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Improved adiabatic calculations of the vibrational-rotational states of HD$^+$

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Potential curves have been calculated for the ground electronic state of HD$^+$ within the framework of an improved adiabatic approximation. Both the $J=0$ and $J=1$ rotational states have been examined in detail using the new approach. This formulation takes into account the symmetry-breaking effects due to the unequal masses of the two nuclei, in contrast to the standard adiabatic approximation. The technique is found to yield significant improvement over the standard adiabatic approach for the highly excited vibrational states of HD$^+$.

I. INTRODUCTION

In a previous paper[1] a new adiabatic approximation which exhibits the correct dissociation limits for diatomic molecules with unequal masses was formulated. This earlier study contained a minimal basis-set calculation for the systems HD$^+$ and $dt\mu$. The present work contains an accurate calculation on HD$^+$ which has been performed using a slightly modified version of this new adiabatic approximation. Potential curves have been calculated for the $J=0$ and $J=1$ rotational states of the $1s\sigma$ electronic ground state. Splittings for the $J=1$ $2p\pi$ states, of interest with regard to Λ doubling, have also been calculated.

Earlier investigations of the vibrational-rotational levels of HD$^+$ near the dissociation limit have noted that in order to obtain accurate results it is necessary to take into account the symmetry-breaking effect of the unequal nuclear masses. Hunter, Yau, and Pritchard[2] observed the dissociation error inherent in the usual adiabatic procedure for HD$^+$ and noted that the problem could be overcome on a nonadiabatic level by using a pair of coupled differential equations to obtain the vibrational-rotational spectrum. Carrington and Kennedy[3,4] have obtained correct dissociation by coupling the $1s\sigma_g$ and $2p\sigma_u$ Born-Oppenheimer wave functions together using matrix elements of the complete (nonadiabatic) Hamiltonian. The resulting matrix is then diagonalized to yield effective potential curves which can be integrated to yield the vibrational-rotational levels. Wolniewicz and Poll[5] utilize the $1s\sigma_g$ and $2p\sigma_u$ states to construct approximate nonadiabatic wave functions which are obtained by integrating a pair of coupled differential equations. The resulting wave functions are then used to construct zeroth-order eigenfunctions in a perturbation scheme to obtain accurate energies.

Macek and Jerjian have discussed the adiabatic hyperspherical scheme[6] in which the zeroth-order Hamiltonian $H_0^{\mathrm{AH}}(R)$ acts upon the Hilbert space of the angular coordinates Ω, with the hyperradius R appearing only as a parameter. This adiabatic approximation leads to potential curves which take into account the symmetry breaking; however, the eigenvalue equation associated with $H_0^{\mathrm{AH}}(R)$ requires the evaluation of matrix elements which are nonstandard, and a complete solution to the hyperspherical adiabatic approximation has not yet been attempted. Macek and Jerjian managed to rewrite $H_0^{\mathrm{AH}}(R)$ as a Born-Oppenheimer Hamiltonian (for a one-electron molecule with unequal charges) plus a perturbation term and have performed a calculation which neglects both this perturbation term and the lowest-order nonadiabatic diagonal correction.

The adiabatic approximation discussed in the present work manifests the symmetry-breaking behavior which is required to obtain correct energies and wave functions near the dissociation limit. It leads to potential curves which may be used to obtain vibrational-rotational levels as well as for other applications not considered here. The vibrational-rotational levels obtained from the method are variational upper bounds to the true nonadiabatic energies. The equations encountered using the present procedure generalize to the many-electron problem and may be solved using the standard quantum-chemistry computer routines. Moreover, the phenomenon of Λ doubling appears without having to resort to perturbation theory.

The organization of this paper is as follows. Section II contains a discussion of the theory, in order to indicate how the formulation of the theory for the present calculation differs from that presented in Ref. 1. Section III describes the computational method used here for the adiabatic calculation. The new potential curve results are presented in Sec. IV. The vibrational levels for the $J=0$ $1s\sigma$ curve are reported and discussed in Sec. V. Section VI contains the conclusions of this work.

II. THEORY

After separating the center-of-mass motion, the Hamiltonian of HD$^+$ is expressed in center of mass of the nuclei (c.m.n.) coordinates[7] (in units where $\hbar=e=1$) as

$$H=-\frac{1}{2\mu}\nabla_R^2-\frac{1}{2(m_a+m_b)}\nabla_r^2+H_e\ , \tag{1}$$

where

$$H_e=-\frac{1}{2m_c}\nabla_r^2+\frac{1}{R}-\frac{1}{r_{ac}}-\frac{1}{r_{bc}}\ , \tag{2}$$

$\mu = m_a m_b/(m_a+m_b)$, $\mathbf{r}$ is the electronic coordinate vector measured from the c.m.n., $\mathbf{R}$ is the internuclear separation vector, and the proton, deuteron, and electron are taken to be particles a, b, and c, respectively. Equation (1) may be rewritten in terms of $\mathbf{L}_R$, the relative angular momentum of the nuclei, as

$$H = -\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]+\frac{\mathbf{L}_R^2}{2\mu R^2} - \frac{1}{2(m_a+m_b)}\nabla_r^2 + H_e \ . \tag{3}$$

It is convenient to regroup terms in Eq. (3) according to

$$H = H_0(R) + H' \ , \tag{4}$$

where

$$H_0(R) = \frac{\mathbf{L}_R^2}{2\mu R^2} - \frac{1}{2(m_a+m_b)}\nabla_r^2 + H_e \tag{5}$$

and

$$H' = -\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right] \ . \tag{6}$$

Note that the Hamiltonian $H_0(R)$ in Eq. (5) operates only on the space of functions of $\mathbf{r}$ (the electronic coordinates) and $\hat{\mathbf{R}}$ (the internuclear orientation). From the usual arguments concerning the completeness of eigenfunctions of a Hermitian operator,[8] the eigenfunctions $\phi_n(\mathbf{r},\hat{\mathbf{R}};R)$ of $H_0(R)$ for a fixed value of R, satisfying

$$H_0(R)\phi_n(\mathbf{r},\hat{\mathbf{R}};R) = U_n(R)\phi_n(\mathbf{r},\hat{\mathbf{R}};R) \ , \tag{7}$$

form a complete set of functions of $\mathbf{r}$ and $\hat{\mathbf{R}}$ for each value of R. Hence the total wave function $\Psi(\mathbf{r},\mathbf{R})$ may be expanded in this set according to

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_m \chi_m(R)\phi_m(\mathbf{r},\hat{\mathbf{R}};R) \tag{8}$$

$$= \sum_m \chi_m(R)\,|\,m;R\,\rangle \ , \tag{9}$$

where $|\,m;R\,\rangle$ is an electronic-internuclear orientation ket, parameterized by R. Inserting Eq. (9) into $H\Psi = E\Psi$ and multiplying on the left by $\langle n;R\,|$ gives the coupled equations

$$\sum_m \langle n;R\,|\,[H_0(R)+H']\,|\,m;R\,\rangle\chi_m(R) = E\sum_m \langle n;R\,|\,m;R\,\rangle\chi_m(R) \tag{10}$$

Using Eqs. (5)—(7), one obtains the system of equations

$$\left[-\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]+U_n(R)-\left\langle n;R\left|\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}\right|n;R\right\rangle - E\right]\chi_n(R) = -\sum_{m(\neq n)}\left[2\left\langle n;R\left|-\frac{1}{2\mu}\frac{\partial}{\partial R}\right|m;R\right\rangle\frac{\partial}{\partial R}\chi_m(R)+\left\langle n;R\left|-\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]\right|m;R\right\rangle\chi_m(R)\right] \ , \tag{11}$$

where Eq. (11) has been written such that all off-diagonal terms in the equation appear on the right-hand side. Equation (11) has been derived by noting that terms of the form $\langle n;R\,|\,\partial/\partial R\,|\,n;R\,\rangle$ and $\langle n;R\,|\,(1/R)\partial/\partial R\,|\,n;R\,\rangle$ are zero (this result requires that these matrix elements are real and that the $|\,n;R\,\rangle$ are normalized to unity for all values of R; this is, in fact, the standard convention and does not impose any computational difficulties). Following Born,[9] the adiabatic approximation is obtained by merely neglecting the off-diagonal terms. Therefore, the adiabatic approximation to the system of Eq. (11) is given by

$$\left[-\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]+U_n(R) - \left\langle n;R\left|\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}\right|n;R\right\rangle\right]\chi_{vn}(R) = E_v\chi_{vn}(R) \ , \tag{12}$$

where the quantum number v has been added to indicate that once $U_n(R)$ and $\langle n;R\,|\,(1/2\mu)\partial^2/\partial R^2\,|\,n;R\,\rangle$ are known, an entire vibrational spectrum may be obtained. For future reference, the above approximation will be designated as the "improved adiabatic" (IA) approximation.

The IA approach differs from the usual method in that the "standard adiabatic" (SA) approximation[9,10] assumes the expansion

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_m \chi_m(\mathbf{R})\phi_m(\mathbf{r};R) \ , \tag{13}$$

where the $\phi_m(\mathbf{r};R)$ are eigenfunctions of the Born-Oppenheimer (BO) Hamiltonian H_e, while the IA method assumes the expansion of Eq. (8) where the $\phi_m(\mathbf{r},\hat{\mathbf{R}};R)$ are eigenfunctions of $H_0(R)$ defined in Eq. (5). One would expect little difference between the results obtained applying the two methods to a $J=0$ state of a *symmetric* system such as H_2^+. However, for a system with *unequal nuclear masses*, such as HD^+, the SA approximation has serious problems with respect to the dissociation energy which are corrected by the IA approach. As discussed in Ref. 1, the $\mathbf{L}_R^2$ operator appearing in the Hamiltonian $H_0(R)$, and the $\partial^2/\partial R^2$ operator appearing in Eq. (12), because they are applied in c.m.n. frame (as opposed to the geometric center of nuclei frame), have the effect of breaking the symmetry. For example, as $R \rightarrow \infty$, the electron in a $1s\sigma$ state goes to a $1s$ state on the heavier nucleus (the deuteron), while the electron in a $2p\sigma$ state goes to a $1s$ state on the lighter nucleus (the proton).

