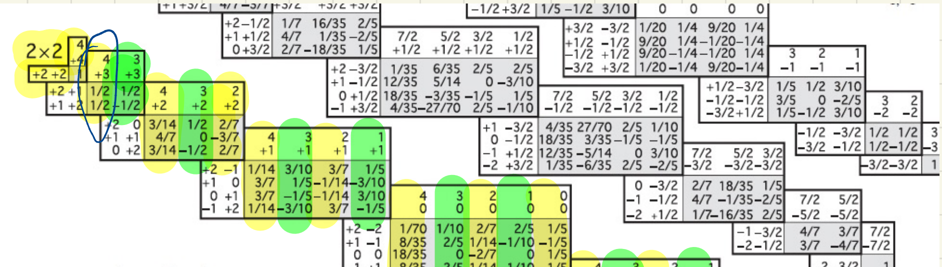


$$d^{3/2}_{3/2,3/2} = \frac{1+\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{3/2,1/2} = -\sqrt{3}\frac{1+\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{3/2}_{3/2,-1/2} = \sqrt{3}\frac{1-\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{3/2,-3/2} = -\frac{1-\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{3/2}_{1/2,1/2} = \frac{3\cos\theta-1}{2}\cos\frac{\theta}{2}$$

$$d^{2}_{2,2} = \left(\frac{1+\cos\theta}{2}\right)^2$$

$$d^{2}_{2,1} = -\frac{1+\cos\theta}{2}\sin\theta$$

$$d^{2}_{2,0} = \frac{\sqrt{6}}{4}\sin^2\theta$$

$$d^{2}_{2,-1} = -\frac{1-\cos\theta}{2}\sin\theta$$

$$d^{2}_{1,1} = \frac{1+\cos\theta}{2}(2\cos\theta-1)$$

$$d^{2}_{1,0} = -\sqrt{\frac{3}{2}}\sin\theta\cos\theta$$

$$\underbrace{L_- = L_{1-} + L_{2-}}$$

$$\checkmark\ |4\,3\rangle = \frac{1}{\sqrt{2}}\left[\,|2\,1\rangle|2\,2\rangle + |2\,2\rangle|2\,1\rangle\,\right]$$

$$\checkmark\ |3\,3\rangle = \cancel{a}\,|2\,1\rangle|2\,2\rangle \mp \cancel{b}\,|2\,2\rangle|2\,1\rangle$$

$$\sqrt{2}$$

$$\sqrt{a^2+b^2} = 1 \qquad \boxed{a = -b}$$

$$\langle\, |21\rangle|22\rangle \,|\, . \,|21\rangle\,|22\rangle \,\rangle = 1$$

$$|\,\langle 21|\,\langle 22|\ \big|\ |22\rangle\,|21\rangle\,\rangle = 0$$

Exchange forces

Not really forces, consequence of sym of states

1D $\psi_a(x), \psi_b(x)$, etc single states

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

$$1 \leftrightarrow \quad \psi_b(x_1)\psi_a(x_2)$$

$$\psi_D(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right]$$

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)\right]$$

Expectation value of the distance squared btw the particles

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$$

Algebra ---

distinguishable

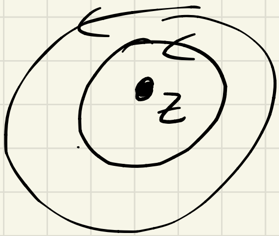
$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle (x_1 - x_2)^2 \rangle_d \mp 2 \left| \underbrace{\int x\, \psi_a^*(x)\, \psi_b(x)\, dx}_{\text{positive } \#} \right|^2$$

Symm state smaller than

$\langle (x_1 - x_2)^2 \rangle_+$ ✓ $\langle (x_1 - x_2)^2 \rangle_-$

Atoms

He $\quad 2p\,2n \quad Z=2$



3-body

Nucleus in stationary approximation

Two electrons H

$$H = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{2}{r_1} + \frac{2}{r_2}\right]$$

$$+ \cancel{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}}$$

Ignoring interaction

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\, \psi_{n'\ell' m'}(\vec{r}_2)$$

$\psi_{n\ell m}$ are H-wavefunctions but with

$Z=2$ instead of $Z=1$

"Bohr radius" is $1/2$ of H-atom a_0

Energies proportional to Z^2

$$E = 4\left(E_n + E_{n'}\right) \qquad E_n = -\frac{R}{n^2}$$

R = Rydberg = 13.6 eV (~~something like that~~)

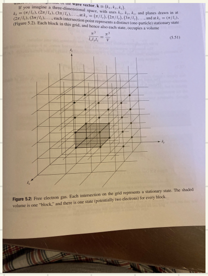
Groun state

$$\psi_0 = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a_0^3}\, e^{-2(r_1+r_2)/a_0}$$

$$E = 4\left(-\frac{13.6}{1} - \frac{13.6}{1}\right) = \underline{\underline{-109\,\text{eV}}}$$

The value ~~a~~ measured $E = -79\,\text{eV}$

30% correction from interaction between the two electrons


... wave vector, $\mathbf{k} \equiv (k_x, k_y, k_z)$.

