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Adiabatic theory of symmetry breaking and dipole moments of isotopic molecules. Correct dissociation of their electronic and muonic ions

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To calculate the nonzero dipole moment of isotopic molecules such as HD or the correct dissociation limit of ions such as HD^+ via the usual approach requires cumbersome, expansive nonadiabatic corrections to the Born-Oppenheimer approximation. Such a complication is herein shown unnecessary; the "best adiabatic" approximation of Pack and Hirschfelder [J. Chem. Phys. **52**, 521 (1970)] provides a single straightforward formalism which gives such effects correctly and yet retains the potential energy curve concept. Simple example calculations show the size of these symmetry-breaking effects to be at the level of high-resolution spectroscopy for HD^+ but very large in ions such as $dt\mu$, which contains a deuteron, a triton, and a negative muon.

I. INTRODUCTION

Symmetric diatomic molecules such as H_2 and D_2 have zero dipole moments and a dipole-forbidden vibration-rotation spectrum, but isotopically mixed molecules such as HD are known to be slightly polar; that is, they have a small permanent dipole moment and an observable dipole-allowed infrared vibration-rotation spectrum.[1-3] However, the usual Born-Oppenheimer (BO) approximation, in which the nuclear masses are taken to be infinite while the electronic motion is treated, gives a zero dipole moment for HD. Furthermore, the usual adiabatic approximation, which only includes first-order energy corrections to the BO approximation, does not break the symmetry and also gives a zero dipole moment. In most previous calculations it has been necessary to go to higher-order perturbation theory or, equivalently, to use a complicated, expensive nonadiabatic formulation to get a nonzero dipole moment.[4-9] In addition, nonadiabatic calculations only yield dipole matrix elements; further approximations[8] are required before a dipole moment function can be extracted.

Similarly, because of reduced mass effects, the D atom has a lower ground-state energy than the H atom, and when a ground-state HD^+ ion dissociates adiabatically (i.e., with the nuclei moving slowly enough that the electron has time to adjust), the proper products are H^+ and D. In contrast, the usual BO and adiabatic[10] approximations dissociate to an equal mixture of $H^+ + D$ and $H + D^+$. The most accurate treatments of HD^+ to date have involved complicated nonadiabatic perturbation methods[11] which nonetheless only approximately correct this dissociation error. Since H and D differ in energy by only 0.0037 eV (29.8 cm^{-1}), the HD^+ dissociation error is small, but a correct treatment of dissociation is likely to be necessary to reproduce forthcoming[12] high-resolution spectra of the high-lying vibration-rotation states of HD^+. Furthermore, when one considers molecular ions containing negative μ mesons, such as $dt\mu$ (we use lower case letters for the particles and upper case letters for atoms containing nuclei and electrons, so that D is de, etc.), which is important in muon-catalyzed fusion, one finds that $d\mu$ and $t\mu$ differ in energy by 48 eV, and proper treatment of the dissociation is essential.

Ponomarev and co-workers[13] have done extensive calculations on $dt\mu$ and similar ions and have recognized this problem. Although they call their method "adiabatic," it is actually a nonadiabatic coupled-channel method for the nuclear motion in which an expansion is made in a large number of BO adiabatic muonic states. These BO adiabatic basis functions have neither the correct dissociation nor the correct orbital exponents at large separations, and that could well be responsible for some of the slow convergence experienced.[13]

Some efforts have recently been made to incorporate the effects just discussed within an adiabatic theory. Guryanov and Rebane[14] and Thorson, Choi, and Knudson[15] have used coordinate transformations to shift the asymmetry in the nuclear masses from the kinetic to the potential energy and have shown that such an approach allows calculation of the correct dipole moment function of molecules such as HD within an adiabatic approximation. However, the complicated coordinates and resulting potential necessitated perturbation expansions which are probably too complicated and slowly convergent to be convenient for muonic systems[15] and do not completely correct the dissociation limit of ions such as HD^+ in low order.[14]

The present work shows that these symmetry-breaking effects are included in the "best adiabatic" (BA) approximation of Pack and Hirschfelder;[16-18] direct variational solution of the BA equation gives such effects exactly to all orders. It is also shown that the BA equations are a straightforward generalization of the usual BO equations and can be solved by the usual quantum chemistry techniques.

In previous work it was shown that the BA approximation handles rotation and rotational degeneracies exactly[16,17] and gives correct decoupling of angular momenta in dissociation.[18] In that work the best adiabatic approximation was variationally defined[17] to give the lowest energies possible with the full Hamiltonian and a product wave function. Hence it gives *the best adiabatic approximation to bound-state energy eigenvalues.* We note here as noted elsewhere[17] that, because the BA approximation gives very narrowly avoided curve crossings, it may often *not* be the best zeroth-order approximation to use in treating dynamical processes involving such curve crossings. Rather, some more diabatic approach may be appropriate.

In the next section of this paper the derivation of the BA approximation is reviewed to show where the symmetry-breaking terms arise. The general theory is given for an N-electron or N-muon diatomic molecule. Then, in Sec. III the one electron or one muon case is considered to clarify the details. There the method is applied to a simple illustrative example, and it is found that the symmetry-breaking, dipole, and dissociation effects can all be demonstrated with a simple minimum-basis-set calculation. Section IV contains our conclusions.

