Summary - and Challenges in Theoretical Materials Science

Much of this lecture:

Can we understand the observed behaviour of a given, real material based on quantum-mechanical first principles?

Spectacularly successful:

- Born-Oppenheimer approximation
- effective single-particle framework:
  - Hartree, Hartree-Fock, Density-functional theory
  - Band structure, k-space
  - Cohesion (electrostatics, covalent, metallic bonding, van der Waals ...)
  - Phonons in solids, thermal properties
  - Transport theory (with some reservation)
- Magnetism
- Superconductivity (conventional)

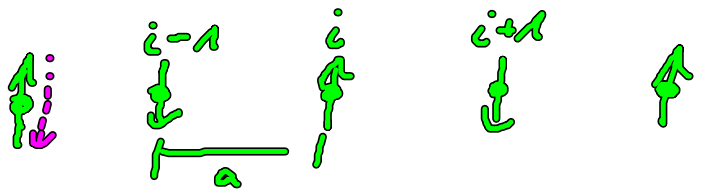
...

However, some basic "openings" left:

- High-T_c superconductivity
- "strong correlation"
- "Emergent phenomena"

Side note: "strong correlation"

breakdown of effective ($\underline{k}$-space / single-particle picture



$\underline{k}$ is good quantum number for quasiparticles...

But what if

$$H = \sum_{\underline{k}\sigma} \epsilon_{\underline{k}} c^{\dagger}_{\underline{k}\sigma} c_{\underline{k}\sigma} + \frac{U}{M} \sum_i n_{i\uparrow} n_{i\downarrow}$$

- "Emergent Phenomena"

Complex many-body interactions create physics which is qualitatively different from the underlying single-particle world.

e.g. fractional quantum Hall effect

But generally: Have the right theories for most mainstream phenomena

Today:

- Can we predict, from first principles alone, the properties of a given "material"?
- For a desired physical property, can we predict "the best" material that best has it?

(e.g. strength of an alloy, catalyst for clean reaction, the highest possible T_c in a d-like magnetic semiconductor)

Main tool at this point,

Kohn-Sham DFT

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{Nuc}(\underline{r}) + V_{Hn}(\underline{r}) + V_{xc}(\underline{r})\right]\psi_i(\underline{r}) = \epsilon_i \psi_i(\underline{r})$$

$$\Rightarrow E_{tot} = E[n(\underline{r})]$$

$$V_{xc}(\underline{r}) = V_{xc}[n(\underline{r})](\underline{r})$$

Still some qualitive failures:

- van der Waals interactions (non-local in nature)
- "strong correlation"

Other challenge: Excited states?
Transport?

[→ GW. corrections..]

Left out a basic flaw:

Real materials are often large, complex

"Multiscale problem"

- QM description happens at Å level
- typical velocities:

Given by $kT \sim 0.04\ eV \sim \frac{1}{2} m v^2 \rightarrow 0.04 \cdot 1.6 \cdot 10^{-19}\ kg\frac{m^2}{s^2}$

$$m \approx m_H = 1.67 \cdot 10^{-27}\ kg$$

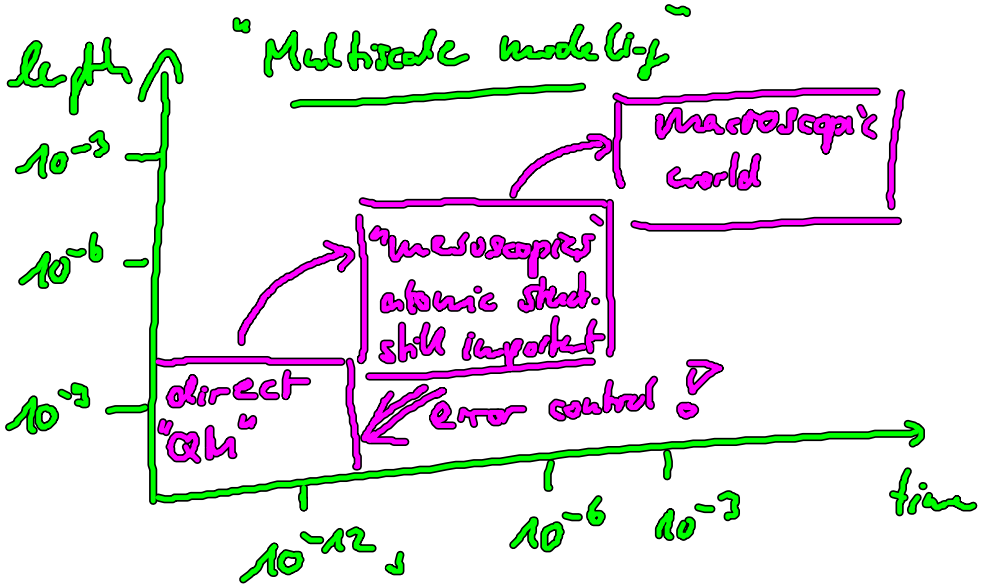
$$\Rightarrow v = \sqrt{\frac{2kT}{m}} \approx \sqrt{008\ \frac{10^{-19}}{10^{-27}}}\ \frac{m}{s} \sim 3 \cdot 10^3\ \frac{m}{s}$$

$$\sim 3 \cdot \frac{10^{-10}\ m}{10^{-13}\ s} = 3\ \frac{Å}{100\ fs}$$

→ need to resolve ~ fs timescale to see

"dynamics" ?

- "Complexity" : ⟶ grows with length scale for real materials.



We know:

- Mesoscopics often described by atomistic model but not necessarily full QM

Examples: "Force fields"

$$E(\{R_I\}) = \sum_{IJ} \frac{D_{IJ}}{2}(|R_{IJ}| - l)^2 + \frac{q_I q_J}{|R_{IJ}|} + \sum_{IJk} (\text{three-body term}) + \dots$$

- [Transport theory in semiconductor structures]

This works qualitatively but not itself "first principles"

- Macroscopic world:
  Continuum models!
  (Heat conduction, fluid dynamics)

- Can we use "first principles" at the QM scale to find the right parameters at the mesoscopic scale?
- Can we use mesoscopics to find the right macroscopic continuum equation?

Example: "Cluster Expansion"

- imagine 3 point lattice
- 2 elements.

$\rightarrow$ $E(A_3)$, $E(A_2B)$, $E(AB_2)$, $E(B_3)$

$\rightarrow$ can rewrite this formally

$$E(\underline{\sigma}) = J_0 + \sum_i J_1 \sigma_i + \sum_{ij} J_2 \sigma_i \sigma_j$$

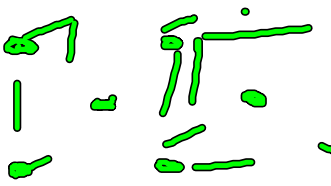
$+ \sum_{ijk} J_3 \sigma_i \sigma_j \sigma_k$

$\sigma_i = 1$ if A on site i

-1 if B on site i

"generalized Ising Hamm.)

We can do this for larger systems too ....

...  3D lattice

$$E(\sigma) = J_0 + \sum_i J_1 \sigma_i + \sum_{ij} \dots + \sum_{ijk} + \dots$$

Physics: J_{ij} will decay with pair distance

→ truncate!

same for MB!

Get complex alloy energetics by:

- Parameterizing a finite # of J from first principles
- Use to predict
  - millions of total E
  - statistical mech.
  - ...