

# 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:

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

Let's define:

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

- **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 kinetic energy operator of the nuclei.
- $\hat{H}_{electronic}(\vec{r}, \vec{R})$  is the electronic Hamiltonian.

Thus,

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

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 equation 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 coordinates) 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  $\mathbf{R}$  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:

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

where

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

Thus, the nuclear Schrodinger equation becomes

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

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:

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

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.

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

We can now separate the intramolecular wavefunction simply as :

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

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:

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

where  $x = R - R_e$ . Substituting the expression 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 respect 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:

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

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:

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