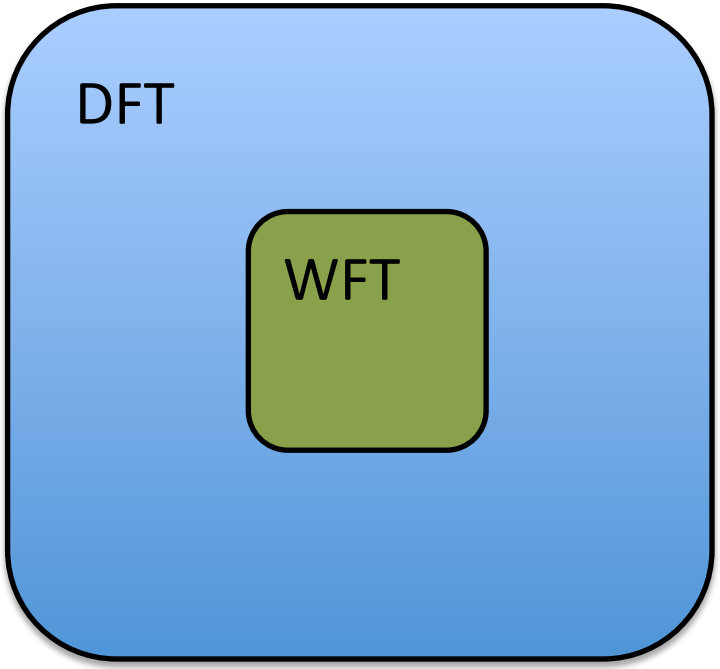
Development and Application of the Projection-Based Embedding Method

Taylor Barnes

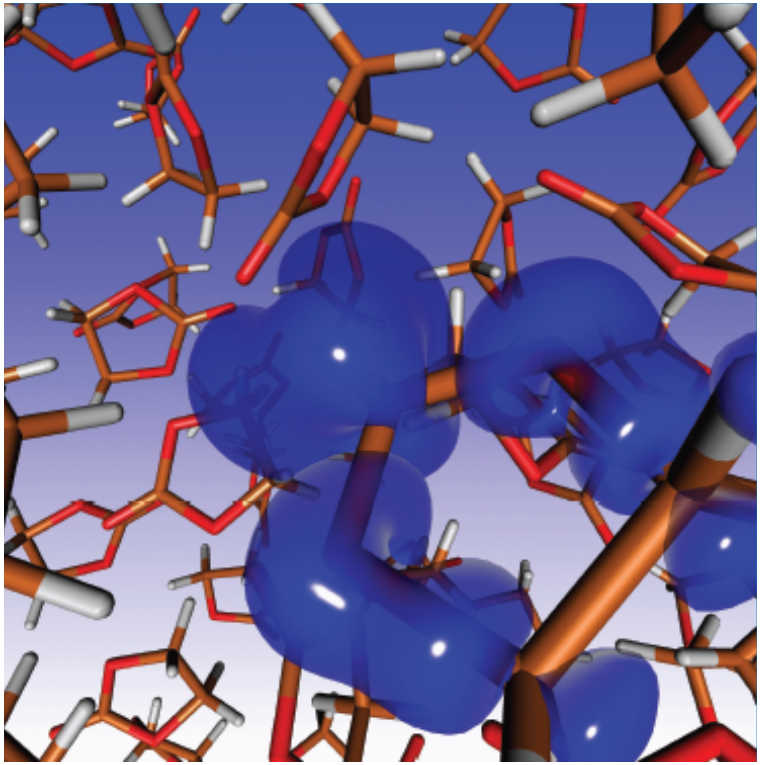
NERSC Annual Meeting, Feb. 24, 2015

Outline

Development of the Accurate Projection-Based WFT-in-DFT Embedding Method



Application: Investigation of the Oxidative Decomposition of Lithium-Ion Battery Solvents



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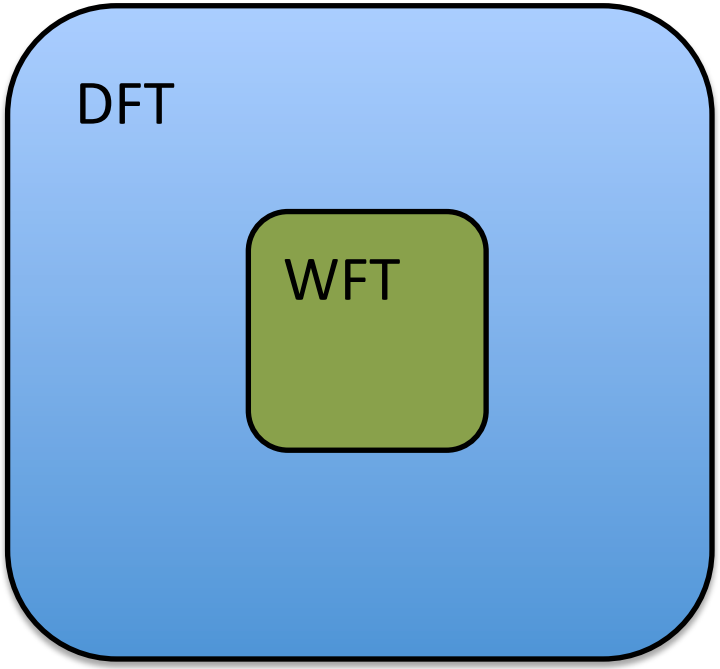

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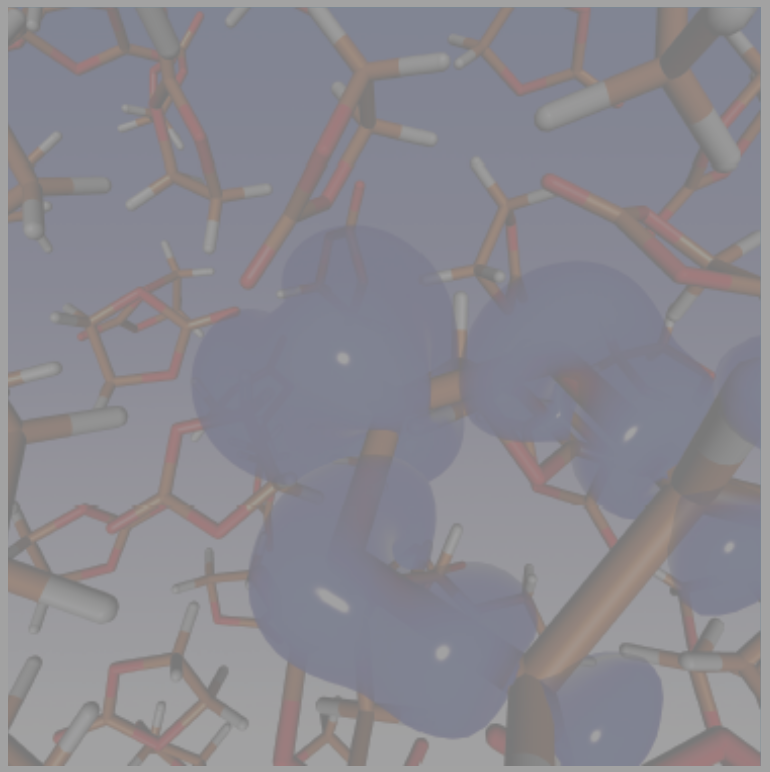
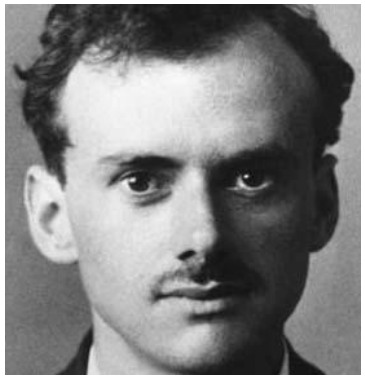


Intro to Computational Chemistry

The Schrödinger equation provides the foundation for computational studies of chemical systems.

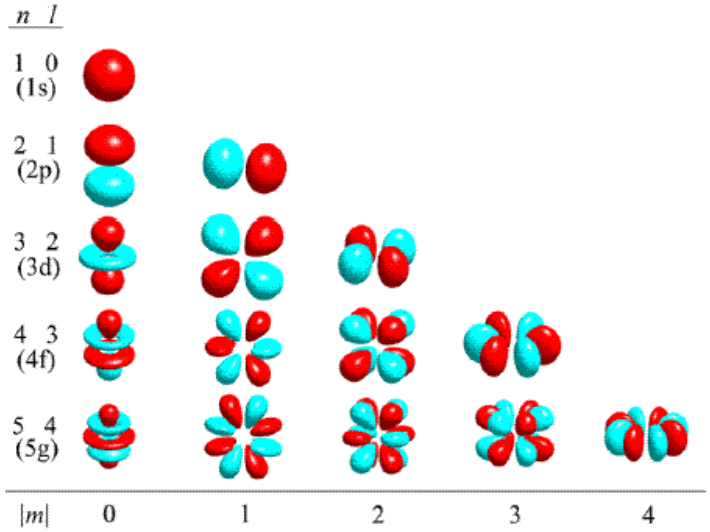
$$\hat{H}\Psi = \epsilon\Psi$$

Erwin Schrödinger



Paul Dirac

Calculation of the molecular orbitals (MOs) of the hydrogen atom is trivial.

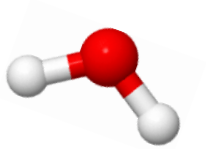


Calculations on many-electron systems are much more challenging:

"the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." - Paul Dirac, 1929

The Scaling Problem

Many wavefunction theory (WFT) methods exist for approximating the solution to the Schrödinger equation.



1 Minute at the CCSD(T) level

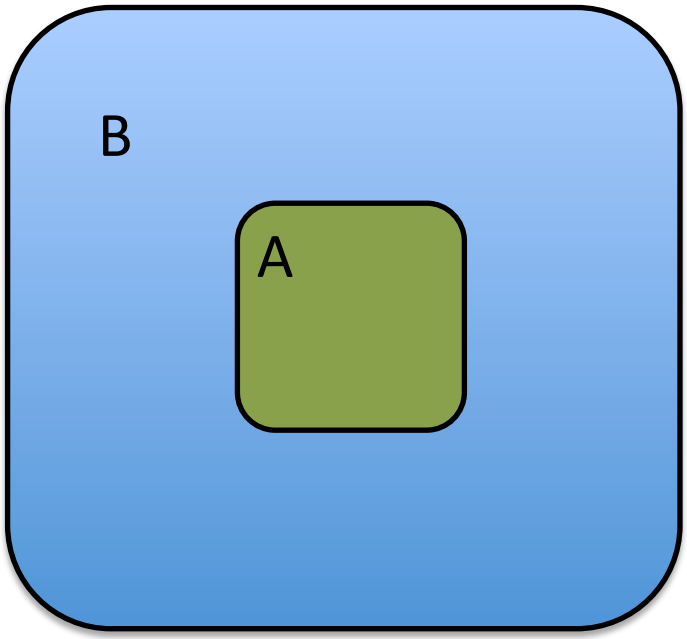
Accuracy ↑		Cost ↑
Full CI	N!	
CCSD(T)	N^7	
CCSD	N^6	
MP2	N^5	
HF	N^2	

20 Years at the CCSD(T) level

Because of the large computational cost of more accurate WFT calculations, they are only practical for systems containing approximately 20 atoms or fewer.

