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Excitation of Molecular Rotation by Slow Electrons*†

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The cross sections for the rotational excitation of H_2 and N_2 by slow electrons are evaluated in a distorted-wave approximation with the use of a simple model potential. The changes from the previous Born-approximation results are quite pronounced, particularly for H_2.

I. INTRODUCTION

EXCITATION of molecular rotation and vibration are among the most important energy-loss mechanisms for slow electrons in molecular gases. Thus the study of these excitation processes is closely related to the study of discharges in gases, the effects of radiation on matter, upper-atmosphere physics, and other problems involving slow electrons.

In this paper, the rotational excitation of homonuclear diatomic molecules is studied wave mechanically. Morse[1] and Carson[2] studied the rotational excitation through the short-range electrostatic interaction which arises when the incident electron approaches the electron cloud of the molecule. Later, Gerjuoy and Stein[3] put emphasis on an interaction with longer range. Molecules are regarded in their treatment as point quadrupoles. For H_2 and N_2, they get effective cross sections which are not inconsistent with the existing experimental data. Stabler[4] made a similar calculation for the molecular ion, taking into account the distortion of the scattered-electron wave function by the Coulomb potential, and this was further considered by Sampson.[5] Dalgarno and Moffett[6] made a correction to Gerjuoy and Stein's result by introducing the nonspherical part of the polarization interaction.

Generally, the asymptotic form of the interaction between a diatomic molecule and an electron is given approximately by

$$V(\hat{s},\mathbf{r})=-\frac{\alpha}{2r^4}-\frac{\mu}{r^2}P_1(\hat{s}\cdot\hat{r})-\left(\frac{\alpha'}{2r^4}+\frac{Q}{r^3}\right)P_2(\hat{s}\cdot\hat{r}). \quad (1)$$

Here and in the following, atomic units are used. Thus distances are measured in units of Bohr radii and energy is measured in units of 27.2 eV. $\mathbf{r}$ is the position vector of the scattered electron relative to the center of mass of the molecule and $\hat{s}$ is the unit vector along the internuclear axis of the molecule (Fig. 1). μ is the electric-dipole moment of the molecule. For homonuclear diatomic molecules, we have $\mu=0$. Q is the electric-quadrupole moment defined by

$$Q=\int q(\mathbf{r}')r'^2P_2(\hat{s}\cdot\hat{r}')d\mathbf{r}', \quad (2)$$

where $q(\mathbf{r}')$ is the charge distribution in the molecule. α and α' are related to $\alpha_{\parallel}$ and $\alpha_{\perp}$, which are the polarizabilities of the molecule along directions parallel and perpendicular to its axis, respectively, by

$$\alpha=\tfrac{1}{3}(\alpha_{\parallel}+2\alpha_{\perp}), \quad (3)$$

$$\alpha'=\tfrac{2}{3}(\alpha_{\parallel}-\alpha_{\perp}). \quad (4)$$

P_1 and P_2 are the Legendre polynomials. Gerjuoy and Stein used the Q term only. Dalgarno and Moffett used the α' term as well as the Q term.

All previous work is based on the Born approximation. The validity of the approximation was discussed by Gerjuoy and Stein. They found that in the transition integral of the Born approximation the main contribution comes from the region corresponding to large separation between the electron and the molecule. If the distant collisions give the main contribution to the transition, the distortion of the electron wave function from a plane wave will have little effect on the resulting cross section. However, a more detailed analysis of the Born calculation shows[7] that the main contribution actually comes from the combination of incident p wave

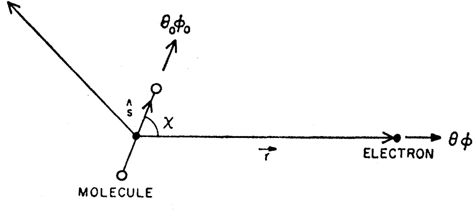

FIG. 1. Coordinates for the electron-molecule collision with Z axis along the direction of incidence.

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[1] P. M. Morse, Phys. Rev. **90**, 51 (1953).

[2] T. R. Carson, Proc. Phys. Soc. (London) **A67**, 909 (1954).

[3] E. Gerjuoy and S. Stein, Phys. Rev. **97**, 1671 (1955); **98**, 1848 (1955).

[4] R. C. Stabler, Phys. Rev. **131**, 679 (1963).

[5] D. H. Sampson, Phys. Rev. (to be published).

[6] A. Dalgarno and R. J. Moffett, Proc. Nat. Acad. Sci. India **A33**, 511 (1963). [*Note added in proof.* A calculation similar to the present one which has recently appeared is by R. C. Mjolsness and D. H. Sampson, Phys. Rev. Letters **13**, 812 (1964).]

[7] K. Takayanagi Joint Institute for Laboratory Astrophysics Report No. 11, 1964 (unpublished).

and outgoing p wave (except for just above threshold where the incident d wave combined with the outgoing s wave gives the main contribution). Since s and p waves should be distorted considerably by the static field of the target molecule in the energy region of interest, the effect of distortion could be important. In this paper, we present a distorted-wave-type calculation for the hydrogen and nitrogen molecules. As will be seen later, the resulting cross sections are considerably different from the results of the Born approximation.

