分類：
編號：
總號： 11-22

Atoms.

He Atom

Zeroth order
spectrum

Variational Method

Hartree method
Pauli exclusion principle.
Periodic table

He Atom

General Discussion, Zeroth Order Approximation

Two electron atom

Hamiltonian

Schrodinger equation

Zeroth order approximation

Ground state

First look at the spectrum

$E_{1,1} = -108.8$ eV -54.4 eV

$E_{1,2} = -68$ eV -13.6 eV

$E_{2,2} = -27.2$ eV $+27.2$ eV

Shift 54.4 eV
↓
the energy required to remove one electron from the ground state to the continuum

⇒ Figure (a)
↓
Zeroth order term.

Electrons are spin $\frac{1}{2}$ particles.

Identical particle effects.

$s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$ ⇒ Total spin of the system can be either 1 or 0

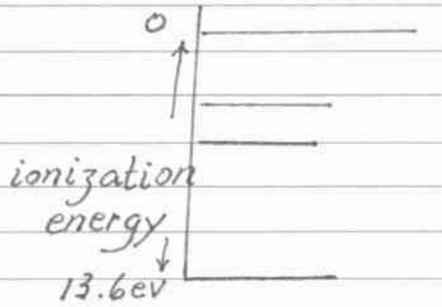
$S = 0$ → singlet

$$\overline{X}_{singlet} = \frac{1}{\sqrt{2}}\left[\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right]$$

Zero order approximation

hydrogen atom

Zeroth order



Helium.

No spin interaction → yet there are spin (through Fermi statistics

Spin wave function $|n, l, m, m_s\rangle$ single particle $s = \frac{1}{2}$

$|n_1, l_1, m_1, m_{s_1}\rangle |n_2, l_2, m_2, m_s\rangle$ are the basis.

4 possible spin state $m_{s_1} = \pm\frac{1}{2}$

$m_{s_2} = \pm\frac{1}{2}$

Use $|n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle$ spin wave function $|s_1, s_2\rangle$

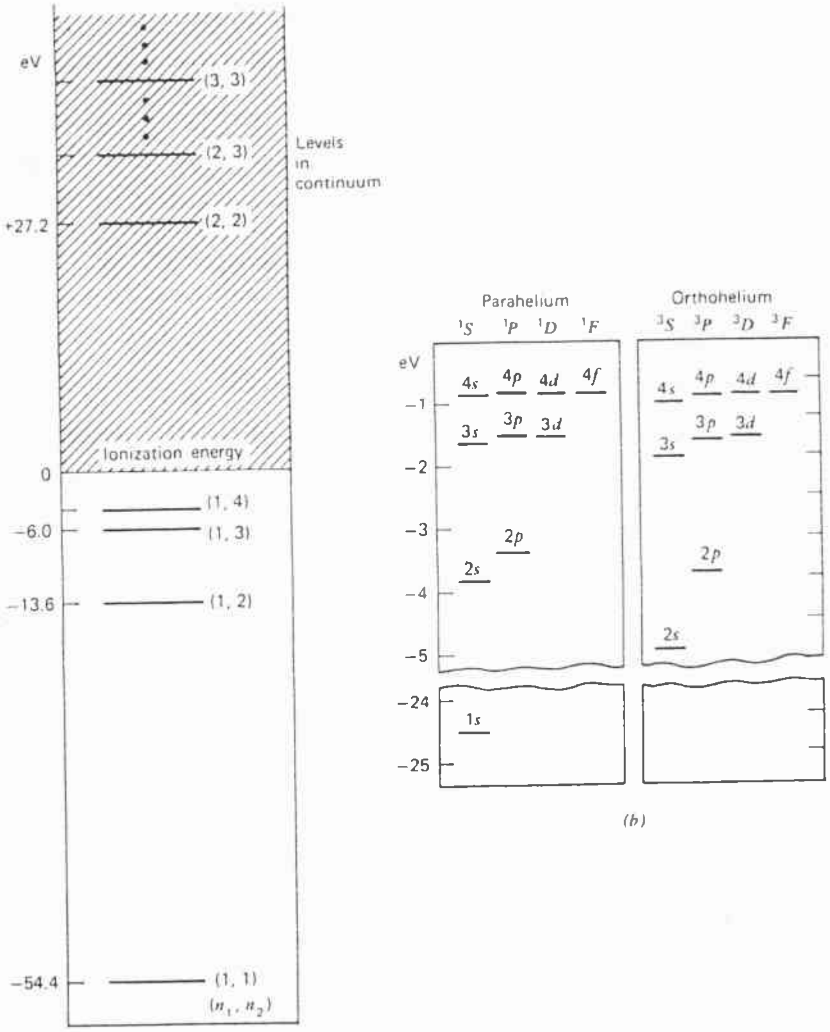
$$|s_1, s_2\rangle \downarrow |S, M_s\rangle$$

$|1, 1\rangle, |1, 0\rangle, |1, -1\rangle$ triplet S orthohelium

$|0, 0\rangle$ singlet A parahelium

Ground state

$$\underbrace{\phi_{100}(r_1)\phi_{100}(r_2) + \phi_{100}(\vec{r}_2)\phi_{100}(r_1)}_{\phi_{100}(r_1)\phi_{100}(r_2)}$$ singlet



(*b*)

(*a*)

(*a*) The spectrum of helium as it would look in the absence of the electron–electron interaction. The zero energy point is chosen at the ionization energy. (*b*) The actual spectrum of helium for the singlet (parahelium) and triplet (orthohelium) states. The level labeling has a suppressed (1*s*), so that the level (2*p*) is approximately described by the (1*s*)(2*p*) orbital.

分類：
編號：
總號： 11-25

Anti-symmetric under $1 \leftrightarrow 2$

$\downarrow$

Parahelium

$S = 1 \longrightarrow$ triplet

$$\chi_{triplet} = \begin{cases} \chi_+^{(1)} \chi_+^{(2)} \\ \frac{1}{\sqrt{2}} (\chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)}) \\ \chi_-^{(1)} \chi_-^{(2)} \end{cases}$$

Symmetric under $1 \leftrightarrow 2$

$\downarrow$

orthohelium.

Ground state

Zeroth order wave function.

$\psi_{1,1} (\vec{r}_1 , \sigma_1 ; \vec{r}_2 , \sigma_2)$

$\downarrow$

wave function.

First order cooreection for the ground state.

Calculation of $\langle H_1 \rangle$

Two different methods

$\downarrow$

$$\langle H_1 \rangle = \frac{5}{4} \frac{e^2}{a_0} = 34 \text{ eV}$$

Positive, rather large.

Experimental result

$-78.975 \text{ eV} \longrightarrow -24.575 \text{ eV}$

$\downarrow$

the graph

First order perturbation result -

$-74.8 \text{ eV} \rightarrow -20.4 \text{ eV}.$

First order energy shift for the excited state

s, t → singlet, triplet

$$\Delta E_1^s > \Delta E_1^t$$

Graph can be understood

↓

the first order correction is large

↓

the first order agreement is not very good.

Heisenberg exchange term.

The Helium Atom

General Discussion, Zeroth Order Approximation

Two-electron atom

$$H = \underbrace{\frac{1}{2m}\vec{P}_1^{\,2} - \frac{Ze^2}{r_1}}_{H_0^{(1)}} + \underbrace{\frac{1}{2m}\vec{P}_2^{\,2} - \frac{Ze^2}{r_2}}_{H_0^{(2)}} + \underset{\substack{\downarrow \\ V}}{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}$$

$Z = 2$ ⟷ He atom

He nucleus ⟷ α - particle

Neglect: (i) effects connected with motion of the nucleus

(ii) relativistic effects

(iii) spin-orbit effects

(iv) effects of the current caused by the motion of one electron, upon the other electron

(v) effects of nuclear spin

Schrodinger equation

$$H\psi(\vec{r}_1, \vec{r}_2) = E\psi(\vec{r}_1, \vec{r}_2)$$

Zeroth order approximation

$$H_0 = H_0^{(1)} + H_0^{(2)}$$

Zeroth order wavefunction

$$\psi_{\substack{n_1, l_1, m_1 \\ n_2, l_2, m_2}}(\vec{r}_1, \vec{r}_2) = \underset{\substack{\downarrow \\ \text{hydrogen-like wavefunction}}}{\phi_{n_1, l_1, m_1}}(\vec{r}_1)\, \phi_{n_2, l_2, m_2}(\vec{r}_2)$$

