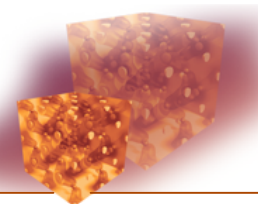


2007 Summer School on Computational Materials Science

Quantum Monte Carlo: From Minerals and Materials to Molecules

July 9 –19, 2007 • University of Illinois at Urbana–Champaign

<http://www.mcc.uiuc.edu/summerschool/2007/qmc/>



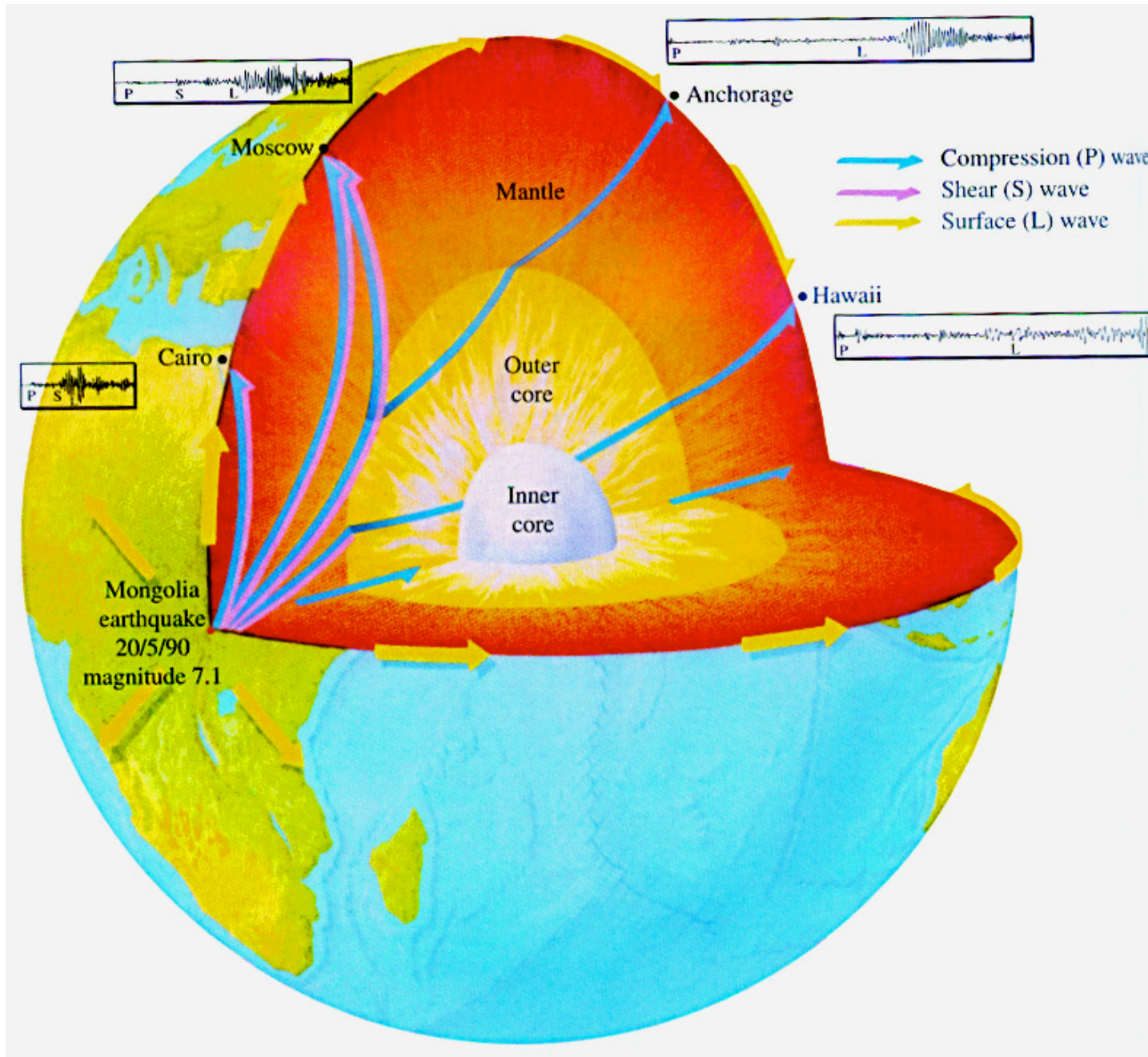
Quantum Monte Carlo on geomaterials

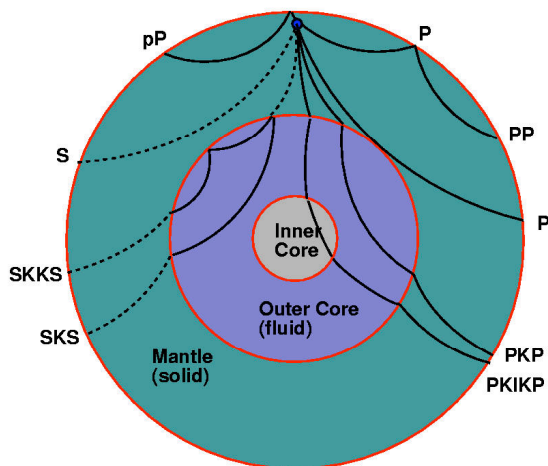
Dario Alfè

[d.alfè@ucl.ac.uk]

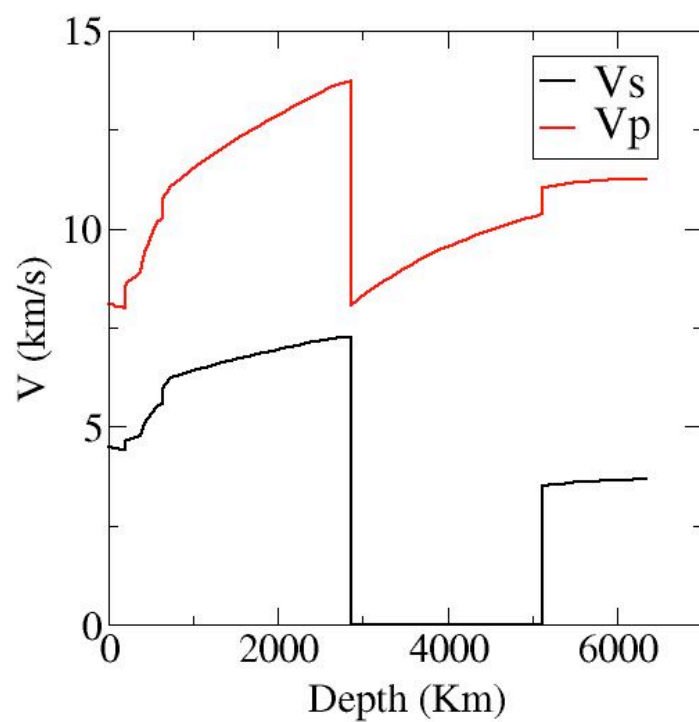
Some properties of interest

- Equations of state (low and high temperature)
- Elastic properties
- Diffusion, viscosity
- Thermodynamic properties
 - Melting
 - Partitioning
 - Thermal conductivity
 - Electrical conductivity
 -

