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Quantal and semiclassical calculations of charge transfer in C^{2+}+He collisions

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A quantal reaction-coordinate treatment is employed to calculate charge-transfer cross sections for $^{12}C^{2+}+^{4}He$ collisions in the impact energy range $300\ eV \leqslant E \leqslant 2.5$ keV, using a molecular basis set. Total cross sections are compared with semiclassical results and with available experimental data. [S1050-2947(97)04007-9]

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In a recent publication [1] cross sections for charge transfer and excitation in C^{2+}+He collisions were calculated for ^{12}C impact energies $E \geqslant 2$ keV (relative velocity $v \geqslant 0.082$ a.u.). This calculation was carried out using a basis set of *ab initio* molecular wave functions that included translation factors, and a semiclassical, impact-parameter treatment. The calculated cross sections showed good agreement with the experimental data [2], for the charge-transfer reaction in which the C^{2+} is in the (metastable) state $1s^22s2p\ ^3P$

$$C^{2+}(1s^22s2p\ ^3P)+\mathrm{He}(1s^2\ ^1S)\rightarrow C^{+}+\mathrm{He}^{+}(1s). \quad (1)$$

However, theoretical and experimental results disagree for the corresponding reaction starting from the C^{2+} ground state

$$C^{2+}(1s^22s\ ^1S)+\mathrm{He}(1s^2\ ^1S)\rightarrow C^{+}+\mathrm{He}^{+}(1s). \quad (2)$$

It was suggested in [1] that these discrepancies might be due to the presence of metastable C^{2+} ions in a proportion bigger than expected in the incident beam. Nevertheless, since the largest differences between theory and experiment were found at relatively low impact energies ($E \simeq 2$ keV), the validity of the impact-parameter method must be checked before a conclusion on the reasons for the discrepancies between theory and experiment at low energies can be reached. Therefore, we have carried out quantal and semiclassical calculations of the cross sections for reactions (1) and (2), extending the range of the calculation to lower impact energies ($300\ eV < E < 2$ keV) where experimental results are not available. The cross section for the excitation process

$$C^{2+}(1s^22s\ ^1S)+\mathrm{He}(1s^2\ ^1S)\rightarrow C^{2+}(1s^22s2p\ ^1P) + \mathrm{He}^{+}(1s) \quad (3)$$

has also been calculated.

The main theoretical difficulty in the use of the molecular expansion is the so-called momentum-transfer problem (see, e.g., [3]). In the semiclassical case, this is solved by including translation factors. In particular, the inclusion of a common translation factor [4] (CTF) leads to a formally convergent expansion which has been employed in many works (see, e.g., [5] and references therein). The situation is different with regards to the application of the quantal method. In this case the solution of the momentum transfer problem lies in the introduction of reaction coordinates (RC) [6] (see Ref. [7] for a review on the RC method). However, this method has been applied only in a few calculations [8–10], and an explicit comparison of CTF and RC approaches has been presented only in Ref. [8]. The RC method is an improvement of the close-coupling molecular expansion in which the coordinates are chosen so that the asymptotic condition can be rigorously fulfilled; further the method can be applied to atom-atom and atom-molecule collisions [11] as well as vibrational problems [12]. In this formalism the total wave function for the collisional system Ψ, solution of the time-independent Schrödinger equation, is expanded in terms of a set of molecular wave functions $\{\psi_j(\mathbf{r},\boldsymbol{\xi})\}$ in the form

$$\Psi(\mathbf{r},\boldsymbol{\xi})=\sum_j F_j(\boldsymbol{\xi})\psi_j(\mathbf{r},\boldsymbol{\xi}), \quad (4)$$

where $\mathbf{r}$ denotes the set of electronic coordinates, $\boldsymbol{\xi}$ is a common RC, and the functions ψ_j are (approximate) eigenfunctions of the Born-Oppenheimer fixed nuclei electronic Hamiltonian $H_{\mathrm{el}}(\mathbf{r},R)$ for a value of the internuclear distance R, numerically equal to ξ

$$H_{\mathrm{el}}(\mathbf{r},R=\xi)\psi_j(\mathbf{r},\xi)=\epsilon_j\psi_j(\mathbf{r},\xi). \quad (5)$$

