Born–Oppenheimer approximation for a harmonic molecule

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Abstract

We apply the Born–Oppenheimer approximation to a harmonic diatomic molecule with one electron. We compare the exact and approximate results not only for the internal degrees of freedom but also for the motion of the center of mass. We address the problem of identical nuclei and discuss other applications of the model and its limitations.
I. INTRODUCTION

The first step in the treatment of a classical or quantum–mechanical isolated system of particles should be the separation of the motion of the center of mass from the internal degrees of freedom. Most textbooks on quantum mechanics and quantum chemistry do that for the hydrogen atom but then consider the nucleus at rest when they discuss many–electron atoms. Such omission is more marked in the case of molecules because they invariably resort to the Born–Oppenheimer (or clamped–nuclei) approximation (BOA) and do not even mention the problem at all. However, an adequate treatment of the motion of the center of mass is most important for the estimation of adiabatic corrections to the potential–energy hypersurface.

In two earlier discussions of the BOA in this journal the authors chose two–particle models: the hydrogen atom and a delta potential in a box. However, the simplest molecule, the hydrogen molecular ion $\text{H}_2^+$, is a three–particle system. Therefore, those earlier discussions are not sufficiently realistic to show many relevant features of the treatment of molecular systems and of the nature of the BOA.

The purpose of this paper is the discussion of the separation of the motion of the center of mass in the BOA. As already mentioned above, this aspect of the problem is not discussed in most textbooks on quantum chemistry and the BOA is almost entirely omitted from those on quantum mechanics. For simplicity we resort to a simple model of three particles (two nuclei and one electron) that interact through Hooke’s forces. Although such harmonic interaction is unphysical, it has the advantage that the Schrödinger equation is solvable analytically and we can thus compare the exact solution with the exact BO one.

In Sec. II we present the model and obtain a dimensionless Hamiltonian operator in a set of variables that allows the exact separation of the motion of the center of mass. In Sec. III we solve the Schrödinger equation exactly. In Sec. IV we obtain the exact BO solution and compare it with an expansion of the exact nonadiabatic result derived in Sec. III. In Sec. V we address the interesting case of identical nuclei and discuss the permutational symmetry of the molecular states and the correlation functions. Finally, in Sec. VI we discuss other applications of the harmonic model and its limitations.
II. Model

Our model consists of three particles of masses $M_1$, $M_2$ and $M_3$ that move in one dimension and interact through forces that follow Hooke’s law

$$\hat{H} = -\frac{\hbar^2}{2M_1} \frac{\partial^2}{\partial X_1^2} - \frac{\hbar^2}{2M_2} \frac{\partial^2}{\partial X_2^2} - \frac{\hbar^2}{2M_3} \frac{\partial^2}{\partial X_3^2}$$

\[ + \frac{1}{2} \left[ K_{12} (X_1 - X_2)^2 + K_{13} (X_1 - X_3)^2 + K_{23} (X_2 - X_3)^2 \right] \]

where $K_{ij}$ are the force constants.

In order to make the Schrödinger equation dimensionless we choose units of length $L$, mass $M$ and force constant $K$ and define the corresponding dimensionless quantities $x_i = X_i / L$, $m_i = M_i / M$ and $k_{ij} = K_{ij} / K$. If we choose $L = \left[ \hbar^2 / (MK) \right]^{1/4}$ and take into account that $\hbar^2 / (ML^2) = \hbar \omega$, where $\omega = \sqrt{K/M}$, we easily derive the dimensionless Hamiltonian operator

$$\frac{\hat{H}}{\hbar \omega} = -\frac{1}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial x_2^2} - \frac{1}{2m_3} \frac{\partial^2}{\partial x_3^2}$$

\[ + \frac{1}{2} \left[ k_{12} (x_1 - x_2)^2 + k_{13} (x_1 - x_3)^2 + k_{23} (x_2 - x_3)^2 \right] \]

From now on we write $\hat{H}$ instead of $\hat{H} / (\hbar \omega)$ and simply remember that the energy is measured in units of $\hbar \omega$. Notice that we may choose $M = M_i$ and/or $K = K_{ij}$ in order to make some particular parameters equal to unity and simplify the Schrödinger equation even further. However, we have decided to keep all the model parameters for clarity.