The "best adiabatic" (BA) approach described in Ref. 1 is an effort to go beyond the IA approach just described. It is an attempt at an approximate solution to the BA equations of Pack and Hirschfelder[11] by utilizing the implicit R dependence of an electronic basis situated on the two nuclei. The BA approach leads to physically appealing values of the energy as $R \rightarrow \infty$ [e.g., the $1s\sigma$ curve goes to *exactly* $-\frac{1}{2}m_b m_c/(m_b+m_c)$, where b is the heavier of the two nuclear masses, which for HD^+ becomes $-\frac{1}{2}m_d/(m_d+m_e)$ a.u., the energy for a $1s$-state electron on the deuteron]. However, our calculations indicate that the potential curves using the BA approach are less reliable than the SA or the IA approach for small and intermediate values of internuclear separation. Calculations of the low-lying vibrational levels using the BA curves lead to somewhat poorer values of the energy than do the SA and IA curves when compared to accurate nonadiabatic results.[12,13] Overall, the IA approximation seems to work better than our attempts at a BA approximation, and we will thus concentrate on the IA approach in the rest of this paper. For purposes of calculation, the masses of the nuclei have been taken to be $m_a = m_p = 1836.152 m_e$ and $m_b = m_d = 3670.481 m_e$ and the electron mass $m_c = m_e$ is used to scale the atomic units.

It should be noted that, as $R \rightarrow \infty$, the IA $1s\sigma$ curve, with H' included through first-order perturbation theory, goes *almost* exactly to $-\frac{1}{2}m_b m_c/(m_b+m_c)$. This is a substantial improvement over the SA $1s\sigma$ curve, which asymptotically goes to $-\frac{1}{2}m_c+(m_a+m_b)m_c^2/4m_a m_b$, owing to its failure to break symmetry. The improvement in the IA approach comes about because the $\mathbf{L}_R^2$ operator in $H_0(R)$ causes the zeroth-order IA wave function $|n;R\rangle$ to move to the heavier nucleus as $R \rightarrow \infty$. However, the wave function is slightly distorted from the $1s$ shape due to the type of kinetic energy terms contributed by the $\mathbf{L}_R^2$ operator. The $\partial^2/\partial R^2$ operator in Eq. (12) supplies the additional kinetic energy terms required for spherical symmetry, but it does so only in a perturbative fashion. Hence, the asymptotic limit of the IA $1s\sigma$ curve agrees with the D-atom ground-state energy through first order in the perturbation H'. For the masses used here for HD^+, the D-atom ground-state energy is $-0.499\,863\,815\,2$ a.u., while the SA and IA asymptotic limits are found to be $-0.499\,795\,734\,7$ a.u. and $-0.499\,863\,814\,4$ a.u., respectively. For computational and experimental purposes, it appears that the difference between the D-atom ground-state energy and the IA asymptotic limit can safely be neglected.

As shown in Ref. 1, the $\phi_n(\mathbf{r},\hat{\mathbf{R}};R)$ may be expanded in terms of body-fixed wave functions $\Psi_n^\Lambda(\mathbf{r};R)$ of definite Λ (angular momentum along the internuclear axis) according to

$$\phi_n(\mathbf{r},\hat{\mathbf{R}};R)=\sum_{\Lambda}\tilde{D}^{J}_{\Lambda M}(\phi_R,\theta_R,0)\Psi_n^\Lambda(\mathbf{r};R)\ , \tag{14}$$

where the coefficients are Wigner D functions;[7] J and M label the total angular momentum of the system and its space-frame z component, respectively, and Λ ranges from $-J$ to J. Once the desired J, M, and R have been fixed, the obvious method of determining the eigenfunction Eq. (14) of the Hamiltonian $H_0(R)$ is to expand the $\Psi_n^\Lambda(\mathbf{r};R)$ in terms of any electronic basis (e.g., Slater, Gaussian, or elliptic orbitals), then perform a linear variational calculation to determine the eigenenergies and eigenstates. For the required Hamiltonian matrix elements, note that the electronic operators in Eq. (5) (i.e., H_e and the mass polarization term) act only upon Ψ_n^Λ, without affecting the D functions. The $\mathbf{L}_R^2/(2\mu R^2)$ operator acts upon both the D functions and the Ψ_n^Λ and may easily be evaluated by using the relation[7]

$$\mathbf{L}_R^2=\mathbf{J}^2-2J_z^2+\mathbf{J}_e^2-J_{e-}J_{+}-J_{e+}J_{-}\ , \tag{15}$$

where $\mathbf{J}$ is the total angular momentum and $\mathbf{J}_e$ is the body-fixed electronic angular momentum as measured about the c.m.n.

Using Eq. (15) and the properties of the Wigner D functions,[7] the required Hamiltonian matrix elements may be expressed in terms of body-fixed basis matrix elements. Note that a general basis term in the expansion of $\phi_n(\mathbf{r},\hat{\mathbf{R}};R)$ is given by $\tilde{D}^{J}_{\Lambda_k M}(\phi_R,\theta_R,0)f_k(\mathbf{r};R)$. For convenience, this will be rewritten in Dirac notation as $|JM\Lambda_k\rangle_{\hat{\mathbf{R}}}\,|k;R\rangle_{\mathbf{r}}$. One obtains, as the general matrix element,

$$\begin{aligned}\langle l;R\,|\,\langle JM\Lambda_l\,|\,H_0(R)\,|\,JM\Lambda_k\rangle_{\hat{\mathbf{R}}}\,|\,k;R\rangle_{\mathbf{r}}={}&\delta_{\Lambda_l,\Lambda_k}\left\langle l;R\,\middle|\,\left[-\frac{1}{2(m_a+m_b)}\nabla_r^2+H_e\right]\middle|\,k;R\right\rangle\\&+\frac{1}{2\mu R^2}\big(\delta_{\Lambda_l,\Lambda_k}\{[J(J+1)-2\Lambda_k^2]\langle l;R\,|\,k;R\rangle+\langle l;R\,|\,\mathbf{J}_e^2\,|\,k;R\rangle\}\\&-\delta_{\Lambda_l,\Lambda_k-1}[J(J+1)-\Lambda_k(\Lambda_k+1)]^{1/2}\langle l;R\,|\,J_{e-}\,|\,k;R\rangle\\&-\delta_{\Lambda_l,\Lambda_k+1}[J(J+1)-\Lambda_k(\Lambda_k-1)]^{1/2}\langle l;R\,|\,J_{e+}\,|\,k;R\rangle\big)\ .\end{aligned} \tag{16}$$

Note that the matrix elements are independent of the value of M.

The only J values to be considered in detail in the present work are $J=0$ and $J=1$. Equation (16) becomes somewhat simpler for these two special cases: for $J=0$,

$$\langle l;R\,|\,\langle 000\,|\,H_0(R)\,|\,000\rangle_{\hat{\mathbf{R}}}\,|\,k;R\,\rangle_{\mathbf{r}}=\left\langle l;R\,\middle|\,\left[-\frac{1}{2(m_a+m_b)}\nabla_r^2+H_e+\frac{\mathbf{J}_e^2}{2\mu R^2}\right]\,\middle|\,k;R\right\rangle \tag{17}$$

and, for $J=1$,

$$\begin{aligned}&\langle l;R\,|\,\langle 1M\Lambda_l\,|\,H_0(R)\,|\,1M\Lambda_k\rangle_{\hat{\mathbf{R}}}\,|\,k;R\,\rangle_{\mathbf{r}}\\ &\quad=\delta_{\Lambda_l,\Lambda_k}\left\langle l;R\,\middle|\,\left[-\frac{1}{2(m_a+m_b)}\nabla_r^2+H_e+\frac{\mathbf{J}_e^2}{2\mu R^2}\right]\,\middle|\,k;R\right\rangle\\ &\qquad+\frac{1}{2\mu R^2}[\delta_{\Lambda_l,\Lambda_k}(2-2\Lambda_k^2)\langle l;R\,|\,k;R\,\rangle-\delta_{\Lambda_l,\Lambda_k-1}\sqrt{2}\langle l;R\,|\,J_{e-}\,|\,k;R\,\rangle-\delta_{\Lambda_l,\Lambda_k+1}\sqrt{2}\langle l;R\,|\,J_{e+}\,|\,k;R\,\rangle]\,.\end{aligned} \tag{18}$$

Once these matrix elements have been evaluated for some choice of basis, one performs a matrix diagonalization, as usual, to obtain the eigenfunctions $\phi_n(\mathbf{r},\hat{\mathbf{R}};R)$ and eigenvalues $U_n(R)$.

