Production of negative hydrogen ions in neutral H + H collisions

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(Received 30 November 1989)

A formulation of collision theory is presented to analyze the process by which H^- and H^+ ions are produced from charge exchange in $H(1s)+H(1s)$ and $H(2s)+H(1s)$ collisions in the energy range of 100 eV to 100 keV. A simple closure approximation to the full Green's function allows an analytic evaluation of the amplitudes. The anomalously large cross sections observed experimentally around 0.5 keV, one maximum near 10–20 keV, and the interference feature around 2–4 keV are reproduced, respectively, in the theory by the excitation-exchange amplitude, the direct amplitude, and their interference. The same theoretical procedure is employed in the treatment of both the $1s$ and $2s$ initial projectile states, providing a unified picture of the H+H collision system at low and intermediate energies.

I. INTRODUCTION

Elementary estimates[1] based on the notion of adiabaticity suggest that the cross section for chemi-ionization in the collision of two ground-state hydrogen atoms

$$H(1s)+H(1s)\rightarrow H^+ + H^- \quad (1a)$$

$$\rightarrow H^- + H^+ \quad (1b)$$

will pass through a maximum value at an energy of the order 10 keV and decrease rapidly at lower energies. More detailed theories[2–7] are in satisfactory agreement with experiments[8–10] in showing a cross section with a maximum value of about 2×10^{-17} cm^2 occurring at an impact energy near 10 keV. The calculations also reproduce the measured high-energy behavior and the rapid decrease down to an energy of 1 keV. In the multistate calculations of Borondo, Martin, and Yanez[7] cross section at 1 keV in the $H(1s)+H(1s)$ initial channel is less than 10^{-18} cm^2 and it appears to be falling to negligible values. In marked contrast to elementary considerations and to the calculations of Borondo, Martin, and Yanez[7] recent experimental measurements[10] yield a cross section which does not continue to fall at energies below 1 keV but instead levels off and oscillates slowly about a mean of 10^{-18} cm^2 down to 63 eV, the lowest energy at which data were obtained. A similar behavior is found for oscillations of H with H_2.[10,11]

Measurements have also been carried out on the charge-transfer reactions of metastable $H(2s)$ atoms in collisions with ground-state $H(1s)$ atoms, one[12] in the low-energy region around 0.5 keV with cross-section value of 10^{-14} cm^2 and another[13] around 5–20 keV, with the peak value of 2×10^{-17} cm^2. There is a gap in the available data in the region of 1–5 keV. Thus the existing measurements for the metastable state channel

$$H(2s)+H(1s)\rightarrow H^+ + H^- \quad (2a)$$

$$\rightarrow H^- + H^+ \quad (2b)$$

seem to suggest two apparently disjoint mechanisms in the two energy regions, with two orders of magnitude difference in the cross sections.

The neutralization process, which is the inverse of (1) and (2), has also been studied extensively in the past[14–16] and several theoretical calculations have been carried out.[17–19] Because of the dominance of the component that leads to the metastable $2s$ and higher excited-state final channels, it is possible to study reaction (2) using these inverse scattering data, but difficult to extract information on reaction (1). No detailed theoretical explanation of the data for (1) in the region $E<2$ keV currently exists.

We report here an exploratory calculation of the processes (1) and (2) using a formulation of collision theories based on distorted-wave theory[20–22] (DWT) in an attempt to provide a unified, albeit qualitative understanding of the processes. Our analysis suggests that the excitation-exchange amplitude T^C that connects the initial and final states by coupling to the intermediate excitation and ionization channels plays an important role at low energies, and that an interference between the direct Born amplitude T^B and the indirect correction amplitude T^C is responsible for the structure observed in the 1–4 keV region for processes (1) and (2). Thus the cross-section behavior observed by Gealy and Van Zyl[10] may not be uncommon in heavy-particle excitation and ionization processes.

II. DISTORTED-WAVE THEORY

We schematically define the processes (1) and (2) as (Fig. 1)

$$(a+e_1)^*+(b+e_2)\rightarrow a+(e_1+e_2+b) \quad (3a)$$

$$\rightarrow (a+e_1+e_2)+b\ . \quad (3b)$$

In the following we denote atoms $A=(a+e_1)$, $B=(b+e_2)$, $C=(e_1+e_2+b)$, and $C'=(a+e_1+e_2)$, and refer to (3a) and (3b) as charge-exchange modes (a) and (b), respectively. The system Hamiltonian may be decomposed according to

