Beyond the Potential Energy Surface: Ab initio Corrections to the Born−Oppenheimer Approximation for H_2O[†]

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It is customary when computing ro−vibrational transitions in molecules to invoke the Born−Oppenheimer separation between nuclear and electronic motion. However, it is known from accurate calculations on H_2^+ and H_2 that the first-order (diagonal adiabatic) and second-order (nonadiabatic) corrections are not negligible and are both important. In the present work, we have made an ab initio implementation of the Bunker and Moss formalism for the nonadiabatic correction and applied it to H_2 and H_2O. From comparison to accurate calculations for H_2, we find that we can obtain good results for the nonadiabatic correction using CI singles to treat the electronically excited states if we scale the results, but we must go beyond the SCF approximation to obtain an accurate diagonal adiabatic correction. For H_2O, we find that the first-order correction is more important than the second-order correction for bending energy levels, but the second-order correction is more important than the first-order correction for stretching energy levels. The correction to rotational levels is also significant. Thus, first- and second-order corrections are vital for accurate ab initio predictions of transition frequencies.

I. Introduction

When we solve the nonrelativistic Schrödinger equation for the bound states of a molecule, the first stage in the calculation is to fix the nuclear positions, removing all terms in the Hamiltonian which involve the nuclear masses, and then to solve for the electronic energy. This level of approximation is called the clamped nuclei approximation. We then allow the nuclei to move, subject to the forces which are a result of the electronic energy determined from the clamped nuclei approximation. This is the customary Born−Oppenheimer (BO) approximation. At the next level of refinement, we retain the electronic wave functions from the clamped nuclei approximation, but we use as the electronic energy the expectation value of the full Hamiltonian. This level of approximation is called the adiabatic approximation, and the difference between the two electronic energies is the Born−Oppenheimer diagonal correction (BODC). This is the first-order correction to the Born−Oppenheimer potential energy surface (PES) and results only in a mass-dependent change to the PES. The ultimate level of refinement is to couple the electron and nuclear motion. In principle, this will give the exact result, and the difference between the results obtained at this level and the adiabatic approximation is the nonadiabatic correction.

The BODC is fairly easy to implement, for it just results in a change to the PES. Formally, the nonadiabatic correction is much more difficult to compute, for explicit coupling to myriad of electronic states is involved, and the PES loses its significance. A significant advance was the derivation of an effective Hamiltonian for the nonadiabatic correction by Bunker and Moss.[1] In that work, they gave the procedure for deriving a correction to the Born−Oppenheimer, single-PES Hamiltonian that includes the nonadiabatic correction, accurate to second order in perturbation theory. This makes the calculation of the nonadiabatic correction essentially the same as the BO approximation once the correction functions are known. This is much more practical than nonperturbative methods.[2] Although they did not do so, their expression for the correction involves quantities that can be explicitly calculated from properties of excited electronic state wave functions. We have recently carried out the first ab initio utilization of the Bunker and Moss formalism and showed that very accurate results could be obtained for H_2^+ and HD^+.[3] In the present work, we extend our ab initio calculations to multielectron systems: H_2 and H_2O. We will use H_2 to test our procedures for a multielectron system, since accurate results exist for H_2,[4] and then use H_2O to make the first ever prediction of the nonadiabatic correction for a system containing more than two electrons.

The BODC for H_2O has been computed by several workers.[5−7] All these calculations were at the SCF level. Bardo and Wolfsberg[5] used normal coordinates and the Eckart conditions to separate out rotational and center-of-mass motion, and this resulted in very complex expressions for the BODC. Handy and co-workers[6] used a much simplier expression for the BODC that they proposed which does not involve internal coordinates or the separation of the center-of-mass motion. Subsequent work by Kutzelnigg[8] has put the Handy formula on much firmer grounds. Wolfsberg and Handy only considered the BODC in the vicinity of the minimum, while Tennyson and co-workers[7] used the Handy formula to produce a BODC surface.

In the course of this work, we will compute the BODC surface at several different levels of electronic structure theory. We have used both the Handy formula and the formula we have derived in the present work, and we obtain identical results. We also compare our SCF BODC to that computed by Tennyson and co-workers and find very similar results. However, we find that it is necessary to go beyond the SCF approximation to achieve accurate results for the BODC.

In the present work, we have implemented the simplest possible representation of the electronically excited states, namely, single-excitation CI. We find that although this level

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of calculation does not give results of quantitative accuracy, a simple scaling greatly improves the reliability of the results. This makes this a very cost-effective calculation.

II. Derivation

Bunker and Moss have given a derivation for diatomics[1] and for H_2O as well.[9] However, since we explicitly evaluate the correction functions, it is valuable to treat some of the steps in the derivation differently. Hence, we will give our derivation for polyatomics. Another difference with most previous workers is that we solve the electronic structure problem for the excited states separately for each isotopomer. This may not be the most efficient procedure but seems to be the most natural. For diatomics, see our work on H_2^+.[3]

We now explicitly give the kinetic energy operator. We assume that there are N nuclei and M electrons. In terms of space-fixed Cartesian coordinates, the kinetic energy operator is given by

$$\mathcal{T} = \mathcal{T}^{\text{nuc}} + \mathcal{T}^{\text{e}} \tag{1}$$

The nuclear kinetic energy operator is

$$\mathcal{T}^{\text{nuc}} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\left[\frac{\partial^2}{\partial X_i^{\,2}} + \frac{\partial^2}{\partial Y_i^{\,2}} + \frac{\partial^2}{\partial Z_i^{\,2}}\right] \tag{2}$$

where m_i is the mass of the nuclei i, and X_i, etc., are the Cartesian coordinates. The electron kinetic energy operator is

$$\mathcal{T}^{\text{e}} = -\frac{\hbar^2}{2m_{\text{e}}}\sum_{i=1}^{M}\left[\frac{\partial^2}{\partial X_i^{\text{e}\,2}} + \frac{\partial^2}{\partial Y_i^{\text{e}\,2}} + \frac{\partial^2}{\partial Z_i^{\text{e}\,2}}\right] \tag{3}$$

We reiterate that at this point, the Cartesian coordinates of the nuclei and electrons are in the space-fixed frame of reference.

Now we assume that we form new vectors describing the nuclear positions, with the only restriction being that the Nth vector gives the center of mass of the nuclei, and that the center of mass is decoupled from the remaining nuclear vectors. We then assume that some sort of vibration−rotational analysis is carried out on the first $N - 1$ vectors, so that the nuclear kinetic energy operator takes the form

$$\mathcal{T}^{\text{nuc}} = \sum_{l,m}\tilde{G}_{lm}\hat{O}_l\hat{O}_m + \mathcal{T}^{\text{ncm}} \tag{4}$$

where $\tilde{G}_{lm}$ is a geometry-dependent coefficient, $\hat{O}_l$ is an operator for vibration if $l = 1$ to $3N - 6$, for rotation if $l = 3N - 5$ to $3N - 3$, and for unity if $l = 3N - 2$. For a specific example of this, see the text after eq 23. The ro−vibrational wave function is expanded in terms of basis functions such as $f_{\nu M_R}(\mathbf{x},x_{\text{b}}) \times D^{(R)}_{M_R M'_R}(\alpha^{LB},\beta^{LB},\gamma^{LB})$, where $\mathbf{x}$ is a collection of all the vibrational coordinates except x_b, x_b is the bending vibrational coordinate used to define the nuclear body fixed axes, and α^{LB}, β^{LB}, and γ^{LB} are the Euler angles determined from the nuclear body fixed frame of reference. The index M_R on f specifies the behavior near linear geometries ($f_{\nu M_R} \propto x_b^{M_R/2}$), and ν specifies the remaining quantum numbers. The final quantity, for the nuclear center of mass, is given by

$$\mathcal{T}^{\text{ncm}} = -\frac{\hbar^2}{2M^{\text{ nuc}}}\left[\frac{\partial^2}{\partial X_{\text{ncm}}^2} + \frac{\partial^2}{\partial Y_{\text{ncm}}^2} + \frac{\partial^2}{\partial Z_{\text{ncm}}^2}\right] \tag{5}$$

Here $M^{\text{ nuc}}$ is the total nuclear mass, and X_{ncm}, etc., are the Cartesian coordinates of the nuclear center of mass.

