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Dissociation of the Hydrogen Molecule Ion by Electron Impact*

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The dissociation cross section of H_2^+ for bombardment by electrons is investigated taking into account the effect of exchange collisions by use of the Born-Oppenheimer approximation. Both the post and prior interactions are considered. Theoretical results are presented for the transition in which the molecule ion is raised from the ground state $1s\sigma\,{}^2\Sigma_g^+$ to the lowest-lying repulsive state $2p\sigma\,{}^2\Sigma_u^+$ and then dissociates. The Franck-Condon principle is assumed throughout, and a classical average is taken over the molecular orientations. Numerical results are given for the dissociation cross sections as a function of energy both with and without the inclusion of exchange effect. The agreement between the post- and prior-interaction cross sections near the threshold energy is poor.

I. INTRODUCTION

THE dissociation of the hydrogen molecule ion has been considered theoretically by Salpeter[1] and by Kerner.[2] Salpeter has made an order of magnitude estimate for the dissociation cross section of H_2^+ at laboratory energies of 1–20 Mev for a collision with stationary gas molecules or ions. Kerner has calculated the cross section for the process in which the molecule ion is excited by electron impact from the ground state $1s\sigma\,{}^2\Sigma_g^+$ to the lowest-lying repulsive state $2p\sigma\,{}^2\Sigma_u^+$, and subsequently dissociates. The calculations, which are based on the Born approximation, do not, however, take into account the effect of electron exchange in which the incoming electron is captured and the originally bound electron is ejected, and which under certain conditions, may be quite appreciable.

In the present investigation we shall consider the dissociation of H_2^+ by excitation of the molecule ion to its lowest-lying excited level with the specific inclusion of exchange effects. The Born-Oppenheimer approximation is used to obtain general results for both the post and the prior interactions, the validity of the Franck-Condon principle being assumed throughout. We further suppose that the molecule ions are randomly oriented, and obtain average cross sections by a classical average over all angles of orientation following Massey and Mohr.[3,4] Effects of Coulomb distortion are neglected in the present treatment. Numerical results for the dissociation cross sections as a function of energy are given for a number of cases of interest. Section II presents the general quantum-mechanical theory, Secs. III and IV are devoted to a detailed discussion of the nonexchange and the exchange contributions, respectively, while Sec. V contains the numerical results.

II. GENERAL CONSIDERATIONS

In this section we shall discuss from a formal point of view the application of the Born-Oppenheimer approximation to the problem of the dissociation of the hydrogen molecule ion. The mathematical treatment follows that of Massey and Mohr,[3] who have considered the closely related problem of the ionization of the hydrogen molecule by an incident electron.

Let $\mathbf{k}_p$, $\mathbf{k}_q$ be the wave number vectors of the incoming and outgoing particle, respectively. The magnitudes k_p and k_q are related by the conservation of energy equation $k_p^2=k_q^2+2\mu\Delta E$, where ΔE is the energy required to raise the molecule from the ground to the first excited state. The differential cross section $d\sigma$ for scattering into $d\Omega$ may be written in the form

$$d\sigma=\frac{k_q}{k_p}\left[\tfrac{3}{4}|f-g|^2+\tfrac{1}{4}|f+g|^2\right], \tag{1}$$

where f and g are the amplitudes for direct and exchange scattering, respectively, and for the post interaction are given by the Born-Oppenheimer expressions

$$f=\frac{-\mu}{2\pi}\int\frac{1}{r_{12}}\exp[i(\mathbf{k}_p-\mathbf{k}_q)\cdot\mathbf{r}_1]\times\psi_p(\mathbf{r}_2)\psi_q(\mathbf{r}_2)^*d\tau_1d\tau_2, \tag{2}$$

$$g=\frac{\mu}{2\pi}\int\left(\frac{1}{r_{1a}}+\frac{1}{r_{1b}}-\frac{1}{r_{12}}\right)\exp[i(\mathbf{k}_p\cdot\mathbf{r}_2-\mathbf{k}_q\cdot\mathbf{r}_1)]\times\psi_p(\mathbf{r}_1)\psi_q(\mathbf{r}_2)^*d\tau_1d\tau_2, \tag{3}$$

