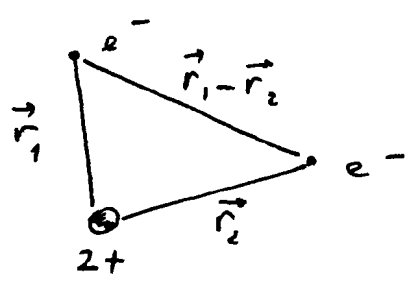


Many-electron systems: Slater determinants give the eigenstates of many-electron non-interacting systems. Coulomb repulsions between the electrons make the problem very non-trivial.

14-1 Helium atom

Hamiltonian:

$$H = \underbrace{\frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1}}_{H_1} + \underbrace{\frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_2}}_{H_2} + \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}}_{V_{12}}$$


$$H = H_1 + H_2 + V_{12}$$

Hartree approximation (assuming $V_{12} = 0$):

$$u(\vec{r}_1, \vec{r}_2) = \underbrace{\Phi_{n_1 l_1 m_1}(\vec{r}_1)}_{\text{quantum numbers}} \times \Phi_{n_2 l_2 m_2}(\vec{r}_2)$$

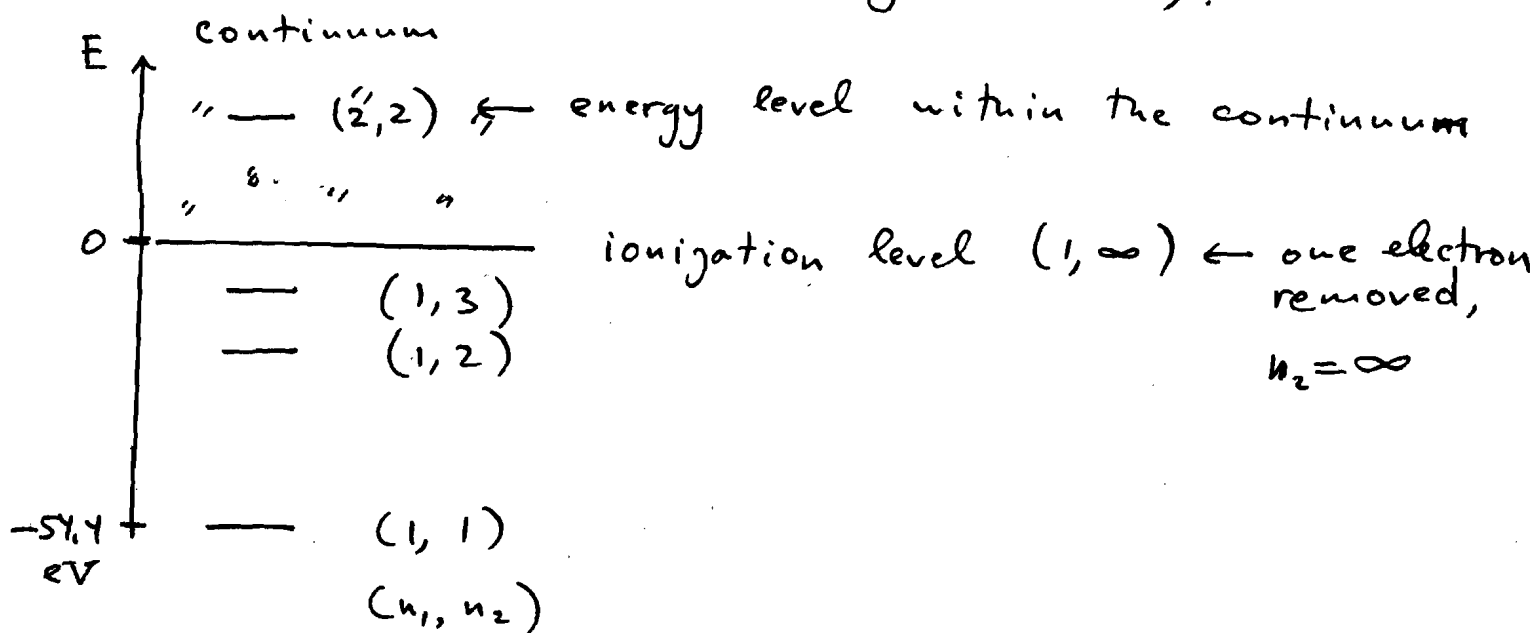
Ground-state energy ($n_1=1, n_2=1$):

$$E = E_{n_1} + E_{n_2} = -2 \times 13.6 \text{ eV} \times \frac{4}{1^2} = -108.8 \text{ eV}$$

