Effect of electron-nuclei interaction on internuclear motions in slow ion-atom collisions

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The electron-nuclei interaction affects the internuclear motion in slow ion-atom collisions, which in turn affects theoretical results for the cross sections of various collision processes. The results are especially sensitive to the details of the internuclear dynamics in the presence of a strong isotope effect on the cross sections, as is the case, e.g., for the charge transfer in low-energy collisions of He^{2+} with H, D, and T. By considering this system as an example, we show that internuclear trajectories defined by the Born-Oppenheimer (BO) potential in the entrance collision channel, which effectively accounts for the electron-nuclei interaction, are in much better agreement with trajectories obtained in the *ab initio* electron-nuclear dynamics approach [R. Cabrera-Trujillo *et al.*, Phys. Rev. A **83**, 012715 (2011)] than the corresponding Coulomb trajectories. We also show that the use of the BO trajectory instead of the Coulomb trajectory in the calculations of the charge-transfer cross sections within the adiabatic approach improves the agreement of the results with *ab initio* calculations.

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I. INTRODUCTION

The theory of slow ion-atom collisions has numerous applications from plasma physics and controlled fusion to astrophysics. Although the theory has a long history and is considered to be well established [1], new findings overlooked by previous studies continue to appear. In a recent paper [2] the strong isotope effect in the charge-transfer process

$$He^{2+} + A(1s) \to He^{+}(n = 2) + A^{+}, \quad A = H,D,T, \quad (1)$$

was predicted using an *ab initio* electron-nuclear dynamics (END) approach described in Ref. [3]. Later, similar results for the different shells of the projectile were reported [4] and the dependence on the target mass was found also for the energy losses and stopping cross sections in the same collision system [5]. These findings motivated a series of studies [6–11] using different methods where the results of Ref. [2] were confirmed and extended to other collision systems. In particular, in Refs. [7,9,10], using the adiabatic approach developed by Solov'ev [12,13], the strong isotope effect was shown to exist also for heavier projectiles. These results, apart from their general interest for collision physics, have important implications for diagnostics and simulation of elementary processes in fusion edge plasmas [14].

The internuclear motion in ion-atom collisions can be treated classically. In this approximation some effective interaction between the nuclei is assumed. The internuclear trajectory determined by this interaction depends on the masses of the nuclei and this is what causes the isotope effect. Indeed, all theoretical methods used in the studies mentioned above involve some internuclear trajectory. Thus, in the END approach [3] used in Refs. [2,4,5] a nontrivial trajectory is self-consistently calculated simultaneously with solving the time-dependent Schrödinger equation for an electron. This approach was shown to yield counterintuitive negative scattering angles for the internuclear motion in the system (1) at certain collision parameters [5], which cannot be explained by any purely repulsive interaction. In the adiabatic approach [12,13], as implemented in Ref. [15] and employed in Refs. [7,9,10], the Coulomb internuclear trajectory with a different dependence on the collision parameters is used. It is clear that in the presence of a strong isotope effect the theoretical results should be sensitive to the trajectory, that is, to the details of the internuclear interaction. However, an exploration of this aspect of the dynamics is lacking.

In this paper we investigate the effect of the electron-nuclei interaction on the internuclear motion and hence on the observable cross sections in slow ion-atom collisions. Our main message is very simple: The internuclear motion should be described by the Born-Oppenheimer (BO) potential corresponding to the entrance collision channel. This potential effectively accounts for the electron-nuclei interaction. We first show (Sec. II) that the inclusion of this interaction enables one to explain qualitatively and reproduce quantitatively the negative scattering angles found in Ref. [5]. This proves that the accurate *ab initio* description of the internuclear motion so essential for the END approach used in Refs. [2,4,5] in the case of slow collisions can be reproduced within the BO approximation. We then analyze (Sec. III) how the modification of the internuclear trajectory caused by the electron-nuclei interaction affects the charge-transfer cross sections calculated within the adiabatic approach [12,13]. Section IV summarizes the paper. Atomic units are used throughout unless otherwise indicated.

