determined from refractivity. (A thermal positron has a velocity of about 10^7 cm sec^{-1}, so that for a molecule of dimension about 10^{-7} to 10^{-8} cm the passing positron looks like a transitory alternating electric field of frequency 10^{14} to 10^{15} sec^{-1} i.e., the frequency of visible light.)

The correlation of λ_{e^+} with α is evidently much stronger than with λ_{Dirac}. In fact from Fig. 4 we can get approximately,

$$\lambda_{e^+}=\alpha^{1.25}/10$$

for all gases, with λ_{e^+} in μsec^{-1} atm^{-1}, α in esu $\times 10^{21}$.

This general relationship seems to demonstrate that the long-range dipole distortion is the predominant mechanism in low-energy positron scattering. This has not previously been clear, either in the positron case, or for slow-electron collisions. There is support for this picture from recent calculations of Cody *et al.*[12]

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[12] W. J. Cody, Joan Lawson, Sir Harrie Massey, and K. Smith, Proc. Roy. Soc. (London) **A278**, 479 (1964).

PHYSICAL REVIEW VOLUME 140, NUMBER 1A 4 OCTOBER 1965

The Transition $1s\sigma_g-2p\sigma_u$ in H_2^+ Induced by Collision with an Electron, Proton, or Hydrogen Atom*

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The first Born approximation to the transition $1s\sigma_g$-$2p\sigma_u$ in H_2^+ is developed. The internal degrees of freedom of the molecular ion are treated explicitly, and in a manner that takes advantage of the dissociative nature of the $2p\sigma_u$ state. The resulting total cross section is found to depend on the initial vibrational state. Numerical results are presented in graphical form for the cases in which this process is caused by collision with an electron, proton, or hydrogen atom. In each case the total cross section is given for all 19 bound vibrational states of the H_2^+ ground state (the $1s\sigma_g$ orbital). In the electron and proton cases the cross section for the lowest ($\nu=0$) vibrational state is observed to be two orders of magnitude lower than the cross section for the last ($\nu=18$) bound vibrational state. The dependence on initial vibrational state in the hydrogen-atom case is not as dramatic as in the bare-charge cases, but simultaneous excitation of the hydrogen atom is demonstrated to be an important factor in the shape and magnitude of the cross section. A method of summing simultaneous excitations is presented for the situation in which one particle undergoes a specific transition and the other particle is left in an unspecified state.

I. INTRODUCTION

PREVIOUS theoretical treatments[1,2] of scattering by the hydrogen-molecule ion H_2^+ indicate that the internal degrees of freedom of this molecular ion must be considered to predict its scattering behavior accurately. This is particularly true because the major mechanism leading to the formation of H_2^+ is $H_2(^1\Sigma_g^+)\rightarrow H_2^+(^2\Sigma_g^+)+e^-$, where the Franck-Condon factors predict a finite probability of occupation[3] of all bound vibrational states of the $^2\Sigma_g^+$ electronic state. These states also have long lifetimes, because they must decay by a quadrupole mechanism; hence any experiment performed with H_2^+ could easily involve all 19 bound vibrational states.[4]

In this paper we investigate the total cross section for the inelastic process

$$a+H_2^+(1s\sigma_g)=a+H_2^+(2p\sigma_u)\,, \qquad (1)$$

where each bound vibrational state of $H_2^+(1s\sigma_g)$ is considered separately and a is an electron, proton, or hydrogen atom. The orbital designating the electronic eigenstate of H_2^+ is given in parentheses. It will then be possible, with a knowledge of the population of vibrational states, to predict an observed cross section by forming the appropriate average of the results for the individual vibrational states.[5] Investigation of transitions to several lower lying electronic states[1] has shown that the reaction indicated by Eq. (1), in the electron case, dominates the discrete transitions proceeding from the ground state. The $2p\sigma_u$ state has no bound vibrational states; hence, in the electron or proton case, the cross sections given here will be good approximations to the dissociation process that results in a proton and hydrogen atom.

The approach will be that of Ref. 1 (to be referred to as I); that is, the total cross section will be calculated in the first Born approximation and it will include the contributions from all eigenstates of nuclear motion for the final electronic configuration. The method used in I for summing the contributions from all final eigenstates of

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* This work was supported by the U. S. Atomic Energy Commission.

[1] James M. Peek, Phys. Rev. **134**, A877 (1964).

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

[3] J. Wm. McGowan and L. Kerwin, Can. J. Phys. **42**, 972 (1964).

[4] S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., Phys. Rev. **119**, 1025 (1960).

[5] See Eq. (13).

nuclear motion was based on the closure relation that results from assuming these eigenfunctions form a complete set. This technique is exact for a given momentum transfer, when the collision energy is such that all states in the sum are possible, but makes it impossible to calculate a total cross section consistent with energy conservation. An alternate method of performing this sum is given in Sec. II where use is made of the fact that all nuclear eigenstates for the $2p\sigma_u$ potential curve lie in the continuum. This derivation removes the difficulty encountered in retaining energy conservation at the expense of introducing an approximation to the continuum wave function. The advantage of the alternative treatment will be discussed. Section III contains the results of calculations based on this theory for the reaction of Eq. (1) when a is either an electron or a proton. Total cross sections are given for all 19 bound vibrational states of the $1s\sigma_g$ state.

