A New Capability for Using Orbital-Dependent Functionals in Density-Functional-Theory Calculations

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Motivation—Density-functional theory (DFT) is widely used at Sandia to obtain information about materials under extreme conditions and defects in semiconductors. The accuracy of this information depends on the *functional* used to describe quantum mechanical interactions between electrons. All functionals currently in use approximate these interactions and, in addition, all but the type noted below depend explicitly on the total electron density. As a result of this density-dependence, each electron incorrectly interacts with itself, yielding non-negligible errors in DFT results. These self-interactions can be eliminated by defining the functional to be the Fock expression, which correctly describes electron exchange inter-actions. However, the Fock expression is challenging to evaluate since it depends on single-electron orbitals. Before the development of the iterative technique described below, finding DFT solutions for the Fock expression was so computationally demanding that less than 10 atoms could be treated when using the plane wave basis sets and periodic boundary conditions preferred by physicists.

Accomplishment—We have developed a new iterative technique for obtaining DFT solutions when using orbital-dependent functionals such as the Fock expression, and have implemented this technique in Sandia's Socorro code. This technique allows calculations to be performed for hundreds of atoms and thus is a significant improvement over prior techniques. Moreover, this technique can also be applied to density-dependent orbitals, thereby making it possible to use *hybrid* (combined density- and orbital-dependent) functionals, which have yielded highly accurate results in quantum chemistry studies.

In developing this new technique, we addressed a difficult technical issue related to the use of periodic boundary conditions: When using the Fock expression, an integral divergence arises in the energy due to the long range of electrostatic interactions. We discovered that this divergence has significant, detrimental consequences for the convergence rate of the energy with respect to numerical sampling: When the divergent term is ignored, the convergence rate is 1/N where N is the number of sampling points (Fig. 1). This is much slower than the exponential convergence found using density-dependent functionals. Our analysis and tests showed that $1/N^2$ convergence can be achieved by using an analytic continuation technique and exponential convergence can be achieved by utilizing an attenuated Coulomb kernel to restrict the range of the electrostatic interactions. Although calculations using the Fock expression and our new iterative technique are significantly faster than prior calculations, they are still roughly an order of magnitude slower than DFT calculations using density-dependent functionals. Compute times using the Fock expression are dominated by double-precision fast-Fourier transforms (FFT). Substantial reductions in these times may be possible in future computers via the use of threaded processes and/or dedicated FFT co-processors.

Significance—To the best of our knowledge, the new capability described herein is available nowhere else in the world. When used with the Fock expression, this capability eliminates self-interaction errors and also yields semiconductor band gaps in good agreement with measured values (Fig. 2). More importantly, this new capability allows hybrid functionals to be seamlessly used in calculations with a plane wave basis. This opens the possibility of obtaining significantly higher accuracy in results for solids and plasmas, akin to what has been found by the quantum chemistry community.

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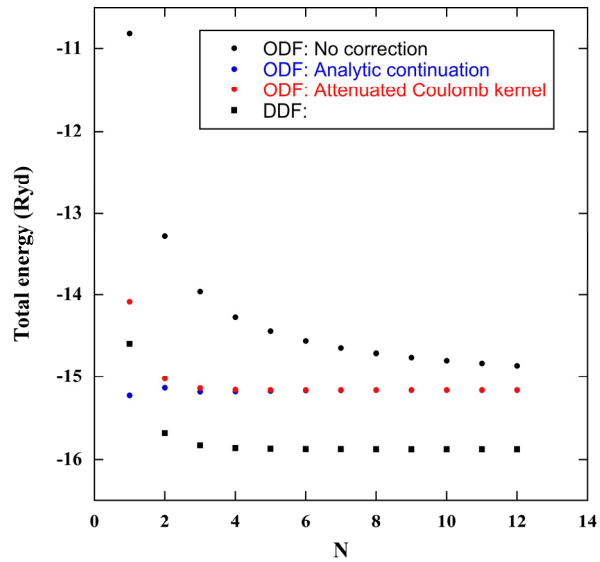

Figure 1. Convergence of the silicon total energy versus the number of sampling points (N) using: an orbital-dependent functional (ODF) with no correction for the integral divergence, analytic-continuation correction, attenuated Coulomb kernel correction; and a density-dependent functional (DDF).

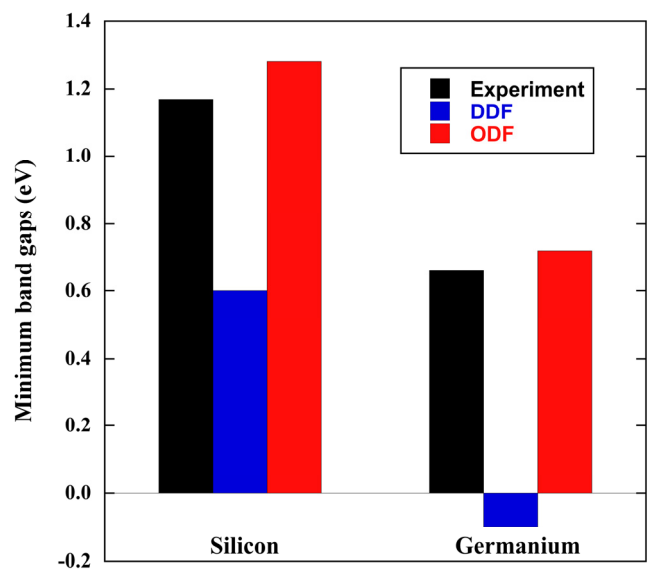

Figure 2. Measured and computed minimum energy gaps for silicon and germanium: Density-Dependent Functional (DDF) and Orbital-Dependent Functional (ODF).