The asymptotic form (1) for the interaction cannot be used for small values of r. The actual interaction will not have singularities such as r^{-3} or r^{-4} at the center of mass, but rather Coulomb singularities at the nuclei. Also the possibility of exchange of incident and molecular electrons will affect the interaction and give it a nonlocal character at small r. Unfortunately, we do not know the correct short-range interaction. In this paper, therefore, we simply cutoff the asymptotic form (1) at $r=R$, as follows:

$$V(\hat{s},\mathbf{r})=-\frac{\alpha}{2R^4}-\left(\frac{Q}{R^3}+\frac{\alpha'}{2R^4}\right)P_2(\hat{s}\cdot\hat{r}),\quad r\leq R \tag{5a}$$

$$=-\frac{\alpha}{2r^4}-\left(\frac{Q}{r^3}+\frac{\alpha'}{2r^4}\right)P_2(\hat{s}\cdot\hat{r}),\quad r\geq R. \tag{5b}$$

For H_2, we adopt the following values for the parameters:

$$\alpha=5.328 \text{ (Ref. 8)},$$
$$\alpha'=1.250 \text{ (Ref. 8)},$$
$$Q=0.464 \text{ (Ref. 9)},$$

and for N_2,

$$\alpha=12.00 \text{ (Ref. 10)},$$
$$\alpha'=4.20 \text{ (Ref. 10)},$$
$$Q=-1.10 \text{ (Ref. 11)}.$$

The negative sign of Q for nitrogen was adopted in accordance with the theoretical calculation of Scherr.[12]

Preliminary calculations showed that the rotational excitation cross section depends rather sensitively on the value chosen for the cutoff distance R. To choose a reasonable value of R, we first studied the elastic scattering resulting from the same potential function. By comparing the calculated elastic cross section with the observed data, we can select a more or less reasonable value of R.

II. ELASTIC SCATTERING

Even if the incident energy is as low as 10^{-3} atomic units, which corresponds roughly to the mean thermal energy at room temperature, the collision time is much shorter than the period of molecular rotation. Therefore, we fix the molecular orientation in calculating the elastic scattering cross section, and then average over all orientations.

The direction of the incident electron beam will be taken as Z direction. The orientation of the molecular axis will be specified by the polar angles θ_0, φ_0. The electronic wave function arising from the l_0th incident partial wave will be expanded as

$$\psi_{l_0}(\mathbf{r})=\sum_{lm} r^{-1}f_{l_0}(lm|k,r)Y(lm|\theta\varphi). \tag{6}$$

$Y(lm|\theta\varphi)$ is the normalized spherical harmonic function. It should be noted that the radial function $f_{l_0}(lm|k,r)$ depends on θ_0 and φ_0 parametrically. By substituting the wave function (6) into the Schrödinger equation, it is found that these radial functions must satisfy a set of coupled equations of the following form:

$$\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-2(lm|V|lm)+k^2 f_{l_0}(lm|k,r)$$
$$=2\sum_{l'm'}{}' (lm|V|l'm')f_{l_0}(l'm'|k,r), \tag{7}$$

where k is the wave number ($k^2/2$ is the incident electron energy in atomic units) and the matrix elements of the interaction V are easily calculated to be

$$(lm|V|l'm')=-\frac{\alpha}{2r^4}\delta_{ll'}\delta_{mm'}$$
$$-\left(\frac{Q}{r^3}+\frac{\alpha'}{2r^4}\right)(lm|P_2(\hat{s}\cdot\hat{r})|l'm'), \tag{8}$$

where

$$(lm|P_2(\hat{s}\cdot\hat{r})|l'm')$$
$$=(4\pi/5)^{1/2}Y^*(2,m-m'|\theta_0\varphi_0)c^2(lm,l'm') \tag{9}$$

and

$$c^2(lm,l'm')=\left(\frac{4\pi}{5}\right)^{1/2}\int\int Y^*(lm|\theta\varphi)Y(2,m-m'|\theta\varphi)$$
$$\times Y(l'm'|\theta\varphi)\sin\theta d\theta d\varphi. \tag{10}$$

$c^2(lm,l'm')$ vanishes unless $l-l'=0$, or ±2. The diagonal matrix element of the interaction potential is given by

$$(lm|V|lm)=-\frac{\alpha}{2r^4}-\left(\frac{Q}{r^3}+\frac{\alpha'}{2r^4}\right)$$
$$\times\frac{l(l+1)-3m^2}{(2l+3)(2l-1)}P_2(\cos\theta_0). \tag{11}$$

It should be understood that for $r\leq R$, r is replaced by R in $(lm|V|l'm')$, in accordance with our potential model (5a), (5b).

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[8] E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. (London) **A65**, 178 (1952).

[9] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).

[10] *Zahlenwerte and Functionen*, edited by H. H. Landolt and R. Börnstein (Springer-Verlag, Berlin, 1951), Vol. I, Part 3, p. 510.

[11] J. D. Poll, Phys. Letters **7**, 32 (1963).

[12] C. W. Scherr, J. Chem. Phys. **23**, 569 (1955).

