Lecture notes
2017/5/11 by Aixi Pan

**The Schrödinger Equation**

Hamiltonian operator:

\[
\hat{H} = \sum_i \frac{p_i^2}{2m_i} + V
\]

For atomic units, \(\hbar = m = 4\pi \varepsilon_0 = a_0 = 1\)

So, nuclei: mass of \(M_i\), charge of \(Z_i\), electrons: mass of \(m_e\), charge of \(-e\).

The above Hamiltonian operator can then be written as:

\[
\hat{H} = \hat{T}_{\text{nuclei}} + \hat{T}_{\text{electron}} + V^{NN} + V^{Ne} + V^{ee}
\]

The Schrödinger equation:

\[
\hat{H} \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) = E \psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M)
\]

Then fixing nuclei to solve the Schrödinger equation for electrons (choose molecular geometry):

\[
\hat{H}^{\text{el}} \psi_{\text{el}}(\{\vec{r}\}; \{\vec{R}\}) = E_{\text{el}} \psi_{\text{el}}(\{\vec{r}\}; \{\vec{R}\})
\]

The (ground state) energy at a particular configuration \(\{\vec{R}\}\),

\[
E_{\text{el}}
\]

We can fit a curve through the points of \(V(\{\vec{R}\})\), then \(V(\{\vec{R}\})\) can be called the potential energy surface (PES). When the potential energy surface has been obtained one can solve for nuclear motion. In accurate calculations one would solve a coupled problem for rotational and vibrational motion. The most common approximations only require the geometry of the minimum (rigid rotor), and the curvature of the potential at the
minimum (harmonic oscillator approximation).

Here we will focus on the electronic structure problem: (approximately) solving the electronic S.E. at a particular nuclear geometry.

**Terms in Electronic Hamiltonian**

For all electrons,

$$\mathcal{T} = -\frac{1}{2} \sum_i \nabla_i^2$$

where \( \nabla_i^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \)

The three terms in Hamiltonian operator:

$$\mathcal{V}^{NN} = \frac{1}{2} \sum_{a \neq b} \frac{Z_a Z_b}{|\vec{R}_a - \vec{R}_b|}$$

$$\mathcal{V}^{Ne} = \sum_i \left( \sum_a \frac{-Z_a}{|\vec{R}_a - \vec{r}_i|} \right) = \sum_i f(\vec{r}_i)$$

$$\mathcal{V}^{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

where \( a \) is constant in \( \mathcal{V}^{NN} \); \( \mathcal{V}^{Ne} \) can be viewed as the sum of the function of \( \vec{r}_i \);

So,

$$\mathcal{T} + \mathcal{V}^{Ne} \equiv \mathcal{H} = \sum_i \mathcal{h}(i)$$

where \( \mathcal{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_a \frac{Z_a}{|\vec{r}_i - \vec{R}_a|} \).

And,

$$\mathcal{V}^{ee} = \mathcal{V} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

then we can get \( \mathcal{H} = \mathcal{h} + \mathcal{V} \).

**Consider: What if \( \mathcal{H} = \mathcal{h} \)?**

It is a “toy problem” in order to sketch true solution which leads to molecular orbital theory. The final result we will obtain is that the solutions will be given by:
where $\mathcal{A}$ denotes an antisymmetrizer (to be discussed), then,

$$\hat{h}(1)\varphi_x(\vec{r}_1) = \varepsilon_x \cdot \varphi_x(\vec{r}_1), \ x = a, b, \ldots, z.$$  

$$E = \varepsilon_a + \varepsilon_b + \ldots, \varepsilon_z.$$  

All complexity for electronic structure is due to $\mathcal{V}^{ee}$.  

Let us go back to the question:

$$\hat{H} = \sum_i \hat{h}(i)$$

For example, let us consider a specific example with 3 electrons, with Hamiltonian

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \hat{h}(3)$$

Assume that $\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \varphi_a(\vec{r}_1) \cdot \varphi_b(\vec{r}_2) \cdot \varphi_c(\vec{r}_3)$,