The total cross section for reaction (1) when a is the hydrogen atom is considered in Sec. IV. The simultaneous excitation of the hydrogen atom is demonstrated to be an important factor in the total cross section. An asymptotic theory, correct at both low and high collision energies, is developed that takes into account all possible final states of the hydrogen atom for a given inelastic process in H_2^+. Correction terms are derived and a comparison of this approximate technique with the term-by-term sum is made. Numerical results for reaction (1) are given for all 19 bound vibrational states of $H_2^+(1s\sigma_g)$ for both the case in which the hydrogen atom remains unexcited and the case in which all possible final states of the hydrogen atom are included.

II. EXCITATION TO A DISSOCIATIVE STATE

The first Born approximation to the total cross section for the excitation of a molecule was shown in I to be

$$Q_\nu = \int_0^\infty dR R^2 |X_\nu(R)|^2 Q(R), \tag{2}$$

where the initial wave function is $\Psi_n = \psi_n(\mathbf{r},R) X_\nu(R) \times Y_{LM}(\delta,\xi)$; $\psi_n(\mathbf{r},R)$ being the initial electronic eigenfunction, $X_\nu(R)$ the initial vibrational wave function, and Y_{LM} a spherical harmonic describing the initial rotational state. The total cross section Q_ν represents the sum over all nuclear eigenstates of the final electronic state, $\psi_{n'}$, and an average over the degenerate levels of the initial rotational state. For the scattering[6] of an electron or proton,

$$Q(R) = \frac{8\pi\mu^2}{k_n^2} \int_{k_n-k_{n'}}^{k_n+k_{n'}} dK K^{-3} |\epsilon(K,R)|^2, \tag{3}$$

where μ is the reduced mass of the scattering system, $k_n = \mu V_0$ where V_0 is the relative velocity between the two colliding systems, $k_{n'} = \{2\mu[(\frac{1}{2})\mu V_0^2 - \Delta E]\}^{1/2}$, and ΔE is the energy loss of the inelastic process. The Born matrix element is defined as

$$\begin{aligned} |\epsilon(K,R)|^2 &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin\delta \, d\delta \, d\xi \left| \int d\mathbf{r} \exp(i\mathbf{K}\cdot\mathbf{r}) \psi_n(\mathbf{r},R) \psi_{n'}^*(\mathbf{r},R) \right|^2, \\ &= \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin\delta \, d\delta \, d\xi \, |\epsilon(K,\delta,\xi,R)|^2, \end{aligned} \tag{4}$$

where δ, ξ orient $\mathbf{R}$ with respect to $\mathbf{K}$, $\mathbf{K} = \mathbf{k}_n - \mathbf{k}_{n'}$ and $K = |\mathbf{K}|$ defines the momentum transfer.

As was pointed out in I, the dependence of k_n', hence ΔE, on the final rotational and vibrational states is ignored in deriving Eqs. (2), (3) and (4). The argument based on closure then makes it impossible to choose ΔE in a manner consistent with energy conservation and does not indicate what method of choosing ΔE is best. This poses a serious problem, especially if the physical process is one in which ΔE may cover a wide range of values. One such situation, under consideration in this paper, is the scattering from $H_2^+(1s\sigma_g)$, initially in a highly excited vibrational state, to the dissociative state $H_2^+(2p\sigma_u)$ where a wide range of dissociation energies is possible. By considering the nature of the final nuclear eigenstate and introducing different approximations, a more detailed knowledge of the scattering process can be obtained. Following Kerner,[2] the final-state function can be written

$$\begin{aligned} \Psi_{n'}^*(\mathbf{r},\boldsymbol{\kappa},\mathbf{R}) &= \psi_{n'}^*(\mathbf{r},R) X_\kappa^{(-)*}(\boldsymbol{\kappa},\mathbf{R}), \\ &= \psi_{n'}^*(\mathbf{r},R) \frac{4\pi}{(8\pi^3)^{1/2}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-i)^l \exp(i\delta_l) Y_{lm}^*(\delta,\xi) Y_{lm}(\theta_0,\varphi_0) F_l^*(\kappa,R), \end{aligned} \tag{5}$$

where $X_\kappa^{(-)}$ satisfies the boundary conditions for dissociation, θ_0, ϕ_0 fix $\boldsymbol{\kappa}$ with respect to $\mathbf{K}$, and δ_l is the phase shift. This wave function refers to an energy in the continuum of $\frac{1}{2}\mu'\kappa^2$ where μ' is the reduced mass of H_2^+. The

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[6] All equations will be given in atomic units unless otherwise specified.

total cross section is then

$$Q_\nu=\int_0^{\kappa_{\max}}\int_0^{2\pi}\int_0^{\pi}\sin\theta\,d\theta_0\,d\phi_0\,\kappa^2d\kappa\int_{k_n-k_{n'}}^{k_n+k_{n'}}dK\frac{8\pi}{V_0{}^2K^3}\frac{1}{(2L+1)}\sum_{M=-L}^{L}\bigg|\int d\mathbf{r}\int d\mathbf{R}\exp(i\mathbf{K}\cdot\mathbf{r})\psi_n(\mathbf{r},R)\psi_{n'}{}^*(\mathbf{r},R)$$
$$\times Y_{LM}(\delta,\xi)\mathrm{X}_\nu(R)\frac{4\pi}{(8\pi^3)^{1/2}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^l\exp(i\delta_l)Y_{lm}{}^*(\delta,\xi)Y_{lm}(\theta_0,\phi_0)F_l{}^*(\kappa,R)\bigg|^2. \quad (6)$$

