Analytical Gradients of Random Phase Approximation correlation energies in a Range-Separated-Hybrid context : Theory and implementation

Bastien Mussard, János G. Ángyán

CRM^2, Université de Lorraine, Nancy, France

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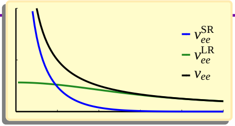
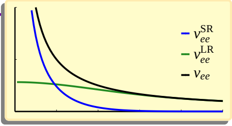
Theoretical Context

Range Separation

Inter-electronic interaction $\dfrac{1}{\mathbf{r}} = v_{ee}^{\mathrm{lr}}(\mathbf{r}) + v_{ee}^{\mathrm{sr}}(\mathbf{r})$



Range Separation



Inter-electronic interaction $\frac{1}{\mathbf{r}} = v_{ee}^{\mathsf{lr}}(\mathbf{r}) + v_{ee}^{\mathsf{sr}}(\mathbf{r})$

$$E = \min_n \left\{ F[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

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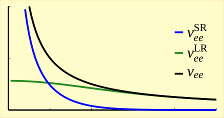

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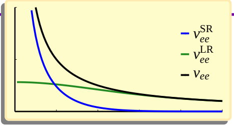
$$E = \min_{n}\left\{ F[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

$$= \min_{n}\left\{ F^{\mathrm{lr}}[n] + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

Range Separation



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$$E = \min_n \left\{ F[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$
$$= \min_n \left\{ F^{\mathrm{lr}}[n] + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$
$$= \min_\Psi \left\{ \langle \Psi | \, \hat{T} + \hat{V}_{ee}^{\mathrm{lr}} \, | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_\Psi] + \int n_\Psi(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}$$

Range Separation

Inter-electronic interaction

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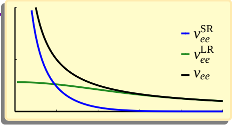
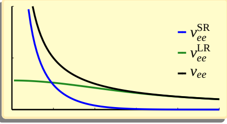


$$\begin{aligned} E &= \min_{n}\left\{F[n] + \int n(\mathbf{r})v_{ext}(\mathbf{r})\right\} \\ &= \min_{n}\left\{F^{\text{lr}}[n] + E_{\text{Hxc}}^{\text{sr}}[n] + \int n(\mathbf{r})v_{ext}(\mathbf{r})\right\} \\ &= \min_{\Psi}\left\{\langle\Psi|\,\hat{T} + \hat{V}_{ee}^{\text{lr}}\,|\Psi\rangle + E_{\text{Hxc}}^{\text{sr}}[n_\Psi] + \int n_\Psi(\mathbf{r})v_{ext}(\mathbf{r})\right\} \end{aligned}$$

Range separated hybrid (RSH)

$$E_{\text{RSH}} = \min_{\Phi}\left\{\langle\Phi|\,\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}^{\text{lr}}\,|\Phi\rangle + E_{Hxc}^{\text{sr}}[n_\Phi]\right\}$$

Range Separation



Inter-electronic interaction $\quad \dfrac{1}{\mathbf{r}} = v_{ee}^{\mathrm{lr}}(\mathbf{r}) + v_{ee}^{\mathrm{sr}}(\mathbf{r})$

$$
\begin{aligned}
E &= \min_{n} \left\{ F[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\} \\
&= \min_{n} \left\{ F^{\mathrm{lr}}[n] + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) \right\} \\
&= \min_{\Psi} \left\{ \langle \Psi | \, \hat{T} + \hat{V}_{ee}^{\mathrm{lr}} \, | \Psi \rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_{\Psi}] + \int n_{\Psi}(\mathbf{r}) v_{ext}(\mathbf{r}) \right\}
\end{aligned}
$$

Range separated hybrid (RSH)

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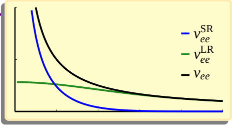
$$

Effective hamiltonian $\quad \hat{H}_0 = \hat{T} + \hat{V}_{ext} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\mathbf{D}] + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[n]$

Range Separation



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Range separated hybrid (RSH)

$$E_{\mathrm{RSH}} = \min_{\Phi}\left\{\langle\Phi|\,\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}^{\mathrm{lr}}\,|\Phi\rangle + E_{Hxc}^{\mathrm{sr}}[n_\Phi]\right\}$$

Effective hamiltonian $\hat{H}_0 = \hat{T} + \hat{V}_{ext} + \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}[\mathbf{D}] + \hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[n]$

total energy $E = E_{\mathrm{RSH}} + E_c^{\mathrm{lr}}$

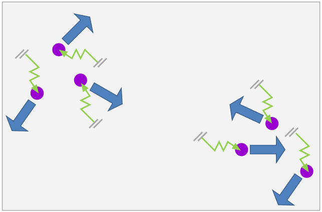
RSH+MP2
RSH+CC
RSH+...

