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SCHOOL ON SYNCHROTRON RADIATION

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Refresher Course in Quantum Mechanics

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Refresher Course in Quantum Mechanics

1. Quantum Mechanics: Who Needs It ?

Experimental facts unaccounted for by classical physics:

- Blackbody radiation (electromagnetic energy in a cavity at temperature T)
- Photoelectric effect

$$\Longrightarrow E = h\nu$$

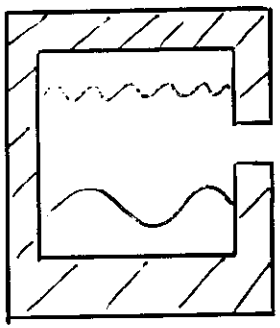
- Stability of the Rutherford atoms against radiation of energy
- Atomic line spectra

$$\Longrightarrow E \text{ is quantized}$$

- Diffraction of electrons (Davisson-Germer experiments)

$$\Longrightarrow \text{Electrons are waves}$$

Black body radiation



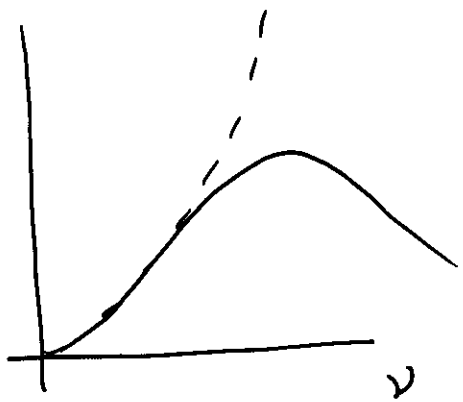
E M field modes in a cavity = harmonic oscillators

At temperature T every oscillator, according to classical statistical physics has average energy $1/2\ kT$

How many modes between ν, $\nu + d\nu$?

$$dN = \frac{V}{(2\pi)^3}\left(\frac{2\pi}{c}\right)^2 \nu^2\, d\nu = \frac{V}{c^3}\,\nu^2\, d\nu$$

$$\frac{dE(\nu,T)}{d\nu} = \frac{V}{c^3}\, kT\, \nu^2$$

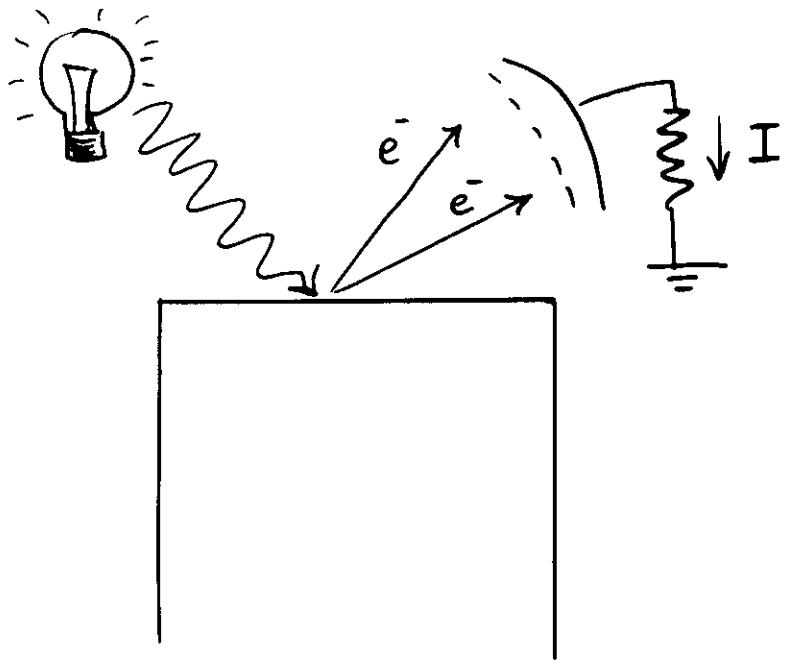


$$\Longrightarrow \quad E = h\nu$$

Planck' s constant :

$$h = 6.6252 \cdot 10^{-27} ergs \cdot s$$

$$\hbar = h / 2\pi = 1.0544 \cdot 10^{-27} ergs \cdot s$$



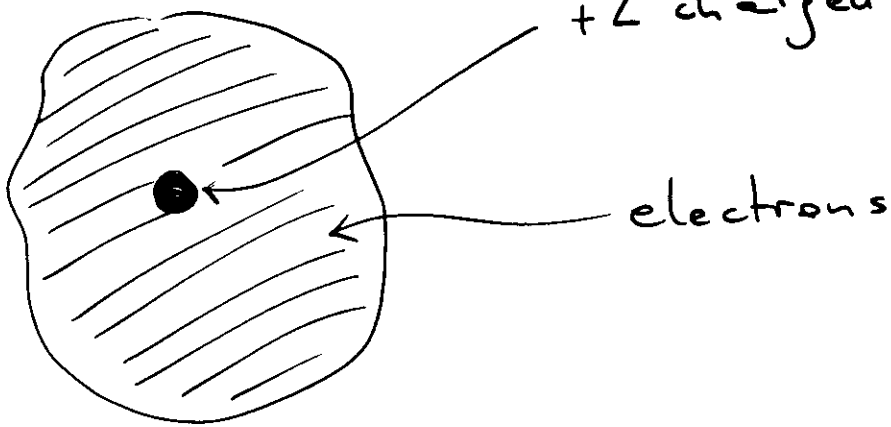
No photoelectrons if

$\nu < \nu_{threshold}$

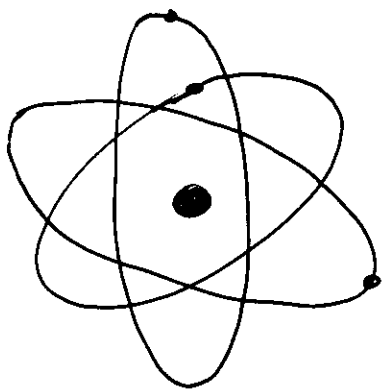
Intensity of light determines intensity of photocurrent, but not electron energy. Electron (kinetic) energy depends only on ν.

$\Longrightarrow \quad E = h\nu$

Rutherford's α-particles scattering experiments show:



'Planetary Model'



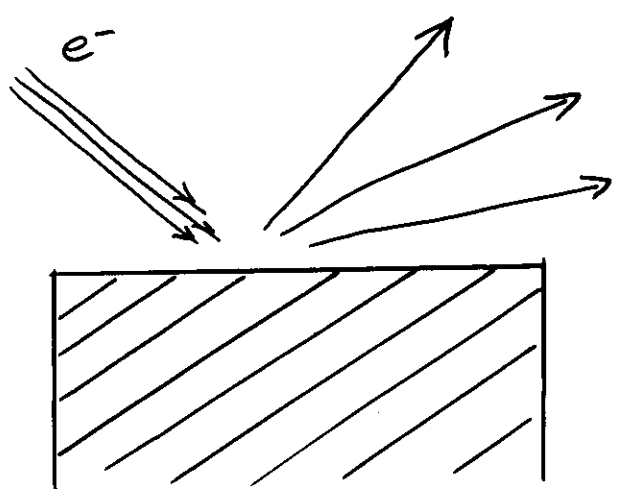
Why electrons do not radiate energy and fall into the nucleus ?