If one gets a solution of (7) with the asymptotic form

$$f_{l_0}(lm|k,r) \xrightarrow[r\to\infty]{} \delta_{ll_0}\delta_{m0}\exp[-i(kr-\tfrac{1}{2}l\pi)] -S(lm|l_00)\exp[i(kr-\tfrac{1}{2}l\pi)], \quad (12)$$

for all possible values of l_0, l, and m, then the elastic-scattering cross section is given by

$$\sigma_{\mathrm{el}}=(\pi/k^2)\sum_{lm}|\sum_{l_0}(2l_0+1)^{1/2} \times i^{l_0}[S(lm|l_00)-\delta_{ll_0}\delta_{m0}]|^2. \quad (13)$$

If the nonspherical part of the potential is not too large, one can apply perturbation theory. To the zeroth approximation, we keep only the diagonal elements of V [as in (11)], leading to a diagonal S matrix,

$$S^{(0)}(lm|l_00)=\delta_{ll_0}\delta_{m0}\exp(2i\eta_{l_00}), \quad (14)$$

where η_{l_00} is the phase shift. The cross section to this approximation is given by

$$\sigma_{\mathrm{el}}=(4\pi/k^2)\sum_{l_0}(2l_0+1)\sin^2\eta_{l_00}. \quad (15)$$

To the first approximation, obtained by using zero-order f's on the right-hand side of (7), one has for the nondiagonal elements of the S matrix,

$$S^{(1)}(lm|l_00)=-(4i/k)\exp(i\eta_{lm}+i\eta_{l_00})\int_0^\infty f^N(lm|k,r) \times(lm|V|l_00)f^N(l_00|k,r)dr, \quad (16)$$

where the zero-order $f^N(lm|k,r)$ is the solution of

$$\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-2(lm|V|lm)+k^2\right\}f^N(lm|k,r)=0, \quad (17)$$

with the conditions

$$f^N(lm|k,0)=0,$$

$$f^N(lm|k,r)\xrightarrow[r\to\infty]{}\sin(kr-\tfrac{1}{2}l\pi+\eta_{lm}). \quad (18)$$

Preliminary calculations showed that the nondiagonal S-matrix elements were fairly small in our problem. Thus the actual calculation was done by using (15). Later, in Figs. 4 and 5, the smallness of the nondiagonal elements of S will be shown for a few selected values of R. In calculating σ_{el}, only $l_0=0$, 1, and 2 were taken into account.

The cross section was calculated for $\theta_0=0$, $\pi/4$, and $\pi/2$. We have assumed that

$$\sigma_{\mathrm{el}}(\theta_0)=\bar{\sigma}_{\mathrm{el}}+\sigma_2P_2(\cos\theta_0)+\sigma_4P_4(\cos\theta_0) \quad (19)$$

gives a good approximation to the θ_0 dependence of the cross section. Then the averaged cross section is given by

$$\bar{\sigma}_{\mathrm{el}}=(1/15)[\sigma_{\mathrm{el}}(0)+8\sigma_{\mathrm{el}}(\pi/4)+6\sigma_{\mathrm{el}}(\pi/2)]. \quad (20)$$

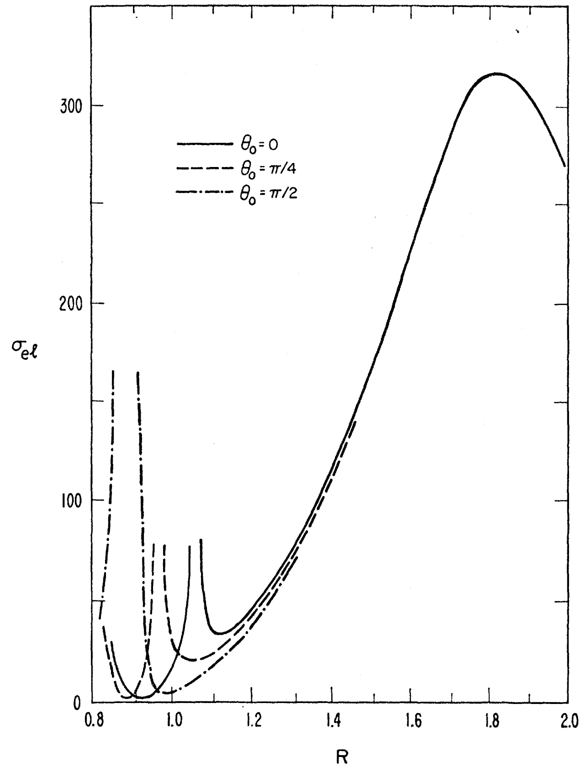

FIG. 2. Elastic-scattering cross section for H_2 for electron energy $k^2/2=0.02$ and various molecular orientations as a function of cutoff parameter.

In the case of H_2, we calculated $\sigma_{\mathrm{el}}(\theta_0)$ as a function of R for a fixed incident energy $k^2/2=0.02$. The result is shown in Fig. 2. The large peak at $R=1.83$ corresponds to the fact that there is a discrete s level with nearly zero energy for this value of R. In other words, the s-wave phase shift (which does not depend on θ_0) for this energy passes through $\pi/2$ at $R\cong1.83$. The peak value of the cross section is found very close to the maximum s-wave cross section $4\pi/k^2=314$. Therefore, the p-wave contribution is very small here. A similar large peak appears to occur for R less than 0.8. The sharp peaks around $R=1.0$ are due to the p-wave phase shift passing through $\pi/2$. Since p-wave scattering depends on the molecular orientation, we get separate peaks for different θ_0.

For hydrogen and nitrogen, the total scattering cross sections were measured many years ago.[13] In the low-energy region under consideration, this is nearly the same as the elastic-scattering cross section. For nitrogen, the cross section has a sharp peak with a maximum of nearly 100 a. u. in the 2–3-eV region, while for hydrogen a much broader peak with a maximum of about 50 a. u. was found in the 1–4-eV region. Both cross sections rise again at lower energies. However, according to a recent analysis of swarm experiments

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[13] E. Brüche, Ann. Physik **82**, 912 (1927); C. Ramsauer and R. Kollath, *ibid.* **4**, 91 (1930); C. E. Normand, Phys. **35**, 1217 (1930).

by Engelhardt and Phelps for hydrogen[14] and by Engelhardt, Phelps, and Risk for nitrogen,[15] it appears that these elastic cross sections do not tend to rise at low energies. Their momentum transfer cross sections, which are practically equal to σ_{el} at very low energy, tend to a finite value of around 30 a. u. for H_2 and a somewhat lower value for N_2. We may thus put the restriction on the cross section that the low-energy value ($k^2/2 \cong 0.02$) should be less than 100 a. u. for H_2 as well as for N_2. This limits the range of R which we need to consider.

