Final Review

One dimentional potential well
(one degree of freedom) — One quantum number
to describe the quantum state and
its energy

rigid box

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L} \qquad E_n = \frac{\pi^2 \hbar^2 n^2}{2 m L^2}$$

Simple harmonic oscillator

$$\psi_n \propto H_n(x) , \qquad E_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

Two- or tree-dimentional potential well
two or three degrees of freedom
need two or three quantum numbers
to charactarize the state, but still only
one energy values.
If ~~ssss~~ different set of quantum numbers
provides same values of energy, ~~the~~
such energy level is <u>degenerate</u>

The exact set of quantum numbers
to use depends on the geometry
of the problem.

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Example 1: Two- or tree dimenthional rigid box

Ractangular geometry — natural Cartesian coordinates

Two (tree) quantum numbers: $n_x, n_y (n_z)$

$$\psi_{n_x, n_y, n_z}(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \, \sin\frac{\pi n_x \cdot x}{L_x} \, \sin\frac{\pi n_y \cdot y}{L_y} \, \sin\frac{\pi n_z \cdot z}{L_z}$$

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

Lowest energy state (ground state)

$n_x = n_y = n_z = 1$

$$E_{111} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right)$$

if a cubic rigid box $L_x = L_y = L_z = L$ $E_{n_x, n_y, n_z} =$

$$E_{ground} = E_{111} = 3\pi^2\hbar^2/2mL^2$$

$$= \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Next excited state: $n_x = 2, n_y = 1, n_z = 1$

1	2	1
1	1	2

Three states have same energe $E_{1st\ excited}$

$$E_{1st} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{4}{L^2} + \frac{1}{L^2} + \frac{1}{L^2}\right) = \frac{3\pi^2\hbar^2}{mL^2} \quad \text{— triple - degenerate}$$

Example 2: centrally-symmetric potential

Spherical symmetry — natural spherical coordinates

Still three quantum numbers — but differently defined

In spherically symmetric potential angular momentum $\hat{L}^2$ and its z-components $\hat{L}_z$ are good quantum numbers

Hydrogen atom — each state is characterized by   n: energy quantum number

ℓ — angular momentum value

m — azimuthal component of the angular momentum

$\Psi_{n\ell m}(r,\theta,\varphi)$

$$\hat{L}^2 \Psi_{n\ell m} = \hbar^2 \ell(\ell+1) \Psi_{n\ell m}$$

The average "length" of the angular momentum vector is $|L| = \sqrt{\hbar^2 \ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$

$$\hat{L}_z \Psi_{n\ell m} = \hbar m \Psi_{n\ell m}$$

The average z-component $|L_z| = \hbar m$

Restrictions on quantum numbers

~~$\ell = 0, \pm \frac{1}{2} ...$~~   ~~non negative int~~

n = 1, 2, 3...   positive integer

ℓ = 0, 1, ... n−1   n possible values

m = 0, ±1, ±2... ±ℓ (2ℓ+1) possible values

In a hydrogen atoms energy depends on "n" only

$$E_n = -\frac{E_R}{n^2}$$

Thus each energy state of H-atom is n^2-degenerate (all different ℓ, m states)

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Molecular spectra

Molecule = 2 (or more) atoms bound together

In addition to electron energy states there are now new degrees of freedom, and thus new quantum numbers

1. Molecular vibrations ⟶ model using simple harmonic oscillator
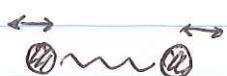
$$E_{vib} = \hbar\omega\left(v + \frac{1}{2}\right) \qquad v = 0, 1, 2\ldots$$

equidistant spectrum

2. Rotation of molecules
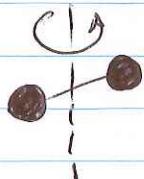
$$E_{rot} = \frac{\hbar^2}{2I}\ell(\ell+1) \qquad \ell = 0, 1, 2.$$

(since the rotational energy is proportional to the angular momentum square $E_{rot} = L^2/2I$)

When we discuss molecules, we usually assume they are always in the ground electronic state, so their energy is a sum of vibrational and rotational energies

$$E_{rot, vib} = \hbar\omega\left(v + \frac{1}{2}\right) + \frac{\hbar^2}{2I}\ell(\ell+1)$$

typically much smaller than $\hbar\omega\left(v+\frac{1}{2}\right)$

Optical transitions

We can calculate the energy levels for different ~~situations~~ situations, and when electrons / molecules change their states they do so by emitting or absorbing quanta of light.

$$E_{ph} = hf = \hbar \omega = \frac{2\pi c}{\lambda} = E_{in} - E_{fin}$$

here $E_{ph} = E_4 - E_2$
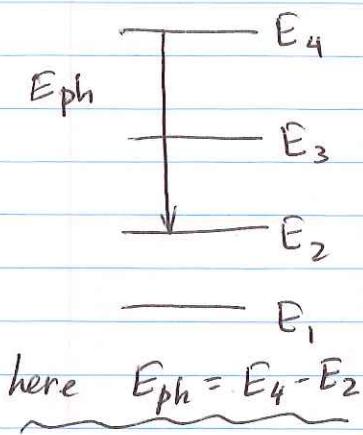
The energy of a photon gives you the information about the separation of two energy levels in an atom or molecule.

This expression is a manifistation of the energy conservation.

