Many Electron Atoms

Helium

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

$$\hat{H}(1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} \; ; \; H(2) = -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2}$$

We want to solve

$$\hat{H}\psi = E\psi$$

Try separation of variables

$$\psi = \varphi(1)\,\phi(2)$$

Can

$$\hat{H}\varphi(1)\phi(2) = E\varphi(1)\phi(2) \quad ?$$

Answer - NO!

Because of the electron-electron interaction the exact wavefunction of He cannot be written as a product of one electron functions.

What to do?

Try to mold approximate solutions using the Variation Method.

Suppose $\tilde{\psi}(1,2) = \varphi(1)\,\varphi(2)$

where $\varphi = \sqrt{\frac{8}{\pi}}\, e^{-2r} = 1s$ for He^+

Note $\hat{H}(1)\,\varphi = -\frac{4}{2}\varphi$ in atomic units

$$\tilde{E} = \frac{\langle \tilde{\psi} | \hat{\mathcal{H}} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \langle 1s(1)\,1s(2) \,|\, \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}} \,|\, 1s\,1s \rangle$$

Now $$\tilde{E} = -2 - 2 + \left(\frac{8}{\pi}\right)^2 \int e^{-4r_1} \frac{1}{r_{12}} e^{-4r_2}\, dV(1)\, dV(2)$$

The integral equals $\frac{10}{8}\left(\frac{\pi}{8}\right)^2$ so

$$\tilde{E} = -4 + \frac{10}{8} = -4 + \frac{5}{4} = -\frac{11}{4} \text{ Hartrees} = -74.8 \text{ eV}$$

$E_{experimental} = -79.0$ eV so 5.3% error

How to improve $\tilde{\psi}$?

Embed parameter & select it to give lowest $\tilde{E}$

$$\varphi = \sqrt{\frac{\zeta^3}{\pi}}\, e^{-\zeta r}$$

$$\tilde{E} = \langle \varphi\varphi | \hat{\mathcal{H}} | \varphi\varphi \rangle = \zeta^2 - \frac{27}{8}\zeta$$

$$\frac{d\tilde{E}}{d\zeta} = 2\zeta - \frac{27}{8} = 0 \Rightarrow \zeta_{opt} = \frac{27}{16} = 1.687$$

$$\tilde{E}(\zeta_{opt}) = \left(\frac{27}{16}\right)^2 - \frac{27}{8}\left(\frac{27}{16}\right) = -\left(\frac{27}{16}\right)^2 = -2.847656 \text{ au}$$

or -77.5 eV & 1.9% error

Can we do better

Instead of putting forth a functional form for the orbital can we determine the best form?

Yes, by using the Calculus of variations.

Write the wave function as

$$\psi(1,2) = \varphi(1)\varphi(2)$$

Form the energy expression

$$\tilde{E} = 2\langle\varphi|\hat{H}|\varphi\rangle + \langle\varphi(1)\varphi(2)|\frac{1}{r_{12}}|\varphi(1)\varphi(2)\rangle = \tilde{E}(\varphi)$$

form the functional derivative

$$\frac{\delta\tilde{E}}{\delta\varphi} = 0$$

This determines that the best orbital φ is a solution to the HF (Hartree-Fock) equation

$$\hat{F}\varphi = \epsilon\varphi$$

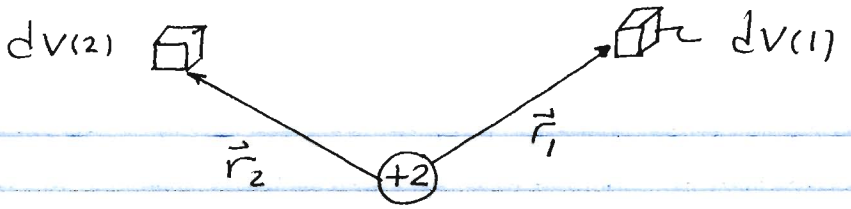
where $$\hat{F} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \int \frac{\varphi^2(2)}{r_{12}}\,dV(2)$$

This equation depends on the solution (!) ϕ so must be solved in an iterative or self consistent manner.

1. guess ϕ
2. form $\hat{F}$
3. solve for new ϕ
4. Compare with guess - if close we are finished. If not close go to 2 & repeat process.

