Comparative study of quantal and semiclassical treatments of charge transfer between O^+ and He

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A comparative study for the electron capture process $O^+(^4S^0,^2D^0,^2P^0)+He \rightarrow O(^3P)+He^+$ is reported. The cross sections are calculated using fully quantal and semiclassical molecular-orbital close-coupling (MOCC) approaches in the *adiabatic* representation. Detailed comparison of transition probabilities and cross sections is made from both MOCC approaches and displays close agreement above ~125 eV/u. The remarkable discrepancies between the earlier semiclassical and quantal MOCC approaches may be attributed to the insufficient step-size resolution in their semiclassical calculation [M. Kimura *et al.*, Phys. Rev. A **50**, 4854 (1994)]. Our results have also been compared with experiment and found to be in good agreement.

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Considerable attention has been paid to investigations of charge transfer for collisions of O^+ and He in recent years [1–6] because of its importance in populating excited states of oxygen and producing its atomic emission spectra in various astronomical environments, such as comets [7], the terrestrial atmosphere [8], and supernova remnants [9]. From the fundamental physics point of view, it is also very important to obtain detailed information on molecular structures and interactions for this system. The validity of classical, semiclassical, and quantal theories describing the collision systems may be checked by comparing measured and evaluated cross sections.

Recently, two experimental studies on charge transfer between O^+ and He arrived at completely contradictive conclusions. The measurement of Kusakabe *et al.* [1] showed that the total capture cross sections from He by metastable $O^+(^2D^0,^2P^0)$ ions at keV energies are similar to or even greater than that for the ground-state $O^+(^4S^0)$, while Wolfrum *et al.* [4] found that the metastable cross sections are too small to be measurable and suggested that this unexpected behavior was caused by efficient suppression of electron capture by one of the metastable ions due to a competing collisionally induced inelastic transition into the companion metastable state. In view of such completely contradictory conclusions, Lindsay and Stebbings [5] remeasured charge-transfer cross sections for the same process. Their ground-state capture cross sections agree well with those of Wolfrum *et al.* [4] and Kusakabe *et al.* [1] above 2 keV and the metastable cross sections are also consistent with the mixed-state data of Kusakabe *et al.* [1]. However, the large differences between the ground-state and metastable cross sections predicted by semiclassical calculations were not observed by Lindsay and Stebbings [5].

More recently, Zhao *et al.* [6] reported a fully quantal investigation of charge transfer between O^+ and He using the molecular-orbital close-coupling (MOCC) method in the *diabatic* representation. They obtained good agreement with most of the measurements mentioned above. However, the calculations of Zhao *et al.* [6] reproduced neither the ground-state nor the metastable-state cross section, as predicted by the semiclassical MOCC approach of Kimura *et al.* [3]. The quantal MOCC and semiclassical MOCC approaches are expected to agree if collision energies are not very low. For example, quantal and semiclassical charge-transfer cross sections and transition probabilities have shown good agreement for several collision systems, such as $Be^{4+}+H$ [10], $C^{2+}+He$ [11], and $S^{2+}+He$ [12] systems in the keV energy region.

The existing discrepancies among various experimental and theoretical results, especially between the semiclassical and quantal calculations for the system stimulated us to carry out a comparative study for charge transfer of O^+ and He using the fully quantal and semiclassical MOCC approaches. In the present Brief Report, we consider the same charge-transfer process,

$$O^+(^4S^0,^2D^0,^2P^0) + He \rightarrow O(^3P) + He^+ - \Delta E, \qquad (1)$$

as that of Kimura *et al.* [3] and Zhao *et al.* [6].

The fully quantal approach employed in this investigation has been formulated earlier in Ref. [13]. Here we present only a brief overview of the MOCC approach. The molecular-orbital close-coupling matrix equations in the *adiabatic* representation are written in the form

$$-\frac{i}{2\mu}[\nabla_{\mathbf{R}}^2 - \mathbf{M}(\mathbf{R}) - \mathbf{P}(\mathbf{R})\cdot\nabla_{\mathbf{R}}]\underline{F}(\mathbf{R}) + \mathcal{E}(R)F(\mathbf{R}) = EF(\mathbf{R}), \qquad (2)$$

where μ is the nuclear-reduced mass of the ion-atom pair, E is the relative collision energy in the center-of-mass frame, $\mathbf{R}$ is the coordinate of the relative nuclear motion, $F(\mathbf{R})$ is the scattering amplitude describing relative motion of the nuclei, $\mathcal{E}(R)$ is a diagonal matrix with elements consisting of adiabatic eigenvalues for each channel state with $|\mathbf{R}|=R$, and $\mathbf{M}$ and $\mathbf{P}$ are the coupling matrices whose expressions are given in Ref. [13].

