This is the 2nd semester of the 2-semester course on atomic and molecular physics. Though we will cover mostly aspects of molecular physics, some "left-over" topics of atomic physics will still appear...

1. Hamiltonian & Born-Oppenheimer approximation

In general, the Hamiltonian for a system of n electrons and N nuclei is given by

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{\nabla_i^2}{M_i} + \sum_{i \neq j}^{N} \frac{q_i^2}{4\pi\epsilon_0 r_{ij}} + \frac{q_i^2}{4\pi\epsilon_0} \sum_{I \neq j}^{N} \frac{Z_I Z_J}{R_{Ij}} - \sum_{I \neq j}^{N} \frac{q_i^2}{4\pi\epsilon_0} \frac{1}{R_{Ii}}$$

where

$$R_{ij} = |\vec{R}_i - \vec{R}_j| : \text{separation of nuclei } I \text{ & } J$$

$$\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j| : \text{separation between electrons } i \text{ & } j$$

$$E_i = |\vec{R}_i - \vec{r}_i| : \text{separation between nucleus } I \text{ & electron } i$$

The 1st two terms are the kinetic energies of the $e^-$ and nuclei, respectively.
The next 3 terms are the potential energy due to the Coulomb interaction

\[ V(\vec{r}, \vec{R}) = V_{el} + V_{nuc,nuc} + V_{nuc,el} \]

This Hamiltonian neglects interactions related to electrons or nuclear spins: it is the non-relativistic Hamiltonian.

For the time being, we consider the molecule at rest in the laboratory frame, i.e., its c.m. is stationary [more about this later].

So, we have the Schrödinger (time ind.) eq.

\[ \hat{H} \psi = E \psi \], with \[ \hat{H} = \hat{T}_{el} + \hat{T}_{nuc} + V(\vec{r}, \vec{R}) \]
and \[ E = E(\vec{r}, \vec{R}) \]

1.2 Separation of electronic and nuclear wavefunctions

Because \( m_e \ll M \), the electron in a molecule moves much faster than the vibrating nuclei.

\( \Rightarrow \) the electron cloud adjust more or less instantaneously to the changing nuclear positions \( \vec{R} \).

So, if \( T_{nuc} \ll T_{el} + V \Rightarrow \) consider it as a perturbation

\[ \hat{H} = \hat{T}_{el} + V + \hat{T}_{nuc} \]
\[ \hat{H} = \hat{H}_0 + \hat{H}' \]
The unperturbed Schrödinger eq. is
\[ \hat{H}_0 \phi^{(d)}(\vec{r}, \vec{R}) = E^{(d)}(\vec{R}) \phi^{(d)}(\vec{r}, \vec{R}) \]

which describes a molecule in which the nuclei are fixed at a given configuration \( \vec{R} \).

\( \Rightarrow \) frozen nucleus approximation

or Born-Oppenheimer approximation

We associate an electronic state \( |m\rangle \) with energy \( E^{(m)}(\vec{R}) \), and \( \phi^{(m)}(\vec{r}, \vec{R}) \) depends only on \( \vec{r} \), i.e. \( \vec{R} \)'s do not enter as variables, but as parameters only [i.e. \( \phi^{(m)} = E^{(m)} \phi^{(d)} \) does not contain differentiation or integration with respect to \( \vec{R} \)'s].

We can then expand the wave function as
\[ \psi(\vec{r}, \vec{R}) = \sum_m \chi_m(\vec{R}) \phi^{(d)}_m(\vec{r}, \vec{R}) \]

So expansion coefficients depend on \( \vec{R} \) only.

