Analysis of Electron Correlation in Simultaneous Electron Transfer and Excitation in Atomic Collisions

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The two-electron process of simultaneous electron transfer and excitation (TE) in atomic collisions is studied within the close-coupling method for the example system $He^+ + H$. The calculated energy dependence of the population of various helium doubly excited states is analyzed for the role of electron correlations in the resonant and nonresonant contributions to the TE process which are included coherently. It is predicted that the impact-parameter–dependent state-selective TE probabilities show conspicuous peak structures.

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Simultaneous electron transfer and excitation (TE) in atomic collisions is a two-electron process in which doubly excited states of the projectile atom (or ion) are formed through the excitation of a projectile electron and, in the same collision event, the capture of an electron from the target atom. Similarly to a time-reversed Auger transition, TE can proceed as a resonant scattering between the quasifree electrons of the traveling target atom with the electrons of the projectile ion. This one-step resonant transfer-excitation (RTE) process populates doubly excited states much in the same way as in the dielectronic recombination[1,2] process, i.e., through the Coulomb interaction of projectile electrons with free or quasifree electrons. For ion-atom collisions, the same doubly excited states of the projectile can be populated in a nonresonant, two-step transfer-excitation (NTE) process which occurs as a sequence of uncorrelated one-electron excitation and transfer events.[1,2] A number of experiments have demonstrated the relative importance of these two TE mechanisms through their respective dependences on the projectile energy, on the projectile charge number, or on the target atoms.[3-8] All these experiments have been interpreted with use of the impulse-approximation, quasifree-electron approach[1] for the RTE process to which any NTE contributions have been added incoherently. Clear evidence for coherence effects between RTE and NTE processes has not been found yet in experiment.

A coherent treatment of the RTE and NTE processes has been presented by Feagin, Briggs, and Reeves,[9] and some first-order perturbation calculations based on that model have been reported by Reeves.[10] While it is convenient and conceptually attractive to express the TE amplitude as a coherent sum of separate RTE and NTE amplitudes, this separation follows from the assumption that the time propagation of each electron proceeds independently of other electrons throughout the collision. To avoid such an independent-electron approximation in the time evolution of the two-electron wave function and to achieve a clearer understanding of the role of interelectronic interaction (electron correlation) in TE processes, in this work we pursue a study of such processes by solving the Schrödinger equation for the two-electron collision system within the close-coupling basis expansion method.[11-13] By a judicious choice of configuration space for the time development of the two-electron wave function within this method, the role of electronic correlation in these collisions can be analyzed and the relative importance of the RTE and NTE processes for various doubly excited states can be assessed not only in the integrated cross sections but particularly in the impact-parameter dependences of TE. Results from this method will be shown to be in harmony with what is known from state-selective TE measurements[14,15] but are at variance with the predictions of the impulse approximation.

As a first application of this method we have chosen to study TE in $He^+ + H$ collisions, which is a particularly simple system for theory and also should allow qualitative comparison with experimental data for $He^+ + H_2$ collisions.[14]

In this work the electron dynamics is described within the framework of the semiclassical close-coupling method with two-electron atomic-orbital basis sets. Details of this method and of the calculational procedures are given elsewhere.[11] Here we stress that, in this method, the interelectronic interaction is included in the Hamiltonian throughout the collision, the electronic wave functions are properly (anti) symmetrized, and plane-wave translational factors are fully taken into account. In choosing the basis set we attempted to use a minimum number of two-electron configurations which are essential for the description of the TE processes. Hence we have included, besides the initial configuration $(1s\ He^+) \circ (1s\ H)$ [where the first (second) orbital is po-

TABLE I. Two-electron singlet configurations $(n_1l_1Z_1)(n_2l_2Z_2)$ which are included in the basis set adopted in this work for representing the helium states. Energies ϵ denote eigenvalues which result from diagonalization of the helium Hamiltonian in this basis and which are associated with the states in the first column.

Helium state	$n_1l_1Z_1$	$n_2l_2Z_2$	ϵ (a.u.)	ϵ (a.u.)
$1\,^1S$	$1s$ 1.19	$1s$ 2.18	−2.877	−2.903[a]
$2\,^1S$	$2s$ 1.21	$1s$ 2.08	−2.139	−2.146[a]
$2\,^1P$	$2p$ 0.97	$1s$ 2.0	−2.122	−2.124[a]
$2s2s(^1S)$	$2s$ 1.58	$2s$ 2.14	−0.772	−0.775[b]
$2p2p(^1D)$	$2p$ 1.13	$2p$ 2.12	−0.675	−0.697[b]
$2s2p(^1P)$	$2p$ 1.21 $2s$ 1.21	$2s$2.61 $2p$2.08	−0.668	−0.688[b]
$2p2p(^1S)$	$2p$ 1.13	$2p$ 2.12	−0.577	−0.615[b]

[a] Reference 16.

