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Adiabatic hyperspherical treatment of HD^+

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We have calculated approximate hyperspherical adiabatic HD^+ potential curves. In contrast to the Born-Oppenheimer adiabatic potential curves, the hyperspherical ones exhibit the correct dissociation limits. The lowest-order vibrational spectrum that we obtain compares favorably with conventional higher-order calculations. The implications of our results for continuum states of HD^+ and for ion-atom scattering in general are discussed. We show that translation factors are not needed in the hyperspherical formulation.

I. INTRODUCTION

Our understanding of molecular structure is currently based on the Born-Oppenheimer adiabatic approximation. In this picture the nuclei of the atoms in the molecule are held fixed, in first approximation, and the Schrödinger equation for the electrons is solved to obtain molecular-energy curves which are functions of the relative location of the nuclei. These curves then provide the effective potentials for the nuclear motion. The Born-Oppenheimer picture is also employed to describe low-energy atom-atom and ion-atom collisions. For purposes of the present discussion we regard wave functions for colliding atoms as continuum functions of diatomic molecules, and thus refer to both bound and continuum states in the same language.

Consideration of atomic collisions reveals the limitations of the Born-Oppenheimer approximation. It is necessary to introduce translation factors,[1-3] sometimes in an *ad hoc* and complicated manner, to allow for translational motion of the electrons relative to the individual nuclei. A related problem concerns the dissociation threshold energies obtained in the Born-Oppenheimer approximation. Because the nuclei are held fixed, the adiabatic molecular-energy curves do not separate to give the correct reaction thresholds. For example, in $H_2{}^+$, the lowest-energy curves equal $-\frac{1}{2}$ a.u. at infinite nuclear separation, whereas the correct energy is $-\frac{1}{2}\mu_{e\mathrm{H}}$, where $\mu_{e\mathrm{H}}$ is the reduced mass of the hydrogen atom. Since the reduced mass is close to unity, this usually is not a serious problem unless high precision is required in bound-state calculations, or unless electron-capture reactions are important for continuum states. In both cases, complicated corrections, including translation factors in the case of electron capture, are required. These problems become more acute for systems where the electron is replaced by the more massive negative muon. Then, the incorrect thresholds cannot be ignored. This is particularly apparent in attempts to describe the autoionizing states of He in terms of an $H_2{}^+$ model.[4] Then one obtains Rydberg series of autoionizing states which converge to series limits that are in error by factors of 2.

The incorrect thresholds of Born-Oppenheimer approximation also imply that the theory of upper and lower bounds on energies and phase shifts, developed primarily by Spruch and co-workers,[5] does not immediately apply. It is necessary to correct the threshold energies and to remove the attendant spurious long-range couplings characteristic of the perturbed-stationary-state approximation.[6]

The purpose of this paper is to point out that an alternative adiabatic approximation, namely, the hyperspherical adiabatic approximation,[7] gives the correct thresholds without introducing electron-translation factors. This is well known in the case of the autoionizing states of He, but it has not been developed in connection with conventional molecular structure. Greene[8] has demonstrated the connection between the hyperspherical adiabatic approximation and the conventional Born-Oppenheimer approximation for the case of $H_2{}^+$, but he introduces approximations which give incorrect thresholds as in the conventional Born-Oppenheimer theory. Here, we reexamine his demonstration for the interesting case of HD^+. For this system the lowest two molecular states in the separated-atom limit are not degenerate owing to the mass difference of the proton and the deuteron. Then the structure of Born-Oppenheimer and hyperspherical adiabatic potential curves are qualitatively different in first approximation. Since this qualitative difference may show up in the vibrational structure of HD^+, we compute the vibrational spectra in the two alternative adiabatic approximations in lowest order. These spectra are compared with each other and with a more accurate calculation[9] which includes higher-order corrections to obtain some quantitative measure of the difference between the two conceptual frameworks for understanding molecular structure.

That the hyperspherical adiabatic approximation gives the correct separated-atom limits follows from the commutation of the generalized angular-momentum operator with the "kinematic rotation" of Smith.[10] Conversely, the kinetic-energy operator of the electron alone does not commute with the kinematic rotations, and thus the Born-Oppenheimer approximation, which separates electron motion for special consideration, gives incorrect thresholds.

Since kinematic rotations play a central role in our discussion, we briefly discuss such rotations and the adiabatic hyperspherical approximation in Sec. II. For definiteness we discuss HD^+ explicitly. The general theory has been given by Smith. This section also establishes the notation used in subsequent sections. Atomic units are used throughout, although it is convenient to write the electron mass m_e explicitly. In Sec. III we obtain an approximate solution for the adiabatic potential curves. Our solution closely follows the theory of Greene;[8] the main difference is that we obtain approximate wave functions which give the correct separated-atom energies. Exact solution of the adiabatic hyperspherical approximation would automatically obtain correct thresholds. Since we employ an approximate solution valid to order $m_e/m_{\rm H}$, it is necessary to explicitly construct an approximation scheme for the adiabatic eigenvalues which preserves correct thresholds at each order. Such a scheme is described in Sec. III and potential curves computed in lowest order. In Sec. IV we obtain the vibrational energy levels in the two approximations and compare with accurate calculations which keep higher-order corrections in the mass ratio $m_e/m_{\rm H}$. The results are discussed in Sec. V.

II. KINEMATIC ROTATIONS AND THE ADIABATIC HYPERSPHERICAL APPROXIMATION

Consider the coordinate systems for the HD$^+$ ion shown in Fig. 1. The vectors $\mathbf{r}_{e\rm H}$ and $\mathbf{r}_{e\rm D}$ represent the electron-proton and electron-deuteron separations, respectively, and the vector $\mathbf{r}_{\rm HD}$ represents the internuclear separation. Since we are interested in the lowest-energy state, and since in the separated-atom limit D + H$^+$ is lower in energy than H + D$^+$, we select the Jacobi coordinates $\mathbf{r}_{e\rm D}$ and $\mathbf{r}_{e\rm D,H}$ of Fig. 1(b) to define the hyperspherical radius R and the hyperangle $\alpha_{e\rm D}$ according to