The most intense emission of light from atoms occurs at discrete frequencies, e.g. for H:

$$h\nu = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \qquad n, n' = 1, 2, \ldots \quad n > n'$$

Quantized energy levels

Electron Diffraction (Davisson - Germer)



"Bragg-like" diffraction spots

Electrons are waves!

Refresher Course in Quantum Mechanics.

2. The basic formalism of Quantum Mechanics

The mathematical apparatus to describe atomic-scale processes

- State of a physical system: state vectors, wavefunctions, probability density. Hilbert space of state vectors, scalar products, norm of a wavefunction.

- Physical Observables: Hermitian operators, eigenvalues, eigenvectors.

- The superposition principle. The measurement of a physical quantity. The expectation value of a physical quantity.

In *classical physics*, the state of a particle at a given time t is specified by the value of its position, **r**(t) and of its velocity **v**(t) (or momentum **p**(t)). Generalization: the state of a system with N degrees of freedom (e.g. N/3 particles) is specified by N coordinates q_i (i=1,2,...N) and momenta p_i.

In *quantum physics*, the state of a particle at a given time is specified by a complex wavefunction of its coordinates, ψ (x,y,z,t). It embodies all what can be known and specified about the state of the particle. Its physical interpretation:

> $|\psi(x,y,z,t)|^2 dxdydz$ ~ probability that at time t a measurement of the particle position will give a result between x,y,z and x+dx, y+dy, z+dz.

Note that $|\psi(x,y,z,t)|^2 dxdydz$ is equal (and not just proportional) to the probability that a measurement of the particle position will give a result between x,y,z and x+dx, y+dy, z+dz, if:

$$\int \left|\psi(x,y,z,t)\right|^2 dxdydz = 1$$

Generalization: for a system of N particles: the wavefunction is $\psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,....\mathbf{r}_N,t)$.

Functions such as ψ (x,y,z) can be thought of as "vectors" in a space of functions.

Definition and properties:

Linear combination of 2 functions ψ_1 and ψ_2, with two arbitrary complex coefficients c_1 and c_2:

$$\psi(x,y,z) = c_1 \psi_1(x,y,z) + c_2 \psi_2(x,y,z)$$

Scalar product of two vectors ψ_1 and ψ_2:

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(x,y,z)\, \psi_2(x,y,z)\, dx\, dy\, dz$$

Generalization for N particles:

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)\, \psi_2(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)\, d^3r_1 \dots d^3r_N$$

Properties:

$$\langle \psi_2 | \psi_1 \rangle = \langle \psi_1 | \psi_2 \rangle^*$$

$$\langle \psi_1 | c_2\psi_2 + c_3\psi_3 \rangle = c_2 \langle \psi_1 | \psi_2 \rangle + c_3 \langle \psi_1 | \psi_3 \rangle$$

$$\langle c_1\psi_1 + c_2\psi_2 | \psi_3 \rangle = c_1^* \langle \psi_1 | \psi_3 \rangle + c_2^* \langle \psi_2 | \psi_3 \rangle$$

$$\langle \psi_1 | \psi_1 \rangle \geq 0 \quad (\text{and } = 0 \text{ only if } \psi_1(x,y,z) \equiv 0)$$

Definition:

ψ_1, ψ_2 are <u>orthogonal</u> if $\langle \psi_1 | \psi_2 \rangle = 0$

Physical Observables:

e.g.
- the position x, y, z, of a particle
- the momentum p_x, p_y, p_z " "
- the z-component of its angular momentum l_z
- its energy E
- the total momentum of a system of particles

In Quantum Mechanics, observables correspond to linear, hermitian (or "self-adjoint") operators in the vector space of wavefunctions

Definitions:

Operator $\hat{O}$: $\hat{O}\psi(x,y,z) = \psi_1(x,y,z)$

It operates (i.e. it performs an operation) on function $\psi(x,y,z)$ to transform it into a different function $\psi_1(x,y,z)$.

Examples of operators:

$\frac{\partial}{\partial x}$: $\hat{O}\psi(x,y,z) \equiv \frac{\partial}{\partial x}\psi(x,y,z) = \psi_1(x,y,z)$

$e^{i\varphi}$: $\hat{O}\psi(x,y,z) = e^{i\varphi}\psi(x,y,z) = \psi_1(x,y,z)$

$x^2\frac{\partial}{\partial x}$: $\hat{O}\psi(x,y,z) = x^2\frac{\partial}{\partial x}\psi(x,y,z) = \psi_1(x,y,z)$

$|\chi(x,y,z)\rangle\langle\chi(x,y,z)|$: $\hat{O}\psi(x,y,z) = \langle\chi(x,y,z)|\psi(x,y,z)\rangle\chi(x,y,z)$

$= \psi_1(x,y,z)$

Linear Operators

An operator is said to be <u>linear</u> if, given any two arbitrary functions, $\psi_1(x,y,z)$ and $\psi_2(x,y,z)$, and two arbitrary complex numbers, c_1 and c_2, it is:

$$\hat{O}\left(c_1\psi_1(x,y,z) + c_2\psi_2(x,y,z)\right) =$$

$$= c_1\,\hat{O}\psi_1(x,y,z) + c_2\,\hat{O}\psi_2(x,y,z)$$

A linear operator is said to be <u>Hermitian</u> (or <u>Self-Adjoint</u>) if, for two arbitrary functions $\psi_1(x,y,z)$ and $\psi_2(x,y,z)$, it is:

$$\langle \psi_1 | \hat{O}\psi_2 \rangle = \langle \hat{O}\psi_1 | \psi_2 \rangle$$

i.e.

$$\int \psi_1^*(x,y,z)\left(\hat{O}\psi_2(x,y,z)\right) dx\,dy\,dz = \int \left(\hat{O}\psi_1(x,y,z)\right)^* \psi_2(x,y,z)\, dx\,dy\,dz$$

Examples of hermitian operators:

- $\hat{O} = x_0$ (a real multiplicative constant)

- $\hat{O} = -i\frac{\partial}{\partial x}$ (for normalizable functions, i.e. functions such that $\int |\psi(x,y,z)|^2 dx\,dy\,dz < \infty$; for such functions, $\psi(\vec{r}) \to 0$ as $|\vec{r}| \to \infty$)

Then: $$\int \psi_1^*(x,y,z)\left(-i\frac{\partial}{\partial x}\psi_2(x,y,z)\right)dx\,dy\,dz =$$

$$= -i\int \psi_1^*(x,y,z)\frac{\partial}{\partial x}\psi_2(x,y,z)\,dx\,dy\,dz$$

(Integrate by parts)

$$= -i\int dy\,dz\left\{\left[\psi_1^*(x,y,z)\,\psi_2(x,y,z)\right]_{x=-\infty}^{x=+\infty} - \int\left(\frac{\partial}{\partial x}\psi_1^*(x,y,z)\right)\psi_2(x,y,z)\,dx\right\}$$

$= 0$!

$$= \int \left(-i\frac{\partial}{\partial x}\psi_1(x,y,z)\right)^* \psi_2(x,y,z)\, dx\, dy\, dz$$

Examples of correspondence between physical observable quantities and operators:

- Position along x (or y, or z): $\hat{O}\,\psi(x,y,z) = x\,\psi(x,y,z)$ [or $y\psi$ or $z\psi$]
- Momentum component p_x: $\hat{O}\,\psi(x,y,z) = -i\hbar\frac{\partial}{\partial x}\psi(x,y,z)$
- Kinetic energy of a particle with mass m, $T = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)$: $\hat{O}\,\psi(x,y,z) = \frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)$

