1. Overview of Quantum Mechanics

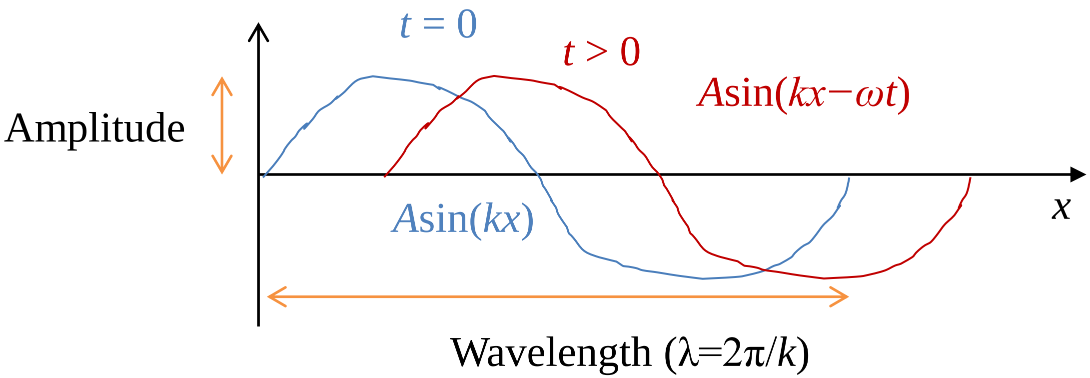
(Bube Chap. 5)

A. Schrödinger Equation
B. Example: Free Particle (1D)
C. Example: Infinite Potential Well (1D)
D. Example: Harmonic Oscillator (1D)
E. Example: Hydrogen Atom (3D)
F. Multielectron Atoms and Periodic Table
G. Example: Tunneling (1D)
H. Mathematical Foundation of Quantum Mechanics

A. Schrödinger Equation

Wave-Particle Duality

In classical physics, particles and waves are distinct identities. Particles are characterized by the position and momentum (velocity) and develop trajectories in the spacetime. On the other hand, the waves are described by phase and amplitude, and display unique phenomena such as interference, diffraction, and superposition. Let's first review the basic quantities that define a wave. We take the example of sinusoidal waves such as sin($kx-\omega t$) or $e^{i(kx-\omega t)}$.



Phase $\phi = kx-\omega t$

Wavenumber $k = 2\pi/\lambda$ (or $1/\lambda$)

The phase at certain x varies in time as sin(ωt). The period T in time is $2\pi/\omega$. The frequency f is $\omega/2\pi$ (in Hz) and ω is the angular frequency.

The speed at which the position with a certain phase moves is called the phase velocity (v_p). It is given as follows:

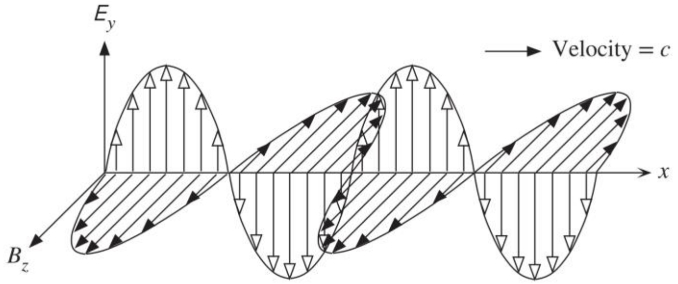
$$kx-\omega t=\phi_0 \rightarrow kdx-\omega dt=0$$

$$\frac{dx}{dt}=\frac{\omega}{k}=v_p$$

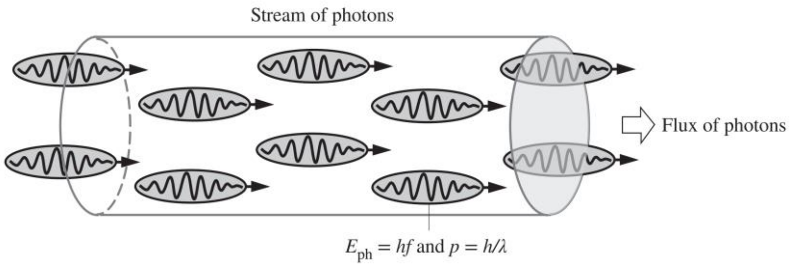
One of the greatest finding in modern physics is the wave-particle duality: particles show wave properties such as interference while the classical waves sometimes have granularity (discreteness) of particles with certain momentum.

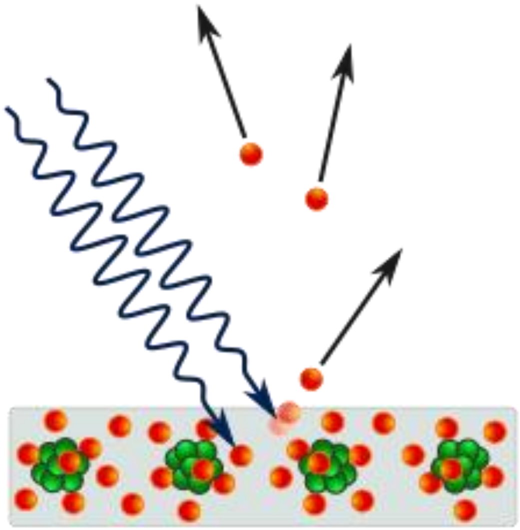
It was Planck (1900) who first noticed the wave-particle duality. He discovered from the research on blackbody radiation that the energy of light waves with angular frequency ω (=$2\pi f$) is quantized by $\hbar\omega$ (= hf or $h\nu$), where $\hbar$ is the Planck constant (**$h = 4.1357\times10^{-15}$ eV·s**) divided by 2π. Each quantized light is called the photon. Therefore, light is a stream of photons. In fact, any waves oscillating with ω have discrete energy levels separated by $\hbar\omega$. Einstein used the Planck's postulate to explain the photoelectric effect, for which he received the Nobel prize.

Light as electromagnetic waves



Light as a stream of photons



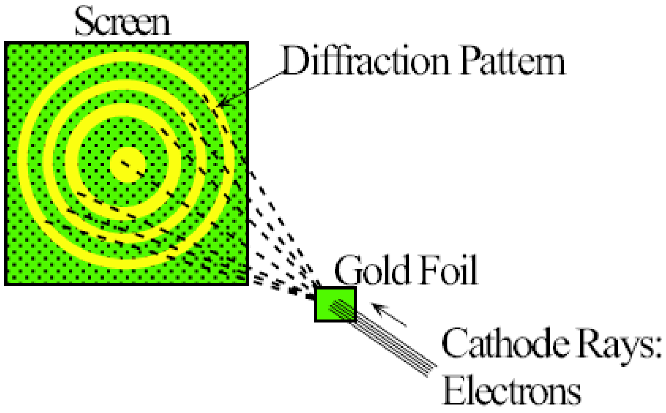


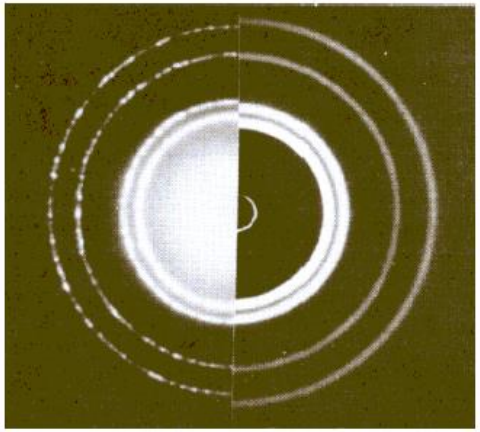
The emission of electrons from a metal plate caused by light quanta – photons.

The wave nature of particles were first hypothesized by de Broglie (1924) who claimed that every matter has a **wave-like nature** with the wavelength is given by the de Broglie relation.

$$\lambda = \frac{h}{p} = \frac{h}{m\upsilon}$$

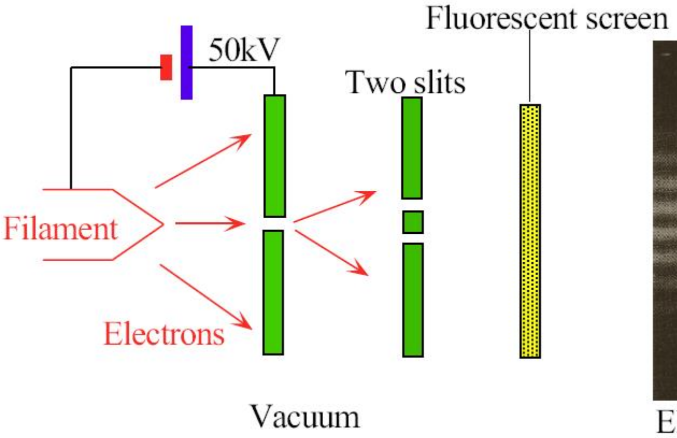
This means that electrons can exhibit diffraction or interference phenomena like waves. It was proved experimentally a few years later independently by Thomson and Davisson-Germer. They observed the predicted interference patterns by passing electrons through crystalline materials.

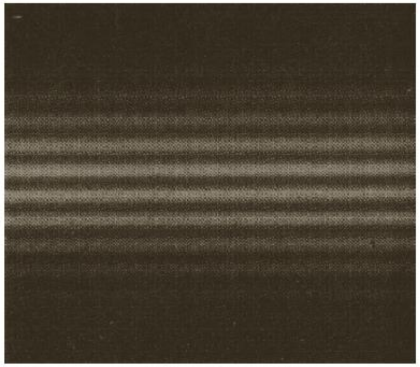




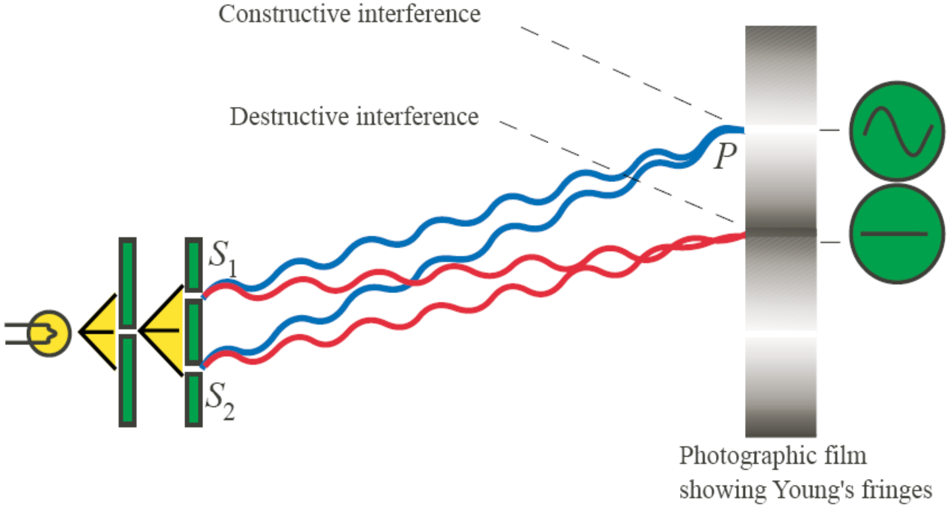
(d) Composite photograph showing diffraction patterns produced with an aluminum foil by X-rays and electrons of similar wavelength. Left: X-rays of $\lambda = 0.071$ nm. Right: Electrons of energy 600 eV.

In a simplified version, electrons also show interreference pattern in double-slit experiment.





Electron diffraction fringes on the screen



$4I_0$ $\quad \overline{S_1P} - \overline{S_2P} = n\lambda$

$0I_0$ $\quad \overline{S_1P} - \overline{S_2P} = (n + \frac{1}{2})\lambda$

The wave-particle duality for particle leads to the probabilistic nature of particles.

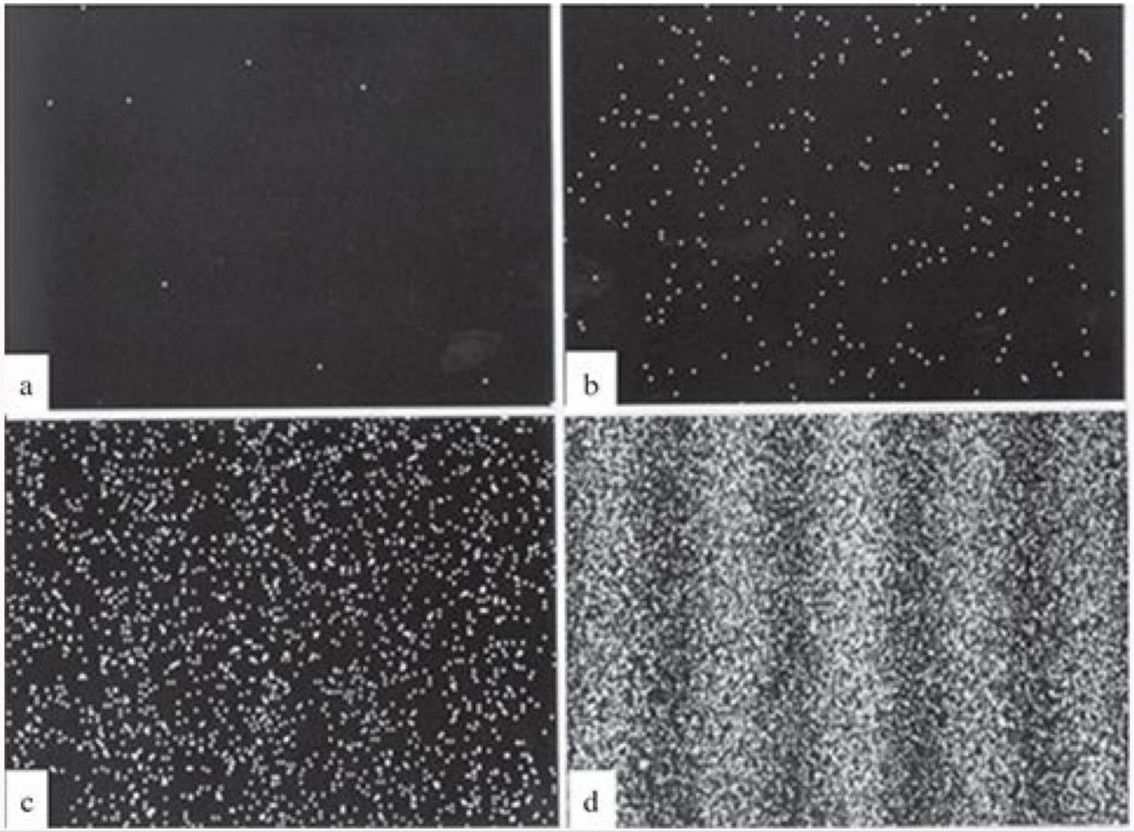


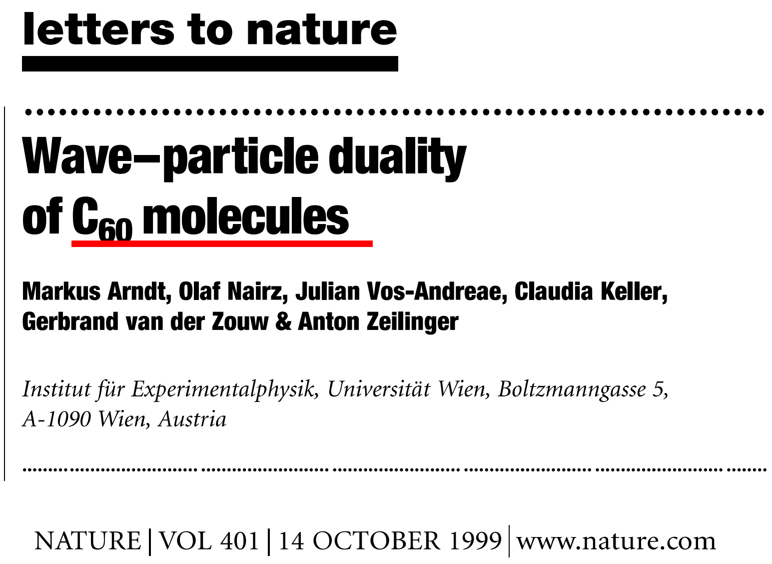
Figure 1.4: Build-up of the electron interference pattern. (a) Eight electrons, (b) 270 electrons, (c) 2000 electrons, (d) 160,000 electrons. Reprinted courtesy of the Central Research Laboratory, Hitachi, Ltd., Japan.

Transmission Electron Microscopy (TEM)

de Broglie wavelength in various situations:

- 50 g golf ball at the speed of 20 ms^{-1}: $\lambda = 6.63\times10^{-34}$ m. This is too short to produce any meaningful observation.
- Proton at 2200 ms^{-1}: $\lambda = 0.18$ nm. This may produce diffraction from crystal but too small penetration depth. Neutron can produce diffraction patterns as it interacts with nucleus rather than electron clouds.
- Electrons at 100 eV: $\lambda = 0.123$ nm

Therefore, the wave nature of matter is observable only when the matter is very light like electron or proton (hydrogen atom).



letters to nature

Wave–particle duality of C_{60} molecules

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NATURE | VOL 401 | 14 OCTOBER 1999 | www.nature.com

Schrödinger Equation

If particles behave like waves, what kind of equation they satisfy? - the Schrödinger equation. The matter can be any known objects such as proton, neutron, electron or molecules, or even human. According to Schrödinger (1926), the particle is described by the (matter) wave function that is a complex function of space and time $\psi(x,y,z,t)$. The first meaning of the wave function is that $|\psi(x,y,z,t)|^2$ is the probability density of finding the particle at (x,y,z) and at time t. This means that the following normalization condition should be satisfied at any time.

$$\rightarrow \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z,t)|^2\, dxdydz = 1$$

Normalization condition

$\psi(x,y,z,t)$ always satisfy the following time-dependent Schrödinger equation which is a kind of differential equation.

