Silica Under Pressure: From DFT to QMC

Carnegie Institute,

August 22-24, 2006

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Outline

Motivation: Physics Inside the Earth

- High pressure phases of silica are important in science and technology
- Silica exhibits a rich phase diagram and is ideal testing ground

Methodology: DFT and QMC

- DFT and and the quality of functionals for silica
- QMC will potentially provide the highest accuracy for silica phases

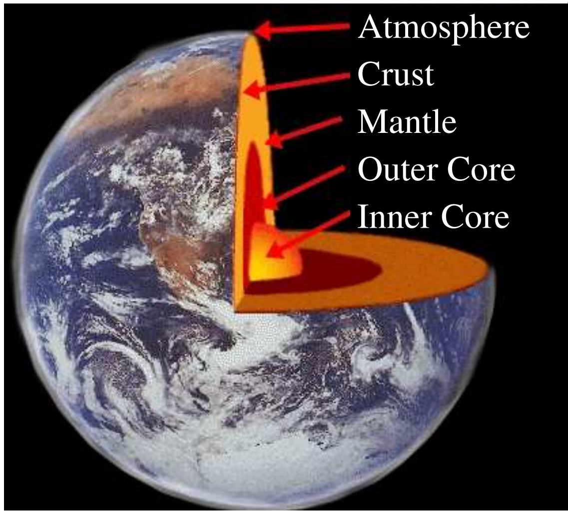
Results: DFT of Silica and What We've Learned From Silicon

- Silica energetics differ in the LDA, PW91, and PBE approximations
- In silicon, ladder of functionals shows new hybrid HSE functional promising

Challenges Ahead in QMC for Silica

- Finite-size and fixed-node errors may be significant in silica
- Methods of correcting finite-size errors are to be implemented

