Electronic Transitions in Slow Collisions of Atoms and Molecules. V. Multichannel Eikonal Approximation for the Differential (p^+, H) Excitation and Rearrangement Collisions

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The multichannel (p^+, H) collisions are investigated in the three-state approximation. In our formulation, precautions are taken to ensure that the state function has the correct asymptotic behavior. Consequently, the spurious long-range interactions coming from the nonadiabatic interactions do not appear in our coupled equations. These coupled equations are solved in the straight-line eikonal approximation. The calculated differential elastic, electron-transfer, and $2p_\pi$-excitation cross sections are compared with recent experimental data and other theoretical results.

I. INTRODUCTION

This is the fifth of a series of papers[1-4] in which we hope to develop a practical and systematic semiclassical procedure for calculating electronic transitions in slow collisions of atoms and molecules. Our effort has been to reduce the coupled equations of the adiabatic state expansion method to a practical form for regimes where the eikonal approximation is valid. The problem was formulated in paper I, where it is shown that the use of the eikonal approximation to describe the motion of the atoms and/or ions permits the coupled equations of the adiabatic state expansion method to be reduced to one-dimensional equations defined along a classical trajectory. The techniques for the evaluation of the wave functions and the Green's functions of the coupled equations in the eikonal approximation were described in paper II. A few illustrative applications were given in paper III as well as in paper II.

Utilizing these techniques, the coupled equations were further reduced in paper IV to a form which allows straightforward computation. As a first example of the application of the coupled equations in the multichannel eikonal approximation, we have in paper IV calculated the energy dependence of the $2p$-excitation cross section for the $He^+(1s) + H(1s) \rightarrow He^+(1s) + H(2p)$ process. In this calculation, we have utilized the multichannel feature of our procedure and investigated the coupling of the asymptotically degenerate channels associated with the $2p_\sigma$ and $2p_\pi$ H states. It is shown that the explicit inclusion of this coupling is a necessary first step to bring the theoretical result into a reasonable agreement with experiment.[5]

The purpose of the present paper is to investigate the application of the coupled equations in the multichannel eikonal approximation to the calculation of the differential cross sections. For the calculation of differential cross sections, unlike the total cross sections, we must treat the phase relation in more detail. Consequently, we need to know more about the adiabatic states of the molecular system to be considered. For this reason, we return to the (p^+, H) system for which the exact states are known.[6] Reasonably accurate calculations of the elastic and $2p$-excitation scatterings, as well as the resonant and $2p$-excitation electron-transfer collisions, have recently become available[7-13] in a wide range of energies (30 eV to 30 keV). These calculations would provide a very useful comparison in assessing the validity of various simplification assumptions adopted in our multichannel eikonal approximation.

After a brief review of the recent developments in the treatment of the (p^+, H) collision, we present in Sec. II a multichannel eikonal approximation for the (p^+, H) collisions. In this approximation we have taken the $1s\sigma_g$, $2p\sigma_u$, and $2p\pi_u$ adiabatic H_2^+ electronic states into consideration. This constitutes one of the simplest models which would provide a reasonable description of the Everhart damping[14] and the $2p$-excitation collisions.[15,16] The method of evaluating the nonadiabatic interaction between these adiabatic states is presented in Sec. II. The results obtained in our calculation are analyzed and compared with available measurements and other theoretical results in Sec. III.

II. EIKONAL APPROXIMATION FOR MULTICHANNEL (p^+,H) COLLISIONS

A. Multichannel (p^+,H) Collisions

The remarkable measurements of Everhart and his associates[14] in the early 1960's have made it apparent that the familiar adiabatic two-state approximation[17] does not provide an adequate description of the elastic and resonant electron-transfer (p^+, H) collisions. One of the salient features which the adiabatic two-state approximation fails to account for is the damping in the electron-transfer probability. One of the physical reasons for this damping has been pointed out by a number of workers[18,19] as being due to the coupling with excited states which are neglected in the adiabatic two-state approximation, and it is this coupling that concerns us in the present paper. A second, comparatively trivial, source of damping is the difference in the amplitudes of scattering in the g and u states at a given angle, which necessarily leads to nonzero minima in the interference pattern. This type of damping is well understood and requires no special comment here.[20,21] The damping due to excited states must be accounted for by including these excited states in the expansion leading to the coupled equations to be solved; the adiabatic representation provides the most common approach to these coupled equations, but other approaches are also useful in various circumstances.[18,20]

We shall consider the former approach and treat the multichannel (p^+, H) collision in the adiabatic state expansion method by including the appropriate excited states. Bates and Williams[19] have shown that the damping in the electron-transfer probability comes primarily from the nonadiabatic coupling of the $2p\sigma_u$ state with the $2p\pi_u$ state at close internuclear separations. The effect due to the nonadiabatic coupling with the $2p\pi_u$ state on the electron-transfer probability was then treated in the impact-parameter approximation. The results are in qualitative agreement with observations in that the electron-transfer probability is no longer oscillating between unity and zero. The results of Bates and Williams were further improved by Smith[21] using an approximate wave treatment. The justification of the procedure is, however, not straightforward.[22] Attempts at solving such three-state coupled equations in terms of the adiabatic molecular states have been made only recently.[9-12]

The three-state approximation has been investigated by Knudson and Thorson[9] in the WKB approximation. In their work, the asymptotic states were constructed in the molecular reference system. As a consequence, spurious long-range interactions appeared in their coupled equations. This spurious long-range interaction which comes from the $2p\sigma_u - 2p\pi_u$ rotational coupling has an R^{-1} dependence. Fortunately, their calculation was carried out at relatively low energies where the errors introduced by this spurious long-range interaction are small. The total $2p_\pi$-excitation cross section has recently been calculated by Rosenthal[12] in the four-ungerade-state approximation. Such spurious long-range interactions were also presented in this calculation.

One way to eliminate the spurious long-range interaction is to explicitly introduce a translational factor in the state function to give the correct asymptotic states.[23] This was done correctly by Bates and Williams[19] in the context of the time-dependent theory. The three-state coupled equations as formulated by Bates and Williams have been solved by McCarroll and Piacentini[11] in the 150-eV–2.84-keV energy region. The results are in reasonably good agreement with experimental observations.[14]

The spurious long-range interactions coming from the nonadiabatic interaction can also be formally eliminated in the formulation of the coupled equations. This has been done in paper I by Chen and Watson in the context of stationary-state scattering theory. This approach has the advantage that the spurious long-range interaction would not appear even in the absence of the translational factor. In the present work, we investigate the application of these coupled equations to the (p^+, H) collision problem in the three-state approximation. We shall solve the three-state coupled equations in the straight-line eikonal approximation.[2,4] A similar procedure has been adopted by McCarroll and Piacentini.[11] The difference lies, however, in the treatment of the longitudinal and transverse components of the momentum transfer. The nonadiabatic interactions used in the present calculation are those obtained using the exact adiabatic H_2^+ molecular electronic states.

