Atomic Structure:

Consider the atomic Hamiltonian for an atom in free space, with no applied fields, \( \vec{E}_{\text{ext}} = 0, \vec{B}_{\text{ext}} = 0 \)

\[
H_A = \sum_i \left( \frac{\hat{p}_i^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j} \frac{1}{r_{ij}} \right)
\]

where \( |\hat{r}_i| = r_i \) \( |\hat{r}_i - \hat{r}_j| = r_{ij} \) \( \vec{R}_{\text{Nucleus}} = 0 \) \( M_{\text{Nucleus}} = \infty \)

(as an aside, to the extent that the electric dipole approximation is good, \( \hat{p} = m\hat{v} \), canonical momentum = kinetic energy)

Note \( H_A \) leaves out relativistic effects which lead to the existence of spin, and spin interactions, and it leaves out nuclear spin interactions. (Well discuss later.)

In general, an \( N \)-electron system has eigenstate wave functions of \( N \) position variables

\[
\psi_i = \psi_i(\hat{r}_1, \hat{r}_2, \ldots \hat{r}_N)
\]

\( \rightarrow \) this multivariable wave function can be complicated to solve.
The easiest way to deal with the problem is in terms of single particle solutions

\[ \Psi_i = \psi_{i_1}(\mathbf{r}_1) \psi_{i_2}(\mathbf{r}_2) \cdots \psi_{i_N}(\mathbf{r}_N), \]

where the best single-particle functions \( \psi_i(\mathbf{r}_i) \) are chosen. This is usually only an approximation to the full solution

\[ \Psi_i = \psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \sum_j C_{ij} \psi_{j_1}(\mathbf{r}_1) \psi_{j_2}(\mathbf{r}_2) \cdots \psi_{j_N}(\mathbf{r}_N) \]

Most general solution

The single particle approximation assumes \( C_{11} = 1 \) and \( C_{ij} = 0 \) for all other \( j \neq 1 \).

This can be a very good solution to the problem if \( \psi_{i_1}(\mathbf{r}) \) and \( \psi_{i_2}(\mathbf{r}) \) etc. are chosen correctly.

In addition, we will have to deal with antisymmetry of the wave function to satisfy Fermion anti-symmetry according to Pauli.

This course assumes you are familiar with the Hydrogen Atom.
Start with our first example: Helium

Assume - non-relativistic
- ignore spin.

\[ |\vec{r}_1 - \vec{r}_2| = r_{12} \]
\[ |\vec{r}_1| = r_1 \]

\[ \hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \]

Solve for
\[ \hat{H} \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1, \vec{r}_2) \rightarrow 2\text{-particle Schrödinger eqn.} \]

Try looking for single-particle solutions by ignoring the electrostatic repulsion between electrons:

\[ H_1 = \frac{\vec{p}_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} \]
\[ H_2 = \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \]

\[ H_x = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \]
\[ H = H_1 + H_2 + H_x \]

Assume \( H_x \) is small:

to zeroth order then, we have Hydrogen-like solutions for each electron

\[ (H_1 + H_2) \psi = E^{(0)} \psi_0 \]
\[ \psi_0 = U_{\text{lin}}(\vec{r}_1) U_{\text{lin}}(\vec{r}_2) \]

\[ E^{(0)} = E_n + E_l + E_m \]

\( n, l, m \) are the quantum numbers of Hydrogen wave functions.
Simplify the notation by calling $n' l m' \rightarrow a$,
$n' l m' \rightarrow b$ (notation: (1) is $F_1$
(2) is $F_2$)

$$\Psi_0 = U_a(1) U_b(2) \quad E^{(0)} = E_a + E_b$$

$\rightarrow$ but there is another state, with the same energy

$$\Psi'_0 = U_a(2) U_b(1) \quad E^{(0)} = E_b + E_a$$

Since these are degenerate, we have to use degenerate perturbation theory, which amounts to diagonalizing the perturbing Hamiltonian $(H_\text{\textscript{int}} = \frac{e^2}{4\pi\varepsilon_0 R_{12}})$ in the space of