II. BEST ADIABATIC APPROXIMATION

A. Theory

Let us consider a system composed of two nuclei a and b and N negatively charged particles. For simplicity we call the negative particles "electrons," but their mass is kept arbitrary so that they may equally well be muons. It is assumed for simplicity that all the negative particles are identical; the generalization to a molecule containing *both* electrons and muons is straightforward.

The nonrelativistic Hamiltonian is used herein, but relativistic corrections can be added as desired.[16] We also use a center-of-mass-relative coordinate system with $\mathbf{R}$ being the vector from a to b and the coordinates of the electrons being measured from the center of mass of the nuclei (CMN). One can just as well formulate everything with the electronic coordinates relative to the geometric center of the nuclei (GCN),[16] but that gives a more complicated-looking Hamiltonian, and we adopt the CMN system as a matter of personal preference; for $N=1$ the CMN system reduces to familiar Jacobi coordinates.

After separation of the center-of-mass motion the Hamiltonian is[16]

$$H'=\frac{1}{2\mu_{ab}}\mathbf{p}_R^2+\frac{1}{2m}\sum_{k=1}^{N}\mathbf{p}_k^2+\frac{1}{2m_{ab}}\mathbf{P}^2+V(\{\mathbf{r}_k\},R)\ , \quad (1)$$

where each of the N electrons has mass m, $m_{ab}=m_a+m_b$, and $\mu_{ab}=m_a m_b/m_{ab}$. Here V is the total Coulombic potential energy of all the particles, and $\mathbf{P}$,

$$\mathbf{P}=\sum_{k=1}^{N}\mathbf{p}_k\ , \quad (2)$$

is the total momentum of the negative particles relative to the nuclei; the term in (1) involving $\mathbf{P}^2$ is usually called the mass polarization. Use of spherical polar coordinates for $\mathbf{R}$ allows H' to be written as

$$H'=-\frac{\hbar^2}{2\mu_{ab}R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}+H_i\ , \quad (3)$$

where the "internal" Hamiltonian is

$$H_i=\frac{\mathbf{L}_R^2}{2\mu_{ab}R^2}+\frac{1}{2m}\sum_{k=1}^{N}\mathbf{p}_k^2+\frac{1}{2m_{ab}}\mathbf{P}^2+V\ . \quad (4)$$

Now, let us briefly sketch the BA approximation. This discussion will aim at simplicity and clarity; a more rigorous variational derivation was given in Ref. 17. It is assumed that the eigenfunctions Ψ of H' can be represented approximately by the product form,

$$\Psi\cong R^{-1}\chi(R)\Phi(\{\mathbf{r}_k\},\hat{\mathbf{R}};R)\ . \quad (5)$$

The factor of R^{-1} is just to simplify the nuclear kinetic energy and Jacobian. It should be noted that, in contrast to the BO approximation, χ *here depends only on the internuclear distance* R. All dependence on the angles $\hat{\mathbf{R}}=(\theta_R,\varphi_R)$ of $\mathbf{R}$ is contained in the *internal* wave function Φ, which is chosen to be normalized at all R,

$$1=\langle\Phi\,|\,\Phi\rangle_i\equiv\int\Phi^*\Phi\,d\mathbf{r}_1\cdots d\mathbf{r}_N d\hat{\mathbf{R}}\ , \quad (6)$$

so that the subscript i on the bracket implies integration over *internal* coordinates. Thus, with Eq. (6), $\Phi(\{\mathbf{r}_k\},\hat{\mathbf{R}};R)$ depends fully on $\hat{\mathbf{R}}$ but only parametrically on R.

With ansatz (5) the expected energy is thus

$$\begin{aligned}E&=\langle\Psi\,|\,H'\,|\,\Psi\rangle\\&=\langle\chi\Phi\,|\,H\,|\,\chi\Phi\rangle\ ,\end{aligned} \quad (7)$$

where now the Hamiltonian and Jacobian simplify to

$$H=-\frac{\hbar^2}{2\mu_{ab}}\frac{\partial^2}{\partial R^2}+H_i\ , \quad (8)$$

and

$$\langle\chi\Phi\,|\,H\,|\,\chi\Phi\rangle=\int(\chi\Phi)^*H\chi\Phi\,d\mathbf{r}_1\cdots d\mathbf{r}_N d\hat{\mathbf{R}}\,dR\ . \quad (9)$$

Substituting Eq. (8) into (7) and using the fact that, with this Jacobian, the operator $-i\hbar\partial/\partial R$ is Hermitian for bound states, one obtains

$$\begin{aligned}E&=\frac{\hbar^2}{2\mu_{ab}}\left\langle\frac{\partial(\chi\Phi)}{\partial R}\,\middle|\,\frac{\partial(\chi\Phi)}{\partial R}\right\rangle+\langle\chi\Phi\,|\,H_i\,|\,\chi\Phi\rangle\\&=\frac{\hbar^2}{2\mu_{ab}}\left[\left\langle\frac{\partial\chi}{\partial R}\Phi\,\middle|\,\frac{\partial\chi}{\partial R}\Phi\right\rangle+\left\langle\chi\frac{\partial\Phi}{\partial R}\,\middle|\,\frac{\partial\chi}{\partial R}\Phi\right\rangle+\left\langle\frac{\partial\chi}{\partial R}\Phi\,\middle|\,\chi\frac{\partial\Phi}{\partial R}\right\rangle\right]+\left\langle\chi\frac{\partial\Phi}{\partial R}\,\middle|\,\chi\frac{\partial\Phi}{\partial R}\right\rangle+\langle\chi\Phi\,|\,H_i\,|\,\chi\Phi\rangle\ .\end{aligned} \quad (10)$$

