Rotational Excitation of Molecular Ions by Electrons*

Douglas H. Sampson

Space Sciences Laboratory, General Electric Company, Valley Forge, Pennsylvania

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The first-order perturbation theory used by R. C. Stabler to compute the cross section for rotational excitation of homonuclear diatomic molecular ions by electrons is shown to be equivalent to an approximation to the method of distorted waves for which quite precise validity criteria can be given and easily applied. It appears to be valid to express the interaction energy by the form $V(\mathbf{r}) = V_0(r) + V_2(r)P_2(\mathbf{r},\mathbf{s})$; however, use of the long-range forms for $V_0(r)$ and $V_2(r)$ for all r is not a valid approximation. Moreover, for $r > r_0$, where r_0 is the approximate radius of the molecular charge cloud, $V_2(r)$ should include the r^{-4} induced-dipole or polarization interaction, which, it is shown, likely gives a contribution only a little less significant than that due to the quadrupole interaction treated by Stabler. Depending on the sign and magnitude of the quadrupole moment and the magnitude and degree of asymmetry of the polarizability, and also depending on the size of the uncertain contribution from the region $r < r_0$, the electron-energy loss rate through rotational excitation can be anywhere between $\sim 100\%$ and a negligible percentage of that due to elastic Coulomb collisions with molecular ions. However, if it is $\gtrsim 10\%$, use of the method of distorted waves, or equivalently the perturbation theory with $V_0(r)$ included in H_0 used by Stabler, is shown to be invalid.

INTRODUCTION

R ECENTLY, an interesting calculation of the cross section for rotational excitation of molecular ions by slow electrons has been reported by Stabler.[1] The principal reason for interest in this process is that it might conceivably be an important energy-loss mechanism for low-energy (below 1 eV) electrons in a partially ionized gas under conditions wherein most of the ions are molecular ions. In I it is concluded that the electron-energy loss rate by this process ranges from about 1 to 20% of that due to elastic Coulomb collisions and hence is of relatively minor importance. However, the basis for arriving at this conclusion is not completely valid for the two following reasons: (1) Essentially, no criteria are given for the validity of the first-order perturbation theory used except to say that it must be valid in the limit of very small angular-dependent electron–molecular-ion interaction, and that it must be invalid in the limit that the computed cross section exceeds the upper theoretical limit $3\pi/k_i^2$ for p-wave scattering imposed by flux conservation. This upper limit can be applied because, as noted by Stabler, the inelastic scattering is almost entirely due to p-wave scattering. (2) A long-range form for the electron–molecular-ion interaction energy is used for all r, while (as shown in Sec. IV of this paper) within the framework of Stabler's theory and using his interaction energy most of the contribution ($\sim 72.5\%$) to the transition matrix element comes from r inside the molecular charge cloud where use of the long-range form for the interaction is invalid. Moreover, the long-range form for the interaction which he has used (Coulomb plus quadrupole interactions) is incomplete in that the induced dipole, or polarization interaction, which gives a comparable contribution to that of the quadrupole interaction, has been omitted.

In the present paper it is shown (Sec. I) that the first-order perturbation theory used by Stabler is exactly equivalent to an approximation to the method of distorted waves for which fairly precise validity criteria (given in Sec. II and applied in Sec. III) can be readily given and applied. The form of the additional induced-dipole long-range interaction is given, and, assuming that the long-range form for the angular-dependent part of the interaction applies for all r and using the approximate low-energy form for the electron radial wave functions used by Stabler, the approximate radial transition matrix element is computed (Sec. III). The result leads to an inelastic cross section slightly in excess of the theoretical upper limit $3\pi/k_i^2$ for reasonable magnitudes of the quadrupole moment Q and polarizability parameter α_2 when Q is positive. However, it is then shown (Sec. IV) that the short-range region, r inside the molecular charge cloud, is actually very important. Finally, the conclusion is reached that the electron–molecular-ion energy-exchange rate due to rotational excitation can be anywhere between a completely negligible amount and $\sim 100\%$ of that due to elastic Coulomb collisions, although it is expected to be more likely under 10% in most cases. This large variation is due to the variation in the long-range contribution from element to element resulting from differences in the magnitudes of Q and α_2 and the sign of Q (for negative Q there is cancellation between the quadrupole and induced dipole contributions), and also is due to the large uncertainty in the short-range interaction energy. The upper limit results when the cross section is set equal to $3\pi/k_i^2$ (which is expected to apply approximately since p-wave scattering still likely dominates for the correct interaction energy). However, applying our criteria for the validity of the method of calculation, we find (Sec. III and Sec. V) that the first-order perturbation-theory approach used by Stabler, or equivalently, the approximate method of distorted waves used here, becomes invalid whenever the cross section exceeds about 10% of the upper limiting value $3\pi/k_i^2$.

