



Missouri University of Science and Technology
Scholars' Mine

Physics Faculty Research & Creative Works

Physics

01 Dec 1968

Rotational Excitation of Polar Molecules by Electrons

Marvin H. Mittleman

Jerry Peacher

Missouri University of Science and Technology, peacher@mst.edu

Balazs F. Rozsnyai

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Physics Commons](#)

Recommended Citation

M. H. Mittleman et al., "Rotational Excitation of Polar Molecules by Electrons," *Physical Review*, vol. 176, no. 1, pp. 180-186, American Physical Society (APS), Dec 1968.

The definitive version is available at <https://doi.org/10.1103/PhysRev.176.180>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

- ¹²W. Buhning, *Z. Physik* **208**, 286 (1968).
¹³D. W. Walker, *Phys. Rev. Letters* **20**, 827 (1968).
¹⁴A. C. Yates, *Phys. Rev. Letters* **20**, 829 (1968).
¹⁵D. Liberman, J. T. Waber, and D. J. Cromer, *Phys. Rev.* **137**, A27 (1965).
¹⁶R. D. Cowan, A. C. Larson, D. Liberman, J. B. Mann, and J. Waber, *Phys. Rev.* **144**, 5 (1966).
¹⁷E. Clementi, *J. Chem. Phys.* **38**, 996 (1963); **38**, 1001 (1963).
¹⁸H. S. W. Massey and C. B. O. Mohr, *Proc. Roy. Soc. (London)* **A177**, 341 (1941).
¹⁹A. C. Yates and T. G. Strand, *Phys. Rev.* **170**, 184 (1968).
²⁰See, e.g., Refs. 8-13.
²¹G. F. Drukarev, *The Theory of Electron-Atom Collisions* (Academic Press, Inc., New York, 1965), p. 148.
²²R. A. Bonham, *J. Chem. Phys.* **36**, 3260 (1962).
²³R. Gáspár, *Acta Phys. Acad. Sci. Hung.* **3**, 263 (1954).
²⁴See, e.g., N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1965), Chap. IV.
²⁵T. Iijima, R. A. Bonham, and T. Ando, *J. Phys. Chem.* **67**, 1472 (1963).
²⁶R. A. Bonham and J. L. Peacher, *J. Chem. Phys.* **38**, 2319 (1963).
²⁷All molecular parameters were obtained from *Tables of Interatomic Distances and Configurations in Molecules and Ions*, edited by L. E. Sutton, Special Publication No. 11 (The Chemical Society, London, 1958).
²⁸L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 104.
²⁹B. V. Noumerov, *Monthly Notices Roy. Astron. Soc.* **84**, 592 (1924).
³⁰M. A. Melkanoff, T. Sawada, and J. Raynal, *Methods in Computational Physics* (Academic Press, Inc., New York, 1966), Vol. 6, p. 1.

Rotational Excitation of Polar Molecules by Electrons

M. H. Mittleman and J. L. Peacher*

Space Sciences Laboratory, University of California, Berkeley, California
and

B. F. Rozsnyai†

Biomedical Research Division, Lawrence Radiation Laboratory, Livermore, California

(Received 19 July 1968)

Rotational excitation of polar molecules is calculated in the approximation that the electron transit time is short compared with rotational periods with the result of an E^{-1} behavior of the cross section. Diffusion cross sections are calculated for $\Delta l = 0, 1, 2$. Significant corrections to the Born approximation are obtained for large dipole moments. The range (in energy) of applicability of the result is discussed in terms of the energy dependence of the corrections, and a novel energy dependence of these corrections is encountered and explained.

I. INTRODUCTION

The full problem of electron scattering by a general atomic or molecular target is much too complex a problem for an exact solution to be even attempted. However, for some values of the incident energy there are solvable approximation schemes which are valid. For example, for low-enough energies it is known that electron-atom scattering is usefully parametrized in terms of the long-range parts of the potential.¹ Similarly for scattering by polar molecules, we can find an energy range of the incident electron in which a solvable approximation scheme is valid.

If the electron moves fast compared with the rotational motion of the molecule, then we may describe the process in terms of electron scattering from a molecule of fixed orientation² and subsequently average over the orientation. If,

further, the electron has low-enough energy so that its wave function does not probe the inner structure of the molecule, i. e., the scattering is dominated by the long-range potential, then we may further approximate the molecule by a point dipole. Thus the scattering in this energy range, which is bounded from above and below, may essentially be described as the scattering of an electron by a fixed point dipole. The numerical solution of this problem has been previously given.³ It is used in the next section to obtain rotational excitation diffusion cross sections. In the third section the approximations described above are treated in more detail. It is found that the domain of applicability is most seriously restricted from below and that the restriction is more severe the greater the dipole moment. If the dipole moment is greater than the critical value the method breaks down. This is discussed briefly in the fourth section.