The integration over the outgoing direction of the dissociating particles θ_0, ϕ_0 can be carried out immediately, yielding

$$Q_\nu=\int_0^{\kappa_{\max}}\kappa^2d\kappa\int_{k_n-k_{n'}}^{k_n+k_{n'}}dK\frac{8\pi}{V_0{}^2K^3}\frac{1}{(2L+1)}\sum_{m=-L}^{L}\sum_{l=0}^{\infty}\sum_{M=-l}^{l}\bigg|\int d\mathbf{r}\int d\mathbf{R}\exp(i\mathbf{K}\cdot\mathbf{r})\psi_n(\mathbf{r},R)\psi_{n'}{}^*(\mathbf{r},R)$$
$$\times Y_{LM}(\delta,\xi)\mathrm{X}_\nu(R)(4\pi/(8\pi^3)^{1/2})Y_{lm}{}^*(\delta,\xi)F_l{}^*(\kappa,R)\bigg|^2. \quad (7)$$

The integration over κ is stopped at the value $\kappa_{\max}$ which is determined by energy conservation. We make the approximation

$$F_l{}^*(\kappa,R)\propto\delta(R-R'), \quad (8)$$

where R' is the classical turning point of the H_2^+ nuclei, with the energy $\frac{1}{2}\mu'\kappa^2$, in the potential of the $2p\sigma_u$ state. The Dirac delta function $\delta(R-R')$ is normalized such that

$$\int d\boldsymbol{\kappa}X(\boldsymbol{\kappa},\mathbf{R}')X^*(\boldsymbol{\kappa},\mathbf{R}'')=\delta(\mathbf{R}'-\mathbf{R}''). \quad (9)$$

The sum over l, m in Eq. (7) can be carried out immediately when $F_l(\kappa,R)$ is taken independent of l. By averaging over the degenerate levels of the initial rotational state and making use of the properties of the Dirac delta function to carry out the integration over R, the total cross section becomes

$$Q_\nu=\int_{R_{\min}}^{\infty}R^2\,dR\int_{k_n-k_{n'}}^{k_n+k_{n'}}dK\frac{8\pi}{V_0{}^2K^3}\int_0^{2\pi}\int_0^{\pi}\sin\delta\,d\delta\,d\xi(1/4\pi)|\mathrm{X}_\nu(R)|^2\bigg|\int d\mathbf{r}\exp(i\mathbf{K}\cdot\mathbf{r})\psi_n(\mathbf{r},R)\psi_{n'}{}^*(\mathbf{r},R)\bigg|^2. \quad (10)$$

Here $R_{\min}$ is the classical turning point associated with $\kappa_{\max}$. From the definitions of Eqs. (3) and (4), Eq. (10) can be written as

$$Q_\nu=\int_{R_{\min}}^{\infty}R^2\,dR|\mathrm{X}_\nu(R)|^2Q(R). \quad (11)$$

The algebra that leads from Eq. (7) to Eq. (11) gives a definite interpretation to $Q(R)$ and the integration over R. $Q(R)$ represents the cross section for the excitation of $H_2^+(1s\sigma_g)$ from the initial vibrational state ν to the state $H_2^+(2p\sigma_u)$, which has an energy in the continuum implied by Eq. (8). Hence, the ΔE to be used in calculating $k_{n'}$ is the energy difference between the initial vibrational state[7] and the final electronic-state potential curve at the internuclear separation R. The integration over R is just the summing of all possible energies in the dissociation continuum. With this interpretation of ΔE, $Q(R)$ will be zero for $R<R_{\min}$, so without further approximation

$$Q_\nu=\int_0^{\infty}R^2\,dR|\mathrm{X}_\nu(R)|^2Q(R). \quad (12)$$

Equation (12) is identical in form to Eq. (2); however, the choice of ΔE is now clearly defined and the one additional approximation to the Born theory is stated by Eq. (8).

The accuracy of the approximation to the final-state nuclear eigenfunction, Eq. (8), must be questioned. It can be inferred from the work of Kerner[2] (see his Fig. 3) that the delta-function dependence on R is not particularly good and it follows that the predicted velocity dependence of the dissociating fragments may be inaccurate. However, in this paper we are not concerned with the velocity distribution and are interested only in the effect of this approximation on the total cross section defined by Eq. (12). Arguments can be made that Eq. (8) is reasonably valid at small or intermediate R and becomes poor at large R where the $2p\sigma_u$ potential curve is relatively flat. The approximation would then be considered good for the lower lying vibrational states

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[7] The author is grateful to Gordon H. Dunn for pointing out the fact that the eigenenergy of the initial vibrational state should be used rather than the energy of the ground-state potential curve at the point R.