Laplacian $\nabla^2\psi(x,y,z) \equiv \frac{\partial^2}{\partial x^2}\psi(x,y,z) + \frac{\partial^2}{\partial y^2}\psi(x,y,z) + \frac{\partial^2}{\partial z^2}\psi(x,y,z)$

Observables → operator correspondence - continues

- Angular momentum of a particle: $\vec{l} = \vec{r} \times \vec{p}$

$$l_x = (y p_z - z p_y): \quad -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\psi(x,y,z)$$

$$l_y = (z p_x - x p_z): \quad -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\psi(x,y,z)$$

$$l_z = (x p_y - y p_x): \quad -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi(x,y,z)$$

$$l^2 = l_x^2 + l_y^2 + l_z^2$$

In general: $\hat{O}^2\psi(x,y,z) = \hat{O}\left(\hat{O}\psi(x,y,z)\right)$

N.B. if $\hat{O}$ is linear, then $\hat{O}^2$ is also linear:

$$\hat{O}^2(c_1\psi_1 + c_2\psi_2) \equiv \hat{O}\left[\hat{O}(c_1\psi_1 + c_2\psi_2)\right] = \hat{O}\left[c_1\hat{O}\psi_1 + c_2\hat{O}\psi_2\right]$$

$$= c_1\hat{O}^2\psi_1 + c_2\hat{O}^2\psi_2$$

Eigenvalues and Eigenvectors of Linear Operators.

Definition

Given a linear operator $\hat{O}$, $\psi_n(x,y,z)$ is an eigenvector of $\hat{O}$ with eigenvalue e_n (a number) if, (for all x, y, z)

$$\hat{O}\,\psi_n(x,y,z) = e_n\,\psi_n(x,y,z)$$

Examples:

$$\hat{O} = \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$$

Eigenvector, (eigenstate, Eigenfunction): $\psi(x,y,z) = \varphi(x,y)\,e^{ik_z z}$

$$\hat{p}_z\,\varphi(x,y)\,e^{ik_z z} = \hbar k_z\,\varphi(x,y)\,e^{ik_z z}$$

Generalizing to components p_x, p_y, show that

$e^{i\vec{k}\cdot\vec{r}} = e^{ik_x x} e^{ik_y y} e^{ik_z z}$ is an eigenvector of

$\hat{p}_x$, eigenvalue $\hbar k_x$

$\hat{p}_y$, " $\hbar k_y$

$\hat{p}_z$, " $\hbar k_z$

Compact notation: $\hat{\vec{p}}\, e^{i\vec{k}\vec{r}} = \hbar\vec{k}\, e^{i\vec{k}\cdot\vec{r}}$

$\vec{p} = -i\hbar\vec{\nabla}$ $\qquad \vec{\nabla} \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

$\hat{O} = \hat{T} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \frac{-\hbar^2}{2m}\nabla^2$

Eigenvector: $\psi(x,y,z) = e^{i\vec{k}\cdot\vec{r}}$

Eigenvalue $\frac{\hbar^2 k^2}{2m}$ (independent of $\vec{k}$ direction!)

$$\hat{O} = \hat{\ell}^2 = \ell_x^2 + \ell_y^2 + \ell_z^2 \qquad \text{(angular momentum)}$$

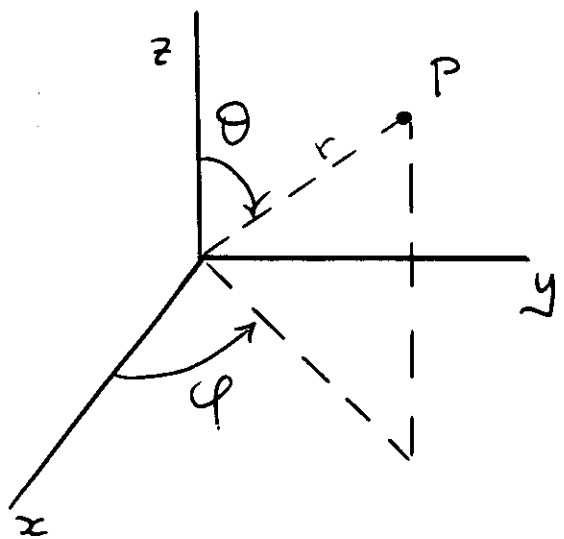
Eigenfunction:

$$\psi(x, y, z) = \chi(r)\, Y_{\ell,m}(\theta, \varphi)$$

$\ell = 0, 1, 2, \ldots$

$m = -\ell, -\ell+1, -\ell+2, \ldots$

$\ldots \ell-1, \ell$



$r = \sqrt{x^2+y^2+z^2}$

$\theta = \cos^{-1} z/r$

$\varphi = \cos^{-1} x/\sqrt{x^2+y^2}$

Eigenvalue: $\hat{\ell}^2 \chi(r)\, Y_{\ell,m}(\theta,\varphi) = \ell(\ell+1)\hbar^2 \chi(r)\, Y_{\ell,m}(\theta,\varphi)$

Also eigenvector of $\hat{\ell}_z$: $\ell_z \chi(r)\, Y_{\ell,m}(\theta,\varphi) = m\hbar\, \chi(r)\, Y_{\ell,m}(\theta,\varphi)$

Table 1. Harmonic Polynomials and Spherical Harmonics.

$$\mathcal{Y}_{lm}(\mathbf{r}) = r^l Y_{lm}(\theta, \varphi)$$

l, m	$\mathcal{Y}_{lm}(\mathbf{r})$	$Y_{lm}(\theta, \varphi)$
0 0	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$
1 0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\,z$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1 ±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,(x \pm iy)$	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{\pm i\varphi}$
2 0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\,(2z^2 - x^2 - y^2)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\,(2\cos^2\theta - \sin^2\theta)$
2 ±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,z(x \pm iy)$	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta e^{\pm i\varphi}$
2 ±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\,(x \pm iy)^2$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{\pm 2i\varphi}$
3 0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}\,(2z^2 - 3x^2 - 3y^2)z$	$\frac{1}{4}\sqrt{\frac{7}{\pi}}\,(2\cos^3\theta - 3\cos\theta\sin^2\theta)$
3 ±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\,(4z^2 - x^2 - y^2)(x \pm iy)$	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\,(4\cos^2\theta\sin\theta - \sin^3\theta)e^{\pm i\varphi}$
3 ±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\,z(x \pm iy)^2$	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\cos\theta\sin^2\theta e^{\pm 2i\varphi}$
3 ±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\,(x \pm iy)^3$	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{\pm 3i\varphi}$

Irreducible tensors containing in addition the components of some other vector $\mathbf{r}'$ may be constructed by polarization of the harmonics with the operator

$$\mathbf{r}' \cdot \nabla \equiv x' \frac{\partial}{\partial x} + y' \frac{\partial}{\partial y} + z' \frac{\partial}{\partial z}$$

Cf. Rose (1954).

