Modélisations quantochimiques des forces de dispersion de London par la méthode des phases aléatoires (RPA) : développements méthodologiques

Soutenance de thèse Bastien Mussard 13 décembre 2013

CRM², Université de Lorraine, Nancy, France

- Dispersion
 - polarisation dynamique mutuelle de nuages d'électrons
 - fluctuations de la densité électronique qui se corrèlent
 - besoin d'une bonne description des corrélations longue portée

RPA

- traitement de la longue-portée
- échange dans la fonction de réponse
- polarisabilité qui conduit au bon comportement à longue-portée (C_6/R^6)

Performances

- moyennes, dû à la qualité de la corrélation courte-portée
- nettement meilleures dans un contexte de séparation de portée

formulation "matrice densité de corrélation" formulation "matrice diélectrique"

formulation "de plasmon"

énergie de corrélation E_c

formulation "de Riccati"

problème à *N*-corps connexion adiabatique

HF DFT RSH

théorème de fluctuationdissipation Gradients

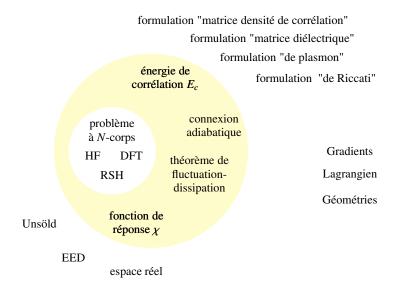
Lagrangien

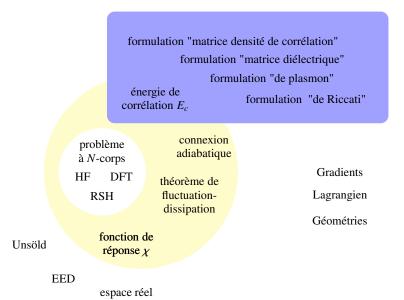
Géométries

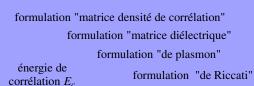
Unsöld fonction de réponse χ

EED

espace réel







problème à *N*-corps

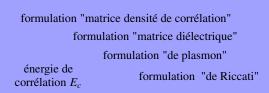
HF DFT RSH connexion adiabatique

théorème de fluctuationdissipation Gradients

Lagrangien

Géométries

Unsöld fonction de réponse χ EED espace réel



problème à N-corps

HF DFT RSH

connexion adiabatique théorème de fluctuationdissipation

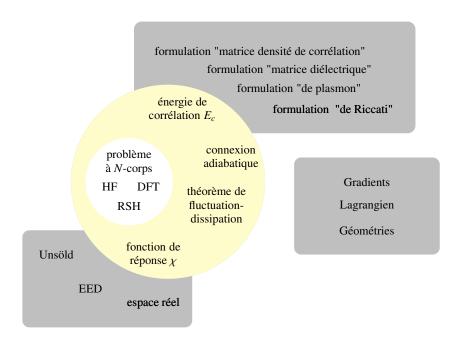
fonction de Unsöld réponse χ **EED**

espace réel

Gradients

Lagrangien

Géométries



Contexte théorique

- montrer le contexte dans lequel sont dérivées les équations qui nous intéressent
- ► comprendre ce qu'est l'énergie de corrélation E_c
- comment sont liées les notions telles que :
 - les fluctuations
 - la réponse d'un système (dissipation)

$$\left(\underbrace{\hat{\mathcal{T}}_e + \hat{V}_{ne}}_{\sum_i \hat{h}_i} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{\mathcal{E}}_{ij}}\right) |\Psi\rangle = E |\Psi
angle$$

$$\left(\underbrace{\frac{\hat{T}_{e} + \hat{V}_{ne}}{\sum_{i} \hat{h}_{i}} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\right) |\Psi\rangle = E |\Psi\rangle}_{\downarrow \downarrow \downarrow \downarrow}$$

$$\left(\underbrace{\frac{\hat{T}_{e} + \hat{V}_{ne}}{\sum_{i} \hat{h}_{i}} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\right) |\Psi\rangle = E |\Psi\rangle}_{}$$

Approche "fonction d'onde"
$$E = \min_{M} \left\{ \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \right\}$$

$$\ket{\phi_i} \ket{\phi_i}$$
 $\frac{1}{r}$

 $\left(\underbrace{\hat{\mathcal{T}}_{e} + \hat{V}_{ne}}_{\sum_{i} \hat{h}_{i}} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\right) |\Psi\rangle = E |\Psi\rangle$

$$E_{\mathsf{HF}} = \langle \Phi_{\mathsf{HF}} | \sum_{i} \hat{n}_{i} + \sum_{ij} \hat{g}_{ij} | \Phi_{\mathsf{HF}} \rangle = \sum_{i} \langle \phi_{i} | \hat{n}_{i} + \hat{v}_{\mathsf{Hx},i} | \phi_{i} \rangle$$

$$E = E_{HF} + \frac{E_c}{E_c}$$

Approche "fonction d'onde"

$$\left(\underbrace{\hat{T}_{e} + \hat{V}_{ne}}_{\sum_{i} \hat{h}_{i}} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\right) |\Psi\rangle = E |\Psi\rangle$$

$$E = \min_{\mathbf{V}} \left\{ \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \right\}$$

$$E_{\mathsf{HF}} = \langle \Phi_{\mathsf{HF}} | \sum_{i} \hat{h}_{i} + \sum_{ij} \hat{g}_{ij} | \Phi_{\mathsf{HF}} \rangle = \sum_{i} \langle \phi_{i} | \hat{h}_{i} + \frac{\hat{\mathsf{v}}_{\mathsf{Hx},i}}{\hat{\mathsf{v}}_{\mathsf{Hx},i}} | \phi_{i} \rangle$$

