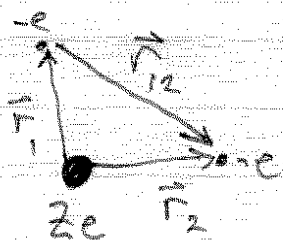


Lecture 11: Two-electron atoms; Helium

Up to now we have treated only the simplest atoms - hydrogenic - consisting of only one electron and a nucleus. Atoms with more electrons are much much more complicated because

- The many-body problem (beyond two-bodies) is not even solvable classically
- Quantum statistics of identical particles

In the next few lectures we will study the basis of these multielectron atoms. A thorough analysis can take a whole semester. To begin with, we consider the simplest case of two-electron atoms.



We take, to good approximation, the center of mass at the nucleus.

Then, ~~more~~ ignoring relativistic effects, for fixed nucleus, the Hamiltonian is

$$H = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

The state describes the two-electron system, $|\Psi(1,2)\rangle$.
 Though we have neglected relativistic (magnetic) effects, the state depends implicitly on spin due to "quantum statistics". The electrons, spin- $1/2$, are fermions. Thus two-electron state must be antisymmetric w.r.t. exchange of the two electrons

$$\hat{P}_{12} |\Psi(1,2)\rangle \equiv |\Psi(2,1)\rangle = -|\Psi(1,2)\rangle$$

This includes both spatial and spin.

Suppose one of the electrons is in state $|\phi_A\rangle|\chi_A\rangle$
↑ spatial wave function ↑ spin state

and the other is in the state $|\phi_B\rangle|\chi_B\rangle$

Then an allowed 2-electron state must anti-symmetrize

$$|\Psi_{12}\rangle = \frac{1}{\sqrt{2}} \left(|\phi_{A_1}\rangle|\chi_{A_1}\rangle \otimes |\phi_{B_2}\rangle|\chi_{B_2}\rangle - |\phi_{B_1}\rangle|\chi_{B_1}\rangle \otimes |\phi_{A_2}\rangle|\chi_{A_2}\rangle \right)$$

$$\text{If } |\chi_A\rangle = |\chi_B\rangle = \begin{cases} |\uparrow\rangle \\ \text{or } |\downarrow\rangle \end{cases} \equiv |\chi\rangle$$

$$\Rightarrow |\Psi_{12}\rangle = \frac{1}{\sqrt{2}} \left(|\phi_{A_1}\rangle|\phi_{B_2}\rangle - |\phi_{B_1}\rangle|\phi_{A_2}\rangle \right) \otimes |\chi\rangle_1|\chi\rangle_2$$

spatial wave function $\Rightarrow |\Psi_{12}\rangle$ antisymmetric

If $|\chi_A\rangle = |\chi_B\rangle$ i.e. $|\uparrow\rangle|\downarrow\rangle$
 or $|\downarrow\rangle|\uparrow\rangle$

$$|\Psi_{12}\rangle = \frac{1}{\sqrt{2}} \left(\frac{|\phi_{A1}\rangle|\phi_{B2}\rangle - |\phi_{B1}\rangle|\phi_{A2}\rangle}{\sqrt{2}} \right) \left[\frac{|\uparrow_1\downarrow_2\rangle + |\downarrow_1\uparrow_2\rangle}{\sqrt{2}} \right]$$

$$+ \frac{1}{\sqrt{2}} \left[\frac{|\phi_{A1}\rangle|\phi_{B2}\rangle + |\phi_{B1}\rangle|\phi_{A2}\rangle}{\sqrt{2}} \right] \left[\frac{|\uparrow_1\downarrow_2\rangle - |\downarrow_1\uparrow_2\rangle}{\sqrt{2}} \right]$$

Symmetric space
antisymmetric spin

Thus there are four natural "eigenstates" for these two-electron orbitals + spin

$$\left(\frac{|\phi_A\phi_B\rangle + |\phi_B\phi_A\rangle}{\sqrt{2}} \right) \otimes \left[\frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \right]$$

