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Time-dependent wave-packet study of the direct low-energy dissociative recombination of HD^+

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Wave-packet methods involving the numerical solution of the time-dependent Schrödinger equation have been used with great success in the calculation of cross sections for dissociative recombination of molecular ions by electron impact in the high energy region where the ''boomerang'' model [L. Dube and A. Herzenberg, Phys. Rev. A **11**, 1314 (1975)] is valid. We extend this method to study low-energy dissociative recombination where this approximation is no longer appropriate. We apply the method to the ''direct'' low-energy dissociative recombination of HD^+. Our results are in excellent agreement with calculations using the multichannel quantum defect method.

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I. INTRODUCTION

Wave-packet methods, that is, numerical solutions of the time-dependent Schrödinger equation, are standard techniques in the study of the dynamics of chemical reactions, dating back to their introduction in this area by Heller in the 1970s [1]. One of the important features of time-dependent methods is the ability it gives one to follow explicitly the time evolving dynamics, providing tremendous insight into the mechanisms of processes and a better understanding of the collision. It is equivalent to having the ability to stop an experiment in midcollision and examine the state distributions to determine the characteristics of the system that are most important in defining the products observed. Since the wave packet is described by its value on a numerical grid of points, there are no serious problems with coupled potential-energy surfaces [2,3] or a three-body continuum [4], which can be difficult to handle with basis set techniques. It easily handles a high density of quantum channels, including the three-body final states. Wave-packet methods have the additional advantage that the cross section is obtained at all energies for a single calculation. In fact, in the case of dissociative recombination (DR) and dissociative excitation (DE) of molecular ions by electrons, a single wave-packet evolution will provide the cross sections and final-state distributions for all electron energies, i.e., all the information for a complete description of the process.

These aspects of the wave-packet technique make it a natural method to use to study DR and DE of molecular ions following collisions with electrons. We have used this method to study DR in H_3^+ [5], HeH^+ [6,7], and DE in HeH^+ [8]. In these previous studies, we found that at high energies where the ''local'' approximation was valid, an *ab initio* approach where the resonance parameters were determined using the complex Kohn variational method and then used as input to the wave-packet method produced good agreement with experiment. These calculations demonstrated the feasibility of the wave-packet method for the calculation of DR and DE, and clearly showed that the time-dependent approach is sound and competitive with any other method that might be considered in this energy region.

However, the wave-packet method for DR, as previously applied, can only be used with the ''local'' approximation; that is, at sufficiently high energy, closure over the intermediate vibrational sum can be assumed to be complete. Domke and Estrada [9] have extended the wave-packet method to the low-energy region in the case of dissociative attachment. However, their work concentrated on the effects of the ''nonlocal'' nature of the interaction, that is, that the coupling between the electron plus neutral continuum and the negative-ion resonance cannot be expressed as a simple function of the internuclear separation. In the case of DR, due to the strength of the Coulomb potential that is explicitly included, the coupling remains local. However, the assumption of closure over intermediate vibrational states is no longer valid.

In Sec. II, we will review the time-dependent wave-packet method as applied to DR. We will derive the extension to the case of low-energy electrons. In Sec. III, we apply this method to the low-energy DR of HD^+, and compare it to available multichannel quantum defect (MQDT) calculations.

II. METHOD

The wave-packet method proceeds by the direct integration of the time-dependent Schrödinger equation:

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=H(\mathbf{r},t)\Psi(\mathbf{r},t), \qquad (1)$$

where, as throughout this paper, atomic units are used. DR proceeds by capture of the electron into a resonant dissociative state. The molecule begins to fragment, moving on the excited-state (resonant) potential-energy surface. During this process, the molecule can re-emit the electron (autoionize), possibly leaving the molecular ion in an excited vibrational state. This is referred to as resonant vibrational excitation (VE). It is possible that autoionization can leave the molecular ion in the vibrational continuum, leading to dissociation of the ion. This is referred to as dissociative excitation (DE). Finally, if no autoionization occurs, the molecule fragments into neutral products. The differential equation governing this ''direct'' DR process has been previously derived [10], and for the case of a diatomic, is given by

$$\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+E_{res}(R)-E\right)\Psi(R)=W, \qquad (2)$$

