PHYSICAL REVIEW A VOLUME 31, NUMBER 1 JANUARY 1985

Novel theory of the HD dipole moment. I. Theory

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(Received 26 June 1984)

A novel theory of the electric dipole moments of homopolar but *isotopically* asymmetric molecules (such as HD, HT, or DT) is formulated, such that electrical asymmetry and the resulting dipole moment arise as purely electronic properties within a suitable Born-Oppenheimer approximation, and nonadiabatic (rovibronic) perturbations play no part in the theory. It is shown thereby that a much simpler and more direct explanation for these dipole moments can be given than that invoking nonadiabatic perturbations: The dipole moment arises from isotopic variation of the local effective electronic reduced mass and its effects on binding energies and sizes of orbitals. It is an *odd* function of the isotopic splitting parameter $\alpha_0 = \frac{1}{2}\lambda m/\mu$, where $\lambda = (M_A - M_B)/(M_A + M_B)$ is the nuclear mass asymmetry for nuclei A,B and (m/μ) is the electron-nuclear mass ratio (for HD, this parameter is 1.36×10^{-4}). A canonical transformation exhibiting these effects (in the form of an asymmetric effective potential) is the basis for the new formulation. Since α_0 is small the resulting dipole moment function is essentially *linear* in α_0, and hence the dipole moment functions for HT and DT may be computed by rescaling the results for HD. Since the problem is purely electronic in the new formulation, variational and convergence studies are easy to carry out. In this and the following paper we formulate the new theory in detail and carry out variation-perturbation calculations of the HD dipole moment. The results are in good agreement with theoretical results obtained by nonadiabatic perturbation theory and demonstrate that this approach to isotopically induced dipole moments is valid.

I. INTRODUCTION

Within the limits of the Born-Oppenheimer approximation as it is normally constructed, a homopolar but isotopically asymmetric molecule such as HD has no permanent electric dipole moment, and hence no electric dipole rotation or vibration-rotation spectra. However, nonvanishing transition moments for such spectra arise when the nonadiabatic corrections to this approximation are considered. The theory of these transition moments has been widely studied,[1-8] from the early work in 1935 by Wick[1] to more recent extensive calculations by Bunker,[5] Wolniewicz and co-workers,[4,6,7] and Ford and Browne.[8] In all these studies the method used is perturbation theory within a full set of electronic, vibrational, and rotational states, since the nonadiabatic perturbation couples electronic and nuclear motions. Such calculations have practical interest since the pure rotation and vibration-rotation spectra have been observed and experimental estimates have been made of the transition moments.[9-13]

However, we can show that HD should have a permanent electric dipole moment, without invoking nonadiabatic perturbations. For deuterium, the electronic reduced mass and binding energy are slightly greater, and the corresponding wave function smaller, than for hydrogen. In the ground state of HD this has two effects: (i) The contribution of the ionic structure H^+D^- is slightly greater than that of H^-D^+; (ii) when the distorting effects of chemical bonding in the molecular-orbital distributions are considered, the smaller size of the D orbital skews the center of charge. Both effects produce a net moment with the sense H^+D^-. Moreover, we can see that this moment should be $\sim \lambda m/\mu$ smaller than the permanent moment of a typical polar molecule, where $\lambda = (M_A - M_B)/(M_A + M_B)$ is the mass asymmetry parameter and m/μ is the electron-nuclear mass ratio. For HD, $\lambda m/\mu = 2.72 \times 10^{-4}$, and the correct value for the HD permanent moment is 8.51×10^{-4} debye. [Only for the isotopic hydrogen molecules will the effect even be this big, since both λ and m/μ are much smaller for a molecule like $^{14}N^{15}N$ ($\lambda m/\mu = 2.6 \times 10^{-6}$), and only the valence electrons can contribute much to a net imbalance.]

In Appendix A we have made a crude application of this simple picture of the HD dipole moment, which yields the qualitatively correct result 4.9×10^{-4} debye (H^+D^-) at $R = R_e$. This suggests that we might *rigorously* reformulate the Born-Oppenheimer separation of electronic and nuclear motions so that the molecular asymmetry of HD appears *directly* in the electronic Hamiltonian (rather than *indirectly* via the nonadiabatic couplings). A permanent electric dipole moment would then arise in the usual way and for the ground electronic state it could be computed variationally within a purely electronic basis set. Transition moments for the vibration-rotation transitions would be related as usual to the dipole-moment derivatives near the equilibrium separation R_e.

In this and the following paper[14] we make just such a reformulation, and we carry out calculations of the permanent electric dipole moment of HD in its $X\,^1\Sigma^+$ ground state near $R=R_e$ with the result 8.51×10^{-4} debye (H^+D^-) at 1.40 a.u., in good agreement with previous theoretical values. *Nonadiabatic couplings play no part whatever in our theory or calculations.*

To do this, we transform to new electronic and nuclear coordinates, chosen so that nonadiabatic couplings depending only on the mass asymmetry parameter vanish exactly.[15] Since it is these couplings which produce the HD dipole moment in the usual formulation, their removal forces the physical asymmetry of the problem to show up elsewhere in the Hamiltonian; in particular, when we make the Born-Oppenheimer separation in the new coordinates, we find the new electronic Hamiltonian no longer has $D_{\infty h}$ symmetry.

For the one-electron case (i.e., the artificial problem of HD^+) this electronic Hamiltonian, to within terms $\sim(\lambda m/\mu)^2$, is just that for an electron moving in the field of two charges $Z_\pm$ $(=1\pm\frac{1}{4}\lambda m/\mu)$ separated by distance R (deuteron has charge Z_+), *plus* a constant electric field of magnitude $\frac{1}{2}\lambda(m/\mu)(e/R^2)$ parallel to the molecule axis, and also orienting the electron in the sense H^+D^-. The "dipole moment" (with respect to the geometric center of HD^+) consists of two parts, a term linear in R resulting directly from the transformation, and a term which arises in response to the Hamiltonian asymmetry; both have the sense H^+D^-. Were there no electron correlation, this simple picture would also hold for HD, but the strong interatomic electron correlation in hydrogen complicates the situation and markedly reduces the overall dipole moment.

In this formulation, both the Hamiltonian asymmetry and the resulting dipole moment $\vec{\mu}_e(R)$ are *odd* and thus essentially *linear* functions of the very small parameter $\alpha_0=\frac{1}{2}\lambda m/\mu$. Hence the HT and DT dipole moment functions may be obtained merely by scaling those for HD, and transition moments for their vibration-rotation spectra require recalculation only of the vibrational matrix elements.

The main goals of this work are conceptual, rather than quantitative: we show that the dipole moment of isotopically asymmetric molecules has a simpler physical explanation than is suggested by the nonadiabatic coupling approach. However, since our scheme is variational, we can test the convergence of the calculations, and we believe the results we have obtained establish the accuracy of the value 8.51×10^{-4} debye to better than 0.1%. The good agreement with the results of Bunker[5] and of Ford and Browne[8] gives high confidence that this value (as contrasted with the experimental result obtained by Trefler and Gush[10]) is the correct one.[16] Because the dipole moment depends so sensitively on electron correlation effects, a much more accurate calculation, or a calculation for the dipole moment at much larger or much smaller internuclear separations, will require a more sophisticated wave function than the James-Coolidge-type expansions[20] used here.

Section II of this first paper defines the transformation to new coordinates and the ensuing Born-Oppenheimer separation. Section III describes the resulting electronic Hamiltonian and its physical interpretation and implementations. Section IV contains a brief discussion of the problem and results from the standpoint of our main goals. In the second paper,[14] we give an account of our calculations, including details about certain new molecular integrals, convergence studies, and tables of vibration-rotation matrix elements for the three isotopically asymmetric hydrogen molecules.

II. NEW COORDINATES AND DYNAMICAL SEPARATION

A. System description

The system consists of electrons 1,2 with masses m_0, and nuclei A,B with masses $M_A\geq M_B$; with respect to a fixed origin these have coordinates $\vec{r}_i^{\,0}$ $(i=1,2)$, $\vec{R}_A^{\,0}$, $\vec{R}_B^{\,0}$. We remove the center-of-mass motion and define the relative coordinates

$$\vec{r}_i=\vec{r}_i^{\,0}-\vec{R}^{\,0}_{\text{c.m.n.}},\quad i=1,2\ , \tag{2.1a}$$

$$\vec{R}=\vec{R}_B^{\,0}-\vec{R}_A^{\,0}\ , \tag{2.1b}$$

where

$$\vec{R}^{\,0}_{\text{c.m.n.}}=(M_A+M_B)^{-1}(M_A\vec{R}_A^{\,0}+M_B\vec{R}_B^{\,0})\ . \tag{2.1c}$$

defines the nuclear center of mass. Then the kinetic energy of relative motion is

$$T=\vec{P}_R^{\,2}/2\mu+(\vec{p}_1^{\,2}+\vec{p}_2^{\,2})/2m_1+(\vec{p}_1\cdot\vec{p}_2)/(M_A+M_B) \tag{2.2}$$

where $\vec{p}_i$ and $\vec{P}_R$ are canonical momenta conjugate to $\vec{r}_i$ and $\vec{R}$, and the reduced masses are

$$\mu=M_AM_B/(M_A+M_B)\ , \tag{2.3a}$$

$$m_1=m_0(M_A+M_B)/(M_A+M_B+m_0)\ . \tag{2.3b}$$

We also introduce the geometric center electron coordinates defined by

$$\vec{\rho}_i=\vec{r}_i-\tfrac{1}{2}\lambda\vec{R}\ , \tag{2.4}$$

where $\lambda=(M_A-M_B)/(M_A+M_B)$ is the mass asymmetry. The electrostatic potential energy $V(\vec{r}_1,\vec{r}_2;\vec{R})$ is invariant under the inversion $\vec{\rho}_i\rightarrow-\vec{\rho}_i$ $(i=1,2)$ at fixed R; that is, the two nuclei appear electrically identical.

