Solvation and embedding schemes in quantum chemistry

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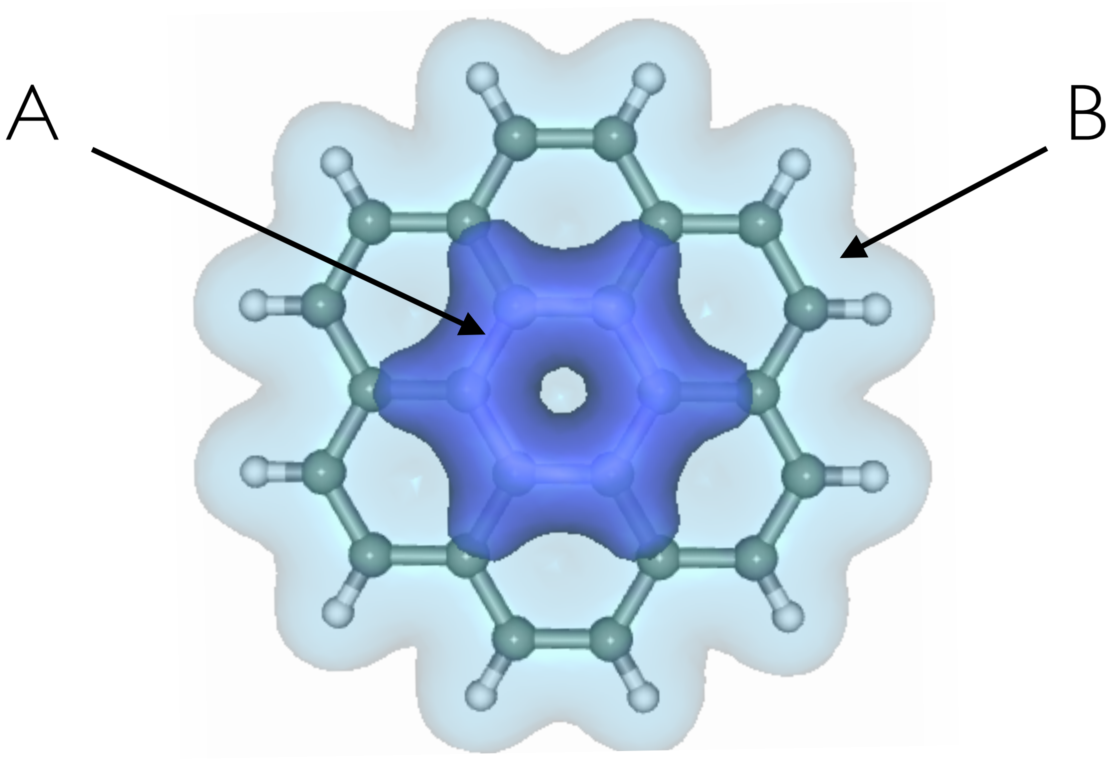
ESQC, Sicily 2019

Lecture 2

Embedding methods

Overview

- Some background theory
- Survey of embedding methods
- WF-in-DFT embedding, and projection-based embedding

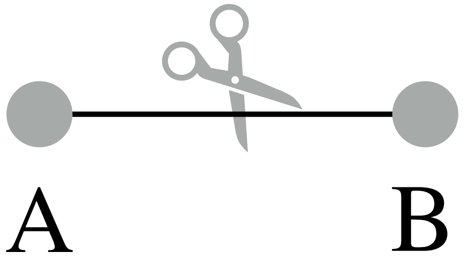


Cutting an arbitrary quantum system

- Suppose we have a system with two parts, A and B
- We often think in terms of the wavefunction for such a system
- Here we will take a look at what really happens when you try to describe the quantum state of a subsystem
- Doing so helps understand what is going on in embedding methods

States of subsystems are weird

H_2



What is the quantum state for atom A?

Pure quantum states and density operators

- We are very familiar with a state represented as a wavefunction $|\Psi\rangle$
- An alternative representation is as a density operator $\rho = |\Psi\rangle\langle\Psi|$
  - ρ is not the electronic density (cf DFT)
  - ρ is not the one-particle reduced density matrix
  - ρ is a way of writing the state that is just as valid as $|\Psi\rangle$, but, as we'll see, much more general
- A quick reminder from linear algebra: $\mathbf{a}^\dagger\mathbf{a}$ is a scalar, but $\mathbf{a}\mathbf{a}^\dagger$ is a matrix
- A quantum state with a wavefunction is a *pure state*

Not all quantum states are pure states

- An operator that represents a quantum state (i.e. one that is a density matrix/operator):
  - Is Hermitian and positive semi-definite
  - Has unit trace: $\operatorname{tr}\rho = 1$
- An example of such an operator is $\rho = \frac{1}{2}|\Psi_1\rangle\langle\Psi_1| + \frac{1}{2}|\Psi_2\rangle\langle\Psi_2|$
- This is a valid quantum state (verify!) but is not associated with a wavefunction
- Such a state is called a *mixed state*
- A physically important example is the thermal state $\rho_{\text{therm}} = e^{-\beta H}/Z$

Some practice

- Is $|\Psi\rangle\langle\Psi|$ a density matrix? (Yes, of course, but let's check…)
  - Is it Hermitian? $(|\Psi\rangle\langle\Psi|)^\dagger = (\langle\Psi|^\dagger)(|\Psi\rangle^\dagger) = |\Psi\rangle\langle\Psi|$ ✓
  - Is it positive? $\langle a|\Psi\rangle\langle\Psi|a\rangle = |\langle\Psi|a\rangle|^2 \geq 0$ ✓
  - Does it have unit trace?

$$\mathrm{tr}\,|\Psi\rangle\langle\Psi| = \sum_i \langle\Phi_i|\Psi\rangle\langle\Psi|\Phi_i\rangle$$

$$= \langle\Psi|\Psi\rangle\langle\Psi|\Psi\rangle + \langle\Psi^\perp|\Psi\rangle\langle\Psi|\Psi^\perp\rangle + \cdots = 1$$ ✓

- So yes, everything is fine and $|\Psi\rangle\langle\Psi|$ is a valid quantum state

Measuring whether a state is pure

- All quantum states satisfy $\operatorname{tr} \rho = 1$
- Pure states additionally satisfy $\operatorname{tr} \rho^2 = 1$
- Mixed states are characterized by $\operatorname{tr} \rho^2 < 1$
- Additionally $\operatorname{tr} \rho^2$ is positive:
    - If λ_i are the eigenvalues of ρ, $\operatorname{tr} \rho^2 = \sum_i \lambda_i^2$

Partial trace

- To figure out state of a subsystem, we need to conduct *partial trace*

- You can understand exactly what this means by looking at the way operators behave on a product Hilbert space $\mathscr{H}_A \otimes \mathscr{H}_B$, but for now we'll just stick to examples

- Take two subsystems A, B and consider the product state $|\Psi\rangle = |\psi_a \psi_b\rangle$

- The density operator is $\rho = |\psi_a \psi_b\rangle\langle\psi_a \psi_b|$

- The state in A can be found by performing partial trace over B:

$$\rho_A = \mathrm{tr}_B\, \rho = \langle\psi_b|\rho|\psi_b\rangle + \langle\psi_b^\perp|\rho|\psi_b^\perp\rangle + \cdots = \langle\psi_b|\psi_a\psi_b\rangle\langle\psi_a\psi_b|\psi_b\rangle$$

$$= |\psi_a\rangle\langle\psi_a|$$

Entanglement and mixed states

- A more complicated case: two two-level subsystems, A and B
- Each subsystem has two basis states, $|0\rangle$ and $|1\rangle$
- The whole problem is spanned by $|00\rangle, |01\rangle, |10\rangle, |11\rangle$
- Let the whole system be in the (pure) state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\big(|00\rangle + |11\rangle\big)$$

- There is correlation in this example: when A is in 0, so is B
- What is the state on A?

