

Lecture Notes, Quantum Physics

Physics 448, Prof. Franz Himpfel

Particles and Waves

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Quantum Physics

First evidence for quantum phenomena (Planck): Quantization of the electromagnetic field energy into photons with energy $h\nu$ provides the exponential cutoff of the blackbody radiation spectrum at high frequencies ν .

Blackbody radiation:

Spectral emittance, i.e., the power P radiated per unit area and frequency interval:

$$dP/d\nu = 2\pi hc^{-2} \cdot \nu^3 / (e^{h\nu/kT} - 1) = \text{const.} \cdot (kT)^3 \cdot F\left(\frac{h\nu}{kT}\right)$$

k = Boltzmann's constant, h = Planck's constant, $\frac{h\nu}{kT}$ dimensionless.

Frequency ν_{max} of maximum emittance:

$\nu_{\text{max}} \sim T$

Total emittance P , integrated over all ν :

$P \sim T^4$

Cosmic background radiation:

Explained as black body radiation from a hot plasma ($H^+ + e^-$) that existed about $3 \cdot 10^5$ years after the Big Bang (short compared to the age of the universe: $1.5 \cdot 10^{10}$ years). The temperature shift from a 4000 K plasma to the observed **3 K microwave radiation** can be viewed as Doppler shift, making Hubble's assumption of a universe expanding with the expansion velocity proportional to the distance from the observer. Thus, we are looking at the outermost, **oldest reaches of the universe**.

Precise data on the spectral and directional distribution of the cosmic background radiation have been obtained by the cosmic background explorer (**COBE**) satellite and a number of follow-up experiments.

Physics Today, July 2000, p. 17

http://space.gsfc.nasa.gov/astro/cobe/cobe_home.html

Particle-Wave Duality

Plane Wave: $\psi(\mathbf{x},t) = \exp[i/\hbar \cdot (\mathbf{p}\mathbf{x}-Et)] = \exp[i(\mathbf{k}\mathbf{x}-\omega t)] = \exp[i2\pi(x/\lambda-t/T)]$

This **wave** corresponds to a **particle** with energy **E** and momentum **p**.

To eliminate \hbar use the angular frequency $\omega = 2\pi\nu = 2\pi/T$ and the wave vector $\mathbf{k} = 2\pi/\lambda$:

$\mathbf{E} = \hbar\omega$ $\mathbf{E} = h\nu \quad (\text{Planck})$
--

$\mathbf{p} = \hbar\mathbf{k}$ $\mathbf{p} = h/\lambda \quad (\text{De Broglie})$

Thus, **E** is related to the frequency ν , and **p** to the wavelength λ via Planck's constant h .

Since **E** is related to **p** via the particle mass m_0 , one can convert **E** to λ , **k** :

Photons:	$\lambda[\text{nm}] = 1.24 / E [\text{keV}]$	$E = pc$	$p = h/\lambda$	$(E = h\nu \quad \nu = c/\lambda)$
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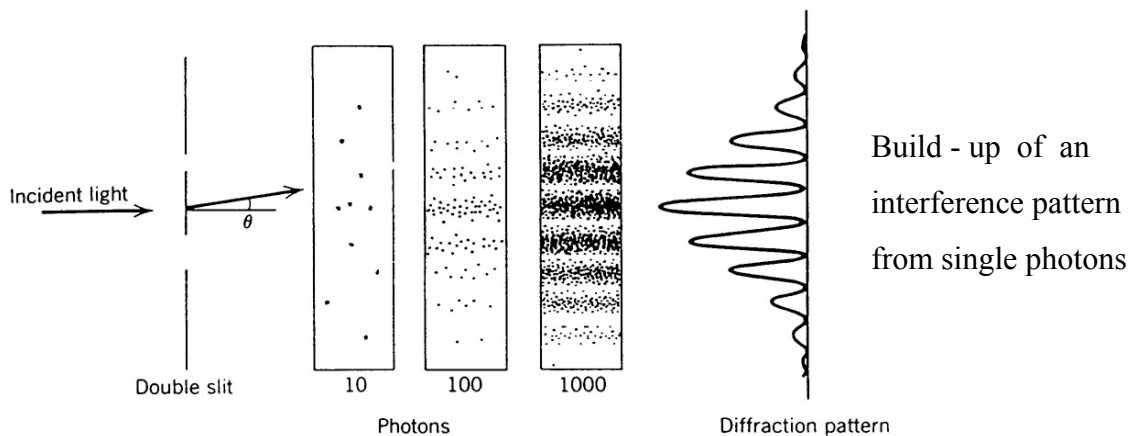
Electrons:	$\lambda[\text{nm}] = 1.23 / \sqrt{E [\text{eV}]}$	$E = p^2/2m_e$	$p = h/\lambda$
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Photons:	$k[\text{nm}^{-1}] = 5.1 \cdot (E [\text{keV}])$
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Electrons:	$k[\text{nm}^{-1}] = 5.1 \cdot \sqrt{E [\text{eV}]}$
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When do we see a particle, when a wave?

Always both: The **wave function ψ** gives the **probability p** of finding a particle: $p = |\psi|^2$



When is quantum physics important?

When **few particles** are involved, for example when the energy of a quantum $h\nu$ is **large** compared to the thermal energy kT (high $h\nu$ cutoff in the blackbody radiation).

Particle Properties of Electromagnetic Waves

The **photon** as a **particle** with energy $E=h\nu$, momentum $p=h/\lambda$, and rest mass $m_0=0$:

Photoemission:

$$\gamma + \text{solid} \Rightarrow e^- \quad \boxed{E_{\max} = h\nu - \Phi}$$

(Φ = work function, see p. 22 for details on photoemission)

Photoelectron spectroscopy is practiced using X-ray tubes (Al K_α) and synchrotron radiation.

For synchrotron radiation centers see:

SRC in Madison ($h\nu=10\text{-}100\text{eV}$, valence electrons): <http://www.src.wisc.edu>

ALS in Berkeley ($h\nu=100\text{-}1000\text{eV}$, core electrons): <http://www-als.lbl.gov/als/>

Bremsstrahlung = Inverse Photoemission:

$$e^- + \text{solid} \Rightarrow \gamma \quad \boxed{h\nu_{\max} = E + \Phi}$$

Inverse photoemission probes **unoccupied** electron states in a solid, whereas **photoemission** probes **occupied** states.

Compton Scattering:

$$\gamma + e^- \Rightarrow \gamma' + e^{-'} \quad \boxed{\lambda' - \lambda = \lambda_C \cdot (1 - \cos\theta)} \quad \boxed{\lambda_C = h/m_e c}$$

Elastic scattering of a photon γ by an electron e^- at rest. The electron picks up energy from the photon. The Compton wavelength λ_C corresponds to the wavelength of a photon with energy $m_e c^2$ (for length scales compare relativity notes p. 12).

Electron-Positron Pair Annihilation and Production:

$$e^- + e^+ \Leftrightarrow 2\gamma$$

Need two photons in order to satisfy energy and momentum conservation. One photon couples to a nucleus in pair production. Used in positron emission tomography (PET) for scanning the brain.

These processes can be treated as **particle collisions** where **energy and momentum are conserved** (see relativity notes p.7). For a solid, only the momentum parallel to the surface is conserved.

Wave Properties of Particles

Diffraction of electrons, x-rays, neutrons, atoms:

Two- or three-dimensional diffraction, depending on how many lattice planes are penetrated:

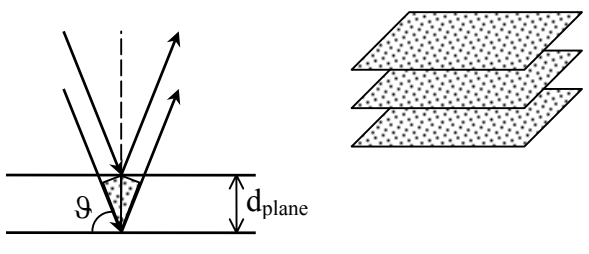
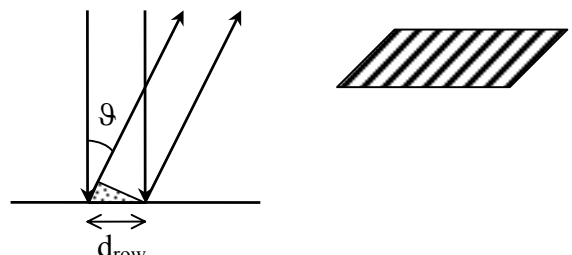
2D: Atom diffraction: Outermost atom layer only.

