Hydrogen Atom

(without Spin)

$$H_0 = \frac{p^2}{2\mu} - \underset{\substack{\downarrow \\ V(r)}}{\frac{ke^2}{r}}$$ ⇒ time - independent Schrodinger equation

Eigenfunction $\psi_{n,\ell,m}(r,\theta,\phi)$ $n > \ell$

Wave function $= R_{n\ell} Y_{\ell m}$ $m = -\ell, -\ell+1, \cdots \ell$

$H_0 \psi_{n\ell,m} = E_n \psi_{n,\ell,m}$ $^2\psi_{n\ell,m} = \ell(\ell+1)\hbar^2$ m, ℓ, n are all integers

$E_n = -\frac{13.6\,eV}{n^2}$ $L_z \psi_{n\ell m} = m\hbar\, \psi_{n\ell m}$

↓

independent of ℓ

(valid only for Coulomb potential)

Energy level

$n = 1$ $\ell = 0$, $m_\ell = 0$

ground state ⇒ lowest energy state

$\psi_{n,\ell,m} = \psi_{1,0,0} = |1,0,0\rangle$

only one state

spectroscopic notation $\underset{\substack{\downarrow \\ \ell = 0}}{1S}$

$n = 2$ $2S$ $\ell = 0$, $m_\ell = 0$ $\psi_{2,0,0} = |2,0,0\rangle$

$2P \left\{ \ell = 1 \right.$ $m_\ell = 1$ $\psi_{2,1,1} = |2,1,1\rangle$

$m_\ell = 0$ $\psi_{2,1,0} = |2,1,0\rangle$

$\psi_{2,1,1} = |2,1,-1\rangle$

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{3/2} \left(1-\frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{11} = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\phi}$$

$$Y_{10} = \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{i\xi}$$

Normalization

$$\int_0^\infty |R_{nl}|^2 r^2 dr = 1$$

$$\int_0^\infty R^*_{n'l'} R_{nl} \, r^2 dr = \delta_{n'} \quad \delta_{ll'}$$

$$\int_0^\pi \int_0^{2\pi} |Y_{lm}|^2 \sin\theta \, d\theta \, d\phi = 1$$

$$\int_0^\pi \int_0^{2\pi} Y^*_{l'm'} Y_{lm} \sin\theta \, d\theta \, d\phi = \delta_{ll'} \delta_{mm'}$$

Orthonormal conditions

All 4 states have the same energy

$\Rightarrow$ degenerate

Any linear combination $\Rightarrow$ still an eigenstate of energy with the same eigenvalue, i.e. E_2

(Spin included) spin included $S = \frac{1}{2}$

$\uparrow$ electron

Spin operator $\vec{S}$

$\hookrightarrow$ operate on spin space

$\Downarrow$

$$[\vec{L}, \vec{S}] = 0$$

$$\vec{\mu} = -\frac{e}{2m_e}\vec{L}$$

$$\vec{\mu}_s = -\frac{g_e e}{2m_e}\vec{S}$$

$$H = H_0 + \frac{Ze^2}{4\pi\epsilon_0}\frac{\vec{L}\cdot\vec{S}}{4m_e^2c^2r^3}g_e = H_0 + H_1$$

$\Downarrow$

$$C \; \vec{L}\cdot\vec{S}$$

$C \downarrow$ constant

$\vec{L}\cdot\vec{S} \downarrow$ spin-orbit interaction

Definition of $\vec{J}$

$\downarrow$ total angular momentum

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

$$\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S}$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}[J^2 - L^2 - S^2]$$

$\downarrow$

important relation in spin-orbit interaction

The wave function

$$\psi_{nlm}(r,\theta,\phi) \longrightarrow \psi_{nlm}(r,\theta,\phi)\chi_{\pm}$$

$\downarrow$

$$|n, l, m, m_s\rangle$$

Furthermore, $H_1 \ll H_0$

$\Rightarrow$ perturbation theory can be used.

With degeneracy $\Rightarrow$ degenerate perturbation theory must be used

$\downarrow$

appropriate linear combination should be used as the starting point, i.e., the unperturbed wave function ψ^0

$|n, \ell, j, m_j\rangle$ is a linear combination of

$|n, \ell, m_\ell, m_s\rangle$

These states are eigenfunctions of $H_0, \vec{L}^2, \vec{J}^2, J_z$ with eigenvalues E_n, $\ell(\ell+1)\hbar^2$, $j(j+1)\hbar^2$, m_j

and

eigenfunctions of H_0, $\vec{L}^2$, L_z, S_z with eigenvalues E_n, $\ell(\ell+1)\hbar^2$, $m_\ell\hbar$, $m_s\hbar$

respectively

Note

$$[H_0, \vec{L}^2] = 0, \quad [H_0, \vec{J}^2] = 0, \quad [H_0, J_z] = 0$$

$$[\vec{L}^2, \underset{\substack{\downarrow \\ (\vec{L}+\vec{S})^2}}{\vec{J}^2}] = 0 \qquad [\vec{L}^2, \underset{\substack{\| \\ L_z + S_z}}{J_z}] = 0 \qquad [J^2, J_z] = 0$$

$\Rightarrow$ there exists simultaneous eigenfunctions of $H_0, \vec{L}^2, \vec{J}^2, J_z$

Relation between $|n, l, j, m_j\rangle$ and $|n, l, m_l, m_s\rangle$

Example (1) $\quad \begin{array}{c} l = 0 \\ \downarrow \\ m_l = 0 \end{array} \qquad \begin{array}{c} s = \frac{1}{2} \\ \downarrow \\ s_z = \frac{1}{2} \end{array}$

$n=1$

$s_z = \frac{1}{2} \Rightarrow j_z = \frac{1}{2}$

$|n, l, m_l, m_s\rangle$

$|1, 0, 0, \frac{1}{2}\rangle = |1, 0, \frac{1}{2}, \frac{1}{2}\rangle$

$s_z = -\frac{1}{2} \Rightarrow j_z = -\frac{1}{2}$

$\begin{array}{c} 2j+1 \text{ states} \\ \Downarrow \\ j = \frac{1}{2} \end{array}$

Example $\quad l = 1 \qquad s = \frac{1}{2}$

$s_z = \frac{1}{2}, \quad m_l = 1 \Rightarrow \underset{\underset{m_j}{\|}}{j_z} = \frac{3}{2} \Rightarrow J = \frac{3}{2}$

$|2, 1, 1, \frac{1}{2}\rangle = |2, 1, \frac{3}{2}, \frac{3}{2}\rangle$

Using $\underset{\underset{L_- + S_-}{\|}}{J_-}$ on $|2, 1, \frac{3}{2}, \frac{3}{2}\rangle \Rightarrow |2, 1, \frac{3}{2}, \frac{1}{2}\rangle$

$\downarrow$

linear combination of

$|2, 1, 0, \frac{1}{2}\rangle$ and $2, 1, 1, -\frac{1}{2}\rangle$

$\Rightarrow$ 4 states which are eigenstate E_2, $J = \frac{3}{2}$

$l = 0 \Rightarrow$ 2 states

$n = 1$ two states $\quad \begin{array}{c} n, l, m_l, m_s \\ |1, 0, 0, \pm\frac{1}{2}\rangle \\ \updownarrow \\ n, l, j, m_j \\ |1, 0, \frac{1}{2}, \pm\frac{1}{2}\rangle \end{array}$

$n = 2 \quad l = 1 \quad$ 6 states with $\begin{array}{l} 4 \quad J = \frac{3}{2} \\ 2 \quad J = \frac{1}{2} \end{array}$

$l = 0 \quad$ 2 states with $J = \frac{1}{2}$

Degenerate perturbation $\Rightarrow \{|n, \ell, j, m_j\rangle\}$ should be used as $\psi^{(0)}$ since $[L^2, H_1] = [J^2, H_1] = 0$

but

$[L_z, H_1] \neq 0$

with $H_1 = c\,\vec{L}\cdot\vec{S} = \frac{1}{2}c\,[J^2 - \vec{L}^2 - \underset{\updownarrow}{\vec{S}}{}^2]$

Energy for $|n, \ell, j, m_j\rangle$ due to $\vec{L}\cdot\vec{S}$ interaction is

$$\frac{c}{2}\left[j(j+1) - \ell(\ell+1) - \frac{3}{2}\cdot\frac{1}{2}\right]\hbar^2$$

Example

$n=1$ $\ell=0$, $j=\frac{1}{2}$ $m_j=\pm\frac{1}{2}$

$\downarrow$

the shift is

$$\frac{c}{2}\underset{\overset{\parallel}{0}}{\left[\frac{1}{2}\left(\frac{1}{2}+1\right) - \frac{3}{4}\right]}\hbar^2$$

2 states

no shift.