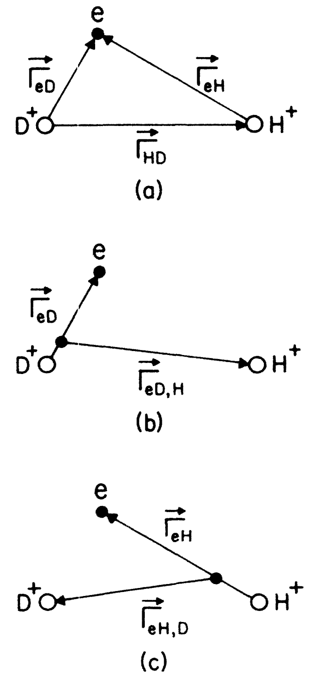

FIG. 1. (a) Interparticle coordinates for the HD$^+$ molecule. (b), (c) Two alternative Jacobi coordinate systems used to describe the HD$^+$ molecule.

$$\mu R^2=\mu_{e\rm D}r_{e\rm D}^2+\mu_{e\rm D,H}r_{e\rm D,H}^2\ , \tag{1a}$$

$$\mu_{e\rm D}r_{e\rm D}^2=\mu R^2\sin^2\alpha_{e\rm D}\ , \tag{1b}$$

$$\mu_{e\rm D,H}r_{e\rm D,H}^2=\mu R^2\cos^2\alpha_{e\rm D}\ , \tag{1c}$$

where the reduced masses $\mu_{e\rm D}$ and $\mu_{e\rm D,H}$ are given by

$$\mu_{e\rm D}=m_em_{\rm D}/(m_e+m_{\rm D})\ , \tag{2a}$$

$$\mu_{e\rm D,H}=(m_e+m_{\rm D})m_{\rm H}/(m_e+m_{\rm D}+m_{\rm H})\ . \tag{2b}$$

Here, $m_{\rm H}$ and $m_{\rm D}$ are the masses of the proton and the deuteron, respectively, and the parameter μ is arbitrary but has the dimensions of mass. The vector $\mathbf{r}_{e\rm D,H}$ locates the position of the proton relative to the electron-deuteron center of mass.

An alternative set of hypercoordinates, appropriate for the first excited state which represents H + D$^+$ at large internuclear separations can be defined in terms of the alternative Jacobi coordinates $\mathbf{r}_{e\rm H}$ and $\mathbf{r}_{e\rm H,D}$ of Fig. 1(c), i.e.,

$$\mu R^2=\mu_{e\rm H}r_{e\rm H}^2+\mu_{e\rm H,D}r_{e\rm H,D}^2\ , \tag{3a}$$

$$\mu_{e\rm H}r_{e\rm H}^2=\mu R^2\sin^2\alpha_{e\rm H}\ , \tag{3b}$$

$$\mu_{e\rm H,D}r_{e\rm H,D}^2=\mu R^2\cos^2\alpha_{e\rm H}\ , \tag{3c}$$

with $\mu_{e\rm H}$ and $\mu_{e\rm H,D}$ defined as in Eqs. (2a) and (2b) with H and D interchanged. The hyper-radius R is identical in the two alternative definitions, however the hyperangle is not. The transformation between the sets of five angular coordinates $\alpha_{e\rm D}$, $\hat{\mathbf{r}}_{e\rm D}$, $\hat{\mathbf{r}}_{e\rm D,H}$ represented by Ω and $\alpha_{e\rm H}$, $\hat{\mathbf{r}}_{e\rm H}$, $\hat{\mathbf{r}}_{e\rm H,D}$ represented by Ω' is called a kinematic rotation. Explicitly we have

$$\mathbf{r}_{e\rm H}=\frac{m_{\rm D}}{m_e+m_{\rm D}}\mathbf{r}_{e\rm D}-\mathbf{r}_{e\rm D,H}\ , \tag{4a}$$

$$\begin{aligned}\mathbf{r}_{e\rm H,D}&=\mathbf{r}_{e\rm D}-\frac{m_{\rm H}}{m_e+m_{\rm H}}\mathbf{r}_{e\rm H}\\&=-\frac{m_e(m_e+m_{\rm H}+m_{\rm D})}{(m_e+m_{\rm H})(m_e+m_{\rm D})}\mathbf{r}_{e\rm D}-\frac{m_{\rm H}}{m_e+m_{\rm H}}\mathbf{r}_{e\rm D,H}\ .\end{aligned} \tag{4b}$$

These relations take on the more transparent form upon defining the kinematic rotation angle γ, and using the definitions of Eqs. (1)–(3),

$$\sin\alpha_{e\rm H}\hat{\mathbf{r}}_{e\rm H}=\cos\gamma\,\sin\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D}-\sin\gamma\,\cos\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D,H}\ , \tag{5a}$$

$$\cos\alpha_{e\rm H}\hat{\mathbf{r}}_{e\rm H,D}=\sin\gamma\,\sin\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D}+\cos\gamma\,\cos\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D,H}\ , \tag{5b}$$

with

$$\tan\gamma=m_e/(\mu_{e\rm D}\mu_{e\rm D,H})^{1/2}\ . \tag{6}$$

For completeness, we write the three interparticle distances of Fig. 1(a) in terms of the $\alpha_{e\rm D}$ hyperangle and the kinematic rotation angles γ and γ':

$$r_{e\rm D}=(\mu/\mu_{e\rm D})^{1/2}R\,\sin\alpha_{e\rm D}\ , \tag{7a}$$

$$\begin{aligned}r_{e\rm H}=(\mu/\mu_{e\rm H})^{1/2}R\,|&\cos\gamma\,\sin\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D}\\&-\sin\gamma\,\cos\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D,H}|\ ,\end{aligned} \tag{7b}$$

$$r_{\mathrm{HD}}=(\mu/\mu_{\mathrm{HD}})^{1/2}R\,|\sin\gamma'\sin\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D}}+\cos\gamma'\cos\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D,H}}|\ , \tag{7c}$$

where

$$\tan\gamma'=(\mu_{e\mathrm{D}}\mu_{e\mathrm{D,H}})^{1/2}/m_{\mathrm{D}}\ . \tag{8}$$

The Schrödinger equation for the three-particle system with the center-of-mass motion separated out can be written in two alternative forms in terms of the two alternative Jacobi coordinate systems,

$$\left[-\frac{1}{2\mu_{e\mathrm{D,H}}}\nabla^2_{e\mathrm{D,H}}-\frac{1}{2\mu_{e\mathrm{D}}}\nabla^2_{e\mathrm{D}}+V\right]\Psi=\varepsilon\Psi\ , \tag{9}$$

$$\left[-\frac{1}{2\mu_{e\mathrm{H,D}}}\nabla^2_{e\mathrm{H,D}}-\frac{1}{2\mu_{e\mathrm{H}}}\nabla^2_{e\mathrm{H}}+V\right]\Psi=\varepsilon\Psi\ . \tag{10}$$

The transformation between the two forms is just the kinematic rotation. Note that the kinetic energy is form invariant to the coordinate transformation.