Best ϕ is called the HF orbital & the associated energy the HF energy. For He $E(HF) = -77.9$ eV This is still in error by 1.1 eV. This should not surprise us as we have seen that separation of variables did not work & $\therefore \Psi(1,2)$ (exact) $\neq \phi(1)\phi(2)$ no matter how "good" ϕ is. The difference between the $E(HF)$ & E (exact) is called "correlation energy". it is called correlation energy

The reason is as follows:



$$\psi^2(1,2)\, dV(1)\, dV(2) = P(1,2)\, dV(1)\, dV(2)$$

represents the probability of electron 1 being at $\vec{r}_1$ in $dV(1)$ while, simultaneously electron 2 is at $\vec{r}_2$ in $dV(2)$. $P(1,2)$ is the associated probability density. In the HF approximation

$$P(1,2) = \psi^2(1,2) = \varphi^2(1)\,\varphi^2(2) = P(1)\,P(2)$$

$\Rightarrow$ The probability of electron 1 being at a given location is independent of the location of electron 2. Indeed they could, in this approximation, be at the same point at the same time. The motion of the two particles is uncorrelated & thus "correlation energy".

In order to improve on the HF energy Hylleraas (1928-30) introduced r_{12} explicitly into the variational wavefunction

$$\psi(1,2) = N\left(e^{-\zeta r_1} e^{-\zeta r_2}\right)(1 + b r_{12})$$

where N is a normalization constant

ζ & b are variational parameters

forming $\langle \psi | \mathcal{H} | \psi \rangle = \tilde{E}(\zeta, b)$ & setting

& $\left(\frac{\partial \tilde{E}}{\partial \zeta}\right)_b = 0$ & $\left(\frac{\partial \tilde{E}}{\partial b}\right)_\zeta = 0$

one finds $\zeta_{opt} = 1.849$

$b = 0.364$

$\tilde{E}_{opt} = -78.7\ eV$, in error by $0.3\ eV$.

He then generalized the trial function to

$$\psi = N e^{-\zeta r_1} e^{-\zeta r_2} \sum_{ijk} (r_1 + r_2)^j (r_1 - r_2)^k r_{12}^i C_{ijk}$$

& included 6 terms in the sum. He obtained an energy that was $\underbrace{0.01\ eV}$ higher than the experimental value.

Some time latter Pekeris took the same trial function, included 1078 terms & calculated the ionization energy of He to be $109,310.68\ cm^{-1}$ whereas the experimental value is $109,310.82 \pm 0.15\ cm^{-1}$.

Electron Spin

There is unambiguous experimental & theoretical evidence that the electron has an intrinsic angular momentum of $\sqrt{3/4}\,\hbar$ which can have either $\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$ projection on an external z axis. Note that

$$\sqrt{\tfrac{3}{4}}\,\hbar = \sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right)}\,\hbar$$

& the similarity with $\sqrt{\ell(\ell+1)}\,\hbar$

suggests that the electron has a angular momentum quantum number $S = 1/2$ with its M_S components following the usual rule $-S \le M_S \le S$ in integer increments.

Since $S = 1/2$ $\quad M_S = \pm 1/2$.

We call $M_S = +1/2$ α & $M_S = -1/2$ β

These functions obey the usual angular momentum equations but with $\hat{S}^2$ replacing $\hat{L}^2$ & $\hat{S}_z$ replacing $\hat{L}_z$. Accordingly

$$\hat{S}^2\alpha = \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\hbar^2\alpha \;;\; \hat{S}_z\alpha = \tfrac{\hbar}{2}\alpha$$

$$\hat{S}^2\beta = \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)\hbar^2\beta \;;\; \hat{S}_z\beta = \tfrac{\hbar}{2}\beta$$

Electron Spin & the Pauli Principle

We must incorporate spin into the He atom trial functions. So instead of ψ we will write $\psi\alpha$ or $\psi\beta$. We then have the following possibilities

$$\psi(1)\,\psi(2)\,\alpha(1)\,\alpha(2)$$
$$\psi(1)\,\psi(2)\,\alpha(1)\,\beta(2)$$
$$\psi(1)\,\psi(2)\,\beta(1)\,\alpha(2)$$
$$\psi(1)\,\psi(2)\,\beta(1)\,\beta(2)$$

We introduce one more postulate: Electrons are indistinguishable from one another. All electrons are the same. This means that if we have $\psi(1,2)$ the probability density $|\psi(1,2)|^2$ must be the same as $|\psi(2,1)|^2$ which means

$$\psi(1,2) = e^{i\chi}\,\psi(2,1)$$

The only values of χ that have been found are $\chi = 0$ & π

When $\chi = 0$ we are dealing with Bosons

When $\chi = \pi$ & $e^{i\pi} = -1$ we are dealing with fermions

Electrons are Fermions so for He

$$\psi(1,2) = -\psi(2,1)$$

& we say that ψ is antisymmetric with respect to electron interchange.