II. DERIVATION AND NUMERICAL RESULTS

The scattering problem of an electron on a molecule is most conveniently described by the integral equation

$$\Psi = \chi + (E - H_0)^{-1} V \Psi, \quad (1)$$

where E is the total energy. H_0 the non-interacting Hamiltonian, and V the electron molecule interaction. The propagator in (1) may be written as

$$(k_i^2 - T + W_{l'} - H_{\text{rot}} + \delta_i - H')^{-1},$$

where k_i^2 is the incident energy of the electron,⁴ T the kinetic-energy operator of the electron $W_{l'}$ and H_{rot} the initial rotational eigenvalue⁵ and Hamiltonian, respectively, and H' is the remaining part of the molecular Hamiltonian (vibrational plus electronic), and δ_i its initial eigenvalue. Our first approximation is to neglect the term $(W_{l'} - H_{\text{rot}})$ in the propagator. This is the approximation that the incident electron motion is fast compared with the rotational motion of the molecule. This is exactly the Born-Oppenheimer approximation applied to a scattering problem.² With this approximation Eq. (1) describes the scattering of an electron from a molecule of fixed orientation. The amplitude for a rotational transition from l' to l is then given by

$$f_{ll'} = - (4\pi)^{-1} \langle \chi_l V \Psi_{l'}^{(+)} \rangle, \quad (2)$$

where $\Psi_{l'}^{(+)}$ is the outgoing wave solution to (1) with initial rotational state l' and χ_l the final state with the scattered electron in a plane-wave state and the molecule in rotational state l . The approximation of neglecting the rotational kinetic energy in (1) allows a factorization of $\Psi_{l'}^{(+)}$ in terms of the solution to the scattering problem with fixed molecular orientation, $\psi_{k_i}^{(+)}$,

$$\Psi_{l'}^{(+)} = \psi_{k_i}^{(+)} \Omega_{l'}, \quad (3)$$

where $\Omega_{l'}$ is the rotational eigenfunction. The final state is similarly factorable so that (2) becomes

$$f_{ll'} = \int d\alpha \Omega_l^* [- (4\pi)^{-1} \langle \chi_{k_f} V \psi_{k_i}^{(+)} \rangle] \Omega_{l'}, \quad (4)$$

where now α represents the rotational coordinates of the molecule. The inner bracket of (4) is just the elastic scattering amplitude for fixed molecular orientation $f(\vec{k}_f, \vec{k}_i; \vec{\alpha})$ so that (4) may be written

$$f_{ll'}(\vec{k}_f, \vec{k}_i) = \int d\alpha \Omega_l^* f(\vec{k}_f, \vec{k}_i; \vec{\alpha}) \Omega_{l'}. \quad (5)$$

The scattering amplitude for fixed molecular orientation may now be obtained from a solution of (1) which still contains the vibrational and electronic part of the molecular Hamiltonian. These may be eliminated in effect by re-expressing (1) in the usual equivalent potential formalism⁶ which suppresses the vibrational and electronic degrees of freedom by introducing a complicated potential operator into the equation for the elastic scattering. Evaluation of this operator is prohibitively difficult except in the limit in which the incident electron is well separated from the molecule. In that case the dominant interaction is the dipole one with corrections from quadrupole, octupole, and shorter-range terms. At low-enough energies we expect the longest-range part of the potential, the dipole part, to dominate, so we replace the entire interaction of the electron with the molecule (including the equivalent potential) by the interaction of an electron with a point dipole. The corrections generated by the shorter-range terms will be small at sufficiently low energies provided that the dipole moment is not too large. These corrections are discussed in the next section.

We have thus reduced the problem to the evaluation of (5) where f on the right-hand side is obtained as the scattering amplitude for the wave function determined by the equation

$$(k^2 + \nabla^2 + \vec{\alpha} \cdot \mathbf{r} / r^3) \psi(r) = 0. \quad (6)$$

This equation has been solved previously with the result⁷

$$f(\vec{k}_f, \vec{k}_i; \vec{\alpha}) = \frac{i}{k} \sum_{n=0}^{\infty} \sum_{m=-n}^n \theta_n^{m(\mu)} e^{im\phi} \{ \theta_n^m(\eta) - \theta_n^m(-\eta) \exp[-i(L_n^m - m)\pi] \}, \quad (7)$$

where the eigenvalue L_n^m and the angular eigenfunction $\theta_n^{m(\mu)}$ are described in detail in Ref. 3. This may also be written as

$$f(\vec{k}_f, \vec{k}_i; \vec{\alpha}) = \frac{2\pi i}{k} \sum_{p,q,m} \rho_{pq}^m Y_{q+|m|,m}(\hat{k}_f, \hat{\alpha}) Y_{p+|m|,m}^*(\hat{k}_i, \hat{\alpha}), \quad (8)$$

where the Y 's are normalized spherical harmonics and the ρ matrix is given by

$$\rho_{pq}^m = \sum_{n=0}^{\infty} \Delta_{n, p-|m|}^m \Delta_{n, q-|m|}^m \{1 - \exp[-i(L_n^m - p)\pi]\}. \quad (9)$$

