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:

\[ H = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|} \]

\[ H = H_1 + H_2 + V_{12} \]

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

\[ u(r_1, r_2) = \Phi_{n_1 e_1 m_1}(r_1) \times \Phi_{n_2 e_2 m_2}(r_2) \]

quantum numbers

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

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

\[ n = 1 \]
Energy diagram (non-interacting electrons):

\[ E \]

- Continuum
  - \(( 2,2 )\) - energy level within the continuum
  - \(( 1,3 )\)
  - \(( 1,2 )\)
  - \(( 1,1 )\)

- Ionization level \((1,\infty) \leftarrow \) one electron removed,
  \( n_2 = \infty \)

- \( -5.4 \text{ eV} \)

**Antisymmetric wave function (ground state)**

\[ U_0(1,2) = \frac{1}{V_2} \left[ U_0(1) U_0(2) - U_0(2) U_0(1) \right] \]

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

The wave function \( U_0(1) \) becomes a product of a coordinate-dependent function and a spinor:

\[ U_0(1) = \Phi_{100}(\vec{r}_1) \chi^{(1)} \]
\[ U_0(2) = \Phi_{100}(\vec{r}_2) \chi^{(2)} \]

\[ U_0(1,2) = \Phi_{100}(\vec{r}_1) \Phi_{100}(\vec{r}_2) \frac{1}{V_2} \left[ \chi^{(1)}(1) \chi^{(2)}(-) - \chi^{(1)}(-) \chi^{(2)}(1) \right] \]

\[ \chi^{(-)} \]

Spin state of a singlet (antisym.)
Question: We know the wave function when two electrons do not interact ($\psi_0(z_i,z_2)$). 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:

$$H = H_0 + H_1, \quad H_0|\psi_n\rangle = E_n^{(0)}|\psi_n\rangle$$

we can do

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

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

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

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$
SE now reads:

\[
\left( H_0 + \lambda H_1 \right) \left\{ |\Phi_n\rangle + \lambda \sum_k C_{nk} |\Phi_k\rangle + \lambda^2 \sum_k C_{nk}^{(2)} |\Phi_k\rangle \right\} = \\
= \left( E_n^{(0)} + \lambda E_n^{(1)} + \ldots \right) \left( |\Phi_n\rangle + \lambda \sum_k C_{nk}^{(1)} |\Phi_k\rangle + \ldots \right)
\]

We now collect terms with the same power of \( \lambda \):

\[
\lambda^0: \quad H_0 |\Phi_n\rangle = E_n^{(0)} |\Phi_n\rangle \quad \text{← unperturbed solution}
\]

\[
\lambda^1: \quad \lambda H_1 |\Phi_n\rangle + \lambda H_0 \sum_k C_{nk}^{(1)} |\Phi_k\rangle = \lambda E_n^{(1)} |\Phi_n\rangle + \\
+ \lambda E_n^{(0)} \sum_k C_{nk}^{(1)} |\Phi_k\rangle
\]

\[
E_n^{(1)} |\Phi_n\rangle = H_1 |\Phi_n\rangle + \sum_k \left( E_k^{(0)} - E_n^{(0)} \right) C_{nk}^{(1)} |\Phi_k\rangle
\]  \hspace{1cm} (x)

Multiply from the left with \( \langle \Phi_k | \) 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 $\tilde{r}$-space:

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

$$= \int d\tilde{r} d\tilde{r}' \varphi_n^*(\tilde{r}) \varphi_n(\tilde{r}) H_1(\tilde{r}, \tilde{r}')$$

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

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

and

$$E_n^{(1)} = \int d\tilde{r} d\tilde{r}' \varphi_n^*(\tilde{r}) \varphi_n(\tilde{r}') H_1(\tilde{r}') \delta(\tilde{r} - \tilde{r}')$$

$$= \int d\tilde{r} |\varphi_n(\tilde{r})|^2 H_2(\tilde{r})$$

First correction for the wave function

Let's take the scalar product of $E_1^{(1)}$ with $\langle \Phi_m | \varphi_m \rangle = 0$

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

$$C_{nk}^{(1)} = \frac{\langle \Phi_m | H_1 | \Phi_n \rangle}{E_n^{(0)} - E_k^{(0)}}$$

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:

\[ E_n^{(2)} = \sum_{\Phi_n} \frac{|\langle \Phi_n | H_1 | \Phi_k \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \]

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

\[ E_2 > E_1 \]

\[ E_2^{(0)} \quad \quad E_2^{(0)} + E_2^{(1)} \quad \quad E_2^{(2)} + E_2^{(1)} + E_2^{(0)} \]

\[ E_1^{(0)} \quad \quad E_1^{(0)} + E_1^{(1)} \quad \quad E_1^{(2)} + E_1^{(1)} + E_1^{(0)} \]