Electron spin — another quantum number, appears naturally only in Dirac (relativistically-invariant) equation

Spin ~~can~~ ~~be~~ angular momentum:
$$\hat{S}^2 \psi_s = \hbar^2 s(s+1) \psi_s$$

Z-component of the spin angular momentum
$$\hat{S}_z \psi_s = \hbar m_s \psi_s$$

All particles have specific ~~va~~ value of spin:
electrons, protons, neutrons — $s = 1/2$ (fermions)
photons, neutrinos $s = 1$ (bosons)

Pauli exclusion principle for fermions
(no such principle for bosons)

No two fermions can occupy the same quantum state.
Thus, √the states of Two electrons must be different by at least one quantum number.

For many bosons the lowest energy state is when all particles are in the ground state

Because of the Pauli exclusion principle only limited number of particles can occupy the ground states, so the fermions will fill up several low energy states according ~~to~~ to their degeneracies

Two - dimensional rigid box
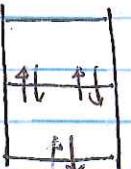
$$E_3 = \frac{4\pi^2\hbar^2}{mL^2}$$ $n_x = 2, n_y = 2$ $m_S = \pm\frac{1}{2}$ 2 diff states

$$E_2 = \frac{5\hbar^2\pi^2}{2mL^2}$$ $n_x = \begin{matrix}1\\2\end{matrix}$ $n_y = \begin{matrix}2\\1\end{matrix}$ $m_S = \pm\frac{1}{2}$ 4 diff. states

$$E_1 = \frac{\hbar^2\pi^2}{mL^2}$$ $n_x = 1, n_y = 1,$ $m_S = \pm\frac{1}{2}$ 2 different states

These three states can hold up to 8 electrons
(fermions)

Multy - electron atom

E_3 $n=3$ $\ell=0$ $m_\ell = 0;$ $\ell=1, m_\ell = \pm 0, 0;$ $\ell=2, m_\ell = 0, \pm1, \pm2$ 18 states
$m_S = \pm\frac{1}{2}$

E_2 $n=2$ $\ell=0$ $m_\ell = 0$ $m_S = \pm\frac{1}{2}$ 8 states
$\ell=1$ $m_\ell = 0, \pm1$

E_1 $n=1$ $\ell=0$ $m_\ell = 0$ $m_S = \pm\frac{1}{2}$ 2 states
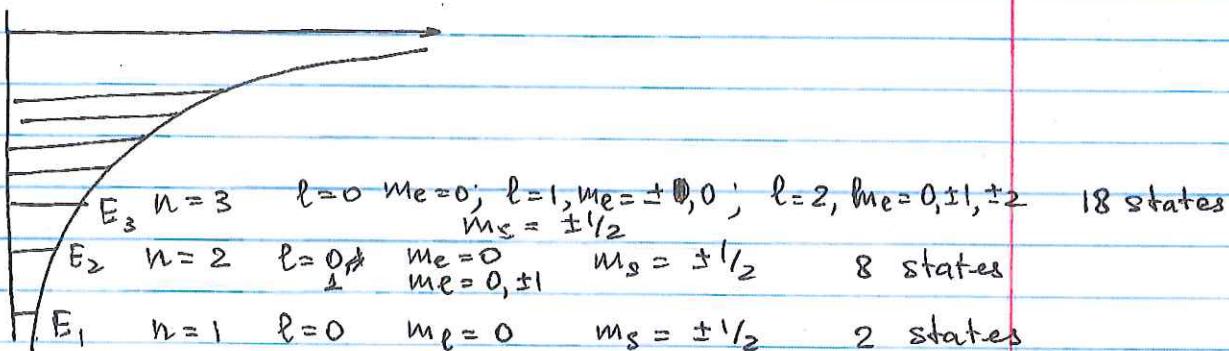
Available energy quantum states structure
determine the "construction" of atoms, as
electrons occupy all low—energy states
according to the Pauli exclusion principle

For example Al $Z=13$
electron configuration $\underset{\underset{2\bar{e}}{n=1}}{1S^2}$ $\underset{\underset{8\bar{e}}{n=2}}{2S^2\,2p^6}$ $\underset{\underset{3\bar{e}}{n=3}}{3S^2\,3p^1}$

1S 2S 2p 3S 3p 3d
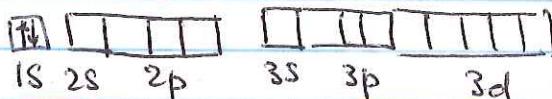
Nuclea physics

We now use the relativistic dynamics again

For non-moving (slowly moving) particles
$E = mc^2$ => mass of a nucleus
is mass of its components – binding energy

↗ # protons _and_ neutrons

$^A_Z X$

↘ # of protons
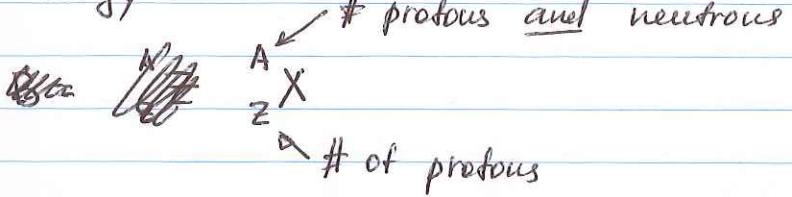
$$B_X = (\cancel{A} \; Z M_p + N M_n - M_X) c^2$$

If a nucleus splits $X \to Y + \alpha$, the mass difference is converted into energy

$$Q = (M_X - M_Y - M_\alpha) c^2$$