Hybrid *Ab Initio* Methods for the Multiscale Design of Advanced Materials

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A multiscale method based on hybrid* ab initio *and the quasicontinuum method is being developed on a rigorous mathematical, physical, and chemical foundation. Rather than being based on classical interatomic potentials, this method will utilize quantum mechanics-based potentials capable of realistically describing the complex chemical bonding required to meet the design needs of advanced materials. Several accomplishments have been made on the project, including the development of an adaptive multilevel finite element first principles solver, the development of core mesh generation technologies, further development of an actor-based model for parallelism, and the development of a highly accurate approach for excited states in large molecular systems at finite temperature.

It is widely appreciated that to apply computational methods to the design of materials encompassing a wide assortment of elements from the Periodic Table, highly efficient methods based as closely as possible on accurate quantum mechanics are needed. We have developed an adaptive multilevel finite element first principles solver using the FeTK finite element libraries (www.fetk.org). The electronic wavefunctions in Density Functional Theory (DFT) are given by the solutions to the eigenvalue problem,

$$H\psi_i = \lambda_i \psi_i$$

where the Hamiltonian operator is given by

$$H\psi_i = \begin{pmatrix} -\frac{1}{2}\nabla^2 + V_{ext} + V_H[\rho] \\ +(1-\alpha)V_x[\rho] + V_c[\rho] \end{pmatrix} \psi_i - \alpha \sum_j K_j \psi_i$$

λ_i is an eigenvalue and the wavefunctions ψ_i satisfy the orthonormality constraints of a symmetric operator. In general, we require the lowest $N_e/2$ eigenvalues, where N_e is the number of electrons in the system. The potential V_{ext} represents the external field imposed on the system, including the ion electron attraction potential. Without modification V_{ext} is singular at the atom positions. The Hartree potential V_H, the local exchange and correlation potentials V_x and V_c, and the exact exchange term $\Sigma K_j \psi_i$, contain the effects of electron-electron interactions.

The matrix representations of the discrete Hamiltonian operator in the finite element basis are always *O(N)* sparse due to the local support nature of finite element basis functions. As shown in Fig. 1, this development also makes use of completely unstructured simplex meshes that have the

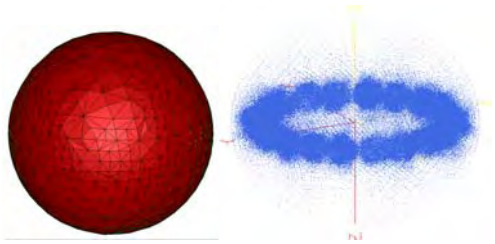

Figure 1. Adaptive mesh refinement for a C_{20} ring obtained from the adaptive multilevel finite element first principles solver.

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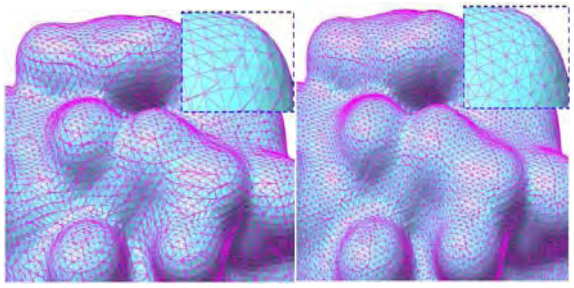
advantage of giving resolution of the near singular features around atomic nuclei using minimal computational resources.

The initial implementation, while robust enough for predicting structural properties, failed to meet the necessary criterion for use with *ab initio* molecular dynamics. In particular it was found that the energy evaluation was not smooth when changing the molecular geometry when a practical refinement was used. This would be disaster for force evaluations needed in a dynamics simulation. Experimenting with meshing strategies based on geometric-based weight functions has shown promise. We have also embarked on several new projects to develop core mesh generation technologies. In particular, we have been developing optimal mesh movement strategies for supplementing (and sometimes replacing) refinement to model multiple spatial scales. These moving-mesh techniques have the advantage of avoiding topological changes to the underlying mesh, and can be implemented using very simple data structures. In addition, we have developed a general mesh generation toolchain for building quality tetrahedral volume meshes around existing structures such as discrete atomic locations, partial lattice submeshes, or complete triangulated surfaces of molecular assemblies (Fig. 2).

With the advent of platforms like BlueGene/L, hiding communication latency is becoming essential in high-end applications. In particular, hiding irregular communication delays for software such as FETK that use "unstructured meshes" is difficult. In this project we are pursuing an actor-based model for parallelism called Thyme. This run-time data-driven substrate has been shown to enable the benefits of latency tolerance without having to manage the low-level details. Using the Thyme



(before) (after)

Figure 2. Illustration of quality improvement algorithm.

library we performed scaling studies for a 256 x 256 x 128 Fast Fourier Transform using a 1D slab decomposition. For modest processor sizes the Thyme library showed improvements over a base algorithm in which the computation and communication were not overlapped. Results using the LLNL Thunder (4-way nodes, connected by quadrics) computer at LLNL are:

	GFLOPS	
Processors	Base	Thyme
32	9200	11000
64	19400	20200

We have also carried out multiscale chemical simulations in biochemistry and environmental chemistry. With Dr. Karol Kowalski (PNNL) we designed a multiscale dynamical approach that combines coupled-cluster theory with molecular dynamics simulations and used it to study the dynamics of the excitation spectrum of cytosine and guanine bases in the native DNA environment. We have also used this method to predict the activation barriers for the reductive dechlorination of carbon tetrachloride, CCl_4, a pollutant of great concern at Hanford.

For further information on this subject contact:

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