Random Phase Approximation

Historical introduction

Random Phase Approximation

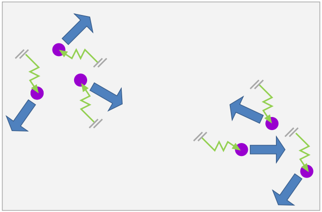
Historical introduction

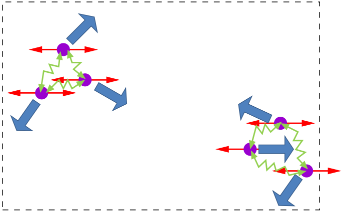


$$\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{champ}} + \hat{H}_{\substack{\text{int.}\\ \text{part./champ}}}$$

Random Phase Approximation

Historical introduction



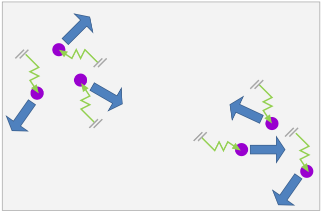


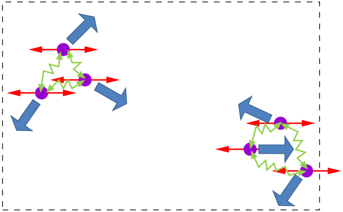
$$\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{champ}} + \hat{H}_{\substack{\text{int.} \\ \text{part./champ}}}$$

$$\hat{H}^{\text{RPA}} = \hat{H}_{\text{part.}} + \hat{H}_{\text{osc.}} + \hat{H}^{\text{sr}}_{\substack{\text{int.} \\ \text{part./part.}}}$$

Random Phase Approximation

Historical introduction





$$\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{champ}} + \hat{H}_{\substack{\text{int.}\\ \text{part./champ}}} \qquad \hat{H}^{\text{RPA}} = \hat{H}_{\text{part.}} + \hat{H}_{\text{osc.}} + \hat{H}^{\text{sr}}_{\substack{\text{int.}\\ \text{part./part.}}}$$

Riccati equations (*i.e.*(d)rCCD formulation)

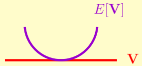
many *flavors*
the simplest is :
$$\begin{cases} E^{\text{lr}}_{c,\text{dRPA-I}} &= \langle \mathbf{KT} \rangle \\ 0 &= 2\left(\mathbf{K} + \mathbf{KT} + \mathbf{TK} + \mathbf{TKT}\right) + \left(\boldsymbol{\varepsilon}\mathbf{T} + \mathbf{T}\boldsymbol{\varepsilon}\right) \end{cases}$$

Analytical Gradients

Analytical Gradients

About Parameters

About Parameters



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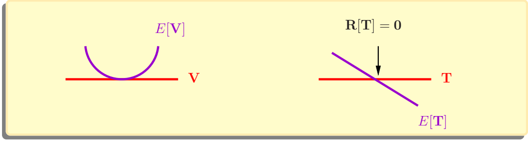
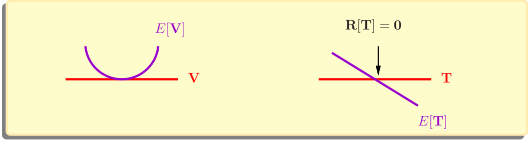


Analytical Gradients

About Parameters

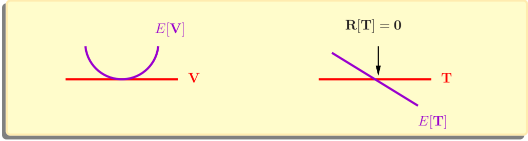


Gradients

$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$

Analytical Gradients

About Parameters



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$$\boxed{\frac{\mathrm{d}E}{\mathrm{d}\kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}}\frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{T}}\frac{\partial \mathbf{T}}{\partial \kappa}}$$