(From now on, we shall suppress the magnetic quantum number)

$$E_{n_1,l_1;n_2,l_2} = -2mc^2\alpha^2\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$$

$$= E_{n_1} + E_{n_2}$$

Ground state : both electrons at $n=1$ state

$$E_{1,0;1,0} = -4mc^2\alpha^2 = -108.8 \text{ eV}$$

First excited state : one electron at $n=1$ and another electron at $n=2$

$$E_{1,0;\substack{2,0\\ \text{or}\\ 2,1}} = -2mc^2\alpha^2\left(1+\frac{1}{4}\right) = -68 \text{ eV}$$

Since in the zeroth order, there is no interaction between the two electrons, the energy required to remove one electron from ground state to ∞ = -54.4 eV

$$E_{1,0,\ \text{electron at } \infty \text{ with zero k.E.}} = -54.4 \text{ eV}$$

⇒ Above $E = -54.4$ eV, there exists a $1s + \underset{\substack{\downarrow\\ \text{free particle}\\ \text{with k.E.}}}{\text{continuum}}$.

$$E_{2;2} = -2mc^2\alpha^2\left(\frac{1}{4}+\frac{1}{4}\right) = -27.2 \text{ eV}$$

⇒ existence of discrete state in the continuum for H_0

Identical particle effect

The total $\underset{\substack{\downarrow\\ \text{product of space, and spin wavefunction}}}{\text{wavefunction}}$, including spin, must be totally anti-symmetric under exchange 1 ↔ 2

Spin wavefunction of two spin $\frac{1}{2}$ particles

$$S = 0 \quad \text{singlet} \longrightarrow \chi_{\text{singlet}} = \underset{\substack{\downarrow\\ \text{anti-symmetric under } 1\leftrightarrow 2}}{\frac{1}{\sqrt{2}}}\left[\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right]$$

⇒ space wavefunction must be symmetric under 1 ↔ 2

⇒ parahelium states.

$S=1$ triplet

$$X_{triplet} \begin{cases} \chi_+^{(1)}\chi_+^{(2)} \\ \frac{1}{\sqrt{2}}(\chi_+^{(1)}\chi_-^{(2)}+\chi_-^{(1)}\chi_+^{(2)}) \\ \chi_-^{(1)}\chi_-^{(2)} \end{cases}$$

$\downarrow$

symmetric under $1 \leftrightarrow 2$

$\downarrow$

space wave function must be
anti - symmetric under $1 \leftrightarrow 2$

$\Rightarrow$ orthohelium

Ground state

$\phi_{100}(\vec{r}_1)$, $\phi_{100}(\vec{r}_2)$ can only form symmetric space wavefunction.

Zeroth order wavefunction

$$\psi_{1,1}^{(0)} = \phi_{100}(\vec{r}_1)\,\phi_{100}(\vec{r}_2)\,X_{singlet}$$

First excited state

$\phi_{100}(\vec{r}_1)$, $\phi_{2\ell m}(\vec{r}_2)$ can form either symmetric and anti-symmetric
(under the exchange of $1 \leftrightarrow 2$) space wavefunction.

$$\psi_{1,2}^{(0),(S)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(\vec{r}_1)\,\phi_{2\ell m}(\vec{r}_2)+\phi_{2\ell m}(\vec{r}_1)\,\phi_{100}(\vec{r}_2)\right]X_{singlet}$$

$$\psi_{1,2}^{(0),(t)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(\vec{r}_1)\,\phi_{2\ell m}(\vec{r}_2)-\phi_{2\ell m}(\vec{r}_1)\,\phi_{100}(\vec{r}_2)\right]X_{triplet}.$$

2. First Order Energy Shift for the Ground State

First order correction for the ground state

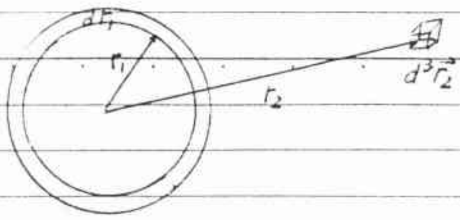
$$\langle H_1 \rangle = \iiint \phi_{100}^*(\vec{r}_1)\,\phi_{100}^*(\vec{r}_2)\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\,\phi_{1,00}(\vec{r}_1)\,\phi_{1,00}(\vec{r}_2)\,d^3\vec{r}_1\,d^3\vec{r}_2$$

$\downarrow$

average potential energy of
repulsion between two electrons

$$= \iiint \underbrace{|\phi_{1,00}(\vec{r}_1)|^2}\,|\phi_{100}(\vec{r}_2)|^2\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\,d^3\vec{r}_1\,d^3\vec{r}_2$$

electrostatic repulsion between two charge clounds each with
charge density distribution $-e|\psi_{100}|^2 \leftarrow \rho$



Consider the interaction between a spherical shell of the first charge distribution of radius r_1 thickness dr_1 with an element of the second charge distribution of volume $d^3\vec{r}_2$ situated at r_2 where $r_2 > r_1$

$$\Rightarrow \quad \frac{\rho_1 4\pi r_1^2 dr_1 \rho_2 d^3\vec{r}_2}{r_2} = \frac{\rho_1 \rho_2 4\pi r_1^2 4\pi r_2^2 dr_1 dr_2}{r_2}$$

Similar expression with $r_2 \leftrightarrows r_1$ clearly hold for $r_2 < r_1$

$$\Rightarrow \quad \langle H_1 \rangle = \iint \frac{\rho_1 \rho_2 4\pi r_1^2 4\pi r_2^2 dr_1 dr_2}{r_>}$$

$$\xrightarrow{} \quad e^2 \left(\frac{32}{a_0^3}\right)^2 \iint \frac{r_1^2 r_2^2 e^{-4r/a_0} e^{-4r_2/a_0} dr_1 dr_2}{r_>}$$

↑ put in the wave function with $Z = 2$

The integral is symmetrical in r_1 and r_2

⇒ we shall clearly get equal contribution from $r_1 < r_2$ and $r_1 > r_2$

$$\Rightarrow \quad \langle H_1 \rangle = 2e^2 \left(\frac{32}{a_0^3}\right)^2 \int_0^\infty dr_0 \int_0^\infty \frac{r_1^2 (r_1 + r_0)^2 e^{-4r_1/a_0} e^{-4(r_1+r_0)/a_0}}{r_1 + r_0} dr_1$$

take into account r_1 may be either $> r_2$ or $< r_2$

we have defined $r_2 = r_1 + r_0$
$r_1 : \; 0 \to \infty$
$r_0 : \; 0 \to \infty$

contribution for the case $r_2 > r_1$

$$= 2e^2 \left(\frac{32}{a_0^3}\right)^2 \int_0^\infty e^{-4r/a_0} dr_0 \int_0^\infty (r_1^3 + r_1^2 r_0) e^{-8r_1/a_0} dr_1$$

Note: $\displaystyle\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}} \quad (\alpha > 0,\ n \geq 0)$

$$\Rightarrow \quad \langle H_1 \rangle = 2e^2 \left(\frac{32}{a_0^3}\right)^2 \int_0^\infty e^{-4r_0/a_0} \left(\frac{3!\, a_0^4}{8^4} + \frac{2!\, a_0^3 r_0}{8^2}\right) dr_0$$

$$= e^2 \int_0^\infty \left(\frac{3}{a_0^2} + \frac{8r_0}{a_0^3}\right) e^{-4r_0/a_0} dr_0$$

$$= \frac{5}{4} \frac{e^2}{a_0}$$

Put in the numerical value

$$\langle H_1 \rangle = \frac{5}{2}\,\frac{e^2}{2a_0} = \frac{5}{2}\cdot 13.6\,\text{eV} = 34\,\text{eV}$$

$\downarrow$

the first order correction is rather large

$\downarrow$ first order perturbation theory may not be reliable.

Ground state energy (up to first order perturbation)

$$= -108.8\,\text{eV} + 34\,\text{eV} = -74.8\,\text{eV}$$

Experimental result. E (ground state) = -78.975 eV.