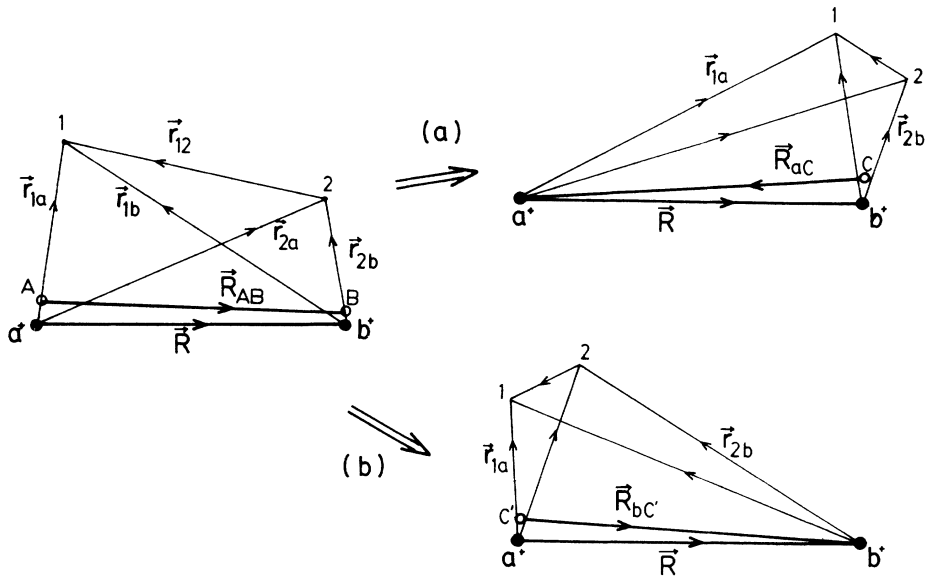

FIG. 1. Various combinations of coordinate systems used in the present calculation are defined for the states before and after the charge exchange. Modes (a) and (b) are also indicated. Different sets of coordinates are needed to treat the rearrangement collisions; for mode (a) $\mathbf{R}_i=\mathbf{R}_{AB}$ and $\mathbf{R}_f=\mathbf{R}_{aC}$, while for mode (b), $\mathbf{R}_f=-\mathbf{R}_{bC'}$.

$$H=H_c+V_c\ ,$$
$$(H-E)\Psi=0\ , \tag{4}$$

where c is a label identifying the scattering channel. The channel eigenvectors satisfy the equation

$$H_c\Phi_{(c,n)}=E\Phi_{(c,n)}\ , \tag{5}$$

where n denotes collectively the internal states of the atoms in channel c. If the incident wave is in channel c, the state vector describing the outgoing scattered wave is

$$\Psi^+_{(c,i)}=\Phi_{(c,i)}+\frac{1}{E+i\epsilon-H_c}V_c\Psi^+_{(c,i)} \tag{6a}$$

or

$$\Psi^+_{(c,i)}=\Phi_{(c,i)}+\frac{1}{E+i\epsilon-H}V_c\Phi_{(c,i)}\ , \tag{6b}$$

where E is the total energy of the system. In the following, we simplify the notation by setting collectively $i\equiv(c,i)$ and $f\equiv(c',f)$.

The transition matrix element for scattering from the initial state i of channel c to a final state f of a rearrangement channel c' is given in the "prior" or "post" form as

$$T_{fi}^{\rm prior}=(\Psi_f^-|V_i|\Phi_i)\ , \tag{7a}$$
$$T_{fi}^{\rm post}=(\Phi_f|V_f|\Psi_i^+)\ . \tag{7b}$$

As is well known, these two forms are related by analytic continuation and are equivalent on the energy shell. Equations (7) may be written alternatively in the form[20–22]

$$T_{fi}^{\rm prior}=(\Psi_f^-|V_i-U_i|\chi_i^+)\ , \tag{8a}$$
$$T_{fi}^{\rm post}=(\chi_f^-|V_f-U_f|\Psi_i^+)\ , \tag{8b}$$

where

$$\chi_i^+=\Phi_i+\frac{1}{E+i\epsilon-H_i-U_i}U_i\Phi_i\ , \tag{9a}$$
$$\chi_f^-=\Phi_f+\frac{1}{E-i\epsilon-H_f-U_f}U_f\Phi_f\ . \tag{9b}$$

Then

$$\Psi_i^+=\chi_i^+\frac{1}{E+i\epsilon-H}(V_i-U_i)\chi_i^+\ , \tag{10a}$$
$$\Psi_f^-=\chi_f^-+\frac{1}{E-i\epsilon-H}(V_f-U_f)\chi_f^-\ , \tag{10b}$$

and T_{fi} may be written in the equivalent prior form as[20]

$$T_{fi}^{\rm prior}=(\chi_f^-|V_i-U_i|\chi_i^+)+\left[\chi_f^-\left|(V_f-U_f)\frac{1}{E+i\epsilon-H}(V_i-U_i)\right|\chi_i^+\right]$$
$$=T_{fi}^{{\rm DWB}i}+T_{fi}^{\rm DWC}\ , \tag{11}$$

where DWBi denotes the distorted-wave Born approximation in the prior form and DWC is for the distorted-wave correction amplitude. The post form is defined as

$$T_{fi}^{\text{post}}=(\chi_f^-|V_f-U_f|\chi_i^+)+\left[\chi_f^-\left|(V_f-U_f)\frac{1}{E+i\epsilon-H}(V_i-U_i)\right|\chi_i^+\right]$$
$$=T_{fi}^{\text{DWB}f}+T_{fi}^{\text{DWC}}\ . \tag{12}$$

