

Double Electron Capture in $H^+ + H^-$ Collisions

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 (Received 9 September 2018; revised manuscript received 14 November 2018; published 8 March 2019)

We have investigated the double electron capture process in the $H^+ + H^-$ collision system for energies from 60 eV to 20 keV. Despite the apparent simplicity of this highly correlated system, all previous calculations fail to reproduce the experimental total cross sections. Moreover, the latter exhibit oscillations that have been previously attributed to quantum interferences between the gerade and ungerade ionic states of the transient molecule formed during the collision. For this process, we present the absolute cross sections obtained from a fully correlated two-active-electron semiclassical atomic-orbital close-coupling approach. Our results reproduce well the experimental data in both magnitude and shape. Furthermore, we demonstrate that the oscillations stem from coherence effects between double electron capture and other two-electron inelastic channels, namely the transfer-excitation processes. This alternative interpretation is supported by a Rosenthal-like model based on a molecular treatment of the collision. Our results shed new light on this old but challenging problem.

DOI: [10.1103/PhysRevLett.122.093402](https://doi.org/10.1103/PhysRevLett.122.093402)

Inelastic electron processes in atomic collisions play a central role in many fields, such as plasma physics [1], astrophysics [2], and radiation chemistry [3]. While single electron processes are fairly well understood, our knowledge on multielectron ones is far from complete. A striking example is the $H^+ + H^-$ collision system. As a benchmark, it has been extensively investigated for more than five decades. Despite its apparent simplicity, a complete description of the electronic dynamics of this system remains a challenge owing to the predominant role of the electronic correlation. Most of the previous works focused on single electron capture (SEC) processes, i.e., the mutual neutralization of H^+ and H^- [4–13]. Studies of double electron capture (DEC) are however more scarce. The cross sections of DEC were firstly measured by Brouillard *et al.* [14] in 1979, for impact energies ranging from 60 to 400 eV. In the same year, Peart and Forrest [15] extended these measurements for energies up to about 1 keV. More recently, Braüning *et al.* [16] resumed this study for higher energies up to 25 keV. The three series of experiments show that the DEC cross section oscillates. These oscillations have been attributed to quantum interferences between the gerade and ungerade ionic states of the transient molecule formed during the collision [16,17]. However, all previous theoretical investigations of DEC process failed to reproduce the experimental oscillations and/or the magnitude of the cross section, illustrating the complexity of this collision system.

In parallel with their experimental investigation, in [14] the authors modeled the DEC process using a semiclassical method based on molecular states of H_2 . They obtained

cross sections that exhibit an oscillatory pattern but were one order of magnitude larger than the experimental ones. Later, semiclassical calculations extended the study to energies up to several keV [9,10]. The cross sections were again too large and the oscillations observed in the theoretical cross sections were not consistent with the measured ones. More recently, Braüning *et al.* [16] and Mezei *et al.* [17] evaluated the DEC cross section using molecular treatments, with a rather simple two-state model in the first case and using a fully quantum treatment in the latter. They both overestimate the cross section by at least one order of magnitude. Furthermore, the latter calculations focused in the low impact energy domain, $E \leq 90$ eV, with a limited overlap with the experimental investigations.

In this Letter, we present extensive *ab initio* calculations which cover a wide collision energy domain overlapping with the three series of experiments. Our calculated cross section reproduces in an unprecedented way the experimental one [14–16] in both magnitude and overall oscillatory structure. Furthermore, our investigation suggests that the observed oscillations come from a more complex mechanism than the one discussed so far.

We use a fully correlated two-active-electron semiclassical atomic-orbital close-coupling (AOCC) method, which has been previously described in e.g., [18–20]. The treatment is semiclassical in that the relative target-projectile motion is described by classical straight-line constant velocity trajectories [21], while the electronic dynamics is treated quantum mechanically, by solving nonperturbatively the time-dependent Schrödinger equation. The latter is solved by expanding the total electronic wave function

into the eigenstates of the isolated collision partners. The semiclassical method and the AOCC expansion are well established approaches and have proven to be accurate in the whole range considered in this work (see [19,23]). In the present calculations, these eigenstates are obtained by diagonalizing the corresponding Hamiltonian matrices in the basis set of properly antisymmetrized products of a set of 45 Gaussian-type orbitals (GTOs) (11 for $l = 0$, 8×3 for $l = 1$, and 2×5 for $l = 2$). This allows the inclusion of 1977 one- and two-electron states, describing elastic, SEC and DEC channels, as well as ionization through the inclusion of 1446 pseudostates of energy lying up to 1 a.u. above ionization thresholds. Convergence tests have been performed by comparing the present results with those from two different basis sets, using 32 (9 for $l = 0$, 6×3 for $l = 1$, and 1×5 for $l = 2$) and 55 (11 for $l = 0$, 8×3 for $l = 1$, and 4×5 for $l = 2$) GTOs [24], respectively. The convergence was evaluated to be about 10% for impact energies above 0.2 keV and smaller than 30% for lower energies.

