PHYSICAL REVIEW A VOLUME 54, NUMBER 1 JULY 1996

Molecular treatment of electron detachment in H^++H^- collisions

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(Received 13 November 1995)

To confirm the appropriateness of ideas recently put forward [L. F. Errea, C. Harel, H. Jouin, L. Méndez, B. Pons, and A. Riera, Phys. Rev. A **52**, R2505 (1995)] concerning the validity of the molecular approach to calculate ionization cross sections, we treat the $H^+ + H^-$ reaction as a widely different benchmark. [S1050-2947(96)03407-5]

PACS number(s): 34.50.−s, 34.70.+e

In a recent publication [1] we have shown that a treatment of atomic collisions based on a molecular expansion modified with a common translation factor (CTF) [2] and including pseudostates is able to yield ionization and capture cross sections with an accuracy close to that of large-scale atomic expansions. For this, we introduced a new criterion, which is to consider the energies E_k^J of the basis states with respect to either nucleus $J=A,B$. For a one-electron system, they have the form

$$E_k^{(J)}=\langle \phi_k|D_J h_J D_J^{-1}|\phi_k\rangle, \qquad (1)$$

where ϕ_k are CTF-modified molecular wave functions, h_J is the asymptotic form of the fixed nuclei Born-Oppenheimer Hamiltonian H_{el} when the electron is attached to nucleus J, and D_J is the asymptotic form of the translation factor in the same limit. The usefulness of this criterion was illustrated [1] by choosing the H^++He^+ reaction as a prototype. In the present work we investigate whether the same idea is applicable to treat the $H^+ + H^-$ reaction. An exposition on previous calculations on this important neutralization process can be found in Ref. [3]. With respect to electron detachment, several calculations [3–5] have been carried out with a one-electron approach. Sidis *et al.* [4] employed a molecular basis modified by a CTF (neglecting a divergent coupling), and augmented with two pseudostates, which were Σ and Π wave functions of the form $H^++H^-(P)$. Fussen and Claeys [5] used a two-state model without translation factors, involving the entrance channel and the Σ pseudostate of Ref. [4]. This latter work concluded that the electron detachment takes place through transitions at large impact parameters, induced by the asymptotic part of the long-range dipole interaction. Ermolaev [3] employed two bases, formed by 29 and 36 atomic orbitals, respectively, with plane-wave translation factors and including pseudostates. He concluded that all methods give a reasonably accurate representation of the experimental data.

The interest of checking the applicability of the criterion proposed in [1] on the H^++H^- benchmark lies in that, in contrast with ‘‘usual’’ ion-atom collisions, transitions leading to electron capture mainly occur in the neighborhood of pseudocrossings between states of predominantly ionic (H^+-H^-) or covalent (H-H) character. Now, ionic-covalent pseudocrossings cannot, even approximately, be represented by a model one-electron system ($Z_1^+e^-Z_2^+$) involving Coulomb potentials; instead, exponential-type effective potentials must be employed [3,6]. Therefore these pseudocrossings are unrelated to the so-called ‘‘hidden crossings,’’ which furnish an important mechanism for both capture and ionization in atomic collisions [7–9], for single-electron ($Z_1^+e^-Z_2^+$) systems. All this points to the interest of the H^++H^- reaction as a different (and, as is well known, rather stringent) benchmark.

Unfortunately, for a two-electron system, a treatment that is completely parallel to that of [1] is not possible with the programs available. Like previous work [3–6], we have therefore used a one-electron description, which is sufficient for the present purposes. In the framework of a semiclassical, impact parameter method, we expanded the electronic wave function in terms of the eigenstates of the one-electron effective Hamiltonian described in [6]. These states were modified with the CTF of Errea *et al.* [10] and the ensuing bases were augmented with pseudostates. These were taken to be probability absorbers [11] $\phi_k^{(1)}$, which are obtained by applying $(H_{\mathrm{el}}-i d/dt)$ on the CTF-modified molecular wave functions, and can be expressed as

$$\phi_k^{(1)}=v_R\phi_k^{(R)}+v_\theta\phi_k^{(\theta)}+v^2\phi_k^{v^2}, \qquad (2)$$

where v is the relative nuclear velocity, and v_R, v_θ its radial and rotational components. In our calculation we separately included the (orthogonalized) radial and rotational absorbers $\phi_k^{(R)}, \phi_k^{(\theta)}$ of the Σ states dissociating into H^++H^- and $H(1s)+H(nl)$, $n\leqslant 3$. Furthermore, given the relatively small individual populations of these pseudostates, we neglected the couplings between them as in Ref. [11].