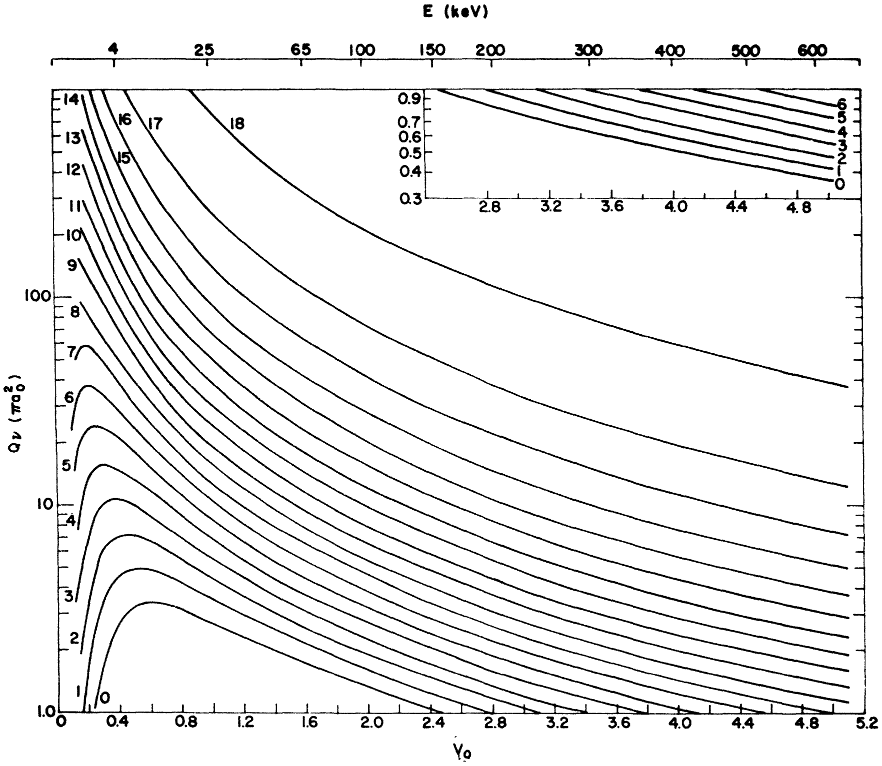

FIG. 1. Q_ν for a proton exciting the transition $1s\sigma_g-2p\sigma_u$ in H_2^+ and all bound vibrational states of the ground state of H_2^+ shown as a function of the relative velocity V_0 of the collision. Q_ν is in units of πa_0^2 and V_0 is in atomic units. The upper scale is the energy in keV of a proton colliding with a stationary hydrogen-molecule ion. The cross sections that go off scale are continued in the upper-right-hand corner.

of the $1s\sigma_g$ electronic state but probably unreliable for the last few bound vibrational states. However, the true situation will not be known until the matrix elements appearing in Eq. (7) have been evaluated. Work of this nature is now in progress.

III. DISSOCIATION BY AN ELECTRON OR PROTON

The total cross section Q_ν defined by Eq. (12) is shown in Fig. 1 for the proton case and in Fig. 2 for the electron case. These figures show the influence of the initial vibrational state and clearly indicate the necessity of having accurate knowledge of the population of vibrational states prevalent during a measurement to make a prediction of the effective cross section. Obviously, if the numbers f_ν represent the initial population of vibrational states of H_2^+, the observed total cross section would be

$$Q_{\text{obs}}=\sum_{\nu=0}^{18} f_\nu Q_\nu \Big/ \sum_{\nu=0}^{18} f_\nu . \tag{13}$$

Since there can be no unique set of f_ν which would apply to all situations, it is necessary to give the individual Q_ν rather than the composite Q_{obs}.

Except at the lowest velocities given in Fig. 1, the cross section for the proton case is independent of mass. Hence, this cross section will apply to the scattering of a bare particle of charge z if Q_ν is replaced by Q_ν/z^2. At higher velocities the electron results approach the mass-independent case. The electron results, Fig. 2, are terminated at these velocities since the cross section can then be obtained from Fig. 1.

The integral defined in Eq. (12) was evaluated in the following manner. The vibrational wave functions used were those tabulated by Cohen, Hiskes, and Riddell.[8] The evaluation of $Q(R)$ has been carried out[1] for a few values of R using the exact electronic eigenfunctions. This turns out to be a laborious task and, since $Q(R)$ is needed over a wide range of R, $0\leq R\leq 20.0$, for which all necessary exact wave functions are not available, the electronic eigenfunctions were approximated by the appropriate linear-combination-of-atomic-orbitals (LCAO) functions

$$\psi^{\pm}=N^{\pm}(\Phi_a\pm\Phi_b)\,, \tag{14}$$

where $N^{\pm}$ is the normalizing constant and Φ_a, Φ_b are unscreened hydrogenic functions centered on nuclei a and b, respectively. The function ψ^+ refers to the $1s\sigma_g$ state and ψ^- refers to the $2p\sigma_u$ state. The evaluation of $Q(R)$ is then relatively simple, the results being a generalization to any R of Ivash's[9] calculation when his screening constant is taken equal to one. The error introduced into the calculation of $Q(R)$ by using the LCAO functions [Eq. (14)] has been shown[10] to be

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[8] S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., University of California Radiation Laboratory Report No. UCRL-8871, 1959 (unpublished).

[9] E. V. Ivash, Phys. Rev. **112**, 155 (1958).