In order to separate the motion of the center of mass from the internal degrees of freedom we define new coordinates as follows:

$$q_1 = \frac{1}{m_T} \left( m_1 x_1 + m_2 x_2 + m_3 x_3 \right), \quad m_T = m_1 + m_2 + m_3$$

$$q_2 = x_2 - x_1$$

$$q_3 = x_3 - x_1$$

Notice that $q_1$ is the coordinate of the center of mass and $q_2$ and $q_3$ are simply the positions of the particles 2 and 3 with respect to particle 1. The latter variables are translationally invariant as it is expected for the internal (spectroscopic) degrees of freedom. More precisely, the displacement of the whole system $x_i \rightarrow x_i + a$ produces $q_1 \rightarrow q_1 + a$, $q_2 \rightarrow q_2$ and $q_3 \rightarrow q_3$. 
The Hamiltonian operator (3) (in units of $\hbar \omega$) becomes

$$\hat{H} = -\frac{1}{2m_T} \frac{\partial^2}{\partial q_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial q_2^2} - \frac{1}{2m_3} \frac{\partial^2}{\partial q_3^2}$$

$$- \frac{1}{2m_1} \left( \frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_3^2} + 2 \frac{\partial^2}{\partial q_2 \partial q_3} \right)$$

$$+ \frac{1}{2} \left[ k_{12} q_2^2 + k_{13} q_3^2 + k_{23} (q_2 - q_3)^2 \right]$$

(5)

### III. EXACT SOLUTION

The Hamiltonian operator (5) is the sum of an operator that depends only on $q_1$

$$\hat{H}_1 = -\frac{1}{2m_T} \frac{\partial^2}{\partial q_1^2}$$

(6)

and another one that depends only on $q_2$ and $q_3$

$$\hat{H}_2 = -\frac{1}{2m_2} \frac{\partial^2}{\partial q_2^2} - \frac{1}{2m_3} \frac{\partial^2}{\partial q_3^2} - \frac{1}{2m_1} \left( \frac{\partial^2}{\partial q_1^2} + \frac{\partial^2}{\partial q_3^2} + 2 \frac{\partial^2}{\partial q_2 \partial q_3} \right)$$

$$+ \frac{1}{2} \left[ k_{12} q_2^2 + k_{13} q_3^2 + k_{23} (q_2 - q_3)^2 \right]$$

(7)

Therefore, each eigenfunction of $\hat{H}$ can be written as the product of an eigenfunction of $\hat{H}_1$ times an eigenfunction of $\hat{H}_2$. The operator $\hat{H}_1$ describes the motion of a free pseudoparticle with mass equal to the total mass of the system. If $\Phi(q_2, q_3)$ is an eigenfunction of $\hat{H}_2$

$$\hat{H}_2 \Phi = \epsilon \Phi$$

(8)

we conclude that the eigenfunctions $\psi(q_1, q_2, q_3)$ of $\hat{H}$

$$\hat{H} \psi = E \psi$$

(9)

are of the form

$$\psi(q_1, q_2, q_3) = e^{i\kappa q_1} \Phi(q_2, q_3)$$

(10)

and

$$E = \frac{\kappa^2}{2m_T} + \epsilon$$

(11)

where $-\infty < \kappa < \infty$.

Notice that the Hamiltonian operator $\hat{H}$ has a continuous spectrum, and that the Hamiltonian for the internal degrees of freedom $\hat{H}_2$ has a discrete (or point) one (which we will
obtain below). This point is most important when one has to calculate expectation values of observables. For example, everybody knows that if the potential–energy function is homogeneous of degree two (that is to say, it satisfies $V(t\mathbf{r}) = t^2 V(\mathbf{r})$) then the virial theorem gives us $\langle \hat{T} \rangle = \langle \hat{V} \rangle$ for an eigenfunction of the Hamiltonian operator. However, this relationship does not apply to the kinetic and potential energies in $\hat{H}$ because the integrals diverge, but it applies to the kinetic and potential energies in $\hat{H}_2$ since its eigenfunctions are square integrable.