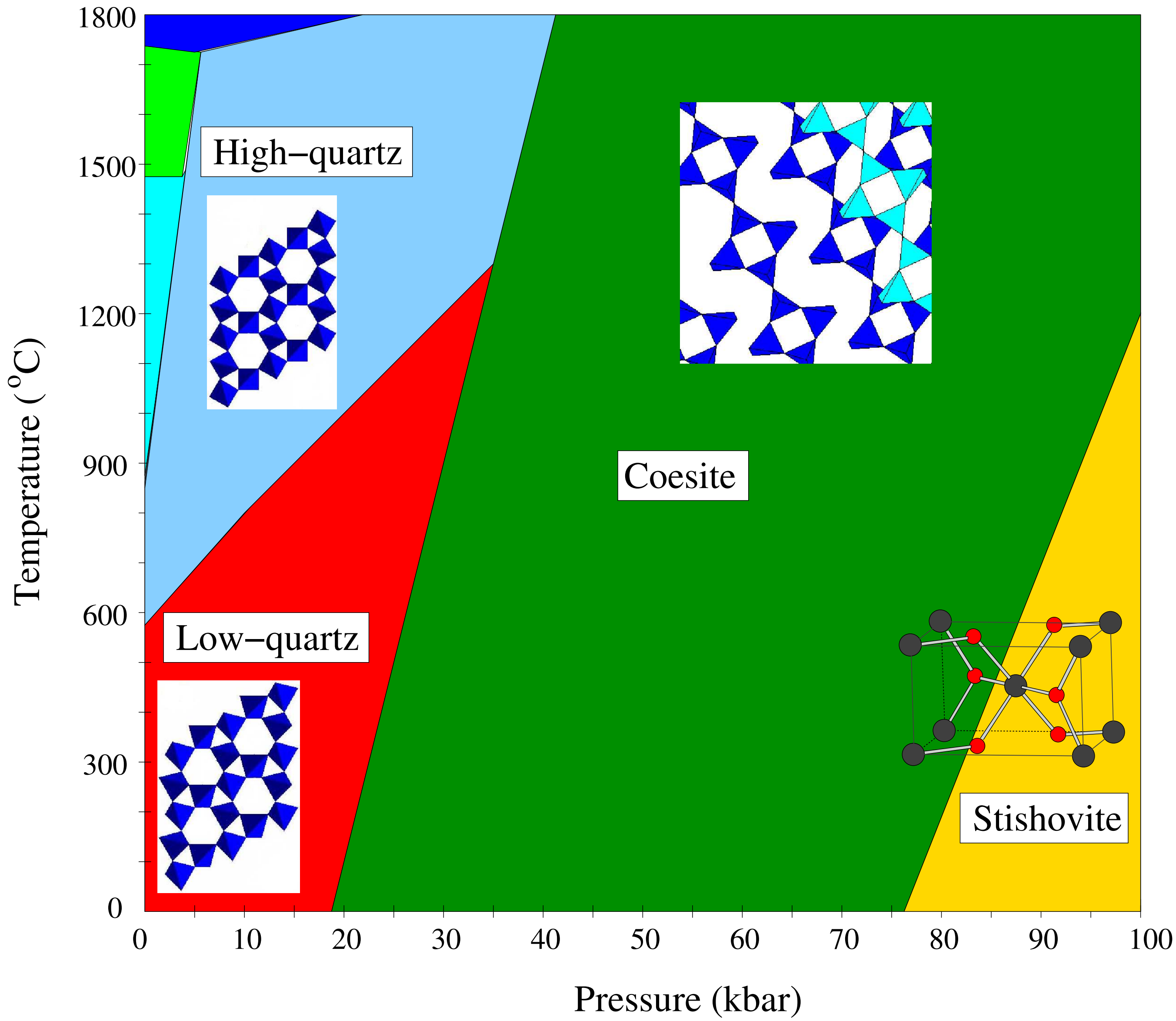
Minerals Under Pressure: Silica



Depth (km)	Pressure (Mbar)	Temperature (C)
0	0	0
2700	~1	870–3700
4300	~3.0	4300
7200	~3.5	6300

- High pressure phases of minerals, such as silica, exist inside the Earth and during meteor collisions.
- Silica is ubiquitous in rock-forming minerals and in modern technology.
- Knowing high pressure behavior of silica is important to understand the interior of Earth.
- Accurate computational methods allow us to explore phases of silica that are difficult to measure directly.
- Silica is found to exist in a rich variety of crystal phases.

