Lecture 27 - Poly-electron atoms

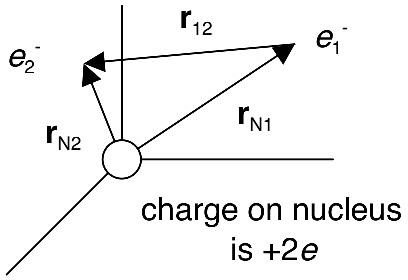
What's important:
- helium atom by approximation
- spin wavefunctions for helium

Text: Gasiorowicz, Chap. 18

Helium atom

We have now solved the Schrödinger equation for an arbitrary charge Z on the nucleus, and examined the specific case where $Z = 1$, the hydrogen atom. As long as there is only one electron present in the atom, these hydrogen-like solutions are perfectly valid for all Z. The next most complex atom (neutral) after hydrogen is helium.

The relevant coordinates for the helium atom can be defined as



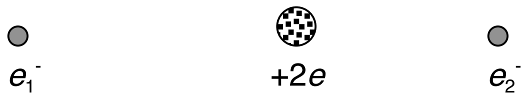
The Hamiltonian operator for the atom then has the form:

$$H = (-\hbar^2/2m_e)\,[\nabla_1^2 + \nabla_2^2] - 2ke^2/r_{N1} - 2ke^2/r_{N2} + ke^2/r_{12}.$$

Kinetic energies of electrons 1 & 2 (center of mass motion factored out)	attraction of electrons to nucleus	repulsion between electrons

If the ke^2/r_{12} term were *not* present then we would have a separable 2-body problem which could be solved analytically. As it is, the Hamiltonian represents a three-body problem that must be solved numerically or by approximation.

A naïve approach to simplifying Hamiltonian is to see what effects the electrons have on each other. By and large, the electrons will not be closeby. Suppose for the moment that they are on opposite sides of the nucleus:



Here, the effect of e_1 on e_2 is to repel it from the nucleus. Thus, e_1 experiences an *effective* coulomb field which can be approximated by

$$-Z' e^2/r_{N1},$$

where Z' is less than Z. Of course, this is only an approximation, and we may have trouble determining Z', but at least it allows us to proceed. So, we write out an *approximate* Hamiltonian H_o as

$$H = (-\hbar^2/2m_e)\,[\nabla_1^{\,2} + \nabla_2^{\,2}] - Z' ke^2/r_{N1} - Z' ke^2/r_{N2}.$$

This Hamiltonian has the classic separation of variables form in the coordinates of electron 1 and 2:

$$H_o = h_o(1) + h_o(2),$$

where

$$h_o = (-\hbar^2/2m_e)\,\nabla^2 - Z' ke^2/r.$$

Thus, we write the solution for the two-electron wavefunction

$$H_o\psi_o(1,2) = E_o\psi_o(1,2)$$

as

$$\psi_o(1,2) = \phi_o(1)\phi_o(2)$$

where spin-statistics are ignored for the moment. The single particle wavefunction satisfies

$$h_o\phi_o = \varepsilon^o\,\phi_o,$$

and

$$E_o = \varepsilon_1^{\,o} + \varepsilon_2^{\,o}.$$

The superscripts and subscripts are admittedly a nuisance, but they emphasize that all of the energies are only approximate. Because h_o has the form of the single particle Schrödinger equation for the Coulomb potential, then ϕ_o and ε^o can be written out immediately:

$$\varepsilon_1^{\,o} = -\,(Z'^2 / 2n_1^{\,2}) \bullet (m_e k^2 e^4/\hbar^2)$$
$$\varepsilon_2^{\,o} = -\,(Z'^2 / 2n_2^{\,2}) \bullet (m_e k^2 e^4/\hbar^2)$$

and

$$E_o = -\,(Z'^2 / 2) \bullet (m_e k^2 e^4/\hbar^2) \bullet (1/n_1^{\,2} + 1/n_2^{\,2}).$$

For numerical purposes, note that the combination

$$m_e k^2 e^4/\hbar^2 = 1 \text{ Hartree} = 27.2 \text{ eV}$$
$$= 2E_{\text{H, gs}} \text{ (ground state energy of the hydrogen atom)}$$

Thus, we see that the ground state energy of the helium atom has

$$n_1 = n_2 = 1$$

and

$$\begin{aligned} E_{o,\,gs} &= -\,(Z'^2 / 2) \cdot (m_e k^2 e^4/\hbar^2) \cdot 2 \\ &= -Z'^2\,(m_e k^2 e^4/\hbar^2) \\ &= 2Z'^2 E_{H,\,gs}. \end{aligned}$$