- Position operator $\vec{r} = (x, y, z)$

Eigenvector: Dirac's δ (delta) function

$$\delta(\vec{r} - \vec{r}_0) = \delta(x - x_0)\,\delta(y - y_0)\,\delta(z - z_0)$$

Eigenvalue (x_0, y_0, z_0)

Properties:

For any $f(\vec{r})$:

$$\int_A d\vec{r}\, f(\vec{r})\,\delta(\vec{r} - \vec{r}_0) = f(\vec{r}_0) \quad \text{if } \vec{r}_0 \in A$$

$$= 0 \quad \text{if } \vec{r}_0 \notin A$$

In particular, $f(\vec{r}) \equiv 1$

$$\int_A \delta(\vec{r} - \vec{r}_0) = 1 \quad \vec{r}_0 \in A$$

$$\int_A \delta(\vec{r} - \vec{r}_0) = 0 \quad \vec{r}_0 \notin A$$

$$\vec{r}\,\delta(\vec{r} - \vec{r}_0) \equiv \vec{r}_0\,\delta(\vec{r} - \vec{r}_0)$$

Important Theorems on Eigenvectors and Eigenvalues

Theorem 1

All eigenvalues of a hermitian operator are real

Theorem 2 (Orthogonality theorem)

If $\hat{O}\psi_1 = e_1\psi_1$ and $\hat{O}\psi_2 = e_2\psi_2$ and $e_1 \neq e_2$, then

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(x,y,z)\,\psi_2(x,y,z)\,dx\,dy\,dz = 0$$

("Eigenvectors of the same operator corresponding to different eigenvalues are orthogonal").

Important Definitions:

- Degenerate eigenvalue.

  If n functions $\psi_{11}(\vec{r}), \psi_{12}(\vec{r}), \ldots \psi_{1n}(\vec{r})$ can be found such that

  $$\hat{O}\,\psi_{1i} = e_1\,\psi_{1i} \qquad \text{for } i = 1, 2, \ldots n$$

  and

  $$\langle \psi_{1i} | \psi_{1j} \rangle = 0 \qquad \text{for } i \neq j$$

  then e_1 is a n-fold degenerate eigenvalue of $\hat{O}$

- Easy to prove:

  Any linear combination

  $$c_1\,\psi_{11} + c_2\,\psi_{12} + \ldots + c_n\,\psi_{1n}$$

  is also an eigenvector of $\hat{O}$ with eigenvalue e_1

- Complete set of functions.

A set of functions $\psi_1, \psi_2, \ldots, \psi_n, \ldots$ in a vector space (for instance, the space of complex functions of three real variable x, y, z which are square integrable, i.e.:

$$\int |\psi(x,y,z)|^2 \, dx\,dy\,dz < \infty \quad)$$

is called complete if <u>any</u> function of the space can be written as a linear combination of $\psi_1, \psi_2, \ldots \psi_n, \ldots$

$$\psi(x,y,z) = \sum_i c_i \psi_i(x,y,z)$$

- If $\psi_1, \psi_2, \ldots \psi_n, \ldots$ are also <u>orthonormal</u>, i.e. $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, they form a complete orthonormal set.

Important theorem:

The eigenfunctions of a hermitian operator form a complete set.

So, if $\hat{O}\psi_n = e_n \psi_n$

Any function ψ can be written

$$\psi = \sum_n c_n \psi_n$$

Linearity of $\hat{O}$ implies

$$\hat{O}\psi = \sum_n c_n \hat{O}\psi_n = \sum_n c_n e_n \psi_n$$

The Physical Interpretation of the Formalism

- Let a physical system be in state described by ψ_n, and let $\hat{O}\psi_n = e_n\psi_n$

  Then <u>measurement</u> of observable corresponding to $\hat{O}$ invariably produces the result e_n.
  In other words: if the system is in an eigenstate of $\hat{O}$, then the physical variable corresponding to $\hat{O}$ has the well defined value e_n.

- Let a physical system be in a generic state ψ.
  Write ψ as linear combination of eigenfunctions of $\hat{O}$, $\psi_1, \dots \psi_n, \dots$

$$\psi(x,y,z) = \sum_n c_n \psi_n(x,y,z)$$

If a measurement of the physical variable is performed,

the possible results are:

e_1 with probability $|c_1|^2 / \sum_n |c_n|^2$

e_2 " " $|c_2|^2 / \sum_n |c_n|^2$

$\vdots$

e_i " " $|c_i|^2 / \sum_n |c_n|^2$

After measurement, with result e_i, the system is left in state ψ_i (Collapse / Reduction of wavefunction)

- Average of results of measurements of physical observable on many identical system in state ψ:

$\langle \psi | \hat{O} | \psi \rangle / \langle \psi | \psi \rangle$ " Expectation value"

Proof: Average is $\sum_i p_i e_i$, but $p_i = \dfrac{|c_i|^2}{\sum_n |c_n|^2}$.

Using orthogonality, can easily show this is $\langle \psi | \hat{O} | \psi \rangle / \langle \psi | \psi \rangle$.

The role of Energy

- In <u>classical physics</u>, a particle of mass m, moving in an external potential has energy which, when expressed as a function of its position and its momentum is

$$H = \frac{p^2}{2m} + V(x,y,z)$$

"Hamiltonian"

$\frac{p^2}{2m}$: Kinetic Energy

$V(x,y,z)$: Potential energy.

- The corresponding <u>quantum-mechanical</u> operator is

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2 \nabla^2}{2m} + V(x,y,z)$$

where $\hat{V}\,\psi(x,y,z) = V(x,y,z)\,\psi(x,y,z)$ (Multiplicative Operator)

- Generalization to system of N particles interacting among themselves with pair interaction (two-body force).

$$\hat{H} = \sum_{i=1,N} \frac{-\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{\substack{i=1,N \\ j=1,N}} V(\vec{r}_i, \vec{r}_j)$$

- Energy plays a very important role in Quantum Mechanics: it determines the time evolution of systems.

(Time-dependent) Schrödinger Equation:

$$i\hbar \frac{\partial}{\partial t} \psi(x,y,z,t) = \hat{H} \psi(x,y,z,t)$$

- Energy eigenstates.

- Suppose that at $t = 0$ $\psi(x, y, z, 0)$ is an eigen_ vector of $\hat{H}$. Then

$$\hat{H}\psi(x, y, z, 0) = E_n \psi(x, y, z, 0)$$

where E_n is one of the eigenvalues of $\hat{H}$.

- Then, at $t = 0$

$$i\hbar \frac{\partial}{\partial t} \psi(x, y, z, t)\Big|_{t=0} = \hat{H}\psi(x, y, z, 0) = E_n \psi(x, y, z, 0)$$

- Solution:

$$\psi(x, y, z, t) = \psi(x, y, z, 0)\, e^{-i \frac{E_n}{\hbar} t}$$

Verify: $i\hbar \frac{\partial}{\partial t} \psi(x, y, z, t) = \psi(x, y, z, 0)\, i\hbar \frac{\partial}{\partial t} e^{-i \frac{E_n}{\hbar} t} = E_n \psi(x, y, z, 0) e^{-i \frac{E_n}{\hbar} t}$

Consequence: for energy eigenstates time dependence is a phase factor.

$$|\psi(x,y,z,t)|^2 \equiv |\psi(x,y,z,0)|^2$$

$\Longrightarrow$ Probability distribution is constant in time

Energy eigenstates are called "stationary states"

N.B. $\psi(x,y,z,t)$ is an eigenstate of $\hat{H}$ at <u>all</u> times t!

