

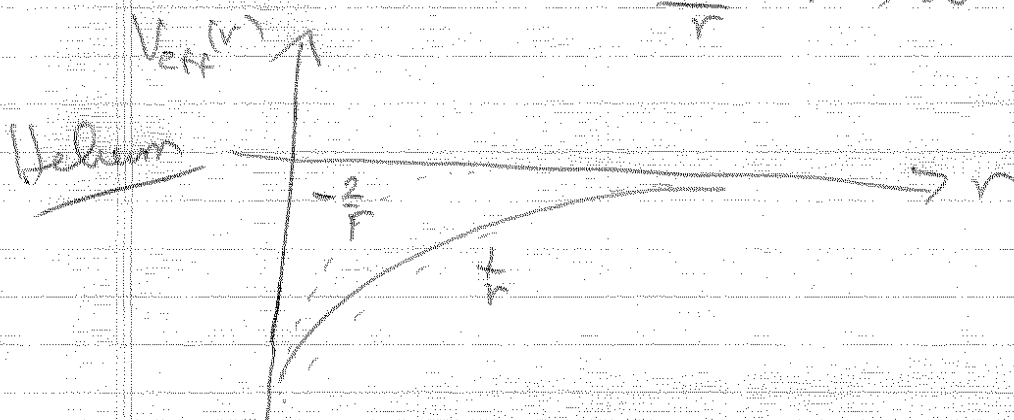
Physics 531: Lecture 12 - Central Potential

- We have seen that ~~before~~ we can get a reasonable approximation to the ground-state of Helium with a variational approach based on some good physical intuition. Last time we considered a trial wave function based on a "screened" Coulomb potential

$$V_{\text{eff}}(r) = -\frac{Z_{\text{eff}}}{r}$$

That is, each electron moves in the average potential of the nucleus and the other electron. We approximated this potential as spherically symmetric and ignored any correlation between the positions of the electrons. Our particular central potential is pretty crude. We do not expect a strict $1/r$ potential since the screening should depend on the distance of the electron from the nucleus. We might expect $V_{\text{eff}}(r)$ to behave as

$$V_{\text{eff}}(r) = \begin{cases} -\frac{Z}{r} & r \rightarrow 0 \\ -\frac{(Z-1)}{r} & r \rightarrow \infty \end{cases} \quad \text{for a 2-electron atom}$$



With a variational approach we might parametrize $V_{\text{eff}}(r)$ somehow to get this asymptotic behavior

Note that with a non $\frac{1}{r}$ potential, the energy will explicitly depend on the angular momentum l , with lower l penetrating to smaller r and thus more tightly bound than states with higher l .

We want to generalize this procedure in some systematic way to multi-electron atoms. ~~that~~
~~is~~ Ignoring relativistic effects

$$\hat{H} = \sum_i \left(\frac{\hat{p}_i^2}{2} - \frac{Z}{r_i} \right) + \sum_{i < j} \frac{1}{r_{ij}}$$

The basic assumption is that the potential seen by the i^{th} electron, ~~is~~ for some energy level is largely spherically symmetric

$$V(\vec{r}_i) = -\frac{Z}{r_i} + \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$= \underbrace{-\frac{Z}{r_i} + S(r_i)}_{V_{\text{eff}}(r_i)} + \Delta V(r_i)$$

where

$$S(r_i) = \left\langle \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right\rangle \text{ is the}$$

screening central potential averaged over the sphere

~~description~~ for a given distribution of the ~~the~~ other $n-1$ electrons. Note: we have a single function $S(r)$ that works for all electrons.

Under this "mean field" approximation with $\Delta V(\vec{r})$ small

$$\hat{H} \approx \sum_i \left(\frac{\vec{p}_i^2}{2} + V_{\text{eff}}(r_i) \right)$$

Each particle is thus effectively independent moving in a mean-field potential of the nucleus and central screening potential.

Each electron eigenstate is thus of the form

$$\Phi_{nlm_l m_s} = (R_{nl}(r) Y_{lm}(\theta, \phi)) \otimes |m_s\rangle \quad \begin{matrix} \text{spin} \\ \text{orbital} \end{matrix}$$

The radial wave functions $u_{nl}(r) = r R_{nl}(r)$

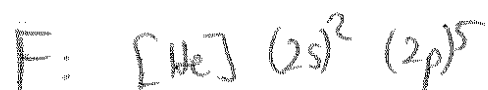
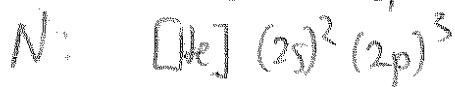
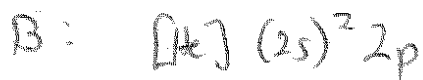
Satisfy $\left(-\frac{1}{2} \frac{d^2}{dr^2} + V_{\text{eff}}(r) + \frac{l^2 l(l+1)}{2mr^2} \right) u_{nl} = E_{nl} u_{nl}$

are not hydrogenic.