The set of coupled equations which is free from the spurious long-range interaction takes the form [see Eqs. (I3.43) and (I3.45)]

$$\Psi_\alpha = \delta_{\alpha 0}\Psi^+_{c0\,\vec{p}} + \sum_{\beta\neq\alpha} G_\alpha J_{\alpha\beta}\Psi_\beta \ , \tag{2.1}$$

with

$$G_\alpha = (E + i\eta - K - W_\alpha - \upsilon_\alpha)^{-1}, \tag{2.2}$$

where $W_\alpha + \upsilon_\alpha$ are the eigenvalues of the adiabatic states φ_α, K is the appropriate kinetic energy operator of the colliding system in the c.m. system, and $J_{\alpha\beta}$ are the appropriately modified nonadiabatic interactions [see Eqs. (I2.16) and (I3.28)]. In Eq. (2.1), we have labeled the initial states as $\alpha = 0$ with incident relative momentum $\vec{p}$. Thus,

the coherent state $\Psi^+_{\text{co}\,\vec{p}}$ represents the elastic scattering [see Eq. (I3.44)]. This set of equations is consistent with formal scattering theory. We shall solve these equations in the eikonal approximation.

In adopting these coupled equations and the eikonal approximation we have restricted our interest to problems which are bounded by the following two inequalities (we are using the notations of paper I):

$$\eta_2 \equiv v/(e^2/\hbar) << 1, \tag{2.3}$$

$$\eta_3 \equiv \hbar/(pa_0) << 1, \tag{2.4}$$

where $\vec{v}$ and $\vec{p}$ are, respectively, the relative velocity and momentum of the colliding atoms, $e^2/\hbar \simeq 2\times 10^8$ cm/sec is a characteristic bound-electron velocity, and a_0 is the Bohr radius. The smallness of the dimensionless parameter η_2 permits a near-adiabatic description of the collisions provided by the coupled equations. The smallness of the dimensionless parameter η_3 permits the coupled equations to be solved in the semiclassical eikonal approximation. For collisions where the inequality for η_2 is not adequately satisfied, coupled equations of the same form would still be obtained [see Eq. (IB.7)].

For collisions when η_2 is not small, the atomic state or atomic pseudostates may for certain cases be used in place of the adiabatic molecular states for the formulation of the coupled equations.[7,8,13] Detailed calculations with very encouraging results are obtained[13] for the (p^+, H) collisions at energies larger than 1 keV. The coupled equations obtained in the atomic state expansion can also be solved in the eikonal approximation.[24] We shall, however, confine our consideration to the adiabatic-state expansion and to the case where η_2 and η_3 are both small.

It has been observed[19,25] that the nonadiabatic coupling between the $2p\sigma_u$ and $2p\pi_u$ states alone would lead to much too large a cross section for the $2p_\pi$ excitation of the hydrogen atom. There are a number of other adiabatic H_2^+ states, namely, the $2s\sigma_g$, $3p\sigma_u$, $3d\sigma_g$, $4f\sigma_u$, and $3d\pi_g$ states, which would lead to the $n=2$ excitation of hydrogen atoms. Schneiderman and Russek[25] have pointed out, based on the calculation of Mukherjee and Russek,[26] that the inclusion of the $3p\sigma_u$ state could significantly reduce the $2p_\pi$-excitation cross section. A detailed two-ungerade state $(2p\sigma_u, 2p\pi_u)$ and a four-ungerade state $(2p\sigma_u, 2p\pi_u, 3p\sigma_u$, and $3p\pi_u)$ calculation have been carried out by Rosenthal.[12] The result indicated that the inclusion of the $3p\sigma_u$ state does improve the agreement with experiment[16] at energies above 2 keV.

It should, however, be pointed out that recently the differential elastic scattering, electron-transfer, and $(n=2)$-excitation cross section, as well as their absolute ratios, have been measured.[15] Thus, by normalizing the differential elastic scattering cross section to the theoretical result at one scattering angle, the absolute differential $(n=2)$-excitation cross section can be obtained. The excitation cross sections so normalized are in good agreement with the three-state theoretical results at energies of 0.7 and 1 keV. The magnitude of the total $(n=2)$-excitation cross section obtained from such normalized differential cross sections is also consistent with the measured total $2p_\pi$-excitation cross section.[16] (One expects the total $2s$- and $2p_\sigma$-excitation cross sections to be small.) Thus, in this energy region ($E \leq 1$ keV), the three-state approximation appears to be reasonable. In the present work, we shall confine our treatment within the three-state ($1s\sigma_g$, $2p\sigma_u$, and $2p\pi_u$) approximation.

B. Multichannel Eikonal Approximation

To solve Eq. (2.1) in the eikonal approximation, we write for the Green's function

$$G_\alpha(\vec{R}, \vec{R}') = -(M_r/2\pi)|\vec{R}-\vec{R}'|^{-1} e^{iS_\alpha(\vec{R},\vec{R}')}, \tag{2.5}$$

and for the wave function

$$\Psi_\beta(\vec{R}') = (2\pi)^{-3/2}\gamma_\beta(\vec{R}')\, e^{iS_\beta(\vec{R}')}. \tag{2.6}$$

Here,

$$S_\alpha(\vec{R}, \vec{R}') = \int_{\vec{R}'}^{\vec{R}} \kappa_\alpha(\vec{R}'')\, ds \tag{2.7}$$

and

$$S_\beta(\vec{R}) = \int^{\vec{R}} \kappa_\beta(\vec{R}')\, ds, \tag{2.8}$$

with

$$\kappa_\alpha = [2M_r(E - W_\alpha - \mathcal{V}_\alpha)]^{1/2}. \tag{2.9}$$

We suppose that the eikonal amplitude γ_β is a relatively slowly varying function of the position. We further suppose that $E \equiv (\frac{1}{2}p^2/M_r)/\mathcal{R} >> 1$ (where $\mathcal{R}$ is the Rydberg constant), so that the path integrals for the eikonals given by Eqs. (2.7) and (2.8) can be evaluated in the straight-line approximation. A detailed investigation of the trajectory problem for the (p^+, H) collision was given in paper II.

