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Semiclassical trajectory effects on C^{6+}-H charge-exchange cross sections at low energy

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Close-coupling charge-exchange calculations for C^{6+}-H collisions have been carried out for impact velocities spanning 2.5×10^4 to 5×10^5 m/s ($\sim$3-to-1300—eV H energy). Six appropriate molecular states were included, among which all radial and angular couplings were evaluated using the proton as an electronic origin following the approach of Piacentini and Salin. Four levels of semiclassical approximations for the nuclear motion were investigated and compared: (1) the usual straight-line impact-parameter approximation, (2) the use of a Coulomb trajectory on a effective $6/R$ potential, (3) the previously developed average approximation, which is a form of multitrajectory theory, and (4) a uniform semiclassical reference-function method of essentially full quantum accuracy. The results are presented and the validity of these various approximations for the nuclear motion is discussed, for the range of collision energies reported.

I. INTRODUCTION

In theoretical treatments of atom-atom (or ions) collisions, it is customary to treat the relative motion of the atoms by classical approximations while retaining a quantum-mechanical description of the electronic motion. This procedure has a range of validity which can be understood from the development of the impact parameter method for atomic collisions: the heavy and energetic nuclei can persist in nearly rectilinear, unperturbed, motion while moving at an appropriate velocity to strongly couple to the electronic motion.[1] As the relative motion slows down from the domain of validity of the impact-parameter method, the electron dynamics tend to couple only among nearly degenerate Born-Oppenheimer states (adiabatic behavior) and the nuclear dynamics tend toward motion on the potential-energy surfaces given by the electronic eigenenergies. This low-energy region of atomic collisions is quite complicated due to the inadequacy of a single classical trajectory to describe the "nuclear part" of the system.

In some circumstances a classical-quantum separation is useful in which the relative classical motion of the nuclei (atomic center-of-mass coordinate) is evaluated on a single effective potential energy surface, which may be dependent on the electronic state of the system.[2] This method can better accommodate large-angle deflections, due to close approach of the nuclei or strong repulsion of inner-core electrons which tend to remain adiabatic while other outer electrons are perturbed. At still lower collision energies, typically less than a few hartrees, a full coupled quantum description of the system becomes necessary[3]; such a description may involve semiclassical approximations for the nuclear wave functions, but it is not equivalent to a simple, single classical trajectory.

The prime motivation for this study is the disagreement between the results of Vaaben and Briggs[4] (VB) and those of Salop and Olson[5] (SO) for the C^{6+}-H collision system. Salop and Olson[6] conjecture that most of the discrepancy at collision velocities less than 10^6 m/s is due to VB's use of an effective potential given by the unscreened nuclear repulsion ($6/R$ in Hartree atomic units) to determine the nuclear classical trajectory. This potential could exclude the atoms from the strong-coupling region near 7 bohrs and thus lower the total charge-exchange cross section.

In Sec. II we briefly describe the electronic basis set; it has been discussed elsewhere in detail. In Sec. III we describe the different semiclassical approaches to the solution of the collision physics, and in Sec. IV we give the results and discussion.

II. ELECTRONIC BASIS

The electronic basis set appropriate for the description of a colliding system at low energy is the set of Born-Oppenheimer (infinite-nuclear-mass adiabatic) states linked to the initial electronic state by near degeneracies. For the C^{6+}-H system these include the six molecular states[7]: (5,4,0), (4,3,0), (4,3,1), (4,2,0), (4,2,1), and (4,3,2) in united-atom notation (n,l,m).[4,5,7] The weakly split crossing of the (5,4,0) state with the (6,5,0) state at 21.36 bohrs remains totally diabatic above 13 eV so that we can properly neglect this state and others in the $n=5$ and 6 united-atom manifold at all but the lowest energy.[8] At this lowest energy the (6,5,0)-(5,4,0) avoided crossing contributes an amount to the total charge-exchange cross section which is about equal to that obtained here from transitions near an internuclear separation of 7 bohrs.[8] The (5,4,0) state that we use thus has a diabatic extension to infinite separation in the initial channel.