Equations (11) and (12) are different only in the direct amplitudes DWB, while the indirect term DWC is the same in both cases. In rearrangement collisions of the type (3) of interest here, $H_c\neq H_{c'}$, and in general $T^{\text{DWB}i}\neq T^{\text{DWB}f}$ when further approximations are introduced in the evaluation of these amplitudes. If $\mathbf{K}_i$ is the initial relative momentum of A and B, and $\mathbf{K}_f$ the final relative momentum of a and C in (3) or $b+C'$, the cross section is given by

$$\sigma_{fi}=g\left(\frac{\mathcal{M}}{2\pi}\right)\frac{4\pi}{2K_i^2}\int_{Q_{\min}}^{Q_{\max}}|T_{fi}|^2Q\,dQ\ , \tag{13}$$

where $\mathcal{M}$ is the reduced mass, $\mathcal{M}=M_AM_B/(M_A+M_B)$, $\mathbf{Q}=\mathbf{K}_i-\mathbf{K}_f$, $Q_{\max}$ and $Q_{\min}$ are the maximum and minimum values of Q, and g is the probability that the two atoms approach in the appropriate symmetry state. For reactions (1) and (2), only the singlet state of the two electrons is allowed, with $g=0.25$.

As described schematically in Eq. (3), suppose a beam of particles A of initial relative kinetic energy E_i is incident upon a gas of stationary particles B. If e_i is the internal energy of A and B and e_f is the internal energy of the rearranged particles a and C in (3) or $b+C'$, the final energy of the relative motion $E_f=E_i+e_i-e_f$. The initial and final momenta satisfy $E_i=\hbar^2K_i^2/2\mathcal{M}$ and $E_f=\hbar^2K_f^2/2\mathcal{M}$ and $Q_{\min}=\mathcal{M}(e_f-e_i)/K_i$. The $Q_{\max}$ may be taken to be infinite.

For the rearrangement collision (3), we set, in obvious notation,

$$V_i=(V_{1b}+V_{12})+(V_{ab}+V_{2a})\equiv V_i'+V_i'' \tag{14}$$

and

$$V_f=V_{1a}+(V_{2a}+V_{ab})\equiv V_f'+V_f''\ . \tag{15}$$

Note that $V_i''=V_f''\equiv V''$. With the choice

$$U_i=V''=U_f\ , \tag{16}$$

we have

$$T_{fi}=(\chi_f^-|V_{i,f}'|\chi_i^+)+\left[\chi_f^-\left|V_f'\frac{1}{E+i\epsilon-H}V_i'\right|\chi_i^+\right]$$
$$=T_{fi}^{Bi,f}+T_{fi}^{C}\ . \tag{17}$$

Approximate evaluation of the first term of Eq. (17)

$$T_{fi}^{Bi,f}=(\chi_f^-|V_{i,f}'|\chi_i^+) \tag{18}$$

has been carried out previously, with different choices for χ U.[3-5] We performed a crude estimate by replacing the distorted waves with their undistorted plane-wave forms

$$\chi_f^-\sim\exp(-i\mathbf{K}_f\cdot\mathbf{R}_f)\psi_{\text{H}^-}(\mathbf{r}_{1b},\mathbf{r}_{2b})\equiv\Phi_f\ , \tag{19a}$$

$$\chi_i^+\sim\exp(+i\mathbf{K}_i\cdot\mathbf{R}_i)\psi_{\text{H}}(\mathbf{r}_{1a})\psi_{\text{H}}(\mathbf{r}_{2b})\equiv\Phi_i\ , \tag{19b}$$

where $\mathbf{R}_f$ is the vector joining H^+ to the center of mass of H^-, $\mathbf{R}_i$ is the vector joining the centers of mass of the two neutral hydrogen atoms, as shown in Fig. 1, $\psi_{\text{H}}(\mathbf{r})$ is the $\text{H}(1s)$ wave function and $\psi_{\text{H}^-}(\mathbf{r}_{1b},\mathbf{r}_{2b})$ is the $\text{H}^-(1s^2)$ wave function for which we adopted the representation[12]

$$\psi_{\text{H}^-}(\mathbf{r}_{1b},\mathbf{r}_{2b})\cong\psi_{\text{H}}(\mathbf{r}_{1b})\phi(\mathbf{r}_{2b})\ . \tag{20}$$

In constructing the H^- wave function ψ_{H^-} as an unsymmetrized product, we have implicitly assumed that one of the electrons acts as a spectator of the transition in which the other electron is captured. In (20), $\phi(\mathbf{r})$ is the normalized form[13]

$$\phi(\mathbf{r})=N_xr^{-1}[\exp(-\gamma r)-\exp(-\delta r)]\ , \tag{21}$$

with $\gamma=0.235$ and $\delta=0.913$. (These constants are slightly different from the ones used previously, but our results are not too sensitive to them.)

