FINAL REPORT

TO THE

U. S. DEPARTMENT OF ENERGY

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On the grant entitled

"Scalable Methods for Electronic Excitations and Optical Responses of Nanostructures: Mathematics to Algorithms to Observables"

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PROJECT PERIOD: 9/15/2003 to 11/14/2004

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Prof. E. A. Carter moved from UCLA to Princeton University in September 2004. This DOE-BES grant/project was transferred to Princeton University and is finishing this year (2009). The PI was not informed until yesterday that there was a need to file a final report on the UCLA portion of the award. After searching through computer files, she was able to reconstruct the point the work had reached during November 2004 when the grant ended at UCLA and started at Princeton. The following technical summary represents only the work completed up to that point, the first 14 months of the project. A final report on the Princeton portion of this grant will give a much more comprehensive and up-to-date picture of the accomplishments of overall project.

This multi-investigator project was concerned with the development and application of new methods and computer codes that would allow realistic modeling of nanosystems. Carter's part in this team effort involved two method/algorithm/code development projects during the first 14 months of this grant. Carter's group has been advancing theory and applications of the orbital-free density functional theory (OF-DFT), the only DFT method that exhibits linear scaling for metals. Such a method offers the possibility of simulating large numbers of atoms with quantum mechanics, such that properties of metallic nanostructures (e.g. nanowires of realistic dimensions) could be investigated. In addition, her group has been developing and applying an embedded correlated wavefunction theory for treating localized excited states in condensed matter (including metals). The application of interest here is spin manipulation at the nanoscale, i.e., spintronics, in which local electron excitations interact with the surrounding material. Her embedded correlation method is ideal for studying such problems. The following work was completed during the first 14 months of this grant:

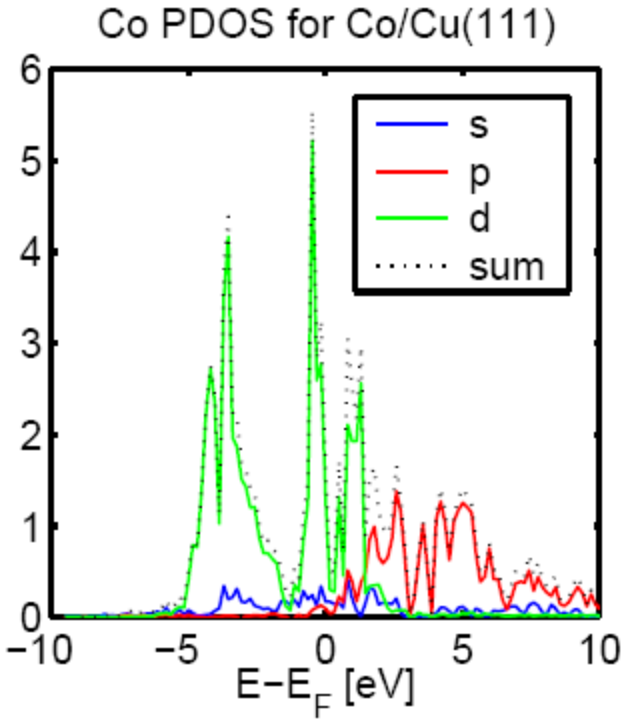
OF-DFT Progress

- A new FORTRAN 90 OF-DFT code was written, with a number of enhancements and algorithm changes to make the code robust. For example, Carter introduced new options for variational parameters into the new code, including the square root of the electron density as well as the electronic density itself. The latter option poses a problem in that the minimization must be done by applying mixed equality-inequality constraints, which require the use of the Active-Set method for constrained minimization, introducing additional algorithmic complexity. However, the algorithm appears to be stable. Carter's new code now can optimize the size and shape of arbitrary periodic unit cells by minimizing the stress tensor, for a variety of kinetic energy density functionals (the key component of OF-DFT). The new code now includes both the LDA and GGA-PBE exchange-correlation functionals. Moreover, the code was written to be compatible with the commercial Kohn-Sham DFT code CASTEP in terms of file formating, so that one can seamlessly go between the two codes for comparison.

- In order to use the OF-DFT approach to study morphological features in materials such as nanostructures or surface cracks, it is critical that the algorithms used allow for the study of aperiodic systems. The OF-DFT code described above relies, as do most condensed matter codes, on the use of 3D periodic boundary conditions so as to utilize Fast Fourier Transforms (FFTs) to keep the scaling as NlnN, where N is some measure of system size. To study aperiodic nanosystems, it will be necessary to work in real space and to utilize an algorithm that retains at least NlnN scaling. As a result, Carter is working to see if the OFDFT energy and potential can be re-expressed profitably in real space using the multigrid technique, in collaboration with Achi Brandt, its inventor. The multigrid technique, a linear iterative solver, will replace the currently-used conjugate-gradient (CG) algorithm for electronic minimization. Carter plans to eliminate the use of FFTs entirely, using a discretized representation of gradients and Laplacians, via use of this O(N) multigrid technique. The multigrid technique will make it easier for the code to be parallelized. It is also expected to be faster than conjugate gradient minimization. Lastly, multigrid can be used with a variety of boundary conditions, including periodic and Dirichlet, both of which will be useful in applications.

Embedded Correlated Wavefunction Theory Progress

- A classic example of spin manipulation is provided by the Kondo effect, where at a critical (low) temperature, bulk nonmagnetic metals with magnetic impurities exhibit quenching of magnetism and an anomalous rise in resistivity as the temperature decreases. Recent scanning tunneling microscopy (STM) experiments for magnetic atoms on nonmagnetic metal surfaces have revealed a very narrow resonance at the Fermi level, which was predicted long ago by Kondo. The effect has been postulated to be due to localized spin fluctuations that singlet-couple the conduction electrons to the impurity d-electrons. No *ab initio* theory has been available to test this assertion. Conventional DFT studies for Co on Cu(111) were completed, a system verified experimentally by STM to exhibit this resonance. It has been shown with Anderson Hamiltonian models that mean field descriptions do not provide the correct description of the Kondo state. Since DFT is a mean field theory, we expect and find incorrect physics, e.g., the magnetic moment is not quenched and the partial density of states exhibits no narrow (10 meV) resonance at the Fermi level (as shown below). The narrow resonance has been attributed to local spin excitations of the many-body open shell singlet ground state.



This is expected to change qualitatively in an embedding theory calculation that explicitly accounts for the open-shell singlet character of the Kondo resonance. In preparation for those calculations, Carter's group re-coded completely her embedding theory into a more versatile quantum chemistry package, namely, MOL-CAS, where all matrix elements involving the embedding potential are now evaluated using Gaussian basis sets combined with a real-space grid. In another advance, while Carter's previous embedding theory relied on norm-conserving pseudopotentials mapped onto quantum chemistry effective core potentials, Carter can now use ultrasoft pseudopotentials in the DFT calculations that are carried out prior to the embedding calculations. Especially for transition metals, this results in a huge computer time savings. This was achieved by developing a scheme for mapping the ultrasoft pseudopotential onto a norm-conserving pseudopotential representation, which in turn can then be mapped onto the quantum chemistry effective core potential representation for use in the embedding theory.

One invited lecture was given on these topics by the PI during the reporting period on Jan. 28, 2004. It was entitled "Embedding and Orbital-Free Density Functional Theories: Current Status and Numerical

Bottlenecks," given at the Nanoscience Workshop, Lawrence Berkeley National Laboratory, Berkeley, California. In subsequent years, many invited lectures were given, and a number of publications resulted from this work, however none were published or given during this initial phase of the work covered by these first 14 months of the project. As stated earlier, a more complete final report will be written upon completion of the entire project later this year.