

<< Transport Properties

- compare 3D to 1D involving electric & thermo transport \Rightarrow conductivity

\rightarrow 3D transport laws (Diffusion Laws)

1. electric conduction : Ohm's law

- σ , the transport param,
is electric conductivity

$$\sigma [=] \frac{\text{Siemens}}{\text{m}}$$

$$[S] = \frac{I}{V} = \frac{C^2 \cdot s}{kg \cdot m^2}$$

- wire of cross section A,
length L, w/ transport mix

$$|J_x| = \sigma \frac{dV}{dx}$$

↑ current flux ↑ transport param
(conductivity) ↓ driving force gradient (voltage)

$$G_e = \frac{1}{R} = \frac{I}{V}$$

↑ electric conductance

$$G_e = \sigma \frac{A}{L}$$

- microscopic model based on Boltzmann theory (Drude Model)

$$\sigma = \frac{\lambda e^2 n \bar{c}}{6 k_B T}$$

↑ electric conductivity

$$(G_e = \frac{\lambda e^2 n \bar{c}}{6 k_B T} \frac{A}{L})$$

- 2- free mean path between collisions of e^- at impurities/interfaces
- e - elementary charge $1.6 \times 10^{-19} C$
- n - # density of drifting e^- $[m^{-3}]$

$$\frac{I}{V} = \sigma \frac{A}{L} \Rightarrow \frac{I}{A} = \sigma \frac{V}{L}$$

↑ flux ↑ gradient (uniform V across L)

c - mean electron gas velocity $[m/s]$

$k_B = 1.38 \times 10^{-23} J/K$
Boltzmann constant

T - absolute temp [K]

2. thermal conduction = Fourier Law (Diffusive)

$$|q_x| = k_c \frac{dT}{dx}$$

↑ heat flux ↑ transport param
(thermo conductivity) ↓ driving force gradient (temp)

$$\cdot \text{ microscopic : } k_c = \frac{1}{2} n \bar{c} \lambda k_B$$

$$\cdot \text{ thermal conductance : } G_{th} = k_c \frac{A}{L}$$

(length scale dependant)

→ 1D Transport

- In 1D, the conductance is length independent

$$G_e = \frac{2e^2}{h} N_e$$

N_e - # of electronic states at Fermi level
(E_F - Fermi energy)

h - Plank's constant
 $6.62 \times 10^{-34} \text{ J}\cdot\text{s}$



$$G_{\text{th}} = \frac{\pi^2 k_B^2 T}{3 h} N_{\text{ph}}$$

N_{ph} - # photon

- both 1D equation of transport does not depend on dimension (length)

<< Miniaturization effect on Surface Energy and Strain

- The surface enclosing the volume imposes a stress (force/area = pressure) on the condensed system

$$f = \gamma + \frac{\partial \gamma}{\partial \epsilon}$$

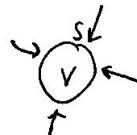
f - surface stress

γ - surface energy per unit area [J/m^2] (for solid)

surface tension [F/m] (for liquid)

ϵ - strain ($\frac{\Delta V}{V}, \frac{\Delta L}{L}$, dimensionless)

e_{coh} - cohesion energy / area



$$\gamma = e_{\text{coh}} \left| \frac{\text{surface atoms}}{\text{bulk atoms}} - \frac{\text{bulk atoms}}{\text{inside}} \right|$$

- energy diff of outside & inside atom

- outside surface $\uparrow E$, inside bulk $\downarrow E$ (happy)

$\frac{\partial \gamma}{\partial \epsilon}$ - stored mechanical energy inside the solid

(for liquid, $\frac{\partial \gamma}{\partial \epsilon} = 0$, cannot store mechanical energy)

- Consider elastic & isotropic solid, we can express the elastic properties with bulk modulus K

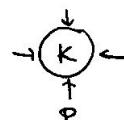
$$\epsilon = -\frac{1}{3K} P$$

P - isotropic pressure

[Pa]

$$P = \frac{4f}{D}$$

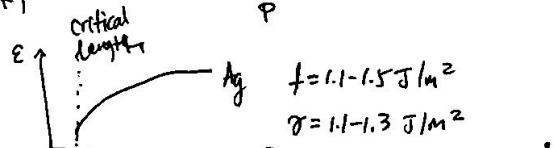
K - bulk modulus
(resist)



$$\epsilon = -\frac{4}{3} \frac{f}{K} \frac{1}{D} \propto \frac{1}{D}$$

ϵ - strain

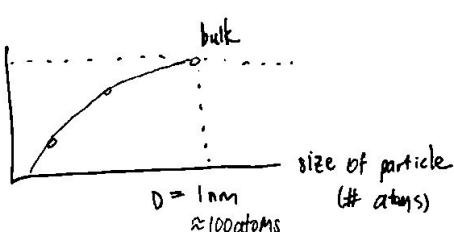
scaling law



- Metal particles smaller than 1nm dimension
⇒ change in crystal structure

e.g. Bulk Ag - FCC structure in 3D
<1nm Ag - truncated octahedron/
icosahedral structure

} change in crystal structure
Scaling law applies



2 April 2021

Ch2 First Step towards Quantum Mechanics - Atomistic Theory of Matter

NME 220

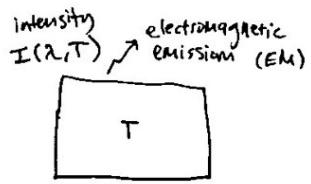
<< Intro to Quantum Mechanics

- All bodies of finite temperature emit light at with a particular intensity depending on their temperature and wavelength $I(\lambda, T)$

- How does the EM radiation interact with matter?

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-
-
-

• To answer the question, quantum mechanics & quantum field theory was born



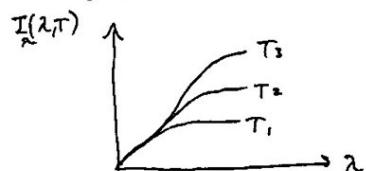
5 April 2021

14 Blackbody Radiation, Rayleigh - Jeans

NME 220

<< Intro to Quantum Mechanics

- $I(\lambda, T)$ [W/m²] - emission rate of EM radiation of hot body per unit area
- typically expressed per unit wavelength $I_\lambda(\lambda, T)$
- An "ideal" radiating body is needed $[W/m^2 \cdot \frac{1}{nm}]$ to develop a theory
- "ideal" - emits radiation at thermal equilibrium
 \Rightarrow "black" - body radiator



- In labs (Wien, Stefan, Planck) - study blackbody cavities
- Investigate irradiation spectrum $I_\lambda(\lambda)$

Applications

- Stealth (radar-absorbent) technology
- solar energy collectors
- efficient infrared heaters for space applications
- antireflective coatings in camera - reduce stray lights

- Wien's displacement law:

$$\lambda_{\max} = \frac{hc}{5k_B T}$$

$$\lambda_{\max, T} = \text{constant} = 2.9 \times 10^{-3} \text{ m}\cdot\text{K}$$

- Numerically integrate over $I_\lambda(\lambda)$, we get irradiation power

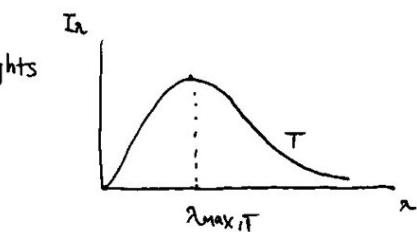
$$I = \int_0^\infty I_\lambda d\lambda = \epsilon \sigma T^4$$

Stefan-Boltzmann law

(radiation power - total radiant heat energy per second and area)

$\epsilon = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$ Stefan-Boltzmann constant

$\epsilon = \text{emissivity}$ ($\epsilon=1$ for black-body)



$$P = IA$$

<< Intro to Quantum Mechanics

• Derive expression of $I_\lambda(\lambda) = ?$

- first attempt : Rayleigh & Jeans (followed by Planck's famous radiation equation, a stepping stone to quantum mechanics)
- Assume all EM oscillations (modes) in the blackbody cavity possess the same average energy $\langle E \rangle$ for given temp T
- N - number density of oscillations (photon modes)

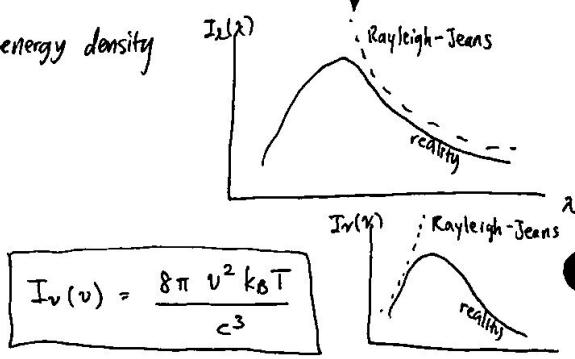
• $\frac{dN}{d\lambda}$ - number density of oscillations per unit wavelength

• $\mu_\lambda(\lambda) = \frac{dN}{d\lambda} \langle E \rangle$ - spectral energy density

$$\Rightarrow I_\lambda(\lambda) = \frac{\mu_\lambda(\lambda)}{c}$$

• $\langle E \rangle = \frac{1}{2} k_B T$

$$\Rightarrow I_\lambda(\lambda) = \frac{2\pi c k_B T}{\lambda^4}$$



Rayleigh & Jean's law for spectral radiation

• Ultraviolet catastrophe - Rayleigh & Jean's law fails at ultraviolet & $\lambda \downarrow, \nu \uparrow$

<< Planck's law

- Based on trial-and-error approach. Max Planck expressed the average mode energy of photons in the blackbody cavity statistically as:

$$\langle E \rangle = \frac{hv}{e^{hv/k_B T} - 1}$$

$\cdot h = 6.626 \times 10^{-34}$ J·s, Planck constant

$\cdot v$ = frequency, [Hz]

$\cdot k_B$ = Boltzmann constant

$\cdot T$ = absolute temp. [K]

- The spectral energy density:

$$u_\lambda(\lambda) = \frac{dN}{d\lambda} \langle E \rangle$$

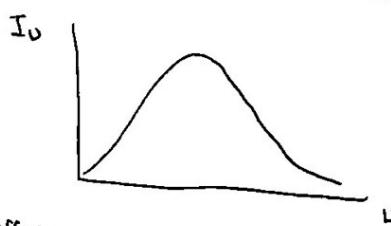
$$u_v(v) = \frac{dN}{dv} \langle E \rangle \quad \left(\frac{dN}{dv} = \frac{8\pi v^3}{c^3} \right)$$

$$u_v(v) = \frac{8\pi hv^3}{c^3} \cdot \frac{1}{e^{hv/k_B T} - 1}$$

- Integrate $u_v(v)$, we get radiation intensity:

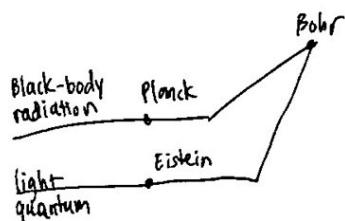
$$\begin{aligned} I(v) &= \frac{c}{4} u(v) \\ &= \frac{c}{4} \int_0^\infty u_v(v) dv \\ &= \underbrace{\frac{2\pi^5 k_B^4}{15 c^2 h^3}}_{\text{Stefan-Boltzmann constant}} T^4 \propto T^4 \end{aligned}$$

- Planck could confirm the Stefan-Boltzmann law



$$u_\lambda(\lambda) = \frac{8\pi hc}{\lambda^5} \left(\frac{1}{e^{hc/\lambda k_B T} - 1} \right)$$

<< Photoelectric Effect



- Planck's effect lacks atomistic description of the energy exchange

- Then comes Hertz Experiment

« Photoelectric Effect (cont.)

• Hertz experiment (1887)

- charge exchange (discharge) increases between electrodes if the negative electrode is exposed to UV light.

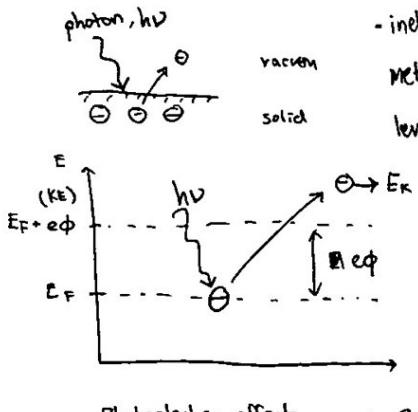
- Other experiments (Lenard 1902) showed that metal electrodes become positive when exposed to UV light

⇒ radiation caused emission of electrons

- Radiation causes electron emission brings the question if it is the light intensity alone that matters.

- In 1905, Einstein postulated that both intensity & frequency matter

• He recognized there's a minimum energy necessary, as well as a certain frequency.
 ⇒ photoelectric effect



- inelastic scattering of photons (light quantum) on metals that raise electrons from the Fermi energy level, E_F , to the vacuum energy level

$$E_k = h\nu - e\phi \geq 0 \quad \text{free moving } e^- \text{ in vacuum}$$

• E_k - kinetic energy in vacuum

• $h\nu$ - photon energy

• $e\phi$ - work function

Photoelectric effect $E = h\nu \geq e\phi$	E_F	$\frac{h\nu}{e\phi} \geq 1$ $h\nu \geq e\phi$	$\frac{h\nu_2}{e\phi} \geq 2$ $h\nu_2 \geq 2e\phi$	$\frac{h\nu_1}{e\phi} \geq 1$ $h\nu_1 \geq e\phi$ $h\nu_1 > e\phi > h\nu_2$
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- If $h\nu < e\phi$, the e^- can only be activated into a higher electronic state, which will decay over time back to the ground state (E_F), emitting a photon.