We used the program PAMPA [12] to calculate the exit probabilities. As has been discussed in [9], the population of the highest capture channels is overestimated by accumulation of ionizing flux. To distinguish this flux from that of genuine electron capture, we applied the criterion proposed in [1]. We ascribed to ionization the probabilities through those basis functions whose energies $E_k^{(A,B)}$ [Eq. (1)] lie in the continuum spectrum of *both* (moving) atoms for the domain of internuclear distances where they are significantly

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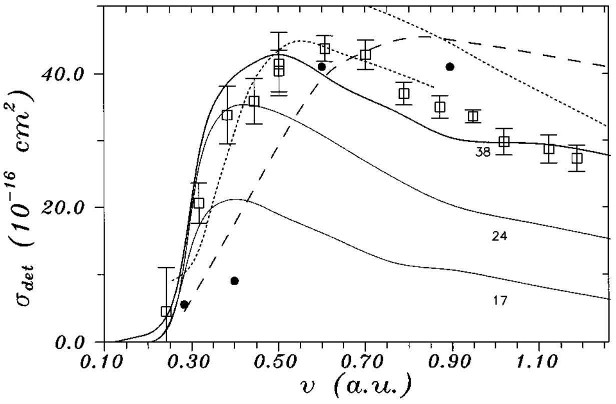

FIG. 1. Electron detachment total cross section as a function of the relative velocity. Theoretical values: —, present molecular results using the bases whose sizes are indicated; · · · ·, results of Ref. [3], including 36 (upper curve) and 29 (lower curve) atomic orbitals; - - -, results of Ref. [5]; ●, results of Ref. [4]. Experimental data: □, Ref. [13].

populated. In particular, we found that states dissociating into H($n=5$) + H(1s) have positive energies in the region of internuclear distances where transitions to them take place; in addition, for impact energies $E>3$ keV, exit probabilities through states dissociating into H($n=4$)+H(1s) (not included in [4] at these energies) should also be ascribed to ionization. Transitions leading to detachment are not localized at the ionic-covalent pseudocrossings and occur through couplings between higher lying covalent states and the entrance channel. The transition region varies from a few atomic units at high velocities up to 40 bohrs at the lowest ones considered.

We present in Fig. 1 our calculated electron detachment cross section for three basis sets, consisting of (i) 17 molecular states [all Σ and Π states dissociating into H(1s) +H(nl), $n\leqslant 4$ and $H^+ + H^-$]; (ii) 24 states [the previous ones plus Σ and Π states dissociating into H(1s) +H(5s,5p,5d,5f)]; (iii) 38 states (the previous ones plus the previously defined 14 pseudostates). Exploratory calculations adding the absorber states associated to the Σ states dissociating into H(1s) + H($n=4$) (46 states) at $v\simeq 0.5$ a.u. yielded cross sections that are indistinguishable from those of Fig. 1. We also include in this figure the previous theoretical [3–5] and the experimental [13] data for $E\leqslant 20$ keV. We notice that for this energy range our results converge reasonably, and our data with the largest (iii) basis set agree with those of previous calculations and measurements. A similar convergence is obtained for the neutralization reactions $H^+ + H^- \rightarrow$ H($n=2$)+H(1s) (Fig. 2) and $H^+ + H^- \rightarrow$ H(Σ) + H(1s) (Fig. 3), for which our results are compared to the accurate data of Refs. [3,14] (this latter employing a plane-wave-modified two-electron atomic expansion), and to experiment [15–17]. We attribute the small discrepancies between our neutralization data and those of Shingal and Bransden [14] to our use of a one-electron model: first, this model does not take into account the ionization of the H^- inner shell, which may not be negligible for $E>1$ keV (see a discussion in [3]); secondly, for $E\leqslant 400$ eV two-electron effects cause the ionic-covalent pseudocrossing at $R\approx 11$ bohrs to be wider than that predicted by the model (see an analysis of this point in [6]). We have checked that an *ad hoc* modification of our energy curves (with a corresponding change in the radial coupling), so as to increase the energy gap at the pseudocrossing, lowers the neutralization cross section by an amount that is of the order of the discrepancy. Furthermore, higher order absorber states [11] would be required to speed up the convergence of this cross section at high energies ($E>3$ keV).