For $J=0$ states once all matrix elements appearing in Eq. (17) are known, performing an IA calculation requires essentially the same amount of labor as a SA calculation. The only difference between the two calculations is that, in the SA approach, only the $\langle l;R\,|\,H_e\,|\,k;R\,\rangle$ matrix elements are involved in the diagonalization, while the

$$\left\langle l;R\,\middle|\,\left[-\frac{1}{2(m_a+m_b)}\nabla_r^2+\mathbf{J}_e^2/(2\mu R^2)\right]\,\middle|\,k;R\right\rangle$$

contribution is perturbatively added to $U_n(R)$ afterwards. Therefore, for $J=0$, the SA and IA approaches require diagonalization of the same size matrix. It should be noted, however, that the SA correction terms calculated for a single diatomic molecule are proportional to the corrections for any of its isotopes, because the SA zeroth-order eigenfunctions are independent of nuclear mass. Hence the SA correction terms for $H_2{}^+$ may be scaled by the appropriate mass factors to obtain the corrections for HD^+, $D_2{}^+$, $dd\mu$, $dt\mu$, etc. Of course, this is not the case with the IA approximation, because the zeroth-order eigenfunctions are inherently nuclear-mass dependent; a separate calculation must be performed for each isotope.

For $J\neq 0$, Eq. (16) indicates the occurrence of nonzero matrix elements between basis terms for which $\Lambda_k=\Lambda_l\pm 1$, resulting from the presence of the $J_{e\pm}$ operators. These coupling operators, of course, do not appear in the zeroth-order Hamiltonian for the SA approach, which is just H_e. Hence, performing a SA calculation with a basis in which Λ_k ranges over $-J\le\Lambda_k\le J$ is simplified because the Hamiltonian matrix factors into blocks between basis terms for which $\Lambda_k=\Lambda_l$, while in an IA calculation using the same basis, no such simplification occurs. Therefore, for $J\neq 0$, performing an IA calculation requires the diagonalization of larger matrices than performing a SA calculation with the same basis set.

Methods for reducing the size of the required matrices are clearly of importance, and two such techniques have been utilized in the calculations performed here for $J=1$. The first approach is a rigorous method for factoring the matrix obtained from Eq. (18) into two uncoupled blocks, using a unitary transformation. This approach requires that the basis ξ_i be constructed according to the procedure

$$\xi_i=\tilde{D}^{\,1}_{\Lambda_i M}(\phi_R,\theta_R,0)f_i(\mathbf{r};R)\,, \tag{19}$$

where, to satisfy the form of Eq. (14), one demands

$$J_{ez}f_i(\mathbf{r};R)=\Lambda_i f_i(\mathbf{r};R)\,. \tag{20}$$

The ordering is such that

$$\begin{aligned}&\Lambda_i=-1\ \text{ for } i=1,\dots,n_1\,,\\ &\Lambda_i=0\ \text{ for } i=n_1+1,\dots,n_0+n_1\,,\\ &\Lambda_i=1\ \text{ for } i=n_0+n_1+1,\dots,n_0+2n_1\end{aligned}$$

with the f_i satisfying

$$f_{i+n_0+n_1}(r,\theta,\phi;R)=f_i(r,\theta,-\phi;R)\quad\text{for } i=1,\dots,n_1\,. \tag{21}$$

Except for the ordering, the only restriction this prescription imposes on the basis is that the $\Lambda=-1$ and $\Lambda=+1$ states be treated symmetrically, certainly a reasonable requirement. Note that the basis consists of n_0 σ-type terms and n_1 of each of the two orientations of π-type terms. Given this form for the basis, the Hamiltonian matrix is found to have the structure

$$\underline{\underline{H}}=\begin{bmatrix}\underline{\underline{H}}_{11} & \underline{\underline{H}}_{01} & 0\\ \underline{\underline{H}}_{01}^{T} & \underline{\underline{H}}_{00} & \underline{\underline{H}}_{01}^{T}\\ 0 & \underline{\underline{H}}_{01} & \underline{\underline{H}}_{11}\end{bmatrix}, \tag{22}$$

where $\underline{\underline{H}}_{00}$ is an $n_0\times n_0$ matrix, $\underline{\underline{H}}_{01}$ is an $n_1\times n_0$ matrix, and $\underline{\underline{H}}_{11}$ is an $n_1\times n_1$ matrix. Note that all the above matrices are real. Superscript T has been used to denote the transpose. The special form of $\underline{\underline{H}}$ allows the transformation to a block-diagonal form by the unitary transformation

$$\underline{\underline{U}}=\underline{\underline{U}}^{-1}=\begin{bmatrix}\sqrt{1/2}\,\underline{\underline{\mathbb{1}}}_{n_1} & 0 & \sqrt{1/2}\,\underline{\underline{\mathbb{1}}}_{n_1}\\ 0 & \underline{\underline{\mathbb{1}}}_{n_0} & 0\\ \sqrt{1/2}\,\underline{\underline{\mathbb{1}}}_{n_1} & 0 & -\sqrt{1/2}\,\underline{\underline{\mathbb{1}}}_{n_1}\end{bmatrix}, \tag{23}$$

where $\underline{\underline{\mathbb{1}}}_{n_0}$ and $\underline{\underline{\mathbb{1}}}_{n_1}$ are the $n_0\times n_0$ and $n_1\times n_1$ identity matrices, respectively. The transformed Hamiltonian $\underline{\underline{H}}'=\underline{\underline{U}}\,\underline{\underline{H}}\,\underline{\underline{U}}^{-1}$ is

$$\underline{H}'=\begin{bmatrix} \underline{H}_{11} & \sqrt{2}\underline{H}_{01} & 0 \\ \sqrt{2}\underline{H}_{01}^{T} & \underline{H}_{00} & 0 \\ 0 & 0 & \underline{H}_{11} \end{bmatrix} . \tag{24}$$

The new basis set is given by

$$\xi_i'=\frac{1}{\sqrt{2}}(\xi_i+\xi_{i+n_0+n_1}) \quad \text{for } i=1,\ldots,n_1 \tag{25}$$

$$\xi_i'=\xi_i \quad \text{for } i=n_1+1,\ldots,n_0+n_1 \tag{26}$$

$$\xi_i'=\frac{1}{\sqrt{2}}(\xi_{i-n_0-n_1}-\xi_i) \quad \text{for } i=n_0+n_1+1,\ldots,n_0+2n_1 . \tag{27}$$

It is clear that the basis terms in Eq. (25) span the space of states denoted in the BO approximation as the π^+ states (symmetric with respect to reflection through any plane containing the two nuclei). Similarly, the basis terms in Eq. (26) span the space of σ^+ states and the basis terms in Eq. (27) span the space of π^- states (antisymmetric with respect to reflection). Hence, the form of the Hamiltonian matrix in Eq. (24) indicates that the π^+ components of the $\pi^\pm$ doublets interact with the σ^+ states, while the π^- components do not. This interaction gives rise to the small splitting of the $\pi^\pm$ doublet known as Λ doubling. In the usual treatment of Λ doubling,[10,14,15] the splitting is calculated using second-order perturbation theory, while here the eigenfunctions of the zeroth-order Hamiltonian exhibit the splitting. Hence, the transformation to the Hamiltonian matrix of Eq. (24) has not only reduced the size of the secular equation but has also elucidated the phenomenon of Λ doubling. It should be noted that the parity-decoupling procedure described above for the $J=1$ case can be performed for any value of J.[16]

We next examine the second approach to reducing the size of the required Hamiltonian matrix for the $J=1$ case. In this procedure, one continues to use the basis given by Eqs. (25)—(27), with the associated Hamiltonian matrix of Eq. (24). However, one makes the approximation that the off-diagonal blocks in Eq. (24), which couple the π^+ terms with the σ^+ terms, can be neglected. While this approach does not manifest the Λ doubling behavior, it has the advantage that one can construct the $J=1$ σ^+ potential curves by merely adding the centrifugal term $(\mu R^2)^{-1}$ to the $J=0$ σ^+ potential curves, as one would do in the SA approximation. Note that this method is still an improvement over the SA approach for unequal nuclear masses because this procedure leads to correct dissociation, while the SA approach does not.

The two methods described above for factoring the $J=1$ Hamiltonian matrix into blocks represent the two extremes in the precision which may be obtained. The transformation to the basis given by Eqs. (25)—(27) is trivial, yet perfectly rigorous, so any approximation method should start from this point. The second approach of ignoring the coupling terms completely is the least-precise procedure that can be used, and between these two extremes there are other possibilities, such as second-order perturbation theory or variation of basis size (e.g., omitting some of the π^+ basis terms if the σ^+ states are of primary interest). However, the present formulation allows one to obtain a higher degree of precision than the SA approach, if this is desired. Finally, note that while only the $J=0$ and $J=1$ rotational states have been discussed explicitly, it is relatively straightforward to apply these ideas to higher rotational states.

Having obtained the eigenfunction $|n;R\rangle$ and the eigenvalue $U_n(R)$ of the Hamiltonian $H_0(R)$ by the above variational procedure, one gets the IA potential curve by adding the correction term $\langle n;R\,|-(1/2\mu)\partial^2/\partial R^2\,|\,n;R\rangle$ appearing in Eq. (12). In the SA approach this term can be calculated either numerically or analytically. The numerical technique[17,18] requires performing two (or more) calculations of the BO electronic eigenfunction for closely spaced values of the internuclear separation about the R of interest and numerically computing the derivative. The analytical approach, suggested by Kolos and Wolniewicz,[19] relies on the virial theorem[20] for the BO Hamiltonian, given by

$$\frac{dE_{\mathrm{BO}}}{dR}=-(1/R)[(\mathcal{E}_P)_{\mathrm{av}}+2(\mathcal{E}_K)_{\mathrm{av}}] \tag{28}$$

$$=-\frac{1}{R}\left[\langle V\rangle+2\left\langle-\frac{1}{2m_c}\nabla_r^2\right\rangle\right] , \tag{29}$$

where $\mathcal{E}_P$ is the potential energy, $\mathcal{E}_K$ is the kinetic energy, and V is the potential energy operator. Note that the relation remains true whether or not the internuclear repulsion term $1/R$ is included. With the virial theorem, dE_{BO}/dR is obtained in terms of readily available matrix elements computed at one value of R. This information can then be used in a system of inhomogeneous equations (obtained by differentiating the secular equation) and the solution allows the computation of $\langle n;R\,|\,(1/2\mu)\partial^2/\partial R^2\,|\,n;R\rangle$ from matrix elements evaluated at just one value of R.