[10] James M. Peek, Phys. Rev. **139**, A1429 (1965).

approximately 30% at $R=2.0a_0$ and 20% at $R=3.2a_0$. The error decreases monotonically from these values as R becomes large and increases as R becomes small. $Q(R)$ calculated in this manner is greater, for all R, than the true first Born value. See Ref. 10 for a more detailed discussion. Because of the fact that $Q(R)$ is a rapidly increasing function of R^1, the error in Q_ν will tend to be that of $Q(R')$ at a value of R' occurring at the largest internuclear separation for which $|X_\nu(R)|^2$ has a maximum. This tends to minimize the effect of the large errors found for $Q(R)$ at small R in the calculation of Q_ν. However, because of this approximation, as well as the untested nature of the approximation defined by Eq. (8), these numerical results should be viewed as semiquantitative in nature.

The limits used in evaluating $Q(R)$ were calculated from the eigenvalues for the initial vibrational state[4] and the exact $2p\sigma_u$ potential curve.[11] The $X_\nu(R)$ are known for increments in R of $0.05a_0$; $Q(R)$ was calculated at these same values of R and the quadrature was carried out using Simpson's Rule.

One additional approximation has the advantage of reducing the computation time by a factor of almost 19 although it does not introduce any simplifications into the calculation. If one takes ΔE as the difference between the $1s\sigma_g$ and the $2p\sigma_u$ potential curves,[11] and hence independent of ν, one table of $Q(R)$ is sufficient to calculate Q_ν for all 19 vibrational states for a given V_0 rather than one table for each of the vibrational states. It was found that this approximation was quite good for high velocities but decreased the cross section by about 10% for $V_0=1.0$. The error was a function of ν, being smallest for the extreme ν and greater for the intermediate ν. Because of these results, the correct values of ΔE were used for $V_0\leq 2.0$ and the approximate values were used for all higher velocities. As an indication of the computation times required, it takes between 20 and 25 min to calculate Q_ν for all ν at a given V_0 on the CDC 3600 when the correct limits are used.

A recent paper by Bates and Holt[12] treats the case of proton excitation of the $2p\sigma_u$ state of H_2^+ as well as other final states of the molecule ion. Their approach is much the same as that used here except they avoid the use of approximate wave functions near the equilibrium internuclear separation and scale the $Q(R)$ calculated with the LCAO functions by an appropriate factor for large R. The limits used by Bates and Holt are calculated from the energy difference between the $1s\sigma_g$ and $2p\sigma_u$ curves. If we note that the vibrational wave functions used in these two calculations may not be identical, the numerical results of these two treatments are in essential agreement with the rough error analysis given in the preceding paragraph.

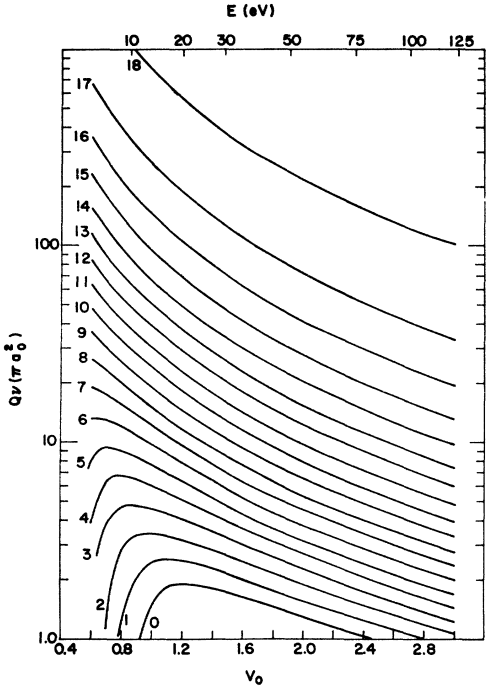

FIG. 2. Q_ν for an electron exciting the transition $1s\sigma_g-2p\sigma_u$ in H_2^+, for all bound vibrational states of the ground state of H_2^+, shown as a function of the relative velocity V_0 of the collision, in atomic units. The upper scale is the energy in eV of an electron colliding with a stationary hydrogen-molecule ion.

IV. DISSOCIATION BY A HYDROGEN ATOM

The reaction of Eq. (1) for the hydrogen-atom case must be written as

$$H(1s)+H_2^+(1s\sigma_g)=H(nl)+H_2^+(2p\sigma_u)\,, \qquad (15)$$

where it is assumed that H is initially in the $1s$ state and may be in any one of its eigenstates after the collision. This corresponds to the conditions of many experiments where a specific process is observed for one particle but nothing is known about the final state of the other particle. The first Born approximation to Q_ν for this case can be found by a simple but lengthy argument which results in redefining $Q(R)$ in Eq. (12) as

$$Q(R,1s)=\frac{8\pi\mu^2}{k_n^2}\int_{k_n-k_{n'}}^{k_n+k_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2 \times|I(1s)-1|^2, \qquad (16)$$

or

$$Q(R,n'l')=\frac{8\pi\mu^2}{k_n^2}\int_{k_n-k_{n'}}^{k_n+k_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2 \times|I(n'l')|^2, \qquad (17)$$

where $n'l'$ cannot refer to the $1s$ state. The quantity $|\epsilon(K,R)|^2$ is defined in Eq. (4) and

$$I(nl)=\int d\mathbf{r}\,\exp(i\mathbf{K}\cdot\mathbf{r})\Phi_{1s}(\mathbf{r})\Phi_{nl}^*(\mathbf{r})\,, \qquad (18)$$

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[11] James M. Peek, Sandia Corporation Report No. SC-RR-65-77, 1965 (unpublished).

