Lecture 17

Many-electron System I – Helium Atom and Pauli Exclusion Principle

Study Goal of This Lecture

- Helium atom - many electron wavefunctions

- Helium atom - variational ground state (screening)

- Eigenstates of a two-spin system

17.1 Helium Atom

Helium atom includes two electrons moving around a fixed nucleus with charge $Z = 2$, we can write down the Hamiltonian as:

$$
\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{1}{4\pi\epsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right) \\
&= \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_1}}_{\hat{H}_1} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_2}}_{\hat{H}_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\hat{H}_{12}} \qquad (17.1) \\
&= \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}.
\end{aligned}
$$

If $\hat{H}_{12} = 0$(or neglected) then the problem is exactly solved. Recall that for a total system composes of independent sub-systems

$$\hat{H}_T = \hat{H}_1 + \hat{H}_2 + \cdots , \tag{17.2}$$

and we can firstly solve all

$$\hat{H}_n \phi_m^n = E_m^n \phi_m^n, \tag{17.3}$$

then the solution of $\hat{H}_T$ is the product states

$$\psi = \prod_n \phi^n. \tag{17.4}$$

If consider as many-electrons, i.e. $\hat{H}_n$ for the n-th electron. Then the product solution is a natural "independent electron" solution. Even when the electron-electron interactions are non-zero, we will see the independent electorn approximation is a good starting point.

Let's consider the Helium atom, we know:

$$\begin{aligned} \hat{H}_1 \phi_1 &= E_1 \phi_1, \\ \hat{H}_2 \phi_2 &= E_2 \phi_2, \end{aligned} \tag{17.5}$$

and total $E = E_1 + E_2$. ϕ_1, ϕ_2 are Helium hydrogen-like atomic orbitals. We know the two ground states (neglect spin for a moment.)

$$\begin{aligned} \hat{H}_1 \phi_{1s}(1) &= E_{1s} \phi_{1s}(1), \\ \hat{H}_2 \phi_{1s}(2) &= E_{1s} \phi_{1s}(2), \end{aligned} \tag{17.6}$$

number 1 and 2 denotes electorn 1 and electron 2 respectively. Therefore, the two-electron wave function

$$\Psi = \phi_{1s}(1)\phi_{1s}(2) = \underbrace{1s(1)1s(2)}_{\substack{\text{electron} \\ \text{configuration}}}. \tag{17.7}$$

The abbreviation $1s(1)2s(2)$ denotes "electron configuration" $\rightarrow$ many-electron wavefunction.

$$\Psi = \Psi(1,2) = \Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \underbrace{R_{10}(r_1)Y_0^0(\theta_1, \phi_1)}_{1s(1)} \cdot \underbrace{R_{10}(r_2)Y_0^0(\theta_2, \phi_2)}_{1s(2)}. \tag{17.8}$$

In Dirac notation:

$$|\Psi\rangle = |1s(1)1s(2)\rangle \equiv |1s(1)\rangle \otimes |1s(2)\rangle . \tag{17.9}$$

17.1.1 The ground state energy at various levels of approximations

- Independent electron:

$$\langle\Psi|\hat{H}_1 + \hat{H}_2|\Psi\rangle = 2E_{1s}(Z=2) \simeq -2 \times 2^2 \times 13.6 = -108.8eV \qquad (17.10)$$

- With electron repulsion:

$$\langle\Psi|\frac{e^2}{4\pi\epsilon_0 r_{12}}|\Psi\rangle \simeq 34eV \qquad (17.11)$$

This integral is best evaluated using an expansion of $\frac{1}{|r_1-r_2|}$ in spherical harmonics function, which we will do it in a practice problem. (This is actually the first-order energy correction in the perturbation theory.)

With this correction, we obtain

$$E \simeq -108.8 + 34 = -74.8eV \qquad (17.12)$$

The exact result measured by adding the first two ionization energy of Helium atom is $-79.0eV$. Therefore, the $\langle\Psi|\hat{H}|\Psi\rangle$ result has error $\simeq 5.3\%$, note that the approximation value is larger than exact one. We can improve the result by going to higher order in the perturbation theory or by using the variational method.