3. First Order Energy Shift for the Excited State

We discuss the stationary state of He atom with one electron in ground state ψ_{100} and other one in excited state $\psi_{2\ell m}$

First order correction

$$\Delta E^{\{s \atop t\}} = \frac{1}{2}\, e^2 \iint d^3\vec{r}_1\, d^3\vec{r}_2 \left\{ \phi_{100}(\vec{r}_1)\, \phi_{2\ell m} \pm \phi_{2\ell m}(\vec{r}_1)\, \phi_{100}(\vec{r}_2) \right\}^*$$

$$\underbrace{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{\text{symmetry under } \vec{r}_1 \leftrightarrow \vec{r}_2} \left\{ \phi_{100}(\vec{r}_1)\, \phi_{2\ell m}(\vec{r}_2) \pm \phi_{2\ell m}(\vec{r}_1)\, \phi_{100}(\vec{r}_2) \right\}$$

$$= e^2 \iint d^3\vec{r}_1\, d^3\vec{r}_2\, \underbrace{|\phi_{100}(\vec{r}_1)|^2}_{\text{direct term} \to J} |\phi_{2\ell m}(\vec{r}_2)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$\pm\, e^2 \iint d^3\vec{r}_1\, d^3\vec{r}_2\, \underbrace{\phi^*_{100}(\vec{r}_1)}_{\text{Heisenberg exchange term} \to K} \phi^*_{2\ell m}(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{2\ell m}(\vec{r}_1)\, \phi_{100}(\vec{r}_2)$$

$$\Delta E_1^{\,t} = J - K$$

$$\Delta E_1^{\,s} = J + K$$

K is positive since we expect $\Delta E_1^s > \Delta E_1^t$

Triplet → space wavefunction is anti-symmetric

→ the two electrons tend to avoid each other

→ decrease electrostatic repulsion between two electrons

The result can be written as

$$\Delta E_1 = J - \frac{1}{2}(1+\vec{\sigma}_1\cdot\vec{\sigma}_2)K$$

Proof: $\vec{S}^2 = \vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1\cdot\vec{S}_2$

$$S(S+1)\hbar^2 = \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2\vec{S}_1\cdot\vec{S}_2$$

$$\Rightarrow \quad \frac{2\vec{S}_1\cdot\vec{S}_2}{\hbar^2} = S(S+1) - \frac{3}{2} = \begin{cases} \frac{1}{2} & \text{triplet} \\ -\frac{3}{2} & \text{singlet} \end{cases}$$

$$\vec{S}_i = \frac{1}{2}\hbar\vec{\sigma}_i$$

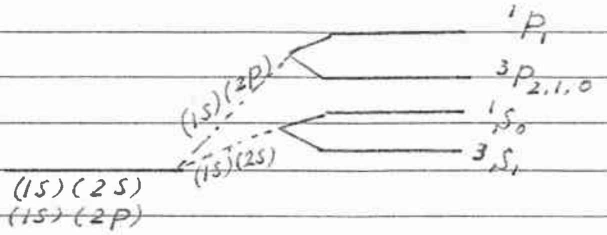
$$\Rightarrow \quad \frac{1}{2}\vec{\sigma}_1\cdot\vec{\sigma}_2 = \begin{matrix} \frac{1}{2} & \text{for triplet} \\ -\frac{3}{2} & \text{for singlet} \end{matrix}$$

$$\frac{1}{2}(1+\vec{\sigma}_1\cdot\vec{\sigma}_2) = 1 \quad \text{for triplet}$$
$$= -1 \quad \text{for singlet}$$

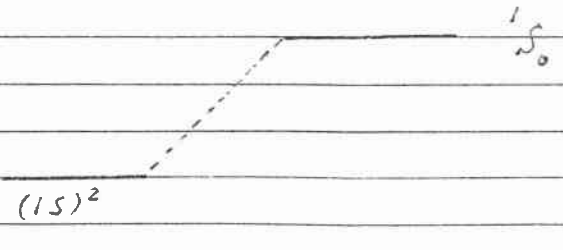
⇒ The energy depend on $\vec{S}$ even though the potential has no spin-dependent

↓

The origin is Fermi-Dirac statistics



$S=0,\ L=1 \Rightarrow J=1$
$S=1,\ L=1 \Rightarrow J=2,1,0$
$S=0 \quad L=0 \Rightarrow J=0$
$S=1 \quad L=0 \Rightarrow J=1$



$S=0,\ L=0 \Rightarrow J=0$

↓

only singlet can exist

The Variational Method.

$\downarrow$

in finding the ground state energy E_0

Theorem

$\int \psi^* H \psi \, d^3x \geq E_0$ for any arbitrary square integrable function ψ which is normalized to unity.

Proof is then given.

Application of variational method.

Example simple harmonic oscillator

Apply the method to find the ground state of He atom

First excited state can be found using the same method with the additional constraint that the wave function should be orthogonal to the ground state wave function.

The Variational Method

The variation method is based on the following theorems

It is very useful in finding the upper bound of the ground state energy E_0

$$\langle H \rangle = \int \psi^* H \psi \, d^3x$$

H is the Hamiltonian, ψ is an arbitrary square integrable function which is chosed to be normalized to unity

$$\underbrace{\int \psi^* \psi \, d^3x = 1}_{\text{constraint equation}}$$

$$\delta \langle H \rangle = \int \delta\psi^* H \psi \, d^3x + \int \psi^* H \delta\psi \, d^3x = 0$$

Here $\delta\psi^*, \delta\psi$ are not independent due to the constraint condition

$$\int \psi^* \psi \, d^3x = 1$$

$$\Rightarrow \quad \int \delta\psi^* \psi \, d^3x + \int \psi^* \delta\psi \, d^3x = 1$$

Use the Lagrangian multiplier method

$$\int \delta\psi^* (H - \lambda) \psi \, d^3x + \int \psi^* (H - \lambda) \delta\psi \, d^3x = 0$$

Now $\delta\psi^*, \delta\psi$ can be considered as independent

$$\Rightarrow \quad H\psi = \lambda\psi$$

Identify $\lambda = E$ $\Rightarrow$ time independent Schrodinger equation

$\updownarrow$

Calculus of variation.

(See Chapter 17 of "Mathematical Methods for Physicists" by G. Arfken)

Claim $\int \psi^* H \psi \, d^3x \geq E_0$ for an arbitrary square integrable function ψ which is normalized to unity

$$\int \psi^* \psi \, d^3x = 1$$

$$\psi = \sum c_n \psi_n$$

where $H\psi_n = E_n \psi_n$

$E_n \geq E_0 \leftarrow$ ground state

$$\int \psi^* H \psi \, d^3x = \sum_n \sum_m c_n^* c_m \int \psi_n^* H \psi_m \, d^3x$$

$$= \sum_n \sum_m c_n^* c_m E_m \delta_{nm}$$

$$= \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2$$

$$= E_0$$

We may use this result to calculate an upper bound on E_0

This can be done by choosing a ψ that depends on a number of parameters $(\alpha_1, \alpha_2, \cdots)$, calculating $\int \psi^* H \psi \, d^3x$ and minimizing this with respect to these parameters

The most difficult part of the method lies in the choice of the best test function $\Rightarrow$ one has to rely on physical and mathematical intuition.

Practical applications.

Make a reasonable guess for $\psi^{(0)} \rightarrow f(x, \alpha, \beta, \cdots)$

α, β are suitable parameters

Compute $E(\alpha, \beta \ \cdots) = \dfrac{\int f^*(x,\alpha,\beta\cdot) H f(x,\alpha,\beta,\cdots)dx}{\int f^*(x,\alpha,\beta\cdot) f(x,\alpha,\beta,\cdots)dx}$

Find values of $\bar{\alpha}$, $\bar{\beta} \cdots$, such that $E(\alpha, \beta, \cdots)$ is minimum

$E(\bar{\alpha}, \bar{\beta}, \cdots) \rightarrow$ approximate ground state energy.

$f(x, \bar{\alpha}, \bar{\beta}, \cdots) \rightarrow$ approximate ground state wavefunction.

Applications of the Variation Method.