$n=2$ $\ell=0$ $j=\frac{1}{2}$, $m_j=\pm\frac{1}{2}$

$\downarrow$

same as above

no shift

$\ell=1$ $j=\frac{3}{2}$ $m_j = \begin{cases} \frac{3}{2} \\ \frac{1}{2} \\ -\frac{1}{2} \\ -\frac{3}{2} \end{cases}$

the shift is

$$\frac{c}{2}\left[\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right]\hbar^2$$

$$= \frac{c}{2}\hbar^2$$

$\downarrow$

fine structure

$l = 1, \quad j = \frac{1}{2}$

The shift is

$$\frac{C}{2}\left[\frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right]\hbar^2$$

$$\parallel$$

$$\frac{C}{2}(-2) = -C$$

Zeeman effect put the hydrogen atom in an external magnetic field

$$H_2 = -\vec{\mu}\cdot\vec{B} \quad \text{(electricity and magnetism)}$$

$$= -(\vec{\mu}_{orbit} + \vec{\mu}_{spin})\cdot\vec{B}$$

$$\vec{\mu}_{orbit} = -\frac{e}{2m_e}\vec{L}$$

$$\vec{\mu}_{spin} = -g_e\frac{e}{2m_e}\vec{S}$$

$$\vec{B} = B\hat{k} \qquad H_2 = \left(\frac{e}{2m_e}L_3 + g_e\frac{e}{2m_e}S_3\right)B$$

An hydrogen atom in an external B field.

$$H = H_0 + H_1 + H_2$$

In general $H_0 \gg H_1, H_2$

↓

we shall use perturbation theory

If we ignore the spin-orbit interaction, then we are dealing with Zeeman effect

$$H = H_0 + H_2 = -(\vec{\mu}_{orbit} + \vec{\mu}_s) \cdot \vec{B} + H_0$$

If we further ignore the spin effect, we are now dealing with the "normal" Zeeman effect.

$$H = H_0 + \frac{eB}{2m_e} L_z + \frac{e g_e}{2m_e} S_z$$

$$[H, S_z] = 0$$

Since $[H, L_z] = 0$, it is appropriate to use $|n, \ell, m, m_s\rangle$ as the starting $\psi^{(0)}$

Shift due to orbital dipole moment is $\frac{eB}{2m_e} m_\ell \hbar$

Shift due to spin dipole moment is $\frac{eB}{2m_e} m_s$

Hyperfine structure

Proton has a spin $\frac{1}{2}$

$$\vec{\mu}_p = \underset{\substack{\downarrow \\ \text{gyromagnetic ratio of the proton.}}}{g_p} \frac{e}{2m_p} \underset{\substack{\downarrow \\ \text{proton spin.}}}{\vec{I}}$$

$$g_p \simeq 5.56$$

Comment :

$\vec{\mu}_p << \vec{\mu}_e$ (note the mass difference)

$g_p \neq 2 \Rightarrow$ indicate it ~~may~~ have internal structure

$$\underset{\substack{\uparrow \\ \text{for hyperfine structure}}}{H'} \propto \frac{\vec{S} \cdot \vec{I}}{r^3}$$

- small
- $l = 0$ is important

$$\vec{F} = \vec{S} + \vec{I}$$

$$\vec{F}^2 = \vec{S}^2 + I^2 + 2S \cdot \vec{I}$$

$\vec{F}$ can be 1 or 0 (proton and electron are both spin $\frac{1}{2}$ particles

$F = 1$ (triplet)

$$\frac{1}{2} [1(1+1) - \tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)] \hbar^2 = \frac{\hbar^2}{4}$$

$F = 0$ $\quad \frac{1}{2} [0(0+1) - \frac{1}{2}(\frac{1}{2}+1)] = -\frac{3}{2}\hbar^2$

Transition from $F = 1$ state to $F = 0$ state

↓

$\Delta E = h\nu$

↓

$\nu = 1420\ \mathrm{Hz}$

↓

$\lambda = 21\ \mathrm{cm}$

Another important application of the nuclear spin

↓

nuclear magnetic resonance

$$\frac{d\vec{I}}{dt} = \vec{\tau} \qquad \vec{\tau} = \vec{\mu}_p \times \vec{B} = \frac{e g_p}{2m_p} \vec{I} \times \vec{B}$$

↓

$$\frac{d\vec{S}}{dt}$$

Proton under the precess with frequency $\omega = \frac{e g_p B}{2m_p}$

$I_z = \pm \frac{1}{2}$

↓

energy difference between spin up and spin down state

$$U = -\vec{\mu}_p \cdot \vec{B}$$

$$\vec{\mu}_p = g_p \frac{e}{2m_p} \vec{I}$$

$$\frac{e g_p}{2m_e} \hbar$$

Add a $\vec{B}'$ field with frequency ω_0

As $\omega_0 \to \omega$ cause the spin-flip ⇒ absorbed or emit photons

↓ resonance

↓ can be detected

↓ reveal the presence of proton

The location of the proton can be observe through the spatial variation of the applied $\vec{B}$ field.

Hydrogen Atom

- An illustration of the structure, technique used in quantum mechanics
- Spin, angular momentum.
- Perturbation theory
  - Non-degenerate
  - Degenerate
  - Time dependent
    - ↳ decay ↔ transition probability
      selection ↓
      Fermi golden rule.

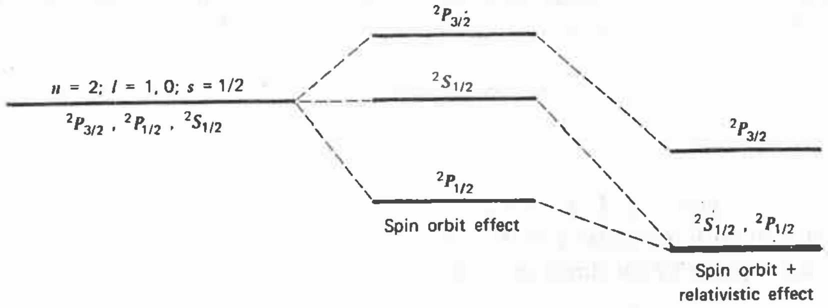

Fig. 17-1. Splitting of the $n = 2$ levels by (1) the spin-orbit coupling (which leaves the S state unaffected) and (2) the relativistic effect. The final degeneracy of the $^2S_{1/2}$ and $^2P_{1/2}$ states is actually lifted by quantum electrodynamic effects. The upward shift of the $^2S_{1/2}$ state is called the Lamb shift.

Spectroscopic Notation.

l	0	1	2	3	4
letter label	s	p	d	f	g

Dirac equation (1928) (electron in Coulomb field)

Relativistic wave equation

⇒ spin, $g_e = 2$, correct spectrum

$\downarrow$

$^2S_{\frac{1}{2}}$ $^2P_{1/2}$ are degenerate

1947 Lamb shift

$\downarrow$

lift the degeneracy of $^2S_{1/2}$ $^2P_{1/2}$

Kusch

$g_e \neq 2$

$g_e = 2\left(1 + \frac{\alpha}{2\pi} + \cdots\right) = 2.0023192$

⇒ Quantum Electrodynamics (Q.E.D)

$$\left.\frac{g_e-2}{2}\right|_{th} = (1159652201.4 \pm 27.1)\cdot 10^{-12}$$

$$\left.\frac{g_e-2}{2}\right|_{exp} = (1159652188.4 \pm 4.3)\cdot 10^{-12}$$

$$\downarrow$$

the study of atomic spectra turned out to be one of the really fruitful sources for the ideas of 20th century physics.

