

Helium:

Schrodinger Equation.

$$\left[\frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{e^2}{r_{12}} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} \right] \psi = E\psi$$

Notice the implicit assumption:

- The nucleus, charge $Z=2$, is assumed to be fixed (i.e. no simple replacement by reduced mass)

In any case, let

$$H_i \equiv \frac{-\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{r_i}$$

Simple model: Ignore electrostatic repulsion term!

In this case $\psi = \psi_1 \psi_2$ with ψ_1 and ψ_2 as solutions to hydrogenic Hamiltonian.

$$H_i \psi_i = E_i \psi_i$$

$$(H_1 + H_2) \psi_1 \psi_2 = (E_1 + E_2) \psi_1 \psi_2$$

$$E^{(0)} = E_1 + E_2 = -2 \times Z^2 \times 13.6 = -109 \text{ eV}$$
$$Z=2$$

Treat $\frac{1}{r_{12}}$ as perturbation:

The wave function for the unperturbed system is

$$\Psi_{1s,1s} = \Psi_{1s} \times \Psi_{1s} \text{ where}$$

$$\Psi_{1s} = \underbrace{2 \left(\frac{Z}{a_0} \right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)}_{\text{radial}} \times \underbrace{\frac{1}{\sqrt{4\pi}}}_{\text{angular}}$$

The expectation value of the repulsion is

$$e^2 \int_0^\infty \int_0^\infty \Psi_{1s,1s}^* \frac{1}{r_{12}} \Psi_{1s,1s} r_1^2 dr_1 r_2^2 dr_2$$

$$= 34 \text{ eV} \quad (Z=2) \quad [\text{Homework}]$$

Thus the binding energy of He is

$$-109 + 34 \text{ eV} = -75 \text{ eV}.$$

Experimentally, the binding energy is

$$\text{He}^0 \rightarrow \text{He}^+ \quad 24.6 \text{ eV}$$

$$\text{He}^+ \rightarrow \text{He}^{++} \quad \underline{544 \text{ eV}}$$

$$\text{Total} \quad \underline{\underline{79 \text{ eV}}}$$

We wish to do better. ("Variational Approach")

We allow for screening of one electron by the other.

So let $Z \rightarrow Z^*$

Then our wavefunction is

$$\Psi_{1s,1s} = \frac{1}{\pi} \left(\frac{Z^*}{a_0} \right)^3 \exp \left[-Z^* \frac{(r_1 + r_2)}{a_0} \right]$$

Kinetic term:

$$A = \iint \Psi_{1s,1s}^* (H_1 + H_2) \Psi_{1s,1s}^* d^3r_1 d^3r_2$$

Each of ∇^2 corresponds to kinetic term (which is one half of potential energy). Thus

$$A = -2 \times \frac{1(Z^*e)^2}{2a_0} = -2Z^{*2} \left(\frac{e^2}{2a_0} \right)$$

$$= -2Z^{*2} I_H$$

The interaction term:

$$\text{where } I_H = \frac{e^2}{2a_0}$$

$$B = \int \Psi_{1s,1s}^* \left(\frac{e^2}{r_{12}} \right) \Psi_{1s,1s} d^3r_1 d^3r_2 = 13.6 \text{ eV}$$

$$= \frac{5}{8} Z^* \frac{e^2}{a_0} = \frac{5}{4} Z^* I_H$$

The attractive electrostatic term:

$$C = Ze^2 \int \psi_{1s,1s}^* \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \psi_{1s,1s} d^3r_1 d^3r_2$$
$$= -4ZZ^* I_H$$

Thus the ground state energy is

$$E_{GS}(Z^*) = \left(4Z^{*2} + \frac{5}{4} Z^* - 4ZZ^* \right) I_H$$

Physical solution \Rightarrow minimize $E_{GS}(Z^*)$

$$\frac{\partial E_{GS}}{\partial Z^*} = 0$$

$$Z^* = Z - \frac{5}{16}$$

$$E_{GS} = -2 \left(Z - \frac{5}{16} \right)^2 I_H$$

$$= -77.45 eV$$

$$\text{Hartree} \equiv 2 \text{ Rydbergs} = 27.211 \text{ eV}$$

$$(\text{Ha}) = \frac{e^2}{a_0}$$

	<u>wave function</u>	<u>parameters</u>	<u>energy (Ha)</u>
	$\exp -Z(r_1+r_2)$	$Z=2$	-2.75
	$\exp(-Z^*(r_1+r_2))$	$Z^* = Z - \frac{5}{16}$	-2.84765
(Hartree)*	$\psi(r_1)\psi(r_2)$	best $\psi(r)$	-2.86168
	$\exp(-Z^*(r_1+r_2))(1+Cr_{12})$	best Z^*, C	-2.89112
	Hylleraas (1929)	10 parameters	-2.90763
	Pekeris (1959)	1078 parameters	-2.90372

↑
agrees with expt.

* Hartree \rightarrow self-consistent approach but using only radial potential

Hylleraas' approach introduces (anti) "correlation" and this was the key to accuracy.