[12] D. R. Bates and A. R. Holt, Proc. Phys. Soc. (London) A85, 691 (1965).

where Φ_{1s}, Φ_{nl} are normalized hydrogen-atom wave functions. Equation (16) applies to a collision in which the hydrogen atom is unexcited and Eq. (17) describes the simultaneous excitation of the two systems.

The analysis for the reaction indicated in Eq. (15) is similar to that given by Bates and Griffing[13] for the collision of two hydrogen atoms and to that of Boyd, Moiseiwitsch, and Stewart[14] for the scattering of He^+ on hydrogen atoms. As in these two papers, the simultaneous excitation of the target while the projectile suffers a specific excitation is found to give an important contribution to the desired cross section.

The total cross section for a single excitation process, defined by Eq. (15) when $nl=1s$, is shown in Fig. 3. Q_ν again is seen to be an increasing function of ν but the dependence is not nearly so dramatic as the e^-, H^+ cases. This is a reflection of difference in behavior of $Q(R)$ and $Q(R,nl)$. That is, for a given V_0, $Q(R)$ as defined by Eq. (3) is proportional to R^2 as R becomes large.[15] Since $|X_\nu(R)|^2$ becomes important for larger R as a larger ν is considered, the R^2 behavior of $Q(R)$ will amplify the difference between various Q_ν [Eq. (12)]. In the hydrogen-atom case, the asymptotic behavior for large R is $Q(R,nl)\sim A+(B/R^2)$, where A and B are constants for a given V_0.[15] If one evaluates Eq. (12) with a function of this form for the large R behavior, it is evident that the extension of $|X_\nu(R)|^2$ to larger R as ν increases will have little effect on the different Q_ν.

The cross section needed to compare with experiment is defined by

$$Q(R,\Sigma)=Q(R,1s)+\textstyle\sum_{n'l'} Q(R,n'l') \qquad (19)$$

where $Q(R,\Sigma)$ is the integrand to be used in Eq. (12) and Σ indicates that all contributions from simultaneous excitations are included. Previous work[13] indicates that only the states $n\leq 3$ plus the continuum give significant contributions to $Q(R,\Sigma)$. This point was verified; the formulas used for $I(n'l')$ were the ones given by McCarroll[16] for the discrete states and the continuum contribution was obtained from results quoted by Bates and Griffing[13] where the ejected electron is described by a wave function for an attractive Coulomb field. An example of the evaluation of Eq. (19) by adding these various terms is shown in Fig. 4 as the solid curve. Evaluating the sum in Eq. (19) by adding the individual terms is a tractable method but somewhat cumbersome. An alternative method of evaluating this sum is now developed.

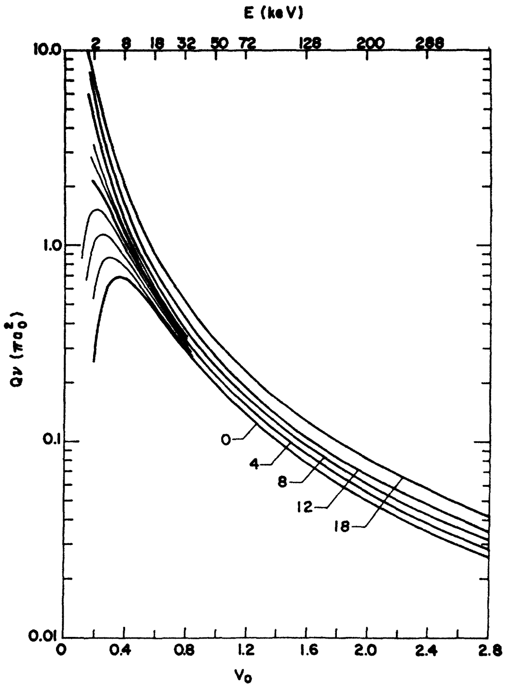

FIG. 3. Q_ν for a hydrogen atom exciting the transition $1s\sigma_g-2p\sigma_u$ in H_2^+, for several vibrational states of the ground state of H_2^+, shown as a function of the relative velocity V_0 of the collision, in atomic units. The cross section is for the hydrogen atom remaining unexcited. The upper scale is the energy in keV of a H_2^+ colliding with a stationary hydrogen atom.

Utilizing the relationship[13]

$$\textstyle\sum_{nl}|I(nl)|^2=1\,, \qquad (20)$$

the approximate relationship

$$\sum_{n'l'} Q(R,n'l')\cong\frac{8\pi\mu^2}{k_n^2}\int_{k_n-\tilde{k}_{n'}}^{k_n+\tilde{k}_{n'}} dK\,K^{-3} \times(1-|I(1s)|^2)|\epsilon(K,R)|^2 \qquad (21)$$

follows. The approximation arises in ignoring the dependence of ΔE on $n'l'$ when changing the order of integration and summation and is emphasized by replacing $k_{n'}$ with $\tilde{k}_{n'}$. In general, $\Delta E=\Delta E(H_2^+)+\Delta E(n'l')$ where $\Delta E(H_2^+)$ is the excitation energy for H_2^+ at the internuclear separation R and $\Delta E(n'l')$ is the energy difference between the $1s$, $n'l'$ states of the hydrogen atom. If we take $\Delta E(n'l')=0.5$ and evaluate $Q(2.0,\Sigma)$ using Eq. (21), the dot-dash curve in Fig. 4 results. It is apparent from Fig. 4 that this method is asymptotically correct at both large and small V_0, but not particularly

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[13] D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953); **A67**, 663 (1954); **A68**, 90 (1955).