The coupling present in the six-state expansion can be represented by the matrix of nonzero elements (x):

$$\begin{array}{ccccccc}
 & (5,4,0) & (4,3,0) & (4,3,1) & (4,2,0) & (4,2,1) & (4,3,2) \\
(5,4,0) & & x & x & x & & \\
(4,3,0) & x & & x & x & & \\
(4,3,1) & x & x & & x & x & x \\
(4,2,0) & x & x & x & & x & \\
(4,2,1) & & & x & x & & x \\
(4,3,2) & & & x & & x &
\end{array}$$

which includes both the radial $(\partial/\partial R)$ and angular $(L^{\pm})$ coupling components of the nuclear gradient operator. Consistent with the energy range of interest, only the first-derivative coupling terms are used.

Following Piacentini and Salin,[9] we choose the electronic origin to lie on the proton in the evaluation of all the electronic matrix elements. The method of computation of the matrix elements is discussed by Green *et al.*[7]

III. SEMICLASSICAL APPROXIMATIONS

The description of the collision is reduced to a set of close-coupled equations among the radius-dependent coefficients of the expansion of the barycentric wave function in the electronic states and rotational eigenfunctions. The arguments are straightforward and lead to the radial equations in the form[10]

$$\underline{G}''+2\underline{DG}'+\underline{AG}+\underline{\kappa}^2\underline{G}=0 \ , \qquad (1)$$

in which only the matrices of the radial derivative $\underline{D}$ and the angular coupling $\underline{A}$ are retained. The second-derivative terms and others may be dropped in the energy range of interest. $\underline{\kappa}^2$ is the diagonal matrix of $(2\mu/\hbar^2)[E-W_i(R)]-P^2/R^2$ where μ is the reduced mass of the nuclei, W_i are the electronic eigenvalues, P is $L+\frac{1}{2}$, and E is the barycentric energy. Four different semiclassical approximations for solving Eq. (1) are the main topic of this report. The more involved of these approximations have been developed and tested elsewhere.[10]

The first approximation makes use of semiclassical uniform (SCUNF) reference functions based on the Langer approximation for the diagonal part of the radial coupled equations. This method leads to results of essentially full quantum accuracy for the solution of Eq. (1); note that the radial motion has only a single turning point in each of the diagonal radial equations in the energy range of interest and also that the SCUNF procedure does not assume in-out decoupling of the radial equations.

The second procedure for solving Eq. (1) is the average approximation (av) of Riley.[10] We include this to demonstrate that it is possible to use an in-out decoupled, computationally fast semiclassical approximation that is nearly of full quantum accuracy for strongly coupled equations. The essence of the method is to replace the nuclear motion wave numbers $\kappa_i(R)$ and $\kappa_j(R)$, which appear in the coupling coefficient in the JWKB-referenced in-out decoupled radial equations between channels i and j, by $\kappa_{ij}^{\mathrm{av}}=[(\kappa_i^2+\kappa_j^2)/2]^{1/2}$. Thus the coupling between each pair i and j occurs as if a trajectory were used on an arithmetic mean of the appropriate pair of diagonal potentials. The nuclear scattering, if decoupled (elastic in molecular frame), retains the full semiclassical JWKB form for each electronic state.

The third procedure is an effective potential method for all channels in Eq. (1). The potential is chosen to be $6/R$ to agree with VB.[4] The $\underline{\kappa}^2$ matrix is replaced by $(2\mu/\hbar^2)(E-6/R)-P^2/R^2$ (in Hartree atomic units) and the equations are in-out decoupled after making the JWKB reference function substitution to reduce to curvilinear classical trajectory form. We denote this procedure and the results as "$6/R$." Our electronic basis includes the most important states in the basis set used by VB. Another difference in the calculations is their use of a switching-function type of translation factor rather than the method of Piacentini and Salin.