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + V(x,y,z)\psi$$

Kinetic energy

Potential energy at (x,y,z)

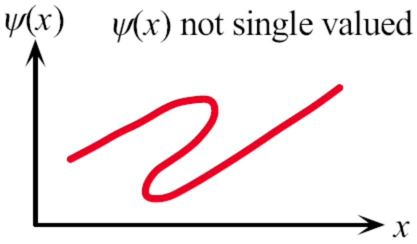
This is similar to the diffusion equation except that time is imagninary.

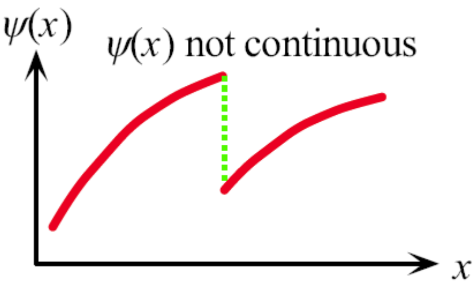
where m is the mass of the particle.

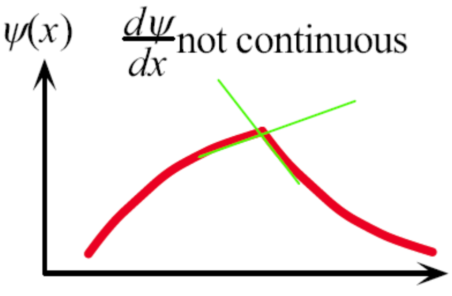
For 1D,

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

There are mathematical conditions that should be satisfied by the wave functions: single-valued, function and first derivatives are continuous







Not in nature

No kinks in nature

(At the point where V diverges, the first derivative can be discontinuous.)

Superposition principle: Since the Schrodinger equation is linear, if ψ_1 and ψ_2 are solutions to the Schrodinger equation, $\psi_1 + \psi_2$ is also a valid solution.

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

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = H\psi$$

A special solution is the steady state or constant-energy state for which

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

$\boxed{E\text{: total energy} = \hbar\omega}$

(similar to photon)

In this special case, the **time-dependent Schrödinger equation** becomes time-independent as follows:

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

This is called time-independent Schrödinger equation or simply Schrödinger equation. Note that this is mathematically an eigenvalue problem. With proper boundary conditions, the solution to this equation produces a set of energy eigenvalues and corresponding energy eigenstates.

For 1D, $$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}y(x)+Vy(x)=Ey(x)$$

B. Example: Free Particle (1D)

When there is no potential over the entire space ($V = 0$), the particle can move freely. Classically, the particle will move with a constant velocity. What is the matter wave corresponding to this state? The Schrodinger equation becomes:

$$\frac{d^2}{dx^2}y(x) + \frac{2m}{\hbar^2}Ey(x) = 0 \rightarrow \frac{d^2}{dx^2}y(x) + k^2y(x) = 0 \quad (E = \frac{\hbar^2k^2}{2m})$$

$$E = p^2 / 2m$$

The solution of this equation is $\underline{\psi(x) = Ae^{ikx}}$ where k is the wave number and can be any real number. sin(kx) or cos(kx) are also valid solutions. However, we will see later that e^{ikx} corresponds to a state with a definite left or right motion while sin(kx) or cos(kx) are the combination of the two. Therefore, we prefer e^{ikx} in the free space. Note that there is no boundary condition for the free particle.

The probability of finding this free particle at x is $|\psi(x)|^2 = |A|^2$, i.e., constant. Therefore, normalization condition will require that $A = 0$! This because the particle moves all over the space and finding the particle inside a specific region is simply zero. Rather, the correct interpretation with finite (nonzero) A is that the wave function here represents a stream of particles moving with the same velocity. (For example, electrons in the double-slit experiment may correspond to this.)

The full wave function $\psi(x,t)$ is given by

$$\psi(x,t) = \psi(x) e^{-i\frac{E}{\hbar}t} = \underline{Ae^{i(kx-\omega t)}}$$

Free Particle (1D)

Wavelength $\lambda = 2\pi/k$. According to the de Broglie relation, $\lambda = h/p$. Therefore, $p = \hbar k$. This is consistent with

$$E = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

In addition, $\underline{E = \frac{\hbar^2 k^2}{2m}} = \hbar\omega \rightarrow \omega = \frac{\hbar k^2}{2m}$

ex. Free electron model

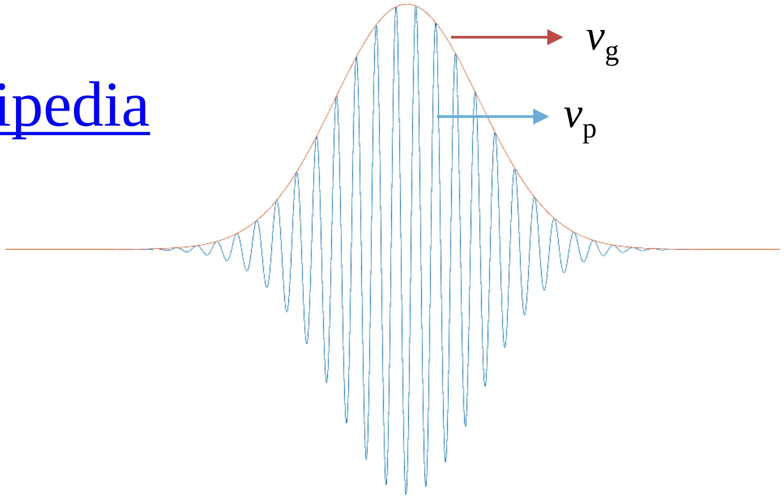
ppt 1-10

Such relation between frequency and wavenumber ($\omega = \omega(k)$) is called the **dispersion relation**.
For the light or photons, $\omega = ck$.

Dispersion Relation: electron, phonon, photon, etc.

The electron described by $Ae^{i(kx-\omega t)}$ is dispersed over the whole space. If there is one electron moving in free space, such a form of wave function may not be appropriate. Rather, a "**wave packet**" with the spread of ~10 nm would best represent such an electron. The figure in the below shows the wave packet with the Gaussian envelope. This state is fairly localized and has a relatively well defined wavelength although it is not the exact energy eigenstate.

Wikipedia



Suppose that the initial wave function is the Gaussian wave packet:

$$\psi(x,0) = \sqrt{\frac{2\pi}{\alpha}}\, e^{ikx} e^{-x^2/2\alpha}$$

The time evolution of the wave function can be obtained by solving the time-dependent Schrödinger equation (numerically or analytically). It is visualized by MATLAB file : wavepacket.m

You can observe that the envelope moves with a velocity that is faster than the phase velocity. The speed of such a localized wave packet is the group velocity and it is given by the following formula.

$$v_g = \frac{dw}{dk} = \frac{\hbar k}{m} = \frac{p}{m} \qquad \text{Bube (2.3)}$$

This is exactly the same as the classical velocity! (In the case of photon, $\omega = ck$ and so $v_p = v_g = c$)

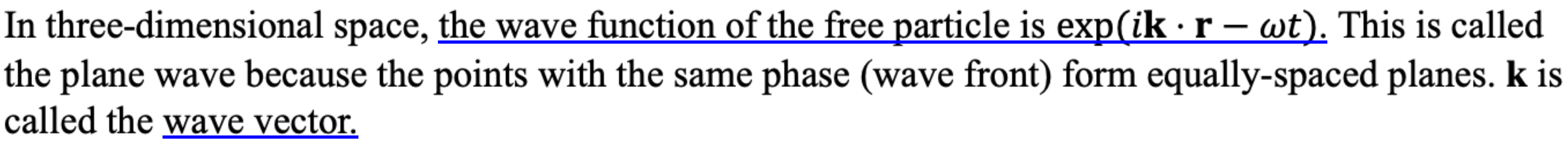
The group velocity is the speed at which energy and charge actually travels through the medium.

Since $\sin(kx) = (e^{ikx} + e^{-ikx})/2$, the state is the combination of right- and left-moving particles.

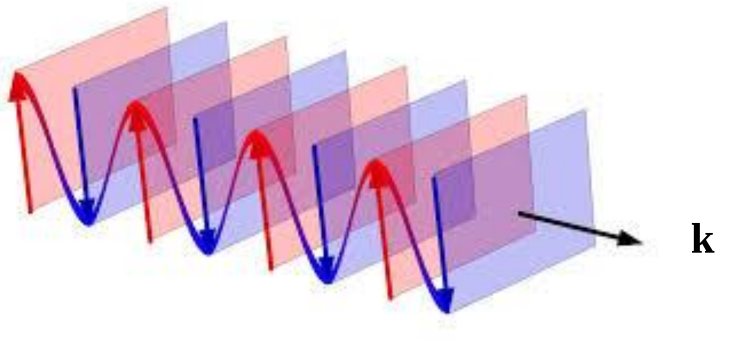
'k' defines a unique energy state of the particle in the free space. Such variables that uniquely specify or label the quantum state are called the quantum numbers.

It was mentioned that $Ae^{i(kx-\omega t)}$ represents a stream of particles. The flux (number of particles passing through a given position per unit time) can be calculated as follows:

$$\text{Flux } j = (\text{density}) \times (\text{velocity}) = |A|^2 \frac{\hbar k}{m}$$

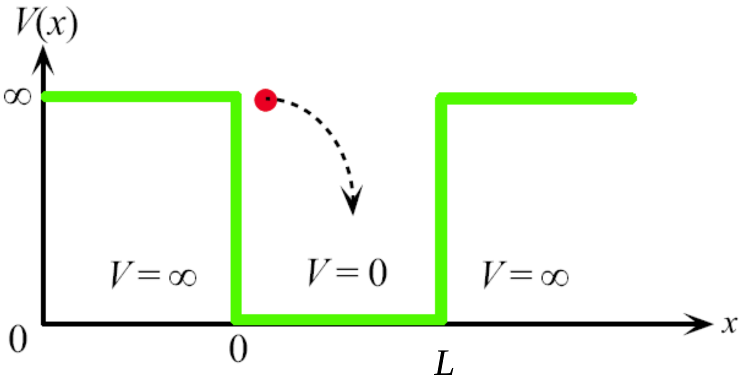


In three-dimensional space, the wave function of the free particle is $\exp(i\mathbf{k}\cdot\mathbf{r}-\omega t)$. This is called the plane wave because the points with the same phase (wave front) form equally-spaced planes. **k** is called the wave vector.



C. Example: Infinite Potential Well (1D)

Suppose that a particle is confined within a certain space and cannot escape. The simplest model describing such a case is the infinite potential well.



Q: What is the classical state?

For $x > L$ or $x < 0$, $\psi(x) = 0$ because particle cannot exist in this region (V is infinite). For $0 < x < L$, the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \rightarrow \frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}E\psi(x) = 0$$

$$\psi(x) = A\sin kx + B\cos kx \quad (\text{or } Ae^{ikx} + Be^{-ikx})$$

(from continuity of ψ(x))

Boundary condition $\psi(0) = \psi(L) = 0$

$$\psi(0) = 0 \rightarrow B = 0$$

$$\psi(a) = 0 \rightarrow \sin kL = 0 \rightarrow kL = n\pi \ (n = 1, 2, ..)$$

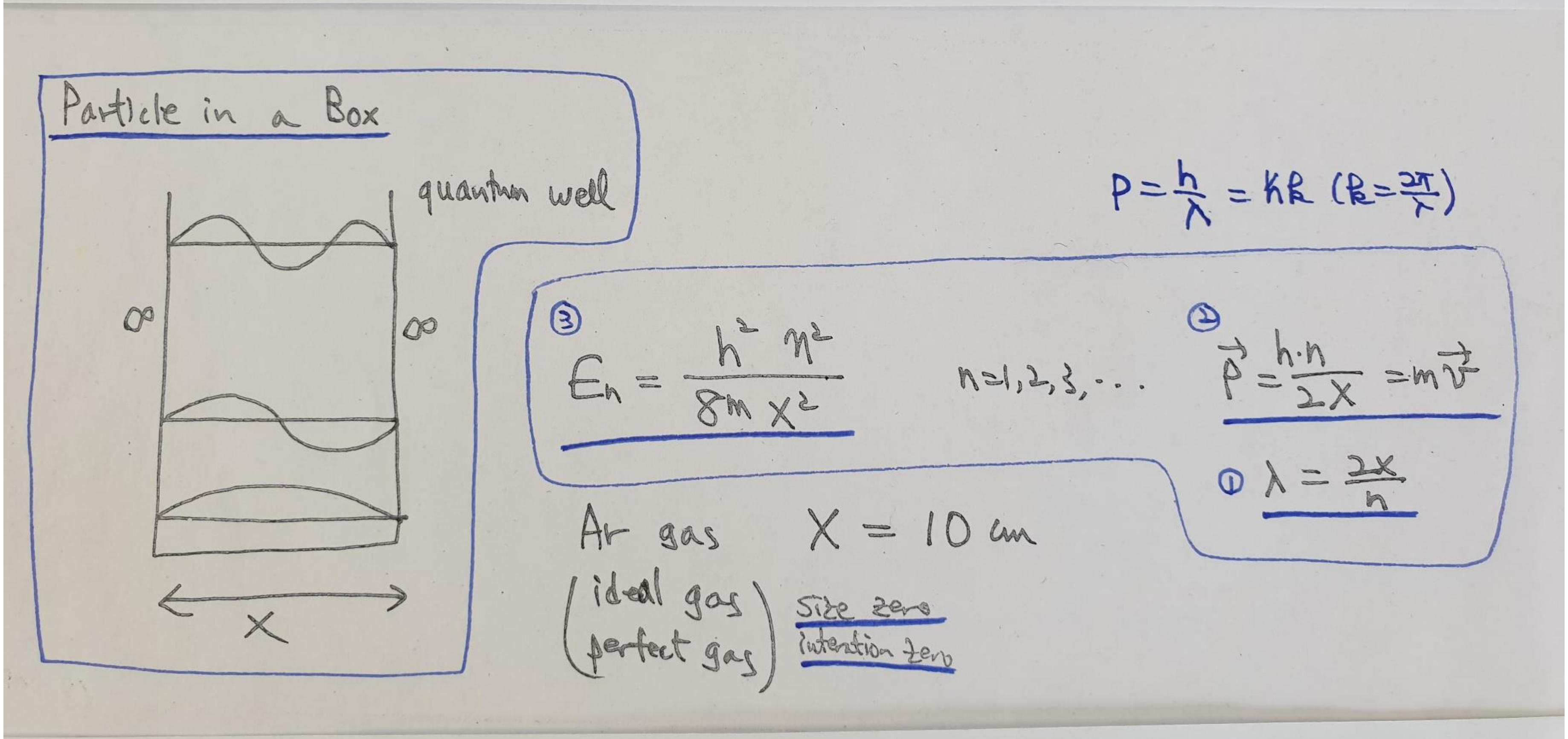
$$\psi_n(x) = A\sin\frac{n\pi}{L}x$$

Normalization condition

$$\int_0^L |\psi|^2\,dx = 1 \rightarrow A = \sqrt{\frac{2}{L}}$$

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

Since *n* (=1,2,3…) specifies the quantum state, it corresponds to the quantum number in the infinite well.



