QMC and DFT Functional Performance for Silica

K. P. Driver, R. G. Hennig, J. W. Wilkins (OSU)
C. J. Umrigar (Cornell), R. E. Cohen, B. Militzer (CIW), G. Scuseria (Rice)

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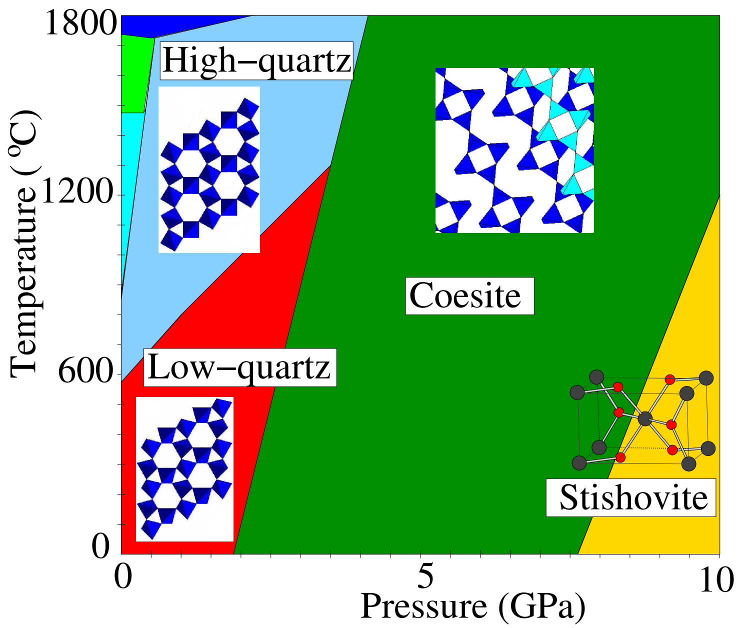
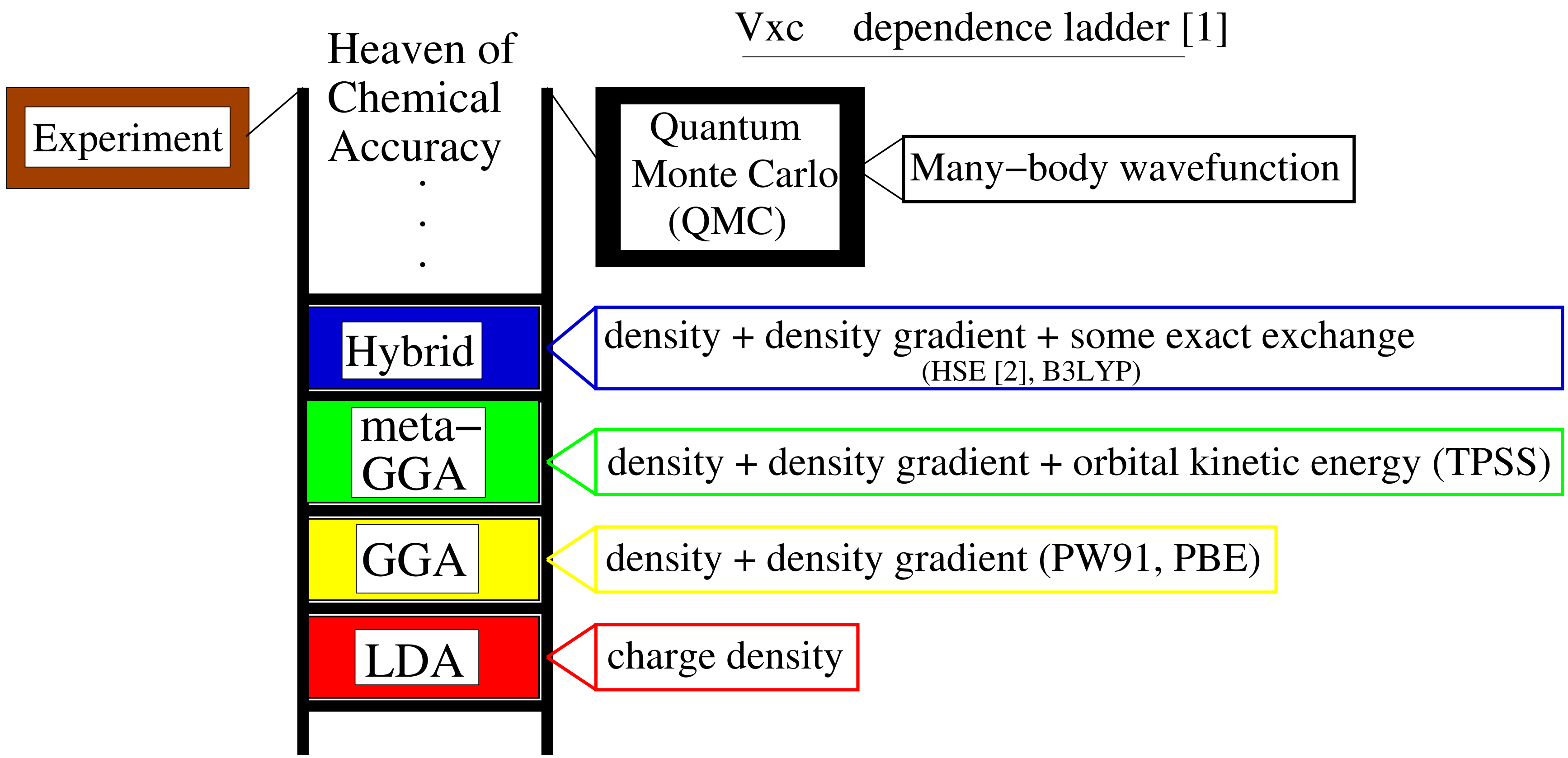
- Silica plays an important role in rock-forming minerals and technology.
- Silica exhibits complex structural phase changes under pressure.
- First principle methods can help extend the range of high pressure study.
- LDA and GGA fail to predict certain properties accurately.
- Goal: Examine accuracy of methods beyond GGA for quartz-stishovite.