II. INTERNUCLEAR POTENTIAL AND TRAJECTORY

We consider a three-body system consisting of two nuclei with charges Z_i and masses M_i, $i = 1,2$, and an electron. The electron is initially bound to the second nucleus in a state with energy E_0. To avoid complexities caused by the Coulomb degeneracy [16], we assume that the initial state is the nondegenerate ground state, so $E_0 = -Z_2^2/2$. The first nucleus (projectile) collides with the bound pair (target). Let $E = \mu v^2/2$ denote the energy of the internuclear motion in the center-of-mass frame, where $\mu = M_1M_2/(M_1 + M_2)$ is the reduced mass of the nuclei and v is their initial relative velocity. The interaction between two bare nuclei is described

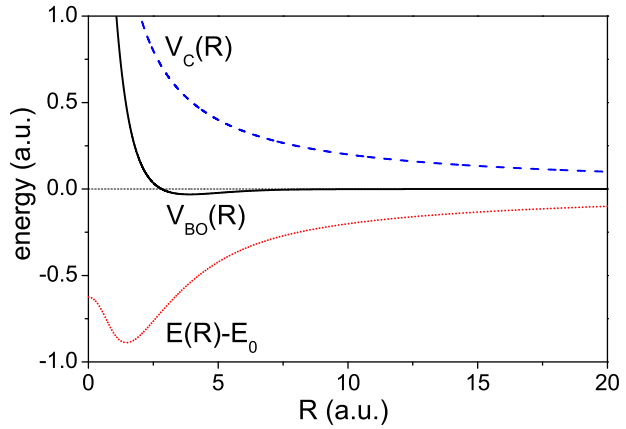

FIG. 1. (Color online) Coulomb (2) and BO (3) internuclear potentials for the system (1).

by the Coulomb potential

$$V_{\rm C}(R) = \frac{Z_1 Z_2}{R}, \tag{2}$$

where R is the internuclear distance. In the BO approximation the internuclear interaction is described by

$$V_{\rm BO}(R) = V_{\rm C}(R) + E(R) - E_0, \tag{3}$$

where $E(R)$ is the electronic energy in the field of the nuclei fixed in space at a distance R from each other, which for the present system is an eigenvalue of the two-center Coulomb problem [17]. Since electronic transitions in slow collisions are suppressed (the adiabatic theorem), we assume that the electronic state defining the potential (3) evolves adiabatically, i.e., is the eigenstate of the two-center Coulomb problem that coincides with the initial state at $R \to \infty$, so $E(R \to \infty) = E_0$. The electronic terms in Eq. (3) represent the electron-nuclei interaction of interest here. The system (1) corresponds to $Z_1 = 2$, $Z_2 = 1$, and $E_0 = -0.5$. The different terms in Eq. (3) for this system are shown in Fig. 1. Note that while the Coulomb potential is repulsive [$dV_{\rm C}(R)/dR < 0$] at all R, the BO potential has a shallow minimum at $R \approx 3.9$ and is attractive [$dV_{\rm BO}(R)/dR > 0$] at larger R.

The potentials (2) and (3) define different trajectories. To judge which of them better describes the internuclear motion the trajectories must be compared with some reliable *ab initio* results. Such results for the system (1) were reported in Ref. [5]. In the END approach [3] used in this work the time-dependent Schrödinger equation for an electron interacting with two moving nuclei is solved. The instantaneous distribution of the electronic density determines the instantaneous forces acting on the nuclei that are used to self-consistently calculate the internuclear trajectory. Thus a nontrivial trajectory appears in the END approach, but there is no a time-independent internuclear potential. As a property of the trajectory characterizing the internuclear dynamics, the authors of Ref. [5] considered the scattering angle. This angle for the system (1) as a function of the collision parameters obtained in the END approach was shown to depend on the target. The results were compared with the predictions of classical mechanics for scattering by two time-independent potentials. At high collision energies ($E \gtrsim 10$ keV/amu), the END results agree with the results for the Coulomb potential (2), but at lower energies the agreement becomes worse. The use of a screened Coulomb potential corresponding to the static electron density distribution in the initial state of the target improves the agreement with the END results at lower energies, but only at large impact parameters. At smaller impact parameters the results differ qualitatively. Namely, it was found that at sufficiently low energies ($E \lesssim 1$ keV/amu) there exists an interval of impact parameters where the scattering angle has negative values. This finding seems to contradict common sense. Indeed, one would expect that the effective internuclear interaction is repulsive, but in this case the scattering angle must be positive. Both potentials considered in Ref. [5] are purely repulsive and cannot reproduce negative scattering angles found in the END calculations. This subtle feature is thus sensitive to the details of the effective internuclear interaction and we focus on it here.