The coordinates $\vec{r}_1$, $\vec{r}_2$, and $\vec{R}$ are those usually employed in making the Born-Oppenheimer separation. If that is done, the electronic Hamiltonian and its eigenfunctions exhibit the centrosymmetric properties of V, and an electric dipole moment cannot arise in the Born-Oppenheimer approximation, but only indirectly, via nonadiabatic couplings. We will not develop this approach; accounts of it may be found in Refs. 5, 21, and 22.

B. Transformation

For clarity we perform the desired transformation in several steps. First, introduce symmetric and antisymmetric electron coordinates $\vec{s}, \vec{t}$,

$$\vec{s}=(\vec{r}_1+\vec{r}_2)/\sqrt{2},\quad \vec{t}=(\vec{r}_2-\vec{r}_1)/\sqrt{2}\ , \tag{2.5}$$

and their canonically conjugate momenta $\vec{p}_s,\vec{p}_t$; the kinetic energy may then be written

$$T=\vec{P}_R^{\,2}/2\mu+\vec{p}_s^{\,2}/2m_2+\vec{p}_t^{\,2}/2m_0\ , \tag{2.6}$$

where

$$m_2=m_0(M_A+M_B)/(M_A+M_B+2m_0)\ . \tag{2.7}$$

Next we define mass-scaled coordinates $\tilde{\vec{s}},\tilde{\vec{R}}$,

$$\tilde{\vec{s}}=\sqrt{m_2}\,\vec{s},\quad \tilde{\vec{R}}=\sqrt{\mu}\,\vec{R}\ , \tag{2.8a}$$

and their conjugate momenta

$$\tilde{\vec{p}}_s=\vec{p}_s/\sqrt{m_2},\quad \tilde{\vec{P}}_R=\vec{P}_R/\sqrt{\mu}\ . \tag{2.8b}$$

Then T has the form

$$T=\tfrac{1}{2}(\tilde{\vec{P}}_R^{\,2}+\tilde{\vec{p}}_s^{\,2})+\vec{p}_t^{\,2}/2m_0\ . \tag{2.9}$$

This *form* is preserved under any orthogonal "rotation" mixing $(\tilde{\vec{R}},\tilde{\vec{s}})$. As the crucial step we now make just such a rotation, to new (scaled) coordinates $(\tilde{\vec{\xi}},\tilde{\vec{\eta}})$:

$$\begin{aligned}\tilde{\vec{\xi}}&=\cos\sigma_0\,\tilde{\vec{R}}+\sin\sigma_0\,\tilde{\vec{s}}\ ,\\ \tilde{\vec{\eta}}&=-\sin\sigma_0\,\tilde{\vec{R}}+\cos\sigma_0\,\tilde{\vec{s}}\ ,\end{aligned} \tag{2.10}$$

where the mixing angle σ_0 is given by

$$\tan\sigma_0=(\lambda/\sqrt{2})(m_2/\mu)^{1/2}\ . \tag{2.11}$$

T now becomes

$$T=\tfrac{1}{2}(\tilde{\vec{P}}_\xi^{\,2}+\tilde{\vec{p}}_\eta^{\,2})+\vec{p}_t^{\,2}/2m_0\ . \tag{2.12}$$

Now we unscale the coordinates $\tilde{\vec{\xi}},\tilde{\vec{\eta}}$, to define a new heavy-particle coordinate $\vec{\xi}$,

$$\vec{\xi}\equiv[(\sec\sigma_0)/\sqrt{\mu}]\tilde{\vec{\xi}} \tag{2.13a}$$

with its conjugate momentum

$$\vec{P}_\xi=(\sqrt{\mu}\cos\sigma_0)\tilde{\vec{P}}_\xi \tag{2.13b}$$

and a new (symmetric) electron coordinate $\vec{\eta}$,

$$\vec{\eta}\equiv[(\sec\sigma_0)/\sqrt{m_2}]\tilde{\vec{\eta}} \tag{2.13c}$$

with its momentum

$$\vec{p}_\eta=(\sqrt{m_2}\cos\sigma_0)\tilde{\vec{p}}_\eta\ . \tag{2.13d}$$

A short calculation yields

$$\vec{\xi}=\vec{R}+\lambda(m_2/\mu)(\vec{s}/\sqrt{2}) \tag{2.14}$$

and the intuitively pleasing result

$$\vec{\eta}=\vec{s}-\lambda\vec{R}/\sqrt{2}=(\vec{\rho}_1+\vec{\rho}_2)/\sqrt{2}\ . \tag{2.15}$$

That is, the canonical electronic coordinate resulting from this transformation is the (symmetrical) *geometric center* coordinate. Now T is given by

$$T=\vec{p}_\xi^{\,2}/2\mu'+\vec{p}_\eta^{\,2}/2m_2\cos^2\sigma_0+\vec{p}_t^{\,2}/2m_0\ , \tag{2.16}$$

where $\mu'=\mu\cos^2\sigma_0$. Finally, noting that $\vec{t}=(\vec{\rho}_2-\vec{\rho}_1)/\sqrt{2}$, we transform back to individual electron coordinates $\vec{\rho}_i$ $(i=1,2)$,

$$\vec{\rho}_1=(\vec{\eta}-\vec{t})/\sqrt{2},\quad \vec{\rho}_2=(\vec{\eta}+\vec{t})/\sqrt{2}\ , \tag{2.17}$$

with corresponding conjugate momenta $\vec{\pi}_1,\vec{\pi}_2$; the *exact* relative kinetic energy then becomes

$$T=\vec{P}_\xi^{\,2}/2\mu'+(\vec{\pi}_1^{\,2}+\vec{\pi}_2^{\,2})/2m'+\vec{\pi}_1\cdot\vec{\pi}_2/4\mu\ , \tag{2.18}$$

where

$$m'=m_0(1+m_0/4\mu)^{-1}. \tag{2.19}$$

Note that m' reduces to m_1, μ' to μ, and $4\mu=(M_A+M_B)$, for $\lambda=0$ $(M_A=M_B)$, as is required for consistency with (2.2).

C. Born-Oppenheimer separation

Now we shall employ the electron coordinates $(\vec{\rho}_1,\vec{\rho}_2)$ and the *heavy-particle coordinate* $\vec{\xi}$ as the dynamical coordinates for a new Born-Oppenheimer separation: that is, *regarding* $\vec{\xi}$ *(not* $\vec{R}$*) as a fixed parameter,* we will solve the electronic eigenvalue problem to obtain electronic eigenstates for the system. As will be shown below, these eigenstates, and the electronic Hamiltonian which defines them, do *not* have g or u symmetry with respect to the inversion $\vec{\rho}_i\to-\vec{\rho}_i$ $(i=1,2)$ *for fixed* $\vec{\xi}$.

In this representation of the problem, asymmetry does *not* arise from the kinetic energy; indeed, T can be shown to have gerade symmetry under the inversion. All asymmetry now appears in the potential energy (when it is expressed in the new coordinates) and hence electrical asymmetry will appear directly in the Born-Oppenheimer electronic eigenstates.

Since we shall work entirely within the Born-Oppenheimer approximation, the heavy-particle coordinate $\vec{\xi}$ appears merely as a *fixed parameter* characterizing electronic eigenstates and energies. The only part played by the heavy-particle kinetic energy, $T_\xi=\vec{p}_\xi^{\,2}/2\mu'$, will be to define the vibrational-rotation states of the molecule associated with a given electronic state. Nonadiabatic couplings will not be considered; they would have a completely negligible effect on the dipole moment, of order $(m/\mu)^3$ or higher.

