Theory of Electron Capture by Molecules: Dissociative Attachment*

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(Received 15 August 1962)

An elementary process for electron capture by molecules, namely, dissociative electron attachment, is investigated, and a general method is given for calculating the cross section for such a process. Application of this method is carried out for the reaction $H_2 + e \rightarrow H^- + H$ with both H^- and H in their ground states. The calculated cross section–energy curve agrees satisfactorily with the experimentally observed curve.

I. INTRODUCTION

THE mechanism for electron capture by molecules is complicated by its many possible fates. Some theoretical aspects of this mechanism have been discussed qualitatively.[1,2] Recently, there have been reported several careful experimental measurements on the cross sections of one of the elementary processes for electron capture by molecules, namely, dissociative electron attachment, in diatomic molecular systems.[3,4] The most important dissociative attachment processes for diatomic molecules are of the Franck-Condon type in which a transition takes place from a stable state of the molecule to a continuum of the negative parent ion. Such direct capture of the incident electron into the repulsive state of the parent ion lying in the Franck-Condon region of the molecule would lead to a dissociation of the molecule under consideration in approximately a vibrational time of the constituent nuclei. Dissociative attachment, however, may also take place in an indirect way in which the incident electron is first captured into a discrete state of the negative parent ion. There follows a radiationless intramolecular decomposition of the Auger type (predissociation) as a result of the overlapping of this discrete state by a continuous range of states. The latter type of capture process is very important for polyatomic molecules, since in such molecules there is predissociation by vibration, in addition to the radiationless transition into a repulsive electronic state or rotational level within a given electronic state.[5]

There seems to have been no attempt made, as reported in the literature, for the calculation of the cross section of such dissociative attachment. The present paper is an attempt to explore the possibilities of such a calculation. We are particularly concerned with dissociative electron attachment by diatomic molecules as an example of the direct capture mechanism. (We prefer to restrict the expression "electron capture from other molecules or atoms" to a somewhat different process, namely, charge transfer.)

In order for the constituent nuclei to absorb the energy released on capture of an electron by their molecule and to move apart, the transition operators for this process must be expressed in terms of certain coupling factors between the nuclear and electronic motion of the molecule. Massey has suggested that the kinetic energy operators of the nuclei are responsible for such a type of capture,[1] and his suggestion was recently discussed by Stanton.[2] In this paper, we start with the Born-Oppenheimer separation (B-O separation),[6] since in this separation procedure one first encounters the interaction terms between the nuclear and electronic motions. In the usual B-O separation procedure, the electronic energy so obtained is regarded as the effective potential for the slower nuclear motion, and the coupling terms between the electronic and nuclear motions are neglected. It is well known that this separation underlies the Franck-Condon principle and gives consistent interpretation and prediction of the characteristics of most molecular spectra. It is, however, not clearly known how the neglected coupling terms affect the molecular system.

As early as 1928, Kronig attributed the predissociation phenomenon to the neglected coupling terms,[7] and later (1929) Van Vleck showed that these coupling terms provide an explanation of the phenomenon of Λ doubling.[8] Only recently has there been an increased interest in the diagonal coupling terms neglected in the B-O separation, with particular attention to configurations in which the nuclei are separated by large distances.[9] More recently, Jepsen and Hirschfelder have studied the possibility that the coupling terms would give inelastic collision probabilities, and have calculated the cross sections for excitation and charge transfer to the 2s state during a proton-hydrogen atomic collision.[10] In this paper, we investigate the possibility that the elementary process of dissociative electron attachment by molecules is also due to these coupling terms.

* Research performed under the auspices of the U. S. Atomic Energy Commission.

[1] H. S. W. Massey, *Negative Ions* (Cambridge University Press, New York, 1950), 2nd ed; J. D. Craggs and H. S. W. Massey, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. 37, p. 314.

[2] R. E. Stanton, J. Chem. Phys. **32**, 1348 (1960).

[3] G. J. Schulz, Phys. Rev. **113**, 816 (1959).

[4] For others, see for example, M. A. Biondi and R. E. Fox, Phys. Rev. **109**, 2012 (1958).

[5] For further discussion, see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), 2nd ed., p. 387; R. S. Mulliken, J. Chem. Phys. **33**, 247 (1960).

[6] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

[7] R. Kronig, Z. Physik **50**, 347 (1928).

[8] J. Van Vleck, Phys. Rev. **33**, 467 (1929)

[9] T. Y. Wu and A. B. Bhatia, J. Chem. Phys. **24**, 48 (1956); T. Y. Wu, *ibid*. **24**, 444 (1956); A. Dalgarno and R. McCarroll, Proc. Roy. Soc. (London) **A237**, 383 (1956); **A239**, 413 (1957).

[10] D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. **32**, 1323 (1960).

In Sec. II, we present the general theoretical approach to the problem of calculation of the cross section for dissociative electron attachment. An application of this approach to the system $H_2 + e \rightarrow H + H^-$ is given in some detail in the remaining sections. Calculation of the coupling matrix elements is shown in Sec. III, and the approximations being made in evaluating these matrix elements are critically examined. In Sec. IV, the distorted nuclear wave equation is solved for the nuclear wave functions in the continuum. The behavior of this function at the boundary conditions is discussed in some detail. Numerical evaluations of the transition matrix elements are then carried out by using these nuclear wave functions as shown in Sec. V. In Sec. VI the results of our application are summarized and the calculated cross sections are compared with the experimental measurements. Finally, in Sec. VII we make some concluding remarks.

II. THEORY

There are different ways in which one may perform the B-O separation. Jepsen and Hirschfelder[10] have shown that the separation carried out in relative coordinates is slightly more accurate than the usual treatment using fixed space coordinates.[11] The separation carried out after the center-of-mass motion has been removed from the equation is not unique, however. For diatomic molecules, the most convenient set of relative coordinates is the set with electron coordinates referred to the center of mass of the nuclei. The Schrödinger equation, in such relative coordinates, for a system of N electrons and two heavy nuclei a and b of masses M_a and M_b, respectively, is[12]

$$\left(-\frac{1}{2\mu}\nabla_R^2 + H\right)\Omega = i\frac{\partial}{\partial t}\Omega, \qquad (1)$$

with

$$H = \frac{1+M_a+M_b}{2(M_a+M_b)}\sum_{i=1}^{N}\nabla_i^2 + V, \qquad (2)$$

where $\mu = M_a M_b/(M_a+M_b)$, ∇^2 is the Laplacian operator, V is the potential energy, $\mathbf{R}$ is the vector from b to a, and the cross terms $\nabla_i \cdot \nabla_j$ in Eq. (1) are neglected. The electronic Schrödinger equation for fixed nuclear configurations becomes

$$H\Psi_n(\mathbf{r},\mathbf{R}) = \mathcal{E}_n(\mathbf{R})\Psi_n(\mathbf{r},\mathbf{R}), \qquad (3)$$

where the electronic coordinates are collectively denoted by $\mathbf{r}$. The Ψ_n's form a complete set in the space of electronic variables, so it is possible to expand the

wave function of the relative system in the form

$$\Omega = \sum_n \int \chi_n{}'(\mathbf{R})\Psi_n(\mathbf{r},\mathbf{R}). \qquad (4)$$