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \left(\hat{h}(1) + \hat{h}(2) + \hat{h}(3)\right) \left(\varphi_a(\vec{r}_1) \cdot \varphi_b(\vec{r}_2) \cdot \varphi_c(\vec{r}_3)\right)$$

$$= \varphi_b(2) \cdot \varphi_c(3) \cdot \left(\hat{h}(1)\varphi_a(1)\right) + \varphi_a(1) \cdot \varphi_c(3) \cdot \left(\hat{h}(2)\varphi_b(2)\right)$$

$$\quad + \varphi_a(1) \cdot \varphi_b(2) \cdot \left(\hat{h}(3)\varphi_c(3)\right) = E \cdot \varphi_a(\vec{r}_1) \cdot \varphi_b(\vec{r}_2) \cdot \varphi_c(\vec{r}_3)$$

so, $E$ is equal to

$$\frac{\varphi_b(2) \cdot \varphi_c(3) \cdot \left(\hat{h}(1)\varphi_a(1)\right) + \varphi_a(1) \cdot \varphi_c(3) \cdot \left(\hat{h}(2)\varphi_b(2)\right) + \varphi_a(1) \cdot \varphi_b(2) \cdot \left(\hat{h}(3)\varphi_c(3)\right)}{\varphi_a(1) \cdot \varphi_b(2) \cdot \varphi_c(3)}$$

$$= \frac{\hat{h}(1)\varphi_a(\vec{r}_1)}{\varphi_a(\vec{r}_1)} + \frac{\hat{h}(2)\varphi_b(\vec{r}_2)}{\varphi_b(\vec{r}_2)} + \frac{\hat{h}(3)\varphi_c(\vec{r}_3)}{\varphi_c(\vec{r}_3)} = \varepsilon_a + \varepsilon_b + \varepsilon_c$$

For every electron,

$$\hat{h}(i)\varphi_a(\vec{r}_i) = \varepsilon_a \varphi_a(\vec{r}_i)$$

The orbitals are eigenfunctions of the same hermitian operator $h$. These orbitals can be chosen to form an orthonormal set, and $E_a$ denotes the so-called orbital energy.

If we now try to get the lowest energy solution we would get the following result:
Obviously, this is unexpected. In Chemistry, we would think we can put 2 electrons in each orbital. That is not the lowest energy solution to the differential equation. What important points have we missed?

**Pauli Principle (anti-symmetric wave function)**

For \( h(1) + h(2) \), \( \varphi_a(r_1)\varphi_b(r_2) \) and \( \varphi_b(r_1)\varphi_a(r_2) \) are degenerate, and the total energy is \( E = \varepsilon_a + \varepsilon_b = \varepsilon_b + \varepsilon_a \).

There exists only one proper solution: \( \varphi(r_1, r_2) = \varphi_a(r_1)\varphi_b(r_2) - \varphi_b(r_1)\varphi_a(r_2) \).

The interchange of two electrons:

\[
\begin{align*}
  r'_2 &\to r_1 & \varphi(r'_2, r'_1) &= -\varphi(r_1, r_2) \\
  r'_1 &\to r_2 & \varphi(r'_1, r'_2) &= \varphi(r_2, r_1)
\end{align*}
\]

\( \varphi(r_1, r_2) = -\varphi(r_2, r_1) \)

\( \varphi_a(r_2)\varphi_b(r_1) - \varphi_b(r_2)\varphi_a(r_1) = -\varphi_a(r_1)\varphi_b(r_2) + \varphi_b(r_1)\varphi_a(r_2) \)

**Slater Determinants (short cut to anti-symmetry)**

For two electrons,

\[
\begin{vmatrix}
  \varphi_a(r_1) & \varphi_a(r_2) \\
  \varphi_b(r_1) & \varphi_b(r_2)
\end{vmatrix}
\]

where the columns labeled by \( r_1, r_2 \ldots \), the rows labeled by orbitals.
\[
\begin{bmatrix}
\varphi_a(r_1) & \varphi_a(r_2) \\
\varphi_b(r_1) & \varphi_b(r_2) \\
\varphi_c(r_1) & \varphi_c(r_2)
\end{bmatrix}
= \varphi_a(r_1)\varphi_b(r_2) - \varphi_a(r_2)\varphi_b(r_1)
\]

For three electrons,
\[
\begin{bmatrix}
\varphi_a(r_1) & \varphi_a(r_2) & \varphi_a(r_3) \\
\varphi_b(r_1) & \varphi_b(r_2) & \varphi_b(r_3) \\
\varphi_c(r_1) & \varphi_c(r_2) & \varphi_c(r_3)
\end{bmatrix}
= \varphi_a(r_1)\varphi_b(r_2)\varphi_c(r_3) - \varphi_a(r_3)\varphi_b(r_1)\varphi_c(r_2) - \varphi_a(r_2)\varphi_b(r_3)\varphi_c(r_1)
+ \varphi_a(r_3)\varphi_b(r_2)\varphi_c(r_1) + \varphi_a(r_1)\varphi_b(r_3)\varphi_c(r_2) - \varphi_a(r_2)\varphi_b(r_3)\varphi_c(r_1)
\]

Slater determinants are antisymmetric product wave functions.