The Δ_{np}^m and L_n^m are eigenvectors and eigenvalues of a tridiagonal matrix whose solution is described in Ref. 3. The result (8) uses $\hat{\alpha}$ as the quantization direction for the incident and final momenta of the electron, but the direction of the vector $\hat{\alpha}$ is integrated over in (5). This is accomplished by expressing the Y 's in terms of Y 's quantized with respect to an arbitrary fixed direction by using the rotation matrices $D_{mm'l}$.⁸

In order to integrate over $\hat{\alpha}$ one must have a representation of the rotational eigenfunctions of the molecule. For a Σ electronic state of the molecule these are just the usual spherical harmonics. We shall now use this case for explicit evaluation of (5) and show below that the result applies to more general cases.

We will not get the angular distribution or concern ourselves with specific initial and final magnetic sublevels. Instead we obtain only a diffusion cross section averaged over initial and summed over final sublevels.⁹

$$\sigma_{ll'} = (2l'+1)^{-1} \sum_{mm'} \int d\Omega_k \int d\Omega_{\alpha} Y_{lm}^*(\hat{\alpha}) f(\vec{k}_f, \vec{k}_i; \vec{\alpha}) Y_{l'm'}(\hat{\alpha}) \cdot (1 - \hat{k}_i \cdot \hat{k}_f). \quad (10)$$

The diffusion cross section is evaluated here since it is the usual quantity obtained from swarm experiments and because the total cross section diverges when calculated by the method described here. The reason for the divergence is the neglect of the energy transfer in the excitation which leads to a larger effective interaction at large distances and a consequent divergence of the cross section in the forward direction. The divergence of the total cross section is however a weak one (logarithmic) so that the diffusion cross section is finite.

Extensive algebra involving $3j$ and $6j$ symbols results in the final expression

$$\sigma_{ll'} = \frac{2l+1}{k^2} \pi \sum_{\lambda=0}^{\infty} (2\lambda+1) \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 Z(\lambda), \quad (11a)$$

where

$$Z(\lambda) = \sum_{st} \left[|Z_{\lambda st}|^2 + \text{Re} Z_{\lambda st} Z_{\lambda, s+1, t+1}^* \left(\frac{(\lambda+s+t+2)(\lambda+s+t+3)(s+t-\lambda+1)(s+t-\lambda+2)}{(2s+1)(2s+3)(2t+1)(2t+3)} \right)^{1/2} \right. \\ \left. - \text{Re} Z_{\lambda st} Z_{\lambda, s+1, t-1}^* \left(\frac{(\lambda+t-s-1)(\lambda+t-s)(\lambda+s-t+1)(\lambda+s-t+2)}{(2s+1)(2s+3)(2t-1)(2t+1)} \right)^{1/2} \right] \quad (11b)$$

$$\text{where } Z_{\lambda st} = \sum_m \rho_{st}^m (-1)^m \begin{pmatrix} \lambda & s & t \\ 0 & m & -m \end{pmatrix}. \quad (11c)$$

The λ sum in (11a) is restricted by the $3j$ symbol to $|\lambda - l'| \leq \lambda \leq l + l'$. The s and t sums in (11b) run over all non-negative values allowed by the $3j$ symbol in (11c), and the m sum in (11c) is also restricted to the values allowed by this $3j$ symbol. The ρ matrix is essentially the output of the code described in Ref. 3. It is then used to evaluate $Z_{\lambda st}$ which in turn is used to evaluate $Z(\lambda)$ from which we get the cross section. The actual evaluation was carried out by using a modified ρ matrix from which the first Born approximation was explicitly removed. The result was to improve the convergence of the sums. The correct result could then be obtained by simply adding back the first Born approximation for the diffusion cross section. The cross section behaves as E^{-1} in this approximation, as has been noted previously.³

We have calculated cross sections for $\Delta l = 0, 1, 2$ for various values of α but have not extended our calculations to higher values of Δl since the model neglects quadrupole, octupole, and higher interactions. The $\Delta l = 2$ transitions require at least 2 dipole interactions or one quadrupole interaction. The $\Delta l = 3$ transitions require at least 3 dipole interactions or one octupole interaction. Thus it is not very meaningful to calculate higher Δl transitions due to the dipole interaction while neglecting higher multipole interactions. Indeed the $\Delta l = 2$ results presented here should be compared with experiment only after very careful consideration of the quadrupole interaction for that molecule. The reader is referred to Sec. IIIb for a further discussion of this point.