Substituting this expression for Ω into Eq. (1) and forming matrix elements in the electronic variables, we obtain the following set of differential integral equations for the $\chi_n{}''$s:

$$\{\nabla_R^2 + 2\mu[E_n - V_n(\mathbf{R})]\}\chi_n{}'(\mathbf{R})$$
$$= -\sum_{n' \neq n} C_{nn'}(\mathbf{R},\nabla_R)\chi_{n'}{}'(\mathbf{R}), \qquad (5)$$

where E_n is the total energy, $V_n(\mathbf{R})$ is the effective nuclear potential energy obtained by including the diagonal coupling terms into the electronic energy $\mathcal{E}_n(\mathbf{R})$, and

$$C_{nn'} = 2A_{nn'}\nabla_R + B_{nn'}, \qquad (6)$$

$$A_{nn'} = \langle\Psi_n|\nabla_R|\Psi_{n'}\rangle, \qquad (7)$$

$$B_{nn'} = \langle\Psi_n|\nabla_R^2|\Psi_{n'}\rangle. \qquad (8)$$

In principle, Eq. (5) can be solved exactly and would provide us with the information for the nuclear motion coupled by the electronic motion. This, however, is not possible in practice. If one assumes that the nondiagonal matrix elements $C_{nn'}$ are so small that they may be neglected except for C_{n0} which involves the initial state "0", Eq. (5) reduces to

$$\{\nabla_R^2 + 2\mu[E_n - V_n(\mathbf{R})]\}\chi_n{}'(\mathbf{R}) = -C_{n0}\chi_0{}'(\mathbf{R}). \qquad (9)$$

Hence, by the distorted-wave method[13] the differential cross section $d\sigma_{f0}$ corresponding to excitation from the initial state "0" to the final state "f" can be expressed as a function of the incident angles (θ_0, φ_0):

$$d\sigma_{f0}(\theta_0,\varphi_0) = (s/16\pi^2 k_0)|H_{f0}|^2 d\Omega_f, \qquad (10)$$

where s is the statistical factor ($s=1$ or 2 for heteronuclear or homonuclear diatomic molecules, respectively), k_0 is the magnitude of the initial propagation vector of the incident electron, $d\Omega_f$ (i.e., $\sin\theta_f d\theta_f d\varphi_f$) is the final solid angle element, and the transition matrix elements are

$$H_{f0} = \langle\chi_f|2A_{f0}\nabla_R + B_{f0}|\chi_0\rangle. \qquad (11)$$

The initial and final nuclear wave functions which appear in Eq. (11) are the solutions of the following corresponding distorted-wave equations:

$$\{\nabla_R^2 + 2\mu[E_0 - V_0(\mathbf{R})]\}\chi_0(\mathbf{R}) = 0, \qquad (12)$$

$$\{\nabla_R^2 + 2\mu[E_f - V_f(\mathbf{R})]\}\chi_f(\mathbf{R}) = 0, \qquad (13)$$

with

$$E_f = K_f^2/2\mu = E_0{}' + E_a - D_e,$$

where $E_0{}'$ is the incident electron energy, E_a is the electron affinity of the constituent atom in question,

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[11] See for example, J. O. Hirschfelder, C. F. Curtiss, and B. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 925.

[12] Atomic units are used throughout this paper except where indicated otherwise.

[13] For a review, see N. F. Mott and H. S. W. Massey, *Theory of Atomic Collision* (Clarendon Press, Oxford, 1949), 2nd. ed.

and D_e is the dissociation energy of the diatomic molecule. In writing down Eq. (10), the final wave function χ_f is assumed to be normalized in the K_f scale.

If the rotational degrees of freedom of the molecule are suppressed, one may consider that the molecule is in a fixed orientation. To find the general differential cross section without specifications to the orientations of the molecular axis, the transition matrix elements are averaged over the incident angles (θ_0, φ_0) of the impinging electron. The cross section σ_{f0} is then obtained by integrating over the sphere $d\Omega_f$:

$$\sigma_{f0} = (s/64\pi^3 k_0) \int\int |H_{f0}|^2 d\Omega_0 d\Omega_f. \tag{14}$$

An application of this formula to a specific problem of interest, namely,

$$H_2 + e \rightarrow H + H^-,$$
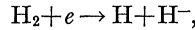
is considered in the following sections. The choice of this application is made, not only because of its relative simplicity, but because of the experimental measurements recently made available[3] and of the importance of this process in astrophysics. The importance of this process arises from the fact that it is credited, in the solar corona, for generating H^- ions,[14] a substance which controls the solar emissivity through bound-free and free-free electron transitions.[15]

III. CALCULATION OF THE COUPLING MATRIX ELEMENTS

For the calculation of the coupling matrix elements A_{f0} and B_{f0}, we consider explicitly the specific application, $H_2 + e \rightarrow H + H^-$, with both H and H^- in their ground state, and proceed from the electronic Schrödinger equation,

$$H\Psi_n = (H_0 + H')\Psi_n = \mathscr{E}_n \Psi_n. \tag{15}$$

If the electrostatic energy of interaction H' between the incident electron and the hydrogen molecule is to be treated as a small perturbation, one may use the power series expansion for the electronic wave function[16]:

$$\Psi_0 = \Psi_0^{(0)} + G^{(+)}(\mathscr{E}^{(0)})H'\Psi_0^{(0)}$$
$$\qquad + G^{(+)}(\mathscr{E}^{(0)})H'G^{(+)}(\mathscr{E}^{(0)})H'\Psi_0^{(0)} + \cdots, \tag{16}$$

where

$$H' = \frac{1}{r_{23}} + \frac{1}{r_{13}} - \frac{1}{|r_3 - R/2|} - \frac{1}{|r_3 + R/2|}, \tag{17}$$

$$H_0\Psi_n^{(0)} = \mathscr{E}_n^{(0)}\Psi_n^{(0)}. \tag{18}$$

The Green function operator $G^{(+)}(\mathscr{E}^{(0)})$ is defined

[14] Y. Öhman, Arkiv Astron. 2, 1 (1955).
[15] S. Chandrasekhar and D. D. Elbert, Astrophys. J. 128, 633 (1958); S. Geltman, Phys. Rev. 104, 346 (1956). See also earlier work therein.
[16] M. Gell-Mann and M. L. Goldberger, Phys. Rev. 91, 398 (1953).

symbolically[16] as

$$G^{(+)}(\mathscr{E}^{(0)}) = \lim_{\epsilon \to 0^+} \frac{1}{\mathscr{E}^{(0)} - H_0 - i\epsilon}.$$

Using the complete orthonormal set $\{\Psi^{(0)}\}$, this operator may be expressed in the integral operator form[17]

$$G^{(+)}(\mathscr{E}^{(0)}) = \lim_{\epsilon \to 0^+} \sum_n \int d\tau_{r'} G_n(r, r'), \tag{19}$$

with

$$G_n(r, r') = \frac{1}{4\pi^3} \int \frac{\Psi_n^{(0)}(k, r)\Psi_n^{(0)*}(k, r')}{k^2 - \kappa_n^2} d\tau_k, \tag{20}$$

$$\kappa_n^2 = k_0^2 - 2(\epsilon_n - \epsilon_0), \tag{21}$$

where ϵ_0 and ϵ_n are the energies of the molecule at the initial and intermediate states, respectively; k_0 and k are the magnitudes of the initial and intermediate propagation vectors of the electron, respectively.