2D+3D: Low energy electron diffraction (LEED, 10-100 eV): A few lattice planes.

3D: High energy electrons (>1keV), x-rays and neutrons.

Determine the charge density with x-rays, and the spin density with neutrons.

Protein crystallography with x-rays: Wayne Hendrickson, Physics Today, Nov. 1995, p. 42.

Three-dimensional	Two-dimensional
<p>Planes of atoms diffract</p>	<p>Rows of atoms diffract</p>
<div style="display: flex; align-items: center; gap: 20px;"> <div style="border: 1px solid black; padding: 2px;">$2d_{\text{plane}} \cdot \sin\theta = n \cdot \lambda$</div> <div style="border: 1px solid black; padding: 2px;">$\theta_{\text{in}} = \theta_{\text{out}}$</div> <div>(Bragg)</div> </div>	<div style="border: 1px solid black; padding: 2px;">$d_{\text{row}} \cdot \sin\theta = n \cdot \lambda$</div> <div>(Optical grating, LEED)</div>
	

For obtaining λ from E , see p. 3.

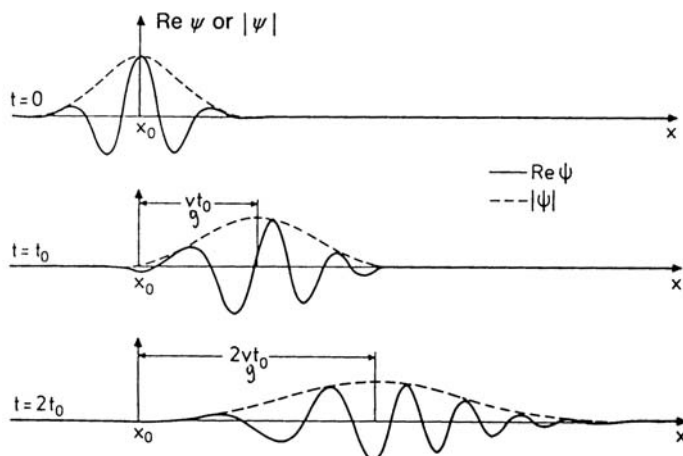
Bragg reflection: Incident radiation with a continuous λ spectrum is monochromatized into discrete λ_n by reflection at a lattice plane. Monochromatic radiation is reflected only if θ_{in} and θ_{out} are matched (θ , 2θ - scan).

Laue pattern: Incident radiation with a continuous spectrum produces exit beams with discrete wavelengths. The angle determines the lattice plane spacing.

Powder Diffraction: Monochromatic radiation produces ring-like diffraction patterns from randomly-oriented crystallites.

Wave Packets

A **wave packet** consists of a sum of plane waves. It spreads (“disperses”) over time if the phase velocity depends on the wavelength λ . Waves with short λ (high frequency ω) move faster due to their higher energy $E = \hbar\omega$. This is characteristic of a non-linear $E(p)$ relation, such as $E = p^2/m_0$.



Group velocity:

$$\boxed{v_{\text{group}} = dE/dp} = d\omega/dk \quad \text{wave packet}$$

Describes the velocity of a wave packet, and the speed of energy and information transfer. Does not exceed c .

Phase Velocity:

$$\boxed{v_{\text{phase}} = E/p} = \omega/k \quad \text{plane wave}$$

Describes the velocity of wave fronts for a plane wave in steady state. v_{phase} can exceed c , for example for light in a medium with refractive index $n < 1$.

Fourier Transform

The superposition of plane waves ψ_n into a wave packet ψ can be viewed in reverse as expansion of ψ into plane waves ψ_n :

$\psi(\mathbf{x}, t) = \sum_n A_n \cdot \exp[i(\mathbf{k}_n \mathbf{x} - \omega_n t)]$	Fourier Series (ψ periodic)
$\psi(\mathbf{x}, t) = \int A(\mathbf{k}, \omega) \exp[i(\mathbf{k} \mathbf{x} - \omega t)] d^3k d\omega$	Fourier Integral (ψ aperiodic)

A **Fourier transform** is an **expansion** of an arbitrary function $\psi(\mathbf{x}, t)$ **into plane waves**.

In the following we restrict ourselves to functions of a single space-time coordinate $f(x)$ or $f(t)$ and write $F(k)$ or $F(-\omega)$ for the amplitude $A(\mathbf{k}, \omega)$. $F(k)$ is the Fourier transform of $f(x)$, likewise $F(-\omega)$ the Fourier transform of $f(t)$.

Real Space xExpansion of $f(x)$ into plane waves:

$$f(x) = (2\pi)^{-1/2} \int F(k) \exp(ikx) dk \quad (1)$$

$$d/dx f(x)$$

$$\int f(x) dx$$

Reciprocal Space kDefinition of the Fourier transform $F(k)$:

$$F(k) = (2\pi)^{-1/2} \int f(x) \exp(-ikx) dx \quad (2)$$

$$ik F(k)$$

$$(2\pi)^{1/2} F(0)$$

Particle Limit δx smallDelta function* $\delta(x)$

$$(2) \Rightarrow$$

 δk largeConstant = $(2\pi)^{-1/2}$ **Wave Limit** δx largePlane wave $(2\pi)^{-1/2} \exp(ik_0x)$

$$\Leftarrow (1)$$

 δk smallDelta function* $\delta(k-k_0)$ **Uncertainty**

$$\delta x = \sqrt{\langle (x-x_0)^2 \rangle} \quad x_0 = \langle x \rangle$$

$\uparrow \uparrow \uparrow$
 root mean square (rms)

$$\delta k = \sqrt{\langle (k-k_0)^2 \rangle} \quad k_0 = \langle k \rangle$$

$$\langle x^n \rangle = \int x^n p(x) dx \quad \int p(x) dx = 1$$

$$\langle k^n \rangle = \int k^n P(k) dk \quad \int P(k) dk = 1$$

Probability $p(x), P(k) = |\psi|^2 = \psi^* \psi$ in quantum mechanics, here $p(x) \sim |f|^2$, $P(k) \sim |F|^2$ **Uncertainty Relation**

$$\delta x \cdot \delta k \geq \frac{1}{2}$$

with $p = \hbar k$

$$\delta x \cdot \delta p \geq \frac{1}{2} \hbar$$

The smallest uncertainty is achieved with a Gaussian wave function $f(x) = \exp[-1/2 (x/\sigma)^2]$.* Definition of the δ -function : $\int \delta(x) f(x) dx = f(0)$ for all functions $f(x)$.

$$\int \delta(x-x_0) f(x) dx = f(x_0)$$

 $\delta(\mathbf{x}) = \delta(x) \cdot \delta(y) \cdot \delta(z)$ in three dimensions.

Similarly for energy and time:

with $E = \hbar\omega$

$\delta\omega \cdot \delta t \geq \frac{1}{2}$
$\delta E \cdot \delta t \geq \frac{1}{2} \hbar$

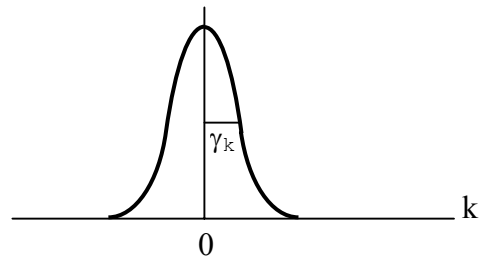
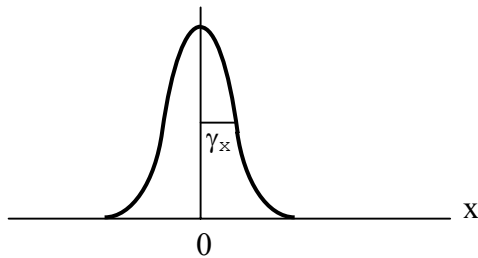
$\delta k, \delta\omega$ are the widths of the k, ω distributions that are required for a wave packet of size $\delta x, \delta t$. As $\delta x, \delta t$ become smaller, the distribution of frequencies $\delta k, \delta\omega$ in the wave packet becomes larger. This is a general **property of wave packets**, which is **quantified** by taking the **Fourier transform**.