Unperturbed solution \quad First-order perturbation \quad Second-order perturbation

**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**

\[
\Delta E = \int d\vec{r}_1 \, d\vec{r}_2 \, \psi_0 (\vec{r}_1, \vec{r}_2) \frac{e^2}{\Psi_0 (\vec{r}_1 - \vec{r}_2)} \psi_0 (\vec{r}_1, \vec{r}_2)
\]

**Crude estimate:**

\[
\Delta E \approx \frac{e^2}{\Psi_0} \frac{1}{f a_0} = \frac{\hbar}{f} \times 27.2 \text{ eV}
\]

\[
\Delta E = \int d\vec{r}_1 \, d\vec{r}_2 \, e|\Phi_{100} (\vec{r}_1)|^2 \frac{1}{\Psi_0 (\vec{r}_1 - \vec{r}_2)} \frac{e^2}{\Psi_0 (\vec{r}_1 - \vec{r}_2)} |\Phi_{100} (\vec{r}_2)|^2
\]

Electronic density of electron 1

Electronic density of electron 2

It was concluded:

\[
\Phi_{100} = \frac{2}{\sqrt{n!}} \left(\frac{\alpha}{\alpha_0}\right) e^{-2r/\alpha_0}
\]

\[
\Delta E = \frac{5}{8} \frac{e^2}{\Psi_0 \alpha_0} = \frac{5}{8} \frac{\hbar}{f} \times 13.6 \text{ eV} \rightarrow 34 \text{ eV}
\]

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

\[
E_{\text{exp}} = -79 \text{ eV}
\]

Something is still missing.
Let us consider the in excited state
\[ \uparrow u = 2 \quad \downarrow u = 2 \]
\[ \uparrow u = 1 \quad \downarrow u = 1 \]

triplet

\[ u_{\pm} (r_1, r_2) \chi_{\pm} \] (we choose \( m = 0 \) for \( u = 2 \))

\[ u_{\pm} (r_1, r_2) = \frac{1}{\sqrt{2}} (\phi_{100}(r_1) \phi_{200}(r_2) \pm \phi_{100}(r_2) \phi_{200}(r_1)) \]

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

Spin variables commute with coordinates

and integration over each set can be taken separately

\[ \langle u_{\pm} (r_1, r_2) | A (r_1, r_2) | u_{\pm} (r_1, r_2) \rangle \]

\[ \times \langle \chi_{+} | \chi_{+} \rangle \]

\[ \frac{1}{4} \]

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

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

\[ \left. \times \langle \chi_{+}^{(2)} | \chi_{+}^{(2)} \rangle \right) \]

\[ = 1 \]
Let's look at the matrix element of the Coulomb operator

\[ \Delta E = \langle U_{12} \rangle \frac{1}{4\pi \varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \langle U_{12} \rangle = J \pm K \]

\[ \frac{1}{2} \left[ \Phi_{100}(\vec{r}_1) \Phi_{2e0}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2) \Phi_{2e0}(\vec{r}_1) \right] \frac{1}{|\vec{r}_1 - \vec{r}_2|} \left[ \Phi_{100}(\vec{r}_1) \Phi_{2e0}(\vec{r}_2) \pm \Phi_{100}(\vec{r}_2) \Phi_{2e0}(\vec{r}_1) \right] \]

\[ J = \frac{1}{4\pi \varepsilon_0} \int d\vec{r}_1 d\vec{r}_2 \ e |\Phi_{100}(\vec{r}_1)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \ e |\Phi_{2e0}(\vec{r}_2)|^2 \]

\[ p(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} p(\vec{r}_2) \]

Electronic density of electron 1

Coulomb repulsion

\[ p_1(\vec{r}_1) \quad p_2(\vec{r}_2) \]
\[ K = \frac{1}{4\pi\sigma_0} \int d\mathbf{r}_1 d\mathbf{r}_2 \ e^{\Phi_{100}(\mathbf{r}_1)} \Phi_{2e0}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \Phi_{100}^{*}(\mathbf{r}_2)\Phi_{2e0}(\mathbf{r}_1) \]

exchange electron density, does not have a classical analogue

**Total energy of the excited state of He:**

\[ E = E_{100} + E_{2e0} + J \uparrow \uparrow K \]

**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:**

States of multielectron systems are labeled as:

- Total spin quantum number
- Orbital angular momentum
- Total angular momentum
For $z < 40$, spin-orbit coupling is less important than repulsion between electrons and $L$ and $S$ separately are considered good quantum numbers

$J = L + S, \quad J = L + S, \quad L + S - 1, \ldots, \quad 1L - S$'

$L$ is the total orbital angular momentum:

$\hat{L} = \hat{L}_1 + \hat{L}_2 + \ldots$

for two electrons

$L = L_1 + L_2, \quad L_1 + L_2 - 1, \ldots, \quad |L_1 - L_2|$

$S = S_1 + S_2, \quad S_1 + S_2 - 1, \ldots, \quad |S_1 - S_2|$

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

\(s = 0, \ 2s + 1 = 1\)
\[L_1 = 0, \ L_2 = 0, \ L = 0\]

\(\rightarrow \ 1s\)

\((1s)(2s)\)

\(s = 1, 0\)
\[L = 0\]

\(\rightarrow \ 3s_0\)

\((1s)(2p)\)

\(s = 1, 0\)
\[L = 1, 0\]

\(\rightarrow \ 1p_1\)

\(2p_1 \quad \rightarrow \ 3p_2\)

Buildup of the periodic table

\(\times\) 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:

\[V_{\text{eff}}(r) = -\frac{\epsilon^2}{4\pi\varepsilon_0} \frac{Z(r)}{r}\]

\(\times\) Neglect spin-orbit coupling (terms of the form \(\delta L \cdot \delta S\)) - one can put two electrons with opposite spins to each orbital (each level is twofold degenerate).
The Ritz variational principle

Q: What if we do not know the exact solution of the SE, 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

\[
|\psi\rangle = \sum_k c_k |1_k\rangle
\]

\[
\langle \psi | H | \psi \rangle = \sum_{n,m} c_n^* c_m \langle n | H | m \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_m |c_m|^2
\]

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?

You choose a probe function depending on parameter(s)

$$\psi_1 \psi_2 = \psi(\xi)$$

The expectation value becomes a function of $$\xi$$:

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

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

$$\Delta E = F_{\text{min}} - E_0$$ 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

$$\psi(r_1, r_2) = \Phi_{100}(r_1) \Phi_{100}(r_2)$$

$$H = \frac{p_1^2}{2m} - \frac{2e^2}{\gamma \xi_0 r_1} + \frac{p_2^2}{2m} - \frac{2e^2}{\gamma \xi_0 r_2} + \frac{e^2}{\gamma \xi_0 |r_1 - r_2|}$$
\( \Phi_{10} = R_{10}(r) \times Y_{00}(\theta, \phi) \), \( Y_{00}(\theta, \phi) = \frac{1}{\sqrt{\pi} \eta} \)

\( R_{10}(r) = 2 \left( \frac{2^* \, 3}{\alpha_0^3} \right)^{1/2} e^{-\frac{2^* \, r}{\alpha_0}} \) \( \alpha_0 \) is the Bohr radius

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

\[
H = H_1^* + H_2^* + V_{12}
\]

\[
H_1^* = \frac{\mathbf{p}_1^2}{2m} - \frac{2^* e^2}{\eta \varepsilon_0 r_1}, \quad H_2^* = \frac{\mathbf{p}_2^2}{2m} - \frac{2^* e^2}{4\eta \varepsilon_0 r_2}
\]

\[
V_{12} = \frac{e^2}{\eta \varepsilon_0 |r_1 - r_2|} + \frac{(2^* - 2)e^2}{\eta \varepsilon_0 r_1} + \frac{(2^* - 2)e^2}{\eta \varepsilon_0 r_2}
\]

Expectation value:

\[
\langle \psi | H | \psi \rangle = -13.6 \text{ eV} \times 2(2^*)^2 + \langle \psi | V_{12} | \psi \rangle
\]

\[
\langle \psi | \frac{2^* - 2}{\eta \varepsilon_0 r_1} | \psi \rangle = \frac{2^* - 2}{\eta \varepsilon_0} \frac{2^* \, 3}{\pi \alpha_0^3} \int \frac{dr}{r} e^{-\frac{2 \, r \, 2^*}{\alpha_0}} =
\]

\[
= \left( \frac{2^* - 2}{\eta \varepsilon_0} \right) \frac{2^* \, 3}{\pi \alpha_0^3} \eta \int_0^\infty r \, dr \, e^{-\frac{2 \, r \, 2^*}{\alpha_0}} =
\]

\[
= \left( \frac{2^* - 2}{\eta \varepsilon_0} \right) \frac{2^* \, 3}{\pi \alpha_0^3} \, \left( \frac{\alpha_0}{2 \, 2^*} \right)^2 = 2 \times 13.6 \text{ eV} \left( \frac{2^* - 2}{2^*} \right) 2^*
\]
Final result:

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

\[ \frac{\partial F(\bar{z}^*)}{\partial \bar{z}^*} = 0 \quad \Rightarrow \quad \bar{z}^* = \bar{z} - \frac{5}{16} \]

\[ E_0 \leq \langle + | H | + \rangle = -13.6 \text{ eV} \times 2 \times \left( \bar{z} - \frac{5}{16} \right)^2 = \]

\[ = -77.3 \text{ eV} \]

\[ E_0^{\text{exp}} = -78.975 \text{ eV} \]