Since the two electrons in the hydrogen molecule are in a symmetric space state and an antisymmetric spin state, the unperturbed electronic wave function $\Psi_n^{(0)}$ may be written as

$$\Psi_n^{(0)}(r) = \psi_n(r_1)\psi_n(r_2)\phi_{k_0}(r_3)(1/\sqrt{2})(\alpha_1\beta_2\alpha_3 - \alpha_2\beta_1\alpha_3), \tag{22}$$

where α and β are the spin states, ϕ is the wave function of the incident electron, and ψ's form the complete orthonormal set of molecular orbital wave functions. Substituting $\Psi^{(0)}$'s from Eq. (22) into Eq. (16) and truncating the power series expansion to two terms, the initial electronic wave function takes the approximate form

$$\Psi_0^{(1)} = \Psi_0^{(0)} + \sum_n \int \psi_n(r_1)\psi_n(r_2)\langle\psi_n(r_1')\psi_n(r_2')G_n(r_3, r_3')$$
$$\times |H'(r')|\psi_0(r_1')\psi_0(r_2')\phi_{k_0}(r_3')\rangle. \tag{23}$$

At the final state, the electronic wave function becomes that of the ground $^2\Sigma_u^+$ state of H_2^-. This wave function is also the eigenfunction of Eq. (15) yielding the nuclear potential $\mathscr{E}_f(R)$ for the final nuclear motion. In the present treatment, we use the valence-bond wave function as the approximate function. Thus, the unnormalized final electronic wave function can be written as

$$\Psi_f = \{\psi_0^a(r_1, r_2)\psi_0^b(r_3) - \psi_0^b(r_1, r_2)\psi_0^a(r_3)\}$$
$$\times (1/\sqrt{2})(\alpha_1\beta_2\alpha_3 - \alpha_2\beta_1\alpha_3) + \text{cyclic terms}, \tag{24}$$

with

$$\psi_0^a(r_i, r_j) = (2 + 2\langle 1s | 1s'\rangle)^{-1/2}$$
$$\times [1s(r_{ai})1s'(r_{aj}) + 1s'(r_{ai})1s(r_{aj})],$$

$$1s(r_{ai}) = \pi^{-1/2}e^{-r_{ai}}, \quad 1s'(r_{ai}) = (0.027/\pi)^{1/2}e^{-0.3r_{ai}},$$

$$\psi_0^b(r_i) = 1s(r_{bi}) = \pi^{-1/2}e^{-r_{bi}},$$

where the $1s$'s are the atomic orbital wave functions

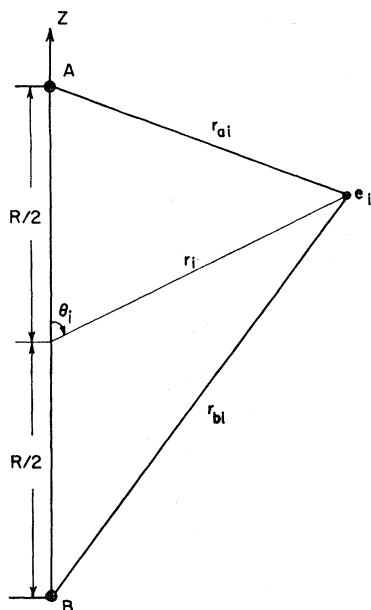[17] G. Gioumousis and C. F. Curtiss, J. Chem. Phys. 29, 996 (1958); J. Math. Phys. 2, 96 (1961).

FIG. 1. The coordi-system used in deter-mining the coupling matrix elements ap-proximately.

having their center at a or b as indicated by superscripts (Fig. 1); $\psi_0{}^a(\mathbf{r}_i,\mathbf{r}_j)$ and $\psi_0{}^b(\mathbf{r}_i)$ are the electronic wave functions for ground states of H^- and H, respectively.[18] The coupling matrix elements A_{f0} and B_{f0} can, therefore, be evaluated by using the expressions for Ψ_0 and Ψ_f from Eqs. (23) and (24), respectively.

In Eq. (23), the wave function of the incident electron may be expressed accurately in terms of spheroidal wave functions[19] and the set of molecular orbital wave functions may be expressed in series of both associated Legendre functions and Laguerre polynomials in the prolate spheroidal coordinates.[20] In terms of these wave functions, the derivatives and integrations become quite involved even for a computer. Our problem consists in finding some simpler functions that would enable us to evaluate the matrix elements and yet would provide a good approximation for the coupling terms. A central-field approximation is adopted for the electronic wave functions.[21,22] The usefulness of this approximation has been demonstrated convincingly for simple molecules of high symmetry,[21] even though, for refined molecular energy calculation, Hagstrom and Shull found that these single center expansions converge slowly.[22] The error that would be introduced in the calculation of the coupling terms by this approximation is, however, not exactly known. Jepsen and Hirschfelder have shown that the nondiagonal $1s\sigma_g$-$2s\sigma_g$ coupling terms for $H_2{}^+$

[18] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).
[19] J. A. Stratton, P. M. Morse, L. J. Chu, and F. J. Corbato, *Spheroidal Wave Functions* (The Technology Press of M.I.T., Cambridge, Massachusetts, 1956).
[20] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1953).
[21] F. A. Matson, J. Chem. Phys. **21**, 928 (1953); J. C. Y. Chen and J. L. Magee, *ibid.* **36**, 1407 (1962); K. Funabachi and J. L. Magee, *ibid.* **26**, 407 (1957); H. W. Jay and R. G. Parr, *ibid.* **28**, 448 (1958).
[22] S. Hagstrom and H. Shull, J. Chem. Phys. **30**, 1314 (1959).

calculated in LCAO approximation are small in comparison with those calculated by using the exact wave functions at internuclear separations of the Franck-Condon region. On the other hand, these same coupling terms calculated in united-atom approximation become too large in comparison with those calculated exactly at the same internuclear separations.[10] In view of these findings, one would expect that the central-field approximation might yield the correct magnitudes for the coupling matrix elements at internuclear separations of the Franck-Condon region.