By introducing a partial-wave decomposition for $F(\mathbf{R})$ as done in Ref. [13], Eq. (2) can be further reduced, and the resulting set of radial coupled equations can be solved with the normalized Fox-Goodwin algorithm of Braga and Belchior [14]. From the numerical results of close-coupling

equations for each partial wave and their asymptotic expressions, the K matrix may be extracted, and thus the scattering matrix S and charge-transfer cross sections are obtained by using the standard relations [15] corresponding to each partial wave. It is important to note that our prescription is different from that of Ref. [14], which starts from the Schrödinger equation in the diabatic representation. We, however, directly adopt an adiabatic basis and thus avoid transformation in order to regain the adiabatic representation.

The semiclassical MOCC approach utilized in the current collision calculations has been detailed in the review of Kimura and Lane [16] and also outlined in Ref. [12], and therefore is omitted here.

Ten molecular states involved in these calculations are $2\ ^2\Sigma^-$, $3\ ^2\Pi$, $2\ ^4\Sigma^-$, and $1\ ^4\Pi$, formed in the approach of $O(^3P)$ with He^+, $1\ ^2\Sigma^+$ and $2\ ^2\Pi$ by $O^+(^2P^0)$ with He, $1\ ^2\Delta$, $1\ ^2\Pi$, and $1\ ^2\Sigma^-$ by O^+ $(^2D^0)$ with He, and $1\ ^4\Sigma^-$ by $O^+(^4S^0)$ with He. The potentials of the ten molecular states and all 19 radial and rotational couplings among the ten states are evaluated from internuclear distance $R=1.5a_0-8.0a_0$ with the multireference single- and double-excitation configuration-interaction (MRD-CI) method [17]. These have been reported earlier in Refs. [3,6,18]. Detailed information on these potentials, such as the comparison of the asymptotic separated-atom energies with the experimental and other theoretical energies, and the dominant and weak couplings can be found therein.

The seven-doublet-state and three-quartet-state close-coupling calculations have been performed for OHe^+ using both the quantal and semiclassical MOCC approaches in the *adiabatic* representation, as described above. In order to make a detailed comparison between the quantal and semiclassical findings, the transition probabilities $P(b)$ times impact parameters b as a function of b are plotted, respectively, at $E=125$ eV/u and 1 keV/u in Figs. 1 and 2. Both quantal and semiclassical $bP(b)$ display similar Stueckelberg-type oscillating structures for capture by the metastable $^2D^0$ and $^2P^0$ ions, while a nonoscillating shape is found for capture by O^+ in the ground state, $^4S^0$ at $E=1$ keV/u. From the two figures, one sees good agreement between the quantal and semiclassical transition probabilities and agreement is excellent at $E=1$ keV. This close agreement illustrates effectiveness of the classical description of nuclear motion. As such a detailed comparison can provide a check on the reliability and accuracy of the theoretical methods employed, the transition probabilities are compared at a few more energies ($E=31.25, 62.5, 500, 625$ eV/u). We found that agreement worsens with decreasing collision energies. Such a tendency is not surprising. This is because as energies get lower, the quantal behavior of nuclei becomes notable and the classical description of nuclear motion is no longer valid. Depending on systems and their states, starting energies where semiclassical theory fails are different. Furthermore, it is observed that the lower the energies are, the more violent the oscillation of $bP(b)$. This feature has also been observed earlier for S^{2+}+He collisions [12]. An explanation has been given therein (see Ref. [12] for details).

