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The Dissociation of H_2^+ by Electron Impact*

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The collision (in Born approximation) of electrons with H_2^+, in which the molecule is raised from the ground state to the lowest lying repulsive state and is therewith dissociated, is discussed as the simplest example of a collision resulting in molecular dissociation. Both the angular distribution of dissociated protons and the excitation of the molecule to a state of definite angular momentum are investigated, and the connection between them is made clear. For the former, rules giving the dominant characteristics of the angular distribution are stated and illustrated by an example; for the latter, a detailed example is given which brings out the scope of the Franck-Condon principle and shows that near the energy of dissociation that gives the Franck-Condon maximum of the scattering amplitude there are also other sizable maxima, i.e., the Franck-Condon principle has a sort of fine structure.

INTRODUCTION

AS the cross section for excitation by electron impact of a vibrational state of a diatomic molecule in a fixed electronic state is very small,[1] it is clear that dissociation of the molecule by an impinging charge must occur predominantly through an alteration of the electronic state from one which gives nuclear binding to one which gives nuclear repulsion. Roscoe[2] and Massey and Mohr[3] have examined the excitation of H_2 to various electronic states; the latter consider the dissociation of the molecule, but without regard to the angular distribution of dissociated atoms or to the details of nuclear motions that reveal details of the Franck-Condon principle. In this report we study, as the simplest example of molecular dissociation, an electron collision with H_2^+ that raises the molecule from the ground $1s\sigma\,{}^2\Sigma_g^+$ state to the $2p\sigma\,{}^2\Sigma_u^+$ repulsive state; we shall show in what sense the Franck-Condon principle has a structure and shall bring out the character of the angular distribution of dissociated atoms. Though several simplifying approximations will be made, the quantitative nature of the results will not be seriously forsaken. We shall treat the collision in Born approximation (neglecting electron exchange effects[4]), the molecular motions in the usual Born-Oppenheimer approximation with the simplest type of molecular-electronic wave functions, the repulsive motion of the protons in the final continuum state by means of essentially a Coulomb field, the initial vibrational motion by means of Fues's diatomic molecule model, and shall introduce some approximations of a mathematical sort.

REDUCTION OF THE SCATTERING AMPLITUDE

In Fig. 1 we label the coordinates of the protons $(\frac{1}{2}\boldsymbol{\rho}, -\frac{1}{2}\boldsymbol{\rho})$, incident electron $(\mathbf{R})$, and molecular electron $(\mathbf{r})$, reckoned from the center of mass which we place at the midpoint of the protons. The Born amplitude for scattering of the incident electron with excitation of the target from the state $\varphi_0(\mathbf{r}, \boldsymbol{\rho})$ to the state $\varphi_k(\mathbf{r}, \boldsymbol{\rho})$ is

$$f_k=-\frac{1}{4\pi}\frac{2m}{\hbar^2}\int e^{i\mathbf{K}\cdot\mathbf{R}}\varphi_k^*v\varphi_0 d\mathbf{r}d\boldsymbol{\rho}d\mathbf{R}, \tag{1}$$

$\mathbf{K}$ being the electron momentum change $\mathbf{k}_0-\mathbf{k}_k$, with $k_i^2=(2m/\hbar^2)(E-E_i)$, $E=\frac{1}{2}m\dot{R}^2+E_0$, and E_i the energy of the ith target eigenstate; v is the interaction energy

$$v=-\frac{e^2}{|\mathbf{R}-\frac{1}{2}\boldsymbol{\rho}|}-\frac{e^2}{|\mathbf{R}+\frac{1}{2}\boldsymbol{\rho}|}+\frac{e^2}{|\mathbf{R}-\mathbf{r}|}.$$

For the target eigenfunctions we write $\varphi_0=\psi_0(\rho, \mathbf{r})\chi_0(\boldsymbol{\rho})$ and $\varphi_k=\psi_k(\rho, \mathbf{r})\chi_k(\boldsymbol{\rho})$, the ψ representing electronic wave functions and depending parametrically on the nuclear separation ρ, the χ representing wave functions for the nuclear motion. Using the well-known simple linear combination of atomic orbitals for the ψ, we write (in atomic units):

$$\begin{aligned}\psi_0&=U_0[u(r_1)+u(r_2)],\\ \psi_k&=U_k[u(r_1)-u(r_2)], \\ U_k{}^0&=2^{-\frac{1}{2}}[1\pm e^{-\rho}(1+\rho+\tfrac{1}{3}\rho^2)]^{-\frac{1}{2}},\end{aligned} \tag{2}$$

with $u(r)=\pi^{-\frac{1}{2}}e^{-r}$; r_1 and r_2 are radial distances, measured from the protons as centers, of the molecular electron. Because of the orthogonality of φ_k and φ_0 in

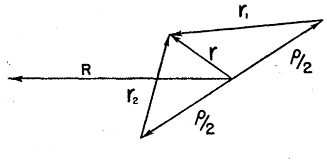

FIG. 1. Labels of the coordinates for an electron $(\mathbf{R})$ impinging on H_2^+ (molecular electron, $\mathbf{r}$; protons, $\frac{1}{2}\boldsymbol{\rho}$ and $-\frac{1}{2}\boldsymbol{\rho}$).

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[1] E. H. Kerner, Phys. Rev. **91**, 1174 (1953).

