In a way similar to the case of the many-electron atom, we can define new variables

\[
\mathbf{R}_{\text{CM}} = \frac{M_A}{M} \mathbf{R}_A + \frac{M_B}{M} \mathbf{R}_B + \frac{m_e}{M} \sum_{i=1}^{\infty} \mathbf{r}_i
\]

\[
\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B
\]

\[
\mathbf{r}_i^c = \mathbf{r}_i - \frac{1}{2} (\mathbf{R}_A + \mathbf{R}_B)
\]

And

\[
\nabla_{\mathbf{R}_A} = \frac{M_B}{M} \nabla_{\text{CM}} + \nabla_{\mathbf{R}} - \frac{1}{2} \sum_{i=1}^{\infty} \nabla_{\mathbf{r}_i}
\]

\[
\nabla_{\mathbf{R}_B} = \frac{M_A}{M} \nabla_{\text{CM}} + \nabla_{\mathbf{R}} - \frac{1}{2} \sum_{i=1}^{\infty} \nabla_{\mathbf{r}_i}
\]

\[
\nabla_{\mathbf{r}_i} = \nabla_{\mathbf{r}_i} + \frac{m_e}{M} \nabla_{\text{CM}}
\]

\[
\Rightarrow \frac{1}{m_e} \sum_{i=1}^{\infty} \nabla_{\mathbf{r}_i}^2 + \frac{1}{M_A} \nabla_{\mathbf{R}_A}^2 + \frac{1}{M_B} \nabla_{\mathbf{R}_B}^2
\]

\[
= \frac{1}{M} \nabla_{\text{CM}}^2 + \frac{1}{M} \nabla_{\mathbf{R}}^2 + \frac{1}{M} \sum_{i=1}^{\infty} \nabla_{\mathbf{r}_i}^2 + \frac{1}{4M} \sum_{i,j=1}^{\infty} \nabla_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} + \frac{1}{M} \nabla_{\mathbf{R}} \sum_{i=1}^{\infty} \nabla_{\mathbf{r}_i}
\]

and

\[
\mathcal{H} = -\sum_{i=1}^{\infty} Z_i q_i e = \sum_{i=1}^{\infty} \frac{Z_i q_i e^2}{|\mathbf{r}_i - \mathbf{r}_c|} - \sum_{i=1}^{\infty} \frac{Z_i q_i e^2}{|\mathbf{r}_i + \mathbf{r}_c|} + \sum_{i>j} \frac{q_i q_j}{r_{c,j}} + \frac{Z_B Z_B q_o e^2}{\mathbf{R}}
\]

\[
L = V(r_c^c, \mathbf{R})
\]

\[
V(r_c^c, \mathbf{R})
\]
The Hamiltonian becomes:

\[
\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2_R - \frac{\hbar^2}{2m_e} \sum_{i=1}^{\overline{m}} \nabla_i^2 + V(r_i, \vec{R}) - \frac{\hbar^2}{8\mu} \sum_{i,j=1}^{\overline{m}} \nabla_i \nabla_j - \frac{\hbar^2}{2\mu} \nabla_R \sum_{i=1}^{\overline{m}} \nabla_i - \frac{\hbar^2}{2M} \nabla_{c.m.}^2
\]

... electronic Hamiltonian

corrections to B.O. (diagonal & C.M. motion)

relative motion of nuclei

We neglect the last 3 terms (i.e. non-B.O. terms & C.M. motion) to describe the "internal" dynamics.

We further can show that

\[
-\frac{\hbar^2}{2\mu} \nabla^2_R = -\frac{\hbar^2}{2\mu} \frac{2}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \hat{\Omega}^2 \frac{2}{MR^2}
\]

where \( \hat{\Omega} \) is the angular momentum of the nuclei.

and \( \hat{\Omega}^2 = \hat{J}^2 + \hat{L}^2 - 2 \hat{J} \cdot \hat{L} \), with \( \hat{J} = \hat{\Omega} + \hat{\mathbf{j}} \) is electronic angular momentum.

\( \hat{L} \) is total angular momentum.

