Full Ambiguity-Free Quantum Treatment of $D^+ + H(1s)$ Charge Transfer Reactions at Low Energies

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Cross sections for the nonresonant charge transfer process $D^+ + H(1s) \rightarrow D(1s) + H^+$ at low energies are calculated in hyperspherical coordinates. The method is free from all the inherent ambiguities associated with the conventional Born-Oppenheimer approach, such as the incorrect asymptotic energies and spurious couplings. However, like the Born-Oppenheimer approach, we show that hyperspherical potential curves and coupling terms have to be calculated only once to obtain results for all partial waves. Feshbach and shape resonances of HD^+ near the $H(1s)$ threshold are also calculated.

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Our understanding of molecular structure is currently based on the Born-Oppenheimer (BO) adiabatic approximation. To see the limitation of this commonly used approach, consider the simplest molecular ions, H_2^+, HD^+, and D_2^+. The BO potential curves for all three are identical and the asymptotic energies of the two lowest curves are all equal to $-1/2$ a.u., whereas the correct limits should be $-(1/2)\mu_H$ a.u. or $-(1/2)\mu_D$ a.u., where μ_H (μ_D) is the reduced mass of $H^+ + e^-$ ($D^+ + e^-$). Since the reduced mass is close to unity, this deficiency does not cause a serious problem unless high precision is required for bound-state calculations, or when isotope effects are important. Clearly, the BO approximation is not a convenient starting point for treating HD^+ since a great deal of effort is needed in order to obtain the energy difference of 3.7 meV between the $D^+ + H(1s)$ limit and the $D(1s) + H^+$ limit.

The failure of the BO approximation is especially severe when it is employed to describe ion-atom or atom-atom collisions at low energies. The problems have been well documented [1]. They include the incorrect boundary conditions, the existence of spurious couplings, and the calculated cross sections not being Galilean invariant. Despite these fundamental ambiguities, the BO approach has been used for more than five decades to describe slow ion-atom and atom-atom collisions since other satisfactory theories have not been found. For collisions at higher energies where the semiclassical impact parameter description is used, the difficulty is partially overcome by introducing somewhat *ad hoc* electron translational factors [2–4]. These factors, defined in terms of nuclear velocities, have no quantum equivalents. Although generalized reaction coordinates which are functions of electronic and nuclear coordinates have been suggested [1], they are quite complicated to implement and have not been applied in scattering calculations except for a recent application in calculating the bound state energies [5]. For the HD^+ system, methods which do not start *exactly* from the BO approximation have been employed for the vibrational energies of the HD^+ ions [6–9] and for the $D^+ + H(1s) \rightarrow D(1s) + H^+$ charge transfer cross sections [10].

In this Letter we present calculations of the above charge transfer process at center-of-mass energies from threshold to 0.1 a.u. The goal of this Letter is twofold: (i) We show that calculations using hyperspherical coordinates are free of all the problems associated with the conventional BO approaches [11]. It avoids the use of complicated reactive coordinates [1] or the equivalent of electron translational factors [12,13]. (ii) We show that many of the adiabatic BO simplifications are also valid in the adiabatic hyperspherical approach. The most important of which is that there is no need to calculate hyperspherical potential curves for states of higher total angular momentum J, since they can be obtained by adding the centrifugal potential energies to the $J = 0$ potential curves, as in the BO approach. This makes the hyperspherical calculation for ion-atom collisions as simple as the BO approach.

The first point above is well known to practitioners of hyperspherical methods, even if they are not as familiar to the general collision physics community. Note that HD^+ is just a special example of the general Coulomb three-body system that also includes familiar members like H^-, He, Ps^-, and $e^+ + H$ [14]. In these cases the hyperspherical approach has been used very successfully to obtain their structure and scattering properties [14–16]. However, in these systems the masses of all three particles are comparable or two of the three are lighter than the third such that there is no need to deal with high angular momentum states in low-energy collisions. In ion-atom collisions, on the contrary, hundreds or thousands of partial waves are needed to achieve a converged calculation even for collisions at thermal energies. In the exact hyperspherical formulation, the potential curves and coupling terms have to be calculated for each J separately. We show in this Letter, however, that the hyperspherical potential curves and coupling terms for the present HD^+ system need to be calculated only once in practical

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applications, just as in the BO approach. This observation makes it possible to perform hyperspherical calculations for ion-atom collisions with the same ease as in the BO approach, yet free from all the problems and ambiguities encountered in the BO approach.