\swarrow z^2
 \nwarrow $n=1$

Energy diagram (non-interacting electrons):

14-2



Antisymmetric wave function (ground state)

$$\psi_0(1,2) = \frac{1}{\sqrt{2}} [\psi_0(1)\psi_0(2) - \psi_0(2)\psi_0(1)]$$

In the absence of spin-orbit coupling, the coordinate and spin variables are independent.

The wave function $\psi_0(1)$ becomes a product of a coordinate-dependent function and a spinor:

$$\psi_0(1) = \Phi_{100}(\vec{r}_1) \chi_+^{(1)}$$

↑ electron 1 "up"

$$\psi_0(2) = \Phi_{100}(\vec{r}_2) \chi_-^{(2)}$$

↓ electron 2 "down"

$$\psi_0(1,2) = \Phi_{100}(\vec{r}_1)\Phi_{100}(\vec{r}_2) \underbrace{\frac{1}{\sqrt{2}} [\chi_+^{(1)}\chi_-^{(2)} - \chi_+^{(2)}\chi_-^{(1)}]}_{\chi_-}$$

spin state of a singlet (antisym.)

Question: We know the wave function when two electrons do not interact ($\psi_0(1,2)$).

Can we use this information to approach the problem of interacting electrons?

11-1 Energy shifts and perturbed eigenstates

There is only a handful of potentials for which the SE is solvable. How to deal with the rest of them?

Let's split a given Hamiltonian into a part that we can solve (H_0) and a part which remains

$$H = \underbrace{H_0}_{\text{we can do}} + H_1, \quad H_0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$$

Let's consider the Hamiltonian $H = H_0 + \lambda H_1$ instead

$$(H_0 + \lambda H_1)|\psi_n\rangle = E_n|\psi_n\rangle$$

$$|\psi_n\rangle = |\phi_n\rangle + \lambda \sum_k C_{nk}^{(1)}|\phi_k\rangle + \lambda^2 \sum_k C_{nk}^{(2)}|\phi_k\rangle + \dots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

δE now reads:

14-5

$$\begin{aligned} (H_0 + \lambda H_1) \left\{ |\Phi_n\rangle + \lambda \sum_k c_{nk}^{(1)} |\Phi_k\rangle + \lambda^2 \sum_k c_{nk}^{(2)} |\Phi_k\rangle \dots \right\} = \\ = \left(E_n^{(0)} + \lambda E_n^{(1)} + \dots \right) \left(|\Phi_n\rangle + \lambda \sum_k c_{nk}^{(1)} |\Phi_k\rangle + \dots \right) \end{aligned}$$

We now collect terms with the same powers of λ :

$$\lambda^0: H_0 |\Phi_n\rangle = E_n^{(0)} |\Phi_n\rangle \leftarrow \text{unperturbed solution}$$

$$\begin{aligned} \lambda^1: \lambda H_1 |\Phi_n\rangle + \lambda H_0 \sum_k c_{nk}^{(1)} |\Phi_k\rangle = \lambda E_n^{(1)} |\Phi_n\rangle + \\ + \lambda E_n^{(0)} \sum_k c_{nk}^{(1)} |\Phi_k\rangle \end{aligned}$$

$$\boxed{E_n^{(1)} |\Phi_n\rangle = H_1 |\Phi_n\rangle + \sum_k (E_k^{(0)} - E_n^{(0)}) c_{nk}^{(1)} |\Phi_k\rangle} \quad (*)$$

