Our ARO-supported work includes key contributions to the development of rigorous quantum embedding methods for the calculation of ground- and excited-state potential energy surfaces. Quantum embedding has long been recognized as a promising strategy for vastly reducing the cost of rigorous electronic structure theory calculations. However, prior to our work in this area, density functional and wavefunction embedding approaches were only applicable to weakly interacting systems, a severe constraint that excluded essentially all condensed-phase and reactive chemical applications. By developing both inversion-based and projection-based strategies to enable

ABSTRACT

Our ARO-supported work includes key contributions to the development of rigorous quantum embedding methods for the calculation of ground- and excited-state potential energy surfaces. Quantum embedding has long been recognized as a promising strategy for vastly reducing the cost of rigorous electronic structure theory calculations. However, prior to our work in this area, density functional and wavefunction embedding approaches were only applicable to weakly interacting systems, a severe constraint that excluded essentially all condensed-phase and reactive chemical applications. By developing both inversion-based and projection-based strategies to enable accurate embedding in the context of strongly interacting (i.e., covalently or hydrogen-bonded) systems, we have expanded the applicability of quantum embedding methodologies, an area of intense interest. In addition to developing new algorithms and software, we have demonstrated that our approach enables simulation of large systems with sub-linear scaling of the required computational time; and we have further demonstrated that it dramatically reduces the cost of accurately describing transition-metal complexes and large molecules and clusters. This work opens new doors for the accurate description of decomposition, catalytic, and electronically non-adiabatic processes in complex systems. This research meets the aims of the Army Research Office by significantly advancing the scope and accuracy of first-principles molecular simulations in complex, reactive systems.
Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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(b) Papers published in non-peer-reviewed journals (N/A for none)

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Scott Habershon, David Manolopoulos, Thomas Markland, Thomas Miller. Ring polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space, Annual Review of Physical Chemistry, (05 2013): 0. doi:

TOTAL: 1
Number of Papers published in non peer-reviewed journals:

(c) Presentations
4. Chemistry Departmental Seminar. Purdue University, Indianapolis, IN. 15 October 2014.
14. 26th Canadian Symposium on Theoretical and Computational Chemistry. Sir George Williams Campus, Concordia University Montreal, Quebec, Canada. 6-11 July 2014.
22. CECAM Workshop on Quantum Dynamics in Molecular and Nano-Materials: Mechanisms and Functionality. Tel Aviv, Israel. 28 November - 1 December 2013.
30. CECAM Workshop on Quantum Dynamics with (Non)Classical Trajectories. Lausanne, Switzerland. 17-20 June 2013.
32. EMBO Conference on From structure to function of translocation machines. Dubrovnik, Croatia. 13-17 April 2013.
35. Workshop on Membrane Biophysics. Telluride Science Research Center, Telluride, CO. 4-8 March 2013.
Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

09/03/2012  5.00 Jason Goodpaster, Taylor Barnes, Nandini Ananth, Thomas Miller. EXACTLY EMBEDDED DENSITY FUNCTIONAL THEORY METHODS FOR THE FIRST-PRINCIPLES MODELING OF REACTIONS IN COMPLEX SYSTEMS, Proceedings of the 27th Army Science Conference. 29-NOV-10, ,

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Received Paper

TOTAL: 

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Patents Submitted

Patents Awarded

Awards

Camille Dreyfus Teacher-Scholar Award (2013)
Associated Students of Caltech (ASCIT) Teaching Award (2012)
National Science Foundation CAREER Award (2011)
American Chemical Society Hewlett-Packard Outstanding Junior Faculty Award (2011)
China Lake Distinguished Speaker, Naval Air Weapons Station, China Lake, CA (2011)
Alfred P. Sloan Research Fellowship (2010)
Editor’s Choice Selection from the Journal of Chemical Physics (2010)

Graduate Students

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**Student Metrics**

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- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: ...... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ...... 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: ...... 0.00
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Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

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Indeed, our recent WFT-in-DFT implementation in the Molpro program has been shared with and is currently being tested and utilized by a range of theoretical chemistry groups, including those of:

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- Prof. Fred Manby (U. Bristol) and Kaito Miyamoto (U. Bristol / Toyota Co.)
Awards Number: W911NF1110256