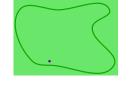
$$E = E_{\mathsf{HF}} + \frac{E_{\mathsf{C}}}{\hat{\mathsf{v}}_{\mathsf{Hx},i}}$$

Approche "fonctionnelle de la densité"

$$E = \min_{n} \left\{ T_e[n] + V_{ee}[n] + \int n(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$$

$$E = \min_{n} \left\{ T_s[n] + E_H[n] + \frac{E_{xc}[n]}{I_{xc}[n]} + \int n(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$$

$$E = \min_{\mathbf{n}} \left\{ T_s[\mathbf{n}] + E_H[\mathbf{n}] + E_{xc}[\mathbf{n}] + \int \mathbf{n}(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$$



$$\begin{split} E &= \min_{\Psi} \left\{ \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \right\} & \sum_{i} \hat{h}_{i} & \sum_{ij} \hat{g}_{ij} \\ E_{HF} &= \left\langle \Phi_{HF} \middle| \sum_{i} \hat{h}_{i} + \sum_{ij} \hat{g}_{ij} \middle| \Phi_{HF} \right\rangle = \sum_{i} \left\langle \phi_{i} \middle| \hat{h}_{i} + \left| \hat{V}_{Hx,i} \middle| \phi_{i} \right\rangle & \frac{1}{r} \\ E &= E_{HF} + \left| E_{c} \middle| E_{c} \right| \end{split}$$
 Approache "fonctionnelle de la densité"

 $\left(\hat{T}_{e} + \hat{V}_{ne} + \hat{V}_{ee}\right)|\Psi\rangle = E|\Psi\rangle$

Approche "fonction d'onde"

$$= \min \left\{ T_0[n] + V_{00}[n] + \int p(\mathbf{r}) v_{00}(\mathbf{r}) \right\}$$

 $E = \min_{\mathbf{n}} \left\{ T_e[\mathbf{n}] + V_{ee}[\mathbf{n}] + \int \mathbf{n}(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$

$$E = \min_{n} \left\{ T_s[n] + E_H[n] + \frac{E_{xc}[n]}{n} + \int n(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$$

Séparation de portée
$$\Xi = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ee}^{lr} | \Psi \rangle + E_{Hxc}^{sr} [n_{\Psi}] + \int n_{\Psi}(\mathbf{r}) v_{ne}(\mathbf{r}) \right\}$$

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

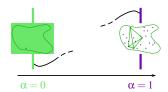
$$E_{RSH} = \min_{\Phi} \left\{ \underline{\langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}^{lr} | \Phi \rangle} + \underline{E_{Hxc}^{sr}[n_{\Phi}]} \right\}$$

 $E = E_{RSH} + \frac{E_{c}^{lr}}{E_{c}^{lr}}$ énergie totale $\frac{1}{r} = v_{ee}^{lr}(r) + v_{ee}^{sr}(r)$

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

$$\begin{split} E_{\alpha} &= \min_{\mathbf{\Psi}} \left\{ \langle \mathbf{\Psi} | \ \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{Ir}} + \alpha \hat{V}_{ee}^{\mathsf{Ir}} \, | \mathbf{\Psi} \rangle + E_{\mathsf{Hxc}}^{\mathsf{sr}} [n_{\mathbf{\Psi}}] \right\} \\ \hat{H}_{\alpha} &= \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{Ir}} + \alpha \hat{V}_{ee}^{\mathsf{Ir}} + \hat{V}_{\mathsf{Hxc}}^{\mathsf{sr}} [\mathbf{\Psi}_{\alpha}] \end{split}$$

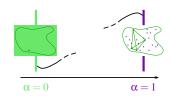
- systèmes soumis à un potentiel intermédiaire
- connexion entre système non-interagissant et le système réel



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

$$\begin{split} E_{\alpha} &= \min_{\mathbf{\Psi}} \left\{ \langle \mathbf{\Psi} | \ \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{Ir}} + \alpha \hat{V}_{ee}^{\mathsf{Ir}} | \mathbf{\Psi} \rangle + E_{\mathsf{Hxc}}^{\mathsf{sr}} [n_{\mathbf{\Psi}}] \right\} \\ \hat{H}_{\alpha} &= \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{Ir}} + \alpha \hat{V}_{ee}^{\mathsf{Ir}} + \hat{V}_{\mathsf{Hxc}}^{\mathsf{sr}} [\mathbf{\Psi}_{\alpha}] \end{split}$$

- systèmes soumis à un potentiel intermédiaire
- connexion entre système non-interagissant et le système réel



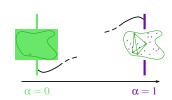
Énergie de corrélation

$$rac{\mathrm{d} E_{lpha}}{\mathrm{d} lpha} = \langle \Psi_{lpha} | \; \hat{W}^{
m lr}_{
m ee} \, | \Psi_{lpha}
angle \hspace{0.5cm} ; \hspace{0.5cm} \hat{W}^{
m lr}_{
m ee} = rac{\mathrm{d} \hat{H}_{lpha}}{\mathrm{d} lpha} = \hat{V}^{
m lr}_{
m Hx,HF}$$