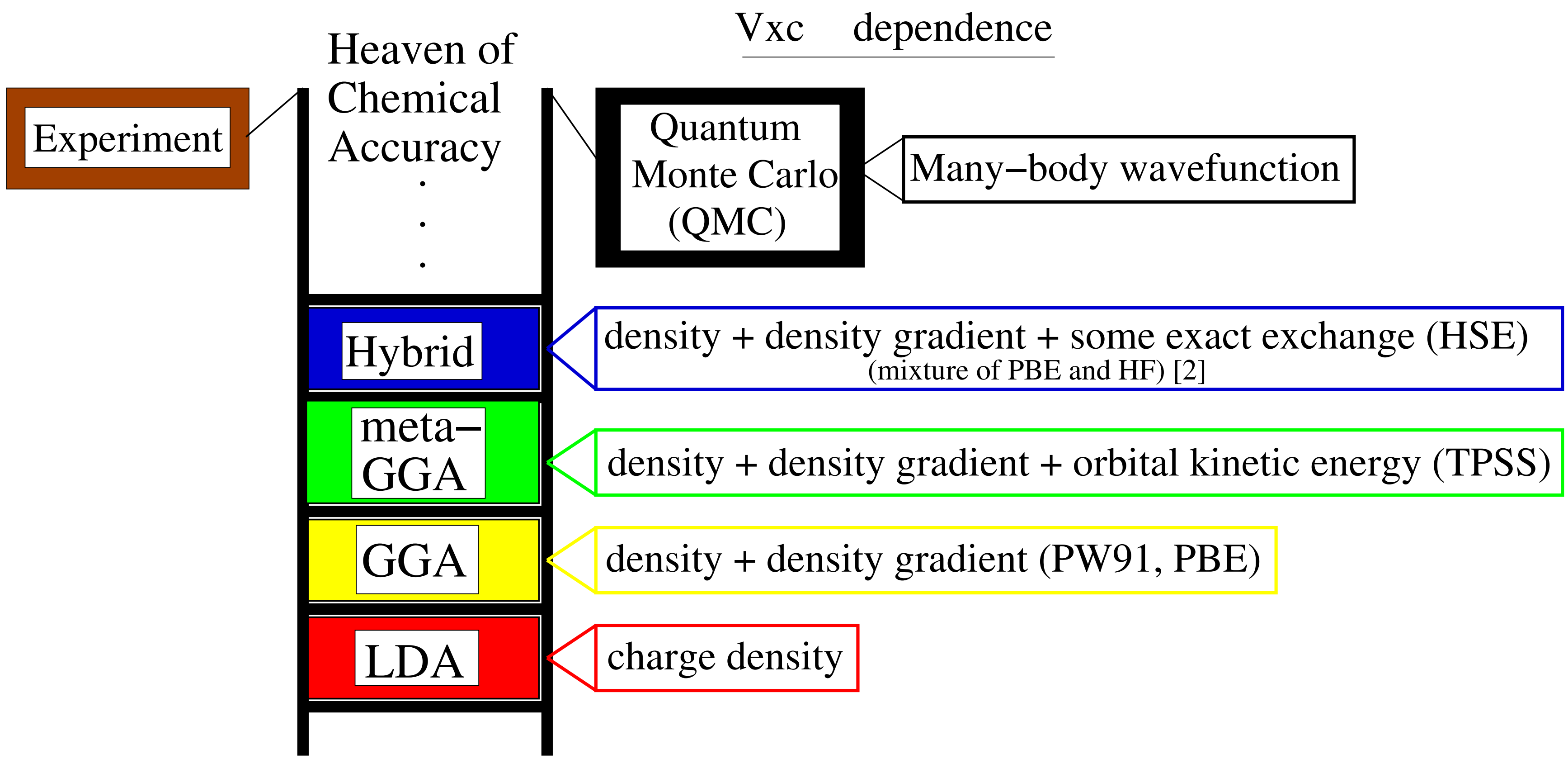
Silica Phase Diagram



- Low pressure phases: SiO_4 tetrahedra; High pressure phases: SiO_6 octahedra.

DFT Calculations: Functional Ladder

$$H_{DFT} = T + V_{Hartree} + V_{XC}[n, ...]$$



[1] J. P. Perdew *et al.* “Climbing the Density Functional Ladder.” Phys. Rev. Lett. 91, 146401 (2003).

[2] J. Heyd and G. Scuseria, J. Chem. Phys. 120, 7274 (2004).

- Get started with DFT to produce orbitals for QMC.
- Determine which functionals work best for silica.

Quantum Monte Carlo Method

Trial Wave Function and Jastrow Factor

$$\Psi_T = (\text{Slater determinant}) \times (\text{Jastrow factor})$$

Density-Functional Calculations

- J. L. Martin's CPW2000, VASP, and Gaussian
- LDA, PW91, PBE, TPSS, B3LYP, HSE functionals

Variational Monte Carlo

- Optimize Jastrow by "energy minimization" [3]

Diffusion Monte Carlo

- Stochastic method of solving the many-body Schrödinger equation
- Projects out the ground state
- 64-atom cell: 6,000 cpu hours and 4 GB per processor

[3] Umrigar and Filippi, Phys. Rev. Lett. (2005).

