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Accurate Calculations of a Solid State Test Set with QMC Methods

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Introduction

Accurate predictions for the properties of functional materials requires accurate *ab-initio* solutions to the many-body Schrödinger equation

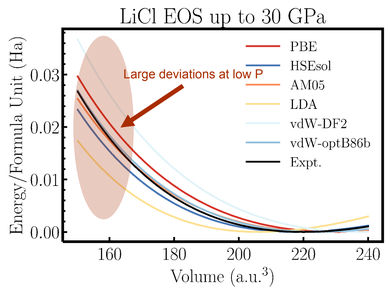
$$\left(\hat{T} + \hat{V}_{\mathrm{Ion-Ion}} + \hat{V}_{\mathrm{Elec-Ion}} + \hat{V}_{\mathrm{Elec-Elec}}\right)|\Psi\rangle = E|\Psi\rangle$$

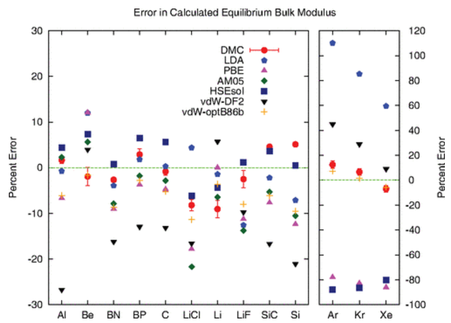
Properties: Cohesion, Optical Properties (gaps), Magnetic Phases, Structural Phase Transitions, etc.

Density Functional Theory (DFT) has been the method of choice due to its cheap cost and reasonable accuracy across many systems and scales.

EOS (T=0K) is one of the simplest metrics for measuring the accuracy of an electronic structure method.

Various DFT approximations can produce large errors in the EOS, especially at high pressure!





Shulenburger & Mattsson[1]

Test set for EOS probes a variety of simple solids with various types of bonding: ionic, covalent, metallic, and Van der Waals

Various DFT have MARE(%) ranging from 6%-26% error from expt.

Previous state-of-the-art DMC makes overall improvement over DFT with 5% mean absolute relative error (MARE). Yet, still room for improvement

We revisit the test set using Diffusion Monte Carlo (DMC) utilizing recent methodological advances to show improved accuracy of EOS

Methodology

QMCPACK[2]

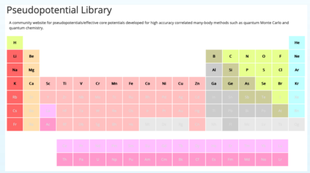
$$|\Psi_0\rangle \propto \lim_{\tau\to\infty} \exp\left[-\tau\mathcal{H}\right]|\Psi_T\rangle$$

$$E_0 = \lim_{\tau\to\infty} \frac{\langle\Psi(\tau)|\mathcal{H}|\Psi_T\rangle}{\langle\Psi(\tau)|\Psi_T\rangle}$$

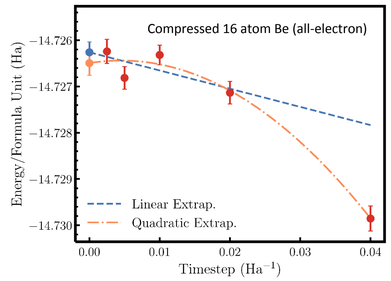
- All Ψ_T use PBE orbitals from Quantum Espresso. DMC has 1,2,3 body J
- Timestep bias controlled by small timestep
- One-body finite-size effects controlled via twist-averaging
- Two-body FS effects corrected with various schemes (e.g. KZK, $S(k)$, MPC, Chiesa, etc.)
- Cold curves are calculated for 12 densities and fit to Vinet EOS to extract V_0 and B_0

Large source of uncertainty in previous DMC came from inaccurate ECPs and thermodynamic limit extrapolations.

Here, we improve upon previous DMC by utilizing recent *explicitly correlated ECPs* designed for many-body calculations and test various finite-size correction schemes.



Approach



Twist averaging[3] alleviates the one-body finite-size effects which arise from shell-filling effects

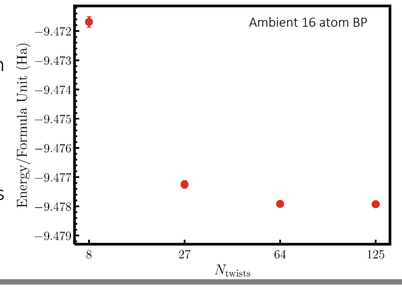
$$E_{\mathrm{TA}}^{\mathrm{QMC}}(N) = \frac{1}{N_{\mathrm{tw}}}\sum_{\mathbf{k}_s} E^{\mathrm{QMC}}(N,\mathbf{k}_s)$$

For all systems, we 4x4x4 or 5x5x5 grids sufficiently converge the energy to within 1mHa/f.u.