In hyperspherical coordinates, the Schrödinger equation takes the form

$$\left[-\frac{1}{2\mu}\left[\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}-\frac{\Lambda^2}{R^2}\right]+V\right]\Psi=\varepsilon\Psi\ , \tag{11}$$

where the generalized angular-momentum operator is defined by

$$\Lambda^2=-\frac{1}{\sin^2\alpha\cos^2\alpha}\frac{d}{d\alpha}\left[\sin^2\alpha\cos^2\alpha\frac{d}{d\alpha}\right]+\frac{L_1^2}{\sin^2\alpha}+\frac{L_2^2}{\cos^2\alpha}\ . \tag{12}$$

The angle α and the subscripts 1 and 2 denote a generic set of hyperangular coordinates. For example, if $\alpha=\alpha_{e\mathrm{D}}$, then $1=(e\mathrm{D})$ and $2=(e\mathrm{D,H})$. The operators $\mathbf{L}_i$ are conventional angular-momentum $\mathbf{r}_i\times\nabla_i$ operators. Because the generalized angular-momentum operator takes the same form in all hyperspherical coordinate systems, it always commutes with kinematic rotations.

In the hyperspherical adiabatic approximation the total wave function Ψ is expanded in a basis set of solutions to the following equation:

$$\left[\frac{\Lambda^2}{2\mu R^2}+V\right]\Phi_\nu(R;\Omega)=U_\nu(R)\Phi_\nu(R;\Omega)\ , \tag{13}$$

i.e.,

$$\Psi=\sum_\nu F_\nu(R)\Phi_\nu(R;\Omega)\ . \tag{14}$$

In the adiabatic approximation, neglecting couplings between the different channels, the total wave function is approximated by $\Psi\sim F_\nu(R)\Phi_\nu(R;\Omega)$ and consequently the hyper-radial equation becomes

$$\left[-\frac{1}{2\mu}\left[\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}\right]+U_\nu(R)\right]F_\nu(R)=\varepsilon F_\nu(R)\ . \tag{15}$$

Because the generalized angular-momentum operator commutes with kinematic rotations, the potentials $U_\nu(R)$ approach the correct thresholds at large R. This was demonstrated in Ref. 7 for the He autoionizing states, but is easily seen to hold generally. The price one must pay for this attractive feature is the use of approximate wave functions, because Eq. (13) has no known solutions in closed form. Accordingly we seek approximate solutions accurate to order m_e/m_{H}. Many different solutions to that order are possible. Indeed, the binding-energy difference of H and D is of order m_e/m_H, and approximate solutions correct to that order could still give incorrect thresholds. Accordingly, we also require that the approximate solutions give the correct threshold energies. Terms neglected in the lowest order could be calculated in higher order using perturbation theory. We therefore give an expression for the "perturbation" operator but do not evaluate its expectation value to obtain the first correction to the energy. This task is left for future studies.

III. APPROXIMATE SOLUTIONS

We consider only states of total angular-momentum zero. For such states, the rotation of the plane containing the three particles gives no contribution to the kinetic energy, and Eq. (13) can be written[11]

$$\left\{-\frac{1}{2\mu R^2}\left[\frac{1}{\sin^2\alpha\cos^2\alpha}\frac{d}{d\alpha}\left[\sin^2\alpha\cos^2\alpha\frac{d}{d\alpha}\right]-\frac{L^2_{\theta_{12}}}{\sin^2\alpha\cos^2\alpha}\right]+V\right\}\Phi_\nu(R;\Omega)=U_\nu(R)\Phi_\nu(R;\Omega)\ . \tag{16a}$$

In accordance with our choice of the Jacobi coordinates $\mathbf{r}_{e\mathrm{D}}$ and $\mathbf{r}_{e\mathrm{D,H}}$ we have

$$V=\frac{1}{\sqrt{\mu}R}\left[\frac{-Z_{\mathrm{H}}\sqrt{\mu_{e\mathrm{H}}}}{|\cos\gamma\sin\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D}}-\sin\gamma\cos\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D,H}}|}-\frac{Z_{e\mathrm{D}}\sqrt{\mu_{e\mathrm{D}}}}{\sin\alpha_{e\mathrm{D}}}+\frac{Z_{\mathrm{H}}Z_{\mathrm{D}}\sqrt{\mu_{\mathrm{HD}}}}{|\sin\gamma'\sin\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D}}+\cos\gamma'\cos\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D,H}}|}\right] \tag{16b}$$

and the combination of L_1^2 and L_2^2 yields

$$L^2_{\theta_{12}}=\frac{-1}{\sin\theta_{12}}\frac{d}{d\theta_{12}}\sin\theta_{12}\frac{d}{d\theta_{12}}\ . \tag{16c}$$

θ_{12} in this case is the angle between the $\hat{\mathbf{r}}_{e\mathrm{D}}$ and $\hat{\mathbf{r}}_{e\mathrm{D,H}}$ directions.

We now rewrite Eqs. (16) in terms of the new variable $s=\tan\alpha_{e\mathrm{D}}$,

$$\left[-\frac{1}{2\mu R^2}\left(\frac{d^2}{ds^2}+\frac{2}{s}\frac{d}{ds}-\frac{L^2_{\theta_{12}}}{s^2}+\frac{3}{(1+s^2)^2}\right)+\frac{V}{(1+s^2)^2}\right]\phi_\nu=\frac{U_\nu(R)}{(1+s^2)^2}\phi_\nu\ , \tag{17a}$$

$$V=\frac{1}{\sqrt{\mu}R}\left[\frac{-Z_{\rm H}\sqrt{\mu_{e\rm H}}}{\cos\gamma s_{e\rm H}}-\frac{Z_{\rm D}\sqrt{\mu_{e\rm D}}}{s}+\frac{Z_{\rm H}Z_{\rm D}\sqrt{\mu_{\rm HD}}}{\cos\gamma' s_{\rm HD}}\right]\ , \tag{17b}$$