Approximations

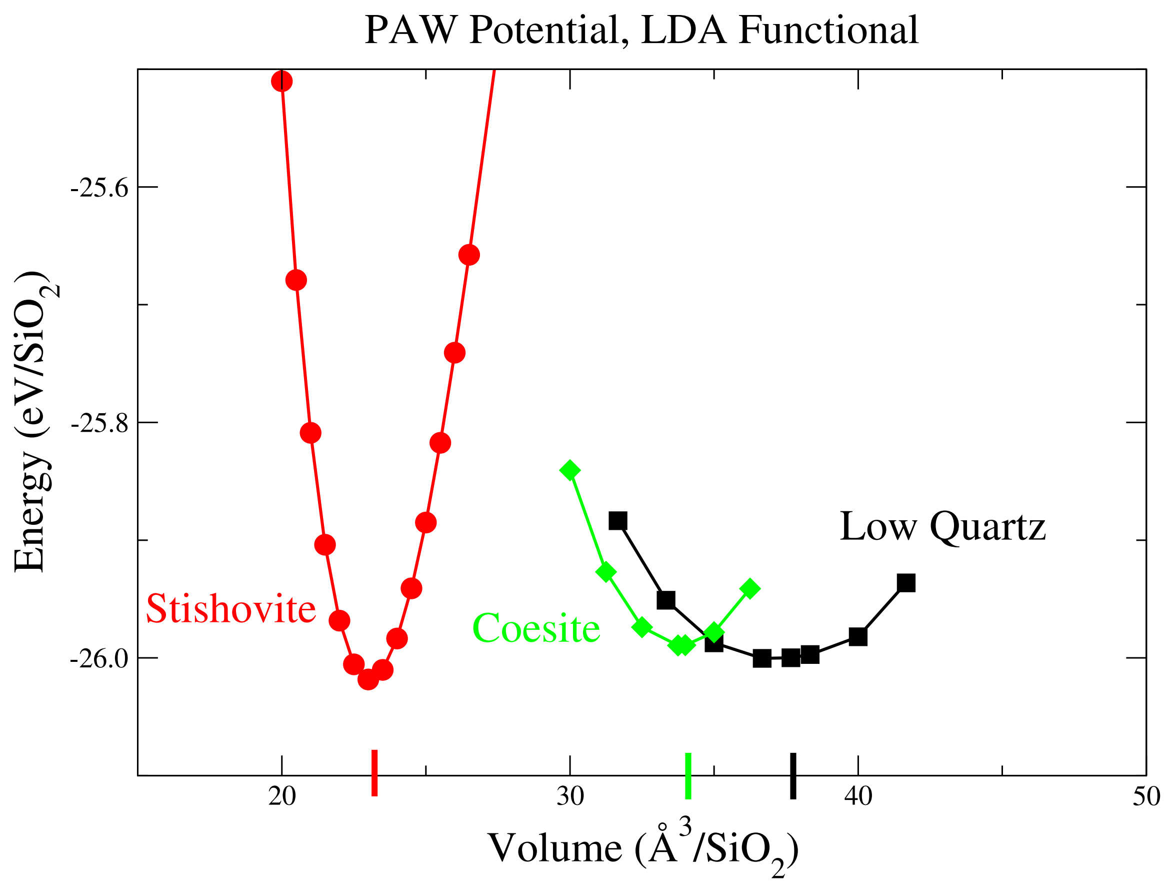
Controlled

- Statistical (increase MC steps)
- Finite-size (use correction scheme)
- Time-step (smaller time step)
- Population control (more walkers)
- Grid-size (decrease grid spacing)

Uncontrolled

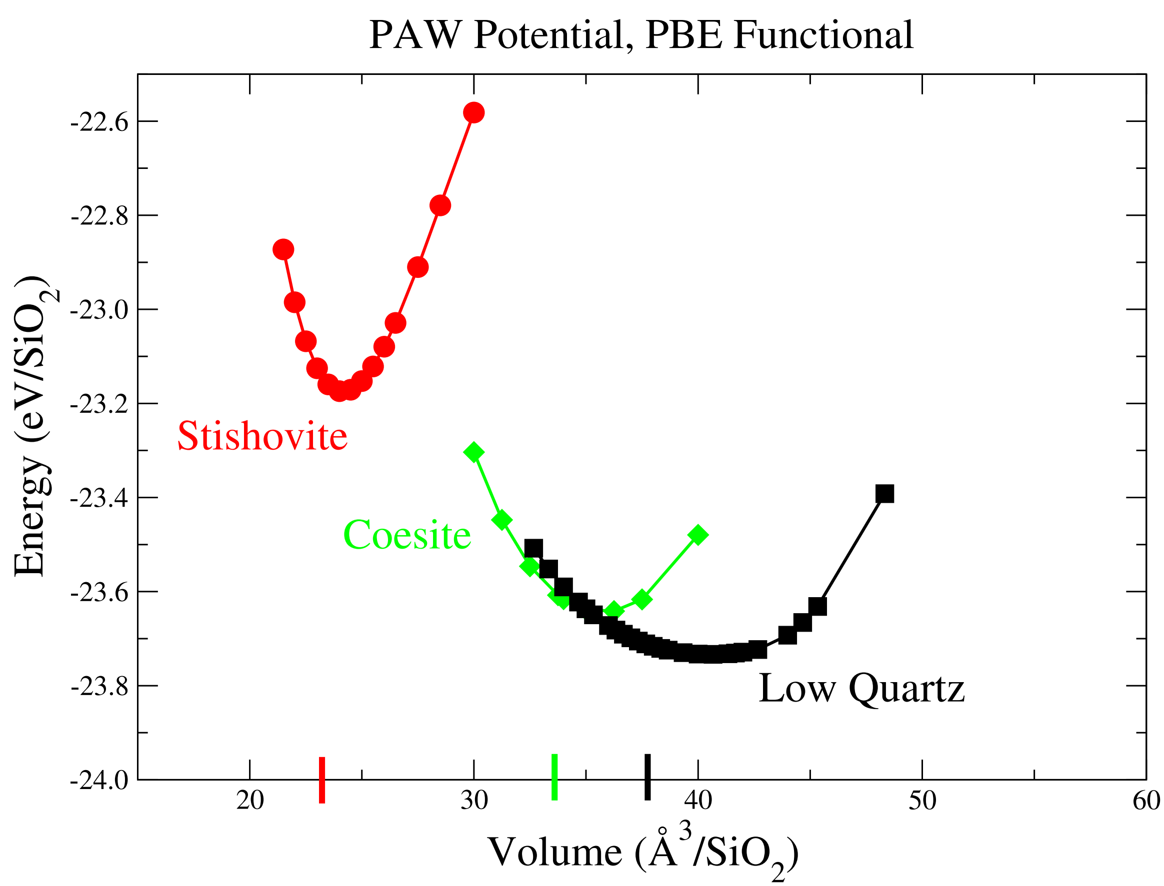
- Pseudopotential**
- Pseudopotential-locality
- Fixed node