In Fig. 1, our calculated DEC cross sections are presented and compared with available experimental [14–16] as well as theoretical [9,10,14,16,17] results. Although slightly higher than the experimental ones at the lowest collision energy, our cross sections are in good agreement with experiments over the whole collision energy range. Furthermore, the cross section shows a clear oscillatory structure whose period increases with increasing impact energies.

Our results are the first ones to reproduce well the experimental data in both magnitude and shape. We now compare our approach to the previous theoretical methods in order to elucidate what ingredients are needed to describe accurately the DEC process in such a complex system.

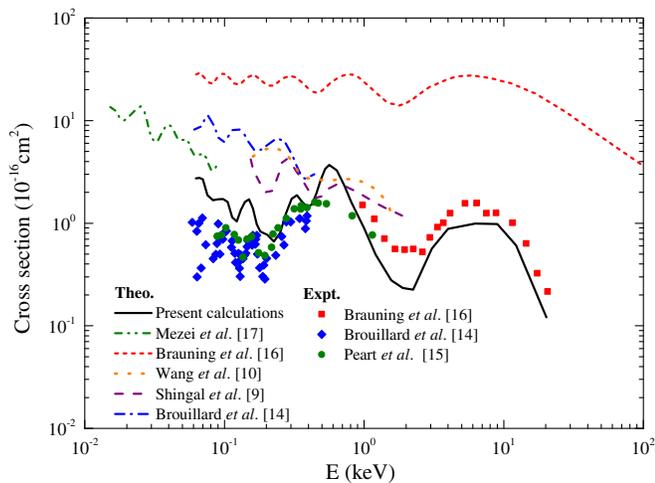


FIG. 1. Double electron capture cross sections as functions of the impact energy. The present results are shown as a black line. Experimental and theoretical results are reported as points and lines, respectively.

The main differences between our calculations and the previous *ab initio* ones [9,10,14,17] are (i) the use of much larger basis sets, (ii) the full treatment of electronic correlation, and (iii) the inclusion of pseudostates which span approximately the electron continuum. The latter point is particularly important since ionization dominates the DEC process: the ionization cross section was measured by Melchert *et al.* [25] and Peart *et al.* [26] in the keV energy range. These cross sections are in the order of 10^{-16} – 10^{-15} cm^2 between 100 eV and 20 keV, in good agreement with our calculations (see Supplemental Material [27]), thus exceeding the DEC cross section. Furthermore, we have performed additional calculations without including the pseudostates (i.e., neglecting ionization). The DEC cross sections increase by up to a factor of 2 at low energies and are very close to the previous results of [17] and [9]. We therefore think that taking into account properly the ionization process is essential to reproduce quantitatively the DEC cross section.

We have further investigated the oscillatory structure in the DEC cross section based on our *ab initio* calculations. In Fig. 2(b) we present as functions of the inverse of the relative velocity, $1/v_p$, the cross sections of the DEC process together with the ones corresponding to the two-electron transfer-excitation (TE) processes, i.e., transfer of one electron to the ground state of the projectile while the second target electron is excited to the L shell. The experimental results [14–16] for DEC are presented in

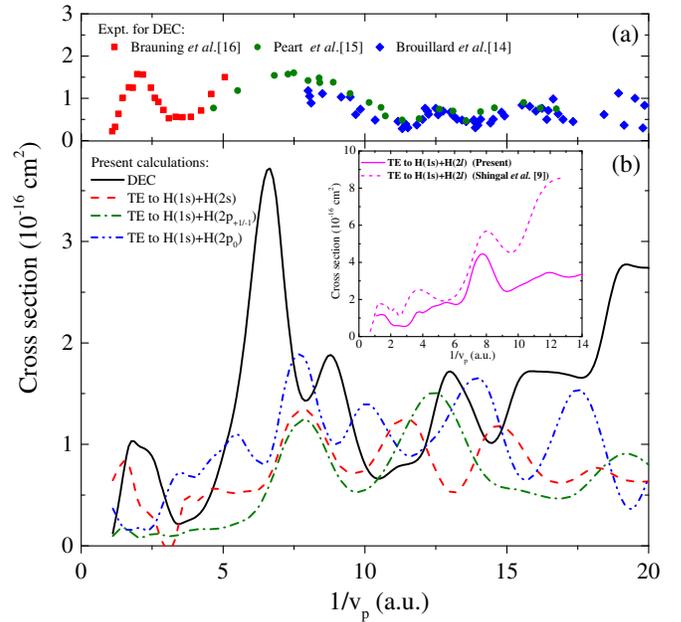


FIG. 2. (a) Experimental results for DEC cross sections as functions of $1/v_p$. (b) Present double electron capture and transfer-excitation (TE) cross sections as functions of $1/v_p$. In the inset, the present cross sections for TE to $H(1s) + H(2\ell)$ are presented and compared with the coupled-channel calculations reported in [9].