The $\Delta l = 0$ transition can come about through 2 or more dipole interactions, or at least 2 quadrupole interactions, so that it is more meaningful to discuss the pure dipole $\Delta l = 0$ transition than the $\Delta l \geq 2$ transitions. In Table I we show various $\Delta l = 0$ diffusion cross sections as a function of α and l . Each is a rapidly rising function of α but an almost flat function of l with a small peak at $l=1$ in each case. In Table II the $\Delta l = 1$ diffusion cross sections are given. In each case the $l-1$ transition is shown. The $l+1-l$ transition may be obtained from the reciprocity relation $(2l+1)\sigma_{l'l} = (2l'+1)\sigma_{ll'}$. It is clear from a comparison of the two tables that the $\Delta l = 0$ transitions contribute significantly for $\alpha \geq 0.6$. The $\Delta l = 1$ cross section does not rise as rapidly as the $\Delta l = 0$ cross section as a function of α but does grow somewhat more rapidly as a function of l . In Fig. 1 we show the ratio of our calculated $\Delta l = 1$ cross section to the first Born-approximation cross section given by

TABLE I. The quantity $[\sigma_{l,l}(\alpha)/\pi a_0^2]E$ (in Ry) as a function of α and l , with α given in units of $\frac{1}{2}ea_0$.

$\alpha \backslash l$	0	1	2	3	4	5	6	7	10	12
0.2	4.639(-4) ^a	5.004(-4)	4.900(-4)	4.882(-4)	4.876(-4)	4.873(-4)	4.871(-4)	4.870(-4)	4.869(-4)	4.868(-4)
0.4	7.575(-3)	8.150(-3)	7.986(-3)	7.958(-3)	7.948(-3)	7.943(-3)	7.941(-3)	7.939(-3)	7.937(-3)	7.936(-3)
0.6	3.983(-2)	4.266(-2)	4.185(-2)	4.172(-2)	4.167(-2)	4.164(-2)	4.163(-2)	4.162(-2)	4.161(-2)	4.161(-2)
0.8	1.342(-1)	1.427(-1)	1.403(-1)	1.399(-1)	1.397(-1)	1.397(-1)	1.396(-1)	1.396(-1)	1.396(-1)	1.395(-1)
1.0	3.659(-1)	3.854(-1)	3.798(-1)	3.789(-1)	3.786(-1)	3.784(-1)	3.783(-1)	3.783(-1)	3.782(-1)	3.782(-1)
1.2	9.683(-1)	1.005	9.944(-1)	9.927(-1)	9.920(-1)	9.917(-1)	9.916(-1)	9.915(-1)	9.913(-1)	9.913(-1)
1.25	1.321	1.360	1.349	1.347	1.346	1.346	1.346	1.346	1.346	1.346

^aThe notation $(-n)$ means a factor of 10^{-n} .

$$\sigma_{l+1,l}^B = \frac{2}{3}(\pi/k^2)\alpha^2(l+1)/(2l+1) \quad (12)$$

as a function of α . The curves for different l are indistinguishable on the scale of the figure for l in the range 0 to 14 indicating that the α^3 and higher contributions to the cross section are very nearly proportional to the α^2 term, the first Born approximation. The correction to the Born result is only significant for $\alpha > 0.8$. In Table III the results for $\Delta l = 2$ transitions are given. They rise rapidly with α and slowly with l but are always small compared with the $\Delta l = 0$ and $\Delta l = 1$ transitions. We expect that our results for $\Delta l = 3$ and higher would be even smaller so that in effect the $\Delta l = 0$ and 1 transitions are all that is needed to compare with experimental results.

The quantity usually measured¹⁰ in a mobility experiment is an effective cross section weighted by the probability of finding the molecule in the initial state l' .

$$Q_{ll'} = N^{-1}\sigma_{ll'}(2l'+1)\exp(-W_{l'}/kT), \quad (13a)$$

$$\text{where } N = \sum_{l'} (2l'+1)\exp(-W_{l'}/kT). \quad (13b)$$

A gross experiment, measuring only the total momentum transfer will measure only $Q = \sum_{ll'} Q_{ll'}$. By using Eq. (10) for $\sigma_{ll'}$ and the completeness of the Y_{lm} , the l sum can be performed with the result that $Q = \sigma'$ where σ' is the cross section calculated by Mittleman and von Holdt.³ It is the total cross section for scattering in a given state l' , and it is independent of l' and is related to the results of this paper by

$$\sigma' = \sum_l \sigma_{ll'}. \quad (13c)$$

Thus Q is temperature-independent in our approximation and we may attribute any temperature dependence in a measurement of it to the breakdown of the fixed orientation approximation.