In paper IV, we have shown that the coupled equations given by Eq. (2.1) can be reduced, in the straight-line eikonal approximation, to the form [see paper IV, Eq. (IV 2.48)]

$$\Psi_\alpha(\vec{R}) = \delta_{\alpha 0}\Psi^+_{\text{co}\,\vec{p}}(\vec{R}) - \sum_{\beta\neq\alpha} \frac{ie^{iS_\alpha(\vec{R})}}{(2\pi)^{3/2}v_\beta} \times \int_{-\infty}^{z} dz'\, J_{\alpha\beta}(z', b)\, \gamma_\beta(z', b)\, e^{-i\phi_{\alpha\beta}(z', b)}, \tag{2.10}$$

with [Eqs. (IV 2.26) and (IV 2.58)]

$$\phi_{\alpha\beta}(z', b) \equiv S_\alpha(\vec{R}') - S_\beta(\vec{R}) \cong -z(k_\beta - k_\alpha \cos\theta) + \delta\Phi_{\alpha\beta}(z, b) + \tfrac{1}{2}[\Phi_\beta(b) - \Phi_\alpha(b)], \quad (2.11)$$

$$\delta\Phi_{\alpha\beta}(z, b) = \int_0^z [(1/v_\alpha) V_\alpha - (1/v_\beta) V_\beta]\, dz', \qquad v_\beta = \lim_{z\to\infty}(\kappa_\beta)/M_r. \quad (2.12)$$

Utilizing Eq. (2.10), the transition matrix for a final state α and relative momentum $\vec{k}_\alpha$ [see Eq. (I 3.46)],

$$\langle \alpha\vec{k}_\alpha | T | 0\vec{p}\rangle = \delta_{\alpha 0}(\lambda_{\vec{k}_\alpha}, U_0 \Psi^+_{co\,\vec{p}}) + \left(\Psi^-_{c\alpha\vec{k}_\alpha}, \sum_{\beta\neq\alpha} J_{\alpha\beta}\Psi_\beta\right), \quad (2.13)$$

may be evaluated to give

$$T_{\alpha 0} = \delta_{\alpha 0}(\lambda_{\vec{k}_\alpha}, U_0\Psi^+_{co\,\vec{p}}) + (2\pi)^{-2}\sum_{\beta\neq\alpha}^{N} v_\beta \times \int_0^\infty b\, db\, J_0(k_\alpha b \sin\theta) Q_{\alpha\beta}(b)\, e^{(i/2)\Phi_{\alpha 0}(b)}, \quad (2.14)$$

with

$$Q_{\alpha\beta}(b) = e^{(i/2)[\Phi_\alpha(b) - \Phi_0(b)]} \lim_{z\to\infty} Q_{\alpha\beta}(z, b), \quad (2.15)$$

$$\Phi_{\alpha 0} \equiv \Phi_\alpha + \Phi_0 = -\int_{-\infty}^{\infty} [k_\alpha U_\alpha(R_0) + p U_0(R_0)]\, dz, \quad (2.16)$$

where the U_α's are defined in terms of the adiabatic potential $\mathcal{U}_\alpha$ [see Eq. (IV 2.12)]. For consistency in notation, we have $\vec{k}_0 = \vec{p}$.

The quantities $Q_{\alpha\beta}(z, b)$ are solutions of the set of coupled first-order differential equations

$$\frac{dQ_{\alpha\beta}(z, b)}{dz} = \Lambda_{\alpha\beta}\delta_{\beta 0} - i\Lambda_{\alpha\beta}\sum_{\gamma\neq\beta}^{N} Q_{\beta\gamma}, \quad (2.17)$$

with

$$\Lambda_{\alpha\beta}(z, b) = v_\beta^{-1} J_{\alpha\beta}(z, b)\, e^{-i\phi_{\alpha\beta}(z,b)}. \quad (2.18)$$

Thus, by solving Eq. (2.17), the transition matrix given by Eq. (2.14) can be evaluated. The potential scattering terms $(\lambda_{\vec{k}_\alpha}, U_0\Psi^+_{co\,\vec{p}})$ can be written in the form [see Eq. (II 5.11)]

$$(\lambda_{\vec{k}_\alpha}, U_0\Psi^+_{co\,\vec{p}}) = [iv_\alpha/(2\pi)^2] \times \int_0^\infty b\, db\, J_0(k_\alpha b\theta)(e^{i\Phi_0(b)} - 1), \quad (2.19)$$

which was first derived by Molière.[27]

In deriving Eqs. (2.10), (2.14), and (2.17) we have supposed that the nonadiabatic interactions $J_{\alpha\beta}$ have cylindrical symmetry. Consequently in Eq. (2.14) only the zeroth-order Bessel function $J_0(z)$ appears in Eq. (2.14). For the intended application to the (p^+, H) problem, the error introduced is less than one percent.[11] The extension to interaction with exponential-type azimuthal angular dependence is given in Ref. 24.

C. Three-State Approximation

In the three-state approximation, Eq. (2.17) reduces to a set of three coupled equations. To simplify our notation, we shall label these states in the numerical order 0, 1, and 2 where 0 and 1 denote, respectively, the asymptotically degenerate $1s\sigma_g$ and $2p\sigma_u$ adiabatic H_2^+ states and where 2 denotes the final $2p\pi_u$ adiabatic H_2^+ state.

From symmetry considerations, it is clear that the nonadiabatic interaction matrix elements $J_{\alpha\beta}$ vanish between gerade and ungerade states. This then uncouples gerade and ungerade interactions and the three coupled equations reduce to a pair of coupled equations for the ungerade states. We have from Eq. (2.17)

$$\frac{d}{dz}\begin{pmatrix} Q_{12}^{(u)} \\ Q_{21}^{(u)}\end{pmatrix} = \begin{pmatrix} 0 \\ \Lambda_{21}^{(u)}\end{pmatrix} - i\begin{pmatrix} 0 & \Lambda_{12}^{(u)} \\ \Lambda_{21}^{(u)} & 0\end{pmatrix}\begin{pmatrix} Q_{12}^{(u)} \\ Q_{21}^{(u)}\end{pmatrix}. \quad (2.20)$$

In terms of the solutions obtained from Eq. (2.20), the transition amplitudes take the forms [see Eqs. (2.14), (2.15), and (2.19)]

$$T_{00}^{(g)} = [iv_0/(2\pi)^2]\int_0^\infty db\, d\, J_0(pb\sin\theta)(e^{i\Phi_0} - 1), \quad (2.21)$$

$$T_{11}^{(u)} = [iv_1/(2\pi)^2]\int_0^\infty b\, db\, J_0(k_1 b\sin\theta) \times\{e^{i\Phi_1}[1 - i\Gamma_1^{(u)}(b)] - 1\}, \quad (2.22)$$

$$T_{21}^{(u)} = [v_1/(2\pi)^2]\int_0^\infty b\, db\, J_0(k_2 b\sin\theta)\, Q_{21}^{(u)}\, e^{i(1/2)\Phi_{21}}, \quad (2.23)$$

$$\Gamma_1^{(u)}(b) = (v_2/v_1)\, Q_{12}^{(u)}(b), \quad (2.24)$$

where the superscripts (g) and (u) are introduced to denote the gerade and ungerade symmetries. From the comparison of Eq. (2.22) with Eq. (2.19), it is clear that the dampings due to the coupling with the $2p_{\pi_u}$ states in the ungerade mode of interaction give rise to the $i\Gamma_1^{(u)}$ term.