Projection-Based Embedding

A – higher level theory
B – lower level theory



- Approximate implementations of the idea:

  QM/MM, ONIOM, FMO,...

- However, we will address this problem in a way that *exactly describes the boundary between subsystems.*

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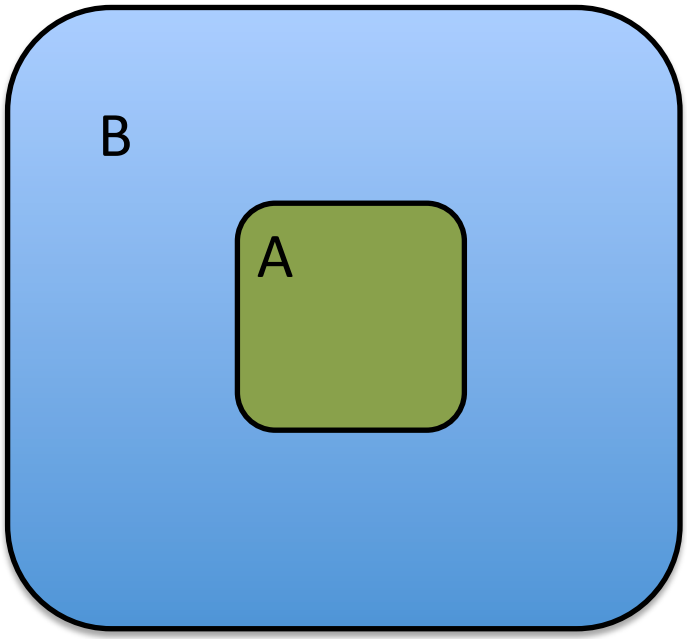

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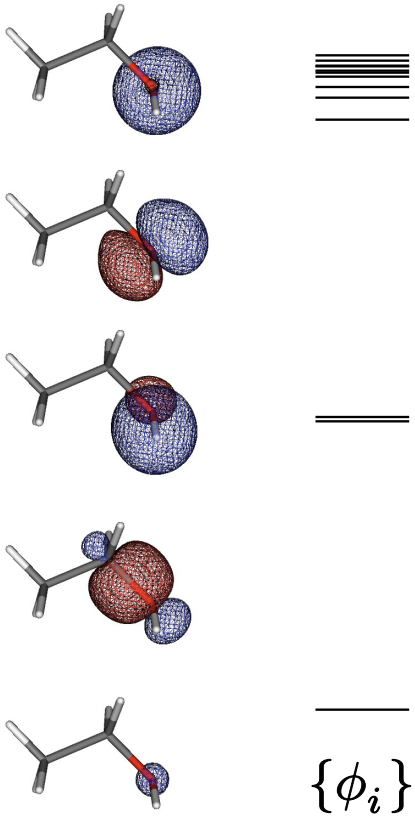
An illustrative example: DFT-in-DFT for ethanol

1. Perform a KS-DFT calculation to obtain a set of MOs:

$$\mathbf{f} = \mathbf{h} + \mathbf{J}[\gamma] + \mathbf{v}_{\mathrm{xc}}[\gamma]$$



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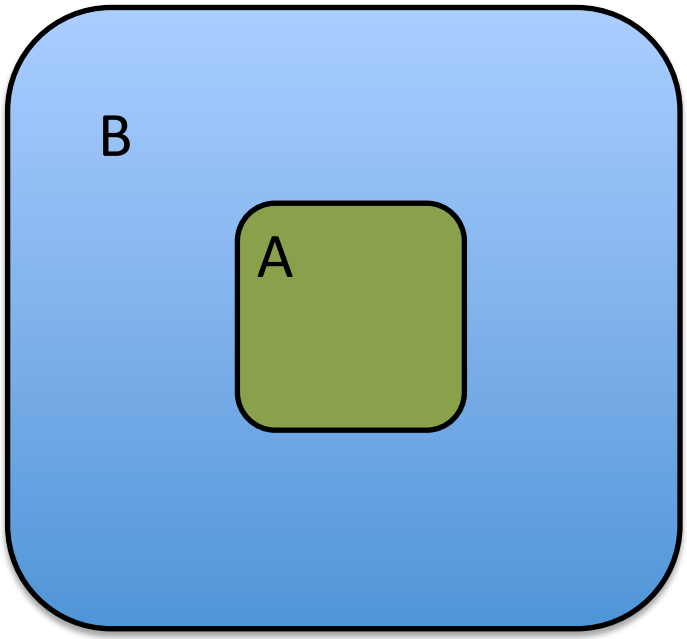

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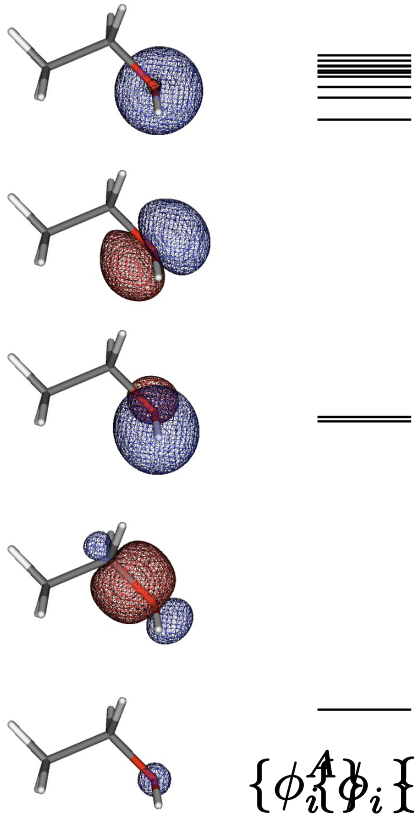
1. Perform a KS-DFT calculation to obtain a set of MOs:

$$\mathbf{f} = \mathbf{h} + \mathbf{J}[\gamma] + \mathbf{v}_{\mathrm{xc}}[\gamma]$$

2. Partition the MOs into two sets.



$$\{\phi_i^A\} \quad \{\phi_i^B\}$$

Projection-Based Embedding

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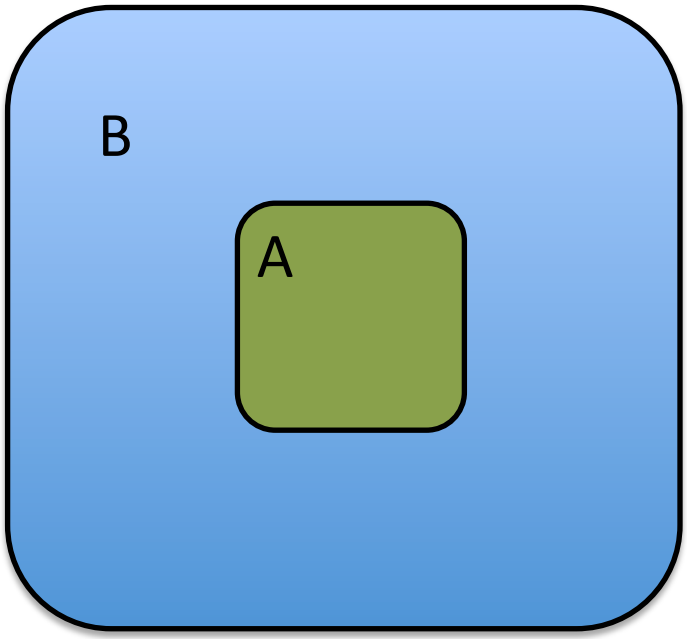

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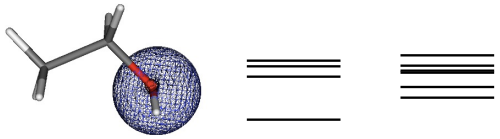
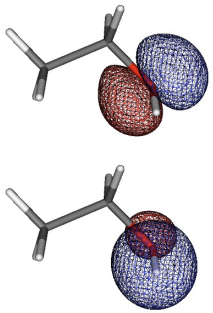
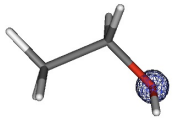


3. Perform a calculation on subsystem A.



$$\mathbf{f}^A = \mathbf{h} + \mathbf{J}[\boldsymbol{\gamma}^A + \boldsymbol{\gamma}^B] + \mathbf{v}_{\mathrm{xc}}[\boldsymbol{\gamma}^A + \boldsymbol{\gamma}^B] + \mu\mathbf{P}^B$$

$$P^B_{\alpha\beta} \equiv \langle\alpha| \left\{ \sum_{i \in B} |\phi^B_i\rangle\langle\phi^B_i| \right\} |\beta\rangle$$



$\{\phi_i^A\}$ $\{\phi_i^B\}$

Projection-Based Embedding

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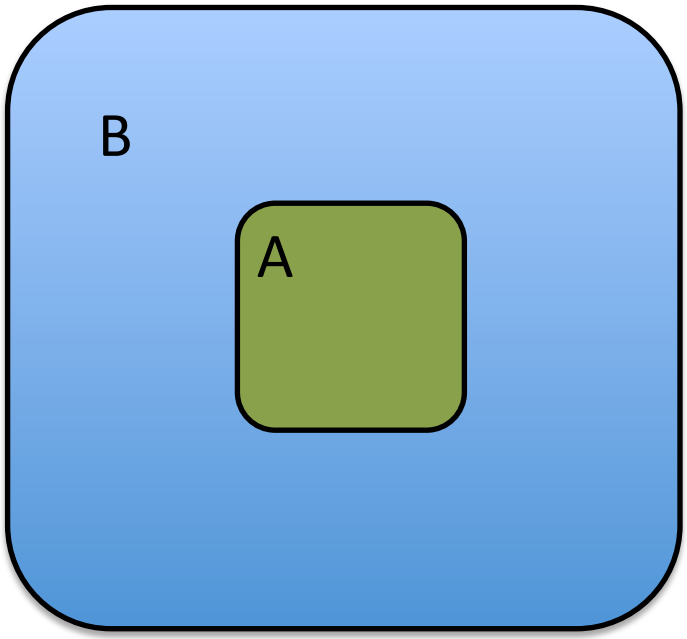

- Approximate implementations of the idea:
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An illustrative example: DFT-in-DFT for ethanol

	Energy / E_h
DFT on full system	-154.827984885
DFT-in-DFT embedding	-154.827984883
Error	0.000000002

PBE functional, 6-31G* basis set

The projection-based embedding calculations do not introduce any error associated with the boundary between subsystems.