Examples:

1. **Gaussian** (ground state of the harmonic oscillator)

$$f(x) = \exp[-\frac{1}{2}(x/\sigma_x)^2]$$

$$F(k) = \sigma_x \cdot \exp[-\frac{1}{2}(k\sigma_x)^2]$$



$p, P = f^2, F^2$ (quantum-mechanical $\delta x, \delta k$):

$$\delta x \cdot \delta k = \frac{1}{2}$$

$p, P = f, F$ (standard deviation σ_x, σ_k):

$$\sigma_x \cdot \sigma_k = 1$$

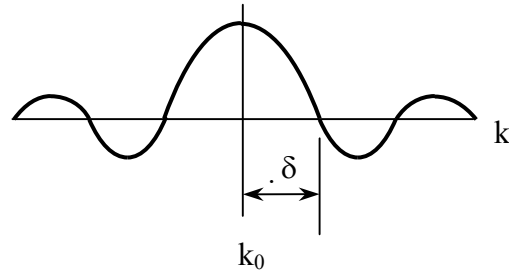
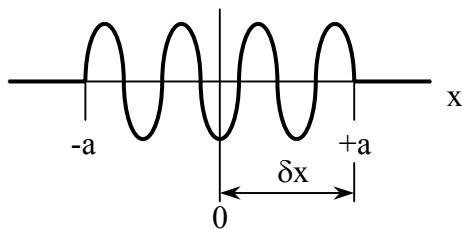
(half width half maximum γ_x, γ_k):

$$\gamma_x \cdot \gamma_k = 2 \ln 2 \approx 1.4$$

2. **Finite wave train** (λ resolution in diffraction)

$$f(x) = \exp[ik_0x] \quad -a \leq x \leq +a \quad k_0 = 2\pi/\lambda$$

$$F(k) = (2/\pi)^{1/2} \sin[(k-k_0)a] / (k-k_0)$$



With $\Delta x = a$, $\Delta k = \pi/a$:

$$\Delta x \cdot \Delta k = \pi$$

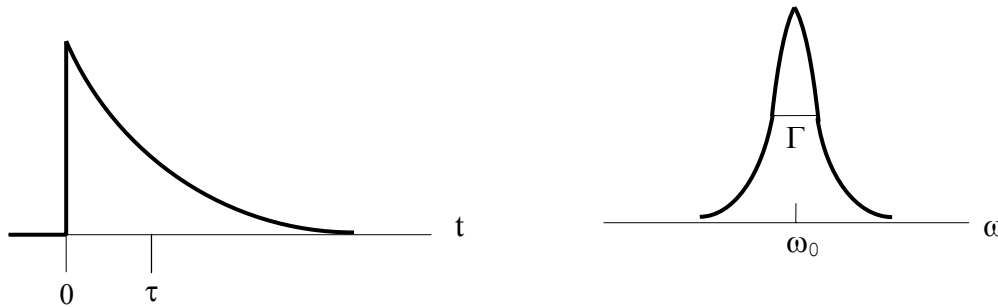
The **resolving power** of a monochromator (Bragg crystal in 3D, grating in 2D, see p. 5) is determined by the length of the wave train = N planes (grooves) $\times n \cdot \lambda$ per plane (groove):

$$\boxed{\lambda_0 / \delta\lambda = N \cdot n} \quad n = \text{diffraction order}$$

3. Lorentzian (damped oscillator, mean free path)

This describes the decay time versus the spectral linewidth. The spatial analog is the mean free path versus the momentum broadening. For quantum mechanical uncertainty one has to take the square of $\psi \sim f$ and of its Fourier transform $\Psi \sim F$. This gives a Lorentzian for $|F|^2$:

$$|f(t)|^2 = \exp[-t/\tau] \quad \tau = 1/2\tau' \quad |F(\omega)|^2 = \frac{1}{2\pi} \cdot \frac{1}{(\omega-\omega_0)^2 + (\Gamma/2)^2} \quad \Gamma = 1/\tau$$



$$f(t) = \exp[-i\omega_0 t - t/\tau'] \quad \text{for } t \geq 0$$

$$F(\omega) = i (2\pi)^{-1/2} \cdot [\omega - \omega_0 + i/\tau']^{-1}$$

With $\Delta t = \tau$, $\Delta\omega = \Gamma = 1/\tau$ (full width half maximum): $\Delta t \cdot \Delta\omega = 1$

Lifetime τ versus Linewidth:

with $E = \hbar\omega$

$$\boxed{\Delta\omega = 1 / \tau}$$

$$\boxed{\Delta E = \hbar / \tau}$$

Mean free path λ versus k-Broadening:

with $p = \hbar k$

$$\boxed{\Delta k = 1 / \lambda}$$

$$\boxed{\Delta p = \hbar / \lambda}$$

For the examples 2 and 3 the quantum-mechanical definition of δk and $\delta\omega$ does not exist because $\langle k^2 \rangle = \int k^2 |F(k)|^2 dk$ diverges. The abrupt step in f causes too many Fourier components at high k .

Course of Action in Quantum Mechanics

Energy $E(\mathbf{p})$	$E = -\mathbf{p}^2/2m + V$	
↓		
Substitution	$E = i\hbar \partial/\partial t, \mathbf{p} = -i\hbar \partial/\partial \mathbf{x}$	Relativity Notes, p. 11
↓		
Schrödinger Equation	$i\hbar \partial\psi/\partial t = [-\hbar^2\nabla^2/2m + V] \psi$	[...] = H = Hamiltonian
↓		
Wave Function	ψ	
↓		
Normalization	$\int \psi^* \psi dx = 1$	Divide ψ by $[\int \psi^* \psi dx]^{1/2}$
↓		
Probability Density	$\psi^* \psi$	Probability of finding a particle
↓		
Observable	$\langle A \rangle = \int \psi^* A \psi dx$	Expectation value of an operator A
↓		
Uncertainty	$\delta A = \frac{\sqrt{\langle (A - \langle A \rangle)^2 \rangle}}{\text{root mean square (rms)}}$	$\delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$
↓		
Uncertainty Relation:	$\delta A \cdot \delta B \geq \left \frac{\langle [A,B] \rangle}{2i} \right $	$[A,B] = A \cdot B - B \cdot A$

Exact Observables \Rightarrow **Eigenvalues** \Rightarrow **Quantum Numbers:**

$A \psi_n = a_n \cdot \psi_n$	A = Operator, a_n = Eigenvalues, ψ_n = Eigenfunctions, $\delta A = 0$
$H \psi_n = E_n \cdot \psi_n$	H = Hamiltonian, $\psi(\mathbf{r},t) = \psi_n(\mathbf{r}) \cdot \exp[-i(E_n/\hbar) \cdot t]$

Complete Set of Quantum Numbers and Basis Functions:

To fully characterize a state one has to find the largest set of operators A,B,... that have common eigenfunctions (for example E, L^2 , L_z). The eigenvalues a_n contain the maximum amount of information that can be measured. The operators A,B,... commute pairwise: $[A,B] = 0$.