In the three-state approximation, the elastic scattering and resonant electron-transfer amplitudes may be obtained by appropriate linear combinations of the elastic transition amplitudes $T_{00}^{(g)}$ and $T_{11}^{(u)}$. We then have

$$\frac{d\sigma_{s,et}}{d\Omega}(1s \to 1s) = (2\pi)^4 M_r^2\, |\tfrac{1}{2}(T_{00}^{(g)} \pm T_{11}^{(u)})|^2. \quad (2.25)$$

It is, however, not possible in the three-state approximation to distinguish electron-transfer

excitation from scattering excitation. We have, therefore, the approximations

$$\frac{d\sigma_s}{d\Omega}(1s \to 2p\pi) = \frac{d\sigma_{et}}{d\Omega}(1s \to 2p\pi) = (2\pi)^4 M_r^2 (v_2/v_1)^{\frac{1}{4}} |T_{21}^{(u)}|^2 . \quad (2.26)$$

The total cross section and electron-transfer probability can be readily determined in terms of these differential cross sections.

D. Nonadiabatic Matrix Elements

To solve the coupled equations, we must first evaluate the nonadiabatic interaction. The matrix elements $J_{\alpha\beta}$ of the nonadiabatic interaction between the adiabatic states φ_α and φ_β were defined in paper I in terms of the incident channel coordinates $(\vec{r}_1, \vec{R}_1)$. Since $J_{\alpha\beta}$, unlike $\Delta_{\alpha\beta}$ and $\Delta_{\alpha\beta}^{(0)}$, are less sensitive to the choice of the coordinates, we shall use the usual coordinates $(\vec{r}, \vec{R})$ for the evaluation of $J_{\alpha\beta}$, where $\vec{R}$ is the vector from the target proton to the incident proton, and $\vec{r}$ is the position of the electron with respect to the mass center of the nuclei. We then have

$$J_{\alpha\beta}(\vec{R}, -i\nabla_R) = \Delta_{\alpha\beta} - \lim_{R\to\infty} \Delta_{\alpha\beta} \equiv \Delta_{\alpha\beta} - \Delta_{\alpha\beta}^{(0)}, \quad (2.27)$$

with

$$\Delta_{\alpha\beta} = -(1/2M_r)[(\varphi_\alpha, \nabla_R^2 \varphi_\beta) + 2(\varphi_\alpha, \nabla_{\vec{R}} \varphi_\beta)\cdot\nabla_{\vec{R}}]. \quad (2.28)$$

This change in coordinates does not introduce an error in $J_{\alpha\beta}$, under the condition $m/M \ll 1$ and Eq. (2.4). In the eikonal approximation, $\Delta_{\alpha\beta}$ to the order of η_3 takes the form

$$\Delta_{\alpha\beta} = -(i\vec{k}_\beta/M_r)\cdot(\varphi_\alpha, \nabla_{\vec{R}} \varphi_\beta), \quad (2.29)$$

where the first term of Eq. (2.28), which is comparatively smaller than the second term, has been neglected in Eq. (2.29).

The electronic coordinates in adiabatic states are usually expressed in terms of the reference system which has the z axis parallel to the molecular axis of symmetry. The collision system is, however, specified in terms of a fixed coordinate system. The atomic states obtained from the adiabatic states in the $\vec{R} \to \infty$ limit depend therefore explicitly on $\vec{R}$. Consequently, the asymptotic expressions of $\Delta_{\alpha\beta}$ [i.e., $\Delta_{\alpha\beta}^{(0)}$, see Eq. (2.27)] are spurious for cases where α and β states belong to the scattering or to the rearrangement channels. It has been shown in paper I that the appropriate nonadiabatic interactions which appear in the coupled equations are $J_{\alpha\beta}$ but not $\Delta_{\alpha\beta}$. By definition $J_{\alpha\beta}$ do not contain $\Delta_{\alpha\beta}^{(0)}$ and are therefore free from the spurious long-range interactions encountered in the work of Knudson and Thorson[9] and of Rosenthal.[12]

Let $\hat{R}$, $\hat{\gamma}$, and $\hat{\eta}$ denote the unit vectors forming the basis of the spherical polar coordinates $\vec{R} = (R, \gamma, \eta)$ in the fixed reference coordinate system. In the moving molecular coordinate, the gradient takes the form[28]

$$\nabla_{\vec{R}} = \hat{R}\frac{\partial}{\partial R} + \hat{\gamma}\frac{1}{R}\left(\frac{\partial}{\partial\gamma} - \frac{i}{\hbar}J_{y'}\right) + \hat{\eta}\frac{1}{R\sin\gamma}\left(\frac{\partial}{\partial\eta} - \frac{i}{\hbar}\cos\gamma(J_{z'} - \tan\gamma J_{x'})\right), \quad (2.30)$$

where $J_{x'}$, $J_{y'}$, and $J_{z'}$ are the Cartesian components of the electronic angular momentum operator in the moving molecular coordinate system.