In this approximation the complete orthonormal set of molecular orbital wave functions $\{\psi_n\}$ is substituted by a complete orthonormal set of hydrogen-like wave functions $\{\psi_n{}^{(0)}\}$ having their centers midway between the nuclei of the symmetric diatomic molecule. The orbital exponents (parameters) are determined by treating them as independent variational parameters in minimizing the electronic energy of their corresponding molecules. Equation (23) then becomes

$$\Psi_0{}^{(1)}=\Psi_0{}^{(0)}+\sum_n \int \psi_n{}^{(0)}(\mathbf{r}_1)\psi_n{}^{(0)}(\mathbf{r}_2)$$
$$\times\langle\psi_n{}^{(0)}(\mathbf{r}_1')\psi_n{}^{(0)}(\mathbf{r}_2')G_n{}^{(0)}(\mathbf{r}_3,\mathbf{r}_3')$$
$$\times|H'(\mathbf{r}')|\psi_0{}^{(0)}(\mathbf{r}_1')\psi_0{}^{(0)}(\mathbf{r}_2')\phi_{k_0}{}^{(0)}(\mathbf{r}_3')\rangle. \quad (25)$$

After taking the gradient and the Laplacian of this wave function with respect to R and making use of the orthonormality of $\psi^{(0)}$'s, we obtain

$$\nabla_R\Psi_0{}^{(1)}=-\psi_0{}^{(0)}(\mathbf{r}_1)\psi_0{}^{(0)}(\mathbf{r}_2)$$
$$\times\nabla_R\langle G_0{}^{(0)}(\mathbf{r}_3,\mathbf{r}_3')|\,|\mathbf{r}_3'-\mathbf{R}/2|^{-1}$$
$$+|\mathbf{r}_3'+\mathbf{R}/2|^{-1}|\phi_{k_0}{}^{(0)}(\mathbf{r}_3')\rangle, \quad (26)$$

$$\nabla_R{}^2\Psi_0{}^{(1)}=-\psi_0{}^{(0)}(\mathbf{r}_1)\psi_0{}^{(0)}(\mathbf{r}_2)$$
$$\times\nabla_R{}^2\langle G_0{}^{(0)}(\mathbf{r}_3,\mathbf{r}_3')|\,|\mathbf{r}_3'-\mathbf{R}/2|^{-1}$$
$$+|\mathbf{r}_3'+\mathbf{R}/2|^{-1}|\phi_{k_0}{}^{(0)}(\mathbf{r}_3')\rangle, \quad (27)$$

where $G_0{}^{(0)}(\mathbf{r}_3,\mathbf{r}_3')$ is the Green's function for a free particle.[23]

$$G_0{}^{(0)}(\mathbf{r}_3,\mathbf{r}_3')=\frac{1}{4\pi^3}\int\frac{\phi_k(\mathbf{r}_3)\phi_k{}^*(\mathbf{r}_3')}{k^2-k_0{}^2}d\tau_k$$
$$=\frac{1}{2\pi}\frac{e^{ik_0|\mathbf{r}_3-\mathbf{r}_3'|}}{|\mathbf{r}_3-\mathbf{r}_3'|}. \quad (28)$$

The appropriate central-field orbital for $1s\sigma_g(\psi_0{}^{(0)})$ electrons in H_2 requires the parameter $Z=0.935$. Equation (27) can be further simplified by applying the well-known Poisson equation in electrostatics:

$$\nabla_R{}^2V=-4\pi\rho(\mathbf{R}), \quad \text{if} \quad V=\int\frac{\rho(\mathbf{r})}{\mathbf{r}-\mathbf{R}}d\tau_r. \quad (29)$$

[23] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

After carrying out the differentiation in R and integration over $\mathbf{r}$, Eqs. (26), (27), and (24) are substituted into Eqs. (7) and (8); the resulting expressions for the coupling matrix elements A_{f0} and B_{f0} are then evaluated by performing the integration in terms of elliptic coordinates (Fig. 1).

IV. THE NUCLEAR WAVE FUNCTIONS OF A DIATOMIC MOLECULE IN THE CONTINUUM

The nuclear wave functions in the continuum are obtained by solving Eq. (13) with the effective nuclear potential given by the Morse function.[24] Writing the wave function in the usual approximate form $[\chi(R)/R]Y(\theta,\varphi)$ and suppressing the nuclear rotational motion, Eq. (13) reduces to a one-dimensional differential equation,

$$\frac{d^2}{dR^2}\chi_f(R)$$
$$+2\mu[E_f-D_e e^{-2\beta(R-R_e)}+2D_e e^{-\beta(R-R_e)}]\chi_f(R)=0. \quad (30)$$

This equation can be simplified by a transformation,

$$Z=2n_0 e^{-\beta(R-R_e)}. \quad (31)$$

Equation (30) becomes

$$\frac{d^2}{dZ^2}\chi_f(Z)+\frac{1}{Z}\frac{d}{dZ}\chi_f(Z)-\left(\frac{n^2}{Z^2}-\frac{n_0}{Z}+\frac{1}{4}\right)\chi_f(Z)=0, \quad (32)$$

where we have defined

$$n_0=(2\mu D_e)^{1/2}/\beta=K_0/\beta,$$
$$n_f=(-2\mu E_f)^{1/2}/\beta=iK_f/\beta=in_f'. \quad (33)$$

We are looking for a solution that is everywhere finite, vanishes at the origin $[R=0$, i.e., $Z_0=2n_0\exp(\beta R_e)]$, and has the asymptotic behavior of a standing spherical wave.

$$\chi_f(R)/R \xrightarrow[R\to\infty]{} (K_f R)^{-1}\sin(K_f R+\delta_f). \quad (34)$$

In view of the boundary conditions, we try a wave function of the form

$$\chi_f(Z)=N_f Z^{n_f}[e^{-Z/2}F_f(Z)]. \quad (35)$$

Substitution of $\chi_f(Z)$ from Eq. (35) into Eq. (32) yields

$$Z\frac{d^2}{dZ^2}F_f(Z)+(1+2n_f-Z)\frac{d}{dZ}F_f(Z)$$
$$-(\tfrac{1}{2}+n_f-n_0)F_f(Z)=0. \quad (36)$$

This equation is the confluent hypergeometric equation known as Kummer's equation[25] having two linearly

independent solutions:

$$F_{1f}(Z)={}_1F_1(\tfrac{1}{2}-n_0+n_f;\ 1+2n_f;\ Z), \quad (37a)$$

$$F_{2f}(Z)=Z^{-2n_f}\,{}_1F_1(\tfrac{1}{2}-n_0-n_f;\ 1-2n_f;\ Z), \quad (37b)$$

where ${}_1F_1$ is the confluent hypergeometric function in Pochhammer's notation

$$_1F_1(a,b,z)=1+\frac{a}{b}Z+\frac{a(a+1)}{b(b+1)}\frac{Z^2}{2!}+\cdots. \quad (38)$$

These series are absolutely convergent for all values of a, b, and z, real or complex, excluding $b=0,-1,-2,\cdots$. Since we are interested in the case $E_f>0$, the quantity n_f is purely imaginary. Both of the two solutions are regular at $Z=0$, and the series for ${}_1F_1$ are everywhere absolute convergent.

