Atomic Structure:

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

$$H_A = \sum_i \left(\frac{\hat{p}_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + e^2 \sum_{i<j} \frac{1}{4\pi\epsilon_0} \frac{1}{r_{ij}} \right)$$

where $|\vec{r}_i| = r_i \quad |\vec{r}_i - \vec{r}_j| = r_{ij} \quad \vec{R}_{Nucleus} = 0$

$M_{Nucleus} = \infty$

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

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

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

$$\psi_j = \psi_i(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$$

→ this multivariable wave function can be complicated to solve.

The easiest way to deal with the problem is n terms of single particle solutions

$$\Psi_i = \psi_{1i}(\vec{r}_1)\psi_{2i}(\vec{r}_2)\cdots\psi_{Ni}(r_N),$$

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

$$\Psi_i = \Psi_i(\vec{r}_1,\vec{r}_2,..\vec{r}_N) = \sum_j C_{ij}\,\overbrace{\psi_{1j}(\vec{r}_1)\psi_{2j}(\vec{r}_2)\cdots\psi_{Nj}(\vec{r}_N)}^{\text{form a complete set.}}\Bigg\}\begin{array}{l}\text{most}\\\text{general}\\\text{solution}\end{array}$$

The single particle approximation assumes $C_{i1} = 1$ $C_{ij} = 0$ for all other $j \neq 1$

This can be a very good solution to the problem if $\psi_{1i}(\vec{r})$ and $\psi_{2i}(r)$ etc. are chosen correctly.

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

This course assumes you are familiar with the Hydrogen Atom.

Start with our first example: Helium

Assume - non-relativistic
- ignore spin.

$|\vec{r}_1 - \vec{r}_2| = r_{12}$

$|\vec{r}_1| = r_1$

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} \underbrace{- \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2}}_{\text{nuclear attraction}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{\text{electron-electron repulsion}}$$

Solve for

$$\hat{H}\,\psi(\vec{r}_1, \vec{r}_2) = E\,\psi(\vec{r}_1, \vec{r}_2)$$ → 2-particle Schrodinger eqn.

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

$$H_1 = \frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1}\,, \qquad H_2 = \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_2}$$

$$H_I = \frac{e^2}{4\pi\epsilon_0 r_{12}}\,, \qquad H = H_1 + H_2 + H_I$$

assume H_I is small:

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

$$(H_1 + H_2)\psi_0 = E^{(0)}\psi_0\,, \qquad \psi_0 = u_{n\ell m}(\vec{r}_1)\, u_{n'\ell' m'}(\vec{r}_2)$$

$$E^{(0)} = E_n + E_{n'}$$

n, ℓ, m are the quantum numbers of Hydrogen wave functions

Simplify the notation by calling $nlm \to a$ $n'l'm' \to b$

notation: (1) is $\vec{r}_1$
(2) is $\vec{r}_2$

$$\psi_0 = u_a(1)\, u_b(2) \qquad E^{(0)} = E_a + E_b$$

→ but there is another state, with the same energy

$$\psi_0' = u_a(2)\, u_b(1) \qquad E^{(0)} = E_b + E_a$$

Since these are degenerate, we have to use <u>degenerate</u> perturbation theory, which amounts to diagonalizing the perturbing Hamiltonian $\left(H_I = \frac{e^2}{4\pi\epsilon_0 r_{12}}\right)$ in the space of

$\psi_0 = u_a(1)\, u_b(2)$, $\psi_0' = u_a(2)\, u_b(1)$.

the electron interaction will lift this degeneracy

using the basis ψ_0 , ψ_0' which in matrix/vector form is $\begin{pmatrix} \psi_0 \\ \psi_0' \end{pmatrix}$. Calculate the matrix elements of H_I :

$$\left.\begin{aligned} H_{11} &= \langle u_a(1) u_b(2) | H_I | u_a(1) u_b(2) \rangle \\ H_{22} &= \langle u_b(1) u_a(2) | H_I | u_b(1) u_a(2) \rangle \end{aligned}\right\} e^2 \int \frac{|u_a(1)|^2 \, |u_b(2)|^2 \, d^3r_1 \, d^3r_2}{4\pi\epsilon_0 r_{12}}$$

$$\left.\begin{aligned} H_{12} &= \langle u_a(1) u_b(2) | H_I | u_b(1) u_a(2) \rangle \\ H_{21} &= \langle u_b(1) u_a(2) | H_I | u_a(1) u_b(2) \rangle \end{aligned}\right\} e^2 \int \frac{u_a^*(1)\, u_b^*(2)\, u_b(1)\, u_a(2)}{4\pi\epsilon_0 r_{12}} \, d^3r_1 \, d^3r_2$$