Helium atom

Helium atom	
Identifiers	
CAS number	7440-59-7 [1] ✓
PubChem	23987 [2]
ChemSpider	22423 [3] ✓
EC number	231-168-5 [4]
UN number	1046
KEGG	D04420 [5] ✗
MeSH	Helium [6]
ChEBI	CHEBI:33681 [7] ✓
RTECS number	MH6520000
ATC code	V03 AN03 [8]
Gmelin Reference	16294
Jmol-3D images	Image 1 [9]
Properties	
Molecular formula	He
Molar mass	4 g mol^{-1}
Appearance	Colourless gas
Boiling point	-269 °C, 4 K, -452 °F
Thermochemistry	
Standard molar entropy S^{o}_{298}	126.151-126.155 J K^{-1} mol^{-1}
Hazards	
S-phrases	S9
✗ (verify) [10] (what is: ✓/✗ ?) Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)	
Infobox references	

This article is about the physics of atomic helium. For other properties of helium, see helium.

A **helium atom** is an atom of the chemical element helium. Helium is composed of two electrons bound by the Coulomb force to a nucleus containing two protons along with either one or two neutrons, depending on the isotope, held together by the strong force. Unlike for hydrogen, a closed-form solution to the Schrödinger equation for the helium atom has not been found. However, various approximations, such as the Hartree-Fock method, can be used to estimate the ground state energy and wavefunction of the atom.

Introduction

The Hamiltonian of helium, considered as a three-body system of two electrons and a nucleus and after separating out the centre-of-mass motion, can be written as

$$H\psi(\vec{r}_1,\, \vec{r}_2) = \left[\sum_{i=1,2}\left(-\frac{\hbar^2}{2\mu}\nabla^2_{r_i} - \frac{Ze^2}{4\pi\epsilon_0 r_i}\right) - \frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right]\psi(\vec{r}_1,\, \vec{r}_2)$$

where $\mu = \frac{mM}{m+M}$ is the reduced mass of an electron with respect to the nucleus, $\vec{r}_1$ and $\vec{r}_2$ are the electron-nucleus distance vectors and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Consider $M = \infty$ so that $\mu = m$ and the mass polarization term $\frac{\hbar^2}{M}\nabla_{r_1}\cdot\nabla_{r_2}$ disappear. The Hamiltonian in atomic units (a.u.) for simplicity is given by

$$H\psi(\vec{r}_1,\, \vec{r}_2) = \left[-\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\psi(\vec{r}_1,\, \vec{r}_2).$$

The presence of the electron-electron interaction term $1/r_{12}$, makes this equation non separable. This means that $\psi_0(\vec{r}_1,\, \vec{r}_2)$ can't be written as a single product of one-electron wave functions. This means that the wave function is entangled. Measurements cannot be made on on one particle without affecting the other. This is dealt with in the Hartree-Fock and Thomas-Fermi approximations.

Hartree-Fock Method

The Hartree-Fock method is used for a variety of atomic systems. However it is just an approximation, and there are more accurate and efficient methods used today to solve atomic systems. The "many-body problem" for helium and other few electron systems can be solved quite accurately. For example the ground state of helium is known to fifteen digits. In Hartree-Fock theory, the electrons are assumed to move in a potential created by the nucleus and the other electrons. The Hamiltonian for helium with 2 electrons can be written as a sum of the Hamiltonians for each electron:

$$H = \sum_{i=1}^{2} h(i) = H_0 + H'$$

where the zero-order unperturbed Hamiltonian is

$$H_0 = -\frac{1}{2}\nabla^2_{r_1} - \frac{1}{2}\nabla^2_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2}$$

while the perturbation term:

$$H' = \frac{1}{r_{12}}$$

is the electron-electron interaction. H_0 is just the sum of the two hydrogenic Hamiltonians:

$$H_0 = \hat{h}_1 + \hat{h}_2$$

where

$$\hat{h}_i = -\frac{1}{2}\nabla^2_{r_i} - \frac{Z}{r_i}, i = 1,2$$

E_n1, the energy eigenvalues and $\psi_{n,l,m}(\vec{r}_i)$, the corresponding eigenfunctions of the hydrogenic Hamiltonian will denote the normalized energy eigenvalues and the normalized eigenfunctions. So:

$$\hat{h}_i\psi_{n,l,m}(\vec{r}_i) = E_{n_1}\psi_{n,l,m}(\vec{r}_i)$$

where

$$E_{n_1} = -\frac{1}{2}\frac{Z^2}{n_i^2} \text{ in a.u.}$$

Neglecting the electron-electron repulsion term, the Schrödinger equation for the spatial part of the two-electron wave function will reduce to the 'zero-order' equation

$$H_0\psi^{(0)}(\vec{r}_1,\vec{r}_2) = E^{(0)}\psi^{(0)}(\vec{r}_1,\vec{r}_2)$$

This equation is separable and the eigenfunctions can be written in the form of single products of hydrogenic wave functions:

$$\psi^{(0)}(\vec{r}_1,\vec{r}_2) = \psi_{n_1,l_1,m_1}(\vec{r}_1)\psi_{n_2,l_2,m_2}(\vec{r}_2)$$

The corresponding energies are (in a.u.):

$$E^{(0)}_{n_1,n_2} = E_{n_1} + E_{n_2} = -\frac{Z^2}{2}\left[\frac{1}{n_1^2} + \frac{1}{n_2^2}\right]$$

Note that the wave function

$$\psi^{(0)}(\vec{r}_2,\vec{r}_1) = \psi_{n_2,l_2,m_2}(\vec{r}_1)\psi_{n_1,l_1,m_1}(\vec{r}_2)$$

An exchange of electron labels corresponds to the same energy $E^{(0)}_{n_1,n_2}$. This particular case of degeneracy with respect to exchange of electron labels is called exchange degeneracy. The exact spatial wave functions of two-electron atoms must either be symmetric or antisymmetric with respect to the interchange of the coordinates $\vec{r}_1$ and $\vec{r}_2$of the two electrons. The proper wave function then must be composed of the symmetric (+) and antisymmetric(-) linear combinations:

$$\psi^{(0)}_{\pm}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}[\psi_{n_1,l_1,m_1}(\vec{r}_1)\psi_{n_2,l_2,m_2}(\vec{r}_2) \pm \psi_{n_2,l_2,m_2}(\vec{r}_1)\psi_{n_1,l_1,m_1}(\vec{r}_2)]$$

This comes from Slater determinants.

The factor $\frac{1}{\sqrt{2}}$normalizes $\psi^{(0)}_{\pm}$. In order to get this wave function into a single product of one-particle wave functions, we use the fact that this is in the ground state. So $n_1 = n_2 = 1,\ l_1 = l_2 = 0,\ m_1 = m_2 = 0$. So the $\psi^{(0)}_{-}$will vanish, in agreement with the original formulation of the Pauli exclusion principle, in which two electrons cannot be in the same state. Therefore the wave function for helium can be written as

$$\psi^{(0)}_0(\vec{r}_1,\vec{r}_2) = \psi_1(\vec{r}_1)\psi_1(\vec{r}_2) = \frac{Z^3}{\pi}e^{-Z(r_1+r_2)}$$

Where ψ_1 and $\psi_2$use the wave functions for the hydrogen Hamiltonian. For helium, Z = 2 from

$$E^{(0)}_0 = E^{(0)}_{n_1=1,n_2=1} = -Z^2 \text{ a.u.}$$

where E $^{(0)}_0 = -4$a.u. which is approximately -108.8 eV, which corresponds to an ionization potential V $^{(0)}_P = 2$ a.u. ($\simeq 54.4$eV). The experimental values are E $_0 = -2.90$a.u. ($\simeq -79.0$eV) and V $_p = .90$a.u. ($\simeq 24.6$eV).