[2] R. Roscoe, Phil. Mag. **31**, 349 (1941).

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

[4] This neglect is justifiable so long as the incident electron energy is not too low, which it mustn't be anyway for the validity of the Born results. See N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), Chaps. 8 and 11.

the coordinate $\mathbf{r}$, the terms $e^2/|\mathbf{R}\pm\frac{1}{2}\boldsymbol{\varrho}|$ in v drop out. The integration over $d\mathbf{R}$ gives $(4\pi/K^2)\exp(i\mathbf{K}\cdot\mathbf{r})$, so that (using atomic units throughout now)

$$f_k=-\frac{2}{K^2}\int e^{i\mathbf{K}\cdot\mathbf{r}}[u^2(r_1)-u^2(r_2)]d\mathbf{r}U(\rho)\chi_k{}^*\chi_0 d\boldsymbol{\varrho}, \quad (3)$$

$$U(\rho)\equiv U_0(\rho)U_k(\rho).$$

Introducing, by Fig. 1, $\mathbf{r}=\mathbf{r}_1+\frac{1}{2}\boldsymbol{\varrho}=\mathbf{r}_2-\frac{1}{2}\boldsymbol{\varrho}$ for the integrals in $d\mathbf{r}$ involving $u^2(r_1)$ and $u^2(r_2)$, respectively, gives, on carrying out the $\mathbf{r}$ integration,

$$f_k=\frac{-64i}{K^2(4+K^2)^2}\int \sin\tfrac{1}{2}(\mathbf{K}\cdot\boldsymbol{\varrho})U(\rho)\chi_k{}^*\chi_0 d\boldsymbol{\varrho}$$

$$=\frac{-64i}{K^2(4+K^2)^2}J(k, K). \quad (4)$$

J will be referred to as the radial integral.

We observe before going ahead that the use of the simple ψ's of Eq. (2) is probably better than might be expected at first sight. For, if better electronic wave functions of the form[5]

$$\psi_0\sim e^{-ar_1}+e^{-ar_2}, \quad \psi_k\sim e^{-br_1}-e^{-br_2},$$

(where a and b are functions of ρ) had been used one would have, instead of $u^2(r_1)-u^2(r_2)$ in Eq. (3), the $\mathbf{r}$ integral

$$\int e^{i\mathbf{K}\cdot\mathbf{r}}\{e^{-(a+b)r_1}-e^{-(a+b)r_2}+[e^{-ar_2-br_1}-e^{-ar_1-br_2}]\}d\mathbf{r}.$$

The contribution to this from the terms in square brackets will be small, at least for the range of small K that is of most importance, while $a(\rho)+b(\rho)$ stays very nearly constant at two (see Fig. 32 of reference 5) down to ρ that are of any consequence in the remaining $\boldsymbol{\varrho}$ integral; the latter contains, for example, the ground state vibrational wave function which is strongly peaked at the relatively large equilibrium nuclear separation distance, and what happens at smaller ρ, where $a+b$ rises, will have negligible effects.

PROPERTIES OF THE RADIAL INTEGRAL

$J(k, K)$ contains now the desired information on the angular distribution of dissociated protons (one of which goes off bearing an electron) and of scattered electrons, and on the range of continuum states χ_k that can be significantly excited.

The χ_0 and χ_k are eigenstates of the Hamiltonians for the nuclear motions in initial and final states:

$$\left(-\frac{1}{2\mu}\nabla_\rho{}^2+V_{0,k}\right)\chi_{0,k}=E_{0,k}\chi_{0,k}, \quad (5)$$

where $V_{0,k}(\rho)$ are the effective nuclear potential energies in these states and μ is the reduced molecular mass. The radial parts of $\chi_{0,k}$, which describe the vibrational motions, satisfy

$$R_{0,k}''+\frac{2}{\rho}R_{0,k}'+\left(2\mu E_{0,k}-2\mu V_{0,k}-\frac{l(l+1)}{\rho^2}\right)R_{0,k}=0, \quad (6)$$

and the angular parts are spherical harmonics. For χ_0 let us take a definite rotation-vibration state,

$$\chi_0=P_{lm}(\cos\theta)e^{im\varphi}R_0(\rho), \quad (7)$$

the polar axis being taken along $\mathbf{K}$ for convenience. In order to answer the question, what is the amplitude for scattering of the incident electron into some small solid angle when the protons dissociate along a specified axis within a small solid angle and with a specified energy in a small energy range, we must normalize χ_k suitably. If the wave function Ψ for the whole problem be written in the usual way as

$$\Psi=e^{ik_\rho\cdot\mathbf{R}}\varphi_0(r, \rho)+\psi_{\text{scatt}},$$

the normalization of χ_k must be chosen so as to provide that ψ_{scatt} in the limit of *large rho* shall give an outward radial flux. The normalization is similar to that for the problem of the ionization of a hydrogen atom by electron impact,[6] and is such that $\chi_k{}^*$ (and not χ_k) has the asymptotic form

$$\chi_k{}^*\rightarrow e^{-ik\rho\cos\theta'}+\frac{e^{ik\rho}}{\rho}g(\theta') \quad (8)$$

$$\cos\theta'=\cos\theta\cos\theta_0+\sin\theta\sin\theta_0\cos(\varphi-\varphi_0),$$

θ_0, φ_0 being the orientation of the axis of dissociation with respect to the polar axis $\mathbf{K}$, and k^2 being $2\mu E_k$; we may place $\varphi_0=0$ by choosing the plane of $\mathbf{k}(\theta_0, \varphi_0)$ and $\mathbf{K}$ to be the xz plane.