Orthonormality:	$\int \psi_n^*(x) \cdot \psi_m(x) dx = \delta_{nm}$	
Completeness:	$\sum_n \psi_n(x) \cdot \psi_n^*(x') = \delta(x-x')$	See p. 7 for the definition of the δ -function.
Expansion of ψ :	$\psi(x) = \int \delta(x-x') \psi(x') dx' = \sum_n \psi_n(x) \cdot \underbrace{\int \psi_n^*(x') \cdot \psi(x') dx'}_{a_n} = \sum_n a_n \psi_n(x)$	

Dirac Brackets:

Definitions: $|n\rangle = \psi_n(x)$ $\langle n|m\rangle = \int \psi_n^*(x) \cdot \psi_m(x) dx$ (scalar)
 $\langle n| = \psi_n^*(x)$ $|m\rangle\langle n| = \psi_m(x) \cdot \psi_n^*(x')$ (operator)
 $\langle n|A|m\rangle = \int \psi_n^*(x) \cdot A \psi_m(x) dx$ (scalar)

Orthogonality: $\langle n|m\rangle = \delta_{nm}$

Completeness: $\sum_n |n\rangle\langle n| = \mathbf{1}$ = unit operator

Expansion of a wave function ψ : $|\psi\rangle = \mathbf{1} \cdot |\psi\rangle = \sum_n |n\rangle \underbrace{\langle n|\psi\rangle}_{a_n} = \sum_n a_n |n\rangle$

Expansion into Plane Waves $|k\rangle$: $|k\rangle = (2\pi)^{-1/2} \exp[ikx]$ (k continuous $\sum_n \Rightarrow \int dk$)

Arbitrary function $f(x) = |f\rangle$: $|f\rangle = \int dk |k\rangle \langle k|f\rangle$

$$f(x) = \int (2\pi)^{-1/2} \exp[ikx] \cdot \underbrace{\int (2\pi)^{-1/2} \exp[-ikx] \cdot f(x) dx}_{F(k)} dk$$

= Fourier inversion theorem (p. 7)

Schrödinger versus Heisenberg Representation:

Expand wave functions ψ and operators A : $A = \mathbf{1} \cdot A \cdot \mathbf{1} = \sum_{m,n} |m\rangle \langle m|A|n\rangle \langle n| = \sum_{m,n} A_{mn} |m\rangle \langle n|$
 Omit unit vectors $|m\rangle, \langle n|$.

$\psi = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix} = \text{Vector}$ $A = \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & & \\ \vdots & & \end{pmatrix} = \text{Tensor}$

Hilbert Space:

Vector space of wavefunctions $\psi_a(x), \psi_b(x'), \psi_c(x''), \dots = |a\rangle, |b\rangle, |c\rangle, \dots$

with the scalar product $\int \psi_a^*(x) \cdot \psi_b(x') dx = \langle a|b\rangle$

Heisenberg Schrödinger
 \downarrow \downarrow
 Scalar = Number = Observable

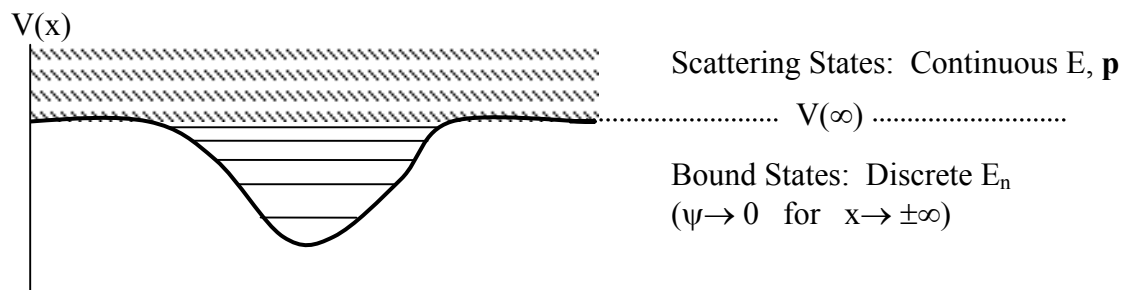
Vector = Wave Function ψ = Physical State

Tensor = Operator A = "Measurement"

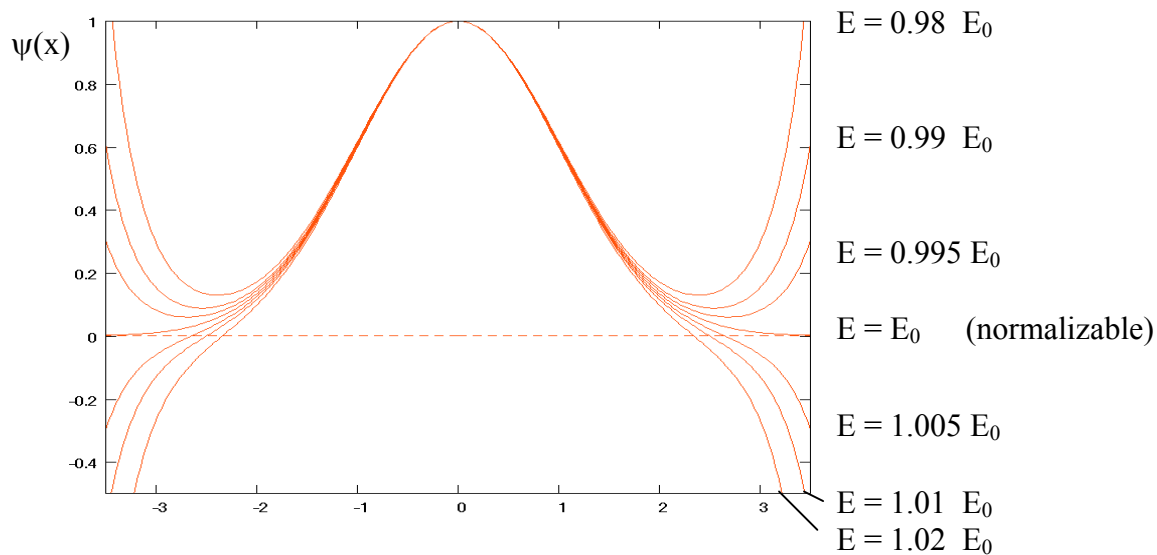
The measurement process (= applying an operator A to ψ) generally changes ψ . Subsequent measurement of B is inaccurate because ψ changed, therefore the uncertainty relation.

General Properties of the Schrödinger Equation:

Discrete versus Continuous Eigenvalues:



Finding Eigenfunctions: Harmonic Oscillator, $n=0$



Oscillatory versus Damped Solutions:

$$\boxed{-\hbar^2/2m_e \psi'' + V \psi = E \psi} \Rightarrow \psi'' \sim (V-E) \psi \Rightarrow (V-E) \text{ determines the curvature of } \psi$$

$E < V$

$$\psi'' \sim +\psi$$

Concave

$$\boxed{\psi \sim \exp(\pm kx)}$$

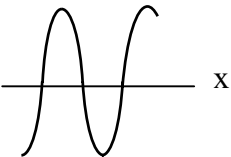


$E > V$

$$\psi'' \sim -\psi$$

Convex

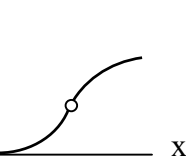
$$\boxed{\psi \sim \exp(\pm ikx)}$$



$E = V$

$$\psi'' = 0$$

Inflection Point



$$\boxed{\begin{aligned} k &= \sqrt{2m_e|V-E|} / \hbar \\ &= 5.1 \text{ nm}^{-1} \sqrt{|V-E| / \text{eV}} \end{aligned}}$$

One-Dimensional Potentials

Particle in a Box:

Counting modes in a cavity,
quantum wells in solids

$$V(x) = 0 \text{ for } 0 \leq x \leq L$$

$$\infty \text{ elsewhere}$$

$$E_n = n^2 \cdot (\pi\hbar)^2 / 2m_e L^2$$

$$\Psi_n(x) = (2/L)^{1/2} \cdot \sin[n \cdot (\pi x/L)]$$

Harmonic Oscillator:

Vibrations and oscillations,
local energy minima

$$V(x) = \frac{1}{2} \kappa \cdot x^2$$

$$E_n = (n + \frac{1}{2}) \cdot \hbar\omega$$

$$\omega = \sqrt{\kappa/m_e}$$

$$\Psi_n(x) = a \cdot \exp[-\frac{1}{2} (x/\sigma)^2] \cdot H_n[x/\sigma]$$

Coulomb Potential:

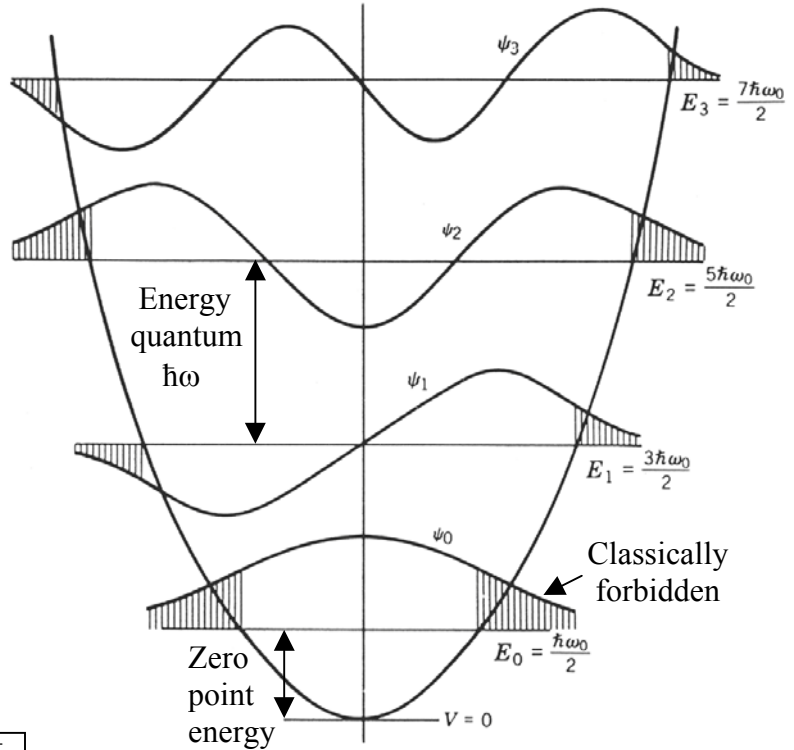
Radial equation for the H atom ($l=0$); Image potential states at a metal surface ($-\frac{1}{4} e^2/z$)

$$V(r) = -e^2/r$$

$$E_n = -R/n^2$$

$$\Psi_n(r) = a \cdot r \cdot \exp[-r/na_0] \cdot L_n[r/na_0]$$

$$\Psi_H(r) = \Psi_n(r) / r$$



$$\sigma = (\hbar/m_e\omega)^{1/2}$$

$$a = (\sigma 2^n n! \sqrt{\pi})^{-1/2}$$

$$H_n[z] = 1, 2z, 4z^2 - 2, \dots \text{ (Hermite polynomials)}$$

$$R = \text{Rydberg} = m_e e^4 / 2\hbar^2 = \frac{1}{2} \alpha^2 m_e c^2 = 13.6 \text{ eV}$$

$$a_0 = \text{Bohr radius} = \hbar^2 / m_e e^2 = \alpha^{-1} \lambda_C = 0.05 \text{ nm}$$

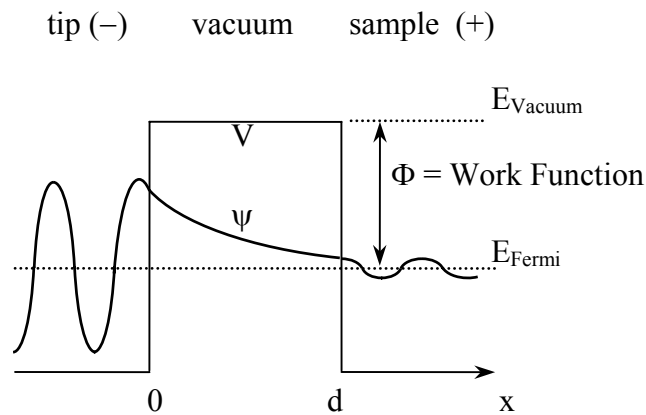
$$a = (a_0^3 n\pi)^{-1/2} \text{ for } \Psi_H \text{ in 3 dimensions}$$

$$L_n[z] = 1, (-z+1)/2, (2z^2-6z+3)/9, \dots$$

Tunneling

$E < V$: Classically-forbidden region ($E_{\text{kin}} < 0$), exponential decay in quantum mechanics.

Scanning Tunneling Microscope (STM):



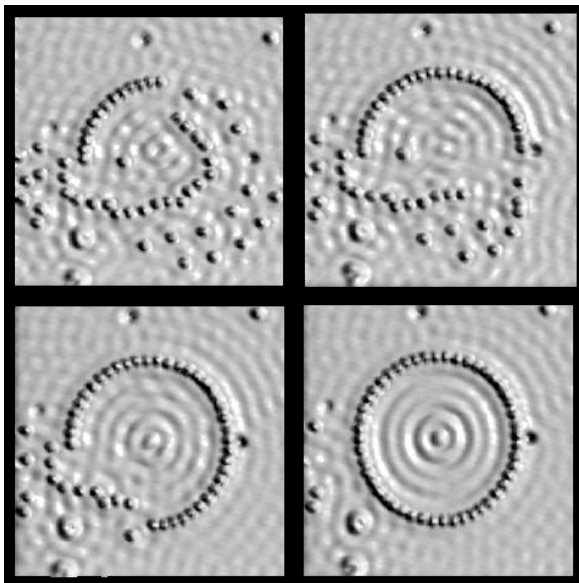
Attenuation of the charge density (\sim tunneling current):

$$|\psi(d)|^2 / |\psi(0)|^2 = \exp(-2kd)$$

$$\psi(x) \sim \exp(-kx)$$

$$k \approx 0.51 \text{ \AA}^{-1} \sqrt{\Phi/eV}$$

For a typical energy barrier $\Phi \approx 4\text{eV}$ the **attenuation** is about a factor of **100 per atom diameter**.



That makes it possible to detect height changes much smaller than an atom. The current is kept constant during a scan by adjusting the tip height d via a piezoelectric material.

The picture shows iron atoms being assembled into a ring at a copper surface. The STM was used for imaging and assembly. The ripples are electron density waves proportional to the wave function $|\psi|^2$ of surface electrons.

(From Crommie and Eigler)

Three-Dimensional Potentials

Separate the variables, i.e. find a coordinate system where the wave function is a product of one-dimensional wavefunctions: $\psi(x,y,z) = \psi_x(x) \cdot \psi_y(y) \cdot \psi_z(z)$

Instead of a partial differential equation (several variables) one solves three ordinary differential equations (one variable each), which is much easier.

Particle in a Box:

$V(x,y,z) = 0$ if $0 \leq x \leq L_x$ and $0 \leq y \leq L_y$ and $0 \leq z \leq L_z$; $V = \infty$ elsewhere.

Using a product wave function $\psi(x,y,z) = \psi_x(x) \cdot \psi_y(y) \cdot \psi_z(z)$ the Schrödinger equation separates into three one-dimensional equations with E replaced by E_x, E_y, E_z . The total energy is:

$$E = E_x + E_y + E_z = (\pi\hbar)^2/2m_e \cdot [\mathbf{n}_x^2 / L_x^2 + \mathbf{n}_y^2 / L_y^2 + \mathbf{n}_z^2 / L_z^2] \quad (\text{compare p. 13})$$

This separation method works for any potential of the form $V(x,y,z) = V_x(x) + V_y(y) + V_z(z)$.

Coulomb Potential:

$$V(x,y,z) = -e^2 / r; \quad r = \sqrt{x^2+y^2+z^2}$$

Polar coordinates r, θ, ϕ separate the variables for **any spherically-symmetric potential $V(\mathbf{r})$** and provide one-dimensional eigenvalue equations for $\psi_r, \psi_\theta, \psi_\phi$ with $\psi(r, \theta, \phi) = \psi_r(r) \cdot \psi_\theta(\theta) \cdot \psi_\phi(\phi)$.