The new electronic and heavy-particle reduced masses m',μ' differ from the old ones m_1,μ by trifling amounts $[\sim\lambda^2(m/\mu)^2]$ and a negligible error *in the dipole moment calculation* is introduced by setting $m'=m_1=m$, $\mu'=\mu$, in what follows.[23]

As the *electronic Hamiltonian* for our problem, we take the definition

$$h_e(\vec{\rho}_1,\vec{\rho}_2;\vec{\xi})\equiv(2m)^{-1}(\vec{\pi}_1^{\,2}+\vec{\pi}_2^{\,2})+V_\xi(\vec{\rho}_1,\vec{\rho}_2;\vec{\xi}) \tag{2.20}$$

where V_ξ is the potential energy expressed in the new coordinates. We have thus omitted the small "masspolarization" term

$$T_{\mathrm{MP}}=(4\mu)^{-1}\vec{\pi}_1\cdot\vec{\pi}_2 \qquad (2.21)$$

from consideration, as is usual in molecular electronic calculations. It also has *gerade* symmetry, and like the nonadiabatic couplings it can affect the *dipole moment* at most by terms of magnitude $\sim(m/\mu)^3$.

III. ELECTRONIC EIGENVALUE PROBLEM

A. Potential energy expressions

In the old coordinates $[\vec{\rho}_i,\ i=1,2;\vec{\mathrm{R}}]$, the potential energy has the simple form

$$V(\vec{\rho}_1,\vec{\rho}_2;\vec{\mathrm{R}})=V_1(\vec{\rho}_1;\vec{\mathrm{R}})+V_1(\vec{\rho}_2;\vec{\mathrm{R}})+e^2/r_{12}+e^2/R\ , \qquad (3.1)$$

where V_1 is the interaction of an electron with the nuclei A,B,

$$V_1(\vec{\rho};\vec{\mathrm{R}})=-e^2\left[\frac{1}{|\vec{\rho}+\frac{1}{2}\vec{\mathrm{R}}|}+\frac{1}{|\vec{\rho}-\frac{1}{2}\vec{\mathrm{R}}|}\right]. \qquad (3.2)$$

In the *new* coordinates $[\vec{\rho}_i,\ i=1,2;\vec{\xi}]$, the potential energy is a new function

$$V_\xi(\vec{\rho}_1,\vec{\rho}_2;\vec{\xi})=V(\vec{\rho}_1,\vec{\rho}_2;\vec{\mathrm{R}}(\vec{\rho}_1,\vec{\rho}_2;\vec{\xi})) \qquad (3.3)$$

obtained by explicit substitution in Eq. (3.1) using the inverse relation

$$\vec{\mathrm{R}}=\cos^2\sigma_0[\vec{\xi}-\tfrac{1}{2}\lambda(m/\mu)(\vec{\rho}_1+\vec{\rho}_2)]\ . \qquad (3.4)$$

The potential energy V_ξ does not have $D_{\infty h}$ symmetry with respect to any point on the $\vec{\xi}$ axis; it does retain $C_{\infty v}$ symmetry about this axis. Two types of terms contribute to the asymmetry.

(1) Internuclear repulsion. The term e^2/R now becomes

$$e^2/R=\frac{e^2}{|\vec{\xi}_0-\alpha_0(\vec{\rho}_1+\vec{\rho}_2)|}\ ,$$

where $\alpha_0=\frac{1}{2}\lambda(m/\mu)\cos^2\sigma_0$ and $\vec{\xi}_0=\cos^2\sigma_0\vec{\xi}$ is simply a rescaled fixed parameter. Since we are interested in finite values of ξ_0 ($\sim$1.4 a.u.) we can use the multipole expansion to obtain

$$\frac{e^2}{R}=\frac{e^2}{\xi_0}+\alpha_0\frac{e^2}{\xi_0^2}(z_1+z_2)+O(\alpha_0^2)\ , \qquad (3.5)$$

an expression which is valid provided $|\vec{\rho}_1+\vec{\rho}_2|\ll\xi_0/\alpha_0$. For brevity, we have not written out the second-order term, which has *gerade* symmetry. The first-order term is just the potential energy due to a constant axial electric field of magnitude α_0e^2/ξ_0^2 which pushes the electrons to negative z (the A-nucleus end).[24]

(2) Electron-nucleus attraction—one-electron case. The second kind of asymmetry appears in the electron-nucleus interaction and is more difficult to understand. To do so let us first consider the one-electron case (e.g., HD$^+$), which yields a very simple result. Repeating the earlier kinematic analysis for the one-electron case, we find

$$\tan\sigma_0'=\tfrac{1}{2}\lambda(m/\mu)^{1/2}\ , \qquad (2.11')$$

$$\vec{\eta}=\vec{\mathrm{r}}-\tfrac{1}{2}\lambda\vec{\mathrm{R}}=\vec{\rho}\ , \qquad (2.15')$$

$$\vec{\xi}=\vec{\mathrm{R}}+\tfrac{1}{2}\lambda(m/\mu)\vec{\mathrm{r}}\ , \qquad (2.14')$$

$$\vec{\mathrm{R}}=\cos^2\sigma_0'[\vec{\xi}-\tfrac{1}{2}\lambda(m/\mu)\vec{\rho}]\ , \qquad (3.4')$$

as the one-electron analogs of the correspondingly numbered equations above. Then the denominators in the potential energy of interaction with nuclei A,B are

$$\vec{\rho}\pm\tfrac{1}{2}\vec{\mathrm{R}}=(1\mp\tfrac{1}{2}\alpha_0')\vec{\rho}\pm\tfrac{1}{2}\cos^2\sigma_0'\vec{\xi}$$

where $\alpha_0'=\frac{1}{2}\lambda(m/\mu)\cos^2\sigma_0'$; this may be rewritten in the form

$$\vec{\rho}\pm\tfrac{1}{2}\vec{\mathrm{R}}=(1\mp\tfrac{1}{2}\alpha_0')(\vec{\rho}\,'\pm\tfrac{1}{2}\vec{\xi}\,')\ , \qquad (3.6)$$

where

$$\vec{\xi}\,'=[1-\tfrac{1}{4}(\alpha_0')^2]^{-1}\cos^2\sigma_0'\vec{\xi}$$

is just a rescaling of the fixed parameter $\vec{\xi}$, and

$$\vec{\rho}\,'=\vec{\rho}+\tfrac{1}{2}\alpha_0'\vec{\xi}\,'$$

simply redefines the (fixed) origin for electron coordinates.[25] But now the electron-nucleus attractions may be rationalized very simply as

$$V_{1\xi}(\vec{\rho};\vec{\xi})=-e^2\left[\frac{Z_A'}{|\vec{\rho}\,'+\frac{1}{2}\vec{\xi}\,'|}+\frac{Z_B'}{|\vec{\rho}\,'-\frac{1}{2}\vec{\xi}\,'|}\right], \qquad (3.7)$$

where the effective charges Z_A',Z_B' are defined

$$Z_{A,B}'=(1\mp\tfrac{1}{2}\alpha_0')^{-1}\ ,$$

Z_A' being the larger. The "nuclei" in this rationalization are separated by the internuclear distance $\vec{\xi}\,'$; moreover, it can also be shown that in this case the internuclear repulsion can be rewritten consistently as

$$\frac{e^2}{R}=e^2\left[\frac{Z_A'Z_B'}{\xi'}+\alpha_0'\frac{Z_A'Z_B'}{(\xi')^2}z'+O((\alpha_0')^2)\right]. \qquad (3.8)$$

Thus, for the one-electron case, transformation from old coordinates $(\vec{\mathrm{r}},\vec{\mathrm{R}})$ to new coordinates $(\vec{\rho},\vec{\xi})$, followed by Born-Oppenheimer separation on surfaces of constant $|\vec{\xi}|$, leads to an electron Hamiltonian for an electron moving in the field of nuclei A',B' with charges Z_A',Z_B' as defined above, and separated by distance ξ'—plus a constant axial electric field of magnitude $\alpha_0'e^2Z_A'Z_B'/(\xi')^2$. $\vec{\rho}\,'$ is simply the electron coordinate measured from the geometric center of this new "molecule." Finally the dipole moment of HD$^+$ [measured with respect to the geometric centre of the original (physical) molecule[26]] is just given by the expectation value of $-e\vec{\rho}$ on the relevant eigenstate $\psi_n(\vec{\rho}\,';\xi')$:

$$\vec{\mu}_{nn}(\xi')=\tfrac{1}{2}e\alpha_0'\vec{\xi}\,'-e\langle\psi_n|\vec{\rho}\,'|\psi_n\rangle\ . \qquad (3.9)$$

$\vec{\mu}_{nn}$ clearly has the polarity H$^+$D$^-$. While this model has little interest for the real ionic system HD$^+$, it gives us important clues for the interpretation of the two-electron case.