Substituting Eqs. (37) back into Eq. (35), one sees that these two linearly independent solutions of Eq. (36) constitute two solutions of Eq. (30) which are complex conjugate to each other. In order to satisfy the boundary condition, $\chi_f(R)\to 0$ as $R\to 0(Z\to Z_0)$, the acceptable solution must be the complete solution of Eq. (30) which can be constructed by taking a linear combination of the two linearly independent solutions.

$$\chi_f(Z)=N_f e^{-Z/2}Z^{in'_f}U(\tfrac{1}{2}-n_0+in_f';\ 1+2in_f';\ Z), \quad (39)$$

$$U(\tfrac{1}{2}-n_0+in_f';\ 1+2in_f';\ Z)$$
$$=(i/2)\{Z_0^{-in_f'}e^{-i\delta_f}F_{1f}(Z)-Z_0^{in_f'}e^{i\delta_f}F_{2f}(Z)\}, \quad (40)$$

where δ_f is the argument of ${}_1F_1(\tfrac{1}{2}-n_0+in_f';\ 1+2in_f';\ Z_0)$, $F_{1f}(Z)$ and $F_{2f}(Z)$ are given by Eqs. (37). This solution is zero at $R=0(Z=Z_0)$, and has the asymptotic form of $\sin(K_f R+\delta_f)$. The eigenfunction, then, is normalized asymptotically according to

$$\int_0^\infty \chi_f(R\to\infty)$$
$$\times\int_{K_f-\Delta K_f}^{K_f+\Delta K_f}\chi_f(K_f',R\to\infty)dK_f'dR=1. \quad (41)$$

We thus obtain the normalized nuclear wave function in a continuum

$$\chi_f(R)=[i/(2\pi)^{1/2}]e^{-Z/2}$$
$$\times\{e^{-i(K_f R+\delta_f)}{}_1F_1(\tfrac{1}{2}-n_0+in_f';\ 1+2in_f';\ Z)$$
$$-e^{i(K_f R+\delta_f)}{}_1F_1(\tfrac{1}{2}-n_0-in_f';\ 1-2in_f';\ Z)\}. \quad (42)$$

In our explicit example, the nuclei, at the initial state, are moving in the lower portion of a strongly attractive potential field, provided by the ground ${}^1\Sigma_g^+$ state of H_2; the usual linear harmonic-oscillator wave functions would therefore give a rather accurate description of their motion.[26] At the final state, the nuclei are moving in the repulsive region of the potential field, provided by the ground ${}^2\Sigma_u^+$ state of H_2^-; their motion is no

[24] P. M. Morse, Phys. Rev. 34, 57 (1929); C. L. Pekeris, ibid. 45, 98 (1933).

[25] See for example, L. J. Slater, Confluent Hypergeometric Functions (Cambridge University Press, New York, 1960).

[26] L. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1935).

longer restricted by quantization. The nuclear wave function in a continuum given by Eq. (42) is therefore used.

Four sets of theoretical potential curves for the ground $^2\Sigma_u^+$ states of H_2^- have been reported in the literature.[27-30] The general shape of the potential curve calculated from superposition of configurations by Fischer-Hjalmars,[30] however, does not agree with the shape obtained by the rest of the calculations.[31] There are controversies as to which basic type of the potential curves is the correct one.[32] In this work we use all of the four theoretical curves, and by comparing the calculated cross sections with the experimental observations we are able to make some comments on the potential curves and the sensitivities of the general characteristics of the cross section–energy curve for the process of dissociative electron capture on the shape of the nuclear

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[27] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys. 4, 439 (1936).
[28] A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. (London) A69, 615 (1956).
[29] B. K. Gupta, Physica 35, 190 (1959); 26, 335 (1960).
[30] I. Fischer-Hjalmars, Arkiv Fysik 16, 33 (1959).
[31] By the use of a valence bond (VB) treatment with two variational parameters, Eyring et al. (reference 27) obtained for the lowest $^2\Sigma_u^+$ state of H_2^- a potential curve with a minimum at an internuclear distance of 1.8 Å, the minimum being 0.906 eV lower than the potential computed for infinite separation of the nuclear. The calculated energy at infinite separation was 1.621 eV higher than the observed value. The authors assumed that the same errors were made at all separations and the curve was lowered by 1.621 eV. Dalgarno and McDowell (reference 28) assumed that the orbital exponents in the wave function of the ground state of H_2^-, in a VB treatment, to be the values obtained for $R=\infty$ multiplied by a common scale factor. By varying this scale factor for each chosen R value, they obtained a potential curve for H_2^- with limiting energy of $H+H^-$ well below the energy of $H+H+e$, in agreement with the well-known stability of H^-. The general features of the potential curves obtained from these two investigations are in fair agreement. Later Gupta (references 29) and Fischer-Hjalmers (reference 30) independently made some more elaborate single configuration calculations for the ground $^2\Sigma_u^+$ state of H_2^-. They obtained almost identical potential curves as the one obtained by Dalgarno and McDowell. Fischer-Hjalmars has also made a calculation for the ground $^2\Sigma_u^+$ state by including the contributions due to configuration interaction of some singly excited states of the H^- atom (reference 30). The shape of the potential curve obtained from this treatment differs drastically from that obtained from the single configuration calculation but resembles that of the ground $^1\Sigma_g^+$ state of the hydrogen molecule between $R=0$ and $R=R_c$, where R_c is the crossing point of the potential curve in question with that of H_2 (see Fig. 2).
[32] It is seen from Fischer-Hjalmars' calculation, for the ground $^2\Sigma_u^+$ state of H_2^- that if one treats the problem of superposition of configurations by restricting the third electron of H_2^- in a very large orbit of H^- leaving the other two in a $1s$ orbital with $Z=1$, one would obtain a curve having a close resemblance to the potential curve for the ground $^1\Sigma_g^+$ state of H_2 between the internuclear separations $R=0$ and $R=R_c$, where R_c is the crossing point of the two curves (references 30 and 31). A speculative interpretation for this finding is that the lowest $^2\Sigma_u^+$ state for the three-electron–two-proton system is $H_2\ldots e$ (one of the three electrons is in the continuum) rather than a bound $^2\Sigma_u^+$ state of H_2^-. Thus the variational method requires their wave functions to be orthogonal. If the orthogonality condition is not satisfied, one cannot be sure that the energy so obtained by variational techniques would be that for the bound $^2\Sigma_u^+$ state of H_2^-, especially when configurations involving one electron in the continuum are introduced in the wave function subject to variation. Davidson's recent calculation seems to favor the above interpretation [E. R. Davidson, J. Chem. Phys. 36, 1080 (1962); see also I. Fischer-Hjalmars, ibid. 36, 1081 (1962)].