where

$$s_{e\rm H}=|\tan\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D}-\tan\gamma\hat{\mathbf{r}}_{e\rm D,H}|\ , \tag{18a}$$

$$s_{\rm HD}=|\tan\gamma'\tan\alpha_{e\rm D}\hat{\mathbf{r}}_{e\rm D}+\hat{\mathbf{r}}_{e\rm D,H}|\ , \tag{18b}$$

and

$$\Phi_\nu=(1+s^2)^{1/2}\phi_\nu\ . \tag{19}$$

Next, we define the new variable r according to

$$\sqrt{m_e}r=\sqrt{\mu}Rs \tag{20}$$

and set

$$\mu=\mu_{e\rm D,H}\ , \tag{21a}$$

$$\sqrt{m_e}r_{eh}=\sqrt{\mu}Rs_{e\rm H}=\sqrt{m_e}\left|r\hat{\mathbf{r}}_{e\rm D}-\left(\frac{m_e}{\mu_{e\rm D}}\right)^{1/2}R\hat{\mathbf{r}}_{e\rm D,H}\right|\ , \tag{21b}$$

$$\sqrt{\mu_{e\rm D,H}}r_{hd}=\sqrt{\mu}Rs_{\rm HD}=\sqrt{\mu_{e\rm D,H}}\left|\left(\frac{m_e}{\mu_{e\rm D,H}}\right)^{1/2}\tan\gamma' r\hat{\mathbf{r}}_{e\rm D}+R\hat{\mathbf{r}}_{e\rm D,H}\right|\ . \tag{21c}$$

Notice that R, as opposed to r_{hd}, is a constant. Equation (17a) now becomes

$$\left[-\frac{1}{2m_e}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{L^2_{\theta_{12}}}{r^2}+\frac{3}{(1+m_er^2/\mu R^2)^2}\right)+\left(\frac{-Z_{\rm H}(\mu_{e\rm H}/m_e)^{1/2}}{\cos\gamma r_{eh}}-\frac{Z_{\rm D}(\mu_{e\rm D}/m_e)^{1/2}}{r}+\frac{Z_{\rm D}Z_{\rm H}(\mu_{\rm HD}/\mu_{e\rm D,H})^{1/2}}{\cos\gamma' r_{hd}}\right)\left(1+\frac{m_er^2}{\mu R^2}\right)^{-3/2}\right]\phi_\nu=\frac{U_\nu(R)}{(1+m_er^2/\mu R^2)^2}\phi_\nu\ . \tag{22}$$

Since no approximations have been made, Eq. (22) is still exact. Now we note that since r and R are of comparable magnitude, and since the kinematic rotation angles γ and γ' are of order $(m_e/m_{\rm H})^{1/2}$, Eq. (22) can be written as

$$\left[-\frac{1}{2m_e}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{L^2_{\theta_{12}}}{r^2}\right)-\frac{Z_{\rm H}(\mu_{e\rm H}/m_e)^{1/2}}{r'_{eh}}-\frac{Z_{\rm D}(\mu_{e\rm D}/m_e)^{1/2}}{r}+\frac{Z_{\rm H}(\mu_{e\rm H}/m_e)^{1/2}}{R}+V_p\right]\phi_\nu=\left[U_\nu^{(0)}(R)+\frac{\frac{15}{4}}{2\mu R^2}\right]\phi_\nu \tag{23}$$

with

$$r'_{eh}=|r\hat{\mathbf{r}}_{e\rm D}-R\hat{\mathbf{r}}_{e\rm D,H}| \tag{24}$$

and the corresponding hyper-radial equation

$$\left[-\frac{1}{2\mu_{e\rm D,H}}\left(\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}+\frac{\frac{15}{4}}{R^2}\right)+E_\nu^{(0)}(R)\right]F_\nu(R)=\varepsilon F_\nu(R)\ , \tag{25}$$

where the "perturbation operator" V_p is of order $m_e/m_{\rm H}$ and is given explicitly by

$$V_p=\left(1+\frac{m_er^2}{\mu R^2}\right)^{-3/2}V-\left(-\frac{Z_{\rm H}(\mu_{e\rm H}/m_e)^{1/2}}{r'_{eh}}-\frac{Z_{\rm D}(\mu_{e\rm D}/m_e)^{1/2}}{r}+\frac{Z_{\rm H}(\mu_{e\rm H}/m_e)^{1/2}}{R}\right)-\left(1+\frac{m_er^2}{\mu R^2}\right)^{-2}\left(U_\nu(R)+\frac{3}{2\mu R^2}\right)+\left(U_\nu^{(0)}(R)+\frac{\frac{15}{4}}{2\mu R^2}\right) \tag{26}$$

with $\mu=\mu_{e\rm D,H}$ and where $E_\nu^{(0)}(R)=[U_\nu^{(0)}(R)+\frac{15}{4}/2\mu R^2]$ is the zeroth-order energy defined by the eigenvalue equation, Eq. (23), with V_p set equal to zero.

The first term in Eq. (23) just has the form of the total kinetic energy in spherical coordinates for a particle in a state with magnetic quantum number equal to zero. Accordingly the zeroth-order equation with V_p omitted is identical in form to the usual equation of the Born-

Oppenheimer approximation with effective charges

$$Z'_{\mathrm{D}}=Z_{\mathrm{D}}(\mu_{e\mathrm{D}}/m_e)^{1/2} \text{ and } Z'_{\mathrm{H}}=Z_{\mathrm{H}}(\mu_{e\mathrm{H}}/m_e)^{1/2} . \tag{27}$$

A similar zeroth-order equation has been introduced in another connection in Ref. 12. Our Eq. (23), although similar in form to Eq. (3.20) of Ref. 12, has a significantly different interpretation. In particular, only one variable R is held fixed in the hyperspherical adiabatic approximation, whereas the vector $\mathbf{r}_{\mathrm{HD}}$ is fixed in the approximation of Ref. 12.

In addition to perturbation corrections to the potential-energy curves, it is also necessary to include the lowest-order nonadiabatic diagonal perturbation (Φ_v,Φ_v'') where primes in this case denote differentiation with respect to R and the inner product is taken with respect to the five angular coordinates Ω.