The projection-based embedding method has been implemented in the Molpro software package.

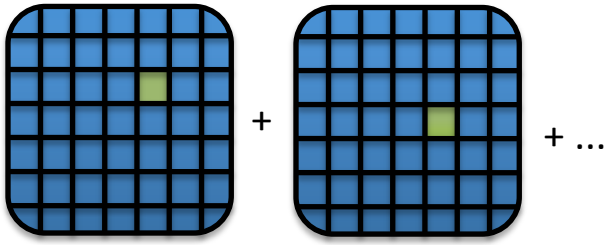
Manby *et al., JCTC,* 8, 2564 (2012).
Barnes *et al., JCP*, 139, 024103 (2013).

Parallelism Through MBE

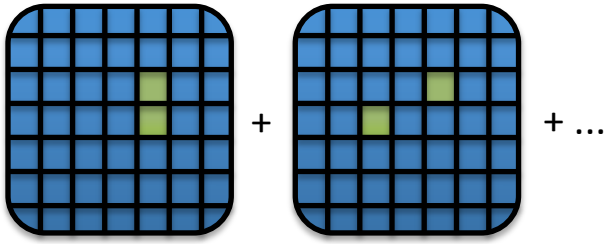
Many-Body Expansion:

First, divide a system into monomers.

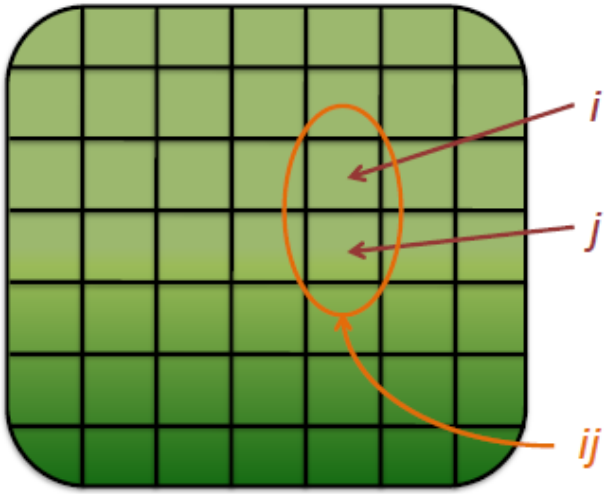
Calculate the WFT energy of each of the monomers ...



... and each of the dimers ...

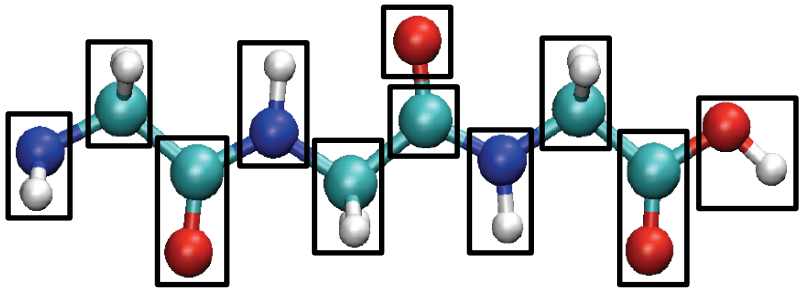


... to estimate the WFT energy of the full system.

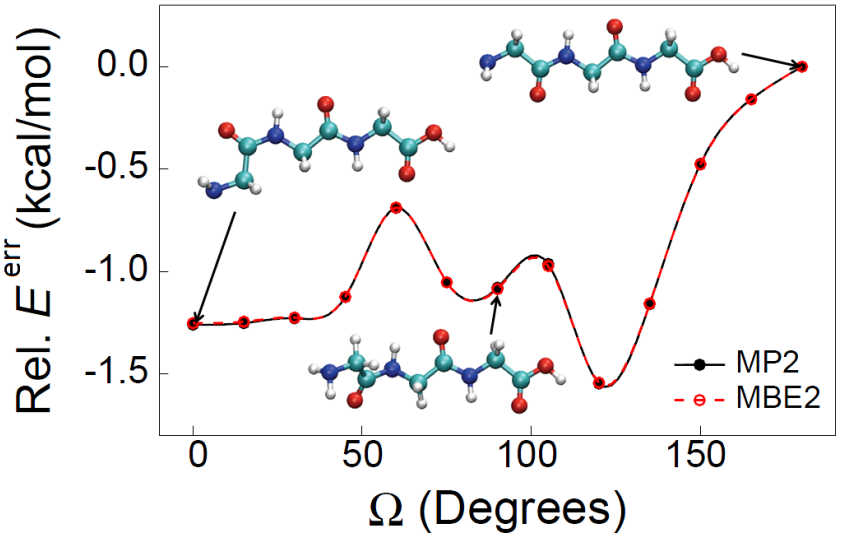


Efficiency:

The accuracy of projection-based embedding facilitates very aggressive partitioning of the monomers:



Accuracy:



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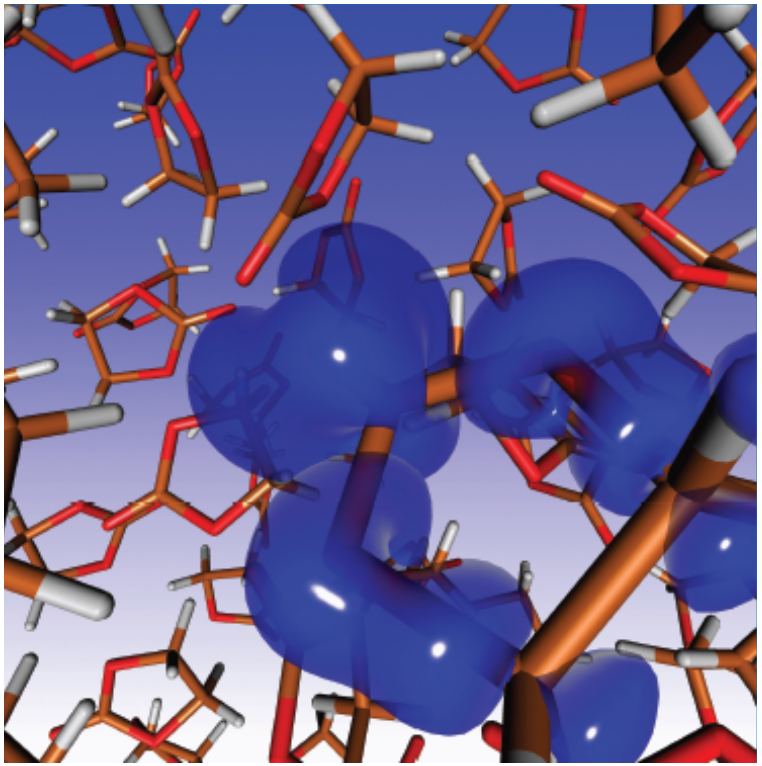
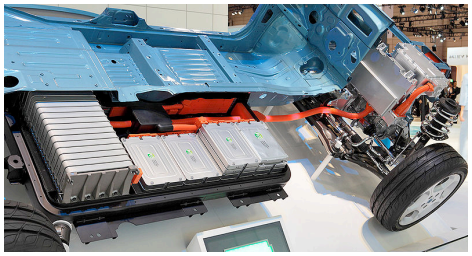
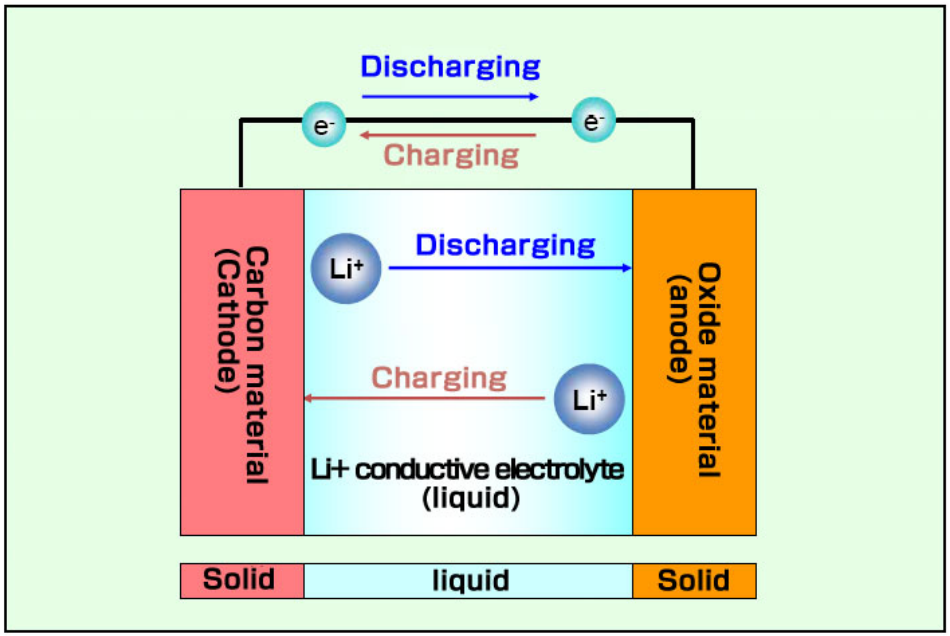


Lithium-Ion Batteries

Commercial Uses:



Structure of a lithium-ion battery:

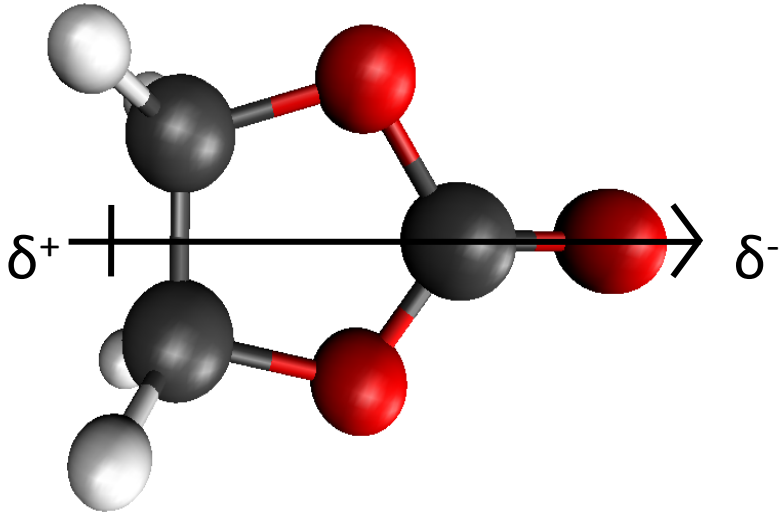


Properties of a good solvent:

- High dielectric constant
- Liquid over a large temperature range
- Inert with respect to the electrodes
- Low viscosity
- Forms an SEI
- Stable against reduction/oxidation
- Non-toxic
- Inexpensive

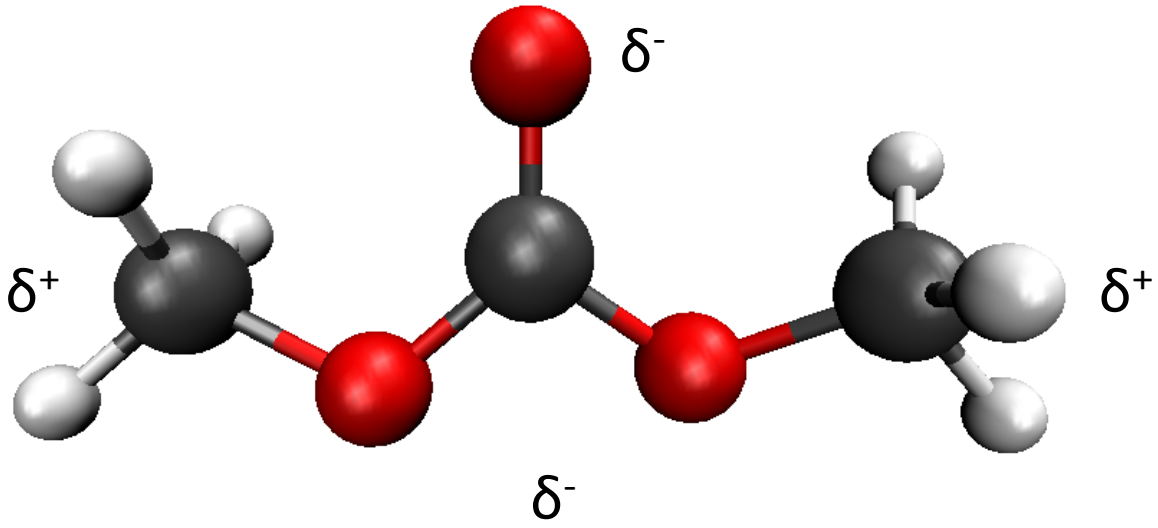
EC and DMC

Ethylene carbonate (EC) and dimethyl carbonate (DMC) are commonly used solvents in commercial lithium-ion batteries.



EC:

- Molecular Dipole: 7 Debye
- Dielectric Constant: 90
- Melting Point: 310 K

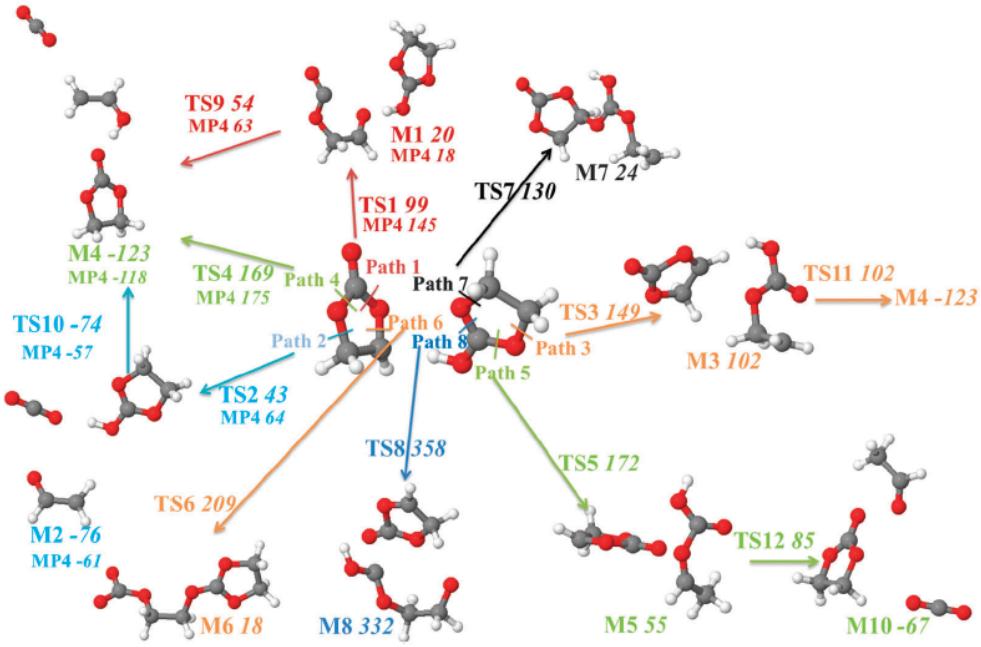


DMC:

- Molecular Dipole: 1 Debye
- Dielectric Constant: 3
- Melting Point: 275 K

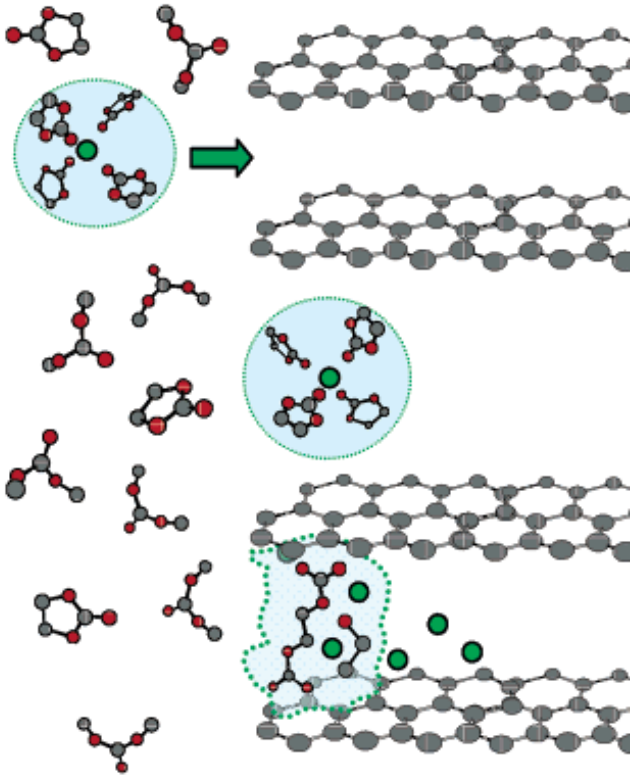
Oxidative Decomposition

When charging at high voltages, EC and DMC can become oxidized by the cathode. This is often followed by numerous oxidation-induced decomposition reactions:



Xing, Borodin, *PCCP* **14**, 12838 (2012)

Formation of a solid electrolyte interphase (SEI) is necessary to prevent excessive solvent decomposition.



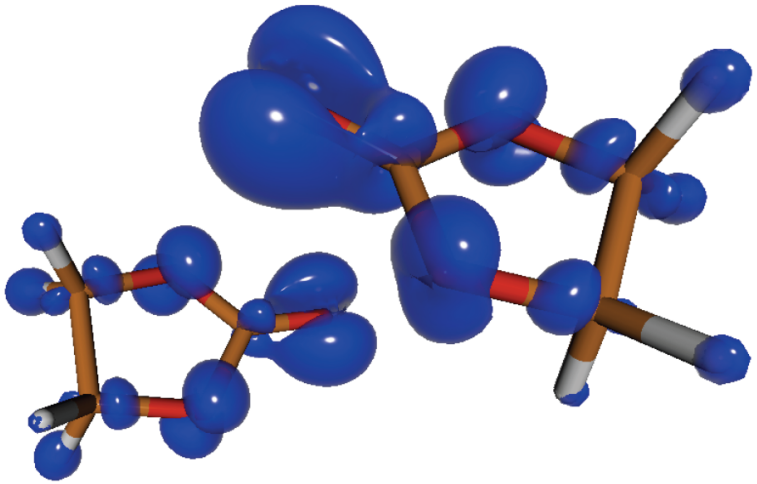
Xu *et al.*, *J. Phys. Chem. C* **111**, 7411 (2007)

Goal: Investigate the effect of solvent interactions on the oxidative stability of EC and DMC.

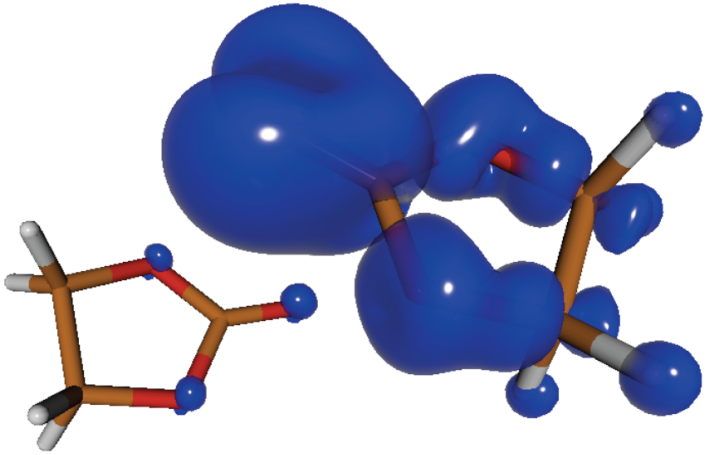
Why Not Use DFT?

The electron hole caused by oxidation of a system of two EC molecules is shown below, at both the B3LYP and HF levels of theory.