Using $\langle \mid \rangle = \langle \langle \mid \rangle_i \rangle_R$, where $\langle \mid \rangle_R$ implies integration only over R, let us look first at integration over the internal coordinates. If, as usual, the internal wave functions are real, or are functions whose only complex parts are phases that are independent of R, one easily proves from (6) that[17,19]

$$\left\langle \frac{\partial \Phi}{\partial R} \middle| \Phi \right\rangle_i = \left\langle \Phi \middle| \frac{\partial \Phi}{\partial R} \right\rangle_i = 0 \; . \tag{11}$$

Thus, Eq. (10) reduces to

$$\begin{aligned} E &= \frac{\hbar^2}{2\mu_{ab}} \left\langle \frac{\partial \chi}{\partial R} \middle| \frac{\partial \chi}{\partial R} \right\rangle_R + \langle \chi \mid \mathscr{E}(R) \mid \chi \rangle_R \\ &= \left\langle \chi \middle| -\frac{\hbar^2}{2\mu_{ab}} \frac{\partial^2}{\partial R^2} + \mathscr{E}(R) \middle| \chi \right\rangle_R \; , \end{aligned} \tag{12}$$

where

$$\mathscr{E}(R) = \frac{\hbar^2}{2\mu_{ab}} \left\langle \frac{\partial \Phi}{\partial R} \middle| \frac{\partial \Phi}{\partial R} \right\rangle_i + \langle \Phi \mid H_i \mid \Phi \rangle_i \; . \tag{13}$$

From Eq. (12) and the variational principal it is obvious that the $\chi(R)$ should satisfy[17]

$$\left[-\frac{\hbar^2}{2\mu_{ab}} \frac{\partial^2}{\partial R^2} + \mathscr{E}(R) - E \right] \chi(R) = 0 \; . \tag{14}$$

Thus, it is clear that the nuclei move on a potential energy curve determined by the internal motion, and it should be noted that Eq. (5) is the most general ansatz which retains this feature. It is also the most general ansatz that allows the dipole moment and similar properties to be given as functions of R.

Now, looking at Eq. (13) one sees that, as discussed elsewhere,[17] $\mathscr{E}(R)$ arises not from the internal Hamiltonian but from the action of the *complete* Hamiltonian H on Φ. [Note that Eq. (13) can be written in terms of $\partial^2/\partial R^2$; the reasons for using the present form are to avoid those higher derivatives and to maintain an obviously self-adjoint form.] Thus, it is clear that the *best adiabatic* (BA) approximation (that is, the adiabatic approximation which gives the *variationally best energy eigenvalues*[20]) is given by the functions Φ which *most nearly diagonalize the complete Hamiltonian H.* Such Φ's have all the *symmetries* of the complete H, but, because of Eq. (6), the Φ's are not on the Hilbert space of all of H, and it is thus clearly impossible to find a set of Φ's which will completely diagonalize H. However, we shall show that it is possible to diagonalize *more* of H than is often thought.

B. Symmetry breaking

Now, let us focus on Eq. (13) with H_i given by Eq. (4) and ask where the symmetry breaking in isotopic molecules arises. In isotopically mixed molecules (i.e., with nuclear charges $Z_a = Z_b$ but $m_a \neq m_b$), it is well known that the usual "electronic" Hamiltonian part of (4),

$$H_e = \frac{1}{2m} \sum_{k=1}^{N} \mathbf{p}_k^2 + V \; , \tag{15}$$

is independent of the nuclear masses and leads to solutions symmetric or antisymmetric (g or u) about the geometric center of the nuclei (GCN). We note that this holds true here even though CMN coordinates are being used. Also, the mass polarization ($\mathbf{P}^2/2m_{ab}$) term depends on the nuclear masses only through the symmetric combination $m_{ab} = m_a + m_b$ and does not break the symmetry either.

To see how the remaining ($\mathbf{L}_R$ and $\partial/\partial R$) terms break the symmetry, we write the internal wave functions as[16,17]

$$\Phi = \sum_{\Lambda} \tilde{D}^{J}_{\Lambda M}(\varphi_R, \theta_R, 0) \psi^{J}_{\Lambda}(\{\mathbf{r}_k\}; R) \; , \tag{16}$$

where J and M label the total angular momentum of the system and its space-frame z component, respectively, and the tilde on the Wigner D functions[16] implies that they are normalized for integration over *two* Euler angles

$$\int \tilde{D}^{J'*}_{\Lambda M'}(\varphi_R, \theta_R, 0) \tilde{D}^{J}_{\Lambda M}(\varphi_R, \theta_R, 0) d\cos\theta_R \, d\varphi_R = \delta_{JJ'} \delta_{MM'} \tag{17}$$

