# Diatomic Molecules

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## 1 Hydrogen Molecule: Born-Oppenheimer Approximation

In this discussion, we consider the formulation of the Schrodinger equation for diatomic molecules; this can be extended to larger molecules. First we will consider the separation of the total Hamiltonian for a 4-body problem into a more tractable form. We will afterward discuss the molecular wavefunctions.

For the hydrogen molecule, we are concerned with 2 nuclei and 2 electrons. The total Hamiltonian, representing the total energy operator, is:

$$\begin{aligned}
\hat{H}(\vec{r},\vec{R}) &= -\frac{\hbar^2}{2M}\left(\nabla_A^2+\nabla_B^2\right)-\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2\right) \\
&- \frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}}-\frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} \\
&- \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}}-\frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}}+\frac{e^2}{4\pi\epsilon_0 r_{12}} \\
&+ \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}
\end{aligned}$$

Let's define:

$$\begin{aligned}
\hat{H}_N(\vec{R}) &= -\frac{\hbar^2}{2M}\left(\nabla_A^2+\nabla_B^2\right) \\
\hat{H}_{electronic}(\vec{r},\vec{R}) &= -\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2\right) \\
&- \frac{Z_A e^2}{4\pi\epsilon_0 r_{1A}}-\frac{Z_A e^2}{4\pi\epsilon_0 r_{2A}} \\
&- \frac{Z_B e^2}{4\pi\epsilon_0 r_{1B}}-\frac{Z_B e^2}{4\pi\epsilon_0 r_{2B}}+\frac{e^2}{4\pi\epsilon_0 r_{12}} \\
&+ \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}
\end{aligned}$$

- **NOTE:** For the present purposes, $\hat{H}_N$ is only a function of $\vec{R}$ and only depends on the coordinates of the nuclei. It is the bf kinetic energy operator of the nuclei.
- $\hat{H}_{electronic}(\vec{r}, \vec{R})$ is the electronic Hamiltonian.

Thus,

$$\hat{H}(\vec{r}, \vec{R}) \quad = \quad \hat{H}_N(\vec{R}) + \hat{H}_{electronic}(\vec{r}, \vec{R})$$

To solve the full Schrodinger equation for electrons and nuclei, one has to make approximations. This is because, as in the hydrogen atom case, there are non-radially symmetric interactions between electrons, nuclei, and electrons-nuclei. The first approximation we make is the **Born-Oppenheimer**

- Due to the large relative difference in electronic and nuclear masses, a first approximation is to assume that the time scales of motion of electrons and nuclei are **separable**. Effectively, the nuclei are at rest relative to the electrons; as the nuclear configuration changes, the electronic degrees of freedom "relax instantaneously". This is also referred to the adiabatic approximation. This is a good assumption for most cases.
- Because we consider the separation in time scales of nuclear and electronic degrees of freedom, we assume a separable ansatz of the form:

$$\Psi(\vec{r}, \vec{R}) = \psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R})$$

Thus, if we consider the usual approach to setting up the Schrodinger equation:

$$\left[\hat{H}_N(\vec{R}) + \hat{H}_{electronic}(\vec{r}, \vec{R})\right] \psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R}) = E\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R})$$

$$\hat{H}_N(\vec{R})\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R}) + \hat{H}_{electronic}(\vec{r}, \vec{R})\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R}) = E\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R})$$

$$\psi_{el}(\vec{r}, \vec{R})\hat{H}_N(\vec{R})\psi_N(\vec{R}) + \psi_N(\vec{R})\hat{H}_{electronic}(\vec{r}, \vec{R})\psi_{el}(\vec{r}, \vec{R}) = E\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R})$$

$$\psi_{el}(\vec{r}, \vec{R})\hat{H}_N(\vec{R})\psi_N(\vec{R}) + \psi_N(\vec{R})E_{el}(\vec{R})\psi_{el}(\vec{r}, \vec{R}) = E\psi_{el}(\vec{r}, \vec{R}) \ \psi_N(\vec{R})$$

$$[\hat{H}_N(\vec{R}) + E_{el}(\vec{R})]\psi_N(\vec{R}) = E\psi_N(\vec{R})$$

Thus, we have arrived at a Schrodinger eqution for just the nuclear coordinates (degrees of freedom). What we see is that apart from the kinetic energy operator, there is an energy depending on only the nuclear coordinates, $E_{el}(\vec{R})$. We see that this is related to the energy (for fixed nuclear coordiantes) of the electronic Schrodinger equation:

$$\hat{H}_{el}(\vec{r}, \vec{R})\psi_{el}(\vec{r}, \vec{R}) = E_{el}\psi_{el}(\vec{r}, \vec{R})$$