Principal Investigator (PI): Thomas F. Miller III
Institution: California Institute of Technology
Title of Research: Exactly embedded density functional theory: A new paradigm for the first-principles modeling of reactions in complex systems

OVERVIEW

Research from the past funding period has focused on the development of ab initio electronic structure to enable the simulation of reaction dynamics in general, condensed-phase systems. The embedded density functional theory (e-DFT) method has been combined with recent theoretical advances, including an exact treatment of the non-additive kinetic energy and a molecular embedding strategy that achieves sub-linear scaling on large-scale parallel computers. The primary objectives of the proposed research are (i) to fully benchmark and refine the new e-DFT approach and (ii) to demonstrate that it provides systematically improvable accuracy for large molecules and condensed-phase systems. Accomplishment of these research objectives meets the aims of the Army Research Office by significantly advancing the scope and accuracy of first-principles molecular simulations in complex, reactive systems.

In recent years, a central achievement of my research program has been to develop simulation methods that reveal, with new depth, the mechanistic details of quantum mechanical processes that are central to chemical reactions. The nature of this achievement is three-fold: firstly, we have worked from the foundation of rigorous quantum statistical mechanics and semiclassical dynamics to develop path-integral methods that significantly expand the scope and reliability of condensed-phase quantum dynamics simulations [1–9]. Secondly, we have overcome fundamental limitations in quantum embedding theories to dramatically improve the description of molecular interactions in systems with subtle electronic properties [10–17]. And finally, we have established a leadership role in the application of such methods to the elucidation of genuinely complex systems, including enzyme reactions and inorganic electron-transfer and proton-coupled electron transfer processes.

With ARO support in the last funding period, the Miller group has made key contributions to rigorous multi-level partitioning methodologies for the calculation of potential energy surface calculations. Multi-level partitioning, or quantum embedding, has long been recognized as a promising strategy for vastly reducing the cost of rigorous electronic structure theory calculations [18–29]. However, prior to our work in this area, accurate density functional and wavefunction embedding approaches were limited to weakly interacting systems, a severe constraint that excluded essentially all condensed-phase and reactive chemical applications. By developing both inversion-based [10–12] and projection-based [13–17] strategies to enable accurate embedding in the context of strongly interacting (i.e., covalently or hydrogen-bonded) systems, we have expanded the applicability of quantum embedding methodologies (Fig. 1A), an area of intense interest. In addition to developing new algorithms and software, we have demonstrated that our approach enables simulation of large systems with sub-linear scaling of the required computational time (Fig. 1C); and we have further demonstrated that it dramatically reduces the cost of accurately describing transition-metal complexes [12, 17] (Fig. 1B) and large molecules, clusters, and liquids [11, 13–16]. This
work opens new doors for the accurate description of decomposition, catalytic, and electronically non-adiabatic processes in complex systems.

Publications from our previous period of ARO funding include:


Expanded Discussion: Embedding methods to bridge length scales in electronic structure.

The use of computational modeling to investigate complex chemical systems faces extraordinary challenges from the perspective of electronic structure theory. Target applications combine large system sizes with subtle interactions, and in many cases, multiple dynamical timescales and electronically nonadiabatic effects. The development of new methods to perform reliable, on-the-fly electronic structure calculations at a computational cost that makes feasible the simulation of chemical reactions in large systems remains a central theoretical challenge.

At its heart, the electronic structure problem requires a compromise between accuracy and feasibility that is dictated by system size. Kohn-Sham density functional theory (KS-DFT) – the workhorse method for condensed-phase systems [32, 33] – is well known to have fundamental deficiencies associated with currently available exchange-correlation (XC) functionals [34, 35]; these deficiencies include both self-interaction errors and failure to describe systems exhibiting significant static correlation. Resulting artifacts include incorrect spin-state predictions for transition metal complexes, charge-transfer errors, and underestimation of hydrogen-transfer barriers [36–38]. Wavefunction theories, such as CCSD(T) and CASPT2, address these problems but are too costly to use for most applications in large systems.