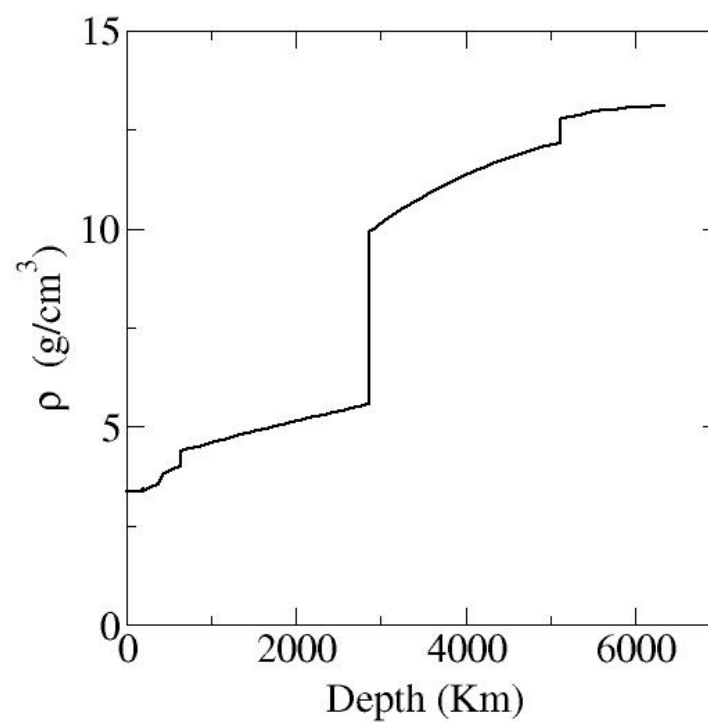




Seismic velocities

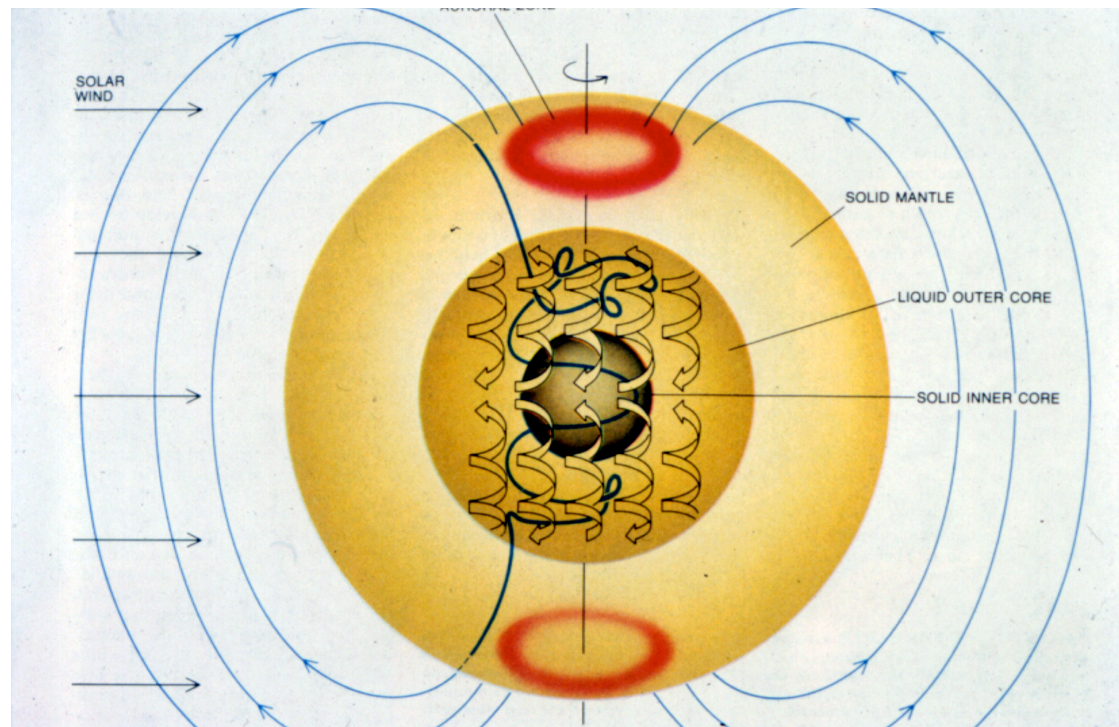


Density



The importance of the core

- The Earth's core is the seat of major global processes.
- Convection in the outer core generates the Earth's magnetic field.
- Heat flow from the core helps drive Mantle convection.



How to find out

- Experimental studies use
 - Diamond Anvil Cell
 - Laser Heating
 - Synchrotron Radiation
 - Shock
- Core P and T still a challenge
- Quantum mechanics
 - Now quantum (density functional theory) molecular dynamics on large systems possible thanks to CPU.
 - Quantum Monte Carlo



Schrödinger equation:

$$\hat{H}\Psi_N = E\Psi_N; \quad \hat{H} = \hat{T} + \hat{V} \quad ?$$

Density Functional Theory:

$$\hat{H}_{KS}\psi_i = \varepsilon_i\psi_i \quad i = 1, N$$

$$\hat{H}_{KS} = \hat{T} + \hat{V} + \hat{V}_H + \hat{V}_{xc}$$

DFT Problems:

- Strong electron correlation in transition-metal, rare-earth, actinide oxides
- Wrong prediction of the electronic structure of MnO, NiO, FeO, etc...
- Incorrect localisation of hole centres in systems such as MgO, SiO₂, ...

Quantum Monte Carlo

Variational Monte Carlo:

Energy E_V depends on Ψ_T

$$E_V = \frac{\int \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R}) d\mathbf{R}}{\int \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) d\mathbf{R}} \geq E_0$$

Diffusion Monte Carlo:

$$-\frac{\partial \phi(\mathbf{x}, t)}{\partial t} = (\hat{H} - E_T) \phi(\mathbf{x}, t)$$

Extracting the ground state: substitute $\tau = it$ $\tau \rightarrow \infty, \quad \phi(\mathbf{x}, \tau) \rightarrow \Phi_0(\mathbf{x})$

Problems:

- Fixed nodes approximation:
- Pseudopotentials

DMC is ~ 1000 times more expensive than DFT

Thermodynamics

- Pure substances (e.g. pure Fe)
 - Free energy
 - Helmholtz: $F(V, T)$
 - Gibbs: $G(p, T) = F + pV$
- Solutions:
 - Chemical potential: $\mu_i = \left(\frac{\partial F}{\partial N_i} \right)_{V, T, N_j}$

The Helmholtz free energy

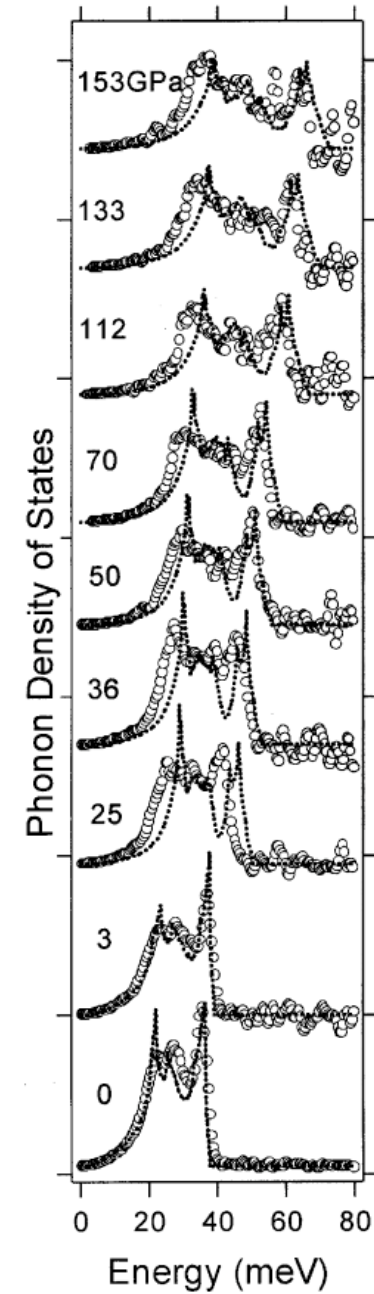
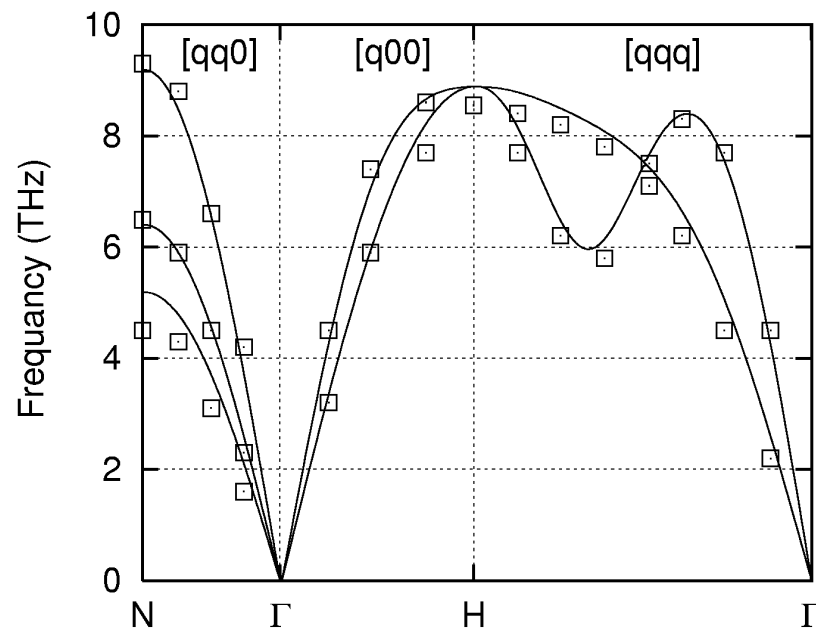
Solids: Low T

$$F(V, T) = F_{perf}(V, T) + F_{harm}(V, T) + \cancel{F_{anharm}(V, T)}$$

$$F_{harm}(V, T) = 3k_B T \frac{1}{N_{\mathbf{q},s}} \sum_{\mathbf{q},s} \ln \left[2 \sinh \left(\frac{\hbar \omega_{\mathbf{q},s}(V, T)}{2k_B T} \right) \right]$$

$\omega_{\mathbf{q},s}$ from linear response or from small displacement (this afternoon)

Example: phonons of Fe



The Helmholtz free energy

Solids: ~~High T~~

$$F(V,T) = F_{perf}(V,T) + F_{harm}(V,T) + \cancel{F_{anharm}(V,T)}$$

$$F_{harm}(V,T) = 3k_B T \frac{1}{N} \sum_{\mathbf{q},s} \ln \left[2 \sinh \left(\frac{\hbar \omega_{\mathbf{q},s}(V,T)}{2k_B T} \right) \right]$$