Timestep errors arise from approximation to the Green's function used for DMC propagation

$$G(\mathbf{R}'\leftarrow\mathbf{R},\tau) \approx G_{\mathrm{diff/drift}} \times G_{\mathrm{branching}}(\mathbf{R}'\leftarrow\mathbf{R},\tau)$$

Timesteps are analyzed in both compressed and ambient density for all systems to choose a sufficiently converged timestep to use for cold curves.



Two-body FS effects:

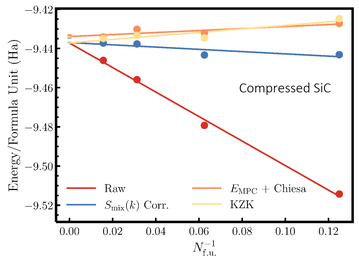
❖ Twist-averaged KZK correction[4,5]
KZK utilizes a finite-size DFT functional to estimate correction

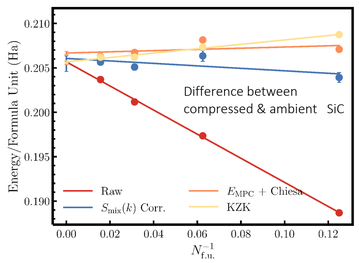
$$E_{corr.}^{\mathrm{KZK}}(N) = E^{\mathrm{LDA}}(\infty) - \frac{1}{N_{\mathrm{tw}}}\sum_{\mathbf{k}_s} E^{\mathrm{KZK}}(N,\mathbf{k}_s)$$

❖ MPC and Chiesa corrections[6,7]
Chiesa: kinetic finite-size effects through long-range behavior of 2 body-Jastrow
MPC: potential interaction by obtaining 1/r in the exchange-correlation hole.

❖ Structure Factor correction[8]
Corrects the potential energy by estimating the discretization error for the structure factor

$$E_{\mathrm{corr.}}^{S(k)}(N) = \left[\int \frac{d\mathbf{k}}{(2\pi)^3} - \frac{1}{V}\sum_{\mathbf{k}\neq 0}\right]\frac{\nu_k S_N(k)}{2}$$

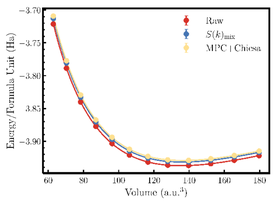




Results

Fit to the Vinet Equation of State using S(k) FS correction

$$E(V) = E_0 + \frac{2B_0V_0}{(B_0'-1)^2}\left[2 - \left(5 + 3\left(\frac{V}{V_0}\right)^{1/3}(B_0'-1) - 3B_0'\right)\right] \times \exp\left(-\frac{3}{2}(B_0'-1)\left[\left(\frac{V}{V_0}\right)^{1/3} - 1\right]\right)$$

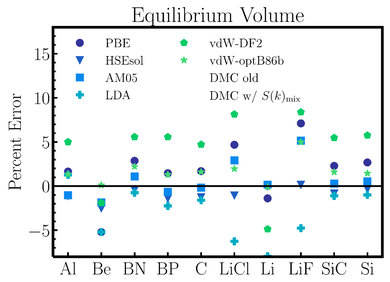


V_0^{expt}: 134.383 a.u.^{3}
V_0^{DMC}: 136.07(3) a.u.^{3}

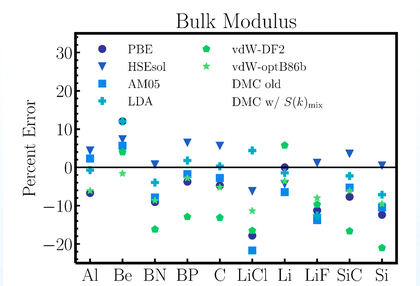
B_0^{expt}: 100.8 GPa
B_0^{DMC}: 99.6(3) GPa

$E_{\mathrm{coh}}^{\mathrm{expt}}$: 4.68(8) eV
$E_{\mathrm{coh}}^{\mathrm{DMC}}$: 4.694(1) eV

Comparison to previous DMC and DFT methods



	LDA	PBE	VdW-DF2	DMC prev.	DMC new
MARE(%)	3.211	3.104	5.538	2.11(5)	1.16(4)
Ar-RE (%)	-16.761	44.575	1.291	1.6(5)	0.001(419)



	LDA	PBE	VdW-DF2	DMC prev.	DMC new
MARE(%)	4.465	8.550	14.257	4.0(4)	4.4(3)
Ar-RE (%)	110.118	-78.0177	32.840	12.4(2.9)	19.9(3.4)

Conclusions

❖ 1st demonstration of ccECPs for solids across variety of materials. Significant improvement over DFT for EOS quantities

❖ Improved accuracy for V_0 compared to previous DMC, comparable accuracy for B_0

❖ All EOS calculations used 16-32 atom supercells with FS corrections to converge energy difference, previous DMC required at least 64-108 atom supercells. Significant reduction in computational cost.

❖ Entire workflow driven by Nexus, will be released as reference and learning tool to do production calculations for new QMC users.

Next steps:
Finish Kr calculations and repeat calculations using AFQMC to develop standard workflow in QMCPACK and compare accuracy to DMC

Investigate FS corrections for more sophisticated TWFs

References

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