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

$$\begin{split} E_{\alpha} &= \min_{\mathbf{\Psi}} \left\{ \langle \mathbf{\Psi} | \ \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{lr}} + \alpha \hat{V}_{ee}^{\mathsf{lr}} \, | \mathbf{\Psi} \rangle + E_{\mathsf{Hxc}}^{\mathsf{sr}} [n_{\mathbf{\Psi}}] \right\} \\ \hat{H}_{\alpha} &= \hat{T} + \hat{V}_{ne} + (1 - \alpha) \hat{V}_{\mathsf{Hx},\mathsf{HF}}^{\mathsf{lr}} + \alpha \hat{V}_{ee}^{\mathsf{lr}} + \hat{V}_{\mathsf{Hxc}}^{\mathsf{sr}} [\mathbf{\Psi}_{\alpha}] \end{split}$$

- systèmes soumis à un potentiel intermédiaire
- connexion entre système non-interagissant et le système réel



Énergie de corrélation

$$\int_{0}^{1} d\alpha \, \frac{dE_{\alpha}}{d\alpha} = \int_{0}^{1} d\alpha \, \langle \Psi_{\alpha} | \, \hat{W}_{\text{ee}}^{\text{lr}} | \Psi_{\alpha} \rangle \qquad ; \qquad \hat{W}_{\text{ee}}^{\text{lr}} = \frac{d\hat{H}_{\alpha}}{d\alpha} = \hat{V}_{\text{ee}}^{\text{lr}} - \hat{V}_{\text{Hx,HF}}^{\text{lr}}$$

$$E_c^{AC} = \int_0^1 d\alpha \, \frac{1}{2} \int_{1.2} w(1,2) P_{c,\alpha}(1,2)$$

Théorème de Fluctuation-Dissipation

$$E_c^{AC} = \frac{1}{2} \int_0^1 d\alpha \int_{1,2} w(1,2) P_{c,\alpha}(1,2)$$

$$P_{c,\alpha}(1,2) = n_{2,\alpha}(1,2) - n_{2,0}(1,2)$$

$$= \langle \Psi_{\alpha} | \delta \hat{n}_{1}(2) \delta \hat{n}_{1}(1) | \Psi_{\alpha} \rangle$$

$$- \langle \Psi_{0} | \delta \hat{n}_{1}(2) \delta \hat{n}_{1}(1) | \Psi_{0} \rangle + \Delta n_{\alpha}$$

Théorème de Fluctuation-Dissipation

 $E_c^{\mathsf{AC}} = \frac{1}{2} \int_0^1 d\alpha \int_{1.2} w(1,2) \Big[\langle \Psi_\alpha | \, \delta \hat{n}(1) \delta \hat{n}(2) \, | \Psi_\alpha \rangle - \langle \Phi_0 | \, \delta \hat{n}(1) \delta \hat{n}(2) \, | \Phi_0 \rangle + \Delta n_\alpha \Big]$

$$E_c^{AC} = \frac{1}{2} \int_0^1 d\alpha \int_{1,2} w(1,2) P_{c,\alpha}(1,2)$$

 $P_{c,\alpha}(1,2)=n_{2,\alpha}(1,2)-n_{2,0}(1,2)$

Fluctuations

$$= \langle \Psi_{\alpha} | \delta \hat{n}_{1}(2) \delta \hat{n}_{1}(1) | \Psi_{\alpha} \rangle$$

$$+ \langle \Psi_{0} | \delta \hat{n}_{1}(2) \delta \hat{n}_{1}(1) | \Psi_{0} \rangle + \Delta n_{\alpha}$$

Théorème de Fluctuation-Dissipation

$$E_c^{\mathsf{AC}} = \frac{1}{2} \int_0^1 d\alpha \int_{1,2} w(1,2) P_{c,\alpha}(1,2) \qquad P_{c,\alpha}(1,2) = n_{2,\alpha}(1,2) - n_{2,0}(1,2) \\ = \langle \Psi_{\alpha} | \delta \hat{n}_1(2) \delta \hat{n}_1(1) | \Psi_{\alpha} \rangle \\ - \langle \Psi_0 | \delta \hat{n}_1(2) \delta \hat{n}_1(1) | \Psi_0 \rangle$$

Fluctuations
$$-\langle \Psi_0 | \delta \hat{n}_1(2) \delta \hat{n}_1(1) | \Psi_0 \rangle + \Delta n_{\alpha}$$

$$E_c^{\text{AC}} = \frac{1}{2} \int_0^1 d\alpha \int_{1.2} w(1,2) \Big[\langle \Psi_{\alpha} | \delta \hat{n}(1) \delta \hat{n}(2) | \Psi_{\alpha} \rangle - \langle \Phi_0 | \delta \hat{n}(1) \delta \hat{n}(2) | \Phi_0 \rangle + \Delta n_{\alpha} \Big]$$

Réponse du système

$$\langle \Psi_{\alpha} | \, \delta \hat{n}(1) \delta \hat{n}(2) \, | \Psi_{\alpha} \rangle = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \, \chi_{\alpha}(1,2;\omega)$$

système répond de la même manière quand il est mis hors équilibre par une force extérieure (dissipation) ou par des fluctuations quantiques

 $E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{1.2}^{\infty} \frac{-d\omega}{2\pi i} w(1,2) \left[\chi_{\alpha}(1,2;\omega) - \chi_0(1,2;\omega) + \Delta n_{\alpha} \right]$

expression exacte de l'énergie de corrélation

Approximation de la phase aléatoire

formulation "matrice densité de corrélation"

formulation "matrice diélectrique"

formulation "de plasmon"
énergie de

connexion

adiabatique

énergie de corrélation E_c

formulation "de Riccati"

