Analytical Gradients of Random Phase Approximation Correlation Energies in Range-Separated-Hybrid Context : Theory and Implementation

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$$E_{\rm RSH}^{\rm SR,LR} = \langle \mathbf{d}^{(0)}\mathbf{f}\rangle + {\rm DC}$$
$$E_{\rm RPA}^{\rm LR} = \langle \mathbf{IT}\rangle$$

(*cf.* [1] for review and [4,5,6] for rCCD)

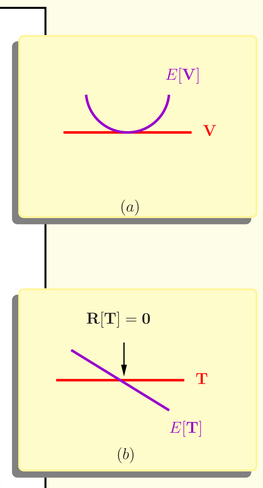
Lagrangian framework

An energy that depends on stationary parameters $\mathbf{V}$ (a) and non-stationary parameters $\mathbf{T}$ associated with rules $\mathbf{R}[\mathbf{T}] = \mathbf{0}$ (b) has a gradient $\frac{\partial E}{\partial x} = E^{(x)}$ of the form :

$$E^{(x)} = \frac{\partial E}{\partial \mathbf{h}}\mathbf{h}^{(x)} + \frac{\partial E}{\partial (\mu\nu|\sigma\rho)}(\mu\nu|\sigma\rho)^{(x)} + \frac{\partial E}{\partial \mathbf{S}}\mathbf{S}^{(x)} + \frac{\partial E}{\partial \mathbf{T}}\mathbf{T}^{(x)}$$

where we wish to avoid the calculation of $\mathbf{T}^{(x)}$. We introduce a Lagrangian (c) that is equal to the energy at the proper parameters *and* is made stationary w.r.t. all its parameters. Its gradient is simply :

$$\mathcal{L}^{(x)} = \frac{\partial \mathcal{L}}{\partial \mathbf{h}}\mathbf{h}^{(x)} + \frac{\partial \mathcal{L}}{\partial (\mu\nu|\sigma\rho)}(\mu\nu|\sigma\rho)^{(x)} + \frac{\partial \mathcal{L}}{\partial \mathbf{S}}\mathbf{S}^{(x)}$$



RSH-RPA lagrangian

$$\mathcal{L} = E_{\rm RSH}^{\rm SR,LR} + E_{\rm RPA}^{\rm LR} + \langle \boldsymbol{\lambda}\mathbf{R}\rangle + \langle \mathbf{zf}\rangle + \langle \mathbf{x}\mathbf{C}^\dagger\mathbf{S}\mathbf{C} - \mathbf{1}\rangle$$

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

In order to calculate the gradient $(E_{\rm RSH}^{\rm SR,LR} + E_{\rm RPA}^{\rm LR})^{(x)}$, the multipliers must make $\mathcal{L}$ stationary w.r.t. $\mathbf{T}$ and $\mathbf{C}$.

RSH-RPA gradients

Stationary condition with respect to $\mathbf{T}$: $\frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \mathbf{I} + \boldsymbol{\lambda}\frac{\partial \mathbf{R}}{\partial \mathbf{T}} = \mathbf{0}$
solved iteratively for $\boldsymbol{\lambda}$ (much like Riccati is solved for $\mathbf{T}$).

Stationary condition with respect to $\mathbf{C}$ with $\mathcal{L}$ rewritten :

$$\mathcal{L} = \langle \left(\mathbf{d}^{(0)} + \mathbf{z} + \mathbf{d}^{(2)}\right)\mathbf{f}\rangle + {\rm DC} + \langle \mathbf{KM}\rangle + \langle \mathbf{K'N}\rangle + \langle \mathbf{JO}\rangle + \langle \mathbf{x}(\mathbf{C}^\dagger\mathbf{S}\mathbf{C} - \mathbf{1})\rangle$$

they boil down to the following **CP-RPA** equations :

$$\left(\boldsymbol{\Theta} - \boldsymbol{\Theta}^\dagger + \mathbf{fz} - \mathbf{zf} + 4\mathbf{g}^{\rm LR}(\mathbf{z}) + 4\mathbf{W}^{\rm SR}[\mathbf{z}]\right)_{ai} = 0$$
$$-\tfrac{1}{4}\left(1 + \tau_{pq}\right)\left(\boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z})\right)_{pq} = (\mathbf{x})_{pq} = (\mathbf{x}_{\rm RPA})_{pq} - 2(\mathbf{f})_{pq}$$