- electron energy - electron volt $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J} = 96.5 \text{ kJ/mol}$

»» Wave - Particle Duality

- special relativity gives mass-energy equivalence

- $E=mc^2$, rest mass energy

- photon - quantum particle of light

- massless particle

- $E=h\nu$ (Einstein photoelectric effect)

- linear momentum p of photon

- $E=pc = h\nu$

- $p_{\text{photon}} = \frac{h\nu}{c} = \frac{h}{\lambda}$

\downarrow
 $c=\lambda\nu$

classically with mass,

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

$$p = \sqrt{2mE}$$

- By assigning the photon a momentum, light was treated as it were a particle.

→ de Broglie duality

- rest mass energy of an e^-

- $E_e = mc^2 = 8.2 \times 10^{-14} \text{ J} \times \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} = 0.51 \times 10^6 \text{ eV} = 0.51 \text{ MeV}$

- $m_e = 9.1 \times 10^{-31} \text{ kg}$

- $c = 3 \times 10^8 \text{ m/s}$

- wavelength of an e^- with KE

- $E_k = \frac{p^2}{2m_e}$
- $p = \frac{h}{\lambda_e}$

$\Rightarrow \boxed{\lambda_e = \frac{h}{\sqrt{2m_e E_k}}} = 1.23 \text{ nm}$

- $h = 6.6 \times 10^{-34} \text{ Js}$ Planck constant

- $= 4.13 \times 10^{-15} \text{ eV.s}$

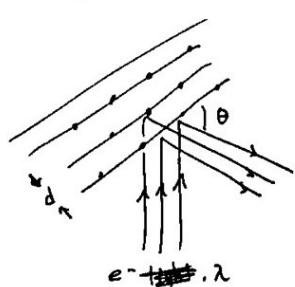
- An e^- in 1V electric field has a KE of $E_k = qV = e \cdot V = 1.6 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

→ Davisson - Germer Experiment (1927)

- in crystal, with atoms

- to get constructive interference

$$\boxed{n\lambda = 2d \sin \theta}$$



• Bragg's law

$$\boxed{\frac{1}{\lambda} = \frac{n}{2d \sin \theta}}$$

• e^- scatters elastically at a crystal exhibit scattering intensity that is similar to wave scattering at surface (diffraction)
⇒ wave characteristic

• Bragg - De Broglie relation

$$\boxed{\frac{1}{\lambda} = \left\{ \frac{n}{2d \sin \theta} \right.}$$

$$\left. \frac{p}{h}, p = \sqrt{2mE} \right.$$

Wave-Particle Duality

$$\text{EX} \quad \frac{1}{\lambda} = \frac{n}{2d \sin \theta} = \frac{\sqrt{2mE}}{\hbar} = \frac{\sqrt{mE}}{\hbar}, E = \text{eV}$$

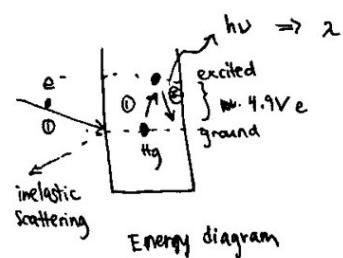
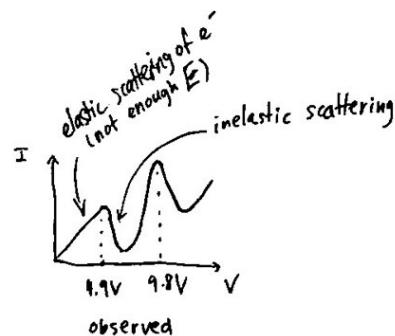
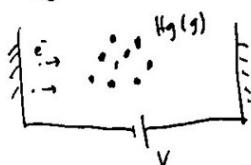
$$e = 1.6 \times 10^{-19} \text{ C}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$\hbar = 6.6 \times 10^{-34} \text{ J-S}$$

→ Frank-Hertz Experiment

gas Hg



compare

Davison-Germer - atoms in lattice, elastic scattering of e^-
Frank-Hertz - free atom, inelastic scattering of e^-

Ch 3 Atom Model & Wave Equation

Early Atom Model

~1900, Thompson recognized e^- as a particle with a mass $\sim \frac{1}{1000}$ of H with constant $\frac{\text{charge}}{\text{mass}}$ ratio $\frac{e}{m}$

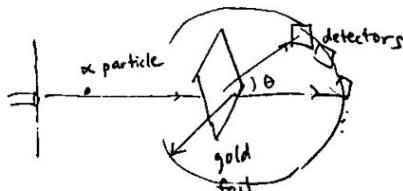
Thompson Model:
(Plum-Pudding)



- need \oplus to balance \ominus
- atom electrically neutral

1911, Ernest Rutherford disproves the model, observing that

- atom is mostly empty space - lots of α particle undeflected
- the nucleus is positively charged in the center, small - α particle deflected small angle
- most mass of the atom is in the nucleus - α particle travels back

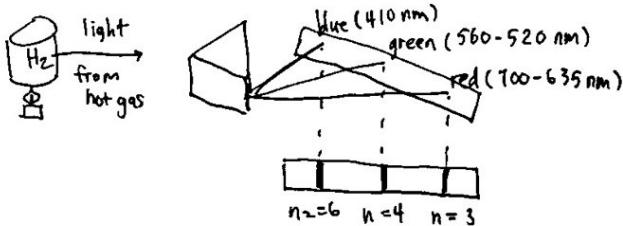


disproves Plum-Pudding Model

states that atom consists of a (+) charged small nucleus. e^- are enveloping the nucleus at relative large distance

<< Hydrogen Emission Spectrum

- 1885-1887 - Johann Balmer & Johannes Rydberg formulated a relationship between the discrete spectral lines from gases



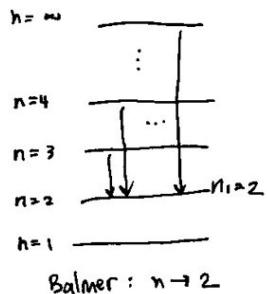
Balmer : $\frac{1}{\lambda} \propto \frac{1}{2^2} - \frac{1}{n^2} \quad (n > 2)$

Lyman lines : $n_1 = 1$ ultraviolet region

Paschen lines : $n_2 = 3$ infrared region

Rydberg : $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

Balmer's formula
(visible light region)



$$n_2 > n_1, \\ n_1 = 1, 2, \dots$$

$$R_H = 1.097 \times 10^7 \text{ m}^{-1}$$

Ex Find frequency range of Lyman series

Lyman : $n_1 = 1$ $n_2 = 2$:
 $n_2 = 2$ (smallest) $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_H \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 0.75 R_H$
 \vdots $n_2 = \infty$:
 $n_2 = \infty$ (largest) $\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - 0 \right) = R_H$

frequency range:

$$\nu = \frac{c}{\lambda} = \begin{cases} 0.75 R_H c = 2.48 \text{ fHz} \\ 1 R_H c = 3.3 \text{ fHz} \\ \sim 3.3 \times 10^{15} \text{ Hz} = 3.3 \text{ fHz} \end{cases}$$

<< Bohr's Model of Atom

- 1913 - Bohr postulated a shell model of atom (hydrogen atom)

- e⁻ travel on distinct and separated stationary orbit (shells) around nucleus

→ Model

Quantized condition

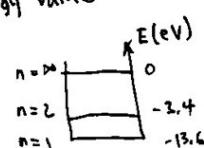
(1) $2\pi r = n \lambda \quad , \quad n = 1, 2, \dots$

- λ - e⁻ wavelength
- r - radius of stable orbital



- (2) Each orbital (shell) is characterized by well-defined energy value

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$$



<< Bohr's Model of atom (cont.)

• Quantization conditions

- (3) Observed spectroscopic EM emission is caused by discrete jumps of e^- from higher stationary states E_j to lower energy state E_i ($i < j$)

$$h\nu = E_{n_j} - E_{n_i}$$

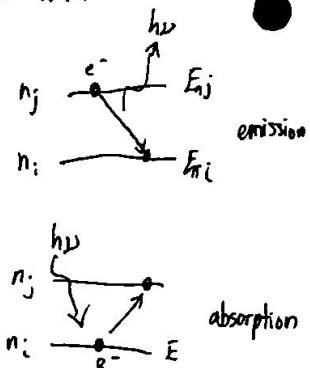
Absorption of EM radiation yields to e^- activation from E_i to E_j

$$h\nu_{j \rightarrow i} = \Delta E = E_j - E_i = -\frac{m e^4}{8 \pi^2 \hbar^3 c} \left(\frac{1}{n_j^2} - \frac{1}{n_i^2} \right)$$

$$\text{ground state: } E_1 = -13.6 \text{ eV}$$

- (4) B^- does not radiate

• (unphysical)



14 April 2021

L8

Wave-Particle Interference & Probability

NME 220

<< Bohr's Model of Atom

• Bohr \rightarrow Rydberg constant

$$\frac{1}{\lambda} = \underbrace{\frac{-m e^4}{8 \pi^2 \hbar^3 c}}_{R_\infty} \left(\frac{1}{n_j^2} - \frac{1}{n_i^2} \right)$$

$$R_\infty \equiv 1.09737 \times 10^7 \text{ m}^{-1} \rightarrow \text{assumed proton has } \infty \text{ mass compared to } e^-$$

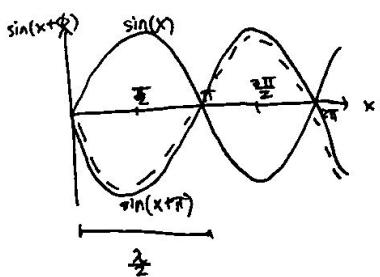
• Dropping the assumption that $m_p = \infty$, we need reduced mass μ .
(proton mass)

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

$$\Rightarrow R_H = R_\infty \frac{\mu}{m_e} = 1.09678 \times 10^7 \text{ m}^{-1}, \text{ confirming Rydberg}$$

<< Wave & Particle Interferences & Probability

\rightarrow Review of Wave & Sine functions

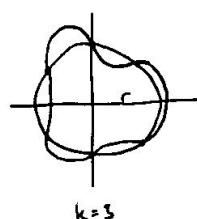


• $\sin(\pi + x)$ is out of phase with $\sin(x)$

$$\Leftrightarrow \sin(\pi + x) + \sin(x) = 0$$

\Leftrightarrow destructive interference

• Moving Wave: $x(x,t) = A \sin(kx - \omega t + \phi)$
amplitude \uparrow \uparrow max amplitude



wave number

$$k = \frac{2\pi}{\lambda}$$

$$v = \frac{dk}{dt} = cor \quad \leftarrow \text{angular velocity}$$

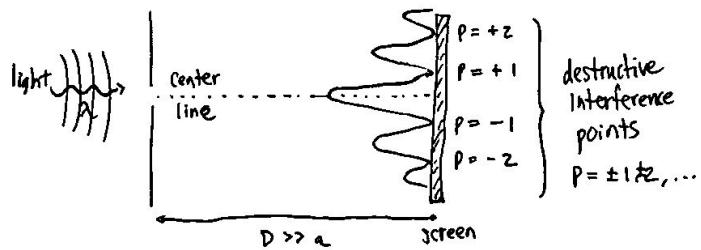
$$\omega = 2\pi v = \frac{2\pi}{\lambda} c = kc \quad \leftarrow \text{angular frequency}$$

$$\omega(k) = ck \quad \leftarrow \text{linear EM wave dispersion relation}$$

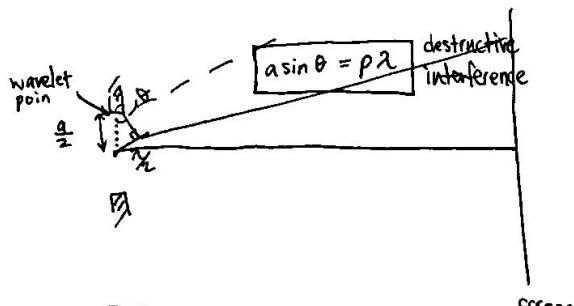
<-- Wave-Particle Interference & Probability (cont.)