The complete first-order correction is thus

$$E_v^{(1)}(R)=(\phi_v,V_p^{(0)}\phi_v)-\frac{1}{2\mu}(\Phi_v,\Phi_v'') , \tag{28}$$

where $U_v(R)$ is set equal to $E_v^{(0)}(R)$ in the expression of Eq. (26) for V_p to obtain $V_p^{(0)}$, and

$$(\phi_v,V_p^{(0)}\phi_v)=\int_0^\infty \phi_v^* V_p^{(0)}\phi_v r^2\,dr\,d\hat{\mathbf{r}}_{e\mathrm{D}}\,d\hat{\mathbf{r}}_{e\mathrm{D,H}} \tag{29}$$

with

$$(\phi_v,\phi_v)=1 . \tag{30}$$

At large distances, the nonadiabatic term cancels some of the perturbation terms of $(\phi_v|\,V_p^{(0)}\,|\phi_v)$. This only happens when the approximate solutions have the correct asymptotic form, and is one of the reasons for selecting the particular form for V_p. Even though it appears that other choices of the effective charge and of the reduced mass μ result in fewer correction terms, we know that the present choice is optimum, at least at large distances. For the exact solution of Eq. (22) none of the questions concerning the reduced mass and the effective charges are relevant. It is only when treating Eq. (22) approximately that these considerations matter.

The hyper-radial Schrödinger equation in the adiabatic approximation is given by Eq. (25). Upon setting $f_v(R)=R^{-5/2}F_v(R)$ we have

$$-\frac{1}{2\mu_{e\mathrm{D,H}}}\left[\frac{d^2}{dR^2}+E_v^{(0)}(R)\right]f_v(R)=\varepsilon f_v(R) . \tag{31}$$

This equation is identical in form to the standard Born-Oppenheimer equation for nuclear motion with rotational angular momentum equal to zero, and with the identification of r_{HD} with R. Because of our choice of $R=r_{\mathrm{HD}}$ and because we include the factor $-\frac{15}{4}/R^2$ in V_p, the radial equation (31) correctly describes a proton moving relative to a deuterium atom at large R, in zeroth approximation. Higher-order calculations of the hyperspherical adiabatic potential curves would include the correction of Eq. (28).

For completeness we note that the matrix elements with integration variable α transform to matrix elements with the integration variable s according to

$$\int_0^\infty |\Phi_v|^2 V\sin^2\alpha\cos^2\alpha\,d\alpha=\int_0^\infty |\phi_v|^2 V\frac{s^2}{(1+s^2)^2}ds . \tag{32}$$

Changing the length scale does not change the magnitude of the integral provided ϕ_v is normalized. Thus we may replace s by r provided this change is made in the normalization integrals also. We must, however, evaluate (Φ,Φ'') using variable α or s kept constant, not r. This is one manifestation of the difference between the hyper-radius R and the internuclear distance r_{HD}.

IV. ZEROTH-ORDER SPECTRUM OF HD$^+$

The exact Born-Oppenheimer and the zeroth-order hyperspherical adiabatic potential curves are shown in Fig. 2. The inset in Fig. 2 shows the behavior of the potential curves at large internuclear separations. These potential curves are obtained using suitable eigenfunction expansions in the appropriate regions of small r_{HD} and large r_{HD}. The expansions lead to three-term recurrence relations, resulting in continued-fraction equations, which are evaluated to a required accuracy.[13] Consequently, no numerical approximations are involved. For small internuclear separations, the potential curves obtained from the two different adiabatic approximations are almost indistinguishable from each other, as concluded and correctly emphasized by Greene. However, the use of effective charges to obtain the hyperspherical adiabatic potentials gives qualitatively different curves at large internuclear separations, leading to the correct dissociation thresholds. This is one of the main differences that distinguishes the two adiabatic approximations. The effect of this difference in the two approaches at larger internuclear separations should be most apparent in the vibrational spectrum of the weakly bound states of the HD$^+$ molecule.

To obtain the vibrational spectrum, the numerical integration over R of Eq. (31) is performed using the Numerov algorithm.[14] Starting with a trial bound-state energy, the solutions of the outward and the inward integrations are matched at a point where the potential is

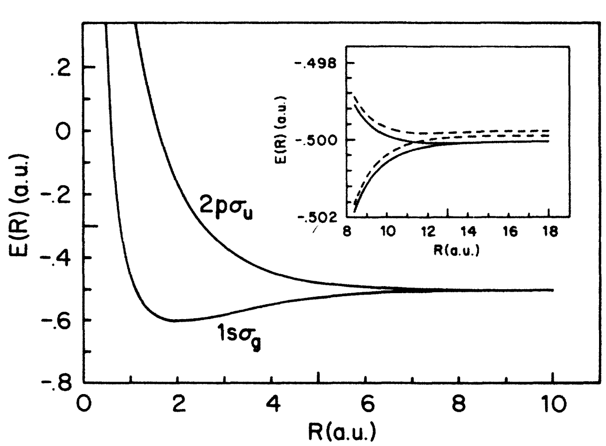

FIG. 2. Adiabatic potential curves for the two lowest states, $1s\sigma_g$ and $2p\sigma_u$, of the HD$^+$ molecule. Solid lines represent the Born-Oppenheimer potential curves, and the dashed lines represent the zeroth-order adiabatic hyperspherical results.

TABLE I. The dissociation energies D_{vJ} of HD$^+$ in cm^{-1}.

v ($J=0$)	Born-Oppenheimer	D_{vJ} (cm^{-1}) Hyperspherical	Ref. 9
0	21 527.2	21 516.4	21 516.073
1	19 614.1	19 603.4	19 603.079
2	17 797.0	17 786.6	17 786.217
3	16 073.5	16 063.1	16 062.630
4	14 440.4	14 430.1	14 429.831
5	12 896.0	12 885.8	12 885.697
6	11 438.6	11 428.4	11 428.466
7	10 066.7	10 056.5	10 056.731
8	8 779.4	8 769.4	8 769.444
9	7 575.9	7 565.6	7 565.920
10	6 455.9	6 445.6	6 445.854
11	5 419.5	5 409.1	5 409.332
12	4 476.2	4 456.8	4 456.863
13	3 600.1	3 589.4	3 589.404
14	2 819.4	2 808.5	2 808.402
15	2 127.1	2 116.1	2 115.845
16	1 525.9	1 514.0	1 514.323
17	1 019.0	1 007.0	1 007.086
18	610.5	598.3	598.111
19	304.9	292.5	292.063
20	107.0	94.4	93.603
21	16.9	10.7	(2.93)
22	0.8		

not too small compared with the energy. The amount of the mismatch then yields a second approximation to the bound-state energy. This procedure is iterated, and the convergence is accelerated with the use of Aitken's δ^2 method,[15] until the eigenenergies converge up to 0.1 cm^{-1}. For the computation of the eigenenergies of the high-lying bound states, the convergence criterion was a stricter 0.01 cm^{-1}.