We use mass-weighted hyperspherical coordinates to describe the three particles in HD^+. In the center-of-mass frame, we choose the first Jacobi coordinate $\vec{R}$ to be the vector from H^+ to D^+, with the reduced mass μ_1; and the second Jacobi coordinate $\vec{r}$ from the center-of-mass of H^+ and D^+ to the electron, with reduced mass μ_2. For this work we define the hyperradius ρ and the hyperangle ϕ by

$$\rho = \sqrt{R^2 + \left(\frac{\mu_2}{\mu_1}\right) r^2}, \tag{1}$$

$$\tan\phi = \sqrt{\frac{\mu_2}{\mu_1}}\,\frac{r}{R}. \tag{2}$$

Using this definition, the hyperradius ρ is very close to the internuclear separation R, and the reduced mass for the motion in ρ is also given by μ_1, as in the BO approximation. By treating ρ as the adiabatic parameter, the calculation in hyperspherical coordinates can be carried out in an essentially identical manner to the familiar BO approach. Thus, for each fixed ρ, a set of hyperspherical potential curves and their nonadiabatic couplings are calculated. There are many different numerical methods available nowadays to calculate the hyperspherical potential curves. In this work, we used a method that is analogous to the linear combinations of atomic orbitals in the standard BO approach. The "atomic orbitals" are Slater-type orbitals expressed in their respective Jacobi coordinates [17–19]. Thus for basis functions representing the $D^+ + H$ arrangement, the Jacobi coordinates are the vector from H^+ to the electron and the vector from the center of mass of $(e^- + H^+)$ to D^+. Another set of Slater-type orbitals representing the $H^+ + D$ arrangement is also used. These "two-center" basis functions have been used to calculate hyperspherical potential curves for other three-body collision systems [17–19]. They are easily implemented for solving the hyperspherical equations for any J. In this work we include about ten Slater-type orbitals for each angular momentum $\ell = 0$, 1, and 2, where ℓ is the orbital angular momentum of the electron with respect to H^+ or to D^+. Such a two-center basis set allows us to obtain the lowest few potential curves and coupling terms accurately. For the present work, we consider collision energies up to 0.1 a.u., so that only the two lowest curves and the coupling between them are needed. The bound state properties and charge transfer cross sections reported below were calculated from solving the hyperradial equations including these two channels only.

1. The adiabatic hyperspherical potential curves and the bound vibrational levels of HD^+.—In Fig. 1 we show in the inset the two lowest $J = 0$ potential curves and the nonadiabatic coupling term $\langle 1|\frac{d}{d\rho}|2\rangle$, where $|1\rangle$ and $|2\rangle$ are the hyperspherical wave functions of the two lowest curves and the integration is over all the angles except for the hyperradius. This figure is used to demonstrate that in the outer region the two potential curves do reach the correct dissociation limits.

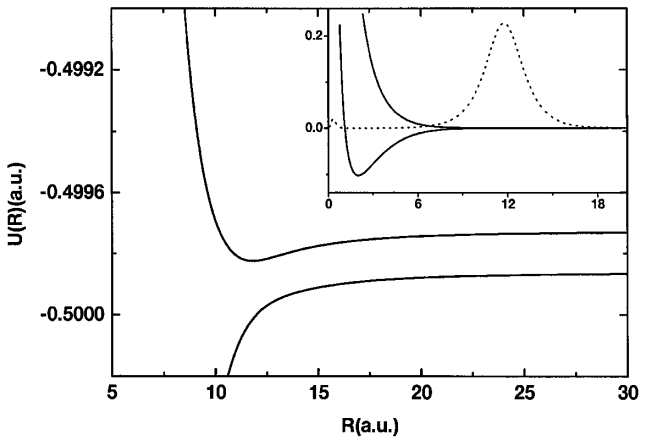

FIG. 1. Hyperspherical potential curves for HD^+, $J = 0$. The main figure details the two lowest curves in the asymptotic region. In the inset, the two curves (solid lines) and the nonadiabatic coupling term (dashed line) in the full range are shown where the potential curves have been rescaled by setting the H($1s$) threshold at zero.

The lowest curve has a deep potential well and was found to support 23 bound states, in agreement with the approximate hyperspherical calculation of Macek and Jerjian [20] and with the accurate calculation of Hara *et al.* [21]. From our potential curve, we obtained the lowest state at 21 515.04 cm^{-1} below the D($1s$) + H^+ threshold. This is to be compared to the result of 21 515.9 cm^{-1} of Hara *et al.* within the same approximation. We comment that the vibrational energies of HD^+ have been reexamined recently by Esry and Sadeghpour [9] using a different method. More detailed discussions of the vibrational states supported by this curve can be found there.

2. Feshbach and shape resonances near the H($1s$) threshold.—In Fig. 1 we notice that the second $J = 0$ curve has a shallow potential well near $\rho = 12$. Using the single channel approximation, this curve was found to support two bound states, at 5.929 and 0.1023 cm^{-1} below the H($1s$) threshold. When channel coupling is included the two states become Feshbach resonances. By fitting the calculated partial wave cross sections to the Breit-Wigner formula with a linear background, we extracted the position of the first resonance as 5.827 cm^{-1} and its width as 4.26 cm^{-1}. We were unable to analyze the second resonance since it is too close to the threshold.