DFT Calculations: Functional Ladder

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

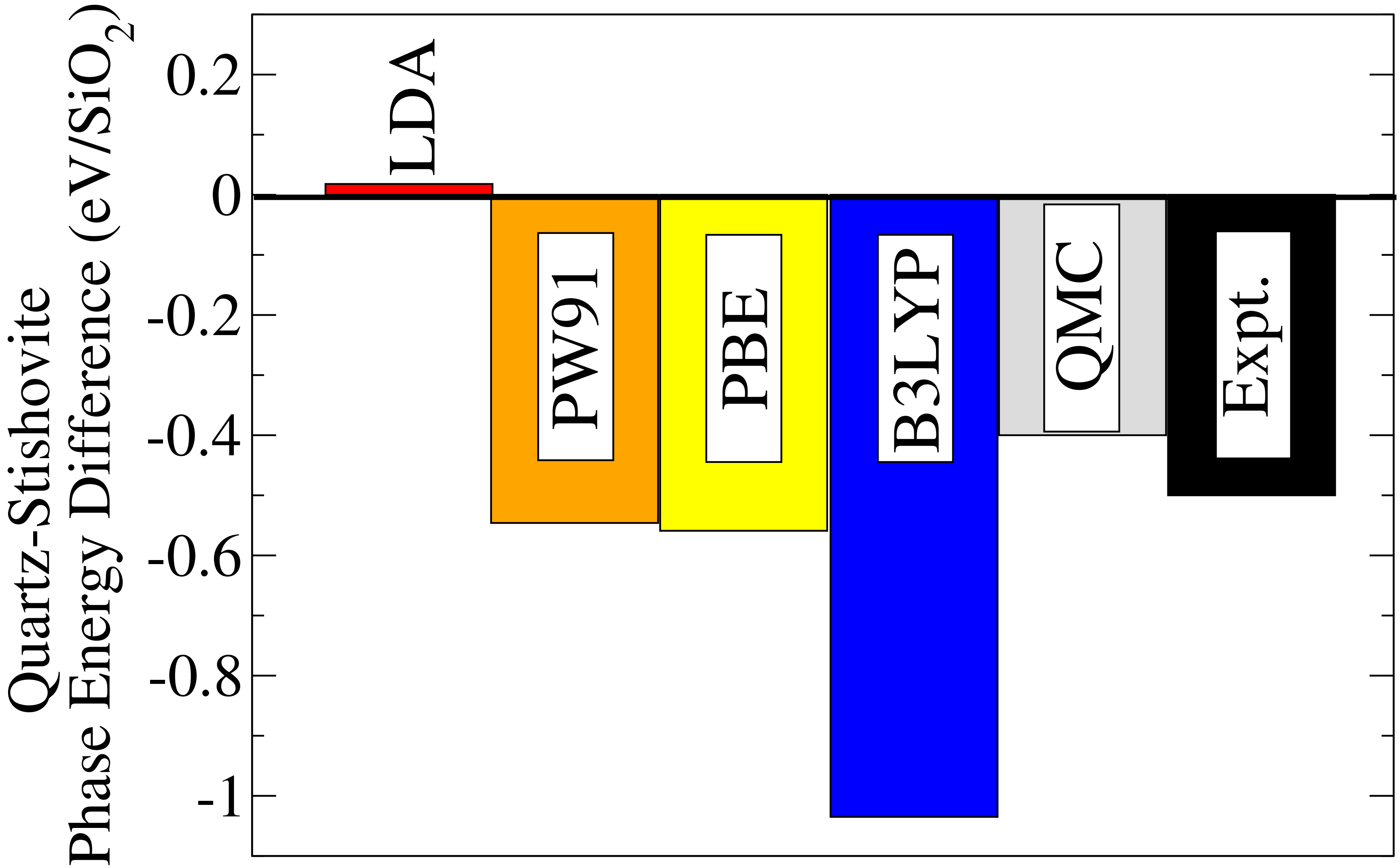


[1] J. P. Perdew *et al.* "Climbing the Density Functional Ladder." Phys. Rev. Lett. 91, 146401 (2003).

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

- Calculate quartz-stishovite energy, transition pressure, and bulk moduli at each rung.
- Compare results with experimental measurements.

