FINAL REPORT

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Grant Title:
Linear Scaling Electronic Structure Methods with Periodic Boundary Conditions.

Period Covered by this Report:
1 September 2001 to 31 May 2007

Objectives

The methodological development and computational implementation of linear scaling quantum chemistry methods for the accurate calculation of electronic structure and properties of periodic systems (solids, surfaces, and polymers) and their application to chemical problems of DOE relevance.

Status of Effort and Recent Progress

During this grant period, we focused our attention on three different projects described below.

1. Assessment of the screened-exchange HSE hybrid functional

Hybrid density functionals, which include a portion of exact Hartree-Fock type exchange, are usually deem the most accurate in the current computational quantum chemistry paradigm for molecules. For periodic systems, we and others have shown that in insulators and semiconductors, hybrids are (almost always) more accurate too. Yet in metals, Hartree-Fock exchange is not practical in its usual form. We have developed a short-range Coulomb HF

exchange hybrid, which retains most of the desirable properties of hybrid functionals, is much faster than standard hybrids, and is practical for metals. Two publications describe these advances:

- Assessment and validation of a screened Coulomb hybrid density functional, J. Heyd and G. E. Scuseria, *J. Chem. Phys.* **120**, 7274-7280 (2004).

- Efficient hybrid density functional calculations in solids: Assessment of the Heyd-Scuseria-Ernzerhof screened Coulomb hybrid functional, J. Heyd and G. E. Scuseria, *J. Chem. Phys*. **121**, 1187-1192 (2004).

2. **Application of our periodic Laplace Atomic Orbital (AO) MP2 method**

Our implementation of the MP2 method for periodic systems was extended to the direct calculation of band gaps and employed to elucidate the importance of van der Waals and dispersion interactions in a prototypical system: trans-polyacetylene. We found that dispersion between different chains (usually neglected) significantly affects the band gap. For details, see:

- Laplace-transformed diagonal Dyson correction to quasiparticle energies in periodic systems, R. Pino and G. E. Scuseria, *J. Chem. Phys*. **121**, 2553-2557 (2004).

- Importance of chain-chain interactions on the band gap of trans-polyacetylene as predicted by second order perturbation theory, R. Pino and G. E. Scuseria, *J. Chem. Phys*. **121**, 8113-8119 (2004).

3. **Development of Resolution of the Identity (RI) Laplace Atomic Orbital MP2 method**

One of the limiting factors for widespread application of our periodic MP2 methodology to a myriad of important applications (eg, carbon nanotube interactions) is its substantial computational cost. One of the major objectives of this grant was the re-write of this code using resolution of the identity techniques. We completed an in-core version of the RI-PBC-MP2 methodology, which is significantly faster than our previous version.

Personnel Supported:

One postdoctoral research associate.
One graduate student.

Unexpended Funds

No unexpended funds by the end of the funding period.

Publications (Cumulative) Acknowledging DOE Support for this Grant

1. Atomic Orbital Laplace transformed second-order Moller-Plesset theory for periodic systems, P. Y. Ayala, K. N. Kudin, and G. E. Scuseria, J. Chem. Phys. **115**, 9698-9707 (2001).

2. Efficient algorithm for band connectivity resolution, O. V. Yazyev, K. N. Kudin, and G. E. Scuseria, Phys. Rev. B **65**, 205117 (2002).

3. Purification of the first-order density matrix using steepest descent and Newton-Rapson methods, R. Pino and G. E. Scuseria, Chem. Phys. Lett. **360**, 117-122 (2002).

4. Linear scaling electronic structure methods in chemistry and physics, S. Goedecker and G. E. Scuseria, Comp. Sci. Eng. **5,** 14-21 **(**2003).

5. Assessment and validation of a screened Coulomb hybrid density functional, J. Heyd and G. E. Scuseria, J. Chem. Phys. **120**, 7274-7280 (2004).

6. Efficient hybrid density functional calculations in solids: Assessment of the Heyd-Scuseria-Ernzerhof screened Coulomb hybrid functional, J. Heyd and G. E. Scuseria, J. Chem. Phys. **121**, 1187-1192 (2004).

7. Laplace-transformed diagonal Dyson correction to quasiparticle energies in periodic systems, R. Pino and G. E. Scuseria, J. Chem. Phys. **121**, 2553-2557 (2004).

8. Importance of chain-chain interactions on the band gap of trans-polyacetylene as predicted by second order perturbation theory, R. Pino and G. E. Scuseria, J. Chem. Phys. **121**, 8113-8119 (2004).

9. Energy bandgaps and lattice parameters evaluated with the Heyd-Scuseria-Ernzerhof screened hybrid functional, J. Heyd, J. E. Peralta, G. E. Scuseria, and R. L. Martin, J. Chem. Phys. **123**, 174101 (2005).

10. Periodic boundary condition calculation using Heyd-Scuseria-Ernzerhof screened Coulomb hybrid functional: Electronic structure of anatanase and rutile TiO_2, H. Nakai, J. Heyd, and G. E. Scuseria, J. Comput. Chem. Jpn. **5**, 7-18 (2006).

11. Theoretical study of CeO_2 and Ce_2O_3 using a screened hybrid density functional, P. J. Hay, R. L. Martin, J. Uddin, and G. E. Scuseria, J. Chem. Phys. **125**, 034712 (2006).

12. Spin-orbit splittings and energy band gaps calculated with the Heyd-Scuseria-Ernzerhof screened hybrid functional, J. E. Peralta, J. Heyd, G. E. Scuseria, and R. L. Martin, Phys. Rev. **B 74**, 073101 (2006).

13. Efficient evaluation of short-range Hartree-Fock exchange in periodic systems and large molecules, A. Izmaylov, G. E. Scuseria, and M. J. Frisch, J. Chem. Phys. **125**, 104103 (2006).

14. Comparison of screened hybrid density functional theory to diffusion Monte Carlo in calculations of total energies of silicon phases and defects, E. R. Batista, J. Heyd, R. G. Hennig, B. P. Uberuaga, R. L. Martin, G. E. Scuseria, C. J. Umrigar, and J. W. Wilkins, Phys. Rev. B **74**, 121102 (2006).

15. Mott transition of MnO under pressure: A comparison of correlated band theories, D. Kasinathan, J. Kunes, K. Koepernik, C. V. Diaconu, R. L. Martin, I. D. Prodan, G. E. Scuseria, N. Spaldin, L. Petit, T. C. Schulthess, and W. E. Pickett, Phys. Rev. B **74**, 195110 (2006).

16. Linear scaling calculation of static and dynamic polarizabilities in Hartree-Fock and density functional theory for periodic systems, A. F. Izmaylov, E. N. Brothers, and G. E. Scuseria, J. Chem. Phys. **125**, 224105 (2006).

17. Theoretical study of ZnO phases using a screened hybrid density functional, J. Uddin and G. E. Scuseria, Phys. Rev. B **74**, 245115 (2006).