	institute for pure & applied mathematics	
Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules		
	July 21 - August 1, 2014	
Monday, July 21, 2014 Morning Session		
	First Principles - Overview	
8:00 - 9:00 9:00 - 9:30 9:30 - 10:30 11:00 - 12:00	Breakfast Welcome and Opening Remarks Matthias Scheffler (Fritz-Haber-Institut der Max-Planck-Gesellschaft) "Overview: Electronic Structure Theory for the Ground State" Kieron Burke (University of California, Irvine (UCI)) "Electronic Structure Beyond the Ground State"	



Theoretical Concepts and Some Examples (Results)

- 1. Electronic-Structure Theory
- 2. Ab initio Atomistic Thermodynamics
- 3. Molecular Dynamics
- 4. Kinetic Monte Carlo Approach

Modeling Materials Properties and Functions: The Many-Body Schrödinger Equation

$$(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With: $\Psi(\mathbf{r_{1}}, \cdots \mathbf{r_{N}}; \mathbf{R_{1}}, \cdots \mathbf{R_{M}})$
 $\hat{T}^{e} = \sum_{k=1}^{N} \frac{\mathbf{p}_{k}^{2}}{2m}$ $\hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{p}_{I}^{2}}{2M_{I}}$
 $\hat{V}^{e-e} = \frac{1}{2} \frac{1}{4\pi\epsilon_{0}} \sum_{k\neq k'}^{N,N} \frac{e^{2}}{|\mathbf{r_{k}} - \mathbf{r_{k'}}|}$
 $\hat{V}^{ion-ion} = \frac{1}{2} \frac{1}{4\pi\epsilon_{0}} \sum_{I\neq I'}^{M,M} \frac{Z_{I}Z_{I'}}{|\mathbf{R_{I}} - \mathbf{R_{I'}}|}$
 $\hat{V}^{e-ion}(\mathbf{r_{k'}}, \mathbf{R_{I}}) = \sum_{k=1}^{N} \sum_{I=1}^{M} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k}}|)$

$$\begin{aligned} &(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi \\ &(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi \\ &\text{With: } \Psi(\mathbf{r_{1}}, \cdots \mathbf{r_{N}}; \mathbf{R_{1}}, \cdots \mathbf{R_{M}}) \\ &\hat{T}^{e} = \sum_{k=1}^{N} \frac{\mathbf{p}_{k}^{2}}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_{I}^{2}}{2M_{I}} \\ &\hat{V}^{e-e} = \frac{1}{2} \frac{\mathbf{p}_{I}^{2}}{\pi c_{e}} \sum_{k \neq k'}^{N} \frac{e^{2}}{|\mathbf{r_{k}} - \mathbf{r_{k'}}|} \\ &\hat{V}^{ion-ion} = \frac{1}{2} \frac{1}{4\pi c_{0}} \sum_{I \neq I'}^{M,M} \frac{Z_{I}Z_{I'}}{|\mathbf{R_{I}} - \mathbf{R_{I'}}|} \\ &\hat{V}^{e-ion}(\mathbf{r_{k}}, \mathbf{R_{I}}) = \sum_{k=1}^{N} \sum_{I=1}^{M} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \mathbf{v}_{k}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \sum_{k=1}^{N} \sum_{I=1}^{M} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \sum_{k=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \sum_{i=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \sum_{i=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{r_{k'}}|) \\ & \sum_{i=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \sum_{I=1}^{N} \mathbf{v}_{I}^{ion}(|\mathbf{R_{I}} - \mathbf{v}_{I'}|) \\ & \sum_{i=1}^{N} \sum_{I=1}^{N}$$



Some Limits of the Born-Oppenheimer Approximation

It does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamical Jahn-Teller effect at defects in crystals
- some phenomena of diffusion in solids
- non-adiabaticity in molecule-surface scattering and chemical reactions
- relaxation and transport of charge carriers $(e^{-} \text{ or } h)$
- etc.



































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Ab initio Atomistic Thermodynamics

Assumption of thermodynamic equilibrium

This means that any information about time-scales is lost. We look at the system after infinite time.

Note that in reality the kinetics *can* be very slow; an extreme example is C-diamond \leftrightarrow graphite.

Sometimes it is important (and possible) to define a *constrained equilibrium*.

Thermodynamics (A Brief Reminder)

Thermodynamic potentials:			
Internal energy	$U(S, V) = E^{\text{tot}} + U^{\text{vib}}$		
Enthalpy	H(S, p) = U + pV		
(Helmholtz) free energy	F(T, V) = U - TS		
Gibbs free energy	G(T, p) = U - TS + pV		
E^{tot} contains energy contributions from chemical binding (structure) as well as electronic excitations, if present. U^{vib} is the energy of vibrations. For poly- atomic systems E^{tot} and U^{vib} are best calculated by DFT.			
At thermodynamic equilibrium the corresponding thermodynamic potential assumes its minumum.			
Chemical potentia = the cost to remove a p	l $\mu = (\partial G / \partial N)_{T, p} =$ particle from the system.		



Ab Initio Atomistic Thermodynamics Effect of a Surrounding Gas Phase on Surface Structure and Composition

C. M. Weinert and M. Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
E. Kaxiras et al., Phys. Rev. B 35, 9625 (1987)
X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998)
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002)













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Brief History of MD

<u>First MD simulation:</u> B.J. Alder and T.E. Wainwright, 1956 - hard sphere liquid, phase transition

First MD simulations with a continuous potential: G.H. Vineyard et al, 1959 -- radiation damage simulation with a pair potential A. Rahman, 1964 - Lennard-Jones liquid

<u>First MD with DFT energetics:</u> R. Car and M. Parrinello, 1985 – Si crystal

Computational cost is almost always dominated by the cost of the force call (evaluating E^{tot} and $dE^{\text{tot}}/d\mathbf{R}$).











Possibilities and Limitations of MD

<u>With force fields (no explicit quantum mechanics)</u>: 10³ - 10⁴ atoms are possible on a single processor Much larger systems are possible via parallelization: several million atoms are now routine; billions of atoms are possible <u>With DFT energies</u>: just ~100 atoms (soon 1000)

Problems:

- Accuracy of the interatomic interaction
- Length scale (number of atoms)
- Time scale limited to ~ 1 ms (with *simple* potentials) and with DFT energies up to 1 ns
- Quantum dynamical effects of the nuclei are typically ignored.
- Non adiabatic dynamics not treated properly

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kMC Summary

- kMC is a numerical solution of the master equation.
- It gives essentially the same information as MD, but can simulate time spans $>10^{12}$ times longer.
- It can be linked to *ab initio* rate processes: free energy barriers, and their *T* dependence. Often transition state theory can be applied. Configurational entropy and resulting (kinetic) barriers are obtained by the kMC simulation. .. and more.
- The main challenge for building a reliable kMC simulation is to find all the important processes.







Summary and Outlook: Interacting Electrons Determine the Properties and Function of Real Materials Important arenas for future theoretical work: Non-adiabatic effects, dissipation ٠ Transport (electrons, ions, heat) ٠ Thermodynamic phase transitions, e.g. melting ٠ Surfaces, nanostructures – in realistic environments • Modeling the kinetics, e.g. of catalysts or crystal growth • (self-assembly and self-organization) Molecules and clusters in solvents, electrochemistry, fuel • cells, external fields Correlated systems, e.g. *f*-electron chemistry ٠ **Biological problems** ٠ The challenges: Find ways to control the xc approximation Develop methods for bridging length and time scales electronic (collective) excitations