Simulations of Silica Phases Beyond the Generalized-Gradient Approximation

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As a fundamental building block of rock-forming minerals, silica has undergone intensive study within Density Functional Theory (DFT). The conventional Local Density and Generalized Gradient Approximations (LDA and GGA) have mixed success in describing silica phases. The LDA, which depends solely on a uniform charge density, tends to describe structural properties well, but fails for the energy differences between silica phases. A striking failure of the LDA is that it predicts the structural energy of stishovite to be lower than alpha-quartz. By allowing for the possibility of gradients in the charge density, GGA drastically improves the energy differences, but, in many cases, gives worse experimental agreement for structural properties. Indeed, experimental bulk moduli tend to agree much better with LDA calculations, rather than GGA. Recently, more advanced functionals have become available by considering effects beyond a gradient correction. Therefore, in this work, silica phase properties have not only been calculated within LDA and GGA, but also with a meta-GGA (TPSS) (Perdew et al., Phys. Rev. Lett. 91, 146401, 2003) and a screened-Coulomb hybrid (HSE) functional (J. Heyd et al., J.Chem.Phys. 118, 8207 2003). The meta-GGA adds orbital kinetic energy into the functional, while the hybrid-HSE functional is a mixture of screened Hartree Fock Exchange and GGA. Both functionals potentially provide a better description of bonding than in LDA and GGA. In fact, past work has shown the HSE functional agrees well with quantum Monte Carlo calculations of pure silicon phases. Results of silica transition pressures and structural energy differences are compared for each of these functionals.