Analytical Gradients

About Parameters

Gradients

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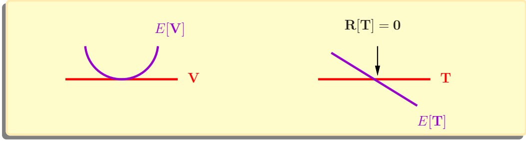
Analytical Gradients

About Parameters



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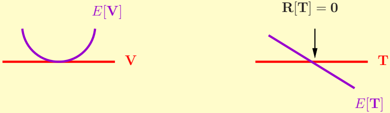
$$\frac{\partial E}{\partial \mathbf{h}}\mathbf{h}^{(\kappa)} + \frac{\partial E}{\partial(\mu\nu|\sigma\rho)}(\mu\nu|\sigma\rho)^{(\kappa)} + \frac{\partial E}{\partial \mathbf{S}}\mathbf{S}^{(\kappa)}$$

About Parameters



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Analytical Gradients

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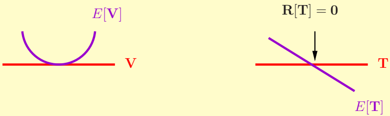

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Fully-variational methods

About Parameters

Gradients

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Fully-variational methods

$$\frac{\partial E_{HF}}{\partial \kappa} =$$

Analytical Gradients

About Parameters

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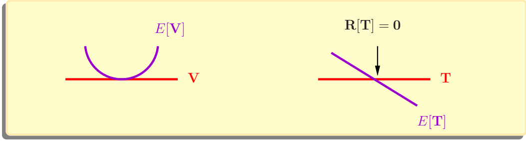
Fully-variational methods

$$\frac{\partial E_{HF}}{\partial \kappa} = \underline{\delta h_{\alpha\beta}} P_{\alpha\beta} + \frac{1}{2}\underline{\delta(\mu\lambda|\nu\sigma)}(P_{\mu\lambda}P_{\nu\sigma} - P_{\mu\sigma}P_{\nu\lambda}) + \underline{\delta S_{\mu\nu}} S^{-1}_{\nu\lambda} F_{\lambda\sigma} P_{\sigma\mu}$$

About Parameters



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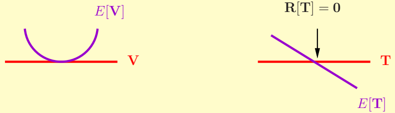
<u>Non-variational methods</u>

Analytical Gradients

About Parameters



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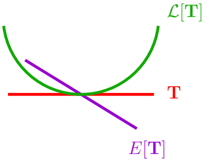
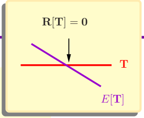
Non-variational methods



Work with an alternative object that **is** variational

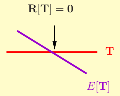
Lagrangian Framework



Remember :

	energy	rules for $\mathbf{T}$
for a non-variational method	$E[\mathbf{V}, \mathbf{T}]$	$\mathbf{R}[\mathbf{T}] = 0$

Lagrangian Framework

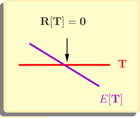


	energy	rules for $\mathbf{T}$
Remember : for a non-variational method	$E[\mathbf{V}, \mathbf{T}]$	$\mathbf{R}[\mathbf{T}] = 0$

introduce the Lagrangian

$$\boxed{\mathcal{L}[\mathbf{V}, \mathbf{T}, \boldsymbol{\lambda}] = E[\mathbf{V}, \mathbf{T}] + \langle \boldsymbol{\lambda} \mathbf{R}[\mathbf{T}] \rangle}$$

Lagrangian Framework



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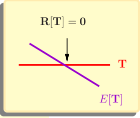
stationary conditions for $\mathcal{L}$

Lagrangian Framework



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introduce the Lagrangian

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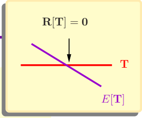
$$\frac{\partial \mathcal{L}}{\partial \mathbf{V}} = \frac{\partial E}{\partial \mathbf{V}} = 0$$

stationary conditions for $\mathcal{L}$

Lagrangian Framework



Remember : for a non-variational method — energy $E[\mathbf{V}, \mathbf{T}]$ — rules for $\mathbf{T}$: $\mathbf{R}[\mathbf{T}] = 0$

introduce the Lagrangian

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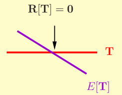
stationary conditions for $\mathcal{L}$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{V}} = \frac{\partial E}{\partial \mathbf{V}} = 0$$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \frac{\partial E}{\partial \mathbf{T}} + \langle \boldsymbol{\lambda} \frac{\partial \mathbf{R}}{\partial \mathbf{T}} \rangle = 0$$