in which ψ_p is the ground-state wave function for the hydrogen molecule ion, ψ_q is the wave function for the excited state of the ion, while the subscripts 1, 2 and a, b are labels for the two electrons and for the two hydrogen nuclei, respectively. The quantities $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of electrons 1 and 2 referred to a common space-fixed origin, while r_{1a}, r_{1b}, and r_{12} are the distances between the two particles designated by the subscripts. For simplicity units have been chosen so that e, m, and $\hbar$ are all unity and, consequently, the Bohr radius $\hbar^2/me^2$ is the unit of distance. In Eqs. (2)

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[1] E. E. Salpeter, Proc. Phys. Soc. (London) **A63**, 1295 (1950).

[2] E. H. Kerner, Phys. Rev. **92**, 1441 (1953).

[3] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A135**, 258 (1932).

[4] The validity of such an averaging process has been considered by Dr. T. K. Fowler (private communication).

and (3), μ is the reduced mass of the system (expressed in units of electronic mass), which for the case of incoming electrons may be taken equal to 1.

The prior interaction expression for g is given by an equation similar to (3), except that r_{1a} and r_{1b} are to be replaced by r_{2a} and r_{2b}, respectively. Since the mathematical formalism for the two interactions is entirely similar, we shall consider in detail the prior interaction only, and simply indicate the final results for the post interaction.

For the wave functions ψ_p and ψ_q we take the approximate expressions

$$\begin{aligned}\psi_p&=A(u_a+u_b),\\ \psi_q&=B(u_a-u_b),\end{aligned}\tag{4}$$

corresponding to the ground state $1s\sigma\ {}^2\Sigma_g{}^+$ and the first excited repulsive state $2p\sigma\ {}^2\Sigma_u{}^+$, respectively.[5] Here $u_a=u(r_a)$ and $u_b=u(r_b)$ are hydrogen-like wave functions centered about the nuclei a and b, respectively, where

$$u(r)=(Z^3/\pi)^{\frac{1}{2}}e^{-Zr},\tag{5}$$

and where $Z=1.228$.[6]

In the next section we shall consider the evaluation of the nonexchange amplitude f using an approach similar to that of Kerner,[2] leaving until a later section the considerably more difficult calculation of g.

III. NONEXCHANGE CONTRIBUTION

Setting $\mathbf{K}=\mathbf{k}_p-\mathbf{k}_q$, we write f in the form

$$f=-\frac{\mu}{2\pi}\int\frac{1}{r_{12}}e^{i\mathbf{K}\cdot\mathbf{r}_1}\psi_p(\mathbf{r}_2)\psi_q(\mathbf{r}_2)^*d\tau_1d\tau_2.\tag{6}$$

Making use of the Bethe integral

$$\int\frac{1}{r_{12}}e^{-i\mathbf{K}\cdot\mathbf{r}_1}d\tau_1=(4\pi/K^2)e^{i\mathbf{K}\cdot\mathbf{r}_2},$$

Eq. (6) becomes

$$f=\frac{-2Z^3AB\mu}{\pi K^2}\int e^{i\mathbf{K}\cdot\mathbf{r}_2}(e^{-2Zr_{2a}}-e^{-2Zr_{2b}})d\tau_2.$$

Choosing the origin of the coordinate system at the midpoint of the molecule, and letting $\mathbf{d}$ represent the vector from nucleus a to nucleus b, so that

$$\mathbf{r}_2=\mathbf{r}_{2a}-\tfrac{1}{2}\mathbf{d}=\mathbf{r}_{2b}+\tfrac{1}{2}\mathbf{d},\tag{7}$$

we find by a straightforward integration that

$$f=\frac{64iZ^4AB\mu}{K^2(4Z^2+K^2)}\sin(\tfrac{1}{2}\mathbf{K}\cdot\mathbf{d}).\tag{8}$$