Liquids:

$$F(V,T) = -k_B T \ln \frac{1}{N! \Lambda^{3N}} \int_V dR e^{-U(R)/k_B T}$$

Thermodynamic integration

$$U_{ref}, F_{ref} \quad U_{\lambda} = (1 - \lambda)U_{ref} + \lambda U$$

$$F_{\lambda} = -k_B T \ln \frac{1}{N! \Lambda^{3N}} \int_V dR e^{-U_{\lambda}(R)/k_B T}$$

$$F - F_{ref} = \int_0^1 d\lambda \frac{dF_{\lambda}}{d\lambda}$$

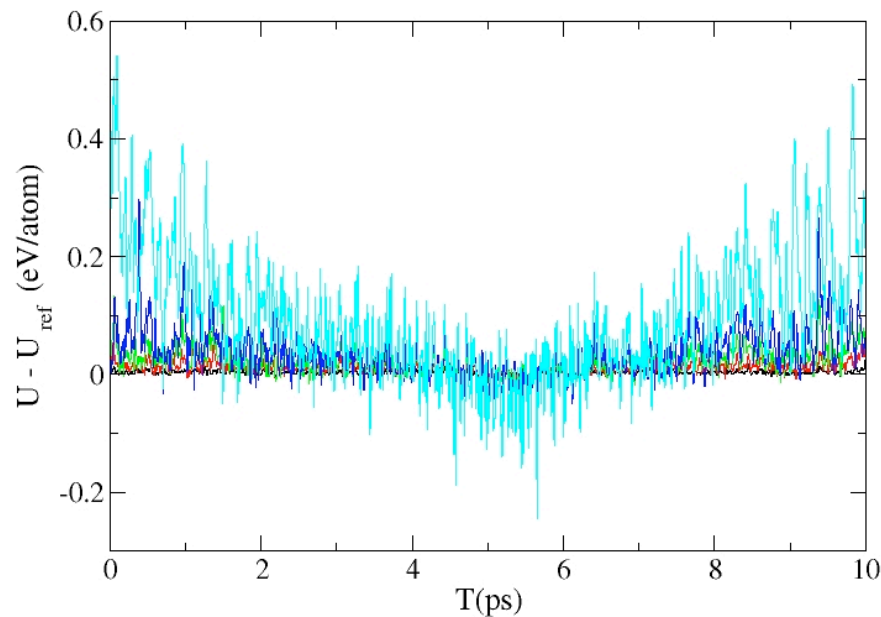
$$\frac{dF_{\lambda}}{d\lambda} = \frac{\int_V dR \frac{\partial U_{\lambda}}{\partial \lambda} e^{-U_{\lambda}(R)/k_B T}}{\int_V dR e^{-U_{\lambda}(R)/k_B T}} = \left\langle \frac{\partial U_{\lambda}}{\partial \lambda} \right\rangle_{\lambda} = \langle U - U_{ref} \rangle_{\lambda}$$

$$F = F_{ref} + \int_0^1 d\lambda \langle U - U_{ref} \rangle_{\lambda}$$

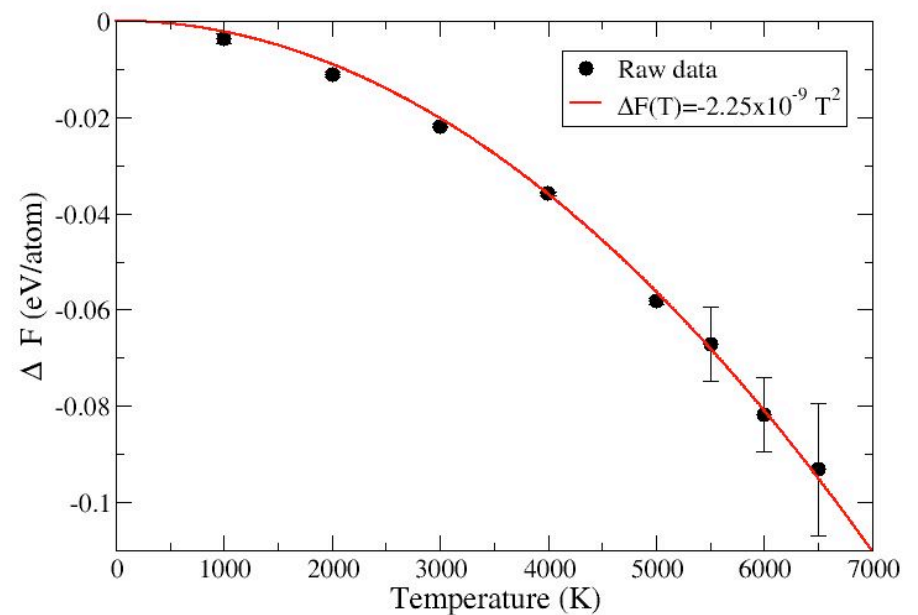
Example: anharmonic free energy of solid Fe at ~350 GPa

$$F = F_{ref} + \int_0^1 d\lambda \langle U - U_{ref} \rangle_\lambda = F_{ref} + \int_0^T dt \frac{d\lambda}{dt} (U - U_{ref})_\lambda$$

T=1000, 2000, 3000, 4000, 6500 K



Anharmonic free energy of Fe at $V=6.97 \text{ \AA}^3/\text{atom}$



Can we use thermodynamic integration with QMC ?

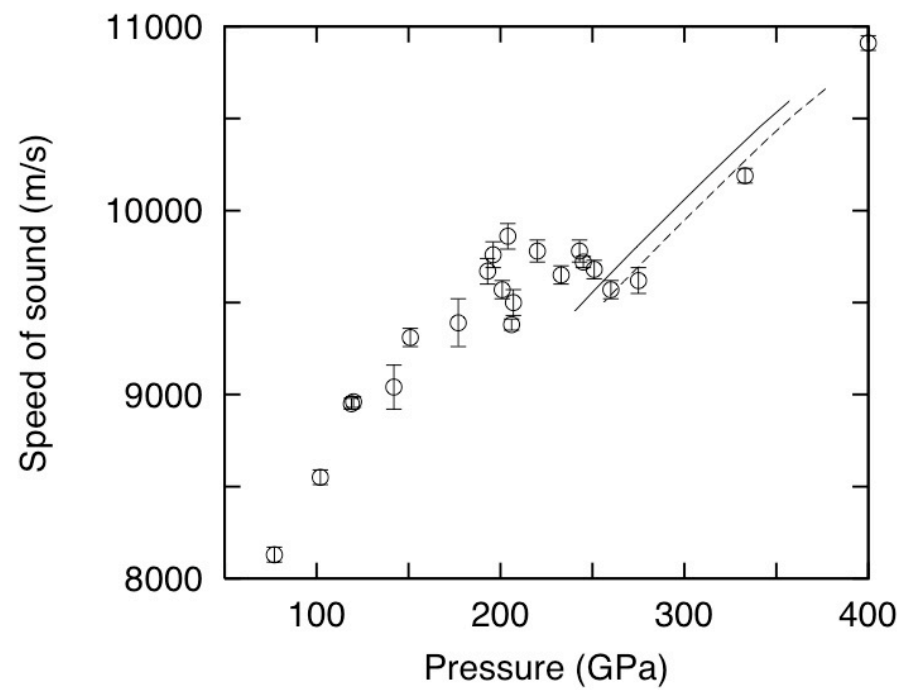
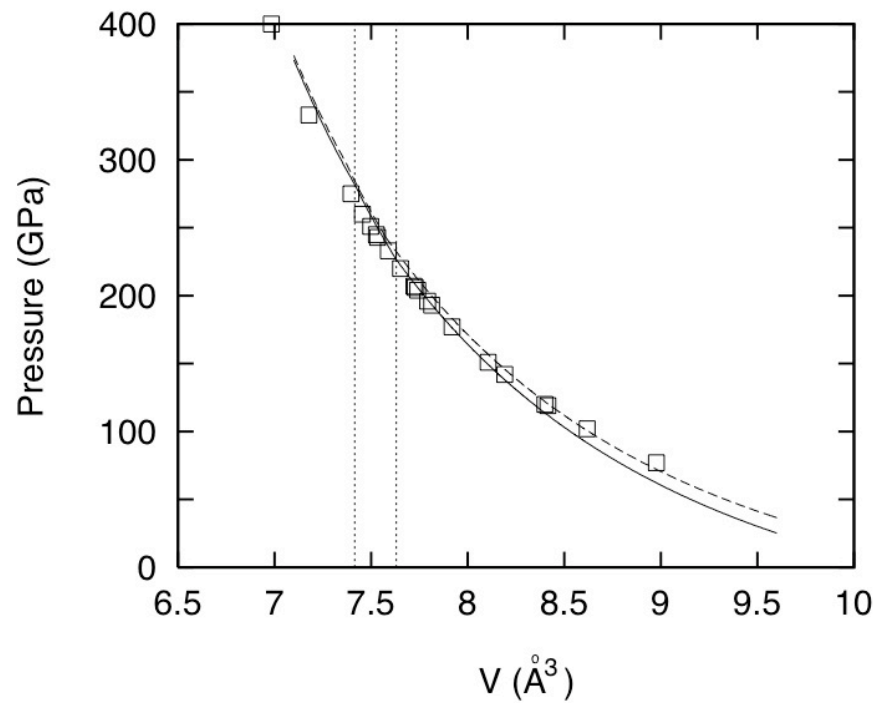
$$F = F_{ref} + \int_0^1 d\lambda \langle U - U_{ref} \rangle_\lambda = F_{ref} + \int_0^T dt \frac{d\lambda}{dt} \langle U - U_{ref} \rangle_\lambda$$

