Quantum Monte Carlo on geomaterials

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Some properties of interest

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

\[ \hat{H} \psi_N = E \psi_N; \quad \hat{H} = \hat{T} + \hat{V} \]

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, SiO$_2$, ...
Quantum Monte Carlo

Variational Monte Carlo:
Energy $E_V$ depends on $\Psi_T$

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

Diffusion Monte Carlo:

\[-\frac{\partial \phi(x,t)}{i \partial t} = \left( \hat{H} - E_T \right) \phi(x,t)\]

Extracting the ground state: substitute $\tau = it$ \hspace{1cm} $\tau \to \infty$, $\phi(x,\tau) \to \Phi_0(x)$

Problems:
- Fixed nodes approximation:
- Pseudopotentials

DMC is $\sim 1000$ 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

\[
F(V, T) = F_{\text{perf}}(V, T) + F_{\text{harm}}(V, T) + F_{\text{anharm}}(V, T)
\]

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

\(\omega_{q,s}\) from linear response or from small displacement (this afternoon)
Example: phonons of Fe
The Helmholtz free energy

Solids: \( T \ll T^* \)

\[
F(V,T) = F_{\text{perf}}(V,T) + F_{\text{harm}}(V,T) + F_{\text{anhar}}(V,T)
\]

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

Liquids:

\[
F(V,T) = -k_B T \ln \left[ \frac{1}{N! \Lambda^{3N}} \int_V dR \ e^{-U(R)/k_B T} \right]
\]
Thermodynamic integration

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

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

\[ F - F_{\text{ref}} = \int_0^1 d\lambda \, \frac{dF_\lambda}{d\lambda} \]

\[ \frac{dF_\lambda}{d\lambda} = \int_V dR \, \frac{\partial U_\lambda}{\partial \lambda} e^{-U_\lambda(R)/k_B T} = \left< \frac{\partial U_\lambda}{\partial \lambda} \right>_\lambda = \left< U - U_{\text{ref}} \right>_\lambda \]

\[ F = F_{\text{ref}} + \int_0^1 d\lambda \, \left< U - U_{\text{ref}} \right>_\lambda \]
Example: anharmonic free energy of solid Fe at ~350 GPa

\[
F = F_{\text{ref}} + \int_{0}^{1} d\lambda \left\langle U - U_{\text{ref}} \right\rangle_{\lambda} = F_{\text{ref}} + \int_{0}^{T} dt \frac{d\lambda}{dt} \left(U - U_{\text{ref}}\right)_{\lambda}
\]
Can we use thermodynamic integration with QMC?

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

\[
U_\lambda = (1 - \lambda)U_{\text{ref}} + \lambda U
\]

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

\[ \frac{1}{2} p_H (V_0 - V_H) = E_H - E_0 \]
Melting
The melting curve of Fe

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

Melting of Ta and Mo:

Coexistence of phases with classical potential:

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

Free energy corrections to full DFT:

\[
\delta T_m = \frac{\Delta G_{\text{ls}}^{\text{ref}} (T_m^{\text{ref}})}{S_{\text{ls}}^{\text{ref}}}
\]
Thermodynamic integration, a perturbative approach:

\[
F = F_{\text{ref}} + \int_0^1 d\lambda \left\langle U - U_{\text{ref}} \right\rangle_{\lambda}
\]

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

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

\[
- \frac{1}{k_B T} \left\{ \int_V dR \left( \frac{\partial U_{\lambda}}{\partial \lambda} \right)^2 e^{-U_{\lambda}(R)/k_B T} \right\} - \left\{ \int_V dR \frac{\partial U_{\lambda}}{\partial \lambda} e^{-U_{\lambda}(R)/k_B T} \right\}^2 = - \frac{1}{k_B T} \left\langle \delta U_{\lambda}^2 \right\rangle_{\lambda}
\]
\[ \delta \Delta U \lambda = U - U_{\text{ref}} - \left\langle U - U_{\text{ref}} \right\rangle _\lambda \]

\[ \left\langle U - U_{\text{ref}} \right\rangle _\lambda = \left\langle U - U_{\text{ref}} \right\rangle _0 - \frac{\lambda}{k_B T} \left\langle \delta \Delta U^2 \right\rangle _0 + o(\lambda^2) \]

\[ \int_0^1 d\lambda \left\langle U - U_{\text{ref}} \right\rangle _\lambda \left\langle U - U_{\text{ref}} \right\rangle _0 - \frac{1}{2k_B T} \left\langle \delta \Delta U^2 \right\rangle _0 \]

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


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)
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
MgO in the rock-salt structure

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ (Å)</th>
<th>$B$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment (a)</td>
<td>4.213</td>
<td>160</td>
</tr>
<tr>
<td>Hartree-Fock all-electron</td>
<td>4.195</td>
<td>184</td>
</tr>
<tr>
<td>Hartree-Fock pseudopot</td>
<td>4.089</td>
<td>196</td>
</tr>
<tr>
<td>QMC pseudopot</td>
<td>4.098 (4.228)</td>
<td>183 (158)</td>
</tr>
</tbody>
</table>

(a) From Y. Fei, Am. Mineral. 84, 272 (1999).
**MgO: the rock-salt/CsCl transition**

<table>
<thead>
<tr>
<th>$p_t$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oganov &amp; Dorogokupets GGA (a)</td>
</tr>
<tr>
<td>other GGA</td>
</tr>
<tr>
<td>LDA</td>
</tr>
<tr>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>Experiments (b)</td>
</tr>
<tr>
<td>Present QMC</td>
</tr>
</tbody>
</table>


MgO: Schottky defect

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

\[ \delta E_N(X) = \alpha z^2 e^2 / \varepsilon L \]

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.

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

\[ \sigma = \frac{(E_{\text{slab}} - E_{\text{bulk}})}{A} \]

<table>
<thead>
<tr>
<th>Method</th>
<th>( \sigma ) (J/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>1.24</td>
</tr>
<tr>
<td>GGA</td>
<td>0.87</td>
</tr>
<tr>
<td>QMC</td>
<td>1.19±0.01</td>
</tr>
<tr>
<td>Experiments</td>
<td>1.04-1.20</td>
</tr>
</tbody>
</table>

$\text{H}_2\text{O}$ adsorption on MgO(001)
DFT-PBE

$E_{\text{ad}} = .46$ eV
H$_2$O adsorption on MgO(001) DFT-LDA

$E_{ad} = .95$ eV
H$_2$O 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, …)