The correctly normalized χ_k for fixed k may be built up from the radial functions $R_l(k\rho)$ of Eq. (6) as

$$\chi_k=\textstyle\sum_s A_sR_s(k\rho)P_s(\cos\theta').$$

Then, using the addition theorem for Legendre functions and writing $x=\cos\theta$, $J(k, K)$ is of the form

$$J(k, K)=\sum_s\sum_{m'=-s}^{+s}\int \sin(\tfrac{1}{2}K\rho x)P_{lm}(x)e^{im\varphi}P_{sm'}(x)$$

$$\times P_{sm'}(x_0)e^{-im'\varphi}dxd\varphi A_s{}^*R_s{}^*UR_0\rho^2d\rho, \quad (9)$$

whence only $m'=m$ in the $\sum_{m'}$ contributes. Since $\sin(\frac{1}{2}K\rho x)$ is odd in x and $P_{jm}(-x)=(-1)^{j-m}P_{jm}(x)$, we have that only those terms in $\sum_s$ contribute for which $l+s$ is odd. Hence, the scattering amplitude for scattered electrons and dissociated protons is given by a superposition of $P_{sm}(\cos\theta_0)$ that is either even or odd

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[5] N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Clarendon Press, Oxford, 1948), Sec. 33.

[6] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A140**, 613 (1933). See also reference 4, Chaps. 11 and 14.

under $\theta_0 \rightarrow \pi - \theta_0$ according as l is odd or even. This states formally what is expected from the symmetry properties of the original amplitude f_k of Eq. (1) and the symmetry of Ψ in the proton coordinates. Note that for m different from zero and for any l no dissociation occurs in the direction $\theta_0 = 0$, and that for $m=0$ and even l (only odd s terms in $J(k, K)$) no dissociation occurs in the direction $\theta_0 = \pi/2$: thus, for excitation from the ground state there is no dissociation at right angles to $\mathbf{K}$. Also for m different from zero there will be no dissociation in the direction $\theta_0 = \pi/2$ when m is odd and l is odd (only even s terms) and when m is even and l even (only odd s terms).

The angular distribution of dissociated protons will be dominated by the terms $P_{l\pm 1, m}(\cos\theta_0)$ in $J(k, K)$, so that, for example, if the molecule is initially in the rotational ground state the dissociated protons will have mainly a $\cos^2\theta_0$ distribution; or if the initial state is an $l=1$ state a spherically symmetric component to the distribution will be important. It is therefore relevant to ask directly for the amplitude for excitation to a state of definite l and E_k (within dE_k), understanding from the preceding discussion that we thereby find a contribution, more or less important depending on what l we select, to the angular distribution of dissociated protons. Also this amplitude will be of interest in itself, apart from questions of angular distribution in the dissociation. In what follows, the main discussion will be around this amplitude but we shall also consider the angular distribution in a little further detail.

EVALUATION OF THE RADIAL INTEGRAL

In Fig. 2 we exhibit the correct[7] potential curves A and B for the nuclear motions in initial and final states, and simple approximations thereto, F and C respectively, that are sufficient to our purposes. F is the Fues potential

$$V_0(\rho) = -D + (2\pi\nu_0)^2\mu\rho_0^2\left(\frac{1}{2} - \frac{\rho_0}{\rho} + \frac{1}{2}\frac{\rho_0^2}{\rho^2}\right),$$

where D, ν_0, ρ_0 are potential curve depth, frequency of small oscillations about equilibrium, and equilibrium nuclear separation. C is a Coulomb potential plus an additive constant chosen to make the potential agree with A near ρ_0,

$$V_k = -\epsilon_0 + \frac{1}{\rho}, \quad \epsilon_0 = 0.65.$$

We should really cut C off at $\rho_1 = (\epsilon_0 - \frac{1}{2})^{-1} = 6.67$ and continue it as C', but little harm will be done by leaving it alone, as ρ_1 is far from the interesting region immediately around ρ_0; we merely restrict the eigenvalue E_k of Eq. (6) to $E_k > -\frac{1}{2}$. V_k of course does not have the detailed structure[7] of A but nevertheless is an adequate representation of it.

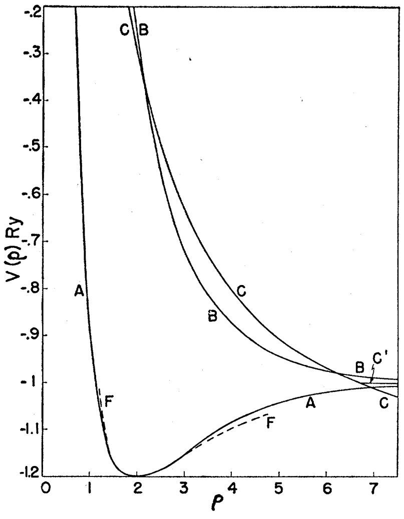

FIG. 2. Potential curves for initial and final nuclear motions. A and B are the correct curves (after Teller, reference 7), F and C, respectively, are the approximate curves that are used, F being the Fues potential, C begin the Coulomb potential $-1.3+2/\rho$ Rydberg. It suffices to use C everywhere, though, strictly, it should be cut off and continued as C'. The nuclear separation ρ is in atomic units.