Entanglement and mixed states

- Procedure: get the density operator for the whole system and perform a partial trace

- Density operator:

$$\begin{aligned}\rho &= \big(|00\rangle + |11\rangle\big)\big(\langle 00| + \langle 11|\big)/2 \\ &= \big(|00\rangle\langle 00| + |00\rangle\langle 11| + |11\rangle\langle 00| + |11\rangle\langle 11|\big)/2\end{aligned}$$

- Partial trace: $\rho_A = \mathrm{tr}_B\, \rho = \langle 0_B|\rho|0_B\rangle + \langle 1_B|\rho|1_B\rangle$

- The result: $\rho_A = \big(|0\rangle\langle 0| + |1\rangle\langle 1|\big)/2$ – a mixed state

- In this state there is entanglement between subsystems A and B

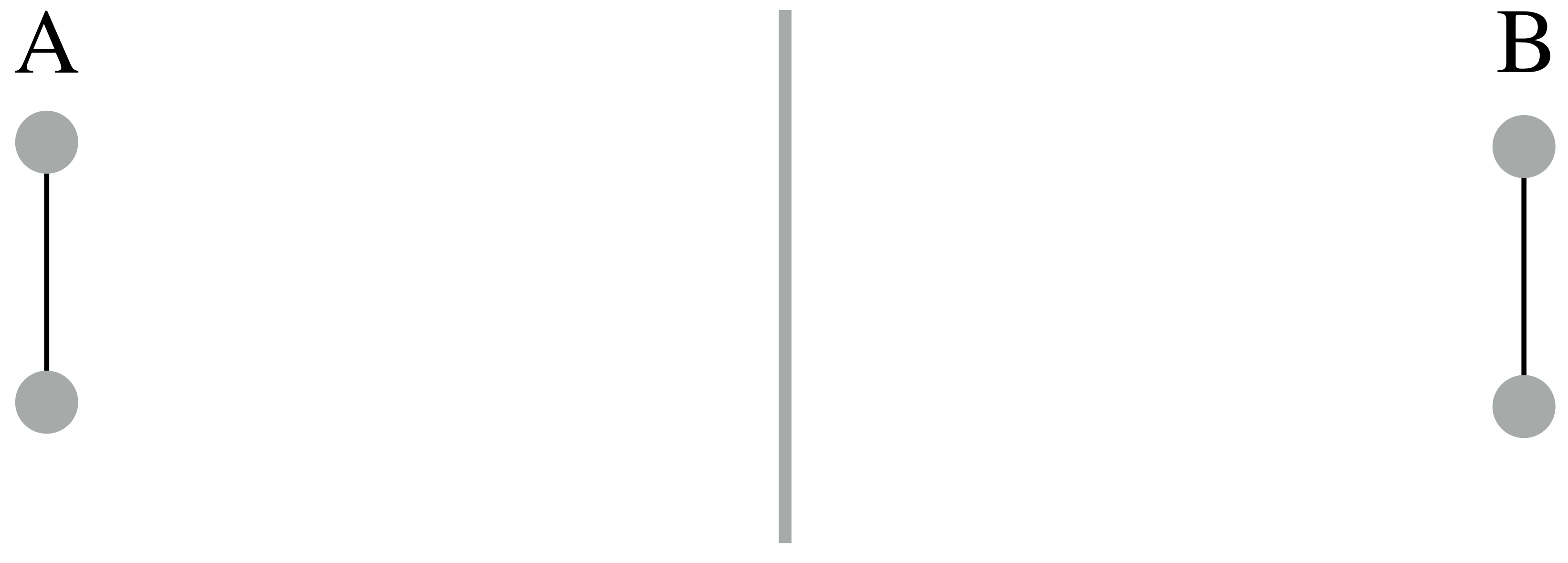
The upshot

- The quantum state of a subsystem where there is any correlation at all between subsystems cannot be represented exactly using a wavefunction

- The quantum state of a subsystem with any interaction at all with an environment cannot be exactly represented using a wavefunction

Mean-field states are not entanglement-free states

- Recalling the example of $|\Psi\rangle = |\psi_a \psi_b\rangle$, we found that the state on A is a pure state (and there is no entanglement between A and B)
- This is always the character of a product state
- However there could be other ways to partition the system, as illustrated by a simple chemical example:



almost no entanglement

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- This is always the character of a product state

- So in general: entanglement is not a property of a system, but of a particular way of partitioning system

- Mean-field states are products, but can still capture loads of entanglement

Cutting molecules in half – real calculations

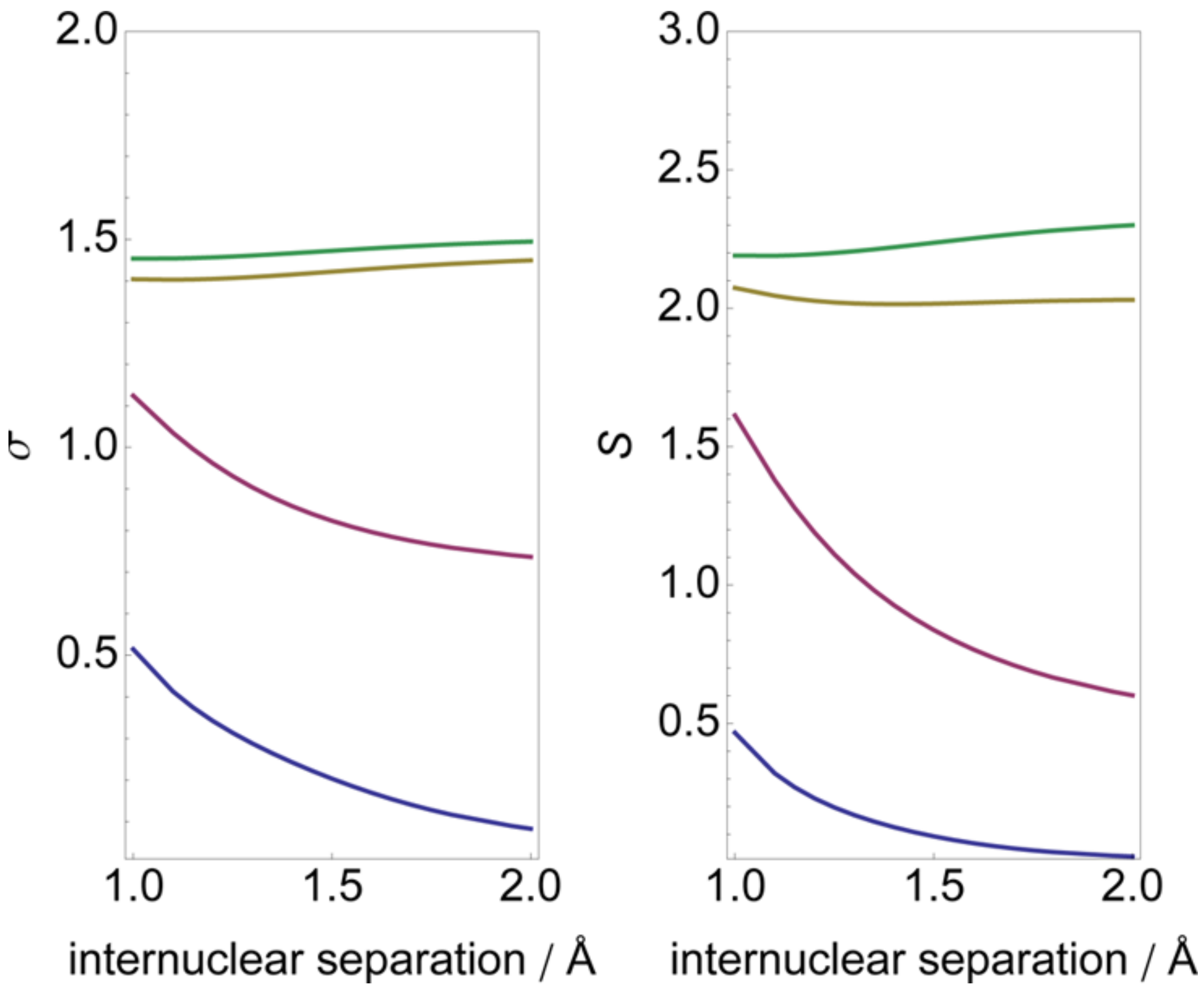


Figure 6. Variance in particle number (left panel) and the von Neumann entropy (right panel) in subsystems of neon dimer (blue), ethane (purple), ethene (gold), and ethyne (green), defined by symmetrically bisecting each system.

$$S = -\operatorname{tr} \rho \log \rho$$

Schmidt decomposition

- Consider a state in a product Hilbert space: $|\Psi\rangle \in \mathscr{H}_A \otimes \mathscr{H}_B$
- Let the dimension of $\mathscr{H}_A$ be d_a, and of $\mathscr{H}_B$ be d_b
- Suppose $d_a < d_b$
- The state can be represented by a Schmidt decomposition

$$|\Psi\rangle = \sum_{i=1}^{d_a} \lambda_i |\alpha_i\rangle \otimes |\beta_i\rangle \text{ with } \alpha_i \in \mathscr{H}_A \text{ and } \beta_i \in \mathscr{H}_B$$