Lagrangian Framework



Remember : for a non-variational method

energy $E[\mathbf{V}, \mathbf{T}]$

rules for $\mathbf{T}$: $\mathbf{R}[\mathbf{T}] = 0$

introduce the Lagrangian

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stationary conditions for $\mathcal{L}$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{V}} = \frac{\partial E}{\partial \mathbf{V}} = 0$$

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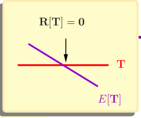
$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\lambda}} = \mathbf{R}[\mathbf{T}] = 0$$

Lagrangian Framework



Remember : energy $E[\mathbf{V},\mathbf{T}]$ rules for $\mathbf{T}$ $\mathbf{R}[\mathbf{T}] = 0$

for a non-variational method

introduce the Lagrangian

$$\boxed{\mathcal{L}[\mathbf{V},\mathbf{T},\boldsymbol{\lambda}] = E[\mathbf{V},\mathbf{T}] + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T}]\rangle}$$

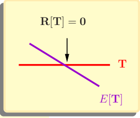
stationary conditions for $\mathcal{L}$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{V}} = \frac{\partial E}{\partial \mathbf{V}} = 0$$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \frac{\partial E}{\partial \mathbf{T}} + \langle \boldsymbol{\lambda}\frac{\partial \mathbf{R}}{\partial \mathbf{T}}\rangle = 0$$

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\lambda}} = \mathbf{R}[\mathbf{T}] = 0$$

Lagrangian Framework



Remember :

for a non-variational method

	energy	rules for $\mathbf{T}$
	$E[\mathbf{V},\mathbf{T}]$	$\mathbf{R}[\mathbf{T}] = 0$

introduce the Lagrangian

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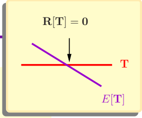
Lagrangian Framework



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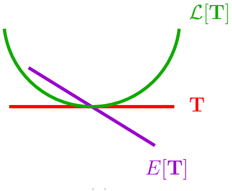

RSH-RPA Analytical Gradients

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RSH+MP2 : Chabbal, S ; Stoll, H. ; Werner, H.-J. ; Leininger, T. Mol. Phys. **108** 3373 (2010)

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RSH+MP2 : Chabbal, S ; Stoll, H. ; Werner, H.-J. ; Leininger, T. Mol. Phys. **108** 3373 (2010)
HF+RPA : Rekkedal, J. ; Coriani, S. ; Iozzi, M. F. ; Teale, A. M. ; Helgaker, T. ; Pedersen, T. B. J. Chem. Phys. **139** 081101 (2013)
PBE+dRPA(DF) : Burow, A. M. ; Bates, J. E. ; Furche, F. ; Eshuis, H. J. Chem. Theory Comput., Just Accepted Manuscript

RSH+RPA Energy and Lagrangian

Remember : $E = E_{\mathrm{RSH}} + E_c^{\mathrm{lr}} = \langle\Phi|\,\hat{T} + \hat{V}_{ext} + \hat{V}_{ee}^{\mathrm{lr}}|\Phi\rangle + E_{Hxc}^{\mathrm{sr}}[n_\Phi] + E_c^{\mathrm{lr}}$

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Notation with fockians

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$$
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&\quad + \left\langle \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{sr}} \right\rangle + \Delta_{\mathrm{DC}}^{\mathrm{sr}}
\end{aligned}
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RSH+RPA (sr+lr) Lagrangian

- two non-variational parameters : amplitudes $\mathbf{T}$, orbital coefficients $\mathbf{C}$
- three constraints : $\mathbf{R}[\mathbf{T},\mathbf{C}] = 0$, $(\mathbf{f})_{ai} = 0$, $\left(\mathbf{C}^{\text{T}}\mathbf{S}\mathbf{C} - \mathbf{1}\right) = 0$

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Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda} \mathbf{R}[\mathbf{T}, \mathbf{C}] \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