The Hamiltonian operator (7) is a particular case of

$$\hat{H} = -\frac{1}{2} \sum_i \sum_j A_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \frac{1}{2} \sum_i \sum_j B_{ij} q_i q_j$$

(12)

In order to obtain its eigenfunctions and eigenvalues we carry out a change of variables of the form

$$q_i = \sum_j c_{ij} y_j$$

(13)

Thus the Hamiltonian operator (12) becomes

$$\hat{H} = -\frac{1}{2} \sum_i \sum_j \left[ C^{-1} A \left( C^{-1} \right)^T \right]_{ij} \frac{\partial^2}{\partial y_i \partial y_j} + \frac{1}{2} \sum_i \sum_j \left( C^T B C \right)_{ij} q_i q_j$$

(14)

where $A$, $B$, and $C$ are matrices with elements $A_{ij}$, $B_{ij}$, and $c_{ij}$, respectively. We choose the matrix $C$ in such a way that

$$C^{-1} A \left( C^{-1} \right)^T = I$$

$$C^T B C = D$$

(15)

where $D$ is a diagonal matrix

$$D_{ij} = \omega_i^2 \delta_{ij}$$

(16)

This approach is well known in the treatment of small oscillations in classical mechanics.$^6$

The resulting Hamiltonian operator is a sum of uncoupled dimensionless harmonic oscillators

$$\hat{H} = -\frac{1}{2} \sum_i \frac{\partial^2}{\partial y_i^2} + \frac{1}{2} \sum_i \omega_i^2 y_i^2$$

(17)

therefore its eigenfunctions are products

$$\Phi_{\{n\}} = \prod_i \varphi_{n_i}(y_i)$$

(18)
and its eigenvalues are given by

$$\epsilon(n) = \sum_{i} \epsilon_{n_i}, \quad \epsilon_{n_i} = \left(n_i + \frac{1}{2}\right) \omega_i$$

(19)

where \(n_i = 0, 1, \ldots\) are harmonic–oscillator quantum numbers, and each \(\omega_i\) is a dimensionless frequency. More precisely,

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial y^2_i} + \frac{1}{2} \omega^2_i y^2_i\right) \varphi_{n_i}(y_i) = \epsilon_{n_i} \varphi_{n_i}(y_i)$$

(20)

It follows from equation (15) that

$$C^{-1}ABC = D$$

(21)

which shows that the problem reduces to the diagonalization of the nonsymmetric matrix \(AB\).

In the particular case of the Hamiltonian operator (7) we have

$$A = \begin{pmatrix} \frac{1}{m_1} + \frac{1}{m_2} & \frac{1}{m_2} \\ \frac{1}{m_1} & \frac{1}{m_1} + \frac{1}{m_3} \end{pmatrix}$$

$$B = \begin{pmatrix} k_{12} + k_{23} & -k_{23} \\ -k_{23} & k_{12} + k_{23} \end{pmatrix}$$

$$AB = \begin{pmatrix} k_{12}(m_1 + m_2) + k_{23}m_1 & m_1m_2 \\ m_1m_2 & k_{12}(m_1 + m_2) + k_{23}m_1 \end{pmatrix} \begin{pmatrix} k_{13}m_2 - k_{23}m_1 & m_1m_3 \\ m_1m_3 & k_{13}(m_1 + m_3) + k_{23}m_1 \end{pmatrix}$$

(22)

The characteristic polynomial for the matrix \(AB\) is

$$w^2 - w \frac{k_{12}m_3(m_1 + m_2) + k_{13}m_2(m_1 + m_3) + k_{23}m_1(m_2 + m_3)}{m_1m_2m_3}$$

$$+ \frac{(m_1 + m_2 + m_3)(k_{12}(k_{13} + k_{23}) + k_{13}k_{23})}{m_1m_2m_3}$$

(23)

where \(w = \omega^2\). The two real positive roots give us the frequencies that we need to obtain the energy eigenvalues according to equation (19):

$$\epsilon_{n_1,n_2} = \omega_1 \left(n_1 + \frac{1}{2}\right) + \omega_2 \left(n_2 + \frac{1}{2}\right)$$

(24)

We do not show those roots explicitly here because they are rather cumbersome.