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

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

where :

$$\mathbf{D}^1 = \mathbf{C}\left(\mathbf{d}^{(0)} + \mathbf{d}^{(2)} + \mathbf{z}\right)\mathbf{C}^\dagger = \mathbf{D}^{(0)} + \mathbf{D}^{(2)} + \mathbf{Z}$$
$$(\mathbf{D}^2)_{\mu\nu,\sigma\rho} = \left((\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)} + \mathbf{Z})_{\mu\nu}\mathbf{D}^{(0)}_{\sigma\rho} - \frac{1}{2}(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)} + \mathbf{Z})_{\mu\sigma}\mathbf{D}^{(0)}_{\nu\rho}\right)$$
$$(\boldsymbol{\Gamma}^2)_{\mu\nu,\sigma\rho} = C_{\mu k}C_{\nu j}C^\dagger_{c\rho}C^\dagger_{b\sigma}(\mathbf{M})_{ia,kc} + C_{\mu k}C_{\nu j}C^\dagger_{b\rho}C^\dagger_{c\sigma}(\mathbf{N})_{ia,kc} + C_{\mu k}C_{\nu b}C^\dagger_{j\rho}C^\dagger_{c\sigma}(\mathbf{O})_{ia,kc}$$

${\rm SR}^{(x)}$ is the derivative of the short-range functional (lengthy)

$\mathbf{d}^{(2)} = \{\mathbf{T}\boldsymbol{\lambda}\} + \{\boldsymbol{\lambda}\mathbf{T}\}$

Validation and (some) Results

Intermolecular energies after optimisation (deviations from W1 ref., in $kJ.mol^{-1}$)

	LDA-dRPA	LDA-MP2
$H_3N{-}NH_3$	-1.26	1.46
$HF{-}FH$	2.49	3.86
$H_2O{-}OH_2$	2.02	4.48
$H_3N{-}OH_2$	1.08	4.14

energies are improved for dimers of the **HB6 subset** of the NCCE31[2] set

Interatomic distances (deviations from exp. data, in pm)

		LDA-dRPA	LDA-MP2
HNC	H−N	0.2	0.4
HCN	H−C	0.1	0.2
CH4	C−H	0.0	-0.1
CH2	C−H	-0.3	-0.4
HOF	**O−F**	**0.8**	**-5.0**

challenging bonds are better described than at the LDA-MP2 level

Conclusion and outlook

- **analytical gradient of the RSH-RPA** correlation energy
- **all-in-one derivation of a SR+LR gradient**
- **implemented in the MOLPRO** package, using pre-existing MP2 gradients[3]
- automatic geometry optimisations are possible
- preliminary results of **correlated multipole moments** calculated at the RSH+RPA level
- improvement of the results is expected for srPBE and for other RPA variants (e.g. SO2)
- extension to **density fitting** is straighforward

- Notations -

- DC stands for « Double-Counting »
- $\mathbf{I}$, $\mathbf{K}$, $\mathbf{K'}$ and $\mathbf{J}$ are two-electronic integrals
- $\langle \mathbf{XY}\rangle = {\rm tr}(\mathbf{XY})$
- $\{\mathbf{XY}\}_{ij} = X_{\mathbf{i}a,kc}Y_{kc,\mathbf{j}a}$; $\{\mathbf{XY}\}_{ab} = X_{i\mathbf{a},kc}Y_{kc,i\mathbf{b}}$
- $\mathbf{g}(\mathbf{X})_{pq} = \mathbf{X}_{rs}\left(\langle pr|qs\rangle - \frac{1}{2}\langle ps|rq\rangle\right)$
- $\mathbf{W}^{\rm SR}[\mathbf{z}]$ is the short-range counterpart of $\mathbf{g}(\mathbf{z})$ (lengthy expression, but good similarity between them)

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