Looking at the four possible spin-space functions we see that

$$\psi(1)\psi(2)\alpha(1)\alpha(2) \quad \& \quad \psi(1)\psi(2)\beta(1)\beta(2)$$

are symmetric WRT electron interchange

$\therefore$ not acceptable.

The remaining two are mixed in that interchanging electrons in one of them gives the other. We can form functions that are symmetric & antisymmetric by taking the sum & difference

$$\psi(1)\psi(2)\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right) \qquad \text{OK}$$

$$\psi(1)\psi(2)\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right) \qquad \neq \text{OK}$$

Normalizing the spin function we see that

$$\Psi(1,2) = \varphi(1)\varphi(2)\left(\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}\right)$$

is an acceptable wavefunction for He. Note that it is a product of a symmetric spatial function & an antisymmetric spin function. Note also

$$\left\langle \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \middle| \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \right\rangle = \frac{1}{2}\left(\langle\alpha\beta|\alpha\beta\rangle - \langle\alpha\beta|\beta\alpha\rangle - \langle\beta\alpha|\alpha\beta\rangle + \langle\beta\alpha|\beta\alpha\rangle \right)$$

but $\langle\alpha\beta|\alpha\beta\rangle = \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle = 1$

$\langle\alpha\beta|\beta\alpha\rangle = \langle\alpha|\beta\rangle\langle\beta|\alpha\rangle = 0$ etc.

How does this influence the energy of He?

$$E = \frac{\langle\Psi|\hat{\mathcal{H}}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\varphi(1)\varphi(2)|\hat{\mathcal{H}}|\varphi(1)\varphi(2)\rangle}{\langle\varphi\varphi|\varphi\varphi\rangle} \frac{\langle\alpha\beta-\beta\alpha|\alpha\beta-\beta\alpha\rangle}{\langle\alpha\beta-\beta\alpha|\alpha\beta-\beta\alpha\rangle}$$

& the spin cancels. Our conclusions about the energy remain intact.

Excited States of He.

Suppose we excite an electron from the 1s to the 2s orbital on He.

What form does the w.f. take?

$$\psi_T(1,2) = \frac{1s(1)\,2s(2) - 2s(1)\,1s(2)}{\sqrt{2}} \quad \left.\begin{matrix} \alpha\alpha \\ \frac{\alpha\beta+\beta\alpha}{\sqrt{2}} \\ \beta\beta \end{matrix}\right\}$$

or

$$\psi_S(1,2) = \frac{1s(1)\,2s(2) + 2s(1)\,1s(2)}{\sqrt{2}} \left(\frac{\alpha\beta-\beta\alpha}{\sqrt{2}}\right)$$

are both acceptable since $\psi_T(1,2) = -\psi_T(2,1)$

& $\psi_S(1,2) = -\psi_S(2,1)$

ψ_T is antisymmetric in space & symmetric in spin

& ψ_S is symmetric in space & antisymmetric in spin

There are three degenerate functions for ψ_T & we call this a triplet state & one for ψ_S & this is a singlet.

	$\hat{S}^2$	$\hat{S}_z$	
$\alpha\alpha$	$\frac{3}{4}\hbar^2$	$+\hbar$	} triplets
$(\alpha\beta+\beta\alpha)/\sqrt{2}$	$\frac{3}{4}\hbar^2$	0	
$\beta\beta$	$\frac{3}{4}\hbar^2$	$-\hbar$	
$(\alpha\beta-\beta\alpha)/\sqrt{2}$	0	0	) singlet

$$\langle \psi_T | \hat{\mathcal{H}} | \psi_T \rangle = \langle 1s\,2s - 2s\,1s | \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}} | 1s\,2s - 2s\,1s \rangle \frac{1}{2}$$

$$= \frac{1}{2}\left(E_{1s} + E_{2s} + E_{2s} + E_{1s}\right) + \left(2J_{1s\,2s} - 2K_{1s\,2s}\right)\frac{1}{2}$$

$$= E_{1s} + E_{2s} + J - K$$

$$\langle \psi_S | \hat{\mathcal{H}} | \psi_S \rangle = E_{1s} + E_{2s} + J + K$$

$1s^1 2s^1$

S — $2K$ — exchange integral — 156277

T — 159856

$6421\ cm^{-1}$ $0.796\ eV$

Many other levels!

Lithium $1s^2 2s^1$

$1s\alpha\ 1s\beta\ 1s\alpha$

$1s$	$1s$	$1s$	
α	α	α	✓
α	α	β	
α	β	α	
β	α	α	
α	β	β	
β	α	β	
β	β	α	
β	β	β	✓

$1s\alpha(1)\left(1s\alpha(2)\,1s\beta(3) - 1s\beta(2)\,1s\alpha(3)\right)$

$1s\,1s\,1s \left(\begin{matrix}\alpha\alpha\beta - \alpha\beta\alpha \\ \alpha\beta\alpha - \alpha\alpha\beta\end{matrix}\right)$

$1s^2 2s^1$

$$\frac{1}{\sqrt{3!}}\begin{vmatrix} \boxed{1s\alpha(1)} & 1s\alpha(2) & 1s\alpha(3) \\ 1s\beta(1) & \boxed{1s\beta(2)} & 1s\beta(3) \\ 2s\alpha(1) & 2s\alpha(2) & \boxed{2s\alpha(3)} \end{vmatrix} = \Psi(1,2,3)$$

$$\Psi(1,2,3) = \mathcal{A}\, 1s\alpha\, 1s\beta\, 2s\alpha$$

Orbitals determined by

$$\hat{f}\,\psi_i = \epsilon_i \psi_i$$

so on

Element	Configuration
He	$1s^2$
Li	$1s^2 2s$
Be	$1s^2 2s^2$
B	$1s^2 2s^2 2p^1$
C	
N	
O	
F	
Ne	

Orbital Energies

	1s	2s	2p	Δsp
H	13.6			
He	24.6			
Li	64.9	5.4		
Be	121.0	9.4		
B	197.0	14.0	5.7	8.3
C	294	19.5	10.7	8.8
N	408	25.6	12.9	12.7
O	543	32.4	15.9	16.5
F	697	40.1	18.6	21.5

An Electron Configuration can imply many wave functions

Consider the carbon atom

$$1s^2\,2s^2\,2p^2$$

The $1s^2\,2s^2$ part is unique. It must be

$$1s\alpha\;1s\beta\;2s\alpha\;2s\beta$$

What about $2p^2$?

D_1 $\quad 2P_{+1}\alpha \;\; 2P_{+1}\beta$

D_2 $\quad 2P_{+1}\alpha \;\; 2P_0\alpha$

D_3 $\quad 2P_{+1}\alpha \;\; 2P_0\beta$

D_4 $\quad 2P_{+1}\beta \;\; 2P_0\alpha$

D_5 $\quad 2P_{+1}\beta \;\; 2P_0\beta$

D_6 $\quad 2P_{+1}\alpha \;\; 2P_{-}\alpha$

D_7 $\quad 2P_{+1}\alpha \;\; 2P_{-}\beta$

D_8 $\quad 2P_{+1}\beta \;\; 2P_{-}\alpha$

D_9 $\quad 2P_{+1}\beta \;\; 2P_{+1}\beta$

D_{10} $\quad 0\alpha \;\; 0\beta$

D_{11} $\quad 0\alpha \;\; -\alpha$

D_{12} $\quad 0\alpha \;\; -\beta$

D_{13} $\quad 0\beta \;\; -\alpha$

D_{14} $\quad 0\beta \;\; -\beta$

D_{15} $\quad -\alpha \;\; -\beta$

We can take these 15 determinants & form the function $\Psi = \sum_{i=1}^{15} c_i D_i$ and determine the c_i and the associated energies using the variation method. We obtain a secular equation like

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots & H_{1,15} \\ H_{12} & H_{22}-E & H_{23} & \cdots & H_{2,15} \\ \vdots & & & & \\ H_{1,15} & & & & H_{15,15}-E \end{vmatrix} = 0$$

Note all overlap integrals $\langle D_i | D_j \rangle = \delta_{ij}$

& $H_{ij} = \langle D_i | \hat{H} | D_j \rangle$

There are 15 roots (possible E's) for this equation & when one solves it by evaluated the H_{ij} useing the Hartree-Fock orbitals one finds only 3 different energies among the 15. It turns out that the energy E_A occurs 9 times; E_B occurs 5 times & E_C once

Also $E_A < E_B < E_C$

What's going on?

Associated with each energy is a wavefunction & because

$[\hat{L}^2, \hat{\mathcal{H}}] = 0$ & $[\hat{S}^2, \hat{\mathcal{H}}] = 0$

these wavefunctions are eigenfunctions of $\hat{L}^2$ & $\hat{S}^2$.