[14] T. J. M. Boyd, B. L. Moiseiwitsch, and A. L. Stewart, Proc. Phys. Soc. (London) **A70**, 110 (1957).

[15] Strictly speaking, the results quoted do not include the change in ΔE as R changes. For a given initial vibrational state, ΔE changes very little as a function of R, for large R, since the $2p\sigma_u$ curve is flat for large R. Also, the energy differences between adjacent vibrational states is small, so the influence of ΔE as a function of R or the initial vibrational state is of secondary importance. Since ΔE becomes a very weak function of R for large R, it can be shown that $Q(R)$ is bounded as $R\rightarrow\infty$, but this occurs at such large R compared to the range of importance in evaluating Eq. (12) that the R^2 behavior is the dominating factor. However, if one considers the "classical" limits, $Q(R)$ is independent of ν but the asymptotic behavior of ΔE is now a strong function of R, $\Delta E\sim aRe^{-R}$, and one finds $Q(R)\sim R^3$ in the large R region. It is shown later in this section that the hydrogen atom case is insensitive to the lower limit, and hence to ΔE, so these omissions are in this case of even less importance.

[16] R. McCarroll, Proc. Phys. Soc. (London) **A70**, 460 (1957).

good in the intermediate range. This asymptotic character also follows from the investigation of Eqs. (19) and (21). As V_0 becomes small, the limits on the integral in Eq. (21) become equal and it is observed that $Q(R,\Sigma) \sim Q(R,1s)$, as it should in this limit. The error introduced by using Eq. (21) to represent the sum can be shown, for large V_0, to be proportional to V_0^{-n} where $n \geq 1$. This same asymptotic character at large V_0 was also found in the treatment of a similar process in hydrogen-atom–hydrogen-atom scattering[13] where their method of using the sum formula, Eq. (20), does not give the correct asymptotic behavior for small V_0.

Correction terms to Eq. (21) for the $n''l''$ state are easily seen to be proportional to

$$\int_{k_n-k_{n'}}^{k_n+k_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2|I(n''l'')|^2 - \int_{k_n-\tilde{k}_{n'}}^{k_n+\tilde{k}_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2|I(n''l'')|^2$$

$$= \int_{k_n-k_{n'}}^{k_n-\tilde{k}_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2|I(n''l'')|^2 + \int_{k_n+\tilde{k}_{n'}}^{k_n+k_{n'}} dK\, K^{-3}|\epsilon(K,R)|^2|I(n''l'')|^2. \quad (22)$$

In Eq. (22) $k_{n'}$ implies we have used the correct $\Delta E(n''l'')$, and $\tilde{k}_{n'}$ is calculated with the approximate $\Delta E(n'l')$. The limits $k_n+k_{n'}$, $k_n+\tilde{k}_{n'}$ are large in the important range of V_0 and, since the integrand of the correction term is quite small for large K, the second term on the right side of Eq. (22) can be ignored. From the fact that $\Delta E(n'l')$ is not very different from 0.5 for any bound $n'l'$, the largest correction term is expected to be the one from the continuum. The dashed line in Fig. 4 shows $Q(2.0,\Sigma)$, including this correction term for continuum. From the agreement with the term-by-term sum, the usefulness of this approach seems to be established.

This technique has another advantage when scattering by complex systems is considered. Note that $Q(R,1s)$ and Eq. (21) require only the ground-state wave function for the hydrogen atom. This will also be true of the analogues to Eqs. (19) and (21) for any atom or molecule. Usually approximate ground-state functions are known but few, if any, excited-state functions are available for complex systems. Equation (21) circumvents this lack of excited-state wave functions required to calculate the individual terms in Eq. (19) and, at the expense of constructing a continuum function, this example indicates that quite high accuracy can be obtained for all V_0.

The total cross section Q_ν, for the reaction of Eq. (14) when H_2^+ is initially in the vibrational state ν, including all simultaneous excitations, is shown in Fig. 5. The method and approximation used in calculating Q_ν was the same as that described in Sec. III. The use of LCAO functions to replace the H_2^+ eigenfunctions has been considered elsewhere[10] and we will repeat here only the observation that this approximation gives values of $Q(2.0,1s)$ which are 7%, or less, higher than the result based on the eigenfunctions. Minor differences in the calculation of Q_ν for this case occurred on two points. The integrands of $Q(r,nl)$ all vanish at small momentum transfer as a positive power of K. This has the effect of making Q_ν much less senstitive on the lower limit than in the electron or proton case, where the integrand of $Q(R)$ behaves like K^{-1}. Hence, Q_ν for this case is much