(3) Electron-nucleus attractions, two-electron case. Using Eq. (3.4), we write

$$\vec{\rho}_i \pm \tfrac{1}{2}\vec{\mathrm{R}} = (1 \mp \tfrac{1}{2}\alpha_0)[\vec{\rho}_i \pm \tfrac{1}{2}(1 \mp \tfrac{1}{2}\alpha_0)^{-1}\vec{\xi}_0 \mp \tfrac{1}{2}\alpha_0(1 \mp \tfrac{1}{2}\alpha_0)^{-1}\vec{\rho}_j] \,, \tag{3.10}$$

where $j \neq i$, and $\alpha_0, \vec{\xi}_0$ were previously defined. Two distinct rationalizations of this expression can be made, a fact we will exploit computationally.

(a) Scheme 1. As for the one-electron case, we shift the (fixed) origin of electron coordinates,

$$\vec{\rho}_i{}' = \vec{\rho}_i + \tfrac{1}{2}\alpha_0\vec{\xi}_0 \tag{3.11}$$

and then manipulation of Eq. (3.10) yields

$$\vec{\rho}_i \pm \tfrac{1}{2}\vec{\mathrm{R}} = (Z_\pm)^{-1}[(\vec{\rho}\,'_i \pm \tfrac{1}{2}\vec{\xi}_0) \mp \tfrac{1}{2}\alpha_0(\vec{\rho}\,'_j \pm \tfrac{1}{2}\vec{\xi}_0) + O(\alpha_0^2)] \,, \tag{3.12}$$

where $Z_\pm = (1 \mp \tfrac{1}{2}\alpha_0)^{-1}$. Again we interpret $Z_\pm$ as effective nuclear charges, $\vec{\xi}_0$ as the internuclear coordinate, and $\vec{\rho}\,'_i$, $i = 1,2$, as electron coordinates measured from the geometric center of this new molecule.

(b) Scheme 2. In this rationalization, we rearrange Eq. (3.10) directly to obtain the form

$$\vec{\rho}_i \pm \tfrac{1}{2}\vec{\mathrm{R}} = (Z_\pm)^{-1}[(\vec{\rho}_i \pm \tfrac{1}{2}\vec{\xi}_0) \mp \tfrac{1}{2}\alpha_0(\vec{\rho}_j \mp \tfrac{1}{2}\vec{\xi}_0) + O(\alpha_0^2)] \,. \tag{3.13}$$

Here $j \neq i$, and $Z_\pm$ and $\vec{\xi}_0$ are the same as before, but now the $\vec{\rho}_i$ themselves are the electron coordinates measured from the geometric centre of the new molecule.

Each of these rationalizations leads to a different electronic Hamiltonian—and a correspondingly different expression for the electric dipole moment function. Of course, each must give the same physical description, i.e., numerical value for the dipole moment. In Appendix C, we prove that the two results must give the same answer in a complete Hilbert space; hence we can use the convergence of results for the two schemes as at least a necessary condition for basis set adequacy.

(4) Notation change. To reinforce the above conclusions, and for the sake of clarity in what follows, we will change the notation (for each scheme) to one which is more usual in molecular electronic calculations.

(a) We will again use the name $\vec{\mathrm{R}}$ for the internuclear separation vector, i.e., $\vec{\xi}_0$ is renamed $\vec{\mathrm{R}}$.

(b) The names $\vec{\mathrm{r}}_i$ will denote the electron coordinates measured from the geometric centre of the new molecule, that is, in Scheme 1, $\vec{\rho}\,'_i$ is renamed $\vec{\mathrm{r}}_i$, while in Scheme 2, $\vec{\rho}_i$ is renamed $\vec{\mathrm{r}}_i$.

(c) Electronic momenta are denoted $\vec{\mathrm{p}}_i$, i.e., $\vec{\pi}_i$ is renamed $\vec{\mathrm{p}}_i$.

We emphasize that this is purely a *notation change.* In the rest of the paper there will be no chance for serious confusion with previous usage.

(5) Electronic Hamiltonians and dipole moments. In both schemes the electronic Hamiltonians for the system can be written

$$h_e(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R) = (2m)^{-1}(\vec{\mathrm{p}}\,_1^2 + \vec{\mathrm{p}}\,_2^2) + V(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R) \,, \tag{3.14}$$

where

$$V(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R) = V_e(\vec{\mathrm{r}}_1; \vec{\mathrm{r}}_2; R) + V_e(\vec{\mathrm{r}}_2; \vec{\mathrm{r}}_1; R) + e^2/r_{12} + e^2/R + (\alpha_0 e^2/R^2)(z_1 + z_2) + O(\alpha_0^2) \,. \tag{3.15}$$

However, in Scheme 1 the electron-nuclear attraction terms are given by

$$V_e^{(1)}(\vec{\mathrm{r}}_i; \vec{\mathrm{r}}_j; R) = -e^2 \left[\frac{Z_A}{|\vec{\mathrm{r}}_{Ai} - \frac{1}{2}\alpha_0\vec{\mathrm{r}}_{Aj}|} + \frac{Z_B}{|\vec{\mathrm{r}}_{Bi} + \frac{1}{2}\alpha_0\vec{\mathrm{r}}_{Bj}|} \right] , \tag{3.16a}$$

while in Scheme 2 they are given by

$$V_e^{(2)}(\vec{\mathrm{r}}_i; \vec{\mathrm{r}}_j; R) = -e^2 \left[\frac{Z_A}{|\vec{\mathrm{r}}_{Ai} - \frac{1}{2}\alpha_0\vec{\mathrm{r}}_{Bj}|} + \frac{Z_B}{|\vec{\mathrm{r}}_{Bi} + \frac{1}{2}\alpha_0\vec{\mathrm{r}}_{Aj}|} \right] . \tag{3.16b}$$

In both equations, $\vec{\mathrm{r}}_{Ai} = \vec{\mathrm{r}}_i + \frac{1}{2}\vec{\mathrm{R}}$, $\vec{\mathrm{r}}_{Bi} = \vec{\mathrm{r}}_i - \frac{1}{2}\vec{\mathrm{R}}$, $Z_A = Z_+$, $Z_B = Z_-$.

We must then solve the purely electronic Schrödinger equations

$$h_e(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R)\psi(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R) = \epsilon(R)\psi(\vec{\mathrm{r}}_1, \vec{\mathrm{r}}_2; R) \tag{3.17}$$

for the $X^1\Sigma^+$ ground-state energy and wave function, for each of the two schemes; then we evaluate the ground-state dipole moment $\vec{\mu}_e$ which is the expectation value of the physical quantity $-e(\vec{\rho}_1 + \vec{\rho}_2)$ (old notation); in new notation, the resulting formula is

$$\vec{\mu}_e(X^1\Sigma^+; R) = \alpha_0 e\vec{\mathrm{R}} - 2e\langle \psi^{(1)}(X^1\Sigma^+) \,|\, \vec{\mathrm{r}}_1 \,|\, \psi^{(1)}(X^1\Sigma^+) \rangle \,, \tag{3.18a}$$

for Scheme 1, and simply

$$\vec{\mu}_e(X^1\Sigma^+; R) = -2e\langle \psi^{(2)}(X^1\Sigma^+) \,|\, \vec{\mathrm{r}}_1 \,|\, \psi^{(2)}(X^1\Sigma^+) \rangle \tag{3.18b}$$

for Scheme 2.

B. Method of calculation

We use a variation-perturbation method to solve the electronic eigenvalue problem. Terms in the electronic Hamiltonian of order α_0^2 and higher are neglected.

(1) Perturbation Hamiltonian. For each scheme, the electronic Hamiltonian (3.14) may be written

$$h_e(\vec{r}_1,\vec{r}_2;R)=h_e^0(\vec{r}_1,\vec{r}_2;R)+\alpha_0 h_e'(\vec{r}_1,\vec{r}_2;R) \qquad (3.19)$$

($\alpha_0=1.36\times10^{-4}$ for HD). The zeroth-order part has $D_{\infty h}$ symmetry and is just the Hamiltonian for the homonuclear system (H_2),

$$h_e^0=\frac{\vec{p}_1^{\,2}+\vec{p}_2^{\,2}}{2m}-e^2\sum_{i=1,2}\left[\frac{1}{r_{Ai}}+\frac{1}{r_{Bi}}\right]+\frac{e^2}{r_{12}}+\frac{e^2}{R}\,, \qquad (3.20)$$

the perturbation h_e' has odd *(ungerade)* symmetry in $D_{\infty h}$ (to lowest order in α_0) and creates electrical asymmetry in the system. For scheme 1, h_e' is formally defined

$$\alpha_0 h_e'^{(1)}=\alpha_0\frac{e^2}{R^2}(z_1+z_2)-e^2\sum_{i=1}^{2}\sum_{\substack{j=1\\ j\neq i}}^{2}\left[\frac{Z_A}{|\vec{r}_{Ai}-\frac{1}{2}\alpha_0\vec{r}_{Aj}|}-\frac{1}{r_{Ai}}+\frac{Z_B}{|\vec{r}_{Bi}+\frac{1}{2}\alpha_0\vec{r}_{Bj}|}-\frac{1}{r_{Bi}}\right] \qquad (3.21a)$$

while for Scheme 2

$$\alpha_0 h_e'^{(2)}=\alpha_0\frac{e^2}{R^2}(z_1+z_2)-e^2\sum_{i=1}^{2}\sum_{\substack{j=1\\ j\neq i}}^{2}\left[\frac{Z_A}{|\vec{r}_{Ai}-\frac{1}{2}\alpha_0\vec{r}_{Bj}|}-\frac{1}{r_{Ai}}+\frac{Z_B}{|\vec{r}_{Bi}+\frac{1}{2}\alpha_0\vec{r}_{Aj}|}-\frac{1}{r_{Bi}}\right]. \qquad (3.21b)$$

Terms of order α_0^2 and higher in Eq. (3.15) have been neglected, and we will also neglect some other higher-order terms which appear in the evaluation of matrix elements of Eqs. (3.21). The terms of order α_0^2 have even *(gerade)* symmetry in any case, and can have no effect on the dipole moment; the next odd-symmetry (u) terms are of order α_0^3. The terms of order α_0^2 *do* make a contribution to the ground-state energies $\epsilon(X^1\Sigma^+)$, which we have ignored since they have a negligible influence on the wave function.