→ Single Slit Interference

- Light passes through a slit with narrow width a ($a \sim \lambda$) observed on opposite screen (distance $D \gg a$)



- magnification of the slit for destructive interference



$$\text{as} \sin \theta = \begin{cases} p\lambda \\ (p + \frac{1}{2})\lambda \end{cases}$$

destructive
constructive

- Location of destructive interference

$$y_1 \approx p \frac{\lambda}{a} D$$

- $p = \pm 1, \pm 2, \dots$ dest. interf. points
- a - slit size
- D - slit - screen distance

→ Dispersion Relations

- 1D harmonic function (wave)

$$u(x,t) = A \sin(kx - \omega t + \phi)$$

- EM wave

$$\omega(k) = ck$$

EM wave has linear relationship $\left\{ \begin{array}{l} \omega - \text{angular velocity} \\ c - \text{speed of light} \\ k - \text{wave number} \end{array} \right\}$ dispersion relation if a wave

- Particle Wave

$$E = h\nu = \frac{p^2}{2m}$$

$$\boxed{p = \frac{h}{\lambda} = \frac{\tau k}{\lambda}}$$

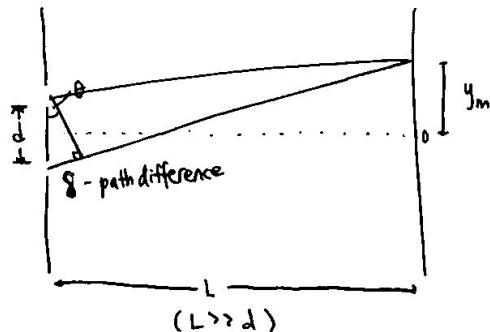
$\lambda = \frac{2\pi}{k}, \tau = \frac{h}{\lambda\tau}$

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

$$\Rightarrow \boxed{\omega(k) = \frac{\hbar^2}{2m} k^2}$$

dispersion relation of particle
quadratic
group velocity & phase velocity

... Wave-Particle Interference
→ Double slit interference



$$\text{path diff: } \delta = d \sin \theta$$

constructive interference:

$$\boxed{\delta = m\lambda = d \sin \theta}, m = 0, \pm 1, \pm 2, \dots$$

For $y_m \ll L$,

$$\sin \theta \approx \tan \theta = \frac{y_m}{L}$$

$$\Rightarrow \boxed{\delta \approx d \frac{y_m}{L}}$$

→ Particle Scattering through Double Slit

EM Wave → particle

slit 1: I_1 intensities

slit 2: I_2

macroscopic classical particle: $I = I_1 + I_2$

quantum particle: $I = I_1 + I_2 + 2 \sqrt{I_1 I_2} \cos \delta$, $\delta = \phi_1 - \phi_2$

We refer intensity I as the probability of finding a particle

$$\boxed{P \equiv I = A^2} \quad . A \text{ is amplitude of wave}$$

Screen maxima

$$\boxed{y_{m,\max} = \frac{m\lambda L}{d}}$$

→ Heisenberg's Uncertainty Principle

without looking through where a particle goes: $I = I_1 + I_2 + 2 \sqrt{I_1 I_2} \cos \delta$

with looking through where a particle goes: $I = I_1 + I_2$

location change Δx

momentum change Δp

$$\boxed{\Delta x \Delta p > \frac{\hbar}{2}}$$

$$\boxed{\Delta E \Delta t > \frac{\hbar}{2}}$$

Heisenberg uncertainty principle

$$\hbar = \frac{h}{2\pi}$$

interference
no interference.

→ Macroscopicity

macroscopicity - quality of a state to be macroscopic
(μ)

↔ lifespan τ_p of a particle to exhibit quantum superposition (coherence)
(ability to exist at multiple spaces at the same time)

$$10^{-14} \text{ s} \propto \frac{\tau_p}{\tau_e}$$

proton
electron

[Ex] a molecule of 2000 atoms shows $\mu = 14.1 \rightarrow \frac{\tau_p}{\tau_e} = 4 \times 10^6$.

Assume $\tau_p = 1 \text{ s}$, then $\tau_e = 4 \times 10^{-7} \text{ yr}$

« QM Wave Equation by Schrodinger

- We describe e^- as a 1D wave \rightarrow wave function
- Assume free e^- , no gravitational, electrostatic field, etc.

$$\psi(x,t) = \psi_0 e^{i(kx - \omega t)}, \text{ where } \psi_0 = A e^{i\phi} \text{ is constant}$$

- $\psi(x,t)$ is called a state function of the electron

- Probability of finding e^- in a given location x

$$P = |\psi(x)|^2$$

A - max amplitude

ϕ - phase

$k = \frac{2\pi}{\lambda}$ wave number

$\omega = 2\pi\nu$ angular frequency

ν = natural frequency

1 Space-differential of $\psi(x,t)$

$$\frac{\partial}{\partial x} \psi(x,t) = i k_x \psi(x,t)$$

$$k_x = \frac{2\pi}{\lambda}, \quad \lambda = \frac{h}{p_x}$$

$$\frac{\partial^2}{\partial x^2} \psi(x,t) = i \frac{p_x}{\hbar} \psi(x,t)$$

$$\Rightarrow \hat{p}_x = \frac{p_x}{\hbar}$$

$$\underbrace{-i\hbar \frac{\partial}{\partial x}}_{\text{operator}} \underbrace{\psi(x,t)}_{\text{eigenfunction}} = \underbrace{p_x \psi(x,t)}_{\text{eigenfunction}}$$

\hat{p}_x eigenvalue

$$\hat{p}_x \equiv -i\hbar \frac{\partial}{\partial x}$$

linear momentum differential operator

- The eigenvalue p_x is a physical observable

- For a free particle, p_x (the eig.value) can have any value \Rightarrow continuous
- under constraints, the continuous condition could be false, being discrete

2 time differential of $\psi(x,t)$

$$\frac{\partial}{\partial t} \psi(x,t) = -i\omega \psi(x,t)$$

$$\omega = 2\pi\nu \quad \Rightarrow \quad \omega = \frac{E}{\hbar}$$

$$\frac{\partial}{\partial t} \psi(x,t) = -i\frac{E}{\hbar} \psi(x,t)$$

$$\underbrace{-i\hbar \frac{\partial}{\partial t}}_{\text{time operator}} \underbrace{\psi(x,t)}_{\text{energy eigenvalue (continuous)}} = E \psi(x,t)$$

$$\hat{t} = -i\hbar \frac{\partial}{\partial t} \quad \text{time operator}$$

$$E = \frac{p_x^2}{2m} \quad (\text{free particle})$$

$$E \psi(x,t) = \frac{p_x^2}{2m} \psi(x,t)$$

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

time-dependent quantum mechanical wave equation for a free particle

- We consider now the particle to be constrained by a potential (e.g. e^- in Coulombic field)

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(x,t) = \underbrace{\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right)}_{\hat{H}} \psi(x,t)}$$

time dependent QM wave equation by Schrodinger (Schrodinger equation)

- Time-independent expression:

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

Hamiltonian operator \hat{H} eigenvalue energy

$$\hat{H} \psi(x,t) = E \psi(x,t)$$

time-independent Schrodinger equation

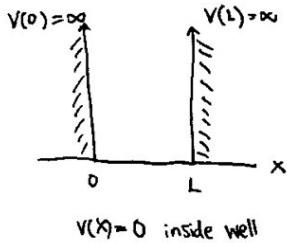
19 April 2021

L10

Particle in ∞ 1D Box

NME 220

<< Particle in Infinite 1D Box



$$V(x) = \begin{cases} 0 & x \in (0, L) \\ \infty & x \in [0, 0] \cup [L, \infty) \end{cases}$$

"Free" e^- motion within box

e^- energy is $E \ll V(x) \Big|_{x=0, L}$

We express e^- by its wave function $\psi(x) = \psi_0 e^{ikx}$

By time-independent Schrodinger equation (SE):

inside box:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E \psi(x)$$

$$\boxed{\frac{d^2 \psi}{dx^2} + k^2 \psi = 0}$$

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

Rewrite with:

$$\lambda = \frac{h}{p}, \quad k = \frac{2\pi}{\lambda}$$

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

has two partial orthogonal soln:

$$\psi_1(x) = e^{ikx}$$

$$\psi_2(x) = e^{-ikx}$$

general soln:

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

2 boundary conditions:

$$\psi(x) = 0 \quad \text{at} \quad \begin{cases} x=0 \\ x=L \end{cases}$$

no penetration condition:

(no probability outside the well, so at boundary should have $\psi(x)=0$)

general soln:

$$\boxed{\psi(x) = C \sin(kx)}$$

wave function of particle in ∞ 1D box

k-wave number

19 April 2020

1D
Particle in ∞ 1D Box
(cont.)Particle in ∞ 1D Box

NME2E0

$$\Psi(L) = C \sin(kL) = 0$$

$\Rightarrow \sin(kL) = 0$ for nontrivial soln

$$kL = n\pi, \quad n = 1, 2, 3, \dots \quad (n=0 \text{ is trivial})$$

$$k_n = \frac{n\pi}{L} \quad \text{discrete wave number, quantized.}$$

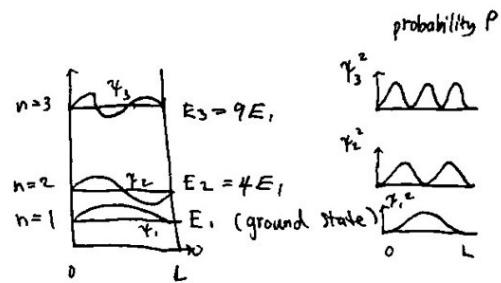
so $p_n = \hbar k_n = \frac{n\pi\hbar}{L}$ quantized momentum

$$E_n = \frac{p_n^2}{2m} = \frac{(n\pi\hbar)^2}{2mL^2}$$
 quantized energy

$$E_1 = \frac{(\pi\hbar)^2}{2mL^2}$$
 ground state

$$E_n = \frac{1}{2m} \left(\frac{\pi\hbar}{L} \right)^2 n^2 = \frac{1}{8m} \left(\frac{\hbar}{L} \right) n^2 \propto n^2$$

$$E_n = E_1 n^2$$



- probability of finding electron of energy E_x at location x :

$$P(x) = |\Psi(x)|^2 \quad ; \quad \Psi(x) = C \sin(kx)$$

- total probability of finding it in the box is 1:

$$P(x) = 1 = \int_0^L P(x) dx = |C|^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx$$

$$1 = |C|^2 \frac{L}{2}$$

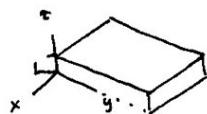
$$C = \sqrt{\frac{2}{L}}$$

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi x}{L} \right) \quad n = 1, 2, 3, \dots$$

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

<< Quantum Well

→ thin film (constrained in 1D)



- within the plane ($x-y$) the electron exhibits a constrained energy spectrum

$$E_{x,y} = \frac{\hbar^2 k_{x,y}^2}{2m}$$

(continuous)

- normal to the film surface (z -dir), e^- exhibits a discrete energy spectrum

- selection of e^- regarding their wavelength
- potential applications
- laser technology

$$E_{n_z} = \frac{\hbar^2 \pi^2}{2mL^2} n_z^2$$

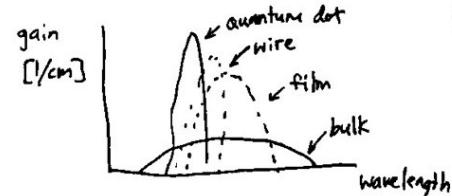
1D box

- $n_z = 1, 2, 3, \dots$
- L - film thickness

- "Gain" material that amplifies the input signal via stimulated emission process

> active laser medium = gain medium

- semiconductors: GaAs, InGAs, GaN
- crystals
- liquid
- glass



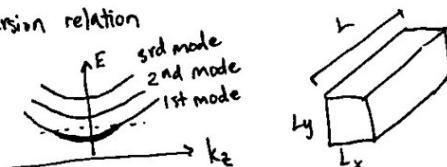
<< Quantum Wire

- total energy in 1D wire in z -dir:

$$E = E_{nx} + E_{ny} + E_z$$

$$= \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) + \frac{\hbar^2 k_z^2}{2m}, \quad n_{x,y} = 1, 2, 3, \dots$$

- dispersion relation



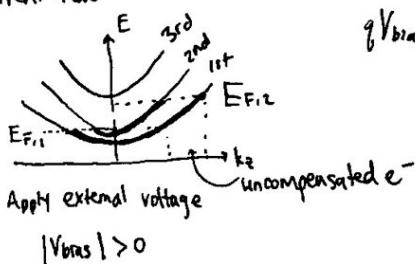
no bias voltage is applied (external)

$$V_{bias} = 0$$

$$E_{F,1} = E_{F,2} \text{ (assumption)}$$

✓ electrical/chemical potential diff.