Substituting Eq. (8) into Eq. (1), and assuming the molecule to be randomly oriented, one obtains, after averaging over all angles

$$d\sigma=\frac{2^{11}A^2B^2Z^8\mu^2k_q}{K^4(4Z^2+K^2)^4k_p}\left(1-\frac{\sin Kd}{Kd}\right).\tag{9}$$

Here

$$K^2=k_p{}^2+k_q{}^2-2k_pk_q\cos\theta,\tag{10}$$

where $\theta=\angle(\mathbf{k}_p,\mathbf{k}_q)$ is the angle of scattering in the center-of-mass system. The total cross section σ is

$$\sigma=\frac{2^{12}\pi Z^8A^2B^2\mu^2}{k_p{}^2}\int_{K_0}^{K_1}\frac{(1-\sin Kd/Kd)}{K^3(4Z^2+K^2)}dK,\tag{11}$$

where $K_0=k_p-k_q$ and $K_1=k_p+k_q$.

The integral in Eq. (11) cannot be evaluated in terms of elementary functions. It can be shown, however, that in the limit of high incident speeds (v_p of the order of 10^9 cm/sec for $H_2{}^+$), σ is given approximately by the formula

$$\sigma\cong\frac{32\pi A^2B^2}{3v_p{}^2}\left(-\frac{11}{12}+\ln\frac{2Zv_p}{\Delta E}\right).\tag{12}$$

Thus, as might be expected for a fast particle, the cross section is independent of the mass of the particle, and for very high speeds has the well-known $\ln E/E$ variation. The dependence of σ on Z under these extreme conditions appears to be small, indicating that it should be relatively insensitive to the specific forms chosen for the molecular wave functions.

IV. EXCHANGE CONTRIBUTION

The exchange term g, as previously mentioned, is considerably more difficult to evaluate than the nonexchange, or direct term. We begin by writing Eq. (3) (taking $\mu=1$) in the form

$$g=g_{12}+g_{1a}+g_{1b},\tag{13}$$

where g_{12}, g_{1a}, and g_{1b} correspond to the Coulomb interactions $r_{12}{}^{-1}$, $r_{1a}{}^{-1}$, and $r_{1b}{}^{-1}$, respectively. The first of these terms, g_{12}, can be readily put in the form

$$\begin{aligned}g_{12}=(ABZ^3I_0i/\pi)[&\sin\tfrac{1}{2}(\mathbf{k}_p-\mathbf{k}_q)\cdot\mathbf{d}\\&+\sin\tfrac{1}{2}(\mathbf{k}_p+\mathbf{k}_q)\cdot\mathbf{d}],\end{aligned}\tag{14}$$

where I_0 is

$$\begin{aligned}I_0=\int\frac{1}{r_{12}}\exp[i(\mathbf{k}_p\cdot\mathbf{r}_{2a}-\mathbf{k}_q\cdot\mathbf{r}_{1a})&\\-Z(r_{1a}+r_{2a})]d\tau_1d\tau_2.&\end{aligned}\tag{15}$$

The evaluation of I_0 is somewhat involved, but follows the general procedure indicated by Massey and Mohr,[3]

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[5] Linus Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

[6] B. N. Finkelstein and G. E. Horowitz, Z. Physik 48, 118 (1928).

Only the final result wlll be given here:

$$I_0=8\pi^3(k_pk_q)^{-\frac{1}{2}}\sum_{l=0}^{\infty}(-1)^lP_l(\cos\alpha)$$
$$\times\int_0^{\infty}dr_1\,r_1^{\frac{3}{2}}J_{l+\frac{1}{2}}(k_pr_1)e^{-Zr_1}$$
$$\times\left\{r_1^{-l-1}\int_0^{r_1}dr\,r^{l+\frac{3}{2}}J_{l+\frac{1}{2}}(k_qr)e^{-Zr}\right.$$
$$\left.+r_1^{l}\int_{r_1}^{\infty}dr\,r^{-l+\frac{1}{2}}J_{l+\frac{1}{2}}(k_qr)e^{-Zr}\right\},\quad(16)$$

in which $\alpha=\angle(\mathbf{d},\mathbf{k}_q)$.