For H_2, with several values of R chosen in the above described manner, we have calculated $\bar{\sigma}_{\mathrm{el}}$ as a function of the incident energy $k^2/2$. The result is shown in Fig. 3. As is seen at once, agreement with the experimental data is not very close for any of the chosen values of R. This indicates the necessity for further refinement in the interaction potential to be used in this scattering problem. Among the values studied, however, $R=1.2$–1.3 is the region where the general behavior and the order of magnitude of the calculated cross section is closest to the experimental one. Thus we have chosen $R=1.2$ and 1.3 for the rotational excitation calculation. For these values of R, $\sigma_{\mathrm{el}}(0)$, $\sigma_{\mathrm{el}}(\pi/4)$, and $\sigma_{\mathrm{el}}(\pi/2)$ are shown in Figs. 4 and 5. Here the calculations were done with and without nondiagonal S-matrix elements. The nondiagonal elements, when included, were calculated by (16). It is seen from these figures that the nondiagonal elements do not change the cross section very much. Dependence on θ_0, however, is fairly strong. We have also computed the elastic-scattering cross section arising from only the spherical part of the potential,

$$V_s = -\alpha/2r^4 \quad \text{for} \quad r \geq R; \quad -\alpha/2R^4 \quad \text{for} \quad r \leq R, \tag{21}$$

and find that it is very close to $\bar{\sigma}_{\mathrm{el}}$, the difference being

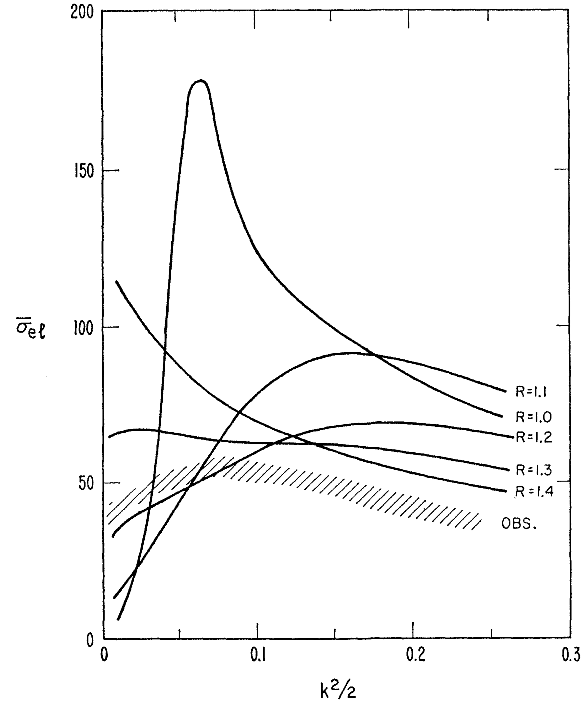

FIG. 3. Average elastic-scattering cross-section curves for H_2 for a number of cutoff radii. The cross hatching corresponds to the experimental data.

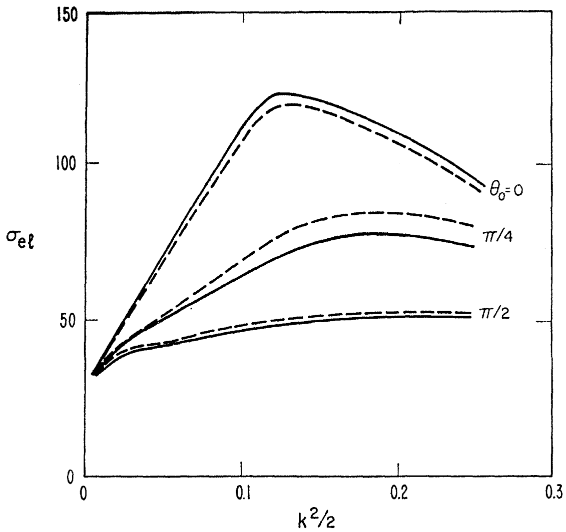

FIG. 4. The effect of the nondiagonal elements of the S matrix on the elastic scattering by H_2 for a number of molecular orientations ($R=1.2$). Solid lines without, dashed lines with, nondiagonal elements of S matrix.

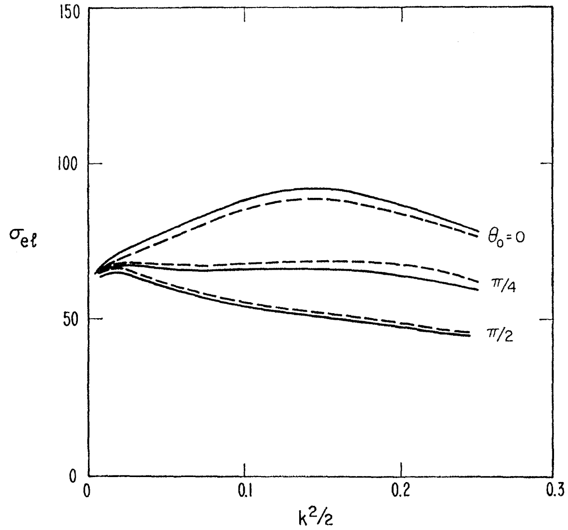

FIG. 5. The effect of the nondiagonal elements of the S matrix on the elastic scattering by H_2 for a number of molecular orientations ($R=1.3$). Solid lines without, dashed lines with, nondiagonal elements of S matrix.