so that $\tilde{D}^{J}_{\Lambda M} = [(2J+1)/4\pi]^{1/2} D^{J}_{\Lambda M}$. The ψ^{J}_{Λ} are many-electron wave functions with the $\mathbf{r}_k$ relative to body-frame (BF) directional axes with the BF z axis lying along $\mathbf{R}$. They have symmetry (Σ, Π, Δ, etc.) labeled by the component Λ of the angular momentum along the BF z axis, and they are further expanded as

$$\psi^{J}_{\Lambda}(\{\mathbf{r}_k\}; R) = \sum_{I} C^{J}_{\Lambda I}(R) \mathscr{A} \prod_{k}^{N} \sum_{j} c^{I}_{kj}(R) \phi_j(\mathbf{r}_k; R) \gamma_k \; , \tag{18}$$

where the γ's are spin functions, the ϕ's are atomic orbitals, the c's are the coefficients of the atomic orbitals in the molecular orbitals, $\mathscr{A}$ is the antisymmetrizer that makes determinants out of products of spin orbitals, and the C are the coefficients of the determinants in ψ. The accuracy of expansion (18) is limited only by the extent to which the set of orbitals and set of determinants used span the electronic Hilbert space.

The atomic orbitals ϕ are themselves usually further expanded as linear combinations of primitive Gaussian or Slater orbitals, but the coefficients in that expansion are independent of R. Also, in common with most present-day quantum chemistry programs, we do not vary any nonlinear parameters in ϕ. Thus ϕ can be written as

$$\phi_j(\mathbf{r}_k; R) = \phi_j(x_k, y_k, (z_k - z_{\alpha j})) \; , \tag{19}$$

where αj is the nucleus (a or b) on which the atomic orbital is centered, and $z_{\alpha j}$ is the position of nucleus αj in the BF CMN coordinate system; namely,

$$z_{\alpha j} = \zeta_{\alpha j} R \; , \tag{20}$$

where $\zeta_a = -m_b/m_{ab}$ and $\zeta_b = m_a/m_{ab}$. Equation (19) displays the only dependence of the ϕ's on R, so that

$$\begin{aligned} \frac{\partial \phi_j}{\partial R} &= \frac{\partial (z_k - z_{\alpha j})}{\partial R} \frac{\partial \phi_j}{\partial (z_k - z_{\alpha j})} \\ &= -\zeta_{\alpha j} \frac{\partial \phi_j}{\partial z_k} \; . \end{aligned} \tag{21}$$

Thus, in the evaluation of $\langle \partial\Phi/\partial R \mid \partial\Phi/\partial R \rangle$ there are terms involving these derivatives of the orbitals and terms involving derivatives of the C and c coefficients. Since the coefficients are determined by solving a secular equation they are not free to satisfy a differential equation, and the terms involving derivatives of the coefficients cannot be included in the secular equation and can only be included afterward as a perturbation. However, the terms involving derivatives of the atomic orbitals on both sides of the bracket can and will be included in our secular equation. They are simply related to the electronic kinetic energy and, via the factors of ζ, can break the symmetry.

The nuclear centrifugal term involving $\mathbf{L}_R^2$ also contributes to symmetry breaking. One has[16]

$$\begin{aligned}\mathbf{L}_R^2 &= (\mathbf{J}-\mathbf{J}_e)^2 \\ &= \mathbf{J}^2 - 2J_z^2 + \mathbf{J}_e^2 - J_{e\_}J_+ - J_{e+}J_- \ , \end{aligned} \tag{22}$$

where $\mathbf{J}$ and $\mathbf{J}_e$ are the total and electronic angular momentum operators, respectively. The raising and lowering operators

$$J_{a\pm} = J_{ax} \pm iJ_{ay} \tag{23}$$

have their usual definitions and actions provided[21] that when working in the BF we take the components of total $\mathbf{J}$ to be formal operators[16] acting on the ψ_Λ^J. The electronic angular momentum is usually given by

$$\mathbf{J}_e = \mathbf{L}_e + \mathbf{S}_e \ , \tag{24}$$

where $\mathbf{L}$ and $\mathbf{S}$ are, respectively, orbital and spin-angular momenta, but in some nonrelativistic treatments,[16] $\mathbf{S}_e$ can be omitted from $\mathbf{J}_e$. Nuclear spins are not presently included but could be added perturbatively to the final results of the present approximation. Further expanding, one has

$$\mathbf{L}_e = \sum_{k=1}^{N} l_k \ . \tag{25}$$

The BF z component of $\mathbf{L}_e$ does not produce symmetry breaking but the other components do. In Eq. (13) the l operators act directly on the atomic orbitals and give

$$\begin{aligned} l_{kx}\phi_j &= -i\hbar\left[y_k \frac{\partial}{\partial z_k} - z_k \frac{\partial}{\partial y_k} \right]\phi_j \\ &= -i\hbar\left[y_k \frac{\partial}{\partial(z_k - z_{\alpha j})} - (z_k - z_{\alpha j}) \frac{\partial}{\partial y_k} \right]\phi_j \\ &\quad + i\hbar z_{\alpha j}\frac{\partial\phi_j}{\partial y_k} \\ &= l_{kx}^{\alpha j}\phi_j + i\hbar\zeta_{\alpha j}R\frac{\partial\phi_j}{\partial y_k} \ , \end{aligned} \tag{26}$$

and similarly,

$$l_{ky}\phi_j = l_{ky}^{\alpha j}\phi_j - i\hbar\zeta_{\alpha j}R\frac{\partial\phi_j}{\partial x_k} \ , \tag{27}$$

where $l_k^{\alpha j}$ is the one-electron orbital angular momentum about nucleus αj. Its action on ϕ_j is simple since the ϕ_j are eigenfunctions of $(l_k^{\alpha j})^2$ and $l_{kz}^{\alpha j}$. The second terms on the right-hand sides of Eqs. (26) and (27) are again kinetic energy type terms that break the symmetry and allow correct dissociation.