The energy that we obtained is too low because the repulsion term between the electrons was ignored, whose effect is to raise the energy levels. As Z gets bigger, our approach should yield better results, since the electron-electron repulsion term will get smaller.

So far a very crude independent-particle approximation has been used, in which the electron-electron repulsion term is completely omitted. Splitting the Hamiltonian showed below will improve the results:

$$H = \bar{H}_0 + \bar{H}'$$

where

$$\bar{H}_0 = -\frac{1}{2}\nabla^2_{r_1} + V(r_1) - \frac{1}{2}\nabla^2_{r_2} + V(r_2)$$

and

$$\bar{H}' = \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2)$$

V(r) is a central potential which is chosen so that the effect of the perturbation $\bar{H}'$ is small. The net effect of each electron on the motion of the other one is to screen somewhat the charge of the nucleus, so a simple guess for V(r) is

$$V(r) = -\frac{Z-S}{R} = -\frac{Z_e}{r}$$

where S is a screening constant and the quantity Z _e is the effective charge. The potential is a Coulomb interaction, so the corresponding individual electron energies are given (in a.u.) by

$$E_0 = -(Z-S)^2 = -Z_e^2$$

and the corresponding wave function is given by

$$\psi_0(r_1 r_2) = \frac{Z_e^3}{\pi} e^{-Z_e(r_1+r_2)}$$

If Z_e was 1.70, that would make the expression above for the ground state energy agree with the experimental value E_0 = -2.903 a.u. of the ground state energy of helium. Since Z = 2 in this case, the screening constant is S = .30. For the ground state of helium, for the average shielding approximation, the screening effect of each electron on the other one is equivalent to about $\frac{1}{3}$ of the electronic charge.[11]

Thomas–Fermi method

Not long after Schrödinger developed the wave equation, the Thomas–Fermi model was developed. Density functional theory is used to describe the particle density $\rho(\vec{r}),\ r \in \mathbb{R}^3$, and the ground state energy E(N), where N is the number of electrons in the atom. If there are a large number of electrons, the Schrödinger equation runs into problems, because it gets very very difficult to solve, even in the atoms ground states. This is where density functional theory comes in. Thomas-Fermi theory gives very good intuition of what is happening in the ground states of atoms and molecules with N electrons.

The energy functional for an atom with N electrons is given by:

$$\xi = \frac{3}{5}\gamma \int_{\mathbb{R}^3} \rho^{5/3}(\vec{r}) d^3\vec{r} + \int_{\mathbb{R}^3} V(\vec{r})\rho(\vec{r}) d^3\vec{r} + \frac{e^2}{2} \int_{\mathbb{R}^3} \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r}-\vec{r'}|} d^3\vec{r} d^3\vec{r'}$$

Where

$$\gamma = (3\pi^2)^{2/3} \frac{\hbar^2}{2m}$$

The electron density needs to be greater than or equal to 0, $\int_{\mathbb{R}^3} \rho = N$, and $\rho \longrightarrow \xi$ is convex.

In the energy functional, each term holds a certain meaning. The first term describes the minimum quantum-mechanical kinetic energy required to create the electron density $\rho(\vec{x})$ for an N number of electrons. The next term is the attractive interaction of the electrons with the nuclei through the Coulomb potential $V(\vec{r})$. The final term is the electron-electron repulsion potential energy.[12]

So the Hamiltonian for a system of many electrons can be written:

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(\vec{r_i}) \right] + \int \frac{e^2 \rho(\vec{r'})}{|\vec{r}-\vec{r'}|} d^3r'$$

For helium, N = 2, so the Hamiltonian is given by:

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(\vec{r_1}, \vec{r_2}) + \int \frac{e^2 \rho(\vec{r'})}{|\vec{r}-\vec{r'}|} d^3r'$$

Where

$$\int \frac{e^2\rho(\vec{r'})}{|\vec{r}-\vec{r'}|}d^3r' = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r_1}-\vec{r_2}|}, \text{ and } V(\vec{r_1},\vec{r_2}) = \frac{e^2}{4\pi\epsilon_0}\left[\frac{2}{r_1}+\frac{2}{r_2}\right]$$

yielding

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)+\frac{e^2}{4\pi\epsilon_0}\left[\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{|\vec{r_1}-\vec{r_2}|}\right]$$

From the Hartree-Fock method, it is known that ignoring the electron-electron repulsion term, the energy is $8E_1$ = -109 eV.

The variational method

To obtain a more accurate energy the variational principle can be applied to the electron-electron potential V_{ee} using the wave function

$$\psi_0(\vec{r_1},\vec{r_2}) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}:$$

$$\langle H\rangle = 8E_1+\langle V_{ee}\rangle = 8E_1+\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2\int\frac{e^{-4(r_1+r_2)/a}}{|\vec{r_1}-\vec{r_2}|}\,d^3\vec{r_1}\,d^3\vec{r_2}$$

After integrating this, the result is:

$$\langle H\rangle = 8E_1+\frac{5}{4a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = 8E_1-\frac{5}{2}E_1 = -109+34 = -75eV$$

This is closer to the theoretical value, but if a better trial wave function is used, an even more accurate answer could be obtained. An ideal wave function would be one that doesn't ignore the influence of the other electron. In other words, each electron represents a cloud of negative charge which somewhat shields the nucleus so that the other electron actually sees an effective nuclear charge Z that is less than 2. A wave function of this type is given by:

$$\psi(\vec{r_1},\vec{r_2}) = \frac{Z^3}{\pi a^3}e^{-Z(r_1+r_2)/a}$$

Treating Z as a variational parameter to minimize H. The Hamiltonian using the wave function above is given by:

$$\langle H\rangle = 2Z^2E_1+2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\langle\frac{1}{r}\rangle+\langle V_{ee}\rangle$$

After calculating the expectation value of $\frac{1}{r}$ and V_{ee} the expectation value of the Hamiltonian becomes:

$$\langle H\rangle = [-2Z^2+\frac{27}{4}Z]E_1$$

The minimum value of Z needs to be calculated, so taking a derivative with respect to Z and setting the equation to 0 will give the minimum value of Z:

$$\frac{d}{dZ}\left([-2Z^2+\frac{27}{4}Z]E_1\right) = 0$$

$$Z = 1.69$$

This shows that the other electron somewhat shields the nucleus reducing the effective charge from 2 to 1.69. So we obtain the most accurate result yet:

$$\frac{1}{2}\left(\frac{3}{2}\right)^6E_1 = -77.5eV$$

Where again, $\mathbf{E_1}$ represents the ionization energy of hydrogen.

By using more complicated/accurate wave functions, the ground state energy of helium has been calculated closer and closer to the experimental value -78.95 eV.[13] The variational approach has been refined to very high accuracy for a comprehensive regime of quantum states by G.W.F. Drake and co-workers[14][15][16] as well as J.D. Morgan III, Jonathan Baker and Robert Hill[17][18][19] using Hylleraas or Frankowski-Pekeris basis functions. It should be noted that one needs to include relativistic and quantum electrodynamic corrections to get full agreement with experiment to spectroscopic accuracy.[20][21]

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11

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The Helium Atom

General Discussion, Zeroth Order Approximation

Two-electron atom

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

$Z = 2 \quad \longleftrightarrow \quad$ He atom

He nucleus $\longleftrightarrow$ 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

$$\psi_{\substack{n_1, l_1, m_1 \\ n_2, l_2, m_2}}(\vec{r}_1, \vec{r}_2) = \underset{\displaystyle \downarrow}{\phi_{n_1, l_1, m_1}}(\vec{r}_1)\,\phi_{n_2, l_2, m_2}(\vec{r}_2)$$

hydrogen-like wavefunction

(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 $n=2$

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

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 $1 \leftrightarrow 2$

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 $1 \leftrightarrow 2$

⇒ parahelium states.

$S=1$ triplet

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

↓

symmetric under $1 \leftrightarrow 2$

↓

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

⇒ orthohelium.

Ground state

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

Zeroth order wavefunction

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

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.

