

Quantum Mechanics

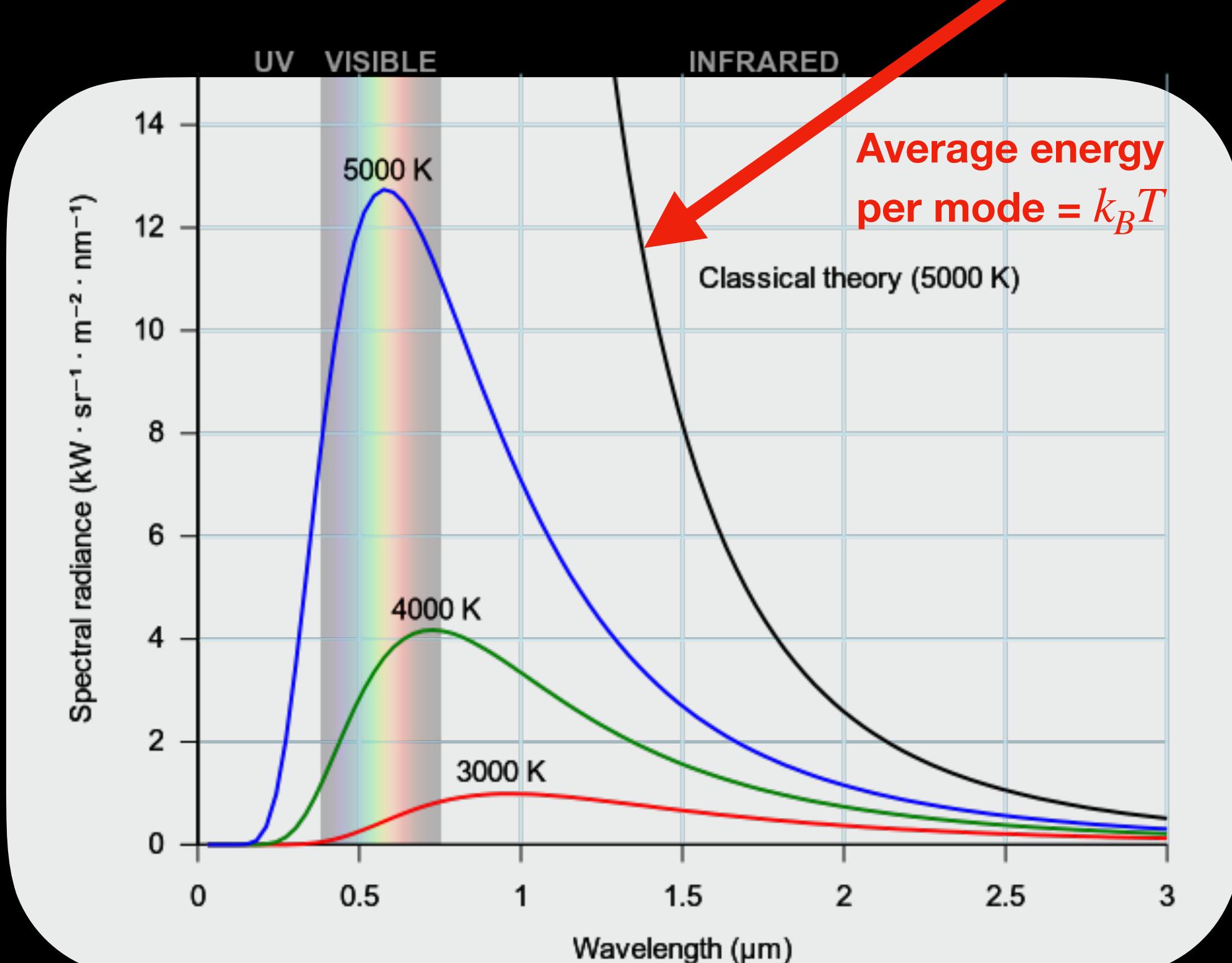
aka
Magic!

Why Quantum?

Blackbody Radiation: Ultraviolet Catastrophe

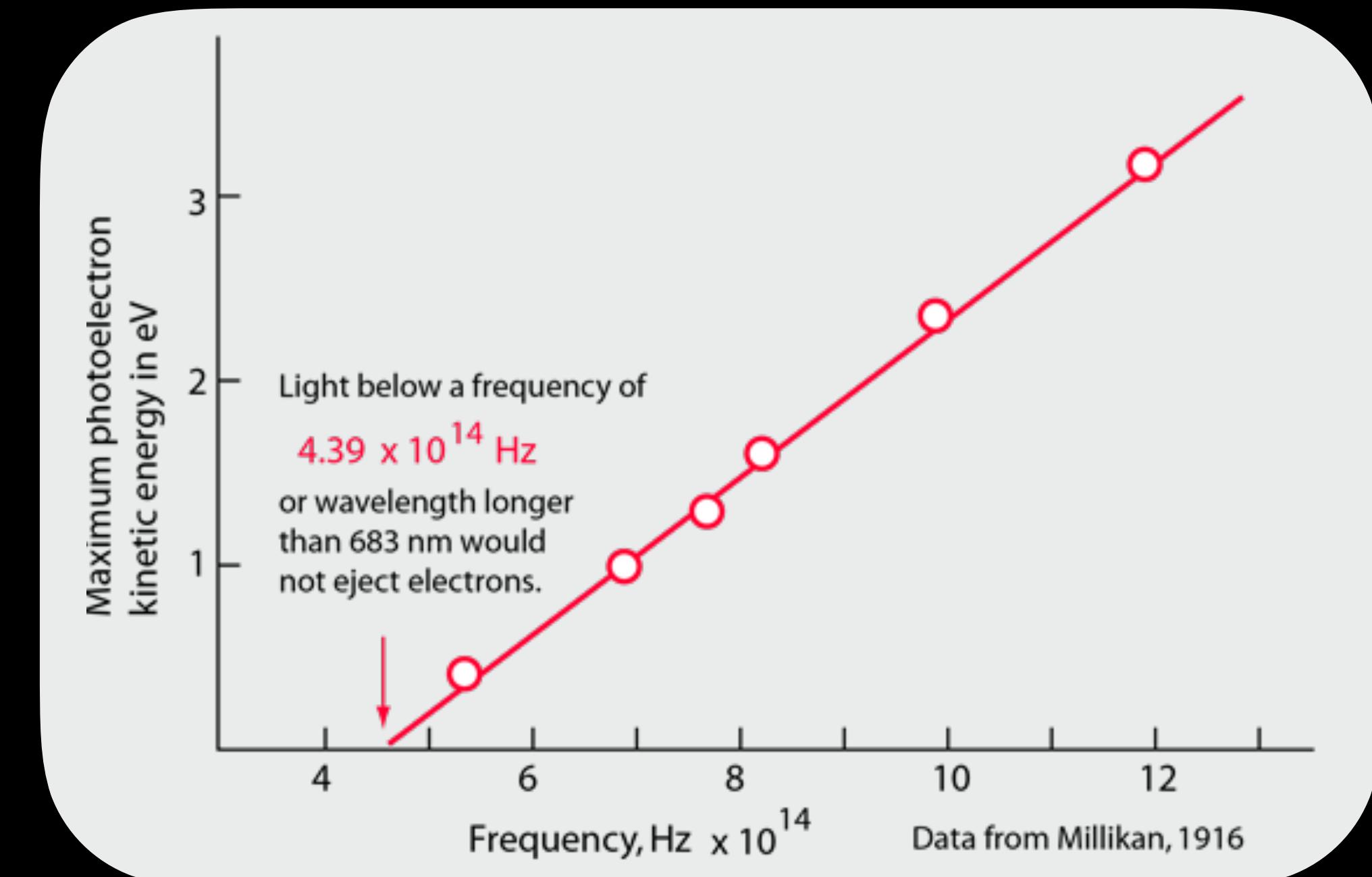
The number of independent standing waves inside a cavity

$$g(\nu)d\nu = \frac{8\pi\nu^2}{c^3}d\nu \quad \text{Rayleigh-Jeans Formula}$$



Wikipedia

Photoelectric Effect



hyperphysics.phy-astr.gsu.edu

Davisson-Germer electron diffraction experiment

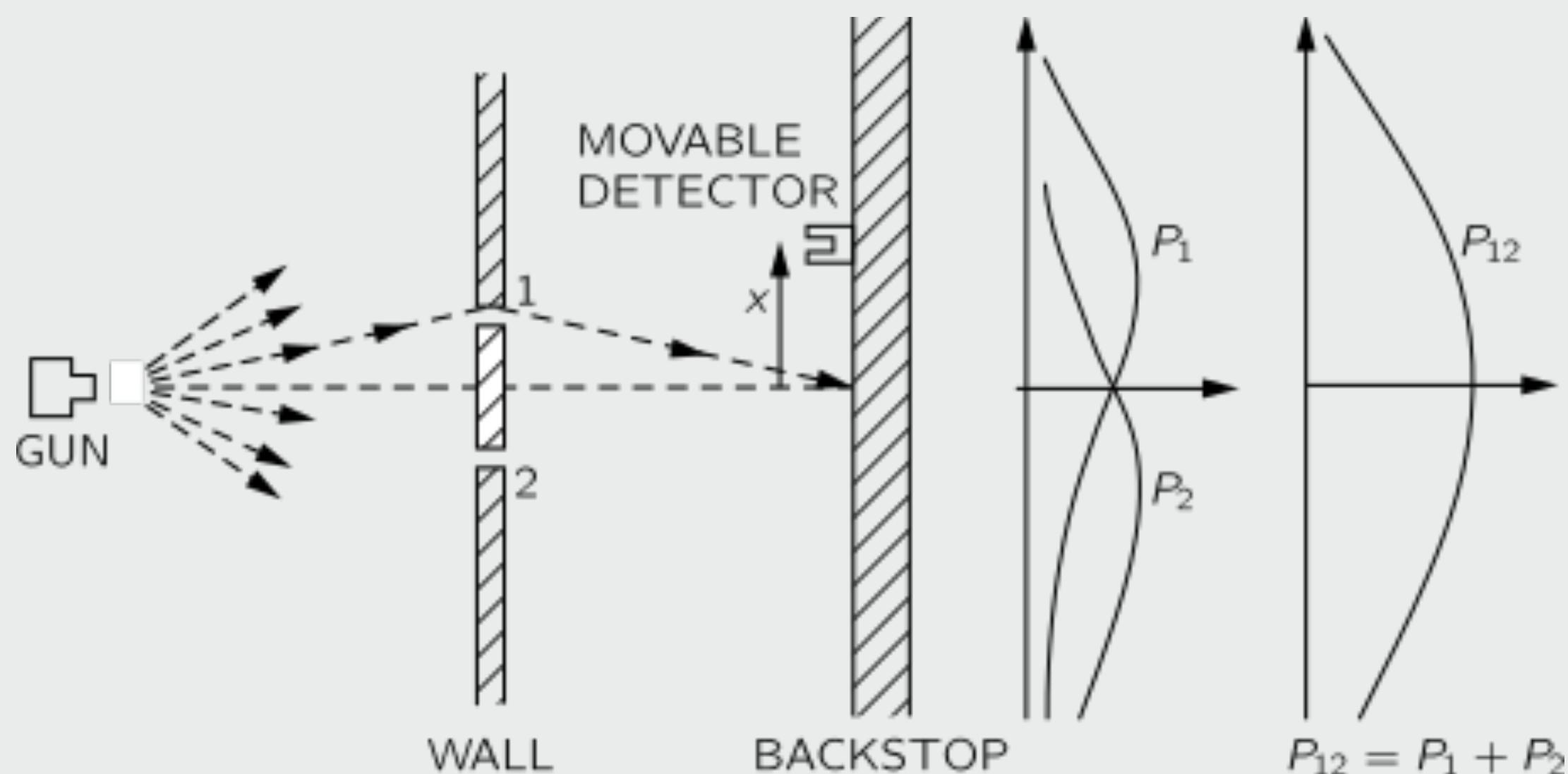
Stability of atomic orbitals

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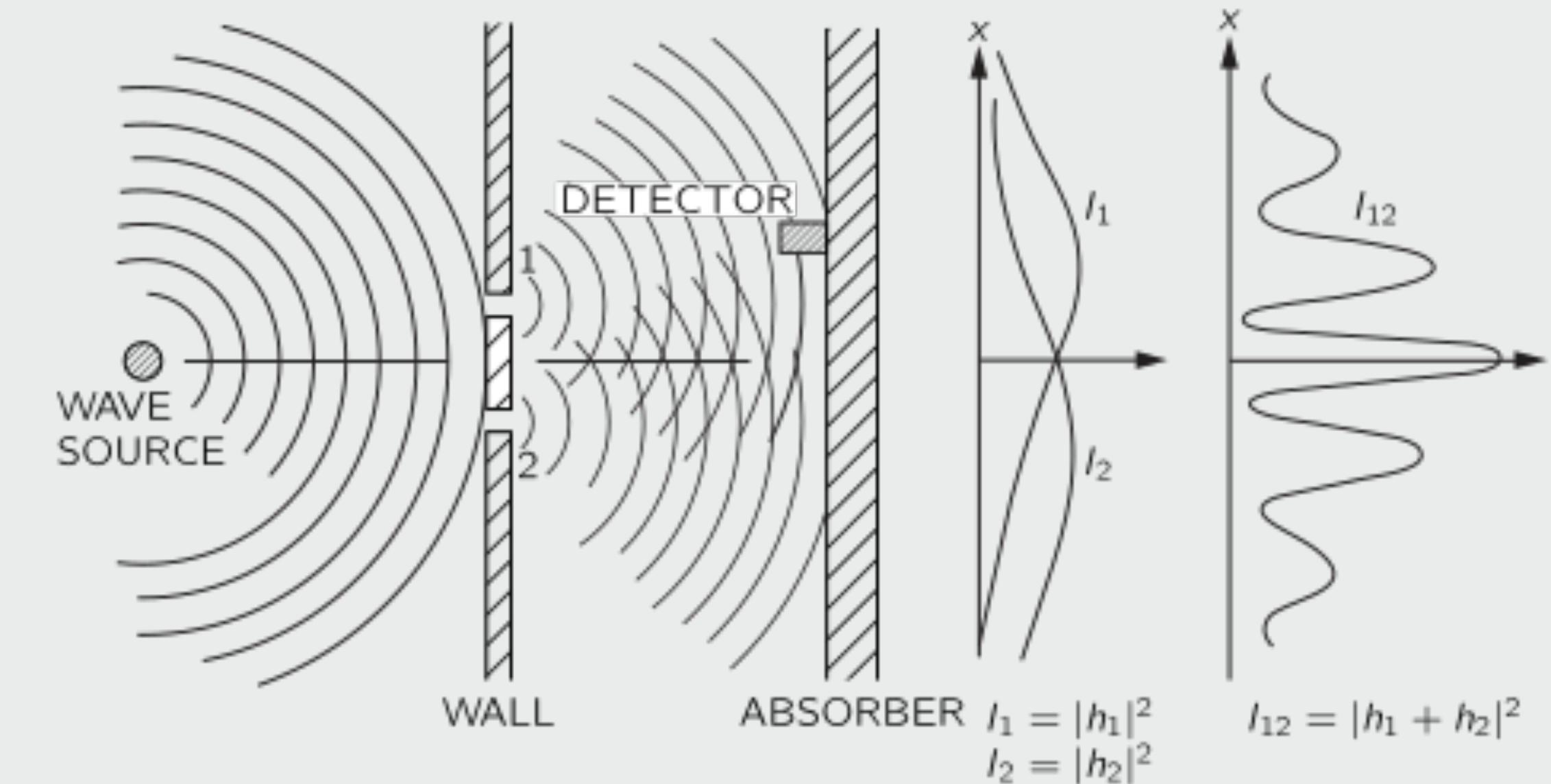
Bullets vs Waves

Feynman Lectures

An experiment with bullets



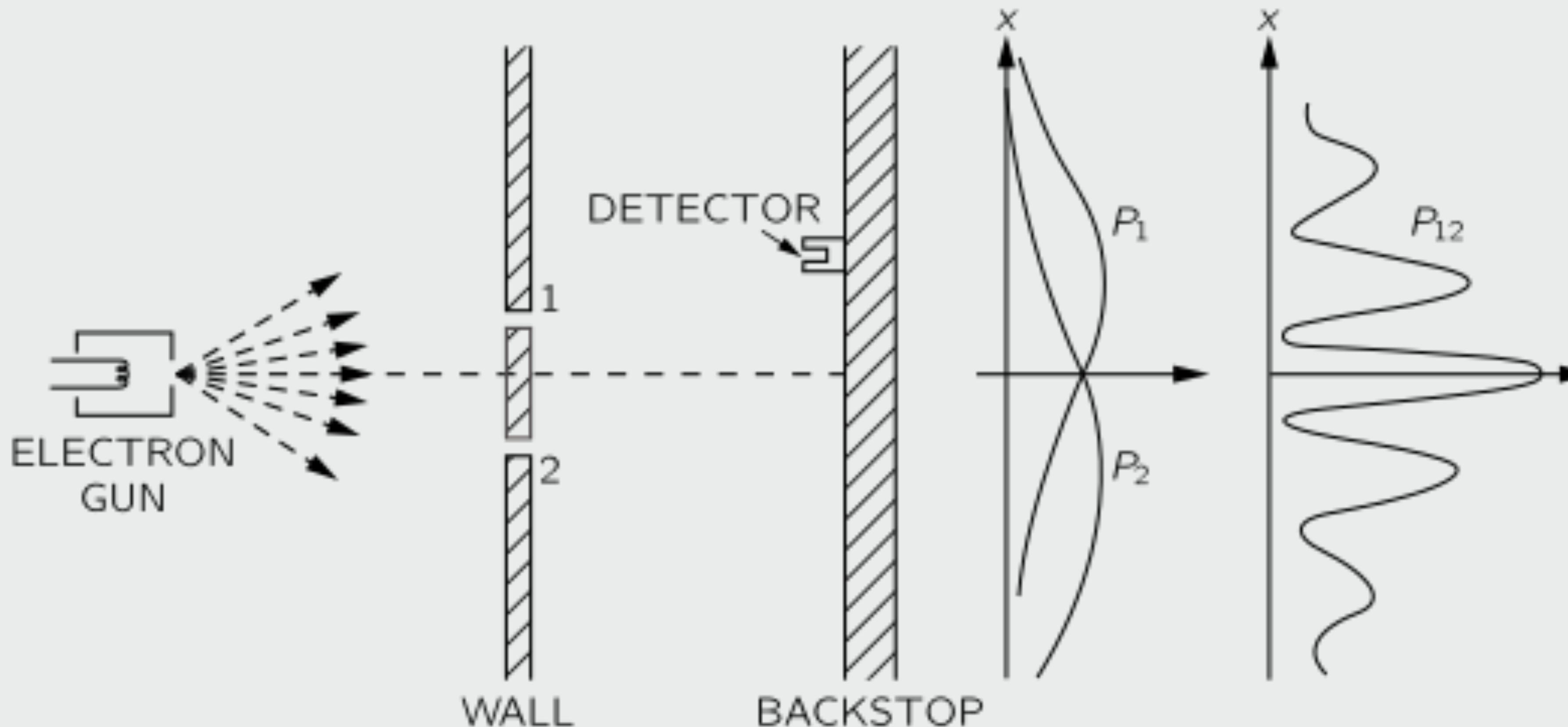
The same experiment with waves



Enter Electrons

Feynman Lectures

The same experiment with electrons



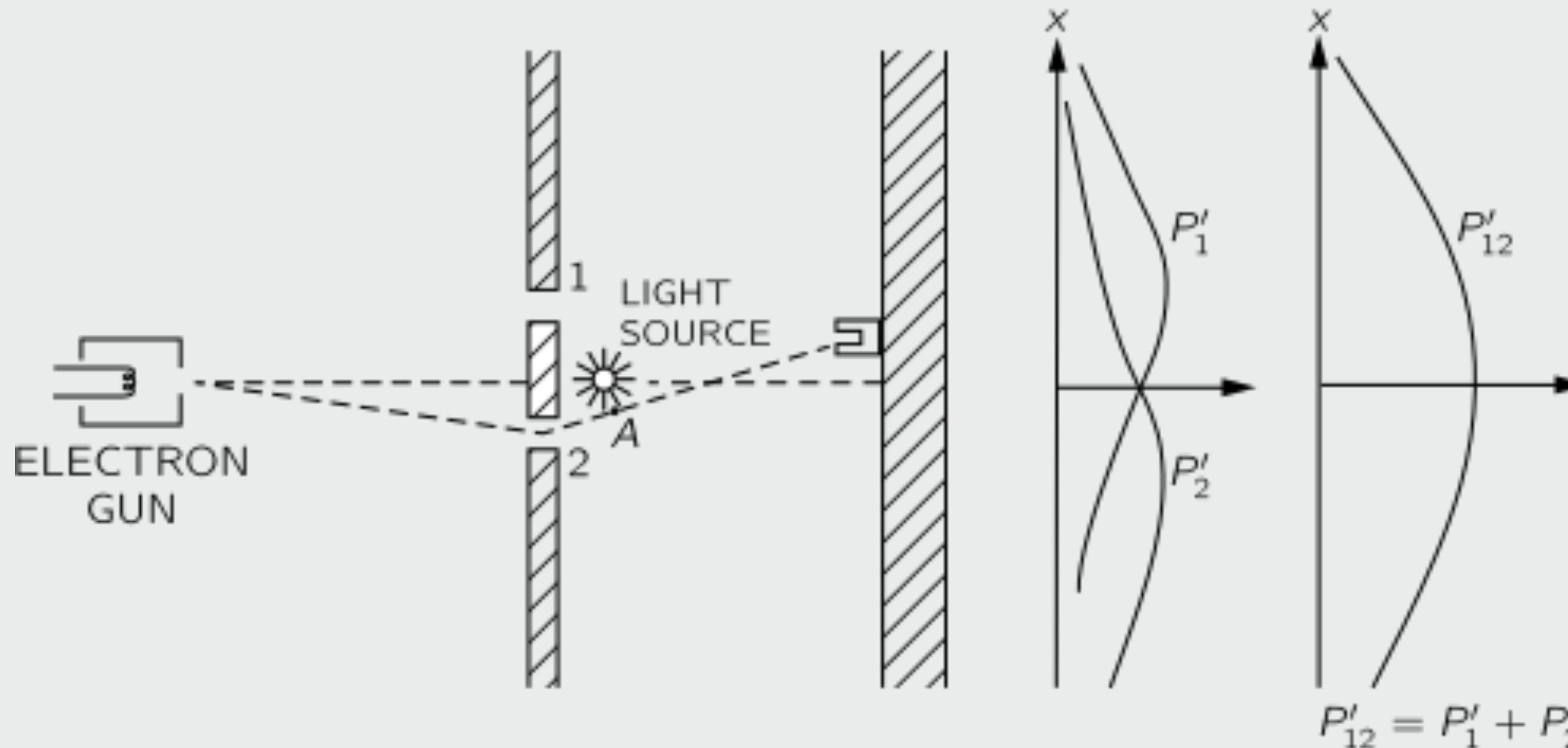
The definition of probability is not changed, but the method to calculate it is completely different

$P_{12} \neq P_1 + P_2$. The two probabilities, P_1 and P_2 are related to two complex numbers

The Ways of Electrons

Feynman Lectures

Which hole?



When we watch them $P_{12} = P_1 + P_2$

Curiouser

Feynman Lectures / Feynman, Hibbs

We are changing the pattern on the screen just by watching the electrons. How is this possible?

To watch them we used light. When an electron collides with a photon its chance of arrival at the detector is possibly altered.

Can we use weaker light and thus expect a weaker effect? A negligible disturbance certainly cannot be presumed to produce the finite change in the distribution.

Light comes in photons of energy $\hbar\nu$ or of momentum \hbar/λ . Weakening the light just means using fewer photons so that we may miss seeing an electron.

The electrons we miss are distributed according to the interference law, while those we do see (and which therefore have scattered a photon) arrive at the detector with the probability $P_{12} = P_1 + P_2$

It might still be suggested that weaker effects could be produced by using light of longer wavelength. But there is a limit to this. If light of too long a wavelength is used, we will not be able to tell whether it was scattered from hole 1 or hole 2.

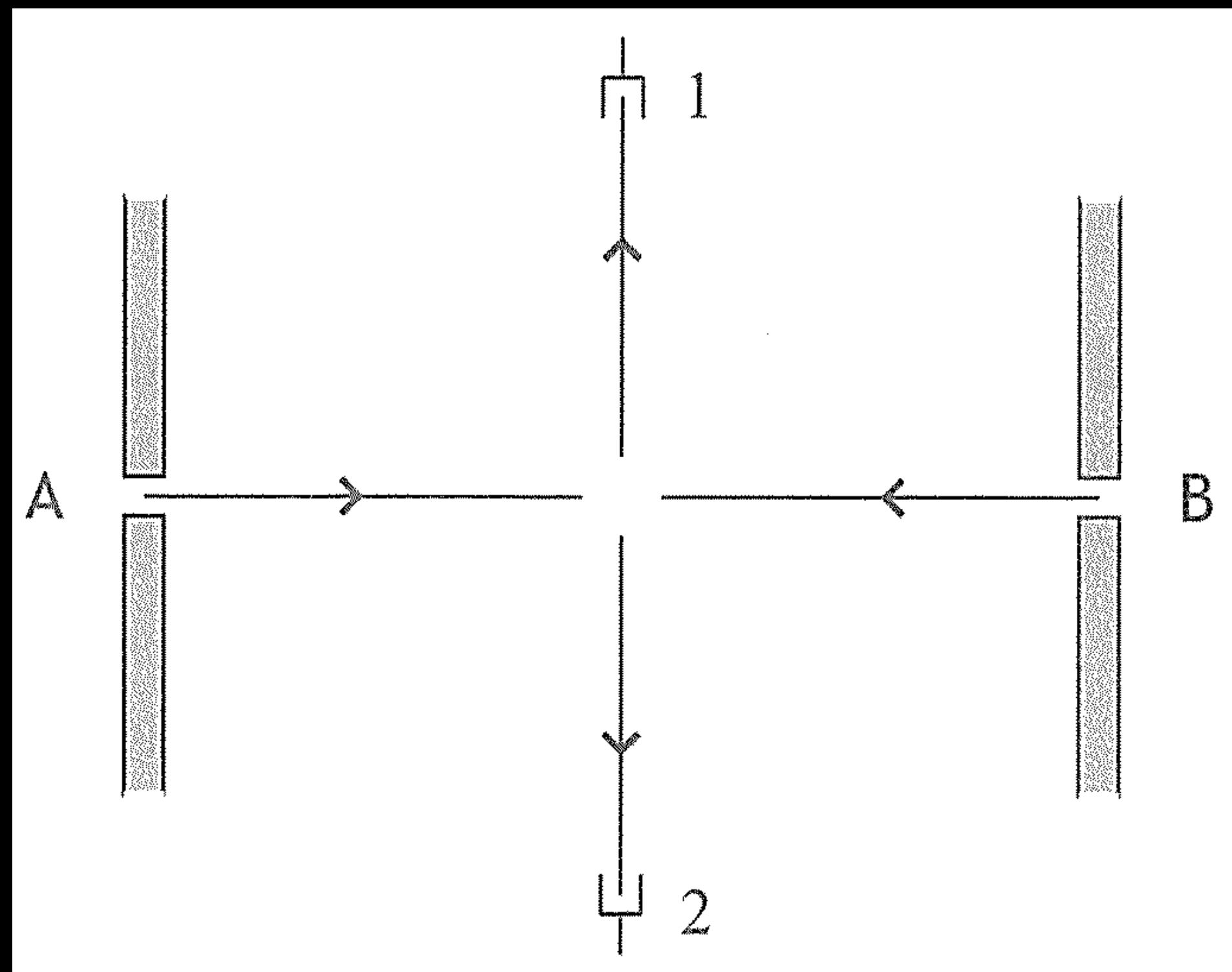
... and Curiouser!

Feynman, Hibbs

The uncertainty principle

Any determination of the alternative taken by a process capable of taking more than one alternatives destroys the interference between alternatives.

- Feynman's qualitative formulation of the uncertainty principle



Let the amplitude of scattering for the particle to start from A and end up at 1 (and the one to start from B and end up at 2) be $\alpha(1,A)$ so that the probability is $p = |\alpha(1,A)|^2$. This is also equal to $|\alpha(2,B)|^2$ as the scattering is by 90° .

If the particles are different (like two different nuclei or two electrons with different spins — assuming the scattering is soft, i.e., can not flip the spins)

$$p(1, A \text{ or } B) = |\alpha(1,A)|^2 + |\alpha(1,B)|^2 = 2p$$

If we wish, we can distinguish the two cases by measuring.

If the particles are alpha particles (i.e., no way to tell them apart)

$$p(1, A \text{ or } B) = |\alpha(1,A) + \alpha(1,B)|^2 = 4p$$

If the particles are electrons with the same spin orientation, i.e., both up or both down

$$p(1, A \text{ or } B) = |\alpha(1,A) - \alpha(1,B)|^2 = 0$$

90° scattering not possible.

The Schrödinger Equation

Unlike classical physics, in Quantum Mechanics we solve the Schrödinger equation to get the “wave function” of a particle

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$
$$\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34} \text{ J s}$$

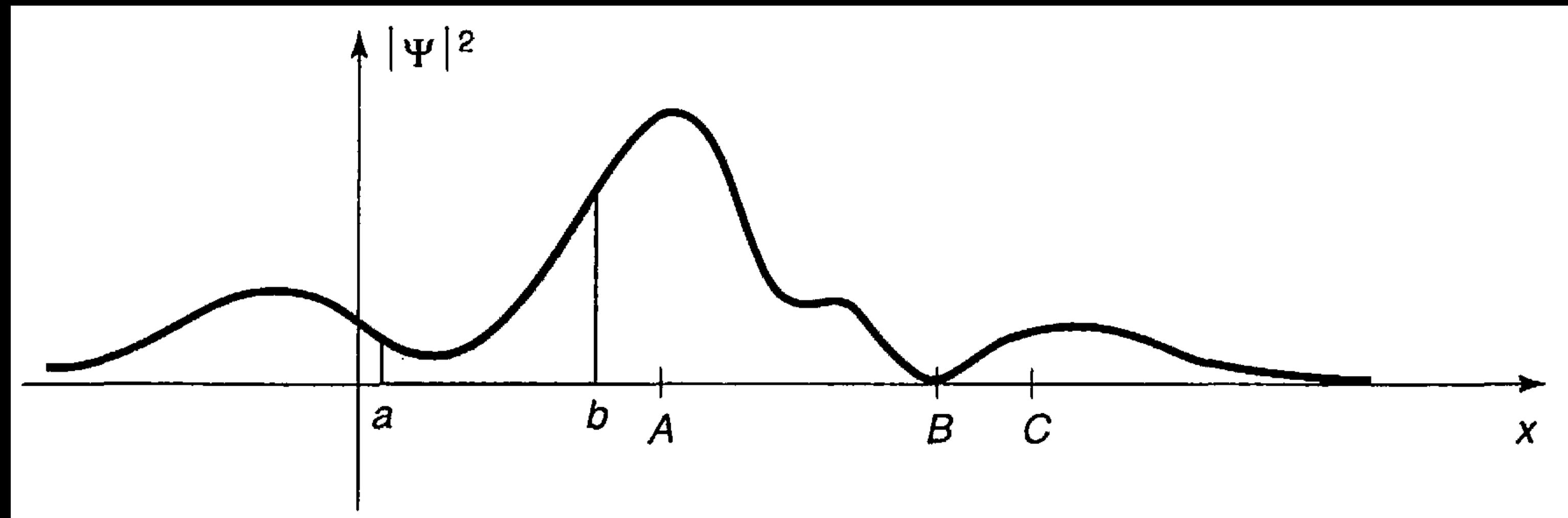
Born's statistical interpretation

The probability of finding the particle between point a and b at time t is given by

$$\int_a^b |\Psi(x, t)|^2 dx$$



PDF



Normalisation

Since $|\Psi(x, t)|^2$ is a PDF, $\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1$

The Schrödinger equation keeps it normalised.

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \left\{ \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \right\} dx$$

$$\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \quad \text{and} \quad \frac{\partial \Psi^*}{\partial t} = -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*$$

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \frac{i\hbar}{2m} \left\{ \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right\} \Bigg|_{-\infty}^{+\infty}$$

Prove
this!

However, since $\Psi(x, t) \rightarrow 0$ as $x \rightarrow \pm \infty$,

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0$$

Where was the Particle?

If, suppose, we locate a particle at point c , what will happen if we measure it immediately again?

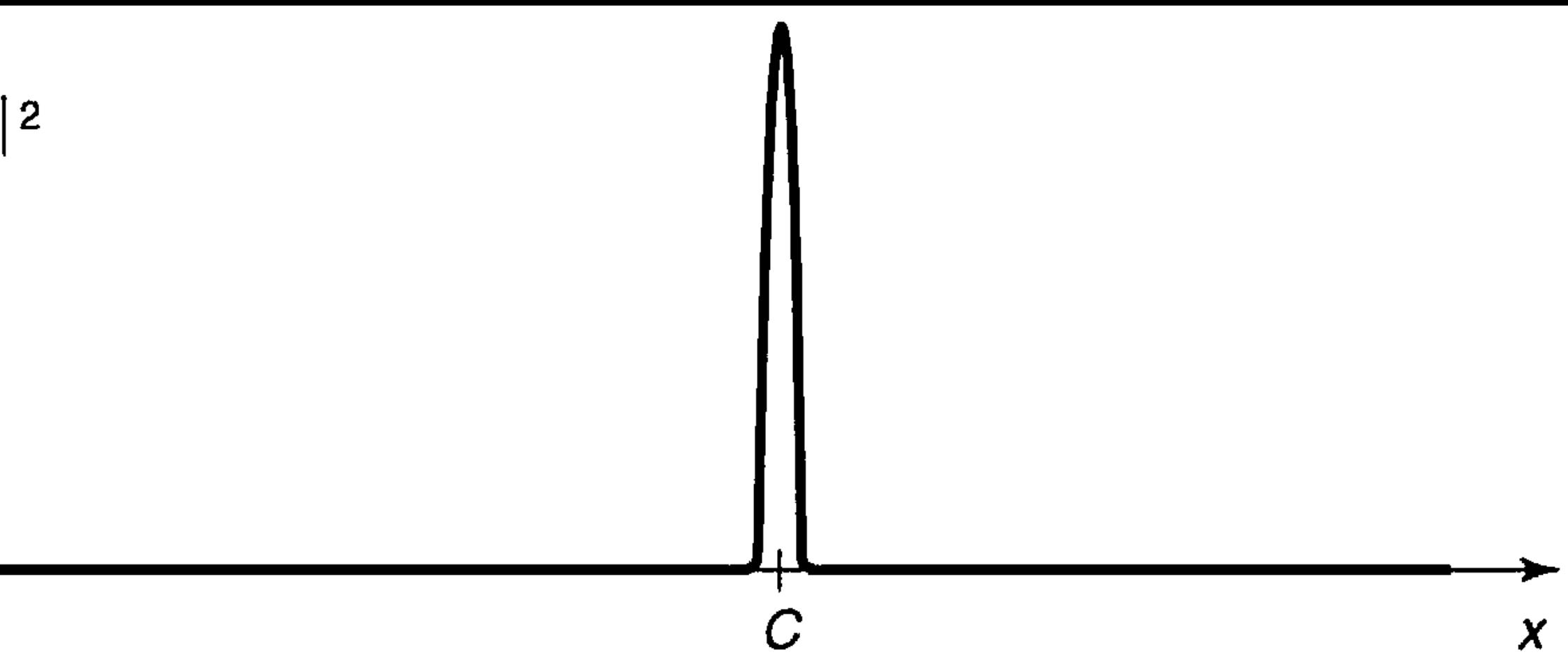
We will find it at c

It was at c . This implies QM is an incomplete theory. There are hidden variables. If we know them, we get back the deterministic picture.

But where was it before we located it for the first time?

It was everywhere. The act of measurement is a physical process that forced it to take a definite position. After the first measurement the wave function collapses to a spike at c .

Bell's experiment has (almost) ruled out the first option.



Is the moon really there when nobody looks? Reality and the quantum theory
N. David Mermin, **Physics Today**, April 1985

$|\Psi(x, t)|^2$ is a PDF

Since $|\Psi(x, t)|^2$ is a PDF of x , if we measure the position of a particle repeatedly a large number of times, what would be the expected outcome?

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \Psi^*(x, t) x \Psi(x, t) dx$$

But, **there is collapse!** The wave function collapses after the first measurement. Hence, the repeated measurement would not be given by the expectation value.

Instead, we should think that if we start with **an ensemble of identically prepared systems** [all with the same wave function $\Psi(x, t)$ —we say, all in the same state $\Psi(x, t)$] and **perform the measurement on all of them at time t** , we would get the expected value.

But what is the use of this?