Symmetric space
antisymmetric spin

$$\left(\frac{|\phi_A\phi_B\rangle - |\phi_B\phi_A\rangle}{\sqrt{2}} \right) \otimes \left\{ \begin{array}{l} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{array} \right.$$

antisymmetric space
Symmetric spin

We recognize, the anti-sym spin = Spin singlet

*The three symmetric spin states = Spin triplet

Thus, though there is no explicit spin-spin interaction the natural eigenstates are ones with coupled spins, eigenstates of

$$\begin{aligned} \vec{S}^2 &= \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2 \\ &= \frac{3}{4} + \frac{3}{4} + \frac{1}{2}\vec{\sigma}_1 \cdot \vec{\sigma}_2 = \frac{3}{2} + \frac{1}{2}\vec{\sigma}_1 \cdot \vec{\sigma}_2 \end{aligned}$$

Crude look at spectrum of bound two electrons

• Independent particle model

In the crudest approximation, the two electrons move independently of one another and separately orbit the nucleus. This will be a reasonable approximation ~~but~~ for $Z \gg 1$, but clearly fail for smaller Z such as He or H^- ion. In this

approximation, we neglect the electron-electron repulsion $\Rightarrow \hat{H} = \hat{H}_1 + \hat{H}_2$ where $\hat{H}_i = \underbrace{\frac{\vec{p}_i^2}{2m_i} - \frac{Ze^2}{r_i}}_{\text{Hydrogenic}}$

The two electron orbitals are thus

$$|2\psi\rangle_{12\pm} = \underbrace{|n_A l m_A\rangle}_{A A A} \underbrace{|n_B l m_B\rangle}_{B B \pm} |X\rangle_{\mp} \quad \begin{array}{l} |X\rangle_{-} \rightarrow \text{singlet} \\ |X\rangle_{+} \rightarrow \text{triplet} \end{array}$$

~~Note~~ $|n_A l m_A; n_B l m_B\rangle = \frac{|n_A l m_A\rangle |n_B l m_B\rangle \pm |n_B l m_B\rangle |n_A l m_A\rangle}{\sqrt{2}}$

$|n l m\rangle = \text{Hydrogenic orbital}$

To zeroth Order: $E_{n_A, n_B}^{(0)} = E_{n_A}^{(0)} + E_{n_B}^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{n_A^2} + \frac{1}{n_B^2} \right)$
in a.u.

For the "electron configuration" $(n_A l_A) (n_B l_B)$

This is a very crude approximation, only possibly useful for large Z two-electron ions where the electrons are held close to the nucleus and have relatively weak repulsion from one another.

For He, $Z=2$ $E_{(1s)^2}^{(0)} = -4 \text{ a.u.} = -108 \text{ eV}$

The actual (experimental) value = $-2.9 \text{ a.u.} = -79 \text{ eV}$

Clearly not such a great approximation.

Note: The energy with one electron ionized and the other bound at level n_A is

$$E_{n_A, \infty}^{(0)} = -\frac{Z^2}{2n_A^2}$$

Is ~~even~~ less than the energy associated with two electrons excited above $1s$, i.e. $n_A > 1, n_B > 1$

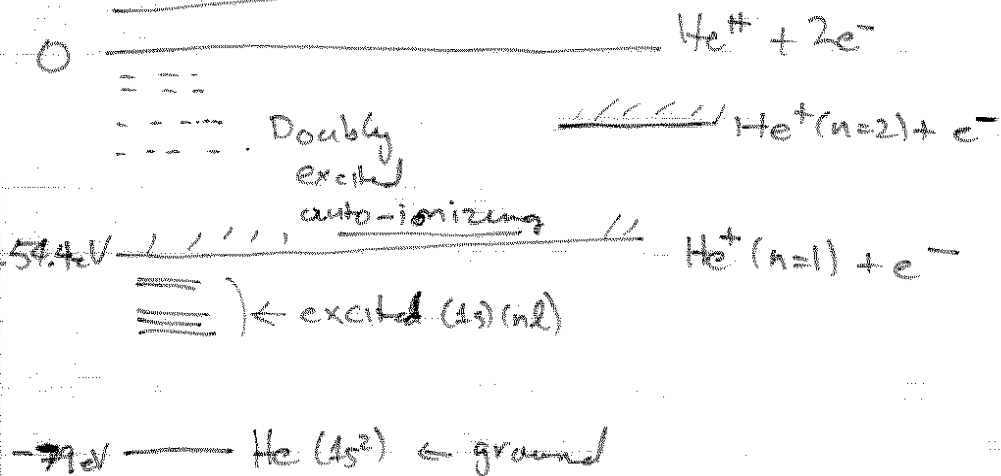
$$E_{n_A > 1, n_B > 1}^{(0)} \geq -\frac{Z^2}{4} > -\frac{Z^2}{2n_A^2} \Rightarrow \text{Excited states with}$$

two bound electrons constructed only

from configurations $(1s)(nl)$

^ second orbital

Sketch of Helium spectrum



Correction via perturbation theory

To the degree that one can consider the electron repulsion small compared to the attraction to the nucleus, we can calculate the shift to our crude zeroth order approximation ^{with} our hydrogenic orbitals.