Fig. 2(a) for comparison. To our knowledge, the state-to-state cross section for the TE processes have never been reported experimentally.

In Fig. 2(b) both the DEC and TE cross sections show clear periodic oscillations but with opposite phases, which suggests that the oscillatory patterns come from coherence effects between DEC and TE processes. Such interpretation is different from previous explanations [16] that attributed the oscillations to the interferences between the gerade and ungerade molecular curves describing the ion-pair (elastic and double capture) channels. As discussed in [16], the period of the oscillations should depend on the energy difference between the gerade and ungerade states of the pseudomolecule formed. However, using the potential energy curves of H_2 one has to introduce in the model *ad hoc* (i) cutoff and (ii) increase of the magnitude of the energy splitting in order to achieve a good agreement with the experimental oscillations (see [16] for a detailed discussion). As shown below, a simple model based on our interpretation reproduces well the period observed experimentally and in our *ab initio* results without the need of adjusted parameters.

To support our interpretation of the oscillations as interferences between DEC and TE processes, we have extended a model proposed by Rosenthal and Foley [29] to explain the oscillations observed in the total cross section (i) for excitation of helium by helium ion impact (see also [30] for more details on the model) and (ii) recently, for ionization and negative ion formation in $H + H$ collisions [31]. Similar interferences between inelastic channels leading to oscillations in total cross sections have also been observed; see, e.g., for two-electron exchange [32] and references therein. In the model proposed in [29,30] the oscillations are interpreted through a molecular representation of the scattering event: the two inelastic processes take place due to a transition occurring at small impact parameters between two states of the transient molecule. These states couple again at large distances, leading to the interference patterns. In this model, the amplitude of each pathway acquires a different phase in the internuclear distance region where the curves cross, i.e., between R_x where the initial nonadiabatic transition takes place and $R_0 > R_x$ where the corresponding states mix again. At the latter distance, the amplitudes of the two inelastic channels are then coherently mixed which leads to the oscillations of the cross section. In this model the period of the oscillations is given by the cumulated energy difference ΔE between the two molecular states between R_x and R_0

$$T = \frac{2\pi}{\int_{R_x}^{R_0} \Delta E dR} \quad (1)$$

when presented as functions of $1/v_p$.

We have extended this model to our collisional system. A selection of the important H_2 adiabatic potential energy

curves of the $^1\Sigma_g$ and $^1\Sigma_u$ states (noted below g and u states, respectively) converging asymptotically to $H^+ + H^-$ and $H(1s) + H(2\ell)$ are shown in Fig. 3. At the internuclear distance $R \approx 15$ a.u. [11,33] the states 4_g and 3_u , corresponding asymptotically to $H^+ + H^-$ (elastic and DEC channels), exhibit strong radial couplings with, respectively, the states 2_g and 1_u [correlated asymptotically to the TE and SEC channels $H(1s) + H(2\ell)$]. As the target and projectile approach each other on the way in the 4_g and 2_g (3_u and 1_u) states couple at $R \approx 15$ a.u. Each pathway acquires a different phase according to the energy of the molecular state. There is another strong radial coupling for each symmetry at shorter R (about 1 a.u.) [11,33] which mix again these states. Finally, the amplitudes of the inelastic channels acquire a different phase and are coherently mixed at $R \approx 15$ a.u. on the way out. Following the model in [29,30], the period of the oscillations in the DEC and TE cross sections are half that given in Eq. (1). The factor 2 between this period and the one expressed in Eq. (1) and in [29,30] comes from the accumulated phase of the inelastic amplitudes on the way in and on the way out in our case while in [29,30] the phase difference takes place only on the way out.

