

# 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:

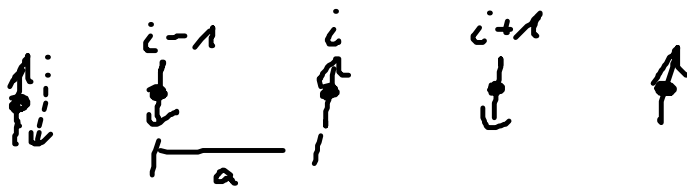
- Born-Oppenheimer approximation
- effective single-particle frameworks:
  - Hartree, Hartree-Fock, Density-functional theory
  - Band structure,  $k$ -space
  - Cohesion  
(electrostatics, covalent, metallic bonding,  
van der Waals ...)
  - Phonons in solids, thermal properties
  - Transport theory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

However, some basic "openings" left:

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

Side note: "strong correlation"

breakdown of effective ( $\underline{L}$ -space) single-particle picture



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

But what if

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

### • "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 has it?

(e.g. strength of an alloy, catalyst for chem. reaction, the highest possible  $T_c$  in a dilute magnetic semiconductor)

Main tool at this point,

Kohn-Shan DFT

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

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

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

Still some qualitative failures:

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

Other challenge: Excited states?  
Transport?

[ $\rightarrow$  GW corrections...]

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Left out a basic idea:

Real materials are often large, complex

"Multiscale problem"

• QM description happens at  $\text{\AA}$  level

• typical velocities:

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

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

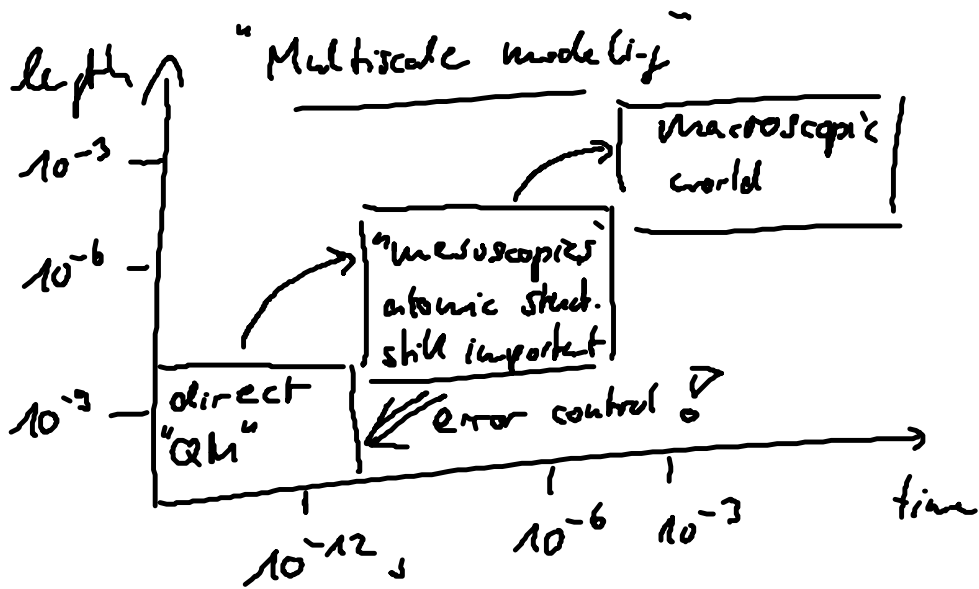
$$\Rightarrow v = \sqrt{\frac{2kT}{m}} \approx \sqrt{0.08 \frac{10^{-19}}{10^{-27}} \frac{\text{m}}{\text{s}}} \sim 3 \cdot 10^3 \frac{\text{m}}{\text{s}}$$

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

$\rightarrow$  need to resolve  $\sim \text{fs}$  timescale to see

"dynamics" ?

- "Complexity" :  $\rightarrow$  grows with length scale for real materials.



We know:

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

Examples: "Force fields"

$$E(\{\mathbf{R}_i\}) = \sum_{ij} \frac{D_{ij}}{2} (|\Delta \mathbf{R}_{ij}| - l)^2 + \frac{q_i q_j}{|\Delta \mathbf{R}_{ij}|} + \sum_{ijk} (\text{three-body term} \dots) + \dots$$

- [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  
QMC scale to find the right parameters at  
the macroscopic scale?

• Can we use mesoscopics to find the right  
macroscopic continuum equation?

Example: "Cluster Expansion"

• • • imagine 3 part lattice  
• • • 2 elements.

→  $E(A_3)$ ,  $E(A_2B)$ ,  $E(AB_2)$ ,  $E(B_3)$

→ can rewrite this (formally)

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

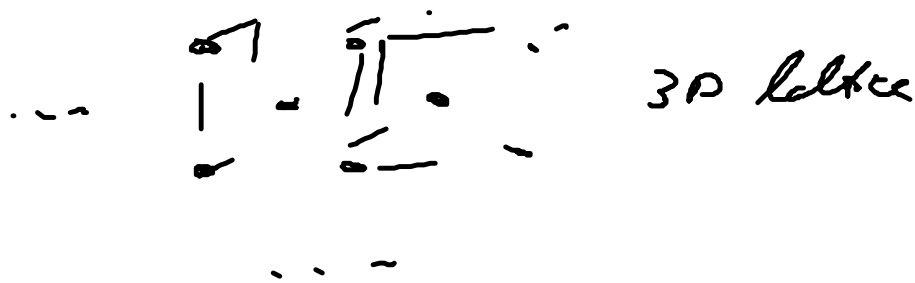
$$+ \sum_{ijk} J_3 \sigma_i \sigma_j \sigma_k$$

$$\sigma_i = 1 \quad \text{if A on site } i$$

$$-1 \quad \text{if B on site } i$$

"generalized Ising (Ham.)"

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



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

Physics:  $J_{ij}$  will decay with pair distance  
 $\rightarrow$  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.
  - ...