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[14] A. G. Engelhardt and A. V. Phelps, Phys. Rev. **131**, 2115 (1963).

[15] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Phys. Rev. **135**, A1566 (1964).

within a few percent. Thus, at least in this case, the elastic cross section based on the spherically averaged potential is not very different from the averaged cross section based on a nonspherical potential.

For N_2, the mean cross section $\bar{\sigma}_{el}$ as a function of R at $k^2/2=0.01$ is given in Fig. 6. As in the case of hydrogen, the steep rises for $R>1$ 8 and $R<1.2$ are due to the s wave and the sharp peak at $R\cong1.43$ is due to the p wave. In this case, the three θ_0 values give p-wave peaks very close to one another, so that the resultant $\bar{\sigma}_{el}$ does not have well-separated peaks. The corresponding phase shifts are shown in Fig. 7. Here again, we have to omit the range of R where the low-energy cross section becomes around 100 a. u. or more. Thus, by studying several values of R within the two minimum regions in Fig. 6, we found that $R=1.75$–1.8 is the best choice. The cross section $\bar{\sigma}_{el}$ as a function of $k^2/2$ is shown in Fig. 8 for a few values of R. Again, the crudeness of our potential does not allow us a very good fit with the experimental data.

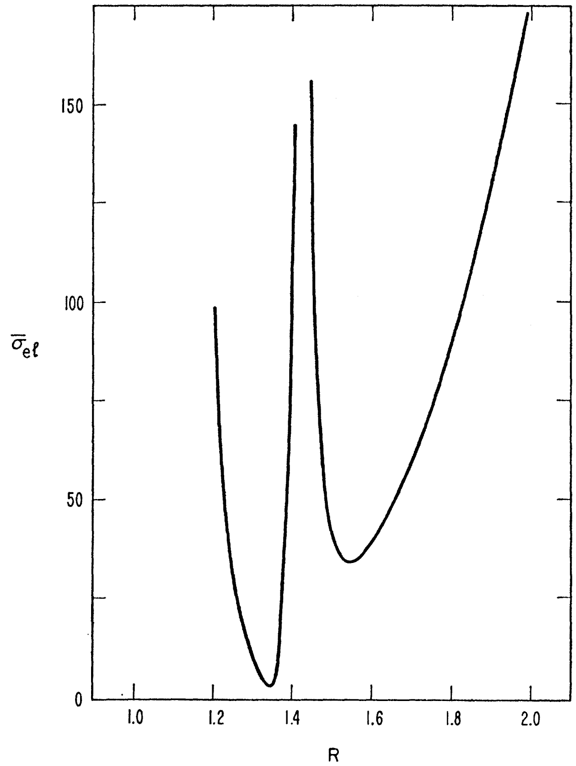

FIG. 6. Average elastic-scattering cross section for N_2 for electron energy $k^2/2=0.01$ as a function of cutoff parameter.

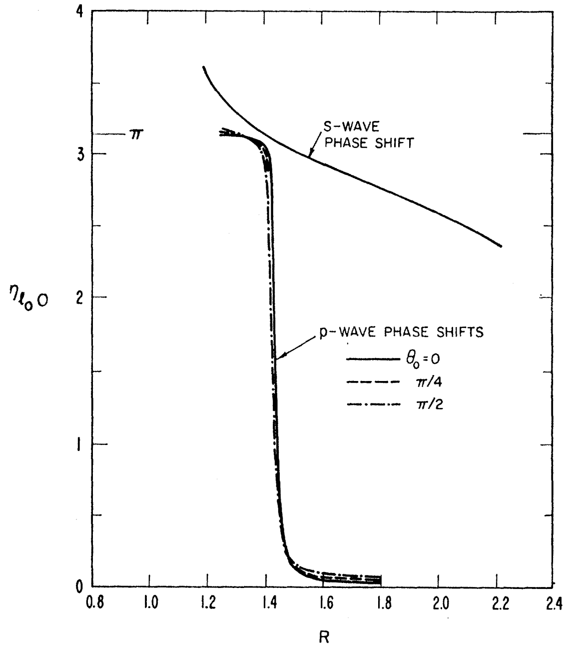

FIG. 7. s- and p-wave phase shifts for N_2 for electron energy $k^2/2=0.01$ as a function of cutoff parameter.

III. ROTATIONAL EXCITATION

In the distorted-wave approximation, the cross section for the rotational transition $J\rightarrow J'$ is given by

$$\sigma(J\rightarrow J')=4\pi\frac{k'}{k}\frac{1}{2J+1}\sum_{M}\sum_{M'}\sum_{l'm'}\delta_{M,M'+m'}\times\left|\frac{1}{kk'}\sum_{l}(2l+1)^{1/2}i^{l}e^{i\eta_l}\int_0^\infty f(l'|k',r)\times(l'm'J'M'|2V_{ns}|l0JM)f(l|k,r)dr\right|^2, \quad (22)$$