For the IA approximation, the numerical approach can also be used in the evaluation of the $(1/2\mu)\partial^2/\partial R^2$ matrix elements. The present calculations have been performed in this manner; for the problem considered, a two-point differentiation scheme, with an interval on the order of 10^{-5} a.u., yields sufficient accuracy. It is interesting to note, however, that the virial theorem can be extended to apply to the Hamiltonian $H_0(R)$ of Eq. (5) and one finds that the derivative of $U(R)$ defined in Eq. (7) is given by

$$\frac{dU}{dR}=-\frac{1}{R}\left[\langle V\rangle+2\left\langle-\frac{1}{2m_c}\nabla_r^2-\frac{1}{2(m_a+m_b)}\nabla_r^2+\frac{\mathbf{L}_R^2}{2\mu R^2}\right\rangle\right] . \tag{30}$$

The only difference between the right-hand sides of Eqs. (29) and (30) is the inclusion of the mass polarization and $\mathbf{L}_R^2/(2\mu R^2)$ operators in the kinetic energy term. Since these additional operators do indeed arise from kinetic energy operators, this difference is to be expected. Numerical computations performed here have confirmed Eq. (30) to the accuracy of the calculation and this relation may serve as a useful computational check. The existence of a virial theorem for the IA approximation may also allow the computation of the $\partial^2/\partial R^2$ matrix elements analytically, from matrix elements evaluated at a single value of R. Investigation of this possibility has been left for future work.

III. COMPUTATIONAL METHOD

The wave functions obtained in this paper have been constructed using a two-centered Slater orbital basis of the form

$$f_i(\mathbf{r};R)=r_{c_i}^{n_i-1}e^{-\alpha_i r_{c_i}}Y_{l_i m_i}(\theta_{c_i},\phi_{c_i}) , \qquad (31)$$

where the c_i denote the center (a or b) on which the orbital has been situated, the remainder of the notation being standard. Previous calculations[12,13,17,21–26] of energies and adiabatic corrections of $H_2{}^+$ and HD^+ have been performed using a basis consisting of functions of elliptic coordinates, because this type of basis is most appropriate for the solution of the BO eigenfunctions. However, as discussed in Ref. 1, matrix elements of the $\mathbf{L}_R^2$ and $\partial^2/\partial R^2$ operators, applied in the c.m.n. frame, are especially easy using a two-centered basis, and not as straightforward if an elliptic basis is used. In addition, a Slater basis having correct behavior for large R (e.g., one containing basis terms that are adequate to describe the $1s\sigma$ state going to a $1s$ state on a deuteron) is simple to construct, while this may prove difficult with an elliptic basis, depending on how flexible the elliptic basis functions have been chosen to be.

The simplest wave function examined here is the $J=0$ $1s\sigma$ state. The basis for this wave function consists of 34 Slater orbitals on each of the two centers. The basis set contains terms with n_i ranging from 1 to 9 and l_i ranging from 0 to 5, with many of the higher n_i+l_i values within this range excluded. The value of m_i is required to be zero as is clear from Eq. (14) for a $J=0$ $1s\sigma$ state. Note that the Slater basis tends to become the appropriate basis at the united-atom limit and for large values of R. However, for the small to intermediate values of internuclear separation, the Slater basis is less appropriate and achieving high accuracy requires including a large number of powers of r and multipoles in the basis. To make better use of the basis in this difficult region, an optimization of the nonlinear parameters α_i was performed for a subset of the basis at $R=1.0$ a.u. For a basis this large, adding higher powers of r and higher multipoles proved to be more effective than adding terms redundant in powers of r and multipoles with different exponents. Table I contains the basis terms used to calculate the $J=0$ $1s\sigma$ state, along with the values of the nonlinear parameters α_i obtained from the optimization at $R=1.0a_0$.

For the $J=1$ σ and π states, one includes not only the previous set of Slater orbitals used for the $J=0$ σ states but also a basis set which is adequate to span the electronic π states. The π-state basis set has been obtained by taking the previously described Slater basis for σ states, deleting the $l_i=0$ terms and changing all m_i from 0 to 1. The resulting basis consists of 23 orbitals on each center. Note that the Hamiltonian matrix elements involving the $m_i=-1$ terms are the same as those for the $m_i=1$ terms, as seen from Eq. (22), so the $m_i=-1$ terms need not be included in the basis.

Given the above basis, it is straightforward to evaluate all matrix elements of the $J=0$ and $J=1$ states using Eqs. (17) and (18) and standard Slater-orbital matrix-element routines. All matrix-element evaluations have been performed to double precision on a Cray 1 (28 digits). For small enough R, the above basis will, of course, lead to numerical linear-dependence difficulties. In order to eliminate this problem, a transformation to a new basis is performed by diagonalizing the overlap matrix and discarding all eigenvectors associated with eigenvalues less than some specified (positive) threshold value. Although the overlap matrix is positive definite by construction, numerical inaccuracies can lead to negative eigenvalues. The eigenvectors associated with negative (or extremely small

TABLE I. Slater-orbital basis (situated on each of the two centers) used for $J=0$ σ-state calculations.

i	n_i	l_i	m_i	α_i
1	1	0	0	1.030 00
2	1	0	0	0.500 00
3	2	0	0	0.984 32
4	2	0	0	0.500 00
5	2	1	0	1.129 45
6	2	1	0	0.500 00
7	3	0	0	1.948 31
8	3	1	0	1.006 57
9	3	2	0	2.861 05
10	4	0	0	1.011 01
11	4	1	0	1.011 01
12	4	2	0	1.011 01
13	4	3	0	1.011 01
14	5	0	0	1.032 05
15	5	1	0	1.032 05
16	5	2	0	1.032 05
17	5	3	0	1.032 05
18	5	4	0	1.032 05
19	6	0	0	1.198 84
20	6	1	0	1.198 84
21	6	2	0	1.198 84
22	6	3	0	1.198 84
23	6	4	0	1.000 00
24	6	5	0	1.000 00
25	7	0	0	1.322 91
26	7	1	0	1.322 91
27	7	2	0	1.322 91
28	7	3	0	1.322 91
29	8	0	0	1.322 91
30	8	1	0	1.322 91
31	8	2	0	1.322 91
32	9	0	0	1.322 91
33	9	1	0	1.322 91
34	9	2	0	1.322 91

positive) eigenvalues of the overlap matrix are, of course, the least numerically reliable basis terms, so this procedure is an effective approach for eliminating linear dependence problems.

Before utilizing the basis to calculate the IA potential curves, the basis was tested by using it to perform SA calculations and comparing the results with previous accurate calculations[17,21–24] (which used functions of elliptic coordinates for the basis). Note that in order to observe the quantitative differences between the SA, IA, and nonadiabatic (i.e., exact) approaches to the solution of the HD^+ energies, it is desirable to be able to calculate potential curves to within an accuracy of 1×10^{-7} a.u. The BO potential curve was calculated using the 68-term Slater-orbital basis and found to be not quite as accurate as desired at small and intermediate internuclear separations, although the accuracy becomes progressively better as R is increased. As an indication of how deficient the basis is, the error in the potential curve at some selected values of internuclear separation was found to be 1.0×10^{-6} a.u. at $1.0a_0$, 3.9×10^{-7} a.u. at $2.0a_0$, 1.6×10^{-7} a.u. at $5.0a_0$, and 9.2×10^{-9} a.u. at $10.0a_0$. All these errors are due to the computed energy being too high, as expected from the variational nature of the calculation. Although this accuracy appears to be inadequate for R less than $5.0a_0$, the accuracy problem can, in practice, be sidestepped, as will be discussed below. Next, the perturbative corrections which must be added to the BO curve (in order to obtain the SA curve) were evaluated using the BO electronic eigenfunctions constructed from the 68-term Slater basis. These correction terms were found to be in excellent agreement with previous high accuracy results,[17,24] with errors less than 1×10^{-8} a.u. for all internuclear separations greater than $R=0.7a_0$. For the internuclear separations equal to and smaller than $0.7a_0$ this accuracy was achieved after reoptimizing some of the exponents at each value of R examined.

Despite the slight deficiency in the Slater basis, one can nevertheless use this basis to compute the IA potential curves to the needed accuracy if accurate BO curves can be obtained from some other source. The calculations indicated that the BO energy was somewhat inadequate, while the perturbative correction terms were more than accurate enough. Note that the primary difference between the SA and IA approaches is that the IA approach includes the mass polarization and $\mathbf{L}_R^2$ operators in the zeroth-order Hamiltonian exactly, while the SA approach treats them only to first-order perturbation theory. However, one would expect first-order perturbation theory to work extremely well, unless the $1s\sigma_g$ potential curve is in a region of R where it is close to another potential curve corresponding to a state with which the $1s\sigma_g$ state has nonzero coupling. In other words, the IA approach should yield substantially different results from the SA approach only when BO potential curves become degenerate or nearly degenerate. Examining the $1s\sigma_g$ potential curve and the $2p\sigma_u$ curve, whose corresponding states become coupled when one takes into account the unequal masses of the nuclei, one finds that the curves become appreciably close only beyond $5a_0$. Therefore, within $5a_0$, the somewhat inaccurate value of the IA potential curve can be improved by subtracting out the $1s\sigma_g$ BO curve obtained from the Slater basis, then adding the correct BO curve. Beyond $5a_0$, recall that the accuracy already appeared to be almost adequate; however, even this region can be corrected by the subtraction-addition procedure if both the $1s\sigma_g$ and $2p\sigma_u$ BO curves are in error by essentially the same amount, as is found to be the case in the present calculation.

