

Adaptive Finite Element Method for Solving the Exact Schrödinger Equation of Density Functional Theory: Is it Computable?

Eric Jon Bylaska*, Mike Holst†, and John H. Weare‡

Results of the application of an adaptive finite element (FE) based solution using the Finite Element ToolKit (FETK) library of Holst to Density Functional Theory (DFT) approximation to the electronic structure of atoms and molecules are reported, including H, He, Li, Ne, H_2^+ , Li_2 , and a C_{20} monocyclic ring.

The severe problem associated with the rapid variation of the electronic wave functions in the singular regions of the atomic centers was treated by implementing completely unstructured tetrahedral meshes that resolve these features around atomic nuclei. This concentrated the computational work in the regions in which the shortest length scales were necessary and provided for low resolution in regions for which there was no electron density. The accuracy of the solutions improved significantly when adaptive mesh refinement was applied, and it was found that the essential difficulties of the Kohn-Sham eigenvalues equation were the result of the singular behavior of the atomic potentials.

Even though the matrix representations of the discrete Hamiltonian operator in the adaptive finite element basis are always sparse with a linear complexity in the number of discretization points, the overall memory and computational requirements for the solver implemented were found to be quite high. The number of mesh vertices per atom as a function of the atomic number Z and the required accuracy ϵ was estimated to be $v(\epsilon, Z) \approx 122.37 * \frac{Z^{2.2346}}{\epsilon^{1.1173}}$, and the number of floating point operations per minimization step for a system of N_A atoms was found to be $O(N_A^3 * v(\epsilon, Z))$ (e.g. $Z = 26$, $\epsilon = 0.0015$ au, and $N_A = 100$, the memory requirement and computational cost would be ~ 2 terabytes and ~ 25 petaflops). Despite the high cost of the method, it was found that strategies for fixing the error near the singularities, such as a geometric based refinement strategy or an overlapping grid method, can be used to reduce the errors ("cancellation of errors") in structure and bond energies of the system.

*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352 Research supported by DOE ASCR Multiscale Mathematics program ...

†Department of Mathematics, University of California, San Diego, La Jolla, California 92093, supported by DOE ASCR Multiscale Mathematics program ...

‡Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, supported by DOE BES Geosciences program ...