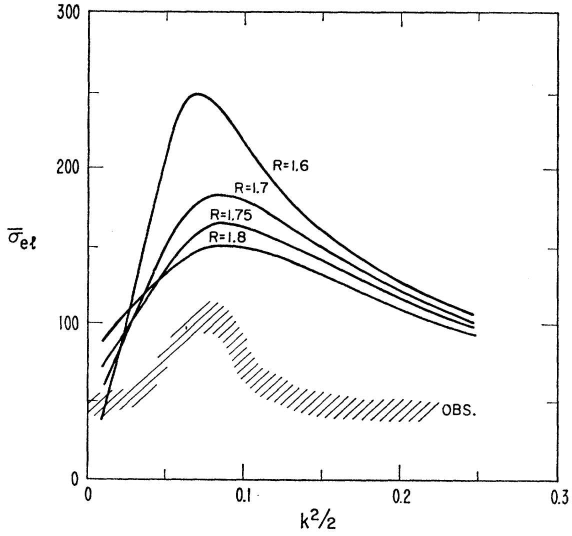

FIG. 8. Average elastic-scattering cross-section curves for N_2 for a number of cutoff radii. The cross-hatching corresponds to the experimental data.

TABLE I. Calculated rotational excitation cross sections for H_2, given in atomic units (a_0^2).

	$J\to J+2$							
	$0\to 2$		$1\to 3$		$2\to 4$		$3\to 5$	
k^2	$R=1.2$	$R=1.3$	$R=1.2$	$R=1.3$	$R=1.2$	$R=1.3$	$R=1.2$	$R=1.3$
0.004	0.1067	0.1027	...	...	...	...	...	...
0.007	...	...	0.0726	0.0689	...	...	...	...
0.01	0.2565	0.2417	0.1188	0.1122	0.0669	0.0627	0.0176	0.0160
0.015	...	...	...	...	...	...	0.0860	0.0793
0.03	0.5249	0.4420	0.2920	0.2473	0.2305	0.1963	0.1949	0.1669
0.1	1.795	1.137	1.049	0.6658	0.8749	0.5572	0.7875	0.5032
0.2	4.538	2.276	...	...	...	...	...	...
0.3	6.721	3.087	4.009	1.842	3.415	1.570	3.142	1.445
0.4	7.184	3.329	4.301	1.992	...	...	...	...
0.6	5.328	2.786	3.198	1.671	...	...	...	...
1.0	2.286	1.464	1.373	0.8792	1.178	0.7540	1.092	0.6985
2.0	0.6581	0.4910	0.3949	0.2947	...	...	...	...
3.0	0.3683	0.2785	0.2210	0.1671	...	...	...	...

where k and k' are the initial and the final electron wave numbers, V_{ns} is the nonspherical part of the potential given in (5), and JM and lm are the quantum numbers of molecular rotation and orbital angular momentum, respectively. The transition matrix element of the potential is given by

$$(l'm'J'M'|2V_{ns}|l\,0JM)$$

$$=-2\left(\frac{Q}{r^3}+\frac{\alpha'}{2r^4}\right)(l'm'J'M'|P_2(\hat{s}\cdot\hat{r})|l\,0JM)$$

$$=-2\left(\frac{Q}{r^3}+\frac{\alpha'}{2r^4}\right)c^2(JM,J'M')c^2(l'm',l0).\qquad(23)$$

The distorted-wave f's are the solution of the radial equations of the form

$$\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-2V_s+k^2\right\}f(l|k,r)=0\qquad(24)$$

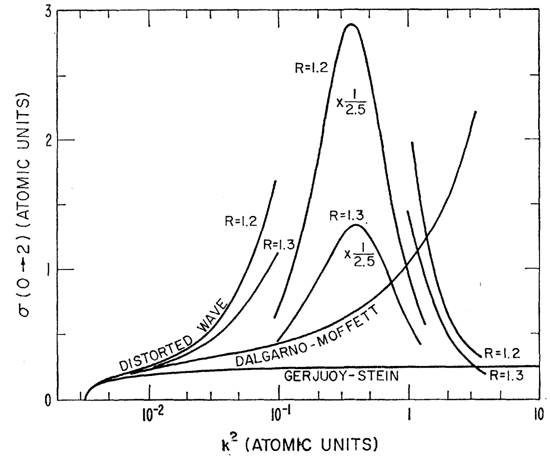

FIG. 9. Comparison of present results for the rotational excitation ($0\to 2$) of H_2 by electron impact with the curves of Gerjuoy-Stein and Dalgarno-Moffett ($k^2=1$ corresponds to 13.6 eV).

with the conditions

$$f(l|k,0)=0,$$

$$f(l|k,r)\xrightarrow[r\to\infty]{}\sin(kr-\tfrac{1}{2}l\pi+\eta_l).\qquad(25)$$

For the transition $J\to J+2$,

$$\Delta k^2=k^2-k'^2=12(\tfrac{2}{3}J+1)B,\qquad(26)$$

where B is the rotational constant of the molecule in atomic units, and

$$B=2.70\times10^{-4}\quad\text{for } H_2$$
$$=9.11\times10^{-6}\quad\text{for } N_2.\qquad(27)$$

The resulting rotational excitation cross sections for $J=0\to J=2$ are shown in Figs. 9 and 10 for hydrogen and nitrogen, respectively. In both cases the distorted-wave calculation gives a cross section larger than the Dalgarno-Moffett approximation in the intermediate energy region and a much smaller result in the higher energy region. The cross sections for transitions between higher J-values behave qualitatively in the same way as does the cross section for $J=0\to J=2$. Numerical results for the effective cross section are given in Tables I and II.