Multiply from the left with $\langle \Phi_n |$ and use $\langle \Phi_n | \Phi_k \rangle = \delta_{nk}$:

$$E_n^{(1)} = \langle \Phi_n | H_1 | \Phi_n \rangle$$

We received a first correction to the energy $E_n^{(0)}$ telling us that we can obtain it by taking the expectation value of the perturbing potential. Now we can use the known solution of the SE to get a first estimate of the energy:

in \vec{r} -space :

$$E_n^{(1)} = \int d\vec{r} d\vec{r}' \langle \Phi_n | \vec{r} \rangle \langle \vec{r} | H_1 | \vec{r}' \rangle \langle \vec{r}' | \Phi_n \rangle = \\ = \int d\vec{r} d\vec{r}' \Phi_n^*(\vec{r}) \Phi_n(\vec{r}') H_1(\vec{r}, \vec{r}')$$

If $H_1 = H_1(\vec{r})$, then

$$\langle \vec{r} | H_1 | \vec{r}' \rangle = H_1(\vec{r}') \langle \vec{r} | \vec{r}' \rangle = H_1(\vec{r}') \delta(\vec{r} - \vec{r}')$$

and

$$E_n^{(1)} = \int d\vec{r} d\vec{r}' \Phi_n^*(\vec{r}) \Phi_n(\vec{r}') H_1(\vec{r}') \delta(\vec{r} - \vec{r}') \\ = \int d\vec{r} |\Phi_n(\vec{r})|^2 H_1(\vec{r})$$

First correction for the wave function

Let's take the scalar product of $E_n^{(1)}$ with $\langle \Phi_m |$, $m \neq n$

$$0 = \langle \Phi_m | H_1 | \Phi_n \rangle + \sum_k (E_k^{(0)} - E_n^{(0)}) c_{nk}^{(1)} \langle \Phi_m | \Phi_k \rangle$$

$$c_{nm}^{(1)} = \frac{\langle \Phi_m | H_1 | \Phi_n \rangle}{E_m^{(0)} - E_n^{(0)}}$$

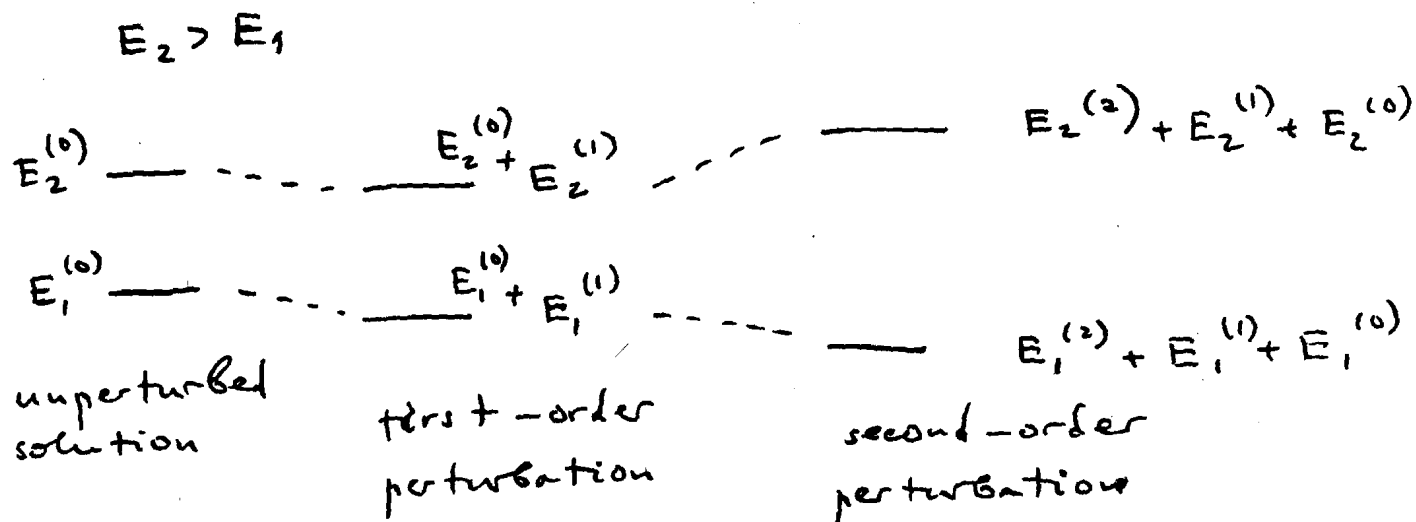
To first approximation

$$|\Psi_n\rangle = |\Phi_n\rangle + \lambda \sum_{k \neq n} \frac{\langle \Phi_k | H_1 | \Phi_n \rangle}{E_k^{(0)} - E_n^{(0)}} |\Phi_k\rangle$$