$$\Psi_0 = U_a(1) U_b(2), \quad \Psi'_0 = U_a(2) U_b(1).$$

The electron interaction will lift this degeneracy

Using the basis $\Psi_0, \Psi'_0$ which in matrix form is

$$\begin{pmatrix} \Psi_0 \\ \Psi'_0 \end{pmatrix}.$$ Calculate the matrix elements of $H_\text{\textscript{int}}$:

$$H_{11} = \langle U_a(1) U_b(2) | H_\text{\textscript{int}} | U_a(1) U_b(2) \rangle \quad \left\{ e^2 \int \frac{|U_a(1)|^2 |U_b(2)|^2 d^3 r_1 d^3 r_2}{4\pi\varepsilon_0 R_{12}} \right\}$$

$$H_{22} = \langle U_b(1) U_a(2) | H_\text{\textscript{int}} | U_b(1) U_a(2) \rangle \quad \left\{ e^2 \int \frac{|U_b(1)|^2 |U_a(2)|^2 d^3 r_1 d^3 r_2}{4\pi\varepsilon_0 R_{12}} \right\}$$

$$H_{12} = \langle U_a(1) U_b(2) | H_\text{\textscript{int}} | U_b(1) U_a(2) \rangle \quad \left\{ e^2 \int \frac{|U_a(1)|^* |U_b(2)|^* U_b(1) U_a(2) d^3 r_1 d^3 r_2}{4\pi\varepsilon_0 R_{12}} \right\}$$

$$H_{21} = \langle U_b(1) U_a(2) | H_\text{\textscript{int}} | U_a(1) U_b(2) \rangle \quad \left\{ e^2 \int \frac{|U_b(1)|^* |U_a(2)|^* U_a(1) U_b(2) d^3 r_1 d^3 r_2}{4\pi\varepsilon_0 R_{12}} \right\}$$

Where state 1 = $\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \Psi_0$, state 2 = $\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \Psi'_0$.

Vector form \( \rightarrow \)
Define the "direct" integral to be

J = H_{11} = H_{22}.

Define the "exchange" integral

K = H_{12} = H_{21}.

To find the new eigenvalues and eigenvectors to
First order, we have to diagonalize the Hamiltonian:

\[
(H_0 + H_T) \psi_0' = \begin{bmatrix} E^{(0)} & 0 \\ 0 & E^{(0)} \end{bmatrix} + \begin{bmatrix} J & K \\ K & J \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = E \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}
\]

\[
H_0 \uparrow
\]

\[
E^{(0)} = E_a + E_b.
\]

\[
\text{diagonalizes with}
\]

\[
\psi_s' = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]

\[
U_S = \frac{1}{\sqrt{2}} \left[ U_{a(1)} U_{b(2)} + U_{b(1)} U_{a(2)} \right]
\]

\[
E_s' = E^{(0)} + J + K
\]

\[
\psi_a' = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]

\[
U_A = \frac{1}{\sqrt{2}} \left[ U_{a(1)} U_{b(2)} - U_{b(1)} U_{a(2)} \right]
\]

\[
E_a' = E^{(0)} + J - K
\]
Note: Since we diagonalized with respect to $H_z$

$$\left< U_s \left| \frac{e^2}{4\pi\epsilon_0 r_{1z}} \right| U_A \right> = 0$$

clearly $U_A$ is antisymmetric when $r_1$ and $r_2$ are exchanged, and $U_s$ is symmetric.

$\Rightarrow$ the Hamiltonian commutes with permutation of particles, and we get symmetric or anti-symmetric eigensolutions, without reference (yet) to the Pauli symmetrization postulate.