**Spin**

The spin angular momentum,
\[
\hat{S}_x, \hat{S}_y, \hat{S}_z
\]
\[
\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2
\]
\[
[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, [\hat{S}_x, \hat{S}_z] = i\hbar\hat{S}_y, [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x
\]

Crucially, the spin operators satisfy commutation relations, which are exactly the same as those for angular momentum operators,
\[
\hat{L}_x, \hat{L}_y, \hat{L}_z
\]
\[
\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2
\]
\[
\hat{L}_z = -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})
\]

Then,
\[
\{ \hat{L}^2 | l, m \} = l(l + 1)\hbar^2 | l, m \}
\]
\[
\hat{L}_z | l, m \} = m\hbar | l, m \}
\]

where \( l = 0, 1, 2, \ldots \); \( m = -l, -l + 1, \ldots, l - 1, l \).

The eigenvalue structure of the angular momentum operators can be derived using only the commutation relations, and introducing the ladder operators,
\[ S_+ = S_x + iS_y \]
\[ S_- = S_x - iS_y \]

Given the analogy of \( \mathcal{L} \) and \( \mathcal{S} \),

\[
\begin{aligned}
\{S^2 |s,m_s\} &= s(s + 1)\hbar^2 |s,m_s\rangle \\
S_x |s,m_s\rangle &= m_s\hbar |s,m_s\rangle
\end{aligned}
\]

The commutation relations allow for both integer \( S \) values, and for half-integer \( S \) values. For spatial angular momentum only integer values are allowed, since functions should be single valued \( (e^{im\phi}) \) part of the solutions.

However, for spin there is not such a restriction and half-integer spin is very important. Electrons are spin 1/2 particles, and we can denote the possible spin-eigenstates as

\[
\begin{aligned}
\left| s = \frac{1}{2}, m_s = \frac{1}{2} \right| &= |\alpha\rangle \\
\left| s = \frac{1}{2}, m_s = -\frac{1}{2} \right| &= |\beta\rangle
\end{aligned}
\]

If electron spin has been considered to wave function, we can know that,

\[
\begin{pmatrix}
\varphi_a(\vec{r}_1)\alpha & \varphi_a(\vec{r}_2)\alpha & \varphi_a(\vec{r}_3)\alpha \\
\varphi_b(\vec{r}_1)\beta & \varphi_b(\vec{r}_2)\beta & \varphi_b(\vec{r}_3)\beta \\
\varphi_c(\vec{r}_1)\alpha & \varphi_c(\vec{r}_2)\alpha & \varphi_c(\vec{r}_3)\alpha
\end{pmatrix} \neq 0
\]

To interpret this equation as an antisymmetrized product, we simply note that a determinant is antisymmetric under interchange of two rows, or under a change of orbitals. In the textbooks, often a spin coordinate is associated with a particle. Nobody knows what that would be. It is not needed if we use the concept of the Slater determinant.

Finally, we now naturally get the Pauli principle. We have introduced spin orbitals. The \( \alpha \) and \( \beta \) spin orbitals are degenerate, and have the same orbital energy (in our example).

We can populate each spin-orbital at most once in the Slater determinant. This implies at most two electrons for each spatial orbital: The Pauli Principle.
Summary

1. When solving spatial one-electron Schrödinger equation,

\[ H = \hbar = \sum_i \hat{h}(i) \]
\[ h(\vec{r}_i) = \varphi_a(\vec{r}_i)E_a \]

2. Spin-orbitals \( \varphi_a(r)\sigma \)

The orthonormal solutions to \( \varphi(r) \),

\[ \int \varphi_a^*(\vec{r})\varphi_b(\vec{r})d\vec{r} = \delta_{ab} \]

\[ \delta_{ab} = \begin{cases} 
1 & \text{if } a = b \\
0 & \text{if } a \neq b 
\end{cases} \]

Go from spatial orbitals to spin orbitals,

\[ \langle \varphi_a(r)\sigma_1 | \varphi_b(r)\sigma_2 \rangle = \int \varphi_a^*(\vec{r})\varphi_b(\vec{r})d\vec{r} \cdot \langle \sigma_1 | \sigma_2 \rangle = \delta_{ab}\delta_{\sigma_1\sigma_2} \]

3. Pauli principle (Aufbau principle to get ground states)

4. Hartree-Fock

Approximate solution to \( H\psi = E\psi \),

-- \( \psi_{HF} \) is a single determinant

-- Only solve for lowest energy state