The above procedure has been used to calculate the IA $1s\sigma$ potential curve and appears to yield potential curves which are accurate to within 1×10^{-8} a.u. (which is about an order of magnitude more accurate than is really necessary to adequately compare the various adiabatic approaches with the exact nonadiabatic results). In addition, the shifts due to the σ^+-π^+ coupling for the $J=1$ $1s\sigma$ state and the $J=1$ $2p\pi^\pm$ splitting have been calculated, in order to indicate the strength of the coupling. Since these values are shifts, they are essentially perturbative corrections and should be valid to the number of digits presented. The Slater basis for the π states was tested by utilizing the basis to calculate the $2p\pi$ BO curve and associated SA corrections, then comparing the results with previous accurate calculations.[23,25] The errors found were only slightly worse than those found for the $1s\sigma$ calculations. The basis was also used to compute the $\langle 2p\pi_u \,|\, iL_y \,|\, 2p\sigma_u \rangle$ matrix element, which appears to be in good agreement with previous calculations;[27,28] however, accurate comparison is difficult because these earlier calculations are displayed only in graphical form.

The computational approach taken here appears to be an effective procedure for obtaining the potential curves to the necessary accuracy, though perhaps not as elegant as one might wish. Some of the basis problems experienced here for small and intermediate values of R could be eliminated if an elliptic basis was used instead. However, the necessary matrix elements of the $\partial^2/\partial R^2$ and $\mathbf{L}_R^2$ operators, as applied in the c.m.n. frame, are nonstandard for the case of unequal nuclear masses.

The present calculations indicate little difference between results obtained using the IA and SA approaches for small and intermediate R. Hence, for other states of HD^+ (and, indeed, other systems) it might be adequate to utilize previously calculated SA results for the smaller R region, then perform the IA calculation, with a two-centered basis (Slater or Gaussian orbitals), for larger R.

IV. POTENTIAL-CURVE RESULTS

Results for the $J=0$ $1s\sigma$ state are presented in Table II. The table includes not only the IA potential curve but also the BO and SA potential curves, for comparison. The BO potential curve has been computed using the algorithm described by Wind[21] and is in good agreement with previous high-accuracy calculations[17,21–23] at those values of R for which comparison is possible. Also note that both the SA and IA potential curves have been calculated using precisely the same matrix elements; the difference between the computations arises from how the matrix elements are partitioned between the zeroth-order Hamiltonian (i.e., involved in the diagonalization) and the perturbation term. The expression for the BO energy is

TABLE II. Electronic potential curves obtained using the Born-Oppenheimer, standard adiabatic, and improved adiabatic formulations for the $J=0$ $1s\sigma$ state of HD^+. To obtain total potential energy, add $1/R$.

R (a_0)	$W_{1s\sigma}^{BO}$ (a.u.)	$W_{1s\sigma}^{SA}$ (a.u.)	$W_{1s\sigma}^{IA}$ (a.u.)
0.00	−2.000 000 00	−1.999 591 47	−1.999 591 55
0.10	−1.978 242 06	−1.977 830 60	−1.977 830 79
0.20	−1.928 620 30	−1.928 213 25	−1.928 213 40
0.30	−1.866 704 08	−1.866 310 24	−1.866 310 38
0.40	−1.800 754 06	−1.800 378 14	−1.800 378 26
0.50	−1.734 988 00	−1.734 631 57	−1.734 631 69
0.60	−1.671 484 71	−1.671 147 58	−1.671 147 69
0.70	−1.611 196 27	−1.610 877 38	−1.610 877 49
0.80	−1.554 480 09	−1.554 178 02	−1.554 178 12
0.90	−1.501 381 60	−1.501 094 82	−1.501 094 91
1.00	−1.451 786 31	−1.451 513 32	−1.451 513 41
1.10	−1.405 502 78	−1.405 242 16	−1.405 242 25
1.20	−1.362 307 86	−1.362 058 34	−1.362 058 43
1.30	−1.321 971 39	−1.321 731 79	−1.321 731 88
1.40	−1.284 269 24	−1.284 038 51	−1.284 038 59
1.50	−1.248 989 87	−1.248 767 06	−1.248 767 15
1.60	−1.215 937 22	−1.215 721 48	−1.215 721 56
1.70	−1.184 931 56	−1.184 722 13	−1.184 722 21
1.80	−1.155 809 19	−1.155 605 37	−1.155 605 46
1.90	−1.128 421 57	−1.128 222 75	−1.128 222 83
2.00	−1.102 634 21	−1.102 439 83	−1.102 439 91
2.10	−1.078 325 42	−1.078 134 96	−1.078 135 04
2.20	−1.055 385 08	−1.055 198 08	−1.055 198 17
2.30	−1.033 713 49	−1.033 529 54	−1.033 529 63
2.40	−1.013 220 31	−1.013 039 00	−1.013 039 08
2.50	−0.993 823 51	−0.993 644 50	−0.993 644 59
2.60	−0.975 448 58	−0.975 271 55	−0.975 271 64
2.70	−0.958 027 66	−0.957 852 30	−0.957 852 39
2.80	−0.941 498 86	−0.941 324 90	−0.941 324 99
2.90	−0.925 805 63	−0.925 632 82	−0.925 632 91
3.00	−0.910 896 20	−0.910 724 30	−0.910 724 40
3.20	−0.883 242 56	−0.883 071 86	−0.883 071 96
3.40	−0.858 201 68	−0.858 031 45	−0.858 031 55
3.60	−0.835 487 07	−0.835 316 69	−0.835 316 81
3.80	−0.814 852 59	−0.814 681 54	−0.814 681 66
4.00	−0.796 084 88	−0.795 912 76	−0.795 912 89
4.20	−0.778 997 44	−0.778 823 92	−0.778 824 06
4.40	−0.763 425 87	−0.763 250 68	−0.763 250 83
4.60	−0.749 224 09	−0.749 047 09	−0.749 047 24
4.80	−0.736 261 45	−0.736 082 50	−0.736 082 67
5.00	−0.724 420 30	−0.724 239 37	−0.724 239 55
5.25	−0.711 034 84	−0.710 851 43	−0.710 851 64
5.50	−0.699 049 69	−0.698 863 88	−0.698 864 11
5.75	−0.688 299 11	−0.688 111 04	−0.688 111 29
6.00	−0.678 635 72	−0.678 445 53	−0.678 445 82
6.25	−0.669 928 55	−0.669 736 45	−0.669 736 78
6.50	−0.662 061 62	−0.661 867 81	−0.661 868 19
6.75	−0.654 932 51	−0.654 737 17	−0.654 737 62
7.00	−0.648 451 15	−0.648 254 49	−0.648 255 02
7.25	−0.642 538 68	−0.642 340 87	−0.642 341 50
7.50	−0.637 126 30	−0.636 927 49	−0.636 928 24
7.75	−0.632 154 17	−0.631 954 50	−0.631 955 41
8.00	−0.627 570 39	−0.627 370 01	−0.627 371 10
8.25	−0.623 330 03	−0.623 129 03	−0.623 130 35
8.50	−0.619 394 25	−0.619 192 73	−0.619 194 32
8.75	−0.615 729 44	−0.615 527 47	−0.615 529 41
9.00	−0.612 306 56	−0.612 104 23	−0.612 106 57
9.25	−0.609 100 47	−0.608 897 83	−0.608 900 65

TABLE II. (*Continued.*)

R (a_0)	$W^{\mathrm{BO}}_{1s\sigma}$ (a.u.)	$W^{\mathrm{SA}}_{1s\sigma}$ (a.u.)	$W^{\mathrm{IA}}_{1s\sigma}$ (a.u.)
9.50	−0.606 089 36	−0.605 886 47	−0.605 889 84
9.75	−0.603 254 29	−0.603 051 17	−0.603 055 17
10.00	−0.600 578 73	−0.600 375 44	−0.600 380 13
10.25	−0.598 048 27	−0.597 844 81	−0.597 850 22
10.50	−0.595 650 25	−0.595 446 67	−0.595 452 76
10.75	−0.593 373 54	−0.593 169 86	−0.593 176 51
11.00	−0.591 208 32	−0.591 004 55	−0.591 011 59
11.25	−0.589 145 87	−0.588 942 03	−0.588 949 25
11.50	−0.587 178 44	−0.586 974 53	−0.586 981 93
11.75	−0.585 299 10	−0.585 095 14	−0.585 103 21
12.00	−0.583 501 64	−0.583 297 64	−0.583 307 67
12.25	−0.581 780 48	−0.581 576 44	−0.581 590 41
12.50	−0.580 130 56	−0.579 926 49	−0.579 946 51
12.75	−0.578 547 31	−0.578 343 22	−0.578 370 71
13.00	−0.577 026 57	−0.576 822 46	−0.576 857 71
13.25	−0.575 564 56	−0.575 360 43	−0.575 402 79
13.50	−0.574 157 79	−0.573 953 64	−0.574 001 97
13.75	−0.572 803 09	−0.572 598 93	−0.572 651 98
14.00	−0.571 497 52	−0.571 293 35	−0.571 350 02
14.25	−0.570 238 40	−0.570 034 22	−0.570 093 62
14.50	−0.569 023 21	−0.568 819 03	−0.568 880 49
14.75	−0.567 849 66	−0.567 645 47	−0.567 708 47
15.00	−0.566 715 61	−0.566 511 40	−0.566 575 57
15.50	−0.564 558 12	−0.564 353 91	−0.564 419 63
16.00	−0.562 536 38	−0.562 332 16	−0.562 398 80
16.50	−0.560 637 83	−0.560 433 60	−0.560 500 80
17.00	−0.558 851 47	−0.558 647 23	−0.558 714 76
17.50	−0.557 167 57	−0.556 963 33	−0.557 031 07
18.00	−0.555 577 52	−0.555 373 28	−0.555 441 14
18.50	−0.554 073 66	−0.553 869 42	−0.553 937 36
19.00	−0.552 649 15	−0.552 444 91	−0.552 512 90
19.50	−0.551 297 86	−0.551 093 61	−0.551 161 63
20.00	−0.550 014 26	−0.549 810 01	−0.549 878 05
20.50	−0.548 793 39	−0.548 589 14	−0.548 657 19
21.00	−0.547 630 75	−0.547 426 50	−0.547 494 56
21.50	−0.546 522 27	−0.546 318 02	−0.546 386 09
22.00	−0.545 464 25	−0.545 259 99	−0.545 328 06
22.50	−0.544 453 31	−0.544 249 05	−0.544 317 12
23.00	−0.543 486 37	−0.543 282 12	−0.543 350 19
23.50	−0.542 560 63	−0.542 356 37	−0.542 424 45
24.00	−0.541 673 50	−0.541 469 24	−0.541 537 32
24.50	−0.540 822 62	−0.540 618 36	−0.540 686 44
25.00	−0.540 005 80	−0.539 801 54	−0.539 869 62
∞	−0.500 000 00	−0.499 795 73	−0.499 863 81