The RC $\boldsymbol{\xi}$ is expressed in terms of a switching function f (see, e.g., [7]). Keeping terms up to order μ^{-1}, where μ is the reduced nuclear mass in atomic units, one can write

$$\boldsymbol{\xi}=\mathbf{R}+\frac{1}{\mu}\sum_{i=1}^{N}\mathbf{s}_i(\mathbf{r}_i,\mathbf{R}), \quad (6)$$

where N is the total number of electrons and

$$\mathbf{s}_i(\mathbf{r}_i,\mathbf{R})=f(\mathbf{r}_i,\mathbf{R})r_i-\tfrac{1}{2}f^2(\mathbf{r}_i,\mathbf{R})\mathbf{R}. \quad (7)$$

Although expansion (4) is formally convergent, the speed of convergence depends on the particular choice of the RC. Several switching functions have been proposed [5] and applied to define CTFs in general for one-electron systems. In this work we have employed the same switching function used to define the CTF in [1], and that has been also employed by other authors [8–10] in quantal calculations. It has the form

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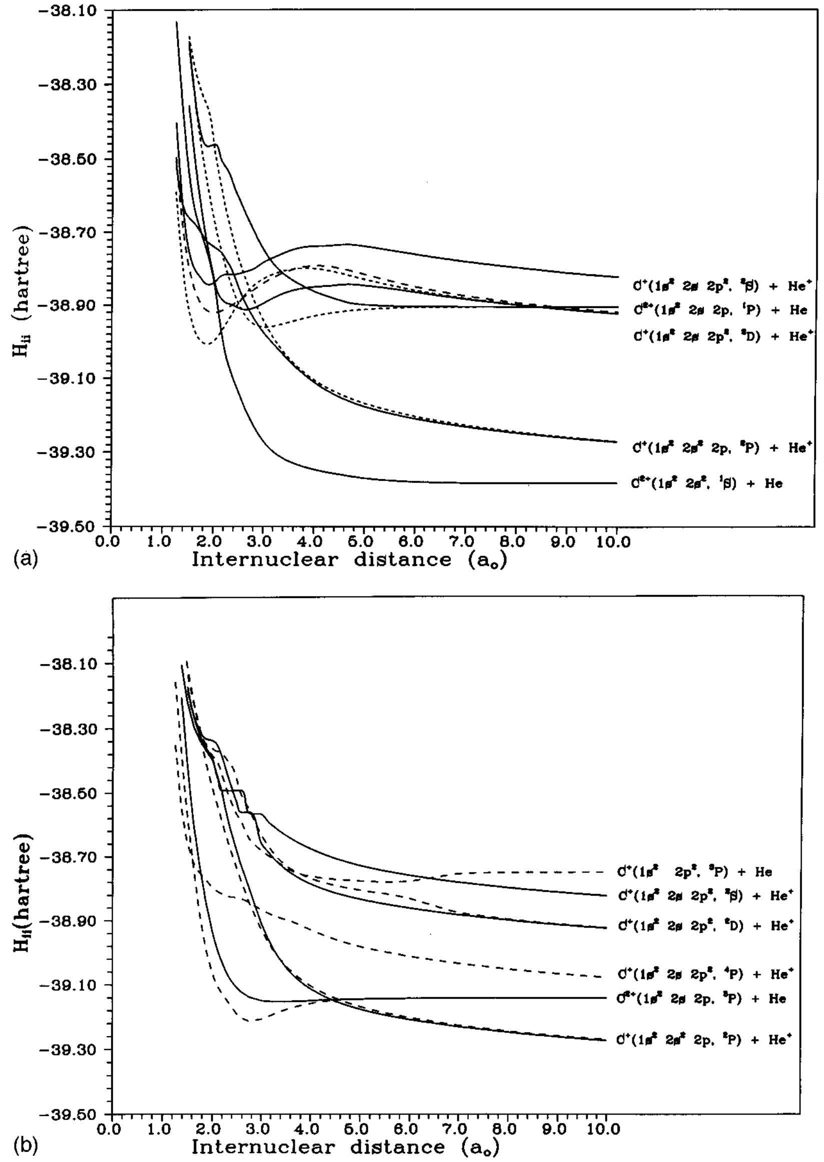