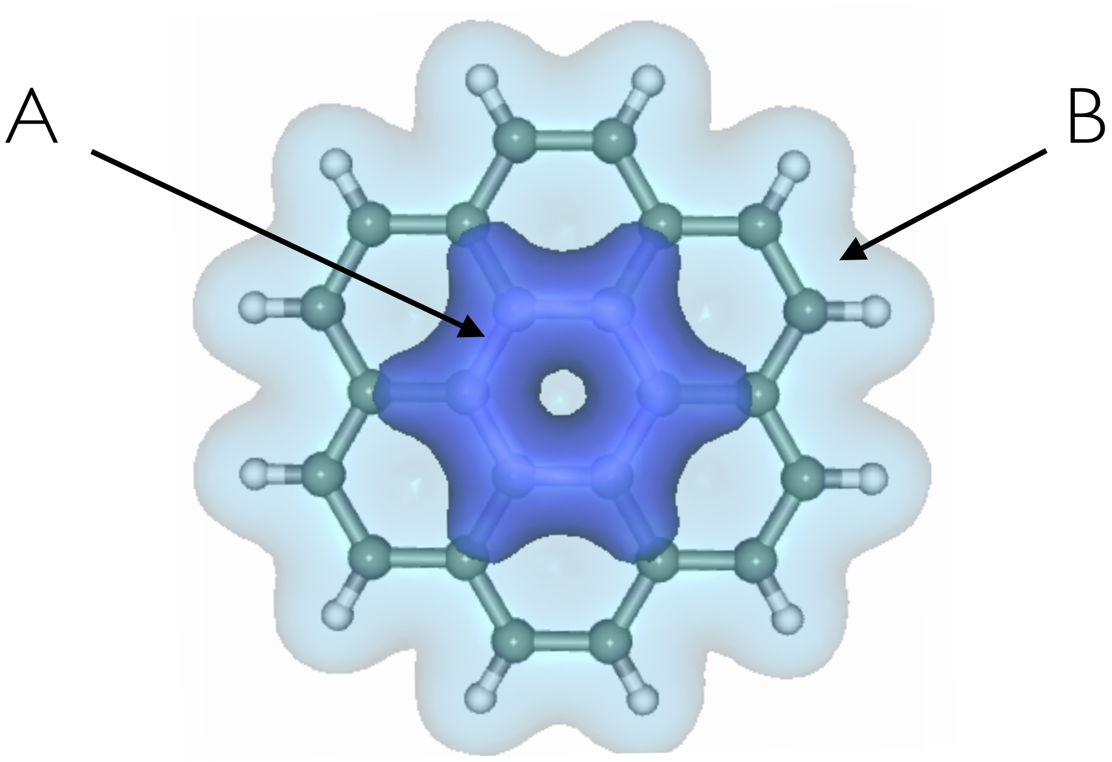
- The significance is that the length of the expansion is determined by the dimensionality of the smaller subsystem

Summary of density matrix section

- Subsystems cannot typically be represented by wavefunctions
- Only a valid approximation when there is almost no interaction

- So how do wavefunction-based embedding methods work at all?
- They work by selecting low-entanglement partitions of the system

Survey of embedding methods



- ONIOM
- Density-matrix-based embedding methods
- Other embedding schemes

ONIOM

- The simplest ever method

$$E^{\mathrm{ONIOM}} = E^{\mathrm{low}}_{A+B} - E^{\mathrm{low}}_{A} + E^{\mathrm{high}}_{A}$$

- Kind-of not really embedding – but simple and used all over the place, both under the name ONIOM, and other names
- Refinements include some degree of embedding, for example using QM/MM to polarise the high and low-level calculations on A
- Gradients: not too much of a problem…

Density-matrix-based embedding methods

- Density matrix embedding theory (DMET) [Garnet Chan] relies on the Schmidt decomposition of the state to provide entanglement with the environment

- The Schmidt decomposition of the exact state is not available, so the idea in DMET is to use a reference mean-field state to provide the decomposition

- For an *n*-orbital subsystem, this provides exactly *n* bath orbitals that model the ways in which the system can be entangled with the environment

Other embedding schemes

- A mean-field based method (embedded mean-field theory – EMFT) also provides mean-field-type entanglement

- Many-body theory also provides an interesting embedding framework: CCSD can be viewed as a remarkably effective way to embed a 2-particle subsystem in a chemical environment

- But usually discussed in a time-dependent framework using Green's functions under the name *dynamical mean-field theory*

Embedding methods based on DFT

- The basic idea
- Past approaches
- Projection-based embedding

Subsystem DFT

- The Kohn-Sham energy is

$$E_{\mathrm{KS}}[\rho] = T_s[\rho] + \int \rho v_{\mathrm{ext}} + J[\rho] + E_{\mathrm{xc}}[\rho]$$

- For a system that can be broken into molecular pieces $\rho = \sum_A \rho_A$

- Energy can be decomposed
  Senatore and Subbaswamy (1986); Cortona (1990)

$$E_{\mathrm{KS}}[\rho] = \sum_A T_s[\rho_A] + \underbrace{\left[T_s[\rho] - \sum_A T_s[\rho_A] \right]}_{\text{could be approximated}} + \int \rho v_{\mathrm{ext}} + J[\rho] + E_{\mathrm{xc}}[\rho]$$

DFT-based embedding methods

- Suppose a system has a ground-state one-particle density ρ
- HK theorem provides that there is a functional for the energy:

$$E_0 = E[\rho]$$

- Cut this density into two parts (such that each part is also a ground-state density):

$$\rho = \rho_A + \rho_B \qquad E_0 = E[\rho_A + \rho_B] = E[\rho_A] + E[\rho_B] + \Delta E[\rho_A, \rho_B]$$

- People have (on several occasions) noticed that you could use "proper" DFT for $E[\rho_A]$ and $E[\rho_B]$ and approximate $\Delta E[\rho_A, \rho_B]$

Wesolowski & Warshel, Carter, Visscher, Neugebauer, Jacob, …

Wavefunction in DFT embedding

- The very simple form of DFT-based embedding

$$E_0 = E[\rho_A] + E[\rho_B] + \Delta E[\rho_A, \rho_B]$$

  suggests there should be no problem in using a wavefunction method

- To set this up, find the potential experienced by electrons in A as a result of interaction with B:

$$v_{\mathrm{emb}} = \frac{\delta \Delta E[\rho_A, \rho_B]}{\delta \rho_A}$$

- Then do a WF calculation in A with v_{emb} as an additional external pot.

The problem with all this

- All of this is exact in principle (so exact WF in exact DFT is exact)
- But the difficulty beyond that of normal DFT is that $\Delta E[\rho_A, \rho_B]$ contains $\Delta T_s[\rho_A, \rho_B] = T_s[\rho_A + \rho_B] - T_s[\rho_A] - T_s[\rho_B]$
- The T_s functional has to be approximated – this is hard, but why?

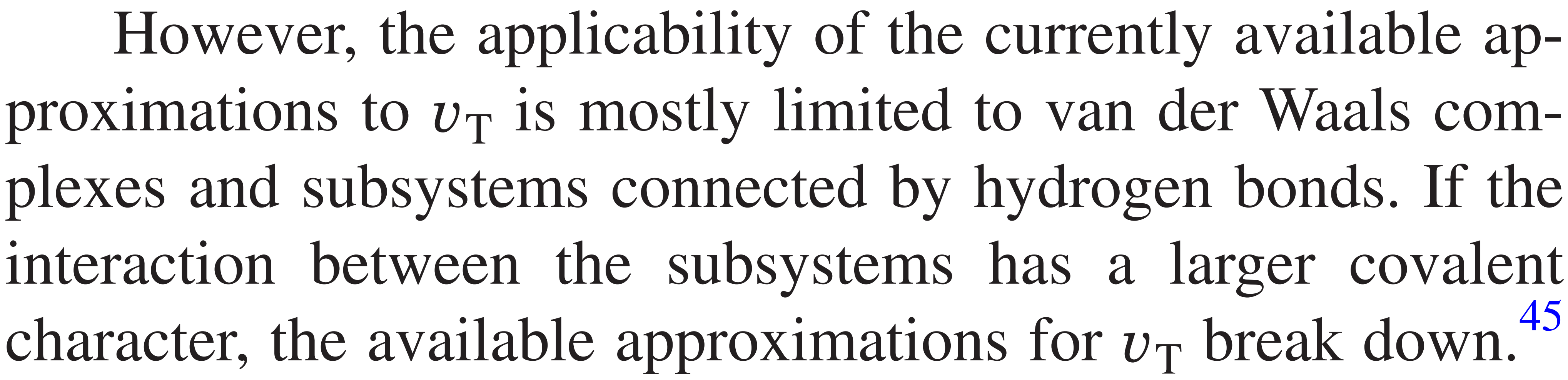
$$E_x[\rho_1] = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \, \frac{|\rho_1(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

$$T_s[\rho_1] = -\frac{1}{2}\int d\mathbf{r} \left[\nabla^2_{\mathbf{r}'}\rho_1(\mathbf{r}, \mathbf{r}')\right]_{\mathbf{r}' \to \mathbf{r}}$$