Particle in a Box

quantum well

$p = \frac{h}{\lambda} = \hbar k \quad (k = \frac{2\pi}{\lambda})$

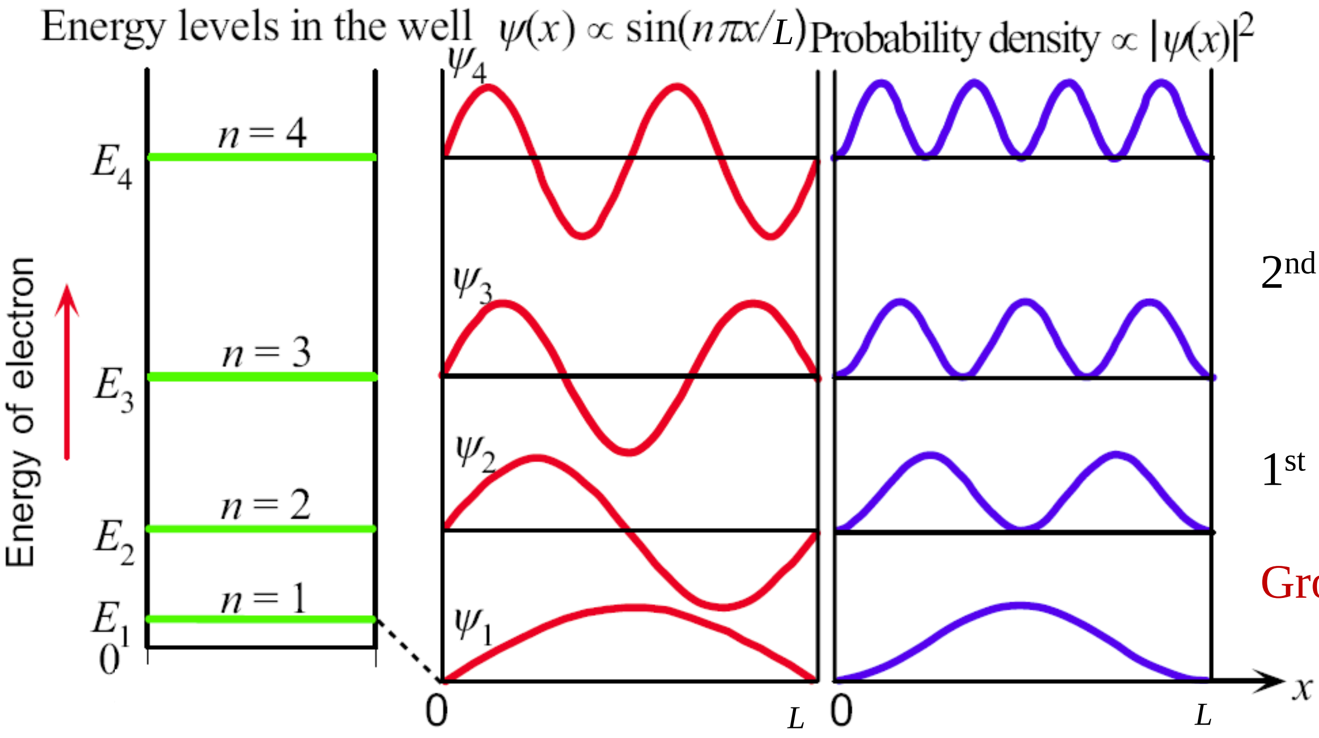
③ $E_n = \frac{h^2 n^2}{8m X^2}$ $\quad n = 1, 2, 3, \ldots$

② $\vec{p} = \frac{h \cdot n}{2X} = m\vec{v}$

① $\lambda = \frac{2X}{n}$

Ar gas $\quad X = 10$ cm

(ideal gas / perfect gas) size zero / interaction zero



2^{nd} excited state (n=3)

1^{st} excited state (n=2)

Ground state (n=1)

Bound state (localized state)

(Note that $\psi'(x)$ is discontinuous at $x = 0$ and
L because V is infinite at those points)

Remarks on the solution of infinite potential well.

i) Energy is **quantized**. (Note that it is only kinetic energy.) Classically, energy can be any non-negative real number. Let's calculate the energy interval (Δε) between 1st and 2nd states. First, a 1-kg object in a macroscopic system with L = 1 m, Δε ~ 10^{-67} J ~ 10^{-48} eV. This is too small energy to be observed. Therefore, the energy is effectively continuous.

Next, if the electron is confined within an atom, L is about 2 Å. In this case, Δε ~ 10 eV which is substantial. Therefore, quantum effects (energy quantization) are expected for electrons bound within the scale of atoms or molecules. This is also known as the quantum confinement effect in nanoscience. (The energy was not quantized in the free particle because the electron was not confined there.) For this reason, the nanoscale potential well is often called the "quantum well".

ii) "Going faster" in classical mechanics → increase n in quantum mechanics. Wavefunction is more oscillatory with shorter wave lengths as the quantum number goes up. Therefore, shorter wave length means higher kinetic energy. Mathematically, this is because the kinetic energy corresponds to the second derivative of the wave functions.

iii) Probability is not uniform but effectively uniform at large n. (Q: what is the probability in the classical mechanics?)

iv) There is a minimum energy (zero-point energy): see uncertainty relation.

v) Parity or symmetry: even parity for n = 1,3,5,.. & odd parity for n = 2,4,6,..

-Tue/9/1/20

Magnitude of Energy = Reference Point?

$\Delta t \, \Delta E \geq h$

Why the ground state energy is not zero? This can be explained in terms of Heisenberg's uncertainty principle for position-momentum. It states that $\Delta x \Delta p_x \geq \hbar/2$ where Δx and Δp_x indicate the uncertainty in the position and momentum, respectively.

If the minimum energy state has the vanishing kinetic energy, the momentum is definitely 0 and so $\Delta p = 0$. On the other hand, $\Delta x = L$, and therefore $\Delta x \Delta p = 0$, disobeying the uncertainty relation. (In the free-particle example, $\Delta p = 0$ but $\Delta x = \infty$.)

(skip)

We can also use the uncertainty relation to estimate the ground-state energy. The uncertainty in the position $\Delta x \sim L$. From the uncertainty relation, the minimum uncertainty is $\Delta p \sim \frac{\hbar}{2L}$. The uncertainty in the momentum mainly comes from the fact that the particle is either moving left or right. Therefore, the particle momentum is about the half of the momentum uncertainty. $p \sim \frac{\hbar}{4L}$. The corresponding kinetic energy is $E = \frac{p^2}{2m} = \frac{\hbar^2}{32mL^2}$, which qualitatively agrees with the ground state energy.

D. Example: Harmonic Oscillator (1D)

The classical harmonic oscillator is simply a mass attached to a spring that follows the Hooke's law. That is to say, $F = -kx$, where $x = 0$ is the equilibrium position. Let's first review on the classical mechanics on the harmonic oscillator.

$$F = -kx = m\frac{d^2x}{dt^2} \rightarrow \frac{d^2x}{dt^2} = -\frac{k}{m}x$$

$$\rightarrow x = A\sin(\omega_0 t) + B\cos(\omega_0 t) \qquad \omega_0 = \sqrt{\frac{k}{m}}: \text{ angular frequency}$$

$$\text{Period: } T = \frac{2\pi}{\omega_0} = 2\pi\sqrt{\frac{k}{m}}, \quad \text{Frequency: } f = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad (\omega_0 = 2\pi f)$$

With an initial condition $x(0) = x_0$ and $v(0) = 0$, $x(t) = x_0 \cos\omega_0 t$ and $v(t) = -\omega_0 x_0 \sin\omega_0 t$

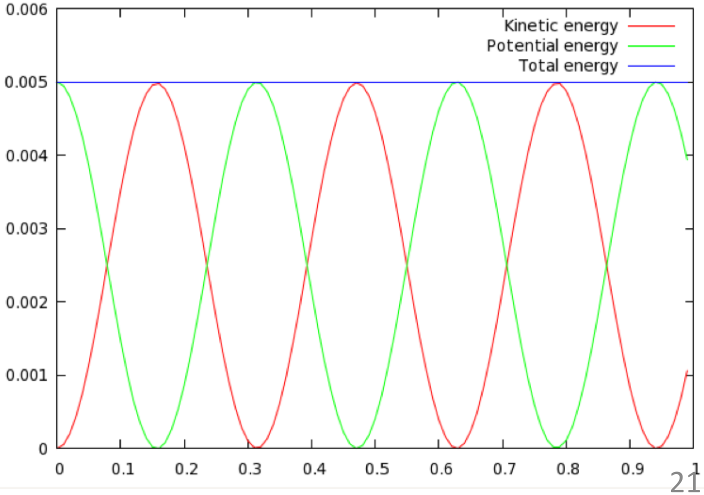
$$\text{Potential energy: } \frac{1}{2}kx(t)^2 = \frac{1}{2}kx_0^2\cos^2\omega_0 t$$

$$\text{Kinetic energy: } \frac{1}{2}mv(t)^2 = \frac{1}{2}m\omega_0^2 x_0^2 \sin^2\omega_0 t$$

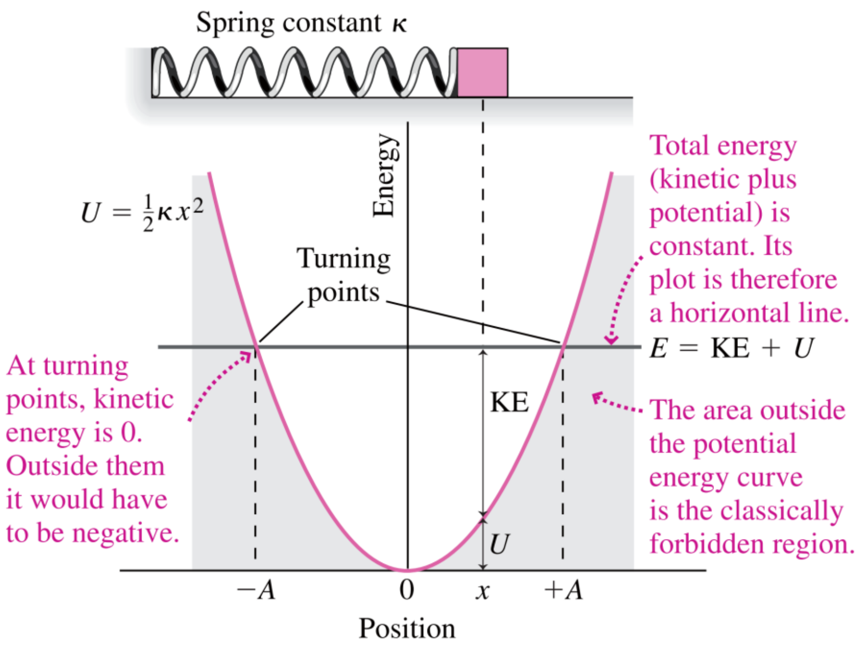
$$= \frac{1}{2}kx_0^2\sin^2\omega_0 t$$

$$\text{Total energy} = \frac{1}{2}kx_0^2$$

Kinetic, potential and total energies as a function of time.



Lattice Vibration = Phonon



Total energy (kinetic plus potential) is constant. Its plot is therefore a horizontal line. $E = \mathrm{KE} + U$

At turning points, kinetic energy is 0. Outside them it would have to be negative.

The area outside the potential energy curve is the classically forbidden region.

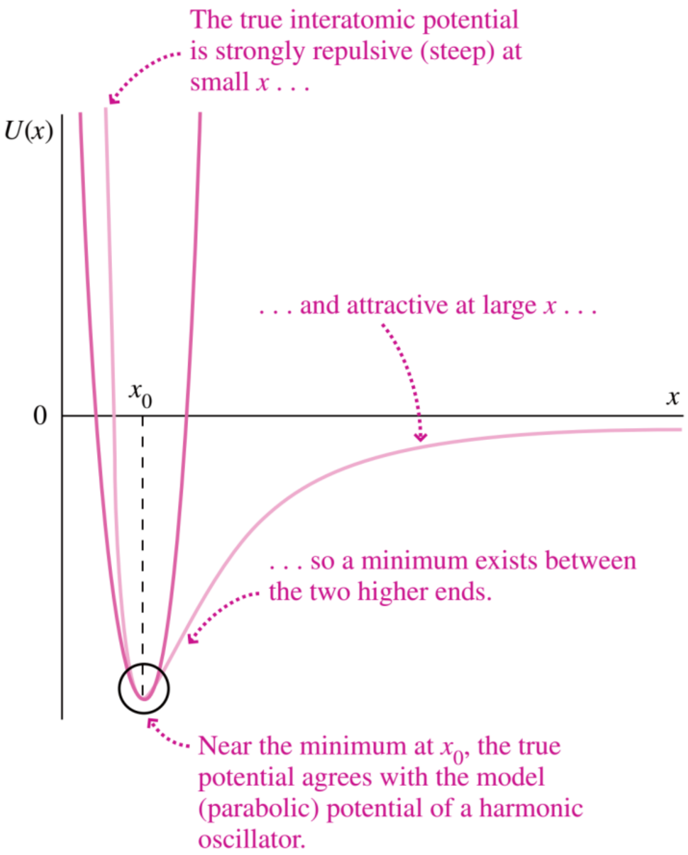


Figure 17 For small oscillations about a point of stable equilibrium, all potential energies resemble a parabola—a simple harmonic oscillator.

The true interatomic potential is strongly repulsive (steep) at small x . . .

. . . and attractive at large x . . .

. . . so a minimum exists between the two higher ends.

Near the minimum at x_0, the true potential agrees with the model (parabolic) potential of a harmonic oscillator.

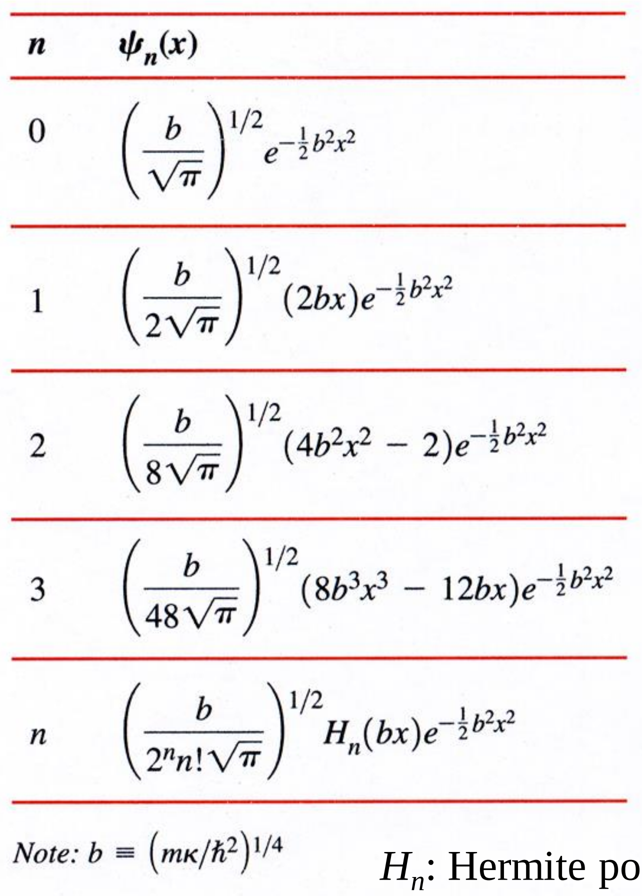
Ex) H_2 molecule

x_0 corresponds to $x = 0$ in the left figure.

The Schrödinger equation for the harmonic oscillator is as follows:

$$-\frac{\hbar^2}{2m}\frac{d^2y(x)}{dx^2}+\frac{1}{2}kx^2y(x)=Ey(x)$$

The boundary condition is that $\psi(\pm\infty)=0$. The solution to this problem requires the series expansion method. Please refer to the standard QM textbook for the solving procedure. Here we just study solutions.



n	$\psi_n(x)$
0	$\left(\frac{b}{\sqrt{\pi}}\right)^{1/2} e^{-\frac{1}{2}b^2x^2}$
1	$\left(\frac{b}{2\sqrt{\pi}}\right)^{1/2}(2bx)e^{-\frac{1}{2}b^2x^2}$
2	$\left(\frac{b}{8\sqrt{\pi}}\right)^{1/2}(4b^2x^2-2)e^{-\frac{1}{2}b^2x^2}$
3	$\left(\frac{b}{48\sqrt{\pi}}\right)^{1/2}(8b^3x^3-12bx)e^{-\frac{1}{2}b^2x^2}$
n	$\left(\frac{b}{2^n n!\sqrt{\pi}}\right)^{1/2}H_n(bx)e^{-\frac{1}{2}b^2x^2}$

Note: $b \equiv (m\kappa/\hbar^2)^{1/4}$

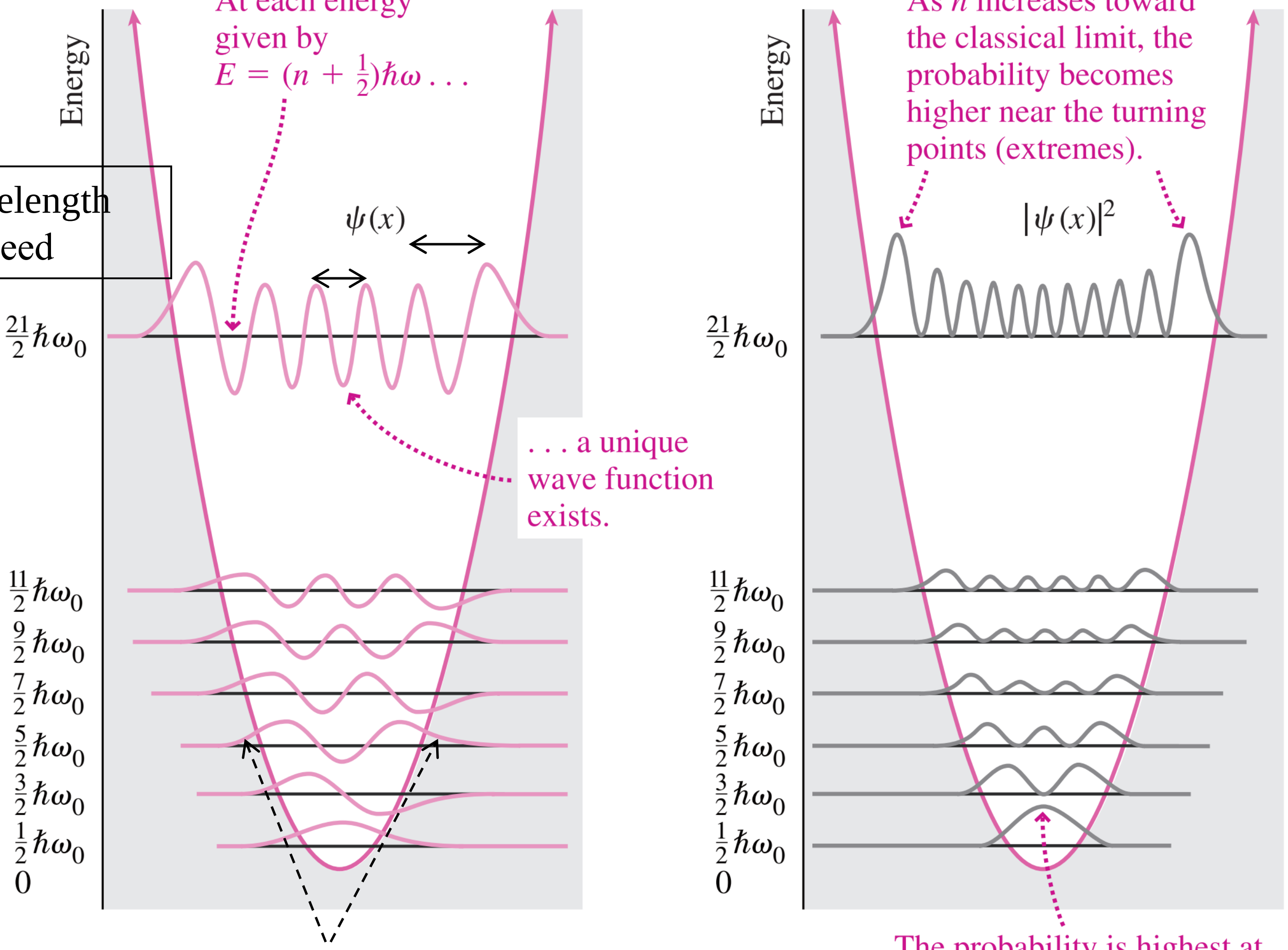
H_n: Hermite polynomial

$$E_n=\left(n+\frac{1}{2}\right)\hbar\omega_0 \quad (n=0,1,2,3,..)$$

This is reminiscent of the photon energy. Recall that ω_0 here is the characteristic angular frequency of the spring while $\omega = E/\hbar$ in the time part of an energy eigenstate varies with energy.