Since the dissociation energy of the molecule is different for the two dissociation channels $H+D^+$ and $D+H^+$, with $D+H^+$ being the lower in energy, and since we are interested in the lowest-energy state, we define the dissociation energy in a particular vibrational and rotational state by

$$D_{vJ}=E_D-E_{vJ} , \tag{33}$$

where E_{vJ} is the energy of the (v,J) state represented by the vibrational v and the rotational J quantum numbers, and E_D is the energy of dissociation in the appropriate channel, the $D+H^+$ in this case.

The complete vibrational spectrum of the $J=0$ rotational states, with the dissociation energies defined as above, is given in Table I. In addition to the present results obtained from the two alternative adiabatic approximations, we also include the more accurate results of Wolniewicz and Poll,[9] who, in their calculations, have taken into account the higher-order relativistic, radiative, and nonadiabatic corrections with an accuracy of the order of 0.001 cm^{-1}. For further testing, we show in Table II a comparison of the Wolniewicz and Poll results with experiment.[16–18]

The spectrum obtained from the Born-Oppenheimer adiabatic potential curve is, as expected, consistently

TABLE II. Comparison of experimental and theoretical transition frequencies for HD$^+$ in cm^{-1}.

Transition (v,J)-(v',J')	Experiment	Theory Ref. 9	(Theor. − expt.)
(0,1)-(1,0)	1869.134[a]	1869.135	(+0.001)
(0,2)-(1,1)	1823.533[a]	1823.533	(0.000)
(1,0)-(2,1)	1856.778[a]	1856.779	(+0.001)
(2,0)-(3,1)	1761.616[a]	1761.616	(0.000)
(2,1)-(3,2)	1797.522[a]	1797.519	(−0.003)
(2,2)-(3,1)	1642.108[a]	1642.111	(+0.003)
(16,0)-(18,1)	926.498[b]	926.490	(−0.008)
(16,1)-(18,2)	932.231[b]	932.220	(−0.011)
(16,2)-(18,3)	933.204[b]	933.207	(+0.003)
(16,3)-(18,4)	929.238[b]	929.238	(0.000)
(16,4)-(18,5)	920.097[b]	920.089	(−0.008)

[a] From Ref. 16.

[b] From Ref. 17.

lower than the hyperspherical adiabatic spectrum by an average of 12 cm^{-1}. This is not surprising considering the fact that in the standard Born-Oppenheimer approximation the nuclei are treated as infinitely heavy. The surprising fact is the excellent agreement between the spectra of the present zeroth order hyperspherical adiabatic approximation and the more accurate calculations of Wolniewicz and Poll. Except for the highest $v=21$ vibrational state, the two calculations yield dissociation energies that agree to within 0.5 cm^{-1}. It should be mentioned that for the $v=21$ state, Wolniewicz and Poll do not include the exact nonadiabatic corrections, because, for this case, the outer turning point is outside the integration range (0.8 to 10.55 a.u.) used in their calculation, yielding unreliable results. Their entry for the $v=21$ state was instead obtained by extrapolation from the values from lower v.

V. DISCUSSION

Our calculations yield a state having the highest vibrational quantum number of $v=22$ with a binding energy of 0.8 cm^{-1} in the case of the Born-Oppenheimer approximation, and $v=21$ with binding energy of 10.7 cm^{-1} in the case of the adiabatic hyperspherical approximation. The highest state obtained by the theoretical calculations of Wolniewicz and Poll has $v=21$ and rotational quantum number $J=1$, with a binding energy of 0.74 cm^{-1}. Experimentally, the highest states detected are the ones with vibrational quantum numbers of $v=17$ and $v=18$. However, efforts are currently underway to determine whether $v=21$ is actually the highest state.[19] Still, with higher rotational levels, the interesting possibility arises for quasibound states of HD$^+$ lying above the dissociation limit which are metastable to dissociation because of the centrifugal barrier.

Whether $v=21$ or $v=22$ is the highest state cannot be answered with certainty in a theoretical calculation without including the higher-order corrections, and the nonadiabatic coupling terms. In the case of the hyperspherical approximation, the inclusion of the correction of Eq. (28) will yield an upper bound to order $m_e/m_{\rm H}$ on the eigenenergies.

Turning our attention to the atomic collision problem in relation to the coupling of the different channels, another important point arises which, though somewhat related to the problem associated with the correct breakup thresholds, distinguishes the hyperspherical adiabatic approximation from the standard Born-Oppenheimer adiabatic approximation. Were it not for the derivative in the hyperspherical Schrödinger equation, Eq. (11), operating also on the parameter R in the basis set $\Phi_\nu(R;\Omega)$, the hyper-radial equation would be completely uncoupled. Since the couplings among the radial functions $F_\nu(R)$ of the different channels result from the matrix projection of the nonzero derivatives $\partial\Phi_\nu/\partial R$ with respect to R (the nonzero gradients of $\nabla\Phi_\nu$ with respect to $\mathbf{r}_{\rm HD}$ in the case of the Born-Oppenheimer approximation), on the basis set Φ_ν, important physical insight is gained by examining in detail these derivatives of the basis functions. To introduce the notation, a brief discussion of the separability of the Schrödinger equation for a one-electron diatomic molecule follows.

It is well known that the Schrödinger equation in this case is separable in elliptic coordinates (λ,η,ϕ) where

$$\lambda=(r_{e{\rm D}}+r_{e{\rm H}})/r_{\rm HD} \quad \text{and} \quad \eta=(r_{e{\rm D}}-r_{e{\rm H}})/r_{\rm HD} \tag{34}$$

with $r_{e{\rm D}}$ and $r_{e{\rm H}}$ representing the electron separations from the two nuclei, and $r_{\rm HD}$ representing the internuclear separation.