The vibrational ground-state wave function $R_0(\rho)$ is

$$R_0 = N_0\rho^\lambda e^{-\alpha\rho}, \quad N_0 = \frac{(2\alpha)^{\lambda+\frac{3}{2}}}{(2\lambda+2)!^{\frac{1}{2}}}, \tag{10}$$

with $\lambda = -\frac{1}{2} + \frac{1}{2}(1+4b)^{\frac{1}{2}}$, $\alpha = (\lambda+1)^{-1}(\rho_0/2b)^{-1}$, and $b = 4\pi^2\nu_0^2\mu^2\rho_0^4/\hbar^2$. The continuum functions $R_k(\rho)$ are

$$R_{k,l} = N_k\rho^l e^{-ik\rho}F(l+1-i\beta, 2l+2, 2ik\rho) = N_kF_l(k\rho), \tag{11}$$

where $\beta = \mu/k$, $k^2 = 2\mu(E_k+\epsilon_0)$, and N_k is a suitable normalization constant; for later use we introduce also $\kappa^2 = 2(E_k+\epsilon_0)$.

The function $U(\rho) = U_0(\rho)U_k(\rho)$ that enters into $J(k, K)$ is a smooth function varying slowly and monotonically near ρ_0 and diverging for small ρ as ρ^{-1}. It can be replaced for purposes of manageability of the ρ integration by a function of the form $a + b\rho^{-1}\exp(-c\rho)$ with very good accuracy; but this is unnecessary because with respect to U, $R_0(\rho)$ is practically a delta function around ρ_0. It would be sufficient to take U outside the integral as $U(\rho_0)$, but at no extra cost we improve on this by representing $U(\rho)$ as c_0/ρ with c_0 adjusted so that $U(\rho_0) = c_0/\rho_0$; this gives $c_0 = 1.234$.

The radial integral for the transition $(0, l, m) \rightarrow (k, t, m')$, say, is now, apart from constant factors,

$$J(k, K) \sim \int \sin(\tfrac{1}{2}K\rho x)P_{lm}(x)P_{tm'}(x)e^{i(m-m')\varphi} \times dx\,d\varphi\,F_t(k\rho)\rho^\lambda e^{-\alpha\rho}\rho\,d\rho, \tag{12}$$

so that $m=m'$ and l and t must be of different parity. We shall discuss a special case of this, illustrative of more general cases, in order to avoid complicating the

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[7] E. Teller, Z. Physik **61**, 458 (1930).

analysis needlessly. To this end we set $l=m=0$. Expanding $\sin(\frac{1}{2}K\rho x)$ in Legendre functions then gives

$$J_t(k, K)=c_0N_0N_k(2t+1)^{\frac{1}{2}} \times\int_0^\infty j_t(\tfrac{1}{2}K\rho)\rho^{\lambda+1}e^{-\alpha\rho}F_t(k\rho)d\rho, \quad (13)$$

where j_t represents the spherical Bessel function and t is an odd integer. For the small-angle scattering of the incident electron $j_t(\frac{1}{2}K\rho)$ may be replaced by $(\pi^{\frac{1}{2}}/(t+\frac{1}{2})!\cdot 2^{2t+1})(K\rho)^t$, and it is at once clear that $t=1$ is by far the most important of all t (J has to be multiplied by K^{-2} to give the amplitude f_k); in terms of our earlier discussion, $\cos^2\theta_0$ dominates the angular distribution of dissociated protons. Reversing the roles of l and t above we obtain the scattering amplitude for the transition from different initial l states to the continuum $t=0$ state; for $l=1$ in particular we are then evaluating the important spherically symmetric contribution to the proton angular distribution for scattering of electrons off the molecule initially in the first rotational state. Detailed results will later be given for this special case as an illustrative example.

For sufficiently small K, which in practice will often cover the whole range of K of primary interest, Eq. (13) involves the integral

$$S(n, t)=\int_0^\infty \rho^n e^{-\alpha\rho}e^{-ik\rho}F(t+1-i\beta, 2t+2, 2ik\rho)d\rho, \quad (14)$$

with $n=\lambda+t+1$ for short. We evaluate S by making use of the representation of the confluent-hypergeometric and hypergeometric functions as contour integrals:[8]

$$F(a, c, x)=\frac{N\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \times\int \exp\left(\frac{xz}{1+z}\right)z^{a-1}(1+z)^{-c}dz, \quad (15)$$

$$F(a, b, c, x)=\frac{N\Gamma(c)}{\Gamma(a)\Gamma(c-a)} \times\int [1+(1-x)z]^{-b}z^{a-1}(1+z)^{b-c}dz. \quad (16)$$

When the real part of $\alpha>0$, $N=1$ and the contour is a straight line from 0 to ∞. For larger K the whole spherical Bessel function must be used, and in any particular case may be written as a combination of trigonometric functions and inverse powers of $\frac{1}{2}K\rho$. Then Eq. (13) involves integrals of the form

$$T\left(n, t, \begin{matrix} c \\ s \end{matrix}\right)=\begin{matrix}\mathrm{Re} \\ \mathrm{Im}\end{matrix}\int_0^\infty \rho^n e^{-\alpha\rho}e^{-ik\rho}e^{\frac{1}{2}iK\rho} \times F(t+1-i\beta, 2t+2, 2ik\rho)d\rho. \quad (17)$$

The Re, Im refer to the real, imaginary parts with respect to iK as first written, but because $F_t(k\rho)$ is itself real, the real and imaginary parts of the whole final result may be taken as well.

