrow j)$$

instead of the exact detailed balancing relationship[1]

$$(2j+1)k_j^2 \sigma(j \rightarrow j') = (2j'+1)k_{j'}^2 \sigma(j' \rightarrow j) .$$

In order to satisfy the exact relationship, Zarur and Rabitz[10] introduced a state-counting function $g(j, j') = \{(2j'+1)/(2j+1)\}^{1/2}$ by which the ECC cross section $\sigma(j \rightarrow j')$ is multiplied.

Figure 2 is a qualitative illustration of the ratio $\sigma(CC)/\sigma(ECC)$ as a function of energy for several values of α. For the $0 \rightarrow 2$ transition, $g(0, 2) = \sqrt{5}$. In Fig. 2, the line at $\sqrt{5}$ refers to the modified ECC cross section and the line at unity to the unmodified cross section. It appears that for weak anisotropies, the unmodified cross sections are more accurate at smaller energies, but the modified cross sections are correct in the limit of high energies.

In the CD approximation, McGuire and Kouri[4] neglected the off-diagonal $(m_j|l^2|m_{j'})$ matrix elements of the orbital angular momentum operator l and replaced the diagonal term $(m_j|l^2|m_j)$ by $\hbar^2 l(l+1)$, where m_j is the projection of the total angular momentum J = j + l on the body-fixed axis. In one formulation, McGuire and Kouri[4] chose $l = J$, and in another[11] they chose $l = |J - j|$.

The choice $l = J$ is equivalent to assuming that j is excited randomly with respect to l. The possible values of l range from $J - j$ to $J + j$, and the average is J. At high energies the assumption that the different values of l contribute in similar amounts is a plausible one that is verified by explicit calculation, and the CD approximation is valid at high energies. It fails at low energies because the choice $l = J$ is not appropriate.

The choice $l = |J - j|$ [11] recognizes that the most effective collisions for causing rotational excitation are those in which the incident atom collides when it is moving in the direction of the rotation. It leads to improved accuracy for the case $Li^+ - H_2$, where the long range anisotropy is significant[9] and there is a large interaction region in which the molecules can become preferentially excited. For our case in which the anisotropy is short ranged there is no preferred orientation for scattering, as indeed is suggested by the insensitivity

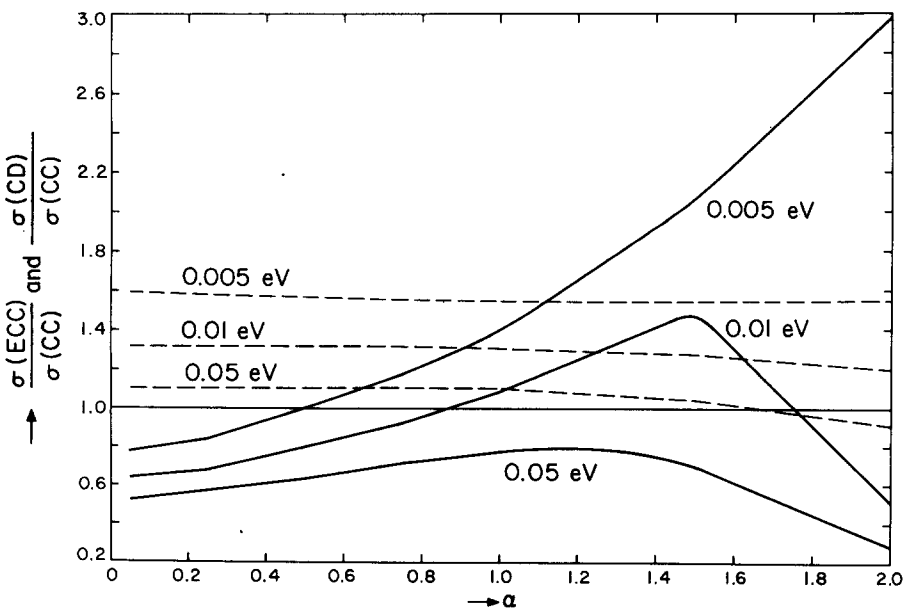

FIG. 1. Behavior of the ECC and CD methods as a function of energy and anisotropy for the process $He + N_2(j=0) \rightarrow He + N_2(j'=2)$. The full curves are the ECC, and the dashed curves are the CD calculations, respectively.

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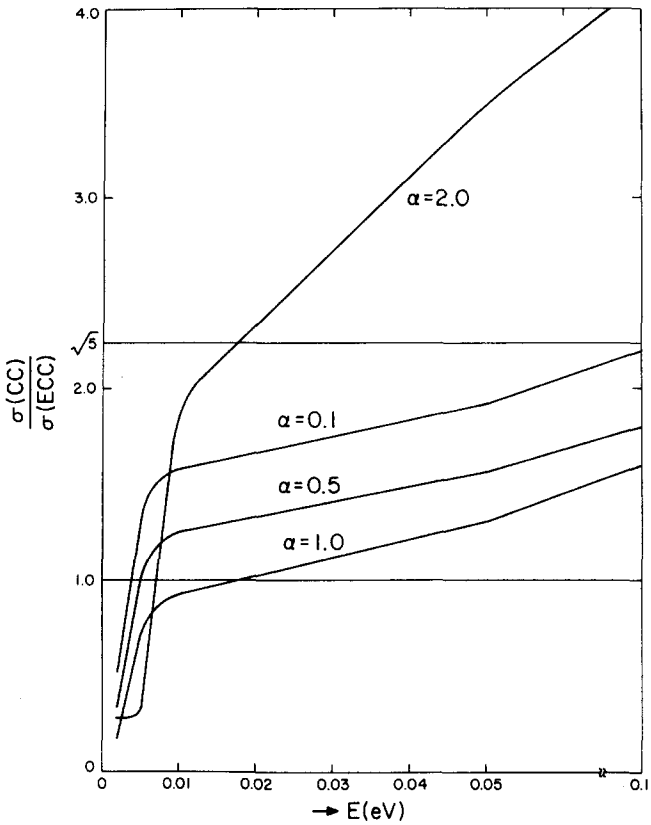

FIG. 2. The ratio $\sigma(CC)/\sigma(ECC)$ as a function of total energy E for $\alpha = 0.1$, 0.5, 1.0, and 2.0 for the process $He + N_2(j=0) \rightarrow He + N_2(j'=2)$.

of the results to α.

Our detailed comments refer to the elastic 0–0 and inelastic 0–2 transitions. We have also carried out calculations for transitions amongst higher rotational levels. A similar behavior occurs, though the CD approximation cross sections are less reliable than for the 0–2 transition. The calculations for collisions of carbon monoxide and hydrogen[5] also show that the CD cross sections for $0-j'$ transitions fall too rapidly as j' increases. Walker and Light[9] have explored in depth the sources of error in the CD approximation by carrying out detailed calculations at one particular energy. They point out that the contributions to the scattering from individual values of the total angular momentum J are often severely underestimated at large J by the CD approximation, an effect which they relate to the incorrect asymptotic behavior of the CD channel energies. The error tends to increase with the rotational quantum number j.

It appears, however, that results of acceptable accuracy can be obtained by the CD approximation at all anisotropies and by the simpler ECC approximation at small anisotropies. Both approximations fail near threshold, but the accuracy of the two approximations improves with increasing energies. Unless interaction potentials of high accuracy are available, the full close-coupling formulation is unnecessary, except close to threshold.

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