Gradients

Lagrangien

Géométries

problème à *N*-corps

HF DFT théorème de RSH fluctuationdissipation

Unsöld fonction de réponse χ

EED

espace réel

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{1,2;1',2'} \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \ w(1,2;1',2') \left[\chi_{\alpha}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$$

"Flavors" de RPA dosage de l'inclusion de l'échange

- dans fonction de réponse χ_{α} : dRPA/RPAx
- dans l'interaction w : intégrales non-antisymétrisées (I) ou antisymétrisées (II)

Intégrations analytiques/numériques

- intégrale analytique sur la fréquence $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ formulation "matrice densité de corrélation" $\mathbf{P}_{c,\alpha}$
- ▶ deux intégrales analytiques $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$ formulation "de plasmon" et "de Riccati" ((d)rCCD)
- lacktriangle intégrale analytique sur la constante de couplage $\left(\int_0^1 dlpha
 ight)$ formulation "matrice diélectrique" $arepsilon=1-\Pi_0 {\sf K}$

Comprendre et Unifier

$$P_{c,\alpha} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha} \quad (1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$$

 χ_{α} $(1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - f_{\alpha}(1,2;1',2';\omega)$ $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$

$$\chi_0(1,2;1',2',\omega) = \sum_{ia} \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1')$$

$$\chi_0(1,2;1',2',\omega) = \sum_{ia} \frac{\gamma_i + \gamma_i +$$

$$1,2;1',2',\omega) = \sum_{ia} \frac{1}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{1}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$$
uation de Bethe-Salpeter

 $\chi_0(1,2;1',2',\omega) = \sum_{\cdot} \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$

Représentation de Lehmann
$$\chi_0(1,2;1',2',\omega) = \sum_{i} \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\psi_-(\varepsilon_2-\varepsilon_1)+in+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(2')}{\psi_-(\varepsilon_2-\varepsilon_1)+in+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_a(2')\psi_a^*(1')\psi_a(2')\psi_a^*(1')\psi_a^$$

$$P_{c,\alpha} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha} \quad (1,2;1',2';\omega) - \chi_{0}(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$$

Représentation de Lehmann

 $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$

$$\chi_0(1,2;1',2',\omega) = \sum_{i,\mathtt{a}} \frac{\psi_i^*(1')\psi_\mathtt{a}(1)\psi_\mathtt{a}^*(2')\psi_i(2)}{\omega - (\varepsilon_\mathtt{a} - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_\mathtt{a}(2)\psi_\mathtt{a}^*(1')\psi_i(1)}{-\omega - (\varepsilon_\mathtt{a} - \varepsilon_i) + i\eta^+}$$

$$\chi_0(1,2;1',2',\omega) = \sum_{ia} \frac{1}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{1}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$$
Équation de Bethe-Salpeter
$$\chi_{\alpha} = (1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - f_{\alpha}(1,2;1',2';\omega)$$

Équation de Bethe-Salpeter

$$(1,2,1,2,\omega) - \sum_{ia} \frac{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$$
uation de Bethe-Salpeter
$$(1,2,1/2/\omega)^{-1} - 2\omega (1,2,1/2/\omega)^{-1} = f(1,2,1/2/\omega)$$

 $=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha \left(\frac{1}{r_1-r_2}+f_x(1,2;1',2')\right)$

$$\frac{-u\omega}{2\pi i} \left[\chi_{\alpha} \quad (1,2;1',2';\omega) - \chi_{0}(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$$
 ation de Lehmann

$$P_{c,\alpha}^{\text{RPA}} = \int_{0}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_{0}(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$$

Représentation de Lehmann

$$\chi_0(1,2;1',2',\omega) = \sum_{i,a} \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$$

Équation de Bethe-Salpeter
$$\chi^{\text{RPA}}(1.2:1'.2':\omega)^{-1} = \chi_0(1.2:1'.2':\omega)^{-1} - \alpha f^{\text{RPA}}(1.2:1'.2')$$

$$\chi_{\alpha}^{\mathsf{RPA}}(1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - \alpha f^{\mathsf{RPA}}(1,2;1',2')$$

$$\chi_{\alpha} (1,2,1,2,\omega) = \chi_{0}(1,2,1,2,\omega) = -\alpha i (1,2,1,2)$$

$$f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{\mathsf{r}_1 - \mathsf{r}_2} + f_{\mathsf{x},\alpha}(1,2;1',2';\omega) + f_{\mathsf{c},\alpha}(1,2;1',2';\omega)$$

$$f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{\mathsf{r}_{1}-\mathsf{r}_{2}} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$$
$$= \alpha f^{\mathsf{RPA}}(1,2;1',2') = \alpha \left(\frac{1}{\mathsf{r}_{1}-\mathsf{r}_{2}} + f_{x}(1,2;1',2')\right)$$

 $P_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$ $\mathbb{P}_{c,\alpha}^{\mathsf{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\mathbb{I}_{\alpha}^{\mathsf{RPA}} - \mathbb{I}_{0} \right]$ Représentation de Lehmann

$$\frac{\psi_{i}^{*}(1')\psi_{a}(1)\psi_{a}^{*}(2')\psi_{i}(2)}{(1-\psi_{a}^{*}(1))\psi_{a}^{*}(1)\psi_$$