TABLE I. The parameters in the Morse function obtained by fitting this function to different calculated potential curves for the ground $^2\Sigma_u^+$ state of H_2^-.

	Origin	D_e	R_e	β
Case I[a]	Eyring et al.[e] Fischer-Hjalmars[f] Gupta[g]	0.0339	3.47	0.65347
Case II[b]	Fischer-Hjalmars[f] Dalgarno and McDowell[h]	0.0059	5.42	0.51094
Case III[c]	Gupta[g]	0.00595	5.80	0.50028
Case IV[d]	Fischer-Hjalmars[f]	0.0933	1.65	1.23143

[a] Simple configuration calculation with the same value for all the orbital exponents, this value being determined by variation for each internuclear distance.
[b] Single configuration calculation with different values for each of the three orbital exponents, these values being determined by variation for each internuclear distance.
[c] W. Mofitt's method of "atoms in molecules" [Proc. Roy. Soc. (London) A210, 224, 245 (1951)].
[d] Superposition of configurations composed of some singly excited states of H^- with fixed values for the orbital exponents, the values of the coefficients for different configurations being determined by variation for each internuclear distance.
[e] See reference 27.   [g] See reference 29.
[f] See reference 30.   [h] See reference 28.

potential field. These potential curves are corrected for the diagonal coupling terms and then fitted to the Morse function

$$V_f(R) = D_e e^{-2\beta(R-R_e)} - 2D_e e^{-\beta(R-R_e)}. \quad (43)$$

The corresponding sets of parameters D_e, R_e, β obtained from different calculated curves of the ground $^2\Sigma_u^+$ of H_2^- are tabulated in Table I. The nuclear wave functions in a continuum are, therefore, obtained for each set of parameters. Figures 2 and 3 show the nuclear eigenfunctions belonging to the continuous spectrum for the two different types of potential curves at $E_f = 5$, 10 (in electron volts).

V. CALCULATION OF THE CROSS SECTION

The cross section σ_{f0} for dissociative electron attachment by a diatomic molecule is given by Eq. (14), where the initial vibronic state of H_2+e is collectively denoted by "0" (the rotational motion of the nuclei is suppressed). For a given electronic state, there are however detailed cross sections for each possible vibrational state. To specify such vibrational states explicitly, the notation $\sigma_{f0}^{(v)}$ is introduced, where v is the initial vibrational state. After carrying out the integrations over the solid angles Ω_f and Ω_0, Eq. (14) becomes

$$\sigma_{f0}^{(v)} = \sum_{l,m} \omega_m (2l+1) \frac{(l-m)!}{(l+m)!} \left(\frac{s}{4\pi k_0}\right)$$

$$\times |\langle \chi_f | 2A_{f0}(l,m)\nabla_R + B_{f0}(l,m)|\chi_0\rangle|^2$$

$$\equiv \sum_{l,m} \sigma_{f0}^{(v)}(l,m), \quad \omega_m = 1 \quad \text{for} \quad m = 0;$$

$$\omega_m = 2 \quad \text{for} \quad m \neq 0, \quad (44)$$

where we have used the central-field approximation (Sec. III). Since A_{f0} and B_{f0} are slowly varying and

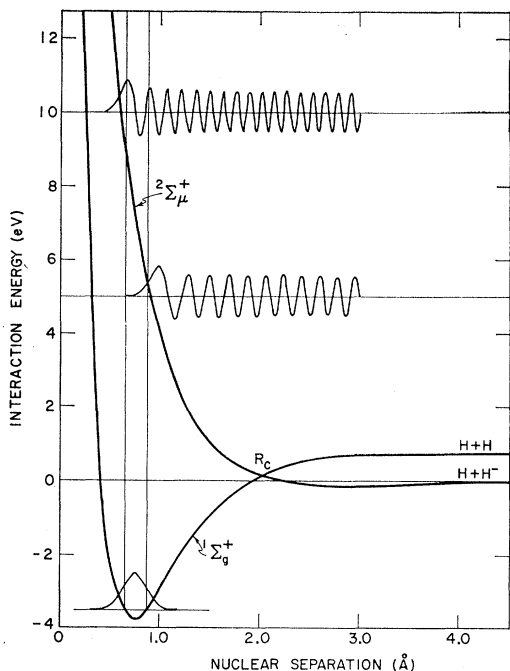FIG. 2. The heavy curves are the Morse curves for the ground $^2\Sigma_\mu^+$ and $^1\Sigma_g^+$ states of H_2^- and H_2, respectively. The Morse curve for H_2^- is obtained by fitting to the potential curves calculated from the best single configuration considerations (see footnote b of Table I). The light oscillating curves are the corresponding eigenfunctions.
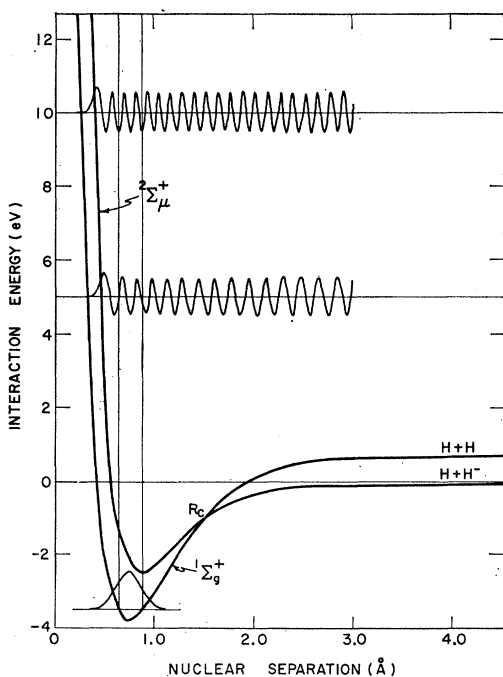

FIG. 3. The heavy curves are the Morse curves for the ground $^2\Sigma_\mu^+$ and $^1\Sigma_g^+$ states of H_2^- and H_2, respectively. The Morse curve for H_2^- is obtained by fitting to the potential curve calculated from superposition of configuration considerations (see footnote d of Table I). The light oscillating curves are the corresponding eigenfunctions.

