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

Bastien Mussard, János G. Ángyán CRM², Université de Lorraine, Nancy, France

Analytical Gradients of

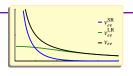
Random Phase Approximation correlation
energies in a Range-Separated-Hybrid
context: Theory and implementation

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Theoretical Context

Inter-electronic interaction

$$rac{1}{\mathbf{r}} = v_{ee}^{\mathsf{Ir}}(\mathbf{r}) + v_{ee}^{\mathsf{sr}}(\mathbf{r})$$



$$rac{1}{\mathbf{r}} = v_{\mathrm{ee}}^{\mathrm{lr}}(\mathbf{r}) + v_{\mathrm{ee}}^{\mathrm{sr}}(\mathbf{r})$$

$$\mathbf{\textit{E}} = \min_{\mathbf{\textit{n}}} \Big\{ \textit{F}[\mathbf{\textit{n}}] + \int \mathbf{\textit{n}}(\mathbf{\textit{r}}) \textit{v}_{\text{ext}}(\mathbf{\textit{r}}) \Big\}$$

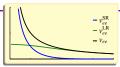
Inter-electronic interaction

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

$$E = \min_{n} \left\{ F[n] + \int_{n} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$
$$= \min_{n} \left\{ F^{\text{lr}}[n] + E^{\text{sr}}_{\text{Hxc}}[n] + \int_{n} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

Inter-electronic interaction

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



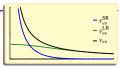
$$E = \min_{n} \left\{ F[n] + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

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

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

Inter-electronic interaction

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



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

Range separated hybrid (RSH)

$$\textit{E}_{\mathsf{RSH}} = \min_{\Phi} \left\{ \langle \Phi | \ \hat{\textit{T}} + \hat{\textit{V}}_{\mathsf{ext}} + \hat{\textit{V}}_{\mathsf{ee}}^{\mathsf{Ir}} \, | \Phi \rangle + \textit{E}_{\mathsf{Hxc}}^{\mathsf{sr}}[\textit{n}_{\Phi}] \right\}$$

Inter-electronic interaction

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

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

$$= \min_{n} \left\{ F^{\text{lr}}[n] + E^{\text{sr}}_{\text{Hxc}}[n] + \int_{\mathbf{n}} \mathbf{n}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

$$= \min_{\mathbf{\psi}} \left\{ \langle \mathbf{\Psi} | \hat{T} + \hat{V}^{\text{lr}}_{\text{ee}} | \mathbf{\Psi} \rangle + E^{\text{sr}}_{\text{Hxc}}[n_{\mathbf{\psi}}] + \int_{\mathbf{n}} n_{\mathbf{\psi}}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

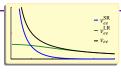
Range separated hybrid (RSH)

$$\textit{E}_{\mathsf{RSH}} = \min_{\Phi} \left\{ \langle \Phi | \ \hat{\textit{T}} + \hat{\textit{V}}_{\mathsf{ext}} + \hat{\textit{V}}_{\mathsf{ee}}^{\mathsf{Ir}} \, | \Phi \rangle + \textit{E}_{\mathsf{Hxc}}^{\mathsf{sr}}[\textit{n}_{\Phi}] \right\}$$

$$\hat{\mathcal{H}}_0 = \hat{\mathcal{T}} + \hat{V}_{\mathsf{ext}} + \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{Ir}}[\mathbf{D}] + \hat{V}_{\mathsf{Hxc}}^{\mathsf{sr}}[n]$$

Inter-electronic interaction

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



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

$$= \min_{n} \left\{ F^{\text{Ir}}[n] + E^{\text{sr}}_{\text{Hxc}}[n] + \int_{n} n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

$$= \min_{n} \left\{ \langle \Psi | \hat{T} + \hat{V}^{\text{Ir}}_{\text{ee}} | \Psi \rangle + E^{\text{sr}}_{\text{Hxc}}[n_{\Psi}] + \int_{n} n_{\Psi}(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \right\}$$

Range separated hybrid (RSH)

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

Effective hamiltonian

$$\hat{\mathcal{H}}_0 = \hat{\mathcal{T}} + \hat{\mathcal{V}}_{\text{ext}} + \hat{\mathcal{V}}_{\text{Hx,HF}}^{\text{Ir}}[\mathbf{D}] + \hat{\mathcal{V}}_{\text{Hxc}}^{\text{sr}}[n]$$

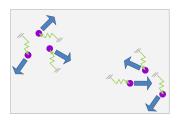
total energy

$$E = E_{RSH} + \frac{E_c^{lr}}{}$$

RSH+MP2 RSH+CC

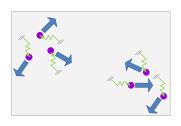
Historical introduction

Historical introduction

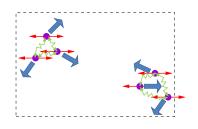


$$\hat{H} = \hat{H}_{part.} + \hat{H}_{champ} + \hat{H}_{int.}_{part./champ}$$

Historical introduction

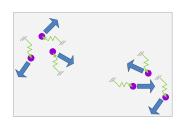


$$\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{champ}} + \hat{H}_{\text{int.}}_{\text{part./champ}}$$

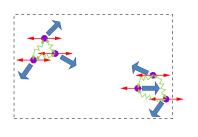


$$\hat{\textit{H}}^{\text{RPA}} = \hat{\textit{H}}_{\text{part.}} + \hat{\textit{H}}_{\text{osc.}}^{\text{sc.}} + \hat{\textit{H}}_{\text{int.}}^{\text{sr}}_{\text{part./part.}}$$

Historical introduction



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



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

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

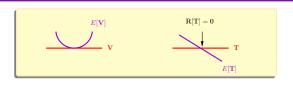
many flavors the simplest is :
$$\begin{cases} E_{c, \mathsf{dRPA-I}}^{\mathsf{Ir}} &= \langle \mathbf{KT} \rangle \\ 0 &= 2 \left(\mathbf{K} + \mathbf{KT} + \mathbf{TK} + \mathbf{TKT} \right) + \left(\varepsilon \mathbf{T} + \mathbf{T} \varepsilon \right) \end{cases}$$