$$W^{\mathrm{BO}}_{1s\sigma}(R)=\left\langle 1s\sigma_g \left| H_e-\frac{1}{R} \right| 1s\sigma_g \right\rangle , \tag{32}$$

where H_e is the BO Hamiltonian and $|\,1s\sigma_g\rangle$ is the BO eigenstate. The expression for the SA energy is

$$W^{\mathrm{SA}}_{1s\sigma}(J=0;\ R)=\left\langle 000 \left| \left\langle 1s\sigma_g \left| \left[H_e-\frac{1}{R}+H'_{\mathrm{SA}} \right] \right.\right.\right.\right.$$
$$\left.\left.\left.\left.\times \right| 1s\sigma_g \right\rangle_{r} \right| 000 \right\rangle_{\hat{\mathbf{R}}} , \tag{33}$$

where

$$H'_{\mathrm{SA}}=-\frac{1}{2(m_a+m_b)}\nabla_r^2-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}+\frac{\mathbf{L}_R^2}{2\mu R^2} . \tag{34}$$

The expression for the IA energy is

$$W^{\mathrm{IA}}_{1s\sigma}(J=0;R)=\left\langle 1s\sigma,J=0 \left| \left[H_0-\frac{1}{R}-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} \right] \right.\right.$$
$$\left.\left.\times \right| 1s\sigma,J=0 \right\rangle , \tag{35}$$

where H_0 is defined in Eq. (5) and $|\,1s\sigma,J=0\rangle$ is the electronic-nuclear orientation eigenstate for this zeroth-order Hamiltonian. The internuclear repulsion term $1/R$ has not been included in the definition of the W's, in order to make the results better behaved (and monotonically decreasing) for purposes of both interpolation and discussion of the small-R behavior of W. The values given have been found to be sufficiently closely spaced in R such that cubic-spline interpolation is capable of yielding additional points which may be needed (e.g., for vibrational calculations) to the necessary accuracy. These values have been used for the calculations of the vibrational levels presented in Sec. V. Including additional calculated points between those listed in Table II failed to change the vibrational levels (to the accuracy considered in this work). The values should be adequate for other possible applications, such as dynamics or multiphoton processes for HD^+. Energies are all given in Hartree atomic units and are believed to be accurate to within ± 1 in the last digit, i.e., to $\pm 1.0\times 10^{-8}$ a.u.

The results listed in Table II indicate that the $J=0$ $1s\sigma$ IA potential curve lies lower than the $J=0$ $1s\sigma_g$ SA potential curve for all internuclear separations. Between $R=0$ and $R=5.0a_0$ the SA and IA curves differ by less than 2×10^{-7} a.u. Note that the $1s\sigma_g$ and $2p\sigma_u$ BO curves lie within 4×10^{-3} a.u. of each other at $8.0a_0$ and asymptotically approach one another as R goes to infinity, so one expects a significant difference between the SA and IA curves for this region of R. Indeed, from Table II one finds that beyond $8.0a_0$ the IA and SA curves begin to separate significantly, reaching a difference of 6.417×10^{-5} a.u. by $15.0a_0$. At $25.0a_0$ the difference has reached 6.808×10^{-5} a.u., which, to the accuracy considered, is the asymptotic value of the difference. Beyond $25.0a_0$, the SA and IA potential curves may be obtained by adding 2.0427×10^{-4} a.u. and 1.3619×10^{-4} a.u., respectively, to the BO electronic potential curve, which will yield results accurate to within 1×10^{-8} a.u. The BO electronic potential curve may be obtained to the necessary accuracy beyond $25.0a_0$ by the asymptotic expansion[29]

$$W^{\mathrm{BO}}_{1s\sigma}(R)\cong -\tfrac{1}{2}-R^{-1}-\tfrac{9}{4}R^{-4}-\tfrac{15}{2}R^{-6}-\tfrac{213}{4}R^{-7}\ \text{a.u.} \tag{36}$$

The united-atom limit of the SA potential curve is of interest and previous discussions of the SA approximation for one-electron diatomics[10,17,24] have not indicated that this limit can, in fact, be obtained analytically. It is convenient to introduce the elliptical coordinates $\lambda=(r_a+r_b)/R$ and $\mu=(r_a-r_b)/R$, where r_a and r_b are the separations of particle c from particles a and b, respectively. Evaluating the necessary matrix elements, one finds that the function $\exp(-m_c R\lambda)$, after normalization, forms a sufficiently accurate small-R approximation of the BO eigenfunction $|1s\sigma_g\rangle$ to yield the correct expansion of the BO energy[30–32] through order R^3, i.e.,

$$W^{\mathrm{BO}}(R)=-2+\tfrac{8}{3}R^2-\tfrac{16}{3}R^3+\cdots\ \text{a.u.} \tag{37}$$

Hence, the function should be adequate to evaluate the SA correction terms in the limit as $R\rightarrow 0$. After performing the necessary integrals, one finds

$$\lim_{R\rightarrow 0}\langle 1s\sigma_g\,|\,H'_{\mathrm{SA}}\,|\,1s\sigma_g\rangle=\frac{(m_a+m_b)m_c^2}{2m_am_b}\ . \tag{38}$$

Therefore, at the united-atom limit the SA potential curve for $1s\sigma$ goes to

$$W^{\mathrm{SA}}_{1s\sigma}(J=0;R\rightarrow 0)=-2m_c+\frac{(m_a+m_b)m_c^2}{2m_am_b} \tag{39}$$

$$=-1.999\,591\,47\ \text{a.u.} \tag{40}$$

for HD^+.

The united-atom limit of the IA potential curve is also of interest and can to a certain extent to be treated analytically. Examining the equal nuclear mass case $m_a=m_b$, it appears that the function $\exp\{-[2m_am_c/(2m_a+m_c)]R\lambda\}$ should serve adequately for small R as the ground-state eigenfunction of $H_0(R)$ defined in Eq. (5). Using this function to evaluate the required matrix elements, one finds that at the united-atom limit, the IA potential curve assumes the value

$$W^{\mathrm{IA}}_{1s\sigma}(J=0;R\rightarrow 0)=-2m_c+\frac{2m_c^2}{2m_a+m_c} \tag{41}$$

for equal nuclear masses. The unequal mass case presents additional analytical difficulties and it appears to be impossible to obtain the united-atom limit in closed form. However, an approximate solution can be obtained, which yields a result where the reduced nuclear mass of Eq. (41), $m_a^2/(m_a+m_a)$ $(=\frac{1}{2}m_a)$, has been replaced by the reduced nuclear mass $m_am_b/(m_a+m_b)$; i.e., for unequal nuclear masses,

$$W^{\mathrm{IA}}_{1s\sigma}(J=0;R\rightarrow 0)\cong -2m_c+\frac{2(m_a+m_b)m_c^2}{4m_am_b+(m_a+m_b)m_c} \tag{42}$$

$$=-1.999\,591\,55\ \text{a.u.} \tag{43}$$

for HD^+. The result of Eq. (43) is in agreement with the variational calculations performed here to the accuracy reported, so apparently the approximation is quite good.

Table III contains potential-curve shifts resulting from the σ^+-π^+ coupling that are pertinent to the calculation of the $J=1$ $1s\sigma$ and $2p\pi$ curves. Values have been computed not only for HD^+ but also for $H_2{}^+$, since these coupling effects are of interest for all systems, whether the nuclear masses are equal or unequal. The shifts listed in Table III are merely the difference in energies obtained by retaining, then omitting the $\underline{H}_{01}$ coupling terms in Eq. (22). Since the $2p\pi^-$ state is not affected by the coupling, the $2p\pi$ shift in Table III is the difference between the $2p\pi^+$ and $2p\pi^-$ potential curves, responsible for the Λ doubling discussed earlier. Values presented in Table III are not adequately dense in R to allow interpolation but are given only to indicate the strength of the coupling as a function of R. A more thorough investigation of the $J=1$ states has been left for future work.

From Table III it is seen that the $2p\pi$ shifts are similar

TABLE III. Energy shifts due to $J_{e\pm}$ coupling for $J=1$ states (in hartree a.u.).