If one repeats the calculation of the electronic wavefunctions and energies for many separations of the nuclear coordinates, one obtains a parametric dependence of the electronic energy on the nuclear positions. This looks like:
Solution of Schrodinger equation for each value of R leads to a set of eigenvalues $E_{el,n}(\vec{R})$ and eigenfunctions $\psi_{el,n}(\vec{r}, \vec{R})$ The minimum energy corresponds to the most stable nuclear geometry.

The recipe is thus:

- fix nuclear coordinates.
- solve Schrodinger equation for fixed coordinate geometry
- obtain eigenfunctions and eigenvalues; the eigenvalues and eigenfunctions have parametric dependence on nuclear coordinates
- solve for nuclear part of ansatz using $E_{el}(\vec{R})$

## 2 Solving the nuclear Schrodinger Equation

From the last section, we saw that the nuclear Schrodinger equation is simply

$$[\hat{H}_N(\vec{R}) + E_{el}(\vec{R})]\psi_N(\vec{R}) = E\psi_N(\vec{R})$$

The kinetic energy operator for the nuclear problem can be separated into a center of mass coordinate and an internal coordinate (the reduced mass for instance). Thus, we still have 2 coordinate, but they are just taken to be another set with the same information. Thus, the kinetic part can be written as:

$$\hat{H}_N(\vec{R}) \quad = \quad -\frac{\hbar^2}{2M_{Total}}\nabla^2_{COM} - \frac{\hbar^2}{2\mu}\nabla^2_{int}$$

where

$$\begin{aligned}
\nabla^2_{int} &= \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{R^2 sin(\theta)}\frac{\partial}{\partial\theta}\left(sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{R^2\sin^2(\theta)}\left(\frac{\partial^2}{\partial\phi^2}\right) \\
\nabla^2_{int} &= \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hat{L}^2(\theta,\phi)}{R^2}
\end{aligned}$$

Thus, the nuclear Schrodinger equation becomes

$$\begin{aligned}
\left[-\frac{\hbar^2}{2M_{Total}}\nabla^2_{COM} - \frac{\hbar^2}{2\mu}\nabla^2_{int} + E(\vec{R})\right]\psi_N(\vec{R}) &= E\psi_N(\vec{R}) \\
\left[-\frac{\hbar^2}{2M_{Total}}\nabla^2_{COM} - \frac{\hbar^2}{2\mu}\left(\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hat{L}^2(\theta,\phi)}{R^2}\right) + E(\vec{R})\right]\psi_N(\vec{R}) &= E\psi_N(\vec{R})
\end{aligned}$$

Now, since the total Hamiltonian is **separable** int center of mass and internal coordinates, we again pose the separable ansatz as:

$$\begin{aligned}
\psi_N(\vec{R}) &= \psi_{translational}\ (\vec{R}_{COM})\psi_{int}(R,\theta,\phi) \\
E &= E_{translational} + E_{int}
\end{aligned}$$

This allows us to obtain (show yourself) two separate Schrodinger equations for center of mass and internal coordinates as:

$$\begin{aligned}
-\frac{\hbar^2}{2M_{Total}}\nabla^2_{COM}\ \psi_{translational}\ (\vec{R}_{COM}) &= E_{trans}\ \psi_{translational}\ (\vec{R}_{COM}) \\
\left[-\frac{\hbar^2}{2\mu}\nabla^2_{int} + E(R)\right]\psi_{int}(R,\theta,\phi) &= E_{int}\psi_{int}(R,\theta,\phi)
\end{aligned}$$

The first equation, for the center of mass, gives solutions of the form of a free particle or PIB; doesn't give much information on molecular nature of molecule. The second equation is the one we are concerned with now.

$$\begin{aligned}
\left[-\frac{\hbar^2}{2\mu}\nabla^2_{int} + E(R)\right]\psi_{int}(R,\theta,\phi) &= E_{int}\psi_{int}(R,\theta,\phi) \\
\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hat{L}^2(\theta,\phi)}{R^2}\right) + E(R)\right]\psi_{int}(R,\theta,\phi) &= E_{int}\psi_{int}(R,\theta,\phi)
\end{aligned}$$