From that equation one can identify the second correction to the energy:

$$E_n^{(2)} = \sum_{k \neq n} \frac{|\langle \Phi_n | H_1 | \Phi_k \rangle|^2}{E_n^{(0)} - E_k^{(0)}}$$

This formula suggests a tendency of the levels to repel each other:



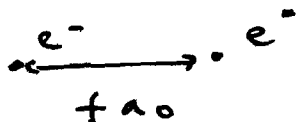
Fundamental result: The existence of excited states results in the attraction between the particles (example: London forces).

14-2. Perturbation result for electron-electron repulsion

First-order perturbation

$$\Delta E = \int d\vec{r}_1 d\vec{r}_2 u_0(\vec{r}_1, \vec{r}_2) \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} u_0(\vec{r}_1, \vec{r}_2)$$

Crude estimate:



$$\Delta E \approx \frac{e^2}{4\pi\epsilon_0} \frac{z}{fa_0} = \frac{z}{f} \times 27.2 \text{ eV}$$

$$\Delta E = \int d\vec{r}_1 d\vec{r}_2 \underbrace{e |\Phi_{100}(r_1)|^2}_{\text{electronic density of electron 1}} \frac{1}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \underbrace{e |\Phi_{100}(r_2)|^2}_{\text{electronic density of electron 2}}$$

If one takes

$$\Phi_{100} = \frac{2}{\sqrt{4\pi}} \left(\frac{z}{a_0}\right) e^{-zr/a_0}$$

the result is:

$$\Delta E = \frac{5}{8} \frac{ze^2}{4\pi\epsilon_0 a_0} = \frac{5}{4} z \times 13.6 \text{ eV} \xrightarrow{z=2} 34 \text{ eV}$$

$$E = E_0 + \Delta E \approx -74.8 \text{ eV}$$

$$E_{\text{exp}} = -79 \text{ eV}$$

} something is still missing!

14-3 Exchange interaction

14-9

Let us consider He in excited state

$$\uparrow n=2$$

$$\downarrow n=2$$

$$\uparrow n=1$$

$$\uparrow n=1$$

triplet

singlet

$$u(12) = u_{\pm}(\vec{r}_1, \vec{r}_2) \chi_{\mp} \quad (\text{we choose } m=0 \text{ for } n=2)$$

$$u_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left(\Phi_{100}(\vec{r}_1) \Phi_{200}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2) \Phi_{200}(\vec{r}_1) \right)$$

$$\chi_+ \leftarrow \text{triplet}, \quad \chi_- \leftarrow \text{singlet}$$

Spin variables commute with coordinates
and integration over each set can be taken
separately

$$\langle u(12) | A(\vec{r}_1, \vec{r}_2) | u(12) \rangle = \langle u_{\pm}(\vec{r}_1, \vec{r}_2) | A(\vec{r}_1, \vec{r}_2) | u_{\pm}(\vec{r}_1, \vec{r}_2) \rangle \times$$

$$\times \underbrace{\langle \chi_{\mp} | \chi_{\mp} \rangle}_{=1}$$

$$\langle \chi_- | \chi_- \rangle = \frac{1}{2} \langle (\chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)}) | \chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)} \rangle =$$

$$= \frac{1}{2} \left(\langle \chi_+^{(1)} | \chi_+^{(1)} \rangle \langle \chi_-^{(2)} | \chi_-^{(2)} \rangle + \langle \chi_-^{(1)} | \chi_-^{(1)} \rangle \times \right. \\ \left. \times \langle \chi_+^{(2)} | \chi_+^{(2)} \rangle \right)$$

$$= 1$$

Let's look at the matrix element of 14-10
the Coulomb operator

$$\Delta E = \langle U_{(12)} \left| \frac{1}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} \right| U_{(12)} \rangle = J \pm K$$