$$U_\lambda = (1 - \lambda)U_{ref} + \lambda U$$

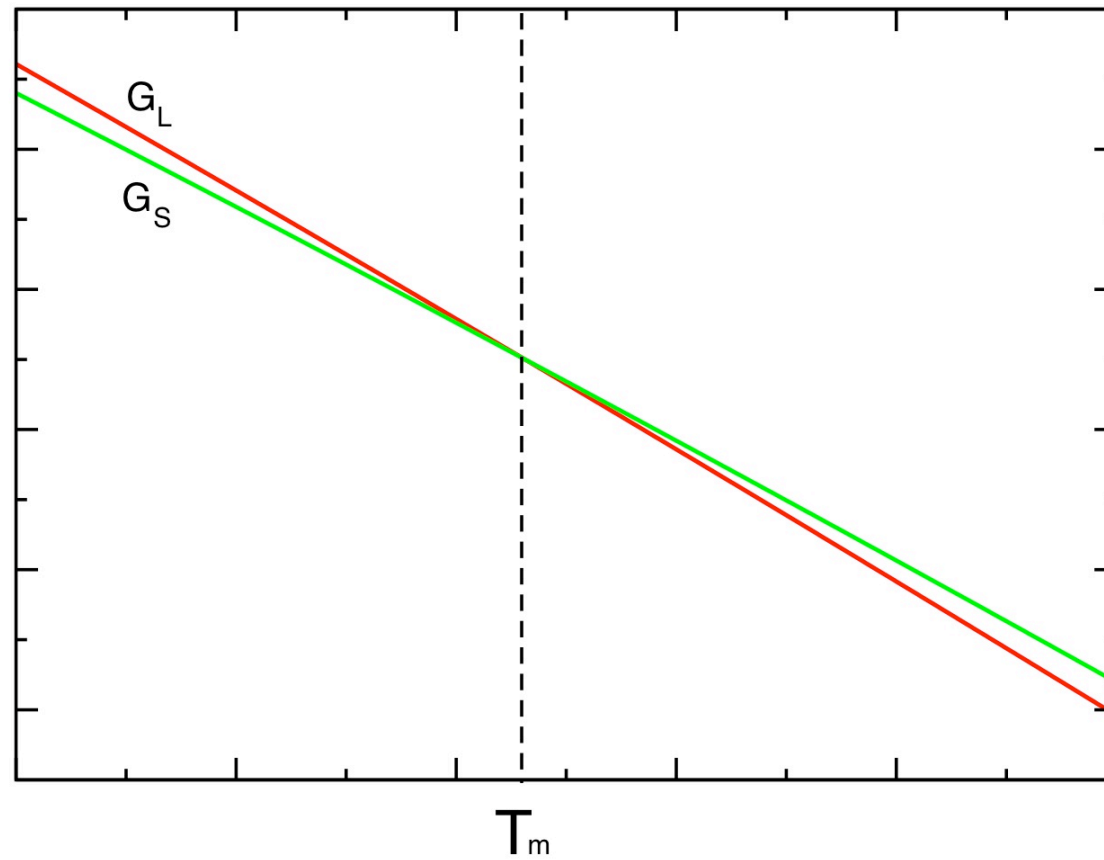
Need to calculate energies and forces with both U_{ref} and U . If we want U to be the quantum Monte Carlo potential energy, then forces are difficult to calculate. However, if U_{ref} is “close” to U we can use a perturbative approach to thermodynamic integration (see later), in which we evolve the system only with U_{ref} forces, and we only need to calculate U energies.

Hugoniot of Fe

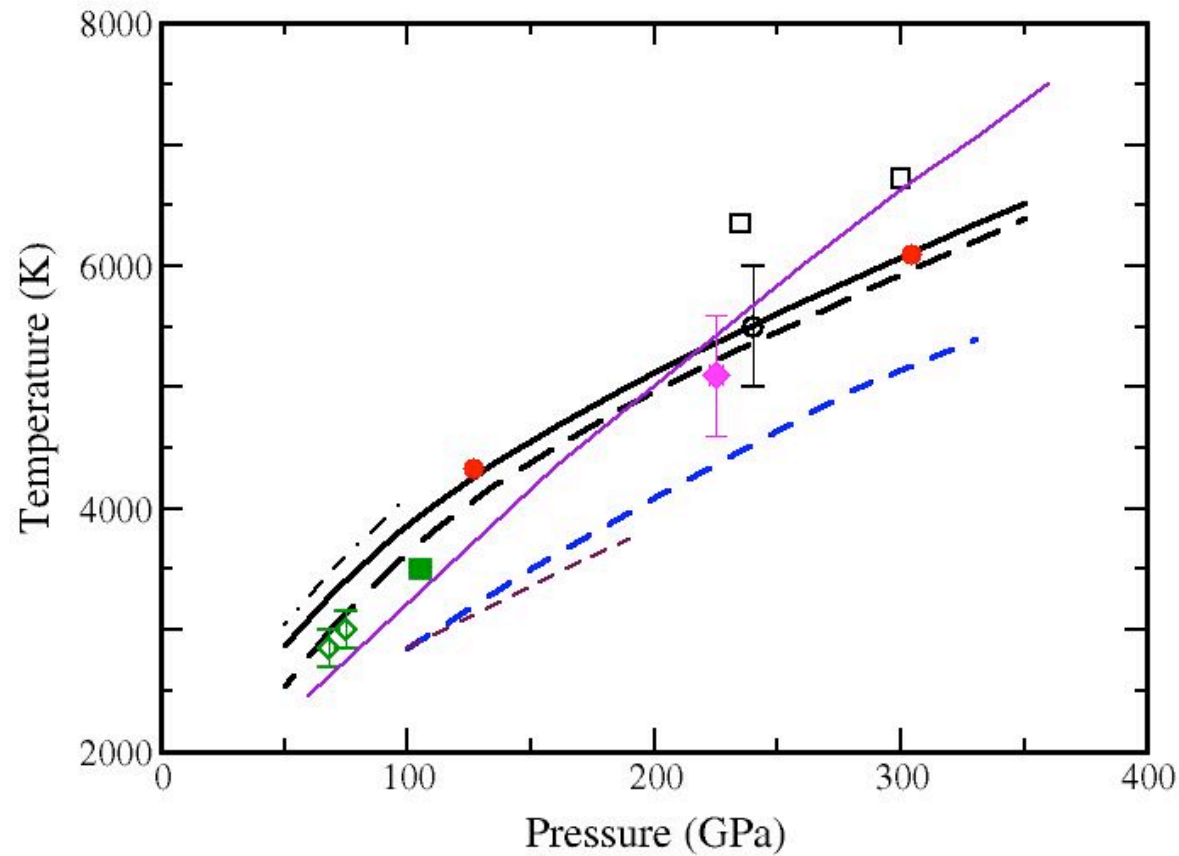
$$\frac{1}{2} p_H (V_0 - V_H) = E_H - E_0$$



Melting

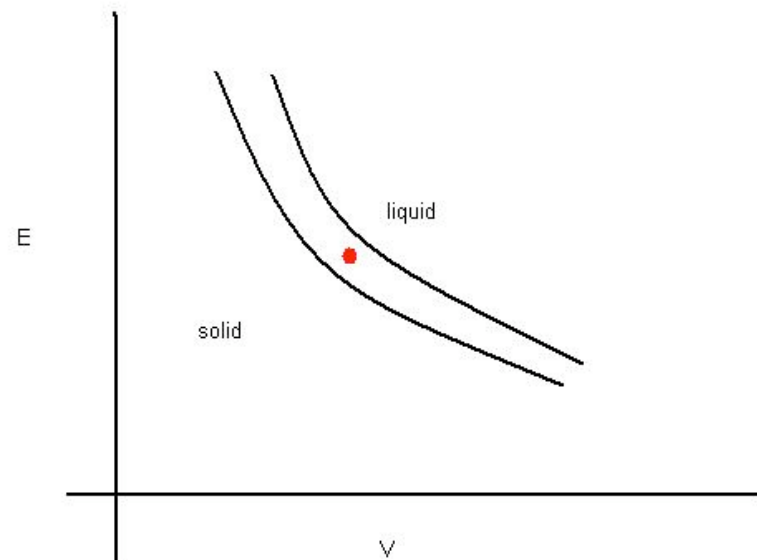
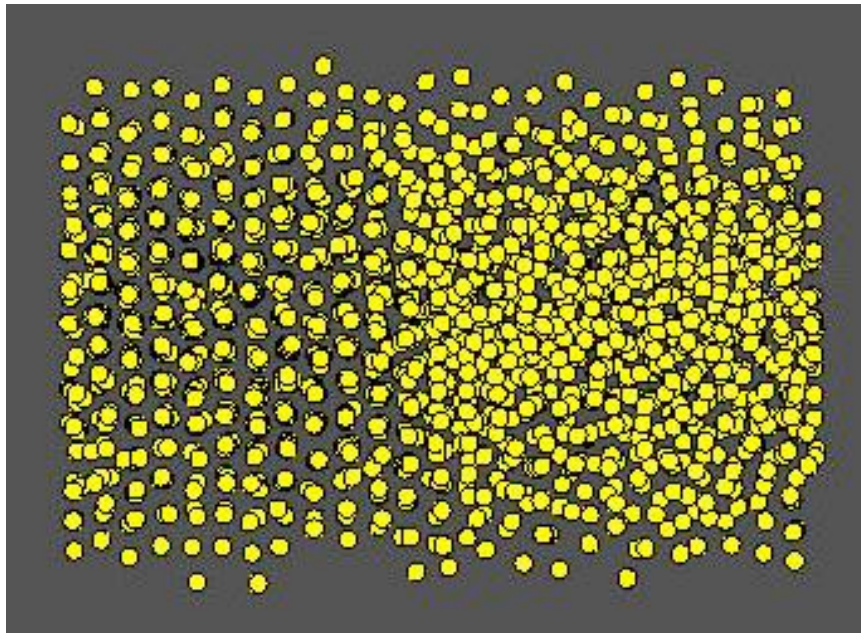


