

Status and Challenges in Quantum Mechanics Based Simulations of Materials Behavior

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- **Why quantum-based simulations?** Even one level up requires inter-atomic potentials that: a) constrain physics via functional form, b) do not exist for all combinations of elements. Quantum mechanics alleviates both a) and b), at a cost...
- **Recommended Strategy for Predictive Materials Simulation:**
 - Must select appropriate theory for given phenomenon and material
 - Must know approximations made and how they effect outcome (error estimates)
 - Method should give right answer for right reason (correct physics, correct phenomenon)
- No universal method works for all materials and all phenomena (sadly)
- **Hierarchy of electronic structure methods (accuracy/efficiency tradeoff)**
- **Properties of interest:** surface reactivity, interfacial structure/bonding/adhesion, dispersion forces, yield/tensile/shear strength, ductility, fracture, band gap, optical spectra, transport (diffusion, electrical and thermal conductivity)
- **Materials of interest (e.g. to industry):** metal oxides/nitrides/carbides, polymers, ceramic coatings, metal alloys, composites, amorphous structures, heterogeneous nanostructures
- **Size of features, e.g. at nanoscale:** 3 nm particle ~1000 atoms => need linear scaling methods
- **Validation** of predictions critical – difficult to design appropriate experiment

First Principles Quantum Mechanics Methods

- **Quantum Chemistry (QC) and Quantum Monte Carlo (QMC)**
 - Pros: exact exchange and correlation (XC) => no assumptions, systematic convergence toward exact results. QC obtains ground and excited states of arbitrary order of excitation
 - Cons: Post-HF QC not periodic & $>O(N^5)$ scaling;
In QMC, TMs, forces problematic
 - Current Solutions: Linear scaling CC/CI/QMC, sub-3D periodicity, periodic embedding theories
- **Density Functional Theory (DFT)**
 - Pros: simple mean field theory, 3D periodicity available, $O(N)$ methods available
 - Cons: approximate XC, no systematic means of improvement, ground state only

Current Solutions?

First Principles Electronic Structure Methods Continued...

- **Beyond DFT – Current Solutions**

- Hybrid XC (includes some exact HF X).
 - Pros: (relatively) simple extension
 - Cons: not appropriate for metals (HF diverges)
- DFT+U (standard DFT for delocalized e-, on-site HF for localized, strongly correlated e-)
 - Pros: eliminates self-interaction error
 - Cons: U-J selection arbitrary, U-J not updated
- Dynamic Mean Field Theory (dynamic DFT+U)
 - Pros: more general than DFT+U, e.g. can treat metal-insulator transition
 - Cons: describe strongly correlated electrons within a Hubbard/Anderson Hamiltonian
- TD-DFT for neutral ($N \rightarrow N$) excited states, absorption spectra
 - Pros: simpler, cheaper than QC methods
 - Cons: Linear response (only single excitations), XC functionals not designed for excited states, excitation energies only accurate to ~ 0.5 eV, 3D periodicity problematic
- GW (DFT input, but XC replaced by “self-energy”, screened XC)
 - Pros: obtain $N \rightarrow N \pm 1$ excitation energies (PES/IPES, IP, EA), band structures (errors ~ 0.3 eV)
 - Cons: results worse when GW done self-consistently and with all electrons! (errors ~ 0.5 eV)
- Bethe-Salpeter equation (DFT + GW input + e-h pair interaction)
 - Pros: obtain neutral excitation energies
 - More complex, expensive formalism, limitations of DFT, GW and only single excitations
- Embedded CI. Pros: systematically improve XC locally, arbitrary order excited states can be treated. Cons: DFT approximations at interface, local excitations only

Select Appropriate Method for Property

Current Status:

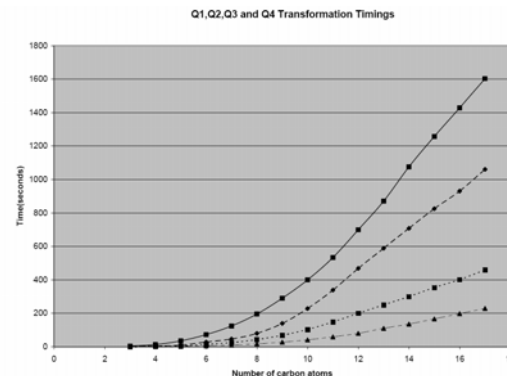
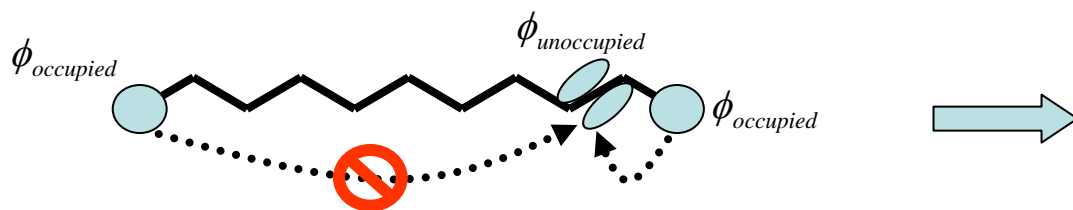
- Surface reactivity and diffusion – DFT-GGA for metal alloys, non-transition metal ceramics – errors < 0.4 eV. Embedded CI can reduce errors to < 0.1 eV, but at greater complexity/expense
- Interfacial structure/bonding/adhesion, yield/tensile/shear strength (requires rescaling), ductility, fracture qualitatively correct with DFT-GGA, but need experimental data for validation
- Band gaps from GW (IP-EA only) and *not from hybrid DFT*
- Optical spectra from BSE or TD-DFT (for neutral single electron excitations)
- Electrical conductivity and conductance in nanostructures (DFT + scattering/Landauer, Kubo-Greenwood/Boltzmann transport) – no consensus on best method, need validation
- Dispersion forces – van der Waals XC functionals, XC hole dipole moment – not yet extended to 3D materials

Select Appropriate Method for Material

- Current Status: no *one* method works for all materials, since all contain approximations...
- Metal alloys, ceramics, semiconductors – DFT-GGA
- Polymers – periodic MP2 for polymer blends, DFT-GGA for polymer/metal or polymer/ceramic interfaces
- Strongly correlated materials, e.g. first row transition metal oxides, actinides – DFT+U, DMFT, embedded CI
- Amorphous structures difficult to model – introduce correlation length artifacts due to finite 3D PBCs, difficult to generate representative structures due to time scale mismatch of MD quench time vs actual quench time
- Heterogeneous nanostructures very challenging:
Large numbers of atoms requires linear scaling, different types of materials may require different methods...

Linear Scaling Electronic Structure Methods

- Linear scaling self-consistent-field methods: DFT & HF (requires band gap, becomes linear at $O(100)$ atoms)
- Orbital-free DFT (linear with no crossover, but only accurate for main group metals)
- Linear scaling QMC (transition metals, forces difficult)
- Linear scaling correlated quantum chemistry methods (coupled cluster, multireference configuration interaction) – only for molecules or local defects...



Length and Time Scale Mismatch between Simulation and Experiment

Typical sim: 100 atoms, ps to ns Typical expt: 10^{23} atoms, hours

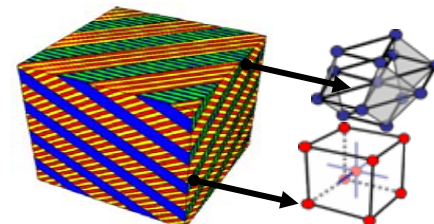
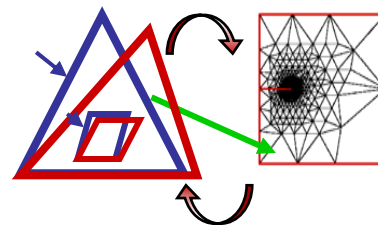
=> Requires methods to bridge scales

– **Length scales:** Angstroms (10^{-10} m) [atoms] to mm [cracks]

- Quantum mechanics \leftrightarrow atomistic molecular dynamics/Monte Carlo \leftrightarrow dislocation dynamics \leftrightarrow grain boundary motion \leftrightarrow phase field/level set microstructure \leftrightarrow continuum
- How to do seamlessly without introducing artifacts/errors?

Current solutions: quasicontinuum, atomistic-discrete dislocation dynamics, coupled QM-MD, informed continuum

– **Major unsolved issues:** heat conduction and mass transfer across scales, uncertainty quantification, unifying mathematical theory, extraction of reduced dimensionality behavior (new concepts, new nonempirical physical laws)



The Ideal Multiscale Model: We are nowhere near there yet...