Thus it is clear where the symmetry-breaking arises. In actual practice one can include all of the H_i of Eq. (4) plus the $\langle \partial\phi_k/\partial R \mid \partial\phi_j/\partial R \rangle_i$ parts of the first term of (13) in the Hamiltonian diagonalized. The necessary integrals are not difficult; all of them are performed in existing adiabatic diatomic computer programs,[8,22] and all, or virtually all, are included in various parts of the new quantum-chemistry codes that give gradients and curvatures of the usual electronic energy.[23] For $J=0$, the generalization of the usual electronic wave function [cf. Eq. (18)] to the Φ of Eq. (16) does not increase the size of the secular equation. For larger J the size of the secular equation increases, but the coupling in Λ is often very weak and allows one to use ψ_Λ^J that depend only weakly on J, so that calculation of the $\mathscr{E}(R)$ of Eq. (13) is certainly feasible even for many-electron diatomic molecules. The whole process is also directly generalizable to polyatomic molecules where it is complicated but feasible for small systems.

III. ILLUSTRATIVE EXAMPLE: THREE-BODY SYSTEMS

To illustrate the concepts of the previous section clearly and simply, without complicated algebra, let us now consider the special case of three-body systems ($N=1$) where there is one "electron" (which can be an electron or a muon) and two nuclei. To show how simply symmetry-breaking and correct dissociation can be realized, we present results of some exceedingly simple approximate calculations. Much more accurate calculations on these systems are underway.[24]

A. Formulas

For $N=1$, only $\mathbf{r}_k = \mathbf{r}_1 = \mathbf{r}$ occurs in (18), the products and antisymmetrizer collapse, the C coefficients degenerate into a normalization constant that can be buried in the c coefficients, and the spin γ factors out, leaving

$$\psi_\Lambda^J(\mathbf{r};R) = \sum_j c_{\Lambda j}^J \phi_j(\mathbf{r};R) \ . \tag{28}$$

Let us consider the lowest-lying electronic states, usually known as the $1s\sigma$ states, that are dominated by $\Lambda=0$ functions. To get a quantitatively accurate BA approximation for $J\neq 0$, one must include $\Lambda=\pm 1(\pi)$ and perhaps even $\Lambda=\pm 2(\delta)$ states in Φ. However, the effects of $\Lambda\neq 0$ states are relatively small in this case; in the older theories they contributed only at the second-order, nonadiabatic level. They are considered later;[24] for now, we set $\psi_\Lambda = 0$ for $\Lambda \neq 0$. Because $\widetilde{D}_{0M}^J$ is simply a spherical harmonic, Eq. (16) reduces to

$$\Phi \cong Y_{JM}(\theta_R,\varphi_R)\psi_0^J(\mathbf{r};R) \ . \tag{29}$$

In addition, to even get a quantitatively accurate BO approximation, one must include in the $\{\phi_j\}$ many atomic orbitals on each nuclear center. However, for the present example, it suffices to take one orbital on each center,

$$\psi_0^J(\mathbf{r};R)\cong\sum_{\alpha=a}^{b}c_\alpha^J(R)\phi_\alpha(x,y,(z-z_\alpha))\ . \tag{30}$$

ϕ_a and ϕ_b are each taken to be normalized, but they are not orthogonal to each other.

For this $N=1$ case $\mathbf{P}=\mathbf{p}$, and Eq. (4) reduces to

$$H_i=(2\mu_{ab}R^2)^{-1}\mathbf{L}_R^2+(2\mu)^{-1}\mathbf{p}^2+V\ , \tag{31}$$

where

$$\mu=mm_{ab}/(m+m_{ab})\ . \tag{32}$$

Also, in what follows we use "mass-weighted atomic units" (m.a.u.). That is, the unit of distance is

$$a_m=\hbar^2/me^2\ , \tag{33}$$

and the unit of energy is e^2/a_m. If the negative particle is an electron, a_m is simply the usual Bohr radius ($a_m=a_0=0.529\,177\,06\times10^{-8}$ cm), and the unit of energy is the hartree ($e^2/a_0=27.211\,608$ eV). However, for a muon ($m_\mu=206.7687m_e$) the natural unit of length a_μ is much shorter ($a_\mu=0.255\,927\,1\times10^{-10}$ cm), and the unit of energy is much larger ($e^2/a_\mu=5626.508$ eV). These units allow easy comparison of electronic and muonic systems.

