

Abstract

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Corrections to the Born-Oppenheimer approximation for a harmonic oscillator

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In this paper, we derive rather simple formulas for the wave-functions and energy corrections to the Born-Oppenheimer approximation for a harmonic oscillator. We derive a coupled pair of equations for these corrections. These equations are valid to first order in the particle-to-oscillator mass ratio m/M and are the time-independent analog to the time-dependent equations for a forced oscillator. Such time-dependent treatments have recently been described for a particle in a box with oscillating walls (the quantum Fermi accelerator) [1,2] and a particle in a harmonic potential with an oscillating spring constant [3]. For slow oscillations compared to the particle motion, this paper describes the corresponding time-independent treatment for the coupling between the particle and oscillator, which is ignored in the Born-Oppenheimer approximation. Our wave functions may be derived from a recent work by Babb and Dalgarno [4] if one applies their diabatic coupling operators to a harmonic-oscillator basis. However, we give here an independent derivation for both wave functions and energies in a harmonic-oscillator basis that simplifies the results in Ref. [4] and that shows an important connection between time-dependent and -independent perturbation theory.

Our theory is particularly useful for describing the electronic-vibrational coupling in molecules and solids. To show its usefulness, we apply it to vibrational states of the H_2^+ electronic and rotational ground state. Recently, Kohl and Shipsey [5] have shown from a variational treatment that the diabatic energy corrections to the H_2^+ electronic ground states are linearly dependent on the vibrational quantum number n (at least up to $n=2$). This behavior is shown to be a direct result of our treatment and is seen in other variational studies as well [6-8].

Let us first consider the standard treatment of H_2^+ in the Born-Oppenheimer approximation. For simplicity, we shall assume that the center of mass is between the two nuclei and shall ignore the mass corrections that give the proper dissociation energy [9]. Our interest here is in the vibrationally dependent diabatic corrections that are more difficult to obtain. Because the electron moves much faster than the nucleus, we may consider the nuclei to be fixed with internuclear distance $R = |\mathbf{R}|$ in order to determine the electron wave function. If \mathbf{r} is the position

of the electron relative to the center of mass, we may write the total wave function as a product of the electron wave function $\psi(\mathbf{r}, R)$ and nuclear wave function $\phi(R)$, or

$$\Psi = \psi(\mathbf{r}, R)\phi(R). \quad (1)$$

We can make a guess for $\psi(\mathbf{r}, R)$. We find the solutions to Schrödinger's equation for fixed R ,

$$(T_r + V_e)\psi_i = W_i(R)\psi_i, \quad (2)$$

where T_r is the kinetic-energy operator for the electron and where the potential between the electron and protons is given by

$$V_e = -e^2/|\mathbf{r} - \mathbf{R}/2| - e^2/|\mathbf{r} + \mathbf{R}/2|. \quad (3)$$

Schrödinger's equation for the electronic ground state $\Psi = \psi_0\phi$ is then

$$-\left[\frac{\hbar^2}{2M}\right]\left[\frac{\partial^2\phi}{\partial R^2}\right]\psi_0 + [e^2/R + W_0(R)]\psi_0\phi = E\psi_0\phi, \quad (4)$$

where we have ignored the terms $(\partial^2\psi_0/\partial R^2)$ and $(\partial\psi_0/\partial R)(\partial\phi/\partial R)$. In atomic units, the electron mass is $m=1$ and the proton reduced mass is $M=918$. We see that the electronic energy W_0 acts like a nuclear potential. The total nuclear potential for the electronic ground state is then

$$V_N(R) = e^2/R + W_0(R), \quad (5)$$

which is approximately a Morse potential. This potential is nearly harmonic at the equilibrium position where

$$\frac{\partial V_N(R_0)}{\partial R} = 0. \quad (6)$$

Near the equilibrium position corresponding to the lower vibrational states, the solution to Eq. (4) is then

$$-\left[\frac{\hbar^2}{2M}\right]\left[\frac{\partial^2\phi_n}{\partial R^2}\right] + V_N(R)\phi_n = E_n\phi_n, \quad (7)$$

where the vibrational energy is given approximately by

$$E_n = W_0(R_0) + \hbar\omega(n + \frac{1}{2}) \quad (8)$$

and the vibrational states ϕ_n are the harmonic-oscillator Hermite polynomials.