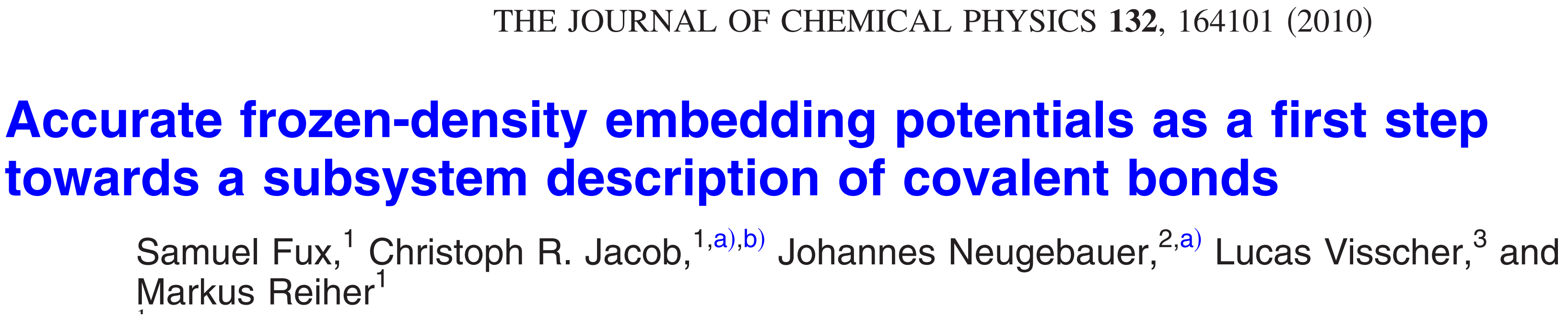
The problem with all this

- Anyway: existing approximations (Thomas-Fermi, GGAs, more advanced functionals) are not accurate enough to allow cutting systems through covalent bonds

- Of course I would say that, but…



> However, the applicability of the currently available approximations to v_T is mostly limited to van der Waals complexes and subsystems connected by hydrogen bonds. If the interaction between the subsystems has a larger covalent character, the available approximations for v_T break down.[45]



THE JOURNAL OF CHEMICAL PHYSICS **132**, 164101 (2010)

Accurate frozen-density embedding potentials as a first step towards a subsystem description of covalent bonds

Samuel Fux,[1] Christoph R. Jacob,[1,a),b)] Johannes Neugebauer,[2,a)] Lucas Visscher,[3] and Markus Reiher[1]

‘Exact’ DFT embedding

- But $T_s[\rho]$ can be calculated exactly (in principle):
  - Find the KS potential for which ρ is the ground-state density
  - Find the KS orbitals in this potential
  - Evaluate the kinetic energy

$$\rho \longrightarrow v_{\mathrm{KS}} \longrightarrow \phi_i \longrightarrow T_s[\rho]$$

Fux, Jacob, Neugebauer, Visscher, Reiher, JCP **132**, 164101 (2010)
Goodpaster, Ananth, Manby, Miller, JCP **133**, 084103 (2010)
Goodpaster, Barnes, Miller, JCP **134**, 164108 (2011)
Huang, Pavone, Carter, JCP **134**, 154110 (2011)
Nafziger, Wu, Wasserman, JCP **135**, 234101 (2011)

The source of the problem

- Why is just doing DFT-in-DFT exactly so hard?
- The trouble comes from trying to partition the system arbitrarily
- If we make the "right" partition we can eliminate all the problems

Non-additivity in kinetic energy

- The non-interacting kinetic energy in KS theory is just

$$T_s[\rho] = \sum_{i \in \mathrm{occ}} \langle \varphi_i | -\tfrac{1}{2} \nabla^2 | \varphi_i \rangle$$

- In other words it *is* additively decomposable

- Let's partition the occupied orbitals into two sets, $A \cup B = \mathrm{occ}$, then

$$\rho = \sum_{i \in A} |\varphi_i^A|^2 + \sum_{i \in B} |\varphi_i^B|^2$$

$$T_s[\rho] = \sum_{i \in A} \langle \varphi_i^A | -\tfrac{1}{2} \nabla^2 | \varphi_i^A \rangle + \sum_{i \in B} \langle \varphi_i^B | -\tfrac{1}{2} \nabla^2 | \varphi_i^B \rangle$$

$$= T_s[\rho_A] + T_s[\rho_B] + \Delta T_s[\rho_A, \rho_B]$$

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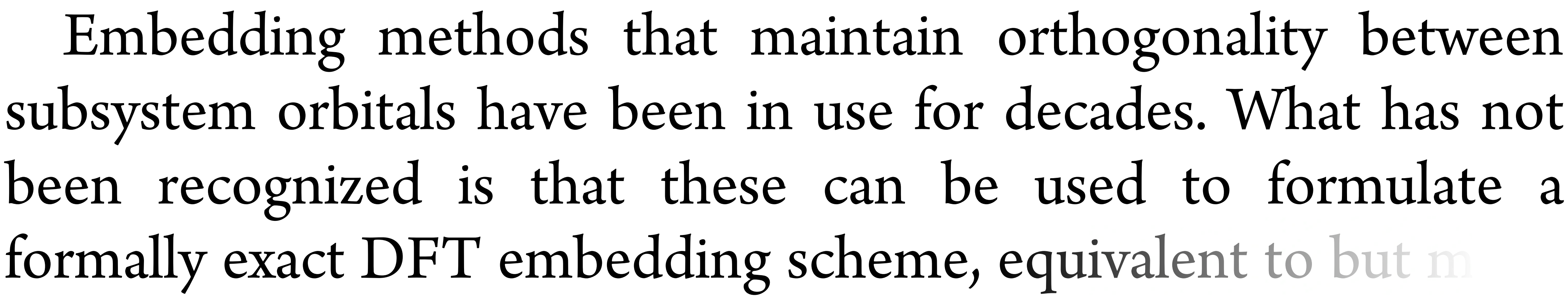
$$= T_s[\rho_A] + T_s[\rho_B] + \xcancel{\Delta T_s[\rho_A, \rho_B]}$$

Manby, Stella, Goodpaster, Miller, *JCTC* **8** 2564 (2012)

Long history of methods based on orthogonalization



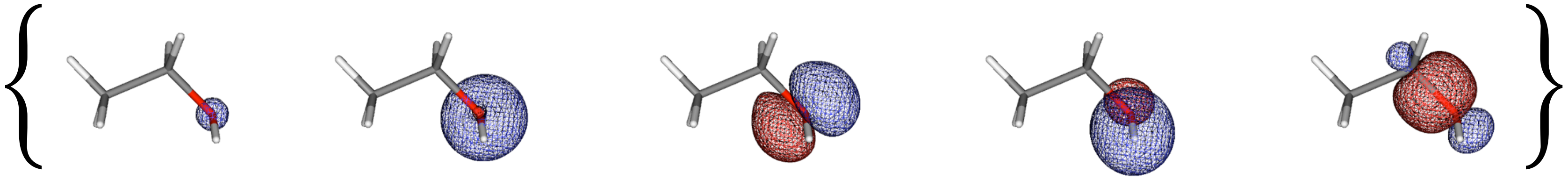
Embedding methods that maintain orthogonality between subsystem orbitals have been in use for decades. What has not been recognized is that these can be used to formulate a formally exact DFT embedding scheme, equivalent to but m

Manby, Stella, Goodpaster, Miller; *JCTC* **8** 2564 (2012)

- Treating π orbitals separately; frozen core orbitals
- Work by McWeeny (self-consistent electron groups)
- Huzinaga method
- Spatially localized local-correlation methods
- Frozen-core calculations

Calculating a subsystem density

- Take ethanol, localize KS orbitals
- Take A =



- Form projector (onto B orbitals):