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wrt. T

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$$\langle \mathbf{K}\mathbf{T} \rangle + \langle \boldsymbol{\lambda}(\mathbf{K} + \mathbf{K}\mathbf{T} + \mathbf{T}\mathbf{K} + \mathbf{T}\mathbf{K}\mathbf{T} + \boldsymbol{\varepsilon}\mathbf{T} + \mathbf{T}\boldsymbol{\varepsilon}) \rangle$$

wrt. T

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f}\rangle$$

wrt. T

$$\tfrac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$

Stationary Conditions

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wrt. T

$$\tfrac{\partial}{\partial T}\{\langle \mathbf{K}\mathbf{T}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{K}\mathbf{T}+\mathbf{T}\mathbf{K}+\mathbf{T}\mathbf{K}\mathbf{T}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\boldsymbol{\varepsilon}\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\boldsymbol{\varepsilon}\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\} = 0$$

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$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

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wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\boldsymbol{\varepsilon}\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\boldsymbol{\varepsilon}\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

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$$\sum_{kc,b} (ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b} (ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

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$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}] \rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{K}\mathbf{T}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{K}\mathbf{T}+\mathbf{T}\mathbf{K}+\mathbf{T}\mathbf{K}\mathbf{T}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\boldsymbol{\varepsilon}\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\boldsymbol{\varepsilon}\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

dh→dh

$$\sum_{kc,b} (ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b} (ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\tfrac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\boldsymbol{\varepsilon}\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\boldsymbol{\varepsilon}\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$\mathbf{dh} \to \mathbf{dh}$

$\mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to \quad \mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + \quad \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}]$

$$\sum_{kc,b} (ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b} (ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}] \rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\tfrac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\varepsilon\mathbf{T}+\mathbf{T}\varepsilon)\rangle\} = 0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathrm{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\varepsilon\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\varepsilon\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$\mathbf{dh} \to \mathbf{dh}$

$\mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to \quad \mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + \quad \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}]$

$-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}]$

$\sum_{kc,b}(ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$

$\sum_{kc,b}(ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$

$\sum_{kc,j}(ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$

$\sum_{kc,j}(aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\varepsilon\mathbf{T}+\mathbf{T}\varepsilon)\rangle\} = 0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\varepsilon\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\varepsilon\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$$\mathbf{dh} \to \mathbf{dh}$$

$$\mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to \quad \mathbf{d} \quad \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + \quad \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}]$$

$$-\tfrac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to -\tfrac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + -\tfrac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}]$$

$$\mathbf{d}\mathbf{f}^{\mathrm{lr}} + \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(2)} + \mathbf{z}]$$

$$\sum_{kc,b}(ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b}(ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j}(ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j}(aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda} \mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\varepsilon\mathbf{T}+\mathbf{T}\varepsilon)\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathrm{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\varepsilon\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\varepsilon\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \boxed{\left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}}} + \boxed{\langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$\mathbf{dh} \to \mathbf{dh}$

$\mathbf{d}\;\; \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to \;\; \mathbf{d}\;\; \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + \;\; \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}]$

$-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}]$

$\mathbf{dg}^{\mathrm{sr}} \to \mathbf{dg}^{\mathrm{sr}} + \mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}]$

$\Delta_{\mathrm{DC}}^{\mathrm{sr}} \to -\mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(0)}]$

$\mathbf{df}^{\mathrm{lr}} +$

$\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(2)} + \mathbf{z}]$

$$\sum_{kc,b}(ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b}(ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j}(ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j}(aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\text{DC}} + \underline{E_c^{\text{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}] \rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\text{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{KT}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{KT}+\mathbf{TK}+\mathbf{TKT}+\varepsilon\mathbf{T}+\mathbf{T}\varepsilon)\rangle\} = 0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\text{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\varepsilon\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\varepsilon\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\text{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\text{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$\mathbf{dh} \to \mathbf{dh}$

$\mathbf{d}\quad \mathbf{g}^{\text{lr}}[\mathbf{d}^{(0)}] \to \quad \mathbf{d}\quad \mathbf{g}^{\text{lr}}[\mathbf{d}^{(0)}] + \quad \mathbf{d}^{(0)}\mathbf{g}^{\text{lr}}[\mathbf{d}]$

$-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\text{lr}}[\mathbf{d}^{(0)}] \to -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\text{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\text{lr}}[\mathbf{d}^{(0)}]$

$\mathbf{dg}^{\text{sr}} \to \mathbf{dg}^{\text{sr}} + \mathbf{d}^{(0)}\mathbf{W}^{\text{sr}}[\mathbf{d}]$