Upon substituting Eqs. (29)—(31) into (4) one finds that the ψ_0^J are independent of J and that integration over the angles $\hat{R}$ can be performed to give

$$\mathscr{E}(R)=\mathscr{E}^{(0)}(R)+\mathscr{E}^{(1)}(R)+(2\mu_{ab}R^2)^{-1}J(J+1)\ . \tag{34}$$

Thus there is an ordinary centrifugal potential in this approximation. The first-order term is an adiabatic correction,

$$\mathscr{E}^{(1)}(R)=(2\mu_{ab})^{-1}\sum_{\alpha=a}^{b}\sum_{\alpha'=a}^{b}\left[\langle\phi_{\alpha'}\,|\,\phi_\alpha\rangle_r\frac{\partial c_\alpha}{\partial R}\frac{\partial c_{\alpha'}}{\partial R}+\left\langle\phi_{\alpha'}\left|\frac{\partial\phi_\alpha}{\partial R}\right.\right\rangle_r c_\alpha\frac{\partial c'_\alpha}{\partial R}+\left\langle\frac{\partial\phi_{\alpha'}}{\partial R}\left|\phi_\alpha\right.\right\rangle_r c_{\alpha'}\frac{\partial c_\alpha}{\partial R}\right]\ , \tag{35}$$

where we have made use of the fact that these c_α turn out to be real. The zeroth-order BA term is

$$\begin{aligned}\mathscr{E}^{(0)}(R)=&\ (2\mu_{ab})^{-1}\sum_{\alpha'\alpha}c'_\alpha c_\alpha\left\langle\frac{\partial\phi_{\alpha'}}{\partial R}\left|\frac{\partial\phi_\alpha}{\partial R}\right.\right\rangle_r\\&+(2\mu_{ab}R^2)^{-1}\sum_{\alpha'\alpha}c'_\alpha c_\alpha\langle\phi_{\alpha'}\,|\,\mathbf{L}_e^2\,|\,\phi_\alpha\rangle\\&+\langle\psi_0\,|\,(2\mu)^{-1}\mathbf{p}^2+V\,|\,\psi_0\rangle\ ,\end{aligned} \tag{36}$$

which clearly contains more than the usual Born-Oppenheimer terms. At this point we take as basis functions ϕ_α, a 1s orbital on each center,

$$\phi_\alpha=(\mu_\alpha/\pi)^{1/2}\exp(-\mu_\alpha r_\alpha)\ , \tag{37}$$

where

$$\mu_\alpha=mm_\alpha/(m+m_\alpha)=m_\alpha/(m_\alpha+1)\ , \tag{38}$$

so that these are the *exact* ground-state solutions for finite-nuclear-mass one-electron atoms. Utilization of Eqs. (21), (26), and (27) then produces

$$\begin{aligned}\mathscr{E}^{(0)}(R)=\sum_{\alpha'\alpha}c'_\alpha c_\alpha[\,&(2\mu_{ab})^{-1}\zeta_\alpha\zeta_{\alpha'}\langle\phi_{\alpha'}\,|\,\mathbf{p}^2\,|\,\phi_\alpha\rangle\\&+\langle\phi_{\alpha'}\,|\,(2\mu^{-1})\mathbf{p}^2+V\,|\,\phi_\alpha\rangle]\ .\end{aligned} \tag{39}$$

The first term in the square bracket here, which is not present in the usual BO and adiabatic theories, is thus very simply related to the "electronic" kinetic energy. It breaks the symmetry as appropriate, causes the electron to become localized on one nucleus or the other at large R, and, via

$$\mu^{-1}+\mu_{ab}^{-1}\zeta_\alpha^2=\mu_\alpha^{-1}\ , \tag{40}$$

shifts the reduced mass of the electron from that relative to the CMN to that relative to the appropriate nucleus to give the atom its exactly correct energy ($-\mu_\alpha/2$ in m.a.u.).

All the integrals in Eq. (39) are easily performed analytically, and application of the variational principle gives a simple two-by-two secular equation which is easily solved to give the coefficients and $\mathscr{E}^{(0)}(R)$. The derivatives of the coefficients needed in Eq. (35) are easily evaluated numerically so that the $\mathscr{E}(R)$ of Eq. (34) is easily generated, and some numerical results are given below.

Now, let us consider the dipole moment. As noted long ago[25] the dipole moment is properly defined relative to the center of mass $\mathbf{C}$ of the system,

$$\boldsymbol{\mu}=\sum_i Z_i(\mathbf{r}_i-\mathbf{C})\ , \tag{41}$$

where the Z_i are the charges of the particles, and the sum runs over *all* the particles in the system. For our present three-body systems with unit charges and the CMN coordinates, this is

$$\boldsymbol{\mu}=m_{ab}^{-1}(m_a-m_b)\mathbf{R}-(1+M^{-1})\mathbf{r}\ , \tag{42}$$

where $M=m_a+m_b+m$. For our present example the only component of $\boldsymbol{\mu}$ with a nonzero expectation value is the BF z component. The integrals are easily evaluated and results are given below.

B. Sample results for HD$^+$ and dtμ

The simple calculations described above have been carried out for an electronic ion (HD$^+$) and a muonic ion (dtμ) to illustrate behavior in these systems. The more massive nucleus is designated nucleus a. The masses of the nuclei are taken to be $m_p=1836.152m_e$, $m_d=3670.481m_e$, and $m_t=5496.918m_e$.