Taking the electronic eigenfunctions as

$$\Psi=X(\lambda)Y(\eta)\exp(\pm im\phi), \quad m=0,1,2,\ldots \tag{35}$$

with the nuclear charges $Z_{\rm H}$ and $Z_{\rm D}$, the "inner" and "outer" equations are given by

$$\frac{d}{d\eta}(1-\eta^2)\frac{dY}{d\eta}+\left[C-p^2(1-\eta^2)-\frac{m^2}{(1-\eta^2)}\right.$$
$$\left.-(Z_{\rm H}-Z_{\rm D})r_{\rm HD}\eta\right]Y=0\,, \tag{36}$$

$$\frac{d}{d\lambda}(\lambda^2-1)\frac{dX}{d\lambda}+\left[-C-p^2(\lambda^2-1)-\frac{m^2}{(\lambda^2-1)}\right.$$
$$\left.+(Z_{\rm H}+Z_{\rm D})r_{\rm HD}\lambda\right]X=0\,, \tag{37}$$

where

$$p^2=-\frac{1}{2}\left[E-\frac{Z_{\rm H}Z_{\rm D}}{r_{\rm HD}}\right]r_{\rm HD}^2$$

and C is the separation constant.

The solutions to these equations can be represented by infinite-series expansions. Hence, the eigenfunctions of Eq. (36) may conveniently be taken in terms of the associated Legendre polynomials as

$$Y(\eta)=\sum_{j=m\ \text{or}\ m+1} f_j P_j^m(\eta)\,, \tag{38}$$

the summation being over even or odd values of j depending on the symmetry. On the other hand, the eigenfunctions of Eq. (37) can be represented using the Jaffe expansion

$$X(\lambda)=(\lambda^2-1)^{m/2}(\lambda+1)^\sigma\exp(-p\lambda)\sum_{j=0}^{\infty}g_j\xi^j \tag{39}$$

in which

$$\sigma=\frac{r_{\rm HD}(Z_{\rm H}+Z_{\rm D})}{2p}-m-1 \tag{40}$$

and

$$\xi=(\lambda-1)/(\lambda+1)\,. \tag{41}$$

The cogent point to notice is the following. Since in the case of the hyperspherical approximation $r_{e{\rm D}}$ and $r_{e{\rm H}}$ are defined in terms of a common scale coordinate R [see Eq. (7)], and because the elliptical coordinates λ and η are dimensionless and they do not involve any R dependence, to first order in $m_e/m_{\rm H}$ we have

$$\lambda=(\mu_{e\mathrm{D,H}}/\mu_{e\mathrm{D}})^{1/2}\sin\alpha_{e\mathrm{D}}+(\mu_{e\mathrm{D,H}}/\mu_{e\mathrm{H}})^{1/2}$$
$$\times\,|\cos\gamma\,\sin\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D}}-\sin\gamma\,\cos\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D,H}}|\ , \tag{42a}$$

$$\eta=(\mu_{e\mathrm{D,H}}/\mu_{e\mathrm{D}})^{1/2}\sin\alpha_{e\mathrm{D}}-(\mu_{e\mathrm{D,H}}/\mu_{e\mathrm{H}})^{1/2}$$
$$\times\,|\cos\gamma\,\sin\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D}}-\sin\gamma\,\cos\alpha_{e\mathrm{D}}\hat{\mathbf{r}}_{e\mathrm{D,H}}|\ . \tag{42b}$$

It follows that the derivatives of Eqs. (38) and (39) with respect to R do not include any derivatives of the series-expansion functions. Only the derivatives of the expansion coefficients come into play. Considering, for example, the expansion (38), we have

$$\frac{\partial Y}{\partial R}=\sum_j \frac{\partial f_j(R)}{\partial R}P_j^m(\eta)\ . \tag{43}$$

On the other hand, in the case of the Born-Oppenheimer approximation, the gradient with respect to $\mathbf{r}_{\mathrm{HD}}$ of the eigenfunctions involves derivatives of the expansion functions, the expansion coefficients, and of the coordinates λ and η, e.g.,

$$\hat{\mathbf{r}}_{\mathrm{HD}}\cdot\nabla Y=\sum_j \frac{\partial f_j}{\partial r_{\mathrm{HD}}}P_j^m(\eta)+\sum_j f_jP_j^{m\prime}(\eta)\frac{\partial\eta}{\partial r_{\mathrm{HD}}}\ . \tag{44}$$

That the gradient of the eigenfunctions, and hence the coupling terms, are dependent on the derivative of the elliptical coordinates implies that the Born-Oppenheimer coupled equations are dependent on the coordinate origin. Bates and McCarrol were the first to show that this defect of the Born-Oppenheimer approximation is removed by introducing translation factors—that are themselves origin dependent—in the molecular eigenfunction expansions. The complete set of coupled equations are then invariant to Galilean transformations of the reference frame. Conceptual and practical difficulties of this procedure for molecular states is attested to by the extensive literature on the subject of "translation factors." In contrast, the coupled equations of the adiabatic hyperspherical approximation are automatically Galilean invariant, i.e., invariant to kinematic rotations. Hence, translation factors are not needed in this case. Of course, one pays a price for this attractive feature; as mentioned above, the adiabatic hyperspherical functions are not known exactly. We show here that they can be obtained to order m_e/m_{H} using standard molecular codes. The use of the adiabatic hyperspherical approximation then provides a prescription on how to obtain the derivative couplings. Derivatives are taken holding the five variables $\alpha_{e\mathrm{D}}$, $\hat{\mathbf{r}}_{e\mathrm{D}}$, $\hat{\mathbf{r}}_{e\mathrm{D,H}}$ constant. Effects of rotational coupling, however, are included in the eigenstates of the $[\Lambda^2/2\mu R^2+V]$ operator. Because the present discussion is limited to $L=0$, such coupling does not appear explicitly in the radial equations.

In the context of continuum states of atomic He and H^-, it has been shown[20] that the adiabatic hyperspherical coordinate R converges only slowly to the independent-particle coordinate of the initial or final channel at large R. In the present case, $R\rightarrow r_{e\mathrm{D,H}}$ as $R\rightarrow\infty$ with $r_{e\mathrm{D}}$ fixed. Since the slow convergence has noticeable effects on $e^-+\mathrm{H}$ s-wave phase shifts, it is useful to examine this effect also in the present context for comparison with similar effects in the Born-Oppenheimer approximation.