- For generic state, write it as superposition of stationary states:

$$\psi(x,y,z,t) = \sum_n c_n(t)\psi_n(x,y,z)$$

Easy to prove, from Schrödinger's equation, that:

$$c_n(t) = c_n(0)\, e^{-i\frac{E_n}{\hbar}t}$$

i.e. $$\psi(x,y,z,t) = \sum_n c_n(0)\,\psi_n(x,y,z)e^{-i\frac{E_n t}{\hbar}} = \sum_n c_n(0)\psi_n(x,y,z,t)$$

One-dimensional motion examples

Assume particle of mass m bound to move on a line $\psi \equiv \psi(x)$

- Free particle (no potential)

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) \qquad -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

General Solution: $\psi(x) = Ae^{\alpha x}$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}Ae^{\alpha x} = -\frac{\hbar^2}{2m}\alpha^2 Ae^{\alpha x}$$

$$E = -\frac{\hbar^2}{2m}\alpha^2$$

However, if $\mathrm{Re}\,\alpha \neq 0$, $\psi(x)$ grows indefinitely either at $x \to \infty$ or at $x \to -\infty$: NOT ACCEPTABLE !

Therefore α must be purely imaginary, $\alpha = ik$

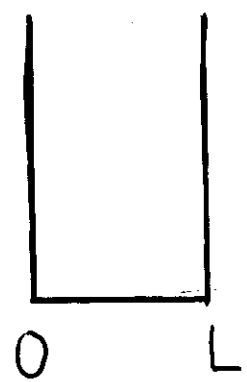
and $E = \frac{\hbar^2 k^2}{2m} > 0 \Rightarrow$ only positive E values

(cfr. to classical physics $T > 0$)

Note e^{ikx} and e^{-ikx} have same energy.

- Particle bound to move on a segment of length L, i.e. between $x = 0$ and $x = L$

$$\psi(x) = 0 \qquad x \geq L \,, \quad x \leq 0.$$



General solution inside $0 < x < L$:

$$e^{ikx} + A e^{-ikx}$$

$\psi(0) = 0 \Rightarrow A = -1 \qquad \psi(x) = 2i \sin kx$

or $\psi(x) = \sin kx$

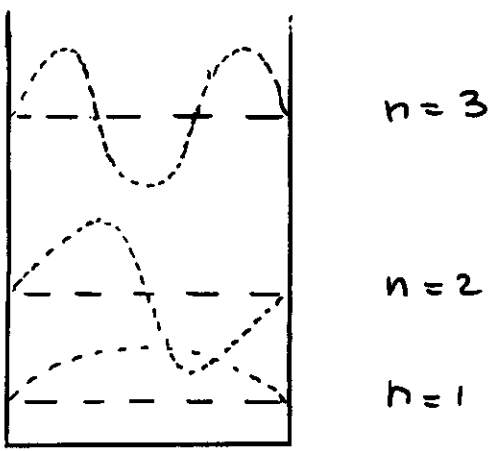
$\psi(L) = 0 \Rightarrow \sin kL = 0$ or $kL = n\pi \quad n = 1, 2, \ldots$

Therefore: $\psi(x) = \sin kx$

Allowed k values $\quad k = \frac{n\pi}{L} \qquad n = 1, 2, \ldots$

Allowed E $\quad E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$

Quantization of energy!



Comments: $E \propto n^2$

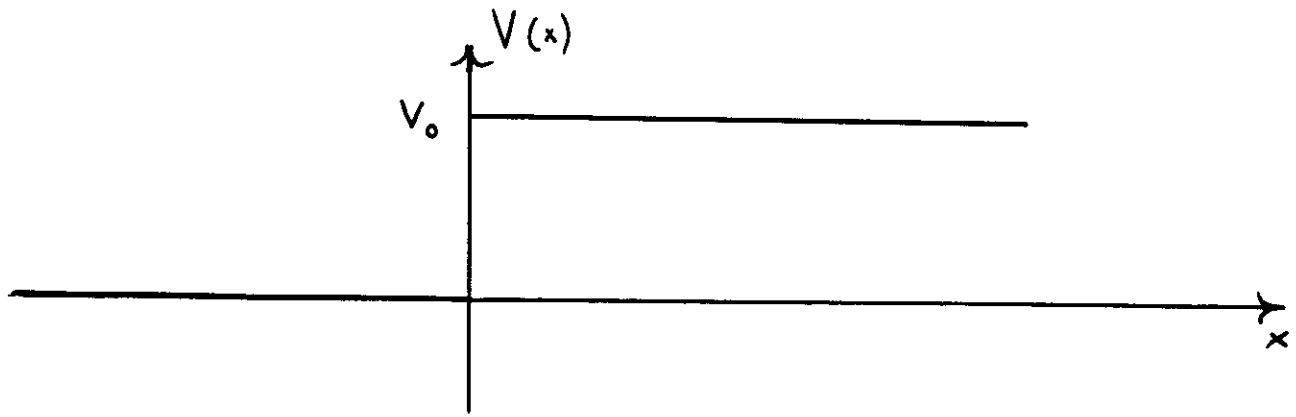
ψ odd or even

# of nodes = $n - 1$

- Potential step

$V(x) = 0 \qquad x < 0$

$V(x) = V_0 \qquad x > 0$



$E < 0$ no solution (wavefunction unbound

$0 < E < V_0$ $\quad x<0: \ \psi(x) \sim e^{ikx} + Ae^{-ikx}$ $\qquad E = \frac{\hbar^2 k^2}{2m}$; $k = \sqrt{\frac{2mE}{\hbar^2}}$

$x>0 \ \ \psi(x) \sim Ce^{-\kappa x}$ $\qquad \kappa = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$

↑ always ≤ 1 for $x \geq 0$!

Coefficients A, C, determined by conditions at $x=0$:

$\psi(x)$ continuous, $\frac{d\psi(x)}{dx}$ continuous;

$$1 + A = C \qquad \text{continuity of } \psi$$

$$ik(1-A) = -\kappa C \qquad \text{continuity of } \frac{d\psi}{dx}$$

$$\Rightarrow \quad ik(1-A) = -\kappa(1+A)$$

$$A = -\frac{\kappa + ik}{\kappa - ik} \qquad C = 1 + A$$

Note: particle in classically forbidden region !!!

$E > V_0$

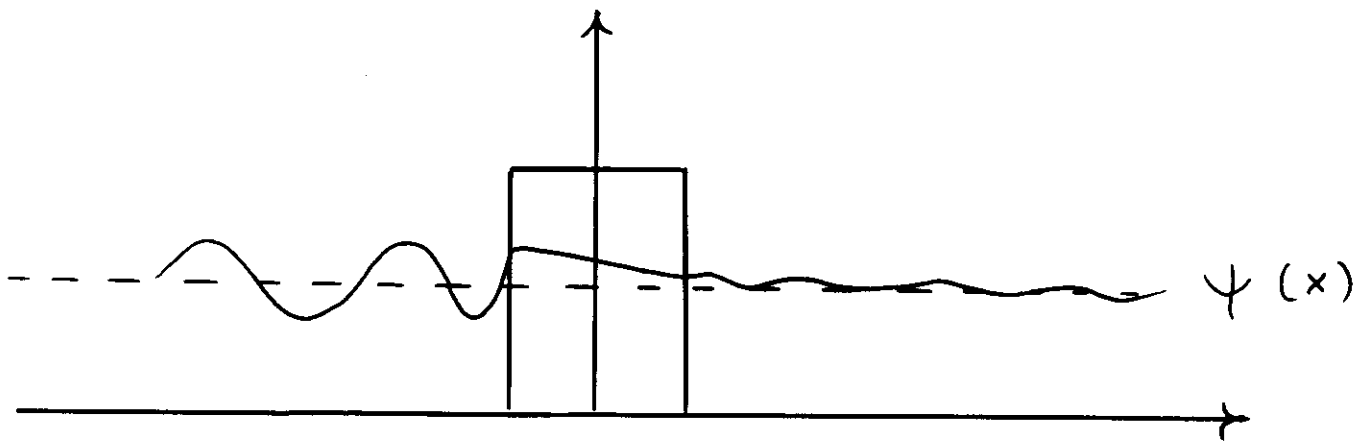
$x < 0 \quad \psi \sim e^{ikx} + Ae^{-ikx}$

$x > 0 \quad \psi \sim Ce^{ik'x}$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$k' = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$$

Tunneling:



Particle can access classically forbidden region, it is only exponentially damped.