We next form a set of relative electronic coordinates. We take the $M + 1$ vectors consisting of the electronic positions and the nuclear center-of-mass position and form M vectors describing the electron positions relative to the nuclear center of mass and one vector describing the position of the center of mass of the nuclei and electrons. Under this transformation, we have

$$\mathcal{T}^{\text{ncm}} + \mathcal{T}^{\text{e}} = \mathcal{T}^{\text{e ncm}} + \mathcal{T}^{\text{mp}} + \mathcal{T}^{\text{cm}} \tag{6}$$

where $\mathcal{T}^{\text{e ncm}}$ is the same as $\mathcal{T}^{\text{e}}$, except the origin of the electronic coordinates is the center of mass of the nuclei−these coordinates will be called $X_j^{\text{e ncm}}$, etc.−and

$$\mathcal{T}^{\text{mp}} = -\frac{\hbar^2}{2M^{\text{ nuc}}}\sum_{i,j}\left[\frac{\partial^2}{\partial X_i^{\text{e ncm}}\partial X_j^{\text{e ncm}}} + \frac{\partial^2}{\partial Y_i^{\text{e ncm}}\partial Y_j^{\text{e ncm}}} + \frac{\partial^2}{\partial Z_i^{\text{e ncm}}\partial Z_j^{\text{e ncm}}}\right] \tag{7}$$

is the mass polarization term, and $\mathcal{T}^{\text{cm}}$ is the kinetic energy operator for the total center of mass. At this point, the electron Cartesians have their origin at the nuclear center of mass but are oriented with respect to the space-fixed frame of reference.

We now transform the electron Cartesians to the nuclear body fixed frame of reference. This potentially only effects $\mathcal{T}^{\text{e ncm}}$ and $\mathcal{T}^{\text{mp}}$. Since these operators are expressed in terms of Cartesians, the transformed operators will have the same form, except the Cartesians are now referenced with respect to the nuclear body fixed frame of reference. The electronic wave function is expanded in terms of the basis functions $\Sigma_{M_L}\psi_{nLM_L}(\mathbf{X}^{\text{e ncm}})D^{(L)}_{M_L M'_L}(\alpha^{\text{LB}},\beta^{\text{LB}},\gamma^{\text{LB}})$, where the values $\mathbf{X}^{\text{e ncm}}$ are the collective electronic coordinates.

Finally, we transform the electron−nuclear wave function to the total angular momentum representation. This is done because the ro−vib−electronic wave function is expanded in terms of basis functions containing the product $D^{(R)}_{M_R M'_R}\ D^{(L)}_{M_L M'_L}$. If we make the substitution

$$D^{(R)}_{M_R M'_R}\ D^{(L)}_{M_L M'_L} = \sum_{JM_JM'_J}(RM_RLM_L|RLJM_J)(RM'_RLM'_L|RLJM'_J)D^{(J)}_{M_J M'_J} \tag{8}$$

and then transform to a simple product basis in the usual way,[11] we obtain a new basis function

$$f_{\nu\ K-M_L}(\mathbf{x},x_b)\psi_{nLM_L}(\mathbf{X}^{\text{e ncm}})D^{(J)}_{KM_J}(\alpha^{LB},\beta^{LB},\gamma^{LB}) \tag{9}$$

The Hamiltonian matrix will be diagonal in J and M_J. In practical calculations, one deals with electronic functions which are not eigenfunctions of L and M_L, which means that the $f_{\nu\ K-M_L}$ must be made independent of M_L. In the present work, we do this by using a basis function having the index K. This substitution is only questionable near linear geometries where the index controls the limiting behavior and is appropriate for the lowest electronic state having $M_L = 0$. In general, the lowest electronic state at linear geometries will depend on $\mathbf{x}$, so the situation becomes complicated. We will assume that the fine details at linear geometries are not important. Since these basis functions no longer are labeled by R, we need to use the relation

$$\hat{R}_\alpha = \hat{J}_\alpha - \hat{L}_\alpha \tag{10}$$

in eq 4 to evaluate matrix elements. Finally, we parity adapt the basis functions in the usual way.[11]

In summary, the exact nonrelativistic kinetic energy operator now takes the form

$$\mathscr{T} = \mathscr{T}^{\mathrm{nuc}J} + \mathscr{T}^{\mathrm{e\ ncm}} + \mathscr{T}^{\mathrm{mp}} + \mathscr{T}^{\mathrm{cm}} \tag{11}$$

where

$$\mathscr{T}^{\mathrm{nuc}J} = \sum_{l,m} \tilde{G}_{lm}\hat{O}_l\hat{O}_m \tag{12}$$

with R_α being replaced by $J_\alpha - L_\alpha$ in $\hat{O}_l$, where $l = 3N - 5$ to $3N - 3$.

The total center of mass is decoupled from all other degrees of freedom and is henceforth dropped.

It should be noted that when carrying out the electronic structure calculations for particular relative positions of the nuclei, the nuclear centers are not to be placed arbitrarily, but rather, the center of mass of the nuclei is at the origin, and the orientation is given by the definition of the nuclear body fixed frame of reference. This means that new calculations are required if one considers different isotopes of any nuclei. The total energy is not affected by shifting and rotating the nuclear positions, but most of the matrix elements of the operators required for the nonadiabatic correction are affected by these changes. This should be contrasted with the Handy method for computing the BODC.[6] There one takes derivatives with respect to a given nuclear position, with the positions of the other nuclei being fixed. Thus, the derivatives are independent of mass. There are two reasons favoring the present method. The first is that all calculations for triatomics can be carried out using C_s symmetry while the Handy method requires no symmetry for some of the derivatives. The second is the formation of the nonadiabatic correction. In contrast to the BODC, which is independent of coordinate system, the nonadiabatic correction functions are manifestly different for different coordinate systems. Thus, the generalization of the Handy method to evaluate the nonadiabatic corrections will involve using derivatives with respect to Cartesian coordinates to generate the various matrix elements which we determine directly below. This has the advantage that the Cartesian derivatives are independent of the masses, but there will be intermediate expressions that are more complicated. Note that if one is going to take advantage of analytic methods of evaluating the derivatives, it will be necessary to take that route, but at this stage of the development, we prefer the present procedure.

It is also convenient to write the nuclear kinetic energy in a symmetric form, namely

$$\mathscr{T}^{\mathrm{nuc}J} = \sum_{l,m} \hat{O}_l^\dagger G_{lm}\hat{O}_m \tag{13}$$

where † means the complex conjugate of the operator acts to left and $G_{lm} = G_{ml}$.

We partition the Hamiltonian operator into two parts, H_0, the clamped nuclei Hamiltonian, and the rest, H', which is just the difference between $\mathrm{T}^{\mathrm{nuc}J} + \mathscr{T}^{\mathrm{mp}}$ and the BO result. The operator H_0 has geometry-dependent eigenvalues W_n and eigenstates $|n\rangle$.

The result of the derivation of the nonadiabatic correction given by Bunker and Moss[1] is that, to the second order, the Hamiltonian operator should be modified by adding the correction

$$\frac{i}{2}\sum_{n\neq 0}\{\langle 0|H'|n\rangle\langle n|S|0\rangle - \langle 0|S|n\rangle\langle n|H'|0\rangle\} \tag{14}$$

where

$$\langle 0|S|n\rangle = \langle 0|S_0|n\rangle + \langle 0|S_1|n\rangle \tag{15}$$

$$\langle 0|S_l|n\rangle = +\frac{i}{2}[\Delta_{0n}{}^{-1},\ \langle 0|H'_l|n\rangle]_+ \tag{16}$$

$$\langle 0|H'_l|n\rangle = \frac{1}{2}\{\Delta_{0n}{}^{-1}[\langle 0|H'_{l-1}|n\rangle, W_n] + [\langle 0|H'_{l-1}|n\rangle, W_0]\Delta_{0n}{}^{-1}\} \tag{17}$$

with $H'_0 = H'$ and $\Delta_{0n} = W_0 - W_n$. The symbols 0 and n denote electronic states, with being 0 the ground electronic state, and $\langle|\rangle$ denotes integration over electronic coordinates. In principle, the sum over excited states n will include all bound electronic excited states as well as all continuum electronic states. In practice, however, we solve the electronic structure problem using a finite basis, so all excited states are descrete and one can explicitly carry out the sum. In principle, one needs much larger basis expansions to describe excited states than just the ground state; however, since all matrix elements involve the projection of the excited states on an operator acting on the ground state, as we will see below, it is sufficient to be able to accurately describe the ground state and its response to the operators.

