tional Method

PH253
1 April 2010

Schrodinger eqn gives us energy from ψ

only got to Kr-Penney $E(k)$ in 1 lec

$$E\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi \equiv \hat{H}\psi$$

- plug in $\psi(r)$, get energy at a point. total energy of system / particle

$$\boxed{E = \frac{\int \psi \hat{H} \psi \, dV}{\int \psi^2 dV}}$$

variational method:
- guess ψ w/some free parameters
- minimize E wrt parameters!

- even if guess is wrong, but physically reasonable, can be quite accurate

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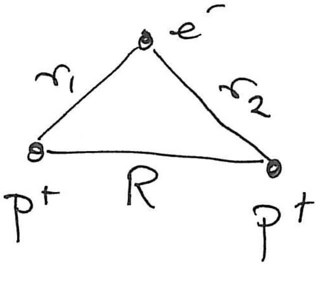
LCAO how to guess ψ?

- for molecules, presume real ψ to be a linear combo of atomic wave functions $\boxed{\psi = \sum_i C_i \varphi_i}$ weights → C_i; φ_i ← site; atomic soln → φ_i
- molecules' orbitals = combos of "bare" atom orbitals

2 atom orbitals → 2 hybrid mol orbitals

$n \rightarrow n$

Say, H_2^+



$$V = -ke^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$\varphi_{1,2} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_{1,2}/a_0} \quad (1s)$$

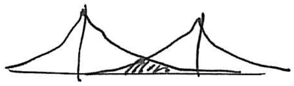
$$\psi = C_1\varphi_1 + C_2\varphi_2$$

what this really assumes is that bonding is a relatively weak perturbation, i.e. weak coupling

new $\Psi = c_1\varphi_1 + c_2\varphi_2$

energy: $$\boxed{E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1c_2 H_{22}}{c_1^2 + c_2^2 + 2c_1c_2 S_{12}}}$$

S_{12} = overlap integral $S_{12} = \int \varphi_1 \varphi_2 \, dV$



H_{ij} = Bond integrals

$H_{11} = H_{22}$ = bare single atom

e^- with one site, KE+PE

$H_{11} = c_1^2 \int \varphi_1 \hat{H} \varphi_1 \, dV$

$= c_1^2$ (energy of H atom)

$H_{12} = H_{21}$ = bonding term, interaction energy (e^- with both sites)

$$\boxed{H_{12} = 2c_1c_2 \int \varphi_1 \hat{H} \varphi_2 \, dV}$$

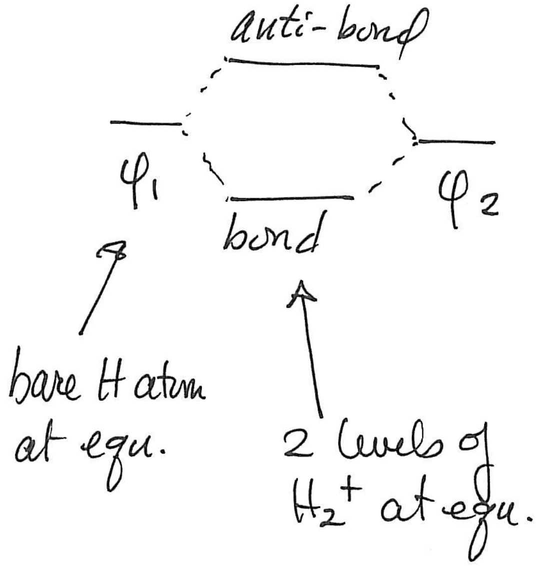
$\boxed{\text{Task: minimize } E \text{ wrt } c_1 \text{ \& } c_2}$ $\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$

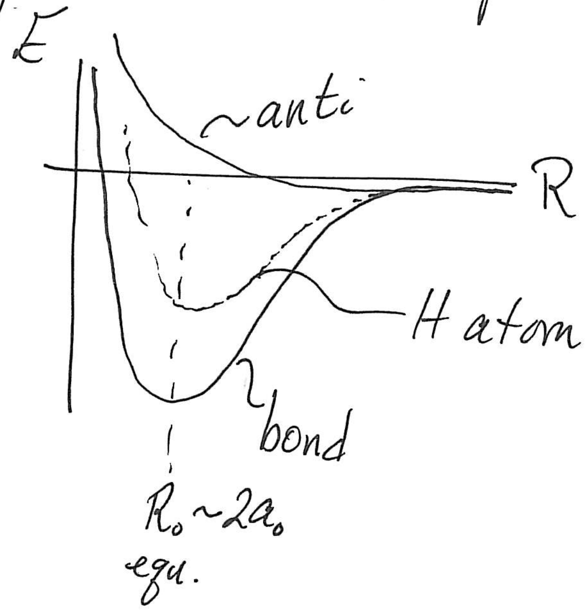
$$\Rightarrow \boxed{E = H_{11} \pm \frac{H_{12} - H_{11} S_{12}}{1 \pm S_{12}}}$$

large R: $S_{12} = H_{12} = 0$ – no coupling/bonding

$\Rightarrow$ H atom + bare proton

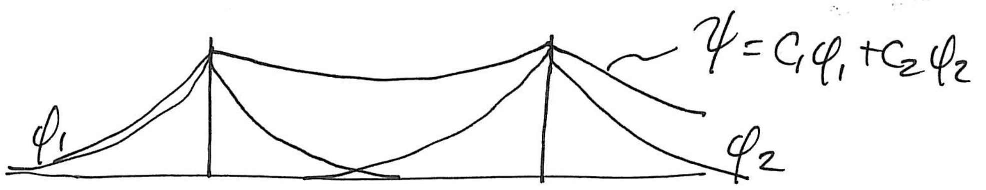
what was 2 equal energy levels is now 2 sep. ones!

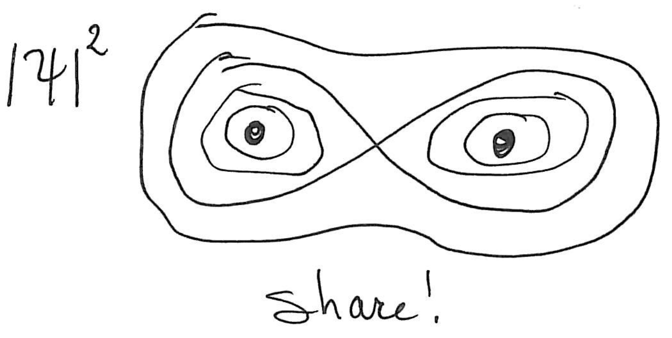




- bond formation: Lower overall energy of ground state at expense of 1st excited state

Bond





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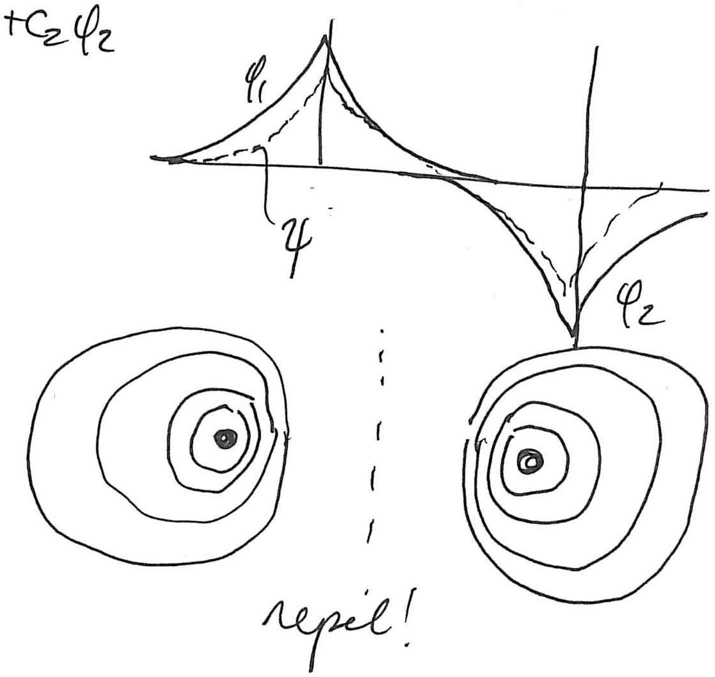
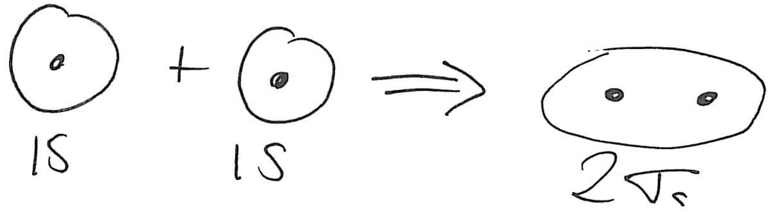
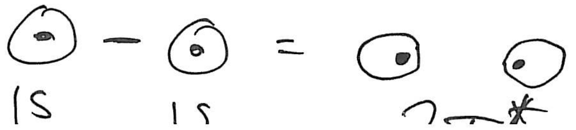






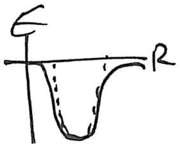
onding : e^- wants to be between protons – σ

Anti : e^- on either outer side – σ*

σ = molecular orbital

2 – s states ⟶ 2 σ states, σ & σ*

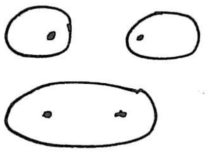
- Can do this for H_2 ($2e^-$, $2p^+$)
  - harder, but straightforward
- from E(R) near equil : forces! elastic const / moduli



- near $R = R_0$, approx with parabola, $E = \frac{1}{2}kx^2$
- small dev. from equil, ≈ SHM / Hooke's law

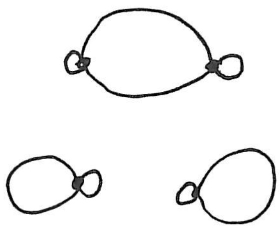
More complex orbital?

s ± s ⟶

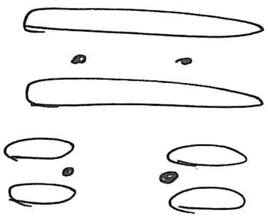


$_z \pm p_z$ ⟶

∞ ± ∞



8 ± 8



Can have s–p or p–p bonding too...

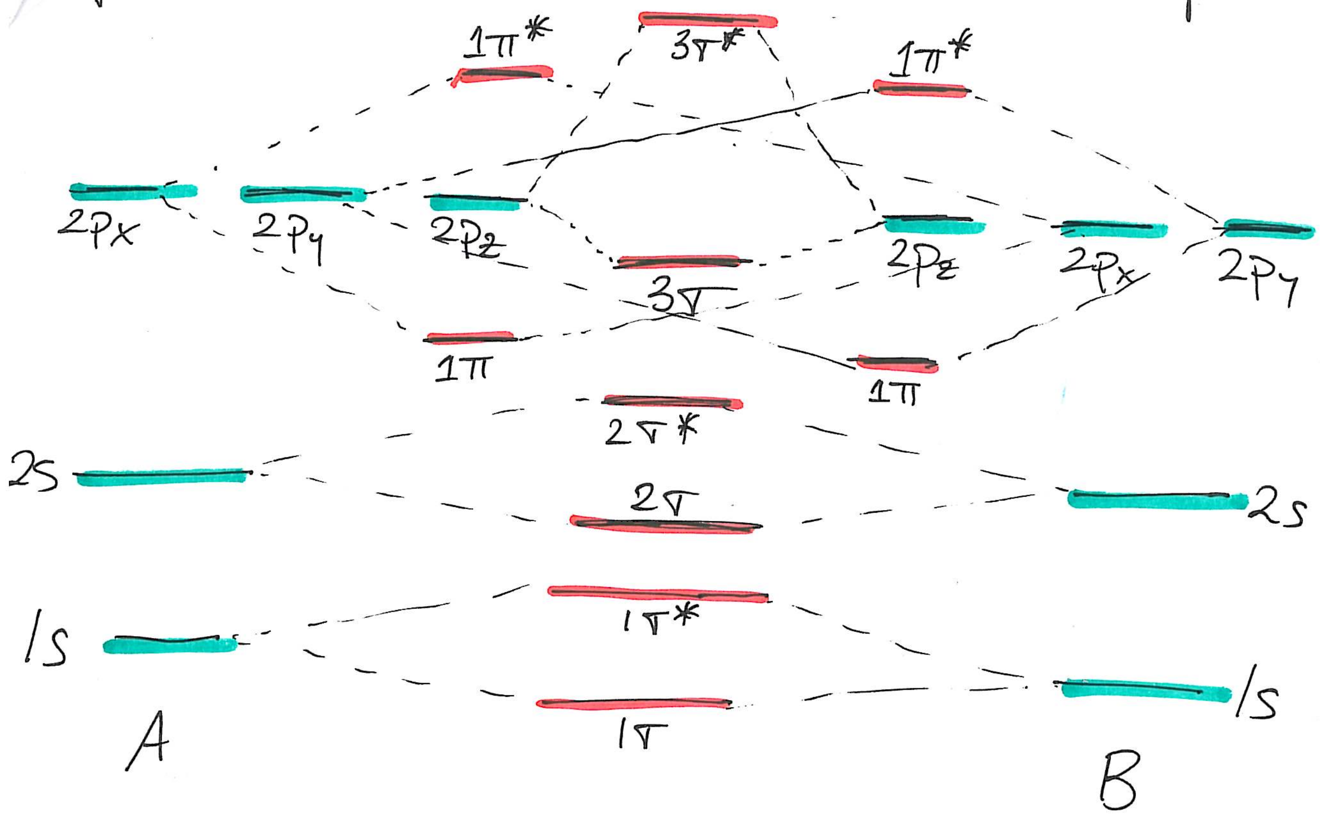
Can't have

8 + O (integral zero)

8 + ∞ "

(and even more ...)

just like atomic orbitals, build up a level diagram



atomic orbitals

1s, 2s, 2p
?
2, 2, 6 e⁻
1, 1, 3 levels (m_ℓ)

$\Longrightarrow$

molecular orbital

1σ, 1σ* < 2σ, 2σ* < 1π < 3σ < 1π* < 3σ*

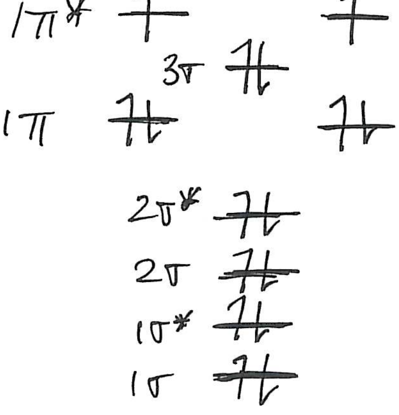
- 2 levels/orbital for π
- 4 e⁻ per orbital (↑↓ ↑↓)

- 1 level per orbital for σ
- 2 e⁻ per orbital (↑↓)

Example: O_2

$O = 1s^2 2s^2 2p^4$

So 8e⁻ x2 = 16e⁻



- 2 unpaired spins
- net magn moment
- still reactive (lone e⁻...)

How about still larger systems?

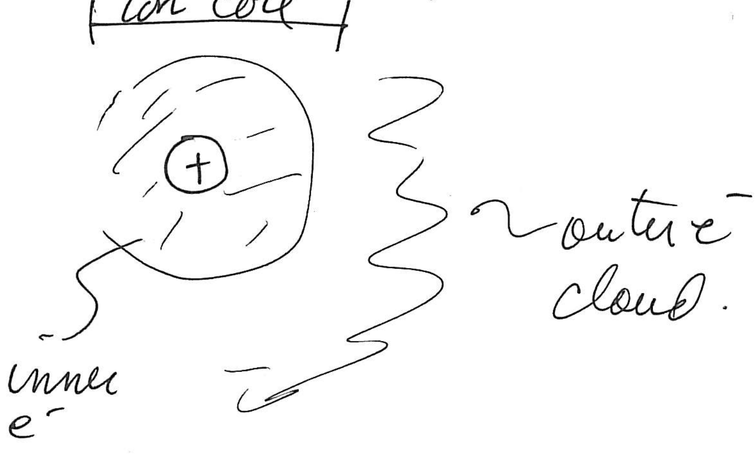
- Variational + LCAO works fine for small molecules
- we are still *hosed* for a whole crystal
- we have missed some nice tricks

Task: figure out metals, semicond, insulator crystals

- inorganic (mostly)
- *periodic* lattice ... we can *use* this!

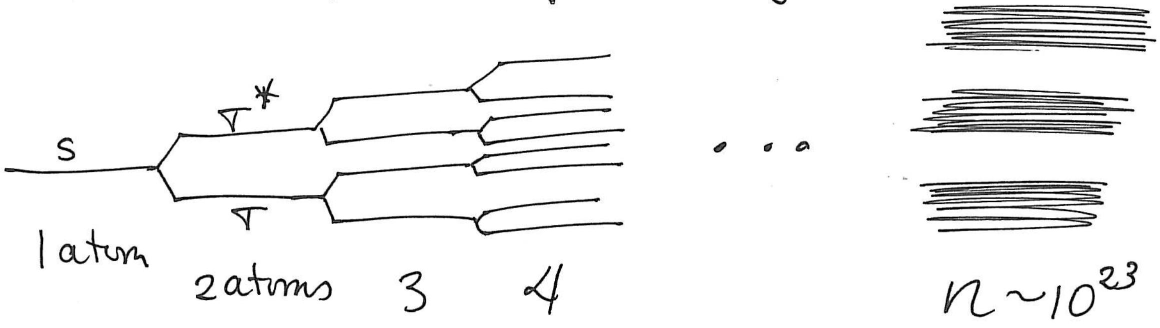
Basic model: periodic array of ⊕ nuclei & core e^-

- inner e^-: stick around nucleus (strong binding)
  $\Rightarrow$ "Screened" ion core
  these stay put - heavy!
- outer e^-: weakly bound, can *migrate* from atom-atom
  - or - participate in bonding



outer e^- cloud · bonding, potentially mobile sual in physics, let's start in 1D and appeal to generalities

- general expectations
  - when we combine 2 atoms, we get 2 new energy levels
    (like coupled oscillators, get $f_1 \pm f_2$)
  - Combining n atoms should give n new levels
    this quickly gets out of hand!



- essentially continuous <u>bands</u> of allowed energies in large n limit ($\sim 10^{23}$)
- Some forbidden regions remain ... Xtal symmetry
  (note: a 1nm × 1nm × 1nm cube of Cu has ~150 atoms)
  - all nanotech way above that yet
  - all practical problems are intractable ...

n Model

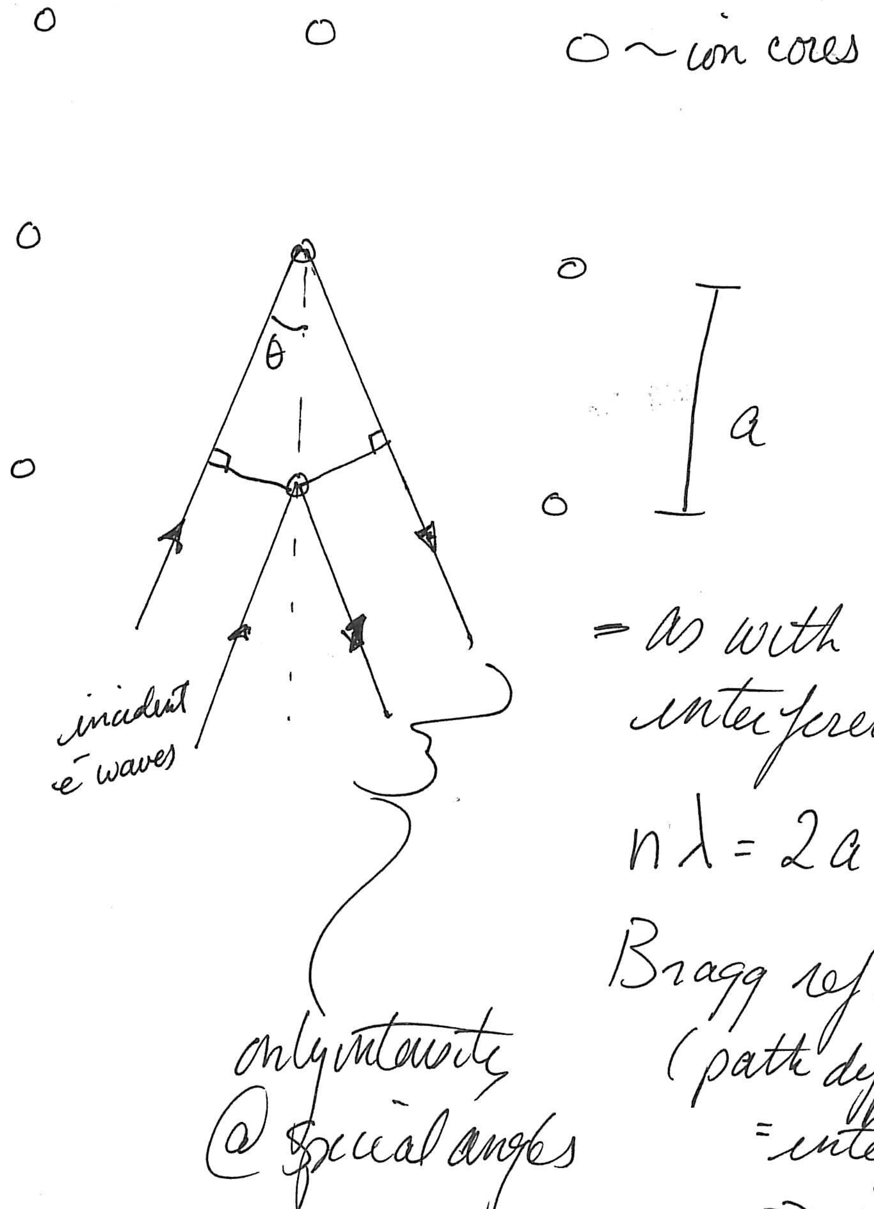
- Let us assume the "free" outer e⁻ look like plane waves
  i.e. like a free electron

$\psi_k = e^{ikx}$

k = wavevector = $\frac{2\pi}{\lambda}$ = spatial periodicity

free e⁻: $E = \frac{\hbar^2 k^2}{2m}$

- what happens when such a wave enters a crystal lattice?
  interference, like light diffraction!



= as with light, constr. interference when

$$n\lambda = 2a\cos\theta \qquad n = 1, 2, 3, \ldots$$

Bragg reflection
(path difference for waves
= integer wavelengths
⇒ constructive)

(9)

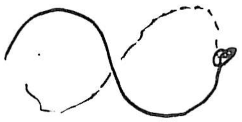
one dimension, there is no angle: just FW a REV

reduces to $n\lambda = 2a$ i.e. $a = n\left(\frac{\lambda}{2}\right)$ lattice period matches $\frac{1}{2}\lambda$ (like 1D well)

- also implies $\boxed{k = \frac{n\pi}{a}}$ only certain wave vectors can propagate in crystal!

  - makes sense: periodicity of ψ matches underlying lattice, V

- wave could also be reflected by an atom



so wave function has → and ← parts

$$\underset{\text{fw/refl}}{\underset{\uparrow}{\psi_{\pm}}} = \frac{1}{\sqrt{2}}\Big(\underset{\substack{\text{fw}\\ \text{trans}}}{e^{ikx}} \pm \underset{\substack{\text{rev}\\ \text{refl}}}{e^{-ikx}}\Big) = \sqrt{2}\begin{pmatrix}\cos kx\\ \sin kx\end{pmatrix}$$

($\sqrt{2}$ for normalization)

basically: waves in a periodic PE

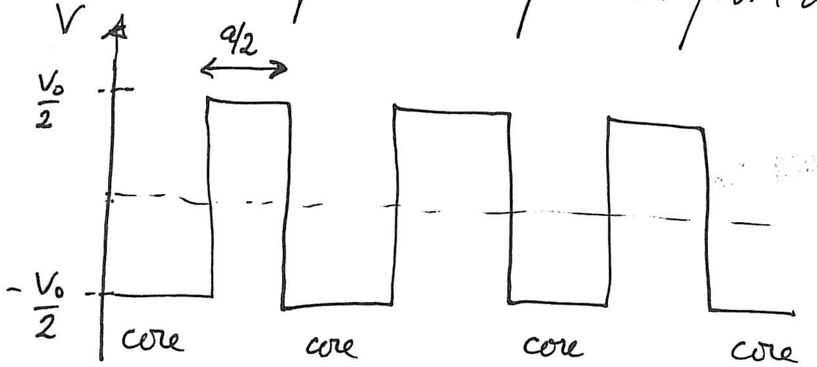
, let's find the energies! (of the e^- in these states only)

- for e^- in states ψ_I, energy varies w/ posn
- let's find their <u>average</u> PE in this crystal

$$V_\pm = \frac{1}{L}\int |\psi_\pm|^2 V(x)\,dx = \frac{1}{L}\int \begin{pmatrix} 2\cos^2 kx \\ 2\sin^2 kx \end{pmatrix} V(x)\,dx$$

↑ Length of xtal

model potential? steps . . . deep attraction to cores, background repulsion from other e^-



(Kronig-Penney Model)

(one can prove that $\psi = u_a(x)e^{ikx}$, where $u_a(x)$ has same symmetry as lattice)

- Since the potential is periodic, we only need to average over <u>one period</u>

$$V_\pm = \frac{1}{a}\int_0^a \begin{pmatrix} 2\cos^2 kx \\ 2\sin^2 kx \end{pmatrix} V(x)\,dx = \frac{1}{a}\int_0^a \begin{pmatrix} 1+\cos 2kx \\ 1-\cos 2kx \end{pmatrix} V(x)\,dx$$

- now $V(x)$ integrates to zero - oscillating function!

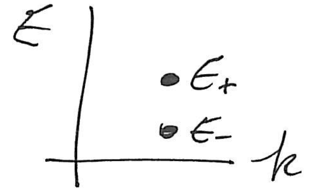
$$V_\pm = \pm\frac{1}{a}\int_0^a \cos 2kx\, V(x)\,dx = \pm V_n \quad \text{since } k = \frac{n\pi}{a}$$

(can do integral, but we don't care)

main point: $V_n \neq 0$, and has <u>opposite signs</u> for $\psi_\pm$

<u>Again</u>:
- e^- waves have certain wave numbers ($k = \frac{n\pi}{a}$) that are <u>reflected</u> by the lattice
- given k, there are transmitted and refl solutions ψ_+ and ψ_- with energies $+V_n$ and $-V_n$
- KE same for both, $K = \frac{\hbar^2 k^2}{2m}$
- total E then $\boxed{E = K + V = \frac{\hbar^2 k^2}{2m} \pm V_n}$

! 2 possible values, but NONE in between - discrete



there is a "gap" in the allowed energies of $2V_n$!

• what if $k \neq \frac{n\pi}{a}$? the energy can vary continuously

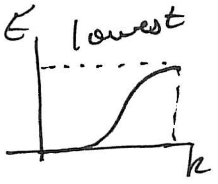
- no longer just pure plane wave, some decay & <u>modulation</u>

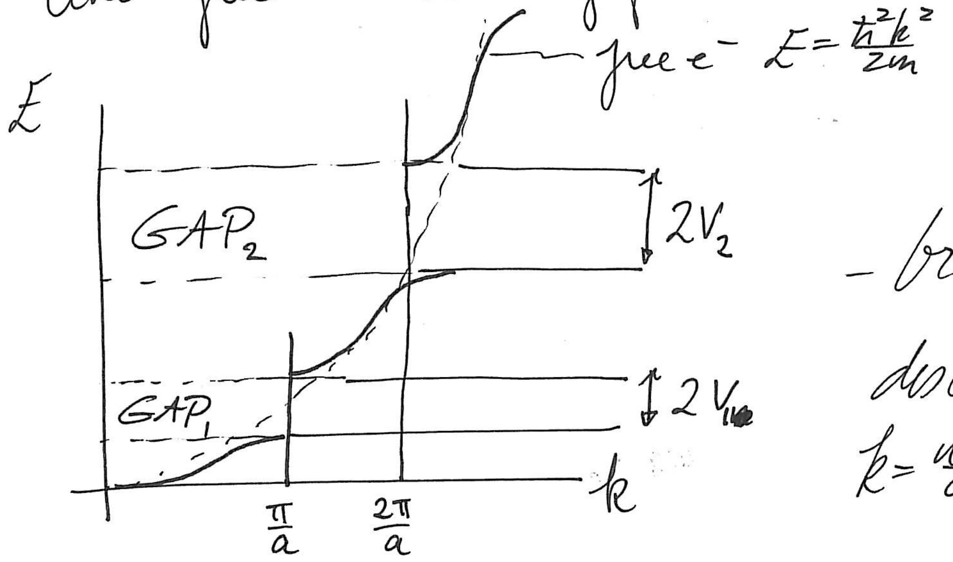
($k \neq \frac{n\pi}{a}$ ⇒ lattice & wave period don't match—beating!

- sum of plane wave part and "interference" w/ lattice

- leads to continuous spectrum outside of "gaps"

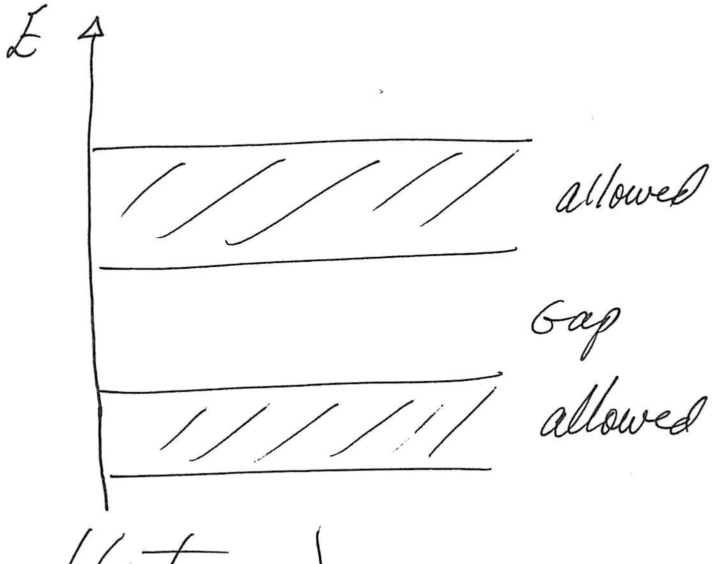
like free-e^- with gaps





- broken parabola
discontinuities at
$k=\frac{n\pi}{a}$ from lattice refl

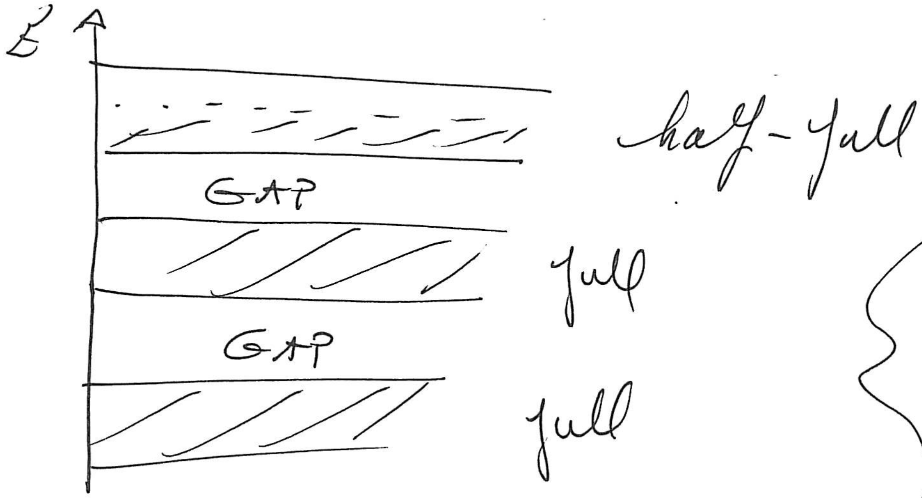
• for many atoms, 3D ... need crystal geometry ⇒ gaps



• now fill allowed states w/ electrons

• where last ones go determines <u>conductor vs insul vs semi</u>

(Got here, 11 lecture)

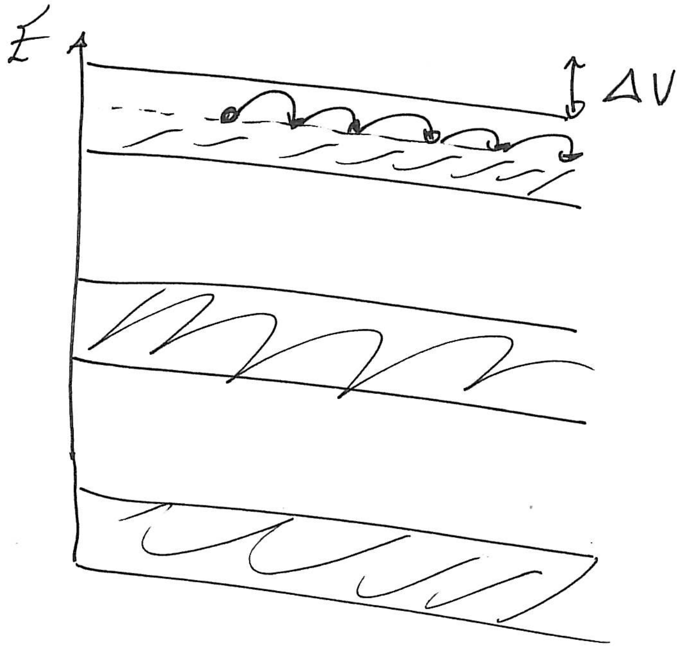


Metal!

highest E electrons (weakest bound) have states available

⇒ can move around

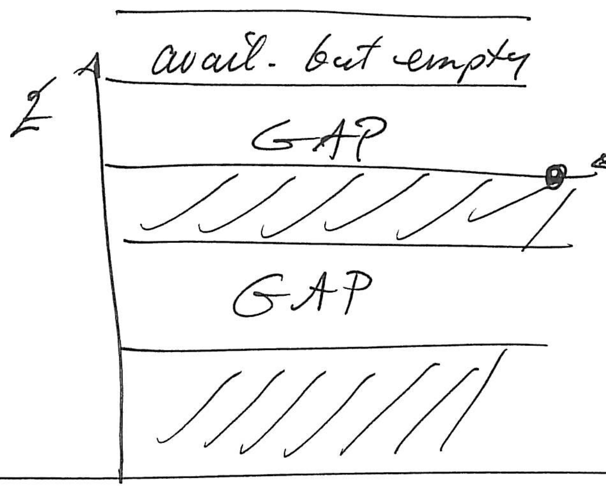
↓ apply voltage



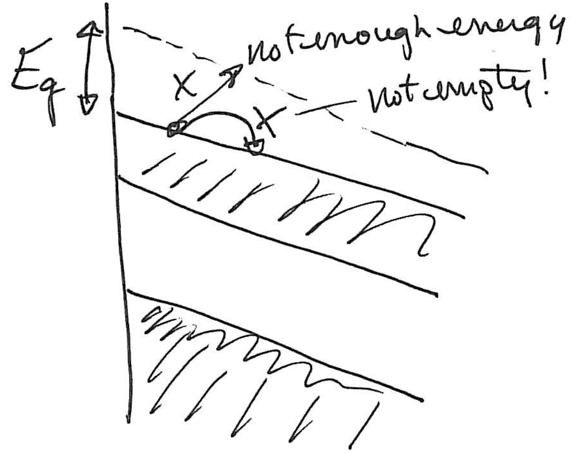
e^- can hop to empty state at same or lower E!

⇒ net flow to RHS

<u>insulator</u>: top-most band filled!



upper e^- has no adjacent states! ~~so~~ applying ΔV does not free up levels



unless $\Delta V \gtrsim E_g$ no chance

(even then... distance involved may be too much!

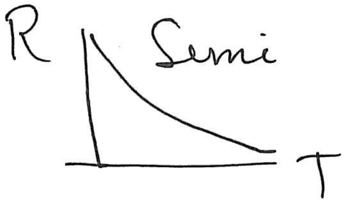
need $\Delta V \gtrsim E_g$ over <u>atomic</u> dist!

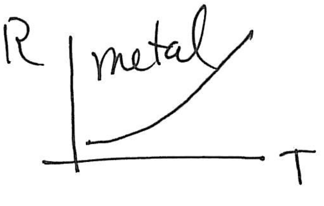
$\Delta V \sim E_g \sim 3\text{-}8\,\text{eV}$ atomic dist $\sim 0.2\,\text{nm}$ $\Rightarrow |\vec{E}| \gtrsim 1.5\times10^{10}\,\frac{\text{V}}{\text{m}}$!

- this is the breakdown voltage, roughly ($\gtrsim 10^9\,\frac{\text{V}}{\text{m}}$ SiO_2)
- ridiculous field ... <u>truly insulating</u> for all practical purposes

Semiconductor

gap is small, so k_BT may allow some e^- to "jump" $\Rightarrow$ slight conductivity





(very susceptible to doping)