↑ Coulomb integral ↑ exchange integral

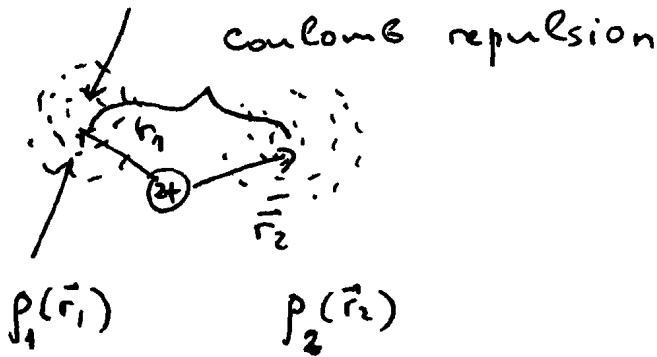
$$\frac{1}{2} \langle \Phi_{100}(\vec{r}_1) \Phi_{200}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2) \Phi_{200}(\vec{r}_1) \left| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right| \Phi_{100}(\vec{r}_1) \Phi_{200}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2) \Phi_{200}(\vec{r}_1) \rangle$$

↓ J contribution ↓ K contribution (cross term)

$$J = \frac{1}{4\pi\epsilon_0} \int d\vec{r}_1 d\vec{r}_2 e^{-|\Phi_{100}(\vec{r}_1)|^2} \frac{1}{|\vec{r}_1 - \vec{r}_2|} e^{-|\Phi_{200}(\vec{r}_2)|^2}$$

$\rho(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \rho(\vec{r}_2)$

↑ electronic density of electron 1 ↑ electron 2



$$K = \frac{1}{4\pi\epsilon_0} \int d\vec{r}_1 d\vec{r}_2 e \underbrace{\Phi_{100}^*(\vec{r}_1) \Phi_{210}(\vec{r}_2)}_{\text{exchange electron density}} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \Phi_{100}(\vec{r}_2) \Phi_{200}^*(\vec{r}_1)$$

exchange electron density,
does not have a classical
analogue

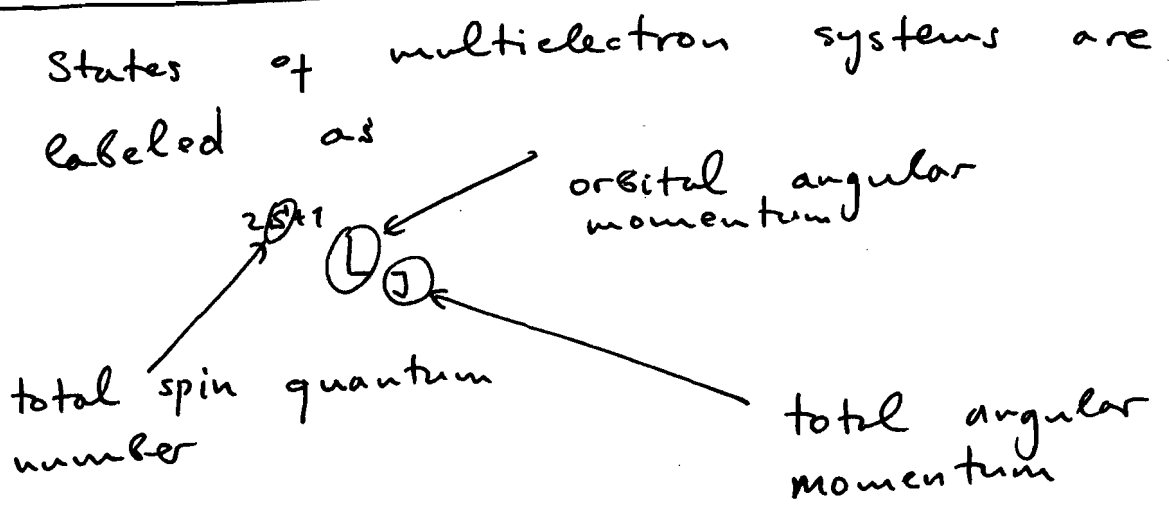
Total energy of the excited state of He:

$$E = E_{100} + E_{210} + J \begin{matrix} \oplus \\ \ominus \end{matrix} \begin{matrix} \leftarrow \text{singlet} \\ \leftarrow \text{triplet} \end{matrix} K$$