At large $r_{e\mathrm{D,H}}$ we have

$$R^{5/2}\Psi\sim\Phi_\nu(R\,;\Omega)\sin(kR+\delta_\nu)\ , \tag{45}$$

$$kR\sim\sqrt{2\mu(\varepsilon-E_{\mathrm{D}})}(\mu_{e\mathrm{D}}r_{e\mathrm{D}}^2+\mu_{e\mathrm{D,H}}r_{e\mathrm{D,H}}^2)^{1/2}/\sqrt{\mu}$$
$$=\sqrt{2\mu_{e\mathrm{D,H}}(\varepsilon-E_{\mathrm{D}})}\left[r_{e\mathrm{D,H}}+\frac{1}{2}\frac{\mu_{e\mathrm{D}}}{\mu_{e\mathrm{D,H}}}\frac{r_{e\mathrm{D}}^2}{r_{e\mathrm{D,H}}}+\cdots\right]$$
$$=kr_{e\mathrm{D,H}}+\tfrac{1}{2}k\frac{\mu_{e\mathrm{H}}}{\mu_{e\mathrm{D,H}}}\frac{r_{e\mathrm{D}}^2}{r_{e\mathrm{D,H}}}+\cdots\ . \tag{46}$$

For small values of k, in the energy ranges where a wave treatment for nuclear motion is required, the error term $\frac{1}{2}k(\mu_{e\mathrm{D}}/\mu_{e\mathrm{D,H}})(r_{e\mathrm{D}}^2/r_{e\mathrm{D,H}})$ is negligible owing to the small factor $\mu_{e\mathrm{D}}/\mu_{e\mathrm{D,H}}$. In the case of $e^-+\mathrm{H}$ phase shifts, the reduced mass is unity and some error is introduced for nonzero k. The comparable factor here is the much smaller parameter $k\mu_{e\mathrm{D}}/\mu_{e\mathrm{D,H}}$. On the other hand, at high energies, where a classical treatment of nuclear motion is appropriate, we have $(\varepsilon-E_{\mathrm{D}})\sim\frac{1}{2}\mu_{e\mathrm{D,H}}v^2$, and

$$\tfrac{1}{2}k\frac{\mu_{e\mathrm{D}}}{\mu_{e\mathrm{D,H}}}\sim\tfrac{1}{2}\mu_{e\mathrm{D}}v\frac{r_{e\mathrm{D}}^2}{r_{e\mathrm{D,H}}}\ . \tag{47}$$

As long as v is much smaller than other characteristic velocities or $r_{e\mathrm{D,H}}$ is quite large, this factor is again negligible.

In contrast, the Born-Oppenheimer approximation employs the asymptotic form

$$\Psi\sim\Phi_\nu\sin(k'r_{\mathrm{HD}}+\delta)\ , \tag{48}$$

where $k'=[2\mu_{\mathrm{HD}}(\varepsilon-E'_{\mathrm{D}})]^{1/2}$, and E'_{D} is the incorrect threshold energy of the Born-Oppenheimer theory. In lowest order in $r_{e\mathrm{D}}/r_{e\mathrm{D,H}}$ and m_e/m_{H}, we have from Eqs. (1c) (6), (7a), (7b), and (8) the result

$$k'r_{\mathrm{HD}}\sim k'\,r_{e\mathrm{D,H}}-\frac{1}{2}\frac{m_em_{\mathrm{H}}}{m_{\mathrm{D}}(m_{\mathrm{H}}+m_{\mathrm{D}})}kr_{e\mathrm{D,H}}$$
$$+\frac{m_e}{m_{\mathrm{D}}}k\hat{\mathbf{r}}_{e\mathrm{D,H}}\cdot\mathbf{r}_{e\mathrm{D}}\ . \tag{49}$$

The last two terms on the right-hand side of Eq. (49) represent corrections of order m_e/m_{H} provided $\mathbf{r}_{e\mathrm{D,H}}$ is small. Note, however, that the second term increases linearly with $r_{e\mathrm{D,H}}$ while the third term remains constant as $r_{e\mathrm{D,H}}\rightarrow\infty$. The comparable correction to the adiabatic hyperspherical phase shift in Eq. (46) decreases as $r_{e\mathrm{D,H}}$ becomes infinite. For small R and moderate or small values of $r_{e\mathrm{D,H}}$, the errors in the Born-Oppenheimer approximation are negligible, but they are still larger than the errors involved in the adiabatic hyperspherical approximation. For large $r_{e\mathrm{D,H}}$ or large k, the corrections to the Born-Oppenheimer approximation are no longer small, and consequently one must introduce translation factors. Because the adiabatic hyperspherical phase converges as $1/r_{e\mathrm{D,H}}$, the translation factors are not needed in this case.

For large values of E such that $k\approx\mu_{\mathrm{HD}}$, we have

$$k' r_{\mathrm{HD}} \sim k' r_{e\mathrm{D,H}} - \tfrac{1}{2} m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right]^2 v r_{e\mathrm{D,H}} + m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right] v \hat{\mathbf{r}}_{e\mathrm{D,H}} \cdot \mathbf{r}_{e\mathrm{D}} \ . \tag{50}$$

Upon setting $r_{e\mathrm{D,H}} \sim vt$ and $v\hat{\mathbf{r}}_{e\mathrm{D,H}} = \mathbf{v}$, we have for the second and third terms of Eq. (50) the result

$$-\tfrac{1}{2} m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right]^2 v r_{e\mathrm{D,H}} + m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right] v \hat{\mathbf{r}}_{e\mathrm{D,H}} \cdot \mathbf{r}_{e\mathrm{D}} \rightarrow -\tfrac{1}{2} m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right]^2 v^2 t + m_e \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{H}}+m_{\mathrm{D}}} \right] \mathbf{v} \cdot \mathbf{r}_{e\mathrm{D}} \ . \tag{51}$$

The right-hand side is now recognized as just the translation factors of Bates and McCarrol. Again, we emphasize that such factors are absent in the adiabatic hyperspherical approximation.

The prescription of treating the translation factors for $L=0$ states that emerges from the adiabatic hyperspherical approximation developed here is quite simple; first, express all wave functions in hyperspherical coordinates and form the relevant radial derivatives holding the hyperangles constant, and next, if desired, reexpress the wave functions in conventional coordinates. The resulting theory is then Galilean invariant. Our application of this approach to the high-vibrational states of the HD$^+$ molecule indicates that this prescription does indeed represent significant improvement over the standard Born-Oppenheimer approximation. Extension to other molecules and nonzero rotational states could prove equally fruitful.

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