We can now separate the intramolecular wavefunction simply as :

$$\begin{aligned}\psi_{int}(R,\theta,\phi) &= \chi(R)\psi_{rotational}(\theta,\phi) = \chi(R)Y_l^m(\theta,\phi)\\ E_{int} &= E_{elec} + E_{vib} + E_{rot}\end{aligned}$$

Consider the angular momentum part of the intramolecular Hamiltonian:

$$\frac{\hbar^2}{2\mu}\frac{\hat{L}^2(\theta,\phi)}{R^2}\psi_{int}(R,\theta,\phi) = \chi(R)\frac{\hbar^2}{2\mu}\frac{\hat{L}^2(\theta,\phi)}{R^2}Y_l^m(\theta,\phi) = \chi(R)\frac{L(L+1)}{2\mu R^2}Y_l^m(\theta,\phi)$$

This gives for the "R" dependent Schrodinger equation for the nuclear intramolecular motion:

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{L(L+1)}{2\mu R^2} + E(R)\right]\chi(R) = E_{int}\chi(R)$$

Now we are left with an equation in R. We can solve this numerically by computing E(R) for various R values. This is cumbersome (though valid). We can also take another approach. First, let's consider expanding E(R) in a Taylor expansion about some equilibrium separation $R_e$ as:

$$\begin{aligned}E(R) &= E(R_e) + (R-R_e)\left(\frac{dE}{dR}\right)_e + \frac{1}{2}(R-R_e)^2\left(\frac{d^2E}{dR^2}\right)_{R_e} + ....\\ &= E(R_e) + \frac{1}{2}k(R-R_e)^2 = E(R_e) + \frac{1}{2}kx^2\end{aligned}$$

where $x = R - R_e$. Substituting the expressin for E(R) and making the transformation to a new function:

$$\psi_{vib} = \chi(R)\ R$$

we obtain the following Schrodinger equation:

$$-\frac{\hbar^2}{2\mu R^2}\ R\ \frac{\partial^2\psi_{vib}}{\partial R^2} + \frac{L(L+1)}{2\mu R^2}\psi_{vib}\ R^{-1} + E(R_e)\psi_{vib}R^{-1} + \frac{1}{2}k(R-R_e)^2\psi_{vib}R^{-1} = E_{int}\psi_{vib}R^{-1}$$

Since $x = R - R_e$ and the derivatives with respect to R and x are equivalent under this transformation, we can take the derivatives with respect to R as with resepct to x. Also, multiplying through by "R", we obtain:

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi_{vib}}{\partial R^2}+\frac{L(L+1)}{2\mu R^2}\psi_{vib}\ +E(R_e)\psi_{vib}+\frac{1}{2}k(R-R_e)^2\psi_{vib}=E_{int}\psi_{vib}$$

Rearranging, we obtain:

$$\begin{aligned}-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi_{vib}}{\partial x^2}+\frac{1}{2}kx^2\psi_{vib} &= \left(E_{int}-\frac{L(L+1)}{2\mu R^2}-E(R_e)\right)\psi_{vib}\\ &= E_{vib}\psi_{vib}\end{aligned}$$

This is exactly the Schrodinger equation for the 1-D quantum harmonic oscillator. We have seen solutions of this type of equation in the form of Hermite Polynomials. The vibrational energy is simply:

$$E_{vib}=\left(n+\frac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}}$$

Some further comments:

$$\begin{aligned}E(R_e) &= E_{elec}(R_e)\\ \frac{J(J+1)}{2\mu R_e^2} &= E_{rot}\\ E_{int} &= E_{elec}+E_{vib}+E_{rot}\end{aligned}$$

The total energy is thus a sum of electronic, vibrational, and rotational energies. Under the **harmonic oscillator approximation** for a diatomic molecule, the energy for vibrational levels resemble the harmonic oscillator energy levels.

The **wavefunction** is a product of electronic and nuclear wavefunctions, with the nuclear function itself a product of translational, vibrational, and rotational wavefunctions:

$$\psi=\psi_{el}(r,R)\psi_{vib}(R)\psi_{rot}(\theta,\phi)\psi_{trans}(R_{COM})$$

Thus, we have considered first-order model of a diatomic and seen the energies and wavefunctions.