In Figs. 3(a) and 3(b), we present electron capture cross sections by O^+ ions in the ground and metastable states, respectively, along with other theoretical and experimental results. The projectile energy concerned ranges from 0.5 to 10 keV. The current quantal and semiclassical MOCC cross sections in the adiabatic representation agree very well in the higher-energy region, but there are larger discrepancies at the lower energies. In particular, the discrepancy attains a factor of about 2 for ^4S at $E_{\mathrm{Lab}}=0.5$ keV. This illustrates the limitation of semiclassical theory, as discussed above. Our quantal MOCC cross sections have been compared with the quantal MOCC results in the diabatic representation [6]. The discrepancy between both quantal results ($<40\%$) is attributed to different estimates of potential and couplings in the interior region of small internuclear distances, where *ab initio* calculations of molecular structures are rather difficult for any theoretical technique. The estimates made in the present work and Ref. [6], which are based on the different representations, are not identical and therefore give rise to the discrepancies depicted in the figures.

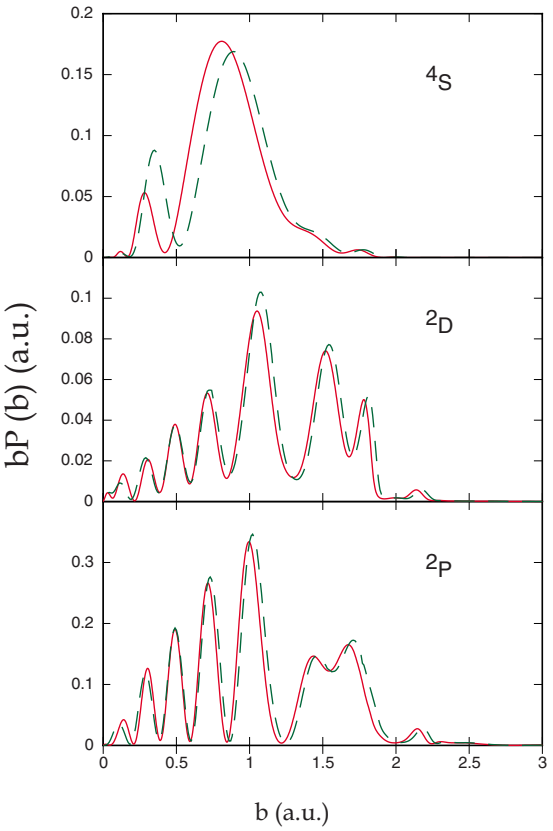

FIG. 1. (Color online) Comparison of quantal (——) and semiclassical (----) MOCC transition probabilities $P(b)$ times impact parameters b for capture by O^+ in the $^4S^0$, $^2D^0$, and $^2P^0$ states as a function of b at $E=125$ eV/u. In the quantal case, we take $b=J/k$.

Over the entire energy region, the semiclassical MOCC cross sections of Kimura *et al.* [3] are larger than the present semiclassical MOCC results for both the metastable $^2D^0$ and $^2P^0$ states. The discrepancy varies widely from a factor of a few to more than 1 order of magnitude. In contrast, for the ground state $^4S^0$, the semiclassical results of Kimura *et al.* [3] are significantly smaller than ours except for energies close to $E_{\mathrm{Lab}}=9$ keV. The discrepancies may stem from an insufficient step-size resolution in their calculations. As the

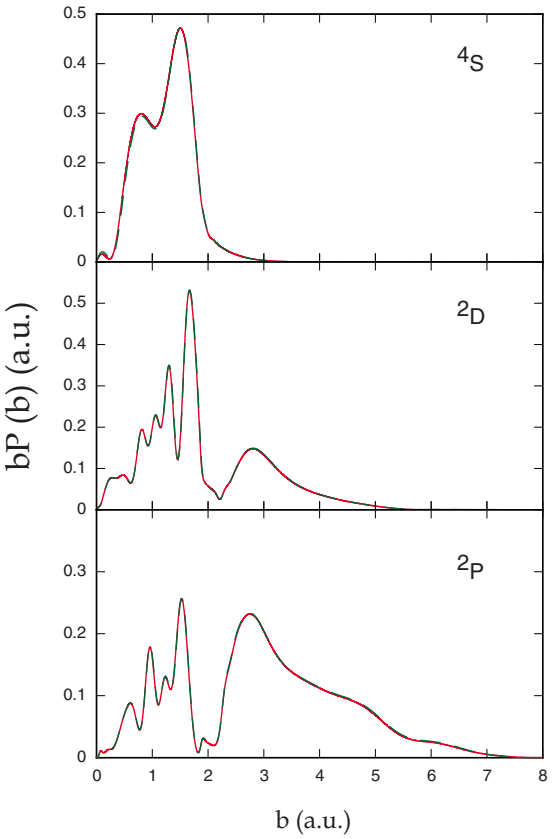

FIG. 2. (Color online) Similar to Fig. 1 but $E=1.0$ keV/u.