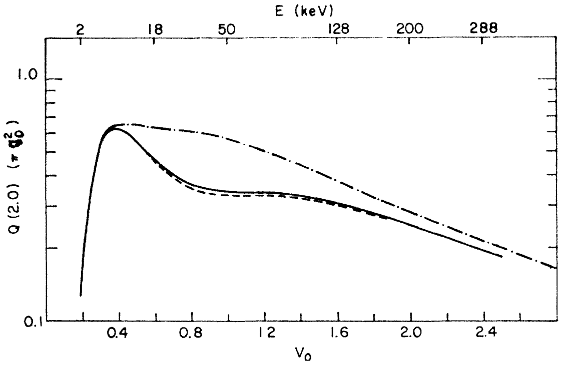

FIG. 4. $Q(2.0)$ for a hydrogen atom exciting the transition $1s\sigma_g-2p\sigma_u$ in H_2^+ shown as a function of the relative velocity V_0 of the collision, in atomic units. The upper scale is the energy of H_2^+ colliding with a stationary hydrogen atom. The solid curve shows the results for Eq. (19) found by adding the terms in the sum individually; the dot-dash curve is based on the approximate sum formula, Eq. (21), and the dashed curve is the result for the same formula plus a correction for the continuum contribution, Eq. (22).

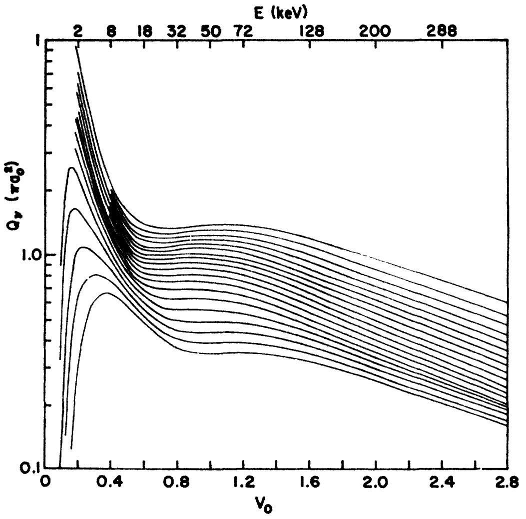

FIG. 5. Q_ν for a hydrogen atom exciting the transition $1s\sigma_g-2p\sigma_u$ in H_2^+ shown as a function of the relative velocity V_0 of the collision, in atomic units. This cross section includes contributions from the simultaneous excitations of the hydrogen atom. The upper scale is the energy in keV of H_2^+ colliding with a stationary hydrogen atom.

less sensitive on the lower limit and the "classical" method of calculating ΔE as the difference between the $1s\sigma_g$ and the $2p\sigma_u$ potential curves is a much better approximation. It was the one used in the computation. Numerical checks showed the error to be less than 1% at $V_0=0.6$ and then to increase slowly as V_0 was made smaller. The method of summing simultaneous excitations made use of the approximate formula given in Eq. (21). The appropriate correction term for the continuum was evaluated according to Eq. (22) and then added to the results from the approximate summation formula.

Comparison of the results that include simultaneous excitation with Fig. 3, which shows the cross section when these events are ignored, demonstrates their importance. It is apparent that the first Born approximation must include these processes when it is possible for them to occur. This is especially significant since their influence is the strongest at the high energies where the Born approximation is most likely to be used. As yet there is no experimental evidence to compare with these results, but the influence of simultaneous excitations on the dependence of the cross section is suggestive when one looks at the results obtained for the H_2^+, H_2 scattering system.[17]

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Minimum-Principle Calculation of the Positron-Hydrogen *s*-Wave Phase Shift*

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The recently developed improved minimum principle for single-channel scattering is applied to a study of the *s*-wave elastic-scattering phase shift η_0 of positrons by atomic hydrogen. The method requires the exact solution of the static one-body equation and of the corresponding static Green's function, and also the orthogonalization of the trial function to the hydrogenic ground-state wave function. The radial part of the trial function $Q\Psi_t$ is chosen to be of the exponential-polynomial form, with linear and nonlinear variational parameters; to simplify the orthogonalization, $Q\Psi_t$ is expanded in Legendre polynomials whose argument is the cosine of the angle between the coordinate vectors of the electron and the positron. Rigorous lower bounds are obtained on η_0 at various energies. The calculation includes the contributions from hydrogenic states with angular momentum l up to $l=5$. For each energy, an estimate is made by extrapolation of the true contribution to η_0 from $0\leq l\leq 5$, and this estimate is used in turn to estimate the contribution from $l>5$ to η_0. The rigorous lower bounds obtained and the estimates are compared with previous estimates of η_0.

I. INTRODUCTION

A LARGE number of calculations have recently been performed of the scattering of electrons by atomic hydrogen, at low[1–4] and at high energies. This is on the one hand a reflection of the increased interest in atomic scattering processes in the atmosphere of the earth and of the sun, for example, and on the other hand of the presence of high-speed computers which make possible large-scale calculations aiming at high accuracy. In view of the concurrent recent interest of the experimentalists and of the consequent improvements in technique, there is little doubt that relatively precise contact will be made shortly between the experimental results and theoretical calculations based on first principles, even for energies at which the distortion of the hydrogen atom is great enough to more or less completely invalidate the Born approximation. We might remark parenthetically that, roughly speaking, such contact has just about been made for scattering by an atom. It would obviously be extremely useful to the experimentalist to be able to normalize cross-section data by the use of reliable theoretical results.

Because of the great similarity of the problems, in the course of studying e^-H scattering the theorists have

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