The fourth and last approximation is to neglect all electronic potential terms in $\underline{\kappa}^2$, which leads to the straight-line impact-parameter (IP) equations in radial form, once JWKB referenced and in-out decoupled. These four approximations for the solution of Eq. (1) are the essence of our study.

IV. RESULTS AND DISCUSSION

For our chosen electronic basis set, the total charge-exchange cross section is the sum of all transitions out of the initial channel. Table I gives the computational results for the four semiclassical approximations listed in Sec. III. The first noteworthy point is that the average approximation (av) is accurate over the whole range of collision energies, as measured by the semiclassical uniform-reference-function method (SCUNF). These results illustrate, as do previous examples,[10–13] that it is possible to use in-out decoupling on multichannel coupled equations without spurious effects arising from the turning-point region.

The most noteworthy point is that the $6/R$ classical-trajectory approximation has not significantly decreased the charge-exchange cross section at the lowest velocity of relevance (10^5 m/s, 52 eV) in the comparison of VB[4] and SO.[5] In fact a slight increase is noted at that velocity, which must be due to a dynamical effect in the coupling arising from a slower effective radial velocity rather than the conjectured[6] exclusion from the strong-coupling region near 7 bohrs. At the lower energy of 13 eV, the use of the $6/R$ effective potential would be disastrous for the reasons brought out by Salop and Olson[6]; however, VB's work does not extend to such low energies. As mentioned in the Introduction, the choice of a single effective potential to determine a curvilinear classical trajectory can possibly be an improvement on the straight-line IP approximation. The data in Table I show that the $6/R$ potential does not serve to accomplish this insofar as the total charge-exchange cross section is a measure. It is worth observing that the IP method begins to fail around 13 eV, and it is completely erroneous at ~3 eV.

Except for the approximately 3-eV data in Table I,[8] we feel that the SCUNF and av cross sections are of good physical accuracy. The cross sections agree with the results given in Ref. 7 to 15% or better. There are several sources of the small differences between the calculations presented here and the more elaborate calculations: (1) Ref. 7 included more electronic states in the basis, (2) Ref. 7 incorporated translation factors, and (3) Ref. 7 simplified the average approximation by dividing the potential curves into nearly degenerate subgroups and using a common potential for each subgroup. The latter affords a useful simplification of the full av procedure used here by reducing the number of distinct potentials involved in the construction of the pairwise-averaged couplings.

Since our present semiclassical results agree with more elaborate calculations[7] and also agree with the completely independent results of SO,[5] and since we have ruled out the serious effect of the $6/R$ potential in the calculations of VB[4] in their range of collision energies, we are somewhat at a loss to reconcile the differences between SO (and the present results) and VB. Translation factors are of little importance in this energy range as shown by the agreement of the Piacentini-Salin procedure used here with the results of calculations with explicit inclusion of the factors.[7] As is known,[1] the choice of electronic origin in IP theory is equivalent to a factorable coordinate-dependent phase change of the total wave function; thus the IP equations (and hopefully the more elaborate semiclassical approximations) can somewhat compensate for the lack of proper rearrangement channel eigenstates by means of completeness in the electronic basis. A modification of this argument would suggest that VB's switching-function translation factor, even if not optimum in some sense, should not be responsible for the difference between their results and the present data.

TABLE I. Total charge-exchange cross sections Q in square angstroms for C^{6+}-H based on the four semiclassical approximations discussed in Sec. III. The initial H velocity and laboratory-frame energy in electron volts are given in the first two columns. The number of digits given in the table is to aid intercomparison of the approximations and is not representative of overall physical accuracy. The lowest-energy results are in overall error due to the neglect of an additional coupling not included in these calculations.

v (10^5 m/s)	E (eV)	Q (Å^2) SCUNF	av	$6/R$	IP
0.25	3.26	0.0190	0.0239	· · ·	0.212
0.5	13	0.518	0.514	3×10^{-5}	0.786
1.0	52	3.90	3.96	4.65	4.10
2.0	209	17.80	17.90	15.77	17.77
5.0	1306	44.85	44.88	44.60	44.91

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