Figures 1(a) and 1(b) show the coefficients of the atom-

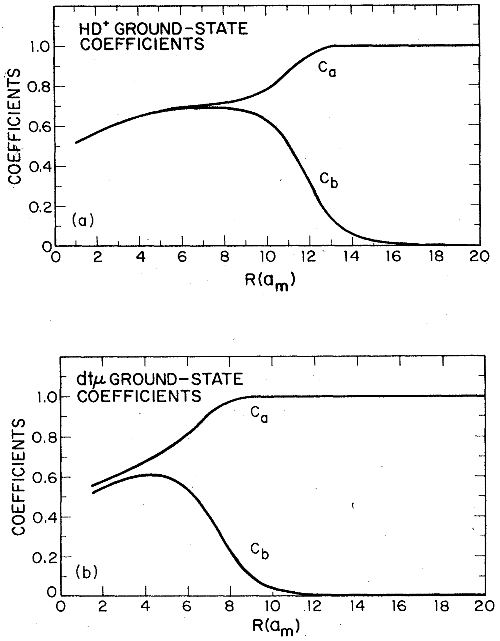

FIG. 1. Ground-state coefficients of the atomic orbitals on each nucleus as a function of internuclear distance (in mass-weighted atomic units). The heavier nucleus is *a*, the lighter *b*. (a) HD^+. At small *R*, the coefficients are nearly equal and the wave function nearly σ_g; at large *R* it dissociates to $D+H^+$. (b) $dt\mu$. The wave function is less symmetric than that of HD^+.

ic orbitals in the ground-state solution of HD^+ and $dt\mu$, respectively. One sees that, for large R, $c_b \to 0$ and $c_a \to 1$, so that the electron or muon stays with the *heavier* nucleus in dissociation. At small distances c_a and c_b are nearly equal for HD^+, so that its wave function almost has σ_g symmetry. However, they are never quite equal; for example, at $R=2.0$, $c_a=0.561\,638$ and $c_b=0.561\,082$. The coefficients in $dt\mu$ have the same qualitative behavior, but, even in the mass-weighted atomic units the large relative size of the non-BO terms makes the coefficients become different at smaller R, and even at small R, the difference in coefficients is visible on the scale of the figure. We note in passing that the coefficients of the first excited state (not shown) are, as expected, roughly those of a σ_u state at small R with the negative particle going with the *lighter* nucleus in dissociation ($c_b \to 1$, $c_a \to 0$).

Figure 2 shows the ($J=0$) potential energy curves of the ground and excited states for both HD^+ and $dt\mu$. On the scale of the drawing the curves of HD^+ look like the BO curves of $H_2{}^+$. However, the dissociation limits of the ground and excited states are $-0.499\,864$ and $-0.499\,728$ a.u., respectively, so that they are split by 1.36×10^{-4} a.u. $=29.8$ cm^{-1} at infinite separation. The well depths or dissociation energies are far too small here due to the small basis set used, but it is interesting to note that the present well is 16.5 cm^{-1} shallower than the equivalent level BO calculation and 14.9 cm^{-1} shallower than the usual adiabatic approximation (first-order corrections to the BO approximation) with this size basis set. It should be necessary to include this effect in theoretical calculations in order to match forthcoming high-resolution vibration-rotation spectra of HD^+ near the dissociation limit.[12]

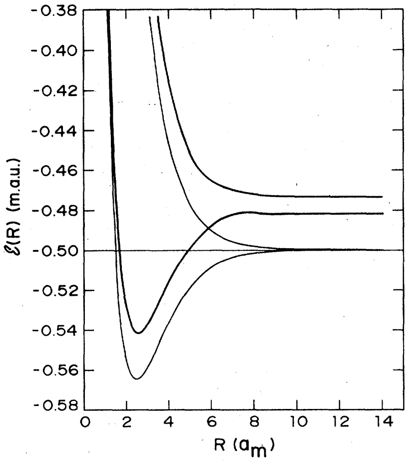

FIG. 2. Small basis set BA potential energy curves for the two lowest states of HD^+ (narrow lines) and $dt\mu$ (heavy lines) vs internuclear distance R. All quantities are in mass-weighted atomic units (m.a.u.).

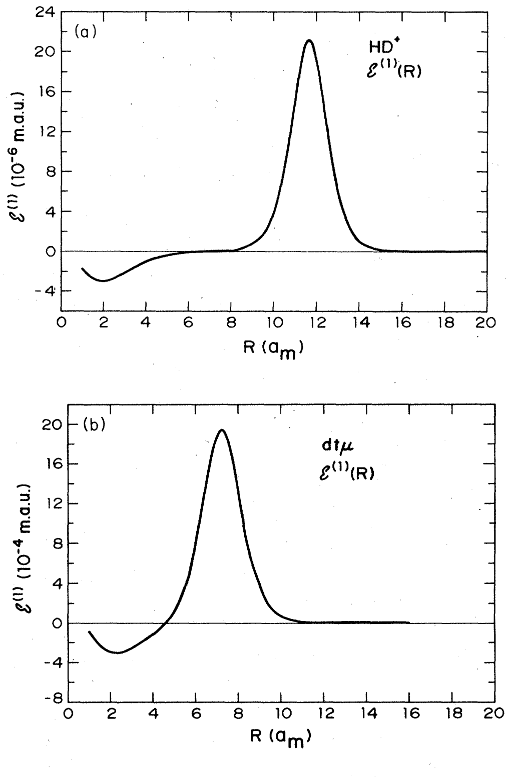

FIG. 3. $\mathcal{E}^{(1)}$ vs R. The contribution due to variation of coefficients. All quantities in mass-weighted atomic units. (a) HD^+. (b) $dt\mu$.