Assuming the classical trajectory lies in straight lines, we may take the local tangent $\hat{\kappa}$ of the classical trajectory in the direction parallel to the z axis of the fixed reference coordinate system. Since

$$\hat{Z}\cdot\hat{R} = \cos\gamma = (Z/R), \qquad \hat{Z}\cdot\hat{\gamma} = -\sin\gamma = -(b/R), \qquad \hat{Z}\cdot\hat{\eta} = 0, \quad (2.31)$$

we obtain from Eq. (2.30)

$$\hat{\kappa}_\beta\cdot\nabla_{\vec{R}} = k_\beta\cos\gamma\frac{\partial}{\partial R} - k_\beta\frac{\sin\gamma}{R}\left(\frac{\partial}{\partial\gamma} - \frac{i}{\hbar}J_{y'}\right), \quad (2.32)$$

where $J_{y'}$ can be expressed in terms of the lowering and rising electronic angular momentum operators. We have

$$iJ_{y'} = \tfrac{1}{2}(J_+ - J_-), \quad (2.33)$$

with

$$J_\pm = \pm e^{\pm i\varphi'}\left(\frac{\partial}{\partial\theta'} \pm i\cot\theta'\frac{\partial}{\partial\varphi'}\right), \quad (2.34)$$

where θ' and φ' are the polar angles of the electron in the moving molecular coordinate system. The nonadiabatic interaction in the straight-line approximation then takes the form

$$\Delta_{\alpha\beta}(\vec{R}) = -\frac{ik_\beta}{M_r}\left[\cos\gamma\left(\varphi_\alpha, \frac{\partial}{\partial R}\varphi_\beta\right) + \frac{\sin\gamma}{R}\left(\varphi_\alpha, \frac{1}{2\hbar}(J_+ - J_-)\varphi_\beta\right)\right]. \quad (2.35)$$

The nonadiabatic interaction between the $2p\sigma_u$ and $2p\pi_u$ has been investigated by Bates and Williams[19] in the united-atom and linear combination of atomic orbitals (LCAO) approximations. This approximate expression was used by McCarroll and Piacentini[11] in their three-state calculation. Evaluations of the $\Delta_{2p\pi_u, 2p\sigma_u}$ nonadiabatic interaction can also be carried out using the exact adiabatic H_2^+ electronic wave functions.[9,12] We have also carried out such a calculation using

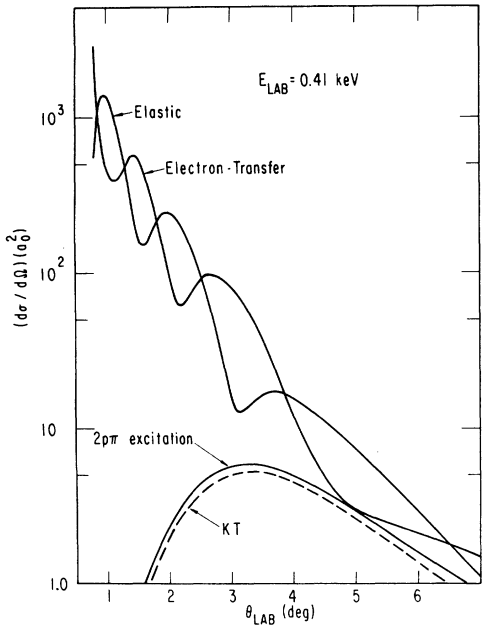

FIG. 1. Angular dependence of the theoretical differential elastic, electron-transfer, and $2p_\pi$-excitation cross sections in the (p^+, H) collision obtained in the three-state straight-line eikonal approximation at a laboratory energy of 410 eV. The differential $2p_\pi$-excitation cross section calculated by Knudson and Thorson (KT, Ref. 9) is shown as the dashed curve.

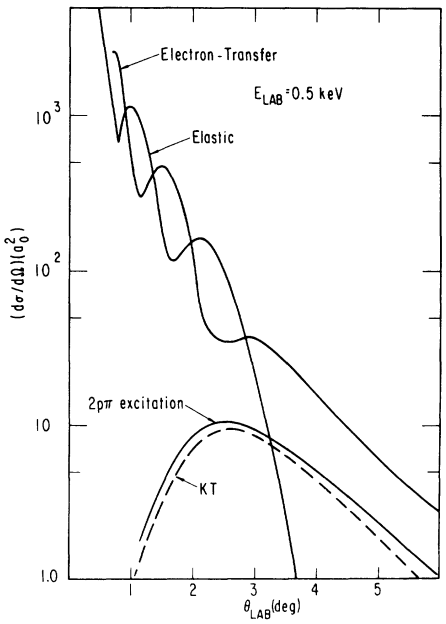

FIG. 2. Angular dependence of the theoretical differential elastic, electron-transfer, and $2p_\pi$-excitation cross sections in the (p^+, H) collision obtained in the three-state straight-line eikonal approximation at a laboratory energy of 500 eV. The differential $2p_\pi$-excitation cross section calculated by Knudson and Thorson (KT, Ref. 9) is shown as the dashed cruve.

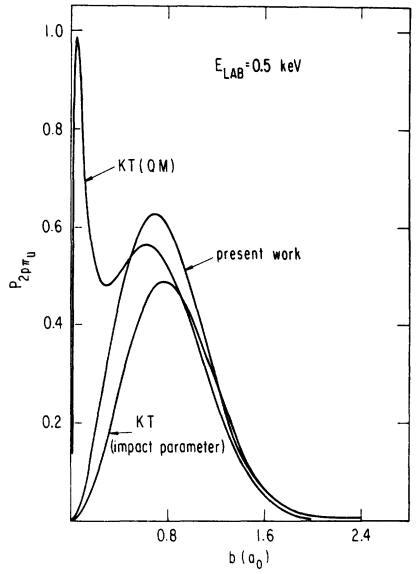

FIG. 3. Comparisons of the $2p_\pi$-excitation probability [see Eq. (3.1)] in the (p^+, H) collision as a function of the impact parameter obtained in the three-state quantum WKB, straight-line eikonal, and impact-parameter approximations.

the exact wave functions. The result agreed with those obtained by Knudson and Thorson[9] and by Rosenthal.[12] The $\Delta_{\alpha\beta}^{(0)}$ term which is expressed in terms of atomic states can be evaluated exactly. We have

$$\Delta_{2p\pi_u, 2p\sigma_u} = i(bv/R)[16\sqrt{2}/81].$$

By subtracting $\Delta_{\alpha\beta}^{(0)}$ from $\Delta_{\alpha\beta}$, we obtain the desired nonadiabatic interaction $J_{\alpha\beta}$. For numerical convenience, we have fitted the nonadiabatic interaction into a simple analytic expression (in

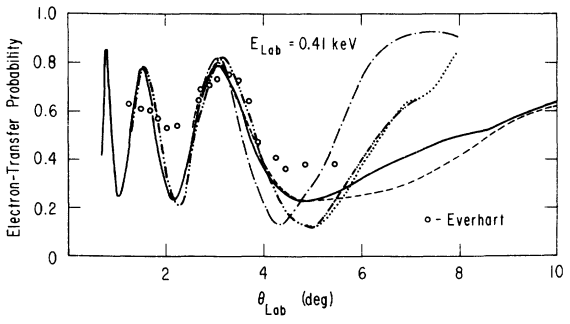

FIG. 4. Comparisons of the angular dependence of the calculated (p^+, H) electron-transfer probability in the three-state straight-line eikonal approximation with that measured by Helbig and Everhart (Ref. 14) and that calculated by McCarroll and Piacentini (dashed line, Ref. 11) and in the two-state straight-line (dash-dot line), angle (dotted line), and classical-trajectory ($O(|\beta|^3 a_0)$) (dash-double dot line) approximations (Ref. 2).

atomic units).

$$J_{2p\pi_u,2p\sigma_u}(R) = +(ibk_2/M_T R^2)\, e^{-1.22R} \times (1+0.9914R+0.9355R^2-0.2757R^3 +0.1486R^4). \quad (2.36)$$

This is the expression that we have used in the calculations reported in the Sec. III.