The melting curve of Fe



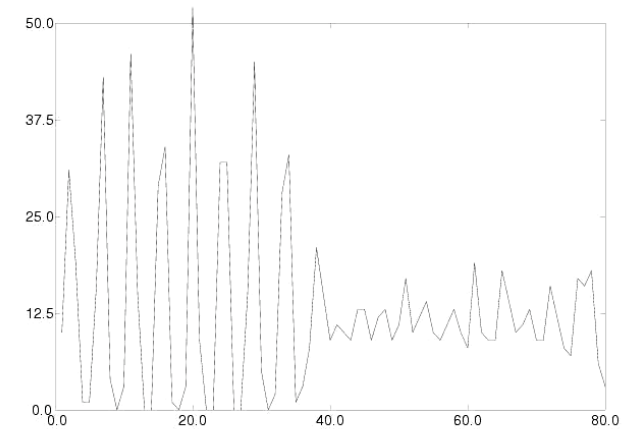
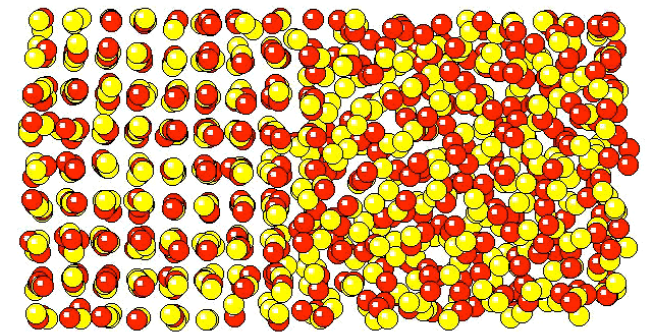
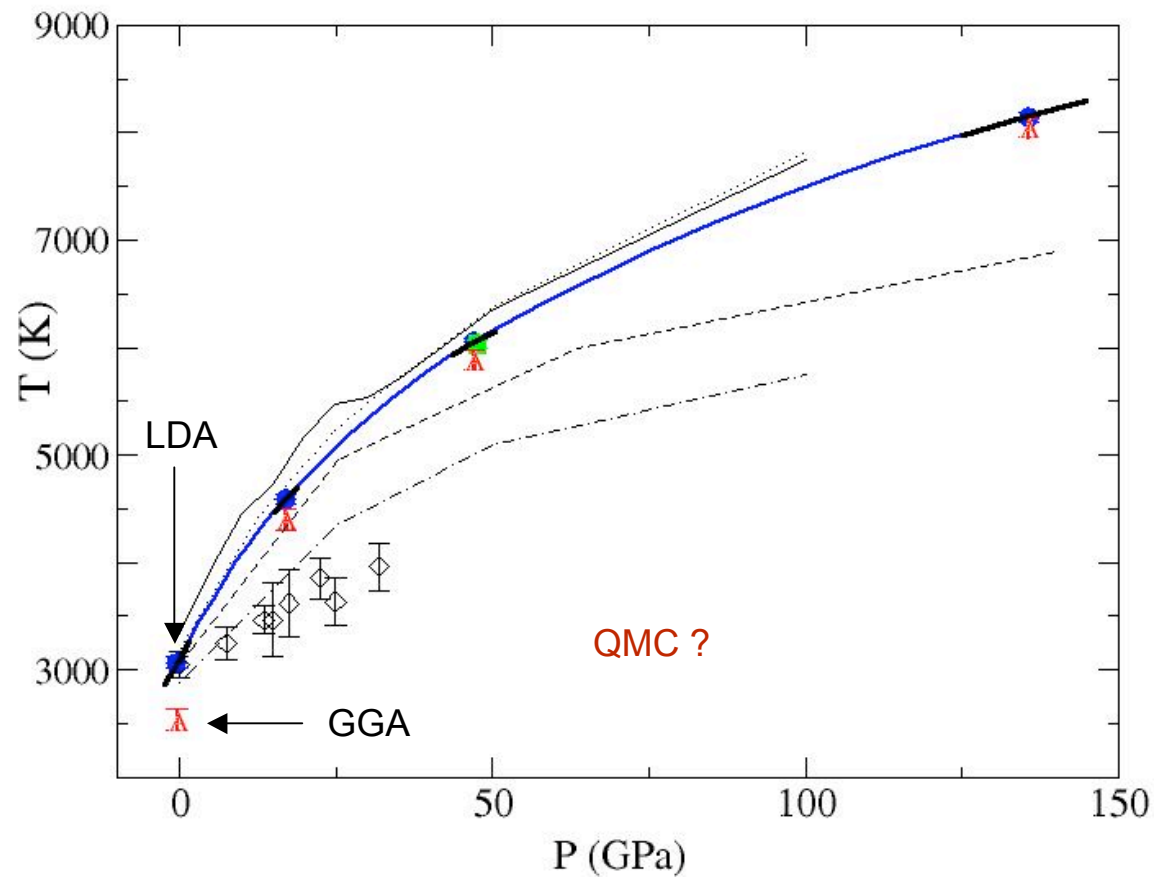
Alfè, Price, Gillan, *Nature*, **401**, 462 (1999); *Phys. Rev. B*, **64**, 045123 (2001);
Phys. Rev. B, **65**, 165118 (2002); *J. Chem. Phys.*, **116**, 6170 (2002)

Melting: coexistence of phases



NVE ensemble: for fixed V , if E is between solid and liquid values, simulation will give coexisting solid and liquid

MgO melting curve



D. Alfè, Physical Review Letters, **94**, 235701, (2005)

Melting of Ta and Mo:

Coexistence of phases with classical potential:

$$U_{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{2} \varepsilon \sum_{i \neq j} \left(\frac{a}{r_{ij}} \right)^n - C \varepsilon \sum_i \left[\sum_{j(\neq i)} \left(\frac{a}{r_{ij}} \right)^m \right]^{1/2}$$

Free energy corrections to full DFT:

$$\delta T_m = \frac{\Delta G^{ls}(T_m^{\text{ref}})}{S_{\text{ref}}^{ls}}$$

Thermodynamic integration, a perturbative approach:

$$F = F_{ref} + \int_0^1 d\lambda \langle U - U_{ref} \rangle_\lambda$$

$$\langle U - U_{ref} \rangle_\lambda = \langle U - U_{ref} \rangle_{\lambda=0} + \lambda \left. \frac{\partial \langle U - U_{ref} \rangle_\lambda}{\partial \lambda} \right|_{\lambda=0} + o(\lambda^2)$$

$$\begin{aligned} \frac{\partial \langle U - U_{ref} \rangle_\lambda}{\partial \lambda} &= \frac{\partial}{\partial \lambda} \left\{ \frac{\int_V dR \frac{\partial U_\lambda}{\partial \lambda} e^{-U_\lambda(R)/k_B T}}{\int_V dR e^{-U_\lambda(R)/k_B T}} \right\} = \\ &= -\frac{1}{k_B T} \left\{ \frac{\int_V dR \left(\frac{\partial U_\lambda}{\partial \lambda} \right)^2 e^{-U_\lambda(R)/k_B T}}{\int_V dR e^{-U_\lambda(R)/k_B T}} - \left(\frac{\int_V dR \frac{\partial U_\lambda}{\partial \lambda} e^{-U_\lambda(R)/k_B T}}{\int_V dR e^{-U_\lambda(R)/k_B T}} \right)^2 \right\} = -\frac{1}{k_B T} \langle \delta \Delta U_\lambda^2 \rangle_\lambda \end{aligned}$$

$$\delta\Delta U_{\lambda} = U - U_{ref} - \langle U - U_{ref} \rangle_{\lambda}$$

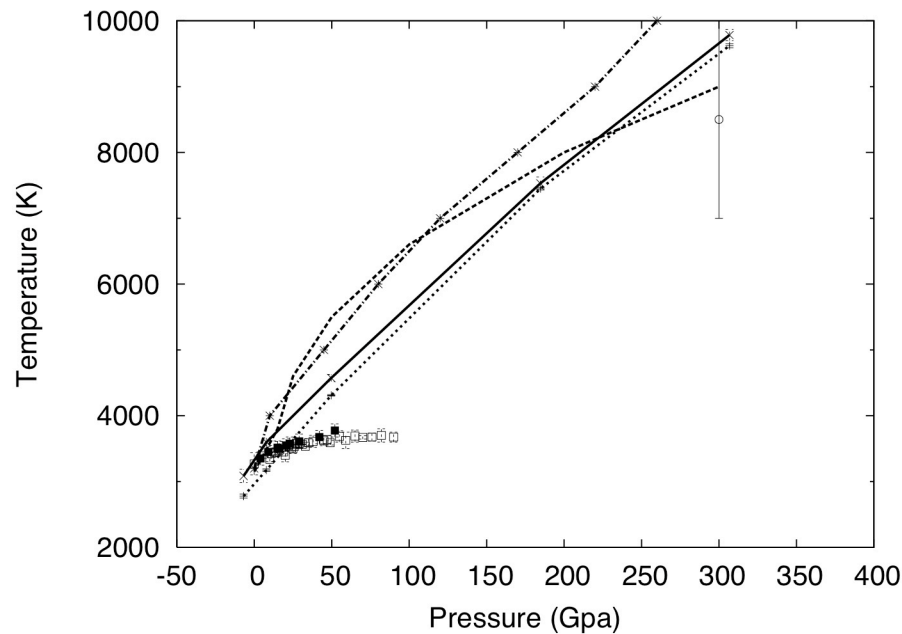
$$\langle U - U_{ref} \rangle_{\lambda} = \langle U - U_{ref} \rangle_0 - \frac{\lambda}{k_B T} \langle \delta\Delta U_0^2 \rangle_0 + o(\lambda^2)$$

$$\int_0^1 d\lambda \langle U - U_{ref} \rangle_{\lambda} = \langle U - U_{ref} \rangle_0 - \frac{1}{2k_B T} \langle \delta\Delta U_0^2 \rangle_0$$

Only need to run simulations with one potential (the reference potential for example). In particular, one can perform thermodynamic integration from DFT to QMC by treating DFT as a reference potential, which can be used to generate MD trajectories. Then QMC energies can be calculated on a number of statistically independent configurations, and the two terms on the r.h.s of the equation above can be obtained.