Phases of Silica: Energy vs. Volume in the LDA



Transition Pressures (GPa)	**LDA**	PBE	PW91	Experiment
Low Quartz to Coesite	**0.5**	4.1	4.4	1.8
Low Quartz to Stishovite	**-2.2**	7.0	6.7	7.2
Coesite to Stishovite	**-0.2**	6.6	6.6	7.2
Energy Difference (eV/SiO_2)				
Coesite - Low Quartz	**0.01**	0.09	0.09	0.04
Stishovite - Low Quartz	**-0.02**	0.56	0.55	0.45

Phases of Silica: Energy vs. Volume using PBE-GGA



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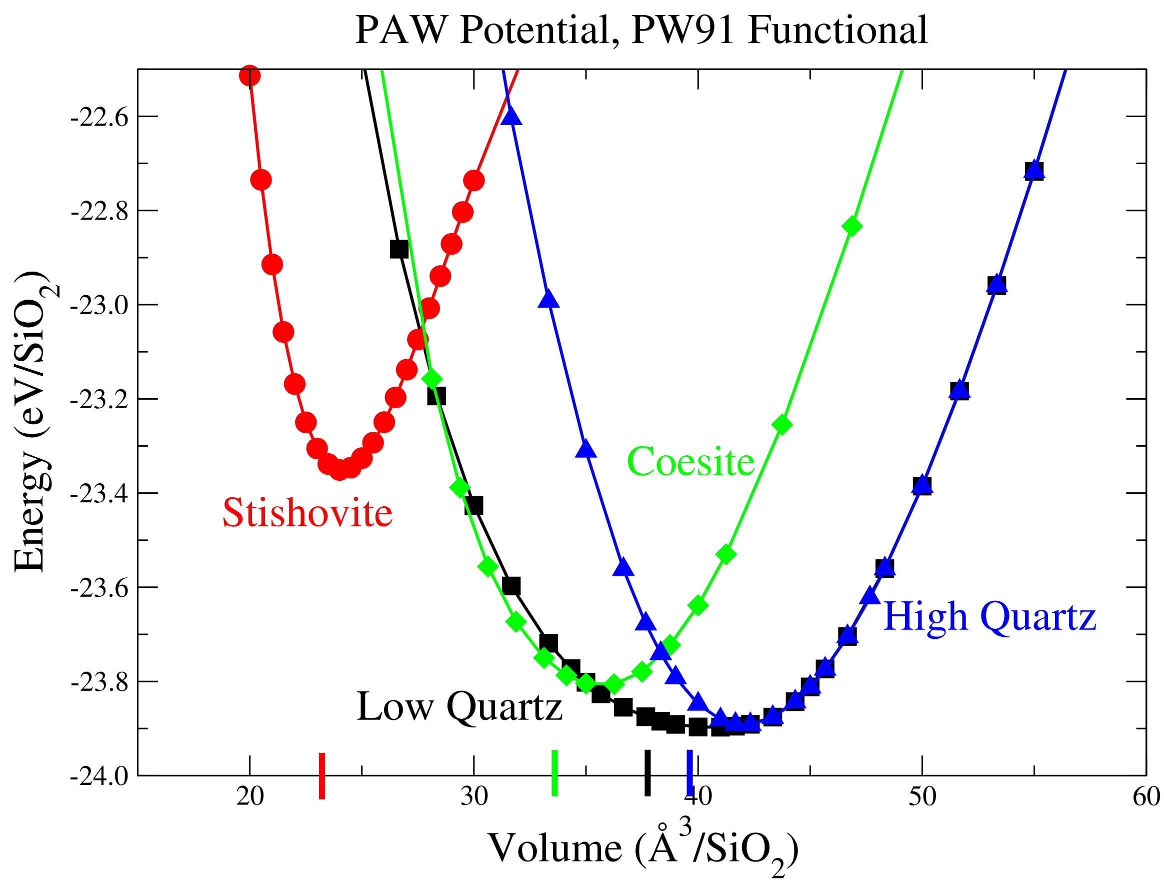