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

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

2. First Order Energy Shift for the Ground State

First order correction for the ground state

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

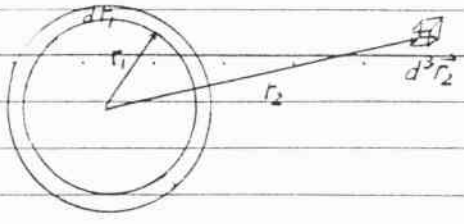
↓

average potential energy of repulsion between two electrons

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

↓

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 $r_2 < r_1$

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

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

put in the wave function with $Z = 2$

The integral is symmetrical in r_1 and r_2

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

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

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

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

$$\int \psi^* H \psi \, d^3x = 2\underset{\underset{2\,\frac{1}{2}\,\frac{Z^2e^2}{a_0}}{\downarrow}}{\left\langle \frac{1}{2m} P_1^2 \right\rangle} - 4\underset{\underset{-4\,\frac{Ze^2}{a_0}}{\downarrow}}{\left\langle \frac{e^2}{r_1} \right\rangle} + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

$$\downarrow$$

this is obtained
through our knowledge
on hydrogen atom

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

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

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2\cos\underset{\downarrow}{\theta})^{1/2}}$$

angle between $\vec{r}_1$ and $\vec{r}_2$

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

$$\int d\Omega_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta) \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2\cos\theta)^{1/2}}$$

$$= -2\pi \frac{1}{2r_1r_2}\left[(r_1^2 + r_2^2 - 2r_1r_2\cos\theta)^{\frac{1}{2}} \right]_{\cos\theta=-1}^{\cos\theta=+1}$$

$$= \frac{\pi}{r_1r_2}(r_1 + r_2 - |r_1 - r_2|)$$

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

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

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

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

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

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

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

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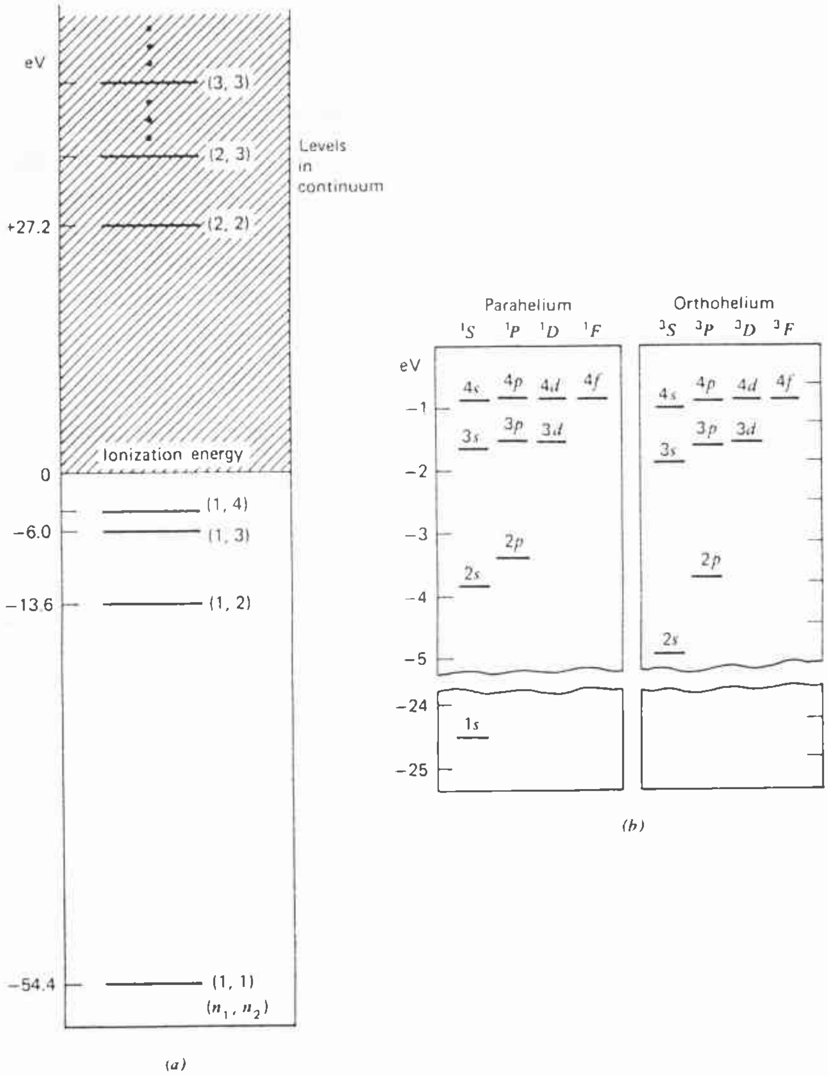


(a)

(b)

(*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.

Put in the numerical value

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

↓

the first order correction is rather large

↓ first order

perturbation theory may not be reliable.

Ground state energy (up to first order perturbation)

$$= -108.8\,eV + 34\,eV = -74.8\,eV$$

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

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

↓

symmetry under $\vec{r}_1 \leftrightarrow \vec{r}_2$

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

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

$$\Delta E_1^t = J - K$$

$$\Delta E_1^s = J + K$$

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

The Variational Method.

↓

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

$$\int \underset{\substack{\downarrow \\ \text{constraint equation}}}{\psi^* \psi} \, d^3x = 1$$

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

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
↑
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

4. Variational Method

Trial wave function

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

$\downarrow$

properly normalized.

Similar to product of hydrogen atom ground state wave function

Z is treated as a free parameter

$$\langle H \rangle = 2\left\langle \frac{1}{2m} P_1^2 \right\rangle - 4\left\langle \frac{e^2}{r} \right\rangle + \left\langle \frac{e^2}{r_{12}} \right\rangle$$

$$\begin{array}{ccc} \downarrow & \downarrow & \downarrow \\ 2\cdot\frac{1}{2}\frac{Z^2e^2}{a_0} & -4\frac{Ze^2}{a_0} & \frac{5}{8}\frac{Ze^2}{a_0} \end{array}$$

$\downarrow$

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

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

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

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

$\Rightarrow$ 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 $H_0 = \underbrace{\left[-\frac{\hbar^2}{2m}\nabla_1^2+U(r_1)\right]+\left[-\frac{\hbar^2}{2m}\nabla_2^2+U(r_2)\right]}_{\text{Two seperate one body problem}}$

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

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

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

where $H\psi_n = E_n \psi_n$

$$E_n \geq E_0 \leftarrow \text{ground state}$$

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

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

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

$$= E_0$$

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

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

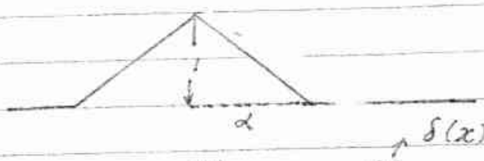
$\hbar$ is taken to be 1
m is taken to be 1

The problem can be exactly solved, $E_{\ldots 1} = 0.5$.

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



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

$$\int_{-\epsilon}^{\epsilon}\frac{d^2 f}{dx^2}\,dx = \left.\frac{df}{dx}\right|_{\epsilon} - \left.\frac{df}{dx}\right|_{-\epsilon} \qquad \frac{d^2 f}{dx^2} = a\,\delta(x)$$

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

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

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

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

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

$\Rightarrow$ 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

$$\psi = \underset{\downarrow\ \text{properly normalized}}{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Z}{a_0}(r_1+r_2)} \quad \rightarrow \quad \text{analogy to hydrogen ground state wave function.}$$

$\downarrow$

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

Z is treated as a parameter

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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.