 $=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha \left(\frac{1}{r_1-r_2}+f_x(1,2;1',2')\right)$

 $\chi_0(1,2;1',2',\omega) = \sum_{\cdot} \frac{\psi_i^*(1')\psi_{\mathfrak{a}}(1)\psi_{\mathfrak{a}}^*(2')\psi_i(2)}{\omega - (\varepsilon_{\mathfrak{a}} - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_{\mathfrak{a}}(2)\psi_{\mathfrak{a}}^*(1')\psi_i(1)}{-\omega - (\varepsilon_{\mathfrak{a}} - \varepsilon_i) + i\eta^+}$

 $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$

Équation de Bethe-Salpeter

 $\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1} = \chi_{0}(1,2;1',2';\omega)^{-1} - \alpha f^{\text{RPA}}(1,2;1',2')$

 $(\Pi_{\alpha}^{\text{RPA}})^{-1} = (\Pi_0)^{-1} - \alpha \mathbb{F}^{\text{RPA}}$

 $(\Pi_0)^{-1} = \omega \Delta - \Lambda_0$

 $P_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$ $\mathbb{P}_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\mathbb{\Pi}_{\alpha}^{\text{RPA}} - \mathbb{\Pi}_{0} \right]$

Représentation de Lehmann

$$\frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\psi_i^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*(1)\psi_a(1)\psi_a^*($$

 $\chi_0(1,2;1',2',\omega) = \sum_{\cdot} \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$

$$^{1}=\chi_{0}(1,$$

 $f^{\text{dRPA}} = w(1,2)[\delta(1,1')\delta(2,2')]$

 $\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1} = \chi_{0}(1,2;1',2';\omega)^{-1} - \alpha f^{\text{RPA}}(1,2;1',2')$

$$(1^{\circ},2^{\circ};\omega)^{-1}-\alpha f^{\circ\circ}$$

$$f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$$

 $(\Pi_0)^{-1} = \omega \Delta - \Lambda_0$

 $(\Pi_{\alpha}^{\mathsf{RPA}})^{-1} = (\Pi_{0})^{-1} - \alpha \mathbb{F}^{\mathsf{RPA}}$

$$= \alpha f^{\text{RPA}}(1,2;1',2') = \alpha \left(\frac{1}{r_1 - r_2} + f_x(1,2;1',2')\right)$$

$$f^{\text{RPAx}} = w(1,2)[\delta(1,1')\delta(2,2') - \delta(1,2')\delta(2,1')]$$

$P_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$

Équation de Bethe-Salpeter

Représentation de Lehmann

 $\chi_0(1,2;1',2',\omega) = \sum_{\cdot} \frac{\psi_i^*(1')\psi_{\mathfrak{a}}(1)\psi_{\mathfrak{a}}^*(2')\psi_i(2)}{\omega - (\varepsilon_{\mathfrak{a}} - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_{\mathfrak{a}}(2)\psi_{\mathfrak{a}}^*(1')\psi_i(1)}{-\omega - (\varepsilon_{\mathfrak{a}} - \varepsilon_i) + i\eta^+}$

Formulation "matrice densité de corrélation" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$

 $\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - \alpha f^{\text{RPA}}(1,2;1',2')$

 $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$

 $=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha \left(\frac{1}{r_1-r_2}+f_x(1,2;1',2')\right)$

 $f^{\text{dRPA}} = w(1,2)[\delta(1,1')\delta(2,2')]$

 $f^{\text{RPAx}} = w(1,2)[\delta(1,1')\delta(2,2') - \delta(1,2')\delta(2,1')]$

 $\mathbb{F}^{dRPA} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}$

 $(\Pi_0)^{-1} = \omega \Delta - \Lambda_0$

 $\mathbb{F}^{\mathsf{RPAx}} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{R} & \mathbf{A}' \end{pmatrix}$

 $\mathbb{P}_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\mathbb{\Pi}_{\alpha}^{\text{RPA}} - \mathbb{\Pi}_{0} \right]$

 $(\Pi_{\alpha}^{\mathsf{RPA}})^{-1} = (\Pi_{0})^{-1} - \alpha \mathbb{F}^{\mathsf{RPA}}$

$P_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$

Équation de Bethe-Salpeter

 $f^{\text{dRPA}} = w(1,2)[\delta(1,1')\delta(2,2')]$

Énergie de corrélation

Représentation de Lehmann

Formulation "matrice densité de corrélation" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$

 $\chi_0(1,2;1',2',\omega) = \sum_i \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$

 $\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - \alpha f^{\text{RPA}}(1,2;1',2')$ $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$ $=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha \left(\frac{1}{r_1-r_2}+f_x(1,2;1',2')\right)$

 $f^{\text{RPAx}} = w(1,2)[\delta(1,1')\delta(2,2') - \delta(1,2')\delta(2,1')]$

 $E_c^{AC} = \int_0^1 d\alpha \, \frac{1}{2} \int_{1.2} w(1,2) P_{c,\alpha}(1,2)$ $E_c^{\text{RPA}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^I . \mathbb{P}_{c,\alpha}^{\text{RPA}}) \qquad E_c^{\text{dRPA}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^I . \mathbb{P}_{c,\alpha}^{\text{dRPA}})$

 $\mathbb{F}^{\mathsf{RPAx}} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix}$ $E_c^{\text{RPA-II}} = \frac{1}{4} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{II}}.\mathbb{P}_c^{\text{RPA}}) \qquad E_c^{\text{dRPA-II}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{II}}.\mathbb{P}_c^{\text{dRPA}})$

