

Updates from UGA

Dr. Justin M. Turney

Friday, November 14, 2014

DCFT

Energy Expression

Exact molecular energy can be expressed as

$$E = h_q^p \gamma_p^q + \frac{1}{4} \bar{g}_{rs}^{pq} \gamma_{pq}^{rs} \quad (1)$$

where

h_q^p : one-electron integrals

\bar{g}_{rs}^{pq} : antisymmetrized two-electron integrals

$\gamma_p^q / \gamma_{pq}^{rs}$: reduced one-/two-particle density matrices

An Alternative Energy Expression

Decompose γ_p^q into an idempotent part and a correction

$$\gamma_p^q = \kappa_p^q + \tau_p^q \quad (2)$$

Decompose γ_{pq}^{rs} to introduce λ_{pq}^{rs} : two-particle density cumulant

$$\gamma_{pq}^{rs} = \gamma_p^r \gamma_q^s - \gamma_p^s \gamma_q^r - \lambda_{pq}^{rs} \quad (3)$$

New energy expression

$$E = \frac{1}{2} (h_q^p + f_q^p) (\kappa_p^q + \tau_p^q) + \frac{1}{4} \bar{g}_{rs}^{pq} \lambda_{pq}^{rs} \quad (4)$$

Now, κ_p^q and λ_{pq}^{rs} can be independently varied (τ_p^q is a function of λ_{pq}^{rs}).

Preliminary Results

Performance of SA-DCFT is tested on S22 database at ODC-12/STO-3G

- $\Delta E = E_{SA-DCFT} - E_{SI-DCFT}$
- Speed-up = $t_{SI-DCFT}/t_{SA-DCFT}$
- The code is not fully spin-adapted (λ -residual equations are not 100% done)

Molecule	ΔE	Speed-up
<chem>C6H6</chem> ... <chem>C8H7N</chem>	3.9×10^{-14}	2.46
<chem>C4H4N2O2</chem> ... <chem>C4H4N2O2</chem>	3.3×10^{-14}	2.48
<chem>C6H6O</chem> ... <chem>C6H6O</chem>	-3.4×10^{-15}	2.53
<chem>C5H5N5</chem> ... <chem>C5H6N2O2</chem>	3.9×10^{-15}	3.02

- More tests are needed (with a larger basis set).

Future Work

- Finish coding the λ -residual part
- Remove redundant quantities from the code
- Symmetry and antisymmetry may be utilized for further adaptation
- Benchmark the SA-DCFT code with sufficient basis set

Concentric Atomic Density Fitting

Concentric Atomic Density Fitting

Theory

Psi4 is being used as a development environment for Concentric Atomic Density Fitting (CADF).

CADF utilizes auxiliary fitting functions for density $\rho_{\mu\nu}$ on the same centers as μ and ν within the Coulomb metric.

The two-electron integral tensor ($\mathbf{g}_{\mu\nu,\lambda\sigma}$) is approximated using a *robust* formulation, accurate to 2nd order in density error:

$$\mathbf{g}_{\mu\nu,\lambda\sigma} \approx \sum_X C_{\mu\nu}^X(X|\lambda\sigma) + \sum_Y C_{\lambda\sigma}^Y(\mu\nu|Y) - \sum_{XY} C_{\mu\nu}^X(X|Y)C_{\lambda\sigma}^Y \quad (5)$$

where μ , ν , λ , and σ represent AOs, and X and Y represent auxiliary functions.

This method is attractive due to its accuracy, efficiency, and scalability, having been tested with up to 1000 MPI instances on 4000 cores.

Concentric Atomic Density Fitting

Current Issues

The *robust* formulation is necessary for accurate energies.

Unfortunately, it causes $\mathbf{g}_{\mu\nu,\lambda\sigma}$ to lose its inherent positive semi-definiteness, which cause variational collapse to a state 100-100,000 Hartrees below canonical Hartree-Fock energy.

Problems generally arise when diffuse regions of electron density are poorly fit. This is problematic as by construction, CADF does not attempt to fit these regions well.

To deal with these issues, we wish to

- (1) construct auxiliary basis sets designed to minimize the number of negative eigenvalues of $\mathbf{g}_{\mu\nu,\lambda\sigma}$ in the CADF-SCF procedure (while still providing accurate energies) and
- (2) devise algorithms to remove negative eigenvalues which may still arise.

Current Use of Psi4

A Psi4 plugin has been written to perform CADF-SCF computations, and aid in the optimization of CADF fitting basis sets.

The plugin runs the CADF procedure using the C++ side of Psi4. It then uses the SciPy optimization module in the Python side of Psi4 to find the “best” fitting basis set.

Additionally, the Psi4 plugin will be used to test any algorithms devised to prevent further violations of positive semi-definiteness during CADF-SCF procedure.

While the true power of the method is its parallelizability in something like MPQC, but Psi4 has been integral in the facile development of Psi4.

Explicitly Correlated Methods

Explicitly Correlated Methods

Explicit correlation methods, which include functions explicitly dependent on the inter-electronic coordinate $f(r_{ij})$ into trial wave functions, have been developed to overcome the slow convergence of energies and properties with basis size in post-mean-field quantum chemical calculations.

For example, MP2-F12, CCSD-F12, etc.

Explicitly Correlated Methods

Yanai and Shiozaki proposed a new class of explicitly correlated theories using an effective Hamiltonian approach with the so-called canonical transformation (CT).

Dynamic correlation is described by a similarity transformation of the Hamiltonian \hat{H} using a unitary operation $e^{\hat{A}}$ with an operator $\hat{A} = -\hat{A}^\dagger$.

$$\begin{aligned}\hat{\hat{H}} &= e^{\hat{A}^\dagger} \hat{H} e^{\hat{A}} \\ &\approx \hat{H} + [\hat{H}, \hat{A}]_{1,2} + \frac{1}{2!} [[\hat{H}, \hat{A}]_{1,2}, \hat{A}]_{1,2} + \dots\end{aligned}$$

Explicitly Correlated Methods

Yanai and Shiozaki proposed a canonical transcorrelated Hamiltonian with the F12 operator.

$$\hat{\hat{H}} \equiv \hat{H} + [\hat{H}, \hat{A}^{F12}]_{1,2} + \frac{1}{2} [[\hat{F}, \hat{A}^{F12}]_{1,2}, \hat{A}^{F12}]_{1,2}$$

with

$$\hat{A}^{F12} = \frac{1}{2} G_{ij}^{\alpha\beta} (\hat{E}_{ij}^{\alpha\beta} - \hat{E}_{\alpha\beta}^{ij})$$

$$G_{ij}^{\alpha\beta} = \frac{3}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | ij \rangle + \frac{1}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | ji \rangle$$

$$F_{12} = -\gamma \exp(-\gamma r_{12})$$

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2$$

Explicitly Correlated Methods

The transformed Hamiltonian

$$\hat{H}^{F12} = \bar{h}_q^p \hat{E}_p^q + \frac{1}{2} \bar{g}_{qs}^{pr} \hat{E}_{pr}^{qs}$$

Where the one- and two-body perturbed elements are given by

$$\bar{h}_q^p = h_q^p + \frac{1}{2} (\bar{C}_{1q}^p \bar{C}_{1p}^q)$$

$$\bar{g}_{qs}^{pr} = g_{qs}^{pr} + \frac{1}{4} (\bar{C}_{2qs}^{pr} + \bar{C}_{2sq}^{rp} + \bar{C}_{2pr}^{qs} + \bar{C}_{2rp}^{sq})$$

Future Work

- Continue coding the method
- Investigate derivatives
- Perform extensive benchmarks against current F12 methods