[b] Reference 17.

sitioned at the place of the He (H) center], six single excitation and single charge-transfer configurations ($1s$ He^+)∘($2lm$ H) and ($2lm$ He^+)∘($1s$ H) (with $l,m=0,1$). Since NTE occurs at rather small internuclear separations where, even at higher collision energies, the electrons may react to the increased molecular binding, also included in the basis are states of the united atom (charge $Z=3$) but otherwise with the same *nlm* quantum numbers. For the *singlet* two-electron configurations on the helium center, states representing single capture, i.e., capture into He $1s^2(^1S)$, $1s2s(^1S)$, and $1s2p(^1P)$, and states representing TE, i.e., transition into He $2s^2(^1S)$, $2p^2(^1D)$, $2s2p(^1P)$, and $2p^2(^1S)$, are included. All these helium states are generated by the diagonalization of the helium Hamiltonian in the basis of hydrogenic configurations given in Table I; the effective charges Z_1,Z_2 of each configuration (cf. Table I) have been chosen so as to minimize the energy expectation value of the associated state. Similarly, in separate calculations with *triplet* configurations, we have included the single-capture states $1s2s(^3S)$ and $1s2p(^3P)$ as well as the TE states $2s2p(^3P)$ and $2p^2(^3P)$. The helium energies calculated in the present basis set, as shown in Table I for the singlet states but also for the triplet states, compare reasonably well with the experimental ones[16] for singly excited states and with the calculations[16] for doubly excited states.

The cross section for the RTE process is expected to peak when the kinetic energy of the quasifree electron on the target is equal to the energy difference in the initial and final electronic states of the collision system. For the $\mathrm{He}^+ + \mathrm{H}$ collision system, the RTE process is expected to peak at 86-96-keV/amu impact energy, depending on the specific final doubly excited state in helium. Calculations have therefore been performed in the impact-energy range 20-150 keV/amu. The resulting cross sections for the population of doubly excited states are given in Fig. 1. This figure shows, at energies $E>50$ keV/amu, a mere steep decrease of cross sections with energy in the case of $2s^2(^1S)$, $2s2p(^1P)$, and $2p^2(^1S)$ states. At lower energies, the TE cross sections for these channels peak, as would be expected for any inelastic processes. However, a pronounced resonancelike structure which seems to be identifiable with the expected RTE peak is obtained for the $2p^2(^1D)$ state. We comment that this feature, i.e., only the $2p^2(^1D)$ state among the doubly excited states exhibits RTE-like resonance, is consistent with the experimental findings in $\mathrm{He}^+ + \mathrm{He}$ and $\mathrm{He}^+ + \mathrm{H}_2$ collisions. From Fig. 1, it is not clear whether the expected RTE peaks for other states are hidden in much larger NTE cross sections or whether they are not present at all. We note that the cross sections for transition into the $2s2p(^3P)$ and into the $2p^2(^3P)$ states (not shown in Fig. 1) also fail to display any resonance feature. In the following we analyze the calculated results in terms of the relative importance of RTE and NTE processes.

In a qualitative discussion, RTE is a one-step process

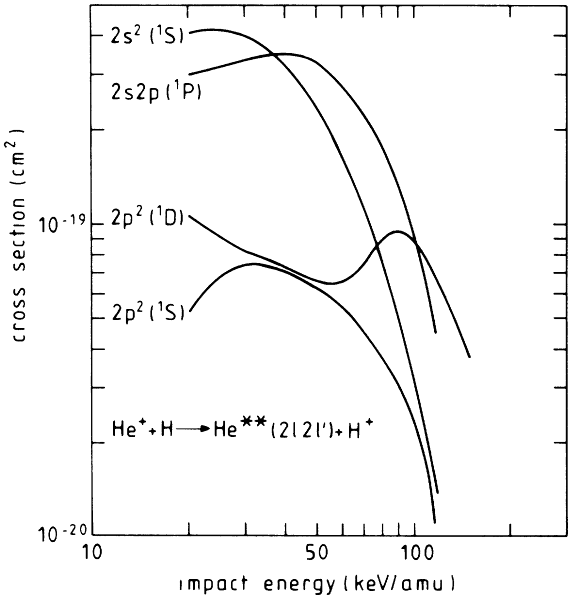

FIG. 1. Calculated state-selective TE cross sections for $\mathrm{He}^+ + \mathrm{H}$ collisions. Only the $2p^2(^1D)$ state shows evidence of an RTE peak.

