Quantum Monte Carlo Calculations of Solids

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How does Quantum Monte Carlo Work?

\( \hat{H}\Psi(R) = [\hat{T} + \hat{V}]\Psi(R) = \left[ -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i>j}^{N} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(R) = E\Psi(R), \)

Project out the many-body ground-state wave function:

\( e^{-\tau\hat{H}} \psi_T(R) = e^{-\tau\hat{H}} \left[ a_0 \psi_0 + a_1 \psi_1 + a_2 \psi_2 + \ldots \right] \)

\( = a_0 e^{-\tau E_0} \psi_0 + a_1 e^{-\tau E_1} \psi_1 + a_2 e^{-\tau E_2} \psi_2 + \ldots \)

Increased weight | Reduced weight | Reduced weight

Approach the ground state iteratively:

\( \psi_{i+1}(R) = e^{-\tau\hat{H}} \psi_i(R) \)

\( \lim_{i \to \infty} \psi_i(R) = \psi_0(R) \)

For small time steps, \( \tau \), split the kinetic and potential operators:

\( e^{-\tau\hat{H}} \equiv e^{-\tau(\hat{T} + \hat{V})} \approx e^{-\tau\hat{T}} e^{-\tau\hat{V}} e^{-O(\tau^2)} \)
Trial Wave Function for High Efficiency and Fermion nodes

\[ \Psi(R) = e^{J(R)} D^{\uparrow}(r_1, \ldots, r_{N^{\uparrow}}) D^{\downarrow}(r_{N^{\uparrow} + 1}, \ldots, r_N) \]

Approximations in current QMC calculations:

- Slater determinant is constructed from DFT orbitals
- Geometries may be taken from DFT
- Pseudopotentials are used in most cases
Three recent QMC Applications

1) Addressing the DFT band gap problem illustrated for solid helium

2) Phase Transitions in Silica Quartz

3) Fundamental high pressure scale for cubic boron nitride
QMC Calculation of the Metallization of Solid Helium under Pressure

Method comparison

- QMC and GW: agreement
- GGA:
  - Underestimates gap by 4eV
  - 40% difference in pressure
  - 20% difference in density

→QMC done with Casino code (Cambridge).

Solid helium metallizes at extreme pressure of 25.7 TPa. This transition is important for the heat transfer in hydrogen-poor white dwarfs. Khairallah & Militzer, Phys. Rev. Lett. 101 (2008) 106407
1) Quartz and Coesite are 4-fold coordinated
2) Stishovite and post-stishovite phases are 6-fold coordinated
3) Stishovite undergoes a ferroelastic transition (2\textsuperscript{nd} order) to CaCl\textsubscript{2}
4) α-PbO\textsubscript{2} is the last structural change before reaching core-mantle boundary
LDA tends to predict structural properties of given phases better than GGA (lattice and elastic constants)
LDA fails to predict the quartz-stishovite transition; GGA gets it correct.
Why? possibly because 6-fold coordinated stishovite has more homogeneous charge density than 4-fold coordinated quartz and coesite. GGA is able to accommodate, but LDA is not.
(However, LDA does better than GGA for the quartz-coesite transition)
DFT functionals can be unreliable; there is no functional which can provide exact results
QMC explicitly computed the exchange and correlation, offering much better accuracy and reliability.

John Wilkins' group works on interstitial defects in silicon, silica, and magnesium silicate calculations with QMC.
QMC and DFT Predictions for the Transition Pressure Enthalpy Differences vs Pressure

On a coarse scale the equation of state looks fine

- The goal: A new pressure scale for diamond anvil experiments
- Calibrate using highly accurate simulations rather than experiments.
- First all electron QMC calculations for solids heavier than H and He.
- The pseudopotential approximation avoided.
- Shown that Goncharov’s experiments are more accurate.

Fabulous 10...15x Speed-Up of QMC on GPU (NVIDIA-CUDA)

- C-BC8 (512 electrons)
- Diamond (256 electrons)
- FeO (352 electrons)
- Diamond (64 electrons)

**Relative to 4 threads**

**Speedup w.r.t. quad-core Xeon E5410**

**Walkers per GPU**

- # elecs ≤ kernel block size

**Legend**

- VMC
- DMC
Speed up is a result of new way to parallelize the QMC algorithm (Esler, Kim & Ceperley at UIUC):

Standard way to distribute work among CPUs using OpenMP/MPI:

Loop over MC generation
  Loop of walkers \textit{on many CPUs}
    Loop over particles
      MC move
      Reweight + branch
      ...
    end
  end
end

New way to distribute work among GPUs

Loop over MC generation
  \hspace{1em} Loop of particles
    Loop over walkers \textit{4096+ threads per GPU}
      MC move
    end
  end
  Loop of particles
    Loop over walkers \textit{4096+ threads per GPU}
      Reweight + branch
    end
  ...
end

Single precision is also used whenever possible.