Then,

\[
\hat{H} = \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^{\overline{m}} \nabla_i^2 + V \right] + \left[ -\frac{\hbar^2}{8\mu} \sum_{i,j=1}^{\overline{m}} \nabla_i \nabla_j - \frac{\hbar^2}{2\mu} \nabla_R \sum_{i=1}^{\overline{m}} \nabla_i - \frac{\hbar^2}{2M} \nabla_{c.m.}^2 \right] - \frac{\hbar^2}{2\mu} \frac{2}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\hat{J}^2}{2\mu R^2} + \frac{\hat{L}^2 - 2 \hat{J} \cdot \hat{L}}{2MR^2} - \hat{H}_{\text{vib}} - \hat{H}_{\text{rot}} + \hat{H}_{\text{c.m.}}
\]

... electronic term
Within the B.O. approximation, we neglect \( \hat{H}_e \), and solve with

\[ \hat{H} = \hat{H}_e + \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}} + \hat{H}_{\text{con}}. \]

Again, separating the nuclear and electronic motion, we get;

\[ \Psi_{m, i} (\vec{r}, R) = \chi_{m, i} (R) \phi_{m, i} (\vec{r}, R), \text{ with } \vec{r} = \{ \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n \} \]

\[ \Rightarrow \Psi_{m, i} (\vec{r}, R) = \chi_{m, i} (R) \phi_{m, i} (\vec{r}, R) \]

Let only distances between nuclei.

So, with \( \hat{H}_e \phi_{m, i} (\vec{r}, R) = E_{m, i} (R) \phi_{m, i} (\vec{r}, R) \)

\[ = U_{m,k} (R) \phi_{m, i} (\vec{r}, R) \]

Lo potential energy curve.

We now have (in the C.M.)

\[ [\hat{H}_{\text{vib}} + \hat{H}_{\text{rot}} + \hat{H}_{\text{con}} + U_{m,k} (R)] \chi_{m, i} (R) = E_{m, i} \chi_{m, i} (R) \]

Here, "m" stands for the electronic state \( |m\rangle \)

"i" stands for all other indices describing the nuclear motion.

We associate an energy with each of the \( \hat{H} \)'s, i.e.

\[ \hat{H}_{\text{vib}} \chi_{m, i} (R) = E_{\text{vib}} \chi_{m, i} (R) \]

\[ \hat{H}_{\text{rot}} \chi (R) = E_{\text{rot}} \chi (R) \] \[ \chi (R) \] \[ \Rightarrow E_{\text{rot}} + E_{\text{con}} = E_{\text{rot}} \]

(From C.M.)
Because \( E_{m,i} \) is a constant (i.e. eigenenergy) we must have

\[
E_{\text{inh}}(R) + E_{\text{rot}}(R) + U_m(R) = E_{m,i} = \text{const}.
\]

\( \text{all must depend on } R \).

The state will be described by

\[
|\gamma\rangle = \hat{v}, \hat{a} \otimes |m\rangle = |m\rangle \otimes |v, j, l\rangle
= |m, v, j, l\rangle \quad \text{or} \quad |m, v, j, l\rangle
\]

we projected onto \( |\gamma, R\rangle \) gives

\[
\mathcal{V}(\gamma, R) = \langle \gamma, R | \gamma \rangle = \langle \gamma, R | m \rangle \langle m | v, j, l \rangle
= \phi_{m, \ell}(\gamma, R) \chi_{m, i}(R) \frac{\hbar^2}{2m} \langle v, j, l \rangle
\]

Note: we have not included the spin of the electron or nuclei yet. These will add more quantum numbers... more later.

So, in general

\[
E_{\text{inh}}(R) = V_2(R)
\]

for upper state

\[
E_{\text{rot}}(R) = V_1(R)
\]

for lower state

\[
E_{\text{vib}}(R) = \{ \text{vib. levels} \}
\]

\[
E_{\text{rot}}(R) = \{ \text{rotational levels} \}
\]

\[
E_{\text{stat}}(R) = \{ \text{stat. levels} \}
\]

\( D_0 \)

\( \approx \) dissociation energy

\( R_e, R_i \) equilibrium separation
1.6 Simplest Molecule: \( \text{H}_2^+ \)

As an example to illustrate the previous points, we consider \( \text{H}_2^+ \).

Although an exact solution exists for a rigid \( \text{H}_2^+ \) molecule using elliptic coordinates, we will use an approximate treatment that can be employed for more complex systems.

1.6.1 Electron states

We will use the approach called molecular orbital calculation using a linear combination of atomic orbitals (MO-LCAO).

For a fixed separation \( R \), the electronic Hamiltonian is

\[
\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{q_e^2}{4\pi\epsilon_0 R_A} - \frac{q_e^2}{4\pi\epsilon_0 R_B} + \frac{q_e^2}{4\pi\epsilon_0 R}
\]

with only one electron.