[1] R. C. Stabler, Phys. Rev. **131**, 679 (1963). Hereafter we refer to this paper as I.

I. APPROXIMATE EQUIVALENCE OF THE THEORY USED BY STABLER TO THE METHOD OF DISTORTED WAVES

The treatment used in I was equivalent to making the assumptions that the molecular ion could be represented by a rigid rotator and the interaction between electron and molecule had the form

$$V(\mathbf{r}) = V_0(r) + V_2(r)P_2(\mathbf{r,s}), \qquad (1)$$

where $\mathbf{r}$ is the position of the electron relative to the center of mass of the molecule and $\mathbf{s}$ is the internuclear separation distance. As is usual in perturbation theory, the total Hamiltonian was split into a zeroth order, or unperturbed, part H_0 and a perturbation H_{eff}'. The $V_0(r)$ part of the interaction was included in H_0,

$$H_0 = H_x + V_0(r) - (\hbar^2/2m)\nabla_r^2, \qquad (2)$$

$$H_{\text{eff}}' = V_2(r)P_2(\mathbf{r,s}). \qquad (3)$$

Here H_x is the Hamiltonian for the isolated molecule. It was assumed that

$$V_2(r) = -Qe^2 a_0^2/r^3, \quad a_0 = \hbar^2/me^2, \qquad (4)$$

where Q is the quadrupole moment of the molecule in units of ea_0^2, and that

$$V_0(r) = -e^2/r. \qquad (5)$$

With this value for $V_0(r)$ the unperturbed wave functions separate into a product of a Coulomb wave function $\psi_{\text{Coul}}(\mathbf{k,r})$ and a spherical harmonic function $Y_j^{m_i}(\Omega_s)$ representing the molecular wave function.

As mentioned in I, from the point of view of perturbation theory it is difficult to assess the reliability of the first-order perturbation theory result for the inelastic cross section. However, this is not the case in the present problem when this first-order perturbation theory is regarded as an approximation to the "method of distorted waves." This is the approach followed by Mjolsness and the author in the treatment of the analogous problem of rotational excitation of neutral molecules.[2] We recall that the expression for the differential scattering cross section obtained by the method of distorted waves is[3,4]

$$I(a, \mathbf{k}_a \to a', \mathbf{k}_{a'}) = \frac{k_{a'}}{k_a}\left(\frac{m}{2\pi\hbar^2}\right)^2$$

$$\times \left| \int F(-\mathbf{k}_{a'}, \mathbf{r})V_{a'a}(\mathbf{r})F(\mathbf{k}_a,\mathbf{r})d^3r \right|^2. \qquad (6)$$

[2] To be published. This work will hereafter be referred to as II. The theory and preliminary numerical results were reported at the 16th Gaseous Electronics Conference; R. C. Mjolsness and D. H. Sampson, Bull. Am. Phys. Soc. **9**, 187 (1964). Although $l=1$ distortion turns out to be most important, only numerical results for $l=0$ distortion were available at the time of this conference.

[3] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1933), 2nd ed., p. 146.

[4] M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 386.