Introducing Eq. (15) into Eq. (14) gives

$$S(n, t)=\frac{\Gamma(2t+2)}{\Gamma(t+1-i\beta)\Gamma(t+1+i\beta)}\int\int\rho^n \times\exp\left\{-\rho\left[\alpha+ik-\frac{2ikz}{1+z}\right]\right\}\frac{z^{t-i\beta}}{(1+z)^{2t+2}}dzd\rho$$

$$=\frac{\Gamma(2t+2)}{|\Gamma(t+1+i\beta)|^2}n!(\alpha+ik)^{-n-1} \times\int\frac{z^{t-i\beta}}{(1+z)^{2t+1-n}}(1+zv)^{-n-1}dz, \quad (18)$$

with

$$v=(\alpha-ik)/(\alpha+ik).$$

Using Eq. (16),

$$S(n, t)=n!(\alpha+ik)^{-n-1} \times F(1+t-i\beta, n+1, 2t+2, 1-v). \quad (19)$$

Similarly

$$T\left(n, t, \begin{matrix} c \\ s \end{matrix}\right)=\begin{matrix}\mathrm{Re} \\ \mathrm{Im}\end{matrix}\, n!(\alpha+ik-\tfrac{1}{2}iK)^{-n-1} F(1+t-i\beta, n+1, 2t+2, 1-u), \quad (20)$$

$$u=(\alpha-ik-\tfrac{1}{2}iK)/(\alpha+ik-\tfrac{1}{2}iK).$$

By a change of variable in Eq. (18) or by

$$F(a, b, c, x)=(1-x)^{-a}F(a, c-b, c, x/(x-1)),$$

Eq. (19) may be written

$$S(n, t)=n!(\alpha+ik)^{-n+t-i\beta}(\alpha-ik)^{-1-t+i\beta} \times F(1+t-i\beta, 2t+1-n, 2t+2, -2ik/(\alpha-ik)), \quad (21)$$

and similarly for T. Now n is in general a large number since λ is large; numerically λ is 38.10 (and α is almost exactly $\frac{1}{2}\lambda$). If we round off λ to an integral value no serious error is committed and then (except for very large t) the F function in Eq. (21) is a polynomial.

Thus S and T are expressed in closed form. However, the results are complicated and we return to Eq. (18) for a more useful approximate result. We write for

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[8] W. Gordon, Ann. Physik 2, 1031 (1929).

Eq. (18)

$$S(n,t)=\frac{\Gamma(2t+2)}{|\Gamma(t+1+i\beta)|^2}n!(\alpha+ik)^{-n-1}\int Q(z)$$

$$\times\exp\left\{i(n+1)\left[\Omega-\frac{\beta}{n+1}\log z\right]\right\}dz,\quad(22)$$

with

$$Q(z)=\frac{z^t[\mathrm{Re}(1+zv)]^{-n-1}}{(1+z)^{2t+1-n}}$$

$$=\frac{z^t}{(1+z)^{2t+1-n}}(1+z^2v_0^2+2zv_0\cos\omega)^{-(n+1)/2},$$

$$\Omega(z)=-\arg(1+zv)=\tan^{-1}\frac{zv_0\sin\omega}{1+zv_0\cos\omega},$$

where v_0 is $|v|$ and

$$\omega=-\arg v=2\tan^{-1}(k/\alpha).$$

For T one has a similar result involving u instead of v. Integrating along the real axis from 0 to ∞ we are in a position to capitalize on the largeness of n by using the method of stationary phase. What we then obtain is the asymptotic form of S (or T) in the limit of both $n(\lambda)$ and $\beta=\mu/k=\mu^{\frac{1}{2}}/\kappa$ large. This seems to place an undesirable restriction on the range of κ which we may wish to examine, but it turns out that for the κ of most interest ($\kappa\sim1$), in the Franck-Condon region, β is indeed comparable with λ and it is just here that the method of stationary phase is valuable. For small κ it is advisable to proceed differently anyway (as discussed below), and for large κ one can use the asymptotic form of $R_{k,l}$ of Eq. (11) directly in the integral for $J(k,K)$ [but already in this range of κ, $J(k,K)$ is very small].

The phase

$$\varphi(z)=\Omega-\frac{\beta}{n+1}\log z$$

is stationary for the roots z_1 and z_2 of

$$\varphi'(z)=0=\frac{v_0\sin\omega}{1+z^2v_0^2+2zv_0\cos\omega}-\frac{\beta/(n+1)}{z}.$$

Both these roots are real positive if κ is not too small. We have also $\varphi''(z_1\text{ or }z_2)=[\beta/(n+1)]/z_1^2$ or z_2^2. For Eq. (22) we get

$$S(n,t)\simeq\frac{\Gamma(2t+2)}{|\Gamma(t+1+i\beta)|^2}n!\,\mathrm{Re}(\alpha+ik)^{-n-1}$$

$$\times\left\{\left(\frac{2\pi}{\beta}\right)^{\frac{1}{2}}z_1Q(z_1)\exp[i(n+1)\varphi(z_1)+\tfrac{1}{4}\pi i]\right.$$

$$\left.+\text{same function of }z_2\right\}.\quad(23)$$

T is to be treated the same way.