(i) $$H = \frac{p^2}{\underset{\underset{-\frac{d^2}{dx^2}}{\downarrow}}{2}} + \frac{x^2}{2}$$

$\hbar$ is taken to be 1

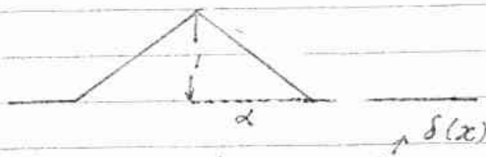
m is taken to be 1

The problem can be exactly solved, $E_{\text{ext}} = 0.5$

Trial wave function

$$f(x) = 1 - \frac{1}{\alpha}|x| \quad \text{for} \quad |x| < \alpha$$
$$= 0 \quad \text{for} \quad |x| > \alpha$$

α is a parameter



$$E_\alpha = \frac{-\frac{1}{2}\int_{-\infty}^{\infty} f(x)\,\overset{\uparrow\,\delta(x)}{\frac{d^2f}{dx^2}}\,dx + \frac{1}{2}\int_{-\infty}^{\infty} x^2 f^2(x)\,dx}{\int_{-\infty}^{\infty} f^2(x)\,dx}$$

$$\int_{-\epsilon}^{\epsilon} \frac{d^2f}{dx^2}\,dx = \frac{df}{dx}\Big|_{\epsilon} - \frac{df}{dx}\Big|_{-\epsilon}$$

$$\frac{d^2f}{dx^2} = a\,\delta(x)$$

$$a = -\frac{2}{\alpha}$$

$f(x) = 0$ for $|x| > \alpha$ ⇒ integration limit, $-\alpha$ to α

$$E_\alpha = \frac{\frac{1}{\alpha} + \frac{\alpha^3}{30}}{\frac{2}{3}\alpha} = \frac{1}{20}\alpha^2 + \frac{3}{2}\frac{1}{\alpha^2}$$

$$\frac{dE_\alpha}{d\alpha} = 0 \Rightarrow \bar{\alpha} = \sqrt[4]{30} = 2.34$$

$$E(\bar{\alpha}) = 0.548$$

⇒ within 10% of the exact value $E_0 = 0.5$

Furthermore $E(\bar{\alpha}) > E_0$

(ii) He Atom Ground State

$$H = \frac{1}{2m}(\vec{P}_1^{\,2} + \vec{P}_2^{\,2}) - \frac{2e^2}{r_1} - \frac{2e^2}{r^2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Trial wave function

$$\underset{\underset{\psi(\vec{r}_1,\vec{r}_2)}{\downarrow}}{\psi} = \frac{Z^3}{\underset{\underset{\text{properly normalized}}{\downarrow}}{\pi a_0^3}}\, e^{-\frac{Z}{a_0}(r_1 + r_2)} \longrightarrow$$

analogy to hydrogen ground state wave function.

Z is treated as a parameter

分類：
編號： A-18
總號： 11-37

$$\int \psi^* H \psi \, d^3x = 2\left\langle \frac{1}{2m} P_1^2 \right\rangle - 4\left\langle \frac{e^2}{r_1} \right\rangle + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

$$\downarrow \qquad\qquad \downarrow$$

$$2\,\frac{1}{2}\,\frac{Z^2 e^2}{a_0} \qquad -4\,\frac{Z e^2}{a_0}$$

$\downarrow$

this is obtained
through our knowledge
on hydrogen atom

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \left[\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\right]^2 e^2 \int_0^\infty r_1^2 dr_1\, e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2\, e^{-2Zr_2/a_0}$$

$$\int d\Omega_1 \int d\Omega_2 \, \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{(r_1^2 + r_2^2 - 2r_1 r_2 \underset{\substack{\downarrow \\ \text{angle between } \vec{r}_1 \text{ and } \vec{r}_2}}{\cos\theta})^{1/2}}$$

Choose the direction of $\vec{r}_1$ to be along z for the $d\Omega_2$ integration

$$\int d\Omega_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \frac{1}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}}$$

$$= -2\pi \frac{1}{2r_1 r_2}\left[(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{\frac{1}{2}}\right]_{\cos\theta = -1}^{\cos\theta = +1}$$

$$= \frac{\pi}{r_1 r_2}\left(r_1 + r_2 - |r_1 - r_2|\right)$$

$$\int d\Omega_1 = 4\pi$$

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = 4e^2\left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1 dr_1\, e^{-2Zr_1/a_0} \int_0^\infty r_2\, dr_2\, e^{-2Z_2/a_0}$$

$$\cdot\,(r_1 + r_2 - |r_1 - r_2|)$$

$$= 4e^2\left(\frac{Z}{a}\right)^6 \int_0^\infty r_1\, dr_1\, e^{-2Zr_1/a_0}\left\{ 2\int_0^{r_1} r_2\, r_2\, \underset{\substack{\downarrow \\ r_1 > r_2}}{dr_2}\, e^{-2Zr_2/a_0}\right.$$

$$\left. + \; 2r_1 \int_{r_1}^{\infty} \underset{\substack{\downarrow \\ r_2 > r_1}}{r_2}\, dr_2\, e^{-2Zr_2/a_0)}\right\}$$

$$= \frac{5}{8}\frac{Ze^2}{a_0}$$

$$\langle H \rangle = \frac{Z^2 e^2}{a_0} - \frac{4Ze^2}{a_0} + \frac{5}{8}\frac{Ze^2}{a}$$

$$\frac{d\langle H\rangle}{dZ} = 0 \Rightarrow \bar{Z} = \frac{27}{16}$$

$$E_0(\bar{Z}) = -2.85\,\frac{e^2}{a_0}$$

4. Variational Method

Trial wave function

$$\psi(\vec{r}_1, \vec{r}_2) = \underset{\underset{\text{properly normalized.}}{\downarrow}}{\left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}}} e^{-\frac{Z}{a_0}(r_1+r_2)}$$

Similar to product of hydrogen atom ground state wave function

Z is treated as a free parameter

$$\langle H \rangle = \underset{\underset{2\cdot\frac{1}{2}\frac{Z^2e^2}{a_0}}{\downarrow}}{2\left\langle \frac{1}{2m}P_1^2 \right\rangle} - \underset{\underset{-4\frac{Ze^2}{a_0}}{\downarrow}}{4\left\langle \frac{e^2}{r} \right\rangle} + \underset{\underset{\frac{5}{8}\frac{Ze^2}{a_0}}{\downarrow}}{\left\langle \frac{e^2}{r_{12}} \right\rangle}$$

$$\downarrow$$

use the technique we have used before

$$= \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right)$$

$$\frac{d\langle H \rangle}{dZ} = 0 \Rightarrow Z = \frac{27}{16} = 1.6875$$

Ground state energy

$$E_0 = \frac{e^2}{a_0}\left(\left(\frac{27}{16}\right)^2 - \frac{27}{8}\frac{27}{16}\right)$$

$$= -5.7\frac{e^2}{2a_0} = -5.7 \cdot 13.6\,\text{eV}$$

$$= -77.52\ \text{eV}$$

⇒ This result is better that the result obtained by first order perturbation theory

In this case, the electron "sees" an effective screened potential (Coulomb type) with an effective charge $Ze = \frac{27}{16}e$

This result show that product wave function is a good approximatio to the exact wave function

⇒ suggest a general procedure

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) \underbrace{- \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}_{V}$$

$$= -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + U(\vec{r}_1) + U(\vec{r}_2) + V(\vec{r}_1, \vec{r}_2)$$

Looking for $U(\vec{r}_1)$ and $U(\vec{r}_2)$ such that $V(\vec{r}_1, \vec{r}_2) = V - U(\vec{r}_1) - U(\vec{r}_2)$ is as small as possible.

Take $H_0 = [-\frac{\hbar^2}{2m}\nabla_1^2 + U(r_1)] + [-\frac{\hbar^2}{2m}\nabla_2^2 + U(r_2)]$

↓

Two seperate one body problem

Solve H_0 and then treat $V(\vec{r}_1, \vec{r}_2)$ as perturbation.

(2S)(2P) of He atom has energy above ionization energy

i.e., He^+, e^- (unbound)

(2S)(2P) $^1P_1$ can decay into $He^+ + e^-$

↓

autoionization

$e^- + He^+$ when the energy of the system = stationary state of He → peak occurs in cross section

↓ resonance

↓ compound state can be formed.

We can also use radiation to excit the He to reach an energy above the ionization energy then it can decay into $e^- + He^+$

⇒ radiation + He ⟶ $e^- + He^4$ can occur

The independent - particle approximation (IPA)

Essential feature:
each electron can be considered to move independently in the average field of the other $Z-1$ electrons plus the nucleus.

In most atoms, it is a good approximation to assume further the distribution of the $Z-1$ other electrons is spherically symmetric around the nucleus.
↓
central - field approximation.
↓
effective potential is of the form
$U(r)$
↳ independent of θ, ϕ.

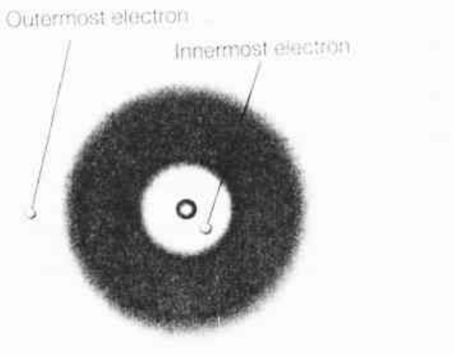
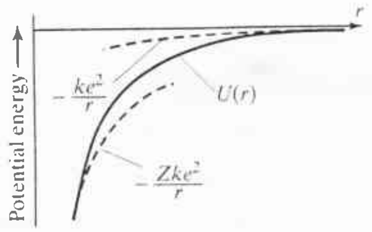


Figure 7.12 How the atom looks to the innermost and outermost electrons, in the Hartree model.