The ground state energy is not zero but $\hbar\omega_0/2$. This is called the zero point energy. The reason is the same as the infinite quantum well.

Figure 18 Wave functions, probability densities, and energies of a harmonic oscillator.



At each energy given by $E = (n + \frac{1}{2})\hbar\omega \ldots$

. . . a unique wave function exists.

As n increases toward the classical limit, the probability becomes higher near the turning points (extremes).

The probability is highest at the center in the ground state, contrary to the classical case.

Shorter wavelength
→ higher speed

Particle exists beyond turning points
due to the tunneling effect.

It is important that any vibration is quantized with the same energy spacing of $\hbar\omega_0$ even if the oscillating substance is not as light as electrons. For example, the effective spring constant of the effective spring constant of a N_2 molecule is 2287 N/m. The angular frequency is given by

$$\omega_0 = \sqrt{\frac{k}{m}} = \sqrt{\frac{2287\ \text{N/m}}{2.33\times 10^{-26}\ \text{kg (nitrogen mass)/2}}} = 4.43\times 10^{14}\ \text{rad/s}$$

Or in terms of frequency, $f = 7.05\times 10^{13}$ Hz. Note that the reduced mass (half of proton mass) is used. Therefore, the energy spacing of this harmonic oscillation is given by

$$\Delta E = \hbar\omega_0 = 4.67\times 10^{-20}\ \text{J} = 0.29\ \text{eV}$$

$\nu \approx 10^{13}$/s in phonon

$k_B = 8.617 \times 10^{-5}$ eV/K

$h = 4.1357\times 10^{-15}$ eV·s

This is a significant energy. In terms of thermal energy, it corresponds to ~3000 K. This means that at room temperatures, there is practically no vibration at all. (See Thermodynamics for the partition function of harmonic oscillators.) That is to say, **vibrational modes** are hardly activated and almost frozen! This also means that the vibrational motion does not contribute to the heat capacity. The vibration can be excited by photon (infrared).

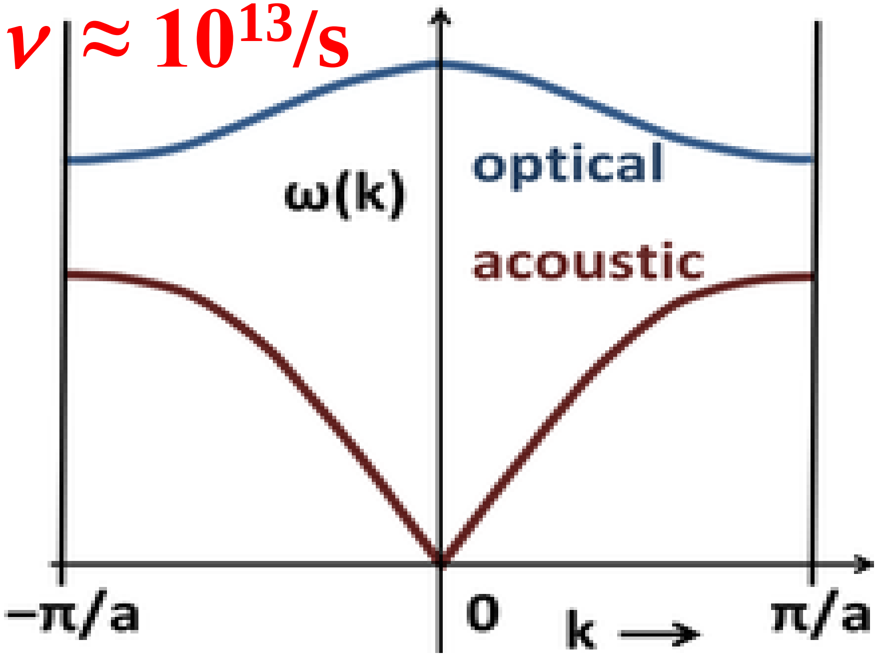
It is only when the frequency is very low that the vibration is thermally activated. The **acoustic phonon** is such oscillations.

optical phonon

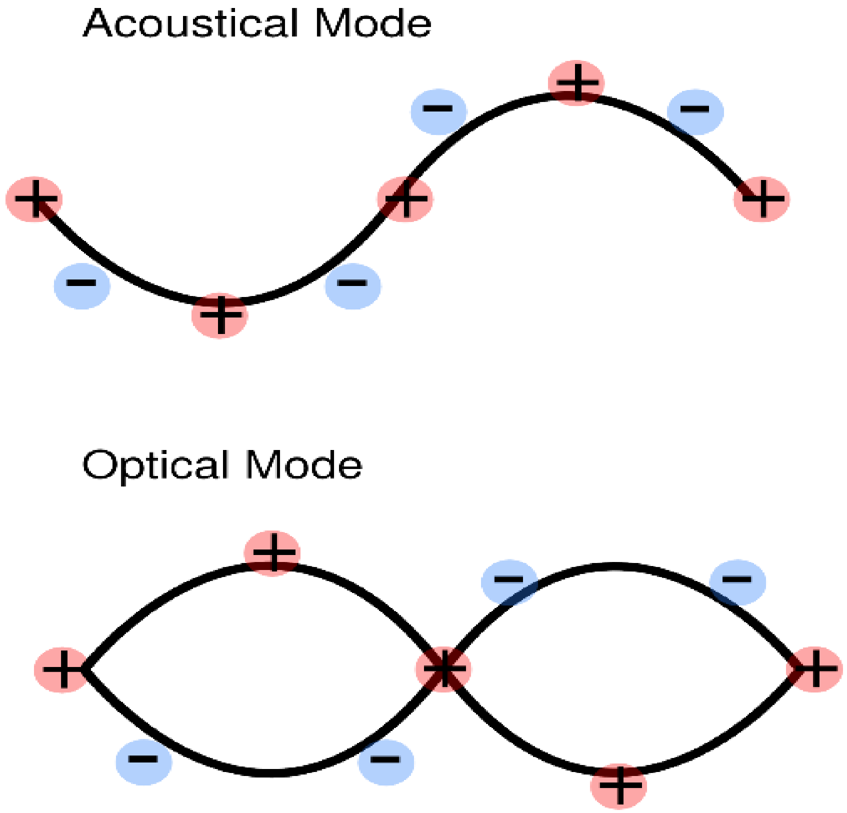
The energy quantization of vibration is perhaps the only quantum effect we see for atoms. In other discussions, atoms can be well described by the classical mechanics. (The exception is hydrogen atom. In some situations, the quantum effect of hydrogen atom is important. Ex. tunneling)

Acoustic and Optical Phonons in a Crystal

$\nu \approx 10^{13}/\mathrm{s}$



Phonon Wavevector *k*


Acoustical Mode

Optical Mode

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \quad (n = 0, 1, 2, 3, ..)$$ ppt 1-23

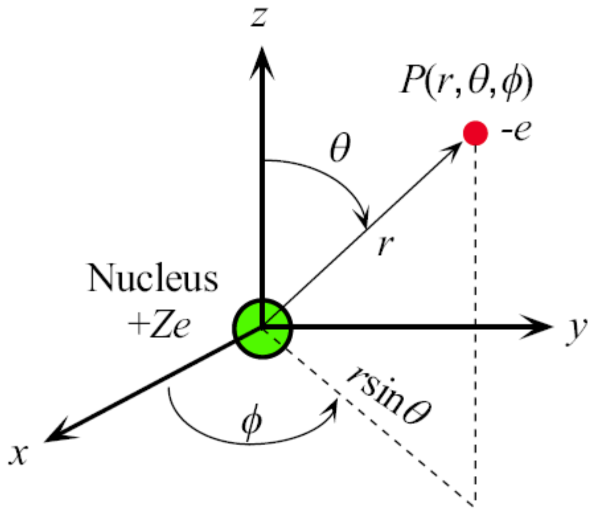
E. Example: Hydrogen Atom

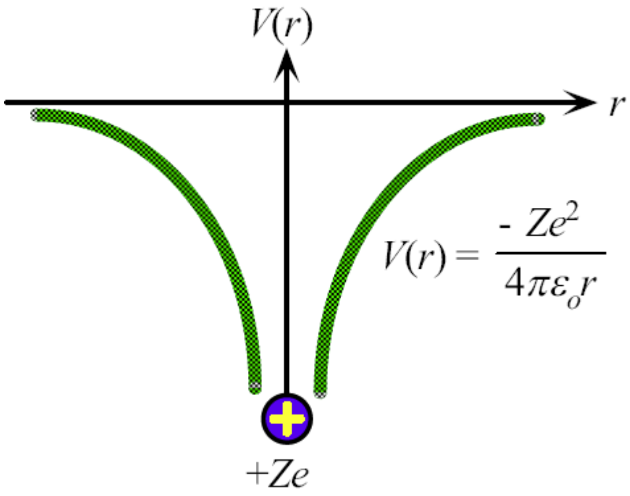
Schrödinger equation in spherical coordinate

The hydrogen atom is the most important problem in quantum mechanics. It is the only system that we can solve exactly among any real materials. From the perfect agreement between theory and spectroscopic data on the hydrogen atom, we are sure that the Schrödinger equation and the way we interpret its solution is correct.

In the hydrogen atom, there is one proton and one electron. We slightly generalized this problem and assume that there is a nucleus with the charge of +*Ze* and only one electron is orbiting around it. This is called the hydrogen-like atom model.

It is convenient to adopt the spherical coordinate with the nucleus at the origin. There are three variables identifying a position: radial distance r ($r \geq 0$), polar angle θ ($0 \leq \theta \leq \pi$), azimuthal angle ϕ ($0 \leq \phi < 2\pi$).





(skip)

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2+V(r)\right]\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

(m_e: electron mass)

Laplacian in spherical coordinate

$$\nabla^2=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)$$

$$=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\hat{L}\quad\left(-\hat{L}=\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right)$$

$$-\frac{\hbar^2}{2m_e}\left\{\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]\right\}\psi(r,\theta,\phi)-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

We will not solve this Schrödinger equation (please refer to any standard QM textbook). Instead, we will learn about the main features of the solution:

i) Quantum numbers.
ii) Energy eigenvalues.
iii) Eigenstates.

Quantum Numbers

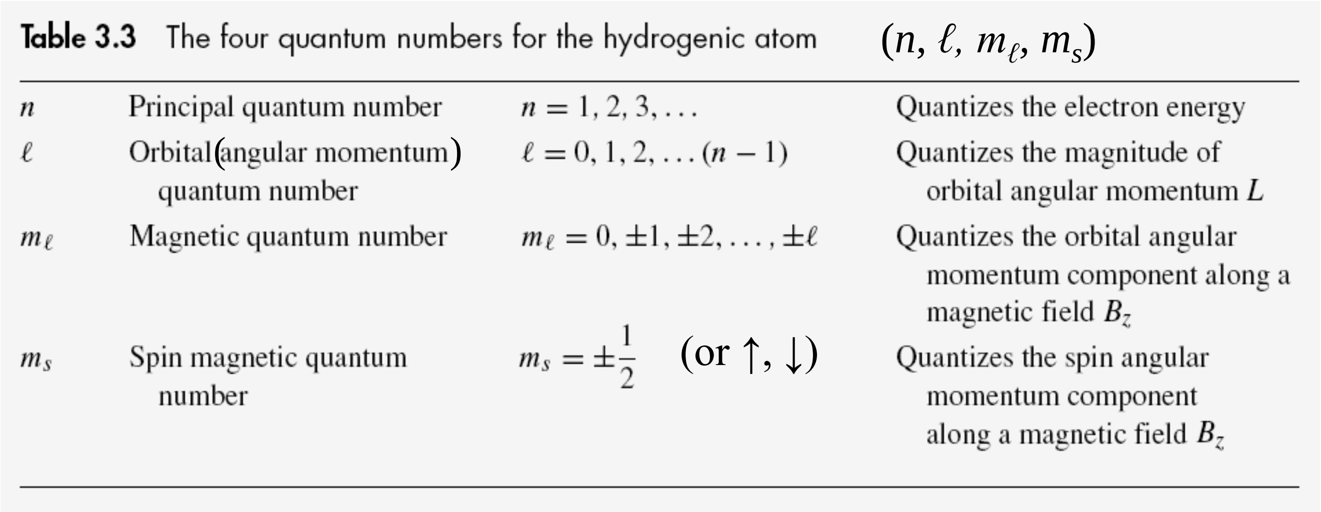
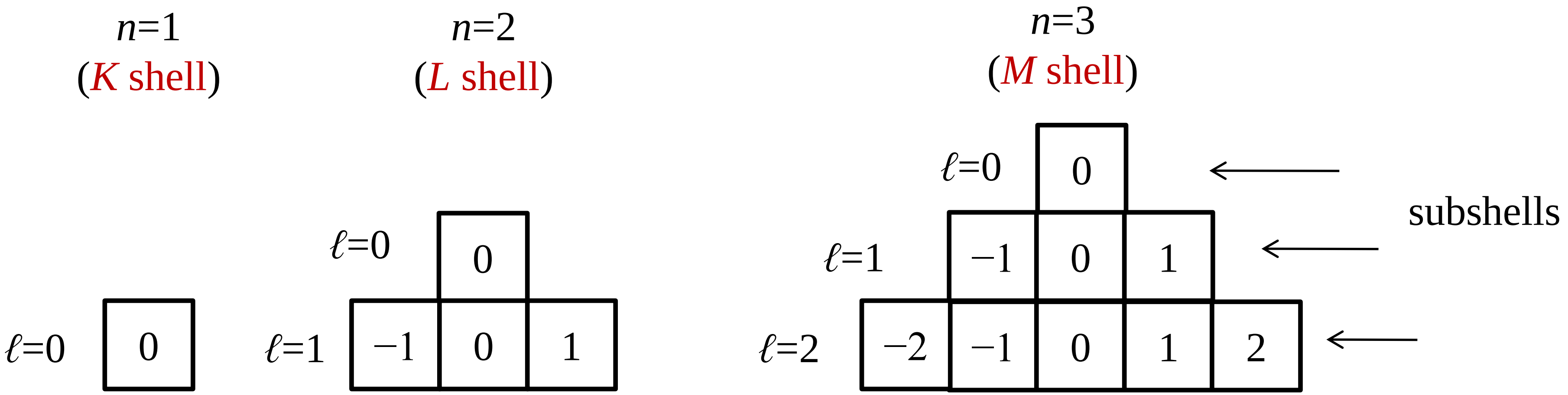


Table 3.3 The four quantum numbers for the hydrogenic atom (n, ℓ, m_ℓ, m_s)

n	Principal quantum number	$n = 1, 2, 3, \dots$	Quantizes the electron energy
ℓ	Orbital (angular momentum) quantum number	$\ell = 0, 1, 2, \dots (n - 1)$	Quantizes the magnitude of orbital angular momentum L
m_ℓ	Magnetic quantum number	$m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$	Quantizes the orbital angular momentum component along a magnetic field B_z
m_s	Spin magnetic quantum number	$m_s = \pm \frac{1}{2}$ (or ↑, ↓)	Quantizes the spin angular momentum component along a magnetic field B_z



0: *s* 1: *p* 2: *d* 3: *f* ...