- Given N electrons, under this approximation we describe an electron ~~configuration~~ "configuration" of orbitals $(n_1 l_1) (n_2 l_2) \dots (n_N l_N)$. Each orbital has a degeneracy of $2 \binom{2l+1}{\uparrow} \binom{2s+1}{\uparrow}$. By the Pauli exclusion principle (following from antisymmetrization of multielectron wave function), no more than one electron can be in the same spin-orbital. This leads to the "build up" picture of the structure of atoms (periodic table) in their ground state.

The periodic table was set up by Mendeleev in 1869 to classify the elements in terms of their similar chemical properties. We now understand the underlying physical reason is the nature of the "valence shell" for these elements.

To build up the elements, electrons are added one by one into the orbitals (nl) until they are filled, $2(l+1)$ electrons. Lowest l are filled first $l=0, 1, \dots, n-1$, and typically (for light elements), however principle g -number



- An orbital (nl) is known as a "subshell"

- All the orbitals with the same principle quantum number ~~are~~ define a "shell" with $2n^2$ electrons

- The valence shell is the ~~last~~ highest ~~lying~~ shell, the filling of this shell defines chemical properties.

Note that because of the non $\frac{1}{r}$ potential, for higher states there is a competition between n and l for which has lower energy.

For example, the $4s$ orbital lies at a lower energy than $3d$, thus potassium $Z=19$, K, has electron configuration $[\text{Ar}] 4s = [\text{Ne}] 3s^2 3p^6 4s$
 $\text{Ca} = [\text{Ne}] (4s)^2$, $\text{Sc} = [\text{Ne}] (4s)^2 3d$

Slater determinants

For a given configuration, the multielectron wave function must be antisymmetric with respect to exchange of any two particles. This can be written using a "Slater determinant"

Suppose we have N -electrons described by a configuration of ~~orbitals~~ spin orbitals $\{\phi_\alpha, \phi_\beta, \phi_\gamma \dots \phi_\nu\}$

where $\alpha = (n, l, m_l, m_s)$, then the normalized wave function is

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_\alpha(1) & \phi_\beta(1) & \dots & \phi_\nu(1) \\ \phi_\alpha(2) & \phi_\beta(2) & \dots & \phi_\nu(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_\alpha(N) & \phi_\beta(N) & \dots & \phi_\nu(N) \end{vmatrix}$$

A determinant is antisymmetric w.r.t. exchange of any two rows, and thus an allowed ~~ψ~~ wavefunction.

Example: $\{ \phi_{1s,\uparrow}, \phi_{1s,\downarrow} \}$

$$\begin{aligned} \Rightarrow \Psi(1,2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s,\uparrow}(1) & \phi_{1s,\downarrow}(1) \\ \phi_{1s,\uparrow}(2) & \phi_{1s,\downarrow}(2) \end{vmatrix} \\ &= \phi_{1s}(1) \phi_{1s}(2) \left\{ \frac{|\uparrow(1)\downarrow(2)\rangle - |\downarrow(1)\uparrow(2)\rangle}{\sqrt{2}} \right\} \end{aligned}$$

Example: $\{ \phi_{1s,\uparrow}, \phi_{1s,\downarrow}, \phi_{2s,\uparrow} \}$

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s,\uparrow}(1) & \phi_{1s,\downarrow}(1) & \phi_{2s,\uparrow}(1) \\ \phi_{1s,\uparrow}(2) & \phi_{1s,\downarrow}(2) & \phi_{2s,\uparrow}(2) \\ \phi_{1s,\uparrow}(3) & \phi_{1s,\downarrow}(3) & \phi_{2s,\uparrow}(3) \end{vmatrix}$$

$$\begin{aligned} &= \frac{1}{\sqrt{3!}} \left(\phi_{1s}(1) \phi_{1s}(2) \phi_{2s}(3) |\uparrow(1)\rangle \otimes \left\{ \frac{|\downarrow(2)\rangle |\uparrow(3)\rangle - |\uparrow(2)\rangle |\downarrow(3)\rangle}{\sqrt{2}} \right. \right. \\ &\quad - (1 \leftrightarrow 2) \\ &\quad \left. \left. - (1 \leftrightarrow 3) \right) \right) \end{aligned}$$