An accurate evaluation of the second term of the transition amplitude (17) is a formidable task. To explore whether or not the inclusion of the second term can reproduce the experimental behavior, we make some severe approximations, especially on the Green's function $G^+=(E+i\epsilon-H)^{-1}$, which appears in T_{fi}^C. Formally, G^+ can be expressed as a sum(s) over the complete spectrum of H with appropriate energy denominator $(E-E_n)^{-1}$. Consistent with the view that one electron is a passive spectator, we represent the spectator electron 2 for (3a), e.g., by the ground-state wave functions. We also replace the denominator by $E-\bar{E}$, where $\bar{E}$ is some mean energy which may depend on the collision energy. Finally, the active electron is represented in G by a complete set of states, all weighted by the same factor $(E-\bar{E})^{-1}$. The summations over the active electron wave functions and the nuclear core wave functions can then be carried out explicitly. We obtain

$$\frac{1}{E+i\epsilon-H}\sim\frac{1}{E-\bar{E}}\psi_{\text{H}}(\mathbf{r}_{2b})\psi_{\text{H}}^*(\mathbf{r}_{2b}')\delta(\mathbf{r}_{1a}-\mathbf{r}_{1a}')(2\pi)^{-3}\int d\mathbf{K}'\exp[i\mathbf{K}'\cdot(\mathbf{R}_i-\mathbf{R}_i')]-i\pi\delta(E-H)\ . \tag{22}$$

A. 1s initial ground-state channel

For the ground-state channel, (3a) and (3b) give identical amplitudes. The direct amplitude for the process (1) can be evaluated analytically for the special choice (16) for the distortion potential U and when the effect of distortion on the

wave functions χ is neglected. Thus we have simply $\chi \cong \Phi$ in this simple approximation, and obtain

$$T_{fi}^{Bf} = -(4\pi)^2 \pi^{-1/2} N_x \frac{1}{1+Q^2+4k^2} \left[\frac{1}{\gamma^2+Q^2} - \frac{1}{\delta^2+Q^2} \right], \tag{23a}$$

$$T_{fi}^{Bi} = -(4\pi)^2 \pi^{-1/2} N_x \frac{2}{(1+Q^2+4k^2)^2} \left\{ \frac{1}{(2+\gamma)^2+Q^2} - \frac{1}{(\delta+2)^2+Q^2} + \frac{1}{Q} \left[\tan^{-1}\left[\frac{Q}{2+\gamma} \right] - \tan^{-1}\left[\frac{Q}{2+\delta} \right] \right] \right\}, \tag{23b}$$

where $k \equiv (m/M)K = K/1840$. Finally, the average amplitude is defined as

$$T_{fi}^{BA} \equiv \tfrac{1}{2}(T_{fi}^{Bi} + T_{fi}^{Bf}) . \tag{24}$$

We have also evaluated numerically the alternative form of T_{fi}^{B} involving the full V_i and V_f of (14) and (15), and obtained matrix elements that differed by a few percent near the maximum around 2 keV. The close agreement occurs because of the dominance of V'' in the Born amplitudes.

The maximum for the full Born cross section occurs at $E_i \cong E = 2$ keV rather than at 10 keV where experiment shows a peak. We see here a defect of the close-coupling method at high energies; many channels are needed merely to take out the effect of V''.

For the excitation-exchange amplitude, we neglect the damping term in the Green's function (22), and also the effect of the distortion potentials U on the initial- and final-state wave functions. Then after considerable analysis we obtain the remarkably simple expression

$$T_{fi}^{C} = \left\langle \chi_f^- \middle| V_f' \frac{1}{E+i\epsilon-H} V_i' \middle| \chi_i^+ \right\rangle$$

$$\approx (4\pi)^2 \pi^{-1/2} N_x \frac{1}{E-\bar{E}} \frac{1}{1+Q^2+4k^2} \left\{ \frac{1}{(\gamma+2)^2+Q^2} - \frac{1}{(\delta+2)^2+Q^2} + \frac{1}{Q} \left[\tan^{-1}\left[\frac{Q}{2+\gamma} \right] - \tan^{-1}\left[\frac{Q}{2+\delta} \right] \right] \right\} \tag{25}$$

and thus

$$T_{fi} \cong T_{fi}^{BA} + T_{fi}^{C} .$$

B. 2s initial metastable state channel

The amplitude for the case in which the metastable H(2s) beam is incident on the H(1s) targets is derived in the same approximation as that used in the case with the 1s initial state. Modes (3a) and (3b) give different amplitudes. For mode (a) of (3a), we have in the post form

$$T_{fi'}^{B(a)} = -N_e N_x (4\pi)^2 [(\tfrac{1}{4}+Q^2+4k^2)^{-1} - (\tfrac{1}{4}+Q^2+4k^2)^{-2}/2][(\gamma^2+Q^2)^{-1} - (\delta^2+Q^2)^{-1}] , \tag{26}$$