III. DIFFERENTIAL CROSS SECTIONS IN (p^+,H) COLLISIONS

Calculations of the differential cross sections for the (p^+, H) elastic, electron-transfer, and $2p_\pi$-excitation collisions are carried out in the three-state approximation described in Sec. II. The coupled differential equations, Eq. (2.20), for the $Q_{\alpha\beta}$ are solved using the Bulirsch-Stoer numerical method.[29] In terms of these $Q_{\alpha\beta}$, the transition amplitudes are then obtained by evaluating the integrals given by Eqs. (2.21)–(2.23). To account for the rapid oscillation of the integrand, the integrations over b are split up into two regions. For $b < 7/k\sin\theta$ the Gaussian quadrature is used, and for $bk\sin\theta > 7$ the integrals are evaluated by utilizing the asymptotic expressions of the Bessel functions to recast the integral in the form

$$\sum_j \int_{b_j}^{b_j+\Delta b_j} db_j\,[g_1(qb)\sin(qb)+g_2(qb)\cos(qb)],$$

where the functions g_1 and g_2 are fairly smooth functions. An explicit evaluation of these integrals is then carried out by cubic-polynomic interpolation of g_1 and g_2. The results are presented and compared with experimental measurements and other theoretical results in graphic forms.

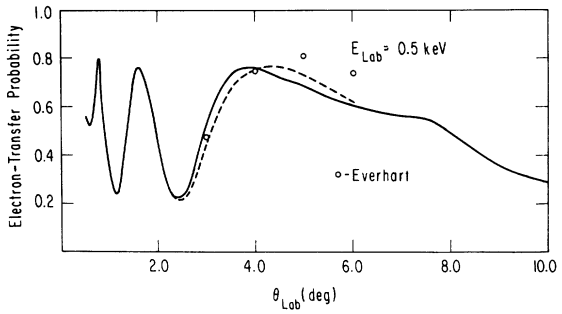

FIG. 5. Comparisons of the angular dependence of the calculated (p^+, H) electron-transfer probability in the three-state straight-line eikonal approximation with that measured by Helbig and Everhart (Ref. 14) and that calculated by Knudson and Thorson (dashed line, Ref. 9).

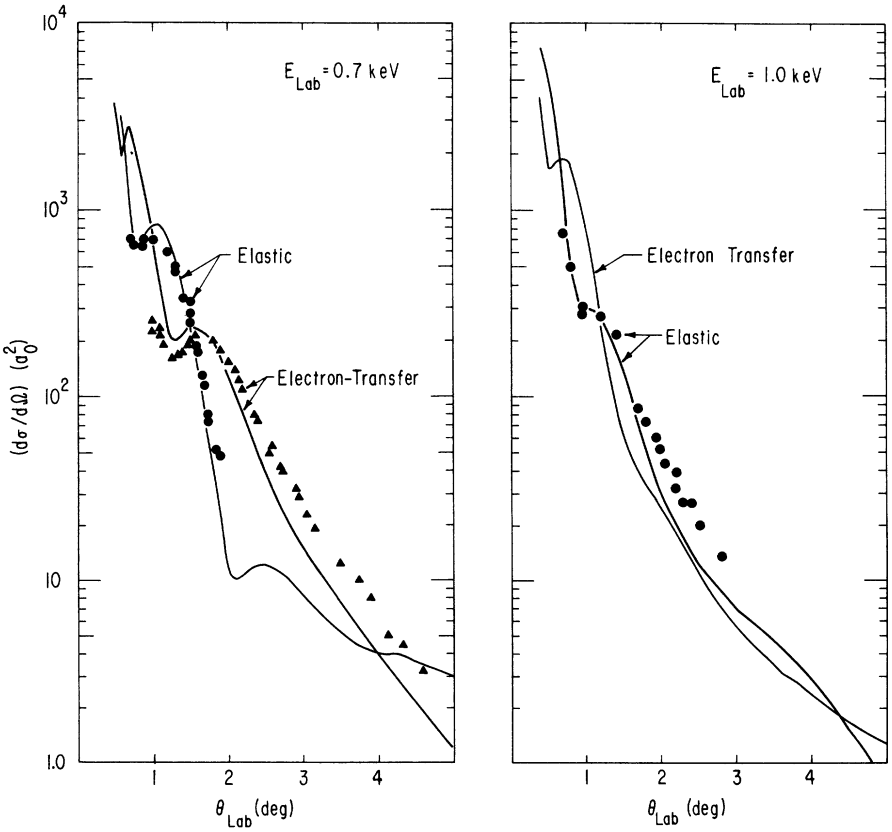

FIG. 6. Comparisons of the angular dependence of the theoretical differential elastic and electron-transfer cross sections obtained in the three-state straight-line eikonal approximation with that measured by Houver *et al.* (Ref. 15). The experimental results are normalized to the theoretical elastic cross section at laboratory angles of 0.8° and 1°, respectively, for energies at 700 and 1000 eV.

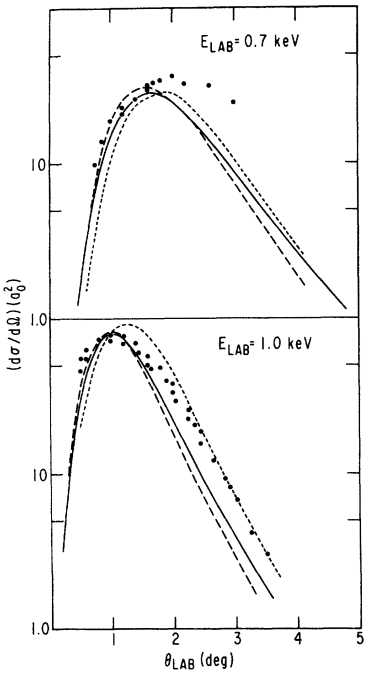

FIG. 7. Comparison of the angular dependence of the theoretical differential $2p_\pi$-excitation cross section obtained in the three-state straight-line eikonal approximation with that of the differential ($n = 2$)-excitation cross section measured by Houver *et al.* (Ref. 15). The magnitude of the experimental data is obtained based on the single-point normalization in Fig. 6. The $2p_\pi$-excitation cross section calculated by McCarroll and Piacentini (Ref. 11) and by McCarroll *et al.* (Ref. 8) are shown as dashed and dotted curves, respectively.