(2) Variation-perturbation equations. If we write

$$|\psi(X^1\Sigma^+)\rangle=|\psi_g\rangle+\alpha_0|\psi_u\rangle\,, \qquad (3.22)$$

then the resulting equations for $|\psi_g\rangle$ and $|\psi_u\rangle$ are

$$(h_e^0-\epsilon)|\psi_g\rangle+\alpha_0^2 h_e'|\psi_u\rangle=0\,,$$
$$(h_e^0-\epsilon)|\psi_u\rangle+h_e'|\psi_g\rangle=0\,. \qquad (3.23)$$

These equations are variational in the sense that effects of the first-order term $\alpha_0 h_e'$ are included to all orders. Now we write $|\psi_g\rangle$ and $|\psi_u\rangle$ as expansions in suitable odd- and even-symmetry (g and u) basis sets,

$$|\psi_g\rangle=\sum_{k=1}^{N_g}b_k|g_k\rangle\,,$$
$$|\psi_u\rangle=\sum_{n=1}^{N_u}c_n|u_n\rangle\,; \qquad (3.24)$$

substitution into Eqs. (3.23) leads to a system of coupled equations for the coefficients $\{b_k\},\{c_n\}$:

$$0=\sum_{k=1}^{N_g}b_k(\langle g_l|h_e^0|g_k\rangle-\epsilon\langle g_l|g_k\rangle)+\alpha_0^2\sum_{n=1}^{N_u}c_n\langle g_l|h_\epsilon'|u_n\rangle,\quad l=1,\ldots,N_g \qquad (3.25a)$$

$$0=\sum_{n=1}^{N_u}c_n(\langle u_m|h_e^0|u_n\rangle-\epsilon\langle u_m|u_n\rangle)+\sum_{k=1}^{N_g}b_k\langle u_m|h_e'|g_k\rangle,\quad m=1,\ldots,N_u\,. \qquad (3.25b)$$

If we neglect the terms of order α_0^2 in Eq. (3.25a), the resulting equations are equivalent to a first-order perturbation theory of the wave function: Given a particular (variational) solution for the even *(gerade)* wave function, we solve the inhomogeneous equation (3.25b) for the odd *(ungerade)* component. To compute the dipole moment, we must also evaluate the matrix elements

$$\langle\psi(X^1\Sigma^+)|\vec{r}_1|\psi(X^1\Sigma^+)\rangle=2\alpha_0\langle\psi_u|z_1|\psi_g\rangle=2\alpha_0\sum_{n=1}^{N_u}\sum_{k=1}^{N_g}c_nb_k\times\langle u_n|z_1|g_k\rangle\,. \qquad (3.26)$$

for use in Eq. (3.18).

(3) Expressions for matrix elements of h_e'. In Appendix B we show that the matrix elements of the operators h_e' for each scheme may be evaluated using the following prescriptions:

$$h_e'^{(J)}=e^2\left\{\hat{V}_1^{(J)}+\hat{V}_2^{(J)}+\sum_{i=1}^{2}\left[\frac{z_i}{R^2}-\frac{1}{2}\left[\frac{1}{r_{Ai}}-\frac{1}{r_{Bi}}\right]\right]\right\}, \qquad J=1,2 \qquad (3.27)$$

where (to first order in α_0) the matrix elements of the operator $\hat{V}_i^{(J)}$ are defined as

$$\langle \chi \,|\, \hat{V}_i^{(1)} \,|\, \Phi \rangle = -\tfrac{1}{2} \int\int d\tau_i\, d\tau_j \left[\frac{1}{2} R \left[\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right] \left[\frac{\partial}{\partial z_i} - \frac{\partial}{\partial z_j} \right] + \left[\frac{1}{r_{Ai}} - \frac{1}{r_{Bi}} \right] (\vec{r}_j \cdot \vec{\nabla}_i - \vec{r}_i \cdot \vec{\nabla}_j) \right] \chi^*(1,2) \Phi(1,2) \tag{3.28a}$$

for Scheme 1, and by

$$\langle \chi \,|\, \hat{V}_i^{(2)} \,|\, \Phi \rangle = -\tfrac{1}{2} \int\int d\tau_i\, d\tau_j \left[-\frac{1}{2} R \left[\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}} \right] \left[\frac{\partial}{\partial z_i} + \frac{\partial}{\partial z_j} \right] + \left[\frac{1}{r_{Ai}} - \frac{1}{r_{Bi}} \right] (\vec{r}_j \cdot \vec{\nabla}_i - \vec{r}_i \cdot \vec{\nabla}_j) \right] \chi^*(1,2) \Phi(1,2) \tag{3.28b}$$

for Scheme 2. In both cases it is understood that $j \neq i$, that the product of the functions $(\chi^* \Phi)$ has odd *(ungerade)* symmetry and that it is nonnegligible only for $r_i, r_j \ll \alpha_0^{-1}$.

IV. DISCUSSION

Figure 1 shows the HD dipole moment function $\mu_e(R)$ vs R obtained from the calculations described in the paper[14] following this. It is also the dipole moment function for HT and for DT, provided it is rescaled by the factors 1.329 32 and 0.332 12, respectively.

The dipole moment function obtained by Ford and Browne[8] is shown for comparison. There is a small but significant difference between their results (and those of Bunker[5]) and ours. While we cannot prove conclusively that our results have completely converged, the stability of our dipole moment to further augmentation of the basis set near R_e, and the close agreement of the values from Schemes 1 and 2 suggests that this is the case. We note that in the vibronic perturbation calculations, certain vibronic energy differences were replaced by average values for the electronic term difference in question, in order to close sums over vibrational states. This could perhaps be a source of error sufficiently large to account for the discrepancy with our results.

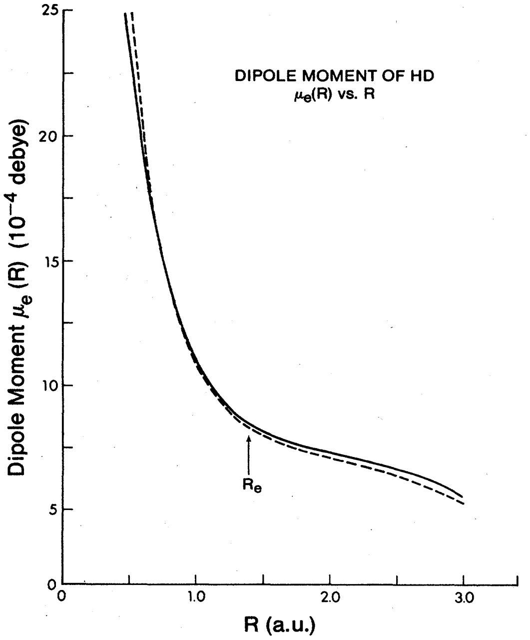

FIG. 1. Dipole moment function $\mu_e(R)$ (in debye) vs internuclear distance R (in a.u.), for HD ($X\,^1\Sigma^+$). Solid curve, results obtained in this work (cf. paper immediately following for details); dashed curve, dipole moment function computed by Ford and Browne (based on vibronic perturbation theory).

In any event the relatively good agreement between these two widely disparate theoretical calculations may be taken to establish the value of the HD permanent dipole moment reliably as over against the older experimental result reported by Trefler and Gush.[10] Within its larger error limits, the more sophisticated and careful recent work by Nelson and Tabisz[13] yields a result in reasonable agreement with the theory.