where we denote the initial excited-state channel by i', i.e., $i' \equiv (i', c)$. Furthermore,

$$T_{fi'}^{C(a)} = \frac{1}{E-\bar{E}} N_e N_x (4\pi)^2 [(\tfrac{1}{4}+Q^2+4k^2)^{-1} - (\tfrac{1}{4}+Q^2+4k^2)^{-2}/2]$$
$$\times \left[[(2+\gamma)^2+Q^2]^{-1} - [(2+\delta)^2+Q^2]^{-1} + \frac{1}{Q} \{ \tan^{-1}[Q/(2+\gamma)] - \tan^{-1}[Q/(2+\delta)] \}/2 \right] . \tag{27}$$

For mode (b) in (3b), we take the "post" form, with $\tilde{V}_f' = V_{2b}$, and obtain

$$T_{fi'}^{B(b)} = -N_e N_x N_0 (4\pi)^3 (1+Q^2)^{-1} 2 (1+Q^2+4k^2)^{-1} [(\gamma+0.5)^{-2} - (\delta+0.5)^{-2} - (\gamma+0.5)^{-3} + (\delta+0.5)^{-3}] \tag{28}$$

and

$$T_{fi'}^{C(b)} = \frac{1}{E-\bar{E}} (4\pi)^3 N_e N_x N_0 (1+Q^2+4k^2)^{-1} (4+Q^2)^{-4} [(4+Q^2)^3 + 3(4+Q^2)^2 + (6-Q^2/2)(4+Q^2) + 6(4-Q^2)]$$
$$\times [(\gamma+0.5)^{-2} - (\delta+0.5)^{-2} - (\gamma+0.5)^{-3} + (\delta+0.5)^{-3}] , \tag{29}$$

where $\tilde{V}_i' = V_{2b}$ was used, and $N_0 = 1/\sqrt{\pi}$, $N_e = 1/\sqrt{8\pi}$.

The cross section is given by Eq. (13) with $e_{i'} \cong -\frac{1}{8}$ a.u., $e_f = -\frac{1}{36}$ a.u., and where the factor of $\frac{1}{4}$ was again included to account for the exclusion of the triplet state in the process (2).

Finally, because of the symmetry between modes (a) and (b), we set

$$T_{fi'}^{B} = (T_{fi'}^{B(a)} + T_{fi'}^{B(b)})/\sqrt{2} ,$$
$$T_{fi'}^{C} = (T_{fi'}^{C(a)} + T_{fi'}^{C(b)})/\sqrt{2} , \tag{30}$$

and

$$T_{fi'} \equiv T^B_{fi'} + T^C_{fi'} \ . \tag{31}$$

III. RESULTS

A. 1s initial-state channel

The cross sections obtained with the amplitudes (24) and (25) are shown in Figs. 2 and 3. They have the same qualitative structure as previous calculations;[3-7] that is, T^{BA} gives a maximum cross section of the order of 10^{-16} cm^2 at the center-of-mass energy of near 10 keV, and a rapid falloff on both sides of the peak. The difference from the cross sections calculated by Janev and Salin[3] arises from their retention of the electron-nucleus interaction in the potential V'. The cross section with T^B alone continues to decrease rapidly at low energies. Therefore the marked change in the behavior at 1 keV seen experimentally must be reflected in the second term of Eq. (17). We evaluated the cross-section expression Eq. (13) by numerical quadrature using a small mesh in Q. Most of the contributions come from the region close to $Q_{\min}$. The cross sections obtained with T^C alone, omitting the first T^B of Eq. (17) and setting $\Delta E \equiv E - \bar{E} = 1.5$ and 1.0 a.u., are also shown in Fig. 2. They are similar in shape to those obtained with T^B, but the maximum is shifted to the lower energy of about 2 keV in the center-of-mass system. $E \equiv E_{\text{c.m.}} = E_{\text{lab}}/2$, where E_{lab} is the impact energy.