R	$1s\sigma$	$2p\pi$
	HD^+	
0.5	-6.93×10^{-6}	$+2.0986\times10^{-3}$
1.0	-1.05×10^{-7}	$+1.4933\times10^{-5}$
1.5	-1.5×10^{-8}	$+1.2399\times10^{-6}$
2.0	-1.1×10^{-8}	$+2.114\times10^{-7}$
2.5	-8.7×10^{-9}	$+5.09\times10^{-8}$
3.0	-7.3×10^{-9}	$+1.45\times10^{-8}$
3.5	-6.5×10^{-9}	$+4.3\times10^{-9}$
4.0	-5.8×10^{-9}	$+9.0\times10^{-10}$
	${H_2}^+$	
0.5	-1.586×10^{-5}	$+4.2325\times10^{-3}$
1.0	-1.98×10^{-7}	$+2.7218\times10^{-5}$
1.5	-1.3×10^{-8}	$+2.2170\times10^{-6}$
2.0	-1.1×10^{-8}	$+3.767\times10^{-7}$
2.5	-1.0×10^{-9}	$+9.06\times10^{-8}$
3.0	-9.4×10^{-9}	$+2.57\times10^{-8}$
3.5	-8.8×10^{-9}	$+7.5\times10^{-9}$
4.0	-8.4×10^{-9}	$+1.6\times10^{-9}$

for HD^+ and ${H_2}^+$, the ${H_2}^+$ shifts being a factor of about 1.8 larger than the HD^+ shifts for most values of R, due to reduced mass effects. Note that the primary contribution to the $2p\pi$ shift comes from $2p\sigma$-$2p\pi$ coupling, which acts essentially the same way for both HD^+ and ${H_2}^+$. On the other hand, the ratio of the $1s\sigma$ shifts for ${H_2}^+$ and HD^+ varies from about 1.0 to 2.3. The difference is apparently due to the fact that for HD^+ the $1s\sigma$ state can couple to the $2p\pi$ state, since neither state is of strict g or u symmetry, while for ${H_2}^+$, exact g and u symmetry applies, and the closest state with which the $1s\sigma_g$ state can couple is the $3d\pi_g$ state.

Although the shifts listed in Table III become significant for smaller R, they should not have any substantial effect on the bound vibrational state energies of the $J=1$ $1s\sigma$ and $2p\pi$ curves. From BO potential curves one finds that the $1s\sigma$ curve attains its minimum at approximately $R=2.0a_0$ and the region of R less than $1.0a_0$ is classically forbidden for all bound vibrational states. From Table III note that, over the classically allowed region of R, the $1s\sigma$ shift due to the σ^+-π^+ coupling is less than 2×10^{-7} a.u., which for most purposes can be neglected. For the $2p\pi$ state, one finds that the BO curve attains its minimum at approximately $R=8.0a_0$ and the region of R less than $4.0a_0$ is classically forbidden for bound states. Table III has not been extended beyond $4.0a_0$ into the classically allowed region because of the smallness of the $2p\pi$ shift here (less than 2×10^{-10} a.u.); the Λ-doubling effect would appear to be too small for experimental observation, for this particular state. Hence, to a very good degree of approximation, the shifts for the two states can be neglected entirely, which simplifies the treatment required. It should be noted that Λ doubling grows with increasing J, so for high enough J the splitting will become too important to neglect.

The effect of σ^+-π^+ coupling can lead to substantial differences between the SA and IA potential curves for small R. As discussed above, these differences do not appear to cause significant changes in the bound vibrational energies obtained for the $J=1$ $1s\sigma$ and $2p\pi$ states. However, the behavior in this region may be of importance for some dynamics problems, so the small-R behavior of the low-lying curves is of interest.

For ${H_2}^+$, the most interesting difference in the behavior of the low-lying potential curves involves the $2p\sigma^+$ and $2p\pi^+$ curves. In the BO approximation, both these curves have the limit -0.5 a.u. as $R\rightarrow0$, not including the nuclear repulsive energy. Note that the following SA and IA results were obtained in a manner similar to Eqs. (38)–(43) by using the small-R approximations

$$|2p\sigma_u\rangle \cong R\mu\lambda\exp(-m_cR\lambda/2)$$

and

$$|2p\pi_u\rangle \cong R[(\lambda^2-1)(1-\mu^2)]^{1/2} \times\exp(-m_cR\lambda/2)\exp(\pm i\phi)\ ,$$

which yield the correct expansions of their respective BO energies,[30] through order R^3. The IA results were obtained by replacing m_c in the above expressions by $2m_am_c/(2m_a+m_c)$ to obtain approximate IA eigenfunctions for the equal-nuclear-mass case which are valid for small R. These results for the equal-nuclear-mass case can then be used to carry over to the unequal-mass case by adjusting the nuclear reduced mass as was done to obtain Eq. (42). The analytical expressions obtained below are in substantial agreement with results from the variational calculations performed in this work. In the SA approximation, adding the adiabatic corrections and the centrifugal term to the BO value leads to the limiting behavior

$$W_{2p\sigma^+}^{\mathrm{SA}}(J=1;R\rightarrow0)\rightarrow\frac{2}{\mu R^2}\ \text{a.u.} \tag{44}$$

for the $2p\sigma^+$ state and

$$W_{2p\pi}^{\mathrm{SA}}(J=1;R\rightarrow0)\rightarrow\frac{1}{\mu R^2}\ \text{a.u.} \tag{45}$$

for the $2p\pi$ states. In these expressions $W_n^{\mathrm{SA}}(J=1;R)$ is the obvious $J=1$ analogue of Eq. (33) given by

$$W_n^{\mathrm{SA}}(J=1;R) =\left\langle 1M\Lambda_n \left| \left\langle n \left| \left[H_e-\frac{1}{R}+H'_{\mathrm{SA}} \right] \right| n \right\rangle_{\hat{\mathbf{r}}} \right| 1M\Lambda_n \right\rangle_{\hat{\mathbf{R}}}\ , \tag{46}$$

where Λ_n is the component of the angular momentum along the internuclear axis of the BO state $|n\rangle$. However, in the IA approximation, the $2p\sigma^+$ and $2p\pi^+$ terms become coupled and analytical arguments (confirmed by numerical calculations) can be used to show that

$$W_{2p\sigma^+}^{\mathrm{IA}}(J=1;R\rightarrow0)\cong-\frac{2m_am_bm_c}{4m_am_b+(m_a+m_b)m_c} \tag{47}$$

for the $2p\sigma^+$ state, where $W_n^{\mathrm{IA}}(J=1;R)$ is the obvious $J=1$ analogue of Eq. (34). As with Eq. (42), this equation is exact for the case of equal nuclear masses, but is only approximate for unequal masses. In addition, an avoided crossing of the $1s\sigma^+$ curve with the $2p\sigma^+$ curve (which occurs for HD^+ but not for $H_2{}^+$, because of symmetry breaking) complicates the identification of Eq. (47) as the limit of the $2p\sigma^+$ curve; for the unequal-mass case, Eq. (47), in fact, becomes the limit of the $1s\sigma^+$ curve. For simplicity let us just consider $H_2{}^+$. If the $2p\sigma^+$-$2p\pi^+$ interaction is dominant, one finds for the $2p\pi^+$ curve that

$$W^{\mathrm{IA}}_{2p\pi^+}(J=1;R\to 0)\to\frac{3}{\mu R^2}\ \text{a.u.}\ , \tag{48}$$

although this behavior eventually breaks down because of an avoided crossing with the $3p\sigma^+$ curve. Since the $2p\pi^-$ state remains uncoupled, it behaves according to $(\mu R^2)^{-1}$, as before. The main point of interest, however, is that in the IA approximation the $2p\sigma^+$ and $2p\pi^+$ curves interact to yield a curve which goes to the united-atom $2p$-state energy of a $Z=2$ one-electron "atom" with nuclear mass $4m_a m_b/(m_a+m_b)$ (exactly for $m_a=m_b$, approximately for $m_a\neq m_b$—with the above caveat that for unequal nuclear masses the $1s\sigma^+$ curve complicates the identifications), as opposed to the characteristic $(\mu R^2)^{-1}$ behavior one obtains from the SA approximation.

The $J=1$ $1s\sigma^+$ curve does not become degenerate with any corresponding π^+ curve in the BO approximation as $R\to 0$. Hence, the SA and IA approximations for this curve lead to the same small-R behavior of

$$W^{\mathrm{SA}}_{1s\sigma}(J=1;R\to 0)=W^{\mathrm{IA}}_{1s\sigma}(J=1;R\to 0)\to\frac{1}{\mu R^2}\ \text{a.u.} \tag{49}$$

Note that this curve does not interact with the $2p\sigma^+$ state of $H_2{}^+$ since $1s\sigma$ is of g symmetry and $2p\sigma^+$ is of u symmetry. However, for HD^+, the symmetry is slightly broken, leading to a very sharp avoided crossing of the $1s\sigma^+$ curve with the $2p\sigma^+$ curve.

Therefore, if the IA approach is used for dynamics, care must be taken concerning the small-R behavior, which is considerably different from that obtained using the SA approach. Some features of the IA approach may be advantageous, while others, such as sharp avoided crossings may lead to numerical difficulties in the dynamical calculations.

V. VIBRATIONAL SPECTRUM FOR THE $J=0$ $1s\sigma$ ROTATIONAL-ELECTRONIC STATE

Using the values of both $W^{\mathrm{SA}}_{1s\sigma}(J=0;R)$ and $W^{\mathrm{IA}}_{1s\sigma}(J=0;R)$ listed in Table II, the vibrational levels may easily be obtained by solving for the eigenvalues of the equation

$$\left[-\frac{1}{2\mu}\left[\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right]+W_{1s\sigma}(J=0;R)+\frac{1}{R}\right]\chi_v(R)=E_v\chi_v(R)\ . \tag{50}$$

This equation is merely Eq. (12) (and its SA analogue) rewritten in a form that makes use of the data in Table II.