FIG. 1. Expectation values H_{ii} of the electronic Hamiltonian for the diabatic states included in the molecular basis set. (a) SInglet subsystem: —, Σ states; . . . , Π states; - - -, Δ states. (b) Triplet subsystem: —, Σ states; - - -, Π states.

$$f(\mathbf{r}_i,R)=\frac{R}{R^2+\beta^2}\,[\mathbf{r}_i\cdot\hat{\mathbf{R}}+\mathbf{R}(p-p_0)]-(p-p_0), \qquad (8)$$

where the electronic position vectors $\mathbf{r}_i$ are referred to the nuclear center of mass, pR is the distance from the nuclear center of masses to the carbon nucleus ($p=1/3$). β and p_0 are two parameters whose values (2.0 and 0.0, respectively) are identical to that employed in the semiclassical calculation [1]. In particular, p_0 indicates the position of the so-called privileged origin [13] (the carbon nucleus in the present calculation). Obviously, the use of the same set of parameters in both calculations does not mean that this is an optimal choice for the RC calculation. Substitution of expansion (4) into the Schrödinger equation leads to the set of differential equations [14]

$$(2\mu^{-1})\nabla_\xi^2 F_j(\boldsymbol{\xi})+\sum_k\,[\mu^{-1}\boldsymbol{M}_{jk}\cdot\boldsymbol{\nabla}_\xi+(E-\varepsilon_k)\delta_{jk}$$
$$+(2\mu^{-1})\langle\psi_j|\nabla_\xi^2|\psi_k\rangle]F_k(\boldsymbol{\xi})=0 \qquad (9)$$

with

$$\boldsymbol{M}_{jk}=\langle\psi_j|\nabla_\xi+\sum_{i=1}^{N}\,(\boldsymbol{\nabla}\mathbf{s}_i)\cdot\boldsymbol{\nabla}+\frac{1}{2}\,\nabla^2(\mathbf{s}_i)|\psi_k\rangle \qquad (10)$$

and where, as in Refs. [9] and [10], we have neglected small terms of order ε_j/μ. Solution of the differential equation (9) with the corresponding boundary conditions yields the scattering matrix S_{ij}^J. If the system is initially represented by the function ψ_i, the total cross sections for transition to state ψ_j, σ_{ij} is given by

$$\sigma_{ij}=\frac{\pi}{k_i^2}\sum_J\,(2J+1)|S_{ij}^J|^2, \qquad (11)$$

where k_i is the initial momentum.

In order to compare quantal and semiclassical results, it is useful to summarize the basic equations leading to the total cross sections in the impact-parameter (IP) method. In this method the nuclei follow rectilinear trajectories with impact parameter b and uniform velocity v, while the electronic