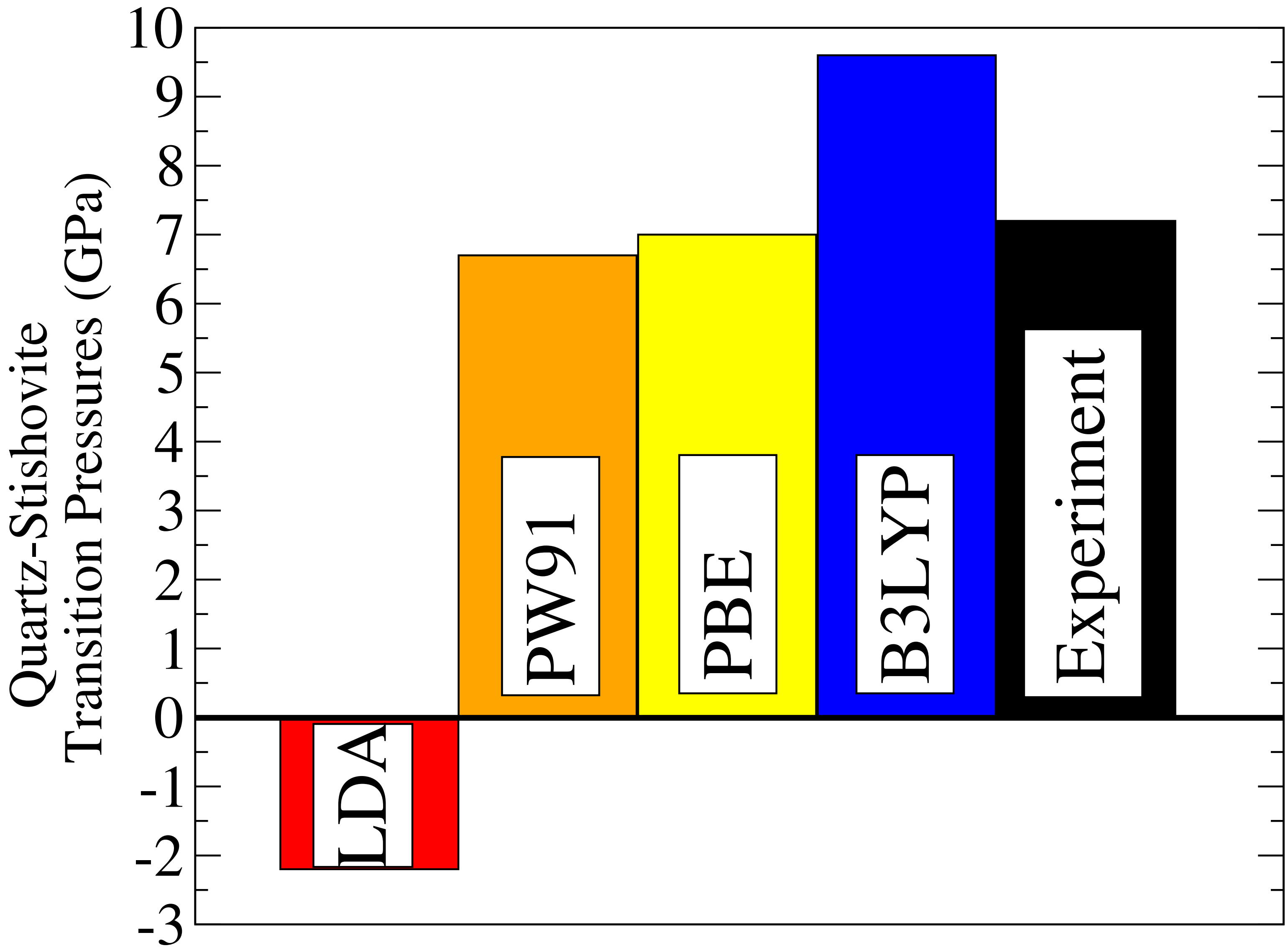
Quartz-Stishovite Phase Energy Difference



- DFT: Plane wave, pseudopotential calculations done in VASP and CPMD.
- QMC: Diffusion Monte Carlo calculation result from CASINO (R.E. Cohen).

LDA underpredicts, GGA and QMC accurate, and B3LYP overpredicts.