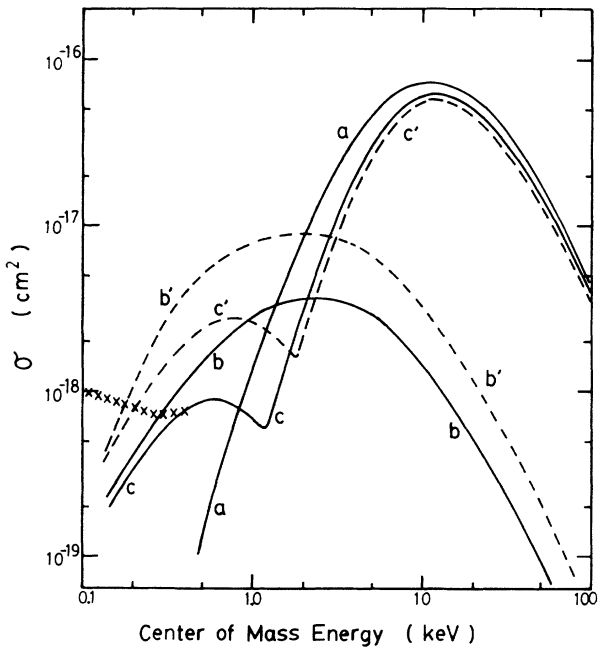

FIG. 2. Theoretical cross sections for the process $H+H \rightarrow H^+ + H^-$ as functions of the center-of-mass energy E, calculated from the "post" form of T^B with V' (curve a), from T^C with $\Delta E = 1.5$ a.u. (curve b) and 1.0 a.u. (curve b'), and from the total $T = T^B + T^C$, (curve c) and (curve c'). The crosses correspond to the result obtained with the E-dependent ΔE, as indicated in Fig. 3.

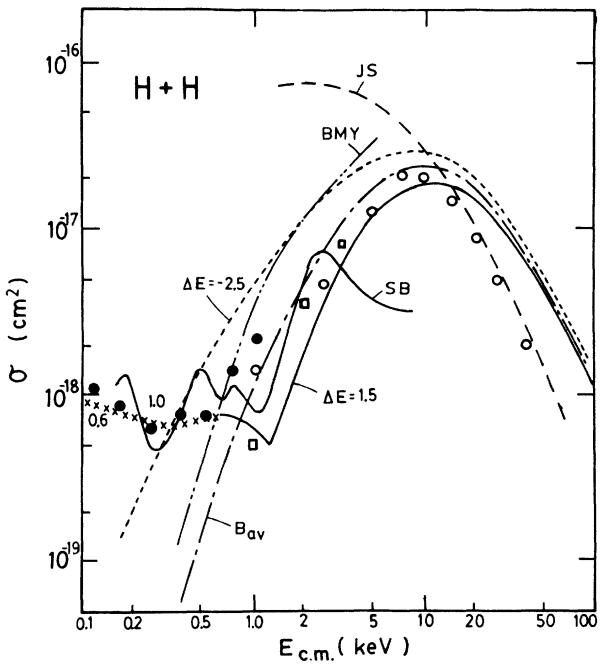

FIG. 3. Theoretical charge-exchange cross sections for the initial ground-state channel are shown for T^{BA} of Eq. (24) and full cross sections corresponding to two different values of ΔE. Below 0.5 keV, the cross sections do not depend on the sign of ΔE. The results of Borondo, Martin, and Yanez (BMY) (Ref. 7) (—··—) are similar to T^{BA} for $E \lesssim 5$ keV and the result of Janev and Salin (JS) (Refs. 2 and 3) are similar to T^{BA} for $E \gtrsim 10$ keV. The result of Shingal and Bransden (SB) is also given. The experimental data are those of McClure (□), Hill *et al.* (○), and Gealy and Van Zyl (●). The crossed curves (×) are obtained with the variations of ΔE with E, as indicated in the figure.

When both terms are retained, the two amplitudes interfere. The high-energy behavior is qualitatively unchanged, but, after passing through the maximum near 10 keV, the downward trend in the cross section at lower energies is interrupted by a minimum and a small maximum before resuming its decline at $E = 0.1$ keV. The decline can be delayed by postulating that $E - \bar{E}$ varies slowly with the relative energy. If we allow ΔE to vary from 1.5 a.u. at 2 keV to 0.6 a.u. at 0.1 keV, we obtain cross sections whose shape and magnitude are similar to the observed values,[8-10] as we show in Fig. 3, in which the theoretical and measured[10] cross sections are presented as functions of the c.m. energy. Figure 3 also shows the effect of a negative value of ΔE; a negative value results in a constructive interference at energies between 1 and 3 keV. Below 1 keV, the cross section is unaffected by the change in the sign of ΔE because the T^B contribution is very small there. The positive values of ΔE that are required to reproduce the data are about 1 a.u., indicating that the change in the kinetic energy of relative motion during the collision may be a critical feature of the process.

The multichannel impact-parameter molecular calculations of Borondo, Martin, and Yanez[7] yield cross sections

which decrease monotonically and rapidly on the low-energy sides of the maximum. Ermolaev[18] has recently reported close-coupling impact-parameter calculations based on an atomic state expansion. His discussion deals with the reverse process to reactions (1) and (2), in which capture into the ground-state atoms is a minor channel. Cross sections for the process (2) may be extracted from his data, but the values for process (1) are too small and probably unreliable numerically. Nevertheless, the theoretical result corresponding to channel (1) appears to be inconsistent with the calculations of Borondo, Martin, and Yanez[7] but more in line with the experiments of Gealy and Van Zyl.[10] Shingal and Bransden[19] have also carried out close-coupling impact-parameter calculations on the neutralization reaction, from which cross sections for reactions (1) and (2) can be deduced. The calculations, carried out for impact energies from 150 eV to 10 keV, may not have converged but do indeed produce a cross section that levels off at energies below 5 keV and oscillates about a mean of $(2-3)\times10^{-18}$ cm^2. Our calculation of T^B with V_i and V_f suggests that the slow convergence of the close-coupling calculations at high energies may be due in part to the large effect of the interaction term V'' which must be canceled if the high velocity behavior of the cross section is to be correctly reproduced. The close-coupling calculations may suffer also because they lack the flexibility to allow T^B and T^C to vary differently with energy.