The main interest in this present work, however, lies in the simpler perspective that it gives us on the origin of these isotopic dipole moments. We see that it is not at all necessary to invoke nonadiabatic or "rovibronic" perturbations to understand the HD dipole moment; it arises directly from asymmetry of the electronic Hamiltonian, provided that we cast that Hamiltonian in an appropriate set of canonical coordinates. The model of this Hamiltonian as having a pair of nuclei with slightly different effective charges is particularly pleasing, since we can link that directly to the orbital-size and binding-energy effects which we know must be associated with the difference in electronic reduced masses for D and for H. The "axial electric field" term is less obvious in meaning but its effect is in the same direction as that of the effective charges. By contrast, one of the real drawbacks of the vibronic perturbation approach is the fact that its ⊥ and || coupling contributions are large and opposite in sign, so that it is not obvious at the outset even what sense the dipole moment must have.

There still remains a small gap in our understanding of the HD dipole moment. We have not tied our calculations directly and rigorously to the arguments about electronic reduced masses which we gave at the beginning of this paper and which we would put forward as the best pedagogical explanation of the problem. We settled for an orthogonal transformation referring electron coordinates to the geometric center of the nuclear system rather than to its center of mass, and the asymmetry then appeared in the potential rather than in the kinematic Hamiltonian. In principle, it would be still more elegant to carry out a transformation which does in fact generate a local electronic reduced mass as a direct feature of the electronic

Hamiltonian. In principle, such a transformation could be achieved, by using the "switching function" approach formalized by Thorson and Delos[27] for the treatment of electronic excitation and charge transfer in slow atom-atom and ion-atom collisions. In practice, it appeared to us that such an approach would have been formidably difficult to carry out accurately.

We may remark that at certain points in our discussion of the electronic model Hamiltonians of Schemes 1 and 2, the reader might feel assailed (as we did) by doubts about the "physical reality" of the "molecules" pictured by these models. Of course, such doubts are the result mainly of unfamiliarity with alternate viewpoints; the same difficulties had to be overcome when one first encountered, in Newtonian mechanics, the proposal that the system of two "real particles" with only mutual interaction be considered *physically equivalent* to a system of two "fictitious particles" whose coordinates are those of the center of mass and the relative motion of the former pair. As long as we do not break up the system into its "real components" by some external intervention device, both viewpoints are *equally real.*

The canonical-transformation strategies adopted in this work stimulate curiosity whether they might lead to useful progress on the general three- or four-body mechanics for bound states of such systems as the muonium molecular ion (i.e., μ^- plus two protons). This may be true, but enthusiasm for this should be tempered by the recognition that simplicity of the present work rests heavily on the very small size of the perturbing parameter α_0, and consequent ability to truncate to first-order terms alone. If consideration of higher-order terms must be made, many additional complications will have to be faced.

ACKNOWLEDGMENT

Support of this research through an Operating Grant from the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

APPENDIX A: A SIMPLE MODEL FOR THE DIPOLE MOMENT OF HD

In this model calculation the dipole moment of HD arises from the difference in electronic reduced masses for deuterium and hydrogen. There are two effects: (1) since D(1s) has a lower energy than H(1s), the ionic configuration H^+D^- is slightly favored over H^-D^+ in the HD ground state; (2) since the D(1s) orbital is slightly smaller, the two-center overlap distribution is skewed in the sense H^+D^-. Both the differential binding energy and orbital size effects are directly related to the parameter $\alpha_0=\frac{1}{2}\lambda m/\mu=1.36\times10^{-4}$ appearing throughout this paper: to first order in α_0

$$\epsilon[\mathrm{H}(1s)]-\epsilon[\mathrm{D}(1s)]=\alpha_0(\mathrm{a.u.}) \tag{A1}$$

and the D(1s) and H(1s) orbital exponents (in a.u.) are

$$\zeta_{\mathrm{D}}=1+\tfrac{1}{2}\alpha_0,\quad \zeta_{\mathrm{H}}=1-\tfrac{1}{2}\alpha_0\ . \tag{A2}$$

Our trial wave function is

$$|\Psi\rangle=|\Psi_0\rangle+\alpha_0 b\,|\Psi_1\rangle \tag{A3a}$$

where

$$\begin{aligned}|\Psi_0\rangle=N_0\{&[\phi_{1s\mathrm{D}}(1)\phi_{1s\mathrm{H}}(2)+\phi_{1s\mathrm{H}}(1)\phi_{1s\mathrm{D}}(2)]\\&+\bar{a}[\phi_{1s\mathrm{D}}(1)\phi_{1s\mathrm{D}}(2)+\phi_{1s\mathrm{H}}(1)\phi_{1s\mathrm{H}}(2)]\}\end{aligned} \tag{A3b}$$

and

$$|\psi_1\rangle=N_1[\phi_{1s\mathrm{D}}(1)\phi_{1s\mathrm{D}}(2)-\phi_{1s\mathrm{H}}(1)\phi_{1s\mathrm{H}}(2)] \tag{A3c}$$

are separately normalized components. The differential contribution of the two ionic configurations is measured directly by the coefficient of $|\psi_1\rangle$, while (to order α_0) the skewing effect of differential orbital size appears as a small dipole moment of the zero-order state $|\psi_0\rangle$.

Calculation of the dipole moment $\vec{\mu}_e$ yields the result

$$\begin{aligned}\vec{\mu}_e(R)=4eN_0^2\{&\alpha_0 b(N_1/N_0)(\bar{a}+S)\vec{\mathrm{R}}\\&-[S(1+\bar{a}^2)+2\bar{a}]\vec{\gamma}\}\end{aligned} \tag{A4}$$

where S is the overlap integral $\langle\phi_{1s\mathrm{D}}|\phi_{1s\mathrm{H}}\rangle$ and $\vec{\gamma}$ is the overlap moment,

$$\begin{aligned}\vec{\gamma}&=+\langle\phi_{1s\mathrm{H}}|\vec{\mathrm{r}}|\phi_{1s\mathrm{D}}\rangle\\&=-\tfrac{1}{4}\alpha_0\vec{\mathrm{R}}e^{-R}(1+R+\tfrac{2}{5}R^2+\tfrac{1}{15}R^3)\ .\end{aligned} \tag{A5}$$

It then remains to compute the coefficient b; using the variation-perturbation method, we find, to lowest order in α_0,

$$\alpha_0 b=\frac{-\frac{1}{2}(\langle\Psi_0|H|\Psi_1\rangle+\langle\Psi_1|H|\Psi_0\rangle)}{\langle\Psi_1|H|\Psi_1\rangle-\langle\Psi_0|H|\Psi_0\rangle}\ . \tag{A6}$$

In evaluating the matrix elements in Eq. (A6), only the lowest-order nonvanishing terms need be kept. These are of zero order in the denominator and first order in α_0 in the numerator. To evaluate the matrix elements, we write

$$H=h_0(1)+h_0(2)+e^2/r_{12}+e^2/R\ , \tag{A7}$$

with special operator rules for the one-electron Hamiltonian:

$$\begin{aligned}h_0|\phi_{1s\mathrm{D}}\rangle&=\epsilon_{1s\mathrm{D}}|\phi_{1s\mathrm{D}}\rangle-(e^2/r_{\mathrm{H}})|\phi_{1s\mathrm{D}}\rangle\ ,\\h_0|\phi_{1s\mathrm{H}}\rangle&=\epsilon_{1s\mathrm{H}}|\phi_{1s\mathrm{H}}\rangle-(e^2/r_{\mathrm{D}})|\phi_{1s\mathrm{H}}\rangle\ .\end{aligned} \tag{A8}$$

The numerator of Eq. (A6) is given explicitly by

$$-\tfrac{1}{2}(\langle\Psi_0|H\,|\Psi_1\rangle+\langle\Psi_1|H\,|\Psi_0\rangle)$$

$$=2N_0N_1\left\{(\bar{a}+s)\left[(\epsilon_{1s\mathrm{H}}-\epsilon_{1s\mathrm{D}})+\left[\left\langle 1s\mathrm{D}\left|\frac{1}{r_\mathrm{H}}\right|1s\mathrm{D}\right\rangle-\left\langle 1s\mathrm{H}\left|\frac{1}{r_\mathrm{D}}\right|1s\mathrm{H}\right\rangle\right]\right]\right.$$

$$-\frac{\bar{a}}{2}\left[\left\langle 1s\mathrm{D}(1)1s\mathrm{D}(2)\left|\frac{1}{r_{12}}\right|1s\mathrm{D}(1)1s\mathrm{D}(2)\right\rangle-\left\langle 1s\mathrm{H}(1)1s\mathrm{H}(2)\left|\frac{1}{r_{12}}\right|1s\mathrm{H}(1)1s\mathrm{H}(2)\right\rangle\right]$$

$$\left.-\left[\left\langle 1s\mathrm{D}(1)1s\mathrm{H}(2)\left|\frac{1}{r_{12}}\right|1s\mathrm{D}(1)1s\mathrm{D}(2)\right\rangle-\left\langle 1s\mathrm{H}(1)1s\mathrm{D}(2)\left|\frac{1}{r_{12}}\right|1s\mathrm{H}(1)1s\mathrm{H}(2)\right\rangle\right]\right\} \tag{A9a}$$

$$=2\alpha_0N_1N_0\{(\bar{a}+s)[1+(1+2R)e^{-2R}]-\tfrac{5}{16}\bar{a}-2Y\}\ , \tag{A9b}$$

where Y is given by the expression

$$Y=R^{-1}e^{-R}[(-\tfrac{63}{64}+\tfrac{43}{32}R+\tfrac{5}{16}R^2+\tfrac{1}{6}R^3)$$

$$+e^{-2R}(\tfrac{63}{64}+\tfrac{25}{32}R+\tfrac{3}{16}R^2)]\ . \tag{A9c}$$

Evaluation of the matrix elements in the denominator of Eq. (A6) is straightforward. The state $|\Psi_0\rangle$ is in fact just the model wave function for the hydrogen molecule ground state studied in 1949 by Coulson and Fischer.[28]

Figure 2 gives the resulting model dipole moment function versus R. While this model is too crude for quantitative predictions (except perhaps for $R \gg R_e$), it obviously shows that the HD dipole moment can be understood without appealing to nonadiabatic perturbations as an explanation.