About Parameters

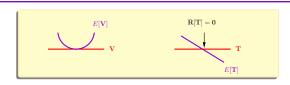
About Parameters



About Parameters



About Parameters



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

About Parameters



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

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

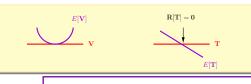
About Parameters



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

$$\frac{dE}{dx} = \frac{\partial E}{\partial x} + \frac{\partial E}{\partial x} \frac{\partial \mathbf{V}}{\partial x} + \frac{\partial E}{\partial \mathbf{T}} \frac{\partial \mathbf{T}}{\partial x}$$

About Parameters

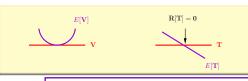


$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$

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

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

About Parameters

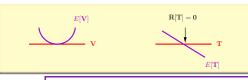


$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$

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

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

About Parameters



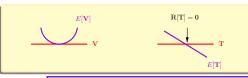
Gradients

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

Fully-variational methods

$$\frac{dE}{d\kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{S}} \mathbf{S}^{(\kappa)}$$

About Parameters



Gradients

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

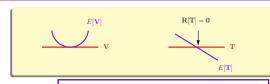
Fully-variational methods

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

$$\frac{dE}{d\kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{I}} \frac{\partial \mathbf{T}}{\partial \kappa}$$

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

About Parameters



Gradients

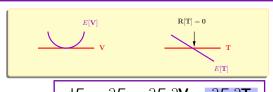
$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$

 $\frac{\mathrm{d}L}{\mathrm{d}\kappa} = \frac{\partial L}{\partial \kappa} + \frac{\partial L}{\partial \nu} + \frac{\partial L}{\partial \nu$

Fully-variational methods

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

About Parameters



Gradients

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

$$\frac{\partial \mathbf{E}}{\partial \kappa} = \frac{\partial \mathbf{E}}{\partial \kappa} + \frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial \mathbf{E}}{\partial \mathbf{V}} \frac{\partial \mathbf{E}}{\partial \kappa}$$

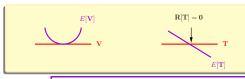
$$\frac{\partial \mathbf{E}}{\partial \mathbf{h}} \mathbf{h}^{(\kappa)} + \frac{\partial \mathbf{E}}{\partial (\mu \nu | \sigma \rho)} (\mu \nu | \sigma \rho)^{(\kappa)} + \frac{\partial \mathbf{E}}{\partial \mathbf{S}} \mathbf{S}^{(\kappa)}$$

Fully-variational methods

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

Non-variational methods

About Parameters



Gradients

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

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

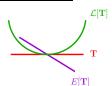
$$\frac{\partial E}{\partial \mathbf{h}} \mathbf{h}^{(\kappa)} + \frac{\partial E}{\partial (\mu \nu | \sigma \rho)} (\mu \nu | \sigma \rho)^{(\kappa)} + \frac{\partial E}{\partial \mathbf{S}} \mathbf{S}^{(\kappa)}$$

Fully-variational methods

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

Non-variational methods





Work with an alternative object that is variational

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



Remember:

for a non-variational method

energy E[V,T] R[T]=0

rules for T

R[T] = 0

introduce the Lagrangian

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

Remember:

for a non-variational method

energy

rules for **T** E[V,T] R[T]=0



introduce the Lagrangian

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

stationary conditions for \mathcal{L}

Remember:

for a non-variational method

E[V,T] R[T]=0

energy rules for T

R[T] = 0

introduce the Lagrangian

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

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

stationary conditions for \mathcal{L}

Remember:

for a non-variational method

E[V,T] R[T]=0

energy rules for T



introduce the Lagrangian

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

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

stationary conditions for
$${\cal L}$$

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

Remember:

for a non-variational method

E[V,T] R[T]=0

energy rules for T



introduce the Lagrangian

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

stationary conditions for \mathcal{L}

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial \mathbf{V}} &= \frac{\partial E}{\partial \mathbf{V}} = 0\\ \frac{\partial \mathcal{L}}{\partial \mathbf{T}} &= \frac{\partial E}{\partial \mathbf{T}} + \langle \mathbf{\lambda} \frac{\partial \mathbf{R}}{\partial \mathbf{T}} \rangle = 0\\ \frac{\partial \mathcal{L}}{\partial \mathbf{\lambda}} &= \mathbf{R}[\mathbf{T}] = 0 \end{aligned}$$

Remember:

for a non-variational method

energy rules for TE[V, T] R[T] = 0

 $\mathbf{R}[\mathbf{T}] = \mathbf{0}$ $E[\mathbf{T}] = \mathbf{0}$

introduce the Lagrangian

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

stationary conditions for
$${\cal L}$$

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

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

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



for a non-variational method

energy rules for T E[V,T] R[T]=0



introduce the Lagrangian

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

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

stationary conditions for \mathcal{L}

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

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

Lagrangian Framework

Remember:

for a non-variational method

energy rules for TE[V, T] R[T] = 0



introduce the Lagrangian

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

stationary conditions for
$${\cal L}$$

$$\mathcal{L}[\mathbf{T}]$$
 \mathbf{T}

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

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

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

RSH-RPA Analytical Gradients

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RSH+MP2: Chabbal, S; Stoll, H.; Werner, H.-J.; Leininger, T. Mol. Phys. $\mathbf{108}$ 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

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

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

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + E_c^{\mathsf{lr}}$$

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

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

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

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

$$\begin{split} \mathbf{f}^{\mathrm{lr}} &= \mathbf{h} + \mathbf{g}^{\mathrm{lr}} \left[\mathbf{d}^{(0)} \right] \\ \Delta^{\mathrm{lr}}_{\mathrm{DC}} &= -\frac{1}{2} \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\mathrm{lr}} \left[\mathbf{d}^{(0)} \right] \right\rangle \\ g^{\mathrm{lr}} \left[\mathbf{d}^{(0)} \right]_{pq} &= d^{(0)}_{rs} \left((pq|rs)^{\mathrm{lr}} - \frac{1}{2} (pr|qs)^{\mathrm{lr}} \right) \end{split}$$

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

Notation with fockians

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

$$\begin{split} \mathbf{f}^{\text{lr}} = & \mathbf{h} + \mathbf{g}^{\text{lr}} \left[\mathbf{d}^{(0)} \right] \\ \Delta_{\text{DC}}^{\text{lr}} = & -\frac{1}{2} \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\text{lr}} \left[\mathbf{d}^{(0)} \right] \right\rangle \\ g^{\text{lr}} \left[\mathbf{d}^{(0)} \right]_{pq} = & d_{rs}^{(0)} \left((pq|rs)^{\text{lr}} - \frac{1}{2} (pr|qs)^{\text{lr}} \right) \\ E_{Hxc}^{\text{sr}}[n] = & \int dr \ F[\xi] \\ g_{ab}^{\text{sr}} = & \int dr \ \sum_{\Delta} \frac{\partial F}{\partial \xi_{\Delta}} \frac{\partial \xi_{\Delta}}{\partial d_{ab}^{(0)}} \end{split}$$

 $\Delta_{\mathrm{DC}}^{\mathrm{sr}} = E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] - \langle \mathbf{d}^{(0)} \mathbf{g}^{\mathrm{sr}} \rangle$

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

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

$$\begin{split} \mathbf{f}^{\mathsf{lr}} = & \mathbf{h} + \mathbf{g}^{\mathsf{lr}} \big[\mathbf{d}^{(0)} \big] \\ \Delta^{\mathsf{lr}}_{\mathsf{DC}} = & -\frac{1}{2} \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\mathsf{lr}} \big[\mathbf{d}^{(0)} \big] \right\rangle \\ g^{\mathsf{lr}} \big[\mathbf{d}^{(0)} \big]_{pq} = & d_{rs}^{(0)} \left((pq|rs)^{\mathsf{lr}} - \frac{1}{2} (pr|qs)^{\mathsf{lr}} \right) \\ E^{\mathsf{sr}}_{\mathsf{Hxc}}[n] = & \int dr \ F[\xi] \\ g^{\mathsf{sr}}_{ab} = & \int dr \ \sum_{A} \frac{\partial F}{\partial \xi_{A}} \frac{\partial \xi_{A}}{\partial d_{ab}^{(0)}} \\ \Delta^{\mathsf{sr}}_{\mathsf{DC}} = & E^{\mathsf{sr}}_{\mathsf{Hxc}}[n] - \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\mathsf{sr}} \right\rangle \end{split}$$

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

Notation with fockians

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

$$\begin{aligned} \mathbf{f}^{\text{lr}} &= \mathbf{h} + \mathbf{g}^{\text{lr}} \left[\mathbf{d}^{(0)} \right] \\ \Delta_{\text{DC}}^{\text{lr}} &= -\frac{1}{2} \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\text{lr}} \left[\mathbf{d}^{(0)} \right] \right\rangle \\ g^{\text{lr}} \left[\mathbf{d}^{(0)} \right]_{pq} &= d_{rs}^{(0)} \left((pq|rs)^{\text{lr}} - \frac{1}{2} (pr|qs)^{\text{lr}} \right) \\ E_{Hxc}^{\text{sr}} [n] &= \int dr \ F[\xi] \\ g_{ab}^{\text{sr}} &= \int dr \ \sum_{A} \frac{\partial F}{\partial \xi_A} \frac{\partial \xi_A}{\partial d_{ab}^{(0)}} \end{aligned} \quad \xi = \{\xi_A\} = \{n, n_\alpha, \nabla n_\alpha, \dots\}$$

▶ two non-variational parameters : amplitudes **T**, orbital coefficients **C**

 $\Delta_{\mathrm{DC}}^{\mathrm{sr}} = E_{\mathrm{Hxc}}^{\mathrm{sr}}[n] - \langle \mathbf{d}^{(0)} \mathbf{g}^{\mathrm{sr}} \rangle$

▶ three constraints : $\mathbf{R}[\mathbf{T}, \mathbf{C}] = 0$, $(\mathbf{f})_{ai} = 0$, $(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}) = 0$

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

Notation with fockians

$$E = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + E_c^{lr}$$

$$= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr} + E_c^{lr}$$

$$+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}$$

 $\Delta_{\mathrm{DC}}^{\mathrm{lr}} = -\frac{1}{2} \langle \mathbf{d}^{(0)} \mathbf{g}^{\mathrm{lr}} [\mathbf{d}^{(0)}] \rangle$ $g^{\mathrm{lr}} [\mathbf{d}^{(0)}]_{pq} = d_{rs}^{(0)} ((pq|rs)^{\mathrm{lr}} - \frac{1}{2} (pr|qs)^{\mathrm{lr}})$ $\mathcal{E}_{\mathrm{Hyc}}^{\mathrm{sr}} [n] = \int dr \ F[\xi] \qquad \xi = \{\xi_A\} = \{n, n_{\alpha}, \nabla n_{\alpha}, \dots\}$

$$\begin{split} \mathbf{g}_{ab}^{\text{sr}} &= \int d\mathbf{r} \ \sum_{A} \frac{\partial F}{\partial \xi_{A}} \frac{\partial \xi_{A}}{\partial d_{ab}^{(0)}} \\ \Delta_{\text{DC}}^{\text{sr}} &= E_{\text{Hxc}}^{\text{sr}}[\mathbf{n}] - \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\text{sr}} \right\rangle \end{split}$$

 $\mathbf{f}^{lr} = \mathbf{h} + \mathbf{g}^{lr} [\mathbf{d}^{(0)}]$

RSH+RPA (sr+lr) Lagrangian

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

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

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

Notation with fockians

 $E = \langle \mathbf{d}^{(0)} \mathbf{f} \rangle + \Delta_{\mathsf{DC}} + E_c^{\mathsf{lr}}$

$$= \frac{\left\langle \mathbf{d}^{(0)} \mathbf{f}^{lr} \right\rangle + \Delta_{DC}^{lr}}{\left\langle \mathbf{d}^{(0)} \mathbf{g}^{sr} \right\rangle + \Delta_{DC}^{sr}} + \mathcal{E}_{c}^{lr}$$

 $g^{\text{lr}}[\mathbf{d}^{(0)}]_{rs} = d_{rs}^{(0)}((pq|rs)^{\text{lr}} - \frac{1}{2}(pr|qs)^{\text{lr}})$

 $E_{H_{XG}}^{sr}[n] = \int dr \ F[\xi] \qquad \xi = \{\xi_A\} = \{n, n_\alpha, \nabla n_\alpha, ...\}$

 $\Delta_{\rm DC}^{\rm lr} = -\frac{1}{2} \langle \mathbf{d}^{(0)} \mathbf{g}^{\rm lr} [\mathbf{d}^{(0)}] \rangle$

 $\mathbf{f}^{lr} = \mathbf{h} + \mathbf{g}^{lr} [\mathbf{d}^{(0)}]$

$$\begin{split} g_{ab}^{\rm sr} &= \int dr \; \sum_{A} \frac{\partial F}{\partial \xi_{A}} \frac{\partial \xi_{A}}{\partial d_{ab}^{(0)}} \\ \Delta_{\rm DC}^{\rm sr} &= E_{\rm Hxc}^{\rm sr}[n] - \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\rm sr} \right\rangle \end{split}$$

RSH+RPA (sr+lr) Lagrangian

▶ three constraints :
$$\mathbf{R}[\mathbf{T}, \mathbf{C}] = 0$$
, $(\mathbf{f})_{ai} = 0$, $(\mathbf{C}^\mathsf{T}\mathbf{SC} - \mathbf{1}) = 0$

two non-variational parameters : amplitudes T, orbital coefficients C

 $\mathcal{L}[\mathsf{T}, \boldsymbol{\lambda}, \mathsf{C}, \mathsf{z}, \mathsf{x}] = \left\langle \mathsf{d}^{(0)} \mathsf{f} \right\rangle + \Delta_{\mathsf{DC}} + \mathcal{E}_c^{\mathsf{lr}} + \left\langle \boldsymbol{\lambda} \mathsf{R}[\mathsf{T}, \mathsf{C}] \right\rangle + \left\langle \mathsf{x}(\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle + \left\langle \mathsf{z} \mathsf{f} \right\rangle$ 8/14

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right
angle + \Delta_{\mathsf{DC}} + \mathcal{E}_c^{\mathsf{lr}} + \left\langle \mathbf{\lambda} \mathbf{R} [\mathsf{T}, \mathsf{C}]
ight
angle + \left\langle \mathbf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1})
ight
angle + \left\langle \mathbf{z} \mathbf{f}
ight
angle$$

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right
angle + \Delta_{\mathsf{DC}} + \mathcal{E}^{\mathsf{Ir}}_c + \left\langle oldsymbol{\lambda} \mathbf{R[T,C]}
ight
angle + \left\langle \mathbf{x(C^\mathsf{T}SC-1)}
ight
angle + \left\langle \mathbf{zf}
ight
angle$$

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{\mathsf{DC}} + \underline{\mathit{E}^{\mathsf{lr}}_\mathit{c}} + \left\langle \mathbf{\lambda}\mathsf{R}[\mathsf{T},\mathsf{C}] \right\rangle + \left\langle \mathbf{x}(\mathsf{C}^\mathsf{T}\mathsf{SC} - 1) \right\rangle + \left\langle \mathbf{zf} \right\rangle$$

wrt. T

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

wrt. T

$$\langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TKT} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle$$

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

$$\begin{aligned} & \frac{\partial}{\partial T} \{ \langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TK} \mathsf{T} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle \} = 0 \\ & - \mathbf{P} = \mathbf{Q} [\mathsf{T}] \frac{\boldsymbol{\lambda}}{\boldsymbol{\lambda}} + \frac{\boldsymbol{\lambda}}{\boldsymbol{\lambda}} \mathbf{Q} [\mathsf{T}]^\mathsf{T} \end{aligned}$$

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{\mathsf{DC}} + \underline{\mathit{E}^{\mathsf{lr}}_\mathit{c}} + \left\langle \textcolor{red}{\textcolor{blue}{\lambda}} \mathsf{R}[\mathsf{T}, \mathsf{C}] \right\rangle + \left\langle \textcolor{red}{\mathsf{x}} (\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle + \left\langle \textcolor{red}{\mathsf{z}} \mathsf{f} \right\rangle$$

$$\frac{\partial}{\partial T} \{ \langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TK} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle \} = 0$$
$$- \mathsf{P} = \mathsf{Q} [\mathsf{T}] \frac{\lambda}{\lambda} + \frac{\lambda}{\lambda} \mathsf{Q} [\mathsf{T}]^{\mathsf{T}}$$

wrt. C

$$\langle \mathsf{K}(\mathsf{T} + \lambda + \lambda \mathsf{T} + \mathsf{T}\lambda + \mathsf{T}\lambda \mathsf{T}) \rangle + \langle \lambda \varepsilon \mathsf{T} + \lambda \mathsf{T}\varepsilon \rangle \dot{=} \langle \mathsf{KM}_{\lambda} \rangle + \langle \mathsf{d}_{\lambda}^{(2)} \mathsf{f} \rangle$$

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

$$\frac{\partial}{\partial T} \{ \langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TK} + \mathsf{T} + \mathsf{T} + \mathsf{T} + \mathsf{T} \rangle) \} = 0$$
$$-\mathsf{P} = \mathsf{Q}[\mathsf{T}] \frac{1}{\lambda} + \frac{1}{\lambda} \mathsf{Q}[\mathsf{T}]^{\mathsf{T}}$$

 $\langle \mathsf{K}(\mathsf{T}+\lambda+\lambda\mathsf{T}+\mathsf{T}\lambda+\mathsf{T}\lambda\mathsf{T})\rangle + \langle \lambda\varepsilon\mathsf{T}+\lambda\mathsf{T}\varepsilon\rangle \doteq \langle \mathsf{KM}_{\lambda}\rangle + \langle \mathsf{d}_{\lambda}^{(2)}\mathsf{f}\rangle$ wrt. C $\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x}(\mathsf{C}^{\mathsf{T}}\mathsf{SC} - \mathbf{1}) \right\rangle$

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

$$\frac{\partial}{\partial T} \{ \langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TK} + \mathsf{T} + \mathsf{T} + \mathsf{T} + \mathsf{T} \rangle) \} = 0$$
$$-\mathsf{P} = \mathsf{Q}[\mathsf{T}] \frac{1}{\lambda} + \frac{1}{\lambda} \mathsf{Q}[\mathsf{T}]^{\mathsf{T}}$$

 $\langle \mathsf{K}(\mathsf{T}+\lambda+\lambda\mathsf{T}+\mathsf{T}\lambda+\mathsf{T}\lambda\mathsf{T})\rangle + \langle \lambda\varepsilon\mathsf{T}+\lambda\mathsf{T}\varepsilon\rangle \doteq \langle \mathsf{KM}_{\lambda}\rangle + \langle \mathsf{d}_{\lambda}^{(2)}\mathsf{f}\rangle$ wrt. C $\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z})\mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x}(\mathsf{C}^{\mathsf{T}}\mathsf{SC} - \mathbf{1}) \right\rangle$

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{\mathsf{DC}} + \underline{F_c^{\mathsf{Ir}}} + \left\langle \mathbf{\lambda} \mathbf{R}[\mathbf{T}, \mathbf{C}] \right\rangle + \left\langle \mathbf{x}(\mathbf{C}^\mathsf{T}\mathbf{SC} - \mathbf{1}) \right\rangle + \left\langle \mathbf{zf} \right\rangle$$

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

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

wrt. C
$$\langle \mathsf{K}(\mathsf{T}+\lambda+\lambda\mathsf{T}+\mathsf{T}\lambda+\mathsf{T}\lambda\mathsf{T})\rangle + \langle \lambda \varepsilon \mathsf{T}+\lambda\mathsf{T}\varepsilon\rangle \dot{=} \langle \mathsf{K}\mathsf{M}_{\lambda}\rangle + \langle \mathsf{d}_{\lambda}^{(2)}\mathsf{f}\rangle$$

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

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

$$\sum_{kc,j} (ab|kc)(\mathsf{M}_{\lambda})_{kc,jb}$$

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

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

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{\text{DC}} + \underbrace{E_c^{\text{lr}} + \left\langle \lambda \mathbf{R}[\mathbf{T}, \mathbf{C}] \right\rangle}_{\mathcal{T}} + \left\langle \mathbf{x}(\mathbf{C}^\mathsf{T} \mathbf{S} \mathbf{C} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z} \mathbf{f} \right\rangle$$
 wrt.
$$\mathbf{T} \qquad \frac{\partial}{\partial T} \{ \langle \mathsf{K} \mathsf{T} \rangle + \langle \lambda (\mathsf{K} + \mathsf{K} \mathsf{T} + \mathsf{T} \mathsf{K} + \mathsf{T} \mathsf{K} \mathsf{T} + \varepsilon \mathsf{T} + \tau \varepsilon) \rangle \} = 0 \\ - \mathbf{P} = \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \lambda \mathbf{Q}[\mathbf{T}]^\mathsf{T}$$
 wrt.
$$\mathbf{C} \qquad \langle \mathsf{K}(\mathsf{T} + \lambda + \lambda \mathsf{T} + \mathsf{T} \lambda + \mathsf{T} \lambda \mathsf{T}) \rangle + \langle \lambda \varepsilon \mathsf{T} + \lambda \mathsf{T} \varepsilon \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\lambda} \rangle + \langle \mathbf{d}_{\lambda}^{(2)} \mathbf{f} \rangle \\ \mathcal{L} = \left\langle \left(\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z} \right) \mathbf{f} \right\rangle + \Delta_{\text{DC}} + \left\langle \mathsf{K} \mathsf{M}_{\lambda} \right\rangle + \left\langle \mathbf{x}(\mathbf{C}^\mathsf{T} \mathbf{S} \mathbf{C} - \mathbf{1}) \right\rangle$$

$$\mathbf{d} \mathbf{h} \rightarrow \mathbf{d} \mathbf{h}$$

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

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

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

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{DC} + \underbrace{E_c^{lr} + \left\langle \boldsymbol{\lambda} R[T,C] \right\rangle}_{\partial T} + \left\langle \mathbf{x} (\mathbf{C^TSC} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z} f \right\rangle$$
 wrt. T
$$\frac{\partial}{\partial T} \{ \langle \mathsf{K}\mathsf{T} \rangle + \langle \boldsymbol{\lambda} (\mathsf{K} + \mathsf{K}\mathsf{T} + \mathsf{T}\mathsf{K} + \mathsf{T}\mathsf{K} + \mathsf{T} + \mathsf{E}\mathsf{T} + \mathsf{T} \rangle) \} = 0$$

$$- \mathbf{P} = \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \boldsymbol{\lambda} \mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$
 wrt. C
$$\left\langle \mathsf{K} (\mathsf{T} + \boldsymbol{\lambda} + \boldsymbol{\lambda} \mathsf{T} + \mathsf{T} \boldsymbol{\lambda} + \mathsf{T} \boldsymbol{\lambda} \mathsf{T}) \right\rangle + \langle \boldsymbol{\lambda} \varepsilon \mathsf{T} + \boldsymbol{\lambda} \mathsf{T} \varepsilon \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\boldsymbol{\lambda}} \rangle + \langle \mathsf{d}_{\boldsymbol{\lambda}}^{(2)} f \rangle$$

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

$$\frac{\mathsf{d} \mathbf{h} \rightarrow \mathsf{d} \mathbf{h}}{\mathsf{d}} \mathbf{d} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow \mathbf{d} \mathbf{g}^{lr} [\mathbf{d}]$$

$$\frac{\sum_{kc,b} (ib|kc)(\mathsf{M}_{\boldsymbol{\lambda}})_{kc,jb}}{\sum_{kc,j} (ab|kc)(\mathsf{M}_{\boldsymbol{\lambda}})_{kc,jb}}$$

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

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + \underbrace{E_c^{lr} + \left\langle \lambda \mathbf{R}[\mathbf{T}, \mathbf{C}] \right\rangle}_{\partial T} + \left\langle \mathbf{x}(\mathbf{C}^\mathsf{T} \mathbf{S} \mathbf{C} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z} \mathbf{f} \right\rangle$$
 wrt.
$$\mathbf{T} \qquad \frac{\partial}{\partial T} \{ \langle \mathsf{K} \mathsf{T} \rangle + \langle \lambda (\mathsf{K} + \mathsf{K} \mathsf{T} + \mathsf{T} \mathsf{K} \mathsf{T} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle \} = 0$$

$$- \mathbf{P} = \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \boldsymbol{\lambda} \mathbf{Q}[\mathbf{T}]^\mathsf{T}$$
 wrt.
$$\mathbf{C} \qquad \langle \mathsf{K}(\mathsf{T} + \lambda \lambda + \lambda \mathsf{T} + \mathsf{T} \lambda + \mathsf{T} \lambda \mathsf{T}) \rangle + \langle \lambda \varepsilon \mathsf{T} + \lambda \mathsf{T} \varepsilon \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\lambda} \rangle + \langle \mathbf{d}_{\lambda}^{(2)} \mathbf{f} \rangle$$

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

$$\mathbf{dh} \rightarrow \mathbf{dh}$$

$$\mathbf{d} \qquad \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow \mathbf{d} \qquad \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}]$$

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

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

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

 $\sum (aj|kc)(\mathbf{M}_{\lambda})_{kc,jb}$

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + \underbrace{E_c^{lr} + \left\langle \lambda \mathbf{R}[\mathbf{T}, \mathbf{C}] \right\rangle}_{\partial T} + \left\langle \mathbf{x} (\mathbf{C}^\mathsf{T} \mathbf{S} \mathbf{C} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z} \mathbf{f} \right\rangle$$
 wrt.
$$\mathbf{T} \qquad \qquad \frac{\partial}{\partial T} \{ \langle \mathsf{K} \mathsf{T} \rangle + \langle \lambda (\mathsf{K} + \mathsf{K} \mathsf{T} + \mathsf{T} \mathsf{K} \mathsf{T} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle \} = 0$$

$$- \mathbf{P} = \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \lambda \mathbf{Q}[\mathbf{T}]^\mathsf{T}$$
 wrt.
$$\mathbf{C} \qquad \qquad \langle \mathsf{K} (\mathsf{T} + \lambda \lambda + \lambda \mathsf{T} + \mathsf{T} \lambda + \mathsf{T} \lambda \mathsf{T}) \rangle + \langle \lambda \varepsilon \mathsf{T} + \lambda \mathsf{T} \varepsilon \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\lambda} \rangle + \langle \mathbf{d}_{\lambda}^{(2)} \mathbf{f} \rangle$$

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

$$\frac{\mathsf{d} \mathbf{h} \rightarrow \mathsf{d} \mathbf{h}}{\mathsf{d}} \qquad \mathbf{d} \qquad \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow \mathbf{d} \qquad \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}] \qquad \mathbf{d} \mathbf{f}^{lr} + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \qquad \mathbf{d}^{lr} \mathbf{f}^{lr} + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \qquad \mathbf{d}^{lr} \mathbf{f}^{lr}$$

$$\mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow \mathbf{d} \qquad \mathbf{d}^{lr} \mathbf{d}^{(0)} \mathbf{d}^{lr} \mathbf{d}^{l$$

$$\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{DC} + \underbrace{E_c^{lr} + \left\langle \lambda \mathbf{R} [\mathsf{T}, \mathsf{C}] \right\rangle}_{\partial T} + \left\langle \mathbf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z} \mathbf{f} \right\rangle$$
 wrt.
$$\mathsf{T} \qquad \qquad \frac{\partial}{\partial T} \{ \langle \mathsf{K} \mathsf{T} \rangle + \langle \lambda (\mathsf{K} + \mathsf{K} \mathsf{T} + \mathsf{T} \mathsf{K} + \mathsf{T} \mathsf{K} \mathsf{T} + \varepsilon \mathsf{T} + \mathsf{T} \varepsilon) \rangle \} = 0$$

$$- \mathsf{P} = \mathsf{Q} [\mathsf{T}] \lambda + \lambda \mathsf{Q} [\mathsf{T}]^\mathsf{T}$$
 wrt.
$$\mathsf{C} \qquad \qquad \langle \mathsf{K} (\mathsf{T} + \lambda + \lambda \mathsf{T} + \mathsf{T} \lambda + \mathsf{T} \lambda \mathsf{T}) \rangle + \langle \lambda \varepsilon \mathsf{T} + \lambda \mathsf{T} \varepsilon \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\lambda} \rangle + \langle \mathsf{d}_{\lambda}^{(2)} \mathsf{f} \rangle$$

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

$$\frac{\mathsf{d} \mathsf{h} \rightarrow \mathsf{d} \mathsf{h}}{\mathsf{d}} \qquad \qquad \mathsf{d} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}] \qquad \qquad \mathsf{d} \mathsf{f}^{\mathsf{Ir}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + -\frac{1}{2} \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + -\frac{1}{2} \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + -\frac{1}{2} \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + -\frac{1}{2} \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] + -\frac{1}{2} \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{(0)} \mathsf{g}^{\mathsf{Ir}} [\mathsf{d}^{(0)}] \qquad \qquad \mathsf{d} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{\mathsf{fl}} \mathsf{d}^{\mathsf{fl}} \mathsf{d}^{\mathsf{fl}} + \mathsf{d}^{$$

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

$$\mathcal{L} = \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{DC} + \underbrace{E_c^{lr} + \left\langle \lambda R[T,C] \right\rangle}_{c} + \left\langle \mathbf{x}(\mathbf{C^TSC} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z}f \right\rangle$$
 wrt.
$$\mathbf{T} \qquad \qquad \frac{\partial}{\partial T} \{ \left\langle \mathsf{KT} \right\rangle + \left\langle \lambda (\mathsf{K} + \mathsf{KT} + \mathsf{TK} + \mathsf{TK} + \mathsf{TE} + \mathsf{TE}) \right\rangle \} = 0$$

$$- \mathbf{P} = \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \boldsymbol{\lambda} \mathbf{Q}[\mathbf{T}]^{\mathsf{T}}$$
 wrt.
$$\mathbf{C} \qquad \qquad \left\langle \mathsf{K}(\mathsf{T} + \boldsymbol{\lambda} + \boldsymbol{\lambda} \mathsf{T} + \mathsf{T} \boldsymbol{\lambda} + \mathsf{T} \boldsymbol{\lambda} \mathsf{T}) \right\rangle + \left\langle \boldsymbol{\lambda} \varepsilon \mathsf{T} + \boldsymbol{\lambda} \mathsf{T} \varepsilon \right\rangle \dot{=} \left\langle \mathsf{KM}_{\boldsymbol{\lambda}} \right\rangle + \left\langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)} f \right\rangle$$

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

$$\mathbf{dh} \rightarrow \mathbf{dh} \qquad \mathbf{dh} \rightarrow \mathbf{dh} \qquad \mathbf{df}^{lr} + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow \mathbf{d} \quad \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}] \qquad \mathbf{df}^{lr} + \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] + -\frac{1}{2} \mathbf{d}^{(0)} \mathbf{g}^{lr} [\mathbf{d}^{(0)}] \qquad \mathbf{dg}^{sr} + \mathbf{d}^{(0)} \mathbf{W}^{sr} [\mathbf{d}] \qquad \mathbf{dg}^{sr} + \mathbf{d}^{(0)} \mathbf{W}^{sr} [\mathbf{d}]$$

$$\mathbf{dg}^{sr} \rightarrow \mathbf{dg}^{sr} + \mathbf{d}^{(0)} \mathbf{W}^{sr} [\mathbf{d}] \qquad \mathbf{dg}^{sr} + \mathbf{dg}^{sr} + \mathbf{dg}^{sr} = \mathbf{dg}^{sr} + \mathbf{dg}^$$

 $d^{(0)}W^{sr}[d^{(2)} + z]$

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

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

Stationary Conditions $\mathcal{L} = \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + \mathcal{E}_c^{\mathsf{lr}} + \left\langle \mathbf{\lambda} \mathbf{R} [\mathsf{T}, \mathsf{C}] \right\rangle + \left\langle \mathbf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle + \left\langle \mathbf{z} \mathbf{f} \right\rangle$

wrt. T
$$\frac{\frac{\partial}{\partial T}\{\langle \mathsf{KT}\rangle + \langle \lambda(\mathsf{K}+\mathsf{KT}+\mathsf{TK}+\mathsf{TK}+\varepsilon\mathsf{T}+\mathsf{T}\varepsilon)\rangle\} = 0}{-\mathsf{P} = \mathsf{Q}[\mathsf{T}]\boldsymbol{\lambda} + \boldsymbol{\lambda}\mathsf{Q}[\mathsf{T}]^\mathsf{T}}$$
wrt. C
$$\frac{\langle \mathsf{K}(\mathsf{T}+\boldsymbol{\lambda}+\boldsymbol{\lambda}\mathsf{T}+\mathsf{T}\boldsymbol{\lambda}+\mathsf{T}\boldsymbol{\lambda}\mathsf{T})\rangle + \langle \boldsymbol{\lambda}\varepsilon\mathsf{T}+\boldsymbol{\lambda}\mathsf{T}\varepsilon\rangle \dot{=}\langle \mathsf{KM}_{\boldsymbol{\lambda}}\rangle + \langle \mathsf{d}_{\boldsymbol{\lambda}}^{(2)}\mathsf{f}\rangle}{\left(\mathsf{d}^{(0)} + \mathsf{d}_{\boldsymbol{\lambda}}^{(2)} + \mathsf{z})\mathsf{f}\right\rangle + \Delta_{\mathsf{DC}}} + \frac{\langle \mathsf{KM}_{\boldsymbol{\lambda}}\rangle}{\langle \mathsf{KM}_{\boldsymbol{\lambda}}\rangle} + \left\langle \mathsf{x}(\mathsf{C}^\mathsf{T}\mathsf{SC} - \mathbf{1})\right\rangle$$

 $-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}]$ $\sum_{kc,j} (ij|kc) (\mathbf{M_{\lambda}})_{kc,jb}$ $\mathbf{dg}^{sr} \rightarrow \mathbf{dg}^{sr} + \mathbf{d}^{(0)} \mathbf{W}^{sr} [\mathbf{d}]$ $dg^{sr}+$

$$\begin{array}{ll} \mathbf{d}\mathbf{g}^{\mathsf{sr}}\!\!\to\!\!\mathbf{d}\mathbf{g}^{\mathsf{sr}}\!\!+\!\mathbf{d}^{(0)}\mathbf{W}^{\mathsf{sr}}[\mathbf{d}] & \mathbf{d}\mathbf{g}^{\mathsf{sr}}\!+\\ \Delta^{\mathsf{sr}}_{\mathsf{DC}}\!\!\to\!\!-\mathbf{d}^{(0)}\mathbf{W}^{\mathsf{sr}}[\mathbf{d}^{(0)}] & \mathbf{d}^{(0)}\mathbf{W}^{\mathsf{sr}}[\mathbf{d}^{(2)}+\mathbf{z}] & \sum\limits_{kc,j} (\mathit{aj}|\mathit{kc})(\mathbf{M}_{\lambda})_{\mathit{kc},\mathit{jb}} \end{array}$$

$$\Delta_{DC}^{sr} \rightarrow -d^{(0)}W^{sr}[d^{(0)}] \qquad \qquad d^{(0)}W^{sr}[d^{(2)} + z] \qquad \qquad \sum_{kc,j} (aj|kc)(M_{\lambda})_{kc}$$

$$\mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(2)} + \mathbf{z}] \qquad \qquad \underbrace{\mathcal{L}^{(a)}_{kc,j}}^{(a)}_{kc,j}$$

$$\left\{ \begin{array}{l} \left(\mathbf{\Theta} - \mathbf{\Theta}^{\mathsf{T}} + \mathbf{f} \mathbf{z} - \mathbf{z} \mathbf{f} + 4 \mathbf{g}^{\mathsf{Ir}}(\mathbf{z}) + 4 \mathbf{W}^{\mathsf{sr}}[\mathbf{z}] \right)_{ai} = 0 \\ \left(1 + \tau_{pq} \right) \left(\mathbf{\Theta} + \tilde{\mathbf{\Theta}}(\mathbf{z}) \right)_{pq} = -4(\mathbf{x})_{pq} \end{array} \right.$$

$$(\mathsf{CP-RP})_{q}$$

(CP-RPA)

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$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z})\mathbf{f}^{-\mathsf{Sr} + \mathsf{Ir}} \right. \left. \left. \right\rangle + \Delta_{\mathsf{DC}}^{-\mathsf{Sr} + \mathsf{Ir}} \right. + \left. \left\langle \mathsf{KM}_{\lambda} \right\rangle \right. + \left\langle \mathsf{x}(\mathsf{C}^\mathsf{T}\mathsf{SC} - \mathbf{1}) \right.$$

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

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



$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f}^{-\mathsf{Sr} + \mathsf{Ir}} \right. \left. \left. \right
angle + \Delta_{\mathsf{DC}}^{-\mathsf{Sr} + \mathsf{Ir}} \right. + \left. \left\langle \mathsf{KM}_{\lambda} \right
angle \right. + \left\langle \mathsf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle$$

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



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

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

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

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

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



$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f}^{-\mathsf{Sr} + \mathsf{Ir}} \right\rangle + \Delta_{\mathsf{DC}}^{-\mathsf{Sr} + \mathsf{Ir}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x}(\mathsf{C}^{\mathsf{T}}\mathsf{SC} - \mathbf{1}) \right\rangle$$

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

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

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

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

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



$$\mathcal{L} = \left\langle (\mathbf{d^{(0)}} + \mathbf{d_{\lambda}^{(2)}} + \mathbf{z}) \mathbf{f^{Sr}} + \mathbf{lr} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{Sr}} + \mathbf{lr} + \left\langle \mathsf{KM_{\lambda}} \right\rangle + \left\langle \mathsf{x}(\mathsf{C^{\mathsf{T}SC}} - \mathbf{1}) \right\rangle$$

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

$$\mathcal{L}^{(\kappa)} = D_{\mu\nu}^{1} H_{\mu\nu}^{(\kappa)} + D_{\mu\nu,\rho\sigma}^{2} (\mu\nu|\rho\sigma)^{\mathsf{lr}(\kappa)} + \frac{\mathsf{\Gamma}_{\mu\nu,\rho\sigma}^{2} (\mu\nu|\rho\sigma)^{\mathsf{lr}(\kappa)}}{\mathsf{\Gamma}_{\mu\nu,\rho\sigma}^{2} (\mu\nu|\rho\sigma)^{\mathsf{lr}(\kappa)}} + \frac{\mathsf{SR}^{(\kappa)}}{\mathsf{SR}^{(\kappa)}} + X_{\mu\nu} S_{\mu\nu}^{(\kappa)}$$

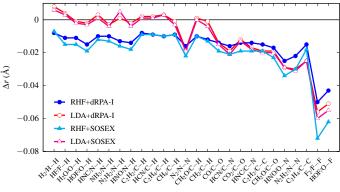
$$(\mathsf{D}^{1})_{\mu\nu} = C_{\mu\rho} \left(\mathsf{d}^{(0)} + \mathsf{d}_{\lambda}^{(2)} + \mathsf{z} \right)_{\rho q} C_{q\nu}^{\dagger} = \left(\mathsf{D}^{(0)} + \mathsf{D}_{\lambda}^{(2)} + \mathsf{z} \right)_{\mu\nu}$$

$$(\mathsf{D}^{2})_{\mu\nu,\sigma\rho} = \left(\frac{1}{2} \mathsf{D}^{(0)} + \mathsf{D}_{\lambda}^{(2)} + \mathsf{z} \right)_{\mu\nu} D_{\rho\sigma}^{(0)} - \frac{1}{2} \left(\frac{1}{2} \mathsf{D}^{(0)} + \mathsf{D}_{\lambda}^{(2)} + \mathsf{z} \right)_{\mu\rho} D_{\nu\sigma}^{(0)}$$

$$\begin{split} (\Gamma^{2})_{\mu\nu,\sigma\rho} &= C_{\mu k} C_{\nu j} C_{c\rho}^{\dagger} C_{b\sigma}^{\dagger} (\mathbf{M}_{\lambda})_{ia,kc} \\ \mathrm{SR}^{(\kappa)} &= \omega_{\lambda}^{(\kappa)} \left(F(\xi_{A}) + \frac{\partial F}{\partial \xi_{A}} \left(\xi_{A}^{\mathbf{d}_{\lambda}^{(2)}} + \xi_{A}^{\mathbf{z}} \right) \right) \\ &+ \omega_{\lambda} \frac{\partial F}{\partial \xi_{B}} \left(\xi_{B}^{\mathbf{d}^{(0)}(x)} + \xi_{B}^{\mathbf{d}_{\lambda}^{(2)}(x)} + \xi_{B}^{\mathbf{z}(x)} \right) + \omega_{\lambda} \frac{\partial^{2} F}{\partial \xi_{B} \partial \xi_{A}} \left(\xi_{A}^{\mathbf{d}_{\lambda}^{(2)}} + \xi_{A}^{\mathbf{z}} \right) \xi_{B}^{(\kappa)} \end{split}$$

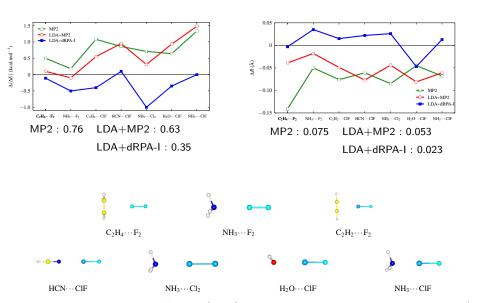
Validation and Results

Bond Lengths of simple molecules



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

Interaction Energies and Intermonomer distances



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