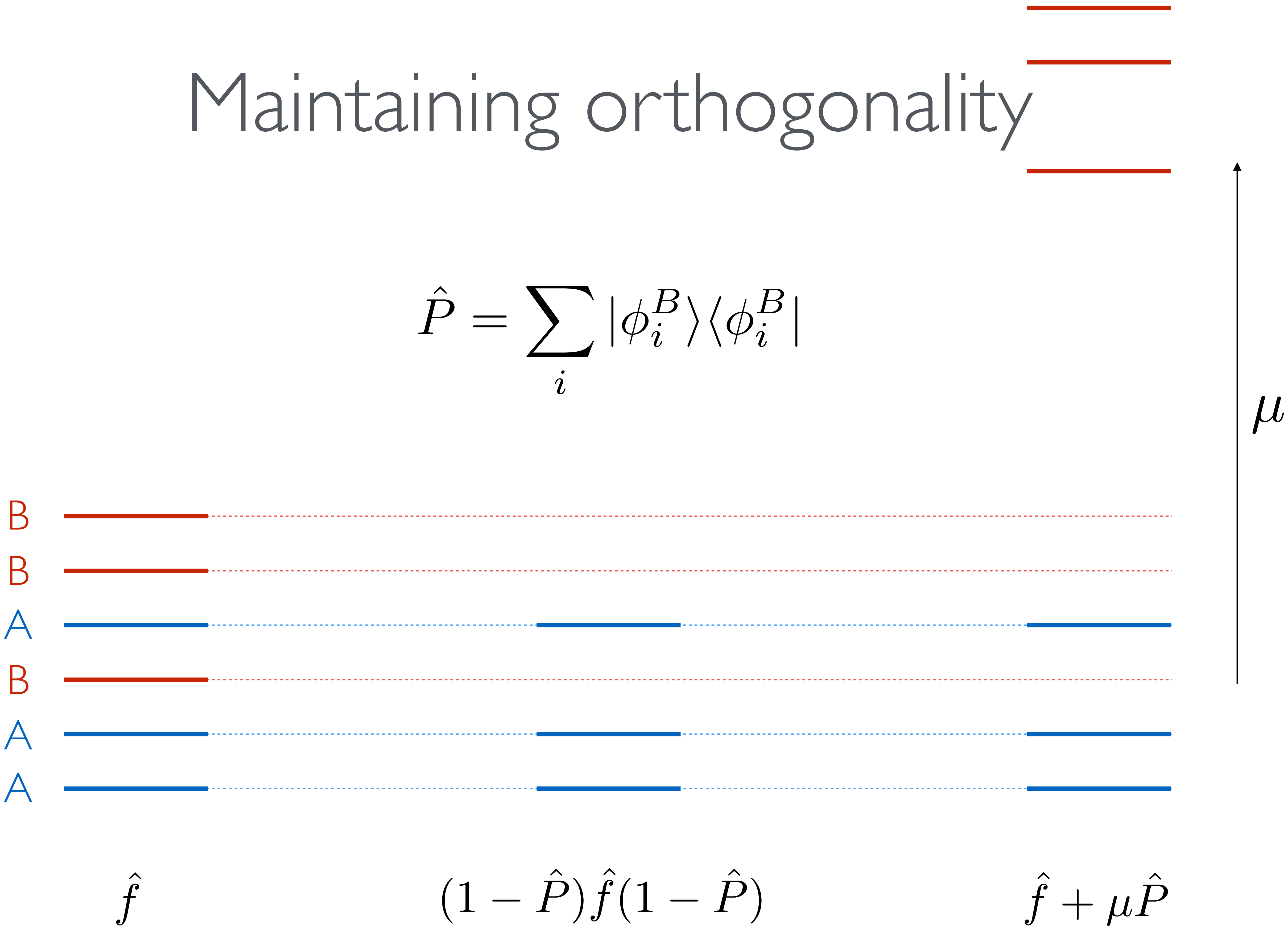
$$\hat{P} = \sum_i |\phi_i^B\rangle\langle\phi_i^B|$$

- Do a 10-electron KS calculation with

$$\hat{f}^A = (1 - \hat{P})\hat{f}(1 - \hat{P})$$

Maintaining orthogonality

$$\hat{P} = \sum_i |\phi_i^B\rangle\langle\phi_i^B|$$



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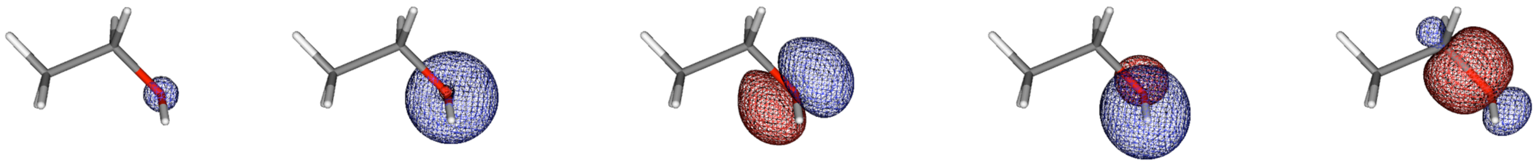


- Form projector (onto B orbitals):

$$\hat{P} = \sum_i |\phi_i^B\rangle\langle\phi_i^B|$$

- Do a 10-electron KS calculation with

$$\hat{f}^A = \hat{f} + \mu\hat{P}$$

Assembling the KS Fock matrix

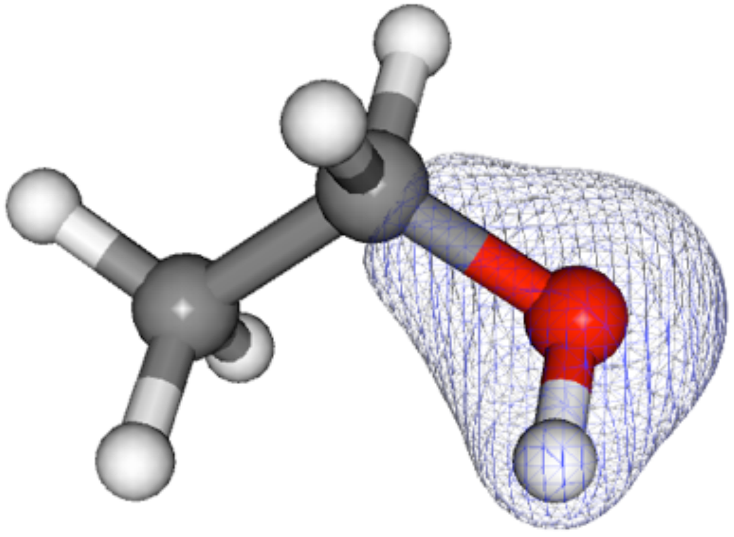
- All done in matrix form

$$\mathbf{F} = \mathbf{T} + \mathbf{V}^{\mathrm{nuc}} + \mathbf{J} + \mathbf{V}^{\mathrm{xc}}$$

- In embedding calculations, extra terms for coupling to subsystem B

$$\mathbf{F} = \mathbf{T} + \mathbf{V}^{\mathrm{nuc}} + \mathbf{J} + \mathbf{V}^{\mathrm{xc}} + \mu\mathbf{P} \qquad \mathbf{P} = \mathbf{S}\mathbf{D}^{\mathrm{B}}\mathbf{S}$$