- current flow



$$qV_{bias} = \Delta E_F = \mu_F E_{F,1} - F_{F,2} \equiv \mu_2 - \mu_1$$

$$I = \frac{2e}{h} (\mu_s - \mu_d)$$

$$V_{bias} = V_{DS} = \frac{-\mu_D - \mu_S}{e} = RI$$

$$\Rightarrow R = \frac{h}{2e^2} \approx 12.9 \text{ k}\Omega$$

$$\Rightarrow G_C = \frac{2e^2}{h}$$

<< Quantum Well Structure

- We attribute energies according to the degree of confinement

- Unconfined (continuous)

$$E_i = \frac{p_i^2}{2m} = \frac{\hbar^2 k_i^2}{2m} \quad i = \text{coord direction}$$

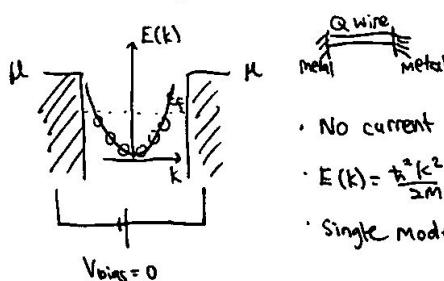
- confined (discrete)

$$E_{nj} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_j^2}{L_j} \right) \quad i = \text{coord direction}$$

Structure	# constrained coord	Quantum Particle Energy
Quantum Well	1	$E = E_{nx} + E_x + E_y$
Quantum Wire	2	$E = E_{ny} + E_{nz} + E_x$
Quantum Dot	3	$E = E_{nx} + E_{ny} + E_{nz}$

- Application: To improve the gain and wavelength speed of active laser media (e.g. QD GaAs laser)

<< Quantum Wire



- No current flow
- $E(k) = \frac{\hbar^2 k^2}{2m}$ free, continuous in 1D
- Single mode

μ - electrochemical potential of metal electrode

E_F - Fermi energy of Q-wire

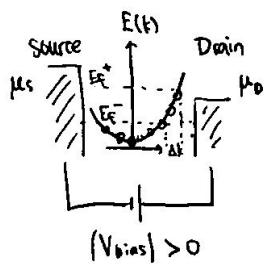
V_{bias} - voltage between electrode

Θ - electron filled state

Δk - wave numbers of uncompensated states

$$\Delta k = k_D - k_S$$

$$k_i = \sqrt{\frac{2m E_F}{\hbar^2}} \quad i = D, S$$



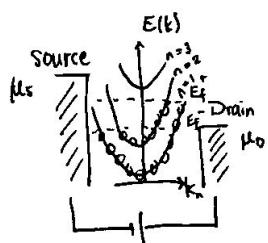
$$\text{current: } I = \frac{2e}{h} (\mu_S - \mu_D)$$

$$\text{voltage: } V_{bias} = V_{DS} = \frac{-(\mu_D - \mu_S)}{e} = RI$$

$$\text{resistance: } R = \frac{h}{2e^2} \approx 12.9 \text{ k}\Omega$$

$$\text{conductance: } G = \frac{2e^2}{h} \approx 7.75 \times 10^{-5} \text{ S}$$

} Independent on length.
(in contrast to classic Ohmic $R \propto L$)



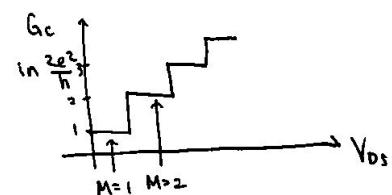
- $n=1, 2$ has uncompensated state, but $n=3$ doesn't

Mode number : M

$$\text{current: } I = \frac{2eM}{h} (\mu_S - \mu_D)$$

$$\text{resistance: } R = \frac{h}{2e^2 M}$$

$$\text{conductance: } G_c = \frac{2e^2}{h} M$$



<< Hydrogen Atom

- $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$
- discrete energy level $E_n = \frac{E_1}{n^2}$; $E_1 = \frac{-Me^2}{8\pi^2\hbar^2}$
- Eigenfunction ψ_{n,l,m_l}
- $n = 1, 2, 3, \dots$ principle quantum # - shell
- $l = 0, 1, 2, \dots, n-1$ orbital quantum # - subshell
- $m_l = -l, -l+1, \dots, 0, \dots, l$ magnetic quantum # - orbital
- Max occupation per orbital: 2
- spin up / down
- Pauli exclusion principle - no two e^- can have an identical set of quantum number

<< Quantum Entanglement, Computing

- Knowing the state of a system quantum mechanically does not imply the knowledge of the states of the parts of the system.
- > EPR-paradox - Assuming to be able to determine the states of the parts of a quantum system and maintain the system state, yielding a physical paradox
- In quantum entangled system, part information is superposed
 - Computing: binary info
 - $\Rightarrow \propto$ info of superposition
 - \Rightarrow Qubit - entangled states of atoms, ions, molecules, or photons
 - promise - ultrafast calculation (e.g. drug development)
 - challenge - quantum decoherence

<< Electron Tunneling

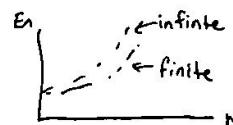
- e^- tunneling through classically forbidden zone (vacuum, insulator)



• Comparison: finite vs. infinite quantum well

$$\cdot \text{infinite: } E_n \propto a n^2$$

$$\cdot \text{finite: } E_n \approx b n^2 + c n + d \quad (b < a)$$



↔ Tunneling Effect

$$\cdot \text{I. } \psi_1 = \psi_{\text{in}} + \psi_{\text{refl}}$$

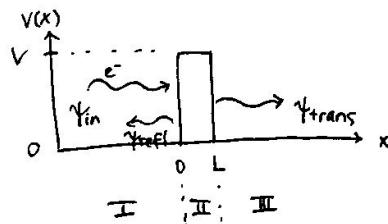
$$\cdot \text{II. } \psi_3 = \psi_{\text{trans}}$$

• II. use continuous condition

$$\cdot \text{I. } -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_1(x) = E \psi_1(x)$$

$$\cdot \text{II. } -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_2(x) + V \psi_2(x) = E \psi_2(x)$$

$$\cdot \text{III. } -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_3(x) = E \psi_3(x)$$



$$\cdot \psi_1 \left\{ \begin{array}{l} \psi_{\text{in}} = B e^{ikx} \\ \psi_{\text{refl}} = B e^{-ikx} \end{array} , \quad k^2 = \frac{2mE}{\hbar^2}, \quad x < 0 \right.$$

$$\cdot \psi_2(x) = C e^{ik'x} + D e^{-ik'x}, \quad k'^2 = \frac{2m(V-E)}{\hbar^2}$$

$$\cdot \psi_3 = \psi_{\text{trans}}(x) = F e^{ikx}$$

• Of interest : for the tunneling current is the transmission probability

$$T(L, V, E) = \frac{|\psi_{\text{trans}}(x)|^2}{|\psi_{\text{in}}(x)|^2} \quad (V, L \text{ large})$$

$$T(L, V, E) \approx 16 \frac{E}{V} (1 - \frac{E}{V}) e^{-2k'L} \quad (\frac{V}{E} \approx 1)$$

$$\approx e^{-2k'L}$$

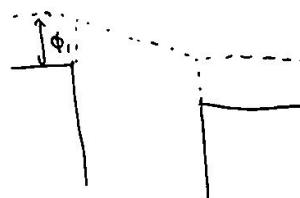
• Tunnel current:

$$I_t \propto V_{\text{bias}} D_s(E_F) \exp\left(\frac{(E_F - V)}{kT} \right)^{\pm L}$$

• $D_s(E_F)$ - density of states, provided # of e^- available at Fermi energy of metal

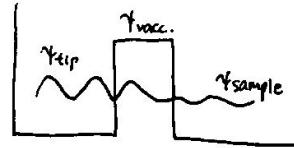
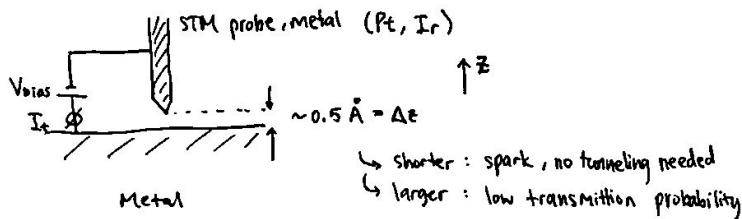
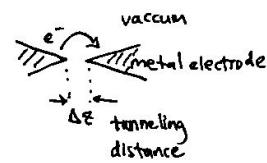
• V in practical application is ϕ , work function

$$\cdot \bar{\phi} = \frac{1}{2} (\phi_1 + \phi_2 - |eV_{\text{bias}}|) \quad (\text{tunnel junction})$$

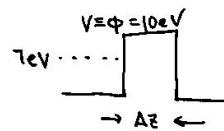


<< Scanning Tunneling Microscopy

- 1928 - Fowler & Fordheim predicted theoretically vacuum tunneling
- 1981 - Binnig & Rohrer introduced the scanning tunnelling microscope (STM)
- nucleation of nanoscience & nanotechnology
- led to more scanning probe methods (SPM)
- atomic force microscope (AFM)
- ↳ renamed: scanning force microscopy (SFM)



Ex Two Au electrodes separated by insulator, $\phi = 10 \text{ eV}$ potential barrier.
Estimate the tunneling probability, assuming 7 eV e^- , and an insulator thickness of 5 nm and 1 nm .



$$T \approx e^{-2k'L}$$

$$\text{where } k' = \sqrt{\frac{8\pi m_e(\phi - E)}{\hbar^2}}$$

$$\Rightarrow T(5 \text{ nm}) = 6.5 \times 10^{-13} \quad \text{unlikely!}$$

$$\Rightarrow T(1 \text{ nm}) = 3.7 \times 10^{-3} \quad \text{not great...}$$

$$\left. \begin{array}{l} m_e = 9.1 \times 10^{-31} \text{ kg} \\ \hbar = 1.055 \times 10^{-34} \text{ J} \cdot \text{s} \\ \phi = 10 \text{ eV} \\ E = 7 \text{ eV} \end{array} \right\}$$

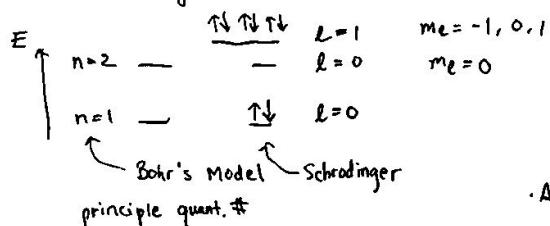
Energy Discretization of Nanoparticles

atom

nano particle

macroscopic bulk solid

. Atom (A eq. H atom)

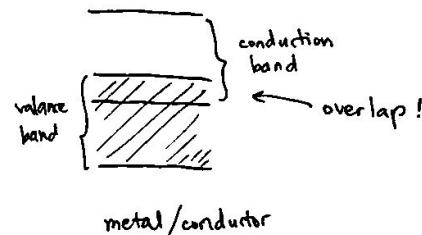
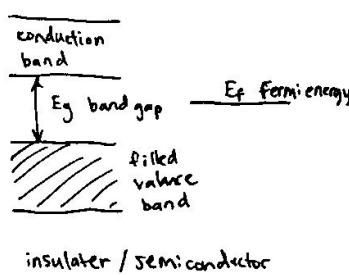
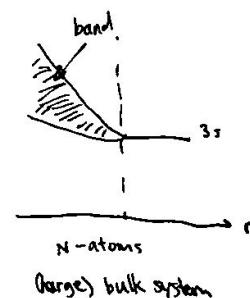
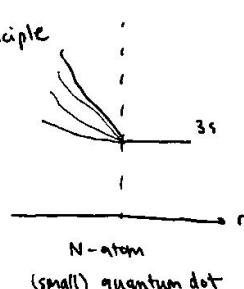
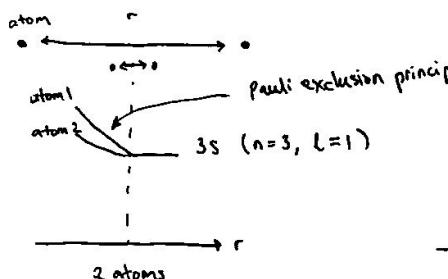
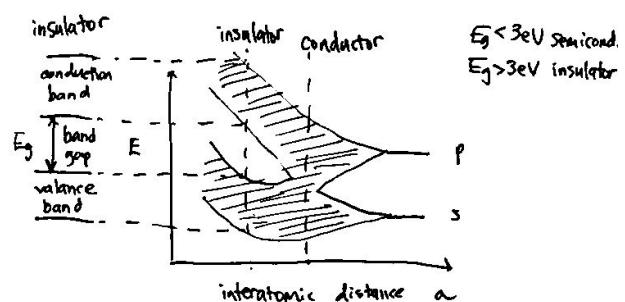
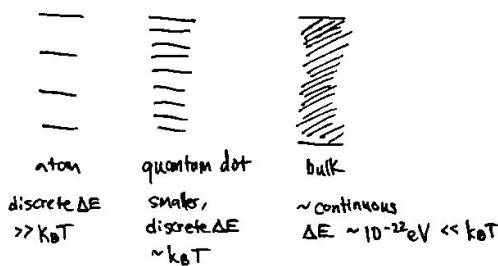


• AE is energy diff. between 2 levels.

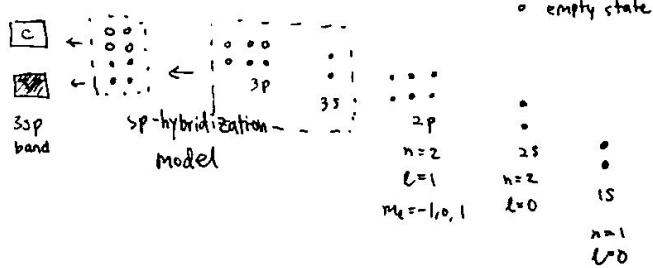
$$k_B T \approx 2.6 \times 10^{-3} \text{ eV}$$

thermal @ 300 K
noise

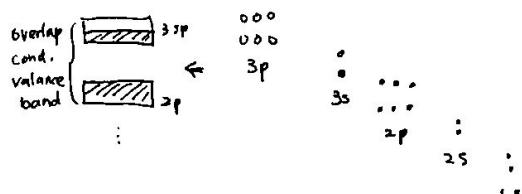
• Bring atom together



EX Silicon atom (Insulator)



EX Sodium (Metal)



Bulk $\xleftarrow[N_e < N_c \wedge \Delta E_i > \Delta E_z]$ Nanoparticle

$$\text{~~~~~} \nabla \Delta E = 10^{-22} \text{ eV}$$

$$n = \frac{N_e}{V}$$

n - # number density

N_e - # free e^-

V - volume

$$\text{~~~~~} \nabla \Delta E \sim \frac{E_F}{N_e} \leftarrow \begin{array}{l} \text{Fermi energy} \\ \text{tot # of free } e^- \text{ (valence)} \end{array}$$

$$\Delta E = \frac{4}{3} \frac{E_F}{N_e}$$

$$N_e < \frac{4}{3} \frac{E_F}{k_B T} \quad \begin{array}{l} \text{valence} \\ \# e^- \text{ to be confined} \end{array}$$

(continuous energy level)