Let us see whether the BO potential (3) can reproduce this feature. The classical scattering angle for a given internuclear potential $V(R)$ as a function of the impact parameter ρ and collision energy E is given by [18]

$$\theta(\rho, E) = \pi - \int_{R_{\rm min}}^{\infty} \frac{2\rho dR}{R^2 F(R)}, \tag{4}$$

where

$$F(R) = \sqrt{1 - \frac{\rho^2}{R^2} - \frac{V(R)}{E}} \tag{5}$$

and $R_{\rm min}$ is the distance of closest approach defined by the equation $F(R_{\rm min}) = 0$. For the Coulomb potential (2) we have $\theta(\rho, E) = \theta_{\rm C}(\rho E)$, where [18]

$$\theta_{\rm C}(\rho E) = 2 \arctan\left(\frac{Z_1 Z_2}{2\rho E}\right). \tag{6}$$

In this case the scattering angle depends only on the product ρE, but this scaling property does not hold for other potentials. We have calculated the scattering angle for the system (1) at a fixed energy $E = 50$ eV/amu also considered in Ref. [5] using the BO potential (3). The results as functions of the parameter ρE are shown by the solid (H), dashed (D), and dash-dotted (T) lines in Fig. 2. They are in perfect agreement over the whole interval of ρE considered with the END results from Ref. [5] shown by symbols. This proves that the internuclear dynamics predicted by the END approach can be well reproduced by the BO potential (3). The attractive part of this potential resulting from incorporating the electron-nuclei interaction is responsible for the appearance of the negative scattering angles found in Ref. [5]. For comparison, the dotted line in Fig. 2 shows the scattering angle for the Coulomb potential (2). Due to the scaling property, the same line describes all three targets in Eq. (1). This line lies rather far from the *ab initio* results and obviously fails to reproduce the negative scattering angles.

It is instructive to compare the Coulomb and BO trajectories in the situation where they have different signs of the scattering angle for the same collision parameters. The scattering angles for the BO trajectories shown in Fig. 2 have minima at rather close values of the impact parameter $\rho = 4.68$, 4.66, and 4.64 for H, D, and T, respectively. Figure 3 shows the Coulomb and BO trajectories calculated near these minima at $E =$

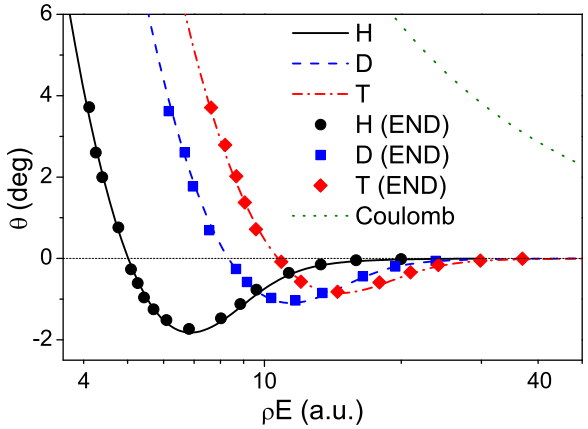

FIG. 2. (Color online) Scattering angle for the internuclear motion in the system (1) at collision energy $E = 50$ eV/amu as a function of the product ρE. Solid, dashed, and dash-dotted lines show the present results for H, D, and T, respectively, calculated using the BO potential (3) in Eq. (4). The symbols indicate the *ab initio* END results from Ref. [5]. The dotted line (the same for all three targets) shows the results for the Coulomb potential (2) from Eq. (6).