If you imagine a three-dimensional space, with axes k_x, k_y, k_z, and planes drawn in at $k_x = (\pi/l_x), (2\pi/l_x), (3\pi/l_x), \ldots$, at $k_y = (\pi/l_y), (2\pi/l_y), (3\pi/l_y), \ldots$, and at $k_z = (\pi/l_z), (2\pi/l_z), (3\pi/l_z), \ldots$, each intersection point represents a distinct (one-particle) stationary state (Figure 5.2). Each block in this grid, and hence also each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \tag{5.51}$$

Figure 5.2: Free electron gas. Each intersection on the grid represents a stationary state. The shaded volume is one "block," and there is one state (potentially two electrons) for every block.

H states

$n=3 \quad \ell=2,1,0 \quad 9$

$n=2 \quad \ell=1,0 \quad m=0,\pm 1, \; m=0 \quad 4$

$n=1 \quad \ell=0=m=0 \quad 1$

$n^2 =$ degeneracy

electrons also have spin degree of freedom $\Rightarrow \times 2$

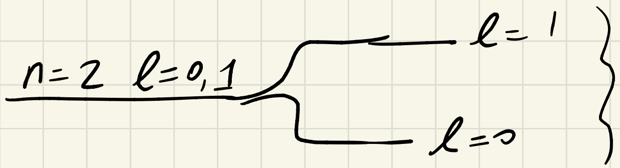
Contact with Chemistry

$n =$ shell Chemistry

Naive picture only works for $n=1,2$

Occupancy in

$$\left.\begin{aligned} n^2 &= 1 \times 2 = 2 \\ n^2 &= 2^2 = 4 \times 2 = 8 \\ n^2 &= 3^2 = 9 \times 2 = 18 \\ &\vdots \end{aligned}\right\} \text{naive picture}$$

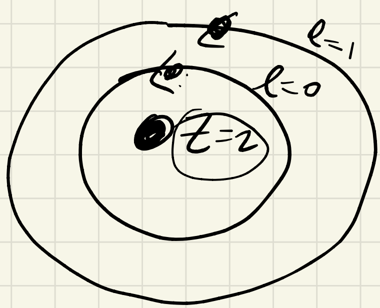


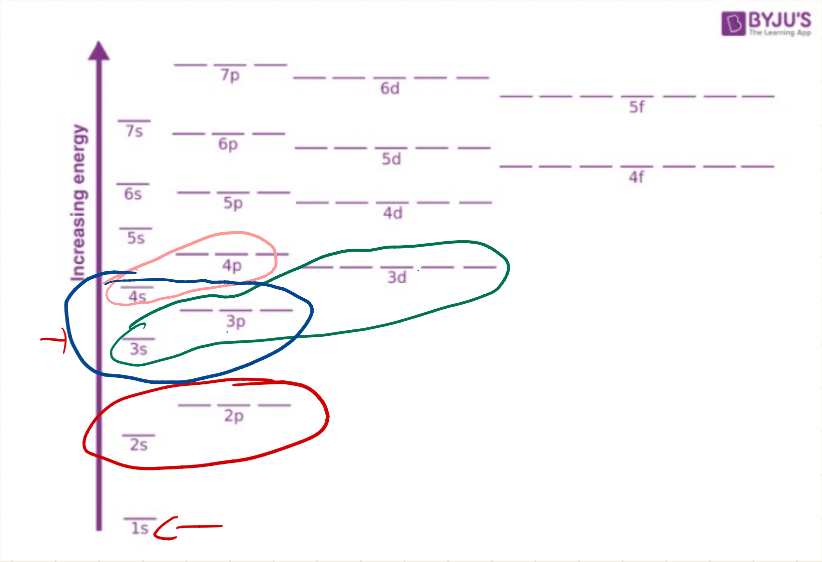
interaction between electron with same n breaks the degeneracy

$\Rightarrow E(n) \to E(n,\ell)$

Hand waving:

$\ell=0$ typical radius is smaller than in $\ell=1$





1(s) $n=1$ $l=0$

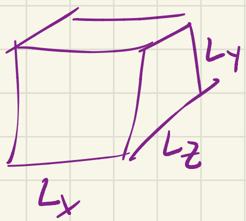
$l=0$ s
$l=1$ p
$l=2$ d
$l=3$ f

SoLiDS

Electrons on outer shells loosely bound – <u>simplest</u> model is that there are some electrons that are <u>free</u>

Treat electrons as free from being bound in the atom, <u>and</u> not interacting with each other

<u>Electron gas (free)</u>



$V(x) = 0$ inside

$0 < x < L_x$

$0 < y < L_y$

$0 < z < L_z$

$V(x) = \infty$ outside

Particle in a box

$$\psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z}$$

$$\boxed{E = \frac{\pi k^2}{m}} \qquad \vec{k} = (k_x \; k_y \; k_z)$$

$$\boxed{k_x = \frac{n_x \pi}{L_x} \quad k_y = \frac{n_y \pi}{L_y} \quad k_z = \frac{n_z \pi}{L_z}}$$

If there was no box, free particles

Wavefunction for free particle is just

a wave $e^{\frac{i \vec{p}\vec{x}}{\hbar}}$ $\vec{p}$ is the momentum

For free particle $\vec{p}$ takes any value

$\vec{k} = \frac{\vec{p}}{\hbar}$ takes any value

In the box you have (almost) free particle states but with only some values of k that are allowed

If electrons were bosons what would be the ground state energy of the system?

$E = \frac{\pi k^2}{m}$ lowest energy for one electron is

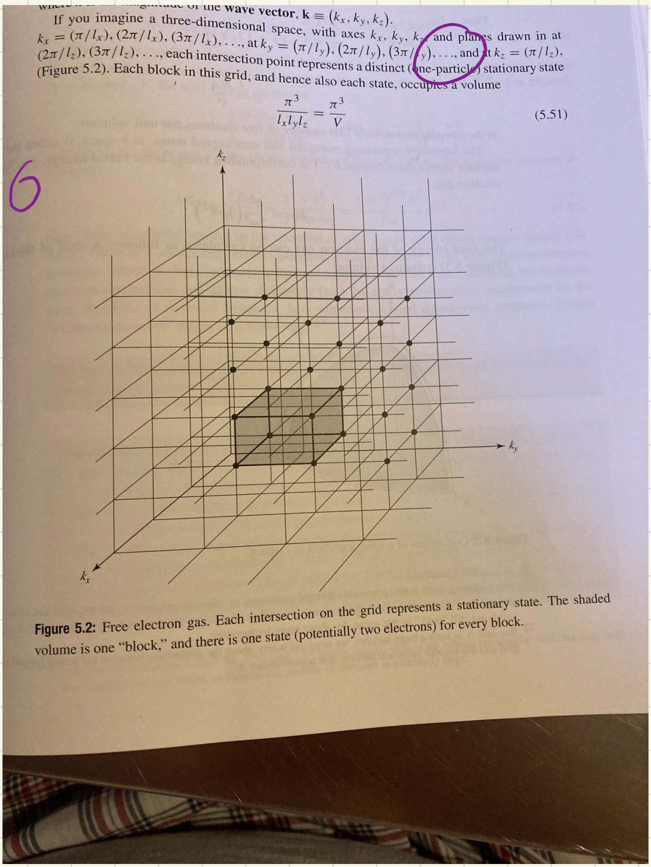
$k = \frac{\pi}{L_x}$

All electrons will pile up

in the lowest state

Electrons are fermions

$\Rightarrow$ They cannot all pile up in the lowest energy state



... wave vector, $\mathbf{k} \equiv (k_x, k_y, k_z)$.

If you imagine a three-dimensional space, with axes k_x, k_y, k_z, and planes drawn in at $k_x = (\pi/l_x), (2\pi/l_x), (3\pi/l_x), \ldots$, at $k_y = (\pi/l_y), (2\pi/l_y), (3\pi/l_y), \ldots$, and at $k_z = (\pi/l_z), (2\pi/l_z), (3\pi/l_z), \ldots$, each intersection point represents a distinct (one-particle) stationary state (Figure 5.2). Each block in this grid, and hence also each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V} \tag{5.51}$$

6

Figure 5.2: Free electron gas. Each intersection on the grid represents a stationary state. The shaded volume is one "block," and there is one state (potentially two electrons) for every block.