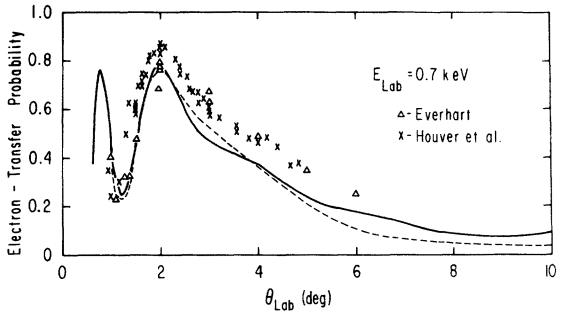

FIG. 8. Comparisons of the angular dependence of the calculated (p^+, H) electron-transfer probability in the three-state straight-line eikonal approximation with that measured by Helbig and Everhart (Ref. 14) and by Houver *et al.* (Ref. 15) and with that calculated by McCarroll and Piacentini (dashed line, Ref. 11) at a laboratory energy of 700 eV.

In Figs. 1 and 2, the angular dependence of the differential elastic, electron-transfer, and $2p_\pi$-excitation cross sections are displayed for two fixed laboratory energies at 410 and 500 eV. The $2p_\pi$-excitation cross section has been calculated by Knudson and Thorson (KT) at these energies.[9] It is seen from Figs. 1 and 2 that their cross section exhibits the same angular dependence, but with slightly smaller magnitude in comparison with the present result.

A comparison of the $2p_\pi$-excitation probability P_{2p_π}:

$$P_{2p_\pi}(b) = \tfrac{1}{4}(v_2/v_1)|Q_{21}^{(u)}|^2 \equiv \tfrac{1}{4}P_{2p\pi_u}, \tag{3.1}$$

which appears in the impact-parameter integral approximation for the total $2p_\pi$-excitation cross section

$$Q_{s,\,et}(1s \to 2p_\pi) \cong 2\pi \int b\,db\,P_{2p_\pi}(b), \tag{3.2}$$

is made in Fig. 3 with those calculated by Knudson and Thorson in the quantum WKB and impact-parameter approximations at an energy of 500 eV. It is apparent that the present straight-line eikonal approximation yields results which are in closer agreement with the quantum WKB results than the impact-parameter approximation.

The electron-transfer probability P_{et} can be obtained from these differential cross sections by the approximate relation

$$P_{et} \cong \frac{\frac{d\sigma_{et}}{d\Omega}(1s \to 1s) + \frac{d\sigma_{et}}{d\Omega}(1s \to 2p_\pi)}{\frac{d\sigma_s}{d\Omega}(1s \to 1s) + \frac{d\sigma_{et}}{d\Omega}(1s \to 1s) + \frac{d\sigma_s}{d\Omega}(1s \to 2p_\pi) + \frac{ds_{et}}{d\Omega}(1s \to 2p_\pi)}. \tag{3.3}$$

Comparisons of the angular dependence of P_{et} with experimental data[14] at these energies are given in Figs. 4 and 5. The damping due to the coupling with the $2p\pi_u$ state is apparent at large angles. We have included in Figs. 4 and 5 the three-state results obtained by McCarroll and Piacentini[11] and by Knudson and Thorson,[9] respectively.

At these relatively low energies, one would expect that the trajectory effect would also be of importance for large-angle collisions. In paper II, we have investigated this trajectory effect in the two-state approximation by following the classical trajectory up to the order $|\beta|^3 a_0$. This result was then compared with those obtained in the straight-line and angle approximations.[2,3,30] For comparison, these results obtained in paper II are

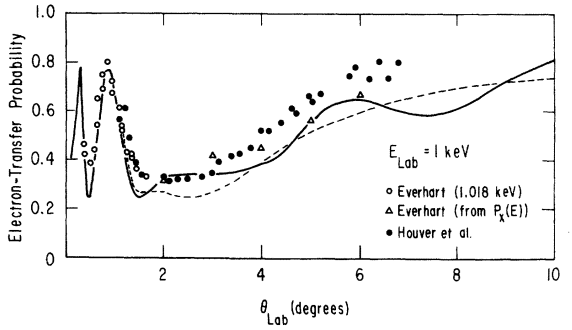

FIG. 9. Comparisons of the angular dependence of the calculated (p^+, H) electron-transfer probability in the three-state straight-line eikonal approximation with that measured by Helbig and Everhart (Ref. 14) and by Houver *et al.* (Ref. 15) and with that calculated by McCarroll and Piacentini (dashed line, Ref. 11) at a laboratory energy of 1 keV.

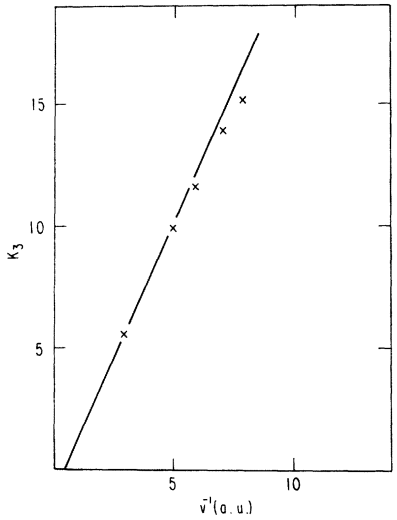

FIG. 10. Comparison of the semiempirical function K_3 [see Eqs. (3.4) and (3.5)] with the theoretical values (denoted by ×) obtained from Eq. (3.15) [see also Eqs. (3.8) and (3.9)] in the three-state straight-line eikonal approximation.

now reproduced in Fig. 4. It is seen that at E_{lab} = 410 eV, the trajectory effect is still appreciable in comparison with effects due to the nonadiabatic coupling with the $2p\pi_u$ state at large angles.

Recently detailed measurements of the differential elastic, electron-transfer, and ($n=2$)-excitation cross sections in the (p^+, H) collision have become available for the first time at slightly higher energies.[15] A comparison of the angular dependence of the theoretical and experimental differential elastic and electron-transfer cross section is made in Fig. 6 at 0.7 and 1 keV laboratory energies. The experimental data are normalized to the theoretical elastic cross section at laboratory angles of 0.8° and 1°, respectively, for energies at 0.7 and 1 keV. At these angles, the elastic cross section goes through dips. The theoretical and experimental data shown in Fig. 6 are in reasonable agreement. The inclusion of the coupling with the $2p\pi_u$ state to allow for the $2p_\pi$ excitation does have a substantial effect on the differential elastic and electron-transfer cross section at the large-angle tails.