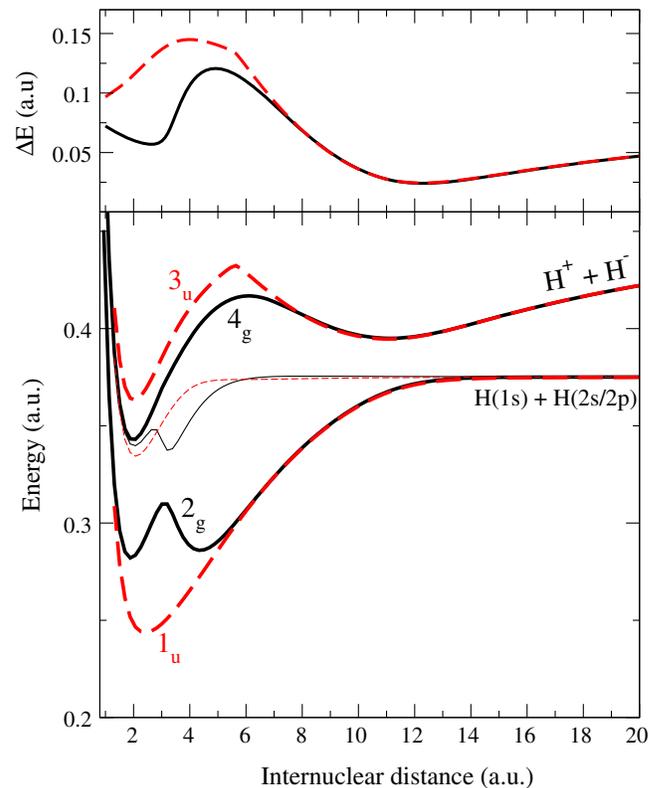


FIG. 3. Bottom: adiabatic potential energy curves of H_2 . The $^1\Sigma_g$ and $^1\Sigma_u$ states (noted g and u , respectively) are shown in black lines and red dashed lines, respectively. The atomic states correlated asymptotically to these molecular states are identified on the curves. Top: energy difference between 4_g and 2_g states (black line) and between 3_u and 1_u states (red dashed line).

It should be noted that our *ab initio* calculations show that only SEC probabilities are nonzero up to impact parameters $b \approx 15$ a.u. (see Supplemental Material [27]), which illustrates the action of the previously discussed radial couplings observed in molecular calculations [11,33]. In contrast, the TE processes are only likely at shorter b (see Supplemental Material [27]) which is a necessary condition to observe the oscillations in the total cross sections [32]. These two observations illustrate the clear effect of the inner crossing advocated in the model.

Using the potential energy curves shown in Fig. 3, we have calculated the energy difference between the 4_g and 2_g states on the one hand and between 3_u and 1_u states on the other hand. The results are shown in the upper panel of Fig. 3. We have integrated these energy differences between $R = 1$ a.u. and 15 a.u., according to the position of the strong radial couplings. Within our model the expected periods are about 3.7 and 3.1 a.u. for g and u symmetry, respectively. These periods agree well with the *ab initio* calculations which predict a period of about 3 a.u. for DEC and TE into $H(2p_0)$ and $H(2s)$ processes, supporting our interpretation, (see Fig. 2).

Our *ab initio* calculations show that the oscillations in the cross section for TE into $H(2p_{\pm 1})$ have a longer period (5–6 a.u., see Fig. 2). To describe this process with our model, one has to include the Π_g and Π_u states of H_2 which can be populated by rotational couplings. To our knowledge, the rotational couplings between states of H_2 are not published. However, our *ab initio* calculations show that probabilities for SEC into $H(2p_{\pm 1})$ extends up to $b = 15$ a.u. as for $H(2p_0)$ and $H(2s)$. It is therefore reasonable to use the same integration range (i.e., $R = 1$ a.u. and 15 a.u.) to develop our model for the Π states [34]: the period of the oscillations is then predicted to be 6.0 and 6.6 a.u. for Π_g and Π_u symmetry, respectively, showing again an overall good agreement with the *ab initio* results.

In conclusion, double electron capture occurring in the course of $H^+ + H^-$ collisions has been a challenge for theoreticians for decades. We have investigated this process with a fully correlated two-active-electron nonperturbative approach. The present extensive calculations cover a wide energy domain from 0.06 to 20 keV overlapping with the three sets of available experimental data. In contrast to all previous calculations, our calculated cross section shows an overall good agreement with the experimental results in both magnitude and shape. Furthermore, our *ab initio* results suggest that the oscillatory structures observed in the double electron capture cross section do not come from interferences between the gerade and ungerade pathways of the ion-pair configuration as previously put forward, but from interferences between double electron capture and transfer-excitation channels. A more complex mechanism involving a two-crossing model is presented and supports this interpretation. Experimental cross section for transfer-excitation processes are not available and we hope that our

results will encourage further experimental works to confirm our interpretation, shedding new light into this challenging many-body quantum problem.

This project has received funding from Agence Nationale de la Recherche through the program ANR-16-CE29-0016-01 and from the LABEXs Plas@par and MiChem (ANR-11-IDEX-0004-02). Y. W. acknowledges the support of the National Key Research and Development Program of China (Grant No. 2017YFA0402300 and No. 2017YFA0403200), the Science Challenge Project (Grant No. TZ2016005), and the National Natural Science Foundation of China (Grant No. 11534011 and No. U1530261).

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