As a fixed initial "guess" for the electronic wavefunction, we assume that it is the sum of two \( \text{H}(1s) \) orbitals (we are interested in the ground electronic state: otherwise, we could use other atomic states).

\[
\phi_e = c_A \psi_A + c_B \psi_B \quad \text{with} \quad 4 \equiv 2(1s)
\]

Now, we minimize the electronic energy, i.e.

\[
E_e = \frac{\langle \phi_e | \hat{H}_e | \phi_e \rangle}{\langle \phi_e | \phi_e \rangle}
\]
Let us define a few parameters:
\[ E_{\text{AA}} = E_{\text{BB}} = \text{Coulomb integral} = \langle \psi_a | \hat{H}_e | \psi_a \rangle \]
\[ \text{or} \quad \langle \psi_b | \hat{H}_e | \psi_b \rangle \]
\[ E_{\text{AB}} = E_{\text{BA}} = \text{resonance (or exchange) integral} \]
\[ = \langle \psi_a | \hat{H}_e | \psi_b \rangle = \langle \psi_b | \hat{H}_e | \psi_a \rangle \]

and \[ S : \text{overlap integral} = \langle \psi_a | \psi_b \rangle \]

Using this notation,
\[ \langle \phi_e | \hat{H}_e | \phi_e \rangle = c_A^2 + c_B^2 + 2c_Ac_B S \]
\[ \langle \phi_e | \hat{H}_e | \phi_e \rangle = c_A^2 E_{\text{AA}} + c_B^2 E_{\text{BB}} + 2c_Ac_B E_{\text{AB}} \]
(we assume \( c_A \) and \( c_B \) to be real coefficients).

\[ \Rightarrow \langle \phi_e | \hat{H}_e | \phi_e \rangle = E_e \langle \phi_e | \phi_e \rangle \]

\[ c_A^2 E_{\text{AA}} + c_B^2 E_{\text{BB}} + 2c_Ac_B E_{\text{AB}} = E_e (c_A^2 + c_B^2 + 2c_Ac_B S) \]

Setting \[ \frac{\partial E_e}{\partial c_A} = \frac{\partial E_e}{\partial c_B} = 0 \]
gives a pair of linear equations which leads to the secular equation:

\[
\begin{vmatrix}
E_{\text{AA}} - E_e & E_{\text{AB}} - E_e S \\
E_{\text{BA}} - E_e S & E_{\text{BB}} - E_e
\end{vmatrix} = 0
\]
The eigenvalues:

\[ E_1 = \frac{E_{AA} + E_{AB}}{1 + S}, \quad E_2 = \frac{E_{AA} - E_{AB}}{1 - S} \]

and eigenfunctions

\[ \phi_1 = \frac{\psi_A + \psi_B}{\sqrt{2(1+S)}} \equiv 1 \sigma_g^+ \]

\[ \phi_2 = \frac{\psi_A - \psi_B}{\sqrt{2(1-S)}} = 1 \sigma_u^+ \]

The Coulomb integral \( E_{AA} \) has two contributions:

\[ |\psi_A|^2 \quad \text{cross section for} \quad \frac{R}{R_{AB}} \quad |\psi_B|^2 \]

Same for \( \psi_B \), i.e.,

\[ |\psi_B|^2 \quad \text{and} \quad |\psi_A|^2 \]

Overlap leads to the molecular interaction.
The exchange integrals $E_{AB}$ & $E_{BA}$ have contributions of overlaps of $\Psi_A$ & $\Psi_B$ with either the two nuclei.

The exchange corresponds to the exchange of the electron from $\Psi_A$ to $\Psi_B$ (or vice versa).

Using the hydrogen atom wave functions, the energies $E_1$ and $E_2$ can be found to be:

$$\Psi_A = (1s)_A = \frac{1}{\sqrt{\pi}} \frac{e^{-r_A/a_0}}{a_0^{3/2}} \quad \text{and} \quad \Psi_B = \frac{1}{\sqrt{\pi}} \frac{e^{-r_B/a_0}}{a_0^{3/2}}$$

\[
E_{1,2} = E_{1s} - \frac{1}{1+S} \frac{e^2}{a_0} \left[ \frac{1}{\rho} - e^{-2\rho} \left( \frac{1}{\rho} + 1 \right) - e^{-\rho} (1 + \rho) \right] + \frac{e^2}{a_0 \rho} \\
\text{where } \rho = R/a_0
\]

\[E(R_a)\]

The exact solution is lower at $D_e = 2.79 \text{ eV}$.
The ground state, $1\sigma_g^+$, is a bonding orbital, while the purely repulsive $1\sigma_u^+$ is an anti-bonding.

Note: This simple treatment gives a bond energy $D_e$ about 50% off. Using an effective Zeff to be varied improves significantly the result. However, a more flexible basis set is needed for really accurate results. More later on Q. Chemistry techniques.

16.2 Vibration and Rotation of $H_2^+$

Now that the electronic curves $E_n^d(R)$ are known, we can address the motion of the nuclei. The move in the effective potentials $V_n(R) = E_n^d(R)$;

$$\left[ -\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V_n(R) \right] \chi_{m;i}(R) = E_{m;i} \chi_{m;i}(R)$$