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Exactly Embedded Wavefunction Methods for Characterizing Nitrogen

THOMAS MILLER
CALIFORNIA INSTITUTE OF TECHNOLOGY

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Air Force Research Laboratory
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Thomas Francis Miller III

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14. ABSTRACT

The final year of research activity witnessed successful completion of the proposed research goals of developing and applying exactly embedded density functional and wavefunction theory methods for the investigation of small-molecular activation catalysis, such as hydrogen and nitrogen reduction. In a significant methodological advance from the past year, we developed an accurate and systematically improvable framework for embedding a correlated wavefunction description of a subsystem in a density functional theory description of the surrounding molecular environment (J. Chem. Phys., 140, 18A507 (2014).). Finally, we applied these newly developed embedding methods to the task of designing new transition-metal catalysts for small-molecule activation. A central challenge in the development of inorganic hydrogen-evolution catalysts is to avoid deleterious coupling of the energetics of metal-site reduction from the kinetics of metal-hydride formation. In work that we are currently preparing for publication, we combined theoretical and experimental methods to investigate a new class of cobalt diimine-dioxime catalysts that shows promise for achieving this aim by introducing an intramolecular proton-shuttle via a pyridyl pendant group.

15. SUBJECT TERMS
density functional theory, quantum embedding, nitrogen reduction, hydrogen evolution

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Applicant/Institution:	California Institute of Technology
Street Address/City/State/Zip:	1200 E. California Boulevard, Pasadena, CA 91125
Principal Investigator (PI):	Thomas F. Miller III
Position Title of PI:	Professor of Chemistry
Mailing Address of PI:	California Institute of Technology 1200 E. California Boulevard, MC 127-72 Pasadena, CA 91125
Telephone Number of PI:	626-395-6588
Email of PI:	tfm@caltech.edu

With AFOSR support in the last funding period (Grant Number: FA9550-11-1-0288), the Miller group developed new electronic structure embedding methods for the investigation of small-molecular activation catalysis, such as hydrogen and nitrogen reduction. In particular, we made a major advances by developing a robust, rigorous, and accurate density functional theory embedding method [1–5]. As is illustrated in Fig. 1, the method enables rigorous quantum embedding calculations in which a small part of a large molecular system is treated using an accurate (and computationally expensive) wavefunction theory (WFT) methods, such as CCSD(T), while the remainder of the system is treated using density functional theory (DFT). This method opens a wide range of application domains that are relevant to the catalysis of small-molecule activation, since the WFT-in-DFT embedding approach enables reactions involving transition-metal complexes to be described using high-accuracy methods, but at only a small fraction of the computational cost. Using these new methods, we have worked in collaboration with experimentalist Jonas Peters (Caltech) to develop a new class of cobalt-based hydrogen evolution catalysts that successfully break the long-standing (and undesirable) correlation between the required overpotential and observed catalytic rate in this important class of earth-abundant catalysts [5].

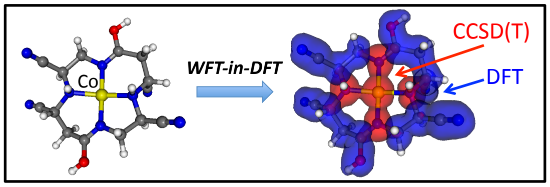

FIG. 1: (Left) The WFT-in-DFT embedding approach is illustrated for cobalt-based hydrogen evolution catalyst is illustrated. Electronic density associated with the region containing the transition metal center is treated at the level of wavefunction theory (CCSD(T), MRCI, CASPT2, etc.), while the remainder of the system is treated at the DFT level. This approach allows high accuracy to be employ in the physical regions that require it, allow for vastly reduced computational cost and systematically improvable accuracy.

Work performed during this function period (Grant Number: FA9550-11-1-0288) has led to the publication of six papers in high-quality journals, including two in preparation:

- "A simple, exact density-functional-theory embedding scheme," F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller III, J. Chem. Theory Comput., 8, 2564 (2012).
- "Density functional theory embedding for correlated wavefunctions: Improved methods for open-shell systems and transition metal complexes," J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, J. Chem. Phys., 137, 224113 (2012).
- "Accurate basis set truncation for wavefunction embedding," T. A. Barnes, J. D. Goodpaster, F. R. Manby, and T. F. Miller III, J. Chem. Phys., 139, 024103 (2013).
- "Accurate and systematically improvable density functional theory embedding for correlated wavefunctions," J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, J. Chem. Phys., 140, 18A507 (2014).
- "Breaking the correlation between energy costs and kinetic barriers in hydrogen evolution: A new class of cobalt (pyridine-diimine-dioxime) catalysts," P. Huo, C. Uyeda, J. D. Goodpaster, J. C. Peters, T. F. Miller III, to be submitted.
- "Projection-based wavefunction-in-DFT embedding," J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, to be submitted. Invited Review Article for *Annu. Rev. Phys. Chem.*

In the following, we describe key aspects of the work from the previous funding period in greater detail.