Now,
\[ \hat{H} \psi = E \psi \Rightarrow (\hat{H} - E) \sum_m \chi_m(\vec{R}) \phi^{(d)}_m(\vec{r}, \vec{R}) = 0 \]

Multiplying by \( \phi^{(d)} \) and integrating over \( \vec{r} \), we obtain equations for the expansion coeff. \( \chi_m(\vec{R}) \):
\[ \int d^3r \phi^{(d)}_m(\vec{r}, \vec{R}) (\hat{H} - E) \sum_n \chi_n(\vec{R}) \phi^{(d)}_n(\vec{r}, \vec{R}) = 0 \]

where \( \hat{H} = \hat{H}_0 + \hat{H}' \)

and \( \int d^3r \phi^{(d)}_m \phi^{(d)}_n = S_{mn} \)
So,

\[(E_{\mu}^{(\text{e})} (\vec{R}) - E) \chi_{\mu}(\vec{R}) + \int d\vec{r} \phi_{\mu}^{*} \hat{H} \sum_{m} \phi_{m}(\vec{R}) \phi_{\mu}^{*} (\vec{r}, \vec{R}) = 0\]

Dropping the "el", i.e. \( \phi_{\mu} = \phi_{\mu}^{el} (\vec{r}, \vec{R}) \), we write

\[
\int d\vec{r} \phi_{\mu}^{*} \hat{H} \left( \sum_{m} \chi_{m}\phi_{m} \right) = \int d\vec{r} \phi_{\mu}^{*} \sum_{m} \left( \hat{H} \chi_{m} \right) \phi_{\mu} \\
+ \int d\vec{r} \phi_{\mu}^{*} \sum_{m} \chi_{m} \left( \hat{H} \chi_{m} \right) \\
- \frac{\hbar^{2}}{2} \int d\vec{r} \phi_{\mu}^{*} \sum_{m} \chi_{m} \sum_{k} \frac{1}{m_{k}} \left\{ \nabla_{k} \phi_{m} \right\} \phi_{\mu} \\
\text{(distributing } \nabla^{2} = \nabla \cdot \nabla \text{ on } \chi \phi = 1)\]

The 1st term is

\[
\int d\vec{r} \phi_{\mu}^{*} \sum_{m} \left( \hat{H} \chi_{m} \right) \phi_{\mu} = \sum_{m} \hat{H} \chi_{m}(\vec{R}) \int d\vec{r} \phi_{\mu}^{*} \phi_{\mu} \\
= \hat{H} \chi_{m}(\vec{R}) \quad [\hat{H} \text{ depends only on } \vec{R}']
\]

The 2nd and 3rd terms can be combined as:

\[
\sum_{m} \text{c.m. } \chi_{m} \text{ with } c_{\text{m.m.}} = \int d\vec{r} \phi_{\mu}^{*} \hat{H} \phi_{\mu} - \frac{\hbar^{2}}{2} \left[ \int d\vec{r} \phi_{\mu}^{*} \\
\times \sum_{k} \frac{1}{m_{k}} \nabla_{k} \phi_{m} \right] \nabla_{k}
\]
This yields
\[(E_n^{(0)}(\vec{r}) + \hat{H}') \chi_n(\vec{r}) + \sum_m \sum \chi_m(\vec{r}) = E \chi_n(\vec{r})]\]

Therefore:
\[
\begin{align*}
\hat{H}_0 \phi(\vec{r}, \vec{R}) &= E^0(\vec{r}) \phi(\vec{r}, \vec{R}) \\
\hat{H}' \chi_n(\vec{r}) + \sum_m \chi_m(\vec{r}) &= [E - E_n^{(0)}(\vec{R})] \chi_n(\vec{r})
\end{align*}
\]

This coupled set of equations for the electronic wavefunctions \(\phi\) and nuclear wavefunctions \(\chi\) is completely equivalent to the Schrodinger equation
\[
\hat{H} \chi(\vec{r}, \vec{R}) = E \chi(\vec{r}, \vec{R})
\]

The coupling matrix elements \(c_{nm}\) describe how different electronic states \(\phi_n\) and \(\phi_m\) are coupled through the nuclear motion.

Note: If \(c_{nm} = 0\), the 2nd eq. describes the motion of the nuclei with kinetic energy \(\hat{H}'\) in the potential \(E_n^{(0)}(R)\).

\[\hat{H}' / \chi_n(\vec{r}) \ [\hat{H}' + E_n^{(0)}(\vec{R})] \chi_n(\vec{r}) = E \chi_n(\vec{r})\]

The potential \(E_n^{(0)}(\vec{R})\) are given by the 1st equation.