Implementation of Quantum Embedding Theories in CP2K

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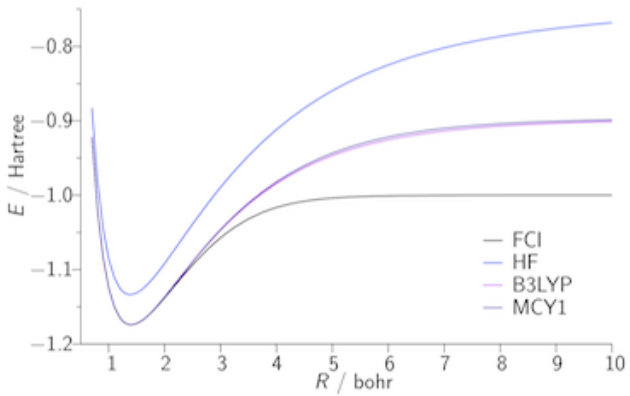
Strong/static correlation problem

H_2 dissociation curves



FCI - "exact", HF - Hartree-Fock, B3LYP and MCY1 - DFT variants (D. Tozer group, Durham)

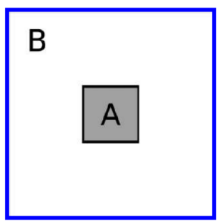
Physics approach: density functional theory (DFT)
Chemistry solution: correlated wave functions (CW)

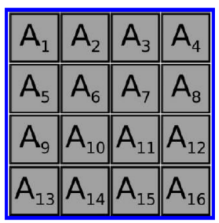
	DFT	CW
scaling	$O(N)$-$O(N^3)$	exponential
static correlation	no	yes
black-box	yes	no
periodic	yes	no

Condensed phase: CW methods non-tractable; DFT not accurate enough.

Subsystems and embedding theories

W. Zurek (Los Alamos): existence of quantum subsystems should be postulated in quantum mechanics.



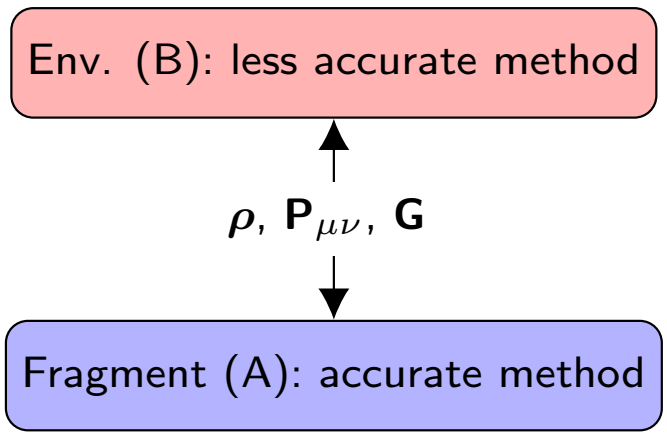


G. K. Chan, Caltech

Different methods for A and B. Similar to:

- QM/MM
- ONIOM
- subsystem DFT
- local quantum-chemical methods

Quantum interaction between subsystems:



- Electron density ρ: Density functional embedding theory, DFET
- One-particle density matrix $\mathbf{P}_{\mu\nu}$: Density matrix embedding theory, DMET
- One-particle Green's function $\mathbf{G}$: Self-energy embedding theory, SEET

Project goals and current status

Status of theories

DFET (Carter, Libisch et al.)

- Very complicated implementation
- Handful state-of-the art applications

DMET (Chan, Knizia et al.)

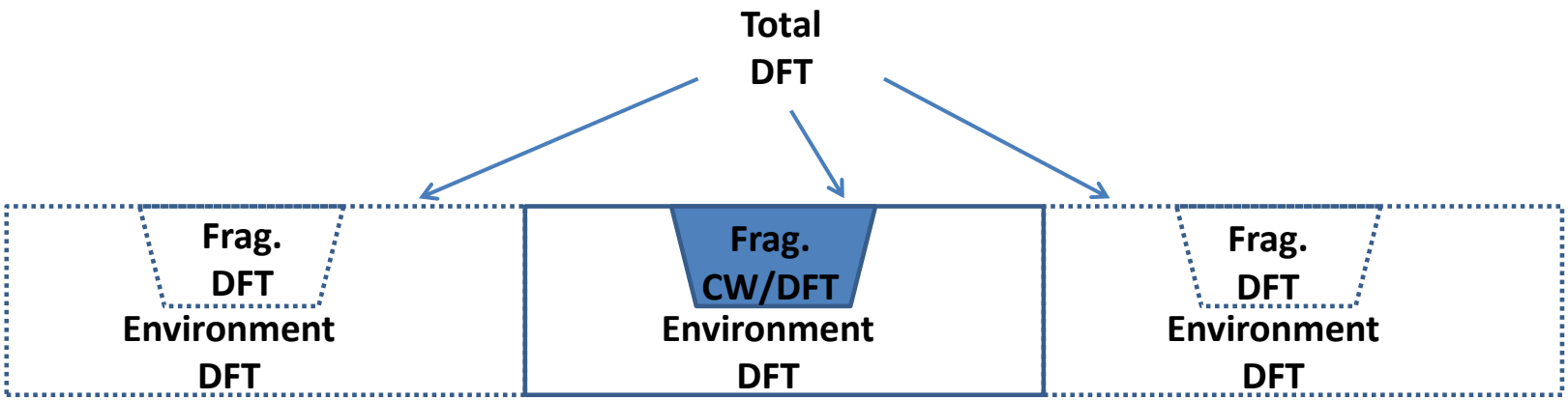
- Proof-of-the-concept
- "Toy" and model applications
- Some solid-state physics applications