$\ll k_B T$ not quantum confined

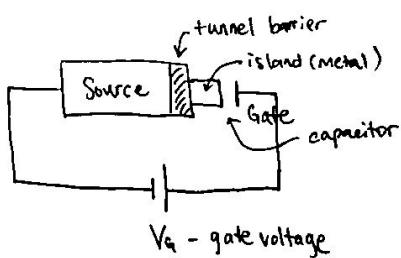
$> k_B T$ quantum confined

(discrete E level)

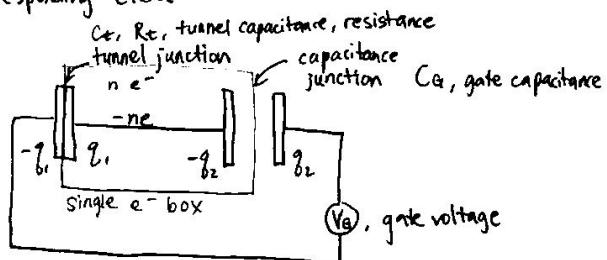
Table

	$n = \frac{N_e}{V}$	E_F (eV)	ΔE (eV)	$(V=1 \text{ nm}^3)$
Cu	8.49	7.05	0.014	For $V=1 \text{ nm}^3$, Cu, Au, Na are quantum confined
Au	5.9	5.53	0.09	\Rightarrow distinct energy level \gg thermal noise
Na	2.65	3.23	0.12	$\nabla > k_B T$

<< Single Electron Box



Corresponding Circuit



- Work moving a charge element dq onto a capacitor is

$$dE = Vdg = \frac{q}{C} dq$$

- q_1, q_2 are charges at capacitor

- total capacitance $C = C_t + C_g$

- Define: $Q = CV_g$ "apparent" continuous system charge

- charging energy (energy required to add e^- of charge $q=e$):

$$E_c = \int_0^e \frac{q}{C} dq = \frac{e^2}{2C}$$

, where $C = C_t + C_g$

- In quantum dot, $C \equiv C_{\text{dot}}$

Gate Voltage:

$$V_g = \frac{q_1}{C_t} + \frac{q_2}{C_g}$$

- What is involved in charging?

- The Gibbs free energy of a system

$$F = H - TS$$

H - enthalpy

S - entropy

TJ - entropic energy

- For our system, H is E_{syst} , TS is lost energy $q_2 V_g$.
(useless)

$$F = E_{\text{syst}} - q_2 V_g$$

- At eqm (fixed n on the island),

$$\frac{dF}{dn} = 0$$

- It follows with calculation,

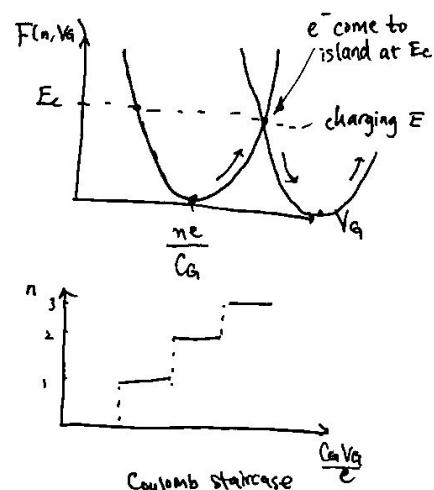
$$F(n, V_g) = \frac{(C_g V_g - ne)^2}{2C} \propto V_g^2$$

- If $F=0$, $C_g V_g = ne$

$$F = E_c, \quad C_g V_g = (n+1)e$$

so

$$E_c = \frac{e^2}{2C} = \frac{(C_g V_g - ne)^2}{2C}$$



<< Single Electron Box

Two major requirements for a working single e^- box:

1. $E_c \gg k_B T$ Coulomb Blockade

Rule of thumb: $E_c > 10k_B T$

$$E_c = \frac{e^2}{2C} = \frac{e^2}{2(C_f + C_a)} > 10k_B T$$

} thermal noise

2. The system has to overcome quantum noise

$R_t \gg \frac{h}{e^2}$ R_t - resistance of tunnel junction

} quantum noise

$\approx 25.8 \text{ k}\Omega$, resistance quantum

Time constant of electric circuit

$$\Delta T_b = R_t C$$

Spherical dot / island

$C_{dot} = 2\pi \epsilon \epsilon_0 D$

D - diameter
 ϵ - permittivity of dot material (relative)

$$E = \frac{e^2}{2C_{dot}} = \frac{e^2}{4\pi\epsilon_0 \frac{D}{2}} = \frac{e^2}{4\pi\epsilon_0 D}$$

material	ϵ
vacuum	1
SiO_2	3.9
Al_2O_3	9

Disk-like quantum dot / island

$C_{dot} = 4\pi\epsilon_0 D$

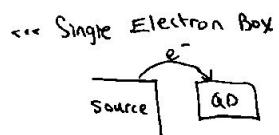
more generally, $C_{dot} \equiv G \cdot 4\pi\epsilon_0 D$

G - geometric parameter

{ $\begin{cases} 2\pi & \text{spherical} \\ 4 & \text{disk} \end{cases}$

$$E_c = \frac{e^2}{2C_{dot}} = \frac{e^2}{2\epsilon_0} \cdot \frac{1}{G \cdot D} \approx (9.0 \text{ eV} \cdot \text{nm}) \cdot \frac{1}{G \cdot D}$$

(General)
 charging density.



$$E_a = E_c + E_k \quad ; \quad E_k = \frac{1}{V D_s(E)}$$

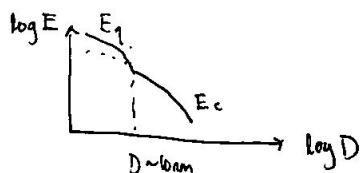
$$D_s(E) = \frac{dN}{dE}$$

E_a - electron addition energy

E_k - quantum kinetic energy

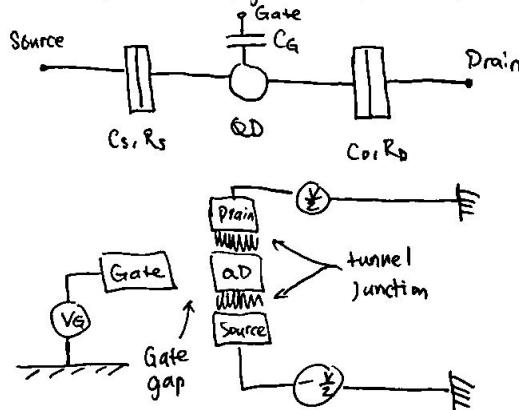
V - volume

D_s - density of state



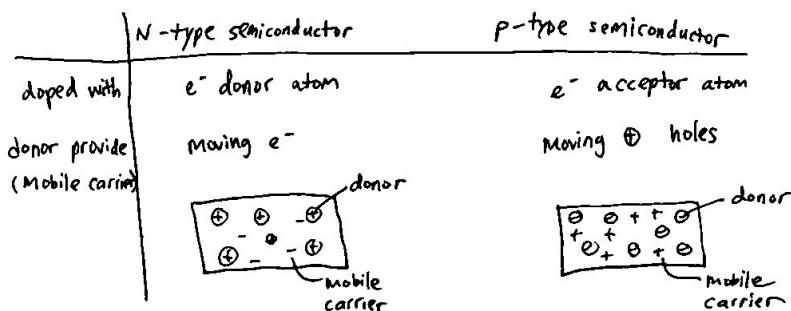
Single Electron Transistor (SET)

- To obtain an electronic logical device, we expand our box by adding a third electrode.

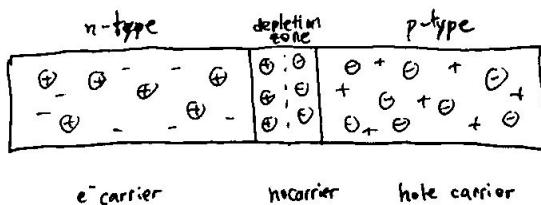


- analogous to a field effect transistor

- semiconductors



- p-n junction : diode



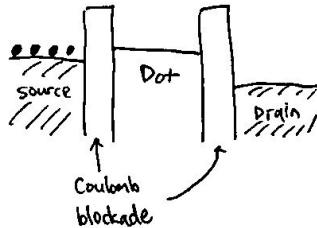
« Single Electron Transistor

• In SET, we have an electrically isolated quantum dot between source & drain

(a) SET in off mode

• Coulomb blockade:

$$E_C = \frac{e^2}{2C_{dot}}$$

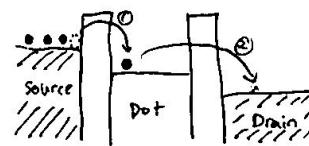


(b) SET in on mode

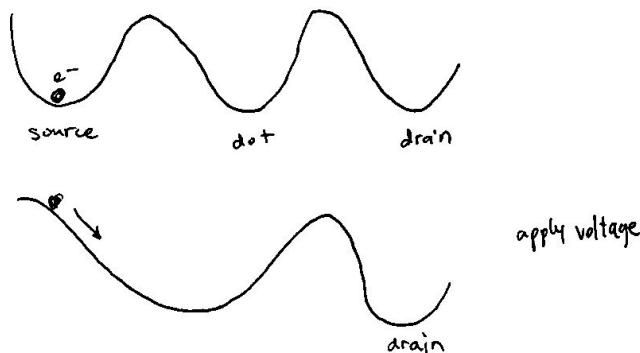
• apply voltage

$$V_G = V_C = \frac{e}{2C_{dot}}$$

minimum voltage for
single e^- transport : $V_C = \frac{E_C}{e}$

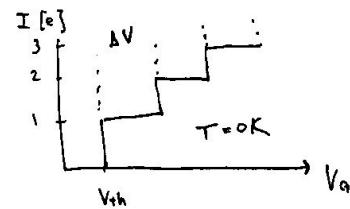


• e^- that travels onto the dot raises the dot's potential energy, so the e^- can travel to the drain



- $V_G = V_C$
- $I = e / s$
- only $1e^-$ at a time

For $V_C + \frac{e}{2C_{dot}} < V_G < V_C + \frac{2e}{2C_{dot}}$
 $I = 2e$



← Electron Distribution

→ Hydrogen Atom

- En - principle energy levels

- $\Psi(\vec{r})$ - electron states represented by wave functions

- $\Psi(\vec{r}) = \Psi_{n,l,m}(r, \theta, \varphi) = \underbrace{R(r)}_{\text{radial fcn}} \underbrace{Y(\theta, \varphi)}_{\text{spherical harmonic fcn}}$

- $Y(\theta, \varphi) = \underbrace{\Theta(\theta)}_{\text{polar fcn}} \underbrace{\Phi(\varphi)}_{\text{azimuthal fcn}}$

Ex1 $\Psi_{100} = R_1(r) \Theta_0(\theta) \Phi_0(\varphi)$

$$\Theta_0 = \frac{1}{\sqrt{2\pi}}, \quad \Phi_0 = \frac{1}{\sqrt{2\pi}} \Rightarrow Y_{00}(\theta, \varphi) = \sqrt{\frac{1}{4\pi}}$$

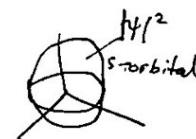
$$\Psi_{100} = \frac{R_1(r)}{\sqrt{4\pi}}$$

Generally,

$$\boxed{\Psi_{n00} = \frac{R_n(r)}{\sqrt{4\pi}}} \quad n=1, 2, 3, \dots$$

$l=0$
 $m=0$

s-orbital, Spherically symmetric



- Radial distribution density

$$P_{nlm} \left| R(r) \right|^2 r^2$$

<< Electron Distribution

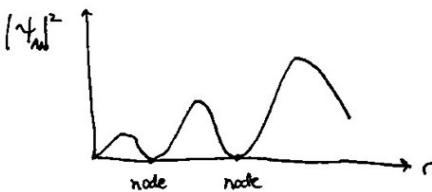
→ Hydrogen Atom

$$\psi_{n,0} = \frac{R_n(r)}{\sqrt[3]{4\pi}} , n=1,2,3,\dots$$

s-orbital, spherical symmetric.

' Radial distribution density

$$P_{n,l}(r) = |R_{n,l}(r)|^2 r^2$$



$$\boxed{\text{Ex1}} \quad \psi_{2,0} : R_n(r) = \frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$

$$\psi_{l,m} = \Theta_l(\theta) \Phi_m(\phi)$$

$$= \frac{\sqrt{6}}{2} \cos \theta \frac{1}{r^{2a_0}}$$

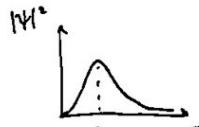
$$\psi_{2,0} = \frac{1}{2\sqrt{6} a_0^{3/2}} \frac{\sqrt{6}}{2\sqrt{\pi}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta \propto r e^{-r/2a_0} \cos \theta$$

→ Probability & Electron Distribution

$$\cdot |\psi_{n,m}|^2 = \psi_{n,m} \psi_{n,m}^* \leftarrow \text{complex conjugate}$$

$$\boxed{\text{Ex2}} \quad \psi_{1,0} = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

$$|\psi_{1,0}|^2 = \left(\frac{2}{a_0^{3/2}}\right)^2 e^{-2r/a_0}$$



$$\cdot \text{Normalization condition : } \iiint_{\text{entire space}} \psi \psi^* d\Omega = 1$$

$$\Rightarrow \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi \psi^* r^2 \sin \theta d\theta d\phi dr$$

$$= \underbrace{\int_0^\infty r^2 R_{nl}^2 dr}_{=1} \underbrace{\int_0^\pi \int_0^{2\pi} Y^* Y \sin \theta d\theta d\phi}_{=1}$$

Radial probability Angular probability

$$> \text{Radial distribution function} - \boxed{P_{n,l}(r) = r^2 R_{n,l}^2}$$

$$> \text{Radial probability density function} -$$

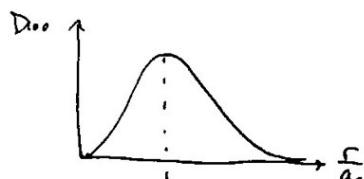
(prob. of finding e^- in a shell)

$$> \text{Radial probability density} -$$

(most likely position of finding e^- in given state)

$$\underbrace{\frac{d}{dr} \left(|\psi_{1,0}|^2 4\pi r^2 \right)}_{\approx D_{1,0}} = 0$$

↑ max

(here, find ground state
 $n=1, l=0, m=0$)

$$\frac{dD_{1,0}}{dr} = \frac{4}{a_0^3} r^2 e^{-2r/a_0} = 0 \Rightarrow r = a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m e^2}$$

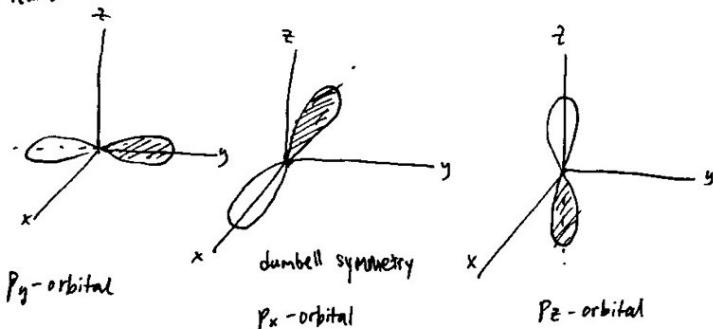
 $\approx 0.053 \text{ nm}$

<< Electron Distribution
> Radial probability density -

$$D_{\text{nem}}(r) = 4\pi r^2 |\Psi_{\text{nem}}|^2$$

→ Orbital Shape & Angular Momentum

- l - angular momentum quantum number
 - gives shape of orbital
 - for $l=1$ (p -orbital)
 - $M_l = \{-1, 0, 1\}$

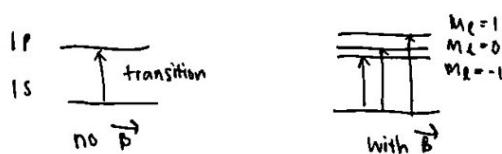


- for $\ell=2$ (d -orbitals)
 - for $\ell=3$ (f -orbitals) } more complex distribution

“Energy Degeneracy

- In H, the principal quantum number, n , dictates the energy level E_n
 $E_n(n) \neq f(l, M_l)$
 - E_n is degenerate regarding l and M_l .

> Zeeman Effect - Magnetic field can make the degeneracy visible



- With spin \rightarrow electronic fine structure (inhomogeneous \vec{B}) - Stern-Gerlach

\Rightarrow spin-orbit-coupling $j = l \pm s$

degeneracy $n^2 \rightarrow 2n^2$ (*n*-rule of degeneracy'; breaks for multi- e^- system)

Angular Momentum

operator: $\hat{L}_E Y_{2,m} = \underbrace{m_2 h}_{\text{observable}} Y_{2,m}$ eigenfunction

$$\hat{z} = i \hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad \text{in Cartesian coord}$$

$$\cdot \text{Magnitude operator: } \vec{L} = \langle \hat{L}_x, \hat{L}_y, \hat{L}_z \rangle$$

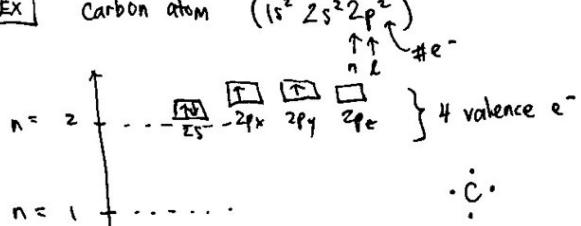
$$\hat{L}^2 = (\vec{L})^2 ; \quad \hat{L}^2 Y_{l,m} = l(l+1) h^2 Y_{l,m}$$

$$L = \hbar \sqrt{l(l+1)} \quad \text{orbital angular momentum}$$

Electron Distribution and Bonding in Molecules

- Covalent bonding is synonymous to overlapping wave functions
- Theory: Molecular Orbital theory (MO)
- bonding $e^- \leftrightarrow$ delocalized e^-
- Delocalized e^- are in outermost shells in atoms, called valence e^- .

EX Carbon atom ($1s^2 2s^2 2p^2$)

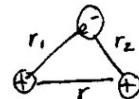


atoms with completely filled subshells are stable
e.g. He ($1s^2$)

$\cdot C \cdot$

Sigma Bonding (σ)

- The simplest molecule, hydrogen ion H_2^+
- 2 protons, 1 e^-
- Coulomb potential $V(r) = \frac{e^2}{4\pi\epsilon_0} \left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r} \right)$



- Building the molecule



ψ_1 and ψ_2 ground state wave functions of e^- for proton 1 and proton 2.

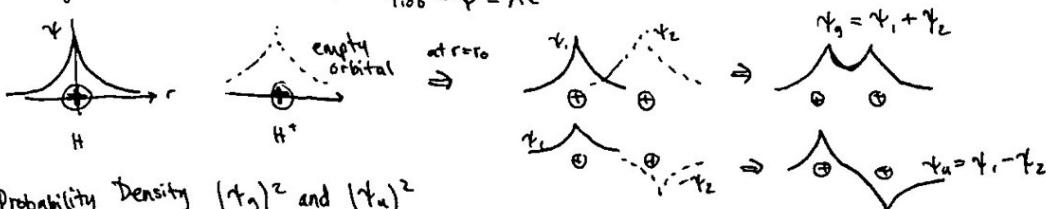
- At of H_2^+ is a linear combination of ψ_1 and ψ_2

$$\text{at } r=r_0 : \quad \psi = \begin{cases} \psi_1 + \psi_2 & \text{linear superposition / fxn overlap} \\ \psi_1 - \psi_2 & \end{cases}$$

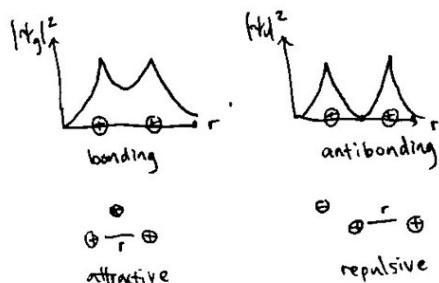
- Define: $\psi_g = \psi_1 + \psi_2$ (even) symmetric linear comb.

$$\psi_u = \psi_1 - \psi_2 \quad (\text{uneven}) \text{ asymmetric linear comb.}$$

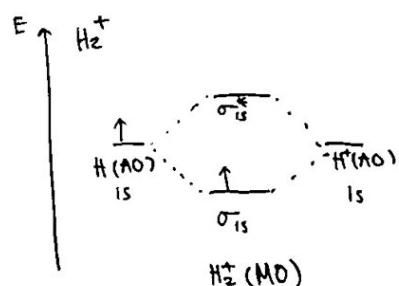
- The ground state wavefunction: $\psi_{1,00} = \psi = A e^{-r/a_0}$



- Probability Density $(\psi_g)^2$ and $(\psi_u)^2$



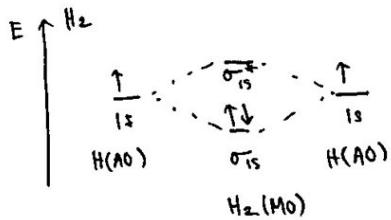
<< Molecular Orbital Energy-Level Diagram



- New notation $\begin{array}{c} \text{AO} \\ \hline s\text{-orbital} \\ (\lambda=0) \end{array}$
- $\begin{array}{c} \text{MO} \\ \hline \sigma\text{-orbital} \end{array}$

- σ -bonds are the strongest covalent bonds

- hydrogen molecule: add a second e^-



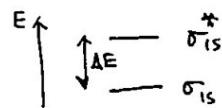
- > LUMO - lowest unoccupied molecular orbital

- > HOMO - highest occupied molecular orbital

- σ_{1s}^* is LUMO

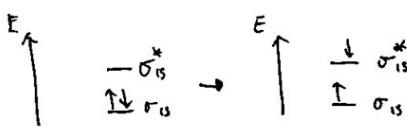
- σ_{1s}^* is HOMO

- $\Delta E \approx 11.2 \text{ eV}$ HOMO-LUMO gap



- $2 \pi 10 \text{ nm}$ UV light

- raise e^- from σ_{1s} $\rightarrow \sigma_{1s}^*$ by $\sigma-\sigma^*$ transition



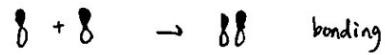
<< Recap

- We discussed prior σ -bonding ($s-s$).
 - Also two p_e -AOs (atomic orbitals) can form σ -bond.

<< p-orbital Overlap



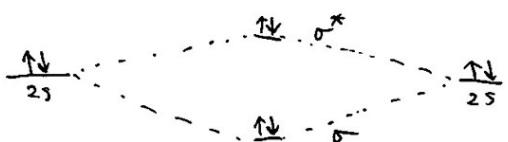
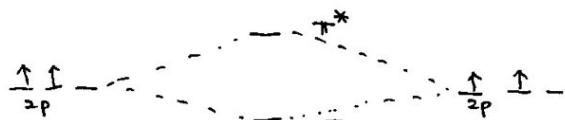
- not axis symmetric
 - π bond
 - σ and π bonding can be either bonding or antibonding



- σ bond always exceeds in strength than π -bond

<< Single & Double Bond

- e.g. C-C and C=C
 - C-C bond (σ bond) 3.69 eV
 - C=C bond (σ, π bond) 6.55 eV (less than 2 σ bond)



AO

Mo

80

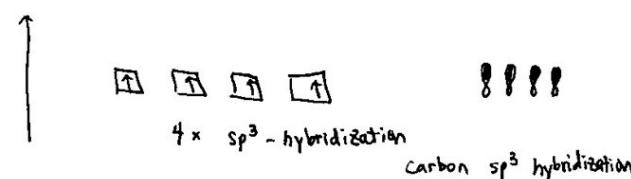
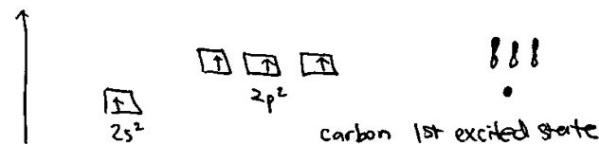
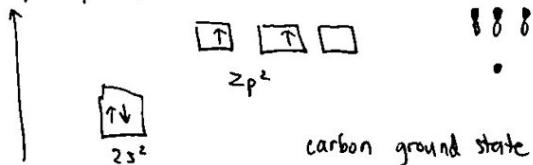
- single bond : s-s or bond
 - double bond : s-s or bond
p_z- bond
 - σ bond provides rotation ∵ axis symmetric
 - π bond cannot be rotated. called "brittle"

<< Non-bonding

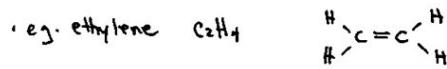
- AOs are the same as MOs if nonbonding

<< $sp^3 \approx sp^2$ - Hybridization

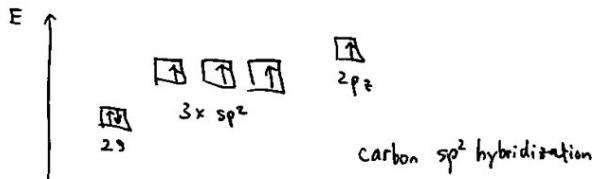
$\rightarrow sp^3$ Hybridization



$\rightarrow sp^2$ hybridization



sp^2 -hybridization requires



<< Mobile Electrons

- Focus on delocalized e^- in molecules \rightarrow electronic applications

<< Delocalized πe^-

- e.g. benzene



- sp^2 hybrids are used to form σ -bonds with neighbor C and π

- Each C donates the remaining $2p e^-$ into the delocalized ring above & below the benzene ring $\Rightarrow e^-$ in the ring delocalized.

- The dispersion of e^- over a larger area provides molecular stability

 - planar geometry of benzene is due to delocalized e^-

 - The $3\pi - \pi^*$ excitations provide small band gaps between HOMO & LUMO

 - lowest singlet $\pi \rightarrow \pi^*$ excitation is 4.9 eV (235 nm) UV light

 - Larger aromatics have smaller E gap

 - can get to visible region

<< HOMO - LUMO Transitions

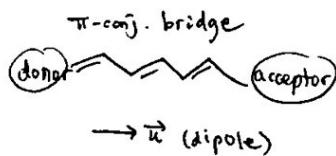
- Chromophores - molecule interact with light
- conjugated molecular system of connected p-orbitals with delocalized e^- and small band gaps between HOMO-LUMO level.
- Chromophore active groups (a group that can interact with light)

- ethylene
- acetylene
- nitrile groups
- ...

\rightarrow photovoltaic applications

 \rightarrow Organic Chromophore

- an e^- donor site
- a π -conjugated bridge
- an acceptor side
- e^- can freely move in the π -bridge
- donor & acceptor site represent spatially separated HOMO & LUMO levels



- . application
 - { molecular engineering system
bandgap engineering
photonics
molecular electrostatics
electro-optical system

<< Introduction

- Modern electronic device technologies depend on availability of delocalized (mobile) e^- .
- Information transfer involving mobile e^- depend on:

(A) availability of electronic states around the kinetic energy of the mobile e^-

(B) the HOMO + LUMO levels

- location of $E_{k,\max}$ (HOMO) = E_F (Fermi Energy at 0K) in respect to any band gap.

(C) system constraints (nano) and temperature

- nano constraint - $dE \rightarrow \Delta E$

- temperature - $k_B T \leq \Delta E$

<< (A) Availability of Electronic States

- The number of available energy states per unit volume and per unit energy at the kinetic energy E of the e^- is called the density of state $D_s(E)$

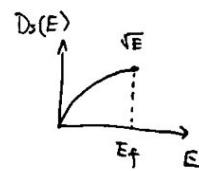
- unit: $D_s(E) [=] \frac{\# \text{ of state}}{\text{J m}^3}$

- high density of state: many states are available for occupation in close vicinity of E

- For s- and p-Metals (s, p valence e^-),

$$D_s(E) \propto \sqrt{E}$$

$$D_s(E) = \frac{8\sqrt{2}\pi M_e^{3/2}}{h^3} \sqrt{E}$$

<< (B) Location of Mobile e^-

- Restrict: metals

- In metals, we have overlapping conduction & valence band

- HOMO level (E_F at 0K) is in conduction band

⇒ mobile e^- carriers

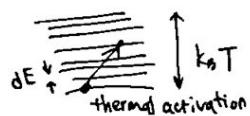
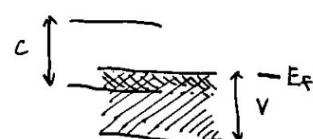
- Consider $k_B T$ at $T > 0$ is much larger than ΔE (ΔE)

⇒ can thermally populate (raise) e^- into higher energy states, given by $D_s(E)$

- thermal activation process

- Classically described by Boltzmann's law

$$f_B(T) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right)}$$



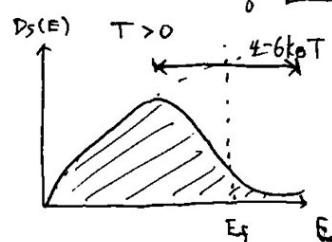
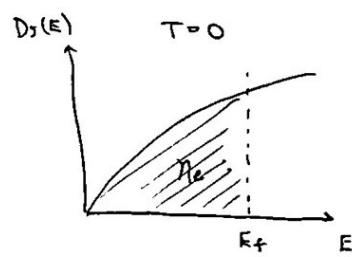
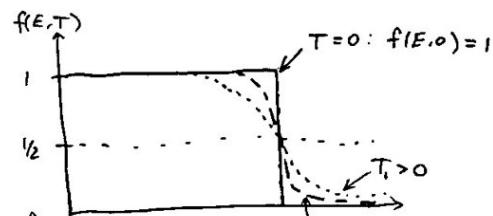
but distribution law does not apply to e^-

- For e^- , the distribution law that takes into account Pauli's exclusion principle is

$$\text{Fermi-Dirac distribution: } f(E; T) = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right) + 1}$$

- The number density of e^- for $E < \infty$

$$n_e = \int_0^\infty f(E) D_s(E) dE$$



\hookrightarrow Unconstrained System

- unconstrained system \rightarrow continuous energy band

- Kinetic energy $E = \frac{p^2}{2m} k^2$

- $E = E_F : E_F = \frac{\hbar^2}{2m} k_F^2$ (k_F is wave number at Fermi edge>)

m - mass of e^-

(usually m^* , effective mass)

- Density of mobile e^- : $n_e = \int_0^\infty f(E) D_s(E) dE$

affected by dim

$$= \frac{16\sqrt{2}\pi m^{3/2}}{3\hbar^3} E_F^{3/2} \quad \text{at } T=0$$

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

$$k_F = (3\pi^2 n_e)^{1/3}, \quad n_e = \frac{N_e}{V}$$

- more general: $n_e \rightarrow N$, # of carriers (e^- , holes)

- wavelength (de Broglie)

$$\lambda = \frac{\hbar}{p} = \left[\frac{2\pi}{k_F} \right] = \lambda_F$$

- Introduce Fermi velocity approx for heavily doped semiconductor

$$V_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m} (3\pi^2 n_e)^{1/3}$$

$$\Rightarrow \boxed{\lambda_F = \frac{2\pi\hbar}{m V_F}}$$

The e^- free mean path $\lambda = v_F \tau$

τ - relaxation time of e^-

\ll 2D - Electron System: Quantum Well

- Discretization of $E_n = n^2 E_1$, $E_1 = \frac{\hbar^2}{8ML^2}$

$$D_s^{3D}(E) \propto \sqrt{E}$$

$$D_s^{2D}(E) = \{D_1, D_2, D_3, \dots\}$$

constant discrete

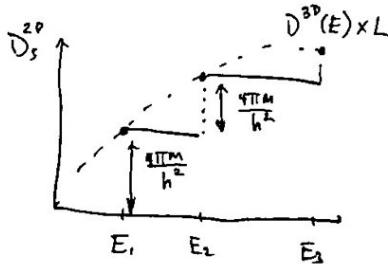
- each jump is the same: $\Delta D_s^{2D} = \frac{4\pi M}{h^2}$

$$D_s^{2D} = D_s^{3D} \times L$$

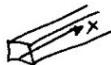
$$= \frac{8\sqrt{2}\pi m^{3/2}}{n^3} \frac{1}{\sqrt{E}} \times L$$

$$D_s^{2D} = \frac{4\pi M}{h^2} n$$

$n=1, 2, 3, \dots$



\ll 1D - Electron Gas:



- $D_s^{1D}(E) \approx \left(\frac{1}{L}\right)^s \frac{dN}{dE} = \left(\frac{1}{L}\right)^s \frac{dN}{dE} \frac{dk}{dE}$

$$n=1 : \frac{\lambda}{2}=L$$

$$n=2 : \lambda=L$$

$$\left. \begin{array}{l} \\ \end{array} \right\} L=\frac{n\lambda}{2}$$

$s = 0, 1, 2, 3$ dimension

L = length scale

N = # of states of standing waves

$$k = \frac{2\pi}{\lambda} \text{ wave #}$$

$$E = \frac{h^2}{2m} k^2 \text{ kinetic energy}$$

Numbers of $n=N^*$ in interval $[-k, k]$

- $L = N^* \frac{\lambda}{2}$ ($k = \frac{2\pi}{\lambda}, \lambda = \frac{2\pi}{k}$)
- $= N^* \frac{2\pi}{2k}$

$$\Rightarrow N^* = \frac{2L}{2\pi} k \quad \text{consider polarization } \uparrow\downarrow \times 2.$$

$$N = 2N^* = 4 \left(\frac{L}{2\pi} \right) k \quad \text{for } [-k, k]$$

$$\frac{dN}{dk} = \frac{2L}{\pi}$$

$$\text{from } E = \frac{h^2}{2m} k^2 \rightarrow k = f(E)$$

$$\frac{dk}{dE} = \sqrt{\frac{M}{2\pi^2 E}}$$

$$\Rightarrow D_s^{1D}(E) = \frac{2}{\pi} \sqrt{\frac{M}{2\pi^2 E}} \propto \frac{1}{\sqrt{E}}$$

SUMMARY:

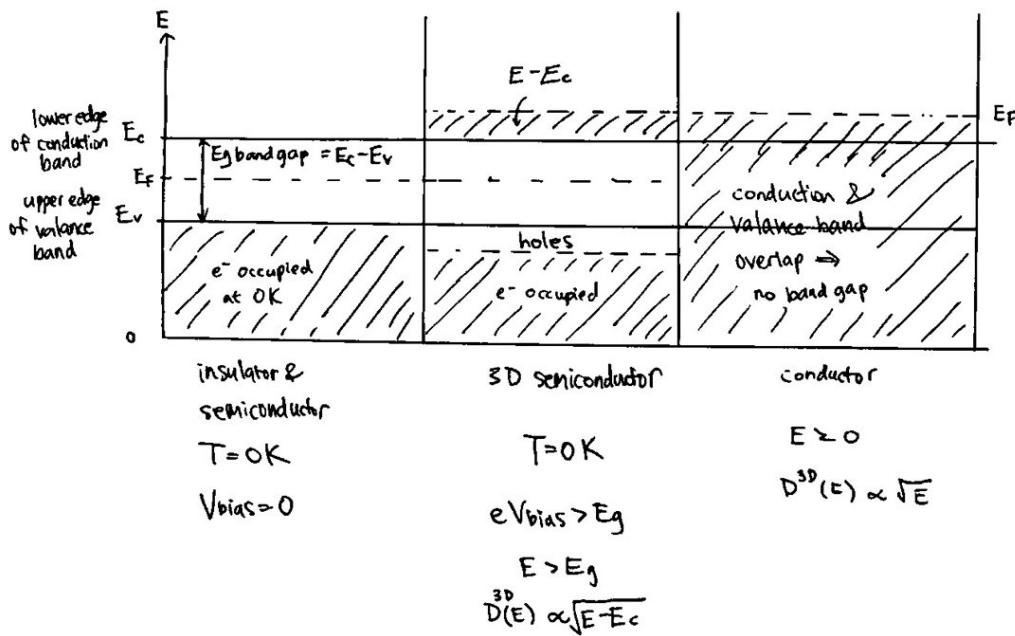
$$3D: D_s^{3D}(E) = \frac{8\pi\sqrt{2}}{h^3} M^{3/2} \frac{1}{\sqrt{E}}$$

$$2D: D_s^{2D}(E) = \frac{4\pi M}{h^2} \quad 0 < E < E_1,$$

$$1D: D_s^{1D}(E) = \frac{\sqrt{2m}}{h} \frac{1}{\sqrt{E}} \quad 0 < E < E_{1,1}$$

$$0D: D_s^{0D}(E) = 2$$

<< Density of State for Mobile Carriers



- E_F - Fermi energy - max energy occupied by e^- at $T=0K$.
- Conductors - E_F within conduction band
- Semiconductors - E_F within the band gap, the forbidden zone
 - $E_v < E_F < E_c$
 - With external V_{bias} , e^- can be raised from valence band into conduction band

<< Semiconductors & Density of States

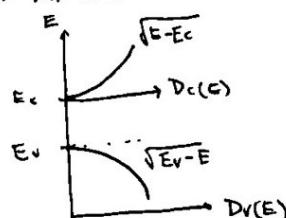
> Density of states = the relevant carriers will differ

- conduction band : electrons

$$D_c(E) \propto \sqrt{E-E_c}$$

- valence band : holes

$$D_v(E) \propto \sqrt{E_v-E}$$



$$\Rightarrow D_c(E) = \frac{8\sqrt{2}\pi M_e^{3/2}}{h^3} \sqrt{E-E_c} \quad \text{for } E > E_c$$

$$D_v(E) = \frac{8\sqrt{2}\pi M_h^{3/2}}{h^3} \sqrt{E_v-E} \quad \text{for } E < E_v$$

• M_e^* , M_h^* are effective mass of e^- and holes

“ Semiconductor Distribution Function & Carrier Density ”

→ Fermi Distribution Function

- for e^-

$$f(E) = \frac{1}{1 + \exp(\frac{E - E_F}{k_B T})}$$

- for holes

$$1 - f(E)$$

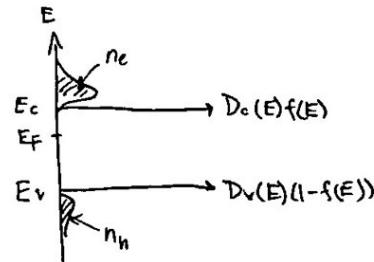
→ Carrier Densities

- for e^-

$$n_e = \int_{E_c}^{\infty} D_c(E) f(E) dE$$

- for holes

$$n_h = \int_0^{E_v} D_v(E) (1 - f(E)) dE$$



→ Calculation & Approximation of Carrier Density

- electron density : $n_e(E) = \int_0^{\infty} f(E) D(E) dE$

- for semiconductor : $E \geq E_c$

$$E - E_F \gg k_B T$$

Boltzmann approx : e^- far above E_F

$$f(E) \approx \exp\left(-\frac{E - E_F}{k_B T}\right)$$

$$\Rightarrow n_e(E) \approx N_{eff,e} \exp\left(-\frac{E_c - E_F}{k_B T}\right) \quad \left\{ \begin{array}{l} E_c - \text{lower edge of conduction band} \\ E_F - \text{Fermi energy} \end{array} \right.$$

(for e^-)

$N_{eff,e} = 2 \left[\frac{2\pi m_e^* k_B T}{h^2} \right]^{\frac{3}{2}} = N_c$

↑ effective density of states
of e^- ($E > M E_c$)

$$\Rightarrow n_h(E) \approx N_{eff,h} \exp\left(-\frac{E_v - E}{k_B T}\right) \quad \left\{ \begin{array}{l} N_{eff,h} = 2 \left[\frac{2\pi m_h^* k_B T}{h^2} \right]^{\frac{3}{2}} = N_v \\ \text{effective density of states of} \\ \text{holes } (E < E_v) \end{array} \right.$$

(for hole)

→ Intrinsic Carrier density

> Intrinsic carrier density - free carriers per unit volume in the conduction and valence band (after thermal excitation in semiconductor)

- for $T > 0K$, $n_i = \begin{cases} n_e |_{T>0} = N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right) & \text{for } e^- \\ p_o |_{T>0} = N_v \exp\left(-\frac{E_v - E_F}{k_B T}\right) & \text{for holes} \end{cases}$

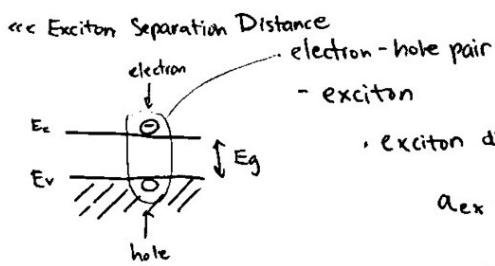
$$n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_c - E_v}{2k_B T}\right)$$

$$E_g = E_c - E_v \text{ band gap}$$

- example use of n_i

- conductivity in solar cells

$$K \propto \mu n \quad \text{where } \mu = \text{carrier mobility}$$



is critical parameter for determining if the system is quantum confined.

$L > a_{ex}$	bulk
$L < a_{ex}$	quantum confined

- Under quantum confinement, we have distinct energy level, we also change the bandgap.

$$\Delta E = \frac{4}{3} \frac{E_F}{N_V}$$

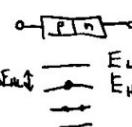
<< Solar Cells

- Intrinsic carrier density $n_i = \sqrt{N_c N_v} \text{ off } \frac{(E_c - E_v)}{2k_B T}$

- important for solar cells

- conductivity $K \propto \mu n_i$, μ - electron mobility

- open circuit voltage $V_{oc} = \frac{\Delta E_{HL}}{q} = \frac{kT}{q} \ln \left(\frac{(N_d - \Delta n) \Delta n}{n_i^2} \right)$



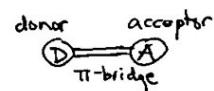
- N_d - donor atom concentration

- Δn - excess e^- generated by photons (photo current)

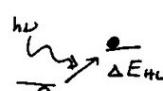
<< Chromophores

- For $g \equiv e = 1.6 \times 10^{-19} C$

$$\gamma V_{oc} = \Delta E_{HL}$$



- Change bridge length, \rightarrow change $\Delta E_{HL} \rightarrow$ change V_{oc}

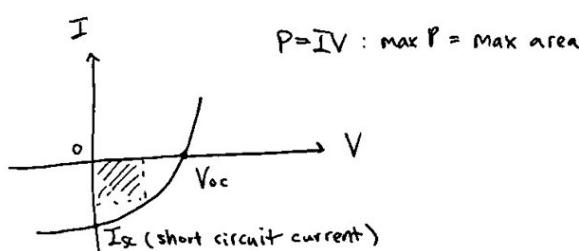
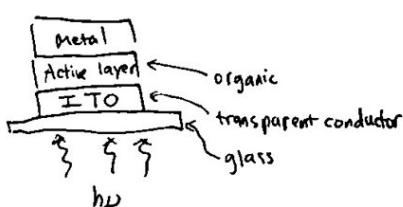


- \uparrow bridge length $\rightarrow \downarrow$ frequency for activation

<< Organic Photovoltaic device (PV)

- Advantage
 - easy to tune property
 - low cost
 - low temp operation
 - mechanically flexible
 - light

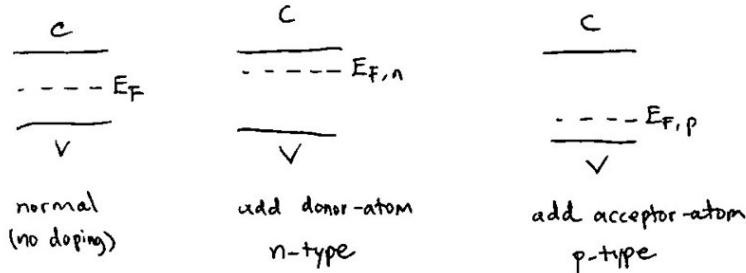
- Disadvantage
 - electron-hole-pair recombination
 - poor coverage of light spectrum
 - thermally unstable



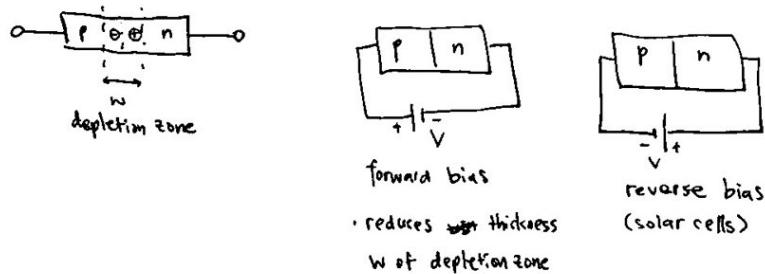
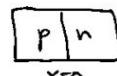
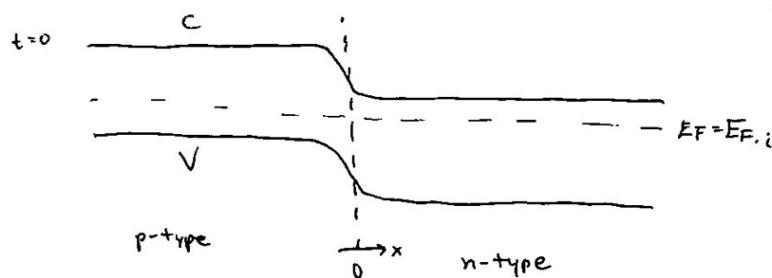
<< Donor/Acceptor Doping

→ p-n junction

- In inorganic semiconductors (e.g. Si), we can add donor dopant (e.g. P) and an acceptor dopant (e.g. B) ⇒ We change E_F Fermi energy.



- Interface (connect) p-type with n-type semiconductor.



$\cdot W=0 :$
Buitin :
voltage

$$V_{bi} = \frac{k_B T}{q} \ln \left(\frac{N_a N_d}{n_i^2} \right)$$

- Photodiode : pn-junction, we are irradiating depletion zone
⇒ free carriers in depletion zones (minority carriers)

$$\cdot \text{Fill factor } \Rightarrow FF = \frac{P_{max}}{V_{oc} I_{sc}}$$

$$\cdot \text{Efficiency } \eta = \frac{P_{max}}{P_{in} \leftarrow \text{solar radiation input}} \Rightarrow$$

$$\eta = \frac{(FF) V_{oc} I_{sc}}{P_{in}}$$

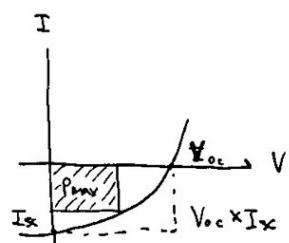
• open circuit voltage

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{I_{ph}}{I_0} + 1 \right)$$

$$\approx \frac{k_B T}{q} \ln \left(\frac{I_{ph}}{I_0} \right)$$

I_{ph} - photo current

I_0 - saturation current density (dark current)



<< Molecular Excitations

- Previously, electronic excitation is in $10^2 - 10^7 \text{ Hz}$ (UV-VIS)

- Molecules can also be excited thermally or by light at lower frequency
 - translational excitation

$$\rightarrow E_{n,\text{trans}}^{3D} = \frac{\hbar^2}{8mV^{\frac{3}{2}}} (n_x^2 + n_y^2 + n_z^2) \quad \text{assume } V=L^3 \Leftrightarrow \text{cube}$$

$n_i = 1, 2, 3, \dots$

- vibrational excitation

$$\cdot E_{n,\text{vib}} = (n + \frac{1}{2}) \hbar \nu \quad n = 0, 1, 2, 3, \dots$$

- \rightarrow range: $300 \times 10^5 - 450 \times 10^{12} \text{ (IR)}$

- rotational excitation

$$\cdot E_{J,\text{rot}} = \frac{J(J+1)\hbar^2}{8\pi^2 I} \quad J = 0, 1, 2, \dots$$

- Energy spacing

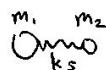
$$\cdot \Delta E_{n,n+1} : \Delta E_{\text{electronic}} \gg \Delta E_{\text{vib}} \gg \Delta E_{\text{rot}} \gg \Delta E_{\text{trans}}$$

$$\cdot k_B T \gg \Delta E_{\text{trans}}$$

<< Bond Vibrations in Molecule

$\rightarrow M_1 \gg M_2$

- Potential: $V(x) = \frac{1}{2} k_s x^2$



- SE: $[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)] \psi(x) = E \psi(x)$ $\rightarrow E \psi(x)$ assume $m_1 \gg m_2 = m$, so m_2 moving.

$$\Rightarrow E_n^{3D} = (n + \frac{1}{2}) \hbar \nu \quad n = 0, 1, 2, \dots$$

$$E_n^{3D} = (n_1 + n_2 + n_3 + \frac{3}{2}) \hbar \nu$$

- For ground state $n=0$

- $E_0 = \frac{1}{2} \hbar \nu$

- $\psi_0(x) = \frac{1}{\alpha \sqrt{\pi}} \exp(-\frac{x^2}{2\alpha^2})$, where $\alpha^2 \equiv \frac{\hbar}{\sqrt{m k_s}}$

- Equidistant energy levels

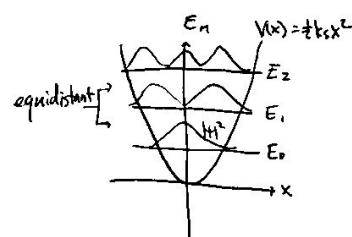
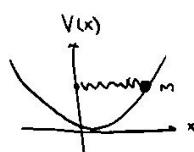
- $\Delta E = h \nu$

- Frequency

$$\boxed{\nu = \frac{1}{2\pi} \sqrt{\frac{k_s}{m}}}$$

$$k_s = m \omega^2$$

$$\omega = 2\pi\nu$$



$\rightarrow M_1 \gg M_2$

- Drop assumption $m_1 \gg m_2$



- Effective mass

$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}}$$

vibrational wave number

- Bond freq:

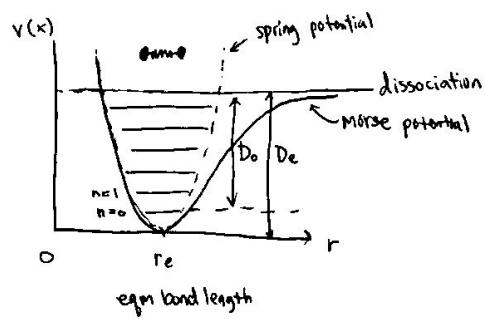
$$\boxed{\nu = \frac{1}{2\pi} \sqrt{\frac{k_s}{\mu}}}$$

$$\boxed{\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_s}{\mu}}}$$

- EM radiation in IR $\Delta E = h\nu$ can activate/relax bonding modes

<< Morse Potential

→ Morse potential - a realistic potential for diatomic molecules



$$V(r) = D_e (1 - \exp(-\alpha(r-r_e)))^2$$

$$\text{where } \alpha = \sqrt{\frac{k_e}{2D_e}}$$

D_e - dissociation energy (rel to $V=0$)

D_o - actual dissociation energy (rel to $n=0: V=\frac{1}{2}h\nu$)

$$D_o = D_e + \frac{1}{2}h\nu$$

<< Rotational Molecular Mode in Diatomic Molecules

- $\nu = \nu_{\text{rot}}$

- $V_i = r_i \omega \quad (\omega = 2\pi\nu)$

- $E_k = \frac{1}{2} I \omega^2$

- $I = m_1 r_1^2 + m_2 r_2^2 = \mu R^2$

- SE: $\hat{H}\psi = E\psi \quad ; \quad \hat{H} = -\frac{\hbar^2}{2I} \nabla^2, \quad V(\vec{r}) = 0$

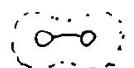
- $-\frac{\hbar^2}{2I} \frac{\partial^2 \psi}{\partial \phi^2} = E\psi$

- Solution: $E_{m_L} = \frac{m_L^2 \hbar^2}{2I}, \quad m_L = 0, \pm 1, \pm 2, \dots$ \uparrow from 2 rotation direction

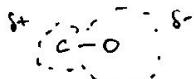
- Zero point energy of rotor $E_0 = 0$

- Wave fn: $\psi = \psi_{\text{rot}} = \sqrt{\frac{1}{2\pi}} \exp(iM_L\phi)$

- Take polar molecule (CO)



- symmetric e^- cloud
- nonpolar



- not sym. e^- cloud
- polar

- Place polar molecules in \vec{E}

- have diff. Energy state: $m_J = 0, \pm 1$

→ 3D Rotor

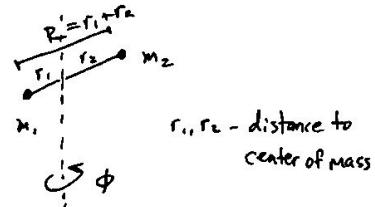
- $E_{\text{rot}}^{3D} = J(J+1) \frac{\hbar^2}{2I}, \quad J = 0, 1, 2, \dots$

- replaced m_L^2 as $J(J+1)$

- Rotational constant $B = \frac{\hbar^2}{2I}, \quad \tilde{B} = \frac{B}{hc} = \frac{\hbar}{8\pi^2 c I}$

- Rotational temperature $\Theta_{\text{rot}} = \frac{B}{k_B} = \frac{\hbar^2}{2I k_B}$

- Rot. energy $E_{\text{rot}} = J(J+1) k_B \Theta_{\text{rot}}$



r_1, r_2 - distance to center of mass