Orbital-Free Density Functional Theory Dynamics: Evolution of Thousands of Atoms with Quantum Forces

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In the last few years, we have been improving both the scaling (expense) and the accuracy of state-of-the-art quantum mechanical theories of condensed matter, which means density functional theory (DFT) [1-5]. Our goal is to develop theoretical methods that can describe accurately the chemical and physical behavior of thousands of atoms, and to link those descriptions to models of solid materials at higher length scales. This talk will discuss progress made toward this objective, where we will outline our recent progress developing accurate kinetic energy functionals [2, 4], which provide the means to treat metals within a linear scaling DFT formalism [5]. Linear scaling means that if the size of the system is doubled, the cost of the calculation only doubles.

Conventional DFT scales cubically with system size and hence only small (≤ 100) numbers of atoms can be treated. In conventional DFT, one solves a mean-field eigenfunction-eigenvalue problem for a set of one-particle "orbitals". If one sums the modulus squared of the occupied orbitals, one obtains the actual physical observable, the electron density. The orbitals are introduced merely so as to obtain the kinetic energy, which in quantum mechanics is represented by the expectation value of the Laplacian, summed over the occupied orbitals. However, introducing orbitals is not desirable, as this is what leads to unfavorable and unphysical scaling of the algorithm. If one could eschew the orbitals, and solve directly for the kinetic energy knowing the density, then one would have a linear scaling algorithm for solving the DFT equations (as all terms can then be evaluated using a series of FFTs). Unfortunately, the functional of the kinetic energy in terms of only the electron density is unknown (and perhaps unknowable). One direction of our current research is to find physically reasonable approximations to the exact functional.

We have developed new kinetic energy density functionals (KEDFs) that satisfy both smoothly varying and rapidly varying density limits of exact linear response theory [2,4]. These new functionals yield accurate structures, bulk moduli, energy differences, vacancy formation energies, densities, and even surface energies and densities (where accuracy is relative to orbital-based DFT, since the KEDFs are an approximation to this). The fact that these new functionals can reproduce surface energies and densities suggests that it may be robust enough to describe any density variation (since vacuum at a surface is the most extreme) and hence any material.

We have used these new functionals to examine, e.g., the electronic structure of nanoparticle arrays, work that would have been impossible with orbital-based DFT [5]. We were able to predict the position of a metal-insulator transition in such an array, using a nonorthogonal tight binding model where the overlaps and energies were extracted from the orbital-free DFT calculation. The particle spacing we find agrees very well with that found experimentally. In addition, we demonstrated that wave function overlaps as small as 1% are enough to induce the transition from insulator to metal.

Unfortunately, there are still technical challenges to overcome before this will be a general technique for studying condensed matter at the thousand atom scale. Right now, sp-bonded metals (alkalis, alkaline earths, group III metals, etc.) can be treated accurately with this technique. Other elements are problematic still because of their tendency to have more localized electronic structure. Work is in progress to resolve such issues [6]. Despite these limitations, the orbital-free DFT method can be used to compute stress-strain relationships directly from DFT [7], which in turn can be passed on to higher length scale simulations such as the quasicontinuum method [8,9].

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We are currently working to implement this approach [10], so that we can use it to study stress-induced failure of metals from first principles.

References