Methods that exploit the intrinsic locality of molecular interactions show significant promise in making tractable the electronic structure calculation of large-scale systems. In particular, embedded density functional theory (e-DFT) offers a formally exact approach to electronic structure calculations in which complex condensed-phase chemical problems are decomposed into the self-consistent solution of individual smaller subsystems [39–46]. The objectives of the e-DFT approach are thus similar to those of more approximate partitioning and fragmentation schemes [47–52], including the QM/MM and ONIOM methods, but e-DFT avoids the uncontrolled approximations (such as link atoms) and errors associated with subsystem interfaces that fundamentally limit these other widely used methods.

However, in practice, previous e-DFT studies have employed substantial approximations in the description of subsystem interactions [42, 53, 54]. The subsystem embedding potentials that emerge in the e-DFT framework include non-additive kinetic potential (NAKP) terms that enforce Pauli exclusion among the electrons of the various subsystems. Without knowledge of the exact functional for the non-interacting kinetic energy, previous e-DFT studies have employed approximate NAKP treatments that break down in cases for which the subsystem densities significantly overlap (which include hydrogen-bonded or covalently bonded subsystems). Prior to our work in this area, e-DFT studies were thus limited to weakly interacting subsystems, a severe constraint that excluded essentially all condensed-phase and reactive chemical applications.

To overcome this constraint, my group has focused on the development of numerically exact methods for obtaining subsystem embedding potentials in e-DFT. We have made key contributions that include (i) the development of optimized-effective-potential-based (OEP-based) methods for the exact evaluation of NAKP contributions to the embedding potential, (ii) the combination of exact embedding potentials with correlated wavefunction theory (WFT) methods to enable seamless WFT-in-DFT embedding for general systems, (iii) the development of a simple, robust method to perform numerically exact e-DFT calculations without any need for OEP operations. By enabling accurate quantum embedding in the context of strongly interacting (i.e., covalently or hydrogen-bonded) systems, we have expanded the applicability of quantum embedding methodologies. In addition to developing key algorithms and software, we have demonstrated that the e-DFT approach enables simulation of large systems with sub-linear scaling of the required computational time; and we have further demonstrated that it dramatically reduces the cost of accurately describing transition-metal complexes [12, 17], large molecules and clusters [14, 15], and liquid mixtures.
that include lithium-ion battery electrolytes [16]. This work provides new tools for the accurate description of catalytic and electronically non-adiabatic processes in complex systems, and it opens the door for widespread adoption of rigorous quantum embedding approaches in computational chemistry.

The remainder of this section describes key aspects of our work in this area. In this developing field, my research group has in particular, we have contributed to the development and application of OEP-based methods for the scalable and accurate treatment of complex systems [10–12]. Moreover, we have recently introduced a new method for the exact treatment of the e-DFT embedding potential that completely mitigates any need for OEP calculations (see Section 2.b) [13]; this approach, which has become one of the most heavily downloaded articles from the Journal of Chemical Theory and Computation (JCTC) for years 2012, 2013, and 2014, provides the needed simplicity and robustness to enable broad utilization by the computational chemistry user community in the near term.

2.a. OEP-based methods for exact embedding.

In our initial contributions to the methodology of e-DFT, we developed accurate and scalable OEP-based treatments for the NAKP in e-DFT. In particular, we introduced a numerically exact protocol for computing the NAKP contributions to the subsystem embedding potentials; we demonstrated the effectiveness of this protocol for systems with both weakly and strongly overlapping subsystem densities [10, 11]; we combined the exact embedding potentials with WFT methods to enable seamless WFT-in-DFT embedding [12]; and we demonstrated the advantageous parallel scaling of the e-DFT approach [11].

2.a.1. DFT-in-DFT embedding: Our original e-DFT protocol [10] utilizes OEP techniques, such as those of Zhao, Morrison, and Parr [58] or Wu and Yang [59], which involve a search for the local potential that yields one-electron orbitals that both reproduce a target electronic density and minimize the orbital-dependent total energy functional. During each iterative update of the subsystem densities and embedding potentials, the OEP calculation is combined with an orbital-dependent expression for the NAKP, and at self-consistency, the iterative procedure yields a total electronic density and a total energy that are identical to those obtained from a KD-DFT calculation performed over the full system. Because the e-DFT calculation yields the same results as the full KS-DFT calculation (for a given orbital basis set and approximate XC functional), no new errors are introduced through the embedded subsystem description; it is in this sense that we achieve a numerically exact DFT-in-DFT embedding protocol.

