Simulations of Silica Phases Beyond the Generalized-Gradient Approximation

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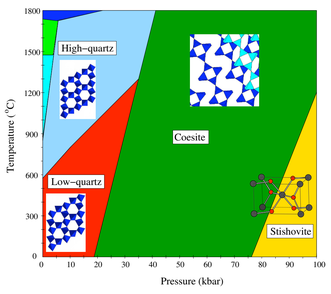
Introduction: Silica



• Silica is ubiquitous in geology and technology, and it exhibits enormous structural complexity.

• High-pressure behavior is particularly important for geophysical information (e.g. seismology).

• Large energy barriers due to strongly covalent bonds impede experimental studies of high-pressure phases and transition pressures.

• Lower pressure phases serve as a testing ground for theoretical models to be employed outside the range of experiment.

• First-principles calculations, such as density functional theory (DFT), are promising for high-pressure study, since they do not rely on experimental input.

• The most common density functionals (LDA, GGA) fail to correctly predict certain fundamental properties of silica [1,2]. Studies of silica beyond GGA are extremely scarce [3].

Acknowledgements

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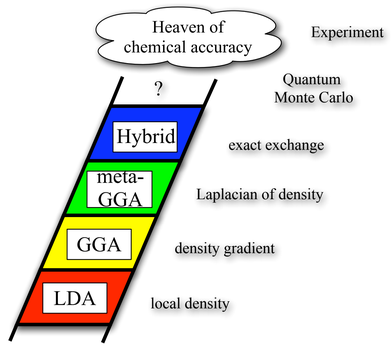
Computational Methodology: Density Functionals and Basis Sets

"Jacob's Ladder of DFT
Exchange-Correlation Functionals"



• **LDA uses exchange and correlation of uniform electron gas**
• **GGA (PBE, PW91) includes gradient corrections to the charge density**
• **Meta-GGA (TPSS) includes higher order corrections in the form of orbital kinetic energy**
• **Hybrid functionals (B3LYP, HSE [4]) contain a percentage of exact Hartree-Fock exchange**

Quantities Obtained from DFT

• DFT provides ground-state total energies.
• Get lattice constants from geometry relaxation.
• Obtain transition pressures by common tangent construction to energy vs. volume curves.
• Get bulk moduli by fitting Birch-Murnaghan equation of state to energy vs. volume curves.

Localized (Gaussian) Basis Sets

• Gaussian-type functions (GTF's) are commonly used to construct localized basis sets, which represent orbitals.

• We have used CRYSTAL03 for gaussian basis set calculations [5]. (HSE and TPSS done in Gaussian code)

• The CRYSTAL03 code is a periodic, first-principles code that contains LDA, GGA, and B3LYP functionals.

• Basis sets are never complete, and it is important to check the convergence of total energy with increasing basis size (see right).

Extended (Plane Wave) Basis Sets

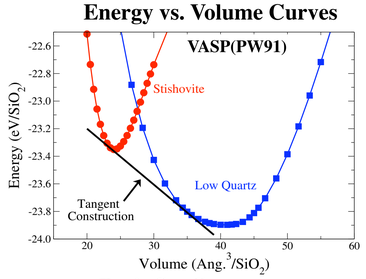
• We have used the VASP code for plane wave calculations [6,7].

• The VASP code is a periodic, first-principles code that contains LDA and GGA functionals, but not B3LYP.

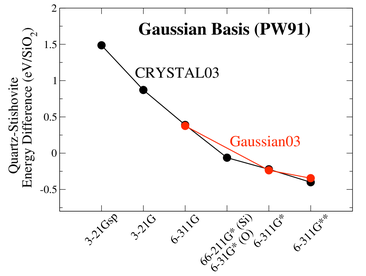
• The number of plane wave basis functions used is determined by a cutoff energy for which the total energy is converged (see right).

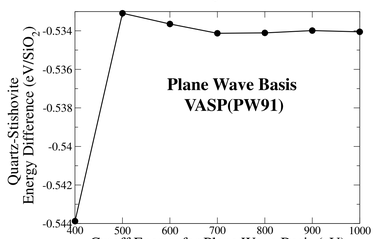
• Plane wave calculations serve as a benchmark for the gaussian-type calculations.