Goals

- Improve the formalism and algorithms
- Make a simple and efficient implementation
- Use accurate DFT and modern CW
- Perform condensed-phase chemistry applications and bring to users

Density functional embedding (cluster-in-solid)

CW embedded in density functional theory (DFT).



$$E_{total} = E_{frag}[\rho_{frag}] + E_{env}[\rho_{env}] + E_{int}[\rho_{frag}, \rho_{env}], \tag{1}$$

Unique embedding potential can be defined:

$$\frac{\delta E_{int}}{\delta \rho_{frag}(\mathbf{r})} = \frac{\delta E_{int}}{\delta \rho_{env}(\mathbf{r})} = V_{emb}(\mathbf{r}). \tag{2}$$

DFT-CW formalism

$$W[V_{emb}] = E_{frag}[\rho_{frag}] + E_{env}[\rho_{env}] + \int V_{emb}(\rho_{frag} + \rho_{env} - \rho_{total})d\mathbf{r} \quad (3)$$

$$\frac{\delta W}{\delta V_{emb}(\mathbf{r})} = \rho_{frag}(\mathbf{r}) + \rho_{env}(\mathbf{r}) - \rho_{total}(\mathbf{r}) \to 0 \quad (4)$$

V_{emb} is optimized so that:

$$\rho_{total}^{DFT} = \rho_{frag}^{DFT} + \rho_{env}^{DFT} \quad (5)$$

V_{emb} is the interaction "felt" by enviromnent/fragment density at the DFT level:

$$E_{emb,frag}^{CW} = E_{frag}^{CW}[\rho_{frag}^{CW}] + \int V_{emb}\rho_{frag}\,d\mathbf{r} \quad (6)$$

$$E_{emb,frag}^{DFT} = E_{frag}^{DFT}[\rho_{frag}^{DFT}] + \int V_{emb}\rho_{frag}\,d\mathbf{r} \quad (7)$$

DFT-CW formalism

Final DFET energy is thus (in the perturbation theory fashion):

$$E_{total}^{DFET} = E_{total}^{DFT} + (E_{emb,frag}^{CW} - E_{emb,frag}^{DFT}) \tag{8}$$

In practice, V_{emb} is expanded in Gaussian functions $g(\mathbf{r})_i$:

$$V_{emb}(\mathbf{r}) = V_{const}(\mathbf{r}) + \sum_i b_i g(\mathbf{r})_i. \tag{9}$$

$W[V_{emb}]$ concave by construction: must be maximized wrt. $\mathbf{b}$.

Algorithm

- Calculate E^{DFT}_{total} and ρ_{total}
  - Construct trial V_emb
  - Calculate fragment and environment with V_emb
  - Check whether $\rho_{frag}(\mathbf{r}) + \rho_{env}(\mathbf{r}) = \rho_{total}(\mathbf{r})$
  - Calculate V_{emb} gradient
  - Update V_{emb}
  - Repeat until converged
- Calculate $E^{CW}_{emb,frag}$ and the total CW/DFT energy

Implementation details

- **MIXED_FORCE_EVAL** environment: no process partitioning
- Potential basis - RI auxiliary basis sets
- V_0 - nuclei reulsion and pseudopotentials
- Quasi-Newton level-shift maximizer
- Yang's regularization
- Full matrixes used
- Current convergence: 10^{-3}
- V_{emb} can be transferred as cube-file

Conceptual basis of DMET

G. Knizia and G. K. Chan, PRL 109: 186404 (2012)

- It principle, an exact theory based on **quantum entanglement** of the fragments
- Communication via one-particle density matrix $\mathbf{P}_{\mu\nu}$
- May be applicable for strongly interacting subsystems (strong coupling embedding)
- Allows crystal-in-crystal embedding

Technical details and challenges

- Unified formalism for CW and DFT, periodic and non-periodic calculations needed
- Improved DMET formalism for a more accurate environment methods
- Improved DFET formalism for a wider class of fragments
- Simple-to-use and efficient combination of CW and DFT software (CP2K)
- Some variants possible within CP2K

Conclusions and suggestions

- DFET in an advanced state in CP2K internally
- DMET is planned
- Ideas for internal CP2K method combinations?
- Ideas for interfacing software?
- Ideas for application?