Turning next to the quantity g_{1a}, a readily performed integration over $d\tau_2$ yields

$$g_{1a}=\frac{-8\pi^{\frac{1}{2}}iBZ^{\frac{5}{2}}I_1\sin(\frac{1}{2}\mathbf{k}_p\cdot\mathbf{d})}{(Z^2+k_p^2)^2},\quad(17)$$

where

$$I_1=\int\frac{1}{r_{1a}}e^{-i\mathbf{k}_q\cdot\mathbf{r}_{1a}}\psi_p(\mathbf{r}_1)d\tau_1=AZ^{\frac{3}{2}}\pi^{\frac{1}{2}}e^{i\frac{1}{2}\mathbf{k}_q\cdot\mathbf{d}}$$
$$\times\left[I_2+\frac{4\pi}{(k_q^2+Z^2)}\right],\quad(18)$$

in which

$$I_2=\int\frac{1}{r_{1a}}\exp[-i\mathbf{k}_q\cdot\mathbf{r}_{1a}-Zr_{1b}]d\tau_1.\quad(19)$$

The evaluation of I_2 is similar to that of I_0. Again, only the final result will be given.

$$I_2=(8\pi^3k_q)^{\frac{1}{2}}\sum_{l=0}^{\infty}i^{-l}(2l+1)P_l(\cos\alpha)S_l,\quad(20)$$

where

$$S_l=-d^{-\frac{1}{2}}\frac{d}{dz}\left\{K_{l+\frac{1}{2}}(Zd)\int_0^{d}J_{l+\frac{1}{2}}(l_qr)I_{l+\frac{1}{2}}(Zr)dr\right.$$
$$\left.+I_{l+\frac{1}{2}}(Zd)\int_d^{\infty}J_{l+\frac{1}{2}}(k_qr)K_{l+\frac{1}{2}}(Zr)dr\right\}.\quad(21)$$

The integrations involved in the expressions for S_l must be performed numerically, in general. Fortunately, the convergence seems to be rapid, the $l=0$ term being sufficient for the purpose of the present computation.

From a comparison of the expression for g_{1a} and g_{1b} (and as might be expected from the symmetries inherent in the problem) the two quantities are related by

$$g_{1b}=-g_{1a}{}^*.\quad(22)$$

The exchange amplitude g_{2a} for the post interaction may be obtained from the expression for g_{1a} by making the following substitutions: (1) $\cos(\frac{1}{2}\mathbf{k}_q\cdot\mathbf{d})e^{-i\frac{1}{2}\mathbf{k}_p\cdot\mathbf{d}}\rightarrow-i\sin(\frac{1}{2}\mathbf{k}_p\cdot\mathbf{d})e^{i\frac{1}{2}\mathbf{k}_q\cdot\mathbf{d}}$, (2) $k_p\leftrightarrow k_q$ in all the remaining terms, and (3) $i^{-l}\rightarrow-i^l$. The amplitude g_{2b} is related to g_{2a} by an equation analogous to Eq. (22).

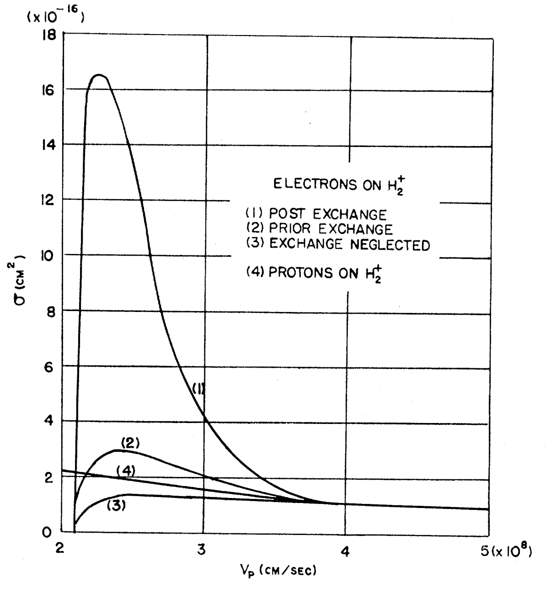

FIG. 1. The total cross section for dissociation of $H_2{}^+$ by charged particles as a function of the incident speed v_p for the following cases: curve (1) for electrons, using the post interaction; curve (2) for electrons, using the prior interaction; curve (3) for electrons, neglecting exchange; and curve (4) for protons.