adiabatic representation is utilized in the semiclassical MOCC calculations, a difficulty arises in solving the set of coupled equations when integrating through a sharp avoided crossing where a radial coupling is strongly peaked. Near such avoided crossings, a small integration step size is required. Larger step sizes result in significant variation in the cross sections leading to unconverged results. The integration step size may have not been small enough in the semiclassical MOCC calculations of Kimura *et al.* [3]. We carefully checked the variation in transition probabilities as well as cross sections with the step sizes to attain convergence at each energy point in the current quantal and semiclassical MOCC calculations. In all cases, the step size required becomes smaller with increasing energies.

The experimental cross sections shown in Fig. 3(a) are from measurements presumed to be for pure $O^+(^4S^0)$ beams or beams with small metastable contamination [4]. The current quantal and semiclassical MOCC results agree well with the measured data except for those of Kusakabe *et al.* [1] below 2 keV. According to Lindsay and Stebbings [5], the discrepancy was caused due to the problem for apparatus operating at the lower energies. Above 5 keV, the current quantal and semiclassical MOCC results are in better agreement with experimental cross sections than those of Ref. [6]. In view of the fact that Kusakabe *et al.*'s [1] $O^+(^4S^0)$ beams have been contaminated with the metastable ions, it is readily inferred that capture cross sections for the metastable states are similar to those for the ground state above around 3 keV. Such a conclusion has been reached by Zhao *et al.* [6] and is also supported by the current calculations.