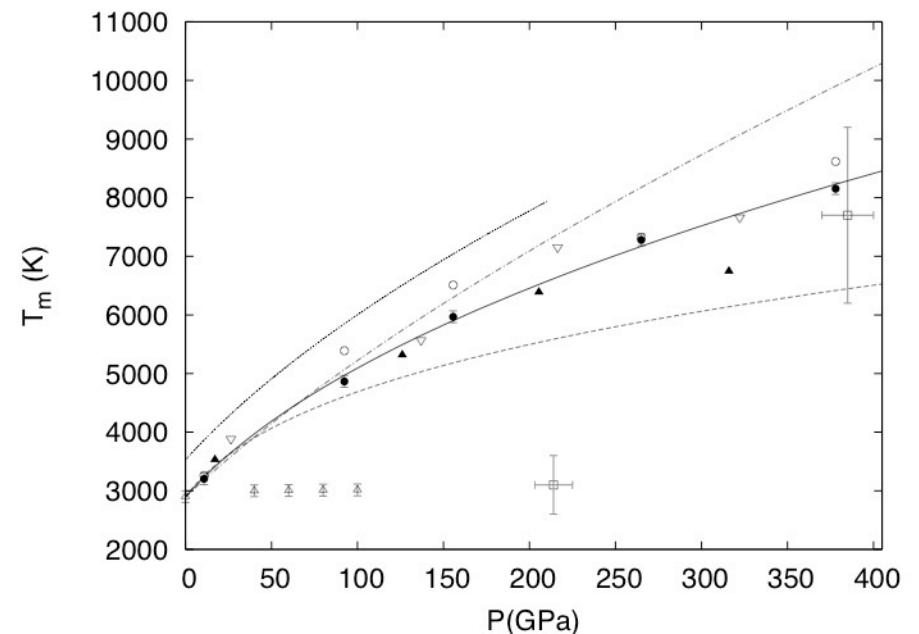
Melting curves of Ta and Mo

Tantalum



S. Taioli, C. Cazorla, M. J. Gillan and D. Alfè,
Physical Review B, **75**, 214103, (2007)

Molybdenum



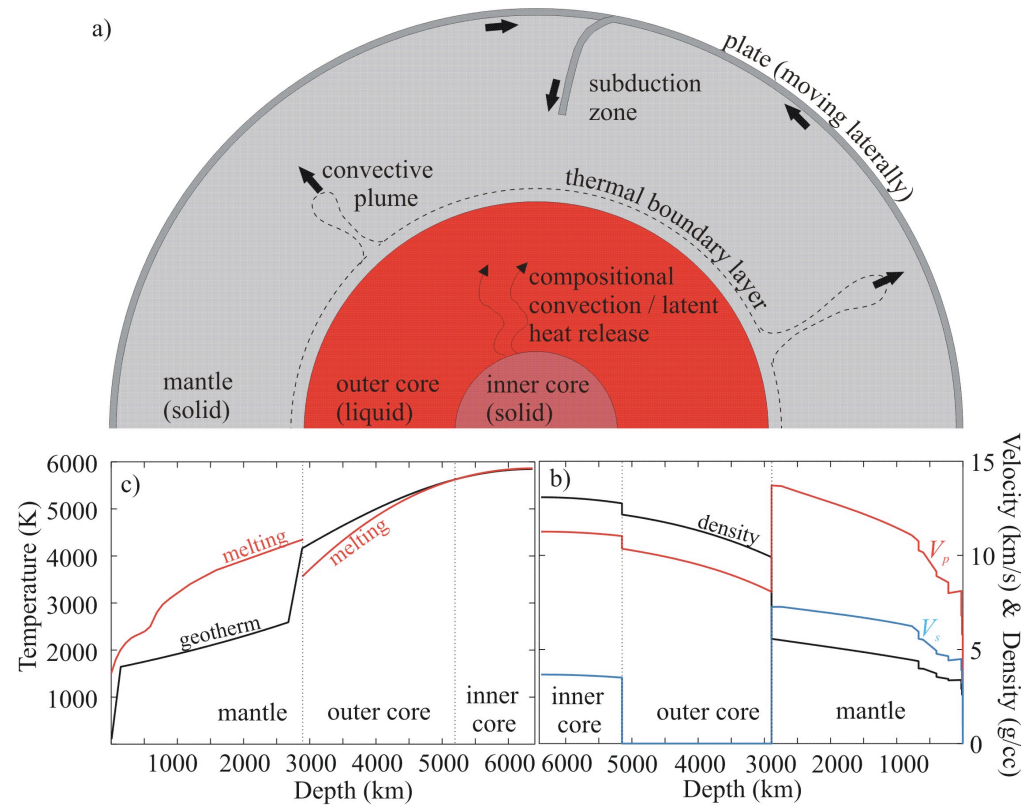
C. Cazorla, S. Taioli, M. J. Gillan and D. Alfè, Journal
of Chemical Physics, **126**, 194502 (2007)

Going beyond DFT: quantum Monte Carlo calculations on MgO

- Feasibility: test equilibrium lattice parameters, bulk moduli, zero temperature transition pressures
- Energetics of point defects (Schottky defects)
- Surface energy, water adsorption energy
- **Refinement of melting curve calculations (future)**
- R. J. Needs, M. D. Towler, N. D. Drummond, P. Lopez-Rios, CASINO user manual, version 2.0, University of Cambridge, 2006.

Why MgO ?

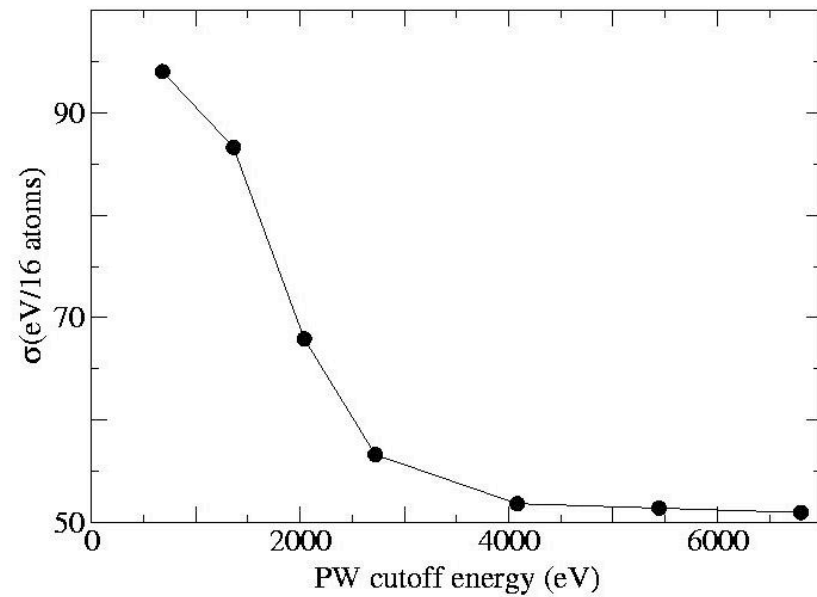
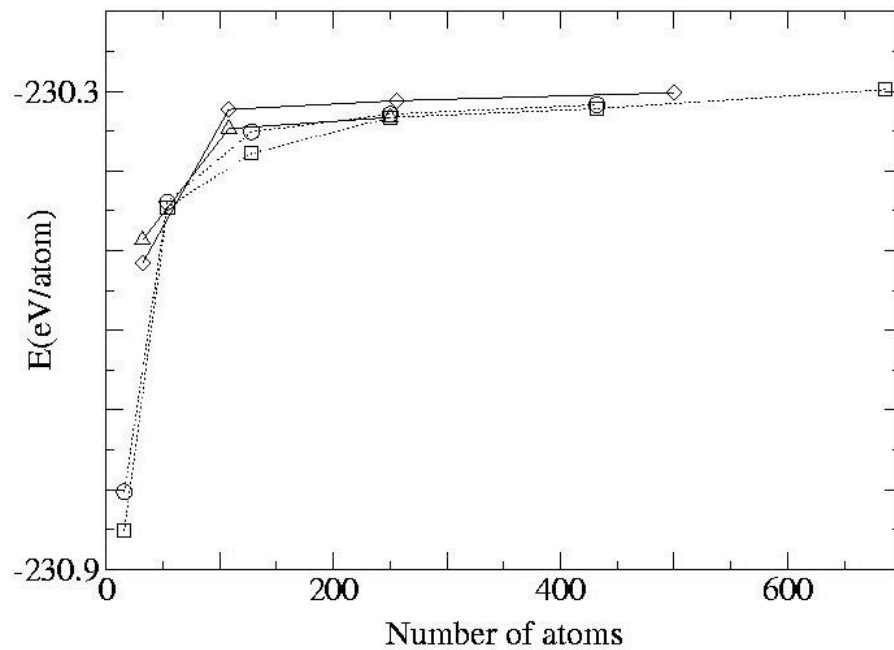
- Earth's lower mantle
 - Mg(Fe)O
 - Mg(Fe)SiO_3



Technical points

Bulk MgO

Finite size errors

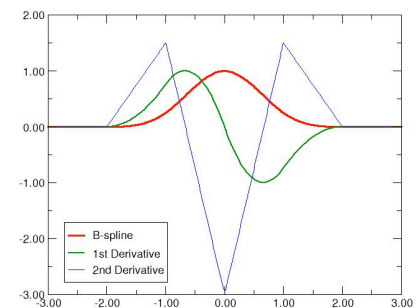


Basis sets:

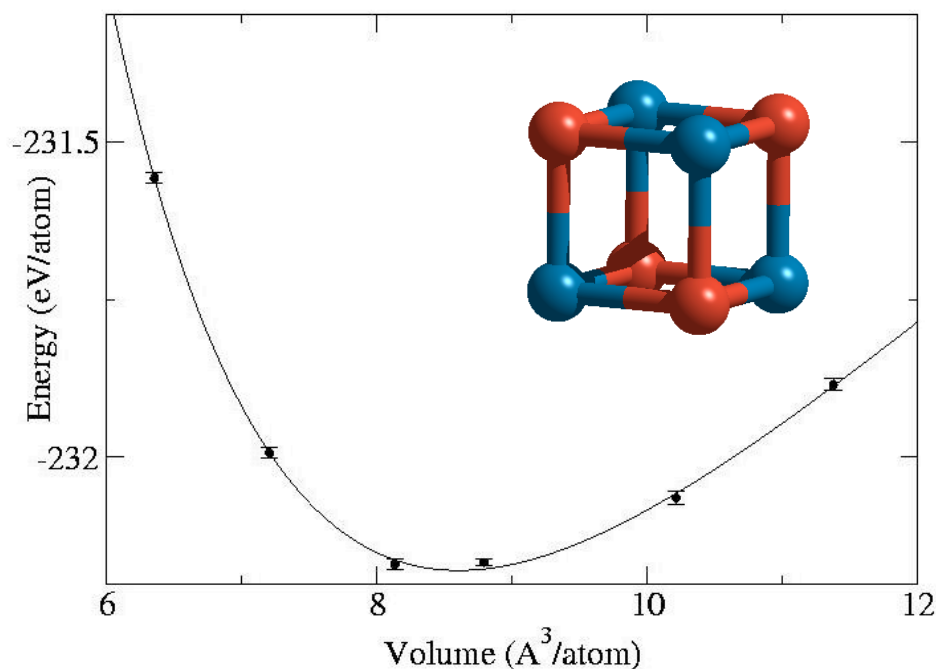
-PW's too expensive

-Blips

(D. Alfè and M. J. Gillan, Phys. Rev. B, **70**, 161101(R), (2004))



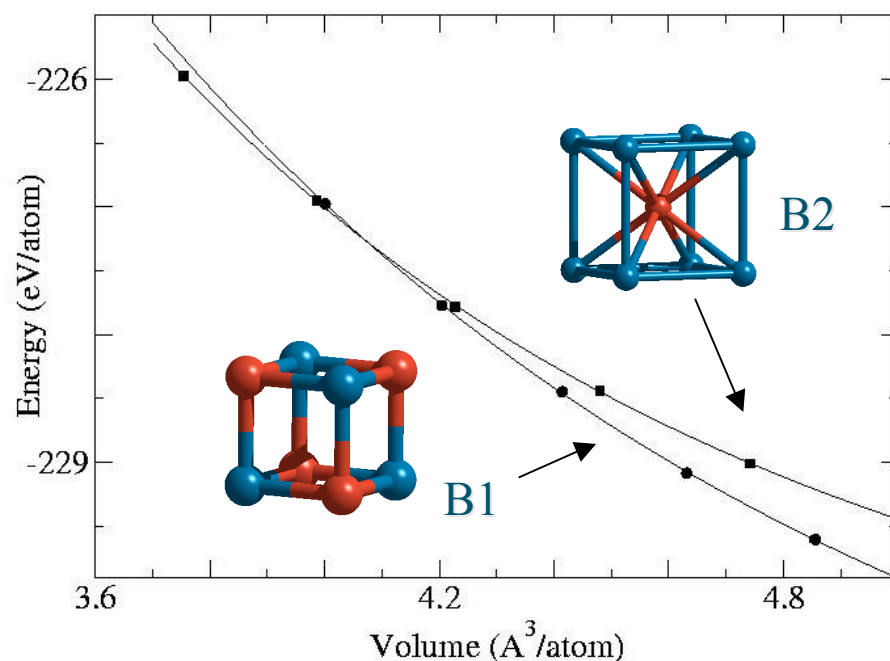
MgO in the rock-salt structure



	a (Å)	B (GPa)
Experiment(a)	4.213	160
Hartree-Fock all-electron	4.195	184
Hartree-Fock pseudopot	4.089	196
QMC pseudopot	4.098 (4.228)	183 (158)

(a) From Y. Fei, Am. Mineral. **84**, 272 (1999).

MgO: the rock-salt/CsCl transition



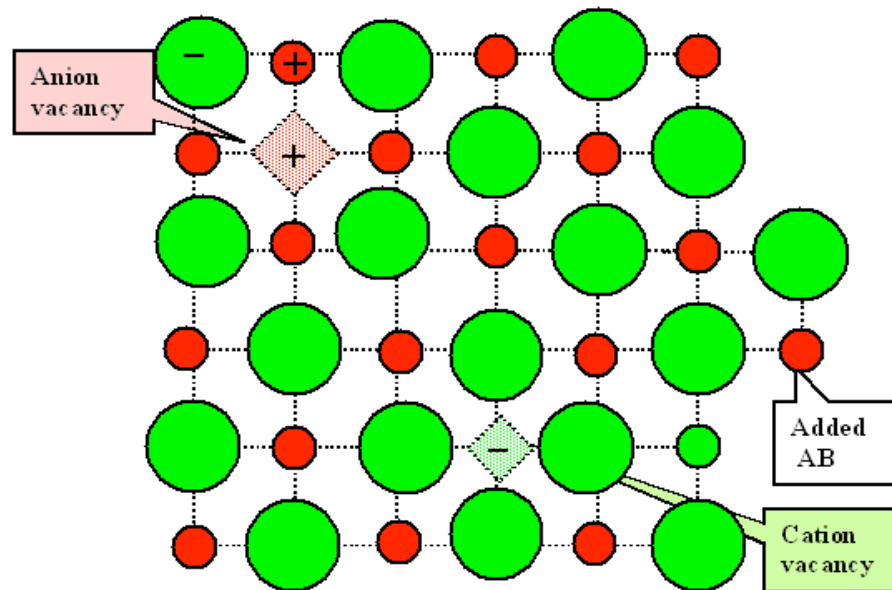
D. Alf  , M. Alfredsson, J. Brodholt, M.J. Gillan, M.D. Towler and R.J. Needs, Phys. Rev. B, **72**, 014114 (2005)

	p_t (GPa)
Oganov & Dorogokupets GGA (a)	509
other GGA	418 – 664
LDA	198 – 1050
Hartree-Fock	220 – 712
Experiments (b)	> 227
Present QMC	597

(a) A. R. Oganov and P.I. Dorogokupets, Phys. Rev. B, **67**, 224110 (2003).

(b) T. S. Duffy, R. J. Hemley, and H.-K. Mao, Phys. Rev. Lett. **74**, 1371 (1995). □

MgO: Schottky defect

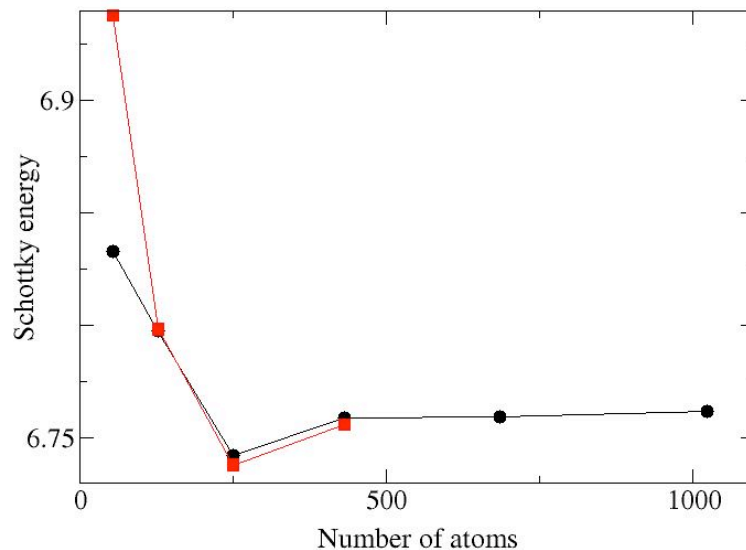


$$E_S = E_N(Mg^{2+}) + E_N(O^{2-}) - 2 \frac{N-1}{N} E_N$$

$$\delta E_N(X) = \alpha z^2 e^2 / \epsilon L$$

Leslie and Gillan, J. Phys. C, **18**, 973 (1985)

MgO: Schottky defect (2)