> The energy is greater than exact value satisfies the variational principle.

17.2 Variational Principle for Helium Atom

Consider the variational principle, using a hydrogen-like $1s$ orbital with a different "variational" charge:

> Note that this is not a true valid wave function since there is no spin!

$$\Psi(\alpha) = \phi_{1s}(Z=\alpha, 1)\phi_{1s}(Z=\alpha, 2)$$
$$= \frac{1}{\pi}\left(\frac{\alpha}{a_0}\right)^3 \underbrace{e^{\frac{-\alpha r_1}{a_0}} e^{\frac{-\alpha r_2}{a_0}}}_{\substack{\text{H-like } 1s \text{ orbital} \\ \text{with effective} \\ \text{nuclear charge } \alpha}}. \qquad (17.13)$$

Variational integral:

$$\langle\hat{H}\rangle = \frac{\int \Psi^*\hat{H}\Psi d\tau}{\int \Psi^*\Psi d\tau} \geq E_{exact}. \qquad (17.14)$$

We find, minimal $\langle\hat{H}\rangle$ by requiring $\frac{d\langle\hat{H}\rangle}{d\alpha} = 0$, notice that:

$$\langle\Psi(\alpha)|\hat{H}_{12}|\Psi(\alpha)\rangle = \frac{5\alpha}{8}\frac{e^2}{4\pi\epsilon_0 a_0}, \qquad (17.15)$$

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$$\hat{H}_1 = \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} = \underbrace{\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{\alpha e^2}{4\pi\epsilon_0 r_1}}_{A} - \underbrace{\frac{(Z-\alpha)e^2}{4\pi\epsilon_0 r_1}}_{B}, \tag{17.16}$$

$$\langle\phi(\alpha)|A|\phi(\alpha)\rangle = -\frac{\alpha^2}{2}\frac{e^2}{4\pi\epsilon_0 a_0}, \tag{17.17}$$

$$\langle\phi(\alpha)|B|\phi(\alpha)\rangle = -\frac{(Z-\alpha)e^2}{4\pi\epsilon_0} \times \int_{-\infty}^{\infty}\int_0^{\pi}\int_0^{2\pi}|\phi_{1s}(Z=\alpha,1)|^2\frac{1}{r_1}r_1^2\sin\theta_1 dr_1 d\theta_1 d\phi_1$$

$$= -\alpha(Z-\alpha)\frac{e^2}{4\pi\epsilon_0}.$$

$$\tag{17.18}$$

Therefore,

$$\begin{aligned}
\langle\Psi(\alpha)|\hat{H}|\Psi(\alpha)\rangle &= \langle\Psi(\alpha)|\hat{H}_1|\Psi(\alpha)\rangle + \langle\Psi(\alpha)|\hat{H}_2|\Psi(\alpha)\rangle + \langle\Psi(\alpha)|\hat{H}_{12}|\Psi(\alpha)\rangle \\
&= 2\langle\Psi(\alpha)|\hat{H}_1|\Psi(\alpha)\rangle + \langle\Psi(\alpha)|\hat{H}_{12}|\Psi(\alpha)\rangle \\
&= \frac{e^2}{4\pi\epsilon_0}\left[-\alpha^2 - 2\alpha(Z-\alpha) + \frac{5\alpha}{8}\right] \\
&= \left[\alpha^2 - 2Z\alpha + \frac{5\alpha}{8}\right]\frac{e^2}{4\pi\epsilon_0} \quad (Z=2) \\
&= \left[\alpha^2 - \frac{27}{8}\alpha\right]\frac{e^2}{4\pi\epsilon_0}.
\end{aligned} \tag{17.19}$$

and then we know the minimal occurs at $\frac{\mathrm{d}}{\mathrm{d}\alpha}\left(\alpha^2 - \frac{27}{8}\alpha\right) = 0 \Rightarrow \alpha_{minimal} = \frac{27}{16}$. This yield $E_{min} = -77.5eV$, the error reduces to about 1.9%. Physically, this corresponds to a "screening" of atomic charges by additional electron. The more sophisticated trial wave function, including p, d-like contribution can be used to further improve the results.