For other than Σ electronic states the rotational states of the molecule are more complicated than the spherical harmonics used in (10). For example, for other than Σ diatomic states the functions must also specify the projection of the electronic orbital angular momentum along the internuclear axis.¹¹ (The m in Y_{lm} specifies the projection of the nuclear angular momentum on a space fixed axis.) The energy of the rotational state depends upon this quantum number so that the sum over initial and the average over final sub-states should be weighted by a factor depending upon the energy of these sub-states. However, the energy splittings are of the same order as the molecular rotational energies which we have neglected. Thus it is consistent to treat them as degenerate states and perform the sums and averages without any weighting factor. In that case completeness relations bring the results back to the form of Eq. (11).

TABLE II. The quantity $[\sigma_{l+1,l}(\alpha)/\pi a_0^2]E$ (in Ry) as a function of α and l , with α given in units of $\frac{1}{2}ea_0$.

$\alpha \backslash l$	0	1	2	3	4	5	6	7	10	12
0.2	2.667(-2) ^a	1.779(-2)	1.600(-2)	1.524(-2)	1.481(-2)	1.455(-2)	1.437(-2)	1.422(-2)	1.397(-2)	1.393(-2)
0.4	1.069(-1)	7.130(-2)	6.415(-2)	6.111(-2)	5.939(-2)	5.832(-2)	5.757(-2)	5.700(-2)	5.599(-2)	5.560(-2)
0.6	2.429(-1)	1.620(-1)	1.457(-1)	1.389(-1)	1.349(-1)	1.325(-1)	1.309(-1)	1.295(-1)	1.272(-1)	1.264(-1)
0.8	4.446(-1)	2.966(-1)	2.267(-1)	2.541(-1)	2.470(-1)	2.425(-1)	2.395(-1)	2.370(-1)	2.328(-1)	2.311(-1)
1.0	7.440(-1)	4.964(-1)	4.466(-1)	4.254(-1)	4.134(-1)	4.060(-1)	4.008(-1)	3.969(-1)	3.898(-1)	3.871(-1)
1.2	1.263	8.433(-1)	7.585(-1)	7.225(-1)	7.020(-1)	6.896(-1)	6.806(-1)	6.739(-1)	6.619(-1)	6.573(-1)
1.25	1.494	9.980(-1)	8.975(-1)	8.549(-1)	8.308(-1)	8.161(-1)	8.055(-1)	7.975(-1)	7.834(-1)	7.778(-1)

^aThe notation $(-n)$ means a factor of 10^{-n} .

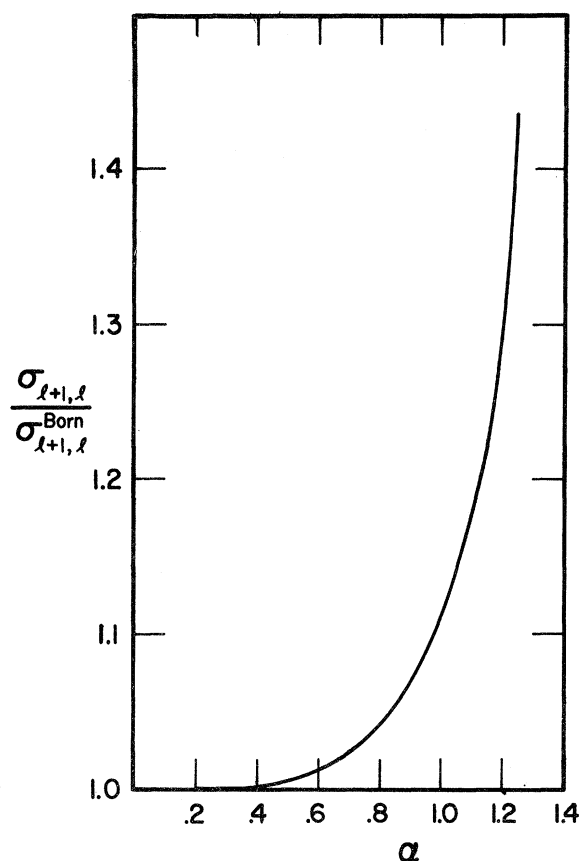


FIG. 1 The ratio of the calculated $\Delta l=1$ cross section to the Born-approximation result as a function of α for all initial states (α is in units of $\frac{1}{2}ea_0$).