$\Delta_{\text{DC}}^{\text{sr}} \to -\mathbf{d}^{(0)}\mathbf{W}^{\text{sr}}[\mathbf{d}^{(0)}]$

$$\mathbf{df}^{\text{lr}} + \mathbf{d}^{(0)}\mathbf{g}^{\text{lr}}[\mathbf{d}^{(2)} + \mathbf{z}]$$

$$\mathbf{dg}^{\text{sr}} + \mathbf{d}^{(0)}\mathbf{W}^{\text{sr}}[\mathbf{d}^{(2)} + \mathbf{z}]$$

$$\sum_{kc,b} (ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,b} (ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\sum_{kc,j} (aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

Stationary Conditions

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)}\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \underline{E_c^{\mathrm{lr}} + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T},\mathbf{C}]\rangle} + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \langle \mathbf{z}\mathbf{f} \rangle$$

wrt. T

$$\frac{\partial}{\partial T}\{\langle \mathbf{K}\mathbf{T}\rangle + \langle \boldsymbol{\lambda}(\mathbf{K}+\mathbf{K}\mathbf{T}+\mathbf{T}\mathbf{K}+\mathbf{T}\mathbf{K}\mathbf{T}+\boldsymbol{\varepsilon}\mathbf{T}+\mathbf{T}\boldsymbol{\varepsilon})\rangle\}=0$$

$$-\mathbf{P} = \mathbf{Q}[\mathbf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathbf{Q}[\mathbf{T}]^{\mathrm{T}}$$

wrt. C

$$\langle \mathbf{K}(\mathbf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathbf{T}+\mathbf{T}\boldsymbol{\lambda}+\mathbf{T}\boldsymbol{\lambda}\mathbf{T})\rangle + \langle \boldsymbol{\lambda}\boldsymbol{\varepsilon}\mathbf{T}+\boldsymbol{\lambda}\mathbf{T}\boldsymbol{\varepsilon}\rangle \doteq \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathrm{DC}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

$\mathbf{dh} \to \mathbf{dh}$

$\mathbf{d}\ \ \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to \ \mathbf{d}\ \ \mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + \ \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}]$

$-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \to -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}]$

$\mathbf{d}\mathbf{g}^{\mathrm{sr}} \to \mathbf{d}\mathbf{g}^{\mathrm{sr}} + \mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}]$

$\Delta_{\mathrm{DC}}^{\mathrm{sr}} \to -\mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(0)}]$

$\mathbf{d}\mathbf{f}^{\mathrm{lr}} +$
$\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(2)} + \mathbf{z}]$

$\mathbf{d}\mathbf{g}^{\mathrm{sr}} +$
$\mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(2)} + \mathbf{z}]$

$$\sum_{kc,b}(ib|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$
$$\sum_{kc,b}(ab|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$
$$\sum_{kc,j}(ij|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$
$$\sum_{kc,j}(aj|kc)(\mathbf{M}_{\boldsymbol{\lambda}})_{kc,jb}$$

$$\begin{cases} \left(\boldsymbol{\Theta} - \boldsymbol{\Theta}^{\mathrm{T}} + \mathbf{f}\mathbf{z} - \mathbf{z}\mathbf{f} + 4\mathbf{g}^{\mathrm{lr}}(\mathbf{z}) + 4\mathbf{W}^{\mathrm{sr}}[\mathbf{z}]\right)_{ai} = 0 & \text{(CP-RPA)} \\ (1+\tau_{pq})\left(\boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z})\right)_{pq} = -4(\mathbf{x})_{pq} \end{cases}$$

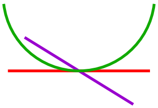
Gradient Expression

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f}\;^{\mathsf{sr}\,+\,\mathsf{lr}} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{sr}\,+\,\mathsf{lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right.$$

Gradient Expression

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f}^{\;\mathsf{sr}\,+\,\mathsf{lr}} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{sr}\,+\,\mathsf{lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right.$$

Since the multipliers are known : simple derivative of a variational object

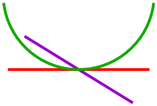


Gradient Expression

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z})\mathbf{f}^{\ \mathrm{sr}\,+\,\mathrm{lr}} \right\rangle + \Delta_{\mathrm{DC}}^{\mathrm{sr}\,+\,\mathrm{lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right.$$