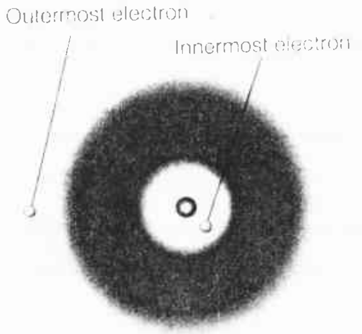
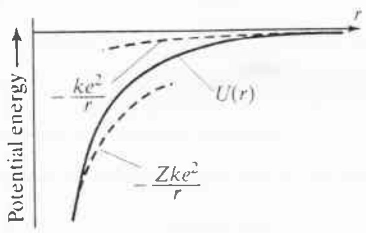
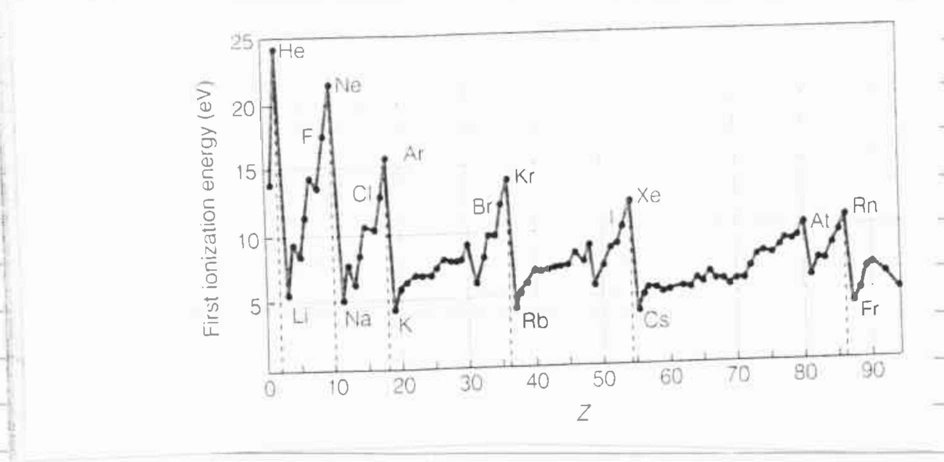


Figure 7.12 How the atom looks to the innermost and outermost electrons, in the Hartree model.



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).

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

$\downarrow$

periodic table of the elements.

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

$$\sim \sum_{i=1}^{Z} \left(\frac{\vec{p}_i^{\,2}}{2m} + U(r_i) \right) + H'$$

↓ hopefully small perturbation

$\psi_{n_i, l_i, m_i}(r, \theta, \phi)$ with eigenvalues $E_{n,l}$

↓ eigenfunction

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

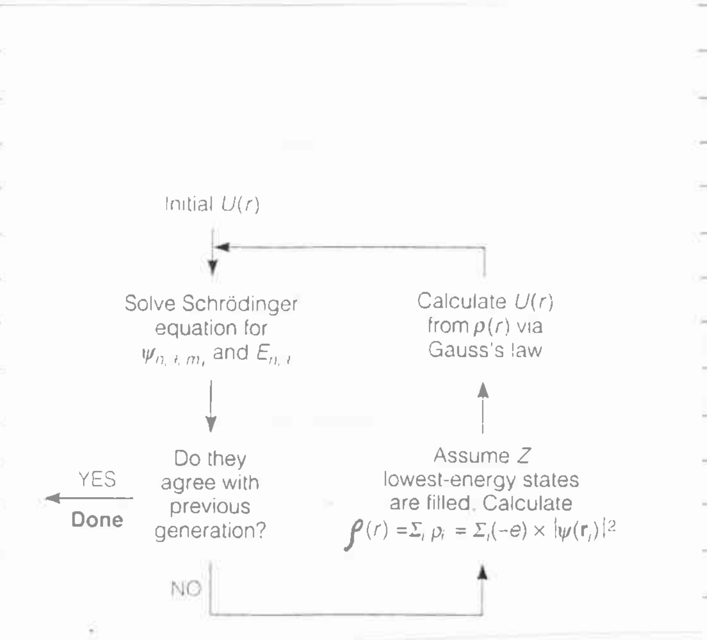
The eigenfunctions

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

↓

the wavefunction need to be antisymmetrized.

Hartree method (self consistent method)



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

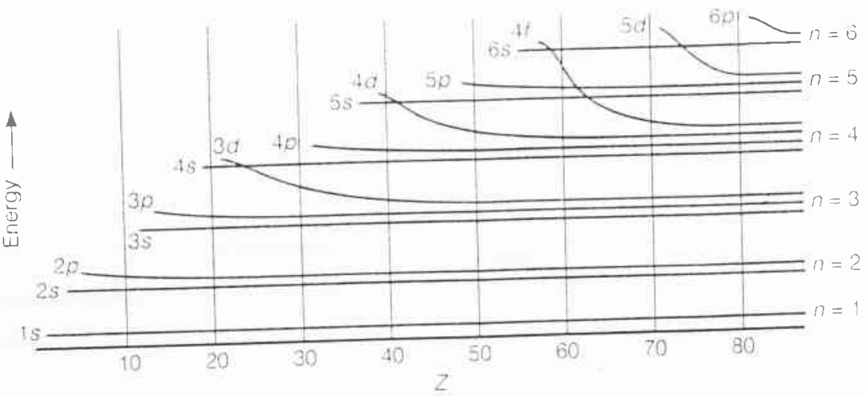


Figure 7.9 The energy ordering of electron states varies with Z.

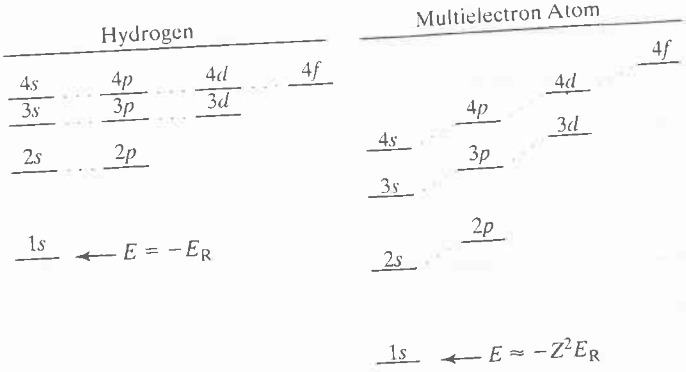


FIGURE 10.3

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 $4s$ level being lower than the $3d$, 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 $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$
$\Updownarrow$
$Z=13$

electronic configuration.

Periodic Table of the Elements

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

Subshell → Typical valence →	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
	+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 20.1797
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 $3d^54s^1$	**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 $4d^45s^1$	**Mo** 42 95.94 $4d^55s^1$	**Tc** 43 (98)	**Ru** 44 101.07 $4d^75s^1$	**Rh** 45 102.906 $4d^85s^1$	**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 $5d^96s^1$	**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 $5d^16s^2$	**Ce** 58 140.115 $4f^15d^16s^2$	**Pr** 59 140.908	**Nd** 60 144.24	**Pm** 61 (145)	**Sm** 62 150.36	**Eu** 63 151.965	**Gd** 64 157.25 $4f^75d^16s^2$	**Tb** 65 158.925 $4f^85d^16s^2$	**Dy** 66 162.50	**Ho** 67 164.930	**Er** 68 167.26	**Tm** 69 168.934	**Yb** 70 173.04
Actinides	**Ac** 89 (227) $6d^17s^2$	**Th** 90 232.038 $6d^27s^2$	**Pa** 91 (231) $5f^26d^17s^2$	**U** 92 238.029 $5f^36d^17s^2$	**Np** 93 (237) $5f^46d^17s^2$	**Pu** 94 (244)	**Am** 95 (243)	**Cm** 96 (247) $5f^76d^17s^2$	**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.

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編號：11-22
11-45

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

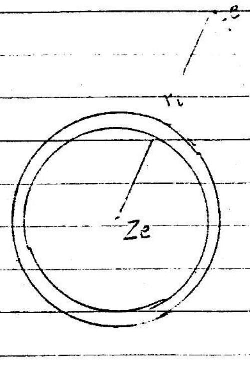
⇒ the above equation is difficult to solve.

Idependent 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

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

↳ density of electron other than the one under consideration.

↑ 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 $r' < r_i$.

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

Contribution from $r' > r_i$

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

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

⇒ 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.