III. CORRECTIONS

(a) High-Energy Correction

Our first approximation was to neglect the terms $W_{l'} - H_{\text{rot}}$ in the propagator in Eq. (1). We shall now retain them to first order to determine the corrections to our result. We write the total amplitude as

$$-4\pi f = \langle \chi_f V \Psi_i^{(+)} \rangle = \langle \chi_f V \chi_i \rangle + \langle \chi_f V (E - H + i\eta)^{-1} V \chi_i \rangle \quad (14)$$

TABLE III. The quantity $[\sigma_{l+2,l}(\alpha)/\pi a_0^2]E$ (in Ry) as a function of α and l , with α given in units of $\frac{1}{2}ea_0$.

$\alpha \setminus l$	0	1	2	3	4	5	6	7	10	12
0.2	9.130(-5) ^a	5.479(-5)	4.696(-5)	4.348(-5)	4.151(-5)	4.024(-5)	3.934(-5)	3.869(-5)	3.744(-5)	3.693(-5)
0.4	1.438(-3)	8.629(-4)	7.396(-4)	6.848(-4)	6.537(-4)	6.337(-4)	6.196(-4)	6.092(-4)	5.895(-4)	5.816(-4)
0.6	7.080(-3)	4.247(-3)	3.641(-3)	3.371(-3)	3.218(-3)	3.119(-3)	3.050(-3)	2.998(-3)	2.902(-3)	2.863(-3)
0.8	2.142(-2)	1.285(-2)	1.102(-2)	1.020(-2)	9.737(-3)	9.437(-3)	9.227(-3)	9.072(-3)	8.781(-3)	8.664(-3)
1.0	4.889(-2)	2.933(-2)	2.515(-2)	2.329(-2)	2.223(-2)	2.154(-2)	2.107(-2)	2.071(-2)	2.005(-2)	1.978(-2)
1.2	8.955(-2)	5.376(-2)	4.608(-2)	4.266(-2)	4.072(-2)	3.946(-2)	3.859(-2)	3.794(-2)	3.673(-2)	3.623(-2)
1.25	9.900(-2)	5.943(-2)	5.094(-2)	4.716(-2)	4.501(-2)	4.362(-2)	4.266(-2)	4.194(-2)	4.060(-2)	4.005(-2)

^aThe notation $(-n)$ means a factor of 10^{-n} .

and define an average energy by

$$k^2 = \frac{1}{2}(k_f^2 + k_i^2) = k_i^2 - \frac{1}{2}\Delta W = k_f^2 + \frac{1}{2}\Delta W, \quad (15a)$$

$$\text{where } \Delta W = W_l - W_{l'}. \quad (15b)$$

Now expanding about this energy in the initial and final plane waves and expanding the propagator in Eq. (14)

$$(E - H + i\eta)^{-1} = a^{-1} + a^{-1}[\frac{1}{2}(W_l + W_{l'}) - H_{\text{rot}}]a^{-1} + \dots, \quad (16)$$

$$\text{where } a = k^2 - T + \mathcal{E}_i - H' + i\eta; \quad (17)$$

and then using the factorization of $\Psi^{(+)}$ into a product of the rotational function and $\psi^{(+)}$, we obtain a correction to the amplitude

$$\delta f = \frac{-i}{16\pi} \frac{\Delta W}{k^2} \langle \Omega_l [\langle \lambda_f \vec{k}_f \cdot \vec{r} V \psi_i^{(+)} \rangle + \langle \psi_f^{(-)} V \vec{k}_i \cdot \vec{r} \lambda_i \rangle] \Omega_{l'} \rangle. \quad (18)$$

The evaluation of the inner integrals in (18) is difficult but the energy dependence may be obtained by noting that $\psi_i^{(+)}$ and $\psi_f^{(-)}$, solutions of the equation for scattering from a point dipole (Eq. 6), are functions of the energy k^2 only through the variable kr , i. e.,

$$\psi = \psi(\vec{k}, kr).$$

A simple scaling of the integration variable in (18) results in

$$\delta f \approx (\Delta W/k^2)(1/k). \quad (19)$$

Then the relative error in the diffusion cross section due to our first approximation is of order $\Delta W/k^2$.¹²

(b) Low-Energy Correction

There is a correction due to our second approximation, that of the replacement of the complicated electron-molecule interaction by the dipole potential in (6). In addition to the dipole interaction there are other potential terms which will contribute additional terms in the amplitude with different energy behaviors. These terms may be para-

metrized in the spirit of a modified effective range expansion¹ provided that the form of the energy dependence is known.

Meaningful solutions of (6) exist for

$$\alpha < \alpha_{\text{crit}} = 1.279. \quad (20)$$

For greater dipole moments the potential is too strongly attractive in some directions. This is reflected by the fact that the eigenvalue L_0^0 appearing in (7) becomes complex. At $\alpha = \alpha_{\text{crit}}$ we obtain $L_0^0 = -\frac{1}{2}$. Our discussion here applies only for dipole moments restricted by (20).