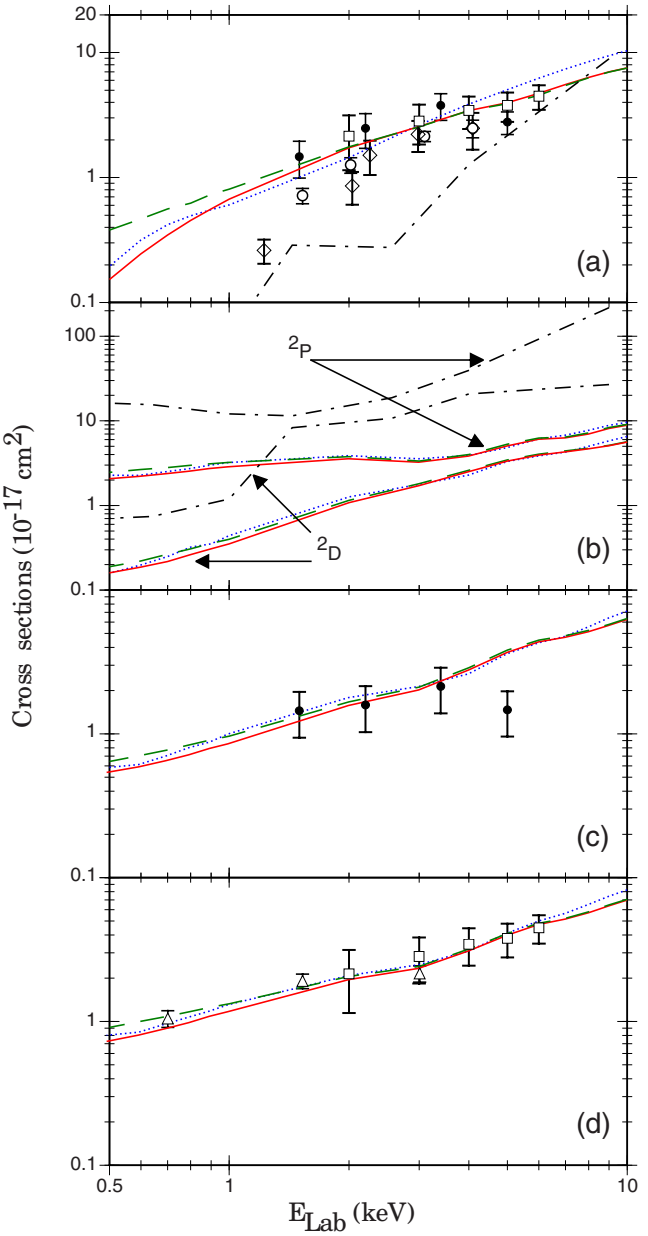

FIG. 3. (Color online) Cross sections for charge transfer between O^+ and He. (a) Capture by $O^+(^4S^0)$. Theory: —— present quantal MOCC; ---- present semiclassical MOCC; ····· Zhao *et al.* [6]; - ·- ·, Kimura *et al.* [3]. Experiment: ○ Kusakabe *et al.* [1]; ◇, Kusakabe *et al.* [1], mostly ground state but small metastable contamination; □ Wolfrum *et al.* [4]; ● Lindsay and Stebbings [5]. (b) Capture by $O^+(^2D^0)$ and $O^+(^2P^0)$. Same notations as in (a). (c) Capture by mixed metastable O^+ ions. Theory: same notations as in (a) with a fraction ratio $O^+(^2P^0):O^+(^2D^0)=1:4$. Experiment: ● Lindsay and Stebbings [5]. (d) Capture by mixed ground-state and metastable O^+ ions. Theory: same notations as in (a) with a fraction ratio $O^+(^4S^0):O^+(^2D^0):O^+(^2P^0)=2:5:3$. Experiment: △ Kusakabe *et al.* [1]; □ Wolfrum *et al.* [4].

In Fig. 3(c), the current quantal and semiclassical MOCC cross sections for capture by the metastable O^+ ions are compared with the measurement of Lindsay and Stebbings [5]. As their experimental techniques cannot differentiate be-

tween $O^+(^2P^0)$ and $O^+(^2D^0)$ and the mixing ratio is unknown, one has to first assume the ratio to make a comparison between experiment and theory. Zhao *et al.* [6] reproduced the experimental data by taking the ratio of $O^+(^2P^0)$ to $O^+(^2D^0)$ to be 1:4 except at $E_{\mathrm{Lab}}=5$ keV. The explanation of the discrepancy at $E_{\mathrm{Lab}}=5$ keV can be found therein. Using the same ratio as that in Ref. [6], we obtain good agreement with the measurement for both the quantal and semiclassical MOCC calculations. It should been emphasized that our results are in contrast with Wolfrum *et al.*'s [4] experimental conclusion that the metastable cross sections are too small to be measurable.

To compare with measurements for capture by unspecified mixed ions in the $^4S^0$, $^2D^0$, and $^2P^0$ states, Zhao *et al.* [12] investigated variations in cross sections with fractions of $O^+(^4S^0)$, $O^+(^2D^0)$, and $O^+(^2P^0)$ and found that 2:5:3 did generate the best agreement with the measurements. In Fig. 3(d), our quantal and semiclassical MOCC cross sections are presented with the same fraction ratio and compared with measurement by Kusakabe *et al.* [6] and also with the quantal MOCC results in the diabatic representation. The measurement by Wolfrum *et al.* [4] is also shown in this figure, as their ion beam is thought to be a mixed beam, although they claim it to be a pure beam. Good agreement is displayed.

In summary, in order to explain the discrepancies among various experimental and theoretical results, especially between quantal and semiclassical MOCC calculations, we have performed a comparative study of charge transfer for collisions of O^+ and He using the fully quantal and semiclassical MOCC approaches in the *adiabatic* representation. It is found that the remarkable discrepancies between the previous semiclassical and quantal MOCC calculations [6] are attributed to the insufficient step-size resolution yielding unconverged results in the semiclassical calculations. Our results have also been compared with experiments and found to be in good agreement with most of the experimental data. The present quantal and semiclassical MOCC calculations support a previously drawn conclusion in the literature [6], namely, the so-called "suppressed electron capture effect" for metastable ions is not a viable mechanism.

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