Separate the kinetic energy into radial and angular parts using the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$:

$$\mathbf{L}^2 = (\mathbf{r} \times \mathbf{p})^2 = \mathbf{r}^2 \mathbf{p}^2 - (\mathbf{r} \cdot \mathbf{p})^2 \quad \Rightarrow \quad E_{\text{kin}} = \mathbf{p}^2 / 2m_e = [\underbrace{(\mathbf{r} \cdot \mathbf{p})^2}_{\text{radial}} + \underbrace{\mathbf{L}^2}_{\text{angular}}] / 2m_e r^2$$

In quantum mechanics: $\mathbf{p} = -i\hbar \mathbf{r} \times \nabla$

(The ordering of \mathbf{r}, ∇ becomes tricky, but the separation into radial and angular terms remains.)

$$r: \quad E_{n,l} \cdot \psi_r = H \psi_r \quad (H = \text{Hamiltonian} = \text{Energy Operator})$$

$$\theta: \quad \hbar^2 \cdot l(l+1) \cdot \psi_\theta = \mathbf{L}^2 \psi_\theta \quad (\mathbf{L} = -i\hbar \mathbf{r} \times \nabla = \text{Angular Momentum Operator})$$

$$\phi: \quad \hbar^2 \cdot m_l^2 \cdot \psi_\phi = L_z^2 \psi_\phi \quad (L_z = z\text{-Component of } \mathbf{L})$$

$$r: \quad E_{n,l} \cdot \psi_r = -(\hbar^2/2m_e) \cdot \left\{ \overbrace{(r \psi_r)'' / r}^{\text{radial}} - \overbrace{[l(l+1) / r^2]}^{\text{angular}} \cdot \psi_r \right\} - e^2/r \cdot \psi_r$$

$$\theta: \quad l(l+1) \cdot \psi_\theta = - [(\sin\theta \cdot \psi_\theta)' / \sin\theta - (m_l^2 / \sin^2\theta) \cdot \psi_\theta]$$

$$\phi: \quad m_l^2 \cdot \psi_\phi = -\psi_\phi''$$

Solutions:

r: $\psi_r \sim \exp(-r/na_0) \cdot L_n [2r/na_0]$

$L_n =$ Laguerre Polynomials (p. 13)

θ : $\psi_\theta \sim P_l^m [\cos\theta, \sin\theta]$

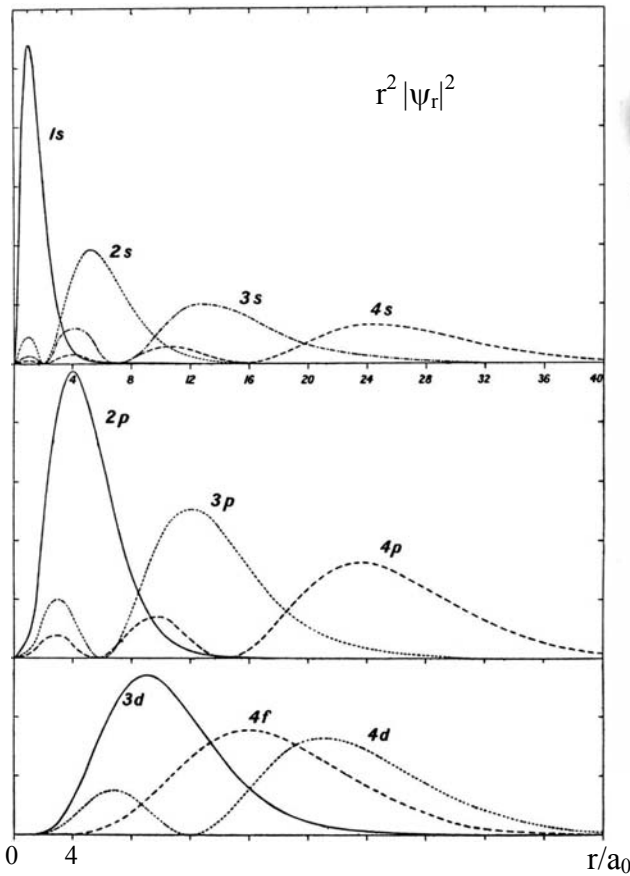
$P_l^m =$ Legendre Polynomials

ϕ : $\psi_\phi \sim \exp[im_l \phi]$

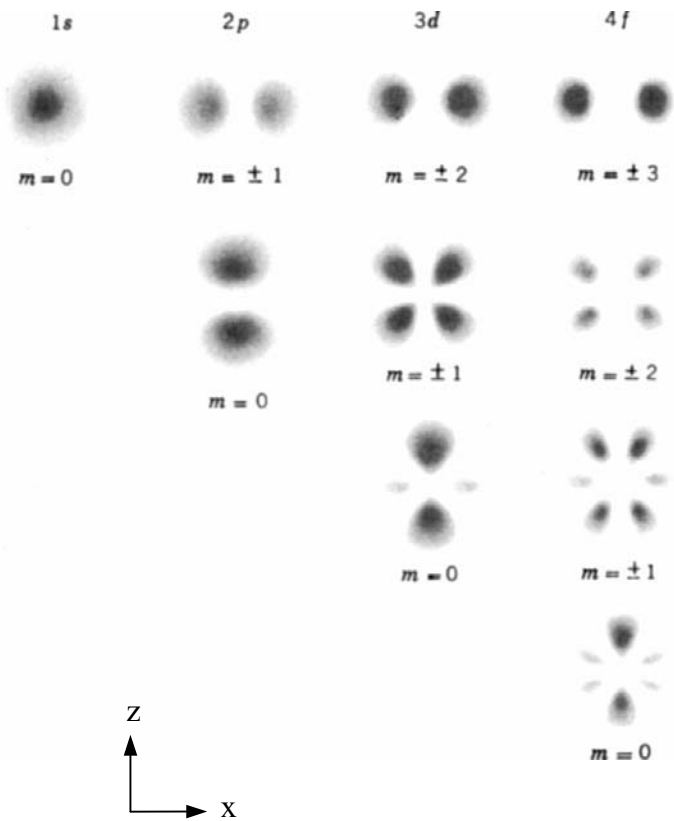
Eigenvalues:

r:	$E_{n,l} = -R / n^2$	$n = 1, 2, \dots$	(R, a_0 : p. 13)
θ :	$L^2 = \hbar^2 \cdot l(l+1)$	$l = 0, 1, \dots, (n-1) = s, p, d, f, \dots$	
ϕ :	$L_z = \hbar \cdot m_l$	$m_l = -l, \dots, +l$	

A complete set of eigenvalues for the H atom includes additional quantum numbers for electron spin, total angular momentum, and nuclear spin (see p. 18-20).