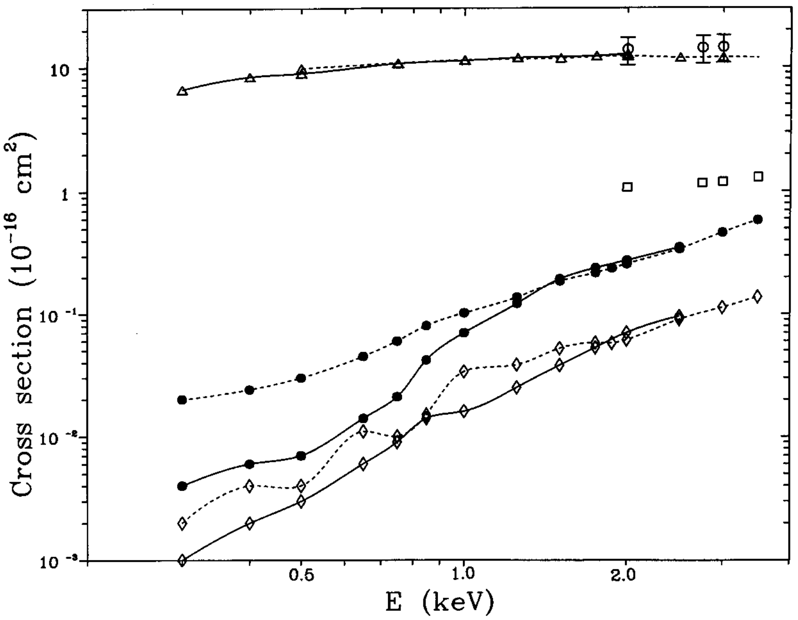

FIG. 2. Total cross sections for reactions (1)–(3) as functions of the impact energy. Results for reaction (1): -△-, quantal result; --△--, semiclassical result; ○, experimental data [2]. Results for reaction (2): -●-, quantal result; --●--, semiclassical result; □, experimental data [2]. Results for reaction (3): -◇-, quantal result; --◇--, semiclassical result.

motion is described by means of the wave function $\Psi^{SC}(\mathbf{r},R(t))$, which is a solution of the impact-parameter equation

$$\left[H_{el}-i\left.\frac{\partial}{\partial t}\right|_{\mathbf{r}}\right]\Psi^{SC}=0 \tag{12}$$

The function Ψ^{SC} is expanded in terms of a set of molecular wave functions $\psi_j(\mathbf{r},R)$ in the form

$$\Psi^{SC}(\mathbf{r},R(t))=D(r,t)\sum_j a_j(t)\psi_j(\mathbf{r},R)\exp\left(-i\int_0^t \varepsilon_j dt'\right), \tag{13}$$

where D is a CTF (see Ref. [1]) that includes the switching function of Eq. (7). Substitution of the molecular expansion into the semiclassical equation yields a set of differential equations for the coeficients $a_j(t)$ of the form

$$i\frac{da_j}{dt}+\sum_k [i\boldsymbol{v}\cdot\boldsymbol{M}_{jk}+v^2N_{jk}]a_k\exp\left[-i\int_0^t(\varepsilon_k-\varepsilon_j)dt'\right]=0, \tag{14}$$

where the dynamical coupling terms $\boldsymbol{M}_{jk}$, N_{jk} depend on the particular CTF chosen. It must be noted that the part of the coupling proportional to v in Eq. (14) is identical to the coupling appearing in the RC expression (9). The quantal terms equivalent to the couplings proportional to v^2 in Eq. (14) are neglected in the approximations leading to Eq. (9) (see, e.g., [7]). Besides, RC and CTF-IP equations can be related by expanding $F_j(\boldsymbol{\xi})$ in powers of μ^{-1}. Explicitly,

$$F_j(\boldsymbol{\xi})=\exp(i\mu\boldsymbol{v}\cdot\boldsymbol{\xi})(F_j^0+\mu^{-1}F_j^1+\cdots), \tag{15}$$

substituting this expansion into Eq. (9) and neglecting terms of order μ^{-1}, in particular, $(2\mu^{-1})\langle\psi_j|\nabla_\xi^2|\psi_k\rangle$, leads to

$$i\boldsymbol{v}\cdot\boldsymbol{\nabla}_\xi F_j^0+i\boldsymbol{v}\sum_k \boldsymbol{M}_{jk}F_k^0-\varepsilon_jF_j^0=0. \tag{16}$$