Effect of μ

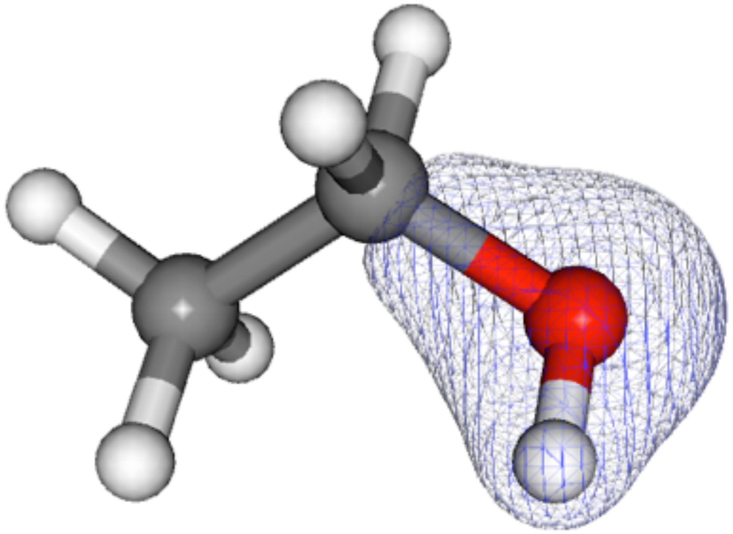


	energy / E_h
PBE on whole system	−154.82798488
PBE in PBE	−154.82800669

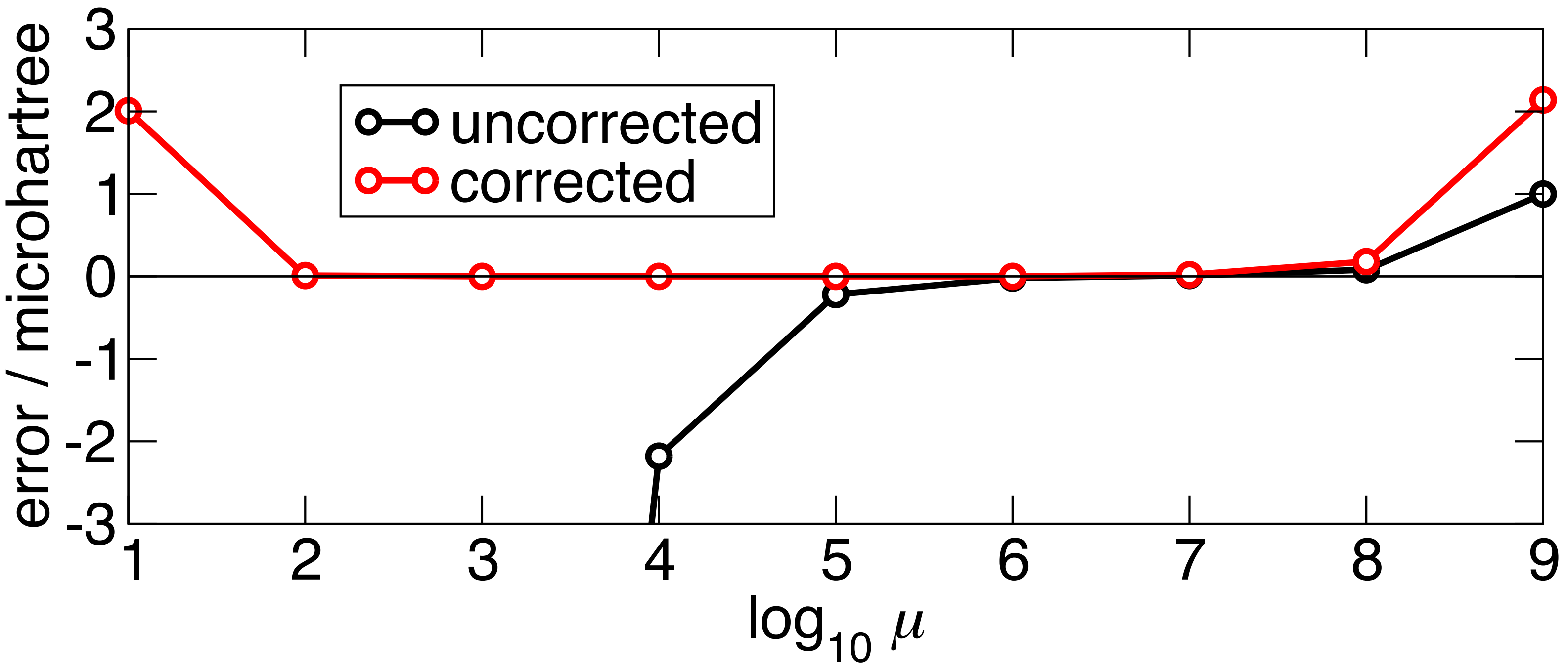
$$\hat{f}_0 = \hat{f} + \mu\hat{P} \qquad \hat{f}_\zeta = \hat{f} + \frac{\mu}{1-\zeta}\hat{P} \qquad \hat{f}_1 = \hat{f} + \infty\hat{P}$$

$$(\hat{f} + \mu\hat{P} + \mu\zeta\hat{P} + \cdots)(|0\rangle + \zeta|1\rangle + \cdots) = (\epsilon_0 + \zeta\epsilon_1 + \cdots)(|0\rangle + \zeta|1\rangle + \cdots)$$

Effect of μ



	energy / E_h
PBE on whole system	−154.82798488
PBE in PBE	−154.82800669
$\mu\,\mathrm{tr}\,\boldsymbol{\gamma}\mathbf{P}$	0.00002181
PBE in PBE + corr.	−154.82798488



Doing something useful

- Embedding with different mean-field methods

$$\mathbf{F} = \mathbf{T} + \mathbf{V}^{\mathrm{nuc}} + \mathbf{J} + \mathbf{V}^{\mathrm{xc},2}(\mathbf{D}^{\mathrm{A}}) - \mathbf{V}^{\mathrm{xc},1}(\mathbf{D}^{\mathrm{A}}) + \mathbf{V}^{\mathrm{xc},2}(\mathbf{D}) + \mu\mathbf{P}$$

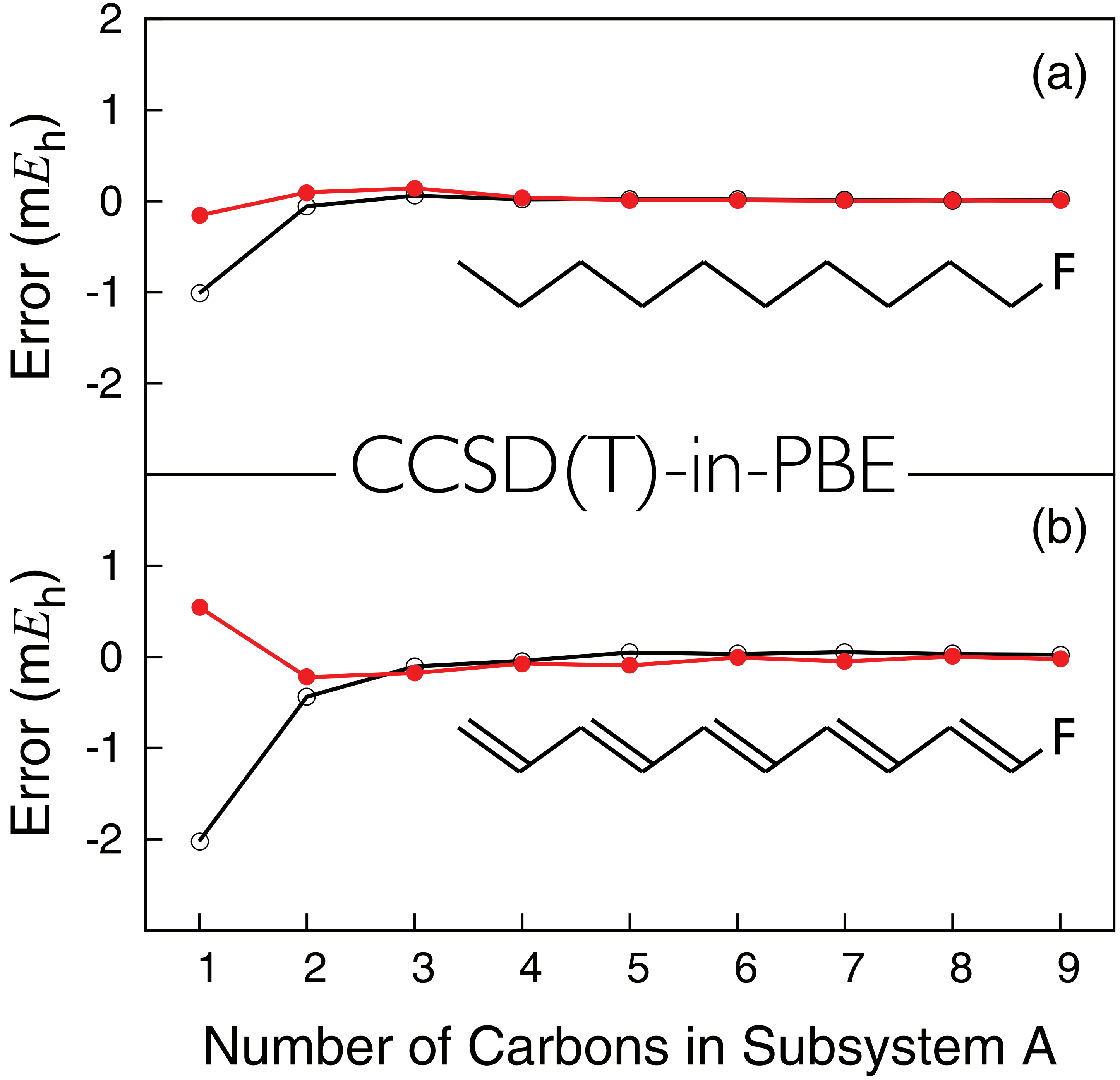
- Solve SCF to update $\mathbf{D}^{\mathrm{A}}$

- Go on to perform a correlated calculation in subsystem A

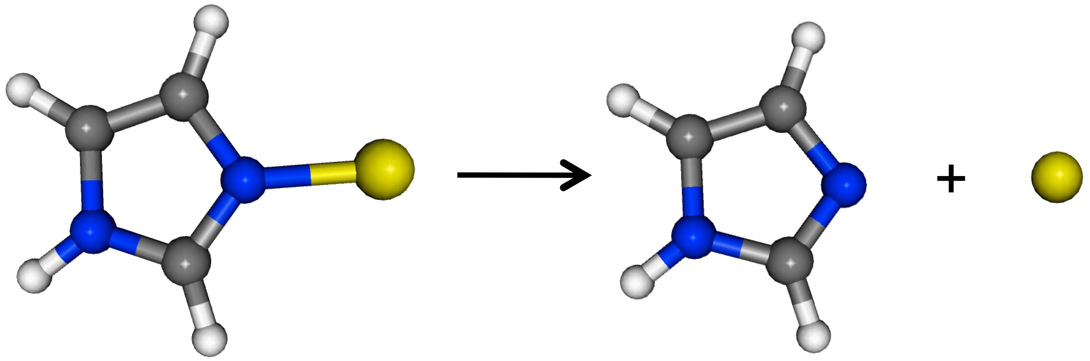
$$E = E_{\mathrm{DFT}} - E_{\mathrm{DFT-in-DFT}} + E_{\mathrm{WF-in-DFT}}$$