A. Detailed Discussion

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 [6–10]. The objectives of the e-DFT approach are thus similar to those of more approximate partitioning and fragmentation schemes, but e-DFT avoids the uncontrolled approximations (such as link atoms) and errors associated with subsystem interfaces that fundamentally limit other widely used methods.

However, in practice, previous e-DFT studies have employed substantial approximations in the description of subsystem interactions [9, 11, 12]. 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.

Projection-based embedding. In the past AFOSR funding period, we made significant breakthroughs in the efficiency and robustness of e-DFT calculations [1, 3, 4]. An exact scheme was developed that correctly accounts for NAKP contributions via a projection technique, while completely avoiding any numerically demanding OEP calculations [1]. This projection-based embedding method 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. This approach provides the needed simplicity and robustness to enable broad utilization by the computational chemistry user community in the near term, as is described in the next subsection.

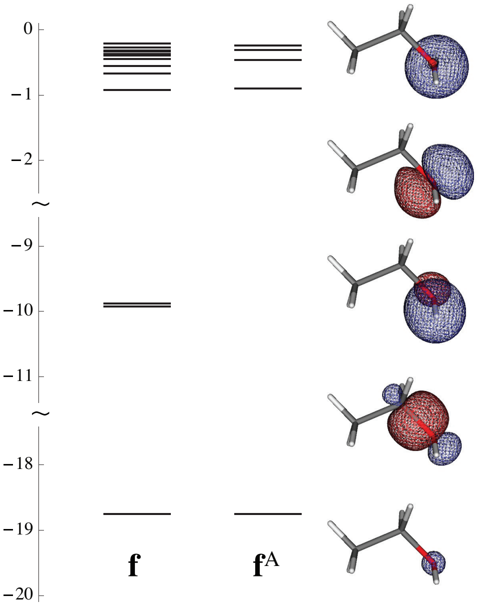

FIG. 2: Demonstration of the projection technique that is employed in the new exact embedding scheme, using the example of embedding the 10 electrons of the -OH moiety of ethanol in the environment produced by the ethyl subsystem. Following projection, the subsystem orbitals are explicitly orthogonalized,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

Numerical tests of the new projection-based embedding 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 (and sometimes larger) 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 [1]. Furthermore, we have developed the method to rigorously and systematically control WFT-in-DFT errors with respect to both basis set truncation [3] and with respect to accuracy of the DFT embedding interactions [4], all while preserving the essential stability, efficiency, and simplicity of the method.

Among the most exciting aspects of the new project-based embedding method is that enables robust and efficient WFT-in-DFT calculations in complex chemical systems, enabling practical applications studies to be performed in a straightforward manner. We have demonstrated this with a major simulation study in which WFT-in-DFT embedding was employed to rationally design a promising new class of cobalt-based catalysts for hydrogen evolution [5]. A central challenge in the development of inorganic hydrogen-evolution catalysts is to avoid deleterious coupling of the energetics of metal-site reduction from the kinetics of metal-hydride formation. We worked in collaboration with the experimental inorganic chemistry group of Jonas Peters at Caltech to discover a new class of cobalt diimine-dioxime catalysts that shows promise for achieving this aim by introducing an intramolecular proton-shuttle via a pyridyl pendant group (Fig. 3).

Using over 200 projection-based CCSD(T)-in-DFT embedding calculations of the Co-based catalyst with a variety of pyridyl substituents, the energetic and kinetic barriers to hydrogen formation were investigated, revealing nearly complete decoupling of the energetics of Co reduction and kinetics of intramolecular Co-hydride formation. This work confirmed that WFT-in-DFT embedding allows for local regions of a molecule to be described using high-accuracy wavefunction methods (such as CCSD(T)), thus overcoming significant errors in the DFT-level description of transition-metal complexes. This study provides a powerful demonstration of the utility of projection-based WFT-in-DFT method for inorganic catalysis applications, as well as revealing a promising design principle for achieving uncoupled and locally tunable intramolecular charge-transfer events in the context of homogenous transition-metal catalysts.