The IPA potential energy $U(r)$ of an atomic electron in the field of the nucleus plus the average distribution of the other $Z-1$ electrons. As $r \to \infty$, U approaches $-ke^2/r$; as $r \to 0$, U approaches $-Zke^2/r$ as in Eq. (10.5).

分類：
編號：
總號： 11-41

The Hartree Model

DOUGLAS RAYNER HARTREE

His Life in Science and Computing

by Charlotte Froese Fischer ***(Vanderbilt University, USA)***

"Dr Fischer's book fills an important gap in the history of individual 20th century scientists. It is also of interest because it documents the immense activity of a very hard-working scientist who did not make any spectacular discoveries and yet contributed to many areas of physical science."

Roy H Garstang
Emeritus Professor, University of Colorado

"Fischer does a good job of outlining the technical context of each of Hartree's contributions .. Extensive references to primary sources are provided, as is a complete listing of Hartree's publications."

The International Meccanoman

Readership: Those interested in the history of science; scientists in quantum chemistry, atomic physics, computer development; astrophysicists, plasma physicists, control theorists.

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$$H = \sum_{i=1}^{Z} \frac{\vec{P}_i^{\,2}}{2m} - \sum_{i=1}^{Z} \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\sim \sum_{i=1}^{Z} \left(\frac{\vec{P}_i^{\,2}}{2m} + U(r_i) \right) + \underset{\substack{\downarrow \\ \text{hopefully small} \\ \text{perturbation}}}{H'}$$

$\underset{\substack{\downarrow \\ \text{eigenfunction}}}{\psi_{n_i, l_i, m_i}(r, \theta, \phi)}$ with eigenvalues $E_{n,l}$

↳ solution of $\left(\frac{-\hbar^2}{2m} \nabla_i^2 + U(r_i) \right) \psi_{\alpha_i} = E_{n_i, l_i} \psi_{\alpha_i}$

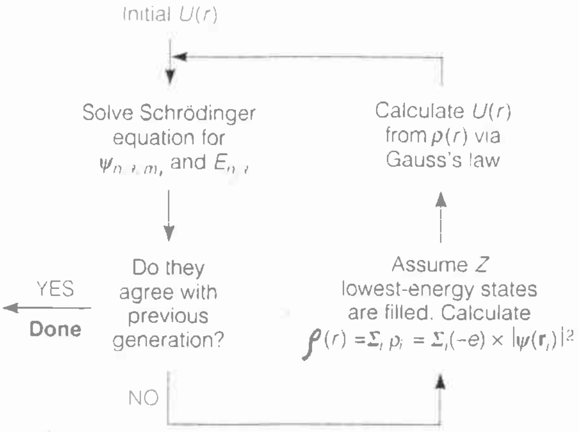
The eigenfunctions

$\prod_i \psi_{\alpha_i}$ with eigenvalue $E = \sum_i E_{n_i, l_i}$

↓

the wavefunction need to be antisymmetrized.

Hartree method (self consistent method)



With the $U_{\downarrow}(r)$, we shall solve the only body central
effective potential
force problem numerically.

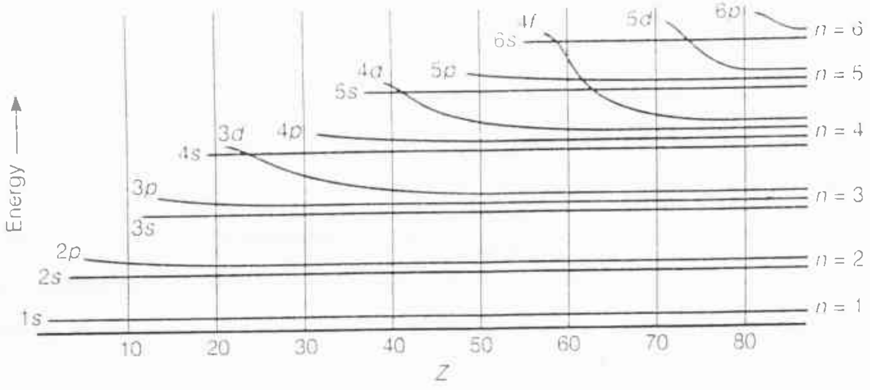


Figure 7.9 The energy ordering of electron states varies with Z.

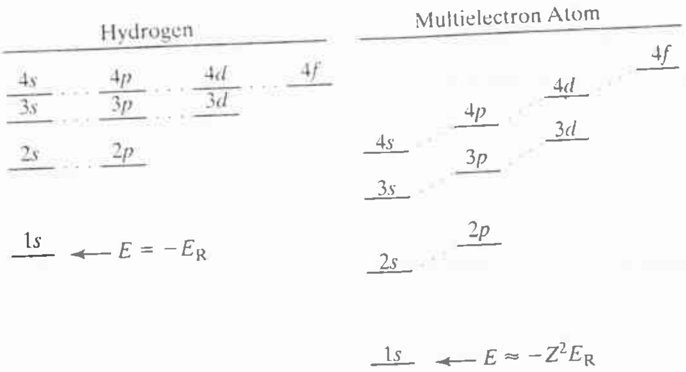


FIGURE 10.3

Schematic energy-level diagrams for a hydrogen atom and for one of the electrons in a multielectron atom. In hydrogen, all states with the same *n* are degenerate. In multielectron atoms states with lower *l* are more tightly bound because they penetrate closer to the nucleus. In many atoms this effect results in the 4*s* level being lower than the 3*d*, as shown here.

Ground state of the atom can be obtained by filling the lowest energy states consistent with Pauli's exclusion principle.

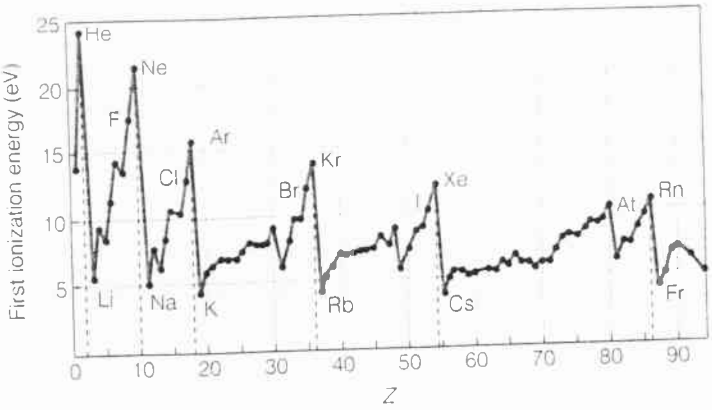
Example

C: $Z=6$, $(1s)^2(2s)^2(2p)^2$

Al $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$
$\Downarrow$
$Z=13$

electronic configuration.

First ionization energy is the energy needed to remove the first electron from the atom.



The chemical properties of the elements are largely determined by the valence electron

Li $Z = 3$ $(1s)^2(2s)$

Na $Z = 11$ $(1s)^2(2s)^2(2p)^6(3s)$

↓

periodic table of the elements.

Periodic Table of the Elements

Symbol — **He** 2 — Atomic number Z
4.0026 — Atomic mass*
Electronic configuration (if different from pattern) — $1s^2$