Energy vs. Volume Curves

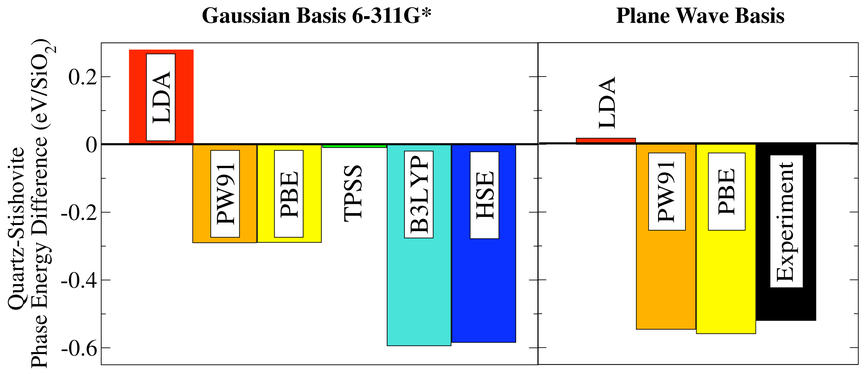


Basis Set Convergence

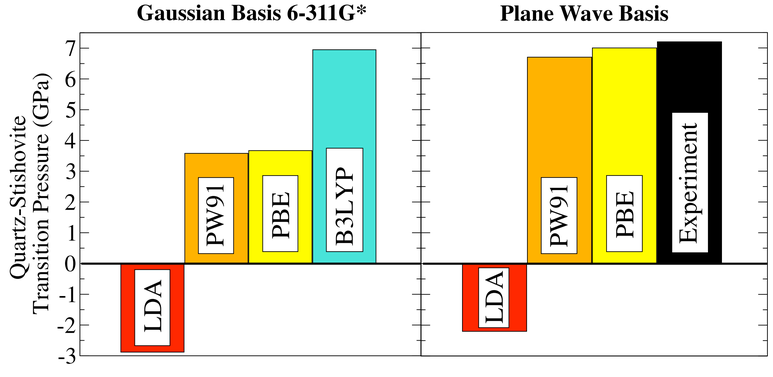




Phase Energy Differences and Transition Pressures

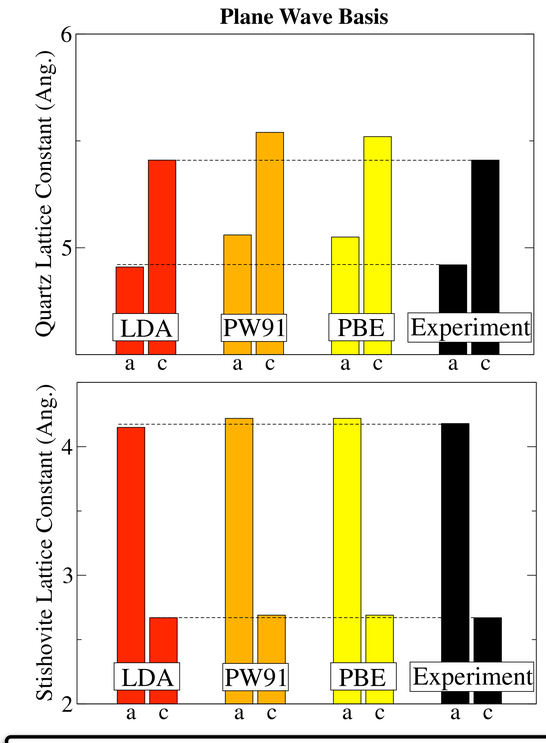


LDA fails to predict correct stability ordering of quartz and stishovite.
GGA's, except for TPSS, improve accuracy and agree with experiment in plane wave basis.
Hybrid functionals agree well with experiment.



LDA incorrectly predicts negative transition pressure.
GGA's improve accuracy and agree with experiment in plane wave basis.
Hybrid functional, B3LYP, agrees well with experiment in the gaussian basis set.

Structural Properties: Lattice Constants



LDA lattice constants are within 1% of experimental measurements.
GGA's typically overestimate lattice constants by 2-3%.

References

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[3] C. M Zicovich-Wilson *et al.*, J. Comput. Chem. **25**, 1873 (2004).
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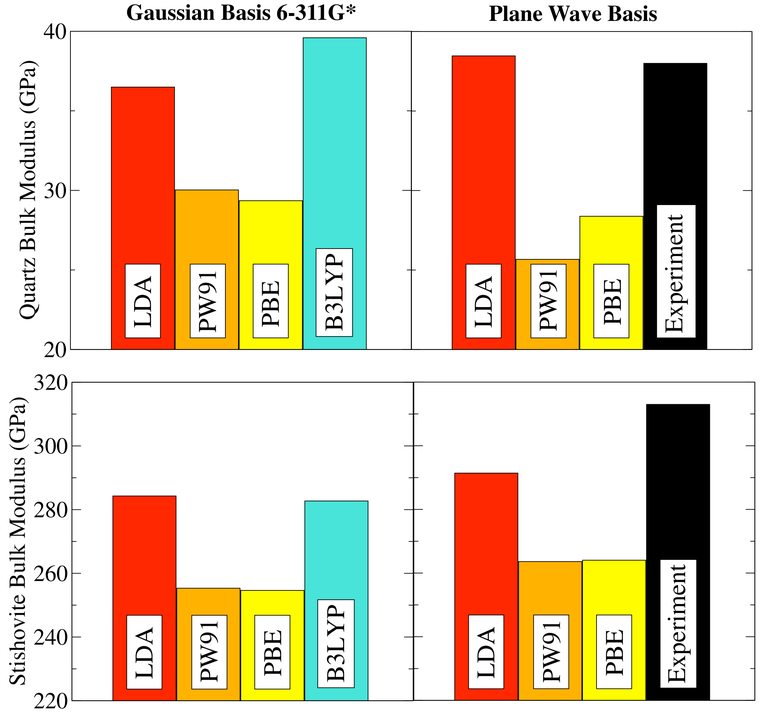
[5] R. Dovesi *et al.*, CRYSTAL03 Users Manual, University of Torino, 2003.
[6] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[7] G. Kresse and J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996).

Elastic Properties: Bulk Moduli



LDA predicts bulk moduli in quantitative agreement with experiment.
GGA's underestimate bulk moduli by more than 50%.
Hybrid functional, B3LYP, agrees with the LDA results.

CONCLUSIONS

• **LDA predicts structural and elastic properties well.**
• **GGA's predicts energy differences well.**
• **Hybrid functional, B3LYP, appears to predict both energies and elastic properties well for the tested basis set. However, definitive results require further testing with larger basis sets.**