Since the measurement also provides the absolute ratios of the differential elastic and ($n=2$)-excitation cross sections, this single-angle normalization in Fig. 6 also determines the absolute magnitude for the differential ($n=2$)-excitation cross section. A comparison of the excitation cross section so normalized with theoretical results is made in Fig. 7. The magnitude of the cross section agrees remarkably well. At these energies, we expect the $2s$ and $2p_\sigma$ excitations to be small so that the ($n=2$) excitation constitutes predominantly the $2p_\pi$ excitation. The magnitude of the total $2p_\pi$-excitation cross section obtained from the differential cross section at these energies is consistent with that measured by Stebbing *et al.*[16] At higher energies, the three-state approximation tends to overestimate the magnitude of the $2p_\pi$-excitation cross section.

The angular dependence of the measured ($n=2$)-excitation cross section is in reasonable agreement with those obtained in the molecular adiabatic state expansion at the small-angle side. For the large-angle tail, the agreement between the theoretical and experimental results is not satisfactory. This is partially owing to the straight-line approximation adopted in the theoretical calculations for the classical trajectories. The trajectory effect is appreciable at these large angles (see Fig. 4). At 1 keV, it is seen from Fig. 7 that the atomic state expansion[8] actually yields an angular dependence which is in better agreement with experiment. This is somewhat surprising since the $2p_\pi$ excitations are induced by the $2p\sigma_u - 2p\pi_u$ rotational coupling at close encounters, where the molecular characters are dominant. One, however, expects that at these energies the additional coupling interaction coming from the translational factors[31] would be of importance. Calculations which include these additional coupling interactions as well as trajectory effects would be instructive.

Comparisons of the theoretical and experimental angular dependence of P_{et} at these energies are given in Figs. 8 and 9. The agreements among the theoretical and experimental results are very reasonable. It is seen from Figs. 8 and 9 together with Figs. 4 and 5 that the angle above which the

damping due to the coupling with the $2p\pi_u$ state becomes appreciable, decreases with increasing energies. In these damping regions, the experimental data in general lie slightly above the theoretical results. In the present calculations, residual oscillations are found to be significant in these damping regions.

As mentioned before, the difference between the two theoretical results in the molecular adiabatic-state expansion obtained by McCarroll and Piacentini and by us comes primarily from the approxition in the momentum transfer.

Shortly after the measurements on the electron-transfer probability first became available, semiempirical equations based on the impact-parameter treatment have been proposed to reproduce the experimental data.[14,18,32] It would be of interest to examine the Lockwood-Everhart semiempirical equation

$$P_{et}^{(c)} \cong K_1(1/v) + K_2(1/v)\sin^2[K_3(1/v)] \tag{3.4}$$

in the framework of the present eikonal coupled equations. In Eq. (3.4), K_1 and K_2 are slowly varying functions of v^{-1}, and K_3 takes the form

$$K_3 = (\pi/h)\langle E_a\rangle v^{-1} - \delta, \tag{3.5}$$

where $\langle E_a\rangle$ is an "effective value" related to the phase integral and δ is a constant phase. For the (p^+, H) system, $\langle E_a\rangle$ and δ have the experimental values of (63.7 ± 1) eV $-A$ and $(0.28 \pm 0.01)\,\pi$, respectively.

From Eqs. (2.14) and (2.19), the elastic scattering amplitude for the gerade and ungerade modes of interactions can be written in the form [i.e., see Eq. (2.29)]

$$T_{00}^{(g)} = [iv_0/(2\pi)^2]\int_0^\infty b\,db\,J_0(k_0 b\sin\theta) \times\{e^{i\Phi_0}[1 - i\Gamma_0^{(g)}(b)] - 1\}, \tag{3.6}$$

$$T_{11}^{(u)} = [iv_1/(2\pi)^2]\int_0^\infty b\,db\,J_0(k_1 b\sin\theta) \times\{e^{i\Phi_1}[1 - i\Gamma_1^{(u)}(b)] - 1\}, \tag{3.7}$$

with

$$1 - i\Gamma_0^{(g)}(b) = 1 - i\sum_{\beta\neq 0}\frac{v_\beta Q_{0\beta}^{(g)}(b)}{v_0} \equiv \eta_g e^{i\gamma_g}, \tag{3.8}$$

$$1 - i\Gamma_1^{(u)}(b) = 1 - i\sum_{\beta\neq 0}\frac{v_\beta Q_{0\beta}^{(u)}(b)}{v_1} \equiv \eta_u e^{i\gamma_u}, \tag{3.9}$$

where the expressions for $\Gamma_0^{(g)}$ and $\Gamma_1^{(u)}$ would be slightly modified for noncylindrical interactions.[24] In the impact-parameter approximation, the total resonant electron-transfer cross section

$$\sigma_{et}(1s \to 1s) = (2\pi)^4 M_r^2 \int |\tfrac{1}{2}(T_{00}^{(g)} - T_{11}^{(u)})|^2\, d\Omega \tag{3.10}$$

reduces to

$$\sigma_{et}(1s \to 1s) = 2\pi\int b\,db\,P_{et}^{(c)}(1s - 1s), \tag{3.11}$$

with

$$P_{et}^{(c)} = \tfrac{1}{4}\,|[e^{i\Phi_0}(1 - i\Gamma_0^{(g)}) - 1] - [e^{i\Phi_1}(1 - i\Gamma_1^{(u)}) - 1]|^2 . \tag{3.12}$$

Substitution of Eqs. (3.8) and (3.9) into Eq. (3.12) yields Eq. (3.4) with

$$K_1(1/v) = \tfrac{1}{4}(\eta_g - \eta_u)^2, \tag{3.13}$$

$$K_2(1/v) = \eta_g\eta_u, \tag{3.14}$$

$$K_3(1/v) = \tfrac{1}{2}(\Phi_0 - \Phi_1) + \tfrac{1}{2}(\gamma_g - \gamma_u). \tag{3.15}$$

A comparison of Eq. (3.5) with experimental values for $\langle E_a\rangle$ and δ with Eq. (3.15) in the three-state approximation is given in Fig. 10. The agreement is reasonably good. Deviations from the straight line are found in the three-state approximation at low velocities. The three-state values for K_1 and K_2 are slowly varying with v^{-1} and stay closely to zero and unity, respectively.

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