Analytical forces for Random Phase Approximation using a Lagrangian framework

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RPA energy

detailed ref : [1]

Among numerous RPA correlation energy expressions that can be found in the literature, we will use the one based on the rCCD formulation[2] :

$$E_c^{\mathrm{RPA}} = \frac{1}{2}\langle \mathbf{BT} \rangle$$

where the RPA amplitudes $\mathbf{T}$ satisfy the **Riccati equation** :

$$\mathbf{R} = \mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}$$

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

Lagrangian framework

We introduce a Lagrangian $\mathcal{L}$:

$$\mathcal{L}(\mathbf{T}, \mathbf{C}, \boldsymbol{\lambda}, \mathbf{z}, \mathbf{x}) = \tfrac{1}{2}\langle \mathbf{BT} \rangle + \langle \boldsymbol{\lambda} \mathbf{R} \rangle + \langle \mathbf{zF} \rangle + \langle \mathbf{xO} \rangle$$

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

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

RPA gradients

Stationary condition with respect to $\mathbf{T}$:

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

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

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

$$\left(\boldsymbol{\Theta} - \boldsymbol{\Theta}^\dagger + \mathbf{Fz} - \mathbf{zF} + 4\mathbf{g}(\mathbf{z})\right)_{ai} = 0$$
$$(1 + \tau_{pq})\left(\boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z})\right)_{pq} = -2(\mathbf{x})_{pq}$$

Once the multipliers are known, the gradient of the energy is easily expressed by matrices in the AO basis :

$$E\,(\mathbf{T}, \mathbf{C})^{(x)} = \langle \mathbf{D}^{①} \mathbf{H}^{(x)} \rangle + \langle \mathbf{X}^{①} \mathbf{S}^{(x)} \rangle + \left(\mathbf{D}^{②} + \boldsymbol{\Gamma}^{②}\right)_{\mu\nu,\rho\sigma} (\mu\nu|\rho\sigma)^{(x)}$$

where :

$$\mathbf{D}^{①} = \mathbf{C}\left(\mathbf{d}^{(2)} + \mathbf{z}\right)\mathbf{C}^\dagger = \mathbf{D}^{(2)} + \mathbf{Z} \quad ; \quad \mathbf{d}^{(2)} = \{\mathbf{T}\boldsymbol{\lambda}\} + \{\boldsymbol{\lambda}\mathbf{T}\}$$
$$\mathbf{X}^{①} = \mathbf{C}\mathbf{x}\mathbf{C}^\dagger$$
$$(\mathbf{D}^{②})_{\mu\nu,\rho\sigma} = \left((\mathbf{D}^{(2)} + \mathbf{Z})_{\mu\nu}\mathbf{D}^{(0)}_{\rho\sigma} - \frac{1}{2}(\mathbf{D}^{(2)} + \mathbf{Z})_{\mu\rho}\mathbf{D}^{(0)}_{\nu\sigma}\right)$$
$$(\boldsymbol{\Gamma}^{②})_{\mu\nu,\rho\sigma} = C_{\mu i}C_{\nu a}C_{\rho j}C_{\sigma b}\left(\boldsymbol{T} + \boldsymbol{\lambda} + \boldsymbol{T\lambda} + \boldsymbol{\lambda T} + \boldsymbol{T\lambda T}\right)_{ia,jb}$$

correlation correction to the 1PDM

Comparison to MP2 gradients

Lagrangian multipliers

1. $\boldsymbol{\lambda} = \mathbf{T}$ 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) $\tilde{\boldsymbol{\Theta}}(\mathbf{z})^{\mathrm{MP2}} = \tilde{\boldsymbol{\Theta}}(\mathbf{z})^{\mathrm{RPA}}$ (keeping in mind that $\boldsymbol{\lambda} = \mathbf{T}$)
   (b) $(\boldsymbol{\Theta})_{ai}^{\mathrm{MP2}} = 2\left(2\{\bar{\mathbf{B}}, \mathbf{T}\} + \mathbf{g}(\mathbf{d}^{(2)})\mathbf{d}^{(0)}\right)_{ai}$
   $(\boldsymbol{\Theta})_{ai}^{\mathrm{RPA}} = 2\left(\{\bar{\mathbf{B}}, \mathbf{T} + \boldsymbol{\lambda} + \mathbf{T}\boldsymbol{\lambda}\mathbf{T}\} + \{\bar{\mathbf{A}}', \mathbf{T}\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{T}\} + \mathbf{g}(\mathbf{d}^{(2)})\mathbf{d}^{(0)}\right)_{ai}$

Contracted matrices

1. $\mathbf{D}^{①}$, $\mathbf{X}^{①}$ and $\mathbf{D}^{②}$ are given by the same expressions in MP2 and in RPA. (keeping in mind that their elements are different).
2. $\mathbf{d}^{(2)} = 2\{\mathbf{TT}\}$: the second order correction to the 1PDM
3. $(\boldsymbol{\Gamma}^{②})_{\mu\nu,\rho\sigma} = C_{\mu i}C_{\nu a}C_{\rho j}C_{\sigma b}\,(2\boldsymbol{T})_{ia,jb}$

- Notations -

$$\langle \mathbf{XY} \rangle = tr(\mathbf{XY})$$
$$(\mathbf{A})_{ia,jb} = F_{ab}\delta_{ij} - F_{ij}\delta_{ab} + \langle ib||ja \rangle = (\boldsymbol{\epsilon})_{ia,jb} + (\mathbf{A}')_{ia,jb}$$
$$(\mathbf{B})_{ia,jb} = \langle ij||ab \rangle$$
$$\{\mathbf{XY}\}_{ij} = X_{\mathbf{i}a,kc}Y_{kc,\mathbf{j}a}$$
$$\{\mathbf{XY}\}_{ab} = X_{i\mathbf{a},kc}Y_{kc,i\mathbf{b}}$$
$$\mathbf{g}(\square)_{pq} = \square_{rs}\left(\langle pr|qs \rangle - \frac{1}{2}\langle ps|rq \rangle\right)$$

Conclusion and outlook

- Most ingredients appearing in the RPA and MP2 gradient expressions are **similar**.
- Additional terms appear in the RPA definition of $\boldsymbol{\Theta}$ and $\boldsymbol{\Gamma}^{②}$
- Gradients of "mixed" RPA energy expressions need further derivation (e.g. Szabo-Oslund variant)
- Extension to **density fitting** is straighforward

. Programming of RPA gradients (in progress) follows a similar structure as that of MP2 gradients.

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