If barrier is finite, it can "tunnel" through and be observable on the right side of the barrier!!

• Harmonic Oscillator

Particle of mass m attracted to $x=0$ by a force proportional to x, i.e. potential energy proportional to x^2:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}\underbrace{m\omega^2}_{\rightarrow k,\ \text{spring constant}} x^2$$

Solutions of $\hat{H}\psi(x) = E\psi(x)$

Eigenvalues: $E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2, \ldots$

Note: Minimum energy $\frac{1}{2}\hbar\omega$

"zero-point" motion!

Eigenfunction of energy E_n:

Def. $q = \sqrt{\frac{m\omega}{\hbar}}\, x$

$$\psi_n(x) = H_n(q)\, e^{-q^2/2}$$

↑ Hermite polynomial

$H_0(q) = 1$

$H_1(q) = 2q$

$H_2(q) = 4q^2 - 2$

$H_3(q) = 8q^3 - 12q$

⋮

$$\frac{dH_n}{dq} = 2n\, H_{n-1}(q)$$

Comment:

# of nodes = n

Even and odd solutions around $x = 0$ alternate with n.

- Generalization to 3 dimensional oscillator easy!

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2} m\omega^2(x^2 + y^2 + z^2)$$

Separable:

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

$$\hat{H}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2$$

Then $\psi(x,y,z) \sim \psi(x)\psi(y)\psi(z)$

Let $\psi(x) = \psi_{n_x}(x)$ $\psi(y) = \psi_{n_y}(y)$ $\psi(z) = \psi_{n_z}(y)$

Then $\hat{H}\psi(x,y,z) = \left(n_x + n_y + n_z + \frac{3}{2}\hbar\omega\right)\psi(x,y,z)$

Comment: degeneracy: there are many different triplets of numbers n_x, n_y, n_z with the same sum $N = n_x + n_y + n_z$

Three-dimensional Central Potentials.

General problem of particle moving in a potential in three-dimensions:

$$\hat{H}\psi(x,y,t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]\psi(x,y,t) = E\psi(x,y,t)$$

An important class of potentials are those with rotation invariance:

$$V(x,y,z) = V\left(\sqrt{x^2+y^2+z^2}\right) = V(r)$$

Examples:

Coulomb potential	$\frac{Ze^2}{r}$
3-dim. isotropic oscillator	$\frac{1}{2}m\omega^2 r^2$
etc.	

General Structure of Solutions for Central Potential

$$\hat{H}\,\psi_{n,\ell,m} = E_{n,\ell}\,\psi_{n,\ell,m}$$

To describe structure of $\psi_{n,\ell,m}(x,y,z)$ use spherical coordinates $x,y,z \longrightarrow r,\theta,\varphi$.

Then $$\psi_{n,\ell,m}(r,\theta,\varphi) = f_{n\ell}(r)\,Y_{\ell m}(\theta,\varphi)$$

- n: principal quantum number
- $\hat{\ell}^2 \to \ell(\ell+1)\hbar^2$
- $\hat{\ell}_z \to m\hbar$
- $f_{n\ell}(r)$: radial function
- $Y_{\ell m}(\theta,\varphi)$: spherical harmonic

Define: $$\chi_{n\ell}(r) = r\,f_{n\ell}(r)$$

Then: $$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]\chi_{n\ell}(r) = E_{n,\ell}\,\chi_{n\ell}(r)$$

"Radial equation"

A two-body central force problem: the H atom.

$M \sim 1850\, m$

$M, +e$ Proton

$m, -e$ Electron

$$\hat{H} = \frac{-\hbar^2}{2M}\nabla_P^2 - \frac{\hbar^2}{2m}\nabla_E^2 - \frac{e^2}{|\vec{r}_P - \vec{r}_E|}$$

Transform to centre of mass and relative coordinates:

$$\vec{R} = \frac{M\vec{r}_P + m\vec{r}_E}{M+m} \quad ; \quad \vec{r} = \vec{r}_P - \vec{r}_E \quad ; \quad \frac{1}{m^*} = \frac{1}{M} + \frac{1}{m}$$

$$\hat{H} = \frac{-\hbar^2}{2(m+M)}\nabla_R^2 - \frac{\hbar^2}{2m^*}\nabla_r^2 - \frac{e^2}{r} = \hat{H}_R + \hat{H}_r$$

$\hat{H}_R$: free particle motion of the whole atom

$\hat{H}_r$: relative

Note: for H atom $\frac{1}{m^*} = \frac{1}{M} + \frac{1}{m} \approx \frac{1}{m}$ because $M \gg m$

Solution of $(\hat{H}_R + \hat{H}_r)\Psi(\vec{R}, \vec{r}) = E\,\Psi(\vec{R}, \vec{r})$

$\Psi(\vec{R}, \vec{r}) = \Psi(\vec{R})\,\psi(\vec{r})$ $\qquad$ $\Psi(\vec{R}) = e^{i\vec{K}\cdot\vec{R}}$

Determine $\psi(\vec{r})$ by solving:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} \right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

↖ Central Potential

$$\psi(\vec{r}) = \psi_{n\ell m}(\vec{r}) = f_{n\ell}(r)\,Y_{\ell m}(\theta, \varphi)$$

$\frac{me^4}{2\hbar^2} = 13.6$ eV Rydberg constant.

$E < 0$ $\qquad$ $n = 1, 2, \ldots$ $\qquad$ $E = -\frac{me^4}{2\hbar^2}\frac{1}{n^2}$ $\qquad$ E independent of ℓ!!

$\ell = 0, 1, \ldots n-1$

$m = -\ell, -\ell+1, \ldots, 0, \ldots \ell$

$E > 0$ $\qquad$ $n = ik$ $\qquad$ $E = \frac{\hbar^2 p^2}{}$

degenerate and contains one 2s state and three 2p states; the second-excited state is nine-fold degenerate and contains one 3s state, three 3p states and five 3d states; and so forth (Fig. XI.1).