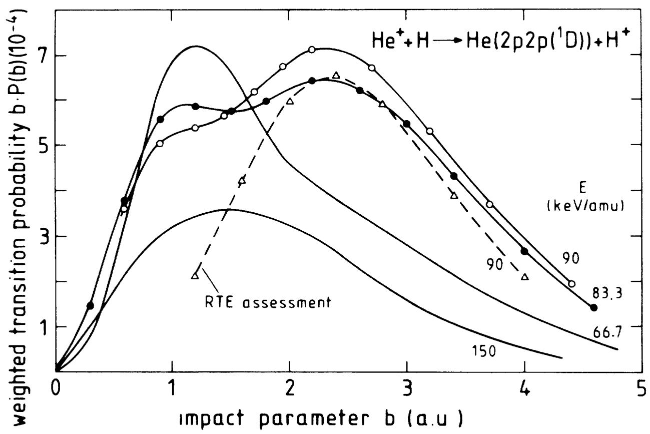

FIG. 2. Impact-parameter dependence of TE probabilities for the $2p^2(^1D)$ state at various energies. Full curves indicate results of the main calculations; the dashed curve, the result of an assessment of the RTE contribution (see text).

involving the interelectronic interaction while the NTE process results from two uncorrelated successive transitions. One may get an indication for the physical processes responsible for the cross sections shown in Fig. 1 by formulating a model in which the two-step population of doubly excited states is deliberately suppressed. This is accomplished in model calculations in which all explicit single-excitation and single-capture states are removed, i.e., by the inclusion of only the initial ($1s$ He$^+$)$\circ$($1s$ H) and the helium doubly excited states in such a "reduced" basis.

Figure 2 shows the impact-parameter–dependent probabilities for the population of $2p^2(^1D)$ states calculated with use of the reduced basis set (broken line labeled RTE) which are compared with the results calculated with the full basis set (full lines). First we note that at about the energy of the resonance of the ^1D state, $E=90$ keV/amu, the result of the full calculation is very close to the result of the calculation with the reduced basis set at impact parameters $b>2$ a.u. This shows that the major part of the ^1D resonance can be associated with the one-step RTE mechanism while the two-step (NTE) mechanism does not seem to be important. On the other hand, at impact parameters $b<2$ a.u., the full calculation at 90 keV/amu shows a shoulder which is not seen in the corresponding curve of the reduced calculation. This shoulder can be attributed to the interference between the RTE and NTE amplitudes. At lower energies, the RTE amplitude diminishes and the peak for the curve from the full calculation can, therefore, be considered as originating from the NTE process. Figure 2 demonstrates that TE to the ^1D state occurs by both RTE and NTE mechanisms in different but partly overlapping regions of impact parameters with varying relative strength depending on the collision energy. It also shows that the TE probabilities at large impact parameters (2-4 a.u.) indeed display resonant behavior as a function of the collision energy.

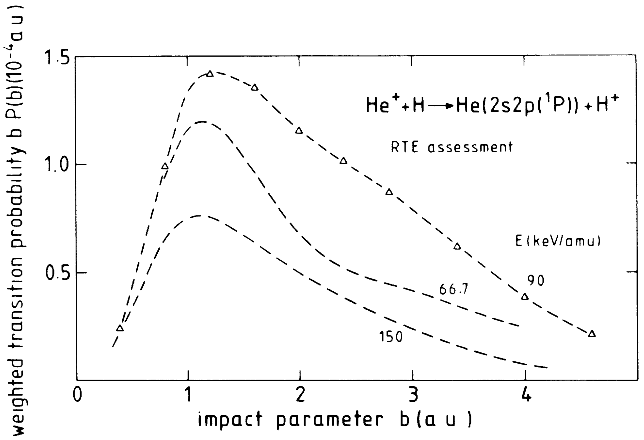

FIG. 3. Assessment of the RTE contribution to the $2s2p(^1P)$ state populations; cf. Fig. 2.

Figure 3 shows an assessment of the RTE contribution for the $2s2p(^1P)$ state. The curve at the approximate resonance energy of 90 keV/amu is clearly enhanced over the other curves; its magnitude is about a factor of 5 smaller than the estimated RTE cross section for the ^1D population (cf. Figs. 2 and 3). Therefore, this population is not noticeable in the total cross sections nor in the impact-parameter-dependence of the full TE process (not shown). A similar behavior has been observed for the $2s^2(^1S)$ state. For the $2p^2(^3P)$ state, the calculation with the reduced basis set (not shown here) does not display any indication of a resonance at about 90 keV/amu. This is consistent with the observation that in the impulse approximation this state does not decay by an Auger transition and, hence, should not be populated