When κ is sufficiently small, the region around $\rho=\rho_0$ is a region of negative kinetic energy for the proton motions and there the Coulomb functions $R_{k,l}$ [Eq. (11)] do not oscillate but vary monotonically. We have in fact that in the limit of small κ, $R_{k,l}$ and therefore $J(k,K)$ [Eq. (12)] are small. As κ increases a point will come when $R_{k,l}$ has a first large maximum near ρ_0 and joins forces with R_0 to make $J(k,K)$ large. As κ increases further $R_{k,l}$ oscillates within the range where R_0 is large and generally $J(k,K)$ becomes small again, though not uniformly with increasing κ since $R_{k,l}$ will reinforce with R_0 when the higher extrema of $R_{k,l}$ are centered near ρ_0. Thus one expects $J(k,K)$ to rise monotonically as κ first increases, pass through a relatively large principal maximum, and then oscillate with more or less rapidly decreasing amplitude. These remarks (which are of course conditioned by the K dependence of $J(k,K)$) restate the Franck-Condon principle and endow it with a "structure" which we exhibit in the example below.

We note first that for sufficiently small κ, when $R_{k,l}$ varies monotonically in ρ near ρ_0, we can without serious error pull it (or ρ times it) outside the radial integral 13:

$$J(k,K)\simeq c_0N_0N_k(2t+1)^{\frac{1}{2}}[\rho_0F_t(k\rho_0)]$$

$$\times\int_0^\infty\frac{1}{\rho}j_t(\tfrac{1}{2}K\rho)\rho^{\lambda+1}e^{-\alpha\rho}d\rho.\quad(24)$$

Further, we can use a WKB approximation for $w_t(\rho_0)=\rho_0F_t(k\rho_0)$:[9]

$$w_t(\rho_0)=(2\cos\eta)^{-\frac{1}{2}}\sin^{t+1}\left(\frac{\eta+\eta_0}{2}\right)\cos^{-t}\left(\frac{\eta-\eta_0}{2}\right)$$

$$\times\exp\left\{-\beta\left(\frac{\pi}{2}-\eta\right)+(t+\tfrac{1}{2})\frac{\cos\eta}{\cos\eta_0}\right\},$$

$$\sin\eta=(k\rho_0-\beta)[\beta^2+(t+\tfrac{1}{2})^2]^{-\frac{1}{2}},\quad(25)$$

$$-\tfrac{1}{2}\pi<\eta<\tfrac{1}{2}\pi,$$

$$\sin\eta_0=\beta[\beta^2+(t+\tfrac{1}{2})^2]^{-\frac{1}{2}},$$

$$0<\eta_0<\tfrac{1}{2}\pi.$$

ILLUSTRATIVE EXAMPLE

As indicated before, we illustrate our general results by the example: initial state, $l=1$; final state, $l=0$. This amplitude for transition to a final state of definite angular momentum gives also the large spherically symmetric component of the angular distribution of dissociated protons resulting from the dissociation of the molecule in the assumed initial rotational state.

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[9] Yost, Wheeler, and Breit, Phys. Rev. **49**, 174 (1936).

For small K we have,[10] from the discussion above,

$$J(k,K)=c_0N_0N_k(3^{\frac{1}{2}}K/6)S(\lambda,0), \tag{26}$$

and for larger K,

$$J(k,K)=c_0N_0N_k3^{\frac{1}{2}}\left\{\frac{T(\lambda-1,0,s)}{\frac{1}{4}K^2}-\frac{T(\lambda,0,c)}{\frac{1}{2}K}\right\}. \tag{27}$$

For sufficiently small κ and also small K,

$$J(k,K)=c_0N_0N_k(3^{\frac{1}{2}}K/6)w_0(\rho_0)(\lambda+1)!/\alpha^{\lambda+2}, \tag{28}$$

while for small κ and larger K,

$$\begin{aligned}J(k,K)&=c_0N_0N_k3^{\frac{1}{2}}w_0(\rho_0)\\&\times\left\{\frac{(\lambda-2)!}{\frac{1}{4}K^2(\alpha^2+\frac{1}{4}K^2)^{(\lambda-1)/2}}\sin\left(\tan^{-1}\frac{K}{2\alpha}\right)\right.\\&\left.-\frac{(\lambda-1)!}{\frac{1}{2}K(\alpha^2+\frac{1}{4}K^2)^{\lambda/2}}\cos\left(\tan^{-1}\frac{K}{2\alpha}\right)\right\}.\end{aligned} \tag{29}$$

We normalize the continuum function on the $W=\frac{1}{2}k^2$ scale, for which

$$N_k=\left(\frac{2k\beta}{\sinh\beta}\right)^{\frac{1}{2}}e^{-\frac{1}{2}\pi\beta}$$

in Eq. (26) and Eq. (27) but $N_k=(2/\pi k)^{\frac{1}{2}}$ in Eqs. (28) and (29).