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

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

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 $\{(n_i, l_i), i=1,2,\cdots Z\}$

$\Rightarrow$ $\{N_{nl}$ for all possible $n, l\}$
$\llcorner$ 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.

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

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

$E_{n,l}$ for $Z \leq 35$ 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 $2(2\cdot 1+1) = 6$.

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 $2\cdot 2^2 = 8$

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

Example (i) Li $Z = 3$

$(1S)^2 \qquad (1, 0, 0, \frac{1}{2}), (1, 0, 0, -\frac{1}{2})$

$(2S) \qquad (2, 0, 0, \frac{1}{2}$ 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 $(ns)^2(np)^6$ ⇒ 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 $U(r_i)$ → 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.

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

for an exchange of any pair of them.

Experiments show that all 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

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

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 $\psi(1,2) = \underset{\llcorner\ \text{particle 1 in state } a}{\psi_a(1)}\,\psi_b(2)$, i.e., can be written as product of wave functions

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

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

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

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

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

(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

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

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 $1 \leftrightarrow 2$

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

$\Rightarrow$ $S = 0$

The first excited state wave function

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

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

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

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 $\to 0$ $\Rightarrow$ the two electrons do not like to be close to each other

$\Rightarrow$ contribution from $\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ tend to be smaller.

$\Rightarrow$ $\underset{\text{state}}{S=1}$ has energy lower than $\underset{\text{state}}{S=0}$.

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

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

$\Rightarrow$ The maximum L is 3.

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

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

Term symbol

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

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

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

In above case the term symbol is

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

Al $\qquad (3s)^2\,(3p)^1$

$L_{12} = 0$

$L_3 = 1$

$\Rightarrow \quad L = 1$

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

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

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

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

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

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

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 $\underset{\text{Russell-Saunders coupling}}{\underset{\updownarrow}{L\text{-}S}}$ coupling scheme

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

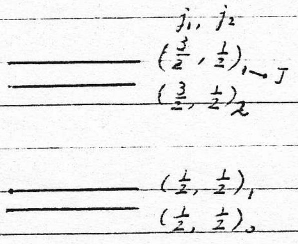
⇒ $j-j$ coupling

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

Example ^{82}Pb 6P7S

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

⇒ $J = 1, 0$; $J = 2, 1$



6P7S
^{82}Pb

3. Quantum mechanics in postulational form

We are now prepared to present the basic postulates of quantum mechanics.

Complementarity postulates

Postulate I. The state of a physical system is represented by a vector (ket) in a linear vector space of infinitely many dimensions.

We shall make the following explanatory remarks:

(1) In view of the uncertainty relation, it is not possible to define, as in classical dynamics, the state of a system by specifying the coordinates and momenta of the particles at any given instant of time.

(2) A vector (ket) is to represent a state to allow the superposition of states. By hypothesis only the direction (not the *sense* such as the "arrow"), but not its length, defines a state. Thus multiplying a ket by any constant does not lead to a different state.

(3) The vector space of infinitely many dimensions is an abstract space, and not the configuration space nor the momentum space of the particles of a system.

(4) The changes of the state of a system are represented by changes in the ket. The Newtonian equations of motion are replaced by an equation for the change of the ket of a system.

Postulate II. All physical quantities ("observables") are represented by linear hermitian operators, which, acting on the state vector (ket), change the state of a system.

(1) Linearity is assumed for a linear theory in the state vectors to allow for superposition of state vectors.

(2) Hermitian operators are employed because hermitian operators have real eigenvalues. Real eigenvalues are needed on account of another basic postulate which connects the mathematical formalism (this and the preceding

postulate) with *physics*—the result of physical observations (see Probability Postulate in the following).

(3) The choice of the eigenvectors of an observable as the basis set of vectors immediately leads to the concepts of representations and transformation of representations. The requirement of invariance of the hermitian charactor of operators leads to unitary transformations.

(4) The transformation theory and the Probability Postulate (see IV below) build up Quantum Mechanics into a coherent system.

Postulate III. The hermitian operators for the coordinate q and the conjugate momentum (in the sense of classical dynamics) obey the commutation relation

$$pq - qp = \frac{\hbar}{i} 1. \tag{V-99}$$

(1) This relation, containing the Planck constant h, causes the system of quantum mechanics to have a fundamental break with classical physics.

(2) Together with the Probability Postulate (that connects the above mathematical formalism with physics), it leads to the uncertainty relation.

(3) In this sense, it may be regarded as the mathematical expression of the Einstein-de Broglie relations.

(4) It is a mathematical expression of the concept of complementarity.

(5) The commutation relation (V-99) may be taken to be a basic principle in quantum mechanics. The postulates I and II have been made for the construction of a mathematical system to cope with the non-classical commutation relation.

The above three postulates are essentially of a mathematical nature and have no real contact with the results of physical measurements. This contact is provided by the Probability Postulate.

Postulate IV. When a measurement is made of a physical quantity (represented by the hermitian operator Q) on a system in a state represented by a vector $|a\rangle$, the expectation value is given by

$$\langle Q \rangle = \langle a|Q|a\rangle, \tag{V-100}$$

(1) This postulate contains the main physical contents of the theory; for it makes theoretical statements of the result of experimental measurements.

(2) If $|a\rangle$ is an eigenstate of Q, say $|a\rangle = |q_k\rangle$, then the expectation value of the measurement is

$$\langle Q\rangle = \langle q_k|Q|q_k\rangle = q_k\langle q_k|q_k\rangle$$
$$= q_k, \tag{V-101}$$

i.e., in this case, the measurement will definitely yield, with certainty, the eigenvalue q_k of Q.

(3) If $|a\rangle$ in (V-100) is an arbitrary state, it can be expanded in the complete set of eigenkets of Q,

$$|a\rangle = \sum_k\!\!\!\!\!\!\int |q_k\rangle\langle q_k|a\rangle \tag{V-102}$$

and

$$\langle a| = \sum_k\!\!\!\!\!\!\int \langle a|q_k\rangle\langle q_k|$$

and

$$\langle Q\rangle = \sum_k\!\!\!\!\!\!\int |\langle a|q_k\rangle|^2 q_k. \tag{V-103}$$

This states that the result of measurement is not a definite one of the eigenvalues, not an in-between value of the q_k's, but *one* of all the q_k's each of which may come out with a probability $|\langle a|q_k\rangle|^2$. The probabilities themselves are definite enough, as they are given by (V-103) but the theory does not tell which *one* of the q_k's will *actually* come out from the measurement.

(4) It is most important to note that the nature of this probability distribution

$$|\langle a|q_k\rangle|^2, \text{ for various } k,$$

is basically different from that in classical statistical physics. In the latter, probability is introduced, when dealing with an extremely large number of molecules, as a substitute for the exact knowledge which exits in principle. In quantum mechanics, even for one atom, a precise knowledge does *not* exist and probability is of an intrinsic nature.

For this reason, quantum mechanics differs from classical physics in a basic way.

(5) Then one may ask why such a probability concept is necessary. For one thing, since two non-commuting operators do not have simultaneous eigenkets, this probability postulate (employed in the derivation of the uncertainty relation) forms at least a *consistent* theory from the point of view of the *anschaulich* thought-experiments in Heisenberg's demonstration of the uncertainty relation on the Einstein-de Broglie relations.

(6) A much deeper and more difficult question is whether it is possible to assume the existence of "hidden variables" and the probability concept arises as the result of a sort of averaging over those hidden variables.[m] If this is the case, the probability will not be "intrinsic" but has the same classical meaning.

From the experimental point of view, when measurements are made, not on one atom, but on a large number of atoms, it is not possible to distinguish between the two kinds of probabilities. The question is a philosophical one—one concerning the nature of quantum mechanics. The concept of an intrinsic probability is repugnant to some philosophers of science; the most prominent ones have been Einstein, Planck and de Broglie. The question has been studied by von Neumann and the answer seems to be that an interpretation of probability in terms of hidden variables is inconsistent in the present system of quantum mechanics. We shall not go into this deep question, but refer to a review of critical studies by Belinfante.