The interaction $\frac{1}{r_{12}}$ is spin independent. Nonetheless, we will see a crucial ~~spin~~ implicit spin dependence through the spin statistics connection.

In the absence of repulsion the states are degenerate

$$|\Psi^{(0)}_{(n_1 m_1)(n_2 m_2)}\rangle_{\pm} = \frac{1}{\sqrt{2}} \left(|n_1 l m_1\rangle_{A1} |n_2 l m_2\rangle_{B2} \pm |n_2 l m_2\rangle_{B1} |n_1 l m_1\rangle_{A2} \right) |X_{\pm}\rangle$$

$|X_{-}\rangle = \text{singlet}$

$|X_{+}\rangle = \text{the one of the triplets}$

$$\text{Shift } \langle \psi_{\pm}^{(0)} | \frac{1}{r_{12}} | \psi^{(0)} \rangle = \frac{1}{2} \int d^3x_1 d^3x_2 \left(\psi_{n_A l_A m_A}^*(\vec{r}_1) \psi_{n_B l_B m_B}^*(\vec{r}_2) \pm \psi_{n_B l_B m_B}^*(\vec{r}_1) \psi_{n_A l_A m_A}^*(\vec{r}_2) \right) \frac{1}{r_{12}}$$

$$= J \pm K$$

where: $J = \int d^3x_1 d^3x_2 |\psi_{n_A l_A m_A}(\vec{r}_1)|^2 |\psi_{n_B l_B m_B}(\vec{r}_2)|^2 \frac{1}{r_{12}}$

= "Direct" term: what we would have written without symmetrization for identical particles

$$K = \int d^3x_1 d^3x_2 \left(\psi_{n_A l_A m_A}^*(\vec{r}_1) \psi_{n_B l_B m_B}(\vec{r}_1) \right) \left(\psi_{n_B l_B m_B}^*(\vec{r}_2) \psi_{n_A l_A m_A}(\vec{r}_2) \right) \frac{1}{r_{12}}$$

= "Exchange" term: Due only to interference under exchange of the two ~~sets~~ identical particles

Note $K \rightarrow 0$ if $\psi_{n_A l_A m_A}(\vec{r})$ and $\psi_{n_B l_B m_B}(\vec{r})$ do not overlap in space

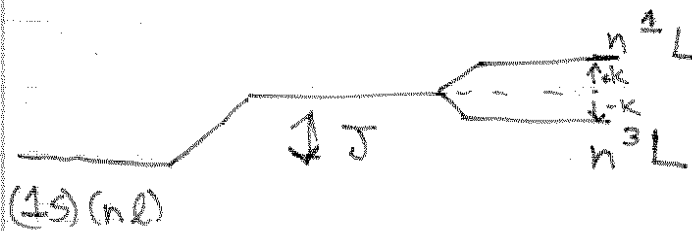
\Rightarrow Spatially separated electrons are distinguishable

\Rightarrow No effect of identical particles

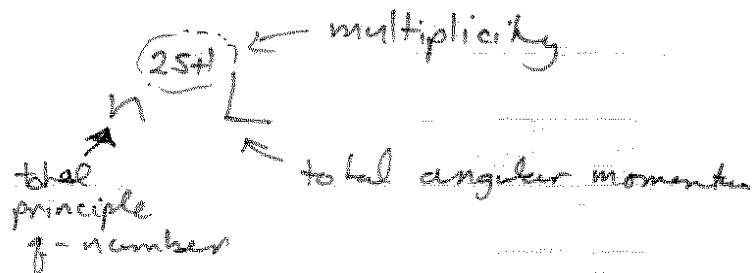
Thus, to first order,

$$E_{(n_A l_A)(n_B l_B)} = -\frac{Z^2}{2} \left(\frac{1}{n_A^2} + \frac{1}{n_B^2} \right) + J \pm K$$