The classical objects are made up of lots of quantum objects. So, roughly, we can think the classical objects as ensemble of quantum states. Then, if we measure the location of a classical object we expect to get the average or the “expected value”, i.e., $\langle x \rangle$. This could work provided **the average quantities obey the classical laws**.

Ehrenfest's Theorem

How to compute $\langle p \rangle$?

We need to compute dynamical quantities like $\langle p \rangle$ or $\langle \vec{L} \rangle$ etc.

$$\begin{aligned}\langle p \rangle &= m\langle v \rangle = m \frac{d\langle x \rangle}{dt} = m \int x \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx = \frac{i\hbar}{2} \int x \frac{\partial}{\partial x} \left\{ \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right\} dx \\ &= -\frac{i\hbar}{2} \int \left\{ \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right\} dx = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx\end{aligned}$$

Every dynamical quantity has its operator. We can compute their expectation values by operating with the corresponding operators.

The diagram illustrates the relationship between position (x) and momentum (p) expectation values and their corresponding operators. It shows arrows pointing from the expectation value equations to the operators they represent.

Position expectation value: $\langle x \rangle = \int \Psi^* x \Psi dx$. The term x is highlighted with a yellow box and arrow.

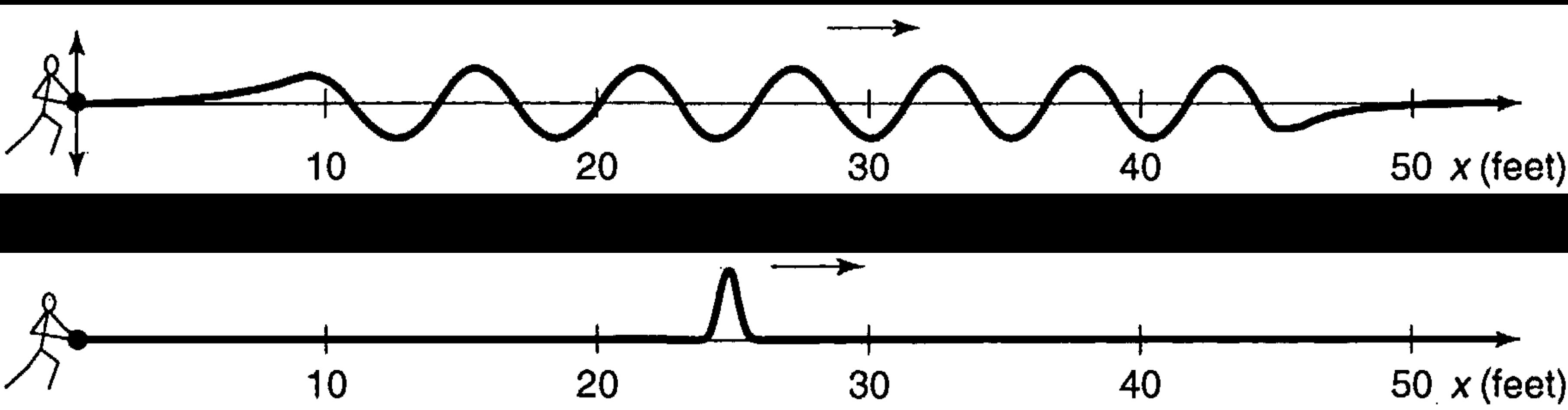
Momentum expectation value: $\langle p \rangle = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx$. The operator $\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)$ is highlighted with a yellow box and arrow.

Total energy expectation value: $\langle T \rangle = \frac{\langle p \rangle^2}{2m} = \int \Psi^* \left(\frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \right) \Psi dx$. The operator $\left(\frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right)^2 \right)$ is highlighted with a yellow box and arrow.

General operator expectation value: $\langle Q(x, p) \rangle = \int \Psi^* Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi dx$. The operator $Q \left(x, \frac{\hbar}{i} \frac{\partial}{\partial x} \right)$ is highlighted with a yellow box and arrow.

The operator \hat{T} is shown above the total energy equation, and the operator $\hat{Q}(x, t)$ is shown below the general operator equation.

The Uncertainty Principle



Every measurement on a state yields some definite answer. However, measurements over identically prepared states vary.

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

Here, σ_q is the standard deviation, i.e., $\sigma_q = \sqrt{\langle q^2 \rangle - \langle q \rangle^2}$

Quantum Mechanics

Solving the Schrödinger Equation

Time-independent Potential, $V = V(x)$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

Can we separate the variables? $\Psi(x, t) = \psi(x) \phi(t)$

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\phi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} \phi$$

The Schrödinger equation can now be written as

$$i\hbar \frac{1}{\phi} \frac{d\phi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V$$

The only way this could be true is if both sides are equal to a constant.

So, we get two equations:

$$\frac{d\phi}{dt} = -\frac{iE}{\hbar} \phi$$

$$\phi(t) = e^{-iEt/\hbar}$$

Time-independent probabilities

$$|\Psi(x, t)|^2 = |\psi(x)|^2 \phi^*(t)\phi(t) = |\psi(x)|^2$$

Steady states or stationary states

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi = E\psi$$

$$\hat{H}\psi = E\psi$$

Time-independent Schrödinger Equation

The stationary states are eigenfunctions of the Hamiltonian operator.

Stationary States

The entire ensemble has the same energy, E

$$\langle H \rangle = \int \Psi^* \hat{H} \Psi dx = \int (\phi^* \phi) (\psi^* \hat{H} \psi) dx = E \int (\psi^* \psi) dx = E$$
$$\langle H^2 \rangle = \int (\psi^* \hat{H} \hat{H} \psi) dx = E^2 \int (\psi^* \psi) dx = E^2 \quad \longrightarrow \quad \sigma_H = 0$$

General solutions are linear combinations

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i E_n t / \hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x, t)$$

Example 2.1 Suppose a particle starts out in a linear combination of just *two* stationary states:

$$\Psi(x, 0) = c_1 \psi_1(x) + c_2 \psi_2(x).$$

(To keep things simple I'll assume that the constants c_n and the states $\psi_n(x)$ are *real*.) What is the wave function $\Psi(x, t)$ at subsequent times? Find the probability density, and describe its motion.

Solution: The first part is easy:

$$\Psi(x, t) = c_1 \psi_1(x) e^{-i E_1 t / \hbar} + c_2 \psi_2(x) e^{-i E_2 t / \hbar},$$

where E_1 and E_2 are the energies associated with ψ_1 and ψ_2 . It follows that

$$|\Psi(x, t)|^2 = (c_1 \psi_1 e^{i E_1 t / \hbar} + c_2 \psi_2 e^{i E_2 t / \hbar})(c_1 \psi_1 e^{-i E_1 t / \hbar} + c_2 \psi_2 e^{-i E_2 t / \hbar})$$
$$= c_1^2 \psi_1^2 + c_2^2 \psi_2^2 + 2c_1 c_2 \psi_1 \psi_2 \cos[(E_2 - E_1)t / \hbar].$$

Combinations can have dynamics

Particle in a Box

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq a, \\ \infty, & \text{otherwise} \end{cases}$$

Outside the walls $\psi(x) = 0$. Inside,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}$$

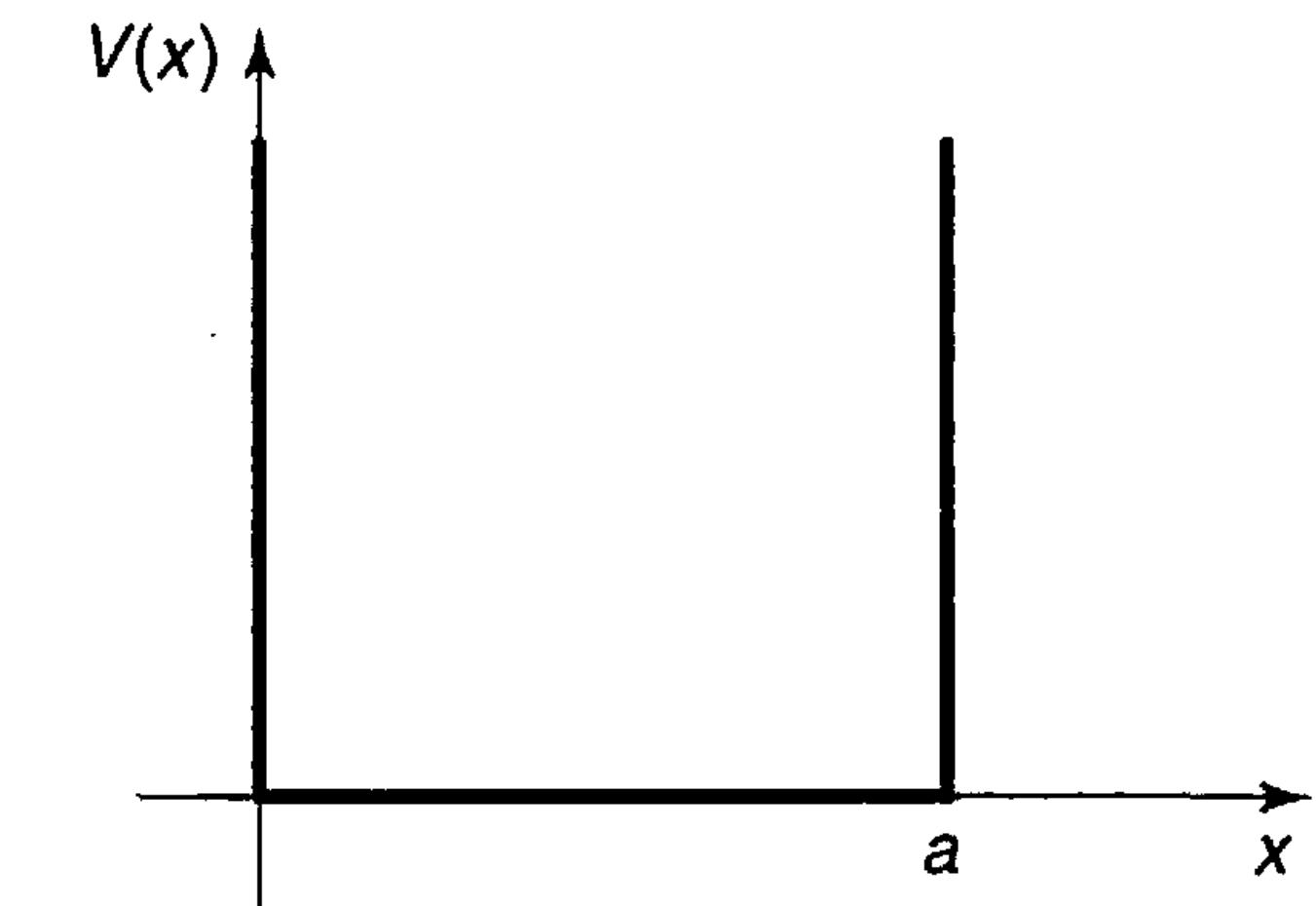
$$\psi(x) = A \sin kx + B \cos kx$$

Boundary conditions

ψ and $d\psi/dx$ are continuous unless $V = \infty$. In that case, only ψ is continuous

We can absorb the minus sign in A

If $E < 0$, there is no normalisable solution to the Schrödinger equation



$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

General solution

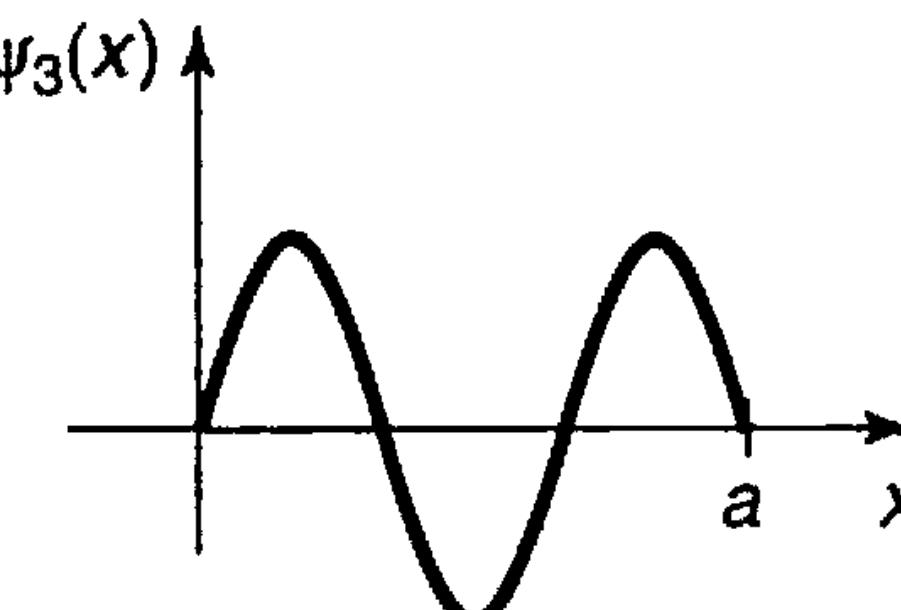
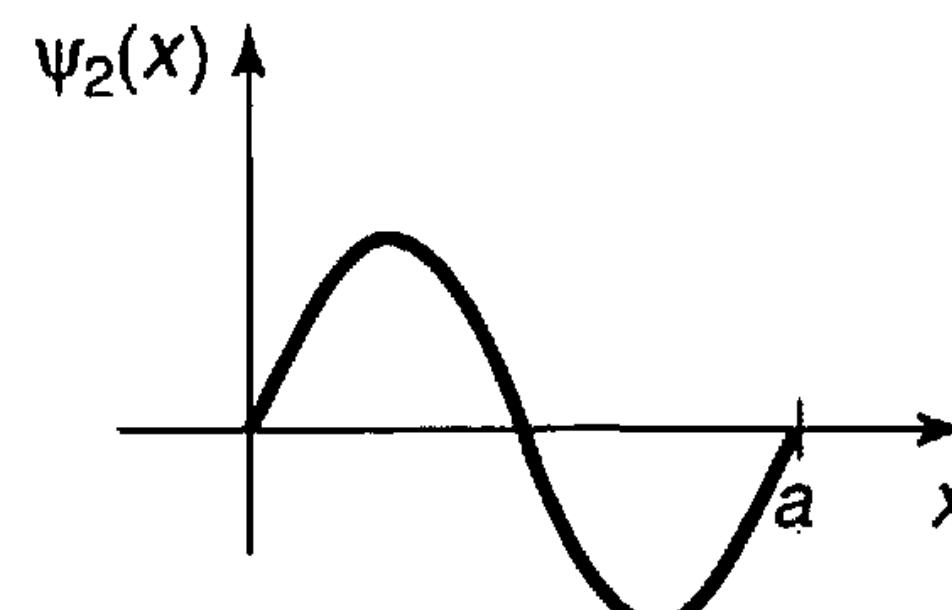
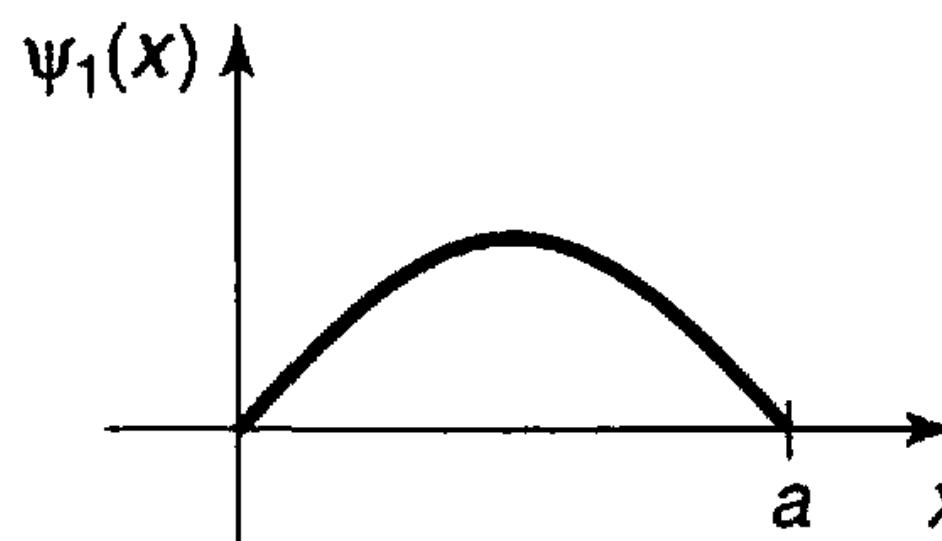
$$ka = 0, \pm\pi, \pm 2\pi, \pm 3\pi, \dots$$

Discrete

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Normalise to get

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$



Particle in a Box

$$E_n = \frac{n^2 h^2}{8ma^2}$$

$$E_4 = \frac{16h^2}{8ma^2}$$

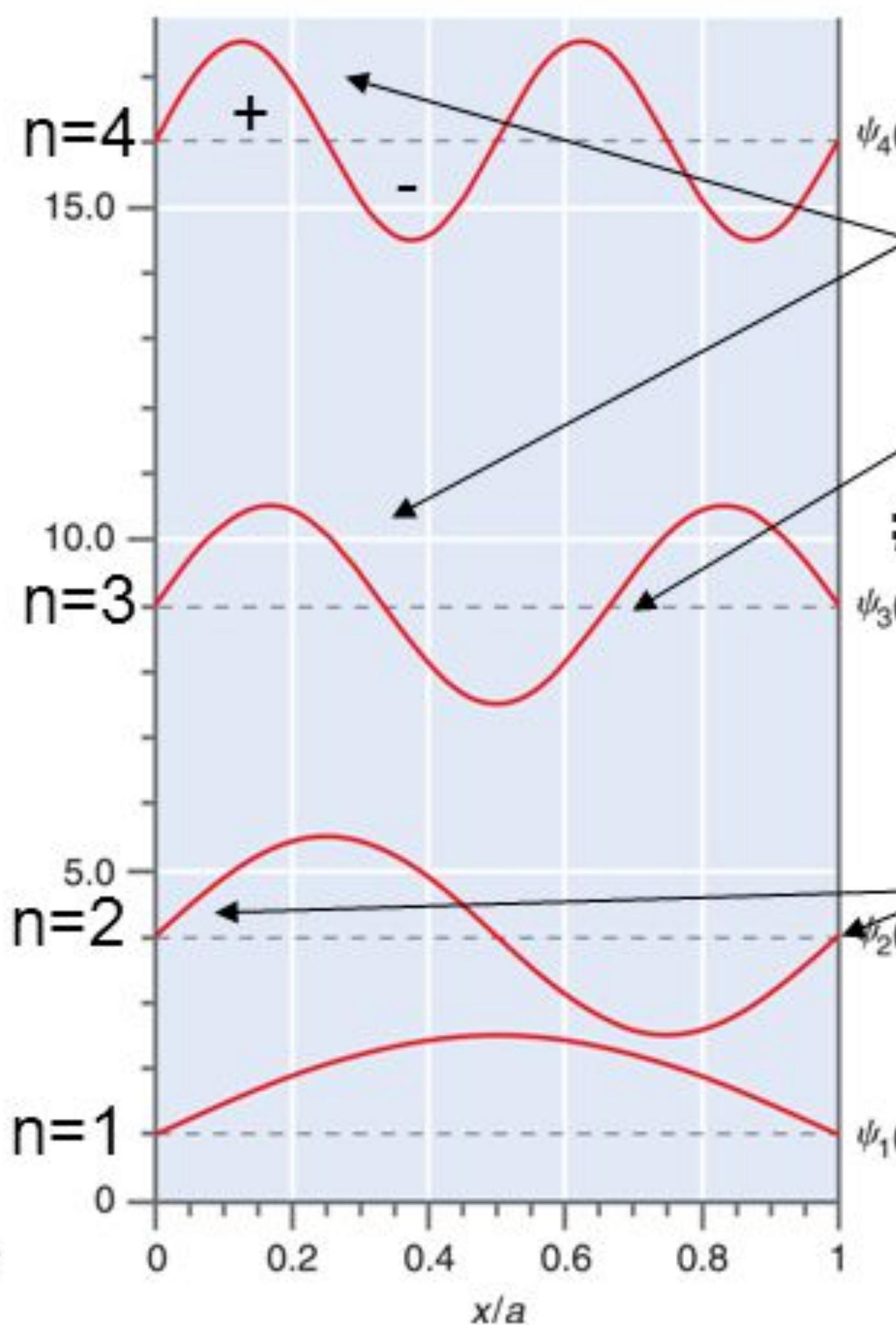
$$E_3 = \frac{9h^2}{8ma^2}$$

$$E_2 = \frac{4h^2}{8ma^2}$$

$$E_1 = \frac{h^2}{8ma^2} \neq 0$$

Ground state

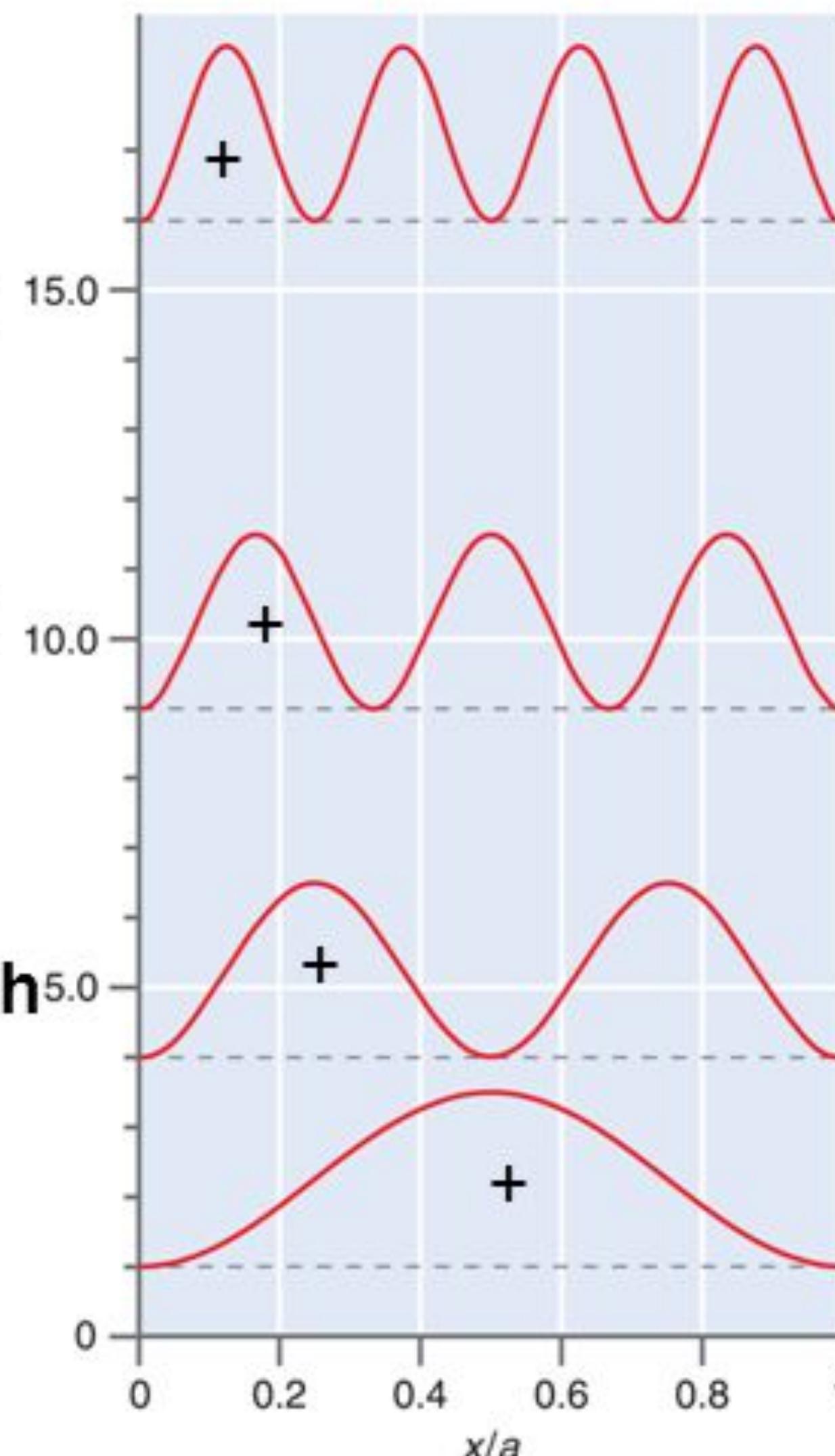
$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$



Normalized
Orthogonal
Node
nodes = n-1
n > 0

$$\lambda = \frac{2a}{n}$$

$$P_n(x) = \frac{2}{a} \sin^2\left(\frac{n\pi x}{a}\right)$$



Particle in a Box

The states are mutually orthogonal (i.e. \perp)

Kronecker delta

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn} \text{ where } \delta_{mn} = \begin{cases} 0, & \text{if } m \neq n \\ 1, & \text{if } m = n \end{cases}$$

If $m \neq n$

$$\begin{aligned} \int \psi_m(x)^* \psi_n(x) dx &= \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx \\ &= \frac{1}{a} \int_0^a \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right] dx \\ &= \left\{ \frac{1}{(m-n)\pi} \sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi} \sin\left(\frac{m+n}{a}\pi x\right) \right\} \Big|_0^a \\ &= \frac{1}{\pi} \left\{ \frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)} \right\} = 0. \end{aligned}$$

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

The states are complete

Any function $f(x)$ can be expressed in terms of them

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

$$\begin{aligned} \int \psi_m(x)^* f(x) dx &= \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x) dx \\ &= \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m \end{aligned}$$

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

$$c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x, 0) dx$$

The probability of getting E_n if you measure energy
 $= |c_n|^2$.

Mathematical Interlude

Wave functions are all square integrable (normalised).

Such functions ($\int |f(x)|^2 dx < \infty$) form a vector space called Hilbert space or L_2 space.

Inner product
A complex number

$\langle \Phi | \Psi \rangle = \int \Phi^*(x, t) \Psi(x, t) dx$ Dirac's bra(c)ket notation

Dual vector space Bra space

Vector space Ket space

If $|\Psi\rangle = c_0 |\Psi_0\rangle + c_1 |\Psi_1\rangle$

$$\langle \Phi | \Psi \rangle = c_0 \langle \Phi | \Psi_0 \rangle + c_1 \langle \Phi | \Psi_1 \rangle$$

Normalisation: $\langle \Psi | \Psi \rangle = 1$

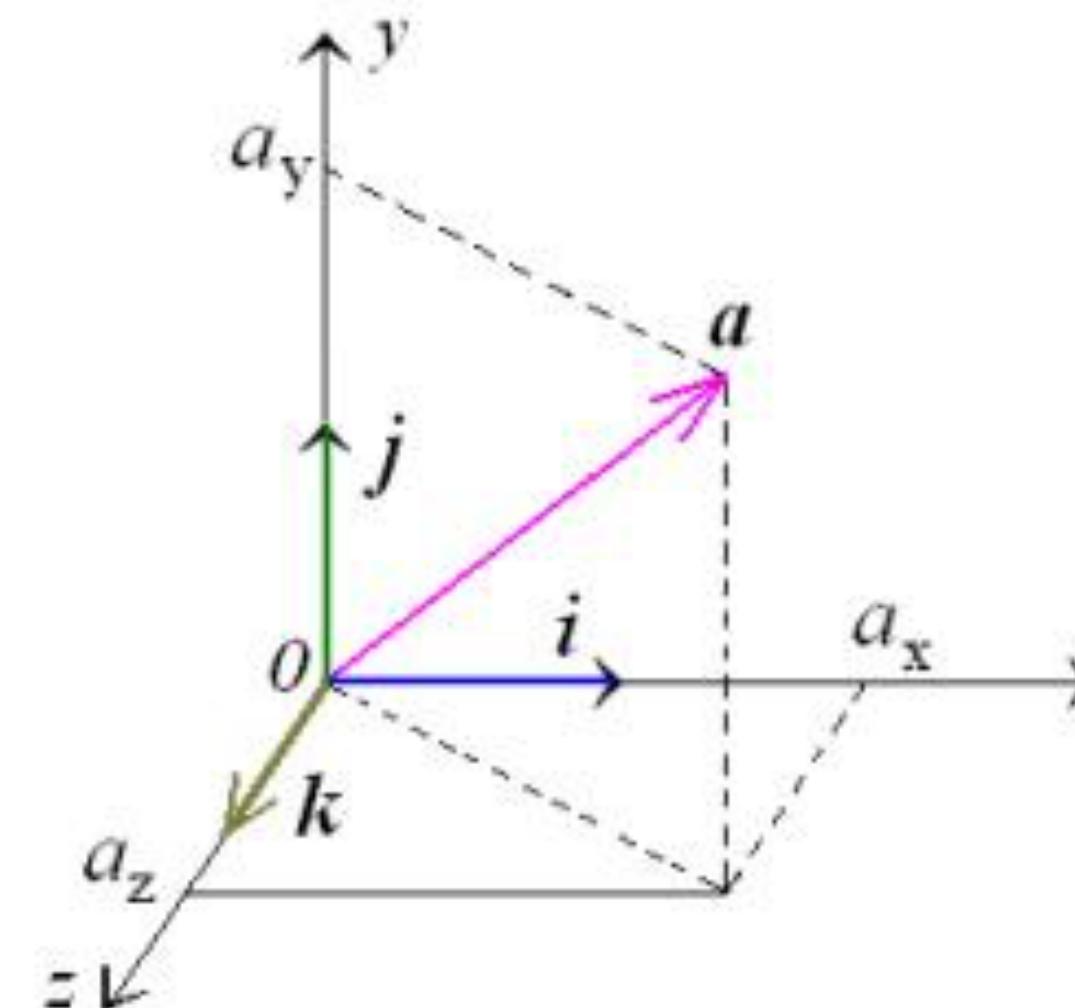
Resolving $\Psi(x, t)$ into mutually orthogonal components

n^{th} unit vector $|\Psi_n\rangle$

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}$$

Orthogonality $\equiv \langle \Psi_m | \Psi_n \rangle = \delta_{mn}$

$c_n = \langle \Psi_n | \Psi \rangle$



$\langle \Psi | \Psi \rangle = |c_0|^2 \langle \Psi_0 | \Psi_0 \rangle + |c_1|^2 \langle \Psi_1 | \Psi_1 \rangle$

Mathematical Interlude

What about operators?

$$\langle f | g \rangle = \langle g | f \rangle^*$$

The expectation value of some observable $Q(x, p)$ is written as $\langle Q \rangle = \int \Psi^*(\hat{Q}\Psi) dx = \langle \Psi | \hat{Q} \Psi \rangle$

The dual vector of $|\hat{Q}\Psi\rangle$ is $\langle \Psi \hat{Q}^\dagger |$. Hence, $\langle \Psi \hat{Q}^\dagger | \Psi \rangle = \int (\hat{Q}^\dagger \Psi^*) \Psi dx = \int (\hat{Q}\Psi)^* \Psi dx = \langle Q \rangle^*$

Also written as $\langle \hat{Q}^\dagger \Psi |$

Observables \equiv Hermitian operators

Since measurement outcomes are real, $\langle \Psi \hat{Q}^\dagger | \Psi \rangle = \langle \Psi | \hat{Q} \Psi \rangle$ or, simply, $\langle \Psi \hat{Q}^\dagger \Psi \rangle = \langle \Psi \hat{Q} \Psi \rangle$, i.e., $\hat{Q}^\dagger = \hat{Q}$

Momentum operator $\langle f | \hat{p} g \rangle = \int_{-\infty}^{\infty} f^* \frac{\hbar}{i} \frac{dg}{dx} dx = \frac{\hbar}{i} f^* g \Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \left(\frac{\hbar}{i} \frac{df}{dx} \right)^* g dx = \langle \hat{p} f | g \rangle$

Measuring an observable \equiv Operating on the state vector with an (hermitian) operator

$\hat{Q} |\Psi\rangle = q_i |\Psi\rangle$ Normally, if measurements are done on an ensemble, different members return different outcomes

If $|\Psi\rangle$ is an eigenvector/eigenfunction of \hat{Q} then we would get the same value, the eigenvalue, from all members

$$\hat{Q} |\Psi\rangle = q |\Psi\rangle \rightarrow \langle Q \rangle = \langle \Psi | \hat{Q} | \Psi \rangle = q \langle \Psi | \Psi \rangle = q \text{ and } \sigma_Q = 0$$

Operator Number

E.g., stationary states are eigenfunctions of the Hamiltonian operator with e.v. E_n

Mathematical Interlude

Two theorems for Hermitian operators ($\hat{Q} = \hat{Q}^\dagger$) in linear algebra

Eigenvalues of Hermitian operators are real

Let $\hat{Q} |\Psi\rangle = q |\Psi\rangle$. Now, $q \langle \Psi | \Psi \rangle = \langle \Psi | \hat{Q} \Psi \rangle = \langle \Psi \hat{Q}^\dagger | \Psi \rangle = q^* \langle \Psi | \Psi \rangle$ **QED**

Eigenvectors/eigenfunctions with different eigenvalues are orthogonal

Let $\hat{Q} |\Phi\rangle = q' |\Phi\rangle$. Now, $q' \langle \Psi | \Phi \rangle = \langle \Psi | \hat{Q} \Phi \rangle = \langle \Psi \hat{Q}^\dagger | \Phi \rangle = q^* \langle \Psi | \Phi \rangle = q \langle \Psi | \Phi \rangle$ **QED**

The degenerate case: If two or more eigenvectors have the same eigenvalues we can find linear combinations that are orthogonal (remember **Gram-Schmidt orthogonalisation?**).

In many cases it is possible to prove that eigenvectors of a Hermitian operator form a complete basis (e.g. particle in a box). In some infinite dimensional cases it is not. There we consider only those operators as our observables for which this is true. Hence, we can span the Hilbert space with these vectors/functions, i.e., express any function in the Hilbert space with them.