Energy Eigenvalues

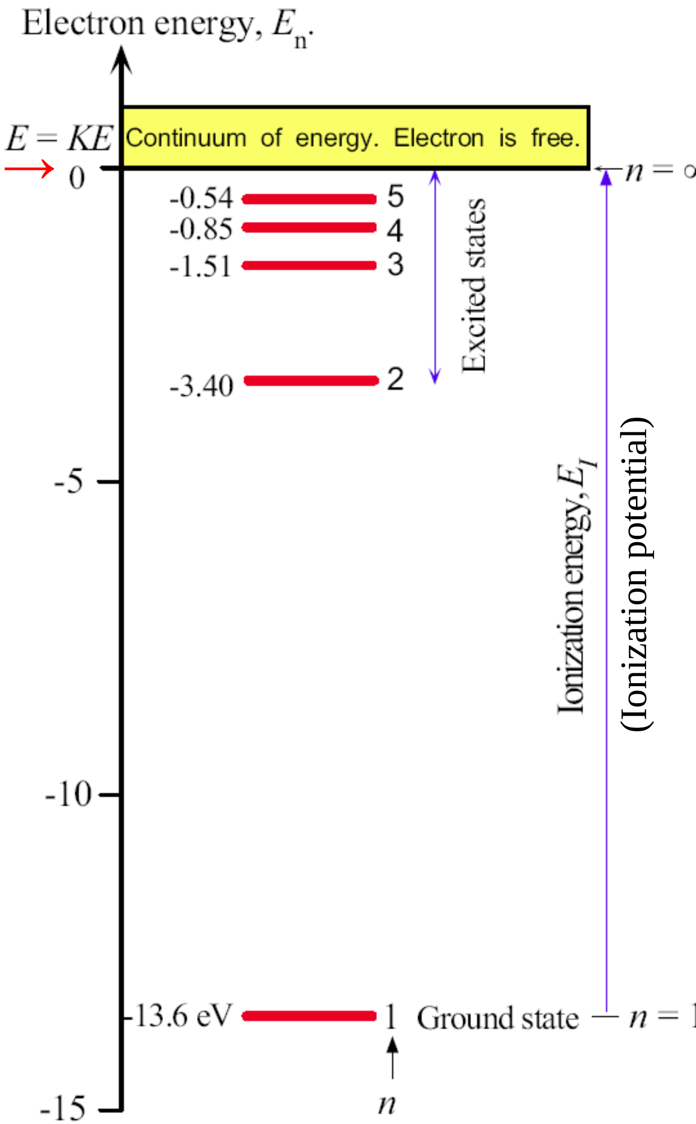
Energy is quantized, and depends only on the principal quantum number *n*.

$$E_n = -\frac{m_e e^4 Z^2}{8\varepsilon_o^2 h^2 n^2} = -\frac{13.6}{n^2} Z^2 \text{eV}$$

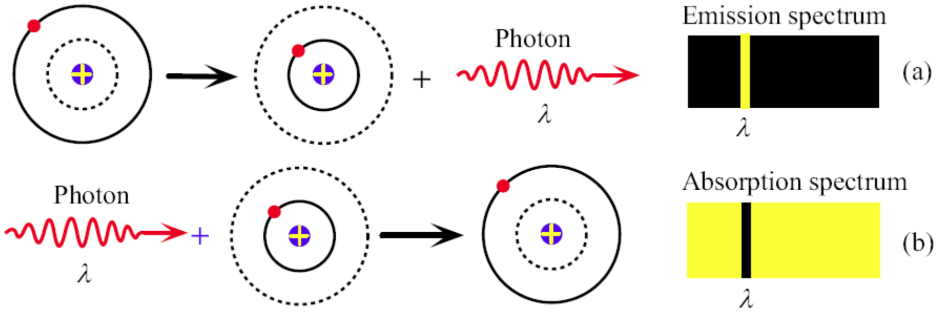
Vacuum Level

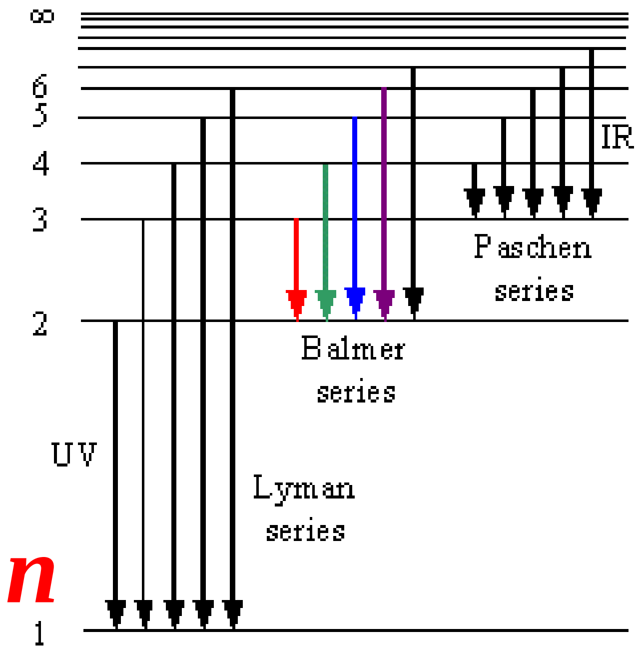
This means that there are many quantum states with the same energy. This is called the degeneracy.

Energy spectrum of H atom



Electrons can **absorb or emit a photon** and make a transition into a new quantum state.





- Balmer series (nm)

Theory: 656, 486, 434, and 410

$1{,}240 / \lambda$ (nm) $= h\nu$ (eV)

Experiment:

410 434 486 656 nm

From the perfect agreement between theory and experiment on this hydrogen atom, with the size of only ~1 Å, we feel confident that the Schrödinger's theory is correct.

Eigenstates

Eigenstates for the hydrogen atom is a product between radial and angular parts:

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = \underset{\substack{\uparrow \\ \text{Radial part}}}{R_{n\ell}(r)}\,\underset{\substack{\uparrow \\ \text{Angular part: spherical harmonics}}}{Y_\ell^{m_\ell}(\theta,\phi)}$$

Principal quantum number

Orbital (angular momentum) quantum number

Magnetic quantum number

Let's first examine the radial part.

Table 4.6: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

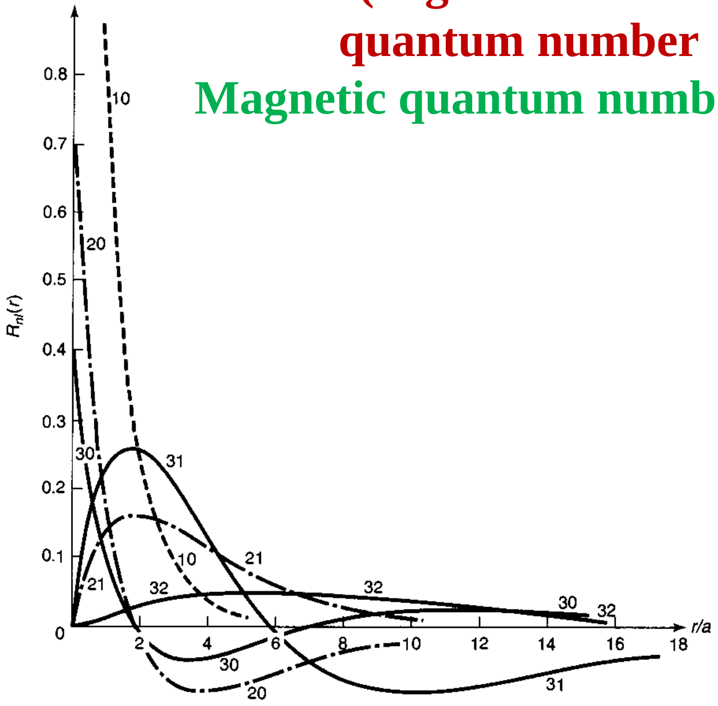
$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1-\frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1-\frac{2}{3}\frac{r}{a}+\frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1-\frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$



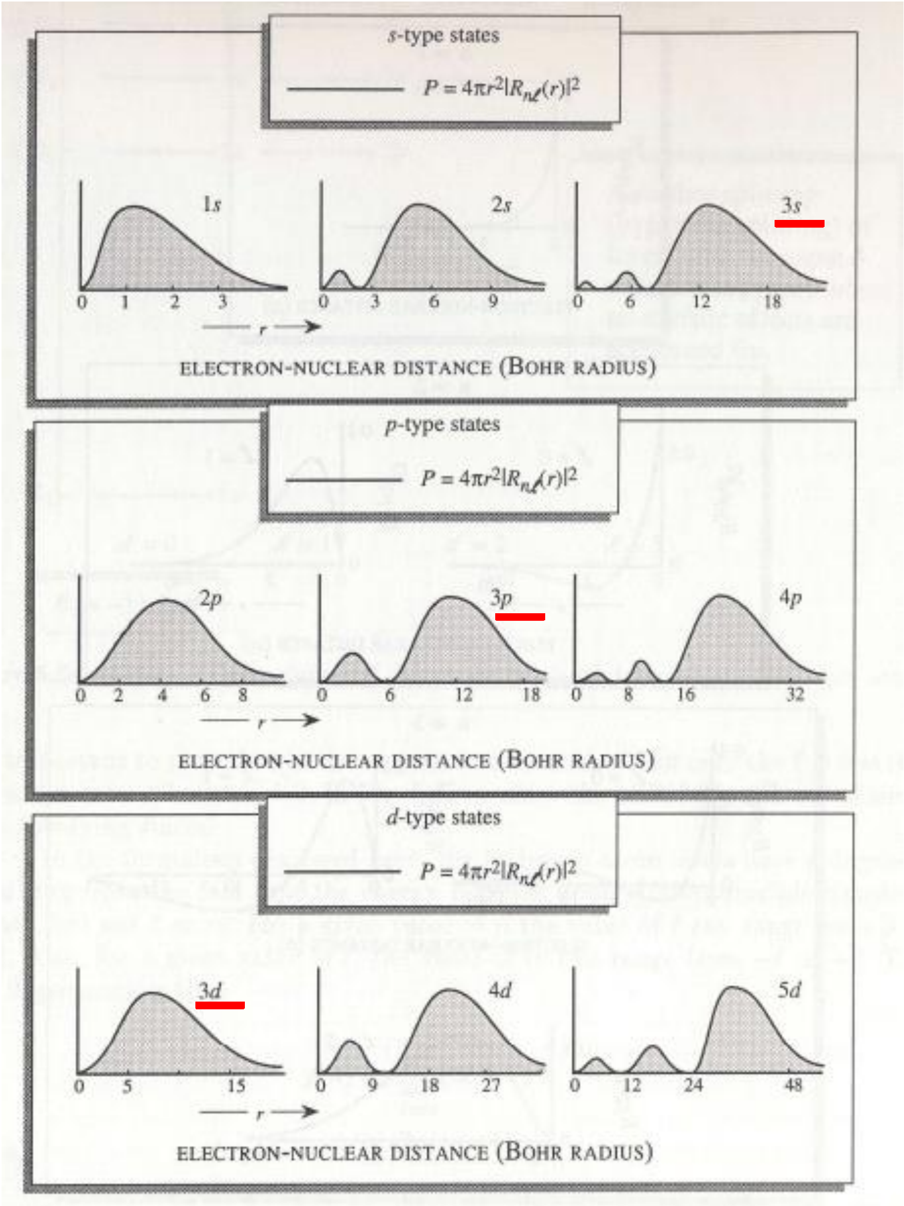
$$a = \frac{4\pi\varepsilon_0\hbar^2}{Zm_e e^2} = \frac{a_0}{Z}$$

a_0: Bohr radius = 0.529 Å

Increasing Z → more localized

Number of nodes = $n-\ell-1$. Higher number of nodes → more oscillations along r → more kinetic energy in the radial direction

The actual radial distribution is given by $P(r) = 4\pi r^2[R_{n\ell}(r)]^2$



- Increasing *n* pushes the distribution outward.
- Electron is more localized for higher ℓ values for the same *n*.

Transition Metal

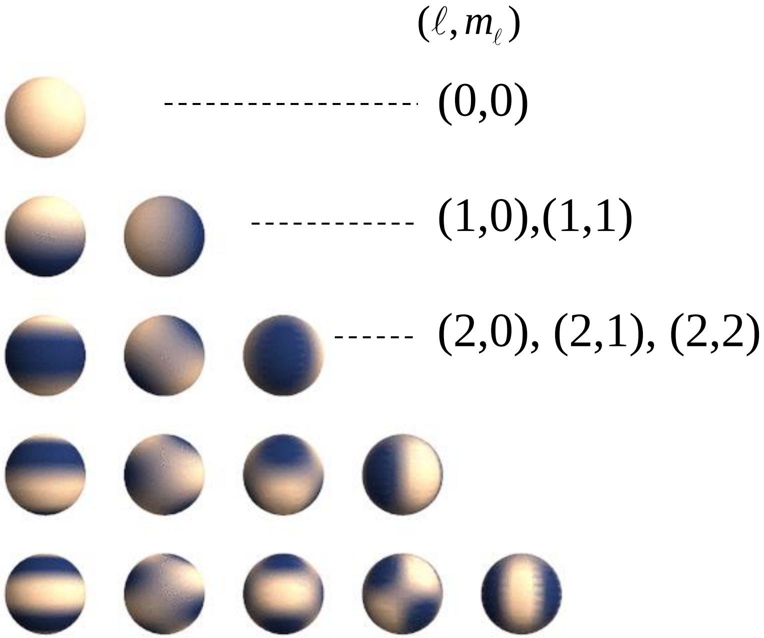
ex. $\mathrm{Co}^{27} = [\mathrm{Ar}]3d^7 4s^2$

(skip)

Second, let's look at the angular part that is simply spherical harmonics. Spherical harmonics is "Fourier series" in the angular space

$$
\begin{array}{ll}
Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} & Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi} \\
Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta & Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta) \\
Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi} & Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi} \\
Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) & Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi} \\
Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi} & Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}
\end{array}
$$

Animated image of real part of spherical harmonics. Bright/dark indicates the sign.

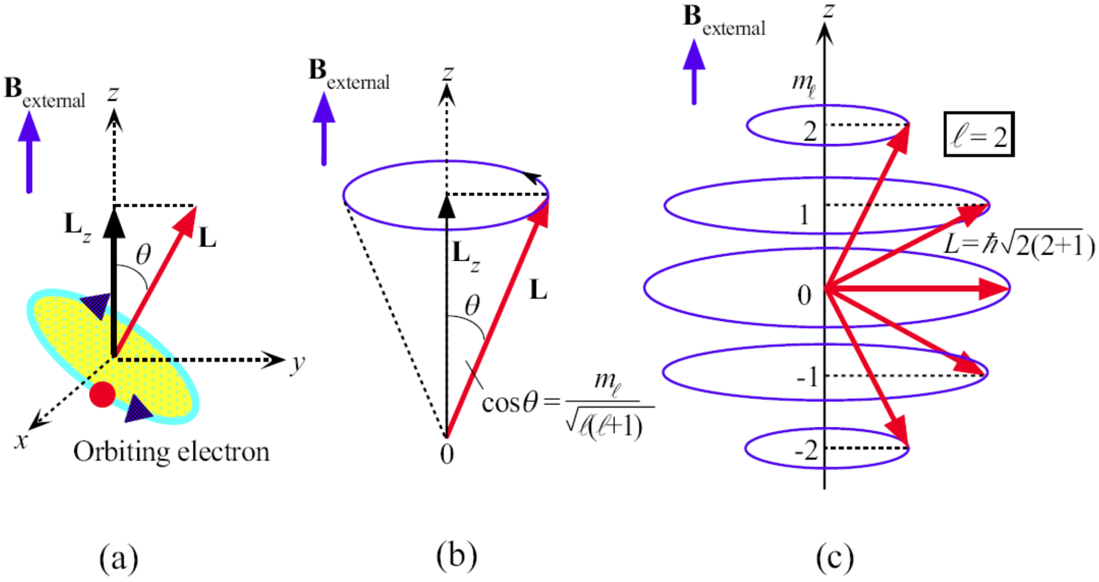


$$Y_\ell^{m_\ell}(\theta,\phi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell - m_\ell)!}{(\ell + m_\ell)!}}\, P_\ell^{m_\ell}(\cos\theta) e^{i m_\ell \phi}$$

Associated Legendre polynomial

The orbital quantum number ℓ reflects how rapidly the electron rotates around the nucleus. The rotation is characterized by the angular momentum vector **L**. (Classically, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$.) The magnitude of **L** is given by $|\mathbf{L}| = L = \hbar\sqrt{\ell(\ell+1)}$. (The angular momentum has the same unit as $\hbar$) About the direction of **L**, we can only know the component of **L** along a specific direction (usually the direction of the magnetic field, if present, is chosen). If it is the z-direction, the z-component of **L** is given by $L_z = m_\ell \hbar$ $(m_\ell = -\ell, .., \ell)$ If one can specify the whole component of **L**, it is at odds with the uncertainty principle.