The differential cross section per unit solid angle of the scattered electron and per unit interval of W of the dissociated protons is

$$\frac{d\sigma}{d\omega dW}=\frac{k_k}{k_0}|f_k|^2=\frac{k_k}{k_0}\frac{64^2}{K^4(4+K^2)^4}J^2(k,K),$$

and, integrating over all angles of scattering, the total cross section per dW is

$$\frac{d\sigma}{dW}=\frac{2\pi}{k_0^2}\int_{k_0-k_k}^{k_0+k_k}KdK\frac{64^2}{K^4(4+K^2)^4}J^2(k,K).$$

The units of σ are atomic units, a_0^2.

In Fig. 3 we show $j(\kappa)=J(k,K)/(3^{\frac{1}{2}}K/6)$ in the small K limit, when this quantity is independent of K, as a function of κ (here the continuum function is normalized on the κ scale). The principal extremum is for κ very close to 1. The neighboring extrema are by no means negligible: the Franck-Condon principle clearly has a structure to it, as previously remarked. Considering the small range of κ in which $J(k,K)$ is large, this structure is to be considered a fine structure.

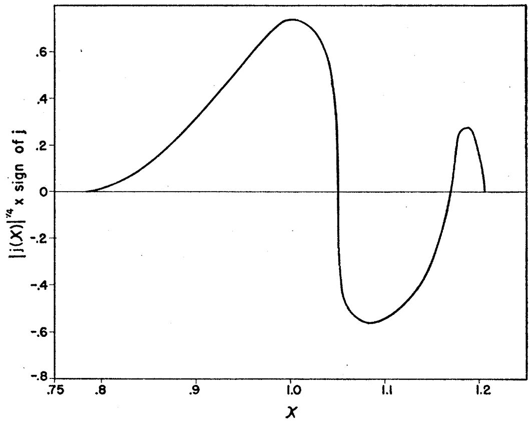

FIG. 3. Illustration of the fine structure of the Franck-Condon principle. $j(\kappa)$ is proportional to the radial integral $J(k,K)$ which gives the scattering amplitude. This example is for the dissociation of H_2 from the initial $l=1$ state to the final $l=0$ state. $j(\kappa)$ for a small region around $\kappa=0.94$ was found by interpolation; the error of the approximation used is such that $j(\kappa)$ should descend somewhat more steeply to the left of the principal maximum than is shown.

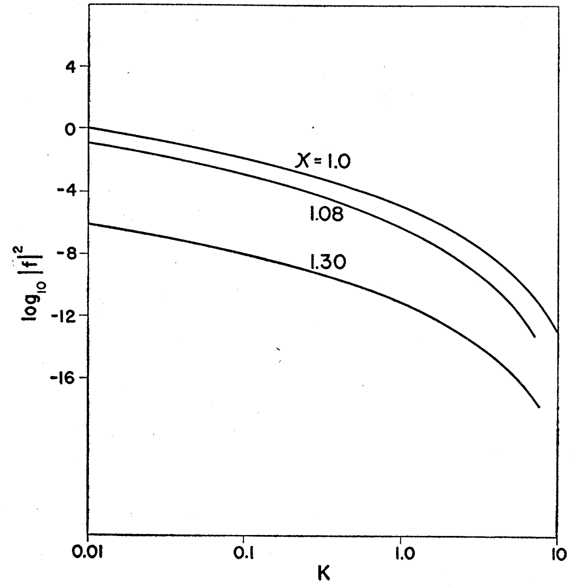

FIG. 4. The modulus of the scattering amplitude, $|f_k|^2$, which gives the differential cross section $d\sigma/d\omega dW$ for the same process as in Fig. 3, for several κ (the upper two curves belong to the κ corresponding to the first extrema of $j(\kappa)$; atomic units are used throughout.

In Fig. 4 we plot $|f_k|^2$ against K for several κ to show the angular distribution of scattered electrons; and in Fig. 5 we give the total cross section $d\sigma/dW$ for $\kappa=1$.

FURTHER REMARKS ON ANGULAR DISTRIBUTION OF DISSOCIATED PROTONS

We conclude by sketching the analysis that gives the complete angular distribution of dissociated protons, leaving a fuller discussion for a later report.

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[10] The roles of t and l in the previous discussion are reversed, as remarked after Eq. (13).

The correctly normalized final-continuum wave function[6] χ_k^* here, apart from a normalization constant, is

$$\chi_k^* = e^{ik\rho}\int_0^\infty y^{i\beta}e^{-y}J_0[2(ik\xi'y)^{\frac{1}{2}}]dy, \quad \xi'=\rho(1+\cos\theta'),$$

with $\cos\theta'$ as given in Eq. (8). Taking the initial state as the ground state, and writing $\sin(\frac{1}{2}\mathbf{K}\cdot\boldsymbol{\varrho})$ $(=\sin\frac{1}{2}Kz$, $\mathbf{K}$ being the polar axis) in exponential form, the radial integral to within constant factors is

$$J(k, K) = \int\int \rho^{\lambda-1}e^{-\alpha\rho}e^{ik\rho}e^{\frac{1}{2}i\mathbf{K}z}y^{i\beta}e^{-y}J_0 dt d\boldsymbol{\varrho} - \text{s.f.}(-K), \quad (30)$$