The Harmonic Oscillator

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

$$H = \frac{1}{2m}[p^2 + (m\omega x)^2]$$

Can we factorise the operator H (as usual, we are sloppy with the hat) like a number? $u^2 + v^2 = (iu + v)(-iu + v)$

Let us define two operators

$$a_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (\mp ip + m\omega x)$$

$$\begin{aligned} a_- a_+ &= \frac{1}{2\hbar m\omega} (ip + m\omega x)(-ip + m\omega x) = \frac{1}{2\hbar m\omega} [p^2 + (m\omega x)^2 - i m\omega (xp - px)] \\ &= \frac{1}{2\hbar m\omega} [p^2 + (m\omega x)^2] - \frac{i}{2\hbar} [x, p] \end{aligned}$$

Commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

$$[x, p]f(x) = \left[x \frac{\hbar}{i} \frac{d}{dx}(f) - \frac{\hbar}{i} \frac{d}{dx}(xf) \right] = \frac{\hbar}{i} \left(x \frac{df}{dx} - x \frac{df}{dx} - f \right) = i\hbar f(x) \rightarrow [x, p] = i\hbar$$

$$a_- a_+ = \frac{1}{\hbar\omega} H + \frac{1}{2} \rightarrow H = \hbar\omega \left(a_- a_+ - \frac{1}{2} \right)$$

$$[a_-, a_+] = 1$$

$$a_+ a_- = \frac{1}{\hbar\omega} H - \frac{1}{2} \rightarrow H = \hbar\omega \left(a_+ a_- + \frac{1}{2} \right)$$

Schrödinger equation

$$\hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right) \psi = E\psi$$

The Harmonic Oscillator

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

$$H = \frac{1}{2m}[p^2 + (m\omega x)^2]$$

$$a_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (\mp ip + m\omega x)$$

$$\begin{aligned} H(a_+\psi) &= \hbar\omega \left(a_+a_- + \frac{1}{2} \right) (a_+\psi) = \hbar\omega \left(a_+a_-a_+ + \frac{1}{2}a_+ \right) \psi \\ &= \hbar\omega a_+ \left(a_-a_+ + \frac{1}{2} \right) \psi = a_+ \left[\hbar\omega \left(a_+a_- + 1 + \frac{1}{2} \right) \psi \right] \\ &= a_+(H + \hbar\omega)\psi = a_+(E + \hbar\omega)\psi = (E + \hbar\omega)(a_+\psi). \\ H(a_-\psi) &= (E - \hbar\omega)(a_-\psi). \end{aligned}$$

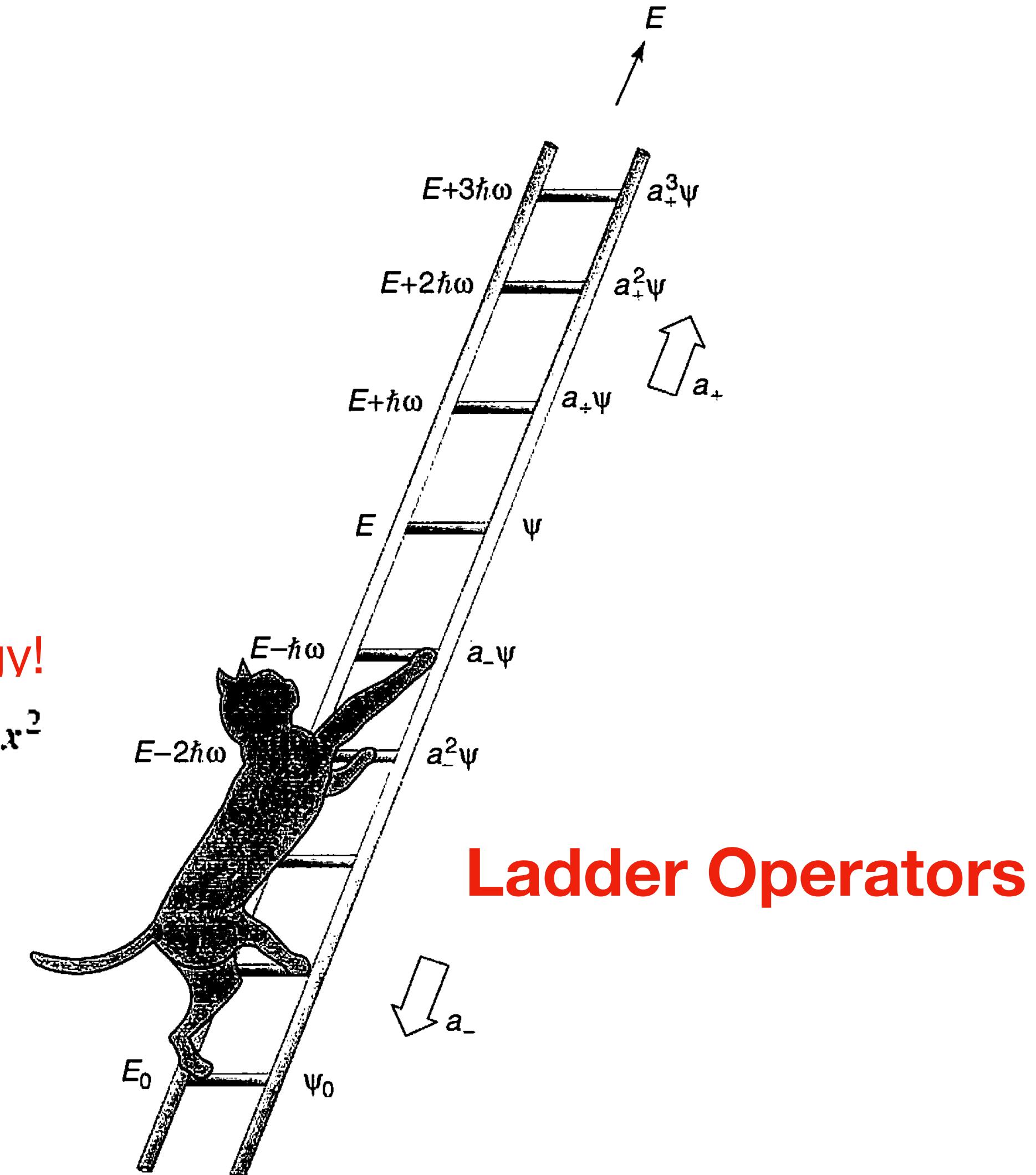
If a_- is applied again and again, we would reach a state with -ve energy!

$$a_-\psi_0 = 0 \quad \text{or} \quad \frac{1}{\sqrt{2\hbar m\omega}} \left(\hbar \frac{d}{dx} + m\omega x \right) \psi_0 = 0 \quad \rightarrow \quad \psi_0(x) = Ae^{-\frac{m\omega}{2\hbar}x^2}$$

Ground state

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar} dx = |A|^2 \sqrt{\frac{\pi\hbar}{m\omega}}$$

$$\begin{aligned} \psi_0(x) &= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2} \\ E_0 &= \frac{1}{2}\hbar\omega. \end{aligned}$$



The Harmonic Oscillator

$$\psi_n(x) = A_n (a_+)^n \psi_0(x), \quad \text{with } E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

It is possible to figure out the constants with simple algebra

Let $a_+ \psi_n = c_n \psi_{n+1}$, $a_- \psi_n = d_n \psi_{n-1}$

Notice

$$\int_{-\infty}^{\infty} (a_{\pm} \psi_n)^* (a_{\pm} \psi_n) dx = \int_{-\infty}^{\infty} (a_{\mp} a_{\pm} \psi_n)^* \psi_n dx$$

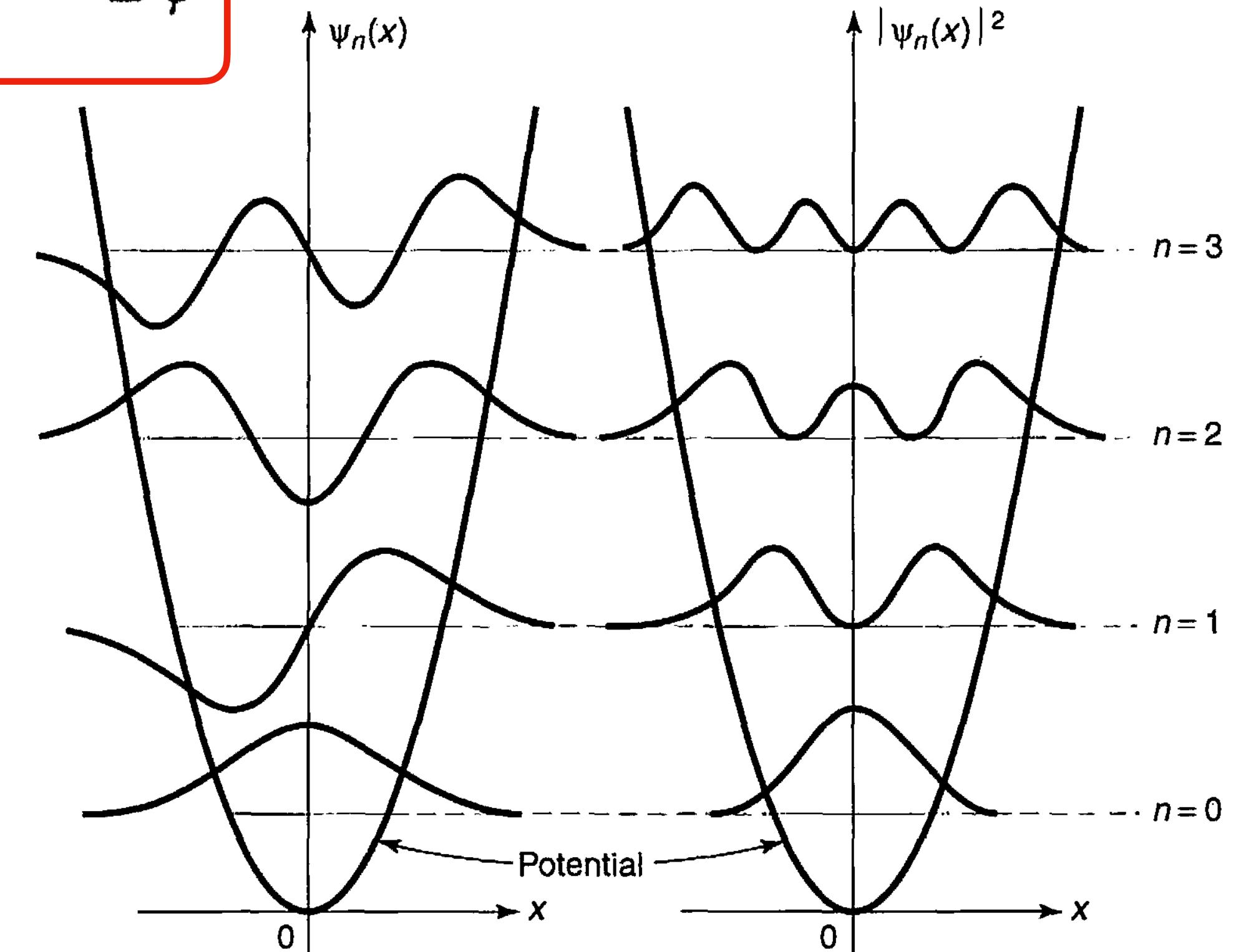
Now

$$a_+ a_- \psi_n = n \psi_n, \quad a_- a_+ \psi_n = (n+1) \psi_n$$

$$\int_{-\infty}^{\infty} (a_+ \psi_n)^* (a_+ \psi_n) dx = |c_n|^2 \int_{-\infty}^{\infty} |\psi_{n+1}|^2 dx = (n+1) \int_{-\infty}^{\infty} |\psi_n|^2 dx$$

$$\int_{-\infty}^{\infty} (a_- \psi_n)^* (a_- \psi_n) dx = |d_n|^2 \int_{-\infty}^{\infty} |\psi_{n-1}|^2 dx = n \int_{-\infty}^{\infty} |\psi_n|^2 dx.$$

$$\hbar\omega \left(a_{\pm} a_{\mp} \pm \frac{1}{2} \right) \psi = E \psi$$



$$a_+ \psi_n = \sqrt{n+1} \psi_{n+1}, \quad a_- \psi_n = \sqrt{n} \psi_{n-1}$$

$$\psi_n = \frac{1}{\sqrt{n!}} (a_+)^n \psi_0$$

Orthogonal stationary states

The Harmonic Oscillator

$$\psi_n = \frac{1}{\sqrt{n!}} (a_+)^n \psi_0$$

$$a_+ \psi_n = \sqrt{n+1} \psi_{n+1}, \quad a_- \psi_n = \sqrt{n} \psi_{n-1}$$

$$\int_{-\infty}^{\infty} \psi_m^* (a_+ a_-) \psi_n dx = n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \int_{-\infty}^{\infty} (a_- \psi_m)^* (a_- \psi_n) dx = \int_{-\infty}^{\infty} (a_+ a_- \psi_m)^* \psi_n dx = m \int_{-\infty}^{\infty} \psi_m^* \psi_n dx.$$

Orthogonal stationary states

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = \delta_{mn}$$

Example 2.5: $\langle V \rangle$ in the n^{th} state: $\langle V \rangle = \left\langle \frac{1}{2} m \omega^2 x^2 \right\rangle = \frac{1}{2} m \omega^2 \int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n dx$

$$a_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (\mp i p + m\omega x)$$

$$= \frac{\hbar\omega}{4} \int \psi_n^* \left[(a_+)^2 + (a_+ a_-) + (a_- a_+) + (a_-)^2 \right] \psi_n dx$$

But $(a_+)^2 \psi_n$ is (apart from normalization) ψ_{n+2} , which is orthogonal to ψ_n , and the same goes for $(a_-)^2 \psi_n$, which is proportional to ψ_{n-2} .

$$\langle V \rangle = \frac{\hbar\omega}{4} (n + n + 1) = \frac{1}{2} \hbar\omega \left(n + \frac{1}{2} \right)$$

The Free Particle

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi} \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}$$

$$\Psi(x, t) = A e^{ik(x - \frac{\hbar k}{2m}t)} + B e^{-ik(x + \frac{\hbar k}{2m}t)}$$

Fixed profile wave traveling right/left
Wavelength $\lambda = 2\pi/|k|$

Momentum $p = \hbar k$

$$\Psi_k(x, t) = A e^{i(kx - \frac{\hbar k^2}{2m}t)}$$

$k \equiv \pm \frac{\sqrt{2mE}}{\hbar}$. with $\begin{cases} k > 0 \Rightarrow \text{traveling to the right,} \\ k < 0 \Rightarrow \text{traveling to the left.} \end{cases}$

Speed of the waves: $v_{\text{quantum}} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}$.

Problem: Solutions are not normalisable!

wave packet

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{i(kx - \frac{\hbar k^2}{2m}t)} dk$$

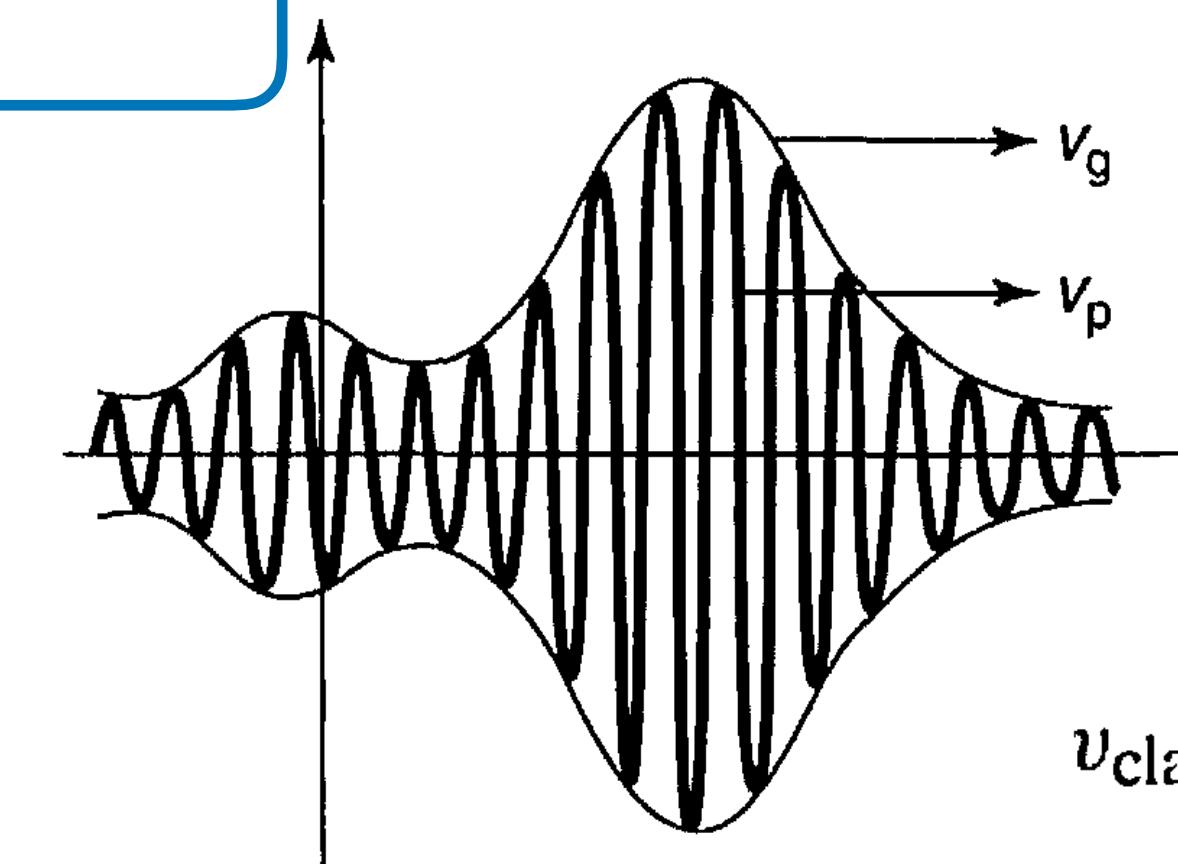
$$\Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \phi(k) e^{ikx} dk$$

$$v_{\text{classical}} = \sqrt{\frac{2E}{m}} = 2v_{\text{quantum}}$$

Plancherel's theorem

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} dk \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx$$

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x, 0) e^{-ikx} dx$$



$$v_{\text{group}} = \frac{d\omega}{dk}$$

$$v_{\text{phase}} = \frac{\omega}{k}$$

$$v_{\text{classical}} = v_{\text{group}} = 2v_{\text{phase}}$$

The Free Particle

Example 2.6 A free particle, which is initially localized in the range $-a < x < a$, is released at time $t = 0$:

$$\Psi(x, 0) = \begin{cases} A, & \text{if } -a < x < a, \\ 0, & \text{otherwise,} \end{cases}$$

where A and a are positive real constants. Find $\Psi(x, t)$.

Solution: First we need to normalize $\Psi(x, 0)$:

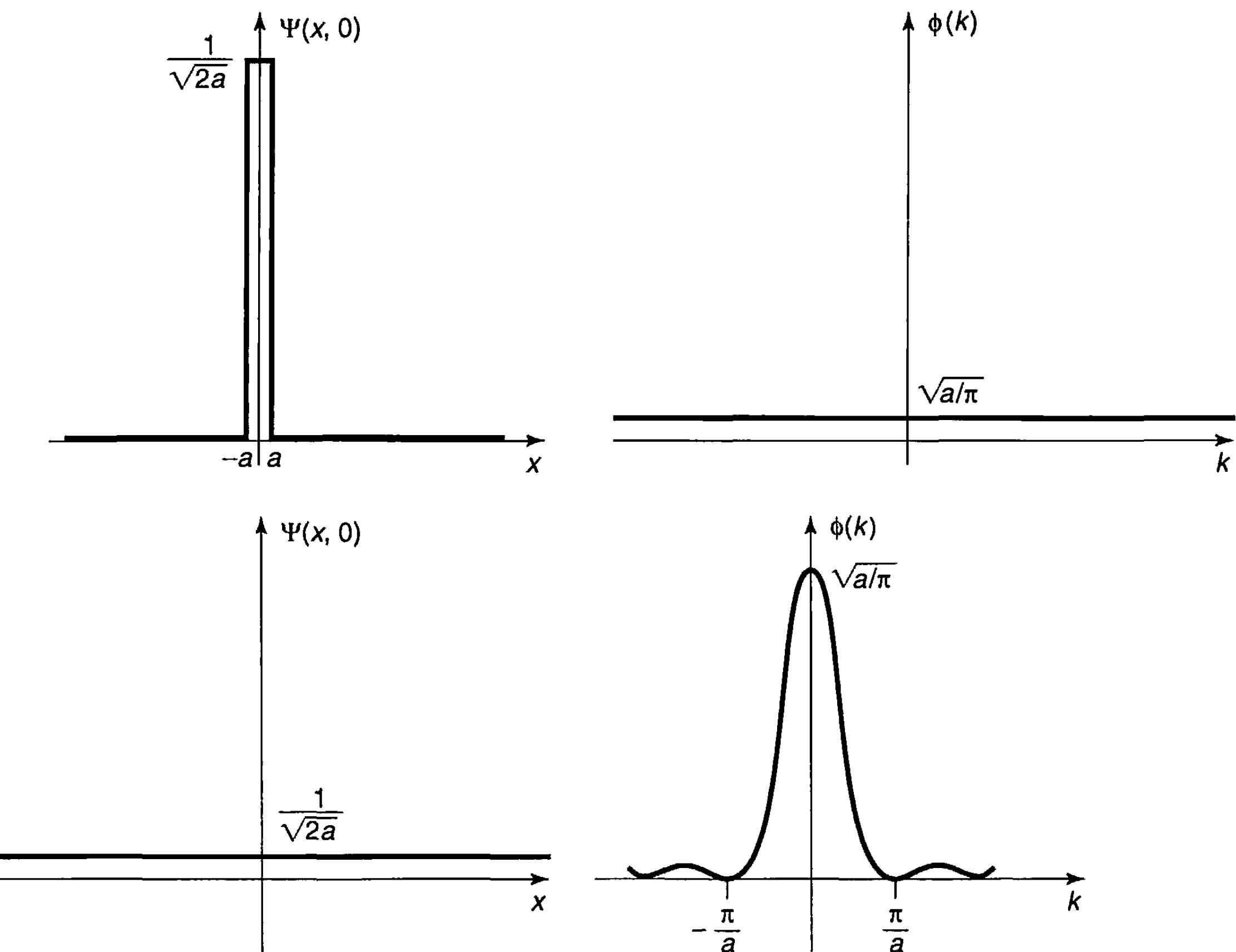
$$1 = \int_{-\infty}^{\infty} |\Psi(x, 0)|^2 dx = |A|^2 \int_{-a}^a dx = 2a|A|^2 \Rightarrow A = \frac{1}{\sqrt{2a}}.$$

Next we calculate $\phi(k)$,

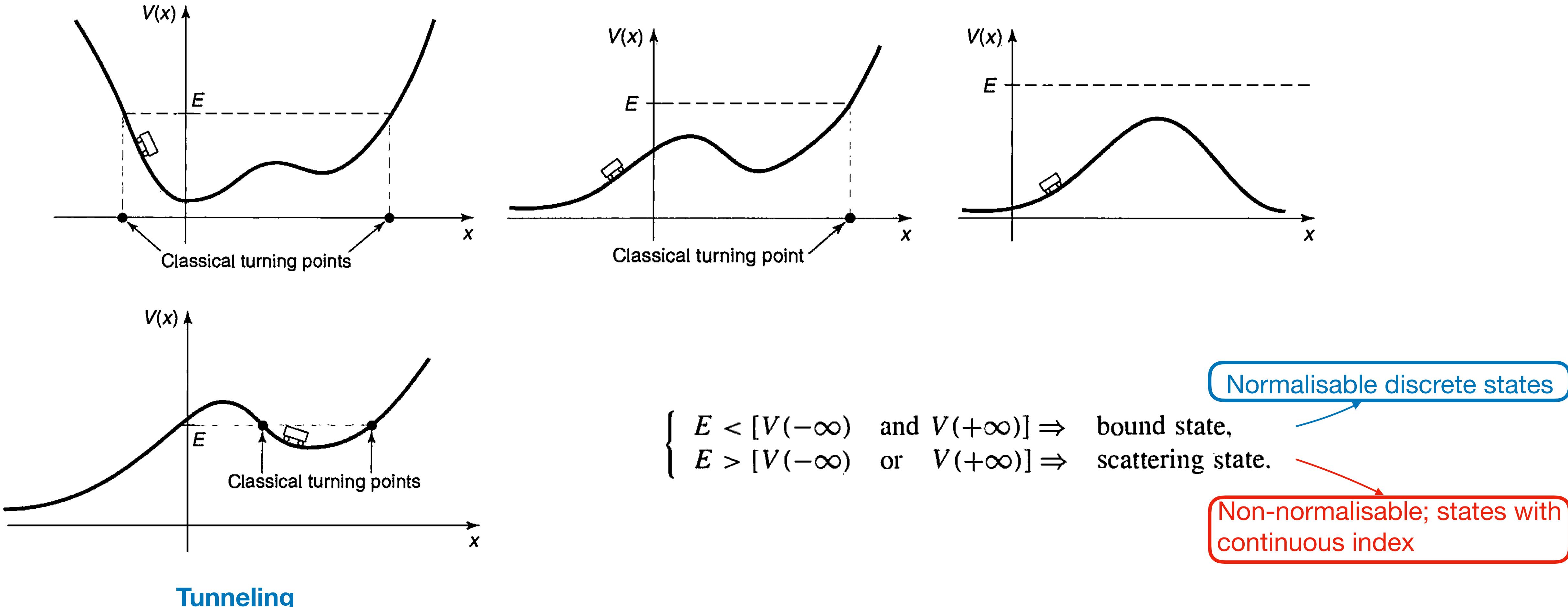
$$\begin{aligned} \phi(k) &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^a e^{-ikx} dx = \frac{1}{2\sqrt{\pi a}} \frac{e^{-ikx}}{-ik} \Big|_{-a}^a \\ &= \frac{1}{k\sqrt{\pi a}} \left(\frac{e^{ika} - e^{-ika}}{2i} \right) = \frac{1}{\sqrt{\pi a}} \frac{\sin(ka)}{k}. \end{aligned}$$

Finally, we plug this back

$$\Psi(x, t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{\sin(ka)}{k} e^{i(kx - \frac{\hbar k^2}{2m}t)} dk.$$



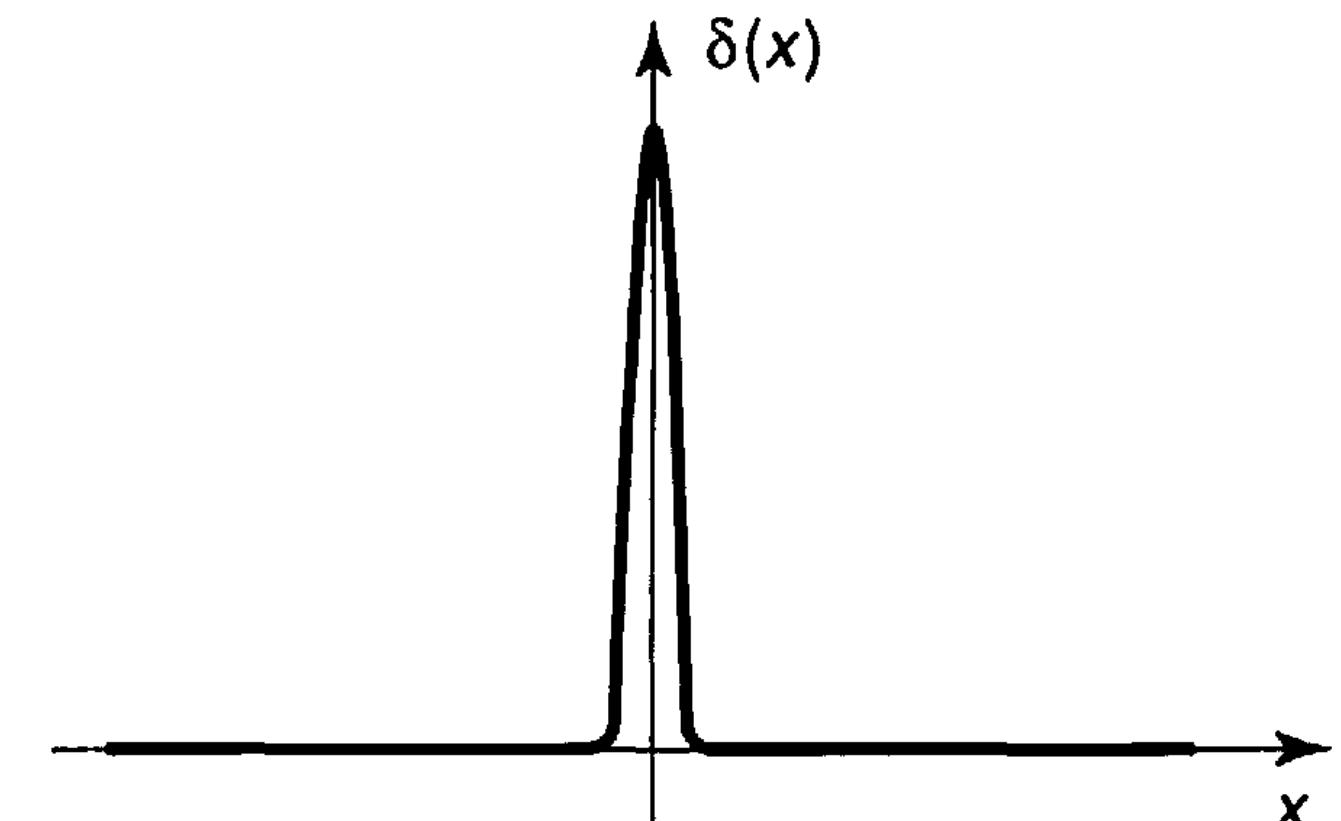
Bound States & Scattering States



Delta Well

Dirac delta function $\delta(x) \equiv \begin{cases} 0, & \text{if } x \neq 0 \\ \infty, & \text{if } x = 0 \end{cases}$, with $\int_{-\infty}^{+\infty} \delta(x) dx = 1$.

$$\int_{-\infty}^{+\infty} f(x)\delta(x-a) dx = f(a) \int_{-\infty}^{+\infty} \delta(x-a) dx = f(a).$$



$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} - \alpha\delta(x)\psi = E\psi \rightarrow \text{both bound states } (E < 0) \text{ and scattering states } (E > 0)$$

Bound States

At $x < 0$ $\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = \kappa^2\psi, \quad \kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$

the first term blows up as $x \rightarrow -\infty$, so we must choose $A = 0$:

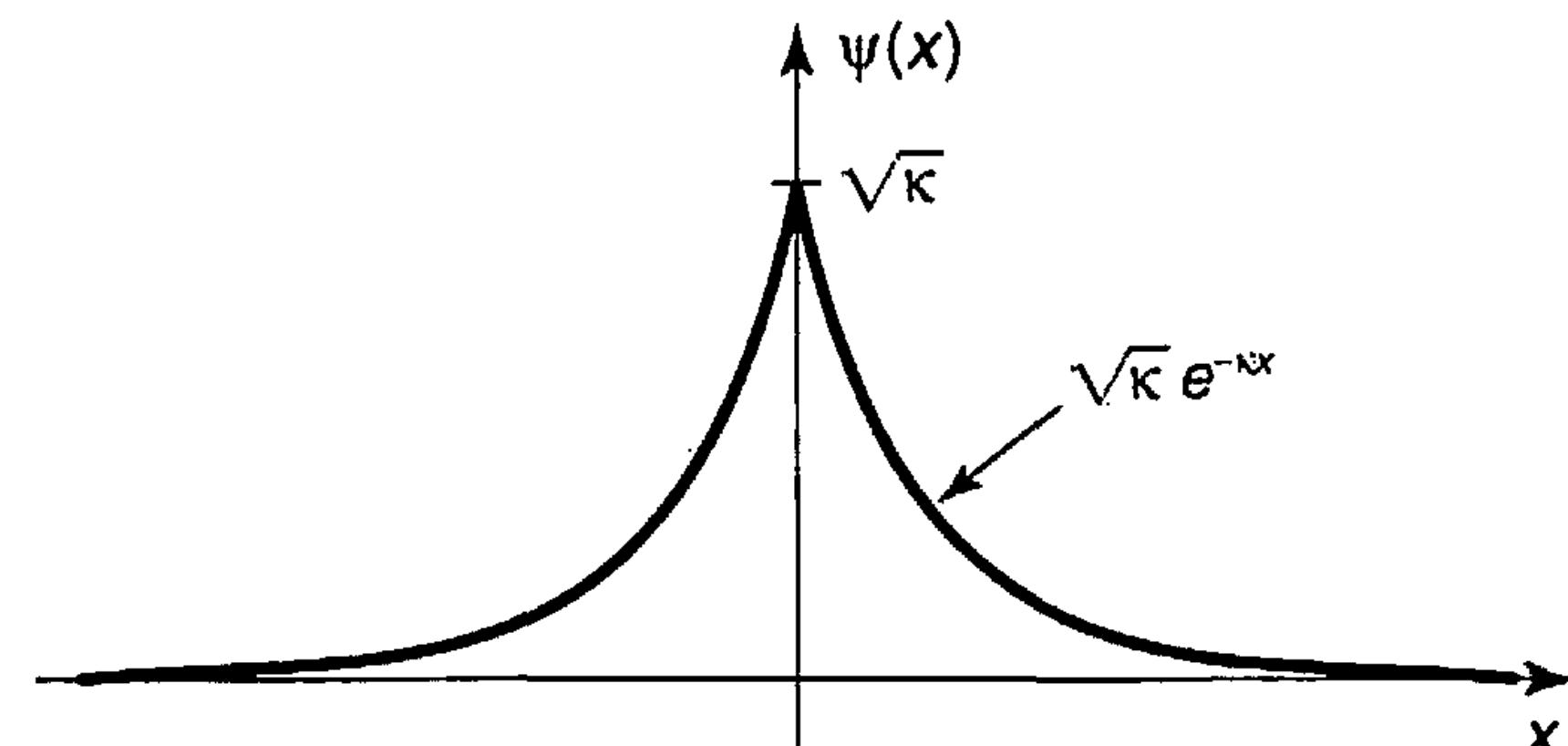
$$\psi(x) = Be^{\kappa x}, \quad (x < 0)$$

At $x > 0$ $\psi(x) = Fe^{-\kappa x}, \quad (x > 0)$

Boundary conditions

1. ψ is always continuous;
2. $d\psi/dx$ is continuous except at points where the potential is infinite.

$$\psi(x) = \begin{cases} Be^{\kappa x}, & (x \leq 0), \\ Be^{-\kappa x}, & (x \geq 0); \end{cases}$$



Delta Well

To determine κ we shall integrate Schrödinger equation about the delta well

$$-\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \frac{d^2\psi}{dx^2} dx + \int_{-\epsilon}^{+\epsilon} V(x)\psi(x) dx = E \int_{-\epsilon}^{+\epsilon} \psi(x) dx$$

$$\Delta\left(\frac{d\psi}{dx}\right) \equiv \lim_{\epsilon \rightarrow 0} \left(\frac{d\psi}{dx}\Big|_{+\epsilon} - \frac{d\psi}{dx}\Big|_{-\epsilon} \right) = \frac{2m}{\hbar^2} \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} V(x)\psi(x) dx. \quad \rightarrow \quad \Delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0).$$

$$\begin{cases} d\psi/dx = -B\kappa e^{-\kappa x}, & \text{for } (x > 0), \quad \text{so } d\psi/dx\Big|_+ = -B\kappa, \\ d\psi/dx = +B\kappa e^{+\kappa x}, & \text{for } (x < 0), \quad \text{so } d\psi/dx\Big|_- = +B\kappa. \end{cases} \quad \rightarrow \quad \Delta(d\psi/dx) = -2B\kappa. \text{ And } \psi(0) = B.$$

$$\kappa = \frac{m\alpha}{\hbar^2}. \quad \rightarrow \quad E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m\alpha^2}{2\hbar^2}.$$

Normalisation

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 2|B|^2 \int_0^{\infty} e^{-2\kappa x} dx = \frac{|B|^2}{\kappa} = 1.$$

Single bound state

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar} e^{-m\alpha|x|/\hbar^2}; \quad E = -\frac{m\alpha^2}{2\hbar^2}.$$

Delta Well

Scattering States

At $x < 0$

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi, \quad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

The general solution is $\psi(x) = Ae^{ikx} + Be^{-ikx}$,

At $x > 0$

$$\psi(x) = Fe^{ikx} + Ge^{-ikx}$$

The continuity of $\psi(x)$ at $x = 0$ requires that

$$F + G = A + B$$

The derivatives are $\begin{cases} d\psi/dx = ik(Fe^{ikx} - Ge^{-ikx}), & \text{for } (x > 0), \quad \text{so } d\psi/dx|_+ = ik(F - G), \\ d\psi/dx = ik(Ae^{ikx} - Be^{-ikx}), & \text{for } (x < 0), \quad \text{so } d\psi/dx|_- = ik(A - B). \end{cases}$

$$\Delta \left(\frac{d\psi}{dx} \right) = -\frac{2m\alpha}{\hbar^2} \psi(0).$$

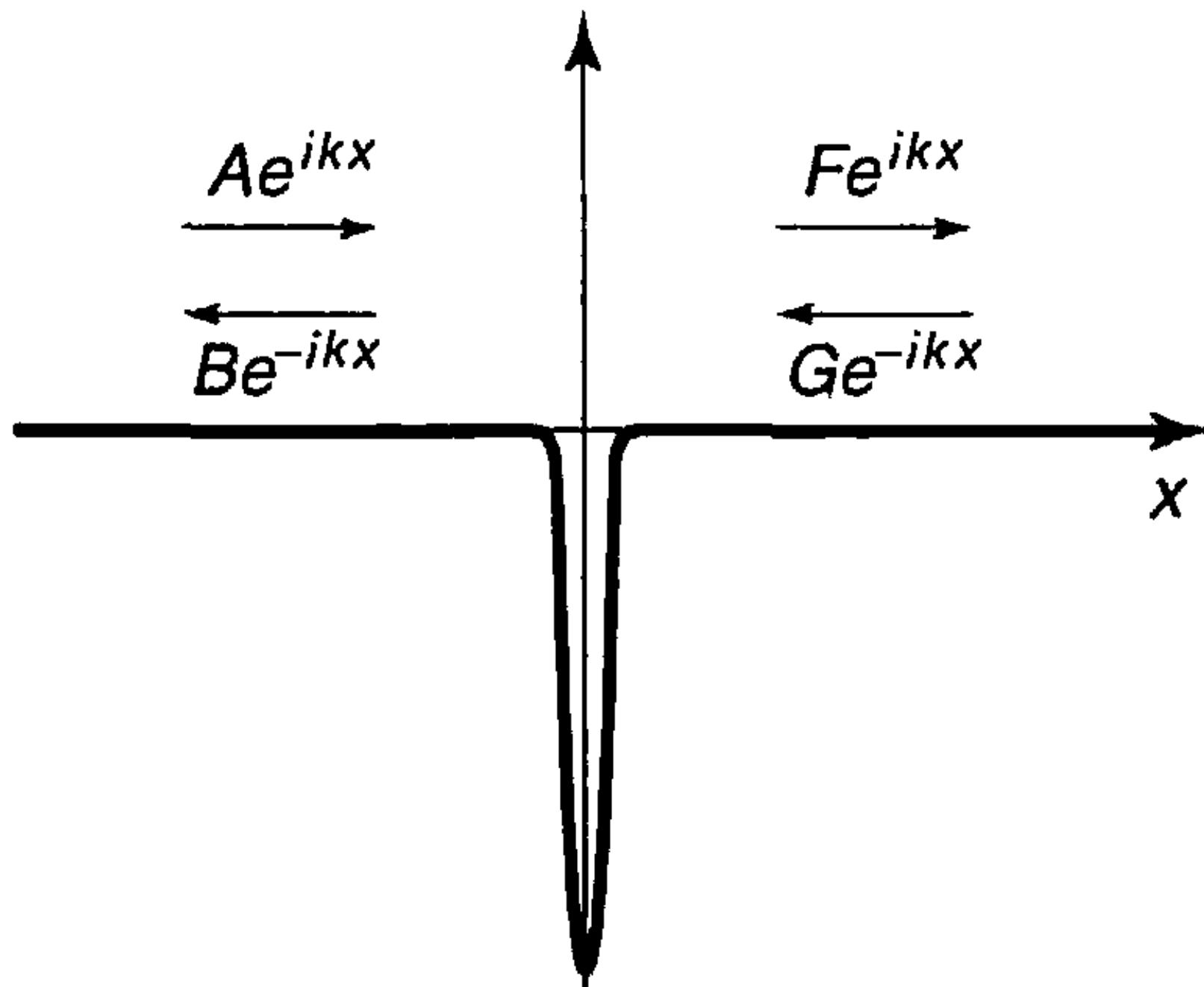


$$ik(F - G - A + B) = -\frac{2m\alpha}{\hbar^2}(A + B)$$

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta), \quad \text{where } \beta \equiv \frac{m\alpha}{\hbar^2 k}.$$

Delta Well

Scattering States



Let's assume $G = 0$, (for scattering from the left)



$$B = \frac{i\beta}{1 - i\beta} A, \quad F = \frac{1}{1 - i\beta} A.$$

Reflection coefficient: $R \equiv \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}$.