Now, if the two electron distributions were so spread out that they had minimal interaction, we would expect $Z' \cong 2$ and

$$\begin{aligned} E_{o,\,gs} &\cong 2 \cdot 2^2 E_{H,\,gs} \\ &= -\,8E_{H,\,gs} = -108.8 \text{ eV}. \end{aligned}$$

Experimentally, it is observed to take 78.98 eV to strip both electrons from a helium atom, so Z' must be less than 2. Using the observed binding energy to solve for Z' gives

$$2Z'^2 \text{ x } 13.6 = 78.89$$

or

$$Z' = 1.70.$$

This is actually not bad, there are models for predicting Z' from wavefunctions and they give $Z' = 1.69$.

Spin wavefunctions

Next, we turn our attention to the wavefunctions occupied by the electrons. Under our approximate Hamiltonian, the spatial part of the ground state wavefunction is just the 1*s* orbit familiar from the hydrogen atom. Because they are fermions, two electrons can only be placed into the **orbital** product state

$$\phi_{1s}(1)\phi_{1s}(2)$$

if the **spin** wavefunction is antisymmetric. There are four different products of the individual spin wavefunctions

$\alpha \equiv |\ 1/2, +1/2>$ $\beta \equiv |\ 1/2, -1/2>$

namely,

$\chi_a = \alpha(1)\ \alpha(2)$ $S_z = +1$

$\chi_b = \alpha(1)\ \beta(2)$ $S_z = 0$

$\chi_c = \beta(1)\ \alpha(2)$ $S_z = 0$

$\chi_d = \beta(1)\ \beta(2)$ $S_z = -1.$

To determine the appropriate combination, we define the permuation operator

$$P(1,2)$$

which exchanges the labels of particles 1 and 2. Then

$$\begin{aligned} P(1,2)\ \chi_a &= +\chi_a \\ P(1,2)\ \chi_b &= +\chi_c \\ P(1,2)\ \chi_c &= +\chi_b \\ P(1,2)\ \chi_d &= +\chi_d \end{aligned}$$

Clearly, χ_a and χ_d are symmetric states, which would be OK for pions and photons, but not for electrons. The way to make an antisymmetric state is to take a linear combination of χ_b and χ_c:

$P(1,2)\ (\chi_b + \chi_c) = +(\chi_b + \chi_c)$
$P(1,2)\ (\chi_b - \chi_c) = -(\chi_b - \chi_c)$

The combination $(\chi_b - \chi_c)$ is correct for the ground state, which can then be written

$$\psi_{gs}(1,2) = \phi_{1s}(1)\phi_{1s}(2)\ (\alpha(1)\beta(2) - \beta(1)\alpha(2)\ )\ / \sqrt{2},$$

where the √2 is included to properly normalize the wavefunction.

What are the various angular momenta of the two-particle states?

1. *Orbital angular momentum* Each 1*s* state has $\ell = 0$, so the total orbital angular momentum $L_{tot} = 0$.

2. *Spin angular momentum* The combination $\chi_b - \chi_c$ has $S_{tot,\ z} = 0$, arising from each of the products $\alpha\beta$. But this doesn't tell us S_{tot}, because even states with $S_{tot} > 0$ must still have an $S_{tot,\ z} = 0$ projection. Here, we have $S_{tot} = 0$ and 1, but the symmetries of each projection must be the same for a given S_{tot}. Thus

$S_{tot} = 1\ \alpha(1)\ \alpha(2)$ $S_z = +1$ even under P(1,2)
$(\alpha(1)\beta(2) + \beta(1)\alpha(2)\ )\ / \sqrt{2}$ $S_z = 0$ even under P(1,2)
$\beta(1)\ \beta(2)$ $S_z = -1$ even under P(1,2)

$S_{tot} = 0\ (\alpha(1)\beta(2) - \beta(1)\alpha(2)\ )\ / \sqrt{2}$ $S_z = 0$ odd under P(1,2)

Thus, the ground state has total spin $S_{tot} = 0$ which is ODD.

3. *Total angular momentum* The total angular momentum $J = L_{tot} + S_{tot}$ is trivially 0.

Spectroscopic notation

Clearly, the addition of angular momentum can be an arduous task, there are many possible combination as the number of electrons increases. A notation commonly used is to identify a state by its total *S*, *L* and *J* by

$$^{2S+1}L_J$$

where *S* and *J* are given their numerical values and *L* = *S P D F* in the atomic sense. Thus, the helium atom ground state is

$$^1S_0.$$