Here $F(\mathbf{k}_{a'},\mathbf{r})$ and $F(\mathbf{k}_a,\mathbf{r})$ are the solutions of the equations

$$[\nabla_r^2 + k_{a'}^2 - (2m/\hbar^2)V_{a'a'}(\mathbf{r})]F(\mathbf{k}_{a'},\mathbf{r}) = 0$$

and

$$[\nabla_r^2 + k_a^2 - (2m/\hbar^2)V_{aa}(\mathbf{r})]F(\mathbf{k}_a,\mathbf{r}) = 0, \qquad (7)$$

which have the form of plane waves plus outgoing waves at infinity. $V_{a'a}(\mathbf{r})$ is the matrix element of the electron-molecule interaction taken between initial and final molecular states. Equations (6) and (7) are seen to be identical with the well-known equations of first-order perturbation theory when the approximation

$$V_{a'a'}(r) \cong V_{aa}(r) \cong V_0(r) \qquad (8)$$

is made. In the present problem, where $V(\mathbf{r})$ is given by Eq. (1),

$$V_{a'a}(\mathbf{r}) = \int Y_{j'}^{m_j*}(\Omega_s)V(\mathbf{r})Y_j^{m_i}(\Omega_s)d\Omega_s$$

$$= V_0(r)\delta_{jj'}\delta_{m_jm_{j'}}$$

$$+ V_2(r)\int Y_{j'}^{m_j*}(\Omega_s)P_2(\mathbf{r,s})Y_j^{m_i}(\Omega_s)d\Omega_s. \qquad (9)$$

Thus, Eq. (8) is valid in the present problem provided

$$\left| V_2(r)\int Y_j^{m_j*}(\Omega_s)P_2(\mathbf{r,s})Y_j^{m_i}(\Omega_s)d\Omega_s \right| \ll |V_0(r)|. \qquad (10)$$

The advantage in making approximation (8) is that then Eqs. (7) do not depend on the rotator states, in contrast to the case when the method of distorted waves is followed exactly. However, when approximation (8) is made and condition (10) is satisfied, we can use the validity criteria for the method of distorted waves to check on the reliability of the result obtained for the cross section. This is much easier to do in the present problem than it is to estimate the second-order perturbation-theory result, as is ordinarily required for testing the validity of first-order perturbation theory.

II. CRITERIA FOR THE VALIDITY OF THE METHOD OF CALCULATION

Use of the method of distorted waves is expected to be a good approximation when the diagonal molecular matrix elements of the interaction potential are large compared with all nondiagonal matrix elements, $V_{a'a'} \gg V_{a''a'}$, $a'' \neq a'$. This results because Eqs. (6) and (7) are obtained from an infinite set of exact coupled differential equations by neglecting all terms proportional to off-diagonal matrix elements except one connecting the final state to the initial state, while terms proportional to the diagonal matrix elements are retained. Thus, a criterion for the validity of the method of distorted waves in the present problem, where Eq. (9)

$w_l(k_i,r)$ is a solution of the equation

$$\left[\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+k_i^2-\frac{l(l+1)}{r^2}\right)-V_0(r)\right]w_l(k_i,r)=0, \quad (21)$$

with an asymptotic form

$$w_l(k_i,r)\big|_{r\to\infty}=\sin(k_i r-\tfrac{1}{2}l\pi+\eta_l). \quad (22)$$

In contrast to the situation when the method of distorted waves is followed exactly, the radial wave functions $w_l(k_i,r)$ and $w_{l'}(k_f,r)$, and hence F_2, are functions of no other quantum numbers than the orbital quantum numbers l' and l because we have made approximation (8).

Also the expression for the inelastic cross section is needed. For the purpose of determining the electron-energy loss rate by rotational excitation, only the total cross section for the transition $j \to j'$ is necessary. With the present formalism, this takes the rather simple form in the distorted-wave approximation.[5]

$$\sigma(j,j')=\frac{4\pi}{(2j+1)}\frac{k_f}{k_i^3}\sum_{J=0}^{\infty}(2J+1)\sum_{l=|J-j|}^{J+j}\sum_{l'=|J-j'|}^{J+j'}(\beta_{j'l'}{}^{Jjl})^2. \quad (23)$$

In testing whether or not conditions (13) and (17) required for the validity of the method are satisfied, one should use the correct form for the interaction energy. The next two sections are devoted largely to a discussion of what this is. However, at this point, we can make a preliminary test to see whether or not condition (13) is satisfied when Stabler's form for the interaction energy is used. Using Eqs. (4) and (5) and f_2 given by Eqs. (15) and (16) in condition (13), we get

$$Qa_0^2/10r^2\ll1. \quad (24)$$

Since $Q\sim1$ and the radius r_0 of the molecular charge cloud is $r_0\sim2a_0$ in most cases, this condition is well satisfied, and Eq. (8) should be valid when $r\geq r_0$, the only region for which Eqs. (4) and (5) are expected to be valid. Actually, it turns out, as shown in Sec. IV, that the region $r<r_0$ cannot be ignored. Also, as we now show, even for $r>r_0$, Eqs. (4) and (5), particularly Eq. (4), should be modified.