where state 1 $= \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \psi_0$, state 2 $= \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \psi_0'$

vector form ↗

Define the "direct" integral to be

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

remember

ψ_0 = state 1 = $U_a(1)\,U_b(2)$

ψ_0' = state 2 = $U_b(1)\,U_a(2)$

Define the "exchange" integral

$$K = H_{12} = H_{21}$$

To find the new eigenvalues + eigenvectors to first order, we have to diagonalize the Hamiltonian:

$$(H_0 + H_I)\,\psi_0 \text{ or } \psi_0' \Rightarrow \left[\underbrace{\begin{pmatrix} E^{(0)} & 0 \\ 0 & E^{(0)} \end{pmatrix}}_{H_0} + \begin{pmatrix} J & K \\ K & J \end{pmatrix} \right] \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$E^{(0)} = E_a + E_b$.

↳ diagonalizes with Eigenvalues $J \pm K$

diagonalizing gives first order correction.

$$\psi_S = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ or } U_S = \frac{1}{\sqrt{2}}\left[U_a(1)\,U_b(2) + U_b(1)\,U_a(2) \right]$$

$$E_S^{(1)} = E^{(0)} + J + K$$

$$\psi_A = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ or } U_A = \frac{1}{\sqrt{2}}\left[U_a(1)\,U_b(2) - U_b(1)\,U_b(2) \right]$$

$$E_A^{(1)} = E^{(0)} + J - K$$

Note: since we diagonalized with respect to H_I

$$\langle u_S | \frac{e^2}{4\pi\epsilon_0 r_{12}} | u_A \rangle = 0$$

clearly u_A is antisymmetric when $\vec{r}_1$ and $\vec{r}_2$ are exchanged, and u_S is symmetric.

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

Apply this to the ground state of Helium:

both electrons in the ground 1s state: $1s^2$

$$u_A = 0 \qquad u_S = u_{1s}(r_1)\,u_{1s}(r_2)$$

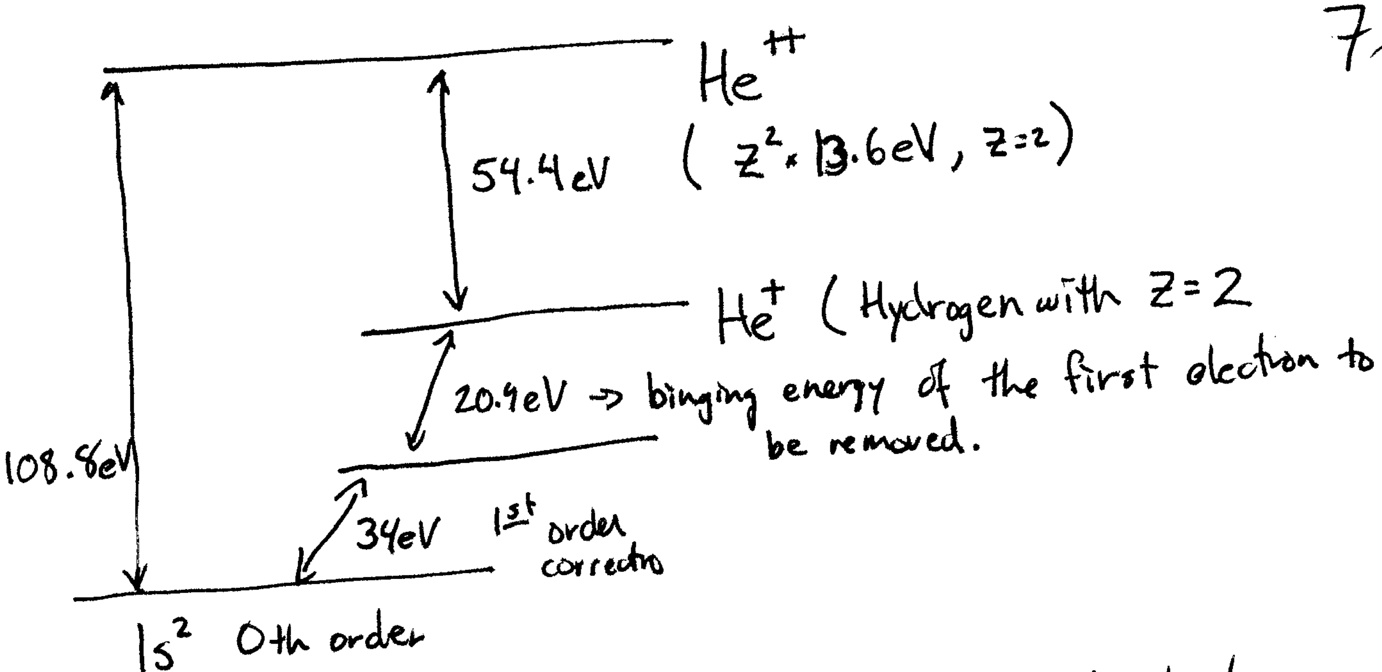
$$E^{(0)} = E_{1s}^{Z=2} + E_{1s}^{Z=2} = -2\,Z^2\,13.6\,\text{eV} = -8 \times 13.6\,\text{eV}$$