It is straightforward to show that we can write

$$\langle 0|H'|n\rangle = \sum_l \hat{O}_l^\dagger\, b_l^{n*} \tag{18}$$

and

$$\langle n|H'|0\rangle = \sum_l b_l^n\hat{O}_l \tag{19}$$

with b_l^n given below. We then find that

$$\langle 0|S|n\rangle = i\sum_l \hat{O}_l^\dagger\, b_l^{n*}\, \Delta_{0n}{}^{-1} - iS^n \tag{20}$$

$$\langle n|S|0\rangle = -i\sum_l b_l^n\, \Delta_{0n}{}^{-1}\hat{O}_l + iS^n \tag{21}$$

where

$$S^n = \Delta_{0n}{}^{-2}\sum_{l=1}^{3N-6} b_l^n\hat{O}_l W_0 \tag{22}$$

Then the correction is given by

$$\sum_{\substack{l,m\\ n\neq 0}} \hat{O}_l^\dagger\, b_l^{n*}\, \Delta_{0n}{}^{-1}\, b_m^n\hat{O}_m - \frac{1}{2}\sum_{\substack{l\\ n\neq 0}} \hat{O}_l^\dagger\, b_l^{n*}\, S^n - \frac{1}{2}\sum_{\substack{l\\ n\neq 0}} S^n b_l^n\hat{O}_l \tag{23}$$

This is the same form as eq 13, so it can be straightforwardly evaluated given the functions $\Sigma_{n\neq 0} b_l^n\, \Delta_{0n}{}^{-1} b_m^n$, etc.

We now specialize to triatomics. Here we have $\hat{O}_1 = \partial/\partial r_1$, $\hat{O}_2 = \partial/\partial r_2$, $\hat{O}_3 = \partial/\partial x$, $\hat{O}_4 = \hat{R}_x = \hat{J}_x - \hat{L}_x$, $\hat{O}_5 = \hat{R}_y = \hat{J}_y - \hat{L}_y$, $\hat{O}_6 = \hat{R}_z = \hat{J}_z - \hat{L}_z$, and $\hat{O}_7 = 1$, where r_i are distances, $x = \cos\theta$, θ is the angle between r_1 and r_2, and $\hat{R}_\alpha$ is an rotational angular momentum operator of the nuclei about the nuclear center of mass, in the frame of reference defined by the nuclei. The geometry-dependent coefficients $\tilde{G}_{lm}$ are given below, and they are obtained from the work of Sutcliffe and Tennyson.[10] The specific expression for the nuclear kinetic energy operators is

$$\mathcal{T}^{\mathrm{nuc}J} = \mathcal{T}^{(1)}_{V} + \mathcal{T}^{(2)}_{V} + \mathcal{T}^{(1)}_{VR} + \mathcal{T}^{(2)}_{VR} \tag{24}$$

where

$$\mathcal{T}^{(1)}_{VR} = -\frac{\hbar^2}{2}\left\{\frac{1}{\mu_1}\frac{\partial^2}{\partial {r_1}^2} + \frac{1}{\mu_2}\frac{\partial^2}{\partial {r_2}^2} + \left(\frac{1}{\mu_1 {r_1}^2} + \frac{1}{\mu_2 {r_2}^2}\right)\left[(1-x^2)\frac{\partial^2}{\partial x^2} - 2x\frac{\partial}{\partial x}\right]\right\} \tag{25}$$

$$\mathcal{T}^{(2)}_{V} = \frac{\hbar^2}{\mu_{12}}\left\{-\frac{x}{r_1 r_2} + \frac{x}{r_2}\frac{\partial}{\partial r_1} + \frac{x}{r_1}\frac{\partial}{\partial r_2} - x\frac{\partial^2}{\partial r_1 \partial r_2} + \frac{x}{r_1 r_2}(1-x^2)\frac{\partial^2}{\partial x^2} + \frac{(1-3x^2)}{r_1 r_2}\frac{\partial}{\partial x} - \frac{(1-x^2)}{r_2}\frac{\partial^2}{\partial r_1 \partial x} - \frac{(1-x^2)}{r_1}\frac{\partial^2}{\partial r_2 \partial x}\right\} \tag{26}$$

$$\mathcal{T}^{(1)}_{VR} = \frac{1}{2}\{M_{xx}(\hat{J}_x - \hat{L}_x)^2 + M_{yy}(\hat{J}_y - \hat{L}_y)^2 + M_{zz}(\hat{J}_z - \hat{L}_z)^2 + M_{xz}[(\hat{J}_x - \hat{L}_x)(\hat{J}_z - \hat{L}_z) + (\hat{J}_z - \hat{L}_z)(\hat{J}_x - \hat{L}_x)]\} + \frac{\hbar}{i}\left[\left(\frac{1-a}{\mu_1 {r_1}^2} - \frac{a}{\mu_2 {r_2}^2}\right)\left(-(1-x^2)^{1/2}\frac{\partial}{\partial x} + \frac{x}{2(1-x^2)^{1/2}}\right)\right](\hat{J}_y - \hat{L}_y) \tag{27}$$

$$\mathcal{T}^{(2)}_{VR} = \frac{\hbar}{\mu_{12} i}\left[(1-x^2)^{1/2}\frac{a}{r_2}\frac{\partial}{\partial r_1} - (1-x^2)^{1/2}\frac{1-a}{r_1}\frac{\partial}{\partial r_2} - \frac{2a-1}{r_1 r_2}x(1-x^2)^{1/2}\frac{\partial}{\partial x} - \frac{a-\frac{1}{2}}{(1-x^2)^{1/2}}\frac{1-2x^2}{r_1 r_2}\right](\hat{J}_y - \hat{L}_y) \tag{28}$$

where M_{ab} is given in eqs 12 and 18 of ref 10. By the appropriate choices of a few parameters relating $\vec{r}_i$ to the atomic positions, it is possible to represent almost all coordinates used for calculations on H_2O. For orthogonal coordinates such as Jacobi or Radau coordinates, $1/\mu_{12} = 0$ so that $\mathcal{T}^{(2)}_{V}$ and $\mathcal{T}^{(2)}_{VR}$ do not occur, while for bond-length−bond-angle coordinates, all are required. The volume element is $dr_1\, dr_2\, dx$.

The parameter a is defined in eq 12 of ref 10 and controls the embedding of the body-fixed z-axis. We will consider $a = 0$ (align embedding), where the body-fixed x-axis is along $\vec{r}_1$, and $a = {}^1/_2$ (bisect embedding), where the body-fixed x-axis bisects the angle between $\vec{r}_1$ and $\vec{r}_2$. The choice of bisect embedding provides good decoupling between vibration and rotation, but align embedding results in simplier matrix elements with fewer singularities. Equations 25, 26, 27, and 28 define the functions $\tilde{G}_{ij}$ of eq 12.

The symmetric form is given by

$$\mathcal{T}^{(1)}_{V} = +\frac{\hbar^2}{2}\left[\left(\frac{\partial}{\partial r_1}\right)^\dagger \frac{1}{\mu_1}\frac{\partial}{\partial r_1} + \left(\frac{\partial}{\partial r_2}\right)^\dagger \frac{1}{\mu_2}\frac{\partial}{\partial r_2} + \left(\frac{\partial}{\partial x}\right)^\dagger \left(\frac{1}{\mu_1 {r_1}^2} + \frac{1}{\mu_2 {r_2}^2}\right)(1-x^2)\frac{\partial}{\partial x}\right] \tag{29}$$

$$\mathcal{T}^{(2)}_{V} = \frac{\hbar^2}{\mu_{12}}\left[-\frac{x}{r_1 r_2} + \frac{1}{2}\left(\frac{\partial}{\partial r_1}\right)^\dagger x\frac{\partial}{\partial r_2} + \frac{1}{2}\left(\frac{\partial}{\partial r_2}\right)^\dagger x\frac{\partial}{\partial r_1} - \left(\frac{\partial}{\partial x}\right)^\dagger \frac{x(1-x^2)}{r_1 r_2}\frac{\partial}{\partial x} + \frac{1}{2}\left(\frac{\partial}{\partial r_1}\right)^\dagger \frac{1-x^2}{r_2}\frac{\partial}{\partial x} + \frac{1}{2}\left(\frac{\partial}{\partial x}\right)^\dagger \frac{1-x^2}{r_2}\frac{\partial}{\partial r_1} + \frac{1}{2}\left(\frac{\partial}{\partial r_2}\right)^\dagger \frac{1-x^2}{r_1}\frac{\partial}{\partial x} + \frac{1}{2}\left(\frac{\partial}{\partial x}\right)^\dagger \frac{1-x^2}{r_1}\frac{\partial}{\partial r_2}\right] \tag{30}$$