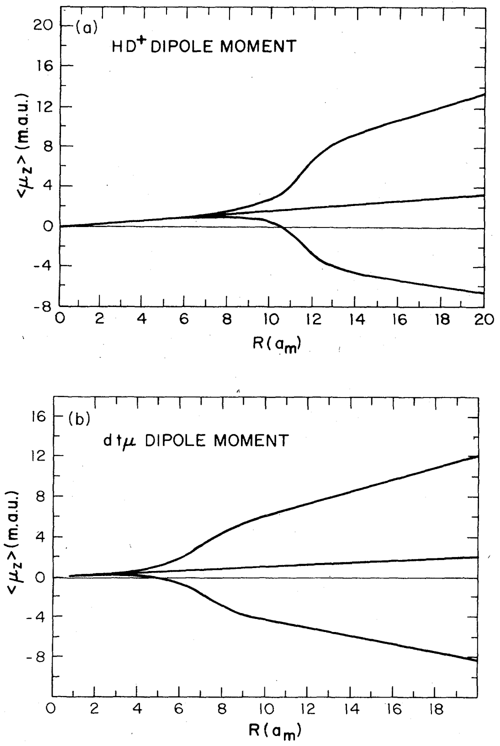

FIG. 4. Dipole moment function vs R. Mass-weighted atomic units. The upper curve is for the ground state, the lower curve is for the first excited state, and the middle curve is the Born-Oppenheimer result for both states. (a) HD$^+$. (b) dtμ.

The asymptotic splitting of the states of dtμ is obvious even on the mass-weighted atomic unit scale of the plot. This 48.0 eV (8.54×10^{-3} m.a.u.) splitting affects the ground-state dissociation energy by about 24 eV relative to the usual adiabatic approximation. Since the $v=1$, $J=1$ state of dtμ, which is very important to its formation and hence to muon-catalyzed fusion, is thought to be bound[13] by only 0.6 eV, it is clear that a proper treatment of symmetry breaking is crucial to any theoretical description of this state.

The term $\mathscr{E}^{(1)}(R)$ coming from the variation of the coefficients with R is plotted in Figs. 3(a) and 3(b) for the ground states of HD$^+$ and dtμ. [The excited state $\mathscr{E}^{(1)}(R)$ are similar and thus not shown.] The qualitative behavior of $\mathscr{E}^{(1)}$ is the same for the two systems, and in HD$^+$ it is small, but in dtμ it is relatively 2 orders of magnitude larger, indicating that the similar terms occurring in nonadiabatic corrections to the BA approximation may need to be included for a quantitative theory of dtμ.

The calculated dipole moment functions for HD$^+$ and dtμ are shown in Figs. 4(a) and 4(b), respectively. Their behavior is seen to be qualitatively similar with the larger mass of the muon enhancing the effect at smaller R for dtμ but with the effect of proper dissociation apparent for both. The BO dipole moment, which is not zero for a molecular ion, is also shown. We note that for HD$^+$ at $R=2.0$ the present BA and BO dipole moments of the ground state *differ* by $6.84\times10^{-4}ea_0$, which is the same order of magnitude as the correct dipole moment of neutral HD for which the BO dipole is zero. From this and from the fact that all the symmetries of the complete Hamiltonian are included in the BA theory, one can be confident that the BA approximation, solved accurately, will give quantitatively accurate dipole moments for all isotopic molecules.

IV. CONCLUSION

The best adiabatic (BA) approximation provides a direct, straightforward variational method that includes all the symmetries of the complete Hamiltonian and thus is capable of quantitative prediction of such symmetry-breaking effects as the dipole moments and dissociation of isotopically mixed diatomic molecules and their electronic and muonic ions. The nonadiabatic complications involved in getting such effects starting from the BO approximation have been shown to be unnecessary. The extra integrals that are required are not difficult to perform, and most, if not all, are already performed in different parts of present-day quantum chemistry computer codes. The secular equation obtained is a generalization of that usually encountered in quantum chemistry calculations and can be solved by the same techniques.

The simple sample calculations performed herein show clearly that the basic effects can be obtained and understood very easily. In HD$^+$ they are small but observable, and in dtμ they are crucial to the resonant formation of the species and any quantitative understanding of muon-catalyzed fusion.

Because of its generality and simple relationship to the older BO methods, the BA approximation appears to be the method of choice for calculating effects due to the unequal nuclear masses in isotopically mixed molecules.

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[20] As noted in the Introduction and in Ref. 17, this BA approximation is not always the most appropriate starting point for dynamical processes involving curve crossings.

[21] If, instead of the present approach, the BF components of **J** are taken to be differential operators acting on the $\tilde{D}$, one must interchange J_+ and J_- due to the often noted reversal of signs in the commutation relations of BF components of angular momentum. For some discussion of this point, see J. D. Louck, J. Mol. Spectrosc. **61**, 107 (1976).

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