Let's slow down and summarize what we learn here:

1. Products of single-electron wavefunctions provide good zeroth-order approximations to the many-electron wavefunctions $\Rightarrow$ electronic configurations.

2. The results can be further improved by using the variational method or perturbation theory.

Note that by using more general single-electron wave function, e.g. including functions of the np, d, f-type, the variational results can be further improved. However, even with the most general single-electron wavefunctions(complete basis), the

result still does not equal the exact ground state energy. Because the "true" ground state cannot be written as a product state. The product state form is already an approximation. When using those approximation methods, we should notice that in chemistry, the typical accuracy should below $1\text{kJ/mol}(\simeq 0.05eV)$.

17.3   Eigenstates of a two-spin system(two electrons)

So far, we have ignored the electron spins. Consider the spin states of the two electrons(no spatial part, pure spin), there are four combinations

$$\alpha(1)\alpha(2), \ \beta(1)\beta(2), \ \alpha(1)\beta(2), \ \alpha(2)\beta(1). \tag{17.20}$$

Now, the first two combinations are valid spin wavefunctions, but the last two are not, because these two wavefunctions means that the two electrons can be identified by its spin states.

In valid many-electron wavefunctions, the electron should be indistinguishable. Therefore, valid spin wavefunctions are:

$$\alpha(1)\alpha(2), \tag{17.21}$$

$$\beta(1)\beta(2), \tag{17.22}$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)], \tag{17.23}$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \tag{17.24}$$

The first three spin functions are symmetric, while the last one is antisymmetry.

- Symmetric: Remains the same with respect to electron interchange(exchange their indexes).

- Antisymmetric: Changes sign with respect to electron interchange.

The properties can also be derived by considering the spin operators: define $\hat{S}_1, \hat{S}_2$ and $\hat{S}_{z1}, \hat{S}_{z2}$, then the total spin operator:

$$\hat{S} = \hat{S}_1 + \hat{S}_2, \tag{17.25}$$

$$\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}, \tag{17.26}$$

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\hat{S}_2$$
$$= \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{z1}\hat{S}_{z2} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+},$$

(17.27)

while $\alpha(\gamma)$, $\beta(\gamma)$ are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, let's check $\alpha(1)\beta(2)$:

$$\hat{S}_z\alpha(1)\beta(2) = (\hat{S}_{z1} + \hat{S}_{z2})\alpha(1)\beta(2)$$
$$= [\hat{S}_{z1}\alpha(1)]\beta(2) + \alpha(1)\hat{S}_{z2}\beta(2)$$
$$= \frac{\hbar}{2}\alpha(1)\beta(2) - \frac{\hbar}{2}\alpha(1)\beta(2)$$
$$= 0 \cdot \alpha(1)\beta(2).$$

(17.28)

It is eigenstate of $\hat{S}_z$ too. So we find that all spin functions are eigenstate of $\hat{S}_z$, but, $\alpha(1)\beta(2)$ is not an eigenstate of $\hat{S}^2$ (Derivation is out side the scope of this class.) All of all, let's see the below table:

Spin functions	$\hat{S}^2$	$\hat{S}_z$
$\alpha(1)\alpha(2)$	$2\hbar^2(S=1)$	$+1$
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	$2\hbar^2(S=1)$	0
$\beta(1)\beta(2)$	$2\hbar^2(S=1)$	-1
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	$0(S=0)$	0

The first three spin functions in the tabel is called spin triplets, and the last one is spin singlet. The linear combintaion is required for $\alpha(1)\beta(2)$ to make the wavefunction the simultaneous eigenfunctions of total spin operator $\hat{S}^2$. This result is the same of considering the indistinguishability of electrons.