Transmission coefficient: $T \equiv \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}$

$$R = \frac{1}{1 + (2\hbar^2 E / m\alpha^2)}, \quad T = \frac{1}{1 + (m\alpha^2 / 2\hbar^2 E)}$$

Tunnelling

If $\alpha < 0$, i.e., a delta barrier instead of a delta well: The bound state vanishes. R and T remain the same.

Quantum Mechanics

Mathematical Interlude

Fourier transform of a delta function

Plancherel's theorem

$$\delta(x) = \frac{1}{2\pi} \int e^{ikx} dk$$



$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} F(k) e^{ikx} dk \iff F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-ikx} dx$$

When the **spectrum** of a hermitian operator is continuous, the individual solutions are not-normalisable.
Nevertheless, there is a sense of orthonormality and completeness among the eigenvectors.

Let $f_p(x)$ be the eigenfunction and p the eigenvalue of the momentum operator.

$$\frac{\hbar}{i} \frac{d}{dx} f_p(x) = p f_p(x). \quad f_p(x) = A e^{ipx/\hbar}$$

$$\int_{-\infty}^{\infty} f_{p'}^*(x) f_p(x) dx = |A|^2 \int_{-\infty}^{\infty} e^{i(p-p')x/\hbar} dx = |A|^2 2\pi\hbar \delta(p - p')$$

If we pick $A = 1/\sqrt{2\pi\hbar}$, so that $f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$.

$$\langle f_{p'} | f_p \rangle = \delta(p - p').$$



$$\langle f_m | f_n \rangle = \delta_{mn}$$

Any (square-integrable) function $f(x)$ can be written in the form

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x) dp = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p) e^{ipx/\hbar} dp.$$

Generalised Statistical Interpretation

If you measure an observable $Q(x, p)$, you would get one of the eigenvalue of $\hat{Q} (\hat{x}, \hat{p})$

If the spectrum of \hat{Q} is discrete, the probability of getting a particular e.value q_n associated with e.vector $f_n(x)$ is

$$|c_n|^2. \quad \text{where } c_n = \langle f_n | \Psi \rangle.$$

Ortho-normalised

If the spectrum of \hat{Q} is continuous with e.values $q(z)$ associated with e.vectors $f_z(x)$, the probability of getting a result in the range dz is

$$|c(z)|^2 dz \quad \text{where } c(z) = \langle f_z | \Psi \rangle$$

$$\langle Q \rangle = \sum_n q_n |c_n|^2.$$

Upon measurement, the wave function collapses to f_n or a narrow range about f_z depending on the precision of the measurement.

Completeness  $\Psi(x, t) = \sum_n c_n f_n(x)$

$$\begin{aligned} 1 &= \langle \Psi | \Psi \rangle = \left\langle \left(\sum_{n'} c_{n'} f_{n'} \right) \middle| \left(\sum_n c_n f_n \right) \right\rangle = \sum_{n'} \sum_n c_{n'}^* c_n \langle f_{n'} | f_n \rangle \\ &= \sum_{n'} \sum_n c_{n'}^* c_n \delta_{n'n} = \sum_n c_n^* c_n = \sum_n |c_n|^2. \end{aligned}$$

$$\begin{aligned} \Phi(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ipx/\hbar} \Psi(x, t) dx; \\ \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{ipx/\hbar} \Phi(p, t) dp. \end{aligned}$$

Generalised Uncertainty Principle

For any observable A , we have

$$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle) \Psi | (\hat{A} - \langle A \rangle) \Psi \rangle = \langle f | f \rangle,$$

where $f \equiv (\hat{A} - \langle A \rangle) \Psi$. Likewise, for any *other* observable, B ,

$$\sigma_B^2 = \langle g | g \rangle, \quad \text{where } g \equiv (\hat{B} - \langle B \rangle) \Psi.$$

Therefore

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2.$$

Now, for any complex number z ,

$$|z|^2 = [\operatorname{Re}(z)]^2 + [\operatorname{Im}(z)]^2 \geq [\operatorname{Im}(z)]^2 = \left[\frac{1}{2i} (z - z^*) \right]^2.$$

Therefore, letting $z = \langle f | g \rangle$,

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} [\langle f | g \rangle - \langle g | f \rangle] \right)^2.$$

But

$$\begin{aligned} \langle f | g \rangle &= \langle (\hat{A} - \langle A \rangle) \Psi | (\hat{B} - \langle B \rangle) \Psi \rangle = \langle \Psi | (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle) \Psi \rangle \\ &= \langle \Psi | (\hat{A}\hat{B} - \hat{A}\langle B \rangle - \hat{B}\langle A \rangle + \langle A \rangle \langle B \rangle) \Psi \rangle \\ &= \langle \Psi | \hat{A}\hat{B} \Psi \rangle - \langle B \rangle \langle \Psi | \hat{A} \Psi \rangle - \langle A \rangle \langle \Psi | \hat{B} \Psi \rangle + \langle A \rangle \langle B \rangle \langle \Psi | \Psi \rangle \\ &= \langle \hat{A}\hat{B} \rangle - \langle B \rangle \langle A \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle \\ &= \langle \hat{A}\hat{B} \rangle - \langle A \rangle \langle B \rangle. \end{aligned}$$

Similarly,

$$\langle g | f \rangle = \langle \hat{B}\hat{A} \rangle - \langle A \rangle \langle B \rangle,$$

so

$$\langle f | g \rangle - \langle g | f \rangle = \langle \hat{A}\hat{B} \rangle - \langle \hat{B}\hat{A} \rangle = \langle [\hat{A}, \hat{B}] \rangle,$$

where

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

is the commutator of the two operators

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right)^2.$$

Energy Time Relation

As a measure of how fast the system is changing, let us compute the time derivative of the expectation value of some observable, $Q(x, p, t)$:

$$\frac{d}{dt}\langle Q \rangle = \frac{d}{dt}\langle \Psi | \hat{Q} \Psi \rangle = \left\langle \frac{\partial \Psi}{\partial t} \middle| \hat{Q} \Psi \right\rangle + \left\langle \Psi \middle| \frac{\partial \hat{Q}}{\partial t} \Psi \right\rangle + \left\langle \Psi \middle| \hat{Q} \frac{\partial \Psi}{\partial t} \right\rangle.$$

Now, the Schrödinger equation says

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

(where $H = p^2/2m + V$ is the Hamiltonian). So

$$\frac{d}{dt}\langle Q \rangle = -\frac{1}{i\hbar}\langle \hat{H} \Psi | \hat{Q} \Psi \rangle + \frac{1}{i\hbar}\langle \Psi | \hat{Q} \hat{H} \Psi \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle.$$

But \hat{H} is hermitian, so $\langle \hat{H} \Psi | \hat{Q} \Psi \rangle = \langle \Psi | \hat{H} \hat{Q} \Psi \rangle$, and hence

$$\boxed{\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle.}$$

Now, suppose we pick $A = H$ and $B = Q$, in the generalized uncertainty principle, and assume that Q does not depend explicitly on t :

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i}\langle [\hat{H}, \hat{Q}] \rangle \right)^2 = \left(\frac{1}{2i} \frac{\hbar}{i} \frac{d\langle Q \rangle}{dt} \right)^2 = \left(\frac{\hbar}{2} \right)^2 \left(\frac{d\langle Q \rangle}{dt} \right)^2.$$

Or, more simply,

$$\sigma_H \sigma_Q \geq \frac{\hbar}{2} \left| \frac{d\langle Q \rangle}{dt} \right|.$$

Let's define $\Delta E \equiv \sigma_H$, and

$$\Delta t \equiv \frac{\sigma_Q}{|d\langle Q \rangle / dt|}.$$

Then

$$\Delta E \Delta t \geq \frac{\hbar}{2},$$

and that's the energy-time uncertainty principle. But notice what is meant by Δt , here: Since

$$\sigma_Q = \left| \frac{d\langle Q \rangle}{dt} \right| \Delta t,$$

Δt represents the *amount of time it takes the expectation value of Q to change by one standard deviation*. In particular, Δt depends entirely on what observable (Q) you care to look at—the change might be rapid for one observable and slow for another. But if ΔE is small, then the rate of change of *all* observables must be very gradual; or, to put it the other way around, if *any* observable changes rapidly, the “uncertainty” in the energy must be large.

Quantum Mechanics

QM in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \text{ with } \int |\Psi|^2 d^3r = 1$$

For $V = V(\mathbf{r})$

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

and

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

The general solution

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$

For $V = V(r)$, i.e. central potentials

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V\psi = E\psi$$

Separable solutions

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi).$$

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + VRY = ERY.$$

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] \right\} + \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} = 0.$$

$$\begin{aligned} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] &= l(l+1); \\ \frac{1}{Y} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right\} &= -l(l+1). \end{aligned}$$

QM in 3D - The angular equation

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1) \sin^2 \theta Y.$$

we try separation of variables: $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$.

$$\left\{ \frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta \right\} + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0.$$

$$\frac{1}{\Theta} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1) \sin^2 \theta = m^2 \quad \text{and} \quad \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2.$$

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \Rightarrow \Phi(\phi) = e^{im\phi}$$

Since $\Phi(\phi + 2\pi) = \Phi(\phi)$. $m = 0, \pm 1, \pm 2, \dots$

The θ equation,

$$\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2] \Theta = 0.$$

The solution is

$$\Theta(\theta) = A P_l^m(\cos \theta),$$

where P_l^m is the **associated Legendre function**,

$$P_l^m(x) \equiv (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x).$$

and $P_l(x)$ is the l th **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l.$$

QM in 3D - The angular equation

Legendre polynomials

$$P_0 = 1$$

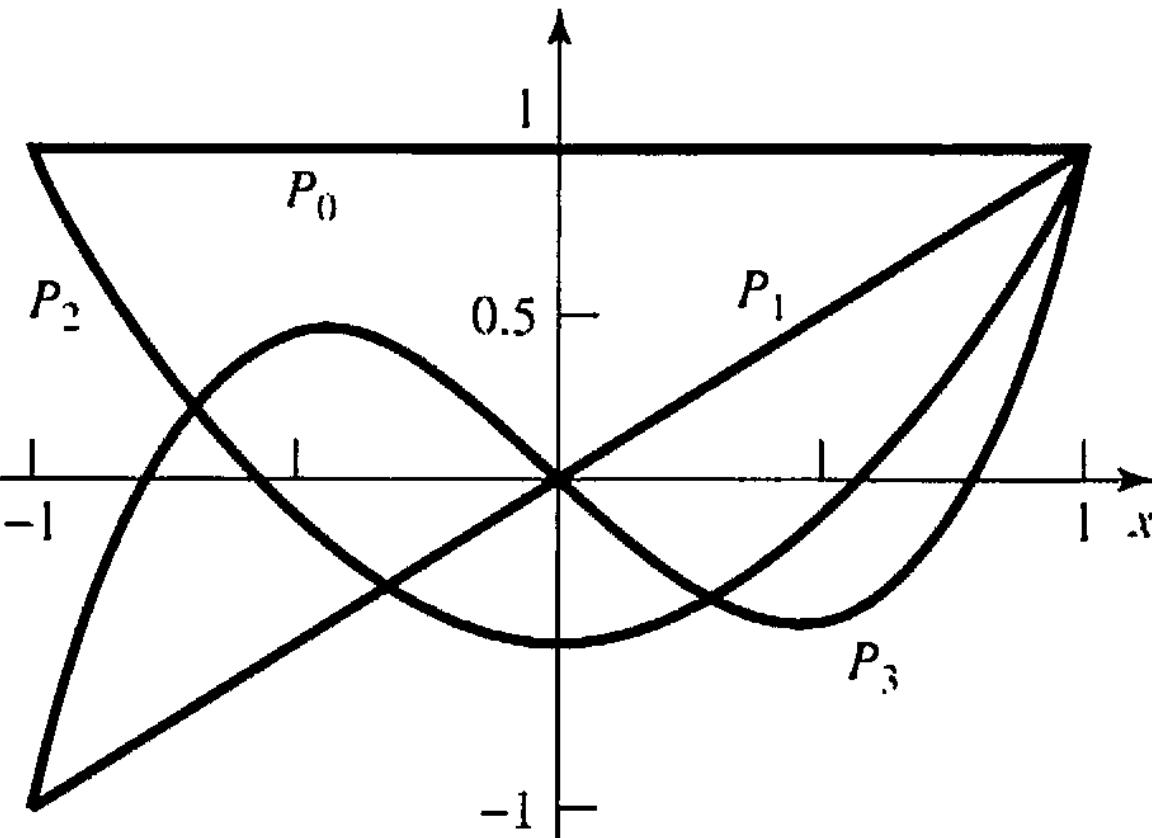
$$P_1 = x$$

$$P_2 = \frac{1}{2}(3x^2 - 1)$$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



(a)

(b)

Rodrigues formula:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l.$$

Notice that l must be a nonnegative *integer*, for the Rodrigues formula to make any sense; moreover, if $|m| > l$, then $P_l^m = 0$.

$$l = 0, 1, 2, \dots; \quad m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l.$$

For example,

$$P_0(x) = 1, \quad P_1(x) = \frac{1}{2} \frac{d}{dx} (x^2 - 1) = x,$$

$$P_2(x) = \frac{1}{4 \cdot 2} \left(\frac{d}{dx} \right)^2 (x^2 - 1)^2 = \frac{1}{2} (3x^2 - 1),$$

Associated Legendre functions

$$P_2^0(x) = \frac{1}{2}(3x^2 - 1), \quad P_2^1(x) = (1 - x^2)^{1/2} \frac{d}{dx} \left[\frac{1}{2}(3x^2 - 1) \right] = 3x\sqrt{1 - x^2}.$$

$$P_2^2(x) = (1 - x^2) \left(\frac{d}{dx} \right)^2 \left[\frac{1}{2}(3x^2 - 1) \right] = 3(1 - x^2),$$

$$P_0^0 = 1$$

$$P_2^0 = \frac{1}{2}(3 \cos^2 \theta - 1)$$

$$P_1^1 = \sin \theta$$

$$P_3^3 = 15 \sin \theta (1 - \cos^2 \theta)$$

$$P_1^0 = \cos \theta$$

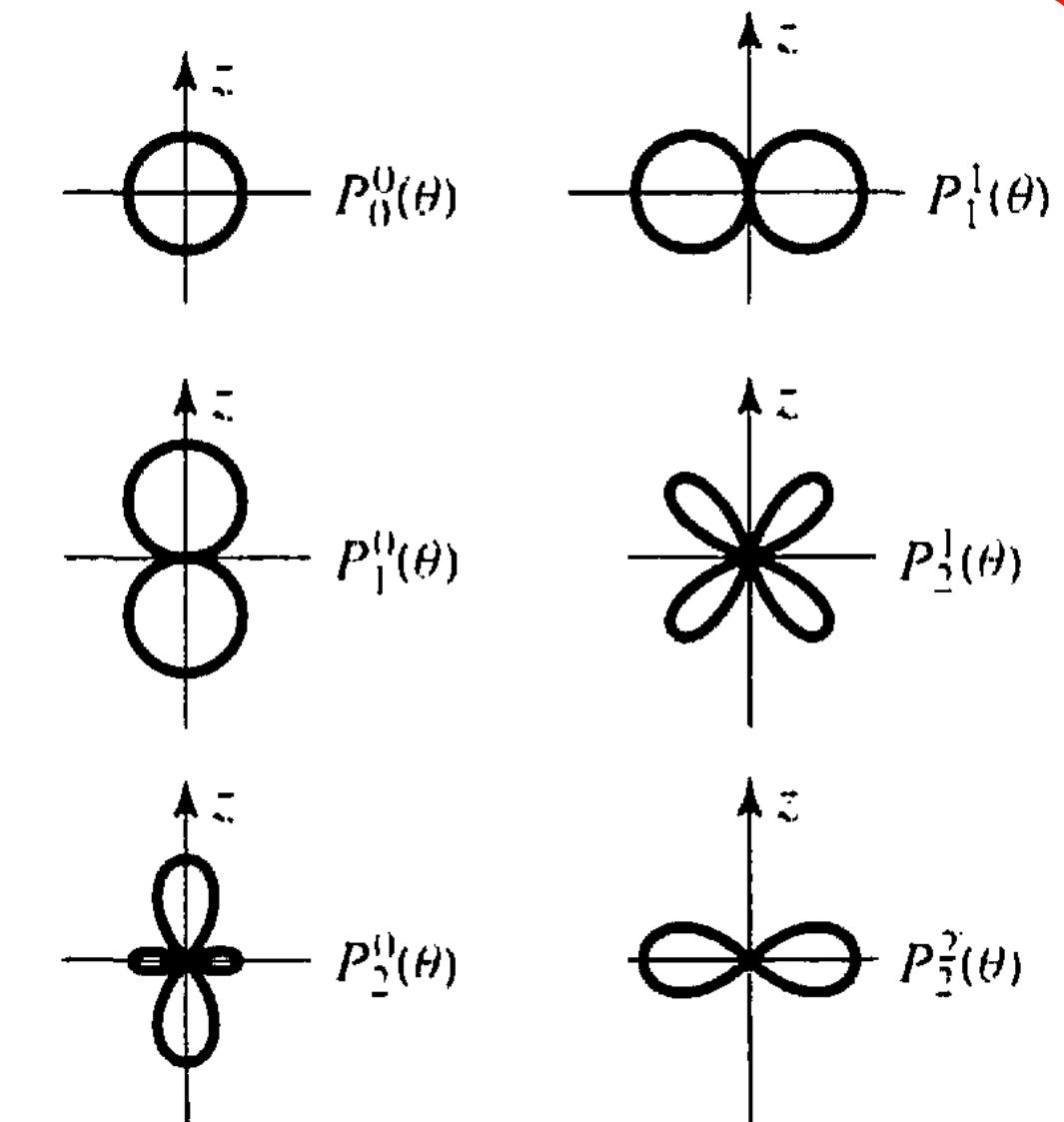
$$P_3^2 = 15 \sin^2 \theta \cos \theta$$

$$P_2^2 = 3 \sin^2 \theta$$

$$P_3^1 = \frac{3}{2} \sin \theta (5 \cos^2 \theta - 1)$$

$$P_2^1 = 3 \sin \theta \cos \theta$$

$$P_3^0 = \frac{1}{2} (5 \cos^3 \theta - 3 \cos \theta)$$



QM in 3D - The angular equation

The normalisation condition

$$\int |\psi|^2 r^2 \sin \theta dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin \theta d\theta d\phi = 1.$$

It is convenient to normalize R and Y separately:

$$\int_0^\infty |R|^2 r^2 dr = 1 \quad \text{and} \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin \theta d\theta d\phi = 1.$$

The normalized angular wave functions⁸ are called **spherical harmonics**:

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos \theta).$$

Orthogonal

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

Azimuthal quantum number: l

Magnetic quantum number: m

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

$$Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$$

$$Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$$

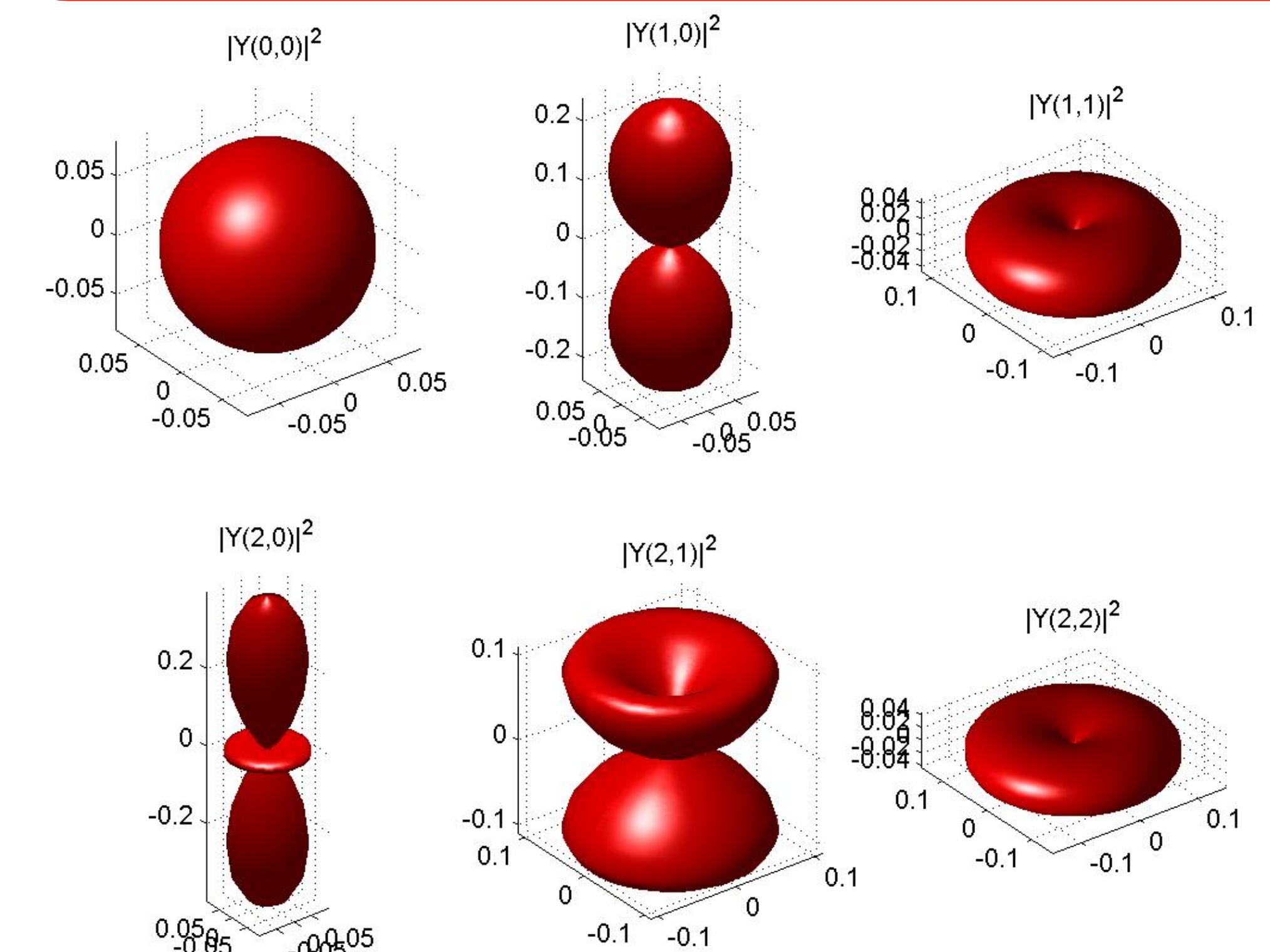
$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$$

$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$$

$$Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$$



QM in 3D - The radial equation

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = l(l+1)R.$$

This equation simplifies if we change variables: Let

$$u(r) \equiv rR(r),$$

so that $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = rd^2u/dr^2$, and hence

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu.$$

We define the effective potential

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2},$$

← Centrifugal term

Normalisation:

$$\int_0^\infty |u|^2 dr = 1.$$

Infinite spherical well $V(r) = \begin{cases} 0, & \text{if } r \leq a; \\ \infty, & \text{if } r > a. \end{cases}$

Inside the well $\frac{d^2u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u$, $k \equiv \frac{\sqrt{2mE}}{\hbar}$.

$$l = 0$$

$$\frac{d^2u}{dr^2} = -k^2u \Rightarrow u(r) = A \sin(kr) + B \cos(kr)$$

$$\cos(kr)/r \rightarrow \infty \text{ as } r \rightarrow 0 \Rightarrow B = 0$$

$$u(a) = 0 \Rightarrow ka = n\pi$$

$$E_{n0} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \dots).$$

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}$$

QM in 3D - The Hydrogen atom

The radial equation

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2m r^2} \right] u = Eu.$$

We are looking for bound state solutions $E < 0$

$$\frac{1}{\kappa^2} \frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \frac{1}{(kr)} + \frac{l(l+1)}{(\kappa r)^2} \right] u. \quad \text{with } \kappa \equiv \frac{\sqrt{-2mE}}{\hbar}.$$

Let $\rho \equiv \kappa r$, and $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$,



$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u.$$

Next we examine the asymptotic form of the solutions. As $\rho \rightarrow \infty$, the constant term in the brackets dominates, so (approximately)

$$\frac{d^2u}{d\rho^2} = u.$$

The general solution is

$$u(\rho) = Ae^{-\rho} + Be^{\rho}.$$

but e^{ρ} blows up (as $\rho \rightarrow \infty$), so $B = 0$. Evidently,

$$u(\rho) \sim Ae^{-\rho}.$$

for large ρ . On the other hand, as $\rho \rightarrow 0$ the centrifugal term dominates

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u.$$

The general solution

$$u(\rho) = C\rho^{l+1} + D\rho^{-l},$$

but ρ^{-l} blows up (as $\rho \rightarrow 0$), so $D = 0$. Thus

$$u(\rho) \sim C\rho^{l+1},$$

for small ρ .

Guess!

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho),$$

QM in 3D - The Hydrogen atom

The radial equation

$$\frac{du}{d\rho} = \rho^l e^{-\rho} \left[(l+1-\rho)v + \rho \frac{dv}{d\rho} \right],$$

and

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho} \left\{ \left[-2l - 2 + \rho + \frac{l(l+1)}{\rho} \right] v + 2(l+1-\rho) \frac{dv}{d\rho} + \rho \frac{d^2v}{d\rho^2} \right\}.$$

In terms of $v(\rho)$, then,

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0.$$

Finally, we assume the solution, $v(\rho)$, can be expressed as a power series in ρ :

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j.$$

Our problem is to determine the coefficients (c_0, c_1, c_2, \dots) . Differentiating term by term:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j.$$

Differentiating again,

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

Plugging these two in our equation for $v(\rho)$ we get,

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$-2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0.$$

The coefficient of ρ^j gives us

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j.$$

QM in 3D - The Hydrogen atom

$$c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j.$$

The radial equation

Now let's see what the coefficients look like for large j (this corresponds to large ρ , where the higher powers dominate). In this regime the recursion formula says

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j.$$

Suppose for a moment that this were *exact*. Then

$$c_j = \frac{2^j}{j!} c_0,$$

so

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho},$$

and hence

$$u(\rho) = c_0 \rho^{l+1} e^\rho,$$

which blows up at large ρ . The positive exponential is precisely the asymptotic behavior we *didn't* want.

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \quad \kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an},$$

The series must terminate!

$$c_{(j_{\max}+1)} = 0,$$

$$2(j_{\max} + l + 1) - \rho_0 = 0.$$

Defining

$$n \equiv j_{\max} + l + 1$$

(the so-called **principal quantum number**), we have

$$\rho_0 = 2n.$$

But ρ_0 determines E (Equations 4.54 and 4.55):

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2},$$

so the allowed energies are

Bohr formula

$$E_n = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots$$

QM in 3D - The Hydrogen atom

The spatial wave functions for hydrogen are labeled by three quantum numbers (n , l , and m):

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_l^m(\theta, \phi),$$

where

$$R_{nl}(r) = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho),$$

and $v(\rho)$ is a polynomial of degree $j_{\max} = n - l - 1$ in ρ , whose coefficients are determined (up to an overall normalization factor) by the recursion formula

$$c_{j+1} = \frac{2(j + l + 1 - n)}{(j + 1)(j + 2l + 2)} c_j.$$

The **ground state** (that is, the state of lowest energy) is the case $n = 1$; putting in the accepted values for the physical constants, we get:

$$E_1 = - \left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = -13.6 \text{ eV.}$$

$$n = 1 \Rightarrow l = m = 0$$

$$\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_0^0(\theta, \phi).$$

$$R_{10}(r) = \frac{c_0}{a} e^{-r/a}.$$

Normalising

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|c_0|^2}{a^2} \int_0^\infty e^{-2r/a} r^2 dr = |c_0|^2 \frac{a}{4} = 1$$

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

QM in 3D - The Hydrogen atom

For arbitrary n , the possible values of l are

$$l = 0, 1, 2, \dots, n-1,$$

and for each l there are $(2l+1)$ possible values of m
degeneracy of the energy level E_n is

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

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho),$$

where

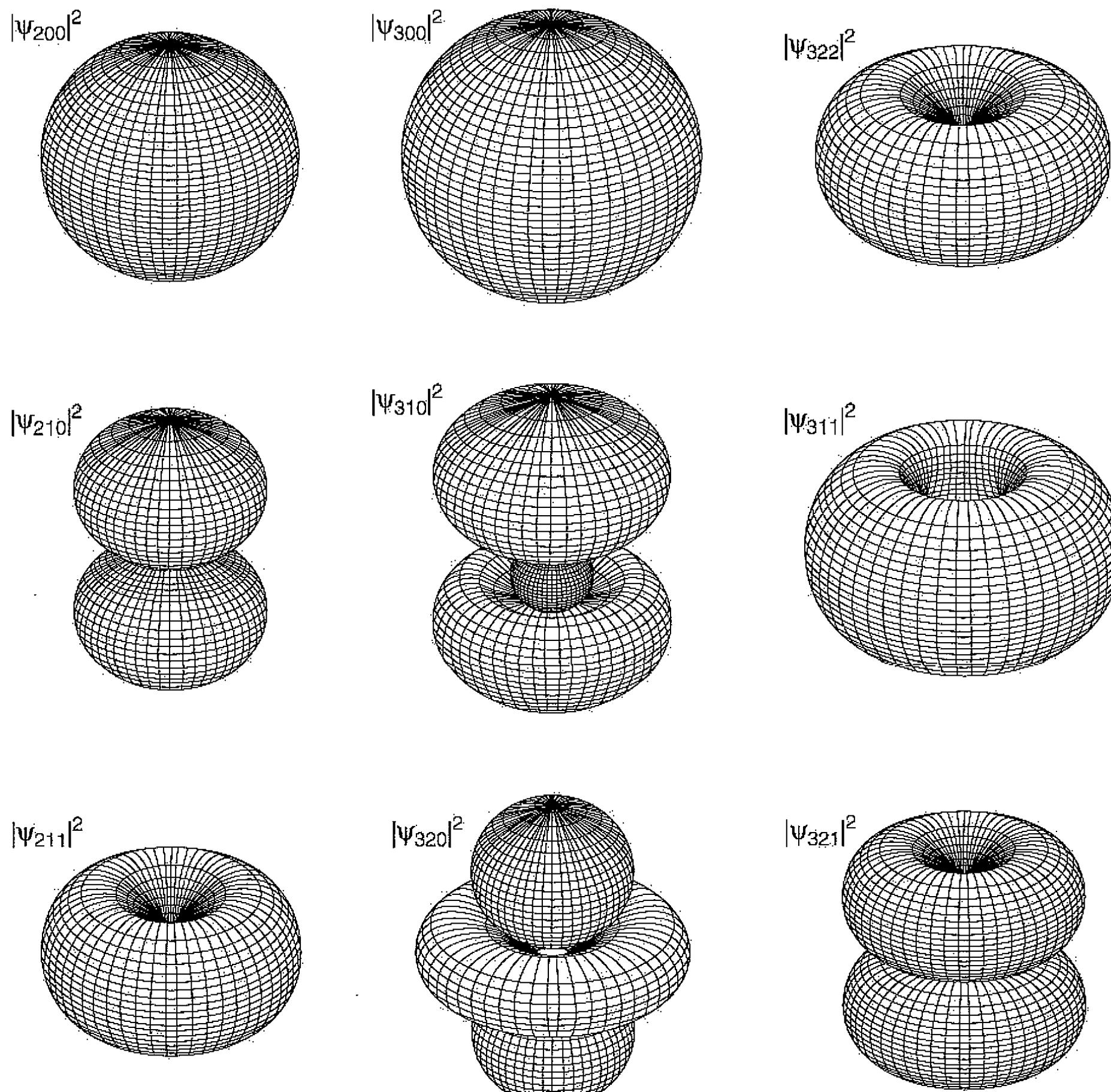
$$L_{q-p}^p(x) \equiv (-1)^p \left(\frac{d}{dx} \right)^p L_q(x)$$

is an associated Laguerre polynomial, and

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q)$$

is the q th Laguerre polynomial.