50 eV/amu and $\rho = 4.68$. At these collision parameters, the attractive part of the BO potential caused by the electron-nuclei interaction prevails, which results in negative scattering angles for the BO trajectories. The geometrical parameters of the

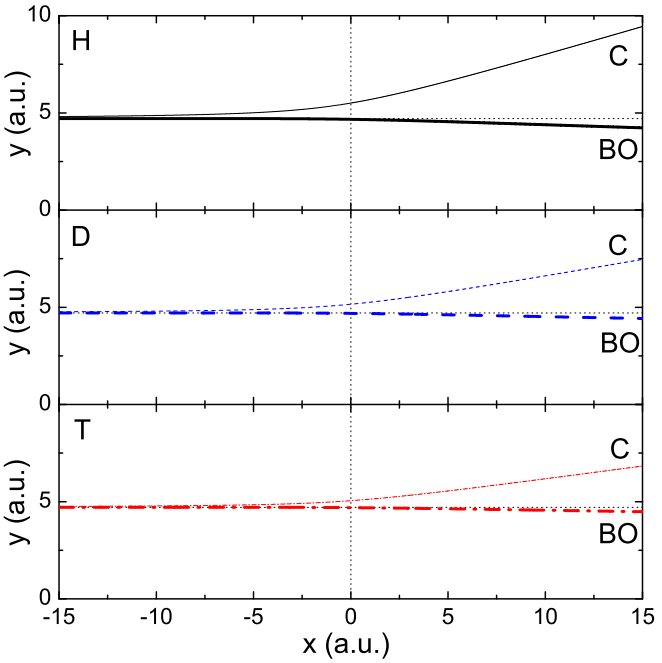

FIG. 3. (Color online) Internuclear trajectories for the system (1) calculated with the Coulomb (thin lines) and BO (thick lines) potentials at energy $E = 50$ eV/amu and impact parameter $\rho = 4.68$ a.u. shown in the collision plane with Cartesian coordinates (x, y) in the center-of-mass frame. The trajectories are oriented in such a way that they coincide with each other and with the corresponding straight-line trajectories shown by horizontal thin dotted lines as $x \to -\infty$, which emphasizes the different signs of the scattering angle for the Coulomb and BO trajectories.

TABLE I. Geometrical parameters of the Coulomb and BO trajectories calculated at $E = 50$ eV/amu and $\rho = 4.68$ a.u. and shown in Fig. 3.

	$V_C(R)$		$V_{BO}(R)$	
Target	θ (deg)	R_{min} (a.u.)	θ (deg)	R_{min} (a.u.)
H	16.5	5.409	−1.82	4.639
D	9.97	5.106	−1.09	4.655
T	7.76	5.008	−0.85	4.661

trajectories shown in Fig. 3 are compared in Table I. The results illustrate two conclusions. First, trajectories defined by the same potential for the different targets differ from each other, which eventually causes the isotope effect. Second, there exists a region of the collision parameters E and ρ where trajectories defined by the BO potential considerably differ from the corresponding Coulomb trajectories. Note that the distance of closet approach R_{min}, whose value has a strong effect on the cross sections (see the next section), exhibits opposite behaviors as the target becomes heavier for the Coulomb and BO potentials.

III. EFFECT ON THE CHARGE-TRANSFER PROCESS

We now investigate how the difference between the Coulomb and BO trajectories affects charge-transfer cross sections in the system (1). To calculate the cross sections, we use the adiabatic approach [12,13] as implemented in the program ARSENY [15]. In this approach the time-dependent Schrödinger equation for an electron in the three-body system discussed in the previous section is solved asymptotically for $v \to 0$. The radial couplings are treated analytically by finding the corresponding hidden crossings (branch points) of the electronic energy as a multivalued analytic function of the complex internuclear distance R. The amplitudes of radial transitions averaged over the Stueckelberg oscillations do not depend on the trajectory. The rotational couplings are treated numerically. They are localized at small R and described in the basis of the united-atom hydrogenlike states $\phi_{nlm}(\mathbf{r})$. The rotation of the internuclear axis causes transitions between states with the same principle n and orbital l quantum numbers, but different projections m of the angular momentum on the internuclear axis. The evolution of the amplitudes $a_m(t)$ of the states with the different m is described by the equations [12]

$$i\dot{a}_m - \epsilon_m a_m + i \sum_{m'=-l}^{l} P_{mm'} a_{m'} = 0, \tag{7}$$

where

$$\epsilon_m = \frac{6m^2 Z_1 Z_2 (Z_1 + Z_2)^2 R^2}{n^3 l(l+1)(2l-1)(2l+1)(2l+3)} \tag{8}$$

is the m-dependent part of the energies of the adiabatic electronic states at small R and

$$P_{mm'} = \langle \phi_{nlm} | \frac{\partial}{\partial t} | \phi_{nlm'} \rangle = \frac{1}{2} \frac{d\varphi}{dt} [\sqrt{(l+m)(l-m+1)}\delta_{m',m-1} + \sqrt{(l-m)(l+m+1)}\delta_{m',m+1}] \tag{9}$$