Physics of the problem: effective repulsion
between equal spins (Pauli exclusion)
reduces the Coulomb repulsion
between them

Exchange forces are very strong and are
responsible for ferromagnetism lowering
the energy of parallel spins

Atomic states:



For $Z < 40$, spin-orbit coupling is less important ^{14-1:} than repulsion between electrons and L and S separately are considered good quantum numbers

$$\vec{J} = \vec{L} + \vec{S}, \quad J = L+S, L+S-1, \dots, |L-S|$$

\vec{L} is the total orbital angular momentum:

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \dots$$

for two electrons

$$L = L_1 + L_2, L_1 + L_2 - 1, \dots, |L_1 - L_2|$$

$$S = S_1 + S_2, S_1 + S_2 - 1, \dots, |S_1 - S_2|$$

A given electronic configuration can produce a number of electronic states with potentially different energies.

The energies of these states are determined by Hund's rules:

- ①. The state with largest S has lowest energy
- ②. For a given S , the state with maximum L lies lowest
- ③. For given S and L , the incomplete shell with less than half electrons will have energies in order of increasing J , more than half filled shell has energies in the order of decreasing J .

Example $(1s)^2$ ground He

$$\left. \begin{array}{l} s=0, 2s+1=1 \\ L_1=0, L_2=0, L=0 \end{array} \right\} \rightarrow {}^1S_0$$

$(1s)(2s)$,

$$\left. \begin{array}{l} S=1, 0 \\ L=0 \end{array} \right\} \rightarrow \begin{array}{l} \text{--- } {}^1S_0 \\ \text{--- } {}^3S_0 \end{array}$$

$(1s)(2p)$,

$$\left. \begin{array}{l} S=1, 0 \\ L=1, 0 \end{array} \right\} \rightarrow \begin{array}{l} \text{--- } {}^1S_0 \\ \text{--- } {}^3S_1 \\ \text{--- } {}^1P_1 \\ {}^3P_1 \text{ --- } {}^3P_2 \\ \text{--- } {}^3P_0 \end{array}$$

Buildup of the periodic table

x Assume that electrons in the atom do not have Coulomb repulsions. They can be considered to stay at Bohr-like orbitals with an effective charge for the nucleus

$$V_{\text{eff}}(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{Z(r)}{r}$$

x Neglect spin-orbit coupling (terms of the form $\propto \vec{L} \cdot \vec{S}$) \rightarrow one can put two electrons with opposite spins to each orbital (each level is twofold degenerate).

14-4. The Ritz variational principle

14-14

Q: What if we do not know the exact solution of the $\mathcal{H}E$, can we estimate the energy?

A (variational principle): Given a normalized function $|\Psi\rangle$ that satisfies the appropriate boundary conditions, then the expectation value of the Hamiltonian is an upper bound to the exact ground state energy:

$$\langle \Psi | H | \Psi \rangle \geq E_0$$

exact energy of the ground state

$$|\Psi\rangle = \sum_k C_k |k\rangle$$

$$\langle \Psi | H | \Psi \rangle = \sum_{n,m} C_n^* C_m \langle n | H | m \rangle =$$

$$= \sum_m |C_m|^2 E_m \geq E_0 \sum_m |C_m|^2$$

since $E_m \geq E_0$

$$\langle \Psi | \Psi \rangle = \sum_m |C_m|^2 = 1$$

$$\langle \Psi | H | \Psi \rangle \geq E_0$$

How does it work?

