The simplest molecule consists of two atoms, called a diatomic molecule. Consider the diatomic molecule AB with a total of 2 electrons.

The Hamiltonian operator for this molecule will consist of five sets of terms:

- the kinetic energy terms for each of the nuclei,
- the kinetic energy terms for the electrons,
- the potential energy of attraction between the electrons and nuclei,
- the potential energy of repulsion between the two electrons, and
- the potential energy of repulsion between the two nuclei.

In atomic units, this is given by

\[
\hat{H} = -\frac{1}{2} \left( \frac{\nabla_A^2}{m_A} + \frac{\nabla_B^2}{m_B} \right) - \frac{1}{2} \left( \nabla_{1A}^2 + \nabla_{1B}^2 \right) - \left( \frac{Z_A}{r_{1A}} + \frac{Z_B}{r_{1B}} + \frac{Z_A}{r_{2A}} + \frac{Z_B}{r_{2B}} \right) + \frac{1}{r_{12}} + \frac{Z_A Z_B}{r_{AB}}
\]

No one has succeeded in solving the Schrödinger equation analytically with this Hamiltonian!

A very important step towards its solution is the Born-Oppenheimer approximation, which is based on recognizing that the electrons in a molecule move many orders of magnitude faster than the nuclei. Therefore, it is justifiable to solve the electronic part of the Schrödinger equation for the instantaneous, fixed, positions of the nuclei.

Invoking the Born-Oppenheimer approximation, therefore, means that we set the first set of terms equal to zero and the last term becomes a constant. Therefore, we wish to solve the equation

\[
\left[ -\frac{1}{2} \left( \nabla_{1A}^2 + \nabla_{1B}^2 \right) - \left( \frac{Z_A}{r_{1A}} + \frac{Z_B}{r_{1B}} + \frac{Z_A}{r_{2A}} + \frac{Z_B}{r_{2B}} \right) + \frac{1}{r_{12}} \right] \psi_{el} = E_{el} \psi_{el}
\]

This electronic energy depends on the value of \( r_{AB} \) because \( (r_{1A}, r_{1B}) \) and \( (r_{2A}, r_{2B}) \) are related to each other through \( r_{AB} \). Therefore, the solution yields

\[
U(r_{AB}) = E_{el}(r_{AB}) + \frac{Z_A Z_B}{r_{AB}}.
\]
Typically, the electronic energy decreases as the distance $r_{AB}$ decreases. On the other hand, the nuclear repulsion energy obviously increases as $r_{AB}$ decreases. If the atoms A and B form a stable molecule AB, the sum of these two terms goes through a minimum as shown in the figure below. The distance at which the energy is a minimum is the preferred internuclear distance, or the equilibrium bond length between A and B, $r_e$.

- Thus, the concepts of bond length and bond angle, for molecules with more than two atoms, arise from the Born-Oppenheimer approximation.
- We cannot think of molecular structure without the concepts of bond length and bond angle.
- Without the notion of molecular structure, there is no chemistry!

Recall that the kinetic energies of the nuclei were set equal to zero in the Born-Oppenheimer approximation. Obviously, the nuclei in a molecule are not stationary but, rather, move relatively slowly compared to the electrons. In fact, nuclear motion is responsible for vibrations, rotations, and reactions of molecules. Therefore, we now return to the full Hamiltonian and examine the nature of the problem that remains:

$$\frac{1}{2} \left( \frac{\nabla^2_A}{m_A} + \frac{\nabla^2_B}{m_B} \right) \psi_{\text{nuc}} + U(r_{AB}) \psi_{\text{nuc}} = \varepsilon \psi_{\text{nuc}},$$

where $U(r_{AB})$ was found by invoking the Born-Oppenheimer approximation. The complete solution to the full Hamiltonian to the problem is, therefore, assumed to be

$$\Psi(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}, r_{AB}) = \psi_{el}(r_{1A}, r_{1B}, r_{2A}, r_{2B}, r_{12}; r_{AB}) \psi_{\text{nuc}}(r_{AB})$$
In analogy with earlier treatments of two masses connected by a spring (the harmonic oscillator), we make the following modifications:

- The two kinetic energy terms corresponding to nuclei A and B are replaced with a single term corresponding to the reduced mass \( \mu \).
- The coordinates describing the positions of the two nuclei A and B are replaced with the internuclear distance \( r_{AB} \).

\[
\left[ -\frac{1}{2\mu} \nabla^2 + U(r_{AB}) \right] \psi_{nuc}(r_{AB}) = \varepsilon \psi_{nuc}(r_{AB}).
\]

The energy \( U(r_{AB}) \) found by invoking the Born-Oppenheimer approximation now plays the role of the potential energy for the movement of the nuclei. Therefore, we refer to it as the molecular potential energy. The movement of the nuclei subject to this potential is called the vibrations of the molecule. In the figure, we compare a model for the molecular potential energy to the more familiar harmonic oscillator potential. It is clear that the harmonic oscillator model we examined in Chapter 11 is a poor, but qualitatively correct, approximation to the molecular potential energy function. We will return to this aspect in more detail in Chapter 13.