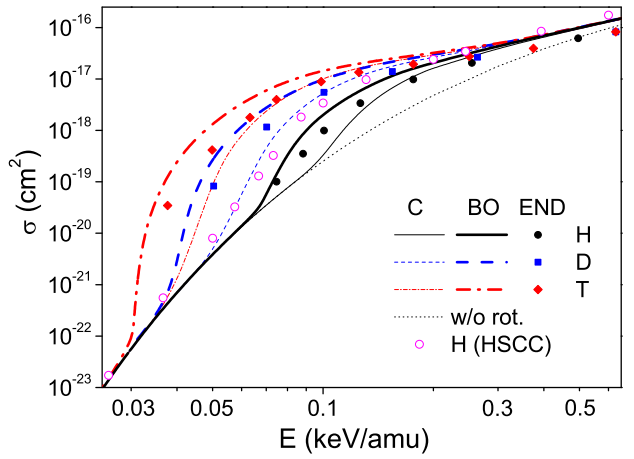

FIG. 4. (Color online) Charge-transfer cross sections for the system (1). Thin and thick lines show the present results obtained in the adiabatic approach [12,13] using the Coulomb and BO internuclear trajectories, respectively. Solid symbols indicate the results of the END approach [3] from Ref. [2]. The thin dotted line (the same for all three targets) shows the adiabatic results calculated without rotational couplings. Open circles indicate the results for H from hyperspherical close-coupling calculations [19].

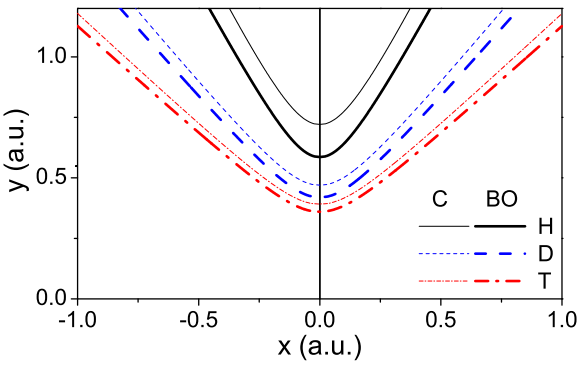

FIG. 5. (Color online) Internuclear trajectories for the system (1) calculated with the Coulomb (thin lines) and BO (thick lines) potentials at energy $E = 100$ eV/amu and impact parameter $\rho = 0.17$ a.u. shown in the collision plane with Cartesian coordinates (x,y) in the center-of-mass frame. The trajectories are oriented to emphasize the different values of $R_{\min}$, which has a strong impact on the rotational coupling.

is the matrix of rotational couplings. The key quantity here is the angle $\varphi(t)$ defining the orientation of the internuclear axis in the collision plane. This angle depends on the trajectory and this is how the trajectory affects the results in the adiabatic approach.

In the original program ARSENY [15] the internuclear trajectory is defined by the Coulomb potential. The Coulomb trajectories for the different targets in the system (1) yield different dependences of the orientation angle $\varphi(t)$ on time, which results in the different contributions of rotational couplings to the charge-transfer cross sections. This isotope effect was studied for a number of collision systems in Refs. [7,9,10]. Here we consider another effect of trajectory caused by the use of the BO potential instead of the Coulomb potential in calculating the angle $\varphi(t)$.