(skip)

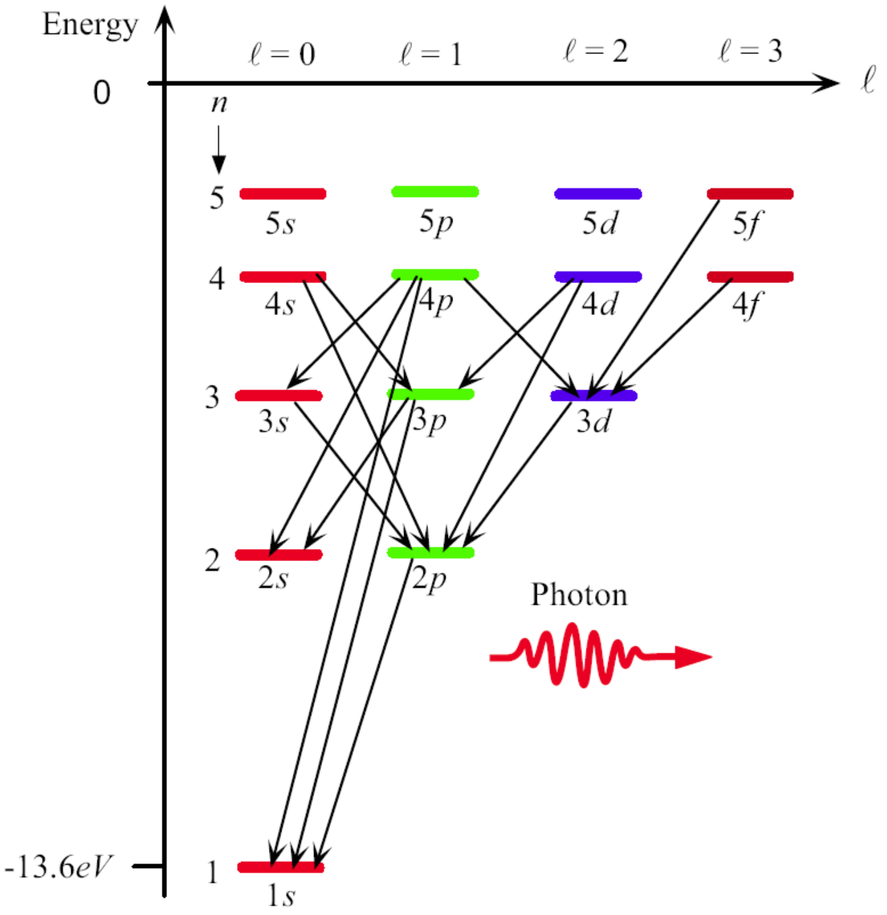


(a) The electron has an orbital angular momentum, which has a quantized component **L** along an external Magnetic field $\mathbf{B}_{\text{external}}$.

(b) The orbital angular momentum vector **L** rotates about the z axis. Its component L_z is quantized; Therefore, the **L** orientation, which is the angle θ, is also quantized. **L** traces out a cone.

(c) According to quantum mechanics, only certain orientations for **L** are allowed, as determined by ℓ and m_ℓ

When an electron in the hydrogen-like atom absorbs or emits a photon by changing its quantum state, the transition should satisfy the **Selection Rules of $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$.** This is because **photon** itself has an **angular momentum** with the magnitude of $\hbar$. The figure below shows the possible transition for emission of one photon.



H atom

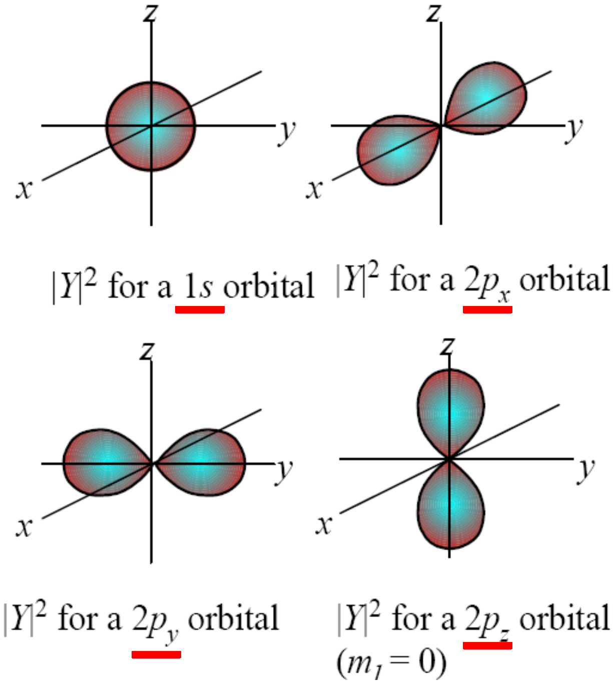
(skip)

Another representation of *p* and *d* orbtials

$$Y_1^0 \propto \cos\theta \propto z \to p_z \text{ orbital}$$

$$Y_1^1 + Y_1^{-1} \propto \sin\theta(e^{i\phi} + e^{-i\phi}) \propto \sin\theta\cos\phi \propto x \to p_x \text{ orbital}$$

$$Y_1^1 - Y_1^{-1} \propto \sin\theta(e^{i\phi} - e^{-i\phi}) \propto \sin\theta\sin\phi \propto y \to p_y \text{ orbital}$$



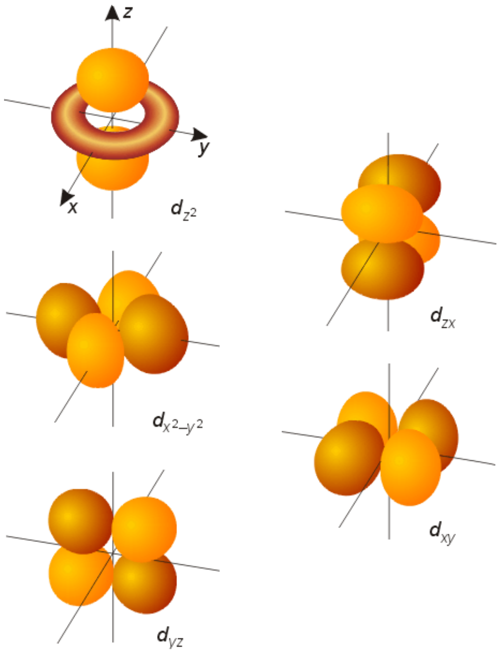
$|Y|^2$ for a 1s orbital

$|Y|^2$ for a 2p_x orbital

$|Y|^2$ for a 2p_y orbital

$|Y|^2$ for a 2p_z orbital ($m_l = 0$)

p orbital

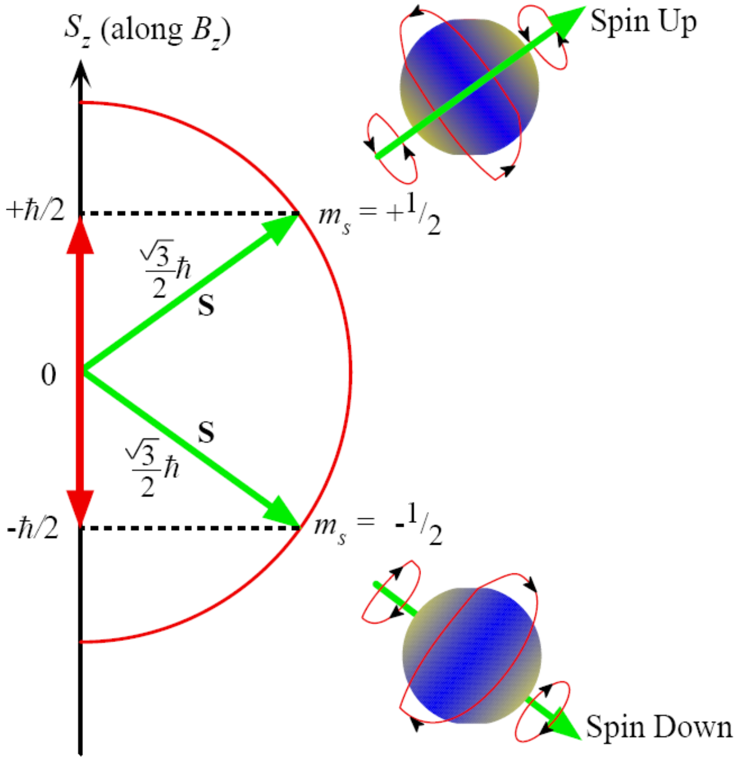


d orbital

(skip)

Electron Spin

It was found in Stern-Gerlach experiment that the electron possesses an intrinsic rotation that is distinct from the spatial rotation. It is analogous to a self-rotation but in fact it is not. (According to the modern particle theory, the electron is a point particle with no spatial extent.) Nevertheless, it has every property of rotation. For instance, it follows the angular momentum conservation. The spin quantum number s is similar to the orbital quantum number ℓ except that s is fixed to ½. Therefore, the magnitude of the spin angular momentum is $S = \hbar\sqrt{s(s+1)} = \frac{\sqrt{3}}{2}\hbar$. Like the orbital quantum number, spin the quantized along a certain direction (z-direction). That is to say, $S_z = m_s\hbar$, where m_s is the spin magnetic quantum number and $m_s = \pm\frac{1}{2}$. These two states are often called spin-up / spin-down or ↑, ↓. Note that spin-up/down do not mean that the angular momentum is point along ±z direction.



Wave functions including the spin part is written like $\psi = \psi_{n\ell m_\ell}(r,\theta,\phi)\otimes|\uparrow\rangle$ or $\psi_{n\ell m_\ell}(r,\theta,\phi)|\uparrow\rangle$

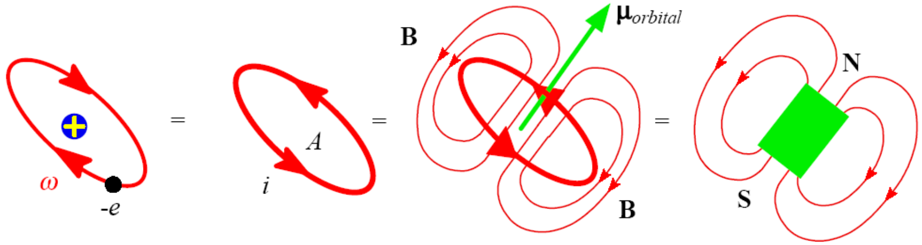
ppt 1-30

(skip)

Magnetic Dipole Moment of Electron

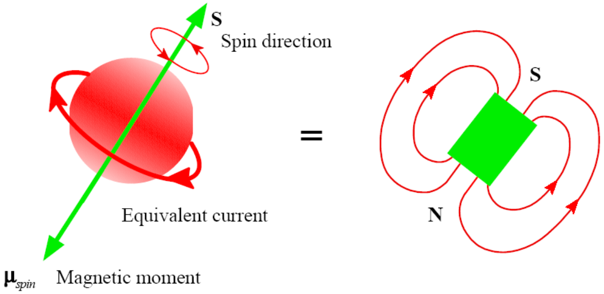
The orbiting electron is equivalent to a current loop that behaves like a bar magnet. The resulting magnetic moment is called the **orbital magnetic moment ($\boldsymbol{\mu}_{\text{orbital}}$)** is given by

$$\boldsymbol{\mu}_{\text{orbital}} = -\frac{e}{2m_e}\mathbf{L}$$



Likewise, the spinning electron can be imagined to be equivalent to a current loop. This current loop behaves like a bar magnet, just as in the orbital case. This produces the **spin magnetic moment ($\boldsymbol{\mu}_{\text{spin}}$).**

$$\boldsymbol{\mu}_{\text{spin}} = -\frac{e}{m_e}\mathbf{S}$$



The total magnetic moment is

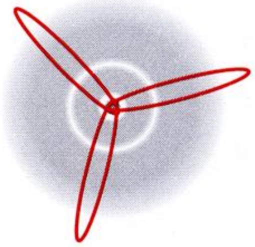
$$\boldsymbol{\mu}_{\text{tot}} = \boldsymbol{\mu}_{\text{orbital}} + \boldsymbol{\mu}_{\text{spin}} = -\frac{e}{2m_e}(\mathbf{L} + 2\mathbf{S})$$

We will come back to this formula when discussing on the magnetic properties.

F. Multielectron Atoms and the Periodic Table

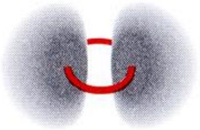
Based on the results of hydrogen-like atom, we can understand other atoms as well.
Starting points are as follows:

- Only one electron can occupy each quantum state: **Pauli exclusion principle**
- Since the inner electrons screen the nuclear charge, the effective nucleus charge is larger as electrons approach the nucleus.
- For a given *n*, energy is lower for lower ℓ orbits because they are more elliptical.



Small ℓ implies less rotational motion, more radial, and a more elliptical orbit.

3*s*
(ℓ = 0)



Large ℓ implies less radial motion, and a more circular orbit.

3*d*
(ℓ = 2)

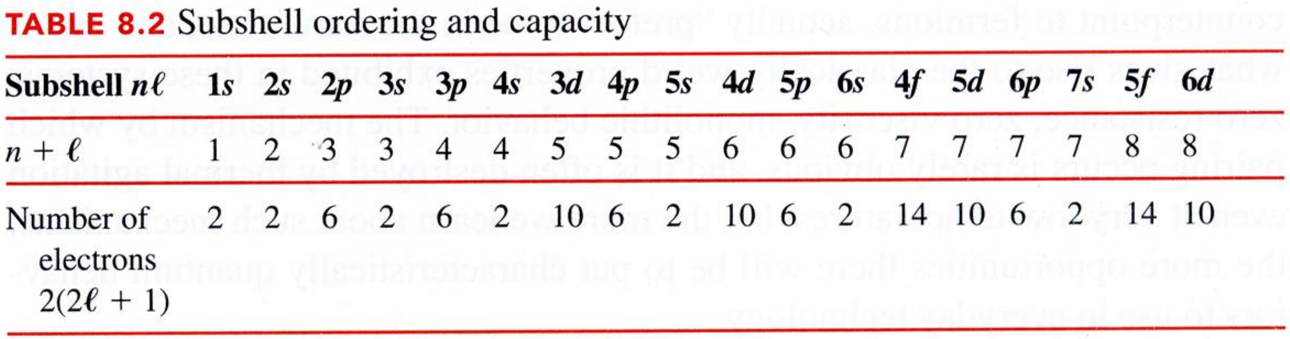


TABLE 8.2 Subshell ordering and capacity

Subshell $n\ell$	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	5d	6p	7s	5f	6d
$n + \ell$	1	2	3	3	4	4	5	5	5	6	6	6	7	7	7	7	8	8
Number of electrons $2(2\ell + 1)$	2	2	6	2	6	2	10	6	2	10	6	2	14	10	6	2	14	10

Rule of thumb: subshell ordering follows $n + \ell$. If this number is the same, the order follows n.