$$\mathcal{T}^{(1)}_{VR} = \frac{1}{2}[(\hat{J}_x - \hat{L}_x)^\dagger M_{xx}(\hat{J}_x - \hat{L}_x) + (\hat{J}_y - \hat{L}_y)^\dagger M_{yy}(\hat{J}_y - \hat{L}_y) + (\hat{J}_z - \hat{L}_z)^\dagger M_{zz}(\hat{J}_z - \hat{L}_z) + (\hat{J}_z - \hat{L}_z)^\dagger M_{xz}(\hat{J}_x - \hat{L}_x) + (\hat{J}_x - \hat{L}_x)^\dagger M_{xz}(\hat{J}_z - \hat{L}_z)] + \frac{\hbar}{2i}\left(\frac{1-a}{\mu_1 {r_1}^2} - \frac{a}{\mu_2 {r_2}^2}\right) \times \left[\left(\frac{\partial}{\partial x}\right)^\dagger (1-x^2)^{1/2}(\hat{J}_y - \hat{L}_y) + (\hat{J}_y - \hat{L}_y)^\dagger (1-x^2)^{1/2}\frac{\partial}{\partial x}\right] \tag{31}$$

and

$$\mathcal{T}^{(2)}_{VR} = \frac{a-\frac{1}{2}}{\mu_{12} r_1 r_2}\frac{\hbar}{i}\left[\left(\frac{\partial}{\partial x}\right)^\dagger x(1-x^2)^{1/2}(\hat{J}_y - \hat{L}_y) + (\hat{J}_y - \hat{L}_y)^\dagger x(1-x^2)^{1/2}\frac{\partial}{\partial x}\right] - \frac{(1-x^2)^{1/2}\hbar}{2\mu_{12} i}\left[a\left(\frac{\partial}{\partial r_1}\right)^\dagger \frac{1}{r_2}(\hat{J}_y - \hat{L}_y) + a(\hat{J}_y - \hat{L}_y)^\dagger \frac{1}{r_2}\frac{\partial}{\partial r_1} + (a-1)\left(\frac{\partial}{\partial r_2}\right)^\dagger \frac{1}{r_1}(\hat{J}_y - \hat{L}_y) + (a-1)(\hat{J}_y - \hat{L}_y)^\dagger \frac{1}{r_1}\frac{\partial}{\partial r_2}\right] \tag{32}$$

The b^n_i values of eq 19 are as follows:

$$b^n_l = 2\tilde{G}_{1l}\left\langle n\left|\frac{\partial}{\partial r_1}\right|0\right\rangle + 2\tilde{G}_{2l}\left\langle n\left|\frac{\partial}{\partial r_2}\right|0\right\rangle + 2\tilde{G}_{l3}\left\langle n\left|\frac{\partial}{\partial x}\right|0\right\rangle - 2\tilde{G}_{l5}\langle n|\hat{L}_y|0\rangle \tag{33}$$

where l =1, 2, 3, and 5

$$b^n_l = -2\tilde{G}_{4l}\langle n|\hat{L}_x|0\rangle - 2\tilde{G}_{6l}\langle n|\hat{L}_z|0\rangle \tag{34}$$

where l = 4 and 6, and

$$b^n_7 = \tilde{G}_{11}\left\langle n\left|\frac{\partial^2}{\partial r_1^2}\right|0\right\rangle + 2\tilde{G}_{12}\left\langle n\left|\frac{\partial^2}{\partial r_1 \partial r_2}\right|0\right\rangle + 2\tilde{G}_{13}\left\langle n\left|\frac{\partial^2}{\partial r_1 \partial x}\right|0\right\rangle - 2\tilde{G}_{15}\left\langle n\left|\hat{L}_y\frac{\partial}{\partial r_1}\right|0\right\rangle + 2\tilde{G}_{17}\left\langle n\left|\frac{\partial}{\partial r_1}\right|0\right\rangle + \tilde{G}_{22}\left\langle n\left|\frac{\partial^2}{\partial r_2^2}\right|0\right\rangle + 2\tilde{G}_{23}\left\langle n\left|\frac{\partial^2}{\partial r_2 \partial x}\right|0\right\rangle - 2\tilde{G}_{25}\left\langle n\left|\hat{L}_y\frac{\partial}{\partial r_2}\right|0\right\rangle + 2\tilde{G}_{27}\left\langle n\left|\frac{\partial}{\partial r_2}\right|0\right\rangle + \tilde{G}_{33}\left\langle n\left|\frac{\partial^2}{\partial x^2}\right|0\right\rangle - 2\tilde{G}_{35}\left\langle n\left|\hat{L}_y\frac{\partial}{\partial x}\right|0\right\rangle + 2\tilde{G}_{37}\left\langle n\left|\frac{\partial}{\partial x}\right|0\right\rangle + \tilde{G}_{44}\langle n|\hat{L}_x^2|0\rangle + \tilde{G}_{46}\langle n|\hat{L}_z\hat{L}_x|0\rangle + \tilde{G}_{46}\langle n|\hat{L}_z\hat{L}_x|0\rangle + \hat{G}_{55}\langle n|\hat{L}_y^2|0\rangle - 2\tilde{G}_{57}\langle n|\hat{L}_y|0\rangle + \tilde{G}_{66}\langle n|\hat{L}_z^2|0\rangle + \langle n|\mathcal{T}^{\mathrm{mp}}|0\rangle \tag{35}$$

In this notation, the BODC is just b_7^0. The excited states in eqs 33 and 35 are of A' symmetry, while those of eq 34 are of A'' symmetry.

A subtlety of these equations is as follows. All quantities occurring in them are either real or are pure imaginary. In our codes, the factors of *i* are not explicitly included. The complicating factor is for G_{l5}, where the *i* is in the denominator, so we store $-Im[G_{l5}]/i$, while, e.g., for $\langle n|\hat{L}_y|0\rangle$, the *i* is in the numerator, and we store $Im[\langle n|\hat{L}_y|0\rangle]/i$. In b_1^n, b_2^n, b_3^n, and b_7^n, the factors $i/i = 1$ occur, but in b_5^n, some terms have *i* in the denominator and some have *i* in the numerator, and it is necessary to put in the extra -1 factor for the G_{l5} terms. A second complication occurs in eq 23. Since b_5^n is pure imaginary, and, e.g., b_3^n is real, the correction multiplying $J_y^\dagger\, {}^{\partial}/_{\partial x}$ is purely imaginary, as is G_{35}. But G_{35} contains *i* in the denominator, while the correction contains *i* in the numerator, so it is necessary to subtract the correction. Another interesting feature is that the matrix elements of the term involving J_y ($l = 7$, $m = 5$) exactly cancel the term involving $J_y^\dagger$ ($l = 5$, $m = 7$).

A valuable experimental parameter which gives a measure of rotational nonadiabaticity is the rotational *g* factor. Experimentally, this is determined by the response of the molecule to magnetic fields. A useful compilation of rotational *g* factors is given in the paper of Flygare and Benson.[12] The rotational *g* factors are defined as[13]

$$g_{\alpha\alpha} = g_{\alpha\alpha}^{\rm nuc} + g_{\alpha\alpha}^{\rm elec} \tag{36}$$

with

$$g_{\alpha\alpha}^{\rm nuc} = \frac{M_{\rm p}}{I_{\alpha\alpha}} \sum_j Z_j (B_j^2 + C_j^2) \tag{37}$$

$$g_{\alpha\alpha}^{\rm elec} = \frac{2M_{\rm p}}{m_{\rm e} I_{\alpha\alpha}} \sum_{n>0} \frac{|\langle 0|\hat{L}_\alpha|n\rangle|^2}{E_0 - E_n} \tag{38}$$

where $M_{\rm p}$ is the proton mass, $m_{\rm e}$ the electron mass, $I_{\alpha\alpha}$ a component of the moment of inertia tensor, Z_j the nuclear charge of atom *j*, and B_j and C_j are the non-α Cartesian coordinates for atom *j*. The nuclear contribution to the *g* factor is straightforwardly computed, and the electronic contribution involves some of the same quantities that are required for the nonadiabatic correction.