The four postulates above have not included considerations regarding of the change of a system in time. For this, a separate postulate is furnished by the Schrödinger equation:

Postulate V. The change of the state of a physical system in time is governed by the equation

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}|a, t\rangle = H|a, t\rangle,$$

or

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial t} + H(q, p, t)\right)\Psi(q, t) = 0, \qquad \text{(V-104)}$$

where $\Psi(q, t)$ is the representative $\langle q, t|a, t\rangle$ of $|a, t\rangle$ in the q-representation.

(1) This equation is an independent postulate, unlike the Schrödinger equation for momentum, (V-64)

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial q} - p\right)\psi_p(q) = 0,$$

which can be derived from the commutation relation $pq - qp = \hbar/i$ on the transformation theory.

---

[m] In the classical kinetic theory of gases, the "hidden variables" are the coordinates and momenta of the individual molecules. With these variables, the dynamical theory is a deterministic one; but on averaging over, and therefore suppressing, these variables, the theory works with probable values.

(2) In classical dynamics, the time variable t and the energy (Hamiltonian) H formally behave as a pair of canonical conjugate variables $(t, -H)$. It might then be thought that, analogously to (q, p), a commutation relation

$$Ht - tH = -\frac{\hbar}{i}1 \tag{V-105}$$

exists, and if so, then one may have a time representation in which the hermitian operators are:

$$t, \qquad H = -\frac{\hbar}{i}\frac{\partial}{\partial t}, \tag{V-106}$$

and an energy representation in which the hermitian operators are

$$H, \qquad t = \frac{\hbar}{i}\frac{\partial}{\partial E}. \tag{V-107}$$

But if two hermitian operators H and t exist that satisfy the commutation relation (V-105), it can be proved that, if E_a, ψ_a are the eigenvalue and eigenvector of H

$$H\psi_a = E_a\psi_a,$$

then

$$H(e^{i\varepsilon t/\hbar}\psi_a) = (E_a - \varepsilon)(e^{i\varepsilon t/\hbar}\psi_a), \tag{V-108}$$

i.e., $E_a - \varepsilon$ is the eigenvalue of H, for arbitrary, real value of ε, with the eigenvector $e^{i\varepsilon t/\hbar}\psi_a$.[n] As ε is real and arbitrary, it follows that H has a continuous spectrum of eigenvalues extending from $-\infty$ to $+\infty$. But this is not true of systems in general; in fact negative infinite total energy is unphysical. Also systems exist whose energy spectrum is not continuous.

Thus no hermitian operator t exists which satisfies a commutation relation like (V-105).[o] For this reason, it is not possible to derive the relations (V-106), (V-107) from a relation like (V-105).

The Schrödinger equation (V-104) must then be based on a different line of arguments.

In Sec. 2, (V-98), it is seen that

$$i\hbar\frac{d}{dt} = \text{a hermitian operator.}$$

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[n] See Prob. 7 at the end of Chap. 2, Sec. 2. Also (V-91a).

[o] This was pointed out by W. Pauli in his article in *Handbuch der Physik*, Bd. 24, 2nd ed. (Springer-Verlag, Heidelberg, 1933).

Hence it is reasonable to *postulate* (V-106)[p]

$$H = -\frac{\hbar}{i}\frac{\partial}{\partial t} \tag{V-109}$$

and hence the Schrödinger equation (V-104).

(3) The Schrödinger equation (V-104)

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial t} + H\right)\Psi(q, t) = 0$$

is a first-order differential equation in t, but second-order with respect to x, y, z. Thus its form is not Lorentz covariant. Attempts to have a relativistic wave equation have been made.[q] These are the Klein-Gordan equation and the Dirac equation.

(4) An argument for an equation which is of the first order in $\partial/\partial t$ is as follows. From the normalization

$$\int \Psi^*(q, t)\Psi(q, t)\, dq = 1,$$

one has

$$\int \left(\Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi\right) dq = 0. \tag{V-110}$$

To solve an initial value problem of an equation of first order in $\partial/\partial t$, one has to specify Ψ at $t = t_0$. For a second order in $\partial/\partial t$, it is necessary to specify Ψ and $\partial\Psi/\partial t$ at $t = t_0$, but (V-110) does not allow arbitrary Ψ and $\partial\Psi/\partial t$.

(5) The Schrödinger equation (V-104) determines $\Psi(q, t)$ in the course of time completely deterministically, and hence the probability $|\Psi(q, t)|^2$, but only the *probability* distribution, and not the actual outcome of an experiment! One may say that quantum mechanics is a "causal theory of probabilities".

(6) There are "constants of motion" of the Schrödinger equation. For example, take a system with central symmetry, i.e., the Hamiltonian H is invariant under parity operation (inversion with respect to a center, see Chap. 3, Sec. 4, (3), (III-115)–(III-120)) If at an instant t_0 the parity of the state of the system is *even*, the parity will remain *even* in time, if the system is not perturbed by external fields, such as electromognetic fields.

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[p] This is the view of Dirac in *The Principles of Quantum Mechanics*, Sec. 27, 4th Ed. (Clarendon Press, Oxford, 1958).

[q] See references to Schrödinger, Klein, Gordon, de Broglie and Fock at the end of Sec. 3 of Chap. 3.

As another example, take an atom with two electrons, such as helium, whose Hamiltonian is symmetric with respect to the interchange of the two electrons. The space part (i.e., without the spins) of the wave function of the two electrons may be symmetric or antisymmetric with respect to this interchange, (although the total wave function including both the space and the spin parts must be antisymmetric, according to Pauli's principle, which constitutes another independent postulate). If at one instant the state is symmetric, this symmetry will remain unchanged in time when the state changes in accordance with the Schrödinger equation, provided the system is not perturbed by external fields affecting the electron spins.

Such "constants of motions" are essentially the consequence of the symmetry properties of the system.

(7) For systems whose Hamiltonian H is not explicitly a function of time, then the assumption of the form

$$\Psi(q,t) = \psi_n(q)\exp\left(-\frac{iE_nt}{\hbar}\right) \tag{V-111}$$

leads to the time-independent Schrödinger equation

$$(H(q,p) - E_n)\psi_n(q) = 0. \tag{V-112}$$

We have seen a few examples of this equation in Chap. 3.

In subsection (6) above, we mentioned that for a system containing identical particles, there is the question of the symmetry of the state vector, or its representative $\psi(q_1, q_2, q_3, \ldots)$ in coordinate representation. This question arises as follows: Take a system containing two identical particles (for example, electrons), and let us denote them simply by the indices 1 and 2. The Schrödinger equation is

$$(H(1,2) - E)\psi(1,2) = 0.$$

Let P be the operator interchanging the two identical particles. Hence in general

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

so that the eigenvalue of P^2 is 1, and those of P are ± 1, and corresponding to them, the function $\psi(1,2)$ is either symmetric with respect to P, i.e.,

$$P\psi_s(1,2) = \psi_s(1,2),$$

or antisymmetric, i.e.,

$$P\psi_a(1,2) = -\psi_a(1,2).$$

Both ψ_s, ψ_a are solutions of the Schrödinger equation because

$$PH(1,2) = H(2,1) = H(1,2).$$

The question is: Does nature allow both kinds of solutions?

The answer to this question came, paradoxically, before the question was asked, i.e., before quantum mechanics was born. For the electrons in atoms, Pauli postulated, the exclusion principle early in 1925. The connection with the symmetry of the wave function was first given by Dirac (1926). This principle can now be stated as follows.

Postulate VI. For a system of identical particles of *half-odd-integral* spin (such as electrons, muons, protons, neutrons), the wave function is *antisymmetric* with respect to the interchange of two particles. For identical particles of *integral spin* (such as pions, deuterons, α-particles), the ψ is *symmetric* with respect to the interchange of two particles.

This principle (including the Pauli principle) really, so to speak, does not belong to the group of postulates that form the system of quantum mechanics. It is directly related to the statistics—the Fermi-Dirac and the Bose-Einstein statistics. The relationship among the symmetry, the spin and the statistics is regarded as a profound law of nature.