III. CONCENTRATION TO THE LONG-RANGE INDUCED-DIPOLE INTERACTION

In addition to the static Coulomb and quadrupole interactions given by Eqs. (1), (4), and (5) there is a fairly long-ranged (r^{-4}) interaction energy of a different type due to the reaction of the bound electrons to the electric field of the free electron. Since the energy of the free electron is low (under 1 eV), the much faster moving bound electrons are able to make several cycles of their motion before the position of the free electron (particularly when r is large) changes significantly. Thus, it is a good approximation to assume that the bound electrons

adjust exactly to the position of the free electron as though it were stationary. The resulting induced-dipole moment $\mathbf{p}$ of the molecule is

$$\mathbf{p}=-|\mathbf{E}|a_0^3[\alpha_{||}\boldsymbol{\varepsilon}_{||}\cos(\mathbf{r},\mathbf{s})+\alpha_{\perp}\boldsymbol{\varepsilon}_{\perp}\sin(\mathbf{r},\mathbf{s})],$$

where $\mathbf{E}=-e\mathbf{r}/r^3$ is the field producing the dipole; $\alpha_{||}$ and $\alpha_{\perp}$ are the polarizabilities in units of a_0^3 of the molecular ion in the direction of $\mathbf{s}$ and a direction perpendicular to $\mathbf{s}$, respectively; $\boldsymbol{\varepsilon}_{||}$ is a unit vector along $\mathbf{s}$; and $\boldsymbol{\varepsilon}_{\perp}$ is a unit vector perpendicular to $\mathbf{s}$ in the $\mathbf{r},\mathbf{s}$ plane. When the electron-ion interaction energy $-\mathbf{p}\cdot\mathbf{E}/2$ due to this polarization, or induced-dipole interaction, is expressed in terms of P_0 and $P_2(\mathbf{r},\mathbf{s})$ and added to the static contribution we find that Eq. (1) still applies, but in place of Eqs. (4) and (5) for the long-range interaction[10] we obtain

$$V_0(r)=-(e^2/r)[1+\alpha_0(a_0/r)^3], \qquad r>r_0 \quad (25)$$

$$V_2(r)=-(Qe^2a_0^2/r^3)[1+(\alpha_2/Q)(a_0/r)], \quad r>r_0 \quad (26)$$

where

$$\alpha_0=\tfrac{1}{6}(\alpha_{||}+2\alpha_{\perp}), \quad \alpha_2=\tfrac{1}{3}(\alpha_{||}-\alpha_{\perp}). \quad (27)$$

The second terms in Eqs. (25) and (26) might significantly overestimate the magnitude of the induced-dipole contributions for the highest free-electron energies of interest because the bound electrons are unable to completely adjust to the position of the free electron. Also, they may give overestimations of the magnitude near $r=r_0$, partly as a result of exchange effects. Of course, none of the terms in Eqs. (25) and (26) are valid for $r<r_0$. We note that since α_0 is generally somewhat greater than α_2, inclusion of the terms involving these quantities does not upset the satisfaction, Eq. (24), of condition (13) for $r>r_0$.

With the induced-dipole interaction included, the central part of the interaction energy is still quite well approximated by the Coulomb term $-e^2/r$ for the region outside the molecular-ion charge cloud because the additional term $\alpha_0(a_0/r)^3$ drops off rapidly with distance and is typically less than unity even at $r=r_0$. On the other hand, the induced-dipole contribution to $V_2(r)$ must be included because it drops off slowly, as r^{-1} relative to the quadrupole contribution, and typically $(\alpha_2/Q)(a_0/r_0)\sim1$.