The results of the different calculations for the system (1) are shown in Fig. 4. Thin lines show our previous results obtained in the adiabatic approach with the use of the Coulomb trajectory [7]. The corresponding thick lines show the present results calculated by the same method, but with the use of the BO trajectory. For comparison, the results of the END approach [2] are shown by solid symbols. All these results demonstrate a strong isotope effect in the energy range considered. In the adiabatic approach this effect is explained by the difference between internuclear trajectories defined by the same potential for the different mass of the target. In addition to the isotope effect, the adiabatic results demonstrate a strong dependence on the potential defining the internuclear trajectory. The difference between the Coulomb and BO trajectories is illustrated in Fig. 5. Here we compare trajectories calculated at energy $E = 100$ eV/amu, where a strong dependence of the cross sections on the trajectory is seen, and impact parameter $\rho = 0.17$, where the rotational couplings that cause this dependence are strong. The rotational couplings are localized at small R, which makes the results sensitive to the distance of closest internuclear approach $R_{\min}$. The smaller this distance is, the larger the effect of rotational couplings and the stronger the dependence on the trajectory. As can be seen from Fig. 5, $R_{\min}$ decreases as the target mass grows from H to T, which results in the growth of the charge-transfer cross section. The values of $R_{\min}$ for the BO potential incorporating the electron-nuclei interaction are smaller than that for the Coulomb potential, which results in a further increase of the cross section.

Figure 4 shows that the use of the BO trajectory instead of the Coulomb trajectory in the adiabatic approach generally improves the agreement of the adiabatic results with the *ab initio* END results [2]. This is explained by the fact that the BO trajectory has smaller $R_{\min}$ than the Coulomb trajectory for the same E and ρ (see Fig. 5) and hence more accurately accounts for the rotational couplings at small R. The improvement is more pronounced at lower energies, while at higher energies the results are less sensitive to the trajectory. For T, the BO trajectory yields better agreement with the END results at energies below $E \approx 0.05$ keV/amu, while for H the agreement becomes better already at energy $E \approx 0.1$ keV/amu. This is because for heavier target the region of strong rotational couplings can be accessed at lower energies.

The thin dotted line in Fig. 4 presents the adiabatic results calculated without taking into account the rotational couplings. In this approximation the adiabatic results do not depend on the trajectory. The relative role of the rotational couplings that cause this dependence decreases at higher energies, so here all the adiabatic results approach the thin dotted line and so do the END results. The rotational couplings (9) also decrease at lower energies, because the derivative $d\varphi(t)/dt$ vanishes as $v \to 0$, so here the adiabatic results for the different targets and trajectories again merge with each other. Unfortunately, the END results from Ref. [2] do not extend to low energies, so this prediction of the adiabatic approach cannot be confirmed.

Both the adiabatic approach [12,13] and the END approach [3] treat the internuclear motion classically and therefore should yield identical results for the same internuclear trajectory. We have demonstrated that the BO trajectory is rather

close to the *ab initio* trajectory used in Ref. [2]. Thus the difference between the results should be attributed to an inaccuracy of the adiabatic approximation and/or possible deficiencies of the numerical scheme for solving the time-dependent Schrödinger equation in Ref. [2]. There exist fully quantum hyperspherical close-coupling (HSCC) calculations for the system (1) with H as the target [19]; the results are shown by open circles in Fig. 4. The HSCC method solves the quantum three-body Coulomb problem without any approximations, provided its numerical implementation yields converged results. Remarkably, the adiabatic results calculated with the BO trajectory are in better agreement with the HSCC results than the END results. Assuming that both *ab initio* calculations [2,19] are numerically converged, this means that the adiabatic approximation partially compensates for an error incurred by the classical description of the internuclear motion.

IV. CONCLUSION

The electron-nuclei interaction affects the internuclear trajectory in slow ion-atom collisions, which in turn affects the values of the charge-transfer cross sections calculated in the adiabatic approach [12,13]. The main conclusion of this work is that the BO potential in the entrance collision channel, which effectively accounts for this interaction, provides a much better description of the internuclear dynamics than the corresponding Coulomb potential. We have demonstrated this by comparing the BO and Coulomb trajectories with the *ab initio* results for the system (1) obtained in the END approach [5]. The BO potential is shown to perfectly reproduce such a subtle feature of the internuclear motion in this system as the negative scattering angles at certain collision parameters found in Ref. [5]. An important consequence of this conclusion is that the BO trajectory should be used instead of the Coulomb trajectory in the implementation of the adiabatic approach, which in fact is fully consistent with the spirit of this approach. We have shown that such a modification of the original implementation [15] indeed leads to better agreement of the adiabatic results with *ab initio* calculations [2,19] of the change-transfer cross sections in the system (1). A similar effect on the adiabatic results is expected for other collision systems studied in Refs. [7,9,10].

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