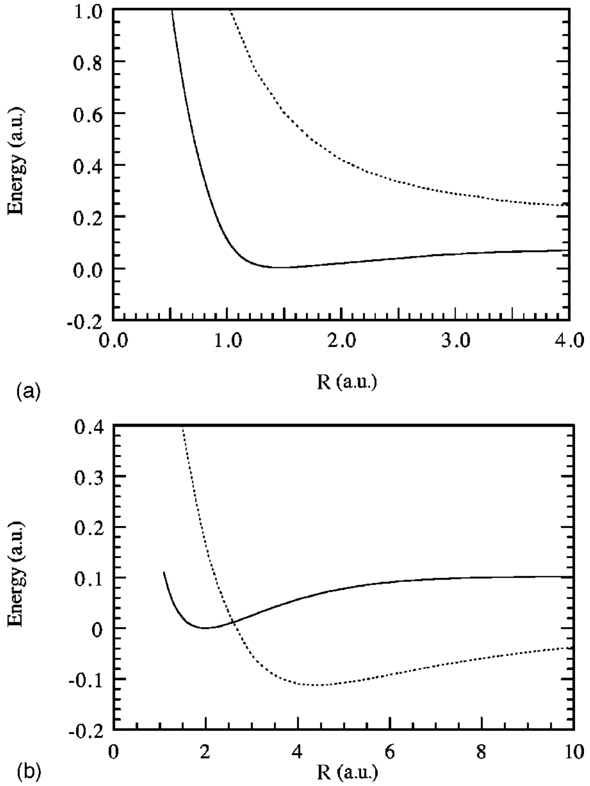

FIG. 1. Potential-energy curves for dissociative recombination. Ion (solid curve) resonance (dotted curve). (a) HeH^+, where vibrational closure [Eq. (5)] is satisfied. (b) H_2^+, where vibrational closure [Eq. (5)] is not satisfied.

where W is defined as

$$W=-V_E(R)\left(\chi_{v_i}(R)-i\pi\sum_j \langle\chi_{v_j}|V_E|\Psi\rangle\chi_{v_j}(R)\right), \quad (3)$$

where χ_{v_j} are the vibrational states of the ion, with χ_{v_i} as the initial vibrational state, μ as the reduced mass of the diatomic, $\Psi(R)$ as the wave function on the dissociating resonant state, and V_E as the electronic-coupling between the electronic-scattering continuum and the resonant state. V_E is related to the autoionization width $\Gamma(R)$ by

$$\Gamma(R)=2\pi|V_E(R)|^2. \quad (4)$$

We note that we assume a ‘‘local’’ form, that is, that the interaction V_E is a function of the internuclear separation only. The sum is a sum over the open vibrational states of the ion and an integral over the continuum vibrational states. For some systems, for example, HeH^+ [see Fig. 1(a)], one can assume that the sum over vibrational levels is complete, that is

$$\sum_j |\chi_{vj}\rangle\langle\chi_{vj}|=1, \quad (5)$$

where again the sum runs over both the bound and continuum vibrational functions, leading to the following equation for the nuclear motion [11]:

$$\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+E_{res}(R)-i\frac{\Gamma(R)}{2}-E\right)\Psi(R) =-V_E(R)\chi_{v_i}(R). \quad (6)$$

This is the so-called ‘‘boomerang’’ model [11]. In this case, the Hamiltonian in Eq. (1) becomes

$$H=-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+E_{res}(R)-i\frac{\Gamma(R)}{2}, \quad (7)$$

and the initial wave packet

$$\Psi(R,t=0)=V_E(R)\chi_{v_i}(R). \quad (8)$$

The cross section is given by

$$\sigma(E)=\frac{2\pi^3}{E}|T(E)|^2, \quad (9)$$

where $T(E)$ is given by the projection of the wave packet $\Psi(R)$ onto the asymptotic scattering wave functions. The projection is done at long times when the wave packet has reached the asymptotic region of the potential and the autoionization loss has gone to zero. $T(E)$ is given by [12]

$$T(E)=\lim_{t\to\infty}\left(-i\int_0^\infty \phi_k(R)\Psi(R)dR\right), \quad (10)$$

where k is the wave number and $\phi_k(R)$ are the energy normalized, asymptotic scattering wave functions. For a diatomic, when the potential is constant, these states are just plane waves given by

$$\phi_k(R)=\sqrt{\frac{\mu}{2\pi k}}e^{ikR}. \quad (11)$$

The generalization of these equations to polyatomic systems is obvious.

Contrast this to the case of HD^+ [see Fig. 1(b)], where at low energies, the sum in Eq. (5) is much smaller than 1, so the action of the Hamiltonian on Ψ in Eq. (1) becomes

$$H(R)\Psi(R)=\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+E_{res}(R)\right)\Psi(R)+O_{nonloc}(R), \quad (12)$$

where the nonlocal operator $O_{nonloc}(R)$ is defined by

$$O_{nonloc}(R)=-i\pi V_E(R)\sum_j \chi_{v_j}(R) \times\left(\int_0^\infty dR'\chi_{v_j}(R')V_E(R')\Psi(R')\right). \quad (13)$$

The initial wave function and definition of the cross section remain the same. Note that now the operation of H on $\Psi(R)$ involves an integration over R, so H becomes a nonlocal operator. The Hamiltonian is also energy-dependent, since as new vibrational channels open, a new term must be included in the sum.