Finally, an averaging over the orientations of the molecule similar to that described in Sec. II should be performed. The process is quite straightforward, though the final equations are rather cumbersome and will not be explicitly given here.

V. NUMERICAL RESULTS

Applying the theory presented in Secs. III and IV, cross sections as functions of v_p for the dissociation produced by the excitation of $H_2{}^+$ from the ground state to the lowest excited state by incident charged particles have been evaluated for the following cases: (1) for electrons using the post interaction, (2) for electrons using the prior interaction, (3) for electrons, neglecting exchange, and (4) for energetic (10^4–10^5 ev) protons. The necessary integrals have been evaluated by numerical integration. Only the $l=0$ contributions have been retained since the $l=1$ terms were found to be smaller by an order of magnitude for the particular energies chosen. The following values for the fixed parameters have been used: $A=0.584$, $B=0.970$, $Z=1.228$, $d=2.01$, $\Delta E=12.4$ ev.

The results are presented graphically in Fig. 1. For electrons the cross sections in all three cases rise from zero at a speed corresponding to a threshold energy of 12.4 electron volts, reach a maximum, and then slowly diminish, as expected. A comparison of the curves with each other shows the importance of the exchange scattering contribution to σ. Unfortunately, the post and prior interactions do not yield results in agreement with each other, except at speeds so high that the effect of exchange collisions is small compared with that of direct collisions. As has been pointed out by Bates *et al.*,[7] this disagreement is due to the approximate nature of the molecular wave functions used. Presumably, a more accurate calculation would yield a cross section intermediate in magnitude, though even then the results would still be approximate. Actually, as a simple estimate for the maximum partial cross sections shows, the post interaction cross sections obtained imply contributions of angular momenta much higher than seems physically plausible. One cannot conclude from this, of course, that the prior interaction results are necessarily correct.

As is more or less evident from a consideration of Eqs. (2) and (3), and as is corroborated by calculations for the present case, the direct amplitude f and the indirect amplitude g are opposite in sign. This difference in sign has the effect of increasing the triplet scattering cross section $\frac{3}{4}|f-g|^2$ relative to pure direct scattering, while at the same time decreasing the singlet contribution $\frac{1}{4}|f+g|^2$. Indeed, somewhere between the region above the threshold, where exchange scattering is dominant, and well above threshold, where direct scattering is of primary importance, there is an energy where the two amplitudes f and g are equal in magnitude and opposite in sign. The scattering should then be entirely triplet in character. In regions where either direct or exchange scattering is dominant the effect of interference between f and g is small, and the usual 3:1 triplet-singlet ratio applies.[8]

Finally, the cross section is presented for the case of incident protons. Essentially the same curve would be obtained for any singly charged ion, provided that the effect of electronic screening be neglected. For ions of charge Z_1 the indicated cross sections must, of course, be multiplied by Z_1^2. Thus, for an incoming beam containing a high percentage of multiply charged ions, σ may be quite appreciable.

It should be emphasized that only contributions of the first excited state of the hydrogen molecule ion to the dissociation cross section have been considered here. The over-all cross section would also include, of course, the effects of transitions to still higher excitation states, though presumably these are small.

ACKNOWLEDGMENTS

The author is indebted to Dr. T. K. Fowler and Dr. Albert Simon for their valuable comments and criticism.

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[7] Bates, Fundaminsky, and Massey, Trans. Roy. Soc. (London) **A243**, 93 (1950).

[8] For a detailed discussion of exchange and direct scattering effects for the atomic case, see reference 7.