We now use the formalism of the latter part of the previous section[11] to make an approximate evaluation of the matrix element F_2, Eq. (20), assuming that only the range $r>r_0$ is important. Then $V_0(r)\simeq-e^2/r$, and, Coulomb wave functions approximately apply for the free electron. Furthermore, since only low electron energies ($\lesssim1$ eV) are of interest, we will follow Stabler

[10] The inclusion of these polarization interaction terms was first reported in a calculation of rotational excitation of N_2 by electrons presented by A. Dalgarno and R. J. Moffett, Proc. Nat. Acad. Sci., India 33A, 511 (1963).

[11] We could as easily have used the method and results of I since it turns out that the angular contribution is the same to good approximation as for the quadrupole interaction; however, we want $\beta_{j'l'}{}^{Jjl}$ explicitly anyway in order to test condition (17).

and use the low-energy expansion of the Coulomb wave functions given by Eq. (I, 12). This leads to

$$w_l(k_i, r) = (\pi k_i r)^{1/2} J_{2l+1} [(8r/a_0)^{1/2}].$$ (28)

Then using Eq. (26), $F_2(k_i l, k_f l')$ given by Eq. (20) becomes

$$F_2(k_i l, k_f l') = -\pi (k_i k_f)^{1/2} Q e^2 a_0^2 \int_0^\infty \frac{dr}{r^2} \left[1 + \frac{\alpha_2 a_0}{Qr} \right] J_{2l+1}[(8r/a_0)^{1/2}] J_{2l'+1}[(8r/a_0)^{1/2}].$$ (29)

This integral is evaluated with the use of the equation[12]

$$\int_0^\infty \frac{dz}{z^\lambda} J_{2l+1}(z) J_{2l'+1}(z) = \frac{(1/2)^\lambda (\lambda-1)! [l+l'-(\lambda-1)/2]!}{[l'-l+(\lambda-1)/2]! [l-l'+(\lambda-1)/2]! [l+l'+(\lambda+1)/2]!}.$$ (30)

The pertinent values of λ are $\lambda = 3$ for the quadrupole contribution and $\lambda = 5$ for the induced dipole contribution [the part in Eq. (29) proportional to α_2]. In the former case ($\lambda = 3$) it was found in I that p-wave scattering contributes 95% of the inelastic scattering cross section. In III, it is shown that about the same is true for $\lambda = 5$. Thus, we obtain the approximate value for the cross section by considering the single term $l = l' = 1$. In this case Eqs. (29) and (30) give

$$F_2(k_i 1, k_f 1) = -\pi (k_i k_f)^{1/2} (Q e^2 a_0/6) [1 + (6\alpha_2/5Q)].$$ (31)

The inelastic cross section is then readily obtained by applying this result together with Eq. (14) to Eqs. (19) and (23), as done in III. When α_2 is set equal to zero, the result agrees exactly with the $l = 1$ contribution to Eq. (I, 30), as is to be expected since the methods of calculation are equivalent. However, when Q is positive, for reasonable values of Q and α_2, say $Q = 1$ and $\alpha_2 = 1.6$, this result for the cross section exceeds $3\pi/k_i^2$. This is an upper theoretical limit imposed by flux conservation[13] on the contribution of p-wave scattering to the inelastic cross section, which, as noted by Stabler, is of particular use in the present problem.

Actually, the fact that invalid results for σ are obtained is to be expected when one inspects Eq. (31). The quantity 6/5 is the average of the quantity a_0/r entering the brackets of Eq. (26). Since $a_0/r_0 \simeq \frac{1}{2}$, this value 6/5 can result only if a considerable contribution, at least to the induced-dipole part, arises from $r < r_0$, where use of the long-range form for the interaction is invalid.

In the next section we consider further the region $r < r_0$. However, at this point we show that regardless of the form of $V_0(r)$ and $V_2(r)$ for $r < r_0$, some general statements can be made about the inelastic cross section as long as Eq. (1) applies. As noted by Stabler, when the angular-dependent part of the interaction energy is proportional to $P_2(\mathbf{r}, \mathbf{s})$, the angular integration yields the selection rule $|l - l'| = 0, 2$ with $l = l' = 0$ forbidden. Thus, since the long-range interaction is given quite accurately by Eqs. (5) and (26), it is highly unlikely that p-wave scattering will not continue to dominate.

[12] G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1944), 2nd ed., p. 403.
[13] Ref. 3, p. 135.

