"All" of chemistry

Basic idea: 2 atoms close-by ⇒

electrons (1) "see" nucleus + electrons (2) →

internal structure may change (eigenwavefunctions)

or even electron transfer may occur (→ ionic bond)

⇒ net attraction (a bit similar to classical attraction between charge + dielectric, but here QM! even 2 neutral objects can attract) ~~Van der Waals forces~~

(exception: permanent dipoles, e.g. H_2O)

→ scattering

→ binding. May lead to sharing of (some) electrons or even transfer (e.g. Na Cl is ionic)

(Note: "metallic" bound later)

Example: ionic bound K Cl

$K \rightarrow K^+ + e^-$: 4.34 eV $\quad e^- + Cl \rightarrow Cl^-$: -3.62 eV

$K^+ Cl^-$ attraction: ⩾ .72 eV.

Equilibrium due to a) ions nuclei get closer, less shielding → repel

b) electrons overlap more → repel

c) Pauli principle

QM in a solid crystal

Simplify: 1D system (chain of N atoms)

Basic idea: each atom "gives up" j electrons ($j = 1, 2 \ldots$) and keeps $Z - j$ ⇒ series of Coulomb potentials at fixed points $0, a, \ldots, Na$:

Look for E.S. solutions to Schrödinger Equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\psi(x) \quad \text{or}$$

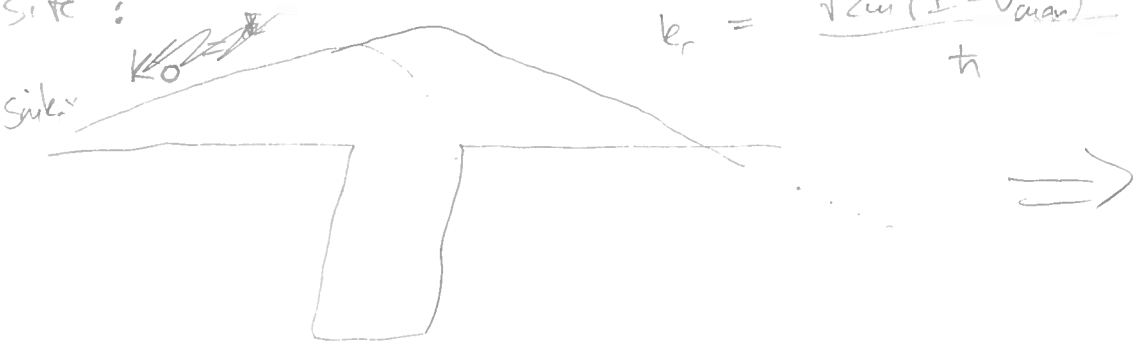
$$\frac{\partial^2}{\partial x^2}\psi = -\frac{2m(E - V(x))}{\hbar^2}\psi$$

General solution: approximate potential by square well

→ assume E just above V_{max}

⇒ curvature small in between sites, strong in each site:

$$k_r = \frac{\sqrt{2m(E - V_{max})}}{\hbar} \qquad E = \frac{\hbar^2 k^2}{2m}$$



Add req.: Bound state! ⇒ at the ends, exponential fall-off ($E<0$!)

Simplification: like U well, require $\psi(0)=\psi(a)=0$

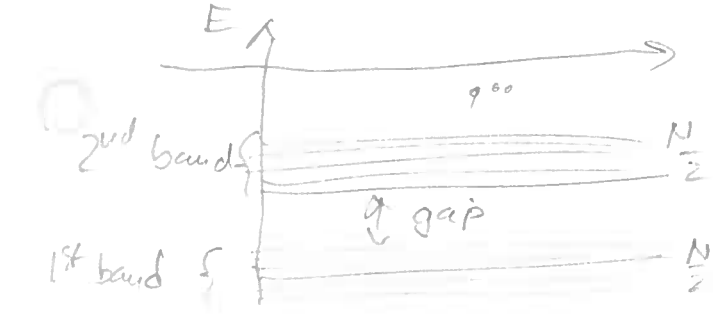
2 conditions → as always, leads to quantization for k_0!

Find minimum k_0 → say we have N oscillations total.

→ next higher → just one oscillation more ($\approx \Delta k \cdot N \cdot a = 2\pi$

etc. → very large (but not ∞!) number of solutions

$k_0 \to k_{band}$. Turns out there are only $\frac{N}{2}$ distinct solutions → "gap" above k_1. However if we keep increasing k → (larger k need to "explain" solutions) eventually solution at sides change enough so we can get another set $\frac{N}{2}$ solutions ($k_2 \to k_3$) ⇒ 2nd band etc. So final structure looks as follows

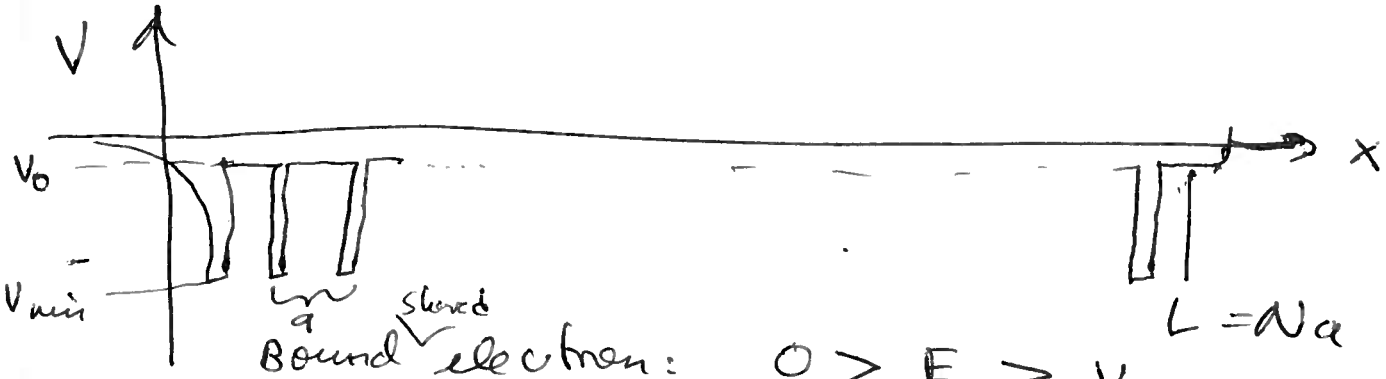


Now add Pauli principle: lowest band can only accept N electrons ($2\times\frac{N}{2}$) ⇒ if $j>1$, several bands filled.

Band structure in simple QM

Alternative Derivation

Toy model 1D



Bound electron: $0 > E > V_0$

Because $E < 0$, outside solution of $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = E\psi$ must be falling-off exponential, $\psi_{out}(x) = A e^{\kappa(x-L)}$ with $\kappa^2 = \frac{2mE}{\hbar^2}$ ⇒ only solutions with $\frac{\psi'}{\psi} = -\kappa$ are allowed inside (continuity of ψ, ψ') at $x = L$

At $x = 0$, of course $\psi_{out} = A e^{+\kappa x}$ ⇒ internal wave must begin with slope $\frac{\psi'}{\psi} = \kappa$. Now just solve 1D EV problem piece by piece: in between binding sites, $V = V_0$ ⇒ small curvature, $-\frac{\partial^2}{\partial x^2}\psi = \frac{E - V_0}{\hbar^2/2m}\psi$ ($E_0 = 0$)

near atom sites, large curvature, $-\frac{\partial^2}{\partial x^2}\psi = \frac{E - V_{min}}{\hbar^2/2m}\psi$

⇒ in limit $E \to V_0$:

→ at end, can have arbitrary $\frac{\psi'}{\psi}$, not usually equal $-\kappa$

Now increase E slightly: get curvature even between sites ⇒ eventually match required $\frac{\psi'}{\psi}$ at $x = L$

→ first (ground state) solution $V_0 < E_0 < 0$