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Phases of Silica: Summary of Functional Data

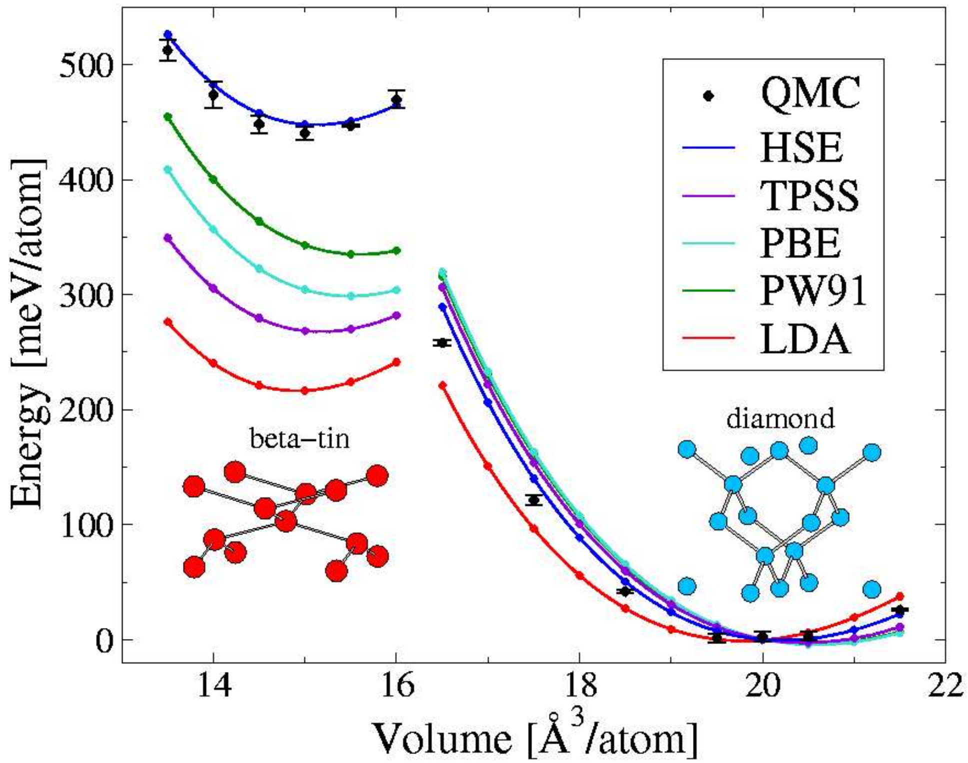
- LDA substantially underestimates transition pressures and phase energy differences.
- GGAs give a more realistic description for high-pressure phases.
- GGAs tend to slightly underestimate transition pressures
  and overestimate energy differences.
- Both LDA and GGA fail to describe the low quartz to coesite transition.