As usually, we identify $\boldsymbol{v}\cdot\boldsymbol{\nabla}_\xi=\partial/\partial t$ and $F_j^0=a_j\exp[-i\int_0^t\varepsilon_j dt']$, obtaining Eq. (14), except for terms proportional to v^2. The total cross section for transition to state j is given by

$$\sigma_{ij}=2\pi\int_0^\infty bP_{ij}(b)db, \tag{17}$$

where the transition probability, $P_{ij}(b)$, is

$$P_{ij}(b)=\lim_{t\to\infty}|a_j(t=\infty)|^2. \tag{18}$$

In practice, the simplest way to solve Eq. (9) is to eliminate the first-order derivative with respect to ξ by means of a transformation to a diabatic representation [15], in which the radial component of the couplings $\boldsymbol{M}_{jk}$ vanishes. In this work we have integrated the radial couplings following the numerical method described in [9] and [16]. The expectation values of the electronic Hamiltonian for the molecular diabatic states (diabatic energies) included in the basis set are shown in Figs. 1(a) and 1(b). The entrance channel of reaction (1) is a statistical mixture of states 2 $^3\Sigma$ and 2 $^3\Pi$ which dissociate into $\mathrm{C}^{2+}(1s^22s2p\ ^3P)+\mathrm{He}(1s^2\ ^1S)$. The dominant mechanism of this reaction involves transitions from these states to 1 $^3\Sigma$ and 1 $^3\Pi$ in the crossings at $R\sim4.5a_0$ in Fig. 1(b). On the other hand, the diabatic energy of the entrance channel of reaction (2) (1 $^1\Sigma$) does not exhibit any crossing for $R>2a_0$. For smaller internuclear distances the large number of crossings between the diabatic energies indicates that there is not a simple mechanism of the charge-transfer reaction in this basis, as discussed in [1]. To calculate the total cross sections, the coupling matrix elements, once tranformed to the diabatic basis set, are substituted into Eq. (9). A partial-wave analysis of the nuclear wave function is carried out which leads to a set of differential equations for the radial waves that is solved numerically. In this work we have used the log-derivative algorithm of Johnson [17] as implemented in Ref. [16]. The calculated cross sections are shown in Fig. 2 together with the semiclassical results [1]

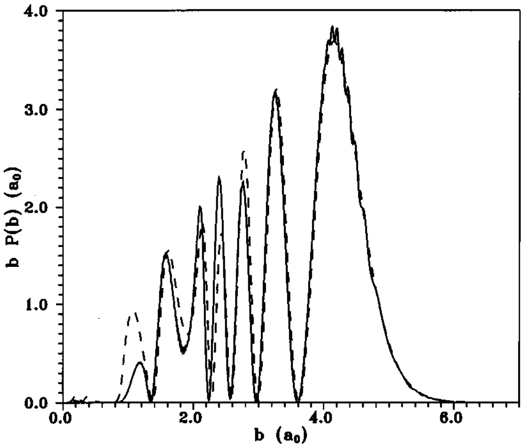

FIG. 3. Opacity for reaction (1) at an impact energy of 1.75 keV vs b. ---, semiclassical result —, quantal result for $bP_{ij}(b)$, where $i=2^3\Sigma$, $j=1^3\Sigma$. In the quantal case $P_{ij}=|S^J_{ij}|^2$, $J=b(2\mu E)^{1/2}$, and in the semiclassical case P_{ij} is the transition probability and b the impact parameter.

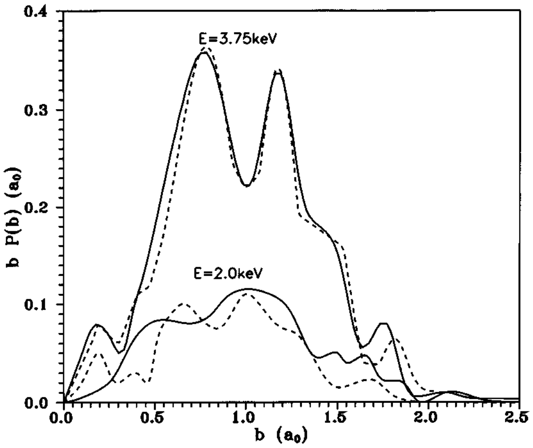

FIG. 4. Opacity $bP(b)$ for reaction (2) at two impact energies: 2 keV and 3.75 keV, where $P(b)$ is the sum over all exit channels, j, of $P_{ij}(b)$. ---, semiclassical result for reaction (2); —, quantal results for reaction (2).