Fig. 1A provides a demonstration of our general e-DFT implementation in the Molpro quantum chemistry package. The figure illustrates the well-known breakdown of approximate treatments of the NAKP for applications involving strongly overlapping subsystem densities. It further shows that our exact treatment of the NAKP overcomes this large error, yielding the first numerical demonstration of DFT-in-DFT embedding for chemical bond-breaking with chemical accuracy [11]. In addition to the Li⁺-Be curve shown in the figure, dissociation curves for the CH₃-CF₃ molecule, transition-metal complexes, and hydrogen-bonded water clusters have been reported [11, 12], demonstrating in all cases that the exact e-DFT protocol preserves excellent agreement with reference KS-DFT calculations, whereas approximate treatments of the NAKP lead to qualitative failures in the calculated energies and equilibrium structures. Further examples have been reported in which the subsystem densities correspond to valence and core electronic shells in atomic systems [10], again illustrating the expected breakdown due to standard NAKP approximations, with errors of 30-80% in the calculated ionization energies; by contrast, the exact protocol is found to be accurate and stable.
FIG. 1: (A) The Li⁺-Be potential energy curve for heterolytic bond cleavage, obtained using our exact OEP-based description for DFT embedding (red) and using approximate (Thomas-Fermi, LC94) descriptions for the embedding potential (blue, green). Results from the reference Kohn-Sham DFT method are also included (black) and are graphically indistinguishable from our e-DFT results. We have demonstrated similar successes for water cluster dissociation, C-C bond cleavage, and transition metal complexes [11]. The inset presents the potential energy curves, shifted vertically and horizontally to align the minimum. (B) WFT-in-DFT embedding results for the [Fe(H₂O)₆]²⁺ cation [12]. Above, the density partitioning is illustrated, for which only the density associated with the transition metal atom (red) is treated at the CCSD(T) level while the density for the surrounding waters (blue) is treated at the DFT level. Below, the low-spin/high-spin energy splitting of the complex (in cm⁻¹) is calculated using standard KS-DFT with various XC functionals (red) and with CCSD(T)-in-DFT embedding with only the transition metal atom treated at the CCSD(T) level (green). The quantum embedding treatment provides results that are far less sensitive to the choice of approximate DFT XC functional and that are generally improved in comparison to the reference CCSD(T) calculation for the full system (black). (C) Wall-clock timings for lattices of hydrogen molecules, ranging in size from 16 to 250 atoms. The black lines indicate ideal quadratic and linear scaling; the blue curve shows the serial implementation of Kohn-Sham DFT in Molpro; the red curve shows the timings for DFT embedding, using a number of processors equal to the number of molecules in the system [11].

2.a.2. WFT-in-DFT embedding: Fig. 1B illustrates the most important practical feature of the e-DFT approach [12]: It provides a versatile, yet rigorous, framework to describe different regions of the system at different levels of electronic structure theory [42–44, 57, 60–65]. In this example calculation for the low-spin/high-spin splitting energy of the hexaaquoiron(II) cation, a subsystem comprised of the Fe atom is treated at the CCSD(T) level of theory, whereas another subsystem comprised of the water ligands is treated using KS-DFT; the e-DFT framework simply is used to determine the external potential that is created for each subsystem by the other. Since the CCSD(T) level of theory is applied only to a single atom, the computational cost for the WFT-in-DFT embedding calculation is reduced by a factor of 50 relative to a CCSD(T) calculation over the full system.