We obtain additional terms in the amplitude by a method suggested by O' Malley.¹³ He gave an argument indicating that the correct energy dependence in a modified effective range formula could be obtained by a method of successive iterations which in lowest order is equivalent to the first distorted-wave Born approximation.¹⁴ We shall therefore add potential terms δV to (6) and obtain the lowest-order corrections by

$$\delta f = - (4\pi)^{-1} \int d^3 r \psi_f^{(-)}(\vec{r}) \delta V \psi_i^{(+)}(\vec{r}). \quad (21)$$

A quadrupole term of the form

$$q P_2(\hat{\alpha} \cdot \hat{r}) [1 - e^{-\beta r}] / r^3 \quad (22)$$

will contribute a correction with an energy dependence

$$\delta f_{\text{quad}} \approx k^2 L_0^0 \quad (23)$$

as will short-range terms. We therefore have a sort of effective range formula whose leading term, obtained from the dipole potential, behaves as k^{-1} while the corrections which must be parametrized are of order k to the power $2L_0^0$. This is different from the usual effective range theory in that the leading term must be parametrized there, while here it is the second term. For dipole moments,

$$\alpha \rightarrow \alpha_{\text{crit}}, \quad L_0^0 \rightarrow -\frac{1}{2}$$

so that the energy dependence of the correction becomes essentially that of the leading term and the expansion loses its utility.

The non-analytic behavior in Eq. (23) is unusual and is indeed an artifact of the calculation. If we take account of the dynamics of the molecule this behavior near $k=0$ disappears. For example, we could investigate the very low-energy scattering of an electron by a molecule in its ground rotational state. The elastic channel may be isolated in the usual way,⁶ and it is found that the longest range potential is proportional to r^{-4} so that the usual modified effective range theory¹ applies. (The same result is obtained for elastic scattering from any rotational state.) Similarly the excitation cross section exhibits no unusual behavior at threshold when the energy difference of the rotational levels is not neglected. It is precisely this neglect which gave the peculiar result of Eq. (23) which we emphasize has no validity when the inequality $(\Delta W/k^2) \ll 1$ does not hold.

IV. DIPOLE MOMENTS GREATER THAN THE CRITICAL VALUE

If the dipole moment is greater than the critical value [Eq. (20)], then the method of Ref. 3 breaks down due to the singularity at the origin. The method may be salvaged by removing the singularity with a cut-off function. We illustrate this for the simplest case where α is greater than α_{crit} so that L_0^0 is complex but all the other L_n^m are real and greater than $-\frac{1}{2}$. Equation (6) may then be replaced by

$$\left[k^2 + \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + Q \left(\frac{L^2}{r^2} + \frac{\vec{\alpha} \cdot \vec{r}}{r^3} \right) \right] Q + P \left(\frac{L^2}{r^2} + \frac{\vec{\alpha} \cdot \vec{r}}{r^3} \right) f(r) P \psi(\vec{r}) = 0, \quad (24a)$$

where L^2 is the angular momentum operator and where

$$P = \theta_0^0(\mu) \langle \theta_0^0(\mu') \rangle, \quad Q = 1 - P, \quad (24b)$$

and for example

$$f(r) = 1, \quad r \geq r_0 \\ = (r/r_0)^2, \quad r < r_0, \quad (24c)$$

where r_0 is of the order of the molecular size.

With this prescription the separation of variables described in Ref. 3 is still possible, and the angular equations and all the radial equations except that for $n=m=0$ are unchanged.

For $n=m=0$ one obtains

$$\left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + k^2 - \frac{\Lambda_{00}}{r^2} f(r) \right) R_{00}(r) = 0, \quad (25)$$

where Λ_{00} is the eigenvalue of the radial equation [Eq. (3) of Ref. 3]. By hypothesis

$$-\Lambda_{00} = \Lambda^2 = a^2 + \frac{1}{4}, \quad (26)$$

where a is real. Equation (25) is readily solvable. The resultant modification of the scattering amplitude [Eq. (7)] is to delete the $n=m=0$ term from the sum and replace it with the term

$$(i/k) \theta_0^0(\mu) [\theta_0^0(\eta) - e^{2i\delta} \theta_0^0(-\eta)], \quad (27)$$

where δ is the phase shift obtained from (25). In the limit $kr_0 \ll 1$ the expression for δ simplifies to give