III. Electronic Matrix Elements

We will evaluate the required electronic matrix elements using a modified version of Molpro2000.1.[14] We have carried out the modifications in two stages. In the first stage, we evaluate the BODC using the MCSCF code and DDR procedure in Molpro. In the second stage, we included a single-excitation CI code to evaluate the nonadiabatic corrections using a SCF description of the ground state.

In general, it is necessary to evaluate the first-order matrix elements $\langle n|\hat{L}_\alpha|0\rangle$ and $\langle n|\partial/\partial y|0\rangle$ and the second-order matrix elements $\langle n|\hat{L}_\alpha\hat{L}_\beta|0\rangle$, $\langle n|\hat{L}_\alpha\, \partial/\partial y|0\rangle$, $\langle n|\partial^2/\partial y^2|0\rangle$, $\langle n|\partial^2/(\partial y \partial z)|0\rangle$, and $\langle n|\mathscr{T}^{\rm mp}|0\rangle$, where *y* and *z* are some vibrational coordinate. The first-order matrix elements have only one-electron contributions, while the second-order matrix elements have both one- and two-electron contributions. As distributed, Molpro2000.1 evaluates $\langle n|\hat{L}_\alpha|0\rangle$, $\langle n|\hat{L}_\alpha\hat{L}_\beta|0\rangle$, and the one electron part of $\langle n|\mathscr{T}^{\rm mp}|0\rangle$. It claims to also evaluate $\langle n|\partial/\partial y|0\rangle$, but the finite difference procedure does not do that correctly. It is fairly straightforward to extend the program to evaluate these matrix elements correctly, as well as to compute the remaining quantities.

Consider $\langle n|\mathscr{T}^{\rm mp}|0\rangle$. The one-electron part is just the matrix element of the electron kinetic energy divided by the total nuclear mass. The two-electron part is easily obtained by modifying the MCSCF properties code to treat the velocity operators in the same way it treats L_α when computing $\langle n|\hat{L}_\alpha\hat{L}_\alpha|0\rangle$. The one-electron velocity operator integrals are already available in Molpro2000.1.

Next, consider the derivative $\langle n|\partial^2/\partial y^2|0\rangle$. We will evaluate this numerically using a modified version of the DDR code in Molpro2000.1. In the DDR procedure, Molpro evaluates the nonadiabatic coupling matrix element $\langle n|\partial/\partial y|n'\rangle$ for $n \neq n'$ by a finite difference. We only consider the central difference formulas. Then the DDR procedure uses

$$\left\langle n\left|\frac{\partial}{\partial y}\right|n'\right\rangle = {\rm Tr}(\gamma_{nn'}^{y} S)/M + {\rm Tr}(\gamma_{nn'} S^{y}) + {\rm Tr}(\gamma_{nn'} S V^{y} V^{T} S) \tag{39}$$

where Tr means trace, *M* is the number of electrons, $\gamma_{nn'}$ is the transition density between states *n* and n', *S* is the overlap matrix in the atomic orbital (ao) basis, *V* is the molecular orbital (mo) eigenvector, and the superscript denotes numerical differentiation with respect to *y*. Specifically

$$\gamma_{nn'}^{y} = [\gamma_{nn'}(y,y+\Delta) - \gamma_{nn'}(y,y-\Delta)]/(2\Delta) \tag{40}$$

where $\gamma_{nn'}(y,y+\Delta)$ is the transition density computed using the mo eigenvectors from *y*, bra (*n*) configuration interaction (CI) coefficients from *y*, and ket (n') CI coefficients from $y + \Delta$

$$S^{y} = [S(y,y+\Delta) - S(y,y-\Delta)]/(2\Delta) \tag{41}$$

where $S(y,y+\Delta)$ is the overlap matrix with bra ao basis functions at *y* and ket basis functions at $y + \Delta$, and

$$V^{y} = [V(y+\Delta) - V(y-\Delta)]/(2\Delta) \tag{42}$$

where $V(y)$ are the mo eigenvectors at *y*. Thus, one carries out calculations at three geometries to get the orbitals and CI coefficients and then uses existing code to compute $S(y,y\pm\Delta)$ and $\gamma_{nn'}(y,y\pm\Delta)$. From this, the DDR code generates the full derivative. In actuality, MOLPRO2000.1 follows a slightly different procedure. First, when using the central difference formula, it also requires the overlap, etc., with the reference geometry, but these terms all cancel out. Second, subroutine OVLADR incorrectly assumes that S^y and SV^yV^TS are skew symmetric, and so it attempts to reduce the error in the calculation by zeroing the diagonals and averaging over the absolute values of the off diagonals. This error is small for multiconfiguration wave functions since the CI contribution (the first term in eq 39) dominates, but for SCF wave functions, this error is catastrophic.

To compute the second derivative we need, we carried out three modifications. First, we forced the CI code to save the transition density computed when $n = n'$. Second, we computed the one electron contribution to the derivative via

$$\left\langle n\left|\frac{\partial^2}{\partial y^2}\right|0\right\rangle_{\rm 1e} = {\rm Tr}(\gamma_{n0}^{yy} S)/M + {\rm Tr}(\gamma_{n0} S^{yy}) + {\rm Tr}(\gamma_{n0} S V^{yy} V^{T} S) + 2{\rm Tr}(\gamma_{n0}^{y} S^{y}) + 2{\rm Tr}(\gamma_{n0}^{y} S V^{y} V^{T} S) + 2{\rm Tr}(\gamma_{n0} S^{y} V^{y} V^{T} S) \tag{43}$$

where

$$\gamma_{n0}^{yy} = [\gamma_{n0}(y,y+\Delta) + \gamma_{n0}(y,y-\Delta) - 2\gamma_{n0}(y,y)]/\Delta^2 \quad (44)$$

etc. Finally, we computed the two-electron contribution

$$\left\langle n\left|\frac{\partial^2}{\partial y^2}\right|0\right\rangle_{2e} = \sum_{ij}\sum_{lm}\delta_{ij,lm}^{n0(2)} M_{ij}^y M_{lm}^y \quad (45)$$

where $\delta_{ij,lm}^{n0(2)}$ is the two-particle density in the mo basis, which is computed by the MCSCF code, but not saved, and

$$M^y = V^T S^y V + V^T S V^y \quad (46)$$

We modified the MCSCF code to pass the two-particle density matrix to the DDR code. It should be noted that the MCSCF code computes the two-particle density matrix in the mo basis of the last iteration. Thus, it is necessary to call the MCSCF code twice if one uses different orbitals for subsequent steps, e.g., natural orbitals.

To compute the mixed second derivative $\partial^2/\partial y\partial z$, we make four calculations at $(y+\Delta,z+\tilde{\Delta})$, $(y-\Delta,z+\tilde{\Delta})$, $(y+\Delta,z-\tilde{\Delta})$, and $(y-\Delta,z-\tilde{\Delta})$. Then we can use the formula

$$\begin{aligned}\left\langle n\left|\frac{\partial^2}{\partial y\partial z}\right|0\right\rangle_{1e} = {} & \mathrm{Tr}(\gamma_{n0}^{yz}S)/M + \mathrm{Tr}(\gamma_{n0}S^{yz}) + \\ & \mathrm{Tr}(\gamma_{n0}SV^{yz}V^TS) + \mathrm{Tr}(\gamma_{n0}^{y}S^{z}) + \mathrm{Tr}(\gamma_{n0}^{y}SV^{z}V^TS) + \\ & \mathrm{Tr}(\gamma_{n0}S^{y}V^{z}V^TS) + \mathrm{Tr}(\gamma_{n0}^{z}S^{y}) + \mathrm{Tr}(\gamma_{n0}^{z}SV^{y}V^TS) + \\ & \mathrm{Tr}(\gamma_{n0}S^{z}V^{y}V^TS) \quad (47)\end{aligned}$$

and

$$\left\langle n\left|\frac{\partial^2}{\partial y\partial z}\right|0\right\rangle_{2e} = \sum_{ij}\sum_{lm}\delta_{ij,lm}^{n0(2)} M_{ij}^y M_{lm}^z \quad (48)$$

with

$$\begin{aligned}\gamma_{n0}^{yz} = {} & [\gamma_{n0}(y+\Delta,z+\tilde{\Delta}) - \gamma_{n0}(y+\Delta,z-\tilde{\Delta}) - \\ & \gamma_{n0}(y-\Delta,z+\tilde{\Delta}) + \gamma_{n0}(y-\Delta,z-\Delta)]/(4\Delta\tilde{\Delta}) \quad (49)\end{aligned}$$

$$\begin{aligned}\gamma_{n0}^{y} = {} & [\gamma_{n0}(y+\Delta,z+\tilde{\Delta}) - \gamma_{n0}(y-\Delta,z+\tilde{\Delta}) + \\ & \gamma_{n0}(y+\Delta,z-\tilde{\Delta}) - \gamma_{n0}(y-\Delta,z-\tilde{\Delta})]/(4\Delta) \quad (50)\end{aligned}$$

$$\begin{aligned}\gamma_{n0}^{z} = {} & [\gamma_{n0}(y+\Delta,z+\tilde{\Delta}) - \gamma_{n0}(y+\Delta,z-\tilde{\Delta}) + \\ & \gamma_{n0}(y-\Delta,z+\tilde{\Delta}) - \gamma_{n0}(y-\Delta,z-\tilde{\Delta})]/(4\tilde{\Delta}) \quad (51)\end{aligned}$$

etc.