Many numerical methods exist for the solution of this equation. The technique used in the present work is Numerov integration.[33] After making an initial guess for E_v, the resulting differential equation is integrated outward from small R and inward from large R to some appropriately chosen matching point. The discrepancy in the logarithmic derivative at the matching point is then used to provide a corrected estimate of the energy E_v. The algorithm is applied iteratively and has been found to be quickly convergent for the problem under consideration. For the accuracy required in the present work, the algorithm requires the potential curve at values more closely spaced than those provided by Table II. As stated earlier, cubic-spline interpolation is used to obtain additional values of W from the table, then the $1/R$ term is added to the interpolated value. This procedure has been repeated with more closely spaced *ab initio* points than given in Table II and no difference, to the accuracy reported, is found in the calculated vibrational levels.

Table IV contains the vibrational-level results in terms of dissociation energies measured relative to the ground state of the D atom, $-m_d/2(m_d+m_e)$ a.u., for both the SA and IA levels. This method for tabulating the vibrational energies allows easy comparison of the results obtained by the two methods. The alternate choice of listing the SA levels relative to the SA curve limit and the IA levels relative to the IA curve limit does not appear to be

TABLE IV. Dissociation energies (relative to D-atom ground-state energy) of the vibrational levels obtained using the IA and SA potential curves for the $J=0$ $1s\sigma$ state of HD^+ (in cm^{-1}).

v	SA	IA
0	21 515.91	21 515.92
1	19 602.78	19 602.80
2	17 785.80	17 785.82
3	16 062.10	16 062.12
4	14 429.20	14 429.22
5	12 884.98	12 885.00
6	11 427.66	11 427.68
7	10 055.86	10 055.88
8	8768.50	8768.53
9	7564.93	7564.96
10	6444.82	6444.85
11	5408.27	5408.30
12	4455.79	4455.82
13	3588.33	3588.36
14	2807.35	2807.39
15	2114.83	2114.87
16	1513.36	1513.42
17	1006.20	1006.28
18	597.31	597.43
19	291.32	291.55
20	92.89	93.55
21	2.24	8.76
22	−14.13	0.32

a reasonable form for presentation because this causes the low-lying levels of the two methods to appear to be substantially different. In fact, there is little difference between the energies of these states, when measured relative to the configuration where all particles are infinitely separated with zero kinetic energy. From the viewpoint of spectroscopy, only the transitional frequencies between the levels listed are of interest, so the zero of the energies is of little physical importance. Energies are presented in cm^{-1}, where the conversion 1 a.u. $=219\,474.635\ \text{cm}^{-1}$ has been used. Note that the SA potential curve asymptotically approaches the value $-\frac{1}{2}+(m_p+m_d)m_e/4m_pm_d$ a.u. For the mass values used, the difference between the SA curve limit and the D-atom ground state is 6.809×10^{-5} a.u. ($14.94\ \text{cm}^{-1}$), which in high-resolution spectroscopy is a significant discrepancy.

Both the SA and IA potential curves are found to have 23 bound states. However, because of the dissociation error of the SA approach, the highest bound state obtained using this curve is actually higher than the dissociation limit used, hence the negative value of the dissociation energy listed. The $v=22$ bound state of the SA and IA curves are extremely weakly bound. To ensure that the integration had converged for the highest state, it was necessary to extend the SA potential curve out to $50a_0$ and the IA potential curve out to $80a_0$.

Wolniewicz[34] has shown that the SA vibrational energies are upper bounds to the exact eigenvalues of the complete Hamiltonian. This proof is easily extended to the case of the IA approximation; therefore the presence of the $v=22$ bound IA vibrational state answers the question that has been posed[6] of whether the $J=0$ $1s\sigma$ state has 22 or 23 bound states. This conclusion, of course, applies only to the nonrelativistic Schrödinger equation, and relativistic and radiative corrections may raise this level above the dissociation threshold. In order to determine if the physical state is actually bound, one must take into account relativistic, radiative, and nonadiabatic corrections. We have investigated including the relativistic corrections computed by Bishop[35] in the manner suggested by Wolniewicz and Poll[26] and found that while the dissociation threshold is lowered by $1.4610\ \text{cm}^{-1}$, the energy of the $v=22$ state is lowered by $1.4607\ \text{cm}^{-1}$, essentially the same amount. Hence the $v=22$ state continues to be bound by $0.32\ \text{cm}^{-1}$ after relativistic effects are included using this procedure. The technique Wolniewicz and Poll have suggested for including the radiative corrections[26] shifts the highest state and the threshold upward by the same amount, $0.2720\ \text{cm}^{-1}$. Hence including both the relativistic and radiative corrections in this manner does not change the binding energy of the $v=22$ level from the original value of $0.32\ \text{cm}^{-1}$, to the accuracy of the present calculations. It thus appears extremely likely that this 23rd level does exist in the physical (nonadiabatic, relativistic, radiative) system. Franck-Condon factors will make transitions between this state and other levels extremely difficult to detect experimentally.

The vibrational levels listed in Table IV indicate that the IA levels are all deeper than those levels obtained from the SA approach. Since both of these adiabatic approximations are upper bounds to the true nonadiabatic levels, this means that the IA approximation has led to more accurate energies for all the levels, as expected. While the lower levels are not appreciably changed, the highly excited levels indicate that the traditional SA approximation is not appropriate for these states. Note that the shift in the vibrational levels is simply a reflection of the shift in the potential curves discussed earlier. The IA potential curve was only slightly lower for the small to intermediate range of R, so the lower vibrational states, sensitive to only this part of the curve, are also slightly lower. However, the IA potential curve was significantly lower for large R, so the higher vibrational states, which are very sensitive to the potential curve at the outer classical turning point, are also significantly lower.

For extremely accurate comparison of the HD^+ levels with experiment, it is necessary to include nonadiabatic corrections (along with relativistic and radiative corrections). Large-scale fully variational calculations are useful for the determination of accurate energies only for states of low-vibrational quantum number[12,13] (typically $v=0$—3). For these low-lying states, the SA and IA values are compared with the BO, the nonadiabatic, and the BA′ (the attempt at a best adiabatic as formulated in Ref. 1) values in Table V.

The higher excited states are also of experimental interest, but the fully variational procedure has not proven to be effective for accurately calculating these energies. Wolniewicz and Poll[13,26] have suggested a procedure that utilizes the framework of the SA approach to calculate the nonadiabatic energies by perturbation theory. To ob-

TABLE V. Energies (in hartree a.u.) obtained for the low-lying $J=0$ levels of HD^+ using approximate [Born-Oppenheimer (BO), standard adiabatic (SA), improved adiabatic (IA), and the attempt at a best adiabatic (BA′) proposed in Ref. 1] and exact [nonadiabatic (NA)] formulations.

Level	Method	Energy
$v=0$	BO	−0.598 090 8
	SA	−0.597 897 5
	BA′	−0.597 893 8
	IA	−0.597 897 6
	NA[a]	−0.597 898 0
$v=1$	BO	−0.589 371 8
	SA	−0.589 180 7
	BA′	−0.589 177 3
	IA	−0.589 180 7
	NA[a]	−0.589 181 8
$v=2$	BO	−0.581 091 1
	SA	−0.580 901 9
	BA′	−0.580 898 7
	IA	−0.580 902 0
	NA[a]	−0.580 903 7
$v=3$	BO	−0.573 235 7
	SA	−0.573 048 1
	BA′	−0.573 045 2
	IA	−0.573 048 2
	NA[b]	−0.573 050 6

[a] Reference 12.

[b] Reference 13.

tain the symmetry-breaking behavior, they have applied this technique using approximate *nonadiabatic* wave functions constructed from coupled $1s\sigma_g$ and $2p\sigma_u$ states[5] and examined the first 22 states of HD^+. If this type of calculation were performed within the framework of the IA approach, it would not be necessary to couple states into nonadiabatic wave functions in order to obtain the symmetry-breaking behavior. Also note that the present calculations indicated the presence of a 23rd state for this system; it may be of interest to calculate nonadiabatic corrections for this state.

VI. CONCLUSION

The IA approximation yields more accurate variational bounds on all vibrational levels than the customary SA approach. For systems with unequal nuclear masses, such as HD^+, the SA approximation is inadequate to describe any physical state which is significantly affected by symmetry breaking, such as the highly excited vibrational states near the dissociation limit. It is clear that the IA approach is better suited to describe such systems.

In addition, the IA approximation requires about the same amount of computational labor as the SA approximation for the $J=0$ states (if a two-centered basis is used, as will usually be the case). For rotational states with $J\neq 0$, the IA approximation is able to describe the Λ doubling in a very natural way, and if this splitting is not important, the computational effort can be reduced to essentially that which is required in the SA approximation. Furthermore, all the calculations required to implement the IA approximation can be performed using currently existing quantum-chemistry computational procedures.

Finally, the implications of the IA approximation should be examined for other applications, such as multiphoton processes and collisions. The IA approximation opens up the possibility of investigating the quasibound states of HD^+, which has not previously been attempted because of the dissociation error of the SA approach.[2] Work is underway at this laboratory to utilize the framework of the IA approximation to construct a basis for a nonadiabatic calculation for the states of $dt\mu$, a molecular system for which the mass ratios are such that no adiabatic approximation can be expected to yield precise results. The molecular viewpoint has proven useful for many physical problems, and the variation on that approach presented here may have additional advantages, depending on the particular problem.

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