$$\tan \delta = \sin(\phi + \xi) / \sin(\phi - \xi), \quad (28a)$$

where $a(\alpha)$ is defined by (26) and

$$\phi = a \ln(\frac{1}{2} k r_0) + \arg \Gamma(1 - ia) - \tan^{-1} \left(\frac{a}{s + \frac{1}{2}} \right), \quad (28b)$$

$$s = \Lambda r_0 \cot \Lambda r_0 - 1, \quad (28c)$$

$$\xi = \tan^{-1} [\tanh(\frac{1}{2} \pi a)]. \quad (28d)$$

This modification of (7) results in a slightly different energy behavior for the cross section of the form

$$\sigma_{ll'} = \frac{1}{k^2} (A_{ll'} + B_{ll'} \sin 2\delta + C_{ll'} \sin^2 \delta), \quad (29)$$

where A , B , C are energy-independent numbers obtained as sums in a form similar to Eq. (11). This result has an energy dependence beyond the simple k^{-2} behavior of Eq. (11) through the slowly varying phase shift δ . We could evaluate the terms A , B , and C as a function of α and the additional parameter γ_0 but considerations analogous to those of Sec. IIIb make this modified method unreliable for comparison with experiment. This conclusion

is reached by asking for the contribution of the neglected quadrupole terms in the potential. We find, by the method of Eq. (21), that the energy behavior of this contribution is similar to that of Eq. (29). That is, this new term has an over-all factor of k^{-2} with additional slow energy dependence through the phase shift. This method will only be useful in cases where the quadrupole moment is small compared with the dipole moment (in natural units). By contrast, the utility of the method for $\alpha < \alpha_{\text{crit}}$ can be based on the smallness of k in addition to the smallness of the quadrupole moment.

*Supported by Advanced Research Projects Agency Contract No. DA HCO-4-67C-0070 and National Aeronautics and Space Administration Grant No. Nsg 243.

†Supported by the U. S. Atomic Energy Commission.

¹T. F. O'Malley, L. Spruch, and L. Rosenberg, Phys. Rev. **125**, 1300 (1962).

²D. M. Chase, Phys. Rev. **104**, 838 (1956).

³M. H. Mittleman and R. E. von Holdt, Phys. Rev. **140**, A726 (1965).

⁴Rydberg units are used throughout.

⁵In the notation W_l , l refers to those quantum numbers necessary to specify the rotational energy. It is the angular momentum only for \sum electronic states.

⁶H. Feshbach, Ann. Phys. (N. Y.) **19**, 287 (1962), or M. H. Mittleman and K. M. Watson, Phys. Rev. **113**, 198 (1959).

⁷Equation (14) of Ref. 3 is incorrect. The factor $\frac{1}{2}$ should be removed. Similarly a factor of 2 should be inserted in the last member of Eq. (12). The numerical results presented are however correct. Dipole moments are measured in units of $\frac{1}{2}ea_0 = 1.27 \times 10^{-18}$ esu. The values of the dipole moments of the three molecules

given in Fig. 3 of Ref. 3 should be multiplied by a factor of 2.

⁸A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, (Princeton University Press, Princeton, New Jersey, 1957).

⁹The exact cross section contains a factor k_f/k_i which has been set equal to unity consistent with the approximation leading to (3). This however is not necessary and in comparison of our numerical results with experiment the factor may be included. The approximation $|\vec{k}_f| = |\vec{k}_i|$ in f is expected not to be crucial but neglecting the factor k_f/k_i will be at lower electron energies.

¹⁰For example, see R. D. Hake and A. V. Phelps, Phys. Rev. **158**, 70 (1967).

¹¹G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

¹²The error made in the total cross section due to this approximation is more significant, since it diverges when calculated by the method used here.

¹³T. F. O'Malley, Phys. Rev. **134**, A1188 (1964).

¹⁴A more formal justification of this procedure has been given by Dr. H. Snodgrass, private communication.

Theory of Polarization of Molecular Line Radiation Excited by Electron Impact*

A. Norman Jette

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

and

Patrick Cahill†

Columbia University Radiation Laboratory, New York, New York

(Received 9 August 1968)

The Percival-Seaton theory for the polarization of atomic impact radiation is extended to the case of diatomic molecules. Similar to the atomic case, it is shown that for excitation by electron impact involving a change of electronic angular momentum along the molecular internuclear axis, the threshold polarization can be determined from the symmetry of the total molecular wave function without a detailed knowledge of the inelastic cross sections. General expressions are developed for the cases of fine and hyperfine splitting, and explicit relations are given for the first two rotational levels of a $^3\Pi_u$ state undergoing a radiative transition to a $^3\Sigma_g$ state in the limit of fine and hyperfine separations being much larger than the natural linewidth. This theory is valid when the radiative state is populated by a direct interaction, and the radiative transition between rotational states is resolved.