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Apply this to the ground state of Helium: both electrons in the ground 1s state: \(1s^2\)

\[ U_A = 0 \quad U_s = U_{1s}(r_1) U_{1s}(r_2) \]

\[ E^{(0)} = E_{1s}^{2s2} + E_{1s}^{2s2} = -2 \cdot 2^2 \cdot 13.6 \text{ eV} = -8 \cdot 13.6 \text{ eV} = -108.6 \text{ eV} \]

\[ E^{(1)} = E^{(0)} + J = -108.8 \text{ eV} + 34 \text{ eV} \]

\[ J = \epsilon \int \left| U_{1s}(r_1) \right|^2 \left| U_{1s}(r_2) \right|^2 \, d^3r_1 \, d^3r_2 = \frac{1}{4\pi\epsilon_0} \frac{5}{8} \frac{e^2}{2a_0} \approx 34 \text{ eV} \]

\(a_0 = \text{Bohr radius}\)
\[ \text{He}^{++} \quad (Z^2 = 13.6 \text{eV}, \ Z=2) \]

\[ \text{He}^+ \quad (\text{Hydrogen with } Z=2) \]

20.4\text{eV} \Rightarrow \text{binding energy of the first electron to be removed.} \\
34\text{eV} \quad 1^{\text{st}} \text{ order correction} \\
1s^2 \quad 0^{\text{th}} \text{ order}

we get the binding energy for removal of 1 electron to be \( 20.4\text{eV} \Rightarrow \text{the actual value is } 24.58\text{eV.} \)

\text{not bad! (there was no exchange } k \text{ to calculate)}

Now look at excited states.

assume \( U_a = 1s \text{ state of Hydrogen} \)

\( U_b = n\ell \text{ state.} \quad (\text{for Helium, doubly excited electrons } n,\ell \text{ are above the ionization limit}) \)

\[ E^{(1)} = E^{(0)} + J \pm K \]

\( \rightarrow \) here we show that it helps to choose \( U_a + U_b \) carefully:
Since the first electron in the 1s state screens other electrons in higher states (particularly if the higher state has a large angular momentum) let's be smart about how we choose $U_A(r) + U_B(r)$ to account for the screening. Split the Hamiltonian as follows:

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{e^2}{4\pi \varepsilon_0} \left( \frac{2}{r_1} + \frac{1}{r_2} \right)$$

$$H_I = \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right)$$

Note that $H_0 + H_I$ is exactly the same, but $H_I$ mimics screening. Also $H_I \to 0$ as $r \to \infty$.

$$E_n \quad \text{J shifts} \quad \text{2k splits} \quad \text{us} \quad \text{ UA}$$

$U_A$ is always lower energy than $U_B$.

In practice, splitting $H_0 + H_I$ like above, significantly improves $E^{(r)}$, so that $E^{(r)}$ doesn't have to be as big.
- Effect of $J$ always raises energy (weakens binding) accounts for screening

- Effect of $K$ always lowers $U_A$ vs. $U_S$. accounts for quantum correlation

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What about spin?

the electron is a spin $\frac{1}{2}$ particle, with two states $+\frac{1}{2}, -\frac{1}{2}$.

label those states $\chi_+ \& \chi_-$

Then to a good approximation

$$\Psi(r) = U_{\text{new}}(r) \chi_{\pm}(r)$$

$$\Psi_0 = U_A(1) \chi_{\pm}(1) U_b(2) \chi_{\pm}(2) \Rightarrow \text{four spin combinations.}$$

Pauli principle says we must always have an anti-symmetric electron wave function. Form symmetric & anti-symmetric spin combinations:

$$U_S \chi_A \quad U_A \chi_S \Rightarrow \text{both are anti-symmetric}$$

$$\chi_S = \begin{cases} \frac{1}{\sqrt{2}} (\chi_+(1) \chi_-(2) + \chi_-(1) \chi_+(2)) & \chi_A = \frac{\chi_+(1) \chi_-(2) - \chi_-(1) \chi_+(2)}{\sqrt{2}} \\ \chi_-(1) \chi_+(2) & \end{cases}$$
these are just the \( S = 1 \) \( \pm m_s = 1,0,-1 \) and \( S = 0 \) total angular momentum states you get when adding two spin \(-\frac{1}{2}\) momenta.

the \( S = 1 \), \( X_s \) state are called triplet states.

the \( S = 0 \), \( X_A \) state is called a singlet state.

So solutions are of the form:

\[
U_s \, X_A \quad \text{or} \quad U_A \, X_s
\]