The energy level is thus split into two singlet manifolds: symmetric space / antisym spin
 antisymmetric space / sym spin \leftarrow triplet



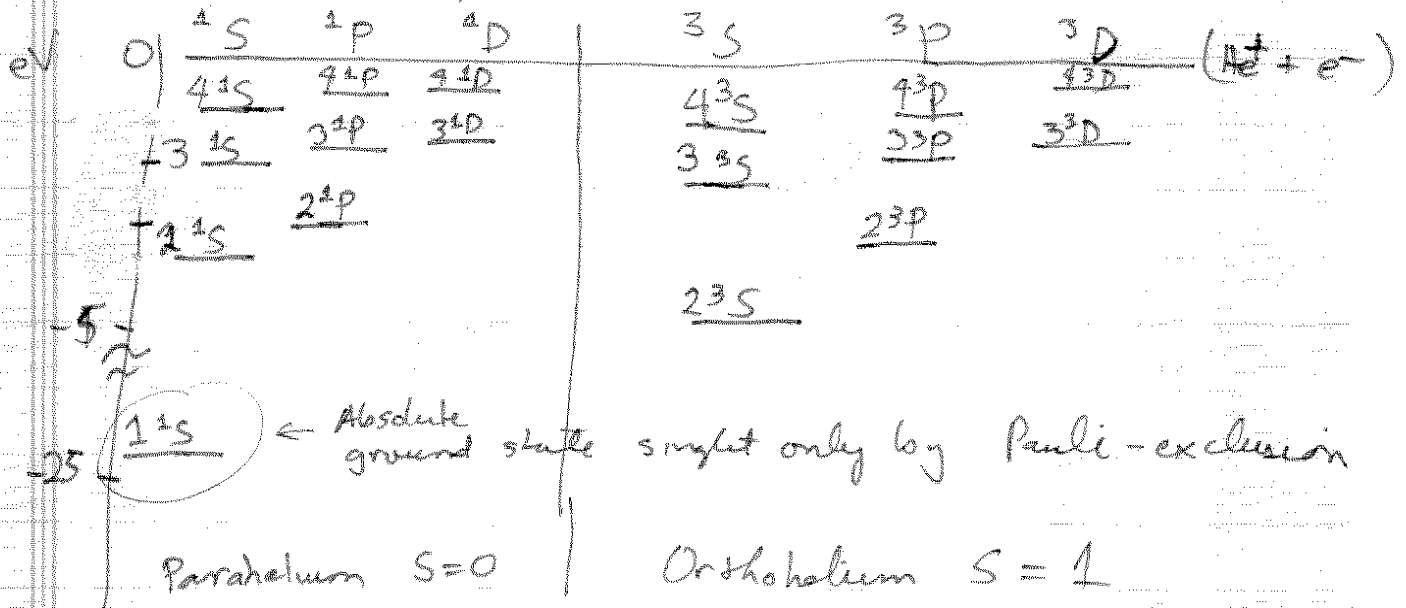
Spectroscopic notation:



The exchange interaction ~~is~~ splits the electron configuration into two terms, singlet and triplet, separated by $2K$. The singlet lies at a higher energy because the spatial wavefunction is symmetric. Thus the exchange term enhances the closeness of the electrons so that they receive an additional repulsion. In contrast, when the two electrons are in a singlet (symmetric spin), the spatial wavefunction is antisymmetric. In this case, the probability that the electrons are near one another is reduced relative to what is experienced by distinguishable particles.

- Fermions in symmetric spin avoid each other
- Fermions in antisymmetric spin bunch together

The division of the ~~spectrum~~^{energy level} into singlet and triplet terms means the allowed (E1) transition are divided into two spectra. This is known as para and ortho helium.



Note: As discussed in homework, the degeneracy in L is broken in non-hydrogenic atoms because the lower angular momentum state penetrate deeper to the nucleus where they are more tightly bound, whereas the higher angular momentum states are at larger radius where the electrons screen the nuclear attraction.

Electromagnetic transitions between $S=0$ and $S=1$ are known as intercombination lines. This can occur by higher multipole, or with spin-orbit, sometime through a small (E1) component.