Our focus for the present is on the nature of the electronic wave functions \( \psi_{el} \) corresponding to the different atomic orbitals on atoms A and B. These molecular electronic wave functions are called molecular orbitals. The formation of molecular orbitals may be said to be a result of the overlap (or linear combination) of atomic orbitals on the different nuclei. This mechanism, the “linear combination of atomic orbitals to form molecular orbitals” is referred to as the LCAO-MO method. The variation method of Chapter 11 plays a central role in the application of this method, as we shall see below.
The LCAO-MO Method: The $\text{H}_2^+$ molecular ion

The $\text{H}_2^+$ molecular ion is the simplest of all molecules, consisting of exactly three particles. Since only one electron is present, the electron-electron repulsion term is absent from the Hamiltonian. Within the Born-Oppenheimer approximation, the Schrödinger equation for the electronic wave function $\psi_{el}$ is

$$-\frac{1}{2} \nabla^2 \psi_{el} - \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \psi_{el} = E_{el} \psi_{el}$$

The single electron could belong to nucleus A, in which case $\psi_{el} = 1s_A = \frac{1}{\sqrt{\pi}} e^{-r_A}$ or it could belong to nucleus B, in which case $\psi_{el} = 1s_B = \frac{1}{\sqrt{\pi}} e^{-r_B}$. It is, however, unphysical to assign the electron to only one of the two nuclei. Therefore, a good variational trial function for this problem is

$$\varphi = c_1 1s_A + c_2 1s_B,$$

where the coefficients $c_1$ and $c_2$ are the variational parameters. It is important to keep in mind that two different origins (one at each nucleus) and coordinate systems are necessary to define these atomic orbitals. In order to solve the problem, we should transform to a common set of coordinates. The suitable coordinates are called “confocal-elliptic coordinates.” [See Eq. (12.4) and the text immediately above and below.] We will gloss over this detail in our treatment below.

We adopt the following notation for the various integrals needed:

$$S = \int (1s_A)^*(1s_B) d\tau$$

$$H_{AA} = \int (1s_A)^*H(1s_A) d\tau$$

$$H_{AB} = \int (1s_A)^*H(1s_B) d\tau$$

$$H_{BB} = \int (1s_B)^*H(1s_B) d\tau$$

In addition, also recall that since the atomic orbitals are normalized,

$$\int (1s_A)^*(1s_A) d\tau = \int (1s_B)^*(1s_B) d\tau = 1$$
Now, the variational functional is given by

$$W = \frac{\int[c_1 1s_A + c_2 1s_B] \hat{H}[c_1 1s_A + c_2 1s_B] d\tau}{\int[c_1 1s_A + c_2 1s_B]^2 d\tau} = \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 + c_2^2 + 2c_1 c_2 S}.$$ 

We now minimize $W$ with respect to the two parameters $c_1$ and $c_2$, i.e.,

$$\frac{\partial W}{\partial c_1} = 0, \quad \text{and} \quad \frac{\partial W}{\partial c_2} = 0$$

This gives rise to two equations which ultimately gives rise to the system of equations

$$c_1(H_{AA} - W) + c_2(H_{AB} - WS) = 0,$$  
$$c_1(H_{AB} - WS) + c_2(H_{BB} - W) = 0.$$ 

A trivial solution is obviously $c_1 = c_2 = 0$. It is a theorem of linear algebra that such a system of equations can have non-trivial solutions if and only if the determinant

$$\begin{vmatrix} (H_{AA} - W) & (H_{AB} - WS) \\ (H_{AB} - WS) & (H_{AA} - W) \end{vmatrix} = 0,$$

where we have recognized that since the nuclei A and B are identical, $H_{AA} = H_{BB}$. This determinant is called the **secular determinant**. Expanding the determinant gives two possible solutions for $W$, the variational energy, as

$$W_\pm = \frac{H_{AA} \mp H_{AB}}{1 \mp S}.$$ 

Substituting $W_+$ into the system of equations above gives rise to the result $c_1 = c_2$, and substituting $W_-$ gives $c_1 = -c_2$. From the normalization condition

$$\int \phi_+^* \phi_+ d\tau = 1,$$

we get

$$\phi_\pm = \frac{1s_A \pm 1s_B}{\sqrt{2(1 \pm S)}}.$$ 

Thus, the linear combination of two atomic orbitals gives rise to two molecular orbitals. Let us now examine the nature of these orbitals.