DOE-COLUMBIA-SC0006613

MANY BODY METHODS FROM CHEMISTRY TO PHYSICS: NOVEL COMPUTATIONAL TECHNIQUES FOR MATERIALS-SPECIFIC MODELLING: A COMPUTATIONAL MATERIALS SCIENCE AND CHEMISTRY NETWORK

FINAL TECHNICAL REPORT

Period Covered: 08/01/2011 TO 07/31/2015

November, 2016

Andrew Millis
Professor of Physics
Columbia University

PREPARED FOR THE US DEPARTMENT OF ENERGY
BASIC ENERGY SCIENCES DIVISION
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Summary

Understanding the behavior of interacting electrons in molecules and solids so that one can predict new superconductors, catalysts, light harvesters, energy and battery materials and optimize existing ones is the ``quantum many-body problem''. This is one of the scientific grand challenges of the 21st century. A complete solution to the problem has been proven to be exponentially hard, meaning that straightforward numerical approaches fail. New insights and new methods are needed to provide accurate yet feasible approximate solutions. This CMSCN project brought together chemists and physicists to combine insights from the two disciplines to develop innovative new approaches. Outcomes included the Density Matrix Embedding method, a new, computationally inexpensive and extremely accurate approach that may enable first principles treatment of superconducting and magnetic properties of strongly correlated materials, new techniques for existing methods including an Adaptively Truncated Hilbert Space approach that will vastly expand the capabilities of the dynamical mean field method, a self-energy embedding theory and a new memory-function based approach to the calculations of the behavior of driven systems. The methods developed under this project are now being applied to improve our understanding of superconductivity, to calculate novel topological properties of materials and to characterize and improve the properties of nanoscale devices.

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Project Goals: the quantum many-body problem of calculating the properties of electrons in atoms, molecules and solids is a grand challenge of contemporary physics. A general solution is believed to by NP-hard [see, e.g. Troyer and Weise, Computational Complexity and Fundamental Limitations to Fermionic Quantum Monte Carlo Simulations, Phys. Rev. Lett. 94, 170201, 2005] and it is important to develop accurate, computationally tractable, approximate solutions. Chemists and physicists approach this problem from different points of view, with chemists typically focusing on small systems (atoms and molecules) and aiming for a high degree of realism, while physicists emphasizing collective properties of large systems and obtaining qualitative information. By bringing chemists and physicists together the project aimed to stimulate the development of new methods leading to new algorithms, enabling the extension of chemistry-based techniques to larger scale problems and collective phenomena and increasing the precision and atomic specificity of physics approaches. The more specific connection arises by way of quantum embedding theories. These theories (of which dynamical mean field theory [Kotliar and Georges, Rev Mod Phys,] is the best-known example) approximate the solution of a full lattice quantum many-body problem in terms of the solution of a quantum impurity model—a finite number of interacting sites connected to a noninteracting bath. As the size of the impurity model increases, the accuracy of the approximation improves, so that methods for more efficiently solving impurity models are desirable.

Project activities: The goal of the project was to bring insights from computational chemistry to condensed matter physics problems and conversely. The project created an intense interaction between the groups of *Garnet Chan* (Chemistry, first Cornell, then Princeton and now CalTech), *Chris Marianetti* (Materials Science, Columbia), *Andrew Millis* (Physics, Columbia) and *David Reichman* (Chemistry, Columbia). Frequent meetings led to projects that succeeded on four levels in creating new methodologies that link chemistry and physics approaches to important aspects of quantum many-body phenomena and provided the seeds from which important methodologies and collaborations have grown. In each case the methods,invented with CMSCN support, have been handed off to the community and are now being used in other contexts.

Density matrix embedding theory [1,2]. This is a new quantum embedding theory. Abbreviated as DMET, it is analogous to dynamical mean field theory but orders of magnitude more tractable computationally because (in first instance) it targets only the ground state, rather than the entire dynamics. As a result, much larger impurity impurity models can be solved. By bringing physics insights and

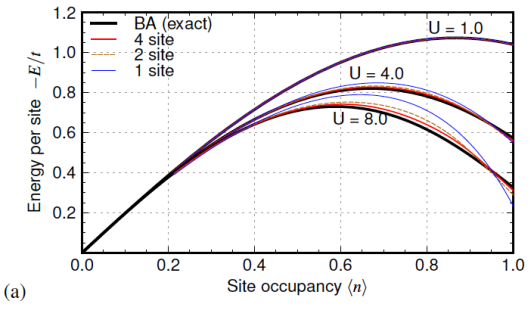

Fig. 1: Energy obtained from 1,2,4 site density matrix embedding theory and Bethe ansatz (BA), from Ref. [1]

benchmark results to the quantum chemistry group of Chan the CMSCN provided crucial impetus and benchmark results for the method, which is now competitive with the best state of the art methods for many-body energetics even for challenging cases such as the doped Hubbard model (see e.g Figs. 6 and 7 of Phys. Rev. X5 041041,(2015)).