B3LYP Electron Hole:



HF Electron Hole:

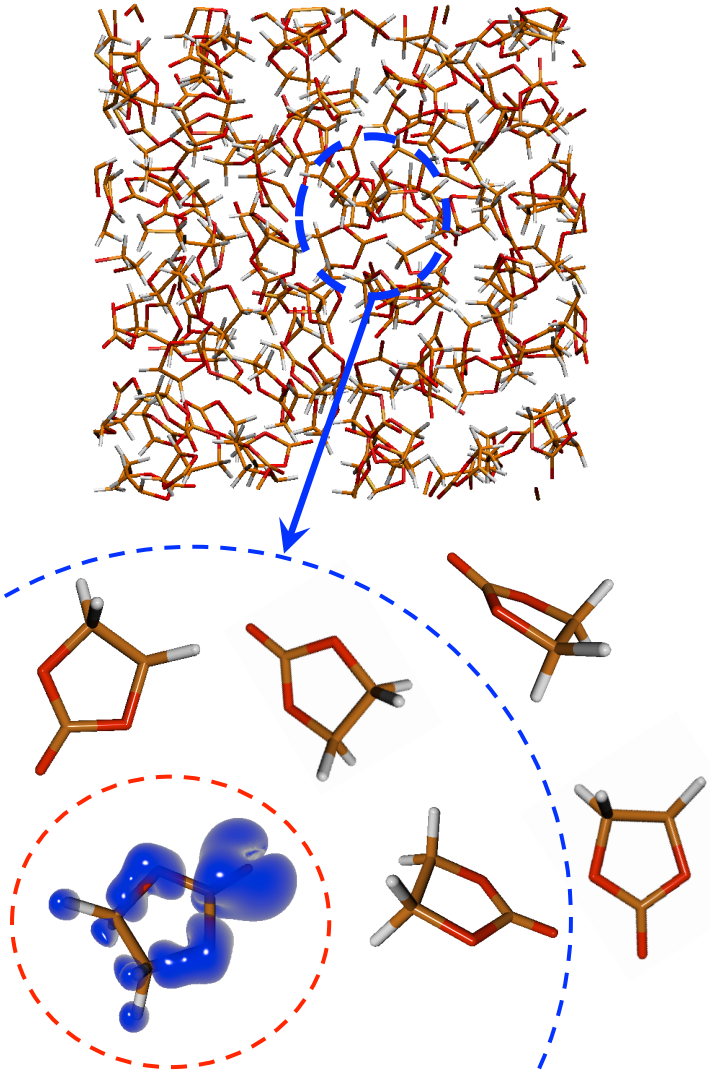


The B3LYP hole is delocalized across both molecules, while the HF hole is localized on a single molecule.

Other DFT functionals (i.e. M05, M05-2X) also produce delocalized holes.

Embedding Strategy

128-Molecule Simulation Cell:



CCSD(T)–in–B3LYP–in–MM

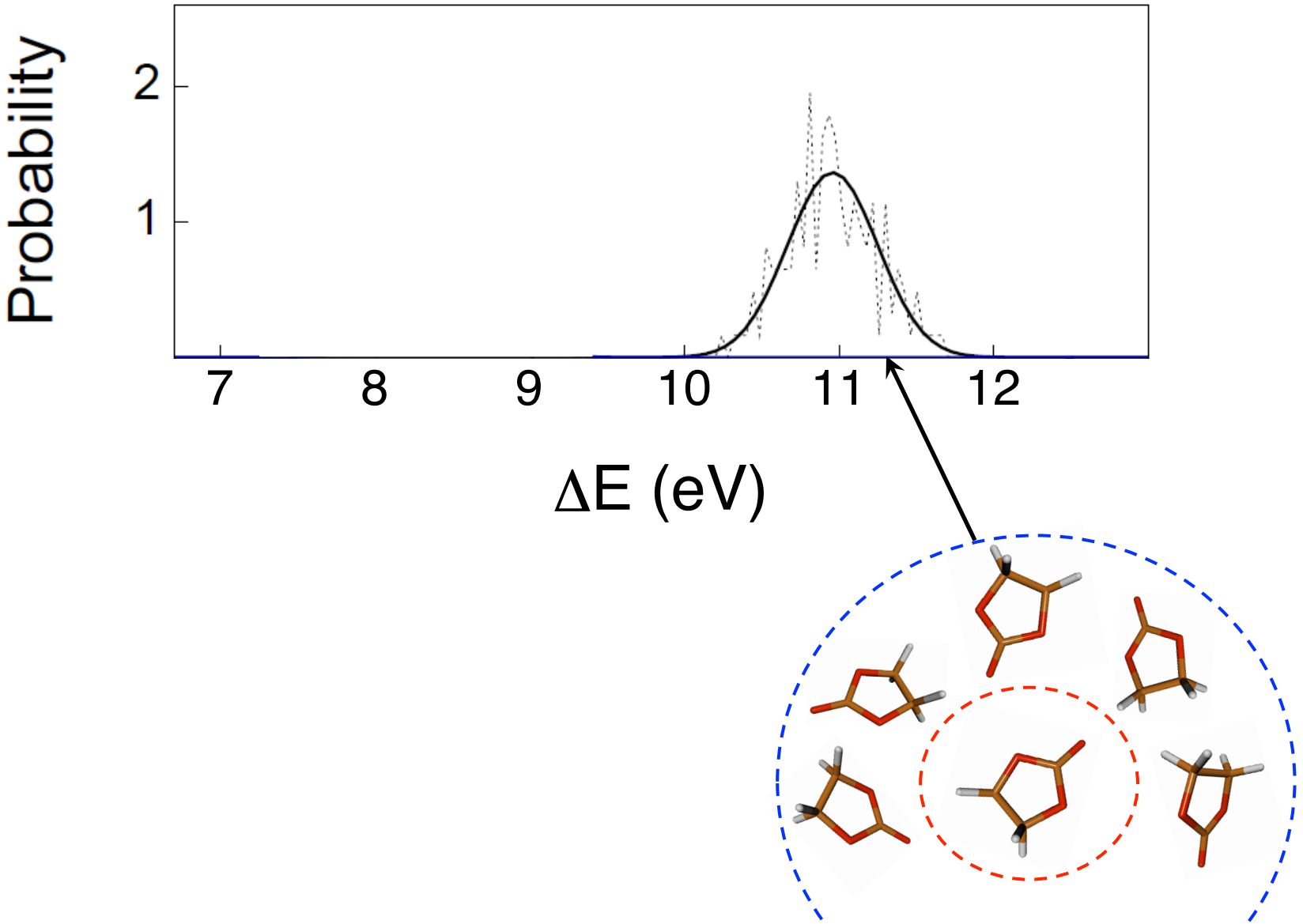
Overall Embedding Strategy:

1. Run molecular dynamics simulations to generate solvent configurations.
2. Calculate the vertical ionization energies for many different solvent configurations using CCSD(T)-in-B3LYP-in-MM embedding.
3. Determine the adiabatic oxidation potentials and reorganization energies using linear response theory

The embedding calculations were performed using NERSC's Edison peta-flop system.

More than 3,000 embedding calculations were performed, costing approximately 5,000,000 CPU hours.