that have been extended to lower nuclear velocities and the experimental data. Quantal and semiclassical results for reaction (1) show excellent agreement in the whole range of impact energies; however, although both calculations yield the same cross sections for reaction (2) in the energy range 1.5 keV $<E<$2.5 keV, they diverge for lower energies. With respect to the comparison with the experiment, good agreement is found for reaction (1), while the disagreement found in [1] for reaction (2) for $E\simeq 2$ keV remains when comparing with the RC values. Even more, the RC values are lower than the CTF-IP ones when the collision energy decreases.

A more detailed comparison of CTF-IP and RC calculations is provided by quantal and semiclassical transition probabilities, which are illustrated in Figs. 3 and 4. In these figures we have plotted the charge-transfer opacity $bP(b)$ for reactions (1) and (2). From the comparison of these two figures one can note the different mechanisms of reactions (1) and (2), already pointed out in [1]. While quantal and semiclassical opacities for reaction (1) show similar Stueckelberg-type oscillating structures, with transitions taking place at relatively large impact parameters ($b\simeq 4.5a_0$), a nonoscillatory shape is found for reaction (2), with transitions occuring at lower impact parameters (or lower angular momenta in the quantal treatment). Besides, noticeable disagreement is found between quantal and semiclassical opacities for reaction (2) at $E\simeq 2$ keV.

In order to analyze the disagreement between quantal and impact-parameter results for reaction (2) we have carried out several tests: First we have checked that the differences do not arise from the couplings proportional to v^2 in the CTF-IP method [Eq. (14)] by setting these couplings equal to zero and checking that the opacities do not change. In a second test we have increased the nuclear reduced mass in the RC calculation for a fixed relative nuclear velocity of 0.0365 a. u. We have checked that the semiclassical cross section is obtained for $\mu>9$ amu. In practice, a difference between quantal and semiclassical calculations is the use in the former one of a diabatic basis set. To study the practical influence of this transformation, we have carried out the CTF-IP calculation using the same diabatic states employed in the RC one. Cross sections obtained from both, diabatic and adiabatic semiclassical calculations are indistinguishable. Finally, we have considered the comparison of both calculations at relatively high velocities. While quantal and semiclassical calculations yield the same cross sections (Fig. 2) for $E\simeq 2$ keV, worse agreement is found for the corresponding opacities (Fig. 4). Good agreement is however recovered for higher energies ($E=3.75$ keV), showing the consistency of both calculations.

As a first conclusion of the present work, RC calculations support both, CTF-IP and experimental cross sections for reaction (1) in the range of impact energies (300 eV–2.5 keV) considered. Secondly, RC and CTF-IP cross sections for reaction (2) agree for $E>1.5$ keV, while remarkable disagreement is found with the experimental values, which reinforces the conclusions of Ref. [1]. Finally, further work is needed to analyze the disagreement between RC and CTF-IP calculations for reaction (2) for $E<1.5$ keV. A possible explanation for this disagreement might be a limitation of the IP approximation for this collision at impact energies below 100 eV/amu. This explanation is supported by the calculation of Ref. [8], in which noticeable trajectory effects were found at similar nuclear velocities. Furthermore, trajectory effects are expected to be more important for reaction (2) than for reaction (1) that takes place at larger impact parameters. On the other hand, given the lack of calculations comparing RC and CTF-IP methods, the effect on the convergence of both expansions of the choice of the switching function is unknown. However, the system considered in this work is not suitable for a convergence study, and a systematic comparison of RC and CTF-IP methods for one-electron systems is desirable.

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