We have also carried out hyperspherical calculations for higher J's and searched for resonances near the H($1s$) threshold. The results are summarized in Table I and compared to other available calculations. For $J = 0$–3, the resonance positions and widths from the present calculation are in good agreement with those from Wolniewicz and Orlikowski [6]. The widths for these resonances are

TABLE I. Energies and widths for Feshbach resonances ($J = 0-3$) and shape resonances ($J = 4-6$). The present hyperspherical calculations are shown in the first two columns. All the energies are given in units of cm^{-1} measured from the H($1s$) threshold at $-0.499\,727\,84$ a.u.

	Energy	Width	Energy	Width[a]	Energy[b]	Width[c]
$J = 0$	−5.827	4.26	−5.868	5.261	−5.840	9.4
$J = 1$	−5.190	3.71	−5.196	4.632	−4.974	8.8
$J = 2$	−3.839	2.79	−3.769	3.336	−3.304	7.1
$J = 3$	−1.496	1.56	−1.478	1.707	−0.987	4.6
$J = 4$	1.190	0.55				
$J = 5$	4.080	2.81				
$J = 6$	7.249	7.62				

[a]Reference [6]; [b]Ref. [21]; [c]Ref. [22].

quite broad and thus the discrepancy is probably due in part to the different procedures used in fitting the resonance parameters from the calculated phase shifts. On the other hand, we notice large discrepancies with the earlier calculations [22,23]. For $J = 4-6$, we found one shape resonance for each J. For J greater than 6, no more resonances associated with the second curve were found.

The Feshbach resonances discussed above become true bound states for H_2^+ and D_2^+ ions and they are stable against predissociation. They have been observed experimentally using laser spectroscopy [24]. Note that these states are supported by the very weak attractive well at large internuclear separations. Similar states have also been observed recently in photoassociation experiments in laser-cooled diatomic alkali-metal atoms [25,26]. The present calculations imply that the spectra of these cold dimers would have an interesting isotope dependence.

3. Charge transfer cross sections.—The $D^+ + H(1s) \rightarrow D(1s) + H^+$ charge transfer reaction cross sections cannot be calculated using the "standard" BO formulation. Calculations based on the modified BO expansion have been used by Hunter and co-workers in a series of papers [10], but their results have not been tested critically in experiments except at energies above 2 eV. We have used the hyperspherical approach to carry out the calculations for center-of-mass energy ranging from threshold to 0.1 a.u. The final results are presented in Fig. 2.

Before discussing the total charge transfer cross sections, the nature of the present calculation should be addressed. In the rigorous hyperspherical approach the potential curves and coupling terms have to be calculated separately for each partial wave J. Since the number of partial waves needed in a converged calculation in ion-atom collisions runs into hundreds or thousands even at subthermal energies, hyperspherical calculations are perceived to be impractical. In the BO approach, the potential curves and coupling terms have to be calculated only once, for example, for $J = 0$. For other J's, the potential curves are obtained from the $J = 0$ curves by adding to each curve a centrifugal potential term $J(J + 1)/(2\mu R^2)$. Meanwhile, the same nonadiabatic coupling terms are used for all J's. In the following we show from actual

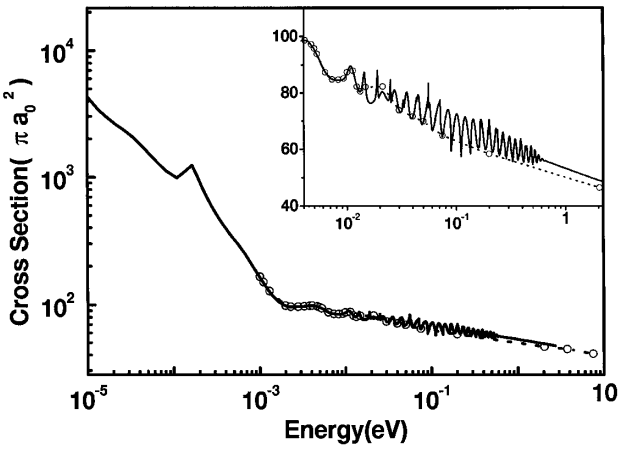

FIG. 2. Total charge transfer reaction cross sections for $D^+ + H(1s) \rightarrow D(1s) + H^+$ at low energies. The present results are shown in solid lines; the results of Hunter and Kuriyan are shown in open circles connected by dotted lines.

calculations that this simplification in the BO approach is also valid in the hyperspherical approach for the present system, and likely for all ion-atom collision systems. We emphasize that this simplification is not valid in general for three-body systems; it is approximately valid only when two of the three particles are much heavier than the third one, i.e., when the system is more "molecular."