Bulk Phase Results



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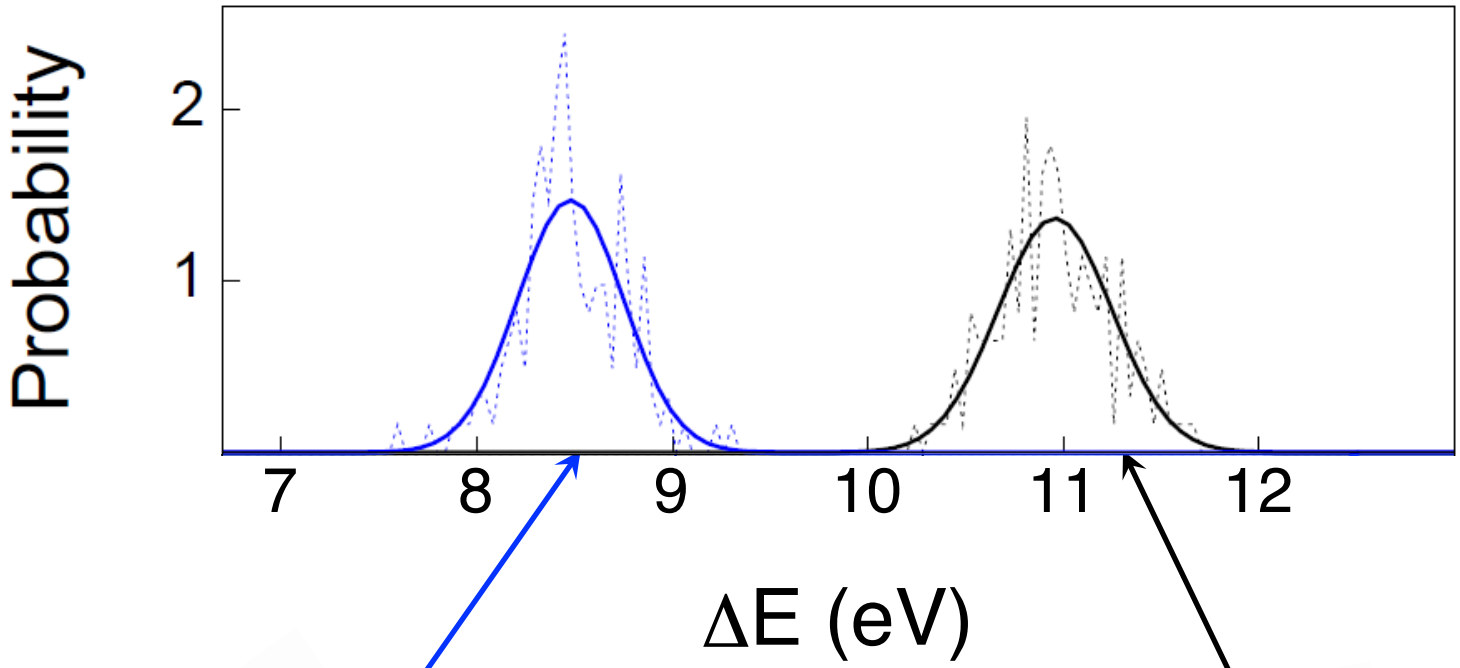
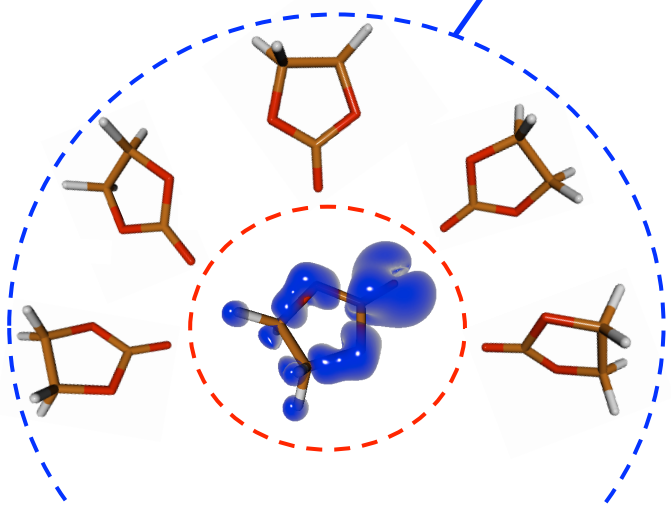
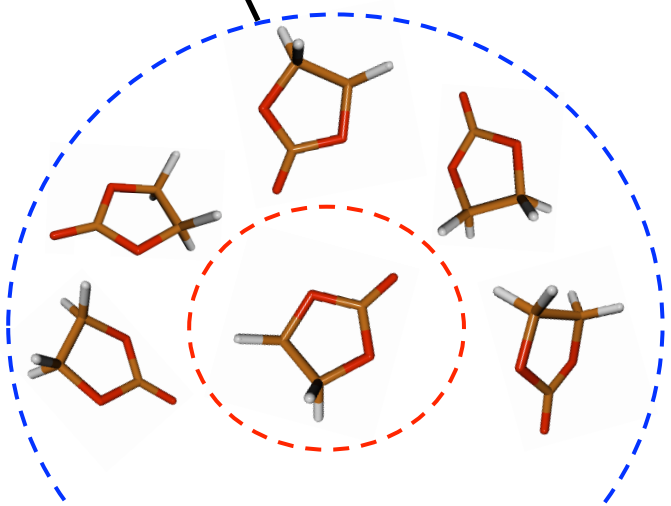
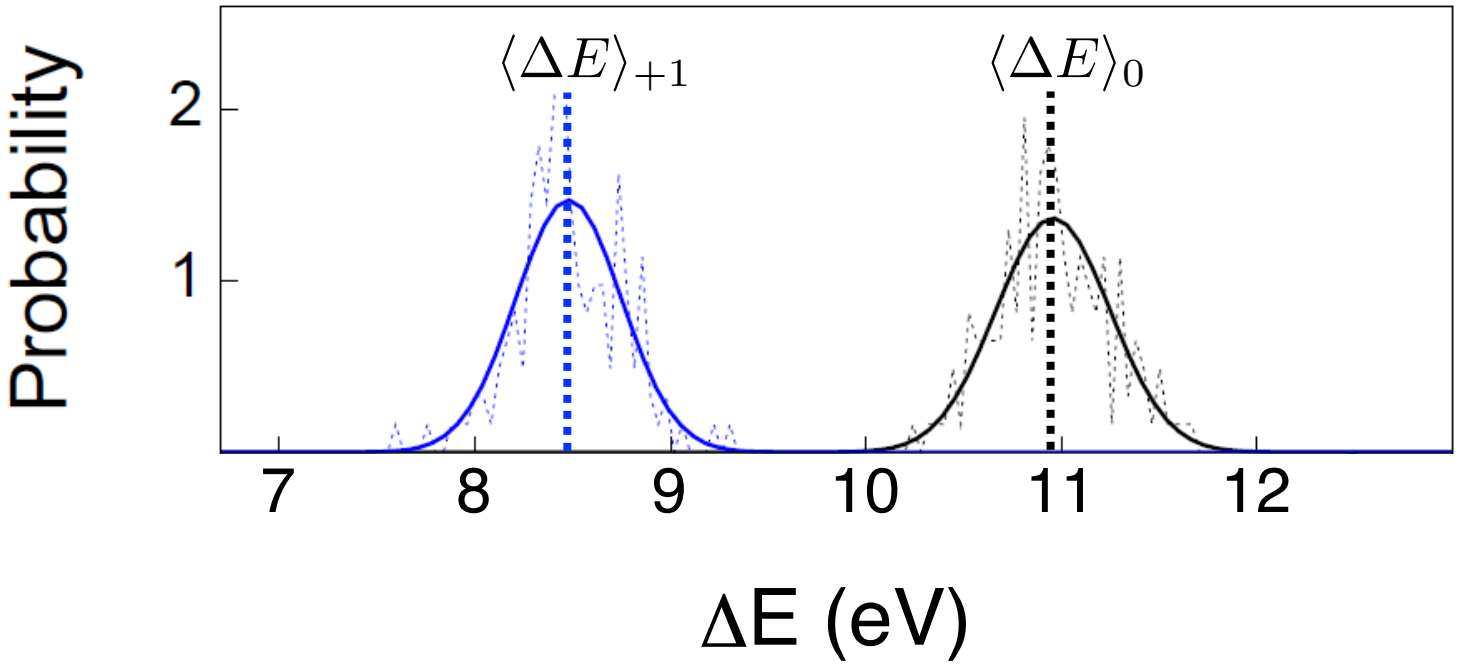






Application of Linear Response Theory



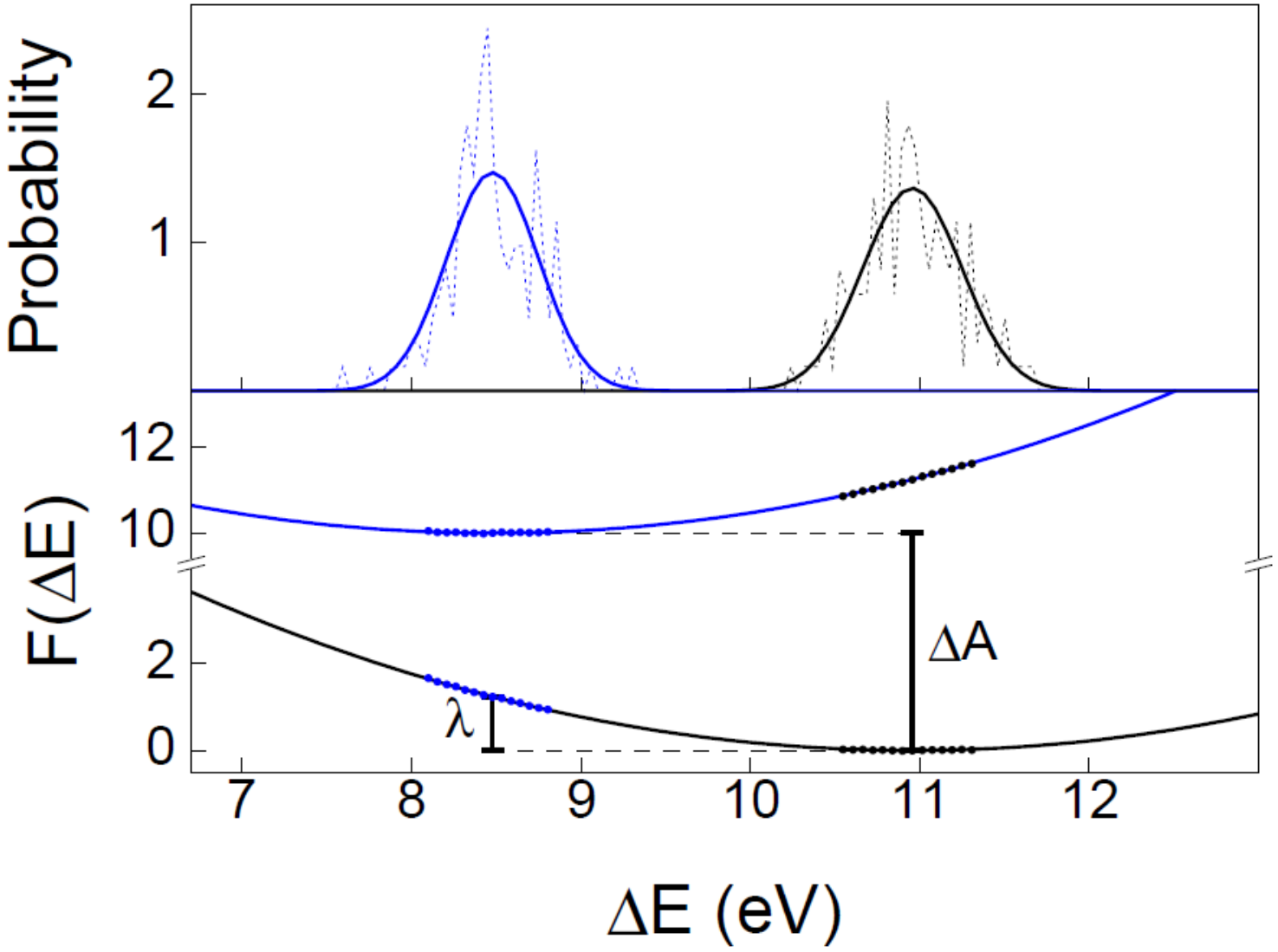
From these distributions, it is possible to calculate the solvent reorganization energy and the free energy of oxidation:

$$\lambda = \frac{1}{2}\left(\langle \Delta E \rangle_0 - \langle \Delta E \rangle_{+1}\right)$$

$$\Delta A = \frac{1}{2}\left(\langle \Delta E \rangle_0 + \langle \Delta E \rangle_{+1}\right)$$

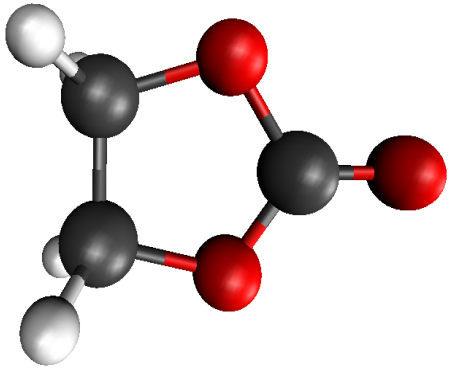
Tateyama, Blumberger, Sprik, Tavernelli, *JCP* **122**, 234505 (2005)

Application of Linear Response Theory

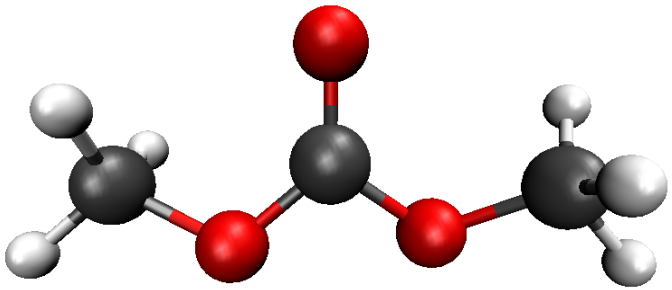


Solvent Reorganization Energy

Neat EC:



Neat DMC:



WFT-in-DFT Embedding:	1.24 eV	1.17 eV

Solvent Reorganization Energy

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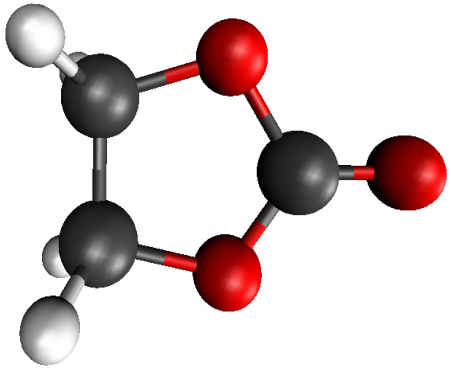
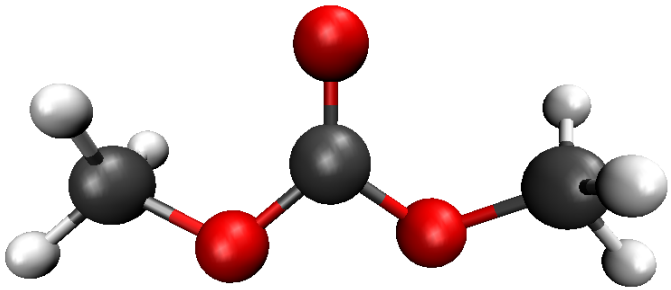
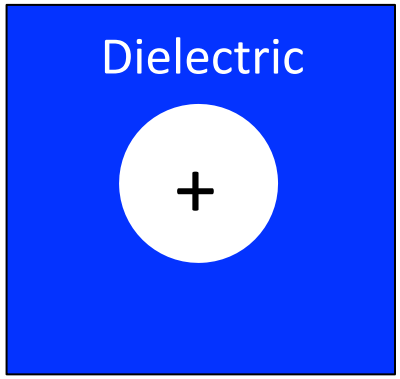


Neat DMC:



WFT-in-DFT Embedding:	1.24 eV	1.17 eV

The Spherical Cavity Model:

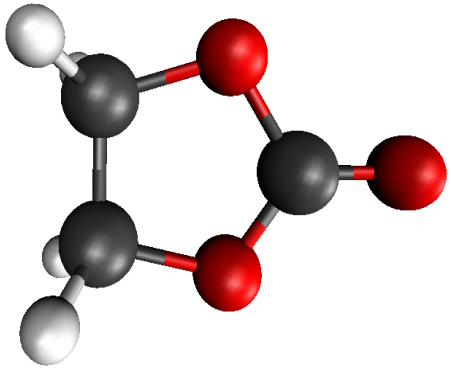


The oxidized molecule is treated as a charged, spherical cavity.

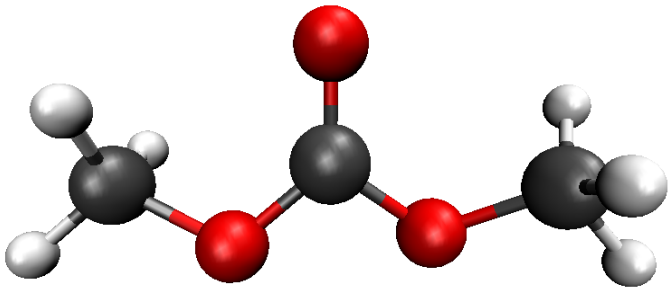
The solvent environment is treated using a homogenous dielectric continuum model.

Solvent Reorganization Energy

Neat EC:

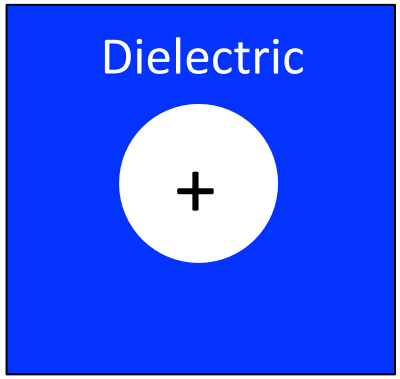


Neat DMC:



WFT-in-DFT Embedding:	1.24 eV	1.17 eV
Spherical Cavity Model:	1.17 eV	0.46 eV

The Spherical Cavity Model:



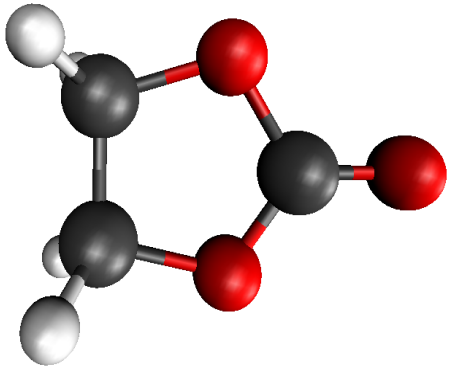
$$\lambda = \frac{e^2}{8\pi\epsilon_o r}\left(\frac{1}{\epsilon_{\text{optical}}} - \frac{1}{\epsilon_{\text{static}}}\right)$$

Cavity radius

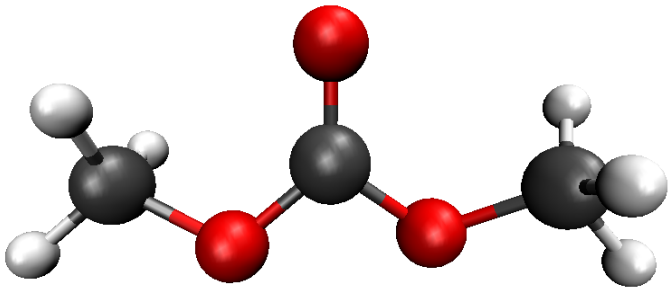
Optical and static dielectric constants

Solvent Reorganization Energy

Neat EC:

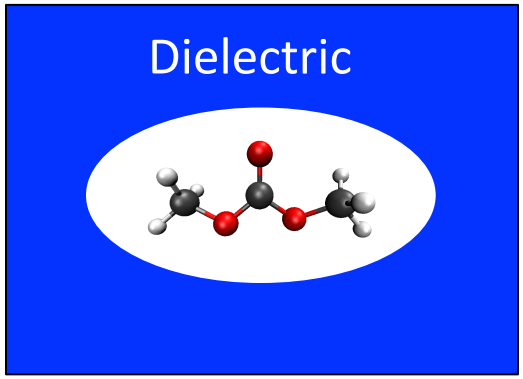


Neat DMC:



WFT-in-DFT Embedding:	1.24 eV	1.17 eV
Spherical Cavity Model:	1.17 eV	0.46 eV
PCM Model:	1.17 eV	0.48 eV

The Polarizable Continuum Model:

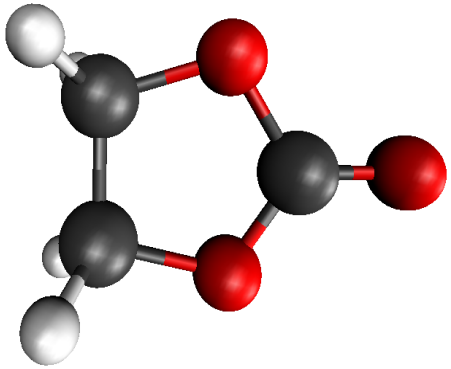


The oxidized molecule is treated explicitly.

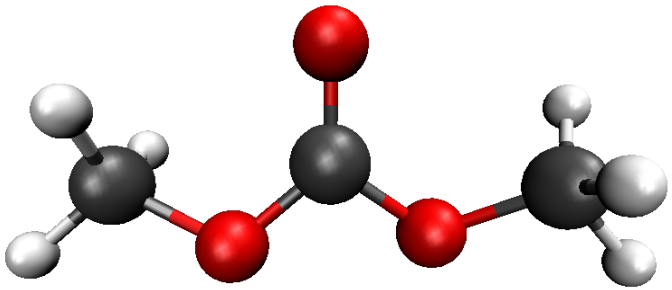
The solvent environment is treated using a homogenous dielectric continuum model.

Solvent Reorganization Energy

Neat EC:



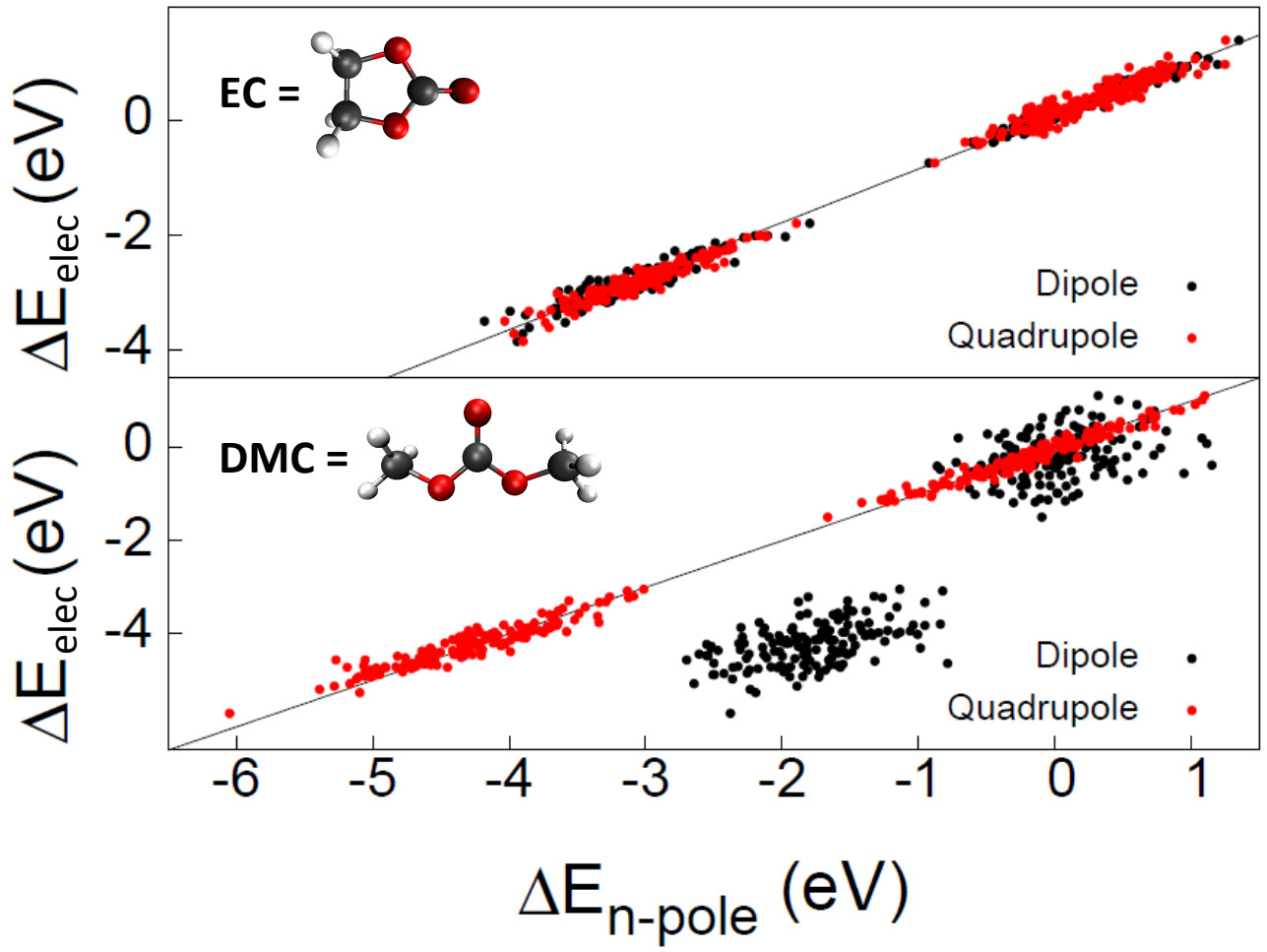
Neat DMC:



WFT-in-DFT Embedding:	1.24 eV	1.17 eV
Spherical Cavity Model:	1.17 eV	0.46 eV
PCM Model:	1.17 eV	0.48 eV

Why do dielectric continuum models significantly underestimate the reorganization energy of DMC?