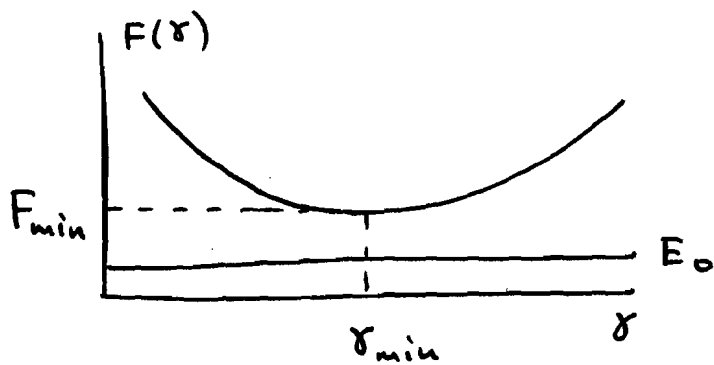
14-15

You choose a probe function depending on parameter(s)

$$\gamma: |\psi\rangle = |\psi(\gamma)\rangle$$

The expectation value becomes a function of γ :

$$F(\gamma) = \langle \psi(\gamma) | H | \psi(\gamma) \rangle$$



Variational principle guarantees that F_{\min} is above the level of E_0

$\Delta E = F_{\min} - E_0$ is the error of choosing an incorrect wave function

Application: The ground-state energy of Helium
Let's choose 1s orbitals for two electrons of He by considering the nuclear charge as a variational parameter

$$\Psi(\vec{r}_1, \vec{r}_2) = \Phi_{100}(\vec{r}_1) \Phi_{100}(\vec{r}_2)$$

$$H = \frac{p_1^2}{2m} - \frac{ze^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

$$\Phi_{100} = R_{10}(r) \times Y_{00}(\theta, \varphi), \quad Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}$$

$$R_{10}(r) = 2 \left(\frac{z^*^3}{a_0^3} \right)^{1/2} e^{-\frac{z^* r}{a_0}} \quad a_0 \text{ is the Bohr radius}$$

Now we need to define the perturbation part of the Hamiltonian consistent with our choice of the probe function:

$$H = H_1^* + H_2^* + V_{12}$$

$$H_1^* = \frac{\vec{p}_1^2}{2m} - \frac{z^* e^2}{4\pi\epsilon_0 r_1}, \quad H_2^* = \frac{\vec{p}_2^2}{2m} - \frac{z^* e^2}{4\pi\epsilon_0 r_2}$$

$$V_{12} = \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} + \frac{(z^* - z)e^2}{4\pi\epsilon_0 r_1} + \frac{(z^* - z)e^2}{4\pi\epsilon_0 r_2}$$

Expectation value:

$$\langle \Psi | H | \Psi \rangle = -13.6 \text{ eV} \times 2(z^*)^2 + \langle \Psi | V_{12} | \Psi \rangle$$

$$\langle \Psi | \frac{z^* - z}{4\pi\epsilon_0 r_1} | \Psi \rangle = \frac{z^* - z}{4\pi\epsilon_0} e^2 \frac{z^{*3}}{\pi a_0^3} \times \int \frac{d\vec{r}}{r} e^{-\frac{2r z^*}{a_0}} =$$

$$= \frac{(z^* - z)e^2}{4\pi\epsilon_0} \frac{z^{*3}}{\pi a_0^3} 4\pi \int_0^\infty r dr e^{-\frac{2r z^*}{a_0}} =$$

$$= \frac{(z^* - z)e^2}{4\pi\epsilon_0} \frac{4z^{*3}}{a_0^3} \times \left(\frac{a_0}{2z^*} \right)^2 = 2 \times 13.6 \text{ eV} (z^* - z) z^*$$

Final result :

$$F(z^*) = \langle \psi | H | \psi \rangle = -13.6 \text{ eV} \left(2z^{*2} + 4z^*(z-z^*) - \frac{5}{4}z^* \right)$$

$$\frac{\partial F(z^*)}{\partial z^*} = 0 \rightarrow z^* = z - \frac{5}{16}$$

$$E_0 \leq \langle \psi | H | \psi \rangle = -13.6 \text{ eV} \times 2 \times \left(z - \frac{5}{16} \right)^2 = -27.3 \text{ eV}$$

$$E_0^{\text{exp}} = -78.975 \text{ eV}$$