Subshell →	ns^1	ns^2	$(n-2)f$	$(n-1)d^1$	$(n-1)d^2$	$(n-1)d^3$	$(n-1)d^4$	$(n-1)d^5$	$(n-1)d^6$	$(n-1)d^7$	$(n-1)d^8$	$(n-1)d^9$	$(n-1)d^{10}$	np^1	np^2	np^3	np^4	np^5	np^6
Typical valence →	+1	+2												+3	+4	+5	−2	1	0
Shell n ↓																			
1	**H** 1 1.00794																		**He** 2 4.0026 $1s^2$
2	**Li** 3 6.941	**Be** 4 9.01218												**B** 5 10.811	**C** 6 12.011	**N** 7 14.0067	**O** 8 15.9994	**F** 9 18.9984	**Ne** 10 20.179
3	**Na** 11 22.9898	**Mg** 12 24.3050												**Al** 13 26.9815	**Si** 14 28.0855	**P** 15 30.9738	**S** 16 32.066	**Cl** 17 35.4527	**Ar** 18 39.948
4	**K** 19 39.0983	**Ca** 20 40.078		**Sc** 21 44.9559	**Ti** 22 47.88	**V** 23 50.9415	**Cr** 24 51.9961 $3d^5 4s^1$	**Mn** 25 54.9381	**Fe** 26 55.847	**Co** 27 58.9332	**Ni** 28 58.6934	**Cu** 29 63.546 $3d^{10} 4s^1$	**Zn** 30 65.39	**Ga** 31 69.723	**Ge** 32 72.61	**As** 33 74.9216	**Se** 34 78.96	**Br** 35 79.904	**Kr** 36 83.80
5	**Rb** 37 85.4678	**Sr** 38 87.62		**Y** 39 88.9059	**Zr** 40 91.224	**Nb** 41 92.9064 $4d^4 5s^1$	**Mo** 42 95.94 $4d^5 5s^1$	**Tc** 43 (98)	**Ru** 44 101.07 $4d^7 5s^1$	**Rh** 45 102.906 $4d^8 5s^1$	**Pd** 46 106.42 $4d^{10} 5s^0$	**Ag** 47 107.868 $4d^{10} 5s^1$	**Cd** 48 112.411	**In** 49 114.82	**Sn** 50 118.710	**Sb** 51 121.757	**Te** 52 127.60	**I** 53 126.904	**Xe** 54 131.29
6	**Cs** 55 132.905	**Ba** 56 137.327	La–Yb	**Lu** 71 174.967	**Hf** 72 178.49	**Ta** 73 180.948	**W** 74 183.85	**Re** 75 186.207	**Os** 76 190.2	**Ir** 77 192.22	**Pt** 78 195.08 $5d^9 6s^1$	**Au** 79 196.967 $5d^{10} 6s^1$	**Hg** 80 200.59	**Tl** 81 204.383	**Pb** 82 207.2	**Bi** 83 208.980	**Po** 84 (209)	**At** 85 (210)	**Rn** 86 (222)
7	**Fr** 87 (223)	**Ra** 88 (226)	Ac–No	**Lr** 103 (260)	**Rf** 104 (261)	**Db** 105 (262)	**Sg** 106 (263)	**Bh** 107 (262)	**Hs** 108 (265)	**Mt** 109 (266)									

	f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}
Lanthanides	**La** 57 138.906 $5d^1 6s^2$	**Ce** 58 140.115 $4f^1 5d^1 6s^2$	**Pr** 59 140.908	**Nd** 60 144.24	**Pm** 61 (145)	**Sm** 62 150.36	**Eu** 63 151.965	**Gd** 64 157.25 $4f^7 5d^1 6s^2$	**Tb** 65 158.925 $4f^8 5d^1 6s^2$	**Dy** 66 162.50	**Ho** 67 164.930	**Er** 68 167.26	**Tm** 69 168.934	**Yb** 70 173.04
Actinides	**Ac** 89 (227) $6d^1 7s^2$	**Th** 90 232.038 $6d^2 7s^2$	**Pa** 91 (231) $5f^2 6d^1 7s^2$	**U** 92 238.029 $5f^3 6d^1 7s^2$	**Np** 93 (237) $5f^4 6d^1 7s^2$	**Pu** 94 (244)	**Am** 95 (243)	**Cm** 96 (247) $5f^7 6d^1 7s^2$	**Bk** 97 (247)	**Cf** 98 (251)	**Es** 99 (252)	**Fm** 100 (257)	**Md** 101 (258)	**No** 102 (259)

---

* In atomic mass units, u. Averaged over naturally occurring isotopes. Values in parentheses are mass numbers of most stable known isotopes.

Atoms with many electrons

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

The nucleus is assumed to be infinitely heavy and located at the origin.

Schrodinger equation

$$\left(\sum_{i=1}^{N} \frac{-\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i\neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right) \psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = E\,\psi(\vec{r}_1, \cdots \vec{r}_N)$$

Potential energy of each atomic electron depends on the position of all other electrons

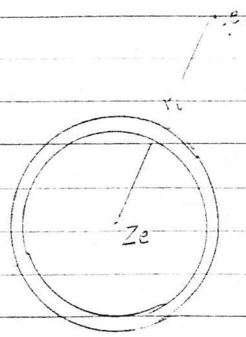
⇒ the above equation is difficult to solve.

Independent electron approximation.

Assumptions

(i) density of all other electrons have spherical symmetry

(ii) density of all other electrons are independent of the ~~position of the~~ position of the electron under consideration.



If ith electron is located at r_i (distance from the nucleus), then it receives a net attraction toward the origin

$$F(r_i) = \Big[Z - \int_0^{r_i} \underset{\llcorner \text{ density of electron other than the one under consideration.}}{\rho(r')}\, 4\pi r'^2 dr' \Big] \frac{e^2}{4\pi\epsilon_0 r^2}$$

↳ this can be obtained from Gauss' theorem

⇒ if ith electron is located at position r_i, its potential energy is $U(r_i)$:

↳ potential from nuclear attraction $\frac{-Ze^2}{4\pi\epsilon_0 r_i}$ reduced by the screening actions of other electrons

Contribution from $r' < r_i$:

$$-\frac{e^2}{4\pi\epsilon_0 r} \Big[Z - \int_0^{r_i} \rho(r')\, 4\pi r'^2 dr' \Big]$$

Contribution from $r' > r_i$

Shell $r' \longrightarrow r' + dr'$

$$\big[e^2 \rho(r')\, 4\pi r'^2 dr' \big] \frac{1}{4\pi\epsilon_0 r'}$$

⇒ total contribution $\frac{1}{4\pi\epsilon_0} e^2 \int_{r_i}^{\infty} \rho(r')\, 4\pi r' dr'$

In this approximation, the approximate Hamiltonian is

$$H_0 = \sum_i \left(\frac{p_i}{2m} + U(r_i) \right)$$

and the Schrodinger equation is

$$\left[\sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right) \right] \psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N) = E\, \psi(\vec{r}_1, \vec{r}_2, \cdots \vec{r}_N)$$

Seperation of variable method

$$\Rightarrow \quad \psi_{\{n_i, l_i, m_{l_i}, m_{s_i}\}}(\vec{r}_1, \cdots \vec{r}_N) = \prod_i \psi_{n_i, l_i, m_{l_i}, m_{s_i}}(\vec{r}_i, \vec{s}_i)$$

$$\text{with} \quad E_{\{n_i, l_i, m_{l_i}, m_{s_i}\}} = \sum_i E_{n_i, l_i}$$

Where $\psi_{n_i, l_i, m_{l_i}, m_{s_i}}(\vec{r}_i, \vec{s}_i)$ and E_{n_i, l_i} are respectively the eigenfunction and eigenvalues of

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] \psi_{n_i, l_i, m_{l_i}, m_{s_i}}(\vec{r}_i, \vec{s}_i) = E_{n_i, l_i}\, \psi_{n_i, l_i, m_{l_i}, m_{s_i}}(\vec{r}_i, \vec{s}_i)$$

Note

(i) This is a one body central problem.

(ii) For central problem, energy eigenvalues are function of n, l.
Only for $\frac{1}{r}$ potential, energy eigenvalues are function of n only.

Pauli's exclusion principle : no two electrons in an atom can have the same set of quantum number n, l, m_l, m_s

Energy of the atom is determined by $\{(n_i, l_i), i=1,2,\dots Z\}$

$\Rightarrow$ $\{N_{nl}$ for all possible $n, l\}$
↳ electron configuration.

Rules for determining the electronic structure of many-electron atoms.

(i) A system of particles is stable (in its ground state) when its total energy is minimum.

(ii) Only one electron can exist in any particular quantum state (n, l, m_l, m_s)

Notations.

Electrons with the same n are said to belong to the same shell.

$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad \cdots$
K L M N O P ⋯ atomic shell.

Electrons with the same n and l are said to belong to the same subshell.

$E_{n,l}$ for $Z \le 35$ can be read off from Figure 10.5 of Beiser
$E_{n,l}$ = − electron binding energy

Usually the larger l, the lesser the binding due to the repulsion of $\frac{l(l+1)\hbar^2}{2\mu r^2}$ term in the effective potential.

Number of maximum electrons in a subshell specified by n, l is
$2(2l+1)$

For example 2p subshell, the maximum number of electrons in it is $2(2\cdot1+1)$
$= 6$

Number of maximum electrons in a shell specified by n is

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2$$

For example $n = 2$, the maximum number of electrons in it is $2\cdot2^2 = 8$

An atomic shell or subshell that contains its full quota of electrons is said to be closed.