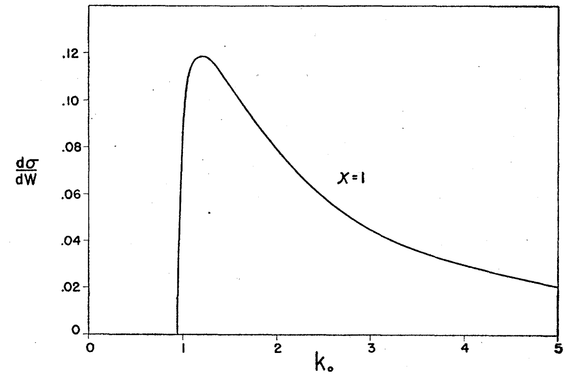

FIG. 5. Total cross section $d\sigma/dW$ for the same process as in Fig. 3, for dissociation of H_2^+ to a continuum state at $\kappa=1$ within dW near where the cross section is largest. Atomic units are used for k_0, units of πa_0^2 for σ.

where s.f.$(-K)$ means "same function of $-K$." Introducing parabolic coordinates $\xi=\rho(1+\cos\theta)$, $\eta=\rho(1-\cos\theta)$, φ, $d\boldsymbol{\varrho}=\frac{1}{2}\rho d\xi d\eta d\varphi$, Eq. (30) may be written

$$J(k, K) = \frac{1}{2}(-1)^\lambda \frac{\partial^\lambda}{\partial\alpha^\lambda}\int \exp\{-\tfrac{1}{2}\alpha(\xi+\eta)+\tfrac{1}{4}iK(\xi-\eta) + \tfrac{1}{2}ik(\xi+\eta)\}y^{i\beta}e^{-y}J_0 dt d\xi d\eta d\varphi - \text{s.f.}(-K).$$

This integral has been treated by Massey and Mohr.[6] One uses the addition theorem for J_0, making use of the fact that

$$\xi' = \xi\cos^2\tfrac{1}{2}\theta_0 + \eta\sin^2\tfrac{1}{2}\theta_0 + 2(\xi\eta)^{\frac{1}{2}}\cos\tfrac{1}{2}\theta_0\sin\tfrac{1}{2}\theta_2\cos\varphi,$$

and finds after reduction

$$J(k, K) = 4\pi(-1)^\lambda \frac{\partial^\lambda}{\partial\alpha^\lambda}(i\beta)! \times \frac{[(\alpha-ik-\frac{1}{2}iK)(\alpha-ik+\frac{1}{2}iK)]^{i\beta}}{[\alpha^2+k^2+\frac{1}{4}K^2-kK\cos\theta_0]^{i\beta+1}} - \text{s.f.}(-K). \quad (31)$$

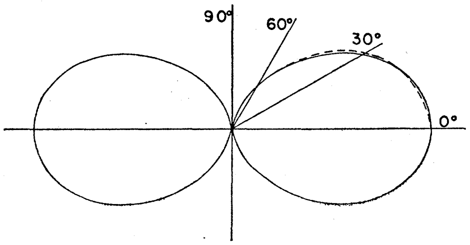

FIG. 6. Angular distribution of dissociated protons resulting from electrons impinging on H_2 in the ground state according to Eq. (32) (solid curve) in comparison with a $\cos^2\theta_0$ distribution (dotted curve) which, as discussed in the text, should dominate the distribution. The two agree everywhere to within $1\frac{1}{2}$ percent. The solid curve refers to the data $\kappa=1.4$, $k_0=10$, $K=$ smallest value (electron scattering in the forward direction); in this case θ_0 is measured from the axis $\mathbf{k}_0$ which is the same as $\mathbf{K}$.

This may be evaluated by writing the derivative as a Cauchy integral and choosing a suitable steepest descent contour in the complex α plane. [Actually it is better to lump $\exp(-\alpha\rho)$ and $\exp(ik\rho)$ together in Eq. (30) and take the derivatives with respect to $\alpha-ik$.]

It is apparent from Eq. (31) that, as discussed before, $J(k, K)$ vanishes for $\theta_0=\pi/2$ and there is no dissociation in the direction perpendicular to $\mathbf{K}$.

For sufficiently large k, χ_k may be adequately represented by the plane wave $\exp(i\mathbf{k}\cdot\boldsymbol{\varrho})$. Then the evaluation of $J(k, K)$ is elementary and gives

$$J(k, K) = \frac{\sin(\lambda+1)\omega_0}{K_0(\alpha^2+K_0^2)^{(\lambda+1)/2}} - \frac{\sin(\lambda+1)\omega_1}{K_1(\alpha^2+K_1^2)^{(\lambda+1)/2}},$$
$$K_{1,0}^2 = k^2+\tfrac{1}{4}K^2 \pm kK\cos\theta_0,$$
$$\omega_{1,0} = \tan^{-1}(K_{1,0}/\alpha). \quad (32)$$

Since the initial state has been taken as a state of zero angular momentum, we expect from our earlier discussion that the angular distribution of dissociated protons will be dominated by $\cos^2\theta_0$. In Fig. 6, where the distribution arising from Eq. (32) is compared with a $\cos^2\theta_0$ distribution, this is verified. The two agree to within slightly more than one percent for all θ_0.

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