Ground State (perturbation theory)

Using the "addition theorem"

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{(r_2)^l}{(r_1)^{l+1}} Y_{l,m}^*(\theta_1, \phi_1) Y_{l,m}(\theta_2, \phi_2)$$

where $r_<$ ($r_>$) is the smaller (greater) of r_1 or r_2
the direct and exchange terms can be calculated

For the ground state, no exchange term
since particles in same spatial wave function

$$\begin{aligned} \Rightarrow E_{(1s)^2}^{(1)} &= \int |\psi_{1s}(\vec{r}_1)|^2 |\psi_{1s}(\vec{r}_2)|^2 \frac{1}{r_{12}} d^3x_1 d^3x_2 \\ &= +\frac{5}{8} Z \text{ au} \quad (\text{see text}) \end{aligned}$$

Thus to first order $E_{(1s)^2} = -Z^2 + \frac{5}{8} Z^2 = -\frac{3}{8} Z^2$

For He this gives $E_{(1s)^2} = -2.750 \text{ au}$ compared to
the exact ~~value~~ result of -2.904 au

For C^{4+} this first order expansion gives

$$E_{(1s)^2} = -32.25 \text{ au} \quad \text{compared to}$$

exact result of -32.41 au

which is pretty good.

Variational approximation

To get a better approximation to the ground state of He, we can use the variational method, discussed at the beginning of the semester. A key idea is the central field approximation. Loosely, to lowest approximation, we assume that each electron moves independently in a "screened" Coulomb potential created by the nucleus and other electron. Crudely, each electron sees a hydrogen ~~atom~~ potential of the form, $-\frac{Z_{\text{eff}}}{r}$. Z_{eff} = Variational parameter

~~Work~~ So that we take as our "trial wave function"

$$\phi(r_1, r_2) = \psi_{1s}^{Z_{\text{eff}}}(r_1) \psi_{1s}^{Z_{\text{eff}}}(r_2) = \left(\frac{Z_{\text{eff}}^3}{\pi}\right)^{1/2} e^{-Z_{\text{eff}} r}$$

$$\text{With energy } E_{(1s)^2}^{(0)} = -\frac{Z_{\text{eff}}^2}{2} - \frac{Z_{\text{eff}}^2}{2} = \frac{Z_{\text{eff}}^2}{2}$$

The energy including interaction

$$E[\phi] = 2 \left\langle \phi \left| \frac{\hat{p}_1^2}{2m} - \frac{Z}{r_1} \right| \phi \right\rangle + \left\langle \phi \left| \frac{1}{r_{12}} \right| \phi \right\rangle$$

$\leftarrow \frac{5}{8} Z_{\text{eff}}$ as before

$$\left\langle \phi \left| \frac{\hat{p}_1^2}{2m} \right| \phi \right\rangle = \left\langle \psi_{1s}^{Z_{\text{eff}}} \left| \hat{T} \right| \psi_{1s}^{Z_{\text{eff}}} \right\rangle = \frac{Z_{\text{eff}}^2}{2}$$

$$\text{and } \left\langle \phi \left| \frac{Z}{r_1} \right| \phi \right\rangle = Z \left\langle \phi \left| \frac{1}{r_1} \right| \phi \right\rangle = Z Z_0$$

$$\text{Since, by virial theorem: } 2 \left\langle T \right\rangle_n = - \left\langle V \right\rangle_n = -2 E_n$$

for coulomb

$$\text{Thus, } E[\phi] = E(z_{\text{eff}}) = z_{\text{eff}}^2 - 2Zz_{\text{eff}} + \frac{5}{8} z_{\text{eff}}^2$$

$$\text{Minimizing: } \frac{\partial E}{\partial z_{\text{eff}}} = 2z_{\text{eff}} - 2Z + \frac{5}{4} z_{\text{eff}}$$

$$\Rightarrow \boxed{z_{\text{eff}} = Z - \frac{5}{16}}$$

$$\Rightarrow \boxed{E_{(2)} \approx -\left(Z - \frac{5}{16}\right)^2}$$

This is more accurate than first order perturbation

For He, this gives $E_{(2)} = -2.848$ (pretty good)

To get a better ~~approx~~ approximation we must take into account the fact the effective potential seen by each electron is not pure Coulombic $\frac{1}{r}$.

For small r $V(r) \approx -\frac{Z}{r}$ (unscreened)

For large r $V(r) \approx -\frac{1}{r}$ (screened by other electron)

In the next lecture we will establish a method for finding the effective potential seen by each electron due to the average of the other electrons + nucleus. This mean-field approximation is the first starting point for any atomic physics calculations, and generally, for dealing with many-body problems.