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na} \left(\frac{2r}{na} \right)^l [L_{n-l-1}^{2l+1}(2r/na)] Y_l^m(\theta, \phi).$$



QM in 3D - Angular Momentum

The operators L_x and L_y do not commute;

$$\begin{aligned} [L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \\ &= yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(xp_y - yp_x) = i\hbar L_z. \end{aligned}$$

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y.$$

L_x, L_y and L_z are incompatible operators $\sigma_{L_x}^2 \sigma_{L_y}^2 \geq \left(\frac{1}{2i}\langle i\hbar L_z \rangle\right)^2 = \frac{\hbar^2}{4}\langle L_z \rangle^2$,

The square of the total angular momentum does commute with each of them.

$$L^2 \equiv L_x^2 + L_y^2 + L_z^2,$$

$$\begin{aligned} [L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\ &= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\ &= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y + L_z(i\hbar L_y) + (i\hbar L_y)L_z \\ &= 0. \end{aligned}$$

$$[L^2, L_x] = 0, \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0, \text{ or, more compactly, } [L^2, \mathbf{L}] = 0.$$

Let's try to find simultaneous eigenstates of L^2 and L_z

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f.$$

Let's use the same old trick!

$$L_{\pm} \equiv L_x \pm iL_y$$

$$\begin{aligned} [L_z, L_{\pm}] &= [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) \\ &= \pm \hbar L_{\pm}. \end{aligned}$$

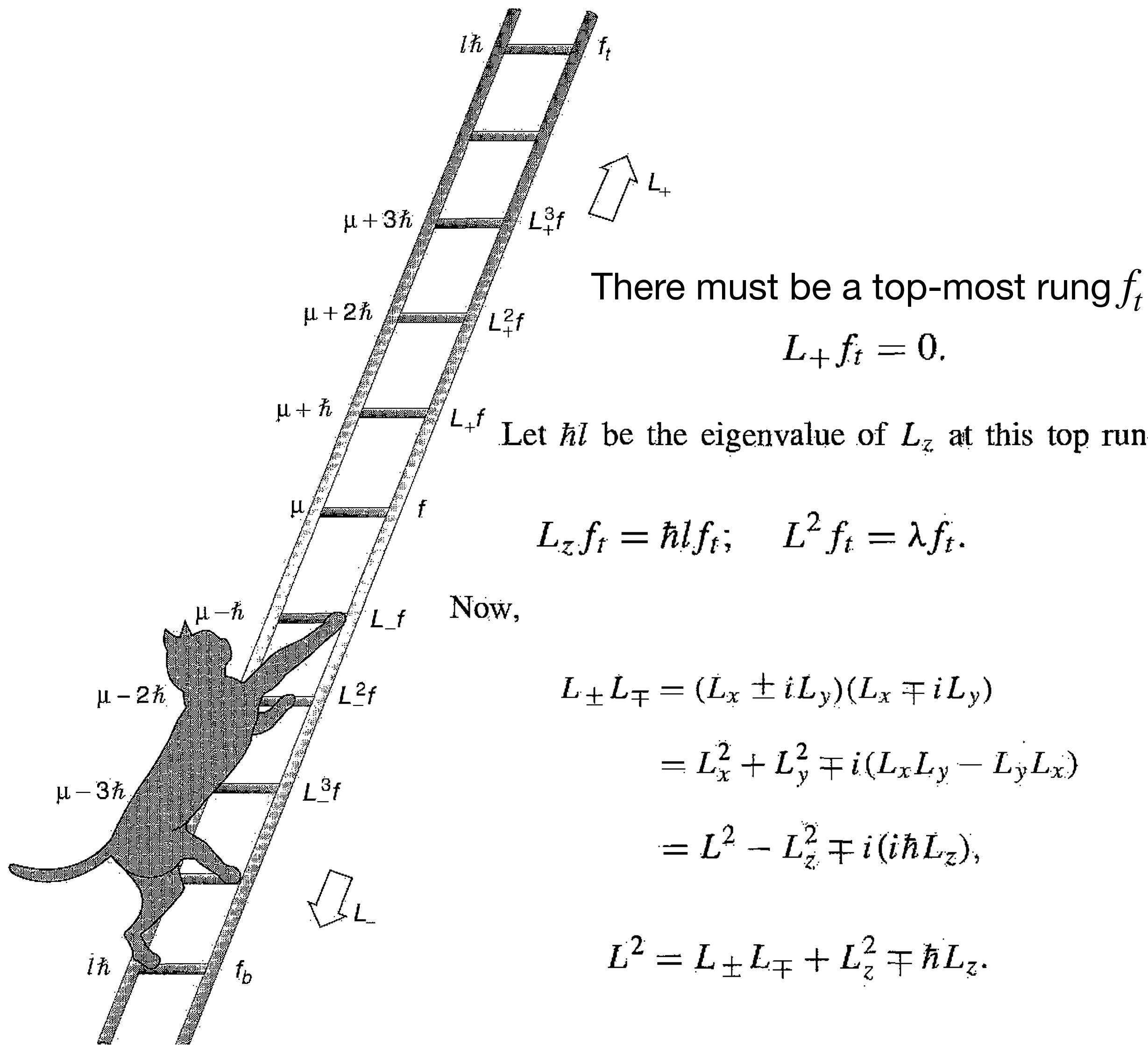
and

$$[L^2, L_{\pm}] = 0.$$

If f is an eigenfunction of L^2 and L_z then so is $L_{\pm}f$

$$\begin{aligned} L^2(L_{\pm}f) &= L_{\pm}(L^2f) = L_{\pm}(\lambda f) = \lambda(L_{\pm}f), \\ L_z(L_{\pm}f) &= (L_z L_{\pm} - L_{\pm} L_z)f + L_{\pm} L_z f \\ &= \pm \hbar L_{\pm}f + L_{\pm}(\mu f) \\ &= (\mu \pm \hbar)(L_{\pm}f). \end{aligned}$$

QM in 3D - Angular Momentum



$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + \hbar^2 l^2 + \hbar^2 l) f_t = \hbar^2 l(l+1) f_t,$$

or, $\lambda = \hbar^2 l(l+1).$

There must be a bottom-most rung f_b

Let $\hbar \bar{l}$ be the eigenvalue of L_z at this bottom rung:

$$L_z f_b = \hbar \bar{l} f_b; \quad L^2 f_b = \lambda f_b.$$

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = (0 + \hbar^2 \bar{l}^2 - \hbar^2 \bar{l}) f_b = \hbar^2 \bar{l}(\bar{l}-1) f_b,$$

or, $\lambda = \hbar^2 \bar{l}(\bar{l}-1).$

Hence, $l(l+1) = \bar{l}(\bar{l}-1),$

$\bar{l} = l+1$ (absurd) or, $\bar{l} = -l.$

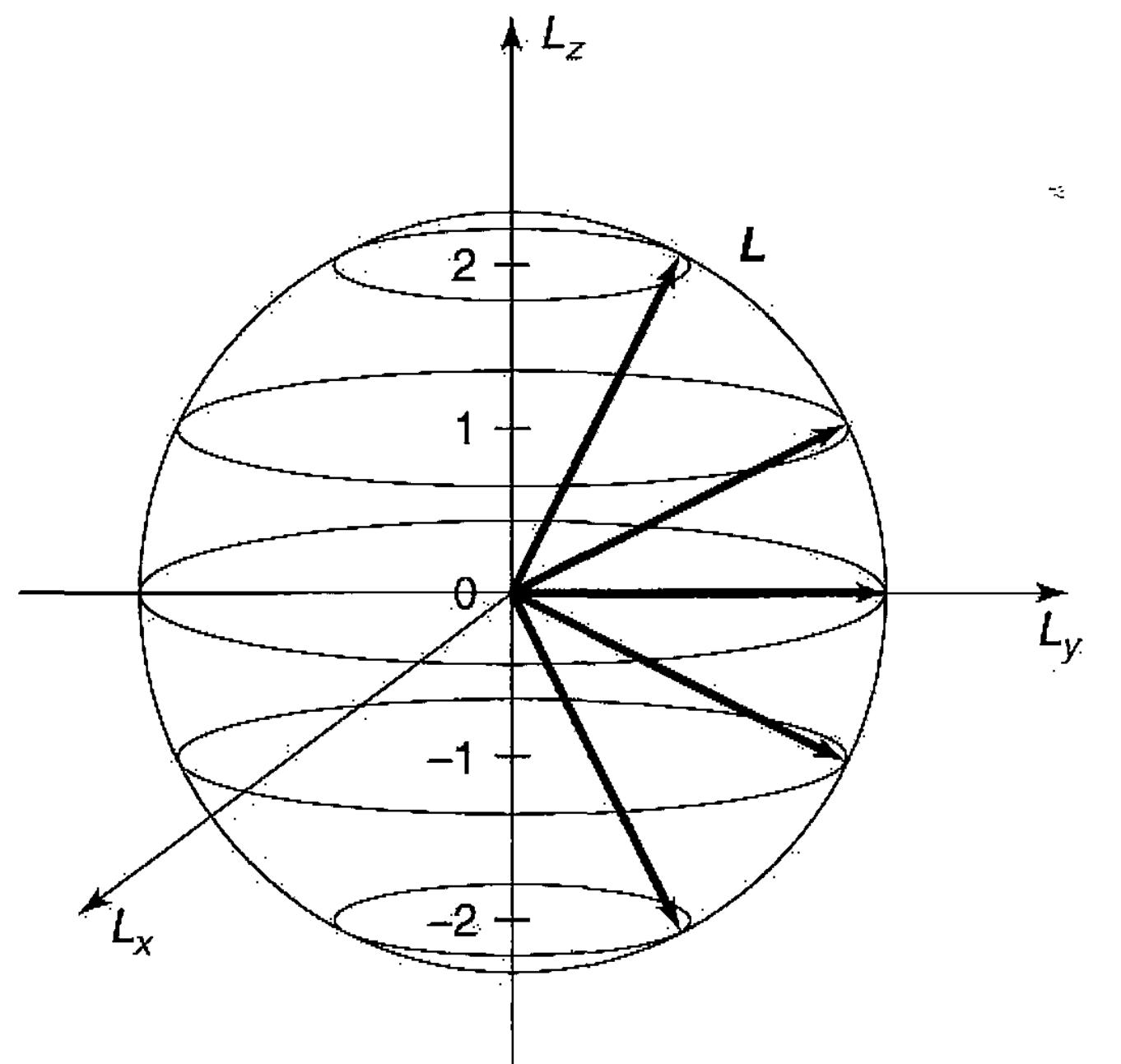
QM in 3D - Angular Momentum

The eigenvalues of L_z are $m\hbar$, where m goes from $-l$ to $+l$ in N integer steps, i.e., $l = N/2$ (an integer or a half-integer).

$$L^2 f_l^m = \hbar^2 l(l+1) f_l^m; \quad L_z f_l^m = \hbar m f_l^m,$$

$$l = 0, 1/2, 1, 3/2, \dots; \quad m = -l, -l+1, \dots, l-1, l.$$

For a given value of l , there are $2l + 1$ different values of m (i.e., $2l + 1$ “rungs” on the “ladder”).



$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi};$$

$$\mathbf{L} = \frac{\hbar}{i} \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + (\hat{r} \times \hat{\phi}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].$$

But $(\hat{r} \times \hat{r}) = 0$, $(\hat{r} \times \hat{\theta}) = \hat{\phi}$, and $(\hat{r} \times \hat{\phi}) = -\hat{\theta}$ (see F)

$$\mathbf{L} = \frac{\hbar}{i} \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right).$$

The unit vectors $\hat{\theta}$ and $\hat{\phi}$ can be resolved into their cartesian components:

$$\begin{aligned}\hat{\theta} &= (\cos \theta \cos \phi) \hat{i} + (\cos \theta \sin \phi) \hat{j} - (\sin \theta) \hat{k}; \\ \hat{\phi} &= -(\sin \phi) \hat{i} + (\cos \phi) \hat{j},\end{aligned}$$

Thus

$$\begin{aligned}\mathbf{L} = \frac{\hbar}{i} \left[& (-\sin \phi \hat{i} + \cos \phi \hat{j}) \frac{\partial}{\partial \theta} \right. \\ & \left. - (\cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right].\end{aligned}$$

QM in 3D - Angular Momentum

Evidently

$$L_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

$$L_y = \frac{\hbar}{i} \left(+\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right),$$

and

$$L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}.$$

We shall also need the raising and lowering operators:

$$L_{\pm} = L_x \pm i L_y = \frac{\hbar}{i} \left[(-\sin \phi \pm i \cos \phi) \frac{\partial}{\partial \theta} - (\cos \phi \pm i \sin \phi) \cot \theta \frac{\partial}{\partial \phi} \right].$$

But $\cos \phi \pm i \sin \phi = e^{\pm i\phi}$, so

$$L_{\pm} = \pm \hbar e^{\pm i\phi} \left(\frac{\partial}{\partial \theta} \pm i \cot \theta \frac{\partial}{\partial \phi} \right).$$

$$L_+ L_- = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + i \frac{\partial}{\partial \phi} \right),$$

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right].$$

$$L^2 f_l^m = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] f_l^m = \hbar^2 l(l+1) f_l^m.$$

But this is precisely the “angular equation”

$$L_z f_l^m = \frac{\hbar}{i} \frac{\partial}{\partial \phi} f_l^m = \hbar m f_l^m,$$

this is equivalent to $L^2 f = \lambda f$ and $L_z f = \mu f$.

Spherical harmonics are eigenfunctions of L^2 and L_z

$$L^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \text{ and } L_z |l, m\rangle = \hbar |l, m\rangle$$

Earlier we were actually looking for simultaneous eigenfunctions of H , L^2 and L_z

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 l(l+1)\psi, \quad L_z\psi = \hbar m\psi. \quad \psi \equiv |n, l, m\rangle$$

We can write the Schrödinger equation as

$$\frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \psi + V\psi = E\psi.$$

Quantum Numbers

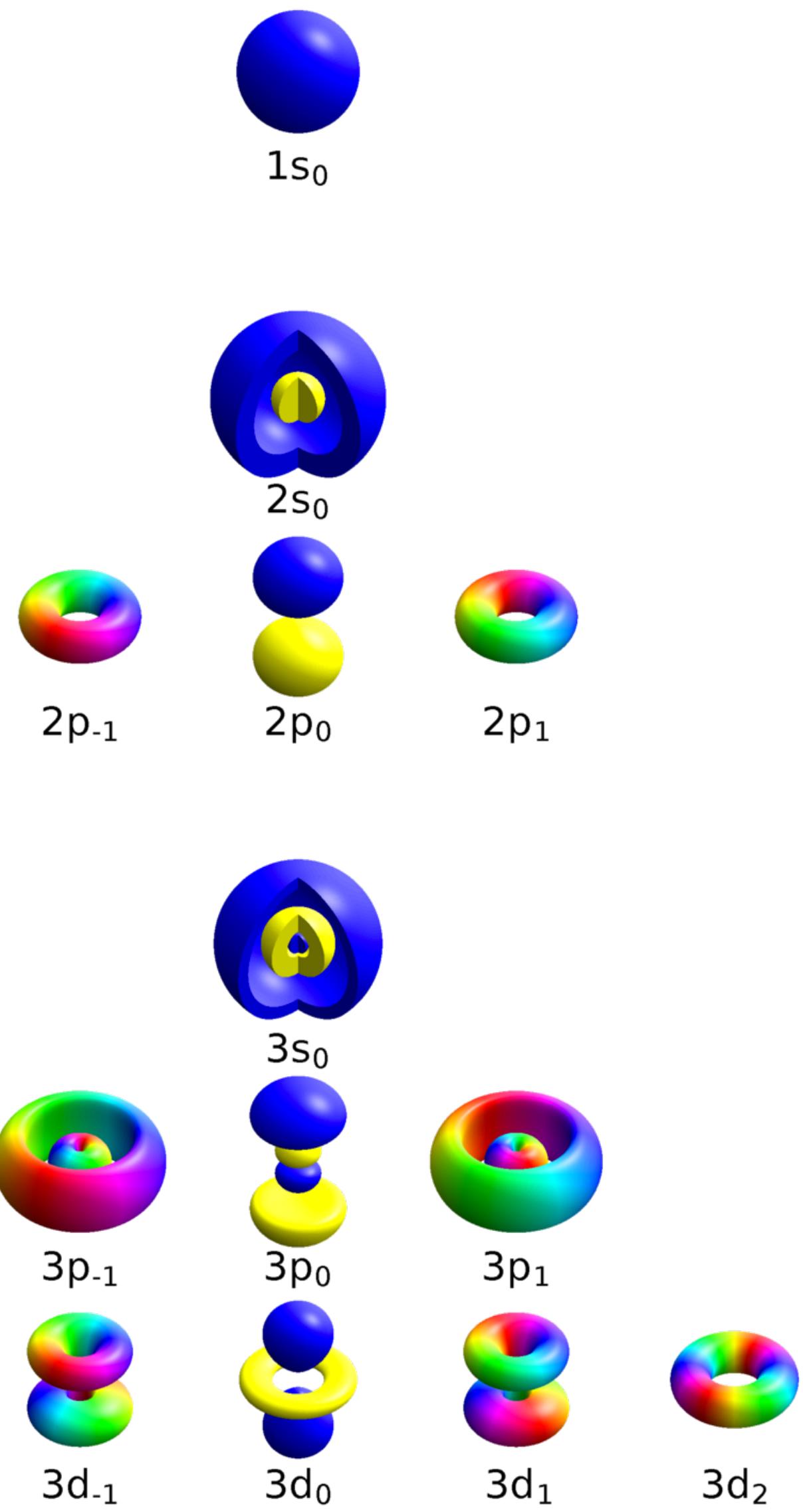
Conserved quantities

$$\psi = |n, l, m\rangle$$

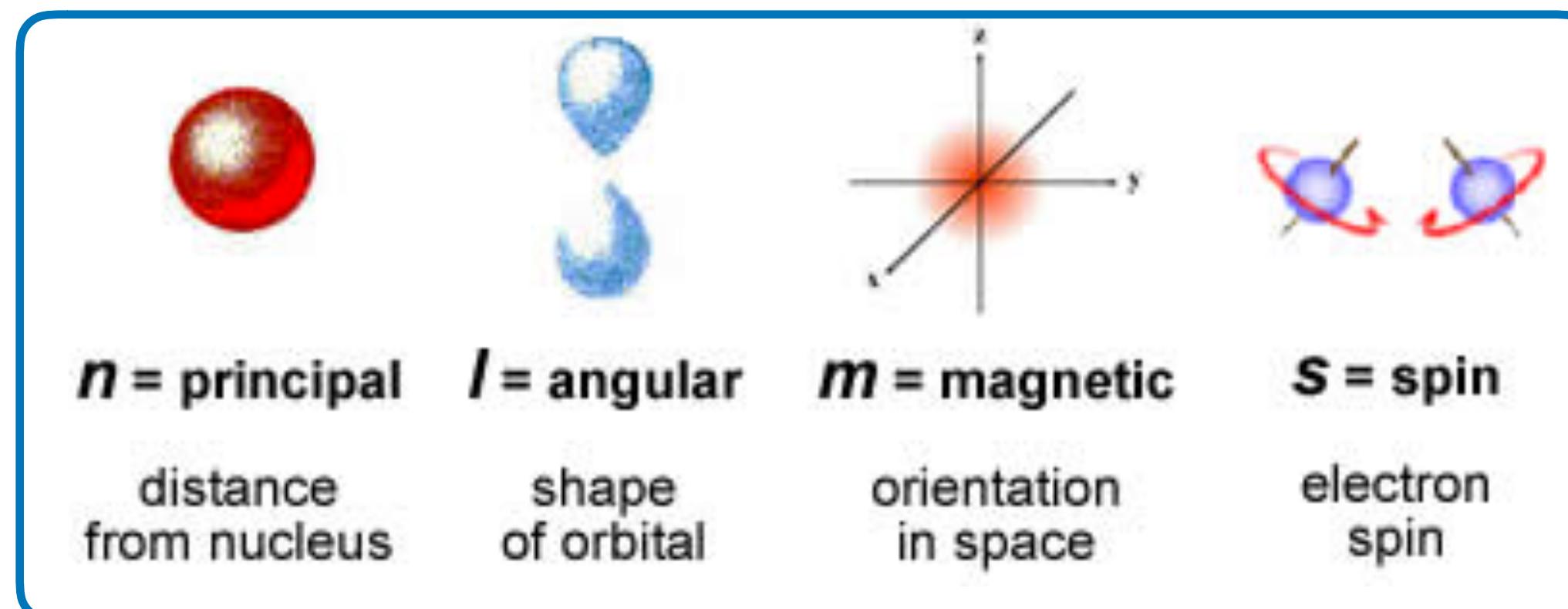
Eigenvalues of hermitian operators that commute with the Hamiltonian. The operators correspond to observables that can be measured together with the system's energy. A specification of all of the quantum numbers of a quantum system characterises the state of the system.

		n=1	n=2	n=3	n=4
s -- sharp	$\ell = 0$	1s	2s	3s	4s
p -- principal	$\ell = 1$		2p	3p	4p
d -- diffuse	$\ell = 2$			3d	4d
f -- fundamental	$\ell = 3$				4f
g	$\ell = 4$				
h	$\ell = 5$				
...					

beyond this point, the notation just follows the alphabet



Address of an electron



The magnetic quantum number determines the energy shift of an atomic orbital due to an external magnetic field.

QM in 3D - Spin

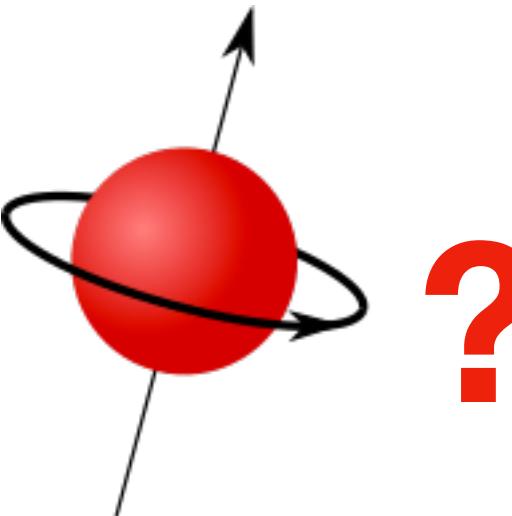
The *algebraic* theory of spin is a carbon copy of the theory of orbital angular momentum,

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y.$$

$$S^2 |s m\rangle = \hbar^2 s(s+1) |s m\rangle; \quad S_z |s m\rangle = \hbar m |s m\rangle;$$

$$S_{\pm} |s m\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s(m \pm 1)\rangle,$$

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots; \quad m = -s, -s+1, \dots, s-1, s.$$



If we write \mathbf{S}^2 as a matrix with (as yet) undetermined elements,

$$\mathbf{S}^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix},$$

then the first equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} \frac{3}{4}\hbar^2 \\ 0 \end{pmatrix},$$

so $c = (3/4)\hbar^2$ and $e = 0$. The second equation says

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{or} \quad \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{3}{4}\hbar^2 \end{pmatrix},$$

so $d = 0$ and $f = (3/4)\hbar^2$. Conclusion:

$$\mathbf{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Spin-1/2

By far the most important case is $s = 1/2$, for this is the spin of the particles that make up ordinary matter (protons, neutrons, and electrons), as well as all quarks and all leptons. Moreover, once you understand spin 1/2, it is a simple matter to work out the formalism for any higher spin. There are just *two* eigenstates: $|\frac{1}{2} \frac{1}{2}\rangle$, which we call **spin up** (informally, \uparrow), and $|\frac{1}{2} -\frac{1}{2}\rangle$, which we call **spin down** (\downarrow). Using these as basis vectors, the general state of a spin-1/2 particle can be expressed as a two-element column matrix (or **spinor**):

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-,$$

with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

representing spin up, and

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

for spin down.

$$\mathbf{S}^2 \chi_+ = \frac{3}{4}\hbar^2 \chi_+ \quad \text{and} \quad \mathbf{S}^2 \chi_- = \frac{3}{4}\hbar^2 \chi_-.$$

QM in 3D - Spin 1/2

Similarly,

$$\mathbf{S}_z \chi_+ = \frac{\hbar}{2} \chi_+, \quad \mathbf{S}_z \chi_- = -\frac{\hbar}{2} \chi_-,$$

from which it follows that

$$\mathbf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Meanwhile,

$$\mathbf{S}_+ \chi_- = \hbar \chi_+, \quad \mathbf{S}_- \chi_+ = \hbar \chi_-, \quad \mathbf{S}_+ \chi_+ = \mathbf{S}_- \chi_- = 0,$$

so

$$\mathbf{S}_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \mathbf{S}_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

Now $S_{\pm} = S_x \pm i S_y$, so $S_x = (1/2)(S_+ + S_-)$ and $S_y = (1/2i)(S_+ - S_-)$, and hence

$$\mathbf{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \mathbf{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

Since \mathbf{S}_x , \mathbf{S}_y , and \mathbf{S}_z all carry a factor of $\hbar/2$, it is tidier to write $\mathbf{S} = (\hbar/2)\boldsymbol{\sigma}$, where

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Pauli Spin Matrices

The eigenspinors of \mathbf{S}_z are

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \left(\text{eigenvalue } + \frac{\hbar}{2} \right); \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \left(\text{eigenvalue } - \frac{\hbar}{2} \right).$$

If you measure S_z on a particle in the general state χ you could get $+\hbar/2$, with probability $|a|^2$, or $-\hbar/2$, with probability $|b|^2$,

$$|a|^2 + |b|^2 = 1$$

But what if, instead, you chose to measure S_x ? What are the possible results, and what are their respective probabilities? According to the generalized statistical interpretation, we need to know the eigenvalues and eigenspinors of \mathbf{S}_x . The characteristic equation is

$$\begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 = \left(\frac{\hbar}{2}\right)^2 \Rightarrow \lambda = \pm \frac{\hbar}{2}.$$

Not surprisingly, the possible values for S_x are the same as those for S_z . The eigenspinors are obtained in the usual way:

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow \begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix},$$

so $\beta = \pm \alpha$.

QM in 3D - Spin 1/2

Evidently the (normalized) eigenspinors of \mathbf{S}_x are

$$\chi_+^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \left(\text{eigenvalue } + \frac{\hbar}{2}\right); \quad \chi_-^{(x)} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} \end{pmatrix}, \left(\text{eigenvalue } - \frac{\hbar}{2}\right)$$

As the eigenvectors of a hermitian matrix, they span the space; the generic spinor χ can be expressed as a linear combination of them:

$$\chi = \left(\frac{a+b}{\sqrt{2}}\right) \chi_+^{(x)} + \left(\frac{a-b}{\sqrt{2}}\right) \chi_-^{(x)}.$$

If you measure S_x , the probability of getting $+\hbar/2$ is $(1/2)|a+b|^2$, and the probability of getting $-\hbar/2$ is $(1/2)|a-b|^2$.

Example 4.2 Suppose a spin-1/2 particle is in the state

$$\chi = \frac{1}{\sqrt{6}} \begin{pmatrix} 1+i \\ 2 \end{pmatrix}.$$

What are the probabilities of getting $+\hbar/2$ and $-\hbar/2$, if you measure S_z and S_x ?

Solution: Here $a = (1+i)/\sqrt{6}$ and $b = 2/\sqrt{6}$, so for S_z the probability of getting $+\hbar/2$ is $|(1+i)/\sqrt{6}|^2 = 1/3$, and the probability of getting $-\hbar/2$ is $|2/\sqrt{6}|^2 = 2/3$. For S_x the probability of getting $+\hbar/2$ is $(1/2)|(3+i)/\sqrt{6}|^2 = 5/6$, and the probability of getting $-\hbar/2$ is $(1/2)|(-1+i)/\sqrt{6}|^2 = 1/6$. Incidentally, the *expectation value* of S_x is

$$\frac{5}{6} \left(+\frac{\hbar}{2}\right) + \frac{1}{6} \left(-\frac{\hbar}{2}\right) = \frac{\hbar}{3},$$

which we could also have obtained more directly:

$$\langle S_x \rangle = \chi^\dagger \mathbf{S}_x \chi = \begin{pmatrix} (1-i) & 2 \\ -\sqrt{6} & \sqrt{6} \end{pmatrix} \begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix} \begin{pmatrix} (1+i)/\sqrt{6} \\ 2/\sqrt{6} \end{pmatrix} = \frac{\hbar}{3}.$$

QM in 3D - Spin 1/2

Electron in a Magnetic Field

A spinning charged particle constitutes a magnetic dipole. Its **magnetic dipole moment**, μ , is proportional to its spin angular momentum, \mathbf{S} :

$$\mu = \gamma \mathbf{S};$$

the proportionality constant, γ , is called the **gyromagnetic ratio**. When a magnetic dipole is placed in a magnetic field \mathbf{B} , it experiences a torque, $\mu \times \mathbf{B}$, which tends to line it up parallel to the field (just like a compass needle). The energy associated with this torque is

$$H = -\mu \cdot \mathbf{B},$$

so the Hamiltonian of a spinning charged particle, at rest in a magnetic field \mathbf{B} , is

$$H = -\gamma \mathbf{B} \cdot \mathbf{S}.$$

Example 4.3 Larmor precession: Imagine a particle of spin 1/2 at rest in a uniform magnetic field, which points in the z -direction:

$$\mathbf{B} = B_0 \hat{k}.$$

The Hamiltonian

$$\mathbf{H} = -\gamma B_0 \mathbf{S}_z = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The eigenstates of \mathbf{H} are the same as those of \mathbf{S}_z :

$$\begin{cases} \chi_+, & \text{with energy } E_+ = -(\gamma B_0 \hbar)/2, \\ \chi_-, & \text{with energy } E_- = +(\gamma B_0 \hbar)/2. \end{cases}$$

Evidently the energy is lowest when the dipole moment is parallel to the field—just as it would be classically.

Since the Hamiltonian is time-independent, the general solution to the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = \mathbf{H}\chi,$$

can be expressed in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{-iE_+t/\hbar} + b\chi_- e^{-iE_-t/\hbar} = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix}.$$

QM in 3D - Spin 1/2

The constants a and b are determined by the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix},$$

(of course, $|a|^2 + |b|^2 = 1$). With no essential loss of generality I'll write $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, where α is a fixed angle whose physical significance will appear in a moment. Thus

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}.$$

To get a feel for what is happening here, let's calculate the expectation value of \mathbf{S} , as a function of time:

$$\begin{aligned} \langle S_x \rangle &= \chi(t)^\dagger \mathbf{S}_x \chi(t) = (\cos(\alpha/2)e^{-i\gamma B_0 t/2} \quad \sin(\alpha/2)e^{i\gamma B_0 t/2}) \\ &\quad \times \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix} \\ &= \frac{\hbar}{2} \sin \alpha \cos(\gamma B_0 t). \end{aligned}$$

Similarly,

$$\langle S_y \rangle = \chi(t)^\dagger \mathbf{S}_y \chi(t) = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_0 t),$$

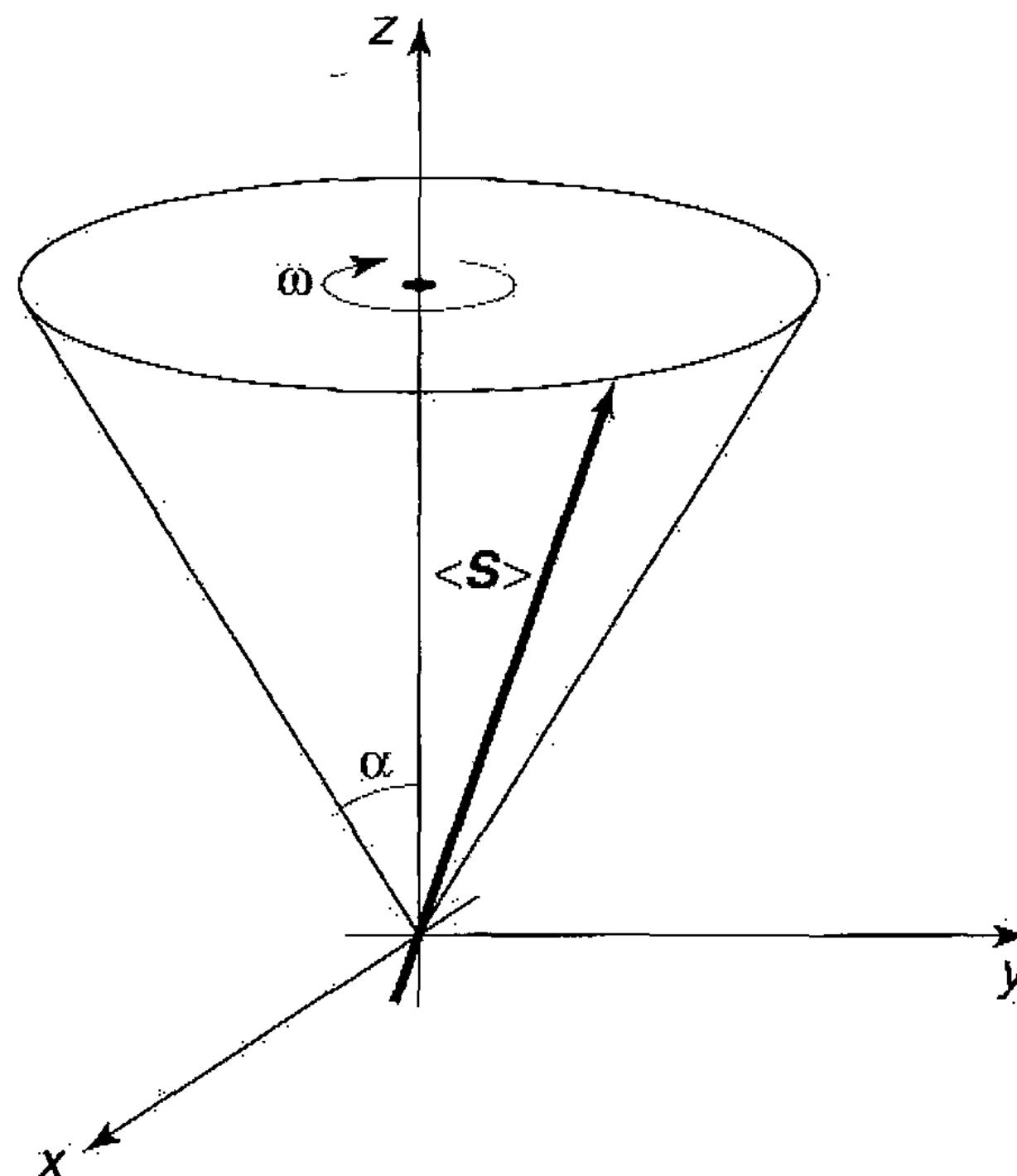
and

$$\langle S_z \rangle = \chi(t)^\dagger \mathbf{S}_z \chi(t) = \frac{\hbar}{2} \cos \alpha.$$

Evidently $\langle \mathbf{S} \rangle$ is tilted at a constant angle α to the z -axis, and precesses about the field at the **Larmor frequency**

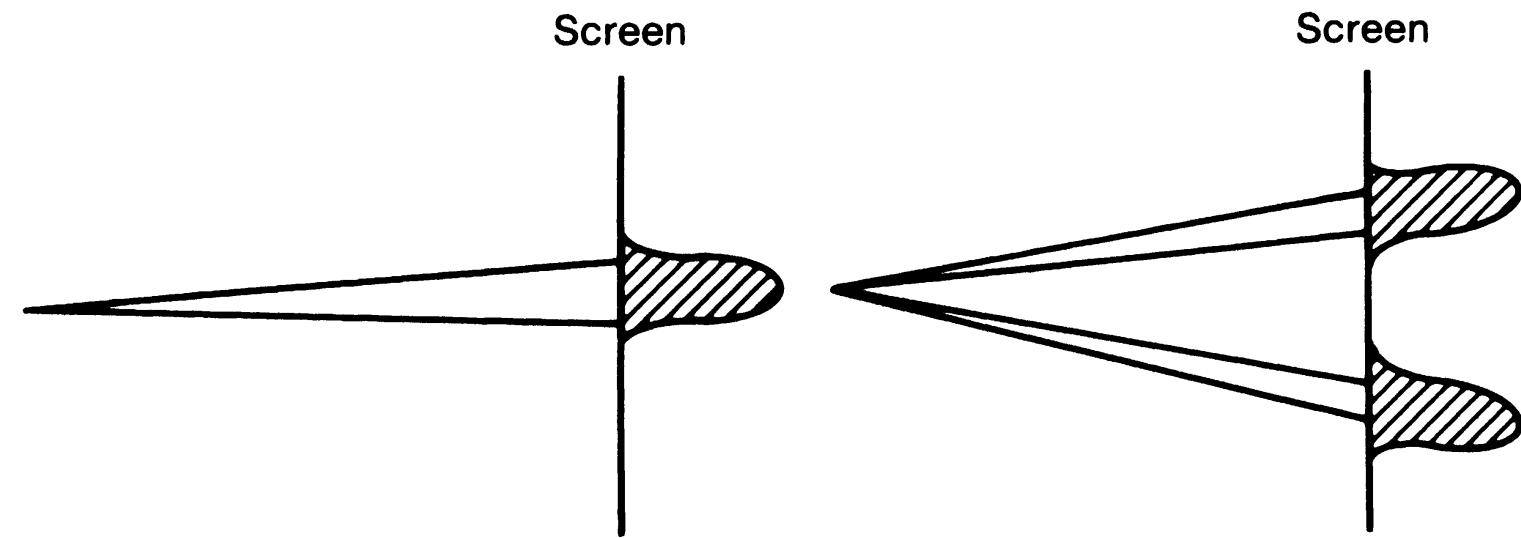
$$\omega = \gamma B_0,$$

just as it would classically



QM in 3D - Spin 1/2

Stern–Gerlach experiment



$$H(t) = \begin{cases} 0, & \text{for } t < 0, \\ -\gamma(B_0 + \alpha z)S_z, & \text{for } 0 \leq t \leq T, \\ 0, & \text{for } t > T. \end{cases}$$

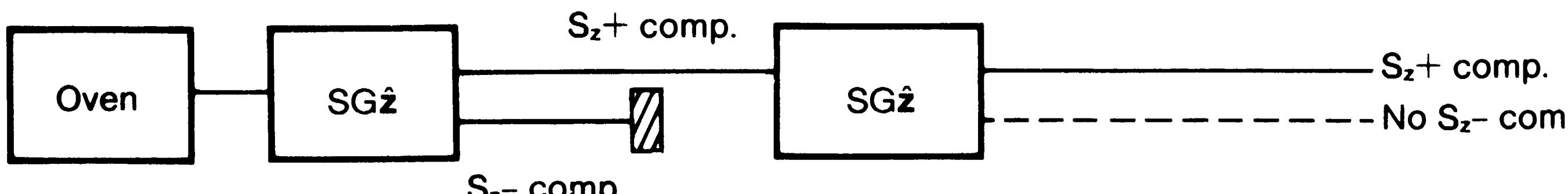
$$\chi(t) = a\chi_+ + b\chi_-, \quad \text{for } t \leq 0.$$

While the Hamiltonian acts, $\chi(t)$ evolves in the usual way:

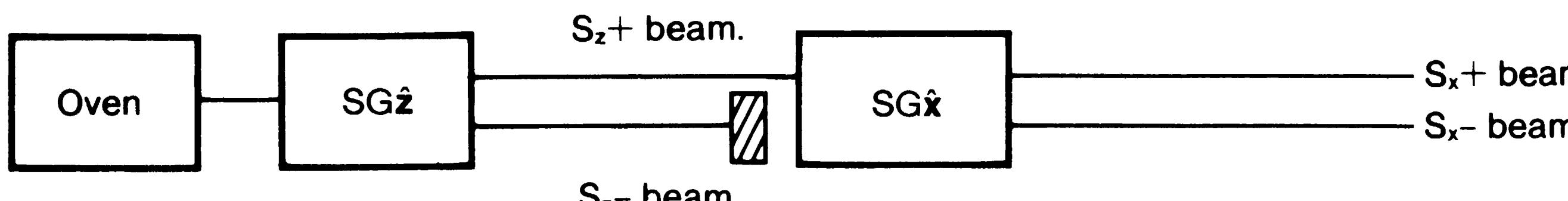
$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar}, \quad \text{for } 0 \leq t \leq T,$$

where

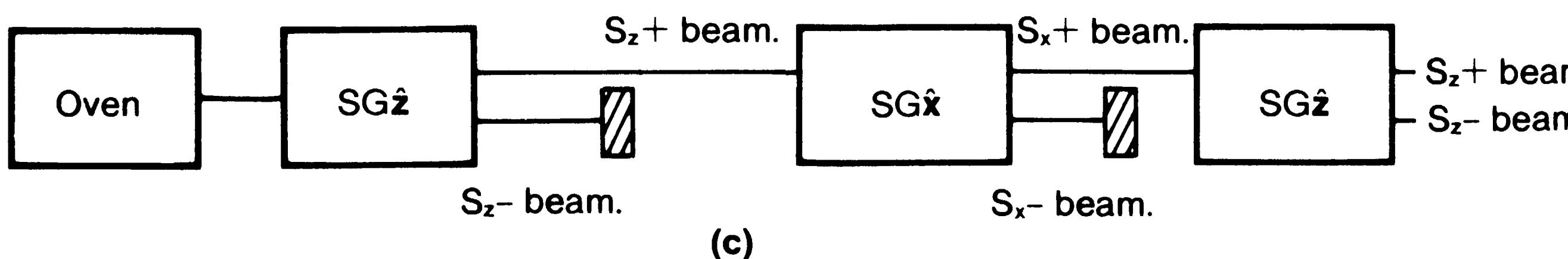
$$E_{\pm} = \mp\gamma(B_0 + \alpha z)\frac{\hbar}{2},$$



(a)



(b)



(c)

and hence it emerges in the state

$$\chi(t) = (ae^{i\gamma TB_0/2}\chi_+)e^{i(\alpha\gamma T/2)z} + (be^{-i\gamma TB_0/2}\chi_-)e^{-i(\alpha\gamma T/2)z},$$

(for $t \geq T$). The two terms now carry *momentum* in the z direction: the spin-up component has momentum

$$p_z = \frac{\alpha\gamma T\hbar}{2},$$

and it moves in the plus- z direction; the spin-down component has the opposite momentum, and it moves in the minus- z direction. Thus the beam splits in two, as before.