Example (i) Li $Z = 3$
$(1s)^2$ $(1, 0, 0, \frac{1}{2})$, $(1, 0, 0, -\frac{1}{2})$
$(2s)$ $(2, 0, 0, \frac{1}{2}$ or $-\frac{1}{2})$
$(1s)^2(2s)$. ← electron configuration

(ii) Na $Z = 11$

$(1S)^2$ 2
$(2S)^2$ 2
$(2p)^6$ 6
10
$(3S)^1$ 1

$(1S)^2(2S)^2(2p)^6(3S)^1$ ← electron configuration

Periodic table : Mendeleev

The elements of each column (group) have ground-state configurations with the same number of electrons in their outermost subshells, all these subshells have the same quantum number l $(nS)^2(np)^6 \Rightarrow 8$ group
⇒ similarities of spectroscopic and chemical properties.

Inert gas → closed shell.

↓

total orbital and spin angular momenta of the electrons in a closed subshell are zero. The electron is a close shell is tightly bound.

their effective charge distributions are perfectly symmetric ⇒ no dipole moment

Atoms with single electron in their outermost shells tend to lose their electrons ⇒ alkali
Atoms whose outer shells lack a single electron of being closed tend to acquire such an electron.

Transition elements

(1) 20 through 29 have similar ionization energies is due to the fact in this region 3d electron and 4S electron have approximately the same energy.

(2) Rare earths 57 - 71

Same $5S^2\ 5p^6\ 6S^2$ configuration.
Incomplete 4f electron

For $Z < 57$ 4f state is highly excited.
$Z < 58$ 4f lies deeper inside the atom ⇒ have virtually no effect on the chemically properties

(3) Actinide elements 89 - 103

Same $6s^2\ 6p^6\ 7s^2$ configuration

Incomplete 5f and 6d electrons

Method of finding $U(r_i)$. Hartree

Given $U(r_i)$ $\rightarrow$ wave function in independent electron approximation

$\rightarrow$ $\rho(r)$

$\rightarrow$ $U(r_i)$

$\Rightarrow$ self consistent requirement.

Procedure

(i) A reasonable guess $U^0(r_i)$

(ii) Solve the one particle Schrodinger equation and find

$$\psi_{n_i,\, l_i,\, m_{l_i},\, m_{s_i}}(\vec{r}_i, \vec{s}_i) \quad \text{and} \quad E_{n_i,\, l_i}$$

(iii) Construct the ground state wave function

$$\prod_i \psi_{n_i,\, l_i\, m_{l_i}\, m_{s_i}}(\vec{r}_i, \vec{s}_i)$$

that minimize the energy and satisfies the Pauli exclusion principle.

(iv) From the wave function $\Rightarrow$ $\rho(r)$

(v) Calculate

$$U'(r_i) = -\frac{e^2}{4\pi\epsilon_0 r}\left[Z - \int_0^{r_i} \rho(r')\, 4\pi r'^2 dr'\right] + \frac{e^2}{4\pi\epsilon_0}\int_{r_i}^{\infty} \rho(r')\, 4\pi r' dr'$$

(vi) Compare $U'(r_i)$ and $U^0(r_i)$

If $U'(r_i)$ and $U^0(r_i)$ are different, then replace $U^0(r_i)$ by $U'(r_i)$ and repeat (ii) - (vi) until a consistent $U(r_i)$ is found.

Identical particle and the exclusion principle.

Let particles 1 and 2 are identical

$\Downarrow$

they are indistinguishable in quantum mechanics

$\Downarrow$

$|\psi(1,2)|^2 = |\psi(1,2)|^2$, otherwise they can be distinguished.

↳ represents $\vec{r}_1, \vec{s}_1$

Two possible solutions

(i) $\psi(1,2) = -\psi(2,1)$ Anti-symmetric

(ii) $\psi(1,2) = \psi(2,1)$ Symmetric.

Generalize to N identical particles

(i) $\psi(1,2,\cdots i, j, \cdots N) = -\psi(1,2,\cdots j, i, \cdots N)$

for an exchange of any pair of them.

Experiments show that all half integer spin identical particles satisfy above condition

$\Rightarrow$ they are said to satisfy Fermi-Dirac statistics and to be fermions

(ii) $\psi(1,2,\cdots i, \cdots j, \cdots N) = \psi(1,2,\cdots j, \cdots i, \cdots N)$

for an exchange of any pair of them.

Experiments show that all integer spin identical particle satisfy above condition

$\Rightarrow$ they are said to satisfy Bose-Einstein statistics and to be bosons

We shall discuss some important consequences of the spin-statistics relations.

In independent electron approximation

$$\psi(1,2,\cdots i,\cdots j,\cdots N) = \psi_{n_1,\ell_1,m_{\ell_1},m_{s_1}}(\vec{r}_1,\vec{s}_1)\,\psi_{n_2,\ell_2,m_{\ell_2},m_{s_2}}(\vec{r}_2,\vec{s}_2)\cdots\psi_{n_i,\ell_i,m_{\ell_i},m_{s_i}}(\vec{r}_i,\vec{s}_i)$$
$$\cdots\psi_{n_j,\ell_j,m_{\ell_j},m_{s_j}}(\vec{r}_j,\vec{s}_j)\cdots\psi_{n_N,\ell_N,m_{\ell_N},m_{s_N}}(\vec{r}_N,s_N)$$

The spin statistics relation they requirement gives

$$\psi_{n_1,l_1,m_{l_1},m_{s_1}}(\vec{r}_1,\vec{s}_1)\,\psi_{n_2,l_2,m_{l_2},m_{s_2}}(\vec{r}_2,\vec{s}_2)\cdots\psi_{n_i,l_i,m_{l_i},m_{s_i}}(\vec{r}_i,\vec{s}_i)\cdots\psi_{n_j,l_j,m_{l_j},m_{s_j}}(\vec{r}_j,\vec{s}_j)$$

$$\cdots\psi_{n_N,l_N,m_{l_N},m_{s_N}}(\vec{r}_N,\vec{s}_N) = -\psi_{n_1,l_1,m_{l_1},m_{s_1}}(\vec{r}_1,\vec{s}_1)\,\psi_{n_2,l_2,m_{l_2},m_{s_2}}(\vec{r}_2,\vec{s}_2)\cdots$$

$$\cdots\psi_{n_i,l_i,m_{l_i},s_i}(\vec{r}_j,\vec{s}_j)\cdots\psi_{n_j,l_j,m_{l_j},m_{s_j}}(\vec{r}_i,\vec{s}_i)\cdots\psi_{n_N,l_N,m_{l_N},m_{s_N}}(\vec{r}_N,\vec{s}_N)$$

If $(n_i, l_i, m_{l_i}, m_{s_i}) = (n_j, l_j, m_{l_j}, m_{s_j})$ then the above equation

$\Rightarrow \psi(1,2,\cdots,N) = -\psi(1,2,\cdots N)$

$\Rightarrow \psi(1,2,\cdots N) = 0$

$\Rightarrow$ No two electrons can have the same set of (n, l, m_l, m_s)

$\Updownarrow$

Pauli exclusion principle

Method of constructing symmetric and anti-symmetric wave function.

If $\psi(1,2) = \psi_a(1)\,\psi_b(2)$, i.e., can be written as product of wave functions

↳ particle 1 in state a

$$\psi_S = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1)\right] \qquad \text{symmetric under } 1 \rightleftharpoons 2$$

↑ normalization

$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1)\right] \qquad \text{anti-symmetric under } 1 \rightleftharpoons 2$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_a(1) & \psi_b(1) \\ \psi_a(2) & \psi_b(2) \end{vmatrix}$$

Generalize to N particle case

If $\psi(1,2,\cdots,N) = \psi_{a_1}(1)\,\psi_{a_2}(2)\cdots\psi_{a_N}(N)$, then

$$\psi_A = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{a_1}(1) & \psi_{a_2}(1) & \cdots & \psi_{a_N}(1) \\ \psi_{a_1}(2) & \psi_{a_2}(2) & \cdots & \psi_{a_N}(2) \\ \vdots & & & \\ \psi_{a_1}(N) & \psi_{a_2}(N) & \cdots & \psi_{a_N}(N) \end{vmatrix}$$

↳ normalization

(i) This is known as Slater determinant. Anti-symmetric under an exchange of any pair of them.

They are the correct wavefunction for N particles in independent electron model.

(ii) If $\{a_i\} = \{a_j\}$, then two columns in above determinant are identical

$\Rightarrow$ the above determinant vanishes $\Rightarrow$ Pauli's exclusion principle.

Addition of spin angular momentum.