most of the contribution to the integration comes from a narrow range of internuclear separation $R = R_e'$ (the equilibrium distance for H_2), they can be taken outside of the integral and Eq. (44) can be written as

$$\sigma_{f0}^{(v)} = \sum_{l,m} \omega_m (2l+1) \frac{(l-m)!}{(l+m)!} \left(\frac{s}{4\pi k_0} \right)$$

$$\times |2a_{lm}\langle \chi_f | \nabla_R | \chi_0 \rangle + b_{lm}\langle \chi_f | \chi_0 \rangle|^2, \quad (45)$$

where $a_{lm} = [A_{f0}(R,l,m)]_{R=R_e'}$, $b_{lm} = [B_{f0}(R,l,m)]_{R=R_e'}$, and the initial and final wave functions are the linear harmonic-oscillator wave functions and the continuum wave function [Eq. (42)], respectively.
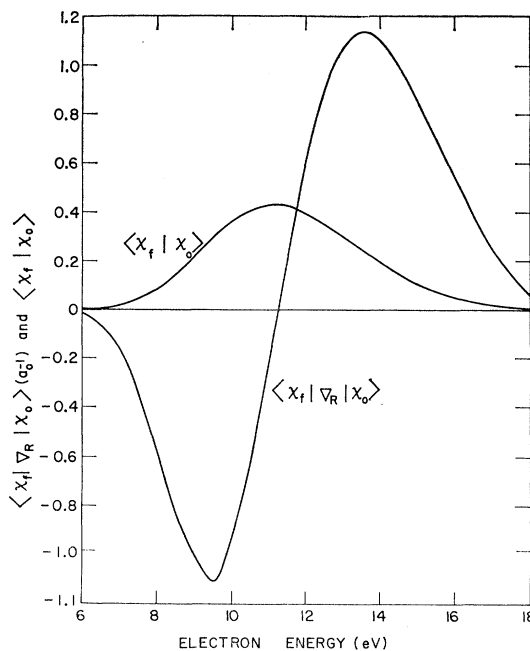

FIG. 4. The overlap $\langle \chi_f | \chi_0 \rangle$ and the gradient $\langle \chi_f | \nabla_R | \chi_0 \rangle$ matrix elements for the continuous and ground nuclear wave functions of H_2^- and H_2, respectively. The effective nuclear potential for the continuous wave function is approximated by a Morse curve of Case II of Table I.

The matrix elements $\langle \chi_f | \nabla_R | \chi_0 \rangle$ and $\langle \chi_f | \chi_0 \rangle$ are numerically evaluated on the IBM 7090 data processing system. It is found for Case II of Table I that $\langle \chi_f | \nabla_R | \chi_0 \rangle$ has a minimum and a maximum at impact electron energies of 9.6 and 13.5 eV, respectively, and that $\langle \chi_f | \chi_0 \rangle$ has, as expected, a maximum at 11.2 eV (Fig. 4). The total cross section $\sigma_{f0}^{(0)}$ for dissociative electron capture by a diatomic molecule is then calculated as a sum of the partial cross sections $\sigma_{f0}^{(0)}(l,m)$. The partial cross sections are calculated as a function of the energy of the incident electrons ranging from 5 to 16 eV. It is observed that strong maxima occur in $\sigma_{f0}^{(0)}(l,m)$ for small values of l and m at energies corresponding to the minimum and the maximum in $\langle \chi_f | \nabla_R | \chi_f \rangle$, and that these maxima decrease in magnitudes as l and m in-

crease. Figure 5 shows this behavior for $l=0$, 1, 2, 3; $m=0$ for $\sigma_{f0}^{(0)}(l,m)$ with the effective nuclear potential for H_2^- approximated by a Morse curve of Case II of Table I. The magnitude of $\sigma_{f0}^{(0)}$, therefore, is not affected by neglecting the contributions to the summation for values of l and m beyond those given. In Fig. 6, the total cross section as a function of the energy of the incident electrons are plotted for different Morse curves used as an approximation to the effective nuclear potential.

VI. COMPARISON OF THE CALCULATED RESULTS WITH EXPERIMENTS

The formation of negative H^- ion by electron impact was first reported by Lozier in connection with the study of ionization properties of the H_2 molecule.[33] He concluded, however, that these ions having maxima occurring at electron energies of 6.6 and 8.8 eV came, not from H_2 molecules, but from impurity molecules of H_2O.
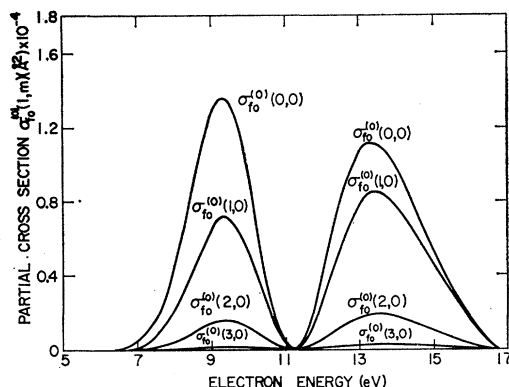
FIG. 5. Calculated partial cross section $\sigma_{f0}^{(0)}(l,m)$ for dissociative electron capture by H_2 molecules with the effective nuclear potential of H_2^- approximated by a Morse curve of Case II of Table I.

This conclusion was recently confirmed in a mass spectrometer experiment by Khvostenko and Dukel'skii.[34] These workers also observed H^- ions coming directly from H_2 molecules as a result of electron impact and determined the approximate cross section for this process. More recently, by a refined ultra-high vacuum technique, Schulz was able to determine accurately the cross section for production of H^- ions by electron impact with hydrogen molecules.[3] His cross section–energy curve is reproduced in Fig. 7. It is seen that the cross section exhibits a plateau around electron energy of 10 eV with a value of 1.2×10^{-4} $Å^2$ and a sharp peak at 14.2 ± 0.1 eV with a value of 3.5×10^{-4} $Å^2$. Schulz interpreted the first plateau to be associated with the reaction $H_2+e \rightarrow H+H^-$, where H and H^- are both in their ground states, and the sharp peak to be associ-

[33] W. W. Lozier, Phys. Rev. **36**, 1417 (1930).

[34] V. I. Khvostenko and V. M. Dukel'skii, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 851 (1957) [translation: Soviet Phys.—JETP **6**, 657 (1958)].
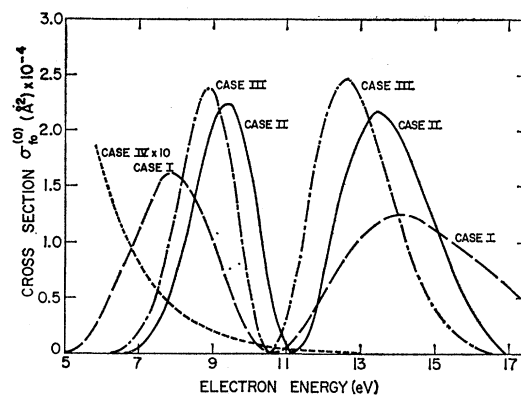
FIG. 6. Calculated total cross $\sigma_{f0}^{(0)}$ for dissociative electron capture by H_2 molecules. Here different cases refer to different approximate nuclear potentials being used (see Table I).

ated with the production of hydrogen atoms in the first excited state, $H_2+e \rightarrow H^*+H^-$.