Also when Eq. (1) applies, only the rotational transitions $j \to j \pm 2$ occur in first-order theory. For p-wave scattering only a single β, Eq. (19), contributes to either transition. Thus, only one term enters Eqs. (17) and (23). Hence, using Eqs. (18) and (23) we obtain

$$\sigma_{l=1}(j, j \pm 2) = \frac{\pi}{k_i^2} \frac{(2J+1)}{(2j+1)} |S^J(j \pm 2, 1; j, 1)|^2.$$ (32)

It is a matter of judgment how well condition (17) should be satisfied, but probably the left-hand side should not exceed 0.3. With this choice we obtain

$$\sigma_{l=1}(j, j \pm 2) \lesssim \frac{0.3\pi}{k_i^2} \frac{(2J+1)}{(2j+1)}$$ (33)

as the range of validity of the method of distorted waves. J has the value $j+1$ for the $j \to j+2$ transition and $J = j - 1$ for the $j \to j - 2$ transition. For large j, usually the situation of interest, $(2J+1)/(2j+1) \approx 1$.

IV. IMPORTANCE OF THE SHORT-RANGE REGION $r < r_0$

An indication of the importance of the region $r < r_0$ is obtained by evaluating numerically the part of the integrals given by Eq. (30) with $\lambda = 5$ and $\lambda = 3$ arising from the range $0 \le r \le r_0$. As previously done, we assume $l = l' = 1$. Taking $r_0 = 2a_0$ as typical of the approximate radius of the molecular charge cloud, we find that this contribution is 92% of the total when $\lambda = 5$, the case of the induced-dipole interaction, and 72.5% of the total when $\lambda = 3$, the case of the quadrupole interaction.

It is interesting to obtain a more realistic approximate value for the importance of the induced-dipole contribution to F_2 relative to the quadrupole contribution to F_2. This is obtained by evaluation of both contributions only for the range $r > r_0$ where the long-range forms, Eqs. (5) and (26), for the interaction energy are approximately valid. Based on the above numbers 92% and 72.5% the result is $[1 - 0.92)/(1 - 0.725)](6\alpha_2/5Q)$ $\simeq 0.35\alpha_2/Q$ in place of $6\alpha_2/5Q$ obtained previously, Eq. (31), assuming the long-range form of the interactions apply for all r. The result is only approximate partly because change in $V_0(r)$ for $r < r_0$ will change the

electron wave function and hence, the matrix elements for $r > r_0$.

Similarly, if the region $r < r_0$ should give a negligible contribution when computed correctly [this would occur if the $V_2(r)$ were small[14] for $r < r_0$ and/or if the correct radial functions were much less than the Coulomb values for most of the range $r < r_0$], an estimation for F_2 on a similar basis (i.e., by neglecting completely the contribution from $r < r_0$) is

$$F_2(k_i 1, k_f 1)|_{l\,\text{est}} = -\pi (k_i k_f)^{1/2} Q e^2 a_0 (0.275/6)$$
$$\times [1 + 0.35\alpha_2/Q] \quad (34)$$

in place of Eq. (31). Using this and Eq. (14) in Eqs. (19), (23), and (18) one obtains

$$\sigma(j \gg 1, j \pm 2)|_{l\,\text{est}} \approx (3\pi/k_i^2) 0.010 Q^2 [1 + 0.35\alpha_2/Q]^2 \quad (35)$$

and

$$\sum_{j'l' \neq jl} |S^J(jl, j'l')|^2\,_{l\,\text{est}} \approx 0.030 Q^2 [1 + 0.35\alpha_2/Q]^2. \quad (36)$$

Usually α_2 is positive and about 1 or 2 times $|Q|$ in magnitude. Thus, when Q is negative, as is apparently the case for neutral nitrogen,[15] severe cancellation occurs in the long-range contribution to F_2; while for positive Q the inclusion of the induced-dipole interaction leads to a substantial increase in the long-range contribution to F_2 and σ. Usually $Q^2(1 + 0.35\alpha_2/Q)^2 \lesssim 3$. Hence, if Eqs. (35) and (36) were correct, the cross section would not even be near the upper limit of $(3\pi/k_i^2)$ and condition (17) required for the validity of the method of distorted waves would be well satisfied as well.