The comparison of our calculations with the experimental data does not definitely establish the sign of ΔE, though there is a strong preference for positive values.

B. 2s metastable state channel

We present in Fig. 4 the cross sections obtained with $T^{B(a)}$, $T^{B(b)}$, T^B, and also with the amplitude $T^{B(b)i}$ which corresponds to the "prior" form with $V_i'=V_{2a}$. Mode (b) dominates at low $E\lesssim1$ keV and mode (a) at $E\gtrsim10$ keV. The amplitude $T^{B(b)i}$ is given by

$$T_{fi'}^{B(b)i}=-(4\pi)^3N_xN_eN_02(1+Q^2)^{-1}(1+Q^2+4k^2)^{-2}\times[(\gamma+0.5)^{-2}-(\delta+0.5)^{-2}-(\gamma+0.5)^{-3}+(\delta+0.5)^{-3}]\,. \quad (32)$$

The second part of the full amplitudes $T^{C(a)}$ and $T^{C(b)}$ are evaluated with $\Delta E=0.5$ a.u. They are very large, especially at small energies, $E\lesssim5$ keV. Figure 5 contains the final cross sections for $T_{fi'}^B$ and $T_{fi'}^C$ given by Eqs. (30) and (31), together with the experimental data. The experimental points in the 10-keV region are those of Hill,

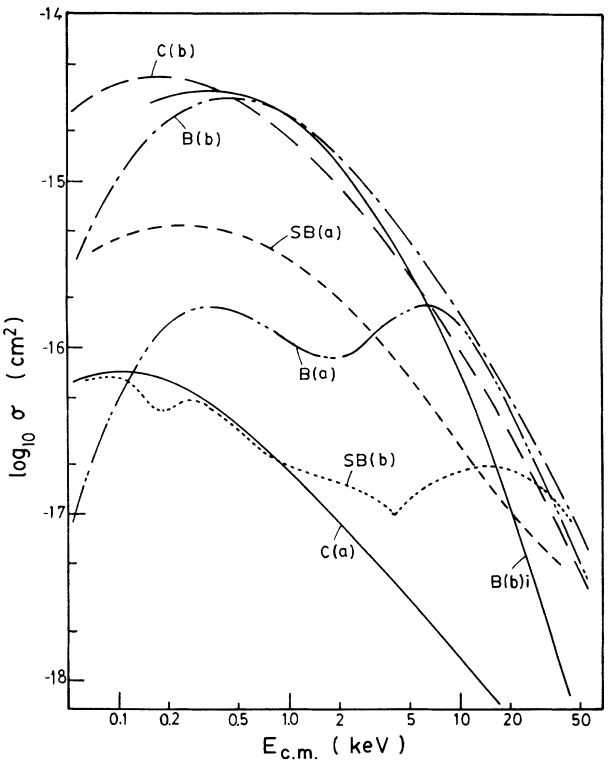

FIG. 4. Charge-exchange cross sections for the metastable initial state are shown which are obtained by the different approximations as discussed in Secs. II and III. The cross sections evaluated with the individual amplitudes T^B and T^C are shown separately, where $\Delta E=0.5$ a.u. was used. The results of Shingal and Bransden (Ref. 19) are also given [SB(a) and SB(b)], which correspond to processes (2a) and (2b).