The exact eigenfunctions for the internal degrees of freedom

$$\Phi_{n_1,n_2}(q_2, q_3) = \varphi_{n_1}(y_2)\varphi_{n_2}(y_3)$$

(25)

clearly show the coupling of the motion of the particles through the variables \(y_i\) that are linear combinations of the \(q_j\). In other words, the problem is completely separable in the variables \(y_i\) but not in the \(q_j\) or \(x_k\).
IV. THE BORN–OPPENHEIMER APPROXIMATION

The BOA is discussed in many textbooks\textsuperscript{2} and also in earlier pedagogical articles in this same journal\textsuperscript{4,5}. For this reason we do not develop it here explicitly and just show its results for the present model. From now on we assume that our three–particle system models a diatomic molecule with just one electron. We choose the particles 1 and 2 to be the nuclei and particle 3 to be the electron; more precisely, we assume that $m_1 \geq m_2 \gg m_3$. We clearly appreciate that the harmonic potential chosen here is not realistic because it describes an attractive interaction between the nuclei. However, since the BOA is based on the different particle masses and not on the nature of the interaction we can apply it successfully and compare its approximate solutions with the exact ones.

In the clamped–nuclei approximation we omit the kinetic energy of the nuclei, which we assume to be at rest at $x_1$ and $x_2$, and solve the Schrödinger equation for the remaining “electronic” Hamiltonian:\textsuperscript{2}

$$\hat{H}_e = -\frac{1}{2m_3} \frac{\partial^2}{\partial x_3^2} + \frac{1}{2} \left[ k_{13} (x_1 - x_3)^2 + k_{23} (x_2 - x_3)^2 \right]$$  \hspace{1cm} (26)

Since the “nucleus–nucleus” interaction $k_{12} (x_1 - x_2)^2 / 2$ is just a constant we add it later to the electronic eigenvalues.

If we rewrite the potential–energy function as

$$\frac{1}{2} \left[ k_{13} (x_1 - x_3)^2 + k_{23} (x_2 - x_3)^2 \right] = \frac{1}{2} (k_{13} + k_{23}) \left[ x_3 - \frac{k_{13}x_1 + k_{23}x_2}{k_{13} + k_{23}} \right]^2$$

$$- \frac{(k_{13}x_1 + k_{23}x_2)^2}{2(k_{13} + k_{23})} + \frac{1}{2} (k_{13}x_1^2 + k_{23}x_2^2)$$

then we realize that the electronic Hamiltonian (26) is just a displaced harmonic oscillator and that the electronic energies are given by

$$\epsilon_{e,n_1}(x_1, x_2) = \sqrt{\frac{k_{13} + k_{23}}{m_3}} \left( n_1 + \frac{1}{2} \right) - \frac{(k_{13}x_1 + k_{23}x_2)^2}{2(k_{13} + k_{23})} + \frac{1}{2} (k_{13}x_1^2 + k_{23}x_2^2)$$  \hspace{1cm} (27)

The nuclear motion is governed by the potential–energy function

$$U(x_1, x_2) = U(x_1 - x_2) = \epsilon_{e,n_1}(x_1, x_2) + \frac{1}{2} k_{12} (x_1 - x_2)^2$$

$$= \sqrt{\frac{k_{13} + k_{23}}{m_3}} \left( n_1 + \frac{1}{2} \right) + \frac{k_{13}k_{23} + k_{12}k_{13} + k_{12}k_{23}}{2(k_{13} + k_{23})} (x_1 - x_2)^2$$  \hspace{1cm} (28)
The final step is the solution of the Schrödinger equation for the nuclear Hamiltonian operator

$$\hat{H}_N = -\frac{1}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2m_2} \frac{\partial^2}{\partial x_2^2} + U(x_1 - x_2)$$  \hspace{1cm} (29)$$