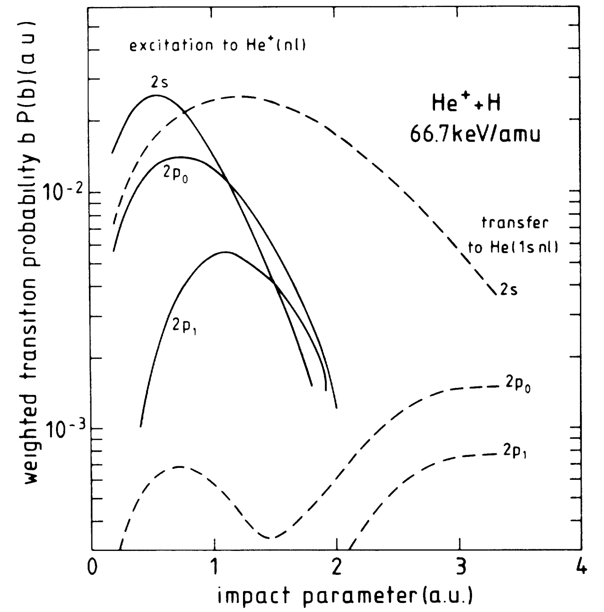

FIG. 4. Approximate one-electron excitation and transfer probabilities to $2s$, $2p_0$, and $2p_1$ states in He$^+$+H collisions at 66.7 keV/amu.

in an inverse Auger process.

In the impulse approximation, the RTE cross section for each doubly excited state is proportional to its autoionization width. The widths for ^1S, ^1P, and ^1D states of helium are 0.140, 0.039, and 0.073 eV, respectively,[17] and hence, all these states, particularly the ^1S state, should show some RTE structures. The fact that only the ^1D state shows evidence of a RTE peak in this investigation as well as in experiments suggest that the impulse approximation is inappropriate for these systems. We note that the collision speed at the RTE resonance energy (about 2 a.u.) is not much larger than the orbital speed of the target electron (about 1 a.u.) and thus the basic assumption of the impulse approximation is violated.

A qualitative assessment of the NTE cross-section contribution may be made by our appropriately combining one-electron transitions. Basic to this analysis is the assumption that each doubly excited state can be represented by its "main" components. For the determination, e.g., of the $2s2p(^1P)$ NTE cross sections, the probabilities

$$P^{\mathrm{NTE}}_{1s1\hat{s}\to 2s2p}=P^{\mathrm{cap}}_{1s1\hat{s}\to 1s2s}P^{\mathrm{ex}}_{1s2s\to 2p2s}+P^{\mathrm{cap}}_{1s1\hat{s}\to 1s2p}P^{\mathrm{ex}}_{1s2p\to 2s2p}+P^{\mathrm{ex}}_{1s1\hat{s}\to 2s1\hat{s}}P^{\mathrm{cap}}_{2s1\hat{s}\to 2s2p}+P^{\mathrm{ex}}_{1s1\hat{s}\to 2p1\hat{s}}P^{\mathrm{cap}}_{2p1\hat{s}\to 2p2s}, \tag{1}$$

(where the state $1\hat{s}$ is a hydrogen state and the others are states of helium) should be integrated over impact parameters. Since we are interested only in a rough assessment of the NTE contribution, we approximate each one-electron transition probability on the right-hand side of (1) to be independent of the quantum number of the spectator electron. The resulting "NTE cross sections" (not shown) agree in *shape* with the results of the full calculations for population of $2s^2(^1S)$ and $2s2p(^{1,3}P)$ states. They are, however, smaller by a factor of 2 to 4 for these states (cf. Fig. 1), indicating that this assessment of NTE cross sections does not hold quantitatively. The NTE contribution for the $2p^2(^1D)$ state is very small, in agreement with the earlier assessment that this state is dominated by the RTE process.

Figure 4 shows the impact-parameter-weighted occupation probabilities for various one-electron excitation and transfer processes taken from the full calculation at 66.7 keV/amu. These probabilities, suitably folded with each other, demonstrate why the cross-section contribution from the NTE process differs largely between the various doubly excited states. We observe that the probability for excitation of the helium ion limits the impact-parameter range for the NTE process to about 2 a.u. Within this range, the $2s$ transfer is the largest, with the $2p$ transfer more than 1 order of magnitude smaller. From this it is clear that the NTE population of $2s2s$ and $2s2p$ helium configurations is larger than the NTE population of $2p2p$ configurations.

In conclusion, the transfer-excitation process has been studied within the close-coupling method. While in the main calculations RTE and NTE processes are included coherently, separate RTE and NTE contributions to the TE cross sections have also been assessed. For the final ^1D state which is populated most strongly by the RTE mechanism we find that, at the energy of the RTE resonance, the RTE and NTE processes give rise to separate peaks in the impact-parameter dependence of the TE process, thus diminishing the chance of seeing interference between RTE and NTE processes in the TE integrated cross sections for this and other systems. We also find that predictions of the impulse approximation about the strength of the RTE process for the various final channels are clearly refuted in the detailed calculations. These results are in agreement with what is known from state-selective experiments available so far, i.e., only the $2p^2(^1D)$ state shows clear RTE resonance character. Our investigation also points out the need to probe experimentally the impact-parameter dependence for indications of interfering TE processes.

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