We now consider corrections to the Born-Oppenheimer approximation resulting from the terms ignored in Eq. (4). We use the notation $|i\rangle = \psi_i$. To first order the diagonal energy correction for the ground state is

$$E^{(1)} = - \left[\frac{\hbar^2}{2M} \right] \left\langle 0 \left| \frac{\partial^2}{\partial R^2} \right| 0 \right\rangle \quad (9)$$

which is referred to as the adiabatic correction. Note that the term $(\partial\psi/\partial R)(\partial\phi/\partial R)$ has no diagonal electron-

ic matrix elements because

$$\left\langle i \left| \frac{\partial}{\partial R} \right| i \right\rangle = 2 \frac{\partial \langle i|i \rangle}{\partial R} = 0 \quad (10)$$

from conservation of normalization. On the other hand, this term dominates for the off-diagonal matrix elements because, for $M \gg m$,

$$\max \left| \frac{\partial\phi}{\partial R} \right| \gg \max \left| \frac{\partial\psi}{\partial R} \right|. \quad (11)$$

Let us use the notation $\psi_i\phi_n = |i,n\rangle$. To first order the contribution of the term $(\partial\psi/\partial R)(\partial\phi/\partial R)$ to the ground-state wave function is

$$\Psi^{(1)} = - \left[\frac{\hbar^2}{M} \right] \sum_{i(\neq 0), n} \left\langle i,n \left| \left[\frac{\partial\psi_0}{\partial R} \right] \left[\frac{\partial\phi_0}{\partial R} \right] \right| i,n \right\rangle / (E - E_{i,n}), \quad (12)$$

where $E_{i,n}$ is the energy of state $|i,n\rangle$ and $E_{0,0} \equiv E$. The corresponding second-order energy correction is then

$$E^{(2)} = \left[\frac{\hbar^2}{M} \right]^2 \sum_{i(\neq 0), n} \left\langle i,n \left| \left[\frac{\partial\psi_0}{\partial R} \right] \left[\frac{\partial\phi_0}{\partial R} \right] \right| \right|^2 / (E - E_{i,n}). \quad (13)$$

This expression cannot be readily simplified because the integral over \mathbf{r} , $\langle i|\partial\psi_0/\partial R\rangle$, is dependent on R . The summations above are not practical for numerical calculations. Indeed, if an electronic state $|i\rangle$ is repulsive, the states $|i,n\rangle$ correspond to the proton continuum. In practice, diabatic corrections that include the term in Eq. (13) are calculated variationally with a large basis set [5-7].

We now derive much simpler expressions for the ground-state corrections $\Psi^{(1)}$ and $E^{(2)}$ which are computationally tractable and give more insight into the physics. We show that, like the Born-Oppenheimer wave functions, the wave-function corrections can also be separated into electronic and vibrational parts. The electronic energy corrections can then be considered as a potential for the vibrations. As we did for the Born-Oppenheimer states themselves, we will first make a guess for the wave-function corrections and then verify that they obey Schrödinger's equation. For the ground-state wave function, we let

$$\Psi = \psi^{(0)}\phi_0 + \psi^{(1)}\phi_1, \quad (14)$$

where ϕ_0 and ϕ_1 are the first two vibrational states of the ground electronic state. We put this wave function Ψ back into the full Schrödinger equation and solve for $\psi^{(0)}$ and $\psi^{(1)}$. But first we make use of the relation for the harmonic-oscillator wave functions:

$$\frac{\partial\phi_n}{\partial R} = K_{n-1}\phi_{n-1} - K_n\phi_{n+1}, \quad (15)$$

where

$$K_n = \sqrt{M\omega(n+1)/2\hbar}, \quad (16)$$

so that

$$\begin{aligned} \frac{\partial\phi_0}{\partial R} &= -K_0\phi_1, \\ \frac{\partial\phi_1}{\partial R} &= K_0\phi_0 - K_1\phi_2. \end{aligned} \quad (17)$$

The full Schrödinger equation with all terms except those with ϕ_2 is now

$$\begin{aligned} (T_r + V_e)\psi^{(0)}\phi_0 - \left[\frac{\hbar^2 K_0}{M} \right] \left[\frac{\partial\psi^{(1)}}{\partial R} \right] \phi_0 - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2\psi^{(0)}}{\partial R^2} \right] \phi_0 + (T_r + V_e)\psi^{(1)}\phi_1 + \left[\frac{\hbar^2 K_0}{M} \right] \left[\frac{\partial\psi^{(0)}}{\partial R} \right] \phi_1 \\ - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2\psi^{(1)}}{\partial R^2} \right] \phi_1 - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2\phi_0}{\partial R^2} \right] \psi^{(0)} - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2\phi_1}{\partial R^2} \right] \psi^{(1)} + (e^2/R)\Psi = E'\Psi. \end{aligned} \quad (18)$$