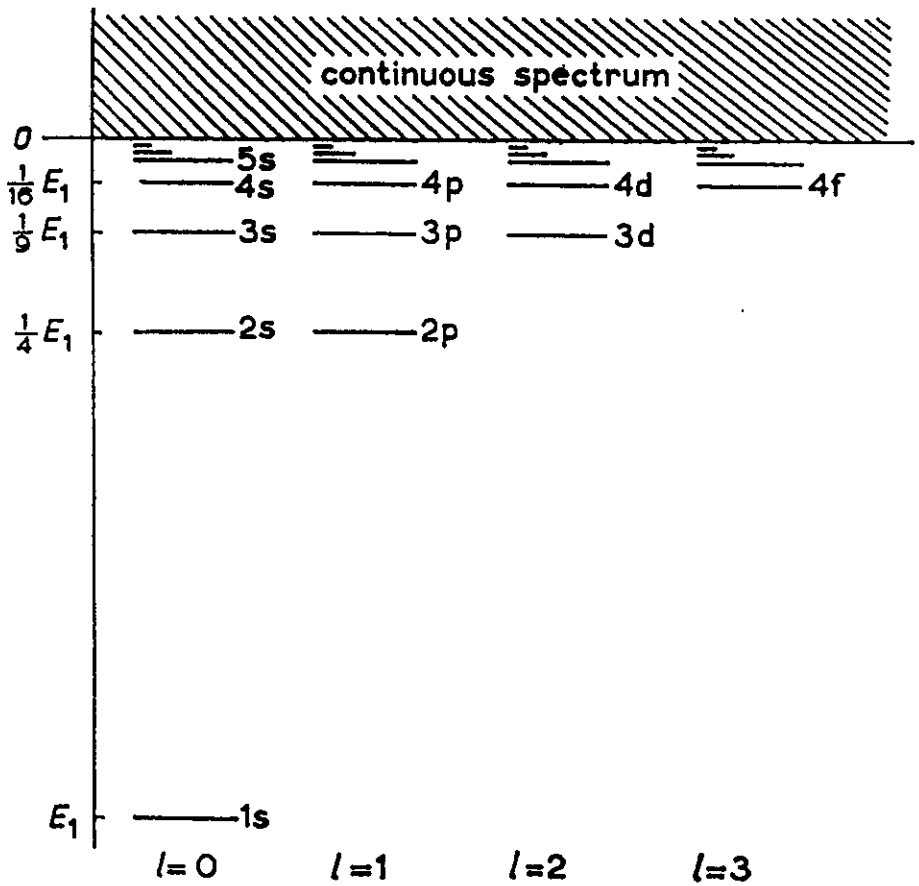


Fig. XI.1. Spectrum of the hydrogen atom.

Eigenfunctions of the H atom. Discrete Spectrum.

$$\psi_{n\ell m}(\vec{r}) = f_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

$$f_{n\ell}(r) = \sqrt{\frac{4(n-\ell-1)!}{a^3 n^4 [(n+\ell)!]^3}} \cdot e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^{\ell} L_{n+\ell}^{(2\ell+1)}\left(\frac{2r}{na}\right)$$

where

$$a = \frac{\hbar^2}{me^2} = 0.529 \times 10^{-8}\ \text{cm} \qquad \text{Bohr radius}$$

$$L_{n+\ell}^{(2\ell+1)}(x) = \frac{d^{(2\ell+1)}}{dx^{(2\ell+1)}} L_{n+\ell}(x)$$

$L_{n+\ell}(x)$ = Laguerre Polynomial

$L_0 = 1$, $L_1 = 1 - x$, $L_2 = 2 - 4x + x^2$

$L_3 = 6 - 18x + 9x^2 - x^3$ ....

Commutation Relation for Operators

- We already know product of 2 operators:

  $\hat{O}_1 \cdot \hat{O}_2$ is the operator which acts on ψ in the following way:

$$\hat{O}_1 \hat{O}_2 \psi = \hat{O}_1 \cdot [\hat{O}_2 \psi]$$

- In general operator product is non-commutative, i.e. $\hat{O}_1 \cdot \hat{O}_2 \neq \hat{O}_2 \cdot \hat{O}_1$

- Definition: Commutator of $\hat{O}_1$ and $\hat{O}_2$

$$[\hat{O}_1, \hat{O}_2] = \hat{O}_1 \hat{O}_2 - \hat{O}_2 \hat{O}_1$$

- Example $[\hat{x}, \hat{p}_x] = [x, -i\hbar \frac{\partial}{\partial x}]$

Consider

$$\hat{x}\,\hat{p}_x\,\psi(x,y,z) = x \cdot -i\hbar\frac{\partial}{\partial x}\psi = -i\hbar\, x\frac{\partial}{\partial x}\psi$$

$$\hat{p}_x\,\hat{x}\,\psi(x,y,t) = -i\hbar\frac{\partial}{\partial x}\left(x\,\psi(x,y,z)\right) = -i\hbar\,\psi(x,y,z) - i\hbar\, x\frac{\partial}{\partial x}\psi$$

$$[\hat{x},\hat{p}_x]\,\psi = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\,\psi = i\hbar\,\psi(x,y,z)$$

Therefore: $[\hat{x},\hat{p}_x] = i\hbar$

- Some useful properties of commutators:

$$[\hat{O}_1,\hat{O}_2] = -[\hat{O}_2,\hat{O}_1]$$

$$[\hat{O}_1,\hat{O}_2\hat{O}_3] = [\hat{O}_1,\hat{O}_2]\,\hat{O}_3 + \hat{O}_2[\hat{O}_1,\hat{O}_3]$$

Physical Meaning of Commutators:

- Theorem

  Two operators which commute have a common complete set of eigenvectors, i.e. they correspond to observables which have precisely defined values in the same physical state.

- Example

  x and y commute $[\hat{x}, \hat{y}] = 0$

  A particle can have perfectly defined simultaneous x and y positions.

  However $[x, p_x] = i\hbar$

  and there is no state in which both x and p_x are measurable with arbitrary precision.

Uncertainty Relations (Heisenberg)

- Definition: for observable $\hat{O}$, the uncertainty in state ψ is defined as

$$\Delta \hat{O} = \sqrt{\langle (\hat{O} - \langle \hat{O} \rangle)^2 \rangle}$$

where $\langle \cdots \rangle$ denotes the expectation (average) value in state ψ

- Theorem:

If $[\hat{O}_1, \hat{O}_2] = i\hbar$

then, for their uncertainty in any state it is:

$$\Delta O_1 \cdot \Delta O_2 \geq \frac{1}{2}\hbar$$

- For example $\Delta x \, \Delta p_x \geq \frac{1}{2}\hbar$

Commutators of Angular Momenta

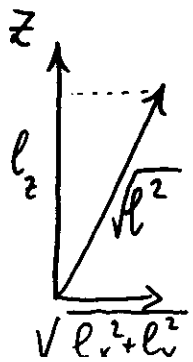
- $\vec{\ell} = \vec{r} \times \vec{p}$:

$$\ell_x = y p_z - z p_y$$
$$\ell_y = z p_x - x p_z$$
$$\ell_z = x p_y - y p_x$$
$$\ell^2 = \ell_x^2 + \ell_y^2 + \ell_z^2$$

$$[\hat{\ell}_x, \hat{\ell}_y] = i\hbar \hat{\ell}_z \qquad [\hat{\ell}_z, \hat{\ell}_x] = i\hbar \hat{\ell}_y \qquad [\hat{\ell}_y, \hat{\ell}_z] = i\hbar \hat{\ell}_x$$

$$[\hat{\ell}^2, \hat{\ell}_x] = [\hat{\ell}^2, \hat{\ell}_y] = [\hat{\ell}^2, \hat{\ell}_z] = 0$$

- Comment. When $\hat{\ell}^2$ is in eigenstate with eigenvalue $\hbar^2 \ell(\ell+1)$, ℓ_z^2 is at most $\ell^2\hbar^2$

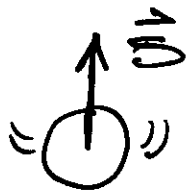


This is because ℓ_x and ℓ_y are not precisely defined so $\ell_x^2 + \ell_y^2 = \ell^2 - \ell_z^2$ cannot be zero!