By comparing the low-energy portion of the experimental curve with the calculated curves, we find that the theory gives the cross section in the correct order of magnitude, and also satisfactory energy dependence for the cross section. These agreements are obtained only for Morse curves of Cases II and III (Table I). Poor agreement for Case I is found, but for Case IV there is no such agreement. The curve obtained for Case IV is shown as a dotted curve in Fig. 6 together with the rest of the calculated curves, and the corresponding values for the cross section are given in Table II. It is seen that the general characteristics of the cross section–energy curve are sensitively dependent on the nuclear potential field in the Franck-Condon region of the parent molecule.

Perhaps the most interesting result from this theory is the prediction of the two resolved peaks in the Franck-
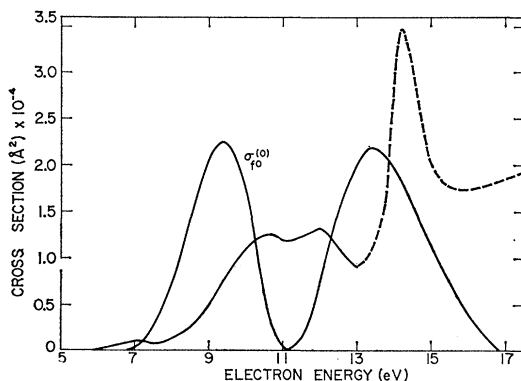
FIG. 7. A comparison of the experimental and theoretical cross section–energy curve for dissociative electron capture by H_2 molecules of the process $H_2+e \rightarrow H+H^-$ with H and H^- in their ground states. The dashed portion of the experimental curve is associated with the processes of $H_2+e \rightarrow H^*+H^-$ and $H_2+e \rightarrow H^++H^-+e$. The theoretical curve is obtained for the effective nuclear potential of H_2^- approximated by a Morse curve of Case II of Table I.

TABLE II. Calculated total cross section $\sigma_{f0}^{(0)}$ for dissociative electron capture by H_2 molecules. Here different cases refer to different approximate nuclear potentials being used (see Table I).

Electron energy, E_0 (eV)	Total cross section $\sigma_{f0}^{(0)}$ (Å^2).			
	Case I	Case II	Case III	Case IV
6.00	3.684×10^{-5}	1.002×10^{-7}	3.251×10^{-7}	1.672×10^{-5}
6.50	7.403×10^{-5}	1.051×10^{-7}	3.074×10^{-6}	
7.00	1.176×10^{-4}	6.497×10^{-6}	1.676×10^{-5}	8.305×10^{-6}
7.50	1.515×10^{-4}	2.597×10^{-5}	5.767×10^{-5}	
8.00	1.614×10^{-4}	7.181×10^{-5}	1.335×10^{-4}	4.098×10^{-6}
8.50	1.415×10^{-4}	1.424×10^{-4}	2.130×10^{-4}	
9.00	1.006×10^{-4}	2.080×10^{-4}	2.356×10^{-4}	2.044×10^{-6}
9.50	5.378×10^{-5}	2.220×10^{-4}	1.694×10^{-4}	
10.00	1.719×10^{-5}	1.656×10^{-4}	6.193×10^{-5}	1.039×10^{-6}
10.50	6.227×10^{-7}	6.592×10^{-5}	1.161×10^{-6}	
11.00	5.533×10^{-6}	8.163×10^{-6}	3.212×10^{-5}	5.420×10^{-7}
11.50	2.656×10^{-5}	1.006×10^{-5}	1.241×10^{-4}	
12.00	5.515×10^{-5}	7.090×10^{-5}	2.097×10^{-4}	2.867×10^{-7}
12.50	8.377×10^{-5}	1.496×10^{-4}	2.460×10^{-4}	
13.00	1.062×10^{-4}	1.981×10^{-4}	2.272×10^{-4}	1.553×10^{-7}
13.50	1.191×10^{-4}	2.175×10^{-4}	1.758×10^{-4}	
14.00	1.246×10^{-4}	1.976×10^{-4}	1.208×10^{-4}	8.603×10^{-8}
14.50	1.206×10^{-4}	1.556×10^{-4}	7.352×10^{-5}	
15.00	1.124×10^{-4}	1.119×10^{-4}	4.146×10^{-5}	4.850×10^{-8}
15.50	9.942×10^{-5}	7.322×10^{-5}	2.149×10^{-5}	

Condon energy range of the ground $^1\Sigma_g^+$ state of H_2 (Fig. 7). This feature is also suggested in the experimental curve by the slight dip in the plateau around electron energy of 10 eV. The magnitude and the location of these two calculated peaks depend more sensitively on the matrix element $\langle \chi_f | \nabla_R | \chi_0 \rangle$ than on $\langle \chi_f | \chi_0 \rangle$. It is possible that the usual mathematical expression for the Franck-Condon principle is no longer quantitatively correct for such transitions, though this principle is still operative. The latter conclusion is further supported by the observation that there is no calculated cross section of any significant magnitude found outside of the Franck-Condon energy region.

In the observed cross-section curve, a small plateau appears at 6.8 eV with a value of the order of $7 \times 10^{-6} \text{ Å}^2$. There is, however, no corresponding plateau obtained in the calculated curve. This is consistent with Schulz's interpretation that this plateau is due to some impurity contained in the system.

VII. CONCLUDING REMARKS

The agreement of the calculated cross section–energy curve with the observed curve for negative H^- ion formation in collisions of electrons with H_2 molecules suggests that the coupling terms between the electronic

and nuclear motion in the molecule are the transition operators responsible for such elementary processes of dissociative electron capture. The possible effects of these coupling terms should, therefore, be taken into consideration in calculation of dissociative phenomena in molecules. The approach described here is, in a sense, in agreement with Massey's proposal,[1] and with Stanton's argument of the impossibility of accounting for capture in terms of the electrostatic interaction between the electron and the neutral molecule.[2]

The fine structure predicted by this theory for the cross section–energy curve in the Franck-Condon energy region of the parent molecule is of interest for further investigation. By using Fischer-Hjalmars' refined potential curve for the ground $^2\Sigma_\mu^+$ state of H_2^-, one fails to get a cross section of any significance to account for the observed negative H^- ion formation. In view of this incapability to account for the observed cross section, it is tempting to believe that this potential curve, between $R=0$ to $R=R_c$ (Fig. 3), is in error (for comments, see footnote 32).

In this calculation we have assumed that errors due to the inconsistency of the final electronic wave function (i.e., the wave function of H_2^-) with the different potential curves being used are negligible. Thus, there are uncertainties in our comparison among the potential curves. The errors due to this inconsistency, however, are believed to be small in view of the fact that the gross feature of the cross section–energy curve is more sensitively dependent on the potential curves being used than on the coupling terms being calculated by the final electronic wave functions. This also follows from the conclusion that the Franck-Condon principle is still operative for such dissociative processes, though in a different fashion.

It is possible that a refined calculation for the coupling matrix elements (Sec. III) would change the values of the cross section. It is unlikely, however, that it would change the order of magnitude and the conclusions. The questions of the effects of the rotational motion of the molecule and of statistical population of the initial state on the agreement between the calculated and observed results are left completely open.