QM in 3D

Addition of Angular Momenta

Suppose now that we have *two* spin-1/2 particles—for example, the electron and the proton in the ground state of hydrogen. Each can have spin up or spin down, so there are four possibilities in all:

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow,$$

where the first arrow refers to the electron and the second to the proton. *Question:* What is the *total* angular momentum of the atom? Let

$$\mathbf{S} = \mathbf{S}^{(1)} + \mathbf{S}^{(2)}.$$

Each of these four composite states is an eigenstate of S_z —the z components simply *add*:

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} + S_z^{(2)}) \chi_1 \chi_2 = (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_1 \chi_1) \chi_2 + \chi_1 (\hbar m_2 \chi_2) = \hbar(m_1 + m_2) \chi_1 \chi_2, \end{aligned}$$

(note that $\mathbf{S}^{(1)}$ acts only on χ_1 , and $\mathbf{S}^{(2)}$ acts only on χ_2 ; this notation may not be elegant, but it does the job). So m (the quantum number for the composite system) is just $m_1 + m_2$:

$$\uparrow\uparrow: m = 1;$$

$$\uparrow\downarrow: m = 0;$$

$$\downarrow\uparrow: m = 0;$$

$$\downarrow\downarrow: m = -1.$$

At first glance, this doesn't look right: m is supposed to advance in integer steps, from $-s$ to $+s$, so it appears that $s = 1$ —but there is an “extra” state with $m = 0$. One way to untangle this problem is to apply the lowering operator, $S_- = S_-^{(1)} + S_-^{(2)}$ to the state $\uparrow\uparrow$,

$$\begin{aligned} S_-(\uparrow\uparrow) &= (S_-^{(1)} \uparrow) \uparrow + \uparrow (S_-^{(2)} \uparrow) \\ &= (\hbar \downarrow) \uparrow + \uparrow (\hbar \downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow). \end{aligned}$$

Evidently the three states with $s = 1$ are (in the notation $|s m\rangle$):

$$\left\{ \begin{array}{l} |\!1\ 1\rangle = \uparrow\uparrow \\ |\!1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |\!1\ -1\rangle = \downarrow\downarrow \end{array} \right\} \quad s = 1 \text{ (triplet).}$$

Meanwhile, the orthogonal state with $m = 0$ carries $s = 0$:

$$\left\{ |\!0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \right\} \quad s = 0 \text{ (singlet).}$$

I claim, then, that the combination of two spin-1/2 particles can carry a total spin of 1 or 0, depending on whether they occupy the triplet or the singlet configuration.

QM in 3D

Addition of Angular Momenta

$$S^2 = (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) \cdot (\mathbf{S}^{(1)} + \mathbf{S}^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}.$$

$$\begin{aligned}\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\uparrow\downarrow) &= (S_x^{(1)} \uparrow)(S_x^{(2)} \downarrow) + (S_y^{(1)} \uparrow)(S_y^{(2)} \downarrow) + (S_z^{(1)} \uparrow)(S_z^{(2)} \downarrow) \\ &= \left(\frac{\hbar}{2} \downarrow\right) \left(\frac{\hbar}{2} \uparrow\right) + \left(\frac{i\hbar}{2} \downarrow\right) \left(\frac{-i\hbar}{2} \uparrow\right) + \left(\frac{\hbar}{2} \uparrow\right) \left(\frac{-\hbar}{2} \downarrow\right) \\ &= \frac{\hbar^2}{4}(2 \downarrow\uparrow - \uparrow\downarrow).\end{aligned}$$

Similarly,

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}(\downarrow\uparrow) = \frac{\hbar^2}{4}(2 \uparrow\downarrow - \downarrow\uparrow).$$

It follows that

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|10\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}}(2 \downarrow\uparrow - \uparrow\downarrow + 2 \uparrow\downarrow - \downarrow\uparrow) = \frac{\hbar^2}{4}|10\rangle,$$

and

$$\mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}|00\rangle = \frac{\hbar^2}{4} \frac{1}{\sqrt{2}}(2 \downarrow\uparrow - \uparrow\downarrow - 2 \uparrow\downarrow + \downarrow\uparrow) = -\frac{3\hbar^2}{4}|00\rangle.$$

we conclude that

$$S^2|10\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} + 2\frac{\hbar^2}{4}\right)|10\rangle = 2\hbar^2|10\rangle, \quad S^2|00\rangle = \left(\frac{3\hbar^2}{4} + \frac{3\hbar^2}{4} - 2\frac{3\hbar^2}{4}\right)|00\rangle = 0,$$

What we have just done (combining spin 1/2 with spin 1/2 to get spin 1 and spin 0) is the simplest example of a larger problem: If you combine spin s_1 with spin s_2 , what total spins s can you get? The answer is that you get every spin from $(s_1 + s_2)$ down to $(s_1 - s_2)$ —or $(s_2 - s_1)$, if $s_2 > s_1$ —in integer steps:

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|.$$

(Roughly speaking, the highest total spin occurs when the individual spins are aligned parallel to one another, and the lowest occurs when they are antiparallel.) For example, if you package together a particle of spin 3/2 with a particle of spin 2, you could get a total spin of 7/2, 5/2, 3/2, or 1/2, depending on the configuration. Another example: If a hydrogen atom is in the state ψ_{nlm} , the net angular momentum of the electron (spin plus orbital) is $l + 1/2$ or $l - 1/2$; if you now throw in spin of the *proton*, the atom's *total* angular momentum quantum number is $l + 1$, l , or $l - 1$ (and l can be achieved in two distinct ways, depending on whether the electron alone is in the $l + 1/2$ configuration or the $l - 1/2$ configuration).

The combined state $|sm\rangle$ with total spin s and z -component m will be some linear combination of the composite states $|s_1 m_1\rangle |s_2 m_2\rangle$:

$$|sm\rangle = \sum_{m_1+m_2=m} C_{m_1 m_2 m}^{s_1 s_2 s} |s_1 m_1\rangle |s_2 m_2\rangle$$

(because the z components add, the only composite states that contribute are those for which $m_1 + m_2 = m$).

The constants $C_{m_1 m_2 m}^{s_1 s_2 s}$ are called **Clebsch-Gordan coefficients**.

Quantum Mechanics

Identical Particles

For a *single* particle, $\Psi(\mathbf{r}, t)$ is a function of the spatial coordinates, \mathbf{r} , and the time, t (we'll ignore spin, for the moment). The state of a *two*-particle system is a function of the coordinates of particle one (\mathbf{r}_1), the coordinates of particle two (\mathbf{r}_2), and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

Its time evolution is determined (as always) by the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi,$$

where H is the Hamiltonian for the whole system:

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

(the subscript on ∇ indicates differentiation with respect to the coordinates of particle 1 or particle 2, as the case may be). The statistical interpretation carries over in the obvious way:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

is the probability of finding particle 1 in the volume $d^3\mathbf{r}_1$ *and* particle 2 in the volume $d^3\mathbf{r}_2$; evidently Ψ must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1.$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt/\hbar},$$

where the spatial wave function (ψ) satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi,$$

and E is the total energy of the system.

Suppose particle 1 is in the (one-particle) state $\psi_a(\mathbf{r})$, and particle 2 is in the state $\psi_b(\mathbf{r})$. (Remember: I'm ignoring spin, for the moment.) In that case $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a simple *product*:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$$

Of course, this assumes that we can tell the particles apart—otherwise it wouldn't make any sense to claim that number 1 is in state ψ_a and number 2 is in state ψ_b ; all we could say is that *one* of them is in the state ψ_a and the other is in state ψ_b , but we wouldn't know which is which. If we were talking *classical* mechanics this would be a silly objection:

All electrons are “identical”. There is no way label them distinctively!

Identical Particles

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *non-committal* as to which particle is in which state. There are actually *two* ways to do it:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)].$$

Thus the theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. Photons and mesons are bosons; protons and electrons are fermions. It so happens that

all particles with *integer* spin are bosons, and
all particles with *half integer* spin are fermions.

This connection between **spin and statistics** (as we shall see, bosons and fermions have quite different statistical properties) can be *proved* in *relativistic* quantum mechanics; in the nonrelativistic theory it is taken as an axiom.

It follows, in particular, that *two identical fermions* (for example, two electrons) *cannot occupy the same state*. For if $\psi_a = \psi_b$, then

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0,$$

and we are left with no wave function at all. This is the famous **Pauli exclusion principle**. It is not (as you may have been led to believe) a weird ad hoc assumption applying only to electrons, but rather a consequence of the rules for constructing two-particle wave functions, applying to *all* identical fermions.

Let us define the **exchange operator**, P , which interchanges the two particles:

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1).$$

Clearly, $P^2 = 1$, and it follows (prove it for yourself) that the eigenvalues of P are ± 1 . Now, if the two particles are identical, the Hamiltonian must treat them the same: $m_1 = m_2$ and $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$. It follows that P and H are compatible observables,

$$[P, H] = 0,$$

and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrödinger equation that are either symmetric (eigenvalue $+1$) or antisymmetric (eigenvalue -1) under exchange:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1).$$

Moreover, if a system starts out in such a state, it will remain in such a state. The *new* law (I'll call it the **symmetrization requirement**) is that for identical particles the wave function is not merely *allowed*, but *required* to satisfy with the plus sign for bosons, and the minus sign for fermions.

Identical Particles

Example 5.1 Suppose we have two noninteracting—they pass right through one another . . . never mind how you would set this up in practice!—particles, both of mass m , in the infinite square well

The one-particle states are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \quad E_n = n^2 K$$

(where $K \equiv \pi^2 \hbar^2 / 2ma^2$, for convenience). If the particles are *distinguishable*, with #1 in state n_1 and #2 in state n_2 , the composite wave function is a simple product:

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E_{n_1 n_2} = (n_1^2 + n_2^2)K.$$

For example, the ground state is

$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a), \quad E_{11} = 2K;$$

the first excited state is doubly degenerate:

$$\psi_{12} = \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a), \quad E_{12} = 5K,$$

$$\psi_{21} = \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a), \quad E_{21} = 5K;$$

and so on. If the two particles are identical *bosons*, the ground state is unchanged, but the first excited state is *nondegenerate*:

$$\frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) + \sin(2\pi x_1/a) \sin(\pi x_2/a)]$$

(still with energy $5K$). And if the particles are identical *fermions*, there is *no* state with energy $2K$; the ground state is

$$\frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) - \sin(2\pi x_1/a) \sin(\pi x_2/a)],$$

and its energy is $5K$.

Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized.

If the two particles are distinguishable, and number 1 is the one in state ψ_a , then the combined wave function is

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

if they are identical bosons, the composite wave function is

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

and if they are identical fermions, it is

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

Let's calculate the expectation value of the square of the separation distance between the two particles,

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

Identical Particles

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

Distinguishable Particles

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

(the expectation value of x^2 in the one-particle state ψ_a),

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b,$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b.$$

In this case, then,

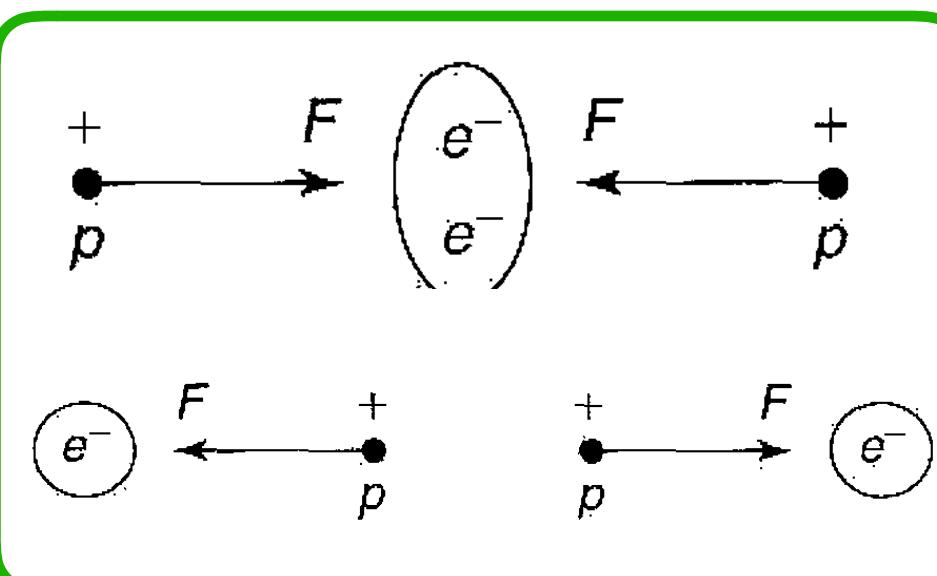
$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b.$$

(Incidentally, the answer would, of course, be the same if particle 1 had been in state ψ_b , and particle 2 in state ψ_a .)

Identical Particles

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

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



Identical Particles

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b). \end{aligned}$$

Similarly, $\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a)$. (Naturally, $\langle x_2^2 \rangle = \langle x_1^2 \rangle$, since you can't tell them apart.)

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2, \end{aligned}$$

where $\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx$.

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2.$$

Difference

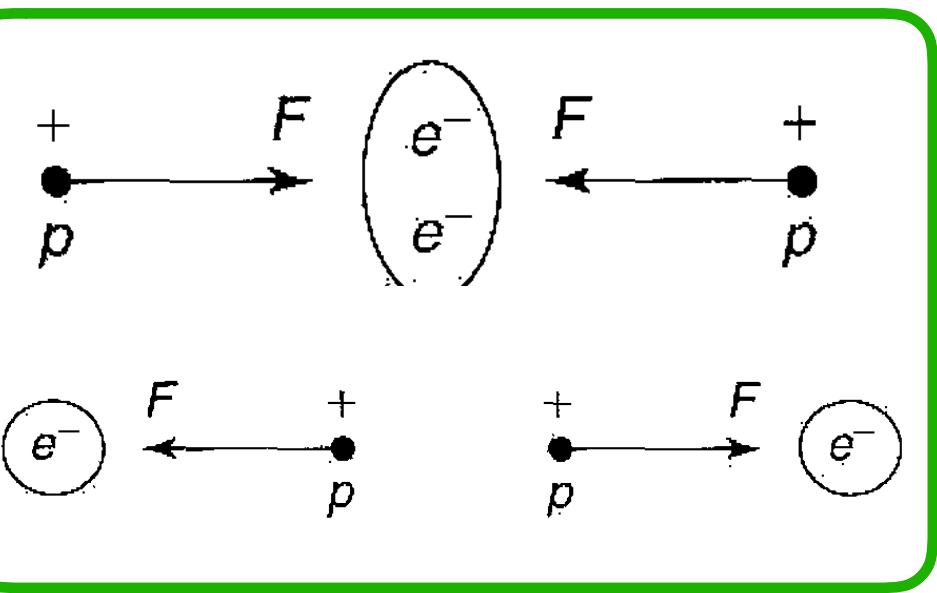
$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2.$$

Identical Particles

Identical Particles

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

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



The *interesting* case is when there *is* some overlap of the wave functions. The system behaves as though there were a “force of attraction” between identical bosons, pulling them closer together, and a “force of repulsion” between identical fermions, pushing them apart (remember that we are for the moment ignoring spin). We call it an **exchange force**, although it’s not really a force at all—no physical agency is pushing on the particles; rather, it is a purely *geometrical* consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart. Nevertheless, it has profound consequences. Consider, for example, the hydrogen molecule (H_2).

Unfortunately, electrons *aren’t* bosons, they’re fermions, and this means that the concentration of negative charge should actually be shifted to the wings tearing the molecule apart!

But wait! We have been ignoring *spin*. The *complete* state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

$$\psi(\mathbf{r})\chi(\mathbf{s}).$$

When we put together the two-electron state, it is the *whole works*, not just the spatial part, that has to be antisymmetric with respect to exchange. Now, the singlet combination is antisymmetric (and hence would have to be joined with a *symmetric* spatial function), whereas the three triplet states are all symmetric (and would require an *antisymmetric* spatial function). Evidently, then, the singlet state should lead to *bonding*, and the triplet to *anti bonding*. Sure enough, the chemists tell us that covalent bonding requires the two electrons to occupy the singlet state, with total spin zero.

Atoms

A neutral atom, of atomic number Z , consists of a heavy nucleus, with electric charge Ze , surrounded by Z electrons (mass m and charge $-e$). The Hamiltonian for this system is

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}.$$

The problem is to solve Schrödinger’s equation, $H\psi = E\psi$, for the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$. Because electrons are identical fermions, however, not all solutions are acceptable: only those for which the complete state (position and spin),

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_Z),$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the *same* state.

Reading task: Read about *He & the Periodic Table*

Solids

In the solid state, a few of the loosely bound outermost **valence** electrons in each atom become detached, and roam around throughout the material, no longer subject only to the Coulomb field of a specific “parent” nucleus, but rather to the combined potential of the entire crystal lattice.

Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions l_x , l_y , l_z , and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, \quad 0 < y < l_y, \text{ and } 0 < z < l_z; \\ \infty, & \text{otherwise.} \end{cases}$$

The Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi,$$

separates, in cartesian coordinates: $\psi(x, y, z) = X(x)Y(y)Z(z)$, with

$$-\frac{\hbar^2}{2m} \frac{d^2X}{dx^2} = E_x X; \quad -\frac{\hbar^2}{2m} \frac{d^2Y}{dy^2} = E_y Y; \quad -\frac{\hbar^2}{2m} \frac{d^2Z}{dz^2} = E_z Z,$$

and $E = E_x + E_y + E_z$. Letting

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar},$$

we obtain the general solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x), \quad Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y), \\ Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z).$$

The boundary conditions require that $X(0) = Y(0) = Z(0) = 0$, so $B_x = B_y = B_z = 0$, and $X(l_x) = Y(l_y) = Z(l_z) = 0$, so that

$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi,$$

where each n is a positive integer:

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots.$$

The (normalized) wave functions are

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right),$$

and the allowed energies are

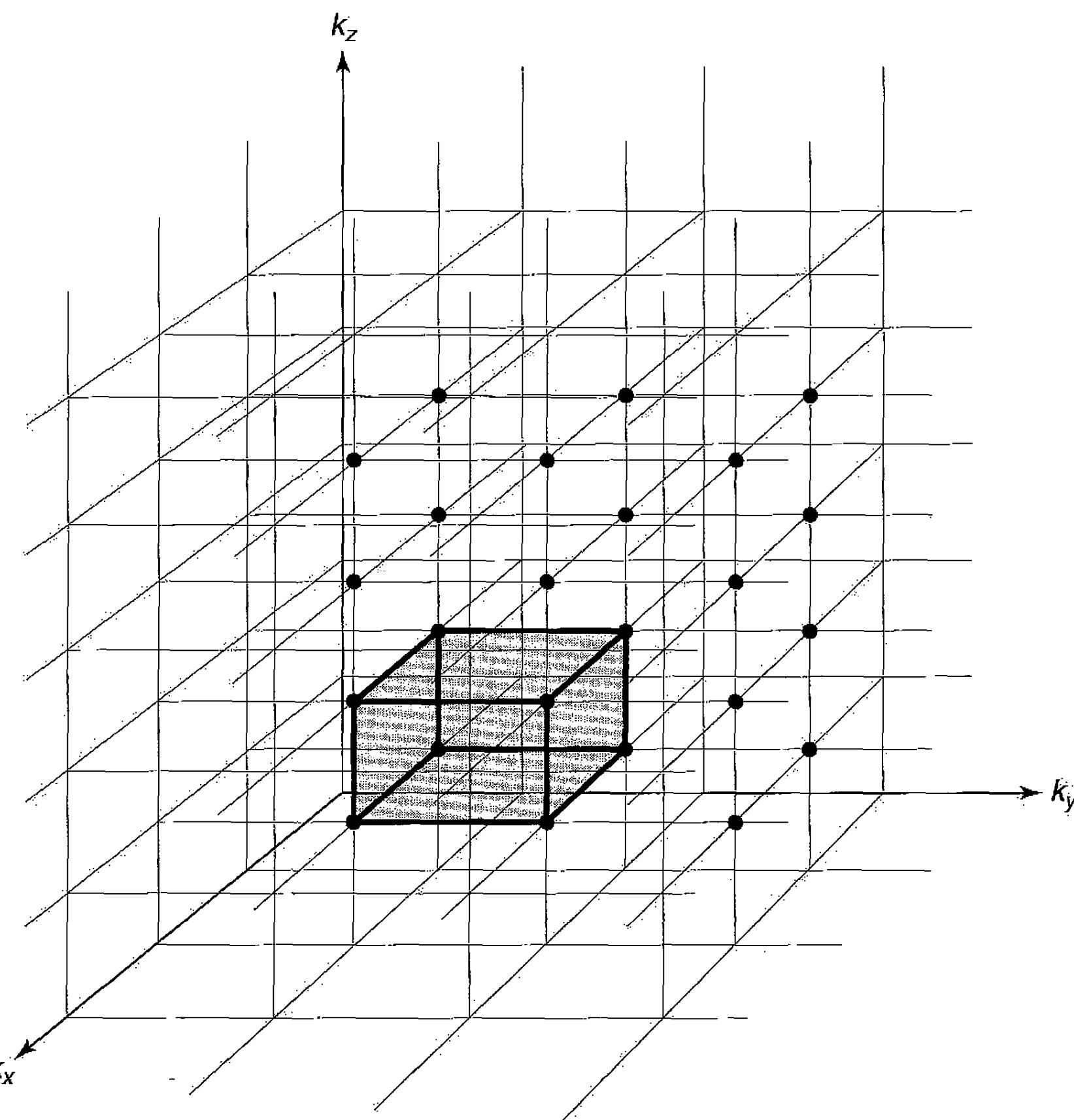
$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m},$$

where k is the magnitude of the **wave vector**, $\mathbf{k} \equiv (k_x, k_y, k_z)$.

Solids

Free Electron Gas

If you imagine a three-dimensional space, with axes k_x , k_y , k_z , and planes drawn in at $k_x = (\pi/l_x)$, $(2\pi/l_x)$, $(3\pi/l_x)$, ..., at $k_y = (\pi/l_y)$, $(2\pi/l_y)$, $(3\pi/l_y)$, ..., and at $k_z = (\pi/l_z)$, $(2\pi/l_z)$, $(3\pi/l_z)$, ..., each intersection point represents a distinct (one-particle) stationary state



Each block in this grid, and hence also each state, occupies a volume

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

of “ k -space,” where $V = l_x l_y l_z$ is the volume of the object itself. Suppose our sample contains N atoms, and each atom contributes q free electrons. (In practice, N will be enormous—on the order of Avogadro’s number, for an object of macroscopic size—whereas q is a small number—1 or 2, typically.) If electrons were bosons (or distinguishable particles), they would all settle down to the ground state, ψ_{111} . But electrons are in fact identical *fermions*, subject to the Pauli exclusion principle, so only two of them can occupy any given state. They will fill up one octant of a *sphere* in k -space, whose radius, k_F , is determined by the fact that each pair of electrons requires a volume π^3/V

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left(\frac{\pi^3}{V} \right).$$

$$\text{Thus } k_F = (3\rho\pi^2)^{1/3}, \text{ where } \rho \equiv \frac{Nq}{V}$$

is the *free electron density* (the number of free electrons per unit volume).

The boundary separating occupied and unoccupied states, in k -space, is called the **Fermi surface** (hence the subscript F). The corresponding energy is called the **Fermi energy**, E_F ; for a free electron gas,

$$E_F = \frac{\hbar^2}{2m} (3\rho\pi^2)^{2/3}.$$

Solids

Free Electron Gas

The *total* energy of the electron gas can be calculated as follows: A shell of thickness dk contains a volume

$$\frac{1}{8}(4\pi k^2) dk,$$

so the number of electron states in the shell is

$$\frac{2[(1/2)\pi k^2 dk]}{(\pi^3/V)} = \frac{V}{\pi^2} k^2 dk.$$

Each of these states carries an energy $\hbar^2 k^2 / 2m$, so the energy of the shell is

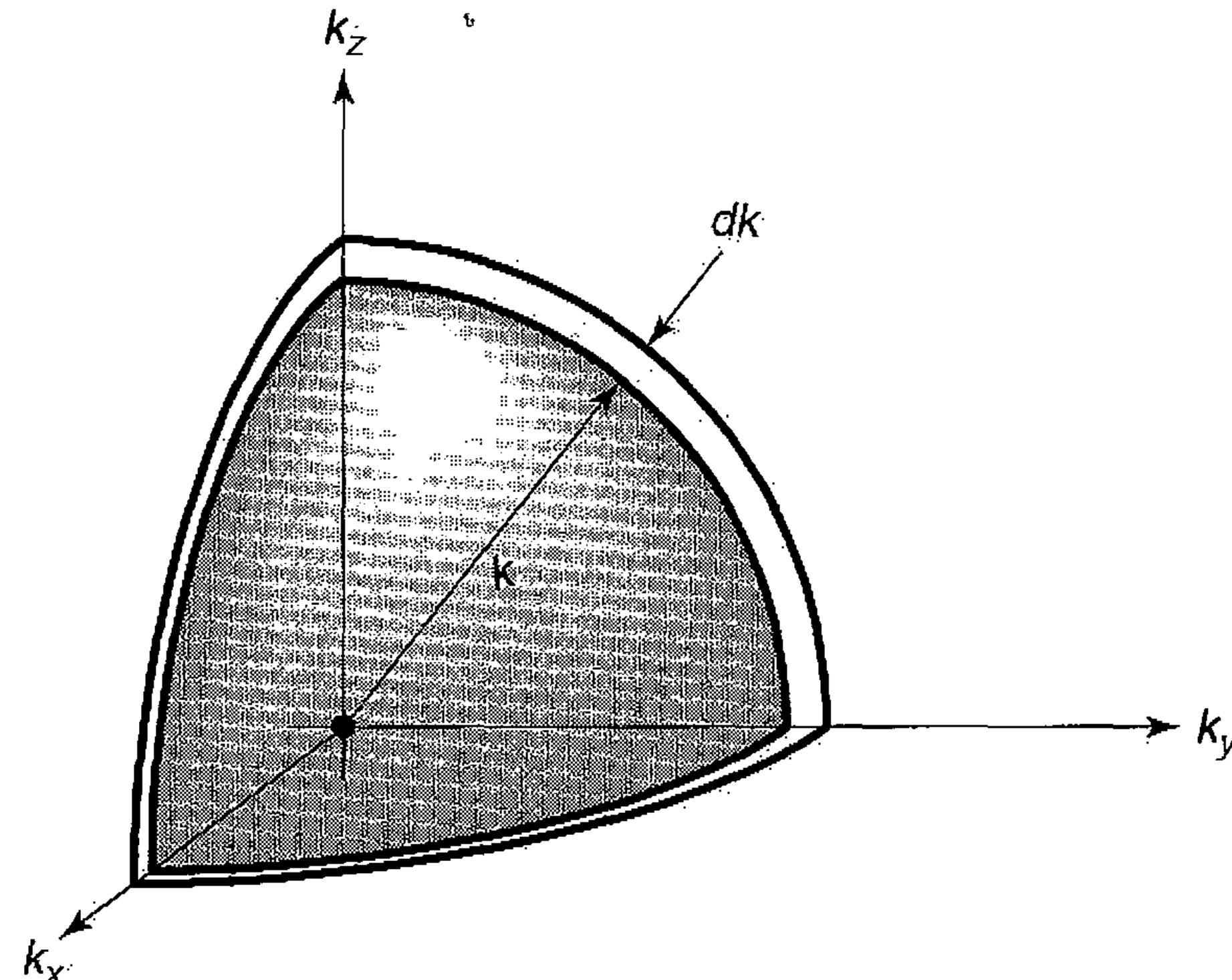
$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk,$$

and hence the total energy is

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3}.$$

This quantum mechanical energy plays a role rather analogous to the internal *thermal* energy (U) of an ordinary gas. In particular, it exerts a *pressure* on the walls, for if the box expands by an amount dV , the total energy decreases:

$$dE_{\text{tot}} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{\text{tot}} \frac{dV}{V},$$



and this shows up as work done on the outside ($dW = P dV$) by the quantum pressure P . Evidently

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} = \frac{2}{3} \frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}.$$

Degeneracy Pressure

Another reading task 😞: Bloch's theory

Quantum Statistical Mechanics

The fundamental assumption of statistical mechanics is that in thermal equilibrium every distinct state with the same *total* energy, E , is equally probable. Random thermal motions constantly shift energy from one particle to another, and from one form (rotational, kinetic, vibrational, etc.) to another, but (absent external influences) the *total* is fixed by conservation of energy. The assumption (and it's a *deep* one, worth thinking about) is that this continual redistribution of energy does not favor any particular state. The temperature, T , is simply a measure of the total energy of a system in thermal equilibrium. The only new twist introduced by quantum mechanics has to do with *how we count the distinct states* (it's actually *easier* than in the classical theory, because the states are generally discrete), and this depends critically on whether the particles involved are distinguishable, identical bosons, or identical fermions.

An Example

Suppose we have just *three* noninteracting particles (all of mass m) in the one-dimensional infinite square well. The total energy is

$$E = E_A + E_B + E_C = \frac{\pi^2 \hbar^2}{2m a^2} (n_A^2 + n_B^2 + n_C^2)$$

where n_A , n_B , and n_C are positive integers. Now suppose, $E = 363(\pi^2\hbar^2/2ma^2)$,

$$n_A^2 + n_B^2 + n_C^2 = 363.$$

There are, as it happens, 13 combinations of three positive integers, the sum of whose squares is 363: All three could be 11, two could be 13 and one 5

(which occurs in three permutations), one could be 19 and two 1 (again, three permutations), or one could be 17, one 7, and one 5 (six permutations). Thus (n_A, n_B, n_C) is one of the following:

(11, 11, 11).

Config. 1

$$(13, 13, 5), (13, 5, 13), (5, 13, 13)$$

Config. 2

$$(1, 1, 19), (1, 19, 1), (19, 1, 1)$$

Config. 3

$(5, 7, 17), (5, 17, 7), (7, 5, 17), (7, 17, 5), (17, 5, 7), (17, 7, 5)$. Config. 4

Config. 4

If the particles are *distinguishable*, each of these represents a distinct quantum state, and the fundamental assumption of statistical mechanics says that in thermal equilibrium they are all equally likely. But I'm not interested in knowing *which* particle is in *which* (one-particle) state, only the total *number* of particles in each state—the **occupation number**, N_n , for the state ψ_n . The collection of all occupation numbers for a given 3-particle state we will call the configuration. If all three are in ψ_{11} , the configuration is

(i.e., $N_{11} = 3$, all others zero). If two are in ψ_{13} and one is in ψ_5 , the configuration is

$$(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, \dots)$$

(i.e., $N_5 = 1$, $N_{13} = 2$, all others zero).

Quantum Statistical Mechanics

An Example ...

If two are in ψ_1 and one is in ψ_{19} , the configuration is

$$(2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, \dots), \quad [5.71]$$

(i.e., $N_1 = 2$, $N_{19} = 1$, all others zero). And if there is one particle in ψ_5 , one in ψ_7 , and one in ψ_{17} , the configuration is

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \dots). \quad [5.72]$$

(i.e., $N_5 = N_7 = N_{17} = 1$, all others zero.) Of these, the last is the *most probable* configuration, because it can be achieved in six different ways, whereas the middle two occur three ways, and the first only one. if we select one of these three particles at random, what is the probability (P_n) of getting a specific (allowed) energy E_n ? The only way you can get E_1 is if it's in the third configuration the

chances of the system being in that configuration are 3 in 13, and in that configuration the probability of getting E_1 is $2/3$, so $P_1 = (3/13) \times (2/3) = 2/13$. You could get E_5 either from configuration 2—chances 3 in 13—with probability $1/3$, or from configuration 4—chances 6 in 13—with probability $1/3$, so $P_5 = (3/13) \times (1/3) + (6/13) \times (1/3) = 3/13$. You can only get E_7 from configuration 4: $P_7 = (6/13) \times (1/3) = 2/13$. Likewise, E_{11} comes only from the first configuration—chances 1 in 13—with probability 1: $P_{11} = (1/13)$. Similarly, $P_{13} = (3/13) \times (2/3) = 2/13$, $P_{17} = (6/13) \times (1/3) = 2/13$, and $P_{19} = (3/13) \times (1/3) = 1/13$. As a check, note that

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} = \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1.$$

That's when the particles are distinguishable. If in fact they are *identical fermions*, the antisymmetrization requirement (leaving aside spin, for simplicity—or assuming they are all in the *same* spin state, if you prefer) excludes the first three configurations (which assign two—or, worse still, three—particles to the same state), and there is just *one* state in the fourth configuration

For identical fermions, then, $P_5 = P_7 = P_{17} = 1/3$ (and again the sum of the probabilities is 1). On the other hand, if they are *identical bosons* the symmetrization requirement allows for *one* state in each configuration so $P_1 = (1/4) \times (2/3) = 1/6$, $P_5 = (1/4) \times (1/3) + (1/4) \times (1/3) = 1/6$, $P_7 = (1/4) \times (1/3) = 1/12$, $P_{11} = (1/4) \times (1) = 1/4$, $P_{13} = (1/4) \times (2/3) = 1/6$, $P_{17} = (1/4) \times (1/3) = 1/12$, and $P_{19} = (1/4) \times (1/3) = 1/12$. As always, the sum is 1.

The purpose of this example was to show you how the counting of states depends on the nature of the particles. In one respect it was actually *more complicated* than the realistic situation, in which N is a huge number. For as N grows, the most probable configuration (in this example, $N_5 = N_7 = N_{17} = 1$, for the case of distinguishable particles) becomes *overwhelmingly* more likely than its competitors, so that, for statistical purposes, we can afford to ignore the others altogether: The distribution of individual particle energies, at equilibrium, is simply their distribution in the most probable configuration. (If this were true for $N = 3$ —which, obviously, it is *not*—we would conclude that $P_5 = P_7 = P_{17} = 1/3$ for the case of distinguishable particles.)

Quantum Statistical Mechanics

The General Case

Now consider an arbitrary potential, for which the one-particle energies are E_1, E_2, E_3, \dots , with degeneracies d_1, d_2, d_3, \dots (i.e., there are d_n distinct one-particle states with energy E_n). Suppose we put N particles (all with the same mass) into this potential; we are interested in the configuration (N_1, N_2, N_3, \dots) , for which there are N_1 particles with energy E_1 , N_2 particles with energy E_2 , and so on.

Question: How many different ways can this be achieved (or, more precisely, how many distinct states correspond to this particular configuration)? The answer, $Q(N_1, N_2, N_3, \dots)$, depends on whether the particles are distinguishable, identical fermions, or identical bosons, so we'll treat the three cases separately.

First, assume the particles are *distinguishable*. How many ways are there to select (from the N available candidates) the N_1 to be placed in the first “bin”?