Making projection-based embedding available for wider use. We have already completed the development of a user-friendly implementation of the new projection-based approach to DFT-in-DFT and WFT-in-DFT embedding in the Molpro quantum chemistry package, which is available to users in over 500 institutions. We recognize that WFT-in-DFT embedding will have application domains that relate to all aspects of simulation and modeling of complex chemical systems, and we anticipate that a sizable user community will benefit from our methodological and software developments. 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.

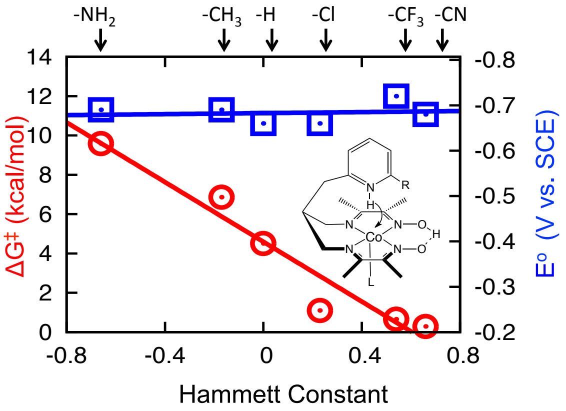

FIG. 3: WFT-in-DFT embedding has been used to discover a new class of cobalt diimine-dioxime catalysts that shows promise for decoupling the energetic ($E°$) and kinetic ($\Delta G^{\ddagger}$) barriers associated with proton- and electron-steps during hydrogen evolution [5].

Indeed, our recent WFT-in-DFT implementation in the Molpro program is being tested and utilized by a range of theoretical chemistry groups, including those of: Prof. Donald Truhlar (U. Minnesota), Prof. Qiang Cui (U. Wisconsin), Prof. Berend Smit (UC Berkeley), Prof. Andres Köhn (U. Stuttgart), Prof. Daniel Lambrecht (U. Pittsburgh), Prof. John Keith (U. Pittsburgh), Prof. Jeremy Harvey (U. Bristol), Dr. Betsy Rice (ARO), Prof. Fred Manby (U. Bristol), and Kaito Miyamoto (U. Bristol / Toyota Co.).

[1] F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller III, *A simple, exact density-functional theory embedding scheme*, J. Chem. Theory Comput., **8**, 2564, (2012).

[2] J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, *Density functional theory embedding for correlated wavefunctions: Improved methods for open-shell systems and transition metal complexes*, J. Chem. Phys., **137**, 224113, (2012).

[3] T. A. Barnes, J. D. Goodpaster, F. R. Manby, and T. F. Miller III, *Accurate basis-set truncation for wavefunction embedding*, J. Chem. Phys., **139**, 024103, (2013).

[4] J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, *Accurate and systematically improvable density functional theory embedding for correlated wavefunctions*, J. Chem. Phys., **140**, 18A507, (2014).

[5] P. Huo, C. Uyeda, J. D. Goodpaster, J. C. Peters, and T. F. Miller III, *Breaking the correlation between energy costs and kinetic barriers in hydrogen evolution: A new class of cobalt (pyridine-diimine-dioxime) catalysts*, in preparation.

[6] G. Senator and K. Subbaswamy, *Density dependence of the dielectric constant of rare-gas crystals*, Phys. Rev. B **34**, 5754 (1986).

[7] P. Cortona, *Self-consistently determined properties of solids without band-structure calculations*, Phys. Rev. B **44**, 8454 (1991).

[8] T.A. Wesolowski and A. Warshel, *Frozen Density Functional Approach for ab-initio Calculations of Solvated Molecules*, J. Phys. Chem. **97**, 8050 (1993).

[9] T.A. Wesolowski, in *Computational Chemistry: Reviews of Current Trends - Vol. 10*, pp. 1-82 (World Scientific, Singapore, 2006).

[10] N. Govind, Y. A. Wang, A. J. R. da Silva, and E. A. Carter, *Accurate Ab Initio Energetics of Extended Systems via Explicit Correlation Embedded in a Density Functional Environment*, Chem. Phys. Lett., 295, 129 (1998).

[11] A. W. Götz, S. M. Beyhan, and L. Visscher, *Performance of Kinetic Energy Functionals for Interaction Energies in a Subsystem Formulation of Density Functional Theory*, J. Chem. Theo. Comput. **5**, 3161 (2009).

[12] M. Iannuzzi, B. Kirchner, and J. Hutter, *Density functional embedding for molecular systems*, Chem. Phys. Lett. **421**, 16-20 (2006).