Equation (35) gives an approximate lower bound for the rotational cross section. The cross section may be even less than that given by Eq. (35) if $V_2(r)$ changes sign for r slightly less than r_0.[14] For then there is cancellation between the net short-range contribution and the long-range contribution to F_2. However, the cross section in this case is expected to be too small to be of any practical interest.

We consider now the form of the interaction for the region $r < r_0$. For homonuclear diatomic molecules, or molecular ions, the symmetry is such that the $n = 1$ term in the expansion

$$V(\mathbf{r}) = \sum_n V_n(r) P_n(\mathbf{r}, \mathbf{s})$$

still vanishes for $r < r_0$. The terms for $n > 2$, although important for a narrow range of r about $s/2$, probably give a negligible contribution to the total inelastic cross section, as indicated by the investigations of Gerjuoy and Stein for neutral molecules.[16] For most values of

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[14] As indicated in II, the sign of $V_2(r)$ changes within the region $r > r_0$ in many cases, which could make the contribution of this region to F_2 small or of opposite sign to that of the long-range region.

[15] P. E. Cade, K. D. Sales, and A. C. Wahl, Bull. Am. Phys. Soc. 9, 102 (1964).

[16] E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).

$r < r_0$, it is difficult to determine the form for $V_0(r)$ and $V_2(r)$ with accuracy; however, probably $V_2(r)$ is of the same order or less than $V_0(r)$ for $r < r_0$ except for a region about $s/2$.

V. CONCLUSIONS AND DISCUSSION

Our conclusions are that, although the forms given by Eqs. (4) and (5) for $V_0(r)$ and $V_2(r)$ are not valid, Eq. (1) is still applicable. Also condition (13) likely holds for most of the important range of r so that Eq. (8) is valid and first-order perturbation theory with V_0 included in H_0 remains approximately equivalent to the method of distorted waves. For $r \gtrsim r_0$, Eqs. (25) and (26) shold be used for $V_0(r)$ and $V_2(r)$ [the second term in the brackets of Eq. (25) is relatively unimportant]. For $r \lesssim r_0$ both forms of $V_0(r)$ and $V_2(r)$ must be radically changed and it is difficult to specify with much accuracy their correct values except that, instead of being singular at $r = 0$, $V(0) = V_0(0) \simeq -2e^2 Z_{\text{eff}}/(s/2)$, where Z_{eff} is the effective charge of the partially screened core of either atom.

Assuming p-wave scattering continues to give most of the contribution to the correctly determined inelastic cross section (as is likely the case), the condition (17) required for the validity of the method of distorted waves is satisfied only if the cross section turns out to be $\lesssim 10\%$ of the theoretical upper limit $3\pi/k_i^2$ [see the discussion surrounding Eqs. (32) and (33)]. The inelastic cross section is approximately bracketed by $3\pi/k_i^2$ on the upper side and by Eq. (35) on the lower side. As seen by inserting $Q^2 = 7.5$ in Eq. (I, 40), the rate of electron energy loss by rotational excitation of molecular ions is about the same as or a little less than that due to elastic Coulomb collisions between electrons and molecular ions when the rotational cross section has the upper limiting value of $3\pi/k_i^2$ [using $Q^2 = 7.5$ rather than 2.5, as in I, is correct because an error by a factor of 3 was made in obtaining Eq. (I, 41) from Eq. (I, 30)]. Thus, if the true rotational cross section is large enough to have much practical significance, i.e., if the electron-energy loss rate due to rotational excitation is between $\sim 10\%$ and the maximum possible value of $\sim 100\%$ of that due to elastic collisions, an accurate determination of this cross section would be desirable, but it would be difficult to accomplish because the method of distorted waves would not be valid. Also, probably of more importance, for the inelastic cross section to be this large the short-range region $r < r_0$ would have to give a large contribution relative to the approximate contribution, Eqs. (34) and (35), of the region $r > r_0$. Thus, a precise knowledge of the interaction energy for the region $r < r_0$ would be required. On the other hand, if the true inelastic cross section is $\lesssim (0.1)3\pi/k_i^2$, rotational excitation of molecular ions is a relatively minor electron-energy loss mechanism. Thus, if the cross section is thought to lie in this region, the principal interest would be only in establishing that this is indeed the case. For this purpose only