APPENDIX B: MATRIX ELEMENTS OF PERTURBATION h_e'

Matrix elements of the operators $\hat{V}_e^{(1)},\hat{V}_e^{(2)}$ defined in Eqs. (3.16a) and (3.16b) must be evaluated carefully. For example, consider a matrix element arising from the first term of (3.16a):

$$-Z_A\int\int d^2r_id^3r_j\chi^*(1,2)\left[\frac{1}{|\vec{\mathrm{r}}_{Ai}-\tfrac{1}{2}\alpha_0\vec{\mathrm{r}}_{Aj}|}\right]\Phi(1,2)\ , \tag{B1}$$

where $\chi(1,2)$ and $\Phi(1,2)$ are arbitrary (L^2-type) basis functions. Since the location of the Coulomb singularity is not fixed in either $\vec{\mathrm{r}}_{Ai}$ or $\vec{\mathrm{r}}_{Aj}$ space, neither multipole expansion nor numerical quadrature can be accurate or convergent. To solve the problem, we transform the integration variables to a new set,

$$\vec{\mathrm{r}}'_{Ai}=\cos\gamma_0\vec{\mathrm{r}}_{Ai}-\sin\gamma_0\vec{\mathrm{r}}_{Aj}\ ,$$
$$\vec{\mathrm{r}}'_{Aj}=\cos\gamma_0\vec{\mathrm{r}}_{Aj}+\sin\gamma_0\vec{\mathrm{r}}_{Ai}\ , \tag{B2}$$

where $\tan\gamma_0=\tfrac{1}{2}\alpha_0$. Since the transformation is orthogonal, its Jacobian is unity and the integral becomes

$$-Z_A\int\int d^3r'_{Ai}d^3r'_{Aj}\left[\frac{1}{r'_{Ai}}\right](\chi^*\Phi)\ ;$$

now the only remaining task is to reexpress $(\chi^*\Phi)$ as explicit function of the new variables. Taking advantage of the small size of α_0, we use the Taylor expansion:

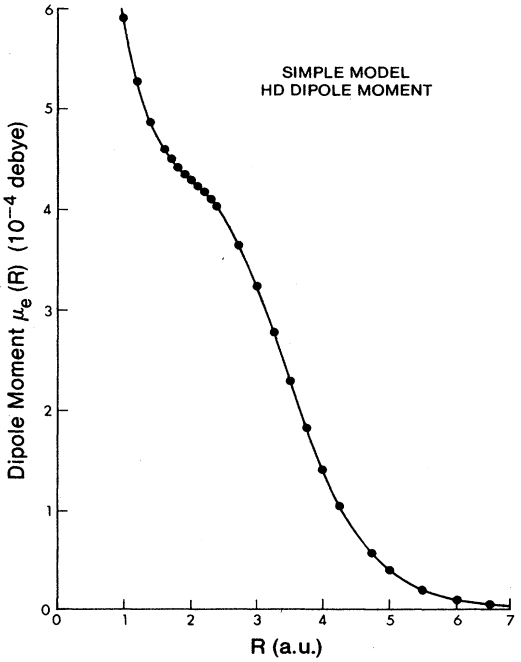

FIG. 2. Dipole moment function $\mu_e(R)$ (debye) vs R (a.u.) for HD ($X^1\Sigma^+$), obtained using crude model calculation described in Appendix A.

$$F(\vec{r}_{Ai},\vec{r}_{Aj};\vec{R})=F(\vec{r}\,'_{Ai},\vec{r}\,'_{Aj};\vec{R})+(\vec{r}_{Ai}-\vec{r}\,'_{Ai})\cdot\vec{\nabla}_{r'_{Ai}}F(\vec{r}\,'_{Ai},\vec{r}\,'_{Aj};\vec{R})+(\vec{r}_{Aj}-\vec{r}\,'_{Aj})\cdot\vec{\nabla}_{r'_{Aj}}F(\vec{r}\,'_{Ai},\vec{r}\,'_{Aj};\vec{R})+\cdots \tag{B3}$$

(where $F=\chi^*\Phi$). Since

$$\vec{r}_{Ai}-\vec{r}\,'_{Ai}=(\cos\gamma_0-1)\vec{r}\,'_{Ai}+\sin\gamma_0\vec{r}_{Aj'},\ \vec{r}_{Aj}-\vec{r}_{Aj'}=(\cos\gamma_0-1)\vec{r}\,'_{Aj}-\sin\gamma_0\vec{r}\,'_{Ai}\ , \tag{B4}$$

we find

$$F(\vec{r}_{Ai},\vec{r}_{Aj};\vec{R})=F(\vec{r}\,'_{Ai},\vec{r}\,'_{Aj};\vec{R})+\tfrac{1}{2}\alpha_0(\vec{r}\,'_{Aj}\cdot\vec{\nabla}_{r'_{Ai}}-\vec{r}\,'_{Ai}\cdot\vec{\nabla}_{r'_{Aj}})F+O(\alpha_0^2)\ . \tag{B5}$$

If we retain explicitly only up through linear terms in α_0, the original integral (B1) now reduces to the expression

$$-(1+\tfrac{1}{2}\alpha_0)\left\langle\chi\left|\frac{1}{r_{Ai}}\right|\Phi\right\rangle-\tfrac{1}{2}\alpha_0\int\int d^3r_i d^3r_j\left[\frac{1}{r_{Ai}}\right](\vec{r}_{Aj}\cdot\vec{\nabla}_i-\vec{r}_{Ai}\cdot\vec{\nabla}_j)(\chi^*\Phi) \tag{B6}$$

(we have dropped the primes on the dummy integration variables). For the corresponding interaction with nucleus B [second term in Eq. (3.16a)] we find, using a similar technique,

$$-Z_B\int\int d^3r_i d^2r_j\chi^*\left[\frac{1}{|\vec{r}_{Bi}+\frac{1}{2}\alpha_0\vec{r}_{Bj}|}\right]\Phi=-(1-\tfrac{1}{2}\alpha_0)\left\langle\chi\left|\frac{1}{r_{Bi}}\right|\Phi\right\rangle$$
$$+\tfrac{1}{2}\alpha_0\int\int d^3r_i d^3r_j\left[\frac{1}{r_{Bi}}\right](\vec{r}_{Bj}\cdot\vec{\nabla}_i-\vec{r}_{Bi}\cdot\vec{\nabla}_j)(\chi^*\Phi)\ . \tag{B7}$$

Noting now that $\vec{r}_{Ai}=\vec{r}_i+\frac{1}{2}\vec{R}$, $\vec{r}_{Bi}=\vec{r}_i-\frac{1}{2}\vec{R}$, subtracting the zero-order terms are required by Eq. (3.21a), and adding on the "constant electric field" terms arising from the nuclear repulsion, we obtain the result summarized by Eqs. (3.27) and (3.28a). A derivation of Eq. (3.28b) proceeds in the same way.

The condition of validity for these results is evidently that the Taylor expansion be accurate when truncated at the first-order term, i.e., that the product $(\chi^*\Phi)$ be nonnegligible only for distances $(r_{Ai},r_{Aj},r_{Bi},r_{Bj},R)\ll(\alpha_0^{-1})$. This will always be true for the basis functions and conditions studied here.

APPENDIX C: EQUIVALENCE OF RATIONALIZATION SCHEMES

We prove here that the two rationalization schemes we have developed give equivalent physical descriptions of the HD dipole moment, within the limiting assumptions (variation-perturbation treatment, terms up to first order in α_0, and $\alpha_0 R\ll 1$): i.e., the value obtained for the dipole moment $\vec{\mu}_e$ is the same for both schemes, provided the problem is solved in the complete Hilbert space.