To demonstrate that hyperspherical calculations for $J \neq 0$ can indeed be obtained by adding a centrifugal potential term $J(J + 1)/(2\mu_1\rho^2)$ to each $J = 0$ potential curve and use the same $J = 0$ coupling terms, we compare the partial wave charge transfer cross sections calculated using this model (the rotor model) with the results from actual hyperspherical calculations for several values of J and energies. The results are shown in Table II. Clearly the rotor model and the actual hyperspherical calculations are in good agreement. (We also checked the model for the resonances of Table I and the results agree to better than four digits.) This confirms that we can use the rotor model in the hyperspherical approach to perform scattering calculations for all the partial waves, just as one would do in the BO approach. This drastic simplification makes it practical to carry out ion-atom collision calculations using the hyperspherical approach at the same degree of ease as the BO approach but free from all the inherent difficulties of the latter.

We have used the rotor model to obtain the total charge transfer cross sections for $D^+ + H(1s) \rightarrow D(1s) + H^+$ for energies between 10^{-5} and 2.7 eV. The results are shown in Fig. 2 where we also compare with the calculation of Hunter and Kuriyan [10] above 10^{-3} eV. Note that the cross section drops rapidly at energies below 10^{-3} eV. Above 10^{-2} eV, it drops at a slower rate. The inset is a replot of the cross section on a linear scale. One can clearly see the oscillatory structure in the cross section for collision energies between 10^{-2} and 1 eV. In this energy region, the cross section for each partial wave for J between 20 and 80 has one or more shape resonances,

TABLE II. Comparison of partial wave charge transfer reaction cross sections calculated from the exact hyperspherical approach (top line) with those calculated from the rotor model (bottom line) for $J \neq 0$. Energies are measured from the H($1s$) threshold in a.u. and the cross sections are given in atomic units. $A(+B) = A \times 10^B$.

E	$J = 1$	$J = 2$	$J = 10$	$J = 50$
1.00(−6)	3.3820(+3)	2.7047(+3)	8.3154(−12)	
	3.3821(+3)	2.7050(+3)	7.3900(−12)	
1.00(−5)	3.0748(+2)	4.5821(+2)	9.2317(−10)	
	3.0748(+2)	4.5825(+2)	8.5130(−10)	
1.00(−4)	3.0013(+1)	4.3884(+1)	5.6740(−2)	
	3.0013(+1)	4.3889(+1)	5.7728(−2)	
5.00(−4)	5.0629	6.8596	8.4297	
	5.0632	6.8610	8.4979	
1.00(−3)	2.1316	2.7411	5.1382	9.3278(−15)
	2.1317	2.7418	5.1761	9.4616(−15)
5.00(−3)			1.6927	1.5330(−2)
			1.7017	1.5333(−2)
1.00(−2)			1.2964	5.4821
			1.3012	5.4835

as well as some oscillatory structures due to the phase shift going through multiples of π. The latter oscillations are analogous to the Stückelberg oscillations in near-resonace charge transfer processes. Summation over the contributions from many partial waves does not smooth out these structures. (The oscillations are seen also in the elastic cross sections.) We comment that the peak near 2×10^{-4} eV has been identified to be due to the local maximum in the $J = 4$ partial wave cross section.

It is interesting that the present results are in reasonable agreement with the calculations of Hunter and Kuriyan [10] above 10^{-3} eV. Nonetheless, the discrepancy is clearly visible if one looks at the comparison in the inset where their results are about 15% lower. Their cross sections do not show oscillations, but that could be due to the fact that their calculations were not done at dense enough points. In their calculations, they started with a modified BO expansion to take into account some of the reduced mass effect (thus the potential curves for HD^+ and $H_2{}^+$ are no longer identical), but their lowest two adiabatic potential curves are still degenerate in the asymptotic region. By taking the sum and difference of these two adiabatic states, they obtained in the new representation two potential curves separated by the energy difference between H($1s$) and D($1s$) for *all* internuclear separations, including the asymptotic limit. Therefore their approach is almost like a "diabatic" representation and the BO spirit is lost altogether. In the present hyperspherical approach, the adiabatic picture is retained and the conceptual framework is very close to the BO approach. The present approach can also be easily generalized to include more channels.

In summary, we have performed the charge transfer cross section calculation for the elementary rearrangement process $D^+ + H(1s) \rightarrow D(1s) + H^+$ at energies below 0.1 a.u. Using hyperspherical coordinates we showed that the calculation is as straightforward as the traditional Born-Oppenheimer approach but without all the inherent limitations of the latter. It is demonstrated that the hyperspherical approach is a practical method for performing accurate calculations for ion-atom collisions at low energies.

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