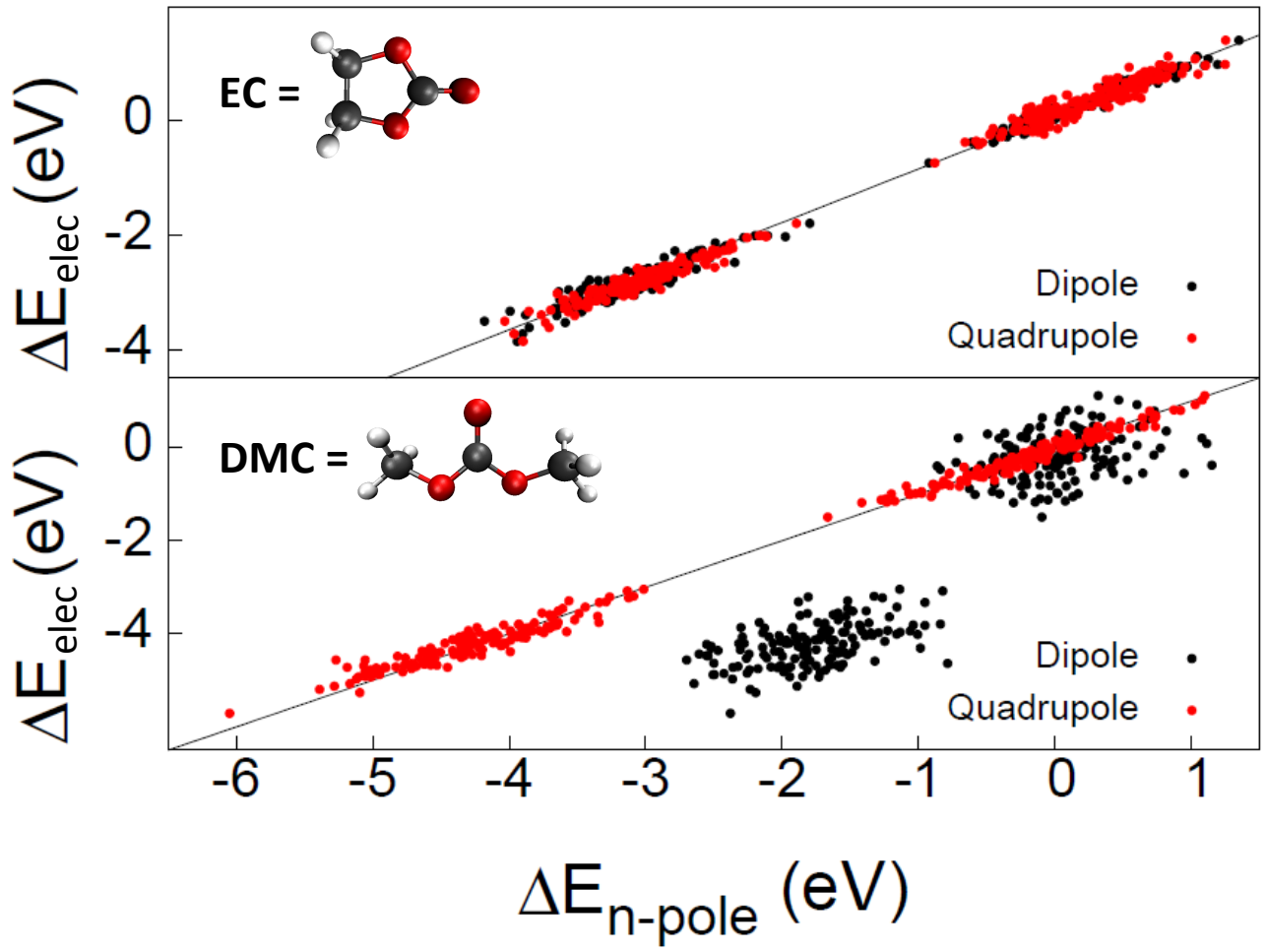
Importance of the DMC Quadrupoles



ΔE_{elec} – Contribution of the intermolecular electrostatic interactions to the IE

$\Delta E_{n\text{-}pole}$ – As ΔE_{elec}, but using a multipole expansion truncated at the n-poles

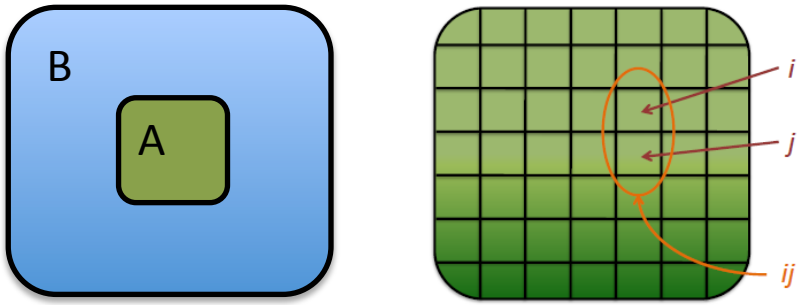
Importance of the DMC Quadrupoles



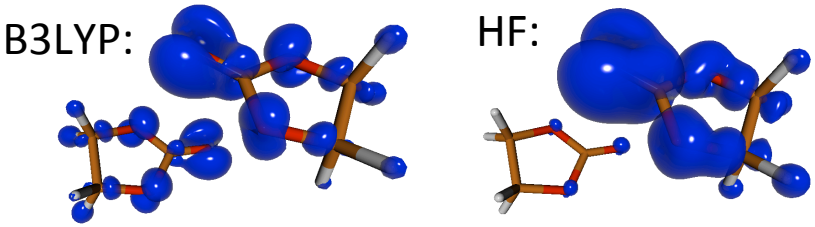
EC intermolecular interactions are primarily dipolar, while DMC intermolecular interactions are largely quadrupolar. Ignoring the quadrupolar interactions leads to underestimation of the DMC reorganization energy.

Summary

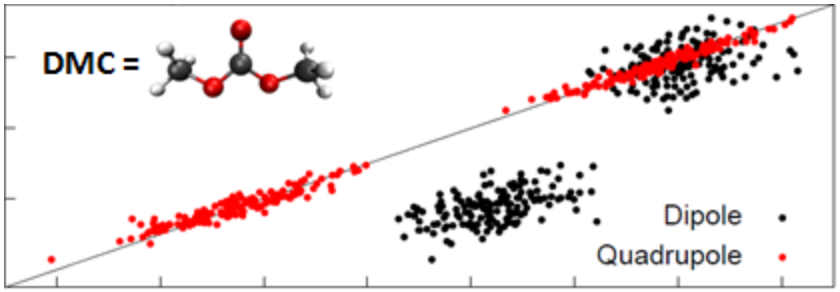
1. The projection-based embedding method enables accurate multiscale modeling.



2. This enables correction of errors from low-level treatments:

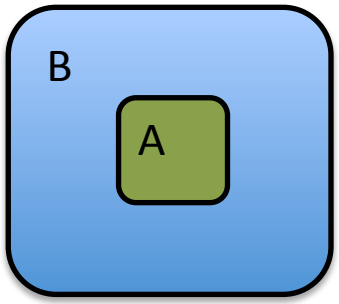


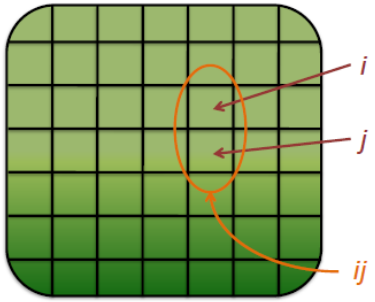
3. It is essential to treat solvent interactions accurately.



Summary

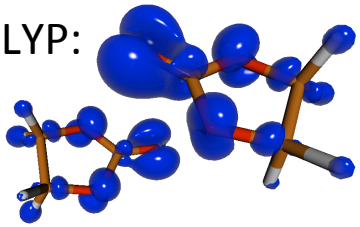
1. The projection-based embedding method enables accurate multiscale modeling.



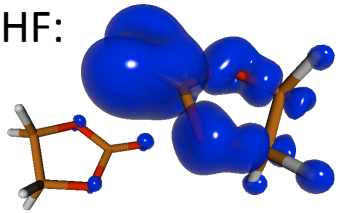


2. This enables correction of errors from low-level treatments:

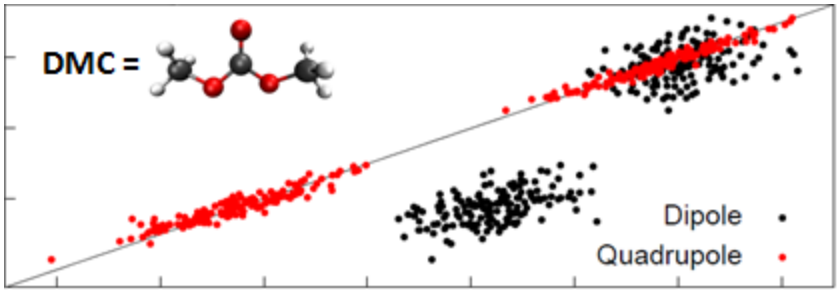
B3LYP:



HF:



3. Projection-based embedding facilitates improved analysis of solvent interactions.



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