Year-End Report

Accurate Electronic Structure Theory of Quantum Dots

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The support by the ISEN Booster Award has significantly advanced our group’s research, resulting in 4 publications in Journal of Chemical Physics and Journal of Chemical Theory and Computation. In addition, the support by ISEN has allowed us to obtain two federal grants: a regular grant from Department of Energy Basic Energy Sciences and the National Science Foundation CAREER Award (to be announced). I have presented 6 invited talks in international conferences, including the Sanibel Symposium, Telluride meetings, and the ACS 2013 Fall meeting. In the following, I will summarize our research achievements during the support by ISEN, and future directions.

Tensor Decomposition of Wave Functions


We have developed a wave function ansatz based on tensor decompositions, $\Psi = \sum_i c_i \prod_f \psi_{i_f}^f$, in order to apply rigorous wave function methods to nanoscale materials including quantum dots. We decided to test our hypothesis using a simple system, a molecular dimer, which iteself is interesting in solar energy conversion.

In the article that we published in J. Chem. Phys., we demonstrated that the active space wave functions of molecular dimers can be compactly represented by a linear combination of monomer wave functions as $\Psi = \sum_i c_i \psi_i^f \otimes \psi_i^f$. This expansion becomes exact when a large number of states are included in the summation. Figure 1 shows the numerical proof of potential exactness using a benzene dimer. Importantly we have found that the Hamiltonian matrix elements between product basis functions can be computed without forming dimer basis functions explicitly:

$$\langle \Phi_{A'} \Phi_{B'} | H | \Phi_{A} \Phi_{B} \rangle = \sum_{\xi} \left( \frac{(-1)^{\phi}}{2} \sum_{\eta} h_{A^A A^B} h_{\xi \eta} h_{B^A B^B} \right),$$

in which $\Gamma_{\xi}^{A'B'} = \langle \Phi_{A'} | \Phi_{B'} \rangle$. Interestingly, our wave function ansatz has a profound connection to low-entanglement wave function ansätze, such as the density matrix renormalization group (or matrix product state wave functions), which we will explore in the future.

Even though we have used a simple system to demonstrate the efficiency and accuracy of our

![Figure 1: Numerical demonstration of potential exactness of our wave function ansatz on the basis of tensor decomposition.](image1)

![Figure 2: Preliminary application of our theory to pentacene dimer. We are currently analyzing the results.](image2)
methods, the ansatz is general and is expected to be applicable to electronic structure of quantum dots with minor modifications. Furthermore, we are interested in applying our theory to singlet fission processes, which are related to carrier multiplication in organic photovoltaic. We are currently analyzing our preliminary numerical data for tetracene and pentacene dimers (Figure 2). The published paper has received immediate attention by the community, and was among the most downloaded communications from the Journal of Chemical Physics in 2013.

We are currently working to generalize this theory to incorporate multiple active regions (that is essential for applications to quantum dots), and to interface our theory to real-space renormalization to realize hierarchical simulations for electronic excited states of nano-scale materials and organic crystals. We have started to investigate the possibility of combining our wave function ansatz to the so-called contractor renormalization group approach (a Hamiltonian analogue of Wilson’s real-space renormalization). The research along this line will be supported by the Department of Energy Basic Energy Sciences funding.

**Relativistic Quantum Chemistry**


We have developed scalable theory and algorithms that account for strong spin–orbit and other relativistic effects in wave-function-based electronic structure simulations. Our approach is based on the four-component Dirac equation, which can account for very large relativistic couplings beyond the perturbative regime. The algorithm uses the so-called density fitting technique, which can be seen as an algorithm to compress the molecular Hamiltonian.

There are three major achievements: (1) By developing an algorithm to evaluate molecular integrals over $r_{12} \otimes r_{12}/r_{12}^2$, molecular electronic simulations with the so-called Breit interaction have been realized for the first time. The Breit interaction is an inter-electronic potential accurate to the order of $\frac{c^2}{\epsilon^2}$ ($c$ is the speed of light), and used to be considered too expensive to be included in molecular simulations. The article that reports this algorithm has been the most downloaded communication from the Journal of Chemical Physics in 2013. (2) We have demonstrated that, with the density fitting approximation to molecular integrals and parallelization of efficient programs, one can routinely perform electronic structure simulations of 100-atom systems or more on the basis of the rigorous Dirac equation. Prior to our research, the biggest systems that could be treated by Dirac approaches were at most 10–20 atoms. Therefore our new algorithm is a breakthrough in this field, extending the applicability of such simulations to molecules of synthetic interest containing heavy elements. (3) We have developed an efficient algorithm for computing analytical nuclear energy gradients, which are to be used as

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*Figure 3: Timing data for Dirac–Hartree–Fock calculations. One self-consistent iteration with the Dirac–Coulomb Hamiltonian took only about 20 minutes using 1024 CPU cores.*
gradients in geometry optimizations and as nuclear forces in on-the-fly dynamics. The properties of electronic excited states of quantum dots are strongly coupled to phonons, and it is important to be able to compute vibronic coupling and perform simulate non-adiabatic on-the-fly dynamics. Our theory helps to realize such simulations.

The theory and algorithms that we have developed are also applicable to magnetic properties of heavy-element complexes. The future research on predictive theory of magnetic molecules, which has been initiated by this research, will be funded by the National Science Foundation CAREER Award (to be announced).