Adaptive Solvers for Dynamical Mean Field Theory [3,4]. Dynamical mean field theory is an approximation to the many-electron problem that can be combined with first-principles band structure to produce chemically realistic theories of materials with strong electronic correlations, and has become the go-to method for treating the properties of these systems. However, it requires the complete solution (full dynamics) of a quantum impurity model and this has proven difficult in many cases. In particular continuous-time quantum Monte Carlo methods [Rev. Mod. Phys. 83 349 (2011)], while widely used to solve these models, suffer from a severe sign problem in many relevant cases, prompting investigation of alternative methods.

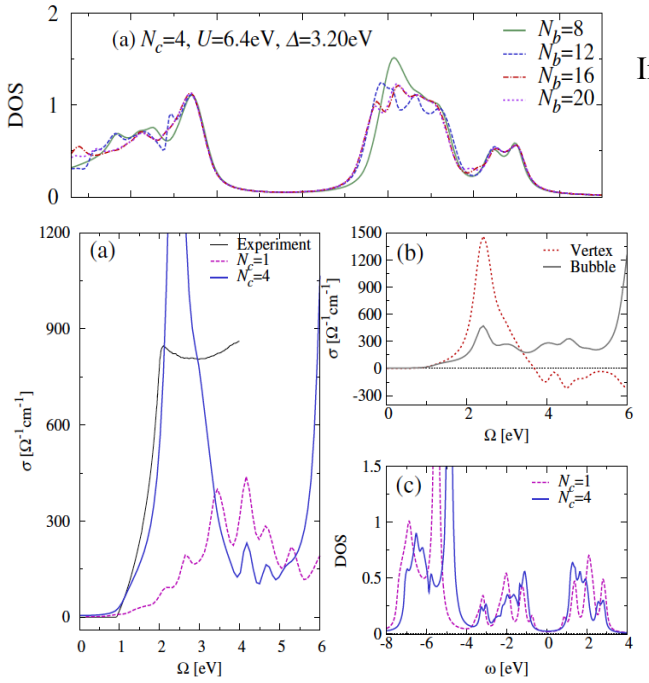

Fig. 2: Upper panel: convergence of many-body density of states with respect to number of bath orbitals. Lower panels: combination of cluster dynamical mean field theory, vertex corrections and oxygen orbitals needed to account for optical absorption in high-Tc cuprates

One widely used method is the `exact diagonalization' approach of Caffarel and Krauth, in which one discretizes the non-interacting bath and then just solves the finite problem exactly. This approach has been limited by the exponential growth of complexity with number of bath orbitals retained. The CMSCN coupled Ara Go (CMSCN-supported postdoc in the Millis group) with the quantum chemical expertise of Chan (and postdoc Zgid) to enable the development of impurity solvers based on a combination of quantum chemical active space methods and adaptively truncated Hilbert spaces. In contrast to the usual chemistry applications, the need for accurate Green functions means that the excited st ate space cannot simply be built on the excitations from the optimized ground state, but needs to be independently and systematically developed. In effect, this method takes advantage of the unusual sparsity structure of impurity models (interactions only on a small subset of the orbitals) to enable solutions with many more bath orbitals per correlated orbital. Results include new insights into the importance of oxygen orbitals in high-Tc

cuprates (see Fig. 3) and into pyrochlore irridates.

Density functional plus dynamical mean field theory. As noted above the dynamical mean field method is a work-horse of condensed matter physics, but many aspects of the method have not been validated. CMSCN-supported interactions between the physics and materials science groups of Millis and Marianetti (CMSCN postdoc Jia Chen) and the quantum chemistry groups of Chan and Reichman identified the spin-crossover molecule $Fe(phen)_2(NCS)_2$ as a suitable comparison system. Our calculations applied condensed matter physics methods to a single molecule and showed quantitatively that relative to other condensed matter physics methods the dynamical mean field method provide a substantially improved account of the energetics of the low spin state (in particular treating correctly the correlated hybridization problem associated with the multireference nature of the low spin state), but do not approach chemical accuracy. The sensitivity of the results to the key issues of the double-counting correction and the interaction parameters were determined and a problem with the spin-dependent density functional plus U approach was uncovered. These results shed new light on the density functional plus dynamical mean field method as applied to real materials.