IV. DISCUSSION OF RESULTS

The qualitative difference between the cross section for hydrogen and that for nitrogen is due to Q having opposite signs. For hydrogen, the Q and α' terms in (1) are additive, but for nitrogen, they tend to cancel one another. This makes the distorted-wave cross section for hydrogen much larger than the Gerjuoy-Stein result and the cross section for nitrogen less than that of Gerjuoy-Stein.

Both for hydrogen and nitrogen, the largest contribution to the cross section comes from the partial cross section corresponding to incident p and outgoing p waves, except in the neighborhood of threshold. For the lth partial wave, the effective scattering potential is

TABLE II. Calculated rotational excitation cross sections for N_2, given in atomic units (a_0^2).

							$J \to J+2$								
	$0 \to 2$		$1 \to 3$		$2 \to 4$		$3 \to 5$	$4 \to 6$	$5 \to 7$	$6 \to 8$	$8 \to 10$	$10 \to 12$	$15 \to 17$	$20 \to 22$	$25 \to 27$
k^2	$R=1.75$	$R=1.8$	$R=1.75$	$R=1.8$	$R=1.75$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$	$R=1.8$
0.0003	0.9643	0.9638	0.4694	0.4686	0.2503	0.2493	...	...	...	...	...	...	...	...	...
0.0005	...	...	...	...	...	...	0.3436	...	...	...	...	...	...	...	...
0.0007	...	...	...	...	...	...	...	0.3585	0.3045	...	...	...	...	...	...
0.001	1.078	1.078	0.6212	0.6209	0.5108	0.5105	0.4518	0.4107	0.3763	...	...	...	...	...	...
0.0015	...	...	...	...	...	...	...	...	...	0.3918	0.3537	0.3165	0.2050	...	...
0.002	...	...	...	...	...	...	...	...	...	...	...	...	...	0.2070	0.0771
0.003	1.063	1.061	0.6296	0.6285	0.5327	0.5318	0.4860	0.4573	0.4374	0.4219	0.3981	0.3789	0.3398	0.3013	0.2580
0.01	1.0203	1.0121	0.6098	0.6049	0.5206	0.5146	0.4758	0.4524	0.4367	0.4252	0.4092	0.3980	0.3787	0.3652	0.3538
0.03	1.129	1.094	0.6762	0.6556	0.5786	0.5611	0.5187	0.4943	0.4784	0.4665	0.4512	0.4411	0.4256	0.4159	0.4087
0.1	1.324	1.247	0.7944	0.7480	0.6807	0.6410	0.5933	0.5662	0.5486	0.5363	0.5200	0.5098	0.4952	0.4873	0.4822
0.3	0.2538	0.2924	0.1523	0.1755	0.1306	0.1504	0.1393	0.1330	0.1288	0.1259	0.1222	0.1199	0.1167	0.1150	0.1140
0.5	0.1151	0.1231	...	0.0738	...	...	...	...	...	...	...	...	...	...	...
1.0	0.0501	0.0490	...	0.0294	...	0.0252	0.0233	0.0223	0.0216	0.0211	0.0205	0.0201	0.0195	0.0192	0.0191
3.0	0.0083	0.0074	...	0.0044	...	...	...	...	...	...	...	...	...	...	...

(including the centrifugal term)

$$V_{\text{eff}}(l)=l(l+1)/2r^2-\alpha/2r^4, \quad \text{for} \quad r\geq R. \tag{28}$$

This potential has a maximum value of

$$V_{\text{eff}}{}^m(l)=[l(l+1)]^2/8\alpha \tag{29}$$

at

$$r=r_m=[2\alpha/l(l+1)]^{1/2}. \tag{30}$$

If the incident electron has an energy greater than this barrier height for $l=1$, the p-wave function will be fairly large in the inner region ($r<r_m$), and the cross section is expected to be enhanced for the energies $k^2/2\geq V_{\text{eff}}{}^m(1)$ over the Dalgarno Moffett result, which does not take account of the distortion effect. This is actually the case as one can see in Figs. 9 and 10. $V_{\text{eff}}{}^m(1)$ in these cases are 0.094 and 0.042 a. u., respectively, and both values for $r_m>R$. The classical turning point occurs at a finite distance for all the partial waves except for the s wave. As the incident energy increases, the electron can penetrate more deeply into the inner region, so that the cross section increases. However, as we have cut off the interaction potential at $r=R$, the transition integral

$$\left(\frac{k'}{k}\right)^{1/2}(kk')^{-1}\int_0^\infty f(l'|k',r) \times(l'm'J'M'|2V_{ns}|l\,0JM)f(l|k,r)dr \tag{31}$$

will eventually decrease toward zero as k^2 increases. In the Dalgarno-Moffett formula, the nonspherical interaction has no cutoff, so that as energy increases, penetration of the p and other higher partial waves will cause the cross section to increase without limit as k^2 increases.

In the neighborhood of threshold, the outgoing electron has a very low energy, so that only an s-wave electron can come out of the interaction region. Only an incident d-wave electron can become a final s-wave electron [$l=0\to l'=0$ forbidden in (23)]. Since the d wave at low energy has a fairly large classical turning radius, the main contribution to the transition integral (31) comes not from the innermost region but the region of $r>R$. Therefore, the cutoff of the interaction at $r=R$ does not affect our result very much. Furthermore, the distortion of the low-energy s and d waves in the region $r>R$ is small as the phase shifts (modulo $n\pi$) are small. This is the reason why we find the distorted-wave cross section in the vicinity of threshold to be very close to the Dalgarno-Moffett result, which has no cutoff in the potential and no distortion correction.