We now make a guess at the solution of Eq. (18). Let us solve the coupled pair of equations below for $\psi^{(0)}$ and $\psi^{(1)}$ at a given R :

$$(T_r + V_e)\psi^{(0)} - \left[\frac{\hbar^2 K_0}{M} \right] \left[\frac{\partial \psi^{(1)}}{\partial R} \right] - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2 \psi^{(0)}}{\partial R^2} \right] = W'_0(R)\psi^{(0)}, \quad (19a)$$

$$(T_r + V_e)\psi^{(1)} + \left[\frac{\hbar^2 K_0}{M} \right] \left[\frac{\partial \psi^{(0)}}{\partial R} \right] - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2 \psi^{(1)}}{\partial R^2} \right] = (W'_0(R) - \hbar\omega')\psi^{(1)}; \quad (19b)$$

then a solution to Eq. (18) will be

$$\begin{aligned} - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2 \phi_0}{\partial R^2} \right] + (W'_0 + e^2/R)\phi_0 &= E'\phi_0, \\ - \left[\frac{\hbar^2}{2M} \right] \left[\frac{\partial^2 \phi_1}{\partial R^2} \right] + (W'_0 + e^2/R)\phi_1 &= (E' + \hbar\omega')\phi_1. \end{aligned} \quad (20)$$

The reader can verify that Eqs. (19) and (20) are indeed solutions to Eq. (18) by direct substitution. We caution the reader that Eqs. (19) and (20) cannot be *derived* from Eq. (18) by projecting with ϕ_0 or ϕ_1 and integrating over R because ψ also depends on R . For M infinite we get back the ground-state Born-Oppenheimer solution in Eq. (2) with $\psi^{(0)} = \psi_0$, $\psi^{(1)} = 0$, and $W'_0 = W_0$ in Eq. (19), so that $\omega' = \omega$ and $E' = E$ and the vibrational equations (20) are the same as (7). For finite M , Eq. (19) depends on the $\hbar\omega'$ from Eq. (20), whereas Eq. (20) depends on the W'_0 from Eq. (19). In principle, these equations can only be satisfied simultaneously if we iterate to convergence. In practice, both W'_0 and ω' are insensitive to the small differences from the Born-Oppenheimer values of W_0 and ω , and no iteration is necessary for H_2^+ for accuracy to order $O(1/M^2)$. If we expand E' in R about the equilibrium distance R_0 , to zeroth order in R we find

$$E' = E + [W'_0(R_0) - W_0(R_0)]. \quad (21)$$

$$\psi^{(0)} = \psi_0 - \left[\frac{\hbar^2}{2M} \right] \sum_{i \neq 0} \left\langle i \left| \frac{\partial^2}{\partial R^2} \right| 0 \right\rangle \left| i \right\rangle / (W_0 - W_i) \quad (24)$$

and

$$\psi^{(1)} = -\hbar V_0 \sum_{i \neq 0} \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \left| i \right\rangle / [W_0 - (W_i + \hbar\omega)]. \quad (25)$$

The wave-function correction $\psi^{(1)}$ is of order $O(1/M)$. One can show that the next-highest-order term, $\psi^{(2)}\phi_2$, would be of order $O(1/M^2)$, and we are justified in omitting the ϕ_2 terms in Eq. (18). These wave functions may be derived from the coupling operators of Ref. [4] applied to a harmonic-oscillator basis if we let $\omega = 0$. The first-order energy correction or adiabatic correction is the same as Eq. (9).

The second-order energy correction is the sum of two terms due to $\psi^{(0)}$ and $\psi^{(1)}$ given by

$$W^{(2)} = E^{(2)} = E_0^{(2)} + E_1^{(2)},$$

where, respectively,

$$E_0^{(2)} = \left[\frac{\hbar^2}{2M} \right]^2 \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial^2}{\partial R^2} \right| 0 \right\rangle \right|^2 / (W_0 - W_i) \quad (26)$$

and

$$E_1^{(2)} = (\hbar V_0)^2 \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \right|^2 / [W_0 - (W_i + \hbar\omega)]. \quad (27)$$

There will also be a change in R_0 and ω due to first- and second-order terms, respectively, in this expansion. So, to find the energy correction in E , we need only to find the corresponding correction in W . Note that the hierarchy established for the Born-Oppenheimer approximation where $|W_0| \gg \hbar\omega$ is also applicable to the corrections where

$$|W'_0 - W_0| \gg \hbar|\omega' - \omega|, \quad (22)$$

and this is why Eqs. (19) and (20) are rapidly convergent and also why our guess is correct.

Physically, this means that the electrons not only respond to the protons' positions, but also to their "velocities"

$$V_n = \hbar K_n / M, \quad (23)$$

giving rise to the diabatic electronic energy corrections $W'_0 - W_0$ found from Eq. (19). The protons then respond to these corrections as an R -dependent effective potential added to W_0 as seen from Eq. (20). We caution the reader that there are diabatic corrections due to the finite mass of the nuclei, which we have ignored because they are independent of vibrations.