Fluorohydrocarbon exchange reaction

$$R\text{–}F + H_2 \longrightarrow R\text{–}H + HF$$

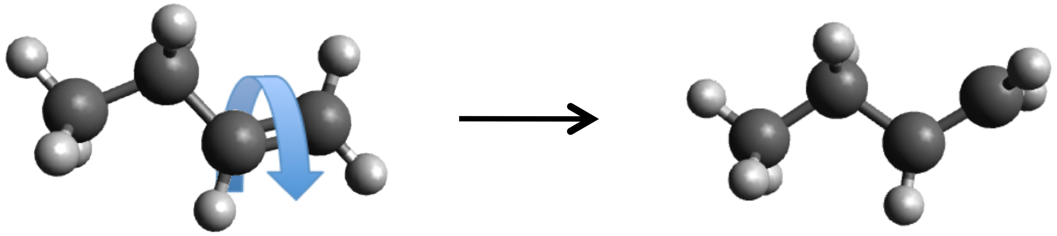


MRCI-in-DFT



method	**error wrt MRCI (mE_h)**
PBE	89.6
CCSD(T)	46.4
MRCI-in-PBE	–5.0

basis = aug-cc-pVTZ; full MRCI = 225.9 mE_h;
active = Fe, N

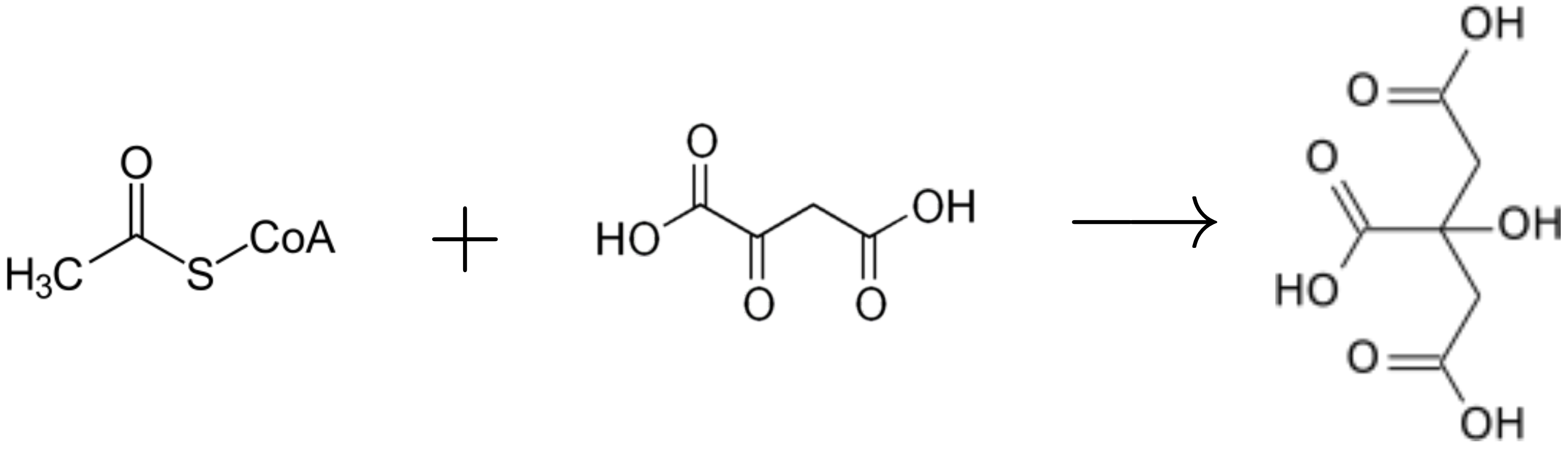


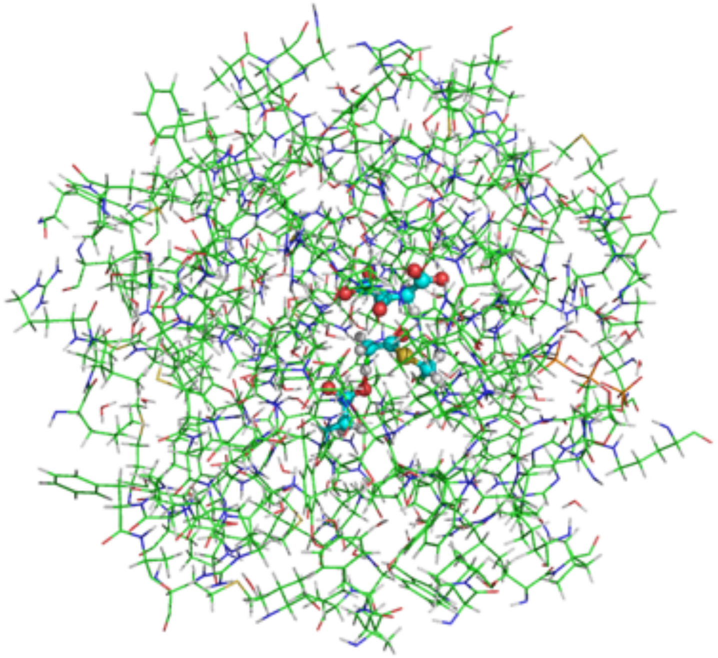
method	**error wrt MRCI (mE_h)**
PBE	79.7
CCSD(T)	63.1
MRCI-in-PBE	2.6

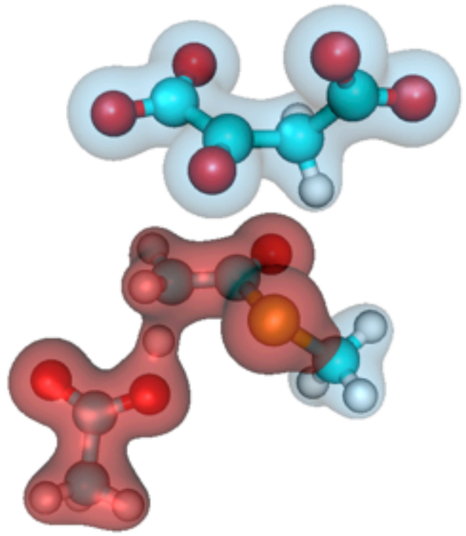
basis = aug-cc-pVTZ; full MRCI = 123.9 mE_h