 $\mathbb{P}_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\mathbb{\Pi}_{\alpha}^{\text{RPA}} - \mathbb{\Pi}_{0} \right]$

 $(\Pi_{\alpha}^{\mathsf{RPA}})^{-1} = (\Pi_{0})^{-1} - \alpha \mathbb{F}^{\mathsf{RPA}}$

 $(\Pi_0)^{-1} = \omega \Delta - \Lambda_0$

 $\mathbb{F}^{\mathsf{dRPA}} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}$

$P_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega) - \chi_0(1,2;1',2';\omega) + \Delta n_{\alpha} \right]$

Équation de Bethe-Salpeter

Représentation de Lehmann

 $f_{\alpha}(1,2;1',2';\omega) = \frac{\alpha}{r_1-r_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega)$

 $f^{\text{RPAx}} = w(1,2)[\delta(1,1')\delta(2,2') - \delta(1,2')\delta(2,1')]$

 $f^{\text{dRPA}} = w(1,2)[\delta(1,1')\delta(2,2')]$

Énergie de corrélation

 $E_c^{\text{RPAx-I}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{I}}.\mathbb{P}_{c,\alpha}^{\text{RPAx}})$

 $\chi_0(1,2;1',2',\omega) = \sum_i \frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+} + \frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta^+}$

 $=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha \left(\frac{1}{r_1-r_2}+f_x(1,2;1',2')\right)$

 $E_c^{\text{RPA}\times\text{II}} = \frac{1}{4} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{RPA}}) \quad E_c^{\text{dRPA}\cdot\text{II}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{dRPA}})$

Formulation "matrice densité de corrélation" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$

 $\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - \alpha f^{\text{RPA}}(1,2;1',2')$

 $E_c^{AC} = \int_0^1 d\alpha \, \frac{1}{2} \int_{1/2} w(1,2) P_{c,\alpha}(1,2)$

 $E_c^{\text{dRPA-I}} = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}^{\text{I}}.\mathbb{P}_{c,\alpha}^{\text{dRPA}})$

 $\mathbb{F}^{dRPA} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}$

 $\mathbb{F}^{\mathsf{RPAx}} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix}$

 $\mathbb{W}^{\mathsf{II}} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix}$

 $\mathbb{W}^{\mathsf{I}} = \begin{pmatrix} \mathsf{K} & \mathsf{K} \\ \mathsf{K} & \mathsf{K} \end{pmatrix}$

 $\mathbb{P}_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\mathbb{\Pi}_{\alpha}^{\text{RPA}} - \mathbb{\Pi}_{0} \right]$

 $(\mathbb{D}_{\alpha}^{\mathsf{RPA}})^{-1} = (\mathbb{D}_0)^{-1} - \alpha \mathbb{F}^{\mathsf{RPA}}$

 $(\Pi_0)^{-1} = \omega \triangle - A_0$

Formulation "de plasmon" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$

$$\Pi_{\alpha}^{-1} = \omega \triangle - A_0 - \alpha \mathbb{F}$$

$$W^{\text{I/II}} = \mathbb{F}^{\text{d/x}}$$

$$E_{c} = \int_{0}^{1} d\alpha \operatorname{Tr}\left(\underline{\mathbb{WP}_{c,\alpha}}\right) = \int_{0}^{1} d\alpha \left. \sum_{n=0}^{\frac{d\omega_{\alpha,n}}{d\alpha}} - \frac{d\omega_{\alpha,n}}{d\alpha} \right|_{\alpha=0} = \sum_{n=0}^{\infty} \omega_{1,n}^{\mathsf{RPA}} - \omega_{1,n}^{\mathsf{TDA}}$$

$$E_{c} = \int_{0}^{1} d\alpha \operatorname{Tr}\left(\underline{\mathbb{WP}_{c,\alpha}}\right) = \int_{0}^{1} d\alpha \left. \sum_{n} \frac{d\omega_{\alpha,n}}{d\alpha} - \frac{d\omega_{\alpha,n}}{d\alpha} \right|_{\alpha=0} = \sum_{n} \omega_{1,n}^{\mathsf{RPA}} - \omega_{1,n}^{\mathsf{TDA}}$$

Formulation "de plasmon" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$ $\frac{\mathbb{Q}_{\alpha}^{-1} = \omega \Delta - \Lambda_{0} - \alpha \mathbb{F}}{\mathbb{Q}^{1/1} = \mathbb{F}^{d/x}}$

$$E_c = \int_0^1 d\alpha \operatorname{Tr}\left(\underline{\mathbb{WP}_{c,\alpha}}\right) = \int_0^1 d\alpha \left. \sum \tfrac{\mathrm{d}\omega_{\alpha,n}}{\mathrm{d}\alpha} - \tfrac{\mathrm{d}\omega_{\alpha,n}}{\mathrm{d}\alpha} \right|_{\alpha=0} = \sum \omega_{1,n}^{\mathrm{RPA}} - \omega_{1,n}^{\mathrm{TDA}}$$