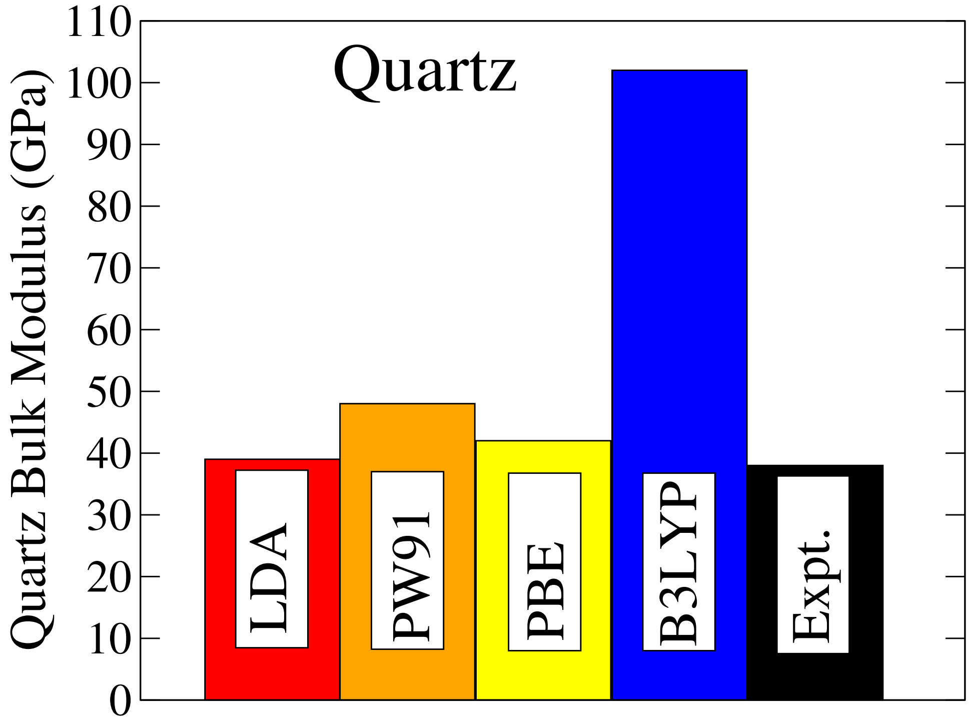
Quartz-Stishovite Transition Pressure

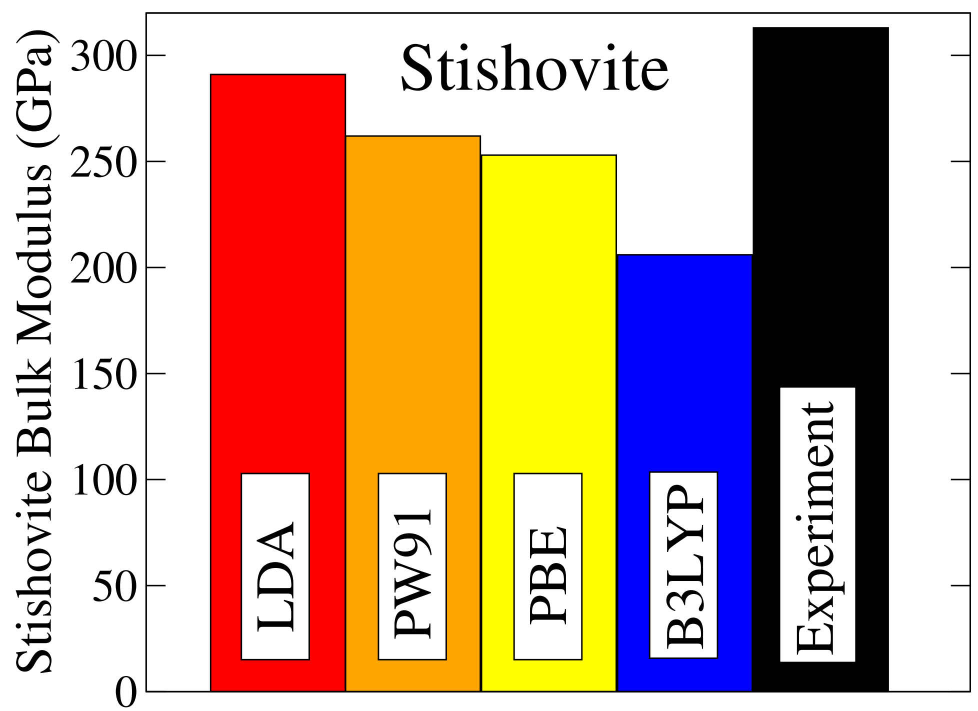


- Transition pressures calculated using the common tanget construction to E(V).

LDA underpredicts; GGA accurate; B3LYP overerpredicts.