The calculations in Fig. 1B were made possible by new techniques that improve the accuracy and stability of WFT-in-DFT embedding calculations [12]. In particular, we derived spin-dependent embedding potentials in both restricted and unrestricted orbital formulations and provided the first implementation of WFT-in-DFT embedding for open-shell systems, and we developed an orbital-occupation-freezing technique to improve the convergence of the OEP operations. The top panel in Fig. 1B illustrates the density partitioning among the two subsystems. Below, the low-spin/high-spin energy splitting of the complex (in cm⁻¹) is calculated using standard KS-DFT with various XC functionals (red) and with CCSD(T)-in-DFT embedding with only the transition metal atom treated at the CCSD(T) level (green). The quantum embedding treatment provides
results that are far less sensitive to the choice of approximate DFT XC functional and that are generally improved in comparison to the reference CCSD(T) calculation for the full system (black). Additional studies of the dissociation curve for the ethylene-propylene dimer [12] reveals that WFT-in-DFT embedding reproduces full CCSD(T) energies to within 0.1 kcal/mol at all distances, thus mitigating errors in the dispersion interactions due to conventional XC functionals while simultaneously avoiding errors due to subsystem partitioning across covalent bonds [12].

These calculations illustrate that WFT-in-DFT embedding, when employed in combination with exact methods for treating the NAKP contributions to the embedding potential, offers significant opportunities for the multi-level (or multi-physics) description of complex systems. WFT-in-DFT embedding achieves the objectives of the QM/MM and ONIOM schemes for interfacing different levels of electronic structure theory; however, in comparison to these widely used methods, WFT-in-DFT embedding exhibits clear advantages that include (i) a more rigorous and systematically improvable approach to multi-level electronic structure calculations and (ii) a more computationally efficient multi-level description, since the rigorous description of the subsystem interfaces allows much smaller WFT subsystems to be employed.

2.a.3. Parallelizability and scaling. Another important feature of the e-DFT approach is that it leads to highly parallel electronic structure methods [11, 54]. For our Molpro implementation of the exact e-DFT protocol, Fig. 1C demonstrates that ideal, constant scaling of the wall-clock computation time with increasing system size can be achieved [11]. Intrinsic linear-scaling complexity arises from the loose coupling among the individual subsystem calculations, and additional parallelization is achieved by treating each subsystem on a different distributed-memory computer processor. The accuracy of the calculated energies and electronic densities do not degrade with increasing system size.

2.b. A simple, exact e-DFT method that avoids OEP calculations.

Earlier this year, we made a significant breakthrough in the efficiency and robustness of e-DFT calculations [13]. An exact scheme was developed that correctly accounts for NAKP contributions via a projection technique, while completely avoiding any numerically demanding OEP calculations. This work introduces three simple innovations: (i) We replaced the iterated DFT-in-DFT with a single conventional KS calculation. (ii) We completely avoided the issue of the NAKP through the use of a level-shifting projection operator to keep the orbitals of one subsystem orthogonal to those of another (Fig. 2). And, (iii) we developed a simple but effective perturbation theory to eliminate practically all dependence on the level-shift parameter.

Numerical tests of the new e-DFT method for a range of molecular systems, including those with conjugated and multiply-bonded subsystems, were shown to consistently yield DFT-in-DFT embedding with errors below $10^{-6}$ kcal/mol; these results mark a dramatic improvement over the system-dependent $0.1 - 1$ kcal/mol errors that can be expected using existing OEP-based approaches. Additionally, we demonstrated that the method allows for accurate and robust WFT-in-DFT embedding calculations and embedded many-body expansions [13]. Moreover, in extremely encouraging preliminary results that we have obtained for (CAS-PT2)-in-DFT embedding for cobalt-based hydrogen reduction catalysts [17], the embedding calculations recover the full accuracy of the full CAS-PT2 method for proton-transfer barriers and driving forces while reducing the cost of the full calculation by over a factor of 700.

The new projection-based embedding approach only relies on existing, stable, well-developed software technologies [13]. It requires nothing more than a KS code, an orbital localization scheme, some elementary matrix operations in the atomic orbital basis, and any wave function method that can accept an arbitrary core Hamiltonian. Since these ingredients are available in
practically all molecular electronic structure codes, we anticipate no barriers to widespread adoption of the approach.

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- Dr. Betsy Rice (ARO)
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FIG. 2: Demonstration of the projection technique that is employed in the new exact embedding scheme, using the example of embedding the 10 electrons of the -OH moiety of ethanol in the environment produced by the ethyl subsystem. Following projection, the subsystem orbitals are explicitly orthogonalized, thus eliminating non-additive kinetic energy contributions [12].


[57] C. Huang, M. Pavone, and E. A. Carter, Quantum mechanical embedding theory based on a unique embedding