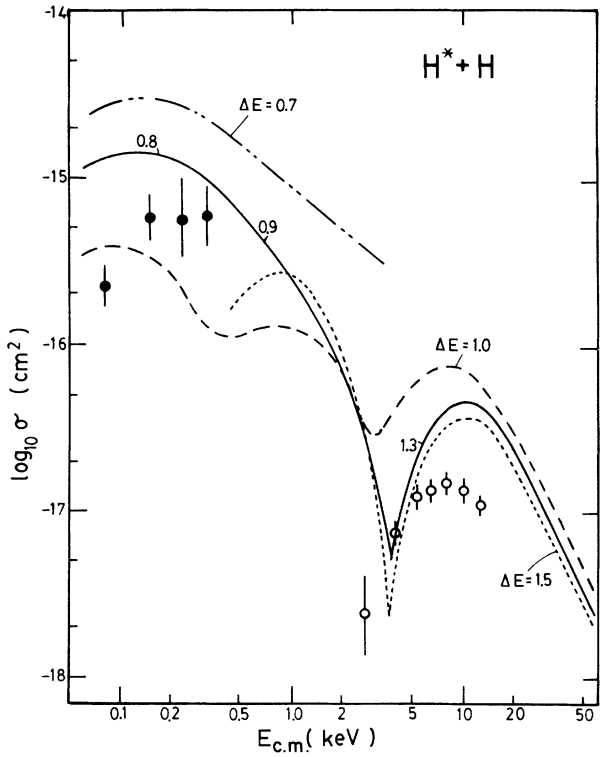

FIG. 5. The total charge-exchange cross section for the initial metastable (2s) state channel is shown, in which T^B and T^C are combined and their interference is included. The curves are labeled by the values of ΔE. The experimental data are from Fussen *et al.* (Ref. 13), Hill, Geddes, and Gilbody (Ref. 9), and Claeys, Brouillard, and Wassenhove (Ref. 12). The dip around $E\cong4$ keV persists in all the approximations examined here, with $\Delta E\gtrsim0.4$ a.u., but disappears for negative ΔE. The solid curve is obtained with varying ΔE, as indicated in the figure.

Geddes, and Gilbody[9] and Claeys, Brouillard, and Wassenhove[12] and near $E \cong 0.1$ keV are those of Fussen *et al.*[13] The two sets of data seem disjoint, but the present calculation connects them nicely, showing that if $\Delta E > 0$ a sharp dip near $E \cong 4$ keV is caused by destructive interference between T^B and T^C. As discussed earlier, a similarly sharp turnup in the cross section was seen in the H(1s)+H(1s) case at $E \cong 2$ keV, again as a result of a strong destructive interference between the two amplitudes T^B and T^C.

The present theory also predicts a sharp increase in the cross section for the H(2s)+H(1s) channel by as much as two orders of magnitude as E decreases from 5 to 0.5 keV. When the sign of $\Delta E = E - \bar{E}$ is reversed, the dip disappears. No data are available in this region; new experiments in the $E = 2$ keV region could be a critical test of some of the approximations introduced here, as the cross section is sensitive to the sign of ΔE in this region. An experiment in the energy region around $E = 4$ keV will determine the sign of ΔE as the predicted cross sections with different signs can differ from each other by two orders of magnitude.

By contrast, the low-energy behavior of the cross section at $E \lesssim 1.0$ keV is nearly independent of the sign of ΔE, but depends more sensitively upon the variation of ΔE as a function of E. Since ΔE could decrease from $\Delta E \gtrsim 0.5$ a.u. to near zero as E goes from $E = 1$ to 0.1 keV, the cross section may increase (the solid curve in Fig. 5), before starting to go down again at very low E. This behavior is again similar to that found in the H(1s)+H(1s) system. The overall feature of the data is reproduced by the present calculation when the actual E dependence of the average excitation energy E is taken within reasonable range.

It is rather remarkable that the cross sections calculated for modes (a) and (b), as shown in Fig. 4, are similar to the values obtained by Shingal and Bransden. The overall features of the cross sections are again well reproduced by the amplitudes $(T^{B(a)} + T^{C(a)})$ and $(T^{B(b)} + T^{C(b)})$, when a suitable value for ΔE is chosen. For mode (a), the two contributions from B(a) and C(a) cross sections more or less add, while for mode (b), they subtract from each other and result in a small fluctuating cross section.

Of course, the final cross section in Fig. 5 was obtained by a coherent sum of these two processes, which, if $\Delta E > 0$, shows a destructive interference at the energies around 4 keV.

IV. CONCLUSION

The recent experimental data[8–13] on the H^- production reactions (1) and (2) at low energies are unexpected in showing large values of the cross sections. Our analysis suggests that the cross-section behavior can be understood as the result of an interference between a direct exchange and excitation-exchange amplitudes and may be a characteristic of low-energy atom-atom excitation and ionization collisions. Since we have applied the same theoretical procedure for reactions (1) and (2), with the same approximations on G and V, we may conclude that the fit for (2) provides a qualitatively model-independent explanation of (1).

Our results are qualitatively consistent with those obtained by extensive close-coupling calculations incorporating translational factors.[19] Many of the approximations we have made could be improved by more extensive computations, in particular, in the evaluation of the Green's function[20–22] G and distorted initial- and final-state wave functions. We believe that our formulation offers an alternative approach to the calculation of atomic collision cross sections.

ACKNOWLEDGMENTS

One of the authors (Y.H.) would like to thank Professor F. Brouillard and the members of the Atomic and Molecular Physics Institute (FYAM) of Université Catholique de Louvain, Louvain la Neuve, for their hospitality, where initial work on $H^* + H$ was done, and the Harvard-Smithsonian Center for Astrophysics for its hospitality. Helpful correspondence with Dr. B. Van Zyl, Dr. A. Salin, and Dr. B. H. Bransden is gratefully acknowledged. This work is partially supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, and Experimental Plasma Physics, Division of Applied Plasma Physics, Office of Energy Research, U.S. Department of Energy.

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