Functional Performance on Bulk Moduli



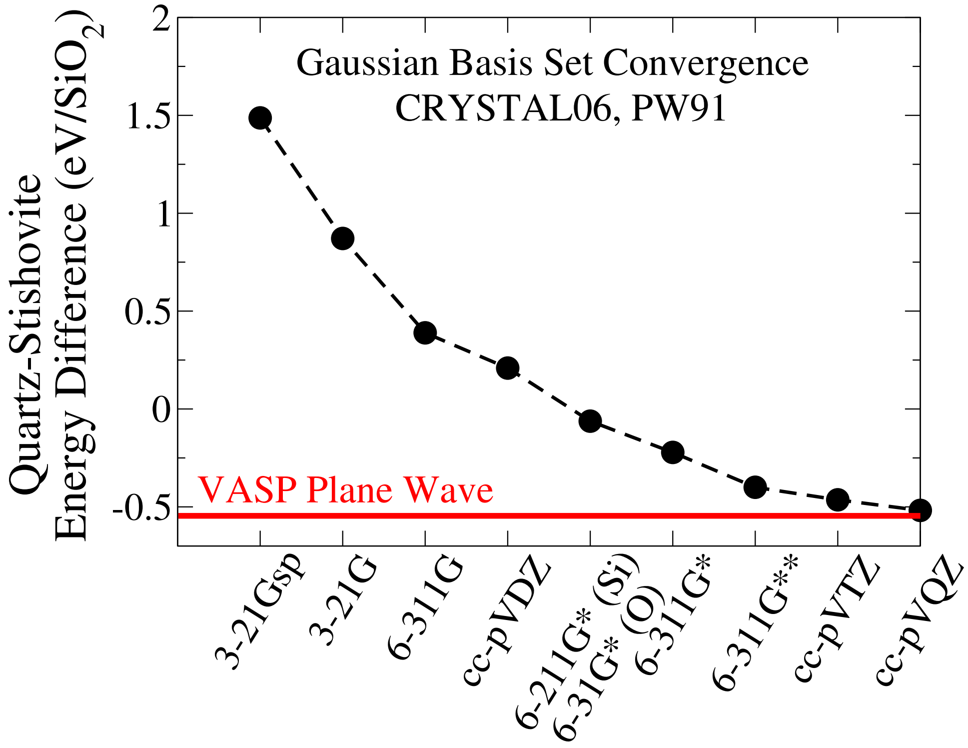


- Bulk Moduli obtain by fitting E(V) with the Birch-Murnaghan equation of state.

- LDA is in close agreement with experiment for both phases.
- GGA slightly overpredicts for quartz; slightly underpredicts for stishovite.
- B3LYP drastically overpredicts for quartz; underpredicts for stishovite.