Answer: the **binomial coefficient**, “ N choose N_1 ,”

$$\binom{N}{N_1} = \frac{N!}{N_1!(N - N_1)!}.$$

For there are N ways to pick the first particle, leaving $(N - 1)$ for the second, and so on:

$$N(N - 1)(N - 2)\dots(N - N_1 + 1) = \frac{N!}{(N - N_1)!}.$$

However, this counts separately the $N_1!$ different *permutations* of the N_1 particles, whereas we don't care whether number 37 was picked on the first draw, or on the 29th draw; so we divide by $N_1!$ Now, how many different ways can those N_1 particles be arranged *within* the first bin? Well, there

are d_1 states in the bin, so each particle has d_1 choices; evidently there are $(d_1)^{N_1}$ possibilities in all. Thus the number of ways to put N_1 particles, selected from a total population of N , into a bin containing d_1 distinct options, is

$$\frac{N!d_1^{N_1}}{N_1!(N - N_1)!}.$$

The same goes for bin 2, of course, except that there are now only $(N - N_1)$ particles left to work with:

$$\frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!},$$

and so on. It follows that

$$\begin{aligned} Q(N_1, N_2, N_3, \dots) &= \frac{N!d_1^{N_1}}{N_1!(N - N_1)!} \frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!} \frac{(N - N_1 - N_2)!d_3^{N_3}}{N_3!(N - N_1 - N_2 - N_3)!} \dots \\ &= N! \frac{d_1^{N_1} d_2^{N_2} d_3^{N_3} \dots}{N_1! N_2! N_3! \dots} = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}. \end{aligned}$$

Quantum Statistical Mechanics

Identical Fermions & Bosons

The problem is a lot easier for *identical fermions*. Because they are indistinguishable, it doesn't matter *which* particles are in *which* states—the antisymmetrization requirement means that there is just *one* N -particle state in which a specific set of one-particle states are occupied. Moreover, only one particle can occupy any given state. There are

$$\binom{d_n}{N_n}$$

ways to choose the N_n occupied states in the n th bin,

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}.$$

The calculation is hardest for the case of *identical bosons*. Again, the symmetrization requirement means that there is just one N -particle state in which a specific set of one-particle states are occupied, but this time there is no restriction on the number of particles that can share the same one-particle state. For the n th bin, the question becomes: How many different ways can we assign N_n identical particles to d_n different slots? There are many tricks to solve this combinatorial problem; an especially clever method is as follows: Let dots represent particles and crosses represent partitions, so that, for example, if $d_n = 5$ and $N_n = 7$,

• • × • × • • • × • ×

would indicate that there are two particles in the first state, one in the second, three

in the third, one in the fourth, and none in the fifth. Note that there are N_n dots, and $(d_n - 1)$ crosses (partitioning the dots into d_n groups). If the individual dots and crosses were *labeled*, there would be $(N_n + d_n - 1)!$ different ways to arrange them. But for our purposes the dots are all equivalent—permuting them ($N_n!$ ways) does not change the state. Likewise, the crosses are all equivalent—permuting them $((d_n - 1)!$ ways) changes nothing. So there are in fact

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n}$$

distinct ways of assigning the N_n particles to the d_n one-particle states in the n th bin, and we conclude that

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

Quantum Statistical Mechanics

The Most Probable Configuration

In thermal equilibrium, every state with a given total energy E and a given particle number N is equally likely. So the *most probable configuration* (N_1, N_2, N_3, \dots) is the one that can be achieved in the largest number of different ways—it is that particular configuration for which $Q(N_1, N_2, N_3, \dots)$ is a maximum, subject to the constraints

$$\sum_{n=1}^{\infty} N_n = N,$$

$$\sum_{n=1}^{\infty} N_n E_n = E.$$

and

The problem of maximizing a function $F(x_1, x_2, x_3, \dots)$ of several variables, subject to the constraints $f_1(x_1, x_2, x_3, \dots) = 0, f_2(x_1, x_2, x_3, \dots) = 0$, etc., is most conveniently handled by the method of **Lagrange multipliers**. We introduce the new function

$$G(x_1, x_2, x_3, \dots, \lambda_1, \lambda_2, \dots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \dots,$$

and set *all* its derivatives equal to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0.$$

In our case it's a little easier to work with the *logarithm* of Q , instead of Q itself—this turns the *products* into *sums*. Since the logarithm is a monotonic function of its argument, the maxima of Q and $\ln(Q)$ occur at the same point. So we let

$$G \equiv \ln(Q) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right],$$

where α and β are the Lagrange multipliers. Setting the derivatives with respect to α and β equal to zero merely reproduces the constraints; it remains, then, to set the derivative with respect to N_n equal to zero.

If the particles are *distinguishable*, then

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)]$$

$$+ \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right].$$

Assuming the relevant occupation numbers (N_n) are large, we can invoke **Stirling's approximation**:

$$\ln(z!) \approx z \ln(z) - z \quad \text{for } z \gg 1,$$

to write $G \approx \sum_{n=1}^{\infty} [N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n]$
 $+ \ln(N!) + \alpha N + \beta E.$

It follows that

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n.$$

Quantum Statistical Mechanics

Setting this equal to zero, and solving for N_n , we conclude that the *most probable occupation numbers*, for distinguishable particles, are

$$N_n = d_n e^{-(\alpha + \beta E_n)}.$$

If the particles are *identical fermions*,

$$G = \sum_{n=1}^{\infty} \{ \ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!] \} + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

This time we must assume not only that N_n is large, but also that $d_n \gg N_n$, so that Stirling's approximation applies to both terms. In that case

$$\begin{aligned} G \approx & \sum_{n=1}^{\infty} \left[\ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n) \ln(d_n - N_n) \right. \\ & \left. + (d_n - N_n) - \alpha N_n - \beta E_n N_n \right] + \alpha N + \beta E, \end{aligned}$$

so

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n.$$

Setting this equal to zero, and solving for N_n , we find the *most probable occupation numbers* for identical fermions:

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1}.$$

Finally, if the particles are *identical bosons*, then we have

$$\begin{aligned} G = & \sum_{n=1}^{\infty} \{ \ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!] \} \\ & + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]. \end{aligned}$$

Assuming (as always) that $N_n \gg 1$, and using Stirling's approximation:

$$\begin{aligned} G \approx & \sum_{n=1}^{\infty} \{ (N_n + d_n - 1) \ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n) \\ & + N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n \} + \alpha N + \beta E, \end{aligned}$$

so

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n.$$

Setting this equal to zero, and solving for N_n , we find the *most probable occupation numbers* for identical bosons:

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}.$$

Quantum Statistical Mechanics

Physical Significance of α and β

The parameters α and β came into the story as Lagrange multipliers, associated with the total number of particles and the total energy, respectively. To carry out the summation, however, we need to know the allowed energies (E_n), and their degeneracies (d_n), for the potential in question. As an example, I'll work out the case of an **ideal gas**—a large number of noninteracting particles, all with the same mass, in the three dimensional infinite square well. This will motivate the physical interpretation of α and β .

we found the allowed energies

$$E_k = \frac{\hbar^2}{2m} k^2,$$

where

$$\mathbf{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right).$$

As before, we convert the sum into an integral, treating \mathbf{k} as a continuous variable, with one state (or, for spin s , $2s + 1$ states) per volume π^3/V of k -space. Taking as our “bins” the spherical shells in the first octant the “degeneracy” the “degeneracy” (that is, the number of states in the bin) is

$$d_k = \frac{1}{8} \frac{4\pi k^2 dk}{(\pi^3/V)} = \frac{V}{2\pi^2} k^2 dk.$$

For distinguishable particles

$$N = \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} k^2 dk = V e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

so

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi\beta\hbar^2}{m} \right)^{3/2}.$$

The second constraint

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} k^4 dk = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

or,

$$E = \frac{3N}{2\beta}.$$

This result is reminiscent of the classical formula for the average kinetic energy of an atom at temperature T :

$$\frac{E}{N} = \frac{3}{2} k_B T,$$

where k_B is the Boltzmann constant. This suggests that β is related to the *temperature*:

$$\beta = \frac{1}{k_B T}.$$

Quantum Statistical Mechanics

Physical Significance of α and β

It is customary to replace α by the so-called **chemical potential**,

$$\mu(T) \equiv -\alpha k_B T,$$

the *most probable number of particles in a particular (one-particle) state with energy ϵ*

	MAXWELL-BOLTZMANN
$n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T} & \\ \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} & \end{cases}$	FERMI-DIRAC
	BOSE-EINSTEIN

The **Maxwell-Boltzmann distribution** is the classical result, for *distinguishable* particles; the **Fermi-Dirac distribution** applies to *identical fermions*, and the **Bose-Einstein distribution** is for *identical bosons*.

The Fermi-Dirac distribution has a particularly simple behavior as $T \rightarrow 0$:

$$e^{(\epsilon-\mu)/k_B T} \rightarrow \begin{cases} 0, & \text{if } \epsilon < \mu(0), \\ \infty, & \text{if } \epsilon > \mu(0). \end{cases}$$

so

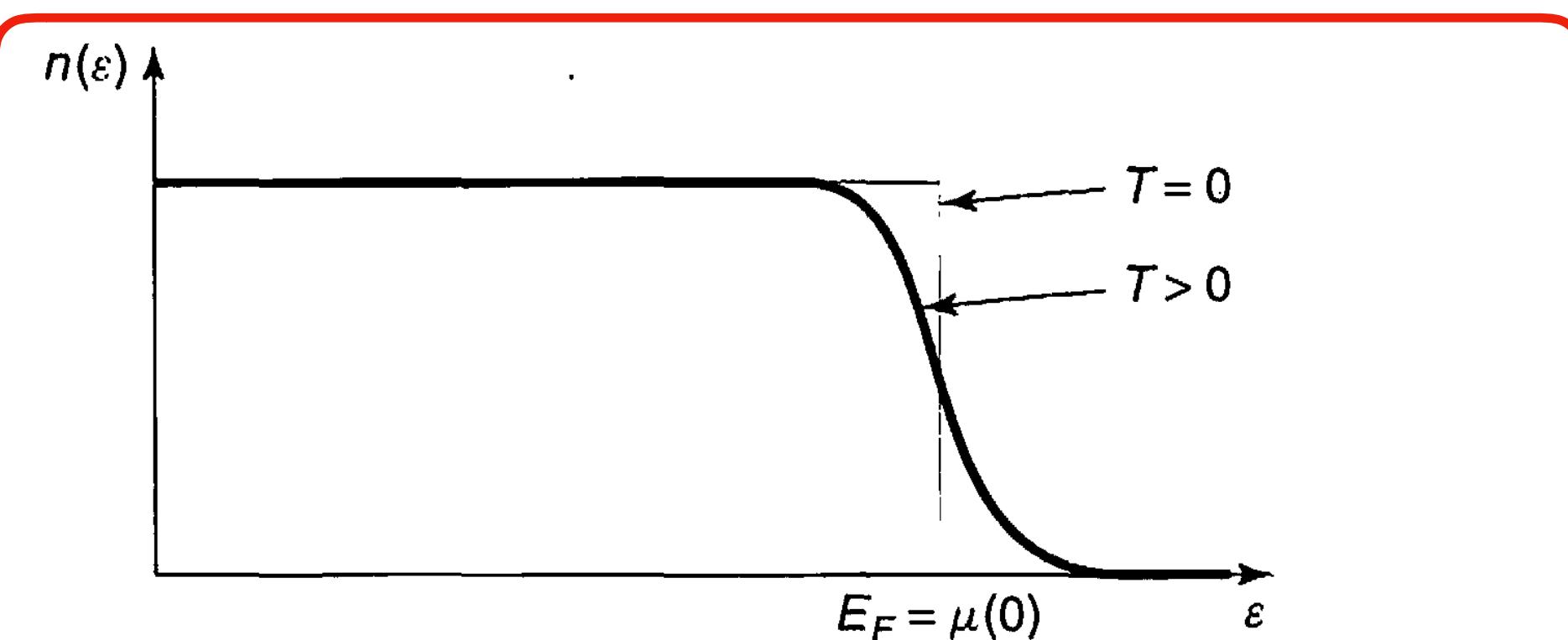
$$n(\epsilon) \rightarrow \begin{cases} 1, & \text{if } \epsilon < \mu(0), \\ 0, & \text{if } \epsilon > \mu(0). \end{cases}$$

All states are filled, up to an energy $\mu(0)$, and none are occupied for energies above this

Evidently the chemical potential at absolute zero is precisely the Fermi energy:

$$\mu(0) = E_F.$$

As the temperature rises, the Fermi-Dirac distribution “softens” the cutoff, as indicated by the rounded curve



Fermi-Dirac distribution for $T = 0$ and for T somewhat above zero.

Returning now to the special case of an ideal gas, for distinguishable particles we found that the total energy at temperature T is

$$E = \frac{3}{2} N k_B T.$$

and the chemical potential is $\mu(T) = k_B T \left[\ln \left(\frac{N}{V} \right) + \frac{3}{2} \ln \left(\frac{2\pi\hbar^2}{mk_B T} \right) \right]$.

Yet another reading task 😞😞: The Blackbody Spectrum

Quantum Mechanics

Time-independent Perturbation Theory

Non-Degenerate Theory

Suppose we have solved the (time-independent) Schrödinger equation for some potential (say, the one-dimensional infinite square well):

$$H^0 \psi_n^0 = E_n^0 \psi_n^0,$$

obtaining a complete set of orthonormal eigenfunctions, ψ_n^0 ,

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}.$$

and the corresponding eigenvalues E_n^0 . Now we perturb the potential slightly. We'd like to find the new eigenfunctions and eigenvalues:

$$H \psi_n = E_n \psi_n,$$

but unless we are very lucky, we're not going to be able to solve the Schrödinger equation exactly, for this more complicated potential. **Perturbation theory** is a systematic procedure for obtaining *approximate* solutions to the perturbed problem, by building on the known exact solutions to the *unperturbed* case.

To begin with we write the new Hamiltonian as the sum of two terms:

$$H = H^0 + \lambda H',$$

where H' is the perturbation (the superscript 0 always identifies the *unperturbed* quantity). For the moment we'll take λ to be a small number; later we'll crank it up to 1, and H will be the true Hamiltonian. Next we write ψ_n and E_n as power series in λ :

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots;$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots.$$

Here E_n^1 is the **first-order correction** to the n th eigenvalue, and ψ_n^1 is the first-order correction to the n th eigenfunction; E_n^2 and ψ_n^2 are the **second-order corrections**, and so on.

$$\begin{aligned} (H^0 + \lambda H')[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots] \\ = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)[\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots], \end{aligned}$$

or (collecting like powers of λ):

$$\begin{aligned} H^0 \psi_n^0 + \lambda(H^0 \psi_n^1 + H' \psi_n^0) + \lambda^2(H^0 \psi_n^2 + H' \psi_n^1) + \dots \\ = E_n^0 \psi_n^0 + \lambda(E_n^0 \psi_n^1 + E_n^1 \psi_n^0) + \lambda^2(E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0) + \dots \end{aligned}$$

Time-independent Perturbation Theory

Non-Degenerate Theory

To lowest order¹ (λ^0) this yields $H^0\psi_n^0 = E_n^0\psi_n^0$, which is nothing new

To first order (λ^1),

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0.$$

To second order (λ^2),

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0,$$

First-order Theory

Taking the inner product with ψ_n^0

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle.$$

But H^0 is hermitian, so

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle,$$

and this cancels the first term on the right. Moreover, $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, so²

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle.$$

This is the fundamental result of first-order perturbation theory; as a *practical* matter, it may well be the most important equation in quantum mechanics. It says that the first-order correction to the energy is the *expectation value* of the perturbation, in the *unperturbed* state.

Example The unperturbed wave functions for the infinite square well are

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right).$$

Suppose we perturb the system by simply raising the “floor” of the well a constant amount V_0

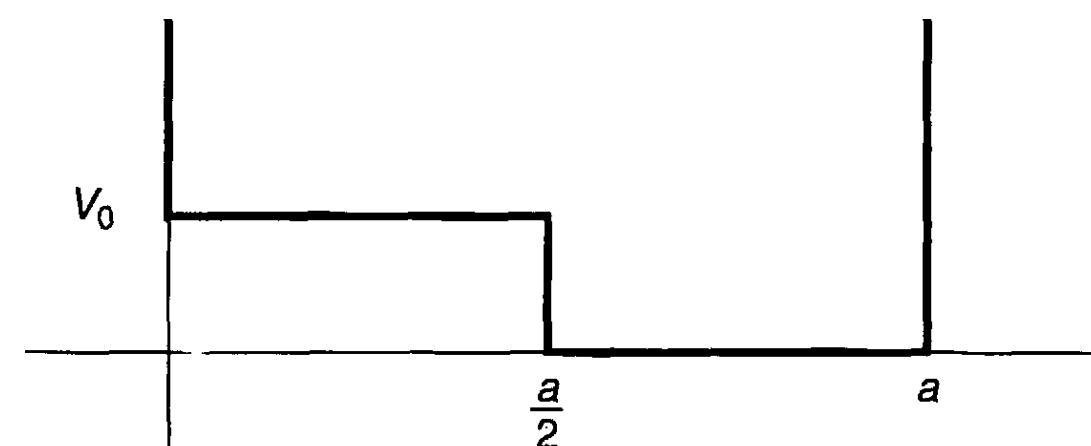
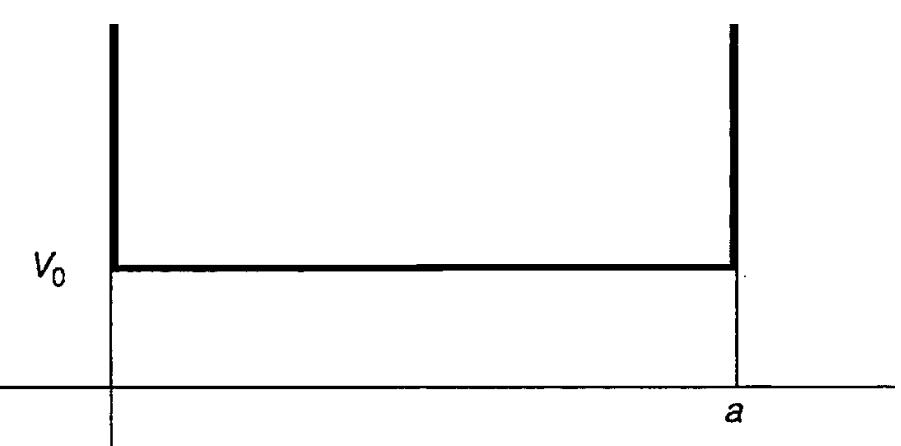
Solution: In this case $H' = V_0$, and the first-order correction to the energy of the n th state is

$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0.$$

The corrected energy levels, then, are $E_n \cong E_n^0 + V_0$; they are simply lifted by the amount V_0 . Of course! The only surprising thing is that in this case the first-order theory yields the *exact* answer. Evidently for a *constant* perturbation all the higher corrections vanish. On the other hand, if the perturbation extends only half-way across the well

$$E_n^1 = \frac{2V_0}{a} \int_0^{a/2} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}.$$

In this case every energy level is lifted by $V_0/2$. That’s not the *exact* result, presumably, but it does seem reasonable, as a first-order approximation.



Time-independent Perturbation Theory

Non-Degenerate Theory

the first-order correction to the *wave function*

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0.$$

The right side is a known function, so this amounts to an inhomogeneous differential equation for ψ_n^1 . Now, the unperturbed wave functions constitute a complete set, so ψ_n^1 (like any other function) can be expressed as a linear combination of them:

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^0.$$

There is no need to include $m = n$ in the sum, for if ψ_n^1 satisfies Equation so too does $(\psi_n^1 + \alpha \psi_n^0)$, for any constant α , and we can use this freedom to subtract off the ψ_n^0 term. If we could determine the coefficients $c_m^{(n)}$, we'd be done.

We have

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \psi_m^0 = -(H' - E_n^1) \psi_n^0.$$

Taking the inner product with ψ_l^0 ,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \langle \psi_l^0 | \psi_m^0 \rangle = -\langle \psi_l^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle.$$

If $l \neq n$, we get

$$(E_l^0 - E_n^0) c_l^{(n)} = -\langle \psi_l^0 | H' | \psi_n^0 \rangle,$$

so

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0},$$

$$\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0.$$

Notice that the denominator is safe (since there is no coefficient with $m = n$) as long as the unperturbed energy spectrum is nondegenerate.

Second-order Energies

We take the inner product of the second order equation with ψ_n^0 :

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle.$$

Again, we exploit the hermiticity of H^0 :

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle,$$

so the first term on the left cancels the first term on the right. Meanwhile, $\langle \psi_n^0 | \psi_n^0 \rangle = 1$, and we are left with a formula for E_n^2 :

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle.$$

But

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0,$$

Time-independent Perturbation Theory

Non-Degenerate Theory

(because the sum excludes $m = n$, and all the others are orthogonal), so

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0}.$$

or, finally,

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}.$$

This is the fundamental result of second-order perturbation theory.

Degenerate Theory

Two-Fold Degeneracy

Suppose that

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \quad \langle \psi_a^0 | \psi_b^0 \rangle = 0,$$

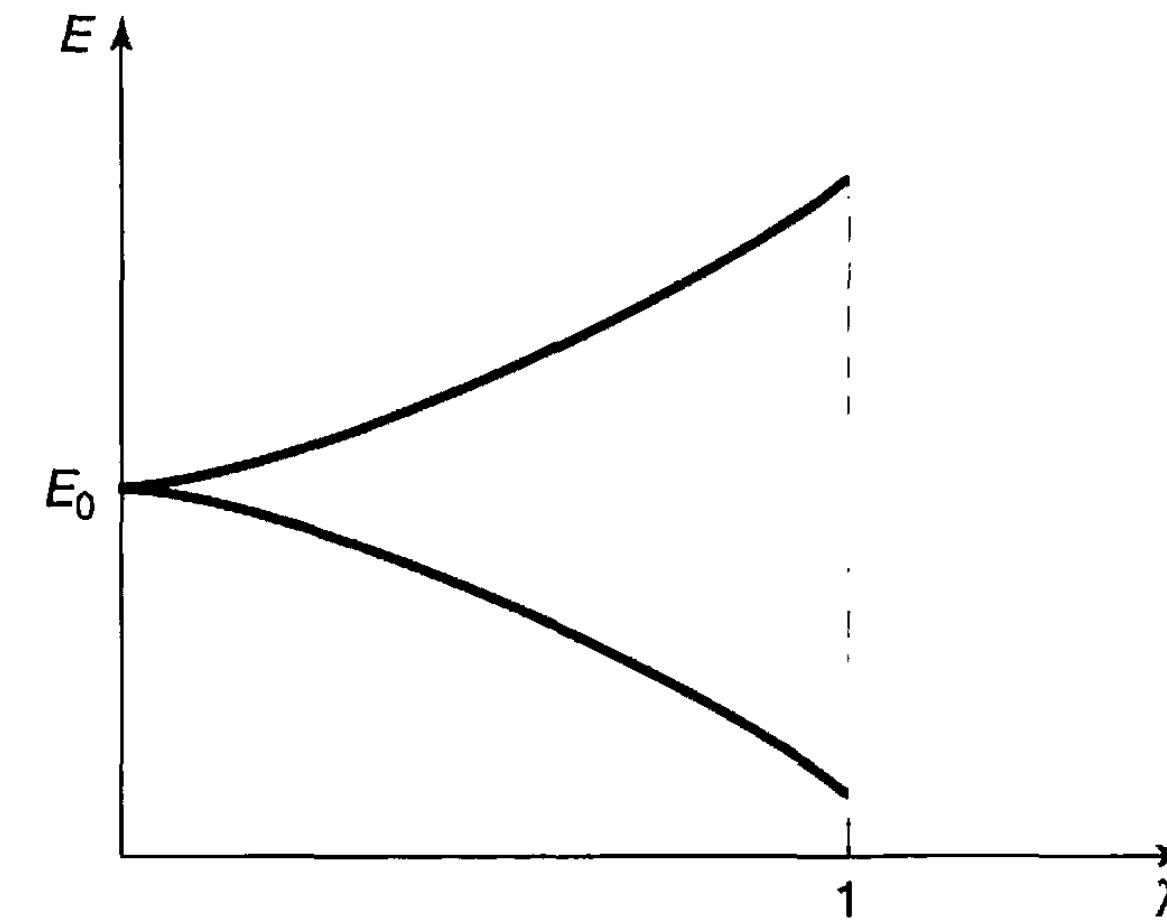
with ψ_a^0 and ψ_b^0 both normalized. Note that any linear combination of these states,

$$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0.$$

is still an eigenstate of H^0 , with the same eigenvalue E^0

Second-order Energies

Typically, the perturbation (H') will “break” (or “lift”) the degeneracy: As we increase λ (from 0 to 1), the common unperturbed energy E^0 splits into two



Going the other direction, when we turn *off* the perturbation, the “upper” state reduces down to *one* linear combination of ψ_a^0 and ψ_b^0 , and the “lower” state reduces to some *orthogonal* linear combination, but we don’t know *a priori* what these “good” linear combinations will be. For this reason we can’t even calculate the *first*-order energy —we don’t know what unperturbed states to use.

We want to solve the Schrödinger equation, with $H = H^0 + \lambda H'$ and

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots, \quad \psi = \psi^0 + \lambda \psi^1 + \lambda^2 \psi^2 + \dots$$

we find

$$H^0 \psi^0 + \lambda (H' \psi^0 + H^0 \psi^1) + \dots = E^0 \psi^0 + \lambda (E^1 \psi^0 + E^0 \psi^1) + \dots$$

Time-independent Perturbation Theory

Degenerate Theory

Two-Fold Degeneracy

But $H^0\psi^0 = E^0\psi^0$, so the first terms cancel; at order λ^1 we have

$$H^0\psi^1 + H'\psi^0 = E^0\psi^1 + E^1\psi^0.$$

Taking the inner product with ψ_a^0 :

$$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle.$$

Because H^0 is hermitian, the first term on the left cancels the first term on the right. exploiting the orthonormality condition we obtain

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1,$$

or, more compactly,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1,$$

where

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle, \quad (i, j = a, b).$$

Similarly, the inner product with ψ_b^0 yields

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1.$$

Notice that the W 's are (in principle) *known*—they are just the “matrix elements” of H' , with respect to the unperturbed wave functions ψ_a^0 and ψ_b^0 . We find:

$$\alpha [W_{ab}W_{ba} - (E^1 - W_{aa})(E^1 - W_{bb})] = 0.$$

If α is *not* zero,

$$(E^1)^2 - E^1(W_{aa} + W_{bb}) + (W_{aa}W_{bb} - W_{ab}W_{ba}) = 0.$$

Invoking the quadratic formula, and noting that $W_{ba} = W_{ab}^*$, we conclude that

$$E_{\pm}^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right].$$

This is the fundamental result of degenerate perturbation theory; the two roots correspond to the two perturbed energies.

But what if α is zero? In that case $\beta = 1$, $W_{ab} = 0$, and $E^1 = W_{bb}$.

This is actually included in the general result with the minus sign (the plus sign corresponds to $\alpha = 1$, $\beta = 0$).

What's more, the *answers*,

$$E_+^1 = W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle, \quad E_-^1 = W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle.$$

are precisely what we would have obtained using *non*degenerate perturbation theory

Time-independent Perturbation Theory

Degenerate Theory

Two-Fold Degeneracy

We have simply been *lucky*: The states ψ_a^0 and ψ_b^0 were *already* the “good” linear combinations. Obviously, it would be greatly to our advantage if we could somehow *guess* the “good” states right from the start—then we could go ahead and use *non*-degenerate perturbation theory. As it turns out, we can very often do this by exploiting the following theorem:

Theorem: Let A be a hermitian operator that commutes with H^0 and H' . If ψ_a^0 and ψ_b^0 (the degenerate eigenfunctions of H^0) are also eigenfunctions of A , with distinct eigenvalues,

$$A\psi_a^0 = \mu\psi_a^0, \quad A\psi_b^0 = \nu\psi_b^0, \quad \text{and } \mu \neq \nu.$$

then $W_{ab} = 0$ (and hence ψ_a^0 and ψ_b^0 are the “good” states to use in perturbation theory).

Proof: By assumption, $[A, H'] = 0$, so

$$\begin{aligned}\langle \psi_a^0 | [A, H'] \psi_b^0 \rangle &= 0 \\ &= \langle \psi_a^0 | AH' \psi_b^0 \rangle - \langle \psi_a^0 | H' A \psi_b^0 \rangle \\ &= \langle A\psi_a^0 | H' \psi_b^0 \rangle - \langle \psi_a^0 | H' \nu \psi_b^0 \rangle \\ &= (\mu - \nu) \langle \psi_a^0 | H' \psi_b^0 \rangle = (\mu - \nu) W_{ab}.\end{aligned}$$

But $\mu \neq \nu$, so $W_{ab} = 0$. QED

Higher-Order Degeneracy

It is easy to see how the method generalizes.

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}.$$

Evidently the E^1 's are the *eigenvalues* of the W -matrix

In the case of n -fold degeneracy, we look for the eigenvalues of the $n \times n$ matrix

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle.$$

In the language of linear algebra, finding the “good” unperturbed wave functions amounts to constructing a basis in the degenerate subspace that *diagonalizes* the matrix W . Once again, if you can think of an operator A that *commutes* with H' , and use the simultaneous eigenfunctions of A and H^0 , then the W matrix will *automatically* be diagonal, and you won’t have to fuss with solving the characteristic equation.

Time-independent Perturbation Theory

Degenerate Theory

Example Consider the three-dimensional infinite cubical well

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < a, 0 < y < a, \text{ and } 0 < z < a \\ \infty, & \text{otherwise.} \end{cases}$$

The stationary states are

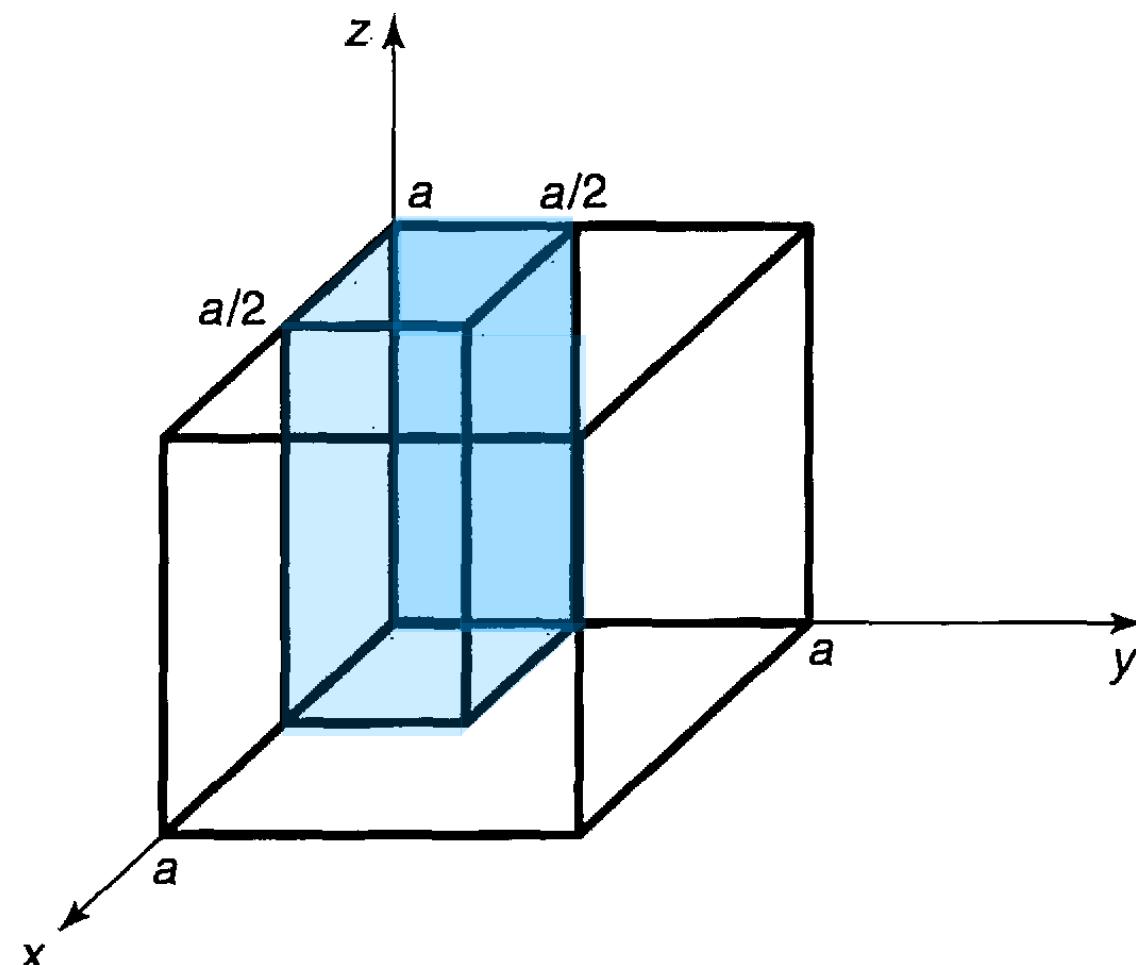
$$\psi_{n_x n_y n_z}^0(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right),$$

where n_x , n_y , and n_z are positive integers. The corresponding allowed energies are

$$E_{n_x n_y n_z}^0 = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2).$$

Notice that the ground state (ψ_{111}) is nondegenerate; its energy is $E_0^0 \equiv 3 \frac{\pi^2 \hbar^2}{2ma^2}$. Now let's introduce the perturbation

$$H' = \begin{cases} V_0, & \text{if } 0 < x < a/2 \text{ and } 0 < y < a/2; \\ 0, & \text{otherwise.} \end{cases}$$



This raises the potential by an amount V_0 in one quarter of the box. The first-order correction to the ground state energy is given by

$$\begin{aligned} E_0^1 &= \langle \psi_{111} | H' | \psi_{111} \rangle \\ &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz \\ &= \frac{1}{4} V_0, \end{aligned}$$

which is pretty much what we would expect.

Time-independent Perturbation Theory

Degenerate Theory

For the first excited state we need the full machinery of degenerate perturbation theory. The first step is to construct the matrix \mathbf{W} . The diagonal elements are the same as for the ground state (except that the argument of one of the sines is doubled);

$$W_{aa} = W_{bb} = W_{cc} = \frac{1}{4} V_0.$$

The off-diagonal elements are more interesting:

$$\begin{aligned} W_{ab} &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin^2\left(\frac{\pi}{a}x\right) dx \\ &\quad \times \int_0^{a/2} \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) dy \int_0^a \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right) dz. \end{aligned}$$

But the z integral is zero (as it will be also for W_{ac}), so

$$W_{ab} = W_{ac} = 0.$$

Finally,

$$\begin{aligned} W_{bc} &= \left(\frac{2}{a}\right)^3 V_0 \int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) dx \\ &\quad \times \int_0^{a/2} \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) dy \int_0^a \sin^2\left(\frac{\pi}{a}z\right) dz = \frac{16}{9\pi^2} V_0. \end{aligned}$$

Thus

$$\mathbf{W} = \frac{V_0}{4} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix}$$

where $\kappa \equiv (8/3\pi)^2 \approx 0.7205$.

The characteristic equation for \mathbf{W} (or rather, for $4\mathbf{W}/V_0$, which is easier to work with) is

$$(1-w)^3 - \kappa^2(1-w) = 0,$$

and the eigenvalues are

$$w_1 = 1; \quad w_2 = 1 + \kappa \approx 1.705; \quad w_3 = 1 - \kappa \approx 0.2795.$$

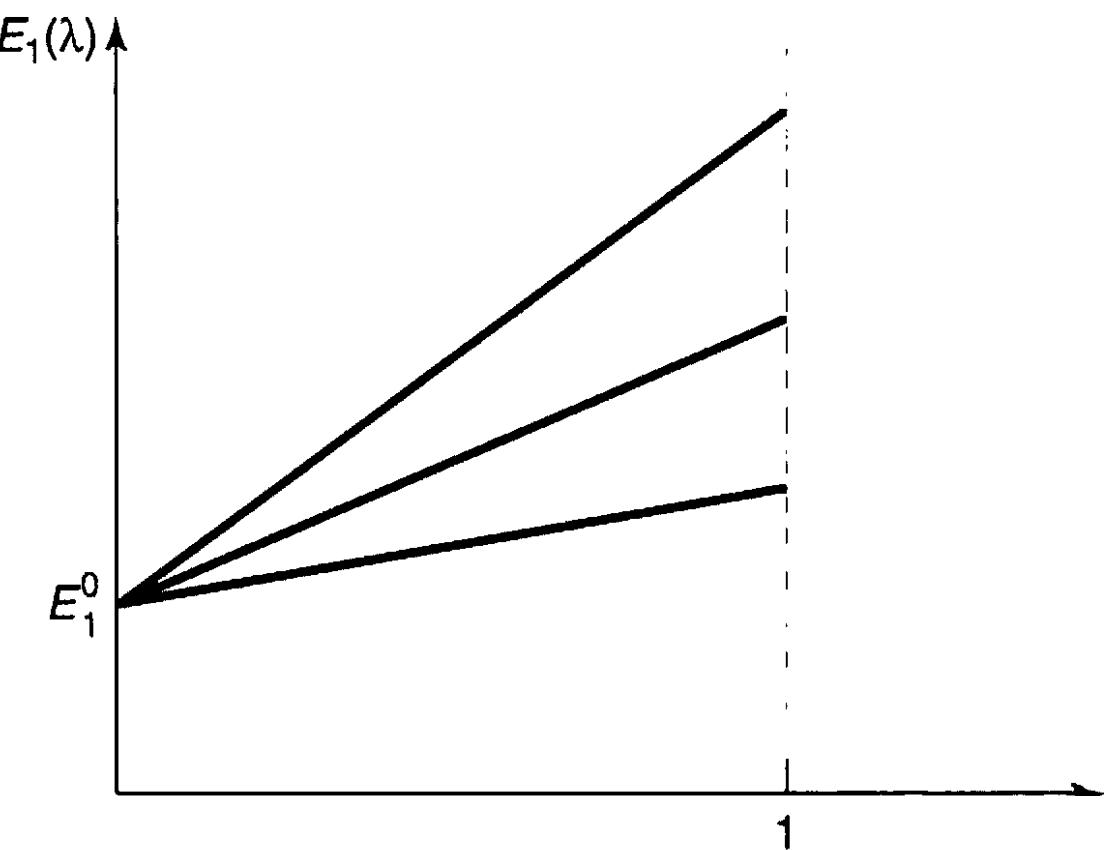
To first order in λ , then,

$$E_1(\lambda) = \begin{cases} E_1^0 + \lambda V_0/4, \\ E_1^0 + \lambda(1+\kappa)V_0/4, \\ E_1^0 + \lambda(1-\kappa)V_0/4, \end{cases}$$

where E_1^0 is the (common) unperturbed energy. The perturbation lifts the degeneracy, splitting E_1^0 into three distinct energy levels. Notice that if we had naively applied *non*degenerate perturbation theory to this problem, we would have concluded that the first-order correction is the same for all three states, and equal to $V_0/4$ —which is actually correct only for the middle state.