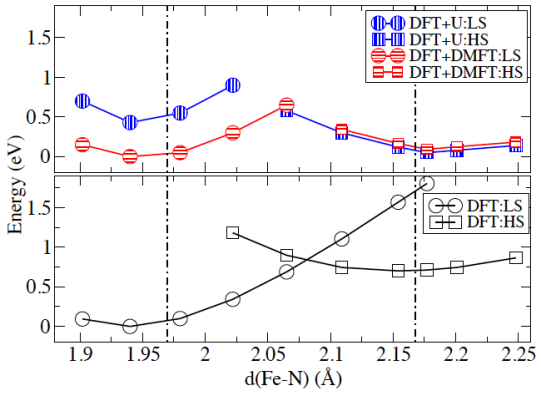

Fig. 3 Energy as a function of metal-ligand bond length for $Fe(phen)_2(NCS)_2$ computed by different condensed matter physics methods. From Ref. 5

Nonequilibrium dynamics of interacting electron systems. One of the most important current questions in interacting electron physics is the nonlinear response to strong applied fields that drive materials far from equilibrium. Nonequilbrium dynamical mean field theory is a promising approach to this problem but numerically exact approaches have been limited to very short times. Insights from chemistry regarding the use of memory function (reduced dynamics, RD) techniques were used by our CMSCN (Millis, Reichman, postdoc Cohen) team to develop algorithms that access much longer times [6]. The essential idea is that the relaxation kernels involve short time physics and may be computed, and then used to obtain the behavior at longer times. Figure 5 shows the time decay of the magnetization after an initial quench;

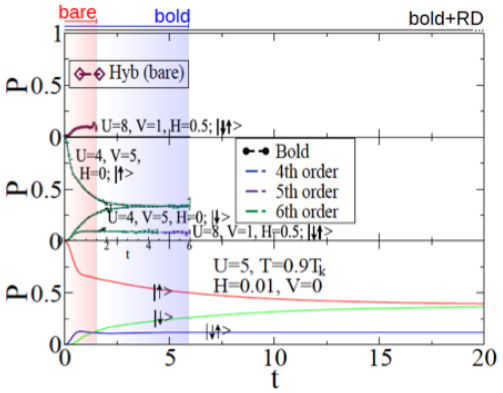

Fig. 4: Occupation probability P of high spin state of quantum dot computed by bare perturbation theory (top), bold-resummed perturbation theory (middle) and reduced dynamics (bottom)

reading from top to bottom one sees the dramatic increase in time accessible from the reduced dynamics methods brought by our chemistry colleagues.

CMSCN Impact: in addition to the development of the new techniques listed above, which have moved beyond the CMSCN and are impacting the area of quantum and energy materials more broadly, it is important to note that collaborations formed through the CMSCN are now producing important results. In particular D. Zgid (chemist, postdoc with CMSCN PI Chan and then with CMSCN PI Millis) has formed a collaboration with E. Gull (former Millis postdoc, author on a CMCSN paper) have combined chemistry and physics insights to develop a very promising ``self energy embedding theory'' which is a related combination of physics and chemistry methods that seems very promising [D. Zgid and E. Gull, Finite temperature quantum embedding theories for correlated systems, arXiv:1611.00395].

Products resulting from the collaboration

[1] "Density matrix embedding: A simple alternative to dynamical mean-field theory" Gerald Knizia and Garnet Kin-Lic Chan, Phys. Rev. Lett. 109, 186404 (2012).

[2] ``Density Matrix embedding: A strong-coupling quantum embedding theory", G. Knizia and G. K. L. Chan, Journal of Chemical Theory and Computation, 9, 1428 (2013)

[3] "Dynamical mean field theory from a quantum chemical perspective", D. Zgid and G Chan, the Journal of Chemical Physics 134, 094115 (2011).

[4] ``Spatial correlations and the insulating phase of the high-Tc cuprates: insights from a configuration interaction based solver for dynamical mean field theory", Ara Go and Andrew J. Millis, Phys. Rev. Lett. 114, 016402 (2015).

[5] ``Density functional plus dynamical mean-field theory of the spin-crossover molecule $Fe(phen)_2(NCS)_2$", Jia Chen, C. Marianetti and A. J. Millis, Phys. Rev. B91 241111 (2015).

[6] Numerically Exact Long Time Magnetization Dynamics Near the Nonequilibrium Kondo Regime, Cohen, Guy; Gull, Emanuel; Reichman, David; Millis, Andrew; Rabani, Eran *American Physical Society, APS March Meeting 2013, abstract #R43.001*