As a check on our numerical procedures, we set $\alpha=0$ in our evaluation of the distorted waves in (24) and allowed V_{ns} in (22) to retain its asymptotic form all the way into the origin. In this way we obtained the Dalgarno-Moffett result to within 5%, which would be the estimate of our numerical errors arising from the numerical solution of (24), the numerical radial integral in (22), and the truncation of the sum in (22) at $l'=10$. Also, if we keep the correct α, while allowing V_{ns} to retain its asymptotic form into the origin, we see that the cross section approaches the Dalgarno-Moffett result at high energies. This is a confirmation that the effect of distortion vanishes in the high-energy limit.

Recently, Schulz[16] directly measured the vibrational

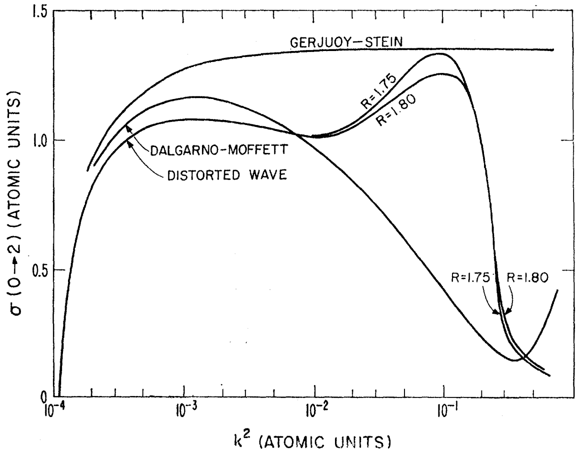

FIG. 10. Comparison of present results for the rotational excitation ($0\to 2$) of N_2 by electron impact with the curves of Gerjuoy-Stein and Dalgarno-Moffett ($k^2=1$ corresponds to 13.6 eV).

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[16] G. J. Schulz, Phys. Rev. **135**, A988 (1964).

excitation cross section of H_2 by slow electron impact. An analysis of swarm experiments by Engelhardt and Phelps,[14] using the Born approximation values for the rotational excitation cross section, yielded a synthesized vibrational excitation cross section for H_2 which was a factor of 2 larger than Schulz's for electron energies >3 eV. Our present results, while still containing major uncertainties, indicate that one must question both the magnitude and shape of the rotational excitation cross sections based upon the Born approximation, which have been used in the swarm experiment analysis. It is hoped that calculations with a more realistic interaction potential can be done in the future.

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Perturbation-Theory Expansions Through 21st Order of the Nonrelativistic Energies of the Two-Electron Systems $(2p)^2\,{}^3P$ and $(1s)^2\,{}^1S$[*]

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The Hylleraas-Scherr-Knight variational perturbation method has been applied to the two-electron systems $(2p)^2\,{}^3P$ and $(1s)^2\,{}^1S$, carrying the calculations through to tenth-order perturbation wave functions. Various forms of expansions for the trial wave functions have been considered, e.g., the Hylleraas form and the Schwartz form, and numerical results are given in naturally spaced groups up to and including 252-term expansions. Estimates of the correct perturbation-energy coefficients through 21st order are tabulated, and the resulting nonrelativistic energies for $Z=2, 3, \cdots, 10$, are given with ten significant figures. To complete the tables the energies of the two states for H^- have also been calculated variationally, using the same expansions of trial wave functions as in the perturbation treatment, and for the $(2p)^2\,{}^3P$ state an extrapolated energy value of -0.2507097 measured in units of Z^2Rh has been obtained.

1. INTRODUCTION

THE $(2p)^2\,{}^3P$ state of the negative hydrogen ion has already been found to be stable.[1] Using a 22-term trial wave function, Wold obtained an energy value of -0.250427, measured in units of Z^2Rh.

In a preliminary investigation for bound states of the negative hydrogen ion[2] an improved 22-parameter wave function has been set up yielding an energy of -0.250618 for H^-. In the same paper the Hylleraas-Scherr-Knight (HSK) variational perturbation method was also applied for the first time to that state, furnishing a second-order and a third-order energy coefficient of -0.078788 and 0.003631, respectively.

The HSK variational perturbation method appears to be very well suited for atomic calculations provided that an electronic computer is available. The results are

TABLE I. Contributions to the perturbation energy coefficients (λ_2–λ_5) for the state $(2p)^2\,{}^3P$.

Order	Contributions to λ_2	Contributions to λ_3	Contributions to λ_4	Contributions to λ_5
3	−0.0744773381	0.0013129555	0.0257976480	−0.0010557398
7	−0.0040427166	0.0009572751	−0.0239069249	0.0015435888
13	−0.0002268368	0.0012021496	−0.0021170919	−0.0016508836
22	−0.0000340131	0.0001651968	−0.0003597004	0.0003557950
34	−0.0000063734	0.0000319708	−0.0000726308	0.0000963727
50	−0.0000014801	0.0000074218	−0.0000171772	0.0000235745
70	−0.0000004035	0.0000020003	−0.0000046640	0.0000065446
95	−0.0000001253	0.0000006093	−0.0000014133	0.0000020143
125	−0.0000000433	0.0000002059	−0.0000004710	0.0000006734
161	−0.0000000164	0.0000000761	−0.0000001707	0.0000002425
203	−0.0000000067	0.0000000303	−0.0000000667	0.0000000934
252	−0.0000000029	0.0000000129	−0.0000000278	0.0000000384

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[1] E. Wold, Phys. Math. Univ. Oslo., No. 13, 1962.

[2] J. Midtdal, Phys. Math. Univ. Oslo., No. 21, 1964.