Time-independent Perturbation Theory

Degenerate Theory



Meanwhile, the “good” unperturbed states are linear combinations of the form

$$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c,$$

where the coefficients (α , β , and γ) form the eigenvectors of the matrix \mathbf{W} :

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \kappa \\ 0 & \kappa & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}.$$

For $w = 1$ we get $\alpha = 1$, $\beta = \gamma = 0$; for $w = 1 \pm \kappa$ we get $\alpha = 0$, $\beta = \pm \gamma = 1/\sqrt{2}$. (I normalized them as I went along.) Thus the “good” states are

$$\psi^0 = \begin{cases} \psi_a, \\ (\psi_b + \psi_c)/\sqrt{2}, \\ (\psi_b - \psi_c)/\sqrt{2}. \end{cases}$$

THE FINE STRUCTURE OF HYDROGEN

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

(electron kinetic energy plus coulombic potential energy). But this is not quite the whole story. We have already learned how to correct for the motion of the nucleus: Just replace m by the reduced mass. More significant is the so-called **fine structure**, which is actually due to two distinct mechanisms: a **relativistic correction**, and **spin-orbit coupling**. Compared to the Bohr energies fine structure is a tiny perturbation—smaller by a factor of α^2 , where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}$$

is the famous **fine structure constant**. Smaller still (by another factor of α) is the **Lamb shift**, associated with the quantization of the electric field, and smaller by yet another order of magnitude is the **hyperfine structure**, which is due to the magnetic interaction between the dipole moments of the electron and the proton.

Bohr energies:	of order	$\alpha^2 mc^2$
Fine structure:	of order	$\alpha^4 mc^2$
Lamb shift:	of order	$\alpha^5 mc^2$
Hyperfine splitting:	of order	$(m/m_p)\alpha^4 mc^2$

Time-independent Perturbation Theory

The Relativistic Correction

The first term in the Hamiltonian is supposed to represent kinetic energy:

$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m},$$

and the canonical substitution $\mathbf{p} \rightarrow (\hbar/i)\nabla$ yields the operator

$$T = -\frac{\hbar^2}{2m}\nabla^2.$$

But this is the *classical* expression for kinetic energy; the *relativistic* formula is

$$T = \frac{mc^2}{\sqrt{1-(v/c)^2}} - mc^2.$$

The first term is the *total* relativistic energy (not counting *potential* energy, which we aren't concerned with at the moment), and the second term is the *rest* energy—the *difference* is the energy attributable to motion.

We need to express T in terms of the (relativistic) momentum,

$$p = \frac{mv}{\sqrt{1-(v/c)^2}},$$

instead of velocity. Notice that

$$p^2c^2 + m^2c^4 = \frac{m^2v^2c^2 + m^2c^4[1-(v/c)^2]}{1-(v/c)^2} = \frac{m^2c^4}{1-(v/c)^2} = (T + mc^2)^2.$$

so

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2.$$

This relativistic equation for kinetic energy reduces (of course) to the classical result, in the nonrelativistic limit $p \ll mc$; expanding in powers of the small number (p/mc) , we have

$$\begin{aligned} T &= mc^2 \left[\sqrt{1 + \left(\frac{p}{mc} \right)^2} - 1 \right] = mc^2 \left[1 + \frac{1}{2} \left(\frac{p}{mc} \right)^2 - \frac{1}{8} \left(\frac{p}{mc} \right)^4 \dots - 1 \right] \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots \end{aligned}$$

The lowest-order relativistic correction to the Hamiltonian is evidently

$$H'_r = -\frac{p^4}{8m^3c^2}.$$

In first-order perturbation theory, the correction to E_n is given by the expectation value of H' in the unperturbed state

$$E_r^1 = \langle H'_r \rangle = -\frac{1}{8m^3c^2} \langle \psi | p^4 \psi \rangle = -\frac{1}{8m^3c^2} \langle p^2 \psi | p^2 \psi \rangle.$$

Now, the Schrödinger equation (for the unperturbed states) says

$$p^2\psi = 2m(E - V)\psi,$$

Time-independent Perturbation Theory

and hence

$$E_r^1 = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = -\frac{1}{2mc^2} [E^2 - 2E\langle V \rangle + \langle V^2 \rangle].$$

So far this is entirely general; but we're interested in hydrogen, for which $V(r) = -(1/4\pi\epsilon_0)e^2/r$:

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right],$$

where E_n is the Bohr energy of the state in question.

To complete the job, we need the expectation values of $1/r$ and $1/r^2$, in the (unperturbed) state ψ_{nlm}

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a},$$

where a is the Bohr radius. The second is not so simple to derive, but the answer is¹

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + 1/2)n^3 a^2}.$$

It follows that

$$E_r^1 = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{(l + 1/2)n^3 a^2} \right],$$

or, eliminating a and expressing everything in terms of E_n

$$E_r^1 = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{l + 1/2} - 3 \right].$$

Evidently the relativistic correction is smaller than E_n , by a factor of about $E_n/mc^2 = 2 \times 10^{-5}$.

You might have noticed that I used *nondegenerate* perturbation theory in this calculation, in spite of the fact that the hydrogen atom is highly degenerate. But the perturbation is spherically symmetrical, so it commutes with L^2 and L_z . Moreover, the eigenfunctions of these operators (taken together) have distinct eigenvalues for the n^2 states with a given E_n . Luckily, then, the wave functions ψ_{nlm} are the “good” states for this problem (or, as we say, n , l , and m are the **good quantum numbers**), so as it happens the use of nondegenerate perturbation theory was legitimate

Time-independent Perturbation Theory

Spin-Orbit Coupling

Imagine the electron in orbit around the nucleus; from the *electron's* point of view, the proton is circling around *it*. This orbiting positive charge sets up a magnetic field \mathbf{B} , in the electron frame, which exerts a torque on the spinning electron, tending to align its magnetic moment (μ) along the direction of the field. The Hamiltonian is

$$H = -\mu \cdot \mathbf{B}.$$

To begin with, we need to figure out the magnetic field of the proton (\mathbf{B}) and the dipole moment of the electron (μ).

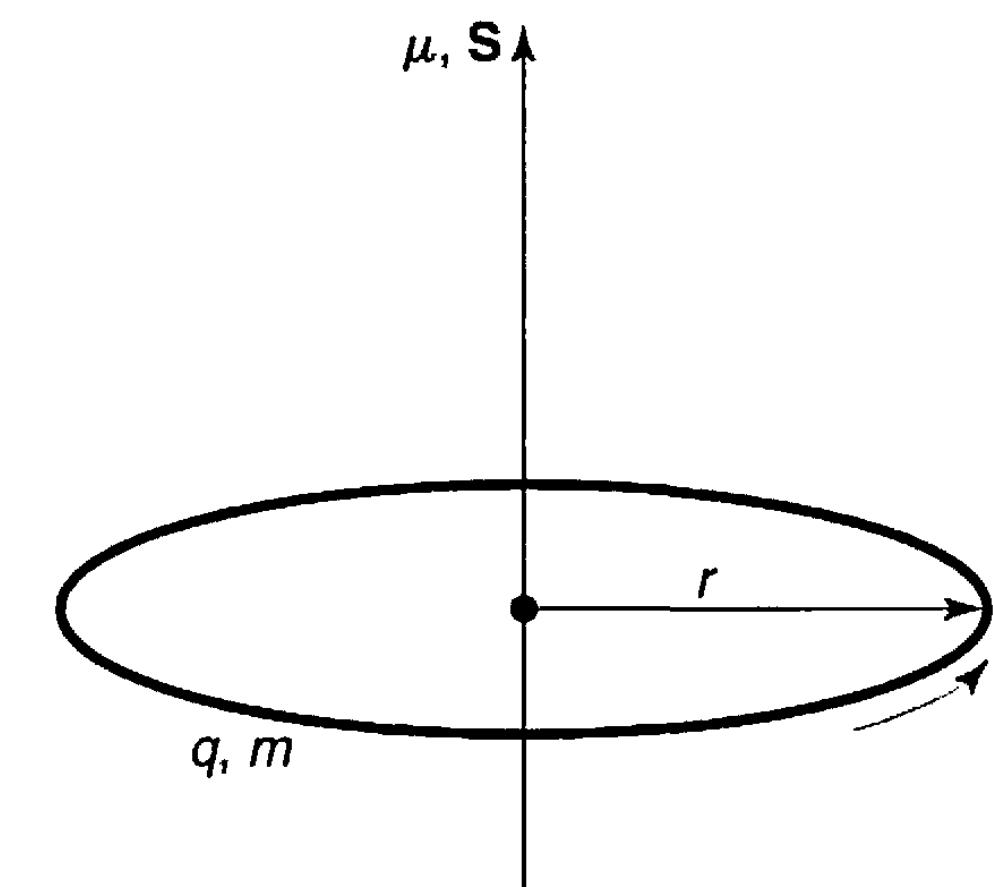
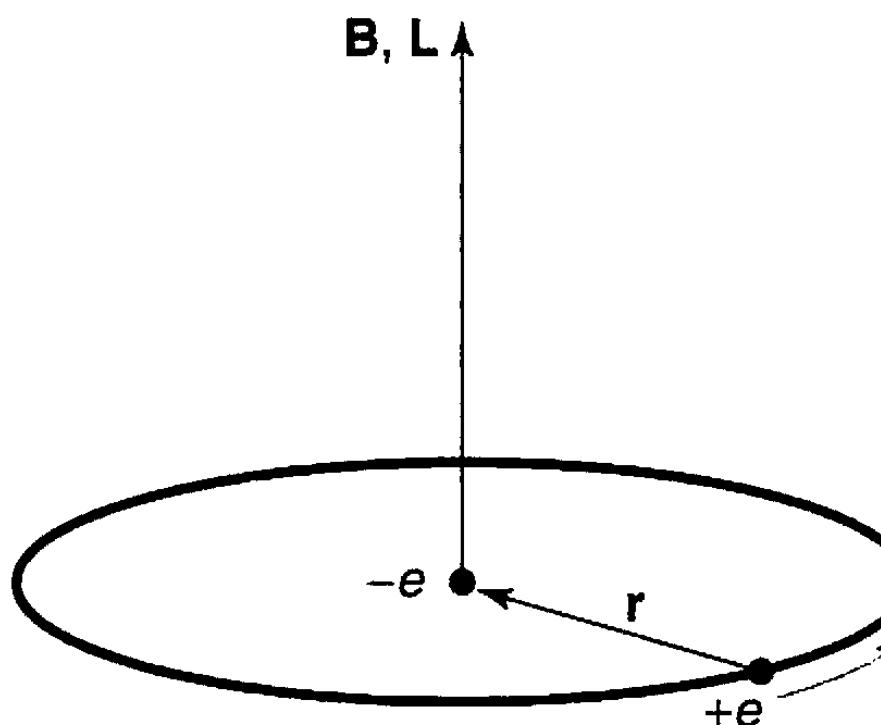
The magnetic field of the proton. If we picture the proton (from the electron's perspective) as a continuous current loop, its magnetic field can be calculated from the Biot-Savart law:

$$B = \frac{\mu_0 I}{2r},$$

with an effective current $I = e/T$, where e is the charge of the proton and T is the period of the orbit. On the other hand, the orbital angular momentum of the *electron* (in the rest frame of the *nucleus*) is $L = rmv = 2\pi mr^2/T$. Moreover, \mathbf{B} and \mathbf{L} point in the same direction, so

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \mathbf{L}.$$

(I used $c = 1/\sqrt{\epsilon_0\mu_0}$ to eliminate μ_0 in favor of ϵ_0 .)



The magnetic dipole moment of the electron. The magnetic dipole moment of a spinning charge is related to its (spin) angular momentum; the proportionality factor is the gyromagnetic ratio

Let's derive it, this time, using classical electrodynamics. Consider first a charge q smeared out around a ring of radius r , which rotates about the axis with period T

The magnetic dipole moment of the ring is defined as the current (q/T) times the area (πr^2):

$$\mu = \frac{q\pi r^2}{T}.$$

If the mass of the ring is m , its angular momentum is the moment of inertia (mr^2) times the angular velocity ($2\pi/T$):

$$S = \frac{2\pi mr^2}{T}.$$

Time-independent Perturbation Theory

The gyromagnetic ratio for this configuration is evidently $\mu/S = q/2m$. Notice that it is independent of r (and T). If I had some more complicated object, such as a sphere (all I require is that it be a figure of revolution, rotating about its axis), I could calculate μ and S by chopping it into little rings, and adding up their contributions. As long as the mass and the charge are distributed in the same manner (so that the charge-to-mass ratio is uniform), the gyromagnetic ratio will be the same for each ring, and hence also for the object as a whole. Moreover, the directions of μ and S are the same (or opposite, if the charge is negative), so

$$\mu = \left(\frac{q}{2m} \right) S.$$

That was a purely *classical* calculation, however; as it turns out the electron's magnetic moment is *twice* the classical value:

$$\mu_e = -\frac{e}{m} S.$$

The “extra” factor of 2 was explained by Dirac, in his relativistic theory of the electron.

Putting all this together, we have

$$H = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} S \cdot L.$$

But there is a serious fraud in this calculation: I did the analysis in the rest frame of the electron, but that's *not an inertial system*—it *accelerates*, as the electron orbits around the nucleus. You can get away with this if you make an appropriate kinematic correction, known as the **Thomas precession**. In this context it throws

in a factor of 1/2:

$$H'_{\text{so}} = \left(\frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} S \cdot L.$$

This is the **spin-orbit interaction**; apart from two corrections (the modified gyromagnetic ratio for the electron and the Thomas precession factor—which, coincidentally, exactly cancel one another) it is just what you would expect on the basis of a naive classical model. Physically, it is due to the torque exerted on the magnetic dipole moment of the spinning electron, by the magnetic field of the proton, in the electron's instantaneous rest frame.

Now the quantum mechanics. In the presence of spin-orbit coupling, the Hamiltonian no longer commutes with L and S , so the spin and orbital angular momenta are not separately conserved. However, H'_{so} does commute with L^2 , S^2 and the *total* angular momentum

$$J \equiv L + S,$$

and hence these quantities *are* conserved. To put it another way, the eigenstates of L_z and S_z are not “good” states to use in perturbation theory, but the eigenstates of L^2 , S^2 , J^2 , and J_z *are*. Now

$$J^2 = (L + S) \cdot (L + S) = L^2 + S^2 + 2L \cdot S,$$

so

$$L \cdot S = \frac{1}{2}(J^2 - L^2 - S^2).$$

Time-independent Perturbation Theory

and therefore the eigenvalues of $\mathbf{L} \cdot \mathbf{S}$ are

$$\frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)].$$

In this case, of course, $s = 1/2$. Meanwhile, the expectation value of $1/r^3$ is

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3},$$

and we conclude that

$$E_{\text{so}}^1 = \langle H'_{\text{so}} \rangle = \frac{e^2}{8\pi\epsilon_0 m^2 c^2} \frac{(\hbar^2/2)[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)n^3a^3},$$

or, expressing it all in terms of E_n :

$$E_{\text{so}}^1 = \frac{(E_n)^2}{mc^2} \left\{ \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right\}.$$

It is remarkable, considering the totally different physical mechanisms involved, that the relativistic correction and the spin-orbit coupling are of the same order (E_n^2/mc^2). Adding them together, we get the complete fine-structure formula

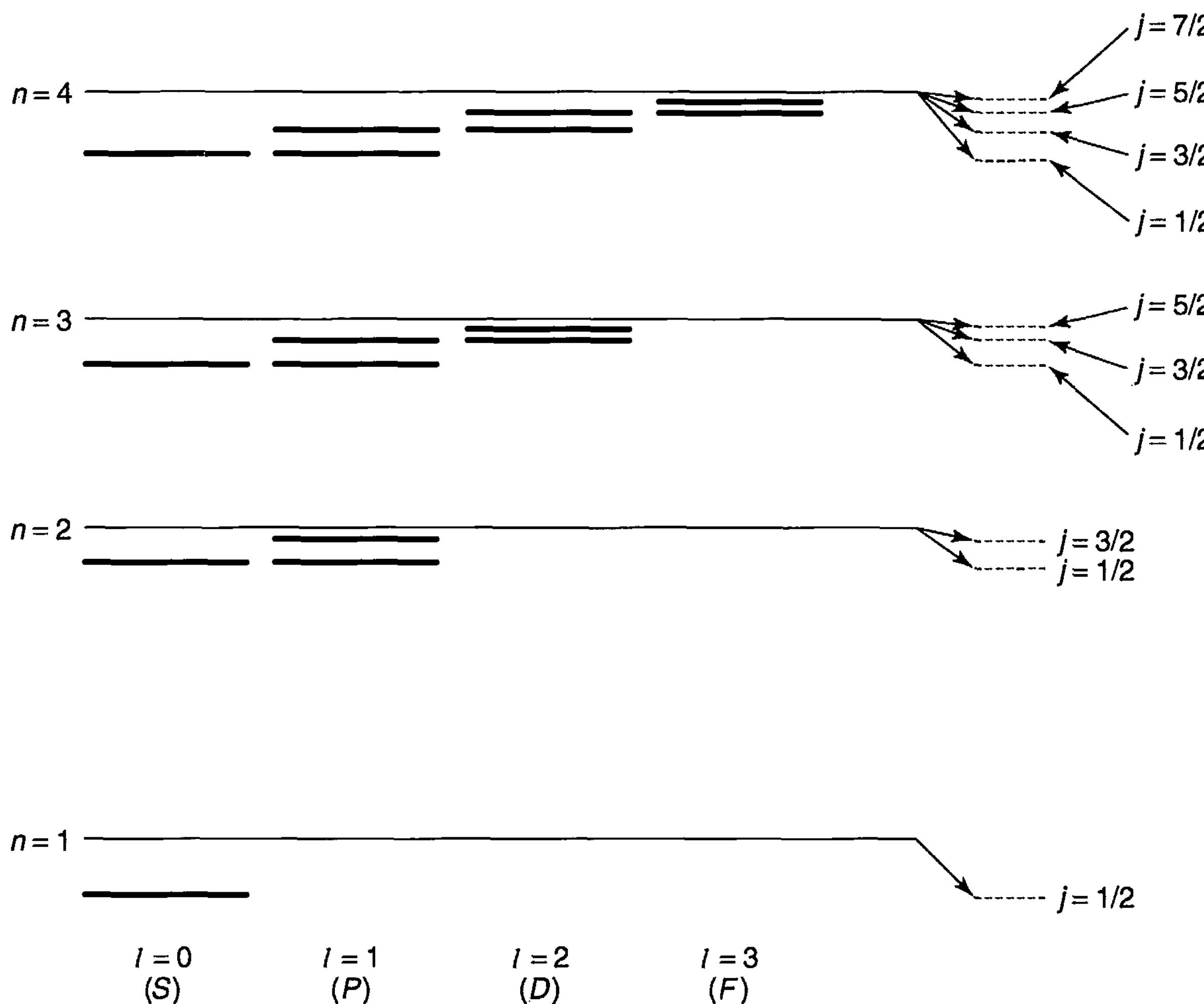
$$E_{\text{fs}}^1 = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right).$$

Combining this with the Bohr formula, we obtain the grand result for the energy levels of hydrogen, with fine structure included:

$$E_{nj} = -\frac{13.6 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right].$$

Fine structure breaks the degeneracy in l (that is, for a given n , the different allowed values of l do not all carry the same energy), but it still preserves degeneracy in j . The z -component eigenvalues for orbital and spin angular momentum (m_l and m_s) are no longer “good” quantum numbers—the stationary states are linear combinations of states with different values of these quantities; the “good” quantum numbers are n , l , s , j , and m_j .

Time-independent Perturbation Theory



THE ZEEMAN EFFECT

When an atom is placed in a uniform external magnetic field \mathbf{B}_{ext} , the energy levels are shifted. This phenomenon is known as the **Zeeman effect**. For a single electron, the perturbation is

$$H'_Z = -(\mu_l + \mu_s) \cdot \mathbf{B}_{\text{ext}},$$

where

$$\mu_s = -\frac{e}{m} \mathbf{S}$$

is the magnetic dipole moment associated with electron spin, and

$$\mu_l = -\frac{e}{2m} \mathbf{L}$$

is the dipole moment associated with orbital motion. Thus

$$H'_Z = \frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}.$$

The nature of the Zeeman splitting depends critically on the strength of the external field in comparison with the *internal* field that gives rise to spin-orbit coupling. If $B_{\text{ext}} \ll B_{\text{int}}$, then fine structure dominates, and H'_Z can be treated as a small perturbation, whereas if $B_{\text{ext}} \gg B_{\text{int}}$, then the Zeeman effect dominates, and fine structure becomes the perturbation. In the intermediate zone, where the two fields are comparable, we need the full machinery of degenerate perturbation theory, and it is necessary to diagonalize the relevant portion of the Hamiltonian “by hand.” In the following sections we shall explore each of these regimes briefly, for the case of hydrogen.

Quantum Mechanics

The Variational Principle

We don't know the solutions or the energies but we want an upper bound on the ground state energy. Claim:

$$E_{\text{gs}} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

where $|\psi\rangle$ is any normalised state.

Proof: Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:

$$\psi = \sum_n c_n \psi_n, \quad \text{with } H\psi_n = E_n \psi_n.$$

Since ψ is normalized,

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2,$$

(assuming the eigenfunctions themselves have been orthonormalized: $\langle \psi_m | \psi_n \rangle = \delta_{mn}$). Meanwhile,

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2.$$

But the ground state energy is, by definition, the *smallest* eigenvalue, so $E_{\text{gs}} \leq E_n$, and hence

$$\langle H \rangle \geq E_{\text{gs}} \sum_n |c_n|^2 = E_{\text{gs}}.$$

Example Suppose we want to find the ground state energy for the one-dimensional harmonic oscillator:

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2.$$

Gaussian trial wave function:

$$\psi(x) = A e^{-bx^2},$$

where b is a constant, and A is determined by normalization:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = |A|^2 \sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}.$$

Now

$$\langle H \rangle = \langle T \rangle + \langle V \rangle,$$

The Variational Principle

where, in this case,

$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2} \left(e^{-bx^2} \right) dx = \frac{\hbar^2 b}{2m}.$$

and

$$\langle V \rangle = \frac{1}{2} m \omega^2 |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2 dx = \frac{m \omega^2}{8b},$$

so

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m \omega^2}{8b}.$$

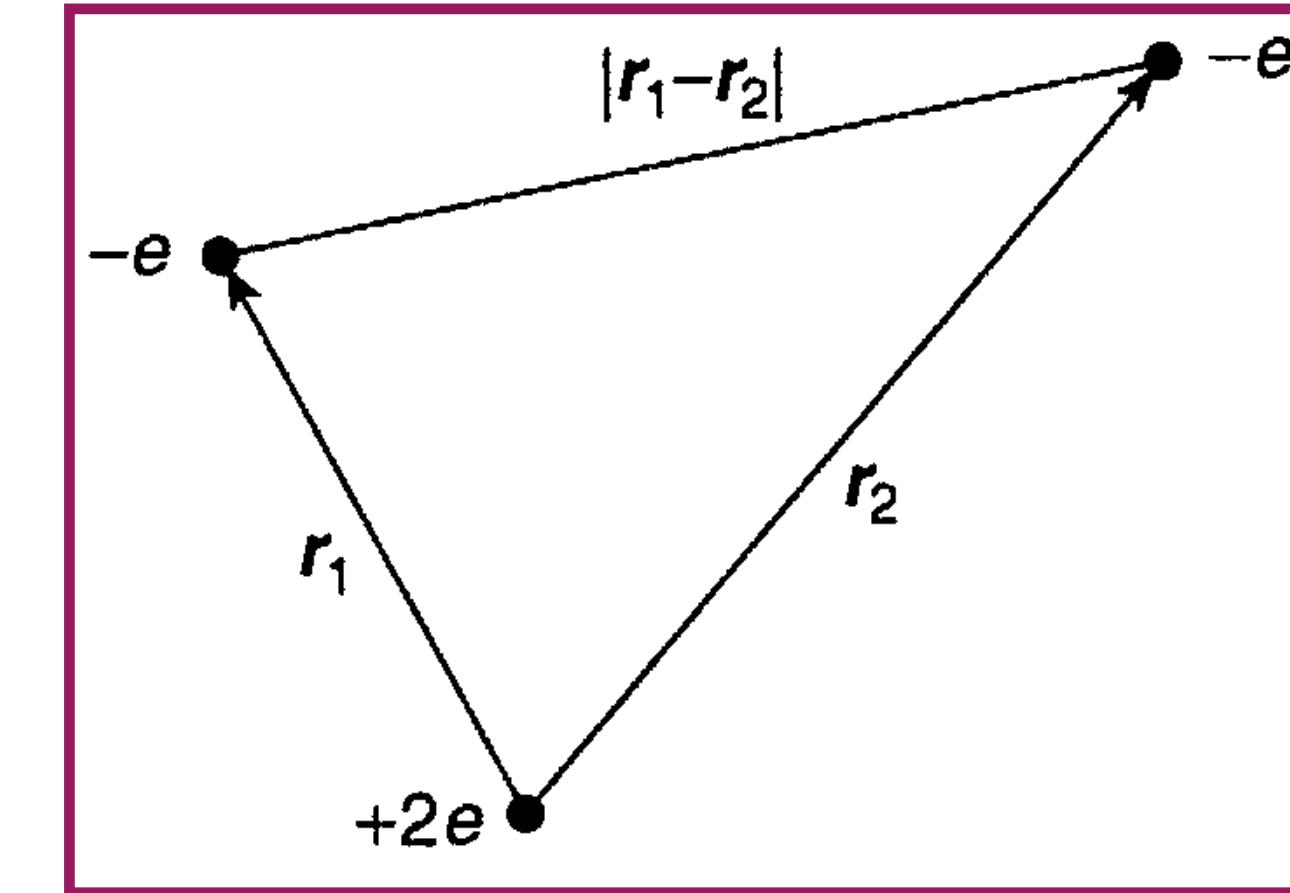
let's minimize $\langle H \rangle$:

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{m \omega^2}{8b^2} = 0 \Rightarrow b = \frac{m \omega}{2\hbar}.$$

Putting this back into $\langle H \rangle$, we find

$$\langle H \rangle_{\min} = \frac{1}{2} \hbar \omega.$$

The Ground State of Helium



The Hamiltonian for this system (ignoring fine structure and smaller corrections) is:

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

Our problem is to calculate the ground state energy, E_{gs} . Physically, this represents the amount of energy it would take to strip off both electrons.

The ground state energy of helium has been measured

$$E_{\text{gs}} = -78.975 \text{ eV} \quad (\text{experimental}).$$

This is the number we would like to reproduce theoretically.

The trouble comes from the electron-electron repulsion,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_1 - r_2|}.$$

The Variational Principle

If we ignore this term altogether, H splits into two independent hydrogen Hamiltonians (only with a nuclear charge of $2e$, instead of e); the exact solution is just the product of hydrogenic wave functions:

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

and the energy is $8E_1 = -109$ eV

To get a better approximation for E_{gs} we'll apply the variational principle, using ψ_0 as the trial wave function. This is a particularly convenient choice because it's an eigenfunction of *most* of the Hamiltonian:

$$H\psi_0 = (8E_1 + V_{ee})\psi_0.$$

Thus

$$\langle H \rangle = 8E_1 + \langle V_{ee} \rangle,$$

where⁸

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2.$$

I'll do the \mathbf{r}_2 integral first; for this purpose \mathbf{r}_1 is fixed, and we may as well orient the \mathbf{r}_2 coordinate system so that the polar axis lies along \mathbf{r}_1

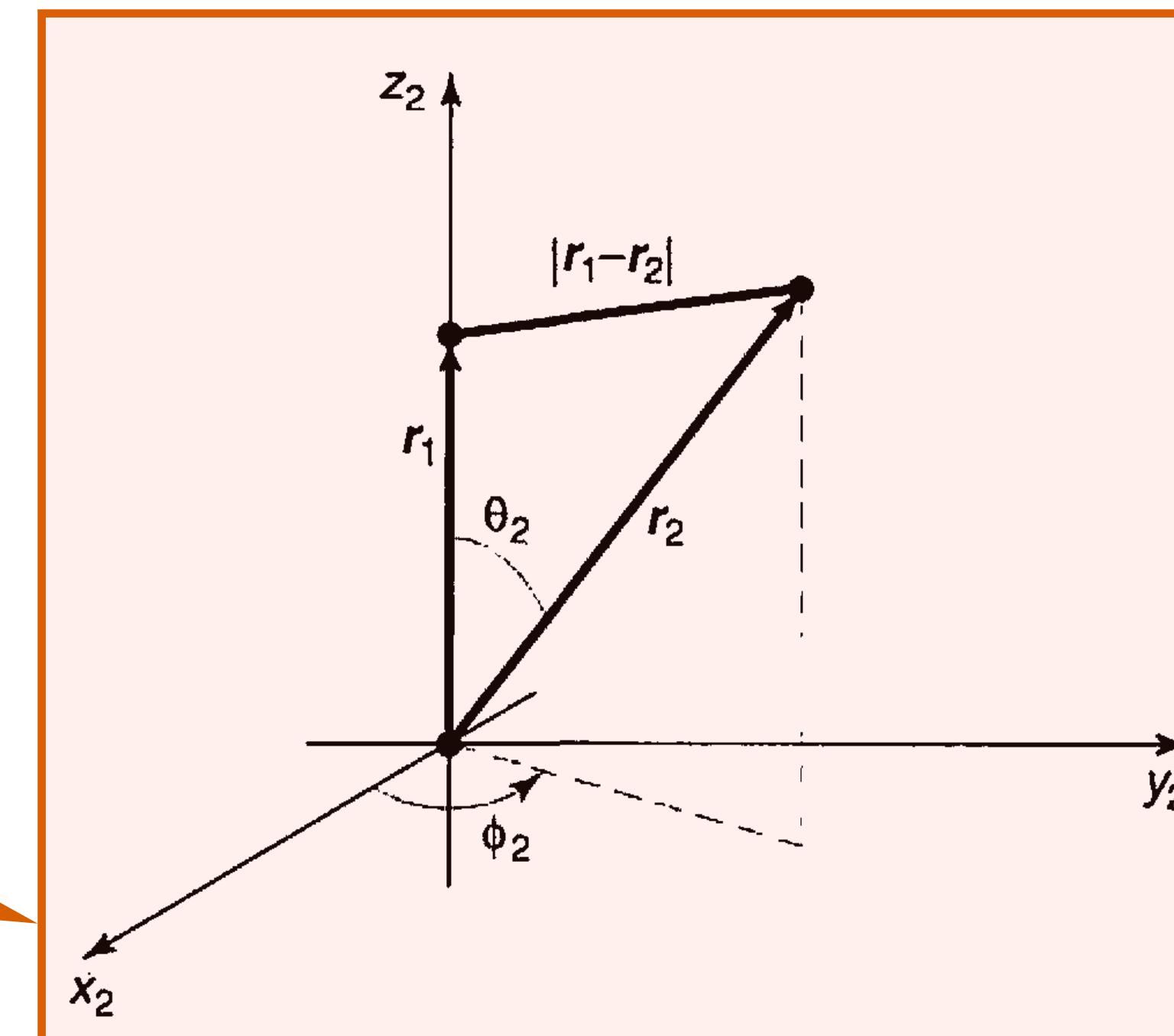
$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}.$$

and hence

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} r_2^2 \sin \theta_2 dr_2 d\theta_2 d\phi_2.$$

The ϕ_2 integral is trivial (2π); the θ_2 integral is

$$\int_0^\pi \frac{\sin \theta_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}} d\theta_2 = \frac{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}}{r_1 r_2} \Big|_0^\pi$$



The Variational Principle

$$= \frac{1}{r_1 r_2} \left(\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2} \right)$$

$$= \frac{1}{r_1 r_2} [(r_1 + r_2) - |r_1 - r_2|] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1, \\ 2/r_2, & \text{if } r_2 > r_1. \end{cases}$$

Thus

$$I_2 = 4\pi \left(\frac{1}{r_1} \int_0^{r_1} e^{-4r_2/a} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2 dr_2 \right)$$

$$= \frac{\pi a^3}{8r_1} \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right].$$

It follows that $\langle V_{ee} \rangle$ is equal to

$$\left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{8}{\pi a^3} \right) \int \left[1 - \left(1 + \frac{2r_1}{a} \right) e^{-4r_1/a} \right] e^{-4r_1/a} r_1 \sin\theta_1 dr_1 d\theta_1 d\phi_1.$$

The angular integrals are easy (4π), and the r_1 integral becomes

$$\int_0^{\infty} \left[r e^{-4r/a} - \left(r + \frac{2r^2}{a} \right) e^{-8r/a} \right] dr = \frac{5a^2}{128}.$$

Finally, then,

$$\langle V_{ee} \rangle = \frac{5}{4a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5}{2} E_1 = 34 \text{ eV},$$

and therefore

$$\langle H \rangle = -109 \text{ eV} + 34 \text{ eV} = -75 \text{ eV}.$$

Not bad (remember, the experimental value is -79 eV). But we can do better.

We need to think up a more realistic trial function than ψ_0 (which treats the two electrons as though they did not interact at all). Rather than completely *ignoring* the influence of the other electron, let us say that, on the average, each electron represents a cloud of negative charge which partially *shields* the nucleus, so that the other electron actually sees an *effective* nuclear charge (Z) that is somewhat *less* than 2. This suggests that we use a trial function of the form

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}.$$

We'll treat Z as a variational parameter, picking the value that minimizes H .

This wave function is an eigenstate of the “unperturbed” Hamiltonian (neglecting electron repulsion), only with Z , instead of 2, in the Coulomb terms. With this in mind, we rewrite H

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right).$$

The expectation value of H is evidently

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

The Variational Principle

Here $\langle 1/r \rangle$ is the expectation value of $1/r$ in the (one-particle) hydrogenic ground state ψ_{100} (but with nuclear charge Z);

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}.$$

The expectation value of V_{ee} is the same as before except that instead of $Z = 2$ we now want *arbitrary* Z —so we multiply a by $2/Z$:

$$\langle V_{ee} \rangle = \frac{5Z}{8a} \left(\frac{e^2}{4\pi\epsilon_0} \right) = -\frac{5Z}{4} E_1.$$

Putting all this together, we find

$$\langle H \rangle = [2Z^2 - 4Z(Z-2) - (5/4)Z] E_1 = [-2Z^2 + (27/4)Z] E_1.$$

According to the variational principle, this quantity exceeds E_{gs} for *any* value of Z . The *lowest* upper bound occurs when $\langle H \rangle$ is minimized:

$$\frac{d}{dZ} \langle H \rangle = [-4Z + (27/4)] E_1 = 0,$$

from which it follows that

$$Z = \frac{27}{16} = 1.69.$$

This seems reasonable; it tells us that the other electron partially screens the nucleus, reducing its effective charge from 2 down to about 1.69. Putting in this value for Z , we find

$$\langle H \rangle = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_1 = -77.5 \text{ eV}.$$

Reading assignment: Hydrogen Molecule Ion