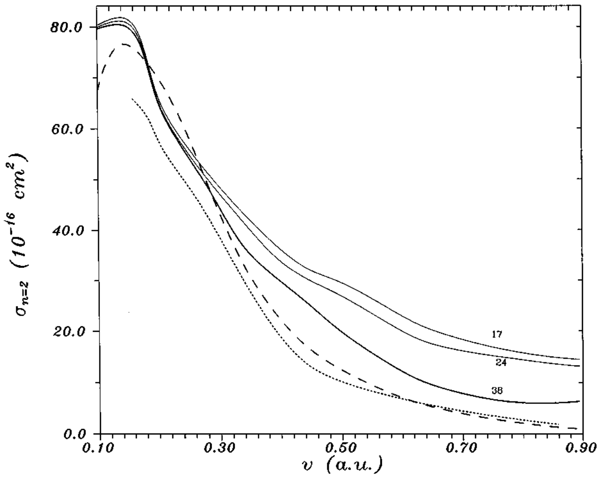

FIG. 2. Calculated total cross section for neutralization into H ($n=2$): —, present molecular results; · · · ·, one-electron atomic orbital calculation of Ref. [3]; - - -, two-electron atomic orbital calculation of Ref. [14] for the reaction $H_A^+ + H_B^- \rightarrow H_A(n=2) + H_B(1s)$.

To sum up, the present work has checked on the generality of the main conclusions of [1] for a very different benchmark, such that accurate theoretical and experimental data are available. The H_2 quasimolecule not being reducible to a

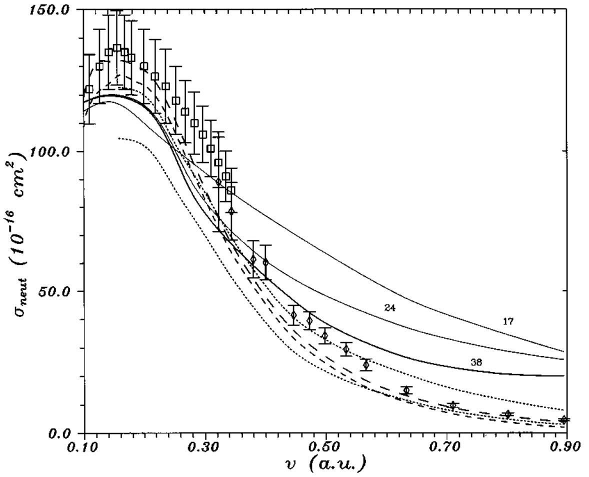

FIG. 3. Neutralization total cross section. Symbols for theoretical results are the same as in Fig. 2, except that two curves are given for Refs. [3,14]. The lower curve of Ref. [3] corresponds to the one-active-electron model while the upper one includes the modified independent-particle model correction. The lower curve of Ref. [14] are the results for the reaction $H_A^+ + H_B^- \rightarrow H_A(n=2) + H_B(1s)$. The upper one also includes the cross section for $H_A^+ + H_B^- \rightarrow H_A(1s) + H_B(n=2)$. Experimental data: □, Ref. [17]; ◇, Refs. [15,16].

three-particle Coulombic system, the usual ‘‘hidden crossing’’ [7,8], or ‘‘relay’’ [9], mechanisms do not apply. As is known, at intermediate energies neutralization yielding H($n=2,3$) mainly occurs in the neighborhood of ionic-covalent pseudocrossings, while detachment takes place for a wide range of distances. In spite of these differences, it is significant that detachment at $E>3$ keV and capture to H($n>3$) at lower energies share a common mechanism in the molecular close-coupling framework. Therefore, as in the usual $X^{q+}+\mathrm{H}$ case [9], we obtain above threshold an accumulation of ionizing flux in the highest exchange levels. The use of the criterion employed in [1] permits us to distinguish this flux from that of genuine electron capture.

This work has been partially supported by the DGICYT Project No. PB93-288-C02 and the ‘‘Acción Integrada Hispano-francesa’’ No. 396B.

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