Radial probability distributions: $r^2 |\psi_r|^2$



Angular wave functions: $\text{Re} [\psi_\theta \cdot \psi_\phi]$

Spin

Spin is the **intrinsic angular momentum** of the electron. Like **L**, it has two quantum numbers:

$\mathbf{S}^2 = \hbar^2 \cdot s(s+1)$	$s = 1/2$	(spin up or down)
$S_z = \hbar \cdot m_s$	$m_s = \pm 1/2$	

Spin is a **relativistic** effect that comes out naturally in the **Dirac equation**, the relativistic generalization of the Schrödinger equation (see relativity notes p. 11 and below). Spin can be added to the non-relativistic Schrödinger equation by multiplying the spatial wave function with a two-component **spin wave function** χ :

$$\Psi_{\text{total}} = \Psi(\mathbf{r},t) \cdot \chi \quad \chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ for } m_s = +1/2 \text{ (spin up)} \quad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \text{ for } m_s = -1/2 \text{ (spin down)}$$

The spin operator **S** is different from the orbital angular momentum operator **L**. It consists of three 2x2 matrices, the **Pauli matrices** $\sigma_{x,y,z}$ which act on the spin wave function χ :

$\mathbf{S} = 1/2 \hbar \cdot (\sigma_x, \sigma_y, \sigma_z)$	$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$	$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
---	---	--	--

$$[\sigma_x, \sigma_y] = \sigma_x \sigma_y - \sigma_y \sigma_x = 2i \sigma_z \text{ etc.}$$

$$\{\sigma_i, \sigma_k\} = \sigma_i \sigma_k + \sigma_k \sigma_i = 2 \delta_{ik}$$

Dirac equation:

This is the relativistic wave equation for spin 1/2 particles. The wave function $\psi = (\psi_1, \psi_2, \psi_3, \psi_4)$ has 4 components (two for spin up/down and two for particle/antiparticle). The 4x4 matrices **Dirac matrices** γ^μ act on ψ . They consist of 2x2 blocks containing $\sigma_{x,y,z}$ and the 2x2 unit matrix **1**:

$$\gamma^\mu = (\gamma^0, \gamma^1, \gamma^2, \gamma^3) \quad \gamma^{1,2,3} = \begin{bmatrix} 0 & \sigma_{x,y,z} \\ -\sigma_{x,y,z} & 0 \end{bmatrix} \quad \gamma^0 = \begin{bmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{bmatrix}$$

$$\{\gamma^\mu, \gamma^\nu\} = 2 g^{\mu\nu} \quad (g^{\mu\nu} = \text{metric})$$

$\gamma^\mu p_\mu \psi = m_e c \cdot \psi$
--

$p_\mu = i\hbar \partial_\mu - q/c A_\mu$

A_μ = electromagnetic four-potential, $q = -e$ for e^-
(Relativity notes p. 10,11)

Total Angular Momentum

General Properties of Angular Momentum Operators \mathbf{J} , \mathbf{L} , \mathbf{S} :

$$\mathbf{J} = (J_x, J_y, J_z) \quad [J_x, J_y] = i\hbar \cdot J_z \quad (\text{cyclical})$$

$$[J_y, J_z] = i\hbar \cdot J_x$$

$$[J_z, J_x] = i\hbar \cdot J_y$$

From these properties one can derive:

$\mathbf{J}^2 = \hbar^2 \cdot j(j+1)$	j integer or half-integer
$J_z = \hbar \cdot m_j$	$m_j = -j, \dots, +j$ in integer increments, $(2j+1)$ states

$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2 \quad \Rightarrow \quad j = j_1 - j_2 , \dots, j_1 + j_2$
--

The sum of two angular momenta is again an angular momentum vector, e.g., for an electron the sum of orbital angular momentum \mathbf{L} and spin \mathbf{S} :

$\mathbf{J} = \mathbf{L} + \mathbf{S}$	$s = 1/2$
$\mathbf{J}^2 = \hbar^2 \cdot j(j+1)$	$j = l - 1/2 , l + 1/2$
$J_z = \hbar \cdot m_j$	$m_j = -j, \dots, +j$

Spin-Orbit Interaction:

This is an extra term $\sim \mathbf{L} \cdot \mathbf{S}$ in the Hamiltonian, again a relativistic effect originating from the Dirac equation. It doubles all levels with $l > 0$ into two states with $j = l - 1/2, l + 1/2$. The level with **smaller j** lies **lower**. Since L_z and S_z do not commute with $\mathbf{L} \cdot \mathbf{S}$, m_l and m_s cease to be good quantum numbers. They are replaced by m_j . Spin-orbit interaction is strong for a large Coulomb potential (heavy elements, deep levels).

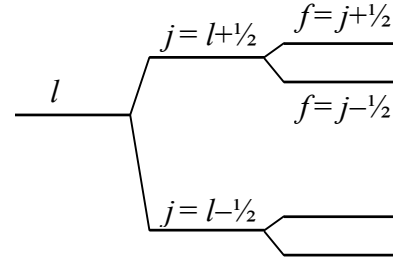
Quantum Numbers of the H Atom:

n, l, s, j, m_j	Terminology:	$2p_{3/2}$ stands for $n=2, l=1, j=3/2$ s, p, d, f, g, \dots stands for $l = 0, 1, 2, 3, 4, \dots$
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They form a complete set for a **single** electron in a spherically-symmetric potential. This single electron label remains useful in many-electron systems (atoms, molecules, solids). Including the proton requires additional quantum numbers for the nuclear spin (see next).

Nuclear Spin, Hyperfine Structure:

Like L and S combining into $\mathbf{J}=\mathbf{L}+\mathbf{S}$ for the electron, \mathbf{J} and \mathbf{I} , the proton spin, combine to a total angular momentum $\mathbf{F}=\mathbf{J}+\mathbf{I}$. Analogous to the spin-orbit interaction $\sim \mathbf{L} \cdot \mathbf{S}$ of the electron there is the hyperfine interaction $\sim \mathbf{J} \cdot \mathbf{I}$ which may be viewed as the energy of the electron in the magnetic field created by the proton spin (see below). The effect is reduced by the mass ratio $m_p/m_e \approx 2000$. The proton spin $i=1/2$ doubles all levels once more into two states with $f=j-1/2, j+1/2$. The $1s_{1/2}$ level in H splits into a singlet ($f=0$) and a triplet ($f=1$) with a transition at the wavelength of **21 cm** (used in radio astronomy).



Electrons in a Magnetic Field (Zeeman Effect):

Energy of a magnetic dipole μ in a magnetic field \mathbf{B} (defines z):

$$E = -\mu \cdot \mathbf{B} = +m_j \cdot g \cdot \mu_B \cdot B$$

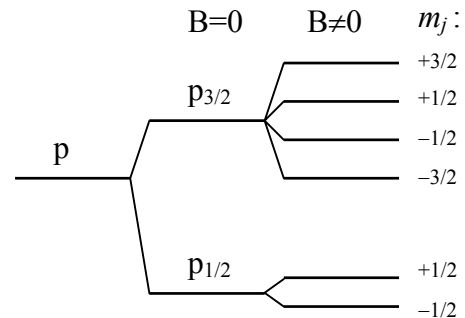
$$\mu_B = e\hbar/2m_e = 5.6 \cdot 10^{-5} \text{ eV/T (Bohr Magnetron)}$$

The sign reversal comes from the negative charge of the electron.

$$g = \frac{\text{magnetic moment in } \mu_B}{\text{angular momentum in } \hbar} = \text{gyromagnetic ratio}$$

$$\left. \begin{array}{l} g = 1 \text{ for pure } \mathbf{L} \\ g = 2 \text{ for pure } \mathbf{S} \end{array} \right\} g(j,l,s) \text{ between 1 and 2}$$

Determine j, m_j from the splitting in a magnetic field: $(2j+1)$ levels.



Perturbation Theory:

Calculate small energy shifts due to an interaction Hamiltonian H_{int} , such as the spin-orbit, hyperfine, and magnetic splittings. Take as unperturbed Hamiltonian $H_0 = -\hbar^2 \nabla^2 / 2m - e^2/r$.

$$H = H_0 + H_{\text{int}}$$

$$H_0 \psi_n^0 = E_n \cdot \psi_n^0$$

$$H \psi_n = (E_n + \Delta E) \cdot \psi_n$$

$$\Delta E \approx \langle \psi_n^0 | H_{\text{int}} | \psi_n^0 \rangle$$

Many-Electron Atoms

Adding angular momenta L_i, S_i, J_i of several electrons: Many-electron levels can be sorted by their angular momenta. First, the largest interactions (splittings) are considered, then the smaller ones as perturbations. The most common sequence is (for low Z):

- 1) **Large ΔE** for different $S = \Sigma S_i \rightarrow S$ ($e^- - e^-$ Coulomb Repulsion)
- 2) **Intermediate ΔE** for different $L = \Sigma L_i \rightarrow L$ ($e^- - e^-$ Coulomb Repulsion)
- 3) **Small ΔE** for different $J = L + S \rightarrow J$ (Spin-Orbit Interaction)

Hund's three rules determine the **signs** of the splittings in the **ground state** (lowest energy):

- 1) **Maximize S** $S_{\max} = |\Sigma m_s|$ + Pauli principle
- 2) **Maximize L** $L_{\max} = |\Sigma m_l|$ + Pauli principle
- 3) **Minimize J** for < half-filled shell $J_{\min} = |L_{\max} - S_{\max}|$
Maximize J for > half-filled shell $J_{\max} = L_{\max} + S_{\max}$

Hund's first rule is due to the fact that electrons with parallel spin are farther apart to satisfy the Pauli principle, which reduces their mutual Coulomb repulsion. This rule is responsible for magnetism. Typical multiplet splittings are about 2eV and produce colors in gems and laser media: Ruby = Cr in sapphire (Al_2O_3), titanium in sapphire (fastest lasers), erbium in SiO_2 (amplifier for optical fibers).