III. RESULTS

This method was applied to the *d*-wave contribution to the direct DR of HD^+. The *d*-wave component dominates at low energy, where this effect is important. This system has been studied by a number of groups. The cross section at very low energy (<120 meV) shows a great deal of structure as a function of energy due to the coupling to the Rydberg states of HD. Schneider *et al.* [13] has used the MQDT method to perform a careful analysis of this cross section, separating the effects of the Rydbergs (the ''indirect'' mechanism) from the ''direct'' mechanism. In our calculation, the curves and couplings are taken from Schneider *et al.* [13] and the wave-packet results are compared to their first order and second-order multichannel quantum-defect results. The first- and second-order MQDT treatments refer to the perturbative expansion of the Lippman-Schwinger equation for the electronic reaction matrix [14,15]. The first-order MQDT includes the electronic interaction between the dissociative state and the electron-ion states only once, with a normalization factor that accounts for autoionization back to the electronic continuum. The second-order MQDT adds a term in which the electronic interaction acts twice and the initial electron-ion state is coupled indirectly with itself and the other ionization channels. In both the first- and second-order treatment, nonadiabatic interactions are included through the variations of the quantum defects with the internuclear distance.

The time-dependent wave packet [solutions to Eq. (7) and Eq. (11)] was calculated on an *R*-grid, and the numerical integration of the wave packet was carried out using the Crank-Nicholson method [16]. Convergence studies were done on both the grid and the time parameters. It was found that a grid of 1000 points with a spacing of 0.2 a.u. in *R* and a time step of 0.2 a.u. for 6000 steps was sufficient to converge the calculation. To determine the cross section using Eq. (10), both the projection of the wave packet onto plane waves and the exact states of the final potential (calculated using a finite difference method [17]) were investigated. It was found that the use of the exact states allowed for more rapid convergence.

We first show results comparing the ''boomerang'' model to the MQDT results, using the Hamiltonian from Eq. (7) and the initial wave function defined in Eq. (8). As can be seen in Fig. 2, the cross section is much lower due to the high autoionization rate resulting from the unphysical loss of flux into closed vibrational states of the ion. In Fig. 2, we also compare the wave-packet results using the same initial wave function, but now using the Hamiltonian defined in Eq. (11). As can be seen in Fig. 2 at very low energies, where only one vibrational channel is open, the wave-packet and both MQDT calculations are in perfect agreement. As the energy is increased, the first-order MQDT results begin to deviate from the second-order and the wave-packet calculation. The small difference between the second-order and wave-packet calculations are due to higher orders that have been neglected in the MQDT, but are accounted for with the wave-packet treatment. The step structure seen in the cross section is due to the opening of new vibrational channels. This leads to additional autoionization into the channel and therefore a lower cross section.

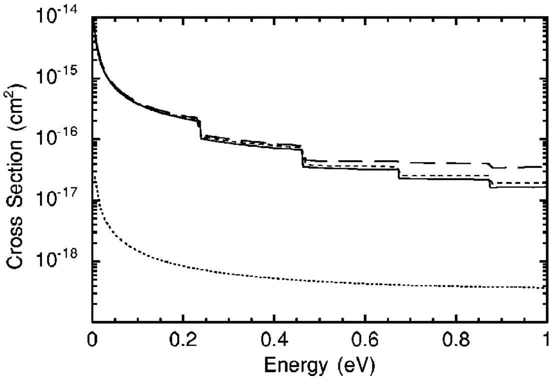

FIG. 2. Cross section for *d*-wave contributions to the direct DR of HD^+. The present time-dependent wave-packet results (solid line) are compared to time-dependent wave-packet results using the ''boomerang'' approximation (dotted line), the first-order MQDT treatment (long dashed line), and the second-order MQDT treatment (short dashed line).

IV. CONCLUSIONS

The time-dependent wave-packet method has just been applied to just a handful of DR and DE problems. We have shown that this method can be used to study low-energy DR, where the boomerang model is no longer valid. For diatomics, this represents an interesting alternative to the MQDT treatments that are already available. Although the wave-packet method can be used in systems where the crossing of the resonance and ion is near the equilibrium of the ion, and the nonlocal form must be employed, it is more efficient at high energy where a number of resonant states are involved in the DR process and a large number of channels are open. The real power of the wave-packet method is in the study of DR and DE in polyatomic systems where more than one degree of freedom is important.

One issue that has not yet been addressed is the inclusion of Rydberg states in the calculation. Unlike dissociative attachment, at very low energies the cross section for DR is strongly affected by the effects of Rydberg states (the ''indirect'' mechanism). We are currently developing a time-dependent method that explicitly includes the Rydbergs in the calculation, leading to a coupled set of time-dependent Schrödinger equations that must be solved.

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