To evaluate the mixed angular momentum derivative operator, we can use essentially the same procedures, except now we need matrix elements such as $L_\alpha(y,y+\Delta)$. It is easy to modify the code that evaluates the overlap matrix $S(y,y+\Delta)$ to return $L_\alpha(y,y+\Delta)$ instead. Then it is straightforward to compute

$$\left\langle n\left|\hat{L}_\alpha\frac{\partial}{\partial y}\right|0\right\rangle_{1e} = \mathrm{Tr}(\gamma_{n0}^{y}L_\alpha) + \mathrm{Tr}(\gamma_{n0}L_\alpha^{y}) + \mathrm{Tr}(\gamma_{n0}L_\alpha V^{y}V^TS) \quad (52)$$

and

$$\left\langle n\left|\hat{L}_\alpha\frac{\partial}{\partial y}\right|0\right\rangle_{2e} = \sum_{ij}\sum_{lm}\delta_{ij,lm}^{n0(2)} M_{ij}^y L_{\alpha lm} \quad (53)$$

where

$$L_\alpha = V^T L_\alpha V \quad (54)$$

Thus, we can evaluate the BODC for any wave function that we can get out of the MC-SCF code. In practice, since all the finite difference formulas have errors proportional to even powers of the stepsize, we carry out calculations at two stepsizes and use Richardson extrapolation[15] to improve the results.

We initially tried using this same procedure to compute the nonadiabatic correction functions but ran into problems. Specifically, as formulated, we need a sum over excited states, and doing a state averaged MCSCF for each level becomes very expensive and is hard to ensure a good description of the ground state in the presence of the excited states. There also is the issue of how many states are required for convergence, and curve crossing as a function of geometry. Thus we think that a reliable procedure will (i) optimize the ground state without reference to excited states and (ii) include all excited states. The simplest example of this is to use a SCF description of the ground state and a single-excitation CI description of the excited states. We have written a program to evaluate all the required matrix elements for a single-excitation CI from a closed shell SCF wave function using the formulas given in ref 18.

In our calculations on H_2^+,[3] we found that it was important to include diffuse basis functions when computing the excited states; thus, we use the augmented basis functions of Duning and co-workers.[16] Also note that the excited states are not given accurately by these basis sets since they are optimized for the ground state, but the ground-state wave function response seems to be computed accurately since all matrix elements involve the ground state.

IV. Results

We take the atomic mass of H to be 1.007 825 032 1 u and the atomic mass of O to be 15.994 914 622 1 u, and we convert the atomic mass to atomic units using the relation $1m_e = 5.485\ 799\ 11 \times 10^{-4}$ u. We then subtracted off Z m_e to get the nuclear mass. The conversion factor from atomic units to cm^{-1} units was computed from the speed of light, 299 792 458 M/s, Planck's constant, $6.626\ 068\ 76 \times 10^{-34}$ J s, and the factor $1E_h = 4.359\ 743\ 81 \times 10^{-18}$ J, all which were obtained from the NIST web page http://physics.nist.gov.

A. H^2. We take the accurate H^2 potential and BODC from Table 2 of Schwartz and LeRoy.[17] This potential includes relativistic and radiative corrections.

We carried out calculations of the nonadiabatic correction for H_2 for 31 bond lengths, covering 0.4−10 Å. At small bond lengths, the spacing was 0.1 Å. These calculations used the aug-cc-pVTZ basis set and gave the SCF BODC as well as the nonadiabatic corrections.

The SCF PES was used to compute the derivatives in eq 22. We also calculated the BODC using CASSCF wave functions at these same geometries. These calculations used the cc-pVTZ basis set. Several different active spaces were used, and these involved different number of A_g, B_{3u}, B_{2u}, and B_{1u} orbitals. The orbitals in the active space were chosen by looking at the occupation numbers of the natural orbitals from a larger calculation at the equilibrium geometry. In our vibrational calculations, we interpolated the corrections using the nine-point Lagrangian interpolation of the correction times R^4. We solved for the vibrational energy levels using a finite basis expansion of the type described in the appendix of ref 19.

In Table 1, we give the adiabatic corrections to the bound vibrational levels for nonrotating H_2 computed using the BODC from different sources. We compare the accurate results with

TABLE 1: Adiabatic Corrections to the Vibrational Energy Levels of H_2 (in cm^{-1})

			CASSCF		
v	accurate	SCF	1,0,0,l[a]	2,0,0,1[a]	2,1,1,1[a]
0	0.00	0.00	0.00	0.00	0.00
1	−1.41	−2.03	−1.09	−1.24	−1.39
2	−2.57	−3.94	−1.93	−2.22	−2.52
3	−3.48	−5.75	−2.51	−2.94	−3.38
4	−4.12	−7.46	−2.83	−3.39	−3.96
5	−4.49	−9.11	−2.90	−3.56	−4.27
6	−4.58	−10.69	−2.70	−3.47	−4.29
7	−4.38	−12.22	−2.24	−3.10	−4.03
8	−3.88	−13.71	−1.55	−2.46	−3.49
9	−3.10	−15.18	−0.63	−1.59	−2.70
10	−2.04	−16.62	0.49	−0.49	−1.69
11	−0.76	−18.05	1.77	0.78	−0.50
12	0.70	−19.42	3.20	2.20	0.82
13	2.34	−20.57	4.77	3.74	2.25
14	4.21	−20.65	6.55	5.46	3.83

[a] Number of A_g, B_{3u}, B_{2u}, and B_{1u} orbitals in the active space.

TABLE 2: Nonadiabatic Corrections to the Vibrational Energy Levels of H_2 (in cm^{-1})

v	nonad[a]	ratio[b]	err[c]	scaled err[d]
0	−0.44	0.883	0.06	−0.003
1	−1.18	0.885	0.15	−0.013
2	−1.84	0.880	0.25	−0.007
3	−2.41	0.872	0.35	0.015
4	−2.90	0.863	0.46	0.055
5	−3.31	0.852	0.58	0.112
6	−3.64	0.839	0.70	0.186
7	−3.87	0.825	0.82	0.278
8	−4.00	0.810	0.94	0.380
9	−4.02	0.794	1.04	0.478
10	−3.90	0.781	1.09	0.545
11	−3.61	0.789	0.97	0.461
12	−3.11	0.765	0.95	0.518
13	−2.34	0.802	0.57	0.248
14	−1.18	0.820	0.26	0.093

[a] Ab initio prediction from the present work. [b] Ratio between column 2 and accurate results.[4] [c] Difference between column 2 and accurate results. [d] Difference between column 2 scaled by 1.14 and accurate results.

