RPA energy

Among numerous RPA correlation energy expressions that can be found in the literature, we will use the one based on the rCCD formulation[1]:

\[ E_{\text{RPA}}^{\text{E}} = \frac{1}{2} \langle \mathbf{BT} \rangle \]

where the RPA amplitudes \( \mathbf{T} \) satisfy the Riccati equation:

\[ \mathbf{R} = \mathbf{B} + \lambda (\mathbf{A} + \mathbf{TB}) + (\mathbf{A} + \mathbf{BT}) \lambda = 0 \]

solved iteratively for \( \lambda \) (much like Riccati is solved for \( \mathbf{T} \)).

The RPA correlation energy \( E_{\text{RPA}}^{\text{E}} \equiv E(\mathbf{T}, \mathbf{C}) \) is non-variational with respect to the excitation amplitudes \( \mathbf{T} \) and the orbital coefficients \( \mathbf{C} \).

Lagrangian framework

We introduce a Lagrangian \( \mathcal{L} \):

\[ \mathcal{L}(T, C, \lambda, z, x) = \frac{1}{2} \langle \mathbf{BT} \rangle + (\mathbf{AR}) + (z\mathbf{F}) + (x\mathbf{O}) \]

that associates the multipliers \( \lambda, z \) and \( x \) to the three rules the energy must fulfill: (1) the Riccati equation \( \mathbf{R} = 0 \) that define the amplitudes; (2) the Brillouin theorem \( (F_{aj} = 0) \) and (3) the orthonormality of the orbitals \( (O = C^{\dagger}SC - 1 = 0) \) that constrain the orbital coefficients.

In order to calculate the gradient \( \frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \mathbf{E}^{(T)} \), the multipliers must make \( \mathcal{L} \) stationary w.r.t. \( \mathbf{T} \) and \( \mathbf{C} \).

RPA gradients

Stationary condition with respect to \( \mathbf{T} \):

\[ \frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \mathbf{B} + \lambda (\mathbf{A} + \mathbf{TB}) + (\mathbf{A} + \mathbf{BT}) \lambda = 0 \]

solved iteratively for \( \lambda \) (much like Riccati is solved for \( \mathbf{T} \)).

Stationary condition with respect to \( \mathbf{C} \) boils down to the following form of CPHF equations:

\[ (\Theta - \Theta) + \mu x - \mathbf{z} \mathbf{F} + 4g(\mathbf{z}) = 0 \]

\[ (1 + \tau_{xy})(\Theta + \Theta) = -2(x)_{xy} \]

Comparison to MP2 gradients

Lagrangian multipliers

1. \( \lambda = \mathbf{T} \) make the Hylleraas functional stationary condition w.r.t. \( \mathbf{T} \)
2. \( \mathbf{x} \) and \( \mathbf{z} \) are obtained from the same CPHF equations, with
   (a) \( \Theta(\mathbf{z})^{\text{MP2}} = \bar{\Theta}(\mathbf{z})^{\text{RPA}} \) (keeping in mind that \( \lambda = \mathbf{T} \))
   (b) \( \Theta(\mathbf{z})^{\text{MP2}} = 2[\bar{\Theta}(\mathbf{B}, \mathbf{T}) + (\mathbf{g}(\mathbf{d}))^{(2)}]_{\mu \nu} \)
   (c) \( \Theta(\mathbf{z})^{\text{RPA}} = 2[\bar{\Theta}(\mathbf{B}, \mathbf{T} + \lambda + \mathbf{T} \lambda) + \bar{\Theta}(\mathbf{B}, \mathbf{T} + \lambda + \mathbf{T} \lambda) + (\mathbf{g}(\mathbf{d}))^{(2)}]_{\mu \nu} \)

Contracted matrices

1. \( \mathbf{D}^{\dagger}, \mathbf{X}^{\dagger}, \mathbf{D}^{\dagger} \) and \( \mathbf{D}^{\dagger} \) are given by the same expressions in MP2 and in RPA.
2. \( \mathbf{d}^{(2)} = 2(\mathbf{T} \mathbf{T}) \) : the second order correction to the 1PDM
3. \( (\mathbf{G})^{(2)}_{\mu \nu, \rho \sigma} = C_{\rho}C_{\nu}C_{\sigma}C_{\rho}C_{\sigma}(2\mathbf{T})_{\mu \nu, \rho \sigma} \)

- Notations -

\( \langle XY \rangle = \text{tr}(XY) \)
\( (\mathbf{A})_{\mu \nu, \rho \sigma} = F_{\mu \rho}d_{\rho \sigma} - (\mathbf{F}_{\mu \rho}d)_{\rho \sigma} + (\mathbf{B})_{\mu \nu, \rho \sigma} = (\mathbf{F})_{\mu \rho}d_{\rho \sigma} \)
\( \langle XY \rangle_{\mu \nu, \rho \sigma} = X_{\mu \nu, \rho \sigma}Y_{\rho \sigma} \)
\( \langle XY \rangle_{\mu \nu, \rho \sigma, \tau \delta} = X_{\mu \nu, \rho \sigma}Y_{\tau \delta} \)
\( g(\mathbf{d})_{\rho \sigma} = \delta_{\rho \sigma} - \frac{1}{2} |\mathbf{d}|_{\rho \sigma} \)

Conclusion and outlook

> Most ingredients appearing in the RPA and MP2 gradient expressions are similar.
> Additional terms appear in the RPA definition of \( \Theta \) and \( \mathbf{F}^{\dagger} \).
> Gradients of “mixed” RPA energy expressions need further derivation (e.g. Szabo-Oslund variant).
> Extension to density fitting is straightforward.

Programming of RPA gradients (in progress)

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1. Ángyán et al. JCTC 7 (2011) 3116