Opportunities to improve accuracy:

-Meta-GGA and Hybrid functionals

-QMC

Past Experience: Silicon Diamond to Beta-tin Transition

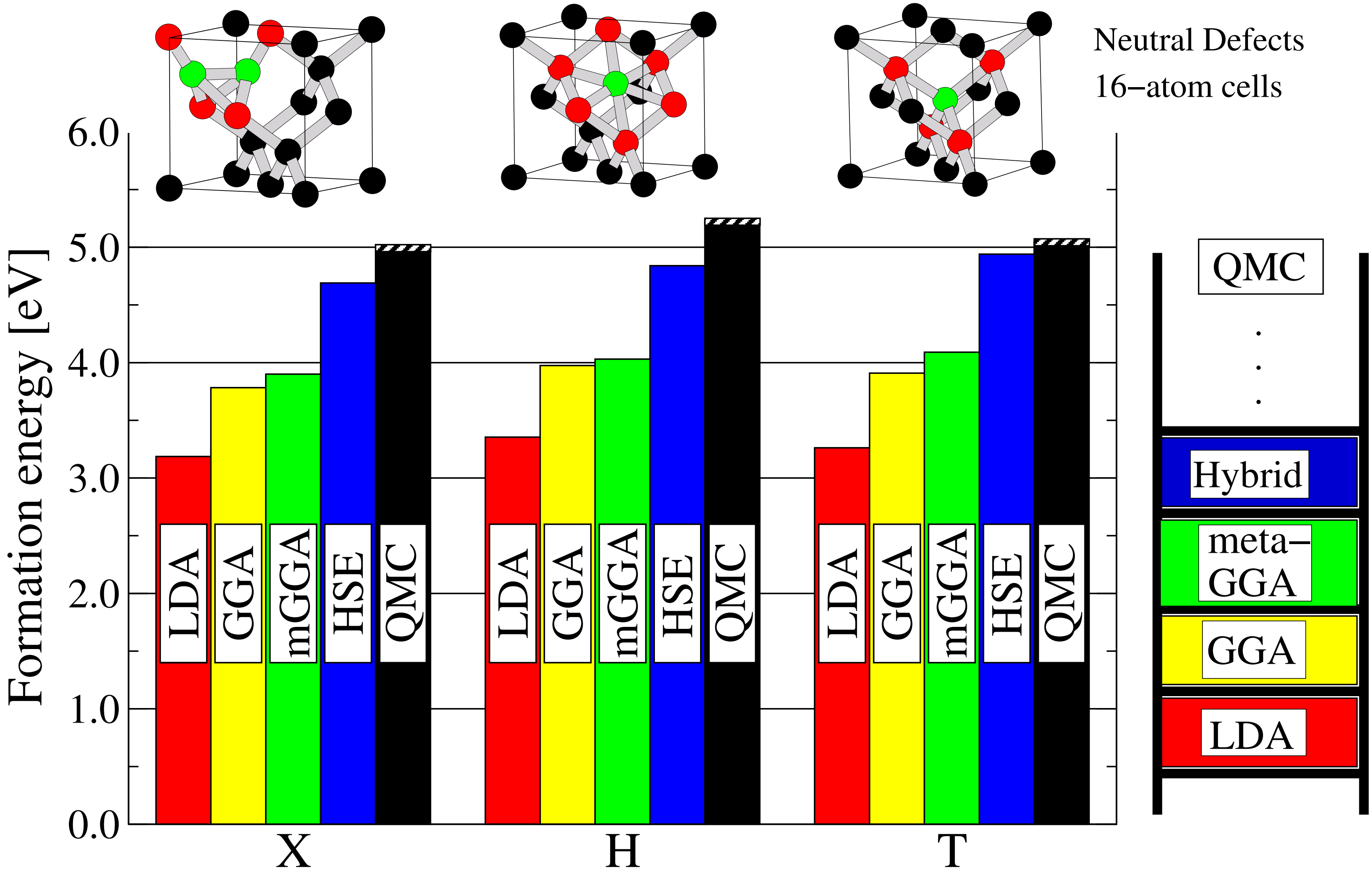


Approximation	LDA	PW91	PBE	TPSS	HSE	DMC[4,5]	Exp.
ΔE [meV]	213	321	284	301	**471**	**440(20)**	
p [GPa]	6	10	8	7	**14**	**14(1), 16.5(5)**	10-13

[4] R. Hennig, [5] D. Alfe, PRB, v70, 2004

- Hybrid HSE functional agrees best with DMC.
- Other functionals underestimate the phase energy difference.
- DMC pressure may be too high from finite size and fixed node errors.