Filled shell: All the $(2l_i + 1) \cdot 2 = 2, 6, 10, 14 \dots$ states with different m_l and m_s are occupied. The total angular momenta L, S, J are zero. A filled shell is particularly stable since an extra electron has to move up into a higher-energy shell with different n_i, l_i due to Pauli's exclusion principle.

Hole: Taking an electron from a filled shell is equivalent to adding a positive charge (= hole). The remaining having $(n-1)$ electrons can be substituted by the single hole. Analogs exist in solid state physics (filled shell \Rightarrow valence band of a semiconductor) and in particle physics (filled shell \Rightarrow sea of electrons in negative energy states of the Dirac equation; hole \Rightarrow positron).

Notation for Many-Electron States: $1s^2 2s^2 2p^5, ^2P_{1/2}$

$1s^2$	stands for $n_i=1, l_i=0, \text{ occupancy } 2$	for individual shells i
$^2P_{1/2}$	stands for $(2S+1)=2$ (doublet), $L=1, J=1/2$	for the combined L, S, J

Dipole Selection Rules:

These rules govern transitions between two levels m, n involving an emitted or absorbed photon, e.g. in optical absorption and emission, photoemission and inverse photoemission, but not in Auger electron emission (see p. 22). The probability of a transition $m \rightarrow n$ can be obtained via the classical electromagnetic radiation of an **oscillating dipole moment**, which is determined quantum-mechanically. An energy eigenfunction $\psi_n(\mathbf{x}, t) = \psi_n(\mathbf{x}) \cdot \exp(-i \frac{E_n}{\hbar} t)$ does not produce an oscillating dipole moment since the time-dependence of ψ_n^* and ψ_n cancels out in the probability density (thereby solving the stability problem of Bohr's model):

$$\psi_n^* \psi_n \sim \psi_n^*(\mathbf{x}) \psi_n(\mathbf{x}) \cdot \exp(+i \frac{E_n}{\hbar} t) \cdot \exp(-i \frac{E_n}{\hbar} t) = \psi_n^*(\mathbf{x}) \psi_n(\mathbf{x})$$

However, the **superposition wave function** $\psi = \psi_m + \psi_n$ creates an oscillating term:

$$\psi_m^* \psi_n \sim \psi_m^*(\mathbf{x}) \psi_n(\mathbf{x}) \cdot \exp[i \frac{(E_m - E_n)}{\hbar} t]$$

Dipole moment: $\mathbf{x}_{mn} = e \cdot \langle m | \mathbf{x} | n \rangle = e \cdot \int \psi_m^*(\mathbf{x}) \cdot \mathbf{x} \cdot \psi_n(\mathbf{x}) dx$

Transition probability: $\sim |\mathbf{x}_{mn}|^2$

Allowed transitions: $\mathbf{x}_{mn} \neq 0$

Allowed Transitions: Symmetries generate conservation laws and allowed transitions. For example, spherical symmetry leads to angular momentum conservation and inversion symmetry to parity conservation. The photon has angular momentum $s_{\text{photon}} = 1$ and parity -1 (vector potential $\mathbf{A} \rightarrow -\mathbf{A}$, dipole $e \cdot \mathbf{x} \rightarrow -e \cdot \mathbf{x}$).

Single Electron Quantum Numbers:

$$e^-_m \leftrightarrow e^-_n + \text{photon}$$

$\Delta l = \pm 1$
$\Delta j = \pm 1, 0$
$\Delta m_j = \pm 1, 0$

Parity $(-1)^l$: $(-1)^{\pm 1} = (-1)^l \cdot (-1)$

Angular momentum: $j_m = |j_n - 1|, j_n, j_n + 1$

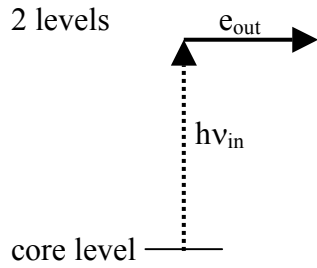
$\mathbf{J}_m = \mathbf{J}_n + \mathbf{S}_{\text{photon}}$

Combined Angular Momenta in Multi-Electron Atoms:

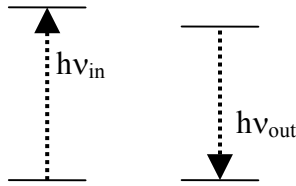
(For LS coupling, where the $e^- - e^-$ repulsion is larger than the spin-orbit interaction; low Z)

$\Delta S = 0$	Total spin ($-e \cdot \mathbf{x}$ does not affect spin wavefunctions)
$\Delta L = \pm 1$	Total orbital angular momentum
$\Delta J = \pm 1, 0$ (not $0 \rightarrow 0$)	Total overall angular momentum

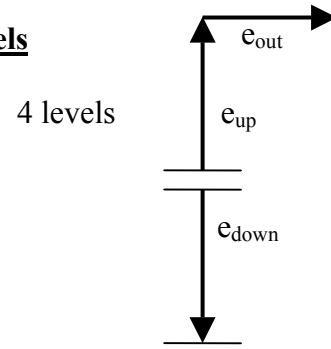
Spectroscopies of Atomic Levels



Photoemission
(UPS, XPS, ESCA)

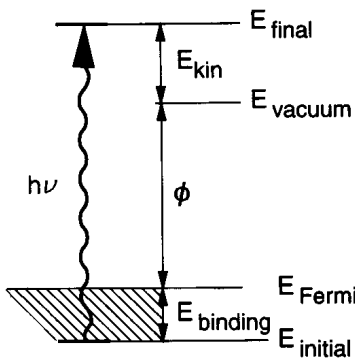


Absorption Emission
(XAS, NEXAFS)

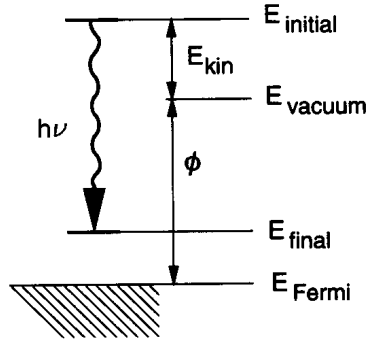


Auger Decay

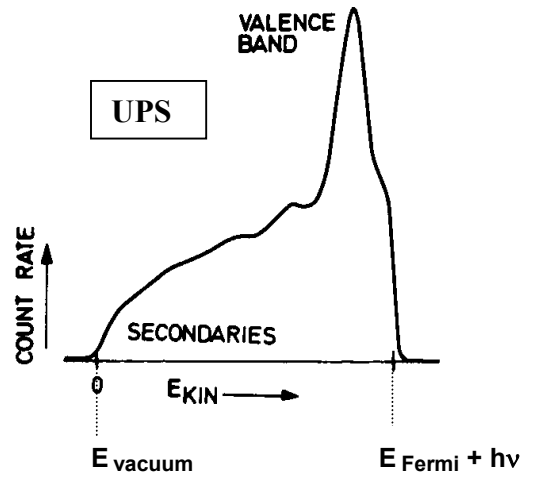
Used for the identification of elements by the core levels (bottom level), for example in astrophysics and materials science.



Photoemission
(UPS)



Inverse Photoemission



XPS