TABLE 3: Components of BODC for H_2O at the Vibrationally Averaged Geometry

	CASSCF[a]	SCF[b]
$\langle 0 \vert \mathscr{T}^{\mathrm{mp}} \vert 0 \rangle$	464.6558 cm^{-1}	463.3701 cm^{-1}
$\Sigma_{\alpha\beta}\tilde{G}_{\alpha\beta}\langle 0 \vert \hat{L}_\alpha \hat{L}_\beta \vert 0 \rangle$	57.8320 cm^{-1}	55.7876 cm-1
$\langle 0 \vert \partial^2/\partial\theta^2 \vert 0 \rangle$	−0.55769	−0.53541
$\tilde{G}_{33}\langle 0 \vert \partial^2/\partial x^2 \vert 0 \rangle$	20.5443 cm^{-1}	19.7233 cm^{-1}
$\langle 0 \vert \partial^2/\partial {r_1}^2 \vert 0 \rangle$	−0.49480	−0.46135
$\tilde{G}_{11}\langle 0 \vert \partial^2/\partial {r_1}^2 \vert 0 \rangle$	29.5715 cm^{-1}	27.5726 cm^{-1}
total	602.1752 cm^{-1}	594.0261 cm^{-1}

[a] Using the cc-pVTZ basis. [b] Using the aug-cc-pVTZ basis.

those obtained using the BODC computed using the aug-cc-pVTZ basis set at the SCF level and the BODC computed using the cc-pVTZ basis set using CASSCF wave functions with different active spaces. Since the SCF wave function does not dissociate properly and the zero of energy for the calculations including the BODC is most naturally taken to be at dissociated atoms, for the purpose of this comparison, we have arbitrarily set the zero energy so that the adiabatic correction for the ground vibrational level is zero. The SCF BODC significantly overestimates the accurate adiabatic correction. For the fundamental, it gives a correction about 50% too large, and furthermore, it clearly breaks down very badly as the amount of vibrational excitation increases. In contrast, the results from the CASSCF wave functions are always qualitatively correct, and as we increase the size of the active space, the results become closer to the accurate results. The largest calculation agrees quite well with the accurate results all the way up to dissociation. This clearly shows that the reason for the poor performance of the SCF method is its lack of electron correlation. The relative errors from the CASSCF calculations are more constant than the relative errors from the SCF calculations, so scaling can improve the results.

We now consider the prediction of nonadiabatic effects. The rotational g factor of H_2 as determined from experiment is 0.882 91,[12] and at R_0, we compute 0.9105 using the aug-cc pVTZ basis using single-excitation CI. This means that we recover about 77% of $g^{\mathrm{elec}}_{\alpha\alpha}$, which is the rotational nonadiabatic effect (see eq 36). In Table 2, we give the nonadiabatic corrections to the bound vibrational levels for nonrotating H_2 computed using the aug-cc-pVTZ basis using single-excitation CI. We use the accurate BODC in these calculations. We find that we obtain from 79% to 89% of the accurate result. Notice that in contrast to the BODC computed at the SCF level, the nonadiabatic correction behaves reasonably well all the way up to dissociation. If we scale the corrections by the factor 1.14, the errors in the transition frequencies for the low-lying levels are only a few times 0.01 cm^{-1}. This is a very encouraging result.

B. H_2O. We carried out calculations of the nonadiabatic corrections at a set of geometries generated as follows. We generated a grid with Θ running from 70° to 150° in steps of 10° and with R_1 and R_2 running from 0.825 to 1.225 Å in steps of 0.05 Å, where R_i are the two OH bond lengths and Θ is the HOH angle. We then retained only those points satisfying $R_1 \geq R_2$, and the energy computed from V^{emp} from ref 19 is less than 11 000 cm^{-1} higher than the minimum. For the ro− vibrational calculations, we interpolated the correction functions by fitting them using

$$\sum_{ijk} C_{ijk}(r_1 - \tilde{r})^i (r_2 - \tilde{r})^j (x - \tilde{x})^k \tag{55}$$

with $i, j \leq 8$, $k \leq 8 - i - j$, and $\tilde{r}$ and $\tilde{x}$ parameters being near in value to the equilibrium values. Some correction functions are symmetric with respect to interchanging r_1 and r_2, while some are antisymmetric, and when we use Jacobi coordinates or align embedding, some are asymmetric. In the former cases, we augment the data for $R_1 \geq R_2$ with data for $R_1 < R_2$ constructed from the appropriate symmetry relations. In the later case, we carried out calculations for $R_1 < R_2$. The coefficients C_{ijk} were determined by least-squares fitting, and the points were equally weighted. It should be noted that the expansion we use will not extrapolate properly. This is not a problem for the present results, for we evaluate the matrix elements of the corrections using the basis optimized for the BO approximation, so our functions do not sample regions where the expansions break down.

For this work, we take the BO PES to be the one denoted $V^{5Z} + \Delta V^{\mathrm{core}}$ from ref 19. This is the most accurate purely ab initio PES available. We ignore relativistic effects. We use the aug-cc-pVTZ basis set to compute the nonadiabatic correction functions and the SCF BODC. The oxygyn 1s-like orbital was always doubly occupied in the single-excitation CI calculations. We have also computed the BODC at the CASSCF level. Here we use the cc-pVTZ basis set, and the active space consists of eight electrons in 6a′ and 2a″ orbitals. This is the same active space used to compute V^{5Z}. In Table 3, we give the various quantities that go into the BODC computed at the vibrationally

TABLE 4: Unique Nonadiabatic Correction Functions for H_2O at the Vibrationally Averaged Geometry for Radau Coordinates, Bisect Embedding (in atomic units)[a]

$-\partial/\partial r_1{}^{\dagger}1.0275213 \times 10^{-7}\ \partial/\partial r_1$

$\partial/\partial r_2{}^{\dagger}3.8808313 \times 10^{-9}\ \partial/\partial r_1$

$-\partial/\partial\theta^{\dagger}2.6324533 \times 10^{-9}\ \partial/\partial r_1$

$-\partial/\partial\theta^{\dagger}1.4062589 \times 10^{-8}\ \partial/\partial\theta$

$-\mathrm{J}_x^{\dagger}9.8205515 \times 10^{-9}J_x$

$-J_y^{\dagger}6.0550853 \times 10^{-10}\ \partial/\partial r_1$

$-J_y^{\dagger}7.3757478 \times 10^{-9}J_y$

$-J_z^{\dagger}1.7082113 \times 10^{-8}J_z$

$3.1006092 \times 10^{-8}\ \partial/\partial r_1$

$-8.0263252 \times 10^{-10}\ \partial/\partial\theta$

$-2.9553018 \times 10^{-7}$

[a] For these coordinates, the reduced mass equals the proton mass.

averaged geometry of $R_0 = 0.974$ Å and $\Theta_0 = 104.2°$. This was determined from the $V^{5Z} + \Delta V^{\mathrm{core}}$ PES. The dominant term in the BODC is the mass polarization term. In Table 4, we give the nonadiabatic correction for Radau coordinates computed at the vibrationally averaged geometry. In all calculations, the derivatives in eq 22 were computed from the SCF PES. In Table 1S we give our calculated values of the CASSCF BODC, and in Table 2S, we give a fit to the CASSCF BODC in terms of R_1, R_2, and Θ.

In Table 5, we give results from various BODC. Our ro−vibrational calculations are well converged and use the algorithm of ref 19; for simplicity, the hyperspherical transformation is not performed. We label the vibrational levels by local mode quantum numbers. We see good agreement between the results we obtain using the BODC reported by Tennyson and coworkers[7] and our SCF BODC. When we go to the CASSCF BODC, we see good agreement with the SCF results for low-lying bending overtones but sizable disagreement for stretching overtones. At first sight, this seems unreasonable, but comparison with Table 1 shows that the shift between SCF and CASSCF for the stretches is very similar to what we observed for H_2. Thus, it appears that the SCF BODC provides a good description of the bending motion for low-lying levels but does a very poor job on stretching levels. Further convergence tests are required to ascertain the accuracy of the present CASSCF BODC.

We now turn to nonadiabatic corrections. A big issue for H_2O is verifying that we are doing the calculations properly. To ensure this, we have carried out calculations using several different kinetic energy operators. We performed separate electronic structure calculations and fits for each choice. We used the H + OH Jacobi coordinates with align embedding, Radau coordinates with both align and bisect embedding, and bond-length−bond-angle coordinates with bisect embedding. We carried out calculations for total angular momenta 0 and 10. If all things are done properly, all choices of coordinates should give the same results within the accuracy of second-order perturbation theory. After each programming error and procedural deficiency was corrected and the level of agreement improved, it was tempting to consider the program correct. However we continued exploring, and the final result was very small differences. The calculations with Jacobi and Radau coordinates gave the same results to within their convergence errors. The differences between the calculations using bond-length−bond-angle coordinates and Radau coordinates were small but not zero. Our final calculations showed apparently random differences of a few 0.0001 cm^{-1} for stretching levels, which is very satisfactory. For bending levels, the differences ranged from 0.001 to 0.005 cm^{-1} and were more systematic. We have not been able to identify the source of this difference, but since it is negligible in practice, we will assume our codes are working properly. The difference for $J = 10$ between align and bisect embedding is essentially zero.