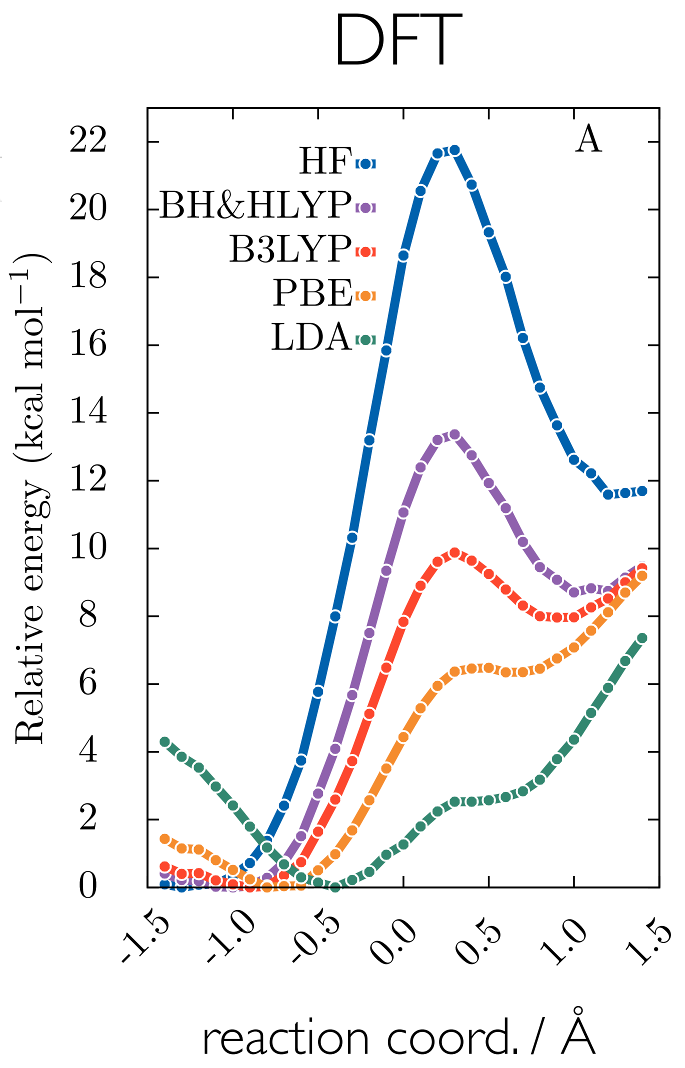
Jason Goodpaster

Citrate synthase: CCSD(T)-in-DFT-in-MM



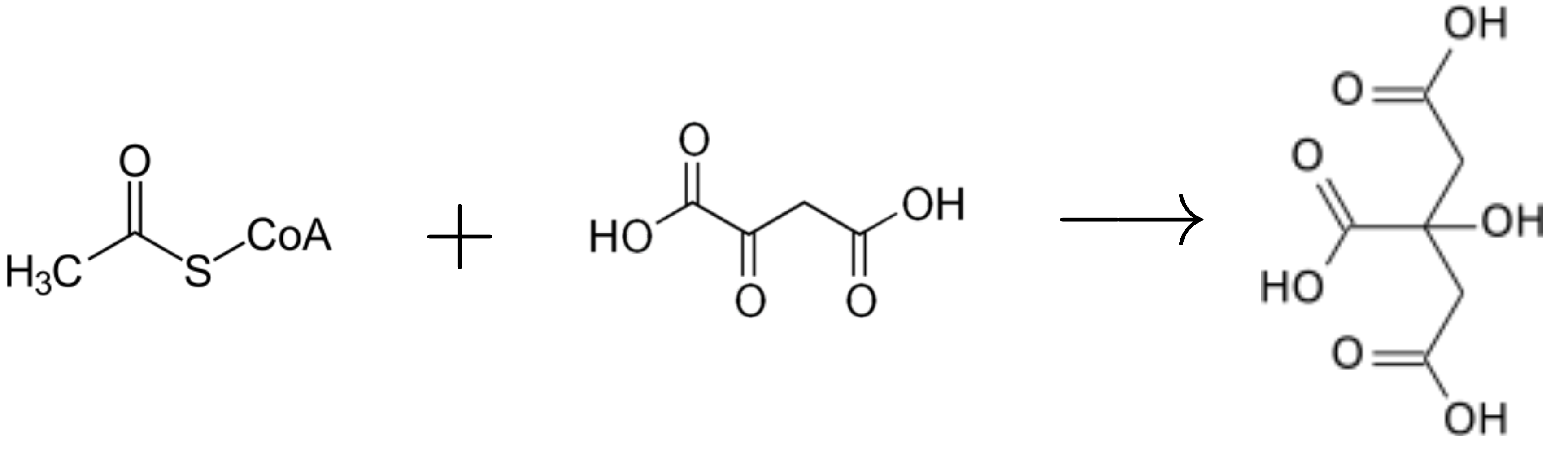


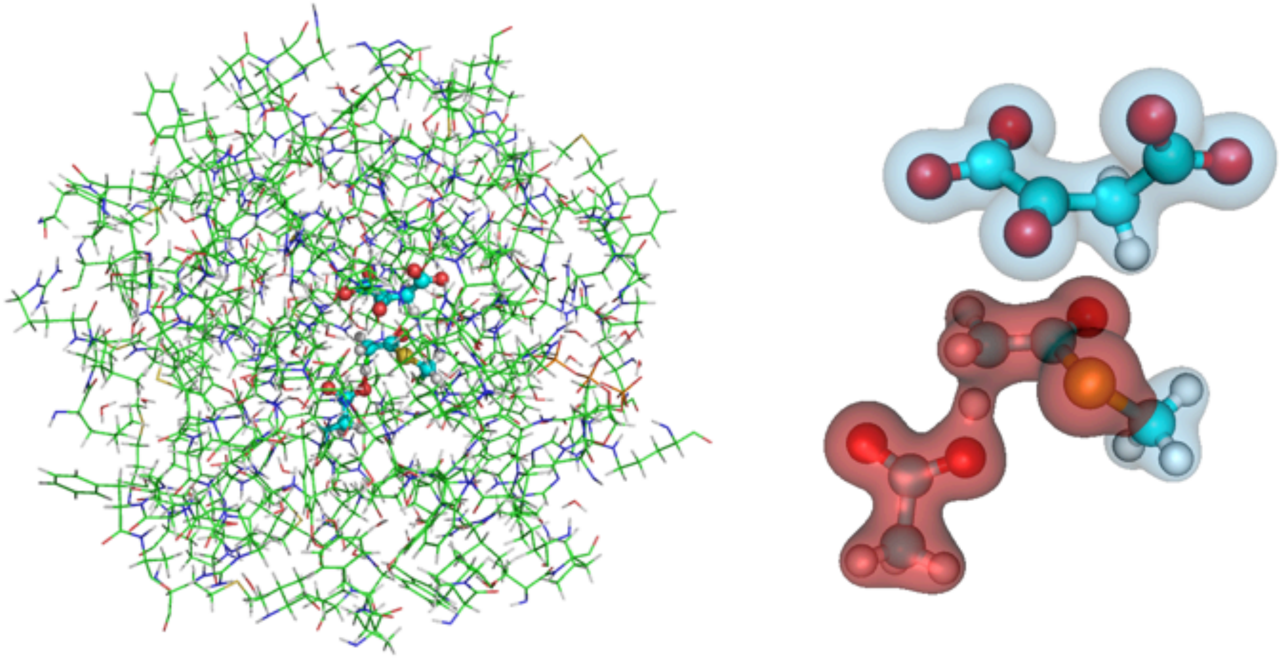




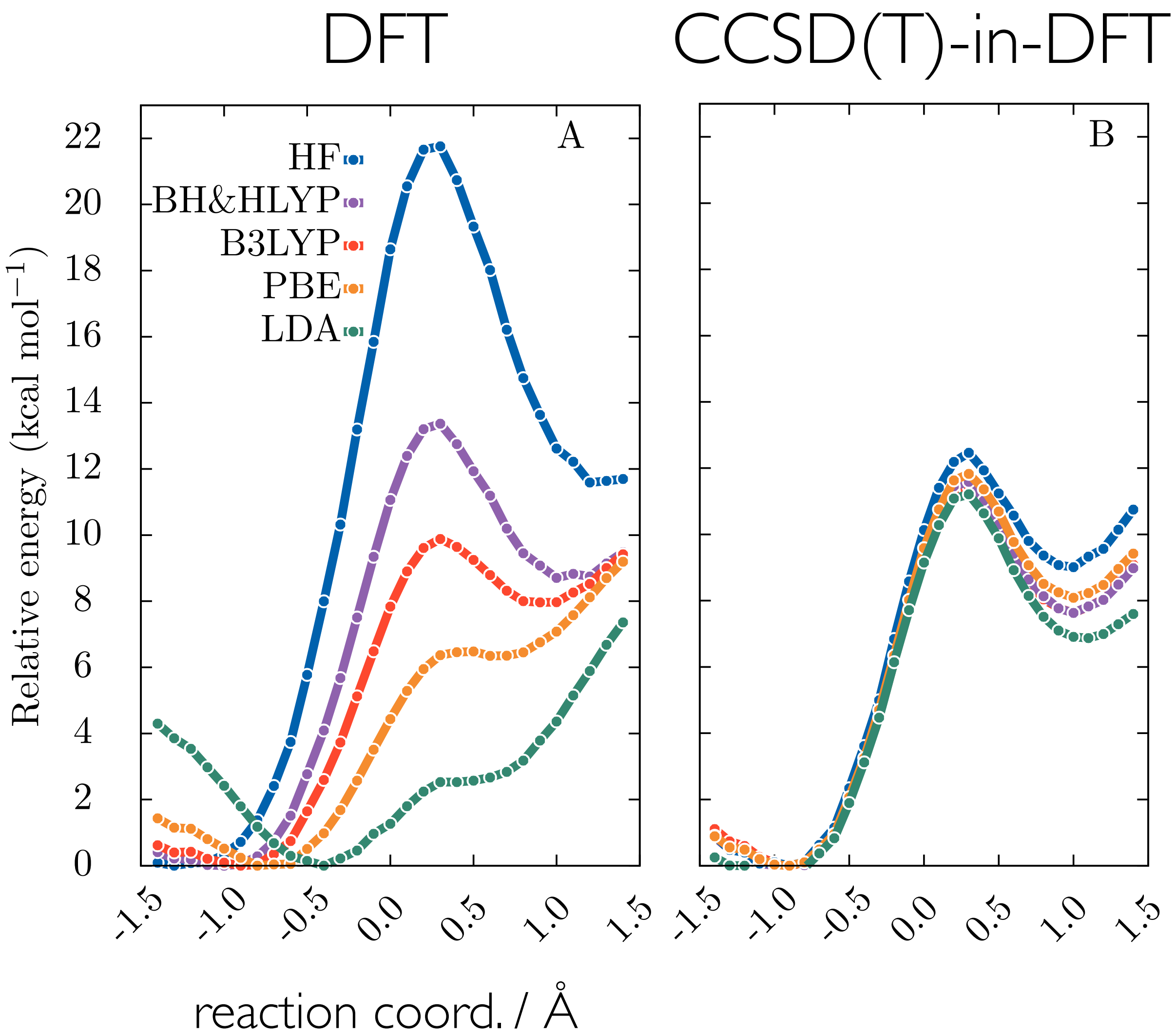
Bennie *et al.*, JCTC **12** 2689 (2016)

Citrate synthase: CCSD(T)-in-DFT-in-MM





Bennie *et al.*, JCTC **12** 2689 (2016)



Summary

- Wavefunctions are suitable descriptions of isolated systems
- States of a bit of a system are not (typically) pure states
- By making low-entanglement partitions, you can often get away with using wavefunctions in subsystems
- But eventually we need more and better embedding schemes that include correlations with the environment (and are widely applicable to chemical problems)