We can now solve the coupled pair of equations [(19)] to find the perturbed electronic wave functions $\psi^{(0)}$ and $\psi^{(1)}$. From first-order perturbation theory we have

TABLE I. Diabatic corrections (in cm^{-1}) and their fit to the form $a + b(2n + 1)$.

	Ref. [8]	Fit	Ref. [7]	Fit	Ref. [6]	Fit	Ref. [5]	Fit
$n=0$	-0.050	-0.050	-0.1321	-0.1363	-0.1296	-0.1282	-0.129	-0.129
$n=1$	-0.140	-0.140	-0.3319	-0.3236	-0.3192	-0.3156	-0.316	-0.316
$n=2$			-0.5068	-0.5110	-0.4918	-0.5031	-0.502	-0.502
$n=3$					-0.6968	-0.6905	-0.636	-0.689
$n=4$							-0.728	-0.875
$a =$	-0.005		-0.042 58		-0.034 51		-0.0362	
$b =$	-0.045		-0.093 68		-0.093 71		-0.0932	

These energies can be readily derived from Eq. (19a) by applying $\langle 0|$ and integrating over the second-order terms using Eqs. (24) and (25). The second-order energy correction $E_0^{(2)}$ due to $\psi^{(0)}$ will be much smaller than $E_1^{(2)}$ due to $\psi^{(1)}$, as already discussed. To our knowledge, these simple energy corrections have not been derived previously. These results are not surprising. For $\omega=0$, Eq. (25) gives the steady-state admixture (except for phase) of excited states to the ground state from time-dependent perturbation theory for protons moving with velocity V_0 . Equation (27) is then the corresponding energy correction for this admixture. This is an obvious result of time-dependent perturbation theory derived from the term

$$i\hbar \frac{\partial}{\partial t} |i\rangle = i\hbar V_0 \frac{\partial}{\partial R} |i\rangle. \quad (28)$$

One may readily generalize these results to find the corrections for the n th vibrational state of the electronic (and rotational) ground state $\psi_0\phi_n$. We simply let

$$\Psi = \psi^{(0)}\phi_n + \psi^{(1)+}\phi_{n+1} + \psi^{(1)-}\phi_{n-1}, \quad (29)$$

where the corrections $\psi^{(1)+}$ and $\psi^{(1)-}$ are of order $O(1/M)$. The wave-function $\psi^{(0)}$ and energy correction $E_0^{(2)}$ are the same as before. The second-order energy correction corresponding to Eq. (27) becomes

$$E_1^{(2)} = (\hbar V_n)^2 \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \right|^2 / [W_0 - (W_i + \hbar\omega)] + (\hbar V_{n-1})^2 \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \right|^2 / [W_0 - (W_i - \hbar\omega)],$$

or, letting $W_0 - W_i \pm \hbar\omega \sim W_0 - W_i$ and using Eqs. (16) and (23), we find

$$E_1^{(2)} \sim [(2n+1)\hbar^3\omega/2M] \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \right|^2 / (W_0 - W_i), \quad (30)$$

and the diabatic energy corrections for H_2^+ are negative and depend linearly on the vibrational quantum number n as found by Kohl and Shipsey [5].

If we fit the diabatic energy corrections in Refs. [5]–[8] to the form $a + b(2n + 1)$, then the slope is given by

$$[b \text{ (cm}^{-1}\text{)}] = E_1^{(2)} / [(2n+1)hc] \sim (\hbar^2\omega/4\pi cM) \sum_{i \neq 0} \left| \left\langle i \left| \frac{\partial}{\partial R} \right| 0 \right\rangle \right|^2 / (W_0 - W_i). \quad (31)$$

Similar sums have been recently evaluated by Babb and Shertzer [10], but they are beyond the scope of this work. In Table I we show the slope derived from separate least-squares fits to the diabatic corrections of Refs. [5–8]. The fitted slopes from Refs. [5–7] are in very good agreement and clearly show the linear dependence on $2n + 1$ to the accuracy of the variational calculation. Only the first three vibrational levels in Ref. [5] were used in the fit in Table I because the rapid deviation from linearity for $n > 2$. On the other hand, the fit of the first three levels in Ref. [5] is exactly linear and in excellent agreement with the fit of Ref. [6].

The sum in Eq. (31) is very slowly converging because $(\partial/\partial R)|0\rangle$ is discontinuous at the protons, whereas the

wave functions $|i\rangle$ are continuous. This accounts for the overestimation of b in Ref. [8], where only a few electronic states above the ground state were used. In fact, evaluating only the first term in Eq. (31) for the ground state $1s$ coupling to the $2s$ state gives $b = -0.040$, in close agreement with the value of Ref. [8] in Table I, and also gives an estimate for the order of magnitude of b .

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