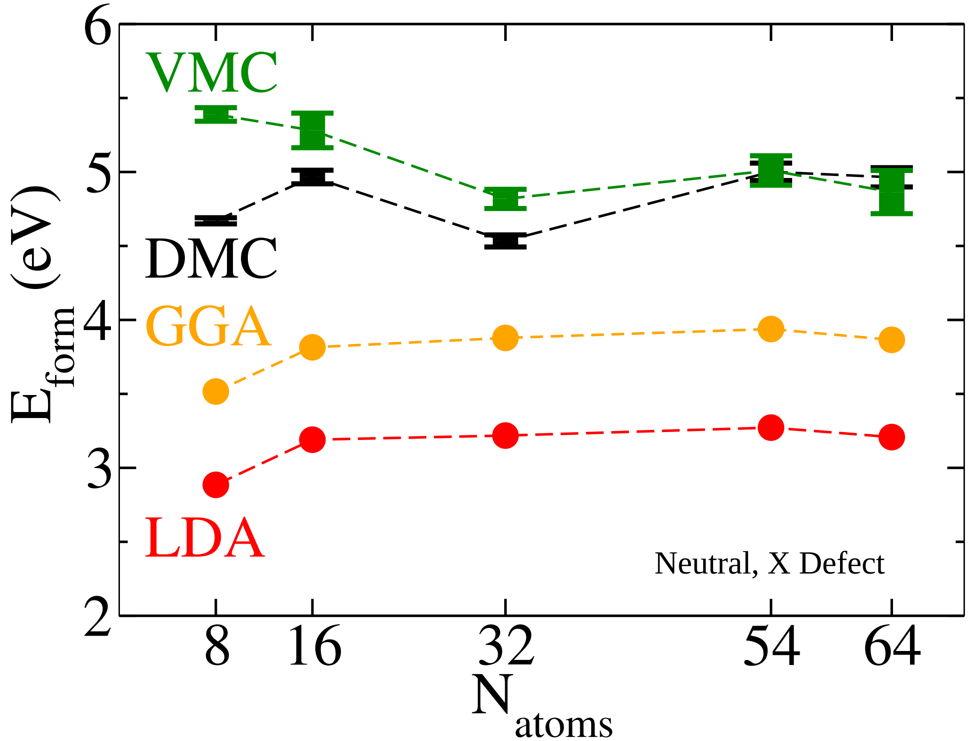
Accuracy of Functionals for Silicon Interstitials



- Single interstitial results agree with earlier QMC by Leung *et al* [5].
- Observe systematic improvement of density functionals, and HSE is accurate.

[5] W. K. Leung, R. J. Needs, G. Rajagopal, S. Itoh and S.Ihara, Phys. Rev. Lett. 83, 2351 (1999).

Finite Size Errors in Silicon



- Finite Size errors are fictitious correlations introduced by PBCs.
- Finite size errors in silicon defects disappear in the subtraction.
- When comparing different phases, such cancellation isn't expected.
- For silica, finite-size correction is needed for accuracy in QMC.

Finite size correction schemes to be implemented in Umrigar code:

1) Fraser "Model Periodic Coulomb" correction (PRB, v53, p1814 (1996))

2) Chiesa "Structure Factor" correction (PRL, v97, p076404-1 (2006))

Summary of Progress and Future Goals

- In Preparation for QMC, several high pressure of phases of silica have been studied within DFT (LDA, PW91, and PBE) - and more phases/functionals to come.

- Continued exploration of the DFT functional ladder for silica may prove useful for calculations outside of the (size/time) scope of QMC.

- Implementing finite size correction methods into Umrigar code is important for accuracy and will improve efficiency (allow use of smaller systems).

- Try QMC to achieve highly accurate silica phase energies and transition pressures.