Formulation "de Riccati"
$$\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$$
 et $\left(\int_{0}^{1} d\alpha\right)$

$$egin{aligned} \mathbf{R}[\mathbf{T}] &= \mathbf{B} + \left[\mathbf{A}', \mathbf{T}
ight]_+ + \mathbf{T}\mathbf{B}\mathbf{T} + \left[arepsilon, \mathbf{T}
ight]_+ = \mathbf{0} \ & E_c^{\mathsf{dRPA-I}} &= rac{1}{2} \operatorname{tr} \left\{ \mathbf{B}^{\mathsf{dRPA}} \mathbf{T}^{\mathsf{dRPA}}
ight\} \ & E_c^{\mathsf{RPAx-II}} &= rac{1}{4} \operatorname{tr} \left\{ \mathbf{B}^{\mathsf{RPAx}} \mathbf{T}^{\mathsf{RPAx}}
ight\} \end{aligned}$$

équivalent à (d)rCCD

$$E_c^{ extsf{d/x-I}} = \int_0^1 dlpha \operatorname{tr}\left\{\mathbf{P}_lpha^{ extsf{d/x}}\mathbf{K}\right\}$$

$$E_c^{\mathrm{d/x-II}} \rightsquigarrow E_c^{\mathrm{d/x-IIa}} = \int_0^1 d\alpha \operatorname{tr} \left\{ \mathbf{P}_{\alpha}^{\mathrm{d/x}} \mathbf{B} \right\} \qquad (\mathbf{1} + \mathbf{P}_{\alpha})^{-1} \approx (\mathbf{1} - \mathbf{P}_{\alpha})$$

$$E_c^{\mathsf{d}/\mathsf{x-I}} = \int_0^1 d\alpha \operatorname{tr}\left\{\mathbf{P}_\alpha^{\mathsf{d}/\mathsf{x}}\mathbf{K}\right\}$$

$$E_c^{\mathrm{d/x\text{-}II}} \leadsto E_c^{\mathrm{d/x\text{-}IIa}} = \int_0^1 d\alpha \operatorname{tr}\left\{\mathbf{P}_{\alpha}^{\mathrm{d/x}}\mathbf{B}\right\} \qquad (\mathbf{1} + \mathbf{P}_{\alpha})^{-1} \approx (\mathbf{1} - \mathbf{P}_{\alpha})$$

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$

$$egin{aligned} \mathbf{0} &= \mathbf{K} + \left[\mathbf{K}, \mathbf{T}
ight]_{+} + \mathbf{T} \mathbf{K} \mathbf{T} + \left[oldsymbol{arepsilon}, \mathbf{T}
ight]_{+} \ & E_{c}^{\mathsf{dRPA-I}} = \ \mathrm{tr} \left\{ \mathbf{K} \mathbf{T}
ight\} \end{aligned}$$

$$E_c^{\text{dRPA-I-}} = \text{tr}\{\mathbf{BT}\}$$

$$\int_0^1 d\alpha \, \mathbf{P}_{\alpha} \, \text{et } \mathbf{T} ?$$
Jansen, Liu, Ángyán; *J. Chem. Phys.* (2010)

, ,

$$E_c^{\mathsf{d}/\mathsf{x-I}} = \int_0^1 d\alpha \, \mathsf{tr} \left\{ \mathbf{P}_\alpha^{\mathsf{d}/\mathsf{x}} \mathbf{K} \right\}$$

$$E_c^{\text{d/x-II}} \leadsto E_c^{\text{d/x-IIa}} = \int_0^1 d\alpha \operatorname{tr} \left\{ \mathbf{P}_{\alpha}^{\text{d/x}} \mathbf{B} \right\} \qquad (\mathbf{1} + \mathbf{P}_{\alpha})^{-1} \approx (\mathbf{1} - \mathbf{P}_{\alpha})$$

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$

$$\begin{aligned} \mathbf{0} &= \mathbf{K} + \left[\mathbf{K}, \mathbf{T}\right]_{+} + \mathbf{T} \mathbf{K} \mathbf{T} + \left[\boldsymbol{\varepsilon}, \mathbf{T}\right]_{+} \\ & E_{c}^{\mathsf{dRPA-I}} = \ \mathsf{tr}\left\{\mathbf{K} \mathbf{T}\right\} \\ & E_{c}^{\mathsf{dRPA-I-SOSEX}} = \ \mathsf{tr}\left\{\mathbf{B} \mathbf{T}\right\} \end{aligned}$$

$$\int_0^1 d\alpha \, \mathbf{P}_{\alpha} \, \text{et } \mathbf{T} ?$$
Jansen, Liu, Ángyán; *J. Chem. Phys.* (2010)

Hesselmann; Phys. Rev. A (2012)

$$\begin{aligned} \mathbf{0} &= \frac{\mathbf{B}}{\mathbf{B}} + \left[\frac{\mathbf{B}}{\mathbf{B}}, \mathbf{T}\right]_{+} + \mathbf{T}\frac{\mathbf{B}}{\mathbf{B}} \mathbf{T} + \left[\varepsilon, \mathbf{T}\right]_{+} \\ E_{c}^{\mathrm{RPAX2}} &= \ \mathrm{tr}\left\{\mathbf{KT}\right\} \end{aligned}$$

$$E_c^{\text{d/x-I}} = \int_0^1 d\alpha \operatorname{tr} \left\{ \mathbf{P}_\alpha^{\text{d/x}} \mathbf{K} \right\}$$

$$E_c^{\text{d/x-II}} \leadsto E_c^{\text{d/x-IIa}} = \int_0^1 d\alpha \operatorname{tr} \left\{ \mathbf{P}_{\alpha}^{\text{d/x}} \mathbf{B} \right\} \qquad (\mathbf{1} + \mathbf{P}_{\alpha})^{-1} \approx (\mathbf{1} - \mathbf{P}_{\alpha})$$

