Discrete Models:
Material Properties from Electrons and Atoms

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Acknowledgements:
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Motivation: ICME

Aim: Linking materials models at multiple length scales
→ design products
→ design materials
→ processing

Key: Standardization of information exchange
→ Are suitable interfaces between the codes sufficient?
List of quantum chemistry codes:

http://en.wikipedia.org/wiki/Quantum_chemistry_computer_programs

Popular codes:

- **WIEN2k**
  - all electron code
  - + most accurate, applications
  - - Computationally very expensive
- **VASP**
  - plane wave, PAW pseudopotentials
  - + accurate, applications
- **SIESTA**
  - atomic orbitals, pseudopotentials
  - +“fast”
  - - Accuracy more difficult to control

Do we need for ICME just an interface to one (or a few) of these codes?
Electronic and atomistic scale

Most fundamental level
→ All subsequent levels rely on availability and accuracy of electronic structure calculations
→ Can it be used to replace experimental parameters by ab initio (i.e. computed) ones?

Key questions:
→ Are the higher level approaches describing the correct physics?
→ Can we control the errors?
→ Can we perform these calculations on todays (super-) computers?
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Physics
Parameters
Errors

Which parameters?
Targeted errors

higher level(s)

Electronic and atomistic scale
Key questions:
→ Are the higher level approaches describing the correct physics?
→ Can we control the errors?
→ Can we perform these calculations on today's (super-) computers?
Example: H-embrittlement

→ H distribution around an edge dislocation

Does ICME mean that we simply replace empirical parameters by ab initio computed ones?

Identify/construct realistic higher-level models

Example: H-embrittlement

→ H distribution around an edge dislocation

realistic dislocation structure

→ full dislocation splits into two partials

inclusion of H-H interaction

→ dislocation stabilized nano-hydrides

Replacing empirical/fitted parameters in higher scale models by ab initio ones is likely to fail

→ Quantum-mechanically informed models!

Pezold, Lymperakis, JN, Acta Mat. 59, 2696 (2011)
Key questions:
→ Are the higher level approaches describing the correct physics?
→ **Can we control the errors?**
→ Can we perform these calculations on today’s (super-) computers?
Main error types:

**Model-related errors:**
→ e.g. finite size effects due to periodic boundaries

**Algorithmic errors:**
→ e.g. pseudopotentials vs all-electron calculations

**Discretization errors:**
→ e.g. basis set, k-point sampling

**Theory-related errors:**
→ e.g. choice of exchange-correlation functional in density functional theory

- can be systematically reduced
- inherent errors
Errors that can be systematically reduced

Only limitation:
  → available computer performance

Critical issue for ICME:
  → none of the presently existing codes allows automatic error reduction
  → presently this has to be done by hand and requires broad knowledge of underlying physics and algorithms
  → main source of discrepancies in literature

Development of frameworks that allow a fully automatic determination of ab initio parameters with a target for these errors (sensitivity analysis)

→ Our approach: Python based workbench (PyCMD)
**Python based CM Workbench (PyCMW)**

- **Generic input** → VASP, LAMMPS, SPHINXS, KMC
- **Code specific input** → POSCAR, INCAR

Create a project
- list of jobs
- high throughput

**Central storage**
- SQL Database
- HDF5
- NAS

Submit and run job
- compress and translate file
- monitor queues
- cleanup

**Code specific output** → e.g. OUTCAR

**Generic output** → energy_tot (eV)

Identify missing data
- Ecut, k-points

Visualize data

Analyze errors
- $\Delta E_{\text{tot}}$, $\Delta a_{\text{lat}}$

Collect project data

Analyze data
- convergence

** MPIE, Department of Computational Materials Design **
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Inherent errors

Errors that cannot be reduced on the expense of more computer time

Example: Error in bulk modulus vs error in lattice constant for various metals

None of the existing xc-functionals provides a superior performance!

Typical errors:
→ length: ~ 1 %
→ elastic const.: ~ 10 %

For ICME we need estimates of inherent errors!
**Key questions:**

→ Are the higher level approaches describing the correct physics?
→ Can we control the errors?
→ Can we perform these calculations on today's (super-) computers?

- physics parameters
- errors
- higher level(s)
- Which parameters?
- Targeted errors
Computational Efficiency

Example: Free energy computations (materials properties at finite temperature)

\[ Z(\hat{A}, T) = \sum_{\{\hat{R}_I\}_A} e^{-E_{BOS}(\{\hat{R}_I, Z_I\}_A)/k_BT} \]

10^7 configurations

a few hours
Computational Efficiency

Example: Free energy computations (materials properties at finite temperature)

\[ Z(\hat{A}, T) = \sum_{\{\hat{R}_I\}_A} e^{-E_{BOS}(\{\hat{R}_I, Z_I\}_A)/k_B T} \]

Recent method developments allow efficient coarse graining of huge configuration spaces
What accuracy is achievable?

Example: Thermal expansion coefficient of bulk aluminum

\[ F(V,T) = F_{\text{el}}(V,T) + F_{\text{qh}}(V,T) + F_{\text{qh,el}}(V,T) + F_{\text{ah}}(V,T) + F_{\text{vac}}(V,T) + F_{\text{int}}(V,T) \]

→ Excellent agreement with experiment
→ LDA and GGA provide approximate measure of inherent errors

systematically reducible errors well below 1 meV

MPIE, Department of Computational Materials Design

Grabowski, Ismer, Hickel, JN, PRB 79, 134106 (2009)
What accuracy is achievable?

Example: Heat capacity of bulk calcium

All systematically reducible errors well below 1 meV

Error control is critical to achieve predictive power!

Conclusions

Quantum-mechanically based ab initio techniques provide a firm basis for ICME

But: Simple interface and parameter transfer will in most cases not sufficient!

→ Critical to identify/construct quantum-mechanically informed higher level approaches

→ Develop tools that allow computation with predefined precision

→ Develop methods/tools that allow an estimate of the inherent errors

→ Develop algorithms that allow a computationally efficient sampling of huge configurations spaces