Two spin $\frac{1}{2}$ particle

$\vec{S} = \vec{S}_1 + \vec{S}_2$

S_{1z}	S_{2z}	S_z
$\frac{1}{2}$	$\frac{1}{2}$	1
$\frac{1}{2}$	$-\frac{1}{2}$	0
$-\frac{1}{2}$	$\frac{1}{2}$	0
$-\frac{1}{2}$	$-\frac{1}{2}$	-1

$S = 1, \quad S = 0$

Let $\alpha_1, \alpha_2 \rightarrow$ spin up wave function for particle 1, 2 respectively
$\beta_1, \beta_2 \rightarrow$ spin down wave function for particle 1, 2 respectively.

$\alpha_1 \alpha_2 \quad \longleftrightarrow \quad S = 1, \quad S_z = 1$
$\beta_1 \beta_2 \quad \longleftrightarrow \quad S = 1, \quad S_z = -1$

Note. they are symmetric under exchange $1 \leftrightarrow 2$.

$\alpha_1 \beta_2$, $\alpha_2 \beta_1$ are have $S_z = 0$

$S = 1 \quad S_z = 0$ wave function can be obtained by

$$\underset{\substack{\uparrow \\ \text{symmetric} \\ \text{under } 1 \leftrightarrow 2}}{(S_{1-} + S_{2-})} \; \underset{\substack{\uparrow \\ \text{symmetric} \\ \text{under } 1 \leftrightarrow 2}}{\alpha_1 \alpha_2}$$

$\Rightarrow$ it must be symmetric under $1 \leftrightarrow 2$

$\Rightarrow$ it must correspond to $\frac{1}{\sqrt{2}}(\alpha_1 \beta_2 + \beta_1 \alpha_2)$

The wavefunction for $S = 0, \; S_z = 0 \iff \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \beta_1 \alpha_2)$

If the total wavefunction can be written as

$\psi(1, 2)$ = space part wave function · spin wave function

For $S = 1$ the spin-wavefunction is symmetric then the space part of the wavefunction must be anti-symmetric.

For $S = 0$ the spin-wavefunction is anti-symmetric then the space part of the wavefunction must be anti-symmetric.

Two electron atom

In the independent electron model

The ground state wave function

$\psi(1,2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)$ (spin wave function)

The space wave function is always symmetric under $1 \longleftrightarrow 2$
⇒ spin wave function must be anti-symmetric under $1 \longleftrightarrow 2$
⇒ $S = 0$

The first excited state wave function

$$\psi(1,2) = \begin{matrix} \frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) + \psi_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1)] \cdot (S=0 \text{ wavefunction}) \\ \frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) - \psi_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1)] \cdot (S=1 \text{ wave function}) \end{matrix}$$

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) + \psi_{100}(\vec{r}_2)\psi_{200}(\vec{r}_1)]\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1) \qquad S=0$$

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\psi_{100}(\vec{r}_1)\psi_{200}(\vec{r}_2) - \psi_{100}(\vec{r}_2)\psi_{200}(r_1)]\begin{cases} \alpha_1\,\alpha_2 \\ \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \alpha_2\beta_1) \\ \beta_1\,\beta_2 \end{cases} \qquad S=1$$

In the independent electron model, all these states have the same energy

Correction $H - H_0$

$$= -\sum \frac{Ze^2}{r_i} + \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i U(r_i)$$

For two electron, the correction is

$$V_1 = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} - U(r_1) - U(r_2)$$

For $S=1$ when $\vec{r}_1 \to \vec{r}_2$ the wave function → 0 ⇒ the two electrons do not like to be close to each other
⇒ contribution from $\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ tend to be smaller.

⇒ $S=1$ state has energy lower than $S=0$ state.

Energy of state is further specified by L, S, J

$\vec{L} = \sum \vec{L}_i$

$\vec{S} = \sum \vec{S}_i$

$\vec{J} = \vec{L} + \vec{S}$ LS - coupling

Example $l_1 = 1$, $l_2 = 2$

L can be 3, 2, 1

S can be 0, 1

J can be 3, 2, 1

4, 3, 2 ; 3, 2, 1 ; 2, 1, 0

Example $(3d)^3$ $l = 2$

$L_{12} = 4, 3, 2, 1, 0$

$L_3 = 2$

$L = 6, 5, 4 ; 5, 4, 3, 2, 1 ; 4, 3, 2, 1, 0 ; 3, 2, 1 ; 2$

$S_{12} = 1, 0$

$S_3 = \frac{1}{2}$

$S = \frac{3}{2}, \frac{1}{2} ; \frac{1}{2}$.

$J = \frac{15}{2}, \frac{13}{2}, \frac{11}{2}, \frac{9}{2} ; \frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2} ; \frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}$

$\frac{13}{2}, \frac{11}{2}, \frac{9}{2}, \frac{7}{2} ; \frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2} ; \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} ; \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2} ; \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$

$\frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2} ; \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} ; \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2} ; \frac{5}{2}, \frac{3}{2}, \frac{1}{2} ; \frac{3}{2}$

$\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2} ; \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2} ; \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$

$\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$

$\frac{13}{2}, \frac{11}{2} ; \frac{11}{2}, \frac{9}{2} ; \frac{9}{2}, \frac{7}{2} ; \frac{11}{2}, \frac{9}{2} ; \frac{9}{2}, \frac{7}{2}, \frac{7}{2}, \frac{5}{2} ; \frac{5}{2}, \frac{3}{2} ; \frac{3}{2}, \frac{1}{2} ; \frac{9}{2}, \frac{7}{2} ; \frac{7}{2}, \frac{5}{2} ;$

$\frac{5}{2}, \frac{3}{2} ; \frac{3}{2}, \frac{1}{2} ; \frac{1}{2}, \frac{7}{2}, \frac{5}{2} ; \frac{5}{2}, \frac{3}{2}, \frac{3}{2}, \frac{1}{2}, \frac{5}{2}, \frac{3}{2}$

Hund's rule

(i) The state with largest S lies lowest

(ii) For a given value of S, the state with maximum L lies lowest

(iii) For a given L and S, if the incomplete shell is not more than half filled, the lowest has the minimum value of J, if the shell is more than half-filled the state of lowest energy has $J = L + S$

Above case $S = \frac{3}{2}$

$L = 6$

$(3d)^3$ maximum number of electrons $= 2(2 \times 2 + 1) = 10 \Rightarrow J = \frac{9}{2}$

However this state does not satisfy exclusion principle

With $S = \frac{3}{2}$, it has a $S_z = \frac{3}{2}$ component.

In this case, due to requirement of exclusion principle L_{zi} must all be different

$\Rightarrow$ $L_{z,max} = 2+1+0 = 3$

$\Rightarrow$ The maximum L is 3.

With $S = \frac{3}{2}$, $L = 3$ $\Rightarrow$ $J_{min} = \frac{3}{2}$

The lowest state in this configuration has $L = 3$, $S = \frac{3}{2}$ and $J = \frac{3}{2}$

Term symbol

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

$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad \ldots$

$\quad\;\; S \quad P \quad D \quad F \quad G \quad H \quad I \quad \ldots$

In above case the term symbol is

$$^4F_{3/2}$$

Al $(3s)^2(3p)^1$

$L_{12} = 0$

$L_3 = 1$

$\Rightarrow$ $L = 1$

$S_{12} = 0$ only $(S_z)_{12} = 0$ is allowed

$S_3 = \frac{1}{2}$

$\Rightarrow$ $S = \frac{1}{2}$

$\Rightarrow$ $J = \frac{3}{2}, \frac{1}{2}$

The ground state has $L = 1$, $S = \frac{1}{2}$, $J = \frac{1}{2}$

The term symbol is $^2P_{1/2}$

There are corrections due to spin-orbit interaction

$$V_2 = \sum \left\langle \frac{1}{r}\frac{dU}{dr} \right\rangle_{n_i l_i} \frac{1}{2m^2c^2} \vec{l}_i \cdot \vec{S}_i$$

Usually $V_2 \ll V_1$ ⇒ the L-S coupling scheme
$\updownarrow$
Russell-Saunders coupling

In heavy atoms $V_1 \gg V_2$ ⇒ the states are specified by $j_1, j_2, \cdots j_i \cdots$ and J
⇒ j-j coupling

$\vec{J}_i = \vec{L}_i + \vec{S}_i$
$\vec{J} = \sum \vec{J}_i$

Example ${}^{82}\mathrm{Pb}$ 6P 7S

$j_1 = \frac{1}{2}, \frac{3}{2}$, $j_2 = \frac{1}{2}$

⇒ $J = 1, 0$; $J = 2, 1$