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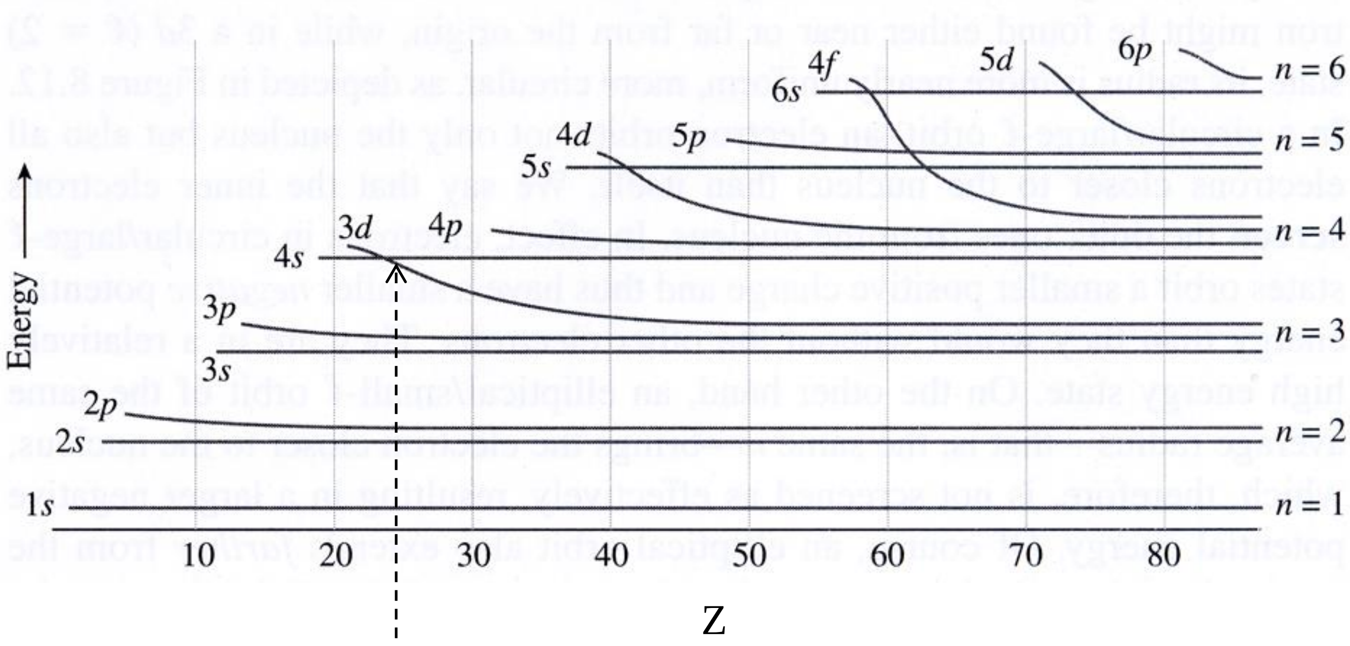
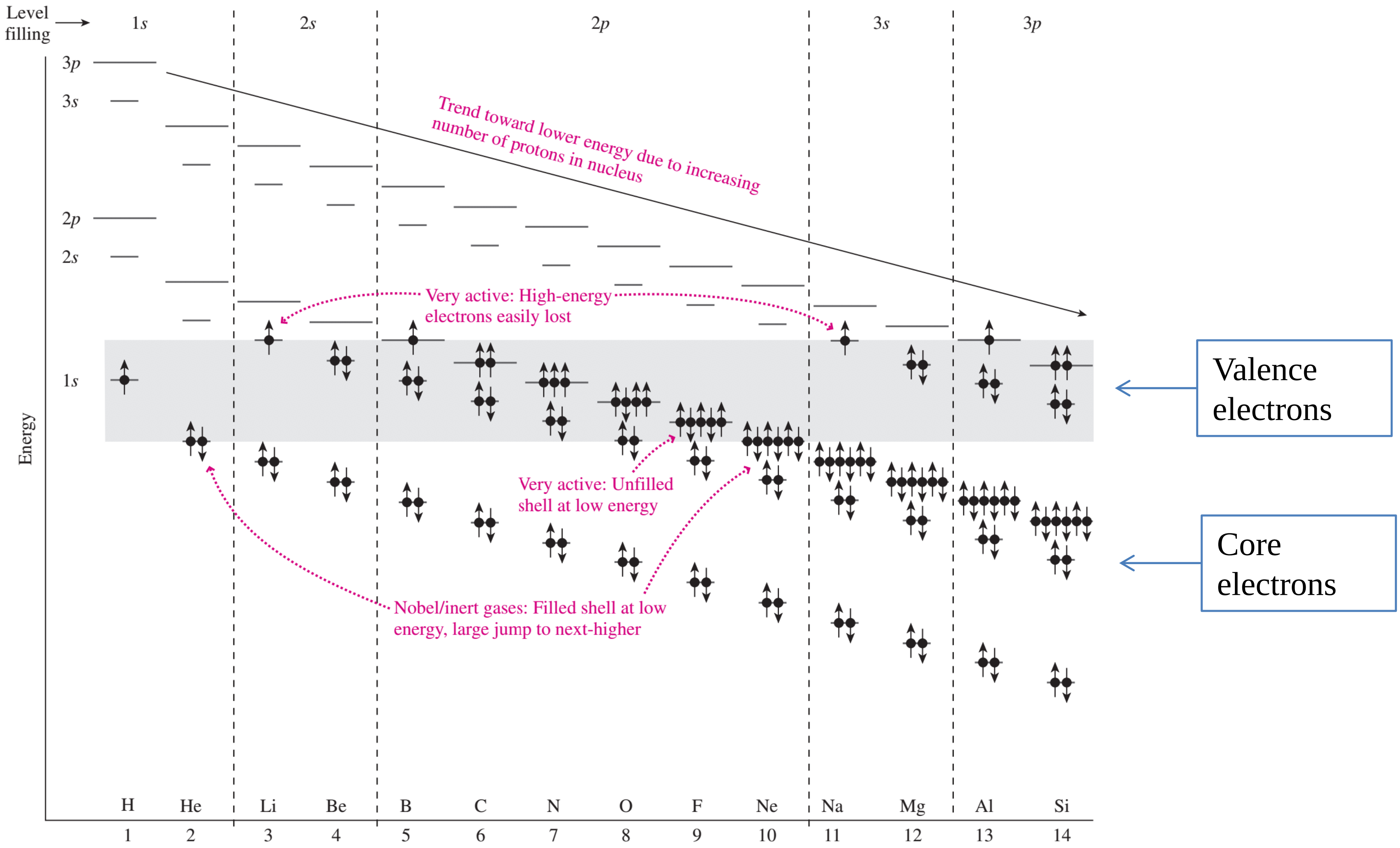
Figure 8.13 The energy ordering of electron states varies with Z.



As the subshells are filled up, the inner subshells tend to be ordered mainly with respect to *n*. This accounts for the apparent anomaly from V (Z = 23: [Ar]$3d^3 4s^2$) to Cr (Z = 24: [Ar]$3d^5 4s^1$).



Trend toward lower energy due to increasing number of protons in nucleus

Very active: High-energy electrons easily lost

Very active: Unfilled shell at low energy

Nobel/inert gases: Filled shell at low energy, large jump to next-higher

Valence electrons

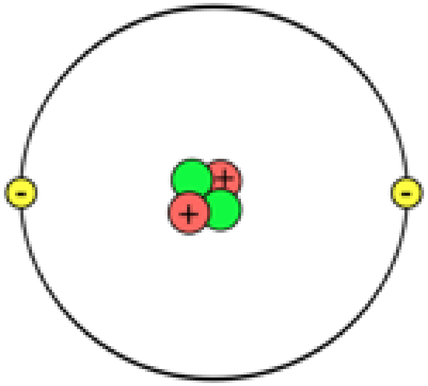
Core electrons

Valence electrons are high in energy and actively involved in the **chemical bonding**. In contrast, core electrons are close to the nucleus and stabilized in energy such that it is chemically inert.

- He: the 1*s* electrons are too tightly bound with large energy so it does not engage in chemical reactions. → Noble gas. 1*s* shell in He is closed.
- Li: high energy electron is easily lost.
- Be: 2*s* subshell is filled. However, since its energy is relatively high, it is still chemically active.
- B, C, N: electrons in 2*p* subshell favors high-spin configuration : Hund's rule (principle of maximum spin multiplicity)– main origin is the reduction in screening of nuclear charges by occupying different orbitals + exchange effects
- O, F, Ne: electron in the downward directions are occupied.
- B-F: 2p subshell is partially occupied and therefore chemically active
- B-N: 2s subshell, albeit filled up, is chemically active → s-p hybridization
- O, F: strongly attracts electrons (O^{2-}, F^{-}) → high electron affinity or electronegativity
- Ionic bonding is formed between Li and F
- Ne is inert or noble gas because closed shell is chemically inert – due to energy and wave function range.
- Chemical behavior of Na and Li (Mg and Be) are similar. (Sizes are bigger.)

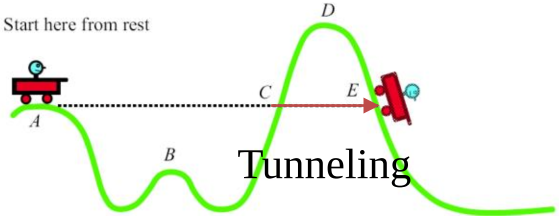
$$\left[-\frac{\hbar^2}{2m}\nabla_1^2-\frac{\hbar^2}{2m}\nabla_2^2-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}+\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\right]\psi(\vec{r}_1,\vec{r}_2)=E\psi(\vec{r}_1,\vec{r}_2)$$

+antisymmetry condition

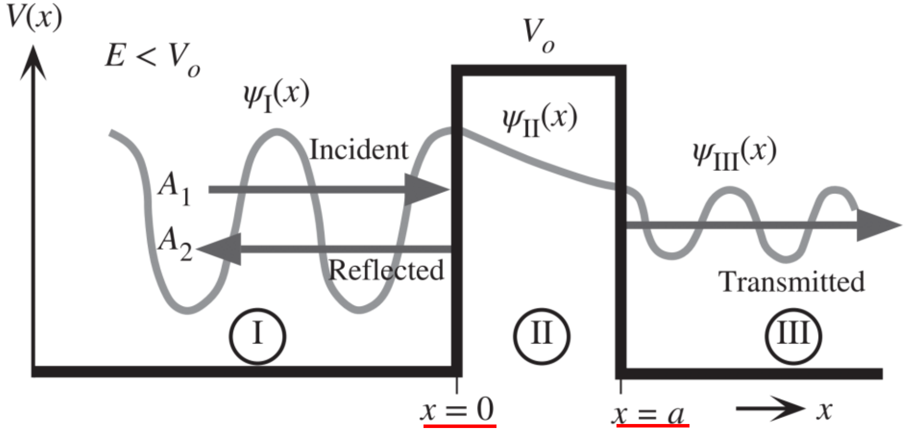


G. Example: Tunneling

Classically, a particle cannot move beyond the turning point. Quantum mechanically, the particle can slightly diffuse through the turning point due to the wave nature, which is called the tunneling phenomena. This can be studied using a square barrier with height of V_0 and particles incident from the left with E (kinetic energy of particles incident from left) is smaller than V_0.



Tunneling



Classically, all the particles are reflected at $x = 0$ because $E < V_0$. In region I & III, potential is zero while it is V_0 in the region II. The Schrödinger equation in each region is as follows:

Region I & III: $-\dfrac{\hbar^2}{2m}\psi'' = E\psi$

Region II: $-\dfrac{\hbar^2}{2m}\psi'' = \left(E - V_0\right)\psi$

$\longrightarrow$

$$\psi_{\text{I}}(x) = A_1 e^{ikx} + A_2 e^{-ikx} \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$\psi_{\text{II}}(x) = B_1 e^{\alpha x} + B_2 e^{-\alpha x} \qquad \alpha^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$\psi_{\text{III}}(x) = C_1 e^{ikx}$$

α = absorption coefficient

In region II, the wave function is a linear combination of exponentially growing and decaying functions. Usually, B_2 is much larger than B_1, and so the wave function decays as $\exp(-\alpha x)$. Here $1/\alpha$ represents the penetration depth of the tunneling particle.

The boundary conditions are ψ and ψ' are continuous at $x = 0$ and $x = a$. These are only four equations so application of the boundary condition gives A_2, B_1, B_2, and C_1 relative to A_1. (A_1 is undetermined because it represents the incident flux.) The transmission coefficient (probability) is the ratio between the incident and transmitted fluxes.

$$T = \frac{j_{\text{transmitted}}}{j_{\text{incident}}} = \frac{|C_1|^2 \frac{\hbar k}{m}}{|A_1|^2 \frac{\hbar k}{m}} = \frac{|C_1|^2}{|A_1|^2} = \frac{1}{1 + D\sinh^2 \alpha a} \quad (D = \frac{V_0^2}{4E(V_0 - E)})$$

Usually, the penetration depth is very short, so $a >> 1/\alpha$ or $\alpha a >> 1$.

$$\sinh \alpha a \approx \frac{1}{2}\exp(\alpha a) \rightarrow T = \frac{16E(V_0 - E)}{V_0^2}\exp(-2\alpha a) \sim \exp(-2\alpha a) = \exp\left(-\frac{\sqrt{8m(V_0 - E)}}{\hbar}a\right)$$

Since the exponential part is very small, T is essentially equal to $\exp(-2\alpha a)$. This expression implies that the transmission probability is highly sensitive many parameters. It increases when mass, a, or $(V_0 - E)$ becomes smaller.

Reflection coefficient: $$R = \frac{j_{\text{reflected}}}{j_{\text{incident}}} = \frac{|A_2|^2 \frac{\hbar k}{m}}{|A_1|^2 \frac{\hbar k}{m}} = \frac{|A_2|^2}{|A_1|^2} = 1 - T$$

$A + R + T = 100\%$

A: absorptance

R: diffused reflectance

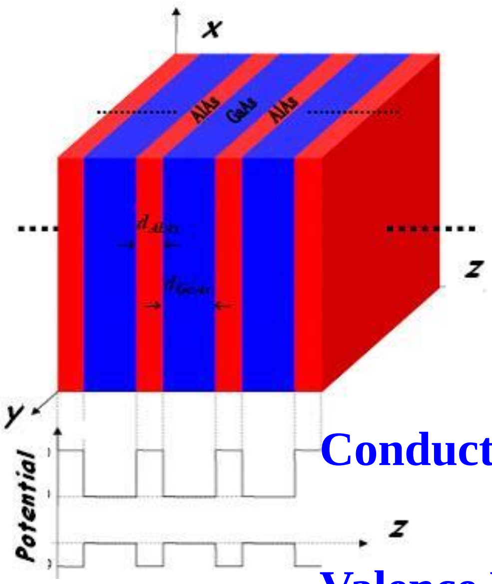
T: transmittance

Examples of Quantum Tunneling

i) Electron spill-over in finite quantum well

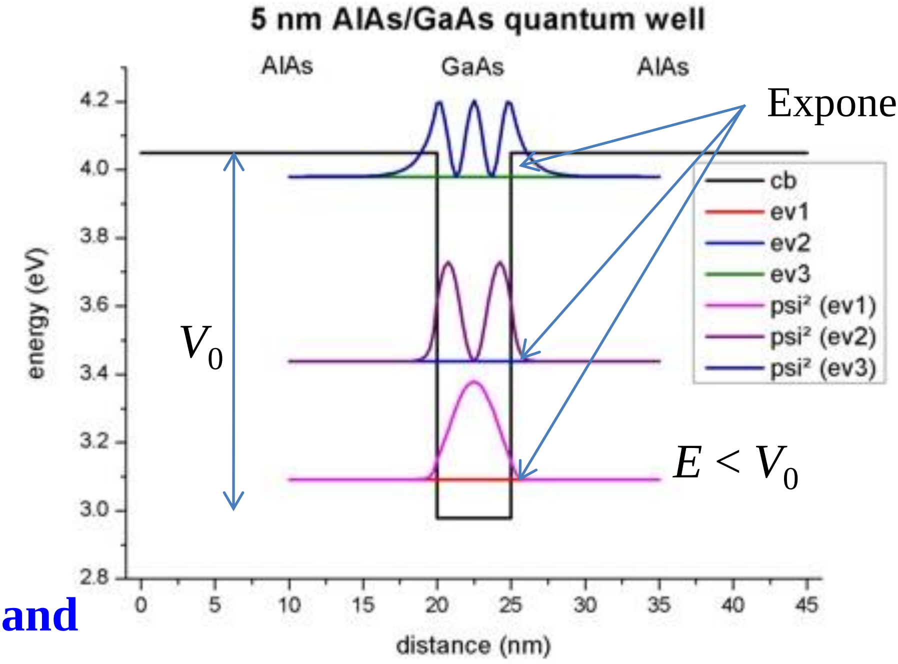
In solid-state, electrons feel the band-gap region as the classically forbidden area with certain energy barrier of V_0.

AlAs/GaAs superlattice



Conduction Band

Valence Band



V_0

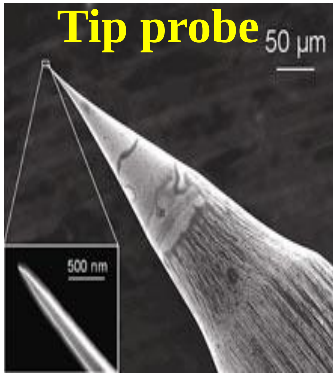
Exponentially decaying tails

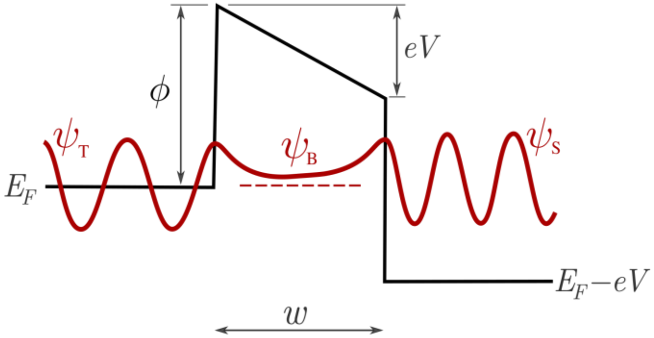
$E < V_0$

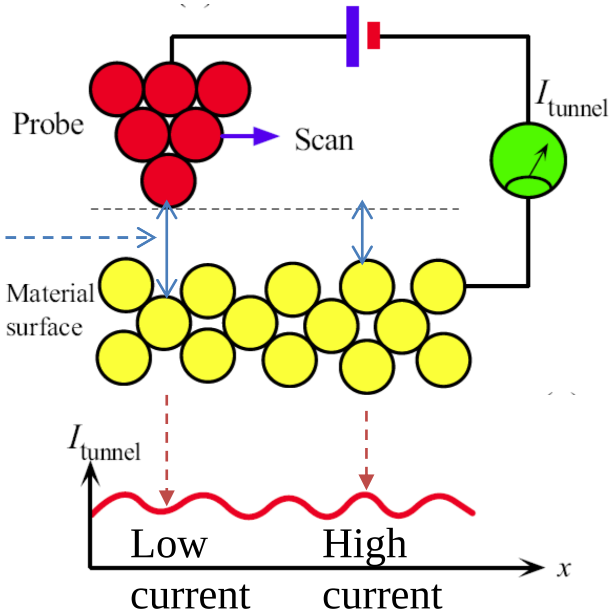
Note that as the energy goes up, the penetration depth increases because $(V_0 - E)$ is smaller.
For E > V_0, unbound state will appear and energy levels are continuous (think about free particles).

ii) Scanning tunneling microscope (STM)

STM tip (tungsten)



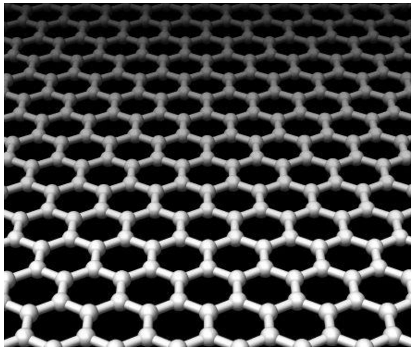




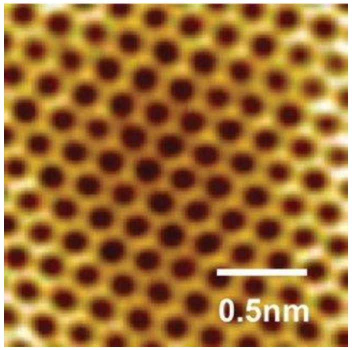
Classically, electrons are confined in the material with certain **work functions**. Therefore, the vacuum space between the tip and the sample is the classically forbidden region. Under the **external bias**, the barrier height is effectively reduced and a small amount of electrons can tunnel to the tip from the material surface, producing weak electric currents. Since the tunneling probability is exponentially sensitive to the tunneling distance, and so the current is high or low depending on whether the tip is on top of an atom or between atoms.