an approximately correct value for the cross section would be required. We note that when the cross section is in this region, condition (17) required for the validity of the method of distorted waves is approximately satisfied. Moreover, the short-range contribution to the radial matrix element F_2 must be about the same or less than the approximate long-range contribution, the contribution from $r > r_0$ given by Eq. (34). Thus, use of the method of distorted waves, or first-order perturbation theory with V_0 included in H_0, and only fairly approximately correct values for $V_0(r)$ and $V_2(r)$ when $r < r_0$ should lead to a sufficiently accurate determination of

the cross section if α_2 and Q are known to indicate whether it is $\gtrsim 0.3\pi/k_i{}^2$, and hence of practical significance, or $\lesssim 0.3\pi/k_i{}^2$, and hence of little practical significance. We think that the latter, is more likely the true situation in most cases. It almost certainly is when Q is negative.[17]

[17] Additional discussion of the short-range region is given in II and III. In the latter it is also shown that within the framework of Stabler's theory the interaction of the electron with the permanent dipole of polar molecular ions such as H_2O^+ or $NH_3{}^+$ gives no contribution to the rotational cross section. This results because the angular part of the matrix element yields the selection rule $|l-l'|=1$, while the radial part yields $l=l'$.

Production of Highly Excited Neutral Atoms for Injection into Plasma Devices

S. T. BUTLER AND R. M. MAY

The Daily Telegraph Theoretical Department, School of Physics,
University of Sydney, Sydney, N.S.W., Australia

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We have considered the production of highly excited states of atomic hydrogen by charge-exchange reactions, discussing first the reaction $H^+ + H(1s) \rightarrow H$ (excited)$+H^+$; we have then used the results for this reaction as a basis with which to compare excited-state production in hydrogen atoms by charge exchange in gases other than atomic hydrogen. We have expressed our results in terms of the equilibrium ratio i_n/i_c, that is, the ratio of the flux of excited states with principal quantum number n to the (constant) flux of protons incident on the neutralizer. We find that with atomic hydrogen as neutralizer the ratio i_n/i_c has a maximum of about $0.75/n^3$ at 20 keV. For alkali atoms such a lithium and sodium, the maximum value of i_n/i_c occurs at about 10 keV, being of similar magnitude to, but probably smaller than, the value for atomic hydrogen. In the case of the inert gases helium, neon, and argon, the maximum value of i_n/i_c occurs in the vicinity of 50–70 keV and again is of similar magnitude to, but probably slightly larger than, the maximum value for atomic hydrogen. The inert gases thus offer a number of advantages over alkali gases as neutralizers: they probably yield as large if not larger values of i_n/i_c at maximum; the maximum occurs at higher energies, so that the natural decay lengths of the excited atoms are correspondingly longer; they may be very much more easily handled experimentally.

1. INTRODUCTION

THE formation of highly excited atomic states from charge-exchange reactions of the type

$$H^+ + H(1s) \rightarrow H(\text{excited}) + H^+$$

is of considerable interest as a source of readily ionizable neutral particles for injection into plasma devices.[1]

In previous publications[2–4] we have calculated the cross section, say $\sigma_n{}^e$, for formation of highly excited atoms with principal quantum number n from the above exchange reaction. This has the form

$$\sigma_n{}^e = \frac{256}{5n^3 p^2 \beta^5} \pi a_0{}^2 , \qquad (1)$$

where a_0 is the Bohr radius; $p = (mv/\hbar)a_0$, where m is the electron mass and v is the speed of the incident ions, and

$$\beta = (p^2+1)^2/4p^2. \qquad (2)$$

Within the framework of first-order perturbation theory, Eq. (1) is accurate to order $1/n^2$. The cross section (1) shows a marked resonance at $p=1$ ($\beta=1$) which corresponds to an incident proton energy of 25 keV. This resonance point corresponds to the condition $\hbar v/e^2 = 1$, that is, for an incident proton speed equal to the average speed of the electron in its initial $1s$ state.

Moreover, as we have commented previously,[2] this first-order perturbation result should be reasonably accurate even at $p \approx 1$; this is indicated by an impact parameter analysis along the lines of that performed by May.[5]

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