## 3 Anharmonic Effects of molecular vibrations

Real molecules are not always well-approximated as harmonic oscillators (particularly at larger separations, near the bond-breaking limits). Thus, the harmonic potential description of a diatomic does not take into consideration states close to dissociation.
The Morse potential (Figure 19.6 , Engel and Reid) shows a description of a potential that is anharmonic about the equilibrium nuclear separation, $R_e$. This is formally defined as:

$$V(x) = D_e \left[1 - e^{-\alpha(x-x_0)}\right]^2$$

- $D_e$ is the dissociation energy referenced to the **zero of the potential**
- $\alpha = \sqrt{\frac{k}{2D_e}}$
- The force constant, k, for this potential is determined by the general prescription for a force constant, namely $k = \frac{d^2V(x)}{dx^2}|_{x=x_e}$
- The **bond energy** is referenced to the quantum mechanical ground state of the oscillating pair

The energy levels for the Morse potential are:

$$E_n = \hbar\omega_0 \left(n + \frac{1}{2}\right) - \frac{(\hbar\omega_0)^2}{4D_e} \left(n + \frac{1}{2}\right)^2$$

**NOTE: in the handbook by Teplyakov and Dybowski, the analogous equation is taken to higher order terms; it is given by**:

$$E_n = \hbar\omega_e \left(n + \frac{1}{2}\right) - \hbar\omega_e x_e \left(n + \frac{1}{2}\right)^2 + \hbar\omega_e y_e \left(n + \frac{1}{2}\right)^3$$

Higher order perturbative terms can be included in the approximation of the vibration to yield higher-order dependence of the energy on the quantum number "n" as seen in the previous equation.
The parameters for $\omega_e$, $x_e$ are given in Table 12.1 in Teplyakov and Dybowski.

**Selection Rule for molecular vibration in absence of rotational coupling :** $\Delta n = \pm 1$

# 4 Rigid Rotor Approximation with Vibrational Distortion

## 4.1 Simple Case: no vibrational distortion

From the above discussion on the nuclear Schrodinger equation, we observe that in the **absence** of coupling of vibrational and rotational motions, the rotational energy of the diatomic is simply:

$$E_{rot} = \frac{\hbar^2}{2\mu R_e^2} J(J+1) = \frac{h^2}{8\pi^2 \mu R_e^2} J(J+1) = h\ B_e\ J(J+1)$$

**Selection for Rigid Rotor Approximation, no coupling to vibrations:** $\Delta J = \pm 1$.

- For **absorption:** $\Delta J = +1$**:**

$$\Delta E_+ = \frac{\hbar^2}{2\mu R_e^2} \left[(J+1)(J+2) - J(J+1)\right] = 2hB(J+1)$$

- **For emission:** $\Delta J = -1$**:**

$$\Delta E_- = \frac{\hbar^2}{2\mu R_e^2} \left[(J-1)(J) - J(J+1)\right] = -2hBJ$$

- **the energy differences are not the same because the energy levels are not equally spaced.**

## 4.2 More complex case: vibrational distortion

For the case of vibrational effects on the rotational dynamics, the energies for a given vibrational-rotational state are given as:

$$E_{J,m_J} \quad = \quad h\ B_n\ J(J+1) \qquad J = 0,1,2,3,4 \qquad m_j = 0, \pm 1, \pm 2, ..., \pm J \quad g_J = 2J+1$$

With the last expression are associated some constants that are defined as :

$$B_n = B_e - \left(n + \frac{1}{2}\right)\alpha_e \qquad B_e = \frac{h}{8\pi^2\ I_e} \qquad I_e = \mu R_e^2$$

The parameter $\alpha_e$ is given in Table 12.1 of Teyplyakov and Dybowski.

### 4.3 Vibration-Rotation Coupling, Centrifugal Distortion, and Electronic Energy

The energy for a diatomic including the various contributions arising from the effects just discussed is:

$$\begin{aligned} E_{n,l} &= E_{electronic} + E_{vibrational} + E_{rotational} \\ &= -D_e + \left(n + \frac{1}{2}\right)\hbar\omega_e - \left(n + \frac{1}{2}\right)^2 \hbar x_e \omega_e + ... + hB_n J(J+1) - hD_c J^2 (J+1)^2 \end{aligned}$$

where:

$$D_c = \frac{4B_e^3}{\omega_e^2}$$