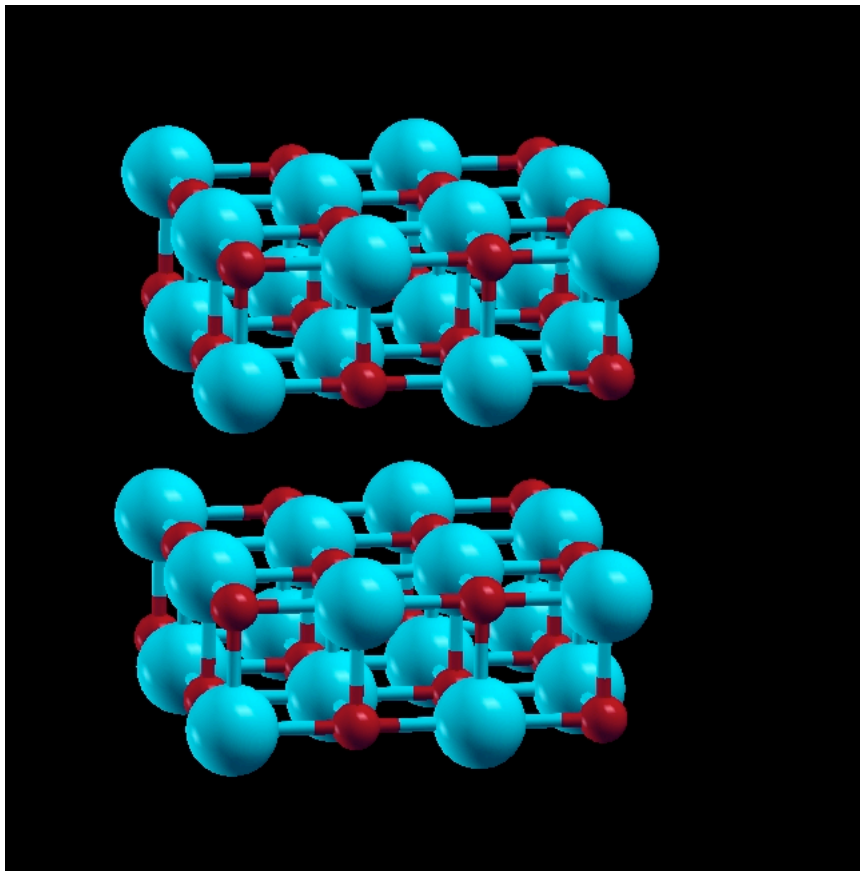
Reference DFT calculations of Schottky energy E_S – system of 54 atoms gives E_S within ~ 0.1 eV.

	E_S (eV)
VASP- PAW	6.75
PWSCF with QMC pseudo	6.99
QMC	7.4 \pm 0.5
Experiments	4-7(a)

(a) WC.Mackrodt, in Computer Simulation of Solids, ed. CRA Catlow and WC Mackrodt (1982)

Conclusion: QMC calculation of defect energetics in oxides is feasible. For MgO, QMC and DFT values of Schottky energy are close to each other.

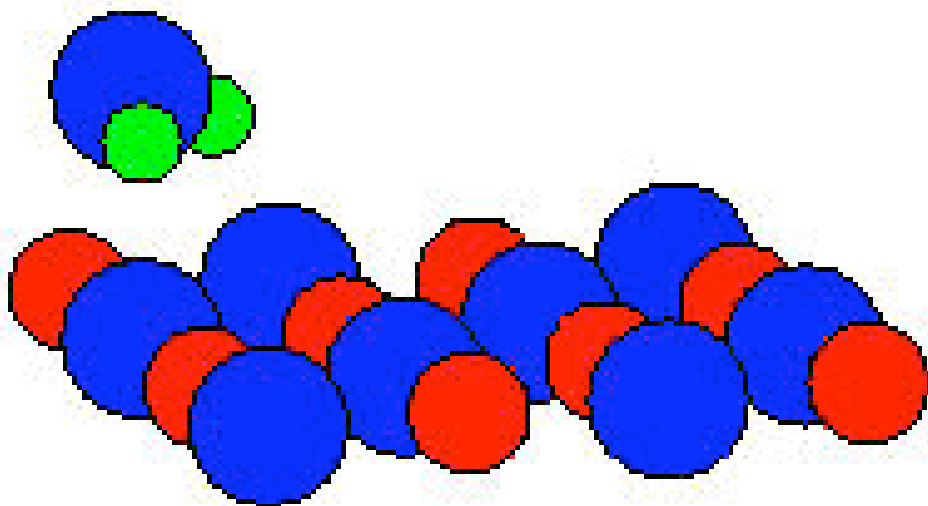
MgO(001) surface energy



$$\sigma = (E_{slab} - E_{bulk}) / A$$

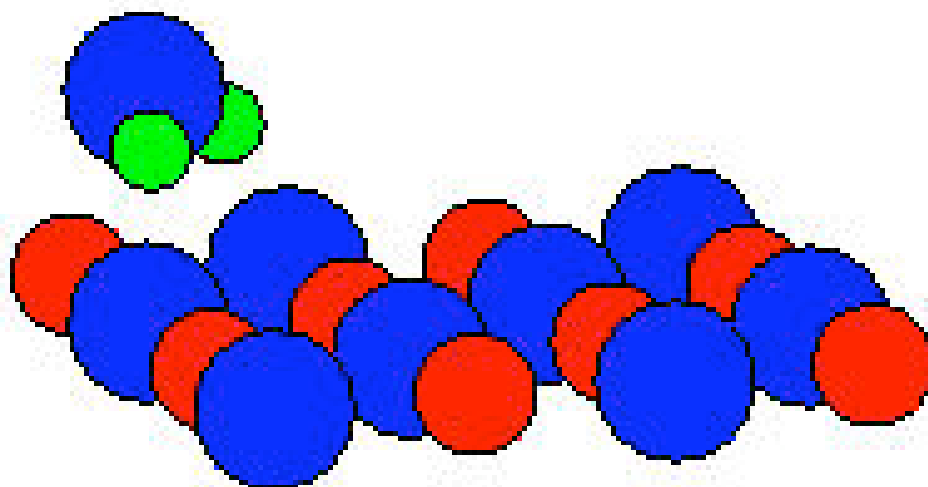
	$\sigma(\text{J/m}^2)$
LDA	1.24
GGA	0.87
QMC	1.19±0.01
Experiments	1.04-1.20

H₂O adsorption on MgO(001) DFT-PBE



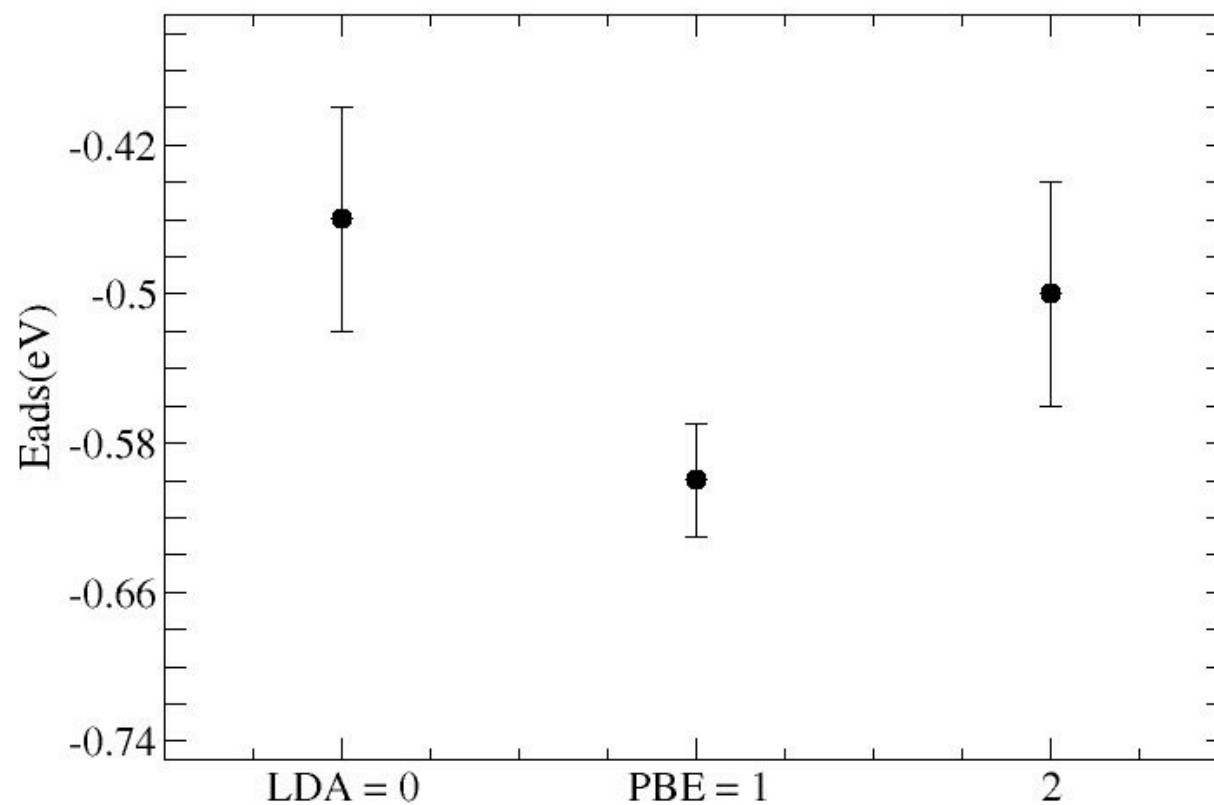
$$E_{\text{ad}} = .46 \text{ eV}$$

H₂O adsorption on MgO(001) DFT-LDA



$$E_{\text{ad}} = .95 \text{ eV}$$

H₂O adsorption on MgO(001) DMC, LDA---PBE line



Water on MgO(001): summary of adsorption energies

- QMC adsorption energy = 0.60(3) eV
- PBE “ “ = 0.46 eV
- LDA “ “ = 0.95 eV
- Experiment “ = 0.75(?) eV

Conclusions

- First principles techniques on geomaterials can help, both at low and high temperatures (free energies).
- Traditional DFT techniques are good for a large class of problems, but there is scope for going beyond it.
- Quantum Monte Carlo is a possibility for going beyond DFT, QMC calculations on MgO are feasible and first results are encouraging.
- Good agreement with experiments for bulk structural parameters, energy of formation of point defects and surface energy.
- Future: using QMC to refine melting properties (MgO, Fe, Mo, Ta, ...)