In doing so, we separate the motion of the center of mass by means of the change of variables

$$R = \frac{1}{m_N} (m_1 x_1 + m_2 x_2), \quad m_N = m_1 + m_2$$

and rewrite the Hamiltonian operator (29) as

$$\hat{H}_N = -\frac{1}{2m_N} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_N} \frac{\partial^2}{\partial q_2^2} + U(q_2), \quad \mu_N = \frac{m_1 m_2}{m_N}$$  \hspace{1cm} (31)$$

The eigenfunctions of this operator are of the form

$$\Phi_N(R, q_2) = e^{i\kappa R} \varphi(q_2)$$  \hspace{1cm} (32)$$

and its eigenvalues are approximations to those of $\hat{H}$:

$$E_{BO}^{k,n_1,n_2} = \kappa^2 \frac{2m_N}{m_3} + \sqrt{k_{13} + k_{23}} \left( n_1 + \frac{1}{2} \right) + \sqrt{\frac{k_{13}k_{23} + k_{12}k_{13} + k_{12}k_{23}}{k_{13} + k_{23}} \mu_N} \left( n_2 + \frac{1}{2} \right)$$  \hspace{1cm} (33)$$

If $\Phi_e(x_3; x_1, x_2)$ is an eigenfunction of the electronic Hamiltonian $\hat{H}_e$ then the full BO eigenfunction is

$$\psi^{BO}(q_1, q_2, q_3) = e^{i\kappa R} \Phi_e(x_3; x_1, x_2) \varphi(q_2)$$  \hspace{1cm} (34)$$

Although the BOA treats the electronic and nuclear motions separately, we appreciate that the BOA solution (34) already couples the nuclear and electronic degrees of freedom through the electronic function $\Phi_e(x_3; x_1, x_2)$ much in the way the exact solution (25) does. Besides, it is worth noticing that the BOA correctly describes the internal degrees of freedom in terms of translationally–invariant coordinates: $q_2$ and $x_3 - (k_{13}x_1 + k_{23}x_2)/(k_{13} + k_{23})$.

Finally, we show that we can obtain the BO eigenvalues from the exact solution (24). Because the BOA is based on the fact that the nuclear masses are much greater than the electronic ones, we substitute $m_1 = u_1/\lambda$ and $m_2 = u_2/\lambda$ into the roots $w_1$ and $w_2$ of the characteristic polynomial (23) and rearrange the results in order to remove the poles (for example, multiplying numerator and denominator by $\lambda^2$). If the undetermined quantities $u_1$ and $u_2$ are of the same order of magnitude as $m_3$ then $\lambda \ll 1$. Then we expand both roots
in Taylor series about $\lambda = 0$: $w_i = w_{i,0} + w_{i,1}\lambda + \ldots$ After tedious algebraic manipulation of the equations (greatly facilitated by any available computer algebra software) we obtain

$$w_1 = \frac{k_{13} + k_{23}}{m_3} + \frac{k_{13}^2 u_2 + k_{23}^2 u_1}{u_1 u_2 (k_{13} + k_{23})} \lambda + \ldots$$

$$= \frac{k_{13} + k_{23}}{m_3} + \frac{k_{13}^2 m_2 + k_{23}^2 m_1}{m_1 m_2 (k_{13} + k_{23})} + \ldots$$

$$w_2 = \frac{(u_1 + u_2) [k_{12}(k_{13} + k_{23}) + k_{13}k_{23}]}{u_1 u_2 (k_{13} + k_{23})} \lambda + \ldots$$

$$= \frac{(m_1 + m_2) (k_{12}k_{13} + k_{12}k_{23} + k_{13}k_{23})}{m_1 m_2 (k_{13} + k_{23})} + \ldots$$