$$= -108.8\,\text{eV}$$

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

$$J = e^2 \int \frac{|u_{1s}(1)|^2\,|u_{1s}(2)|^2}{4\pi\epsilon_0 r_{12}}\,d^3r_1\,d^3r_2 = \frac{1}{4\pi\epsilon_0}\,\frac{5}{8}\,\frac{e^2}{2a_0} \simeq 34\,\text{eV}$$

a_0 = Bohr radius



we get the binding energy for removal of 1 electron to be 20.4eV → the actual value is 24.58eV.

Not bad! (there was no exchange K to calculate)

Now look at excited states.

assume u_a = 1s state of Hydrogen

u_b = $n\ell$ state.

(for Helium, doubly excited electrons $n_1 l_1 n_2 l_2$ are above the ionization limit)

then

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

→ here we show that it helps to choose u_a + u_b carefully:

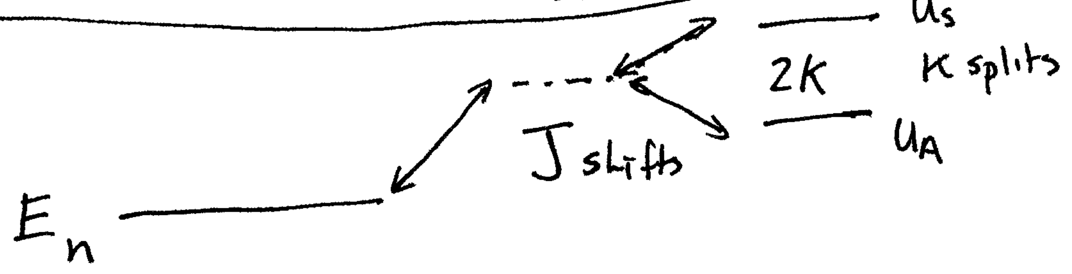
Since the first electron in the 1s state screens electrons in higher states (particularly if the higher state has a large angular momentum) lets be smart about how we choose $U_a(r)$ & $U_b(r)$ to account for the screening. split the Hamiltonian as follows:

$$H_0 = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{1}{r_2}\right)$$

add & subtract $\frac{1}{r_2}$

$$H_I = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}} - \frac{1}{r_2}\right)$$

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



U_A is always lower energy than U_S

in practice, splitting H_0 & H_I like above, significantly improves $E^{(0)}$, so that $E^{(1)}$ 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 ½ particle, with two states +½, −½.

label those states χ_+ & χ_-

Then to a good approximation

$$\psi(1) = U_{n\ell m}(r)\,\chi_\pm(1)$$

$$\psi_0 = U_a(1)\,\chi_\pm(1)\,U_b(2)\,\chi_\pm(2)$$ → four spin combinations.

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

$$U_S\,\chi_A \qquad U_A\,\chi_S$$ → both are anti-symm

$$\chi_S = \begin{cases} \chi_+(1)\,\chi_+(2) \\ \frac{1}{\sqrt{2}}\left(\chi_+(1)\,\chi_-(2) + \chi_-(1))\,\chi_+(2)\right) \\ \chi_-(1)\,\chi_-(2) \end{cases} \qquad \chi_A = \frac{\chi_+(1)\,\chi_-(2) - \chi_+(1)\,\chi_-(2}{\sqrt{2}}$$

these are just the $S=1$ $m_s = 1,0,-1$ and $S=0$ total angular momentum states you get when adding two spin-$1/2$ momenta.

the $S=1$, χ_S states are called triplet states

the $S=0$ χ_A state is called a singlet state.

So solutions are of the form:

$$u_S \chi_A \qquad \text{or} \qquad u_A \chi_S$$