Since the multipliers are known : simple derivative of a variational object

$$\mathcal{L}^{(\kappa)} =$$



Gradient Expression

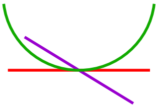
$$\mathcal{L} = \Big\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z})\mathbf{f}^{\ \mathrm{sr}\ +\ \mathrm{lr}} \Big\rangle + \Delta_{\mathrm{DC}}^{\mathrm{sr}\ +\ \mathrm{lr}} + \ \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle \ + \Big\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1})$$

Since the multipliers are known : simple derivative of a variational object

$$\mathcal{L}^{(\kappa)} = D^{1}_{\mu\nu} H^{(\kappa)}_{\mu\nu} + D^{2}_{\mu\nu,\rho\sigma} (\mu\nu|\rho\sigma)^{\mathrm{lr}(\kappa)}$$

$$(\mathbf{D}^1)_{\mu\nu} = C_{\mu p} \left(\mathbf{d}^{(0)} + \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{z} \right)_{pq} C^{\dagger}_{q\nu} = \left(\mathbf{D}^{(0)} + \mathbf{D}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{Z} \right)_{\mu\nu}$$

$$(\mathbf{D}^2)_{\mu\nu,\sigma\rho} = \left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{Z} \right)_{\mu\nu} D^{(0)}_{\rho\sigma} - \frac{1}{2} \left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}_{\boldsymbol{\lambda}}^{(2)} + \mathbf{Z} \right)_{\mu\rho} D^{(0)}_{\nu\sigma}$$



Gradient Expression

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z})\mathbf{f}^{\ \mathrm{sr}\,+\,\mathrm{lr}} \right\rangle + \Delta_{\mathrm{DC}}^{\mathrm{sr}\,+\,\mathrm{lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

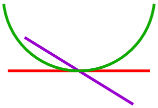
Since the multipliers are known : simple derivative of a variational object

$$\mathcal{L}^{(\kappa)} = D^1_{\mu\nu} H^{(\kappa)}_{\mu\nu} + D^2_{\mu\nu,\rho\sigma}(\mu\nu|\rho\sigma)^{\mathrm{lr}(\kappa)} + \Gamma^2_{\mu\nu,\rho\sigma}(\mu\nu|\rho\sigma)^{\mathrm{lr}(\kappa)}$$

$$(\mathbf{D}^1)_{\mu\nu} = C_{\mu p}\left(\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z}\right)_{pq} C^{\dagger}_{q\nu} = \left(\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z}\right)_{\mu\nu}$$

$$(\mathbf{D}^2)_{\mu\nu,\sigma\rho} = \left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z}\right)_{\mu\nu} D^{(0)}_{\rho\sigma} - \frac{1}{2}\left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z}\right)_{\mu\rho} D^{(0)}_{\nu\sigma}$$

$$(\boldsymbol{\Gamma}^2)_{\mu\nu,\sigma\rho} = C_{\mu k} C_{\nu j} C^{\dagger}_{c\rho} C^{\dagger}_{b\sigma} (\mathbf{M}_{\boldsymbol{\lambda}})_{ia,kc}$$



Gradient Expression

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z})\mathbf{f}^{\,\mathrm{sr} + \mathrm{lr}} \right\rangle + \Delta_{\mathrm{DC}}^{\mathrm{sr} + \mathrm{lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle$$

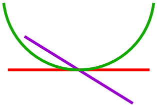
Since the multipliers are known : simple derivative of a variational object

$$\mathcal{L}^{(\kappa)} = D^1_{\mu\nu} H^{(\kappa)}_{\mu\nu} + D^2_{\mu\nu,\rho\sigma} (\mu\nu|\rho\sigma)^{\mathrm{lr}(\kappa)} + \Gamma^2_{\mu\nu,\rho\sigma} (\mu\nu|\rho\sigma)^{\mathrm{lr}(\kappa)} + \mathrm{SR}^{(\kappa)} + X_{\mu\nu} S^{(\kappa)}_{\mu\nu}$$

$$(\mathbf{D}^1)_{\mu\nu} = C_{\mu p} \left(\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z} \right)_{pq} C^{\dagger}_{q\nu} = \left(\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z} \right)_{\mu\nu}$$

$$(\mathbf{D}^2)_{\mu\nu,\sigma\rho} = \left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z} \right)_{\mu\nu} D^{(0)}_{\rho\sigma} - \frac{1}{2} \left(\tfrac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z} \right)_{\mu\rho} D^{(0)}_{\nu\sigma}$$

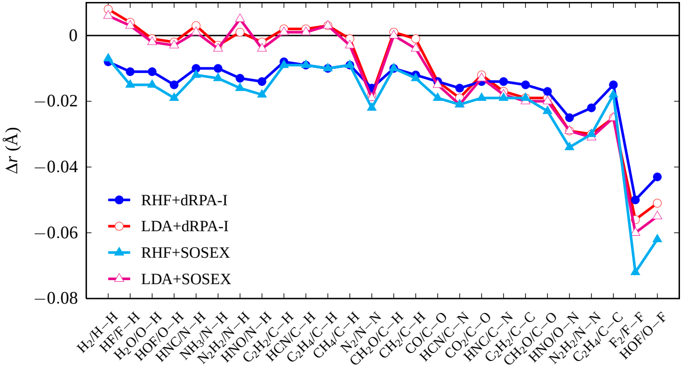
$$(\boldsymbol{\Gamma}^2)_{\mu\nu,\sigma\rho} = C_{\mu k} C_{\nu j} C^{\dagger}_{c\rho} C^{\dagger}_{b\sigma} (\mathbf{M}_{\boldsymbol{\lambda}})_{ia,kc}$$



$$\mathrm{SR}^{(\kappa)} = \omega^{(\kappa)}_{\lambda} \left(F(\xi_A) + \frac{\partial F}{\partial \xi_A} \left(\xi_A^{\mathbf{d}^{(2)}_{\boldsymbol{\lambda}}} + \xi_A^{\mathbf{z}} \right) \right) + \omega_\lambda \frac{\partial F}{\partial \xi_B} \left(\xi_B^{\mathbf{d}^{(0)}(x)} + \xi_B^{\mathbf{d}^{(2)}_{\boldsymbol{\lambda}}(x)} + \xi_B^{\mathbf{z}(x)} \right) + \omega_\lambda \frac{\partial^2 F}{\partial \xi_B \partial \xi_A} \left(\xi_A^{\mathbf{d}^{(2)}_{\boldsymbol{\lambda}}} + \xi_A^{\mathbf{z}} \right) \xi_B^{(\kappa)}$$

Validation and Results

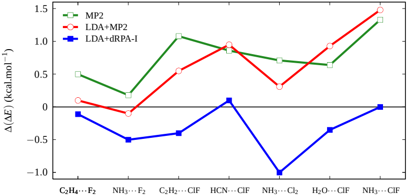
Bond Lengths of simple molecules



RHF+dRPA-I : 0.016, LDA+dRPA-I : 0.013
RHF+SOSEX : 0.021, LDA+SOSEX : 0.014

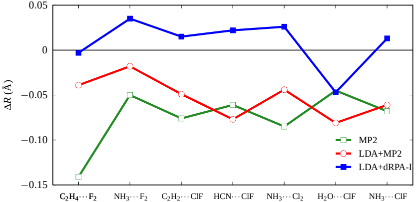
Rekkedal *et al.* Chem. Phys. **139** 081101 (2013)

Interaction Energies and Intermonomer distances



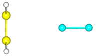
MP2 : 0.76 LDA+MP2 : 0.63

LDA+dRPA-I : 0.35

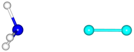


MP2 : 0.075 LDA+MP2 : 0.053

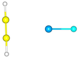
LDA+dRPA-I : 0.023



$C_2H_4\cdots F_2$

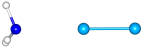


$NH_3\cdots F_2$



$C_2H_2\cdots F_2$

$HCN\cdots ClF$



$NH_3\cdots Cl_2$

$H_2O\cdots ClF$

$NH_3\cdots ClF$

Chabbal *et al.* Mol. Phys. **108** 3373 (2010)

Conclusion & Outlook

Development

- RSH+RPA gradient for the first time
- all-in-one derivation of sr+lr energy gradient for the first time
- HF+RPA [Rekkedal(2013)] and PBE+dRPA(DF) [Burow *et al.* JCTC (just accepted)] has also been done

Implementation

- working implementation in MOLPRO
- gradients of some other RPA energies need further coding
- scaling $O(N^6)$ (possible to $O(N^5)$ and $O(N^4)$)
- the use of srPBE (kernel) is the very next step

Results

- geometry optimization
- intermolecular interaction