9 of them are such that

$\hat{L}^2\psi = 1(1+1)\hbar^2\psi$ or $L = 1$

&

$\hat{S}^2\psi = 1(1+1)\hbar^2\psi$ or $S = 1$

5 are such that

$\hat{L}^2\psi = 2(2+1)\hbar^2\psi$ or $L = 2$

$\hat{S}^2\psi = 0\psi$ or $S = 0$

&

1 is such that

$\hat{L}^2\psi = 0$ or $L = 0$

$\hat{S}^2\psi = 0$ or $S = 0$

and each group has a diff

We characterize these states with a term symbol in which we combine the orbital & spin angular momentum. A generalized term symbol is ^{2S+1}L where

S = the spin quantum number & L is the letter

representing the angular momentum QN L. For example

L	0	1	2	3	4	...
letter	S	P	D	F	G	...

So for the carbon atom we have

^3P, ^1D, ^1S

2S+1 is called the multiplicity of the term & is the number of degenerate spin states associated with an M_L component of the term. Different terms have different energies.

The carbon atom is an example of "equivalent ~~electrons~~ orbitals" This is when the non closed shell elections are in ~~the~~ orbitals with the same principle QN & l. For example

$2p^2$ is an equivalent ~~electron~~ orbital system

while 2p 3p is a non-equivalent ~~electrons~~ orbitals systems.

2s 2p is an equivalent ~~electron~~ orbital system

2p 3d is an non-equivalent

How can we determine the term symbols for carbon?

We can make use of the numerology of angular momentum quantum numbers. Lets revisit the 15 determinants associated with the $2p^2$ configuration. Each determinant has an M_L quantum number & any M_S quantum number associated with it & these are the sums of the m_L & m_S of the individual orbital. For example

$$^2P_+\alpha \; ^2P_0\beta \qquad \text{has} \quad M_L = 1+0 = 1 \quad \& \quad M_S = \tfrac{1}{2} - \tfrac{1}{2} = 0$$

Doing this for each determinant & tabulating the result

M_L	2	1	0	-1	-2
# occurances	1	4	5	4	1

$M_L = 2 \Rightarrow$ $\mathcal{L} \cdot L = 2$ & eliminating these ^1D

M_L	2	1	0	-1	-2
#	0	3	4	3	0

$M_L = 1 \Rightarrow L = 1$ but 3 times $\Rightarrow S = 1$ $(2S+1 = 3)$

$\therefore \; ^3P$.

& left is ^1S

orbitals with the same principal QN are said to belong to the same shell. within a given shell one can have subshells according to l.

This procedure works all the time. However for non equivalent "~~electrons~~" orbitals there is a simpler way

Consider $3d'\,4p'$

we have $l_1 = 2$ & $l_2 = 1$

These can form L when $|l_1 - l_2| \leq L \leq l_1 + l_2$

or $L = 1, 2$ & 3 or P, D & F

There are two electrons each with $s = \frac{1}{2}$ can form

$|s_1 - s_2| \leq S \leq s_1 + s_2$ or $S = 0$ & 1

Combining them $^1P, ^3P; ^1D, ^3D, ^1F, ^3F$

These techniques allow us to determine the terms associated with a given configuration. It does not tell us ~~which is the lowest~~ the relative energies. Hunds rules often allow us to find the term corresponding to the lowest energy.

The term with the highest multiplicity & largest L usually lies lowest.

$(np)^2 \Rightarrow {}^3P, {}^1D, {}^1S$

$\therefore$ ${}^3P$ is ground terms

$(np)^3 \Rightarrow \quad {}^2P, {}^2D, \boxed{{}^4S}$

The term with the maximum multiplicity corresponds to the case when the electrons are distributed among the orbitals so as to have the largest number of parallel spins. This lets us write down the term corresponding to the ground state without determining all of the terms.

Example $(nd)^3$

$M_\ell \quad 2 \quad 1 \quad 0 \quad -1 \quad -2$

$\alpha \quad \alpha \quad \alpha$

$M_\ell = 2+1+0 = 3 \qquad \therefore {}^4F$

Vanadium $4s^2 3d^3 \quad {}^4F$

$V^{++} \quad 3d^3 \quad {}^4F$

How about terms with two classes of electrons - equivalent & nonequivalent

np^2

$p^2 \quad {}^3P, {}^1D, {}^1S$

$s \quad {}^2S$

${}^3P + {}^2S \Rightarrow \boxed{{}^4P} + {}^2P$

${}^1D + {}^2S \Rightarrow {}^2D \qquad {}^1S + {}^2S \Rightarrow {}^2S$

Some Observations