

Frederick R. Manby,[†] Thomas F. Miller III,[‡] Fidel A. Batista Romero,[†] Peter J. Bygrave,[†] Callum B. A. Bungey,[†] Leanne D. Chen,[‡] Feizhi Ding,[‡] Thomas Dresselhaus,[†] Kaito Miyamoto,[†] Rocco Meli,[†] Casper Steinmann,[†] Takashi Tsuchiya,[†] Timothy C. Wiles[†]

[†]University of Bristol and [‡]California Institute of Technology



entos is a new density functional theory code with a focus on mean field embedding and first-principles molecular dynamics simulations. entos is written in modern C++ using state-of-the-art software engineering concepts and nested parallelisation, with the goal of being extensible, easy to maintain and fast.



Functionality	Embedded Mean-Field T	Embedded Mean-Field Theory (EMFT) [1]	
 Hartree-Fock and DFT Time-dependent DFT 	Density matrix partitioning:	Energy expression for DFT-in-DFT embedding:	
 Embedded Mean Field Theory (EMFT) 		$\sum E_{EMFT}[\mathbf{D}] = E^{L}[\mathbf{D}] - E^{L}[\mathbf{D}^{A}] + E^{H}[\mathbf{D}^{A}]$	

- Time-dependent EMFT
- Gaussian basis sets
- LDA, GGA, hybrid and dispersion-corrected functionals
- Coulomb and exact exchange density fitting
- DIIS and Fock extrapolation
- Fock-matrix corrections
- Ab initio Born-Oppenheimer molecular dynamics
- Nuclear quantum dynamics (RPMD)
- Effective core potentials
- Geometry optimisation
- Unsöld UW12 correlation in DFT

Software Engineering

• Extensive use of modern C++

- -Smart pointers
- Move semantics
- Input options from documentation • Extensive unit tests (w/ Catch2) • Nested parallelism (w/ Intel TBB)

aimd(nsteps = 10 $time_step = 0.5$ structure(molecule = 'h2o.xyz') save_trajectory_info = true extrapolation(

type = FMD nsteps = 4polynomial_degree = 2

gradient(



 \mathbf{D}^{AA} : Density matrix of the active region \mathbf{D}^{BB} : Density matrix of the environment $\mathbf{D}^{AB}, \mathbf{D}^{BA}$: Subsystems coupling

Advantages of EMFT:

- Parameter free
- Electron transfer between subsystems
- Reduced number of basis function
- Reduced cost of exchange calculation
- Simple gradient theory

Energy gradients w.r.t. nuclear coordinates:

 $\frac{\partial E}{\partial R}[\mathbf{D}] = \operatorname{Tr}\left(\mathbf{D}\mathbf{F}^{(R)}\right) - \operatorname{Tr}\left(\mathbf{W}\mathbf{S}^{(R)}\right)$

W: energy-weighted density matrix



Time-dependent linear response EMFT [2]





Description of excited states within EMFT.

TD-EMFT eigenvalue equation:

 $(A B \setminus (X))$



- -Generic SCF
- Multiple spin/particle channels
- -Generic Fock operators

dft(xc = 'PBE'basis = 'cc-pVDZ' density_fitting = true df_basis = 'cc-pVDZ-JKFIT'



Geometry Optimisation

Optimisation algorithm: Quasi-Newton method with BFGS Hessian update.



A new ingredient for DFT: Unsöld-W12 correlation [4]

Double-hybrids correlation (MP2):

$$E_c^{\mathsf{PT2}} = -\frac{1}{2} \sum_{ijab} \frac{\langle ij | r_{12}^{-1} | \overline{ab} \rangle \langle ab | r_{12}^{-1} | ij}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

Unsöld-W12 (UW12) correlation energy:

$$E_c^{\text{UW12}} = \frac{1}{2} \sum_{ijab} \langle ij | w_{12} | \overline{ab} \rangle \langle ab | r_{12}^{-1} | ij \rangle, \quad w^{s_{12}}(\mathbf{r}_{12}) = \frac{1}{(2s_{12}+1)} r_c e^{-r_{12}/r_c}$$

 w_{12} : geminal operator

Unsöld-W12 hybrid functional (XCH-BLYP-UW12): $E_{xc}^{\text{XCH-BLYP-UW12}} = \frac{1}{2}E_x^{\text{B88}} + \frac{1}{2}E_x^{\text{HF}} + \frac{3}{4}E_c^{\text{LYP}} + \frac{1}{4}E_c^{\text{UW12}}(r_c)$

Advantages of E_c^{UW12} over E_c^{PT2} : • Rapid basis-set convergence

20	I	I	
15	Atomization Energies	Reaction Barrier Heights	-
	_		

• Decoupling of different DOF • Simple initial Hessian estimate • Easy to apply constraints

 C_2H_5OH 17 5 -12 - 71% C_6H_6O 19 6 -13 -68% $C_3H_8O_3$ 52 13 -39 - 75% $C_9 H_8$ 16 6 -10 -63%

Transformations between cartesian coordinates (CC) and redundant internal coordinates (RIC) have been implemented in an open-source library written in modern C++.

github.com/RMeli/irc

References

[1] M. E. Fornace, J. Lee, K. Miyamoto, F. R. Manby and T. F. Miller, J. Chem. Theory Comput. **11**, 568-580 (2015).

[2] F. Ding, T. Tsuchiya, F. R. Manby and T. F. Miller III, J. Chem. Theory Comput. 13, 4216-4227 (2017).

[3] C. Peng, P. Y. Ayala and H. B. Schlegel, J. Comput. Chem. **17**, 49-56 (1996).

[4] T. C. Wiles and F. R. Manby, Submitted to J. Chem. Theory Comput. (April 2018).

• Avoid divergences in denominator

• Full self-consistent optimisation

• Straightforward gradient theory

• $\mathcal{O}(N^4)$ scaling



Acknowledgements

Some material is based upon work supported by the DOW Chemical Corporation under Award No. 227027AP and The California Institute of Technology and upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. F.R.M. acknowledge the Institute for Advanced Study at the University of Bristol and, together with T.T., support from the EPSRC (EP/M013111/1). T.F.M. additionally acknowledges support from a Camille and Henry Dreyfus Foundation Teacher-Scholar Award and an Alfred P. Sloan Foundation Research Fellowship and, together with F.D. support from the Air Force Office of Scientific Research under Award Number FA9550-17-1-010. F.B.R. is supported by a Newton International Fellowship from the Royal Society (NF170615). C.B., R.M. and T.C.W. are supported by the EPSRC Centre for Doctoral training in Theory and Modelling in Chemical Sciences (EP/L015722/1). K.M. acknowledges the support of Toyota Central R&D Laboratories and C.S. thanks the Danish Council for Independent Research (the Sapere Aude program) for financial support (Grant No. 4181-00370). We thank C. Woods for useful discussions.