A Quantum Observable without Classical Analogue: SPIN

- Electrons, besides orbital angular momentum $\vec{\ell} = \vec{r} \times \vec{p}$ have an intrinsic angular momentum called "Spin" with one allowed value for its square, $S^2 = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2$ and two allowed values for its components, i.e. $S_z = +\frac{1}{2}\hbar$ or $S_z = -\frac{1}{2}\hbar$ ("spin up" or "spin down")

- Helpful (but sometimes dangerous!) to think of electron as a "spinning top"



- Complete description of electron state must include spin. General superposition:

$$\psi(x,y,z)\,(\text{spin up}) \;+\; \varphi(x,y,z)\,(\text{spin down})$$

$\psi(x,y,z)$: prob. of presence of electron at x,y,z, with spin up...

$\varphi(x,y,z)$: ... and with spin down!

- Write this wavefunction as "two-component spinor"

i.e. $$\begin{bmatrix}\psi(x,y,z)\\ \varphi(x,y,z)\end{bmatrix} = \psi(x,y,z)\begin{bmatrix}1\\0\end{bmatrix} + \varphi(x,y,z)\begin{bmatrix}0\\1\end{bmatrix}$$

- In this "two-component" spinor representation, operators become 2×2 matrices.

  In particular:

$$S_x = \frac{1}{2}\hbar\sigma_x \quad , \quad S_y = \frac{1}{2}\hbar\sigma_y \quad , \quad S_z = \frac{1}{2}\hbar\sigma_z$$

  where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} ; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} ; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

  "Pauli Matrices"

- Easy to verify: S_x, S_y, S_z have same commutators as l_x, l_y, l_z

All elementary or composite particles have spin.

- If spin is half-integer (electrons, protons, neutrons, He^3 nuclei, all with $S = 1/2$) the particles are called Fermions

- If spin is integer (Photons, $S = 1$; He^4 nuclei, $S = 0$, etc.) the particles are called Bosons.

Permutation properties of wavefunctions of identical particles:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N) = (-1)^P \Psi(P(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)) \quad \text{Fermions}$$

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \Psi(P(\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)) \quad \text{Bosons}$$

For fermions, this property implies the Pauli exclusion principle:

- Suppose you have two electrons, one in state a, the other in state b:

  Most general wavefunction: $\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)$
  (a and b spinors!)

  But if a, b are the same state, $\underline{\Psi \to 0}$

  Not possible to occupy one state (incl. spin!) with more than one electron

Approximate Methods of Solution.

1. The Variational Method

Based on following

- **Theorem:** Let ψ_0 be ground state wavefunction of Hamiltonian $\hat{H}_0$, i.e. $\hat{H}_0\psi_0 = E_0\psi_0$, with E_0 smallest eigenvalue of H_0. Then for any ψ:

$$\frac{\langle\psi|H_0|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 \qquad \text{and} = E_0 \text{ only for } \psi = \psi_0.$$

- Take a wavefunction family, characterized by parameter p, $\psi(x,y,z,p)$ and look for minimum of

$$\frac{\langle\psi(p)|H_0|\psi(p)\rangle}{\langle\psi(p)|\psi(p)\rangle}, \quad \text{as a function of } p.$$

This is the best approximation to E_0 and ψ_0

2. Perturbation Theory.

Let a problem be characterized by hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$ with $\hat{H}'$ "small" compared to $\hat{H}_0$.

Let all eigenfunctions and eigenvalues of $\hat{H}_0$ be known: $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$

We want to determine ground state eigenvalue E_0 and wavefunction ψ_0 of $\hat{H}$.

It is:

$$E_0 \simeq E_0^{(0)} + \langle \psi_0^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle + \sum_{n \neq 0} \frac{| \langle \psi_0^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle |^2}{E_0^{(0)} - E_n^{(0)}}$$

$$\Psi_0 = \Psi_0^{(0)} + \sum_{n \neq 0} \frac{\langle \Psi_n^{(0)} | \hat{H}' | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}} \Psi_n^{(0)}$$

If $\Psi_0^{(0)}$ is degenerate, however, with eigenvectors

$$\Psi_{01}^{(0)}, \cdots, \Psi_{0n}^{(0)}$$

Then one must find the eigenvalues of matrix

$$H'_{ij} = \langle \Psi_{0i}^{(0)} | H' | \Psi_{0j}^{(0)} \rangle$$

which give correction to (and splitting from) unperturbed value $E_0^{(0)}$

Periodic Perturbations / Fermi's Golden Rule.

- Consider again case in which $\hat{H} = \hat{H}_0 + \hat{H}'$ but now assume $\hat{H}'$ is a <u>periodic</u> <u>perturbation</u>, i.e. it has a time dependence of the form

$$\hat{H}'(t) = \hat{H}'(0)\left(e^{i\omega t} + \text{c.c.}\right)$$

- Examples: the electric field of an EM wave of frequency ω

  the perturbation of the distance and the interaction between atoms caused by an ultrasonic pulse.

- The perturbation can induce <u>transitions</u> between stationary states of $\hat{H}_0$, with energy difference $\pm\hbar\omega$.

- The number of transitions per unit time dN/dt is given by Fermi's "Golden Rule"

$$\frac{dN}{dt} = \frac{2\pi}{\hbar} \sum_f |\langle \psi_0 | \hat{H}'(0) | \psi_f \rangle|^2 \, \delta(E_f - E_0 \pm \hbar\omega)$$

- $\sum_f$: sum over all possible final states
- ψ_0: initial state
- ψ_f: final state
- $\delta(E_f - E_0 \pm \hbar\omega)$: conservation of energy. $+\hbar\omega$ is <u>absorption</u> of one quantum $-\hbar\omega$ is <u>emission</u>

- Case of electromagnetic waves: absorption and emission of photons by atoms.

$$\hat{H}' = \sum_i \vec{A} \cdot \vec{p}_i$$

$\sum_i$: sum over all electrons

$\vec{A}$: vector potential of the radiation

$$\vec{A} = \vec{\epsilon} \cdot \left(e^{i\vec{k}\cdot\vec{r}} \, e^{i\omega t} + \text{c.c.} \right)$$

$\vec{\epsilon}$: polarization vector

Multipole expansion:

$$e^{i\vec{k}\cdot\vec{r}} \sim 1 + i\vec{k}\cdot\vec{r} + \dots$$

1 : electric dipole

$i\vec{k}\cdot\vec{r}$: electric quadrupole + magnetic dipole ...

- Dipole Approximation (Wavelength longer than dimension of atomic wavefunctions)

$$e^{i\vec{k}\cdot\vec{r}} \sim 1$$

$$H'(t) = \vec{\epsilon}\cdot\vec{p}\left(e^{i\omega t} + c.c.\right)$$

$$\frac{dN}{dt} = \frac{2\pi}{\hbar}\sum_f |\langle\psi_0|\vec{\epsilon}\cdot\vec{p}|\psi_f\rangle|^2\,\delta(E_f - E_0 \pm \hbar\omega)$$

$+$ = absorption
$-$ = emission

- Selection rules for transition between one-electron states:

$$\langle\psi_{n\ell m}|\vec{\epsilon}\cdot\vec{p}|\psi_{n'\ell'm'}\rangle \neq 0 \quad \text{if}$$

$\Delta\ell = \ell' - \ell = \pm 1$

$\Delta m = m' - m$ depends on polarization $\vec{\epsilon}$

Δn unrestricted