(35)

The first contribution to $w_1$ gives the large frequency due to the fast motion of the electron (second term in the right–hand side of equation (33)), and the dominant contribution to $w_2$ provides the frequency for the slow motion of the nuclei (third term in the right–hand side of equation (33)). If, in addition, we take into account that $m_T \approx m_N$ and $q_1 \approx R$ when we neglect the electron mass, we clearly appreciate that the BOA yields the leading terms of the expansion of the exact result in negative powers of the nuclear masses (or the ratio of the electron to nuclear mass), even for the contribution of the motion of the center of mass. We have decided to express that ratio conveniently as $\lambda = u_i/m_i$ but other forms are possible.

An alternative mathematical strategy for obtaining the expansions of the roots of the characteristic polynomial is to substitute $w = w^{(0)} + w^{(1)}\lambda + \ldots$ (and, of course, $m_i = u_i/\lambda$) into the characteristic polynomial (23) and expand the resulting expression in powers of $\lambda$. At order zero we obtain two roots $w_1^{(0)} \neq 0$ and $w_2^{(0)} = 0$, and the coefficients of greater powers of $\lambda$ yield further corrections. The result should also be equation (35).

V. IDENTICAL NUCLEI

The particular case of identical nuclei leads to simpler expressions because

$$m_1 = m_2, \ k_{13} = k_{23}$$

(36)

We easily obtain

$$\omega_1^2 = \frac{k_{13}(2m_1 + m_3)}{m_1 m_3}, \ \omega_2^2 = \frac{2k_{12} + k_{13}}{m_1}$$

(37)

and

$$y_2 = \frac{\sqrt{2m_1 m_3 (2q_3 - q_2)}}{2 \sqrt{2m_1 + m_3}}, \ y_3 = \frac{\sqrt{2m_1}}{2} q_2$$

(38)
We appreciate that \( \hat{P}_{12}q_1 = q_1, \hat{P}_{12}q_2 = -q_2 \) and \( \hat{P}_{12}q_3 = q_3 - q_2 \), where \( \hat{P}_{12} \) is the permutation operator that satisfies \( \hat{P}_{12}f(x_1, x_2) = f(x_2, x_1) \). Therefore, \( \hat{P}_{12}y_2 = y_2 \) and \( \hat{P}_{12}y_3 = -y_3 \), so that we conclude that
\[
\hat{P}_{12}\psi(x_1, x_2, x_3) = (-1)^n \psi(x_1, x_2, x_3)
\]
(39)

In this way we can build symmetric and antisymmetric states (including the spin) for boson and fermions, respectively.

At first sight it may seem that when choosing the particle 1 as the coordinate origin we are violating the quantum–mechanical principle that states that identical particles are indistinguishable. However, when we express the resulting wavefunctions in terms of the original variables we realize that we can take into account the correct permutational symmetry explicitly, and, therefore, there is no violation of that principle. That the identical particles are treated exactly in the same way is more clearly seen in the form of the variables that appear in the exact square–integrable eigenfunctions: \( q_2 = x_2 - x_1 \) and \( 2q_3 - q_2 = 2x_3 - (x_1 + x_2)/2 \).

We also realize that the Born–Oppenheimer states exhibit exactly the same symmetry as follows from the fact that the nuclear factor is a function of \( q_2 \) and \( \Phi_e(x_3; x_1, x_2) \) actually depends on \( 2x_3 - (x_1 + x_2)/2 \).

The eigenfunctions are somewhat complicated to write them down explicitly here. However, the correlation functions for the ground state are not so cumbersome. For example,
\[
\rho(x_1, x_2) = \int_{-\infty}^{\infty} \Phi_{0,0}(q_2, q_3)^2 \, dq_3 = \frac{\sqrt{m_1\omega_2}}{2\pi} \, e^{-\frac{m_1\omega_2}{4}(x_1-x_2)^2}
\]
gives us the probability of finding one nucleus at \( x_2 \) if the other one is at \( x_1 \). The fact that it exhibits a maximum at \( x_1 = x_2 \) is a consequence of the unrealistic attractive nucleus–nucleus interaction of our model. This equation clearly shows that we are correctly treating both nuclei as indistinguishable particles.