Pauli Exclusion Principle:

Electrons being fermions their wavefunction must be anti-symmetric to particle interchange

$$\Psi(r_1, r_2) = -\Psi(r_2, r_1)$$

Thus if both electrons are 1s then

$$\Psi(1s, 1s) = -\Psi(1s, 1s)$$

which means $\Psi(1s, 1s) = 0!$

The key is spin. Instead of orbitals (space) we have "spin orbitals"

Consider the general case of helium in excited state: one electron in 1s and the other in "nl" electron index

$$\Psi_{\text{space}} = U_{1s}(1) U_{nl}(2)$$

The exchanged version is

$$\Psi_{\text{space}} = U_{1s}(2) U_{nl}(1)$$

~~to~~ Both are valid. So we consider a linear combination

$$\Psi = a U_{1s}(1) U_{nl}(2) + b U_{1s}(2) U_{nl}(1)$$

$$(H_0 + H') \Psi = E \Psi$$

\swarrow $H_1 + H_2$ (un-perturbed) \nwarrow $\frac{e^2}{r_{12}}$

Since $H_0 \Psi = E^{(0)} \Psi$ $E^{(0)} = E_1 + E_2$
as before

The perturbation is

$$H' \Psi = \Delta E \Psi$$

Consider

$$\langle U_{1s}^*(1) U_{ne}^*(2) | H' | \Psi \rangle = \Delta E \langle U_{1s}^*(1) U_{ne}^*(2) | \Psi \rangle$$

leads to

$$aJ + bK = a\Delta E \quad (1)$$

Consider

$$\langle U_{1s}^*(2) U_{ne}^*(1) | H' | \Psi \rangle = \Delta E \langle U_{1s}^*(2) U_{ne}^*(1) | \Psi \rangle$$

leads to

$$aK + bJ = b\Delta E \quad (2)$$

Equations (1) and (2) can be combined to:

$$\begin{pmatrix} J - \Delta E & K \\ K & J - \Delta E \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0 \quad (3)$$

where "DIRECT" integral

$$\begin{aligned} J &= \iint |U_{1s}(1)|^2 \frac{e^2}{r_{12}} |U_{ne}(2)|^2 d^3r_1 d^3r_2 \\ &= \iint \frac{(-e) |U_{1s}(1)|^2 \times (-e) |U_{ne}(2)|^2}{r_{12}} d^3r_1 d^3r_2 \\ &= \text{repulsion term} \end{aligned}$$

$$K = \iint U_{1s}^*(1) U_{ne}^*(2) \frac{e^2}{r_{12}} U_{1s}(2) U_{ne}(1) d^3r_1 d^3r_2$$

"exchange integral" no classical equivalent

The solution to (3) is

$$\begin{vmatrix} J - \Delta E & K \\ K & J - \Delta E \end{vmatrix} = 0$$

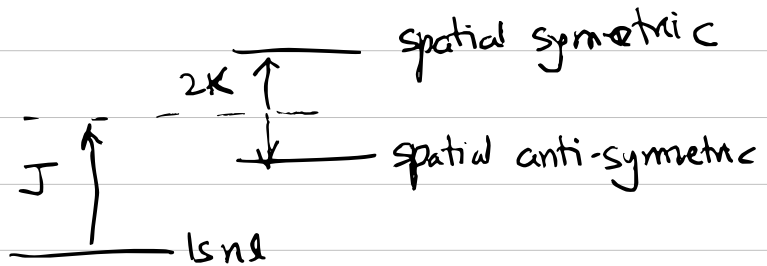
$$\Delta E = J \pm K \quad (4)$$

Substituting (4) into (1) and (2)

$$a = \pm b.$$

So we get eigen wave-functions

$$\begin{aligned} \text{symmetric } \psi^s &= \frac{1}{\sqrt{2}} \{ U_{1s}(1) U_{ne}(2) + U_{1s}(2) U_{ne}(1) \} \\ \text{anti-symmetric } \psi^a &= \frac{1}{\sqrt{2}} \{ \quad \quad \quad - \quad \quad \quad \} \end{aligned}$$



The spin wave-function, has likewise, two forms

symmetric, "S"

$$\begin{aligned} \psi_{spin}^S &= |\uparrow\uparrow\rangle \\ &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \end{aligned}$$

$$= |\downarrow\downarrow\rangle \quad \Rightarrow \text{Triplet}$$

anti-symmetric "A"

$$\psi_{spin}^A = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

\Rightarrow singlet

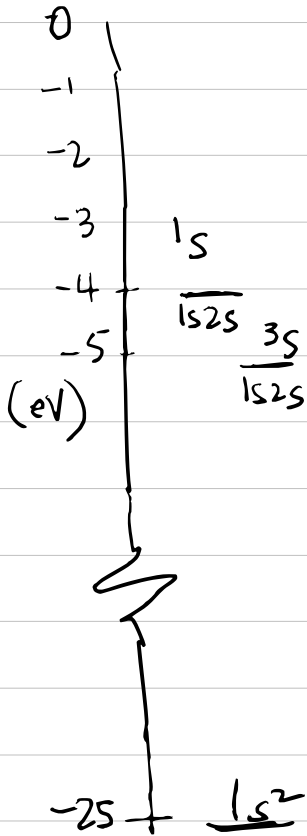
Thus the spin-orbitals are

$$\Psi = \psi_{spin}^A \psi_{space}^S$$

$$\Psi = \psi_{spin}^S \psi_{space}^A$$

Grotrian diagram for Helium:

(see homework)



$n=2$
(hydrogen)

notice how close in energy is $n=2$ of H to $1s2s, 1s2p$ levels.