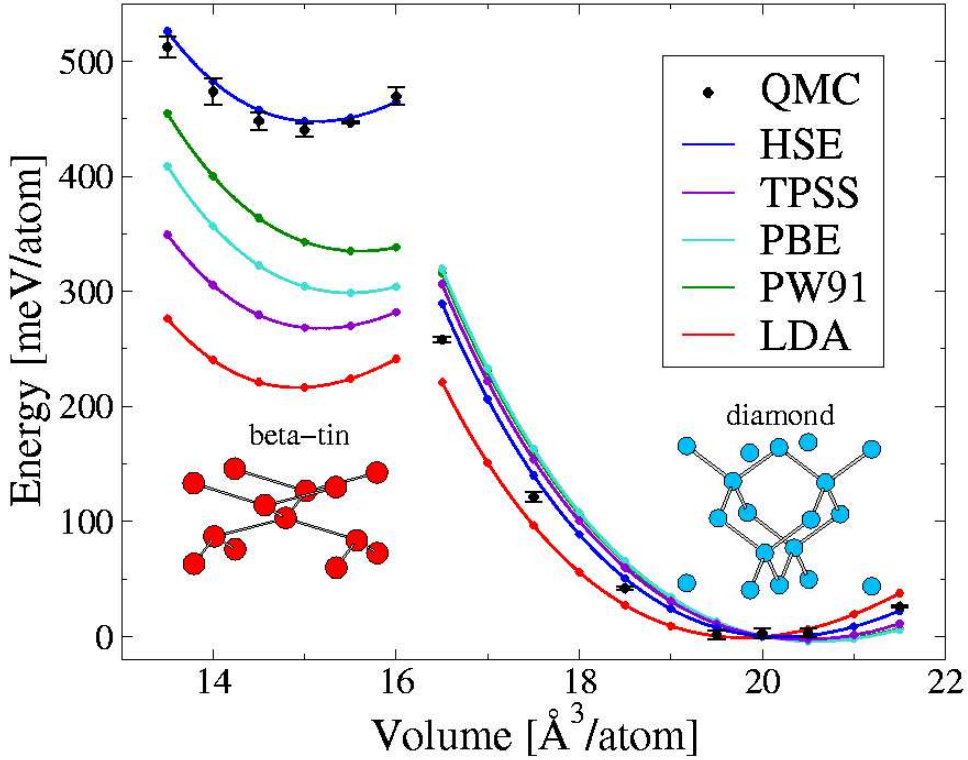
Functionals in progress: HSE and TPSS

- HSE - successful with band gaps[Heyd, 2004] and agrees with QMC[Batista, 2006].
- HSE/TPSS are only available in Quantum Chemistry codes using Gaussian basis sets.
- Quantum Chemistry codes are generally not efficient for solid simulations.
- The first step to doing such an expensive exact exchange calculation is to find which basis set is converged with plane waves.



- cc-pVQZ is necessary for accurate HSE and TPSS results - very expensive (week, >20GB).

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, PRB, 2006, [5] D. Alfe, PRB, 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.

Progress and Future work with QMC

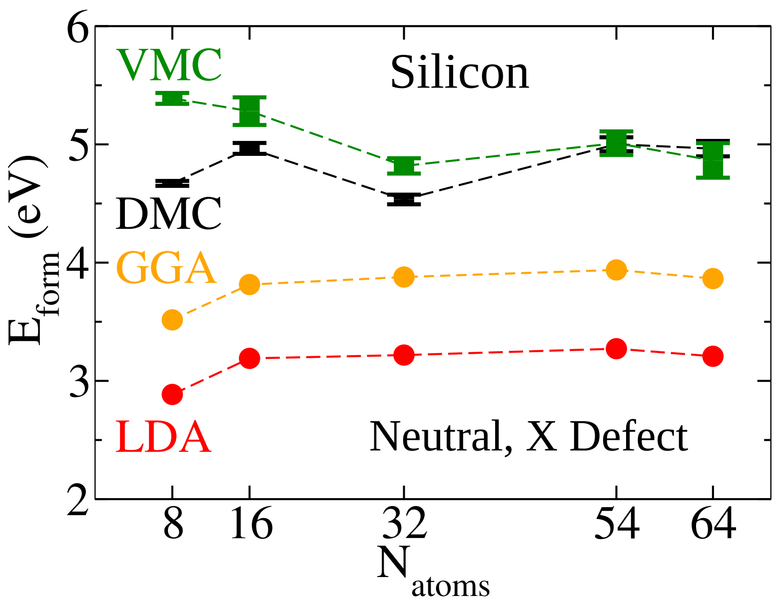
• Finite Size effects are large - need finite size correction scheme for accurate energy differences: Model Periodic Coulomb (Fraser 1996); Structure factor (Chiesa 2006)

1x1x1 cell without MPC: +0.7 eV/SiO2

1x1x1 cell with MPC: -0.7 eV/SiO2

3x3x3 cell with MPC: -0.4 eV/SiO2

Finite size errors in silicon



• Transition pressures and bulk moduli from QMC are feasible. First using input structures from DFT. In the furture, we need QMC forces/MD to do better.

Summary of Progress and Future Goals

- Hybrid functionals tested so far (B3LYP) do not offer improvement over the limitations of LDA and GGA.

- Continued exploration of the DFT functional ladder and other hybrid functionals (HSE, TPSS) may improve accuracy of silica calculations.

- QMC can be used to benchmark functionals, help us understand why DFT functionals fail, and possibly forge a new, accurate functional for silica.

- Implementing finite size correction methods is important for accuracy and efficiency in QMC.