- Would like **one model that bridges atomistic and continuum descriptions seamlessly**, i.e., contains atomistic and continuum limits as special cases.
- All **physics should be defined at the fundamental (atomistic) level** and **coarse-graining should not introduce additional physics or assumptions** (e.g., random noise, viscosity, thermostats, presumption of thermodynamic equilibrium...).
- **Coarsening/refinement should be inhomogeneous** (e.g., full atomistics within defect cores, continuum-like behavior away from defects) **and adaptive**, i.e., local resolution should be provided by the method itself as part of the solution.

Bridging Time Scales: Current Status

Characteristic Time scales:

fs (10^{-15} s) [atomic motion] to minutes/hours [material deformation]

Challenge:

How to capture rare events *and* evolve over long times?

- **Multiple/variable time step** methods don't get to long enough times
- **Rare event** methods (**umbrella sampling**, **blue moon ensemble**) requires advance knowledge of TS and does not get long times either.
- **Kinetic Monte Carlo** (assumes TST for individual steps, usually table lookup of processes/rates, on-the-fly KMC expensive, not deterministic)
- **Accelerated Molecular Dynamics** deterministic, can get to milliseconds with classical interatomic potentials (mostly assume TST, long integration times prohibits use of quantum mechanical forces)
- **Least Action Path Dynamics** can get to arbitrarily long times (must know trajectory endpoints in advance and could miss rare events)
- **Ensemble Dynamics** gets to arbitrarily long times (but only probabilities)

Unfortunately, no general method for getting to long times yet, with accurate forces, without prior knowledge or assumptions...

What's needed next in quantum mechanics theory development for materials simulation?

- Accurate, efficient calculation of dispersion energies/forces from quantum mechanics so that soft materials (polymers, biomolecules, etc.) can be properly treated.
- 3D periodic post-HF quantum chemistry methods for ultimate accuracy.
- Make excited state and strong correlation methods (GW/BSE, DMFT, TD-DFT, embedded CI) linear scaling.
- Coarse grain quantum mechanics to achieve sublinear scaling.
- Experiments to validate predicted observables.
- Seamless modeling across time/length scales with uncertainty quantification.
- Database of validated quantum mechanics data for the purpose of developing interatomic potentials for use in MD

Where to go from here?

Proposal #1: National Thrust on Development of Interatomic Potentials

Sounds really boring.....

BUT essential to accurate modeling and design of materials

- Without potentials, “nanoscale” design is qualitative, not predictive
- Many, many material combinations needed – a large effort.
Only a few groups have experience and patience for this work
- Methods for automation, optimization exist
- Consider how much time and \$\$ is spent now on MD simulations that use “convenient” potentials that may not be accurate
- **THIS IS THE CHEMISTRY OF MATERIALS MODELING**
So treat it like fundamental inorganic chemistry and materials!!

Courtesy of Bill Curtin (Brown U)

Proposal #2: National Thrust on Methods of Multiscale Modeling

Development of Basic Methods (Quasicontinuum-like,
Accelerated MD-like)

(do we need 10 atom/continuum methods?)

(do we need 7 discrete dislocation methods?)

Support for Round-Robin Tests

Support for Parallelization, Engagement of CS

(High Performance Computing is useless without it)

(Funding for code development, optimization, porting is paltry)

Demand/create Open-Architecture models

(Plug-and-play modules for coupled methods)

THIS IS THE PRODUCTION/MANUFACTURING OF MODELING

So treat it like a Major Materials Development Program

**With a stronger, broader, integrated infrastructure,
modeling and simulation capability would expand and be
more predictive**

Courtesy of Bill Curtin (Brown U), with additions by EAC

Proposal #2 1/2: Establish appropriate training in multidisciplinary modeling

Quantum Mechanics

Statistical Mechanics

Molecular Dynamics

Materials Science of Defects and Mechanisms

Continuum Mechanics of Defects

Numerical Methods

Availability of tools (VASP; LAMMPS; ABAQUS)
does not replace understanding, insight.

Use of available codes is deceptively easy

➡ Training of students in **underlying fundamentals** is critical

➡ How do we drive this within existing disciplinary curricula?

Courtesy of Bill Curtin (Brown U)

Simulation Based Science and Engineering: General Investments Needed As Well

- Develop efficient, well-designed HPC-based software
 - Grow the US leadership in scientific software engineering
 - Establish real collaborations between computer engineering and science experts
 - Develop, maintain, optimize, port, parallelize code in the spirit of the European model
- Flexibility of personnel team structure is critical
- Possible Team: domain specialists (engineer/scientist), algorithms specialists, and software engineers/computer scientists
- Encourage research into parallel application software by CS groups