If, on the other hand, we integrate over the coordinate of one of the nuclei we have
\[
\rho(x_1, x_3) = \int_{-\infty}^{\infty} \Phi_{0,0}(q_2, q_3)^2 \, dq_2
\]
\[
= \frac{\sqrt{2m_1m_3\omega_1\omega_2}}{\sqrt{\pi [2m_1\omega_2 + m_3(\omega_1 + \omega_2)]}} \, e^{-\frac{2m_1m_3\omega_1\omega_2}{2m_1\omega_2 + m_3(\omega_1 + \omega_2)}(x_1-x_3)^2}
\]
(41)

that shows the coupling between the electronic and nuclear motions.

The BOA yields remarkably similar expressions: \( \rho^{BO}(x_1, x_2) = \rho(x_1, x_2) \) and
\[
\rho^{BO}(x_1, x_3) = \frac{\sqrt{2m_1m_3\omega_1\omega_2}}{\sqrt{\pi (2m_1\omega_2 + m_3\omega_1)}} \, e^{-\frac{2m_1m_3\omega_1\omega_2}{2m_1\omega_2 + m_3\omega_1}(x_1-x_3)^2}
\]
(42)
Notice that the only difference between the exact \((41)\) and BO \((42)\) correlation functions is the neglect of the small frequency with respect to the large one: \(\omega_1 + \omega_2 \approx \omega_1\). We appreciate that for most purposes the BOA gives a correct description of the system behavior, at least according to the simple harmonic model discussed here.

VI. FURTHER COMMENTS AND CONCLUSIONS

In this paper we have applied the BOA to an exactly solvable model for a diatomic molecule with one electron. We could thus show that the clamped–nuclei approach provides the leading terms of the expansion of the eigenfunctions and eigenvalues in powers of the ratio of the electron to the nuclear mass. In addition to the internal degrees of freedom we also considered the motion of the center of mass that is commonly omitted in most textbooks on quantum mechanics and quantum chemistry\(^1\)). Although molecular physicists are more interested in the internal (spectroscopic) degrees of freedom we explicitly considered the factor that corresponds to the motion of the center of mass for pedagogical purposes. As discussed above for the virial theorem, only the internal degrees of freedom should be taken into account for the calculation of expectation values and transition probabilities. The reader may find a rigorous discussion of the treatment of the motion of the center of mass for actual molecular systems elsewhere\(^3\).

The harmonic potential–energy function of the present model is unrealistic, but such a choice allows us to solve the Schrödinger equation analytically and thus compare the exact solution with the BO one. Unlike earlier oversimplified pedagogical models used to discuss the BOA\(^4,5\), our harmonic molecule contains the minimum number of particles to be a molecule and is therefore more realistic from this point of view. For example, we could address the interesting case of identical nuclei.

The harmonic model is not suitable for the discussion of the Franck–Condon principle\(7\) because all the electronic curves exhibit exactly the same nuclear equilibrium distance \((q_2 = 0)\) and frequency as shown by equation \((28)\). Therefore, the value of an overlap integral is either one or zero because the harmonic–oscillator eigenfunctions are orthogonal.

The three–particle harmonic model is also useful for the study of the mass polarization in atoms\(8\). In fact, if we choose the particles 2 and 3 to be electrons we have a one–dimensional harmonic version of the Helium atom. We can thus, for example, estimate the effect of
neglecting the motion of the nucleus, or discuss the isotope effects on the atomic properties.

Our discussion of the harmonic diatomic molecule may also serve as an introduction to the non Born–Oppenheimer calculation of molecular properties that requires an adequate separation of the motion of the center of mass in the way shown in Sec. [II]

Acknowledgments

The author would like to thank Professor J. F. Ogilvie for useful comments and suggestions.

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