The rotational g factors that we compute at the vibrationally averaged geometry are 0.721, 0.683, and 0.658, which can be compared to the experimental values[12] of 0.718, 0.657, and 0.645. The agreement is very satisfactory, with our calculations recovering from 91% to 99% of the electronic contribution. The component with the smallest experimental uncertainty is the y-component, and if we scale our results by 1.10, we match this value. We will assume that this same scaling is required for all the nonadiabatic correction functions.

In the final columns of Table 5, we give the nonadiabatic corrections we compute for the low-lying vibrational levels of H_2O. We give three sets of results. In the first column, we give the accurate results obtained using the expansion of eq 55. In the next column, we assume that the functions are constant and use the results in Table 6. In the final column, we neglect the cross derivatives. First, consider the accurate results. We see that compared to the adiabatic correction, the trends are very different for bending overtones and stretching overtones. The nonadiabatic correction is small for the bending overtones, while the adiabatic correction is large and negative. In contrast, the nonadiabatic correction is much larger for stretching overtones, and the adiabatic correction is smaller and positive. In fact, the sum of the nonadiabatic correction and the adiabatic correction is quite small for the stretching overtones. Next, consider the effects of assuming the nonadiabatic corrections are constant. The agreement with low-lying levels is very good but deteriorates somewhat as the amount of excitation increases. Finally, consider the last column. These results are nearly in as good agreement with the accurate results as the previous column. Thus, it is easy to include these effects in existing codes by simply scaling the terms in the kinetic energy operator.

In Table 6, we give the adiabatic and nonadiabatic corrections for the rotational levels for $JP = 10+$ for the ground vibrational level. The adiabatic correction function is from the CASSCF calculation using the cc-pVTZ basis, and the nonadiabatic corrections are from the CI singles calculation using the aug-cc-pVTZ basis, scaled by 1.10. The adiabatic and nonadiabatic corrections to the rotational levels are about the same size on average, but the adiabatic correction is both positive and negative, while the nonadiabatic correction is always negative.

It thus seems important to include these effects if high (<1 cm^{-1}) accuracy is required. How do we then rationalize the results of our previous work,[19] where we obtained about 0.05 cm^{-1} accuracy without including nonadiabatic effects? There are several possibilities for this. One is that there is not sufficient experimental data so that the fitted PES can behave nonphysically to make up for the deficiency. This would greatly reduce the predictive power of the PES. Another possibility is as follows. If we neglect the cross terms between vibrational coordinates, and assume that the corrections are constant, as we tried above, we can remove the nonadiabatic part from the vibrational kinetic energy using coordinate scaling and wave function transformation. This would mean, however, that the PES would have very complex isotope dependence, and furthermore, the rotational part of the kinetic energy would be modified. Thus, it should be possible to obtain good results for a single isotope considering purely vibrational levels and, if one is lucky, reasonable results for rotational levels. In contrast, by explicitly including nonadiabatic effects, we expect to be able to treat all isotopomers on an equal footing and obtain accurate predictions for unobserved vibrational and rotational levels.

TABLE 5: Corrections to the Vibrational Energy Levels of H_2O (in cm^{-1})

			adiabatic correction			nonadiabatic correction[b]		
ν_b	ν_s	BO	ZPST[a]	SCF	CASSCF	accurate	const[c]	diag const[d]
0	(0,0)+	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	(0,0)+	1597.60	−0.50	−0.50	−0.46	−0.07	−0.07	−0.07
2	(0,0)+	3157.14	−0.99	−1.00	−0.94	−0.15	−0.14	−0.14
0	(1,0)+	3661.00	−0.06	−0.05	0.39	−0.70	−0.69	−0.72
0	(1,0)−	3758.63	0.12	0.13	0.62	−0.79	−0.77	−0.74
3	(0,0)+	4674.88	−1.49	−1.52	−1.46	−0.23	−0.20	−0.20
1	(1,0)+	5241.83	−0.51	−0.49	−0.01	−0.76	−0.75	−0.78
1	(1,0)−	5336.74	−0.33	−0.31	0.24	−0.87	−0.84	−0.81
4	(0,0)+	6144.64	−2.02	−2.08	−2.03	−0.30	−0.27	−0.26
2	(1,0)+	6784.57	−0.94	−0.94	−0.42	−0.84	−0.82	−0.85
2	(1,0)−	6879.72	−0.74	−0.74	−0.16	−0.94	−0.90	−0.87
0	(2,0)+	7208.80	−0.08	−0.05	0.96	−1.37	−1.35	−1.39
0	(2,0)−	7256.00	0.06	0.09	1.19	−1.43	−1.40	−1.40
0	(1,1)+	7450.86	0.18	0.21	1.22	−1.57	−1.51	−1.46
5	(0,0)+	7555.62	−2.65	−2.74	−2.71	−0.37	−0.32	−0.32
3	(1,0)+	8286.03	−1.38	−1.40	−0.87	−0.91	−0.89	−0.91
3	(1,0)−	8384.72	−1.15	−1.17	−0.58	−1.02	−0.97	−0.94
1	(2,0)+	8771.71	−0.47	−0.44	0.66	−1.43	−1.40	−1.44
1	(2,0)−	8816.00	−0.33	−0.29	0.88	−1.50	−1.45	−1.45
6	(0,0)+	8886.34	−3.51	−3.61	−3.63	−0.41	−0.36	−0.36
1	(1,1)+	9008.72	−0.20	−0.17	0.90	−1.65	−1.56	−1.52
4	(1,0)+	9738.82	−1.90	−1.96	−1.43	−0.97	−0.94	−0.97
4	(1,0)−	9846.98	−1.58	−1.63	−1.05	−1.09	−1.03	−1.00
7	(0,0)+	10105.50	−4.51	−4.62	−4.68	−0.46	−0.39	−0.38

[a] Using the BODC of ref 7. [b] Using CASSCF BODC and nonadiabatic correction functions multiplied by 1.10. [c] Assuming correction functions are constant, with the values taken from Table 4 multiplied by 1.10. [d] Assuming correction functions are constant, with the values taken from Table 4 multiplied by 1.10, except the cross derivatives are neglected.

TABLE 6: Corrections to the Rotational Energy Levels of Ground Vibrational Level of H_2O for $J = 10$ (in cm^{-1})

K_a	K_c	BO	BODC	nonad
0	10	1114.95	−0.08	−0.21
1	10	1114.97	−0.08	−0.21
2	8	1438.58	−0.15	−0.25
3	8	1446.67	−0.11	−0.25
4	6	1617.18	−0.20	−0.27
5	6	1719.18	−0.02	−0.29
6	4	1875.80	0.09	−0.32
7	4	2054.53	0.22	−0.34
8	2	2254.35	0.36	−0.37
9	2	2471.22	0.50	−0.40
10	0	2701.77	0.65	−0.42

V. Conclusions

We have presented the results of ab initio corrections to the Born−Oppenheimer PES. We find that the SCF approximation for the BODC is very poor for stretches. For H_2, a modest CASSCF wave function greatly improves the results. Turning now to the nonadiabatic corrections, we find that for H_2, our simple CI singles calculations recovers about 77% of the rotational nonadiabaticity and about 88% of the vibrational nonadiabaticity. For H_2O, we recover from 91% to 99% of the rotational nonadiabaticity. For diatomics, where there is rigorous separation between vibration and rotation, we can scale the vibrational and rotational parts separately and, thus, obtain very accurate results. For polyatomics, it is no longer possible to rigorously separate vibration and rotation and scale them separately. For triatomics, it will be possible to scale the contributions from excited states of different symmetries (A' and A'') separately. For larger nonlinear polyatomics, it will only be possible to use a single scale factor. Since the scale factor for H_2O is near one, we should be able to obtain reliable results.

We also show that for H_2O, assuming that the nonadiabatic corrections functions are constant and diagonal is a very reasonable approximation; thus, these effects can be easily incorporated into existing codes. This makes the ab initio calculation of the nonadiabatic effects very inexpensive to implement in practice.

Supporting Information Available: A table giving the CASSCF BODC correction function for H_2O and a table giving the fit to the CASSCF BODC correction function for H_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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