Perturbation (electric field): as small as possible

Ball-and-Stick Model



Experiment

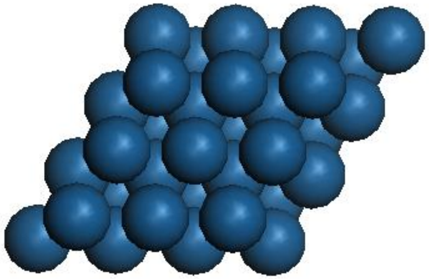


sp^2 bond

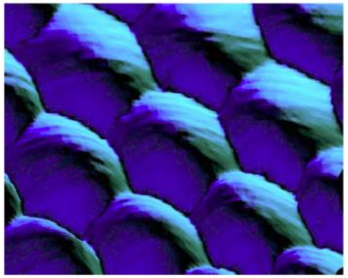
Graphene

STM detects “**electron cloud**” rather than atom itself.

Hard-Sphere Model



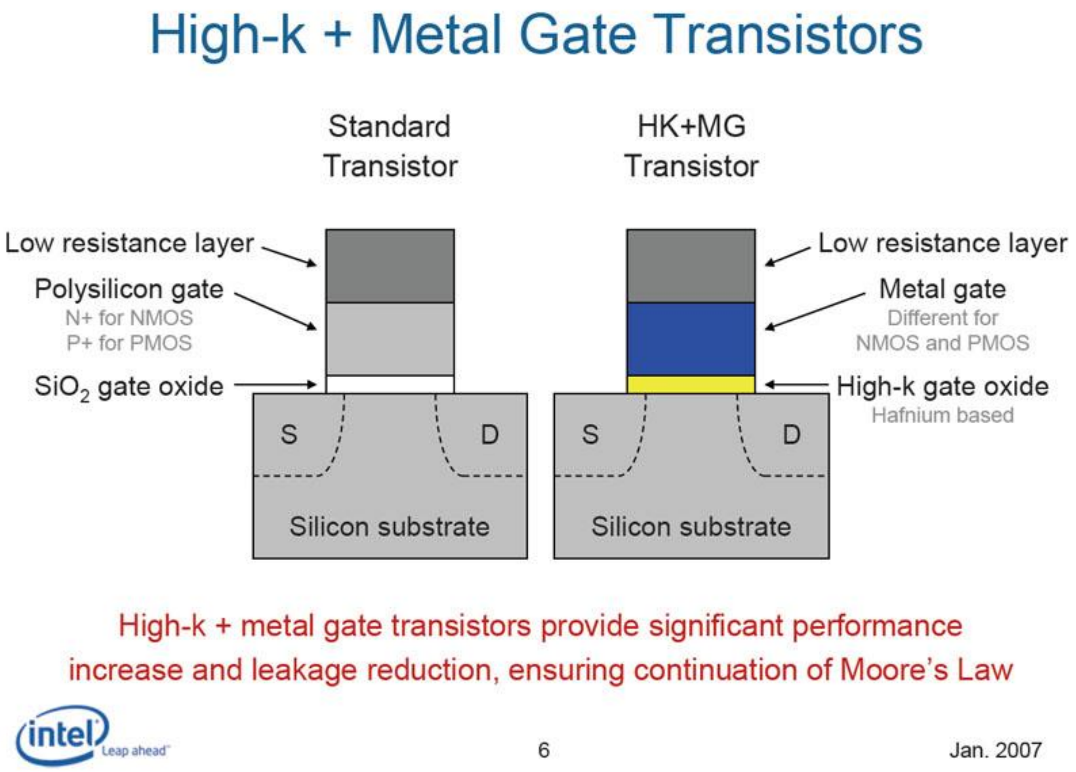
Experiment



Pt(111) surface

iii) Leakage current in nanoscale transistor

The transistor is a critical component in semiconductor devices. The size of the transistor constantly scales down. At the same time, the thickness of gate oxide - an insulator separating the gate electrode and channel layer - also becomes thinner. When the thickness of the oxide is only a few nanometers, the tunneling current through the gate oxide becomes sizeable, which increases power consumption. In order to meet this problem, the industry (pioneered by Intel) changed the material for the gate oxide from SiO_2 to HfO_2 that has high dielectric constant and so can increase the thickness while maintaining the capacitance.


High-k + Metal Gate Transistors

High-k + metal gate transistors provide significant performance increase and leakage reduction, ensuring continuation of Moore's Law

(skip - - -)

H. Mathematical foundation of quantum mechanics

State ------------ Observable ------------ Measurement
↕ ↕ ↕
Wave function Operator Statistical interpretation

Observables (Q) are physical quantities that can be measured. (Ex. momentum, position, energy, etc.) It is usually a function of position and momentum, i.e., $Q(x,p)$. Because of the probabilistic nature, each measurement of an observable for ensemble of identically prepared particles with the same wave function can yield different results. (Ex. In the double-slit experiment, all the electrons are described by single wave function, but each electron marks a spot at different points on the screen, which is equivalent to measuring the position.) We want to formulate the whole procedure within the quantum mechanics. The first step is to define an operator $\hat{Q}$ that corresponds to the observable Q.

- Examples of operator:

Momentum: $\hat{p} = -i\hbar \dfrac{d}{dx}$

Position: $\hat{x} = x$

Kinetic energy: $\mathrm{KE} = \dfrac{p^2}{2m} \rightarrow \hat{T} = \dfrac{1}{2m}\hat{p}^2 = \dfrac{1}{2m}\left(-i\hbar\dfrac{d}{dx}\right)\left(-i\hbar\dfrac{d}{dx}\right) = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}$

Potential energy: $\hat{V} = V(x)$

Energy (Hamiltonian): $H = \hat{T} + \hat{V} = -\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2} + V(x)$

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Mathematical property of operators

i) Each operator has its own set of eigenvalues $\{q_n\}$ and eigenstates $\{\varphi_n\}$ such that

$$\hat{Q}\varphi_n = q_n\varphi_n$$

The eigenvalues are the only values that are observed when Q is measured. The eigenstate φ_n represents a state with the definite value of q_n for the observable Q.

Ex) Momentum eigenstates

$$\hat{p}\psi(x) = p_0\psi(x) \rightarrow -i\hbar\frac{d}{dx}\psi(x) = p_0\psi(x)$$

$$\psi(x) = Ae^{i\frac{p_0}{\hbar}x} = Ae^{ik_0x} \qquad (p_0 = \hbar k_0)$$

Ex) The time-independent Schrödinger equation is the eigenvalue problem of the Hamiltonian. Therefore, $\{\psi_n\}$ in the infinite potential well corresponds to eigenstates of Hamiltonian.

Mathematically, any operator corresponding to a physical observable is Hermitian and its eigenvalues are always real numbers. The collection of eigenvalues $\{q_n\}$ is called the spectrum. There are discrete spectrum and continuous spectrum. For example, momentum of the free particle is a continuous spectrum while the infinite well and harmonic oscillator problems yield discrete energy spectra. In the case of the finite quantum well, there are both discrete ($E < V_0$) and continuous ($E > V_0$) spectra. When eigenstates are bound (free) or localized (extended), they constitute a discrete (continuous) spectra.

ii) Eigenstates are orthonormal to each other

$$\int_{-\infty}^{\infty} \varphi_n^*(x)\varphi_m(x)\,dx = \delta_{n,m}$$

($\delta_{n,m}$: Kronecker delta)

Ex) Eigenstates in infinite quantum well

$$\frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\sin\frac{m\pi x}{L}\,dx = \delta_{n,m}$$

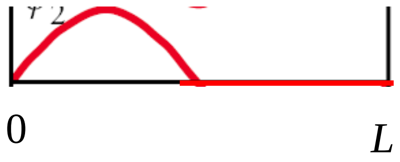
Cf. For continuous spectra, Dirac orthonormality holds: $\int_{-\infty}^{\infty} \varphi_p^*(x)\varphi_q(x)\,dx = \delta(p-q)$

iii) Any wave function can be represented as a linear combination of eigenstates (completeness). Mathematically, eigenstates can expand any function in the Hilbert space.

$$\psi(x) = \sum_n a_n\varphi_n \qquad a_n = \int_{-\infty}^{\infty} \varphi_n^*(x)\psi(x)\,dx$$

$$\int \psi^*\psi = \sum_n\sum_m \int a_n^*\varphi_n^* a_m\varphi_m = \sum_n\sum_m a_n^* a_m \int \varphi_n^*\varphi_m = \sum_n |a_n|^2 = 1$$

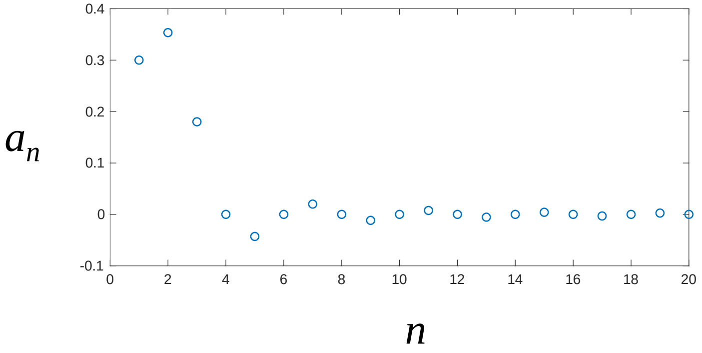
Ex) In the infinite potential, a wave function is as follows:

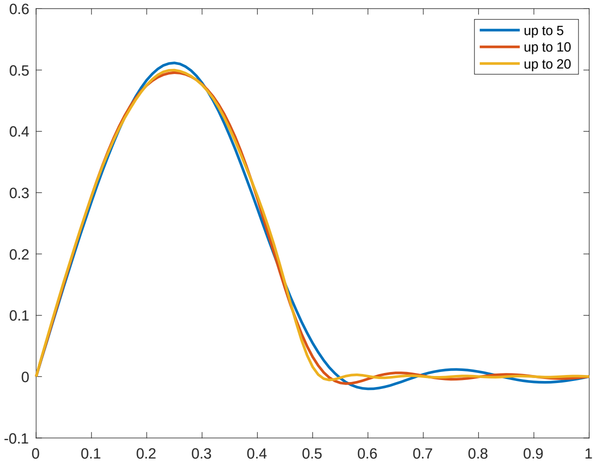


$$\psi(x) = \begin{cases} \sqrt{\frac{4}{L}} \sin\frac{2\pi x}{L} & 0 < x < \frac{L}{2} \\ 0 & \text{otherwise} \end{cases}$$

Expansion with energy eigenstates:

$$\psi(x) = \sum_n a_n \varphi_n \qquad a_n = \int_{-\infty}^{\infty} \varphi_n^*(x)\psi(x)\,dx = \frac{\sqrt{2}}{L}\int_0^{L/2} \sin\frac{n\pi x}{L}\sin\frac{2\pi x}{L}\,dx = \frac{\sqrt{8}}{\pi}\frac{\sin\left(\frac{n\pi}{2}\right)}{4-n^2}$$





Statistical interpretation

For the wave function $\psi(x)$, the expectation value of the measurement is given by:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{Q}\psi(x)\,dx = \langle \psi | \hat{Q} | \psi \rangle$$

Suppose that $\psi(x) = \sum_n a_n \varphi_n$

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi = \sum_n \sum_m \int a_n^* \varphi_n^* \hat{Q} a_m \varphi_m = \sum_n \sum_m a_n^* a_m q_m \int \varphi_n^* \varphi_m = \sum_n q_n |a_n|^2$$

The statistical interpretation: repeated measurements of Q yield one of the eigenvalues, and the probability of observing q_n is $|a_n|^2$.

Therefore, the eigenstate of an operator is the state for which every measurement of the corresponding observable always returns the same eigenvalue. For other states, there is a finite standard deviation or uncertainty (σ_Q or ΔQ) from the probability distribution.

If the measurement returns q_m, the wave function instantly "collapses" to φ_m.

$$\psi(x) = \sum_n a_n \varphi_n \rightarrow \varphi_m$$

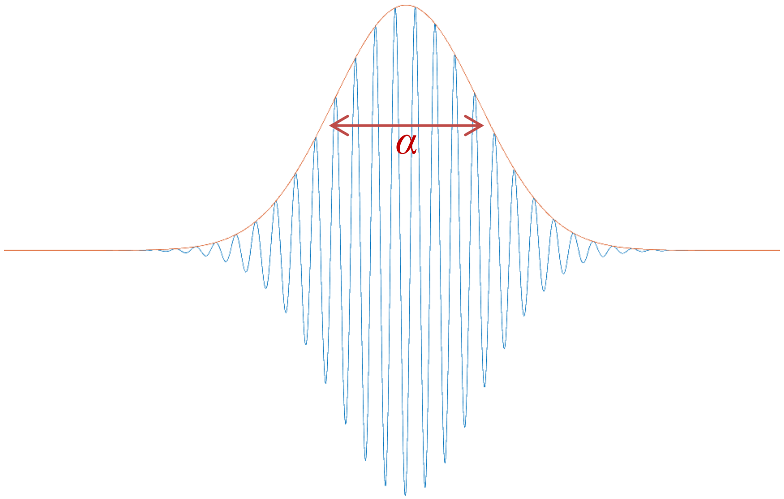
Ex) For the half-wave in the previous example, what is the probability to find the particle in the ground state and 1st excited state?

$$a_1 = \frac{\sqrt{8}}{3p}, \quad a_2 = \frac{\sqrt{2}}{4} \rightarrow p_1 = \frac{8}{9p^2} = 0.09, \quad p_2 = \frac{1}{8} = 0.125$$

Ex) If a wave function in the infinite well is as follows, what is the probability to find the particle in the ground state, 1st excited state, and 2nd excited states? What is the mean energy?

$$y(x) = \frac{1}{\sqrt{2}} y_1(x) + \frac{1}{\sqrt{3}} y_2(x) + \frac{1}{\sqrt{6}} y_3(x)$$

Ex) For the Gaussian wave packet, the position uncertainty is α.



$$\psi(x,0) = \sqrt{\frac{2\pi}{\alpha}}\, e^{ikx} e^{-x^2/2\alpha}$$

Commutation and uncertainty principle

The commutator of two operators $\hat{A}$ and $\hat{B}$ are defined as follows:

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

The two operators are said to commute if their commutator is zero.

Ex) $[x, x^2] = 0$

Ex) $[\hat{x},\hat{p}] = i\hbar$

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

Theorem) When two operators $\hat{A}$ and $\hat{B}$ commute, they have common eigenstates $\{\varphi_n\}$ such that

$$\hat{A}\varphi_n = a_n\varphi_n, \quad \hat{B}\varphi_n = b_n\varphi_n$$

Ex) e^{ikx} in free space is the eigenstate of both momentum and energy operators.

Theorem) When two operators $\hat{A}$ and $\hat{B}$ do not commute, the uncertainties in observables of A and B always satisfy the following relation:

$$\Delta A \Delta B \geq \frac{1}{2}\left|\langle[\hat{A},\hat{B}]\rangle\right|$$

Ex) $\Delta x \Delta p \geq \frac{1}{2}\left|\langle[\hat{x},\hat{p}]\rangle\right| = \frac{\hbar}{2}$

Cf. commutation relation between L^2, L_x, L_y, L_z

(skip)

Operators in three dimensional space

Momentum: $\hat{p} = -i\hbar \dfrac{d}{dx} \quad \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla$

Position: $\hat{x} = x \quad \rightarrow \hat{\mathbf{r}} = x\hat{x} + y\hat{y} + z\hat{z}$

Kinetic energy: $\hat{T} = -\dfrac{\hbar^2}{2m}\nabla^2 = -\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right)$

Potential energy: $\hat{V} = V(\mathbf{r})$

Angular momentum operators:

$$\hat{\mathbf{L}} = -i\hbar(\mathbf{r} \times \nabla)$$

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

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\phi}$$

Ex) Spherical harmonics

$$Y_\ell^{m_\ell}(\theta,\phi) = CP_\ell^{m_\ell}(\cos\theta)e^{im_\ell\phi}$$

$$\hat{L}_z Y_\ell^{m_\ell} = -i\hbar\frac{\partial}{\partial\phi}CP_\ell^{m_\ell}(\cos\theta)e^{im_\ell\phi} = m_\ell\hbar Y_\ell^{m_\ell}$$

Problems from Chap. 1

- 5-22
- 5-25
- 5-26

-Thu/9/3/20