Considering the two electronic Hamiltonians,

$$h_e^{(1)}=h_e^0+\alpha_0 h_e'^{(1)}\ ,$$
$$h_e^{(2)}=h_e^0+\alpha_0 h_e'^{(2)}\ , \tag{C1}$$

we must solve the eigenvalue problem for each case,

$$h_e^{(J)}|\Psi^{(J)}\rangle=\epsilon^{(J)}|\Psi^{(J)}\rangle \tag{C2}$$

by the variation-perturbation method. To do so, we write

$$|\Psi^{(J)}\rangle=|\Psi_g^0\rangle+\alpha_0|\Psi_u^{(J)}\rangle\ , \tag{C3}$$

where $|\Psi_g^0\rangle$ is the *(gerade)* solution of the zero-order problem

$$h_e^0|\Psi_g^0\rangle=\epsilon_j^0(R)|\Psi_g^0\rangle\ . \tag{C4}$$

To determine $|\Psi_u^{(J)}\rangle$ we solve the inhomogeneous equation

$$(h_e^0-\epsilon_g^0)|\Psi_u^{(J)}\rangle=-h_e'^{(J)}|\Psi_g^0\rangle\ ; \tag{C5}$$

if we expand in a complete set of *(ungerade)* eigenstates of h_e^0,

$$|\Psi_u^{(J)}\rangle=\sum_n c_n|\Psi_{nu}^0\rangle\ , \tag{C6}$$

then we find

$$c_n=-\frac{\langle\Psi_{nu}^0|h_e'^{(J)}|\Psi_g^0\rangle}{\epsilon_{nu}^0-\epsilon_g^0} \tag{C7}$$

and without loss of generality we may take c_n to be real.

Given the above, we wish to prove that Eqs. (3.18a) and (3.18b) are equivalent, i.e.,

$$-e\langle\Psi^{(2)}|(\vec{r}_1+\vec{r}_2)|\Psi^{(2)}\rangle+e\langle\Psi^{(1)}|(\vec{r}_1+\vec{r}_2)|\Psi^{(1)}\rangle=\alpha_0 e\vec{R} \tag{C8}$$

(of course only the z component is nonzero). From Eqs. (C3), (C6), and (C7) we obtain

$$-e\langle\Psi^{(J)}|(z_1+z_2)|\Psi^{(J)}\rangle=\alpha_0 e\left[\left\langle\Psi_g^0\left|h_e'^{(J)}\frac{1}{h_e^0-\epsilon_g^0}(z_1+z_2)\right|\Psi_g^0\right\rangle+\left\langle\Psi_g^0\left|(z_1+z_2)\frac{1}{h_e^0-\epsilon_g^0}h_e'^{(J)}\right|\Psi_g^0\right\rangle\right]\ ; \tag{C9}$$

then the result to be proved is that

$$\alpha_0 e\left[\left\langle\Psi_g^0\left|\left[(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\frac{1}{h_e^0-\epsilon_g^0}(z_1+z_2)+(z_1+z_2)\frac{1}{h_e^0-\epsilon_g^0}(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\right]\right|\Psi_g^0\right\rangle\right]=\alpha_0 eR\ . \qquad \text{(C10)}$$

Now we can insert the complete set of *ungerade* eigenstates of h_e^0 into these matrix elements; the left-hand side of (C10) becomes

$$\alpha_0 e\sum_n\left[\langle\Psi_g^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\,|\,\Psi_{nu}^0\rangle\frac{1}{\epsilon_{nu}^0-\epsilon_g^0}\langle\Psi_{nu}^0\,|\,(z_1+z_2)\,|\,\psi_g^0\rangle\right.$$
$$\left.+\langle\Psi_g^0\,|\,(z_1+z_2)\,|\,\Psi_{nu}^0\rangle\frac{1}{\epsilon_{nu}^0-\epsilon_g^0}\langle\Psi_{nu}^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\,|\,\Psi_g^0\rangle\right]. \qquad \text{(C11)}$$

From Eqs. (3.28a) and (3.28b) we have the result

$$\langle\Psi_{nu}^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\,|\,\Psi_g^0\rangle=\int\int d\tau_1 d\tau_2\sum_{i=1}^{2}\left[\frac{e^2R}{2}\left[\frac{1}{r_{Ai}}+\frac{1}{r_{Bi}}\right]\frac{\partial}{\partial z_i}\right](\Psi_{nu}^{0*}\Psi_g^0)\ ; \qquad \text{(C12)}$$

integration by parts (over z_i) yields the result

$$\langle\Psi_{nu}^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})/\Psi_g^0\rangle=-\frac{R}{2}\sum_{i=1}^{2}\int\int d\tau_1 d\tau_2\Psi_{nu}^{0*}\Psi_g^0\left[\frac{\partial}{\partial z_i}\left[\frac{e^2}{r_{Ai}}+\frac{e^2}{r_{Bi}}\right]\right]. \qquad \text{(C13)}$$

But it is easily shown that

$$-\sum_{i=1}^{2}\frac{\partial}{\partial z_i}\left[\frac{e^2}{r_{Ai}}+\frac{e^2}{r_{Bi}}\right]=\left[\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right],h_e^0\right] \qquad \text{(C14)}$$

so it follows that

$$\langle\Psi_{nu}^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\,|\,\Psi_g^0\rangle=\frac{R}{2}(\epsilon_g^0-\epsilon_{nu}^0)\left\langle\Psi_{nu}^0\left|\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]\right|\Psi_g^0\right\rangle\ ; \qquad \text{(C15a)}$$

similarly,

$$\langle\Psi_g^0\,|\,(h_e^{\prime\,(2)}-h_e^{\prime\,(1)})\,|\,\Psi_{nu}^0\rangle=\frac{R}{2}(\epsilon_{nu}^0-\epsilon_g^0)\left\langle\Psi_g^0\left|\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]\right|\Psi_{nu}^0\right\rangle\ . \qquad \text{(C15b)}$$

Substitution of these equations into Eq. (C11) gives us

$$\alpha_0 e\left[\frac{R}{2}\right]\sum_n\left[\left\langle\Psi_g^0\left|\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]\right|\Psi_{nu}^0\right\rangle\langle\Psi_{nu}^0\,|\,(z_1+z_2)\,|\,\Psi_g^0\rangle-\langle\Psi_g^0\,|\,(z_1+z_2)\,|\,\Psi_{nu}^0\rangle\left\langle\Psi_{nu}^0\left|\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right]\right|\Psi_g^0\right\rangle\right]$$
$$=\tfrac{1}{2}\alpha_0 eR\left\langle\Psi_g^0\left|\left[\left[\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right],(z_1+z_2)\right]\right|\Psi_g^0\right\rangle \qquad \text{(C16)}$$

and since the indicated commutator is just equal to 2, this reduces exactly to the result required in Eq. (C10). To prove the theorem, we needed only to insert a complete set of *ungerade* eigenstates of h_e^0, i.e., the completeness of the *ungerade* Hilbert space available to us. On the other hand, no comparable assumptions were required for the *gerade* space.

It follows that agreement of the results from the two schemes is a *necessary* condition for the adequacy of the *ungerade* basis set used in a calculation, but it does *not* prove that the result then obtained for $\vec{\mu}_e$ has converged to the correct value. Nevertheless this does serve as at least some test of basis adequacy.

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[15] J. P. Davis and W. R. Thorson, Can. J. Phys. **56**, 996 (1978) have shown that to treat collision problems in isotopically asymmetric systems (e.g., $H + D^+$, $H^+ + D$), it is important to use a representation in which these terms do not appear, since they introduce couplings which can be shown to be fictitious in a truncated subspace treatment. The present work was stimulated by discussions with P. R. Bunker, who pointed out that since it is just these terms which generate the HD dipole moment in the usual treatments, the sense in which they are "fictitious" must be carefully defined.

[16] We take the view that the theoretical values obtained in this work or in the calculations of Refs. 5—8 are more accurate than the experimental value reported by Trefler and Gush (Ref. 10). An explanation of the error in the result of Trefler and Gush has been given in Refs. 17—19.

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[23] Such approximations would *not* be adequate for the discussion of spectroscopic energies. A correct theory of HD, HT, etc., can be formulated using our approach, and it would give most features of the spectra arising from the asymmetry more directly than the nonadiabatic perturbation approach. To do this however we would need to keep track of reduced masses more carefully, and also consistently retain all terms in the electronic Hamiltonian to order α_0^2 (not done here).

[24] Formally, this perturbation could produce spurious "field ionization" effects at large negative z $(\sim -\alpha_0^{-1})$. However, within the tightly bound basis set used here, no such effects appear; we have proved this by convergence studies in the HD^+ system.

[25] Since the internuclear coordinate $\vec{\xi}$ is *held fixed*, such a transformation does not affect the *electronic* eigenvalue problem.

[26] As P. R. Bunker [Chem. Phys. Lett. **27**, 322 (1974)] has pointed out, this tiny moment is not the one of significant interest for spectroscopic study of HD^+, since the center of mass and the center of charge in the ion are much more grossly separated, by $\frac{1}{2}\lambda R$.

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