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_{0}^{1} d\alpha\right)$

$$\begin{aligned} \mathbf{0} &= \mathbf{K} + \left[\mathbf{K}, \mathbf{T} \right]_{+} + \mathbf{T} \mathbf{K} \mathbf{T} + \left[\boldsymbol{\varepsilon}, \mathbf{T} \right]_{+} \\ & E_{c}^{\mathsf{dRPA-I}} = \operatorname{tr} \left\{ \mathbf{K} \mathbf{T} \right\} \\ & E_{c}^{\mathsf{dRPA-I-SOSEX}} = \operatorname{tr} \left\{ \mathbf{B} \mathbf{T} \right\} \end{aligned}$$

Jansen, Liu, Ángyán; J. Chem. Phys. (2010) Hesselmann; Phys. Rev. A (2012)

Hesselmann; Phys. Rev. A (2012)

$$\mathbf{0} = \mathbf{B} + [\mathbf{B}, \mathbf{T}]_{+} + \mathbf{T}\mathbf{B}\mathbf{T} + [\boldsymbol{\varepsilon}, \mathbf{T}]_{+}$$

$$E_{\boldsymbol{\varepsilon}}^{\mathsf{RPAX2}} = \operatorname{tr}\{\mathbf{KT}\}$$

Comprendre et Unifier

Ángván, Liu. Toulouse, Jansen: J.C.T.C. (2011)

Formulation "matrice diélectrique"
$$\left(\int_0^1 d\alpha\right)$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \operatorname{Tr} \{ \prod_{\alpha}^{d/x} \mathbb{W}^{1/|I|} - \prod_0 \mathbb{W}^{1/|I|} \}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1} \operatorname{Tr} \{ \left(\prod_0 \mathbb{W}^{d/x} \right)^{n-1} \prod_0 \mathbb{W}^{1/|I|} \}$$

$$-\sum_{n=2} \frac{x^n}{n} = \operatorname{Log}(1-x) + x$$

$$\begin{split} E_c^{\text{AC-FDT}} &= \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \operatorname{Tr} \{ \Pi_\alpha^{\text{d/x}} \mathbb{W}^{\text{I/II}} - \Pi_0 \mathbb{W}^{\text{I/II}} \} \\ E_c^{\text{AC-FDT}} &= \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1} \operatorname{Tr} \{ \left(\Pi_0 \mathbb{W}^{\text{d/x}} \right)^{n-1} \Pi_0 \mathbb{W}^{\text{I/II}} \} \\ &- \sum_{n=2} \frac{x^n}{n} = \operatorname{Log}(1-x) + x \end{split}$$

dRPA-I $\mathbb{W}^{\mathsf{d}} = \mathbb{W}^{\mathsf{l}} = \begin{pmatrix} \mathsf{K} & \mathsf{K} \\ \mathsf{K} & \mathsf{K} \end{pmatrix} \quad ; \quad \mathsf{Tr} \left\{ (\Pi_{0} \mathbb{W}^{\mathsf{d}})^{n} \right\} = \mathsf{tr} \left\{ (\Pi_{0} \mathsf{K})^{n} \right\}$

$$E_c^{ ext{dRPA-I}} = rac{1}{2} \int^{\infty} rac{d\omega}{2\pi} \operatorname{tr} \left\{ \operatorname{Log}(\mathbf{1} - \mathbf{\Pi}_0 \mathbf{K}) + \mathbf{\Pi}_0 \mathbf{K}
ight\}$$
 $\epsilon = \mathbf{1} - \mathbf{\Pi}_0 \mathbf{K}$

$$\begin{split} E_c^{\text{AC-FDT}} &= \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \operatorname{Tr} \{ \Pi_\alpha^{\text{d/x}} \mathbb{W}^{\text{I/II}} - \Pi_0 \mathbb{W}^{\text{I/II}} \} \\ E_c^{\text{AC-FDT}} &= \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1} \operatorname{Tr} \{ \left(\Pi_0 \mathbb{W}^{\text{d/x}} \right)^{n-1} \Pi_0 \mathbb{W}^{\text{I/II}} \} \\ &- \sum_{n=2} \frac{x^n}{n} = \operatorname{Log}(1-x) + x \end{split}$$

$$\frac{dRPA-I}{\mathbb{W}^d} = \mathbb{W}^I = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathsf{Tr} \Big\{ (\Pi_0 \mathbb{W}^d)^n \Big\} = \mathsf{tr} \{ (\mathbf{\Pi}_0 \mathbf{K})^n \}$$

$$E_c^{ ext{dRPA-I}} = rac{1}{2} \int_{-\infty}^{\infty} rac{d\omega}{2\pi} \operatorname{tr}\left\{ \operatorname{Log}(\mathbf{1} - \mathbf{\Pi}_0 \mathbf{K}) + \mathbf{\Pi}_0 \mathbf{K}
ight\}$$
 $\epsilon = \mathbf{1} - \mathbf{\Pi}_0 \mathbf{K}$

$$\epsilon = 1 - \Pi_0 \mathsf{K}$$

$$E_c^{ extsf{dRPA-IIIa}} = rac{1}{2} \int_{-\infty}^{\infty} rac{d\omega}{2\pi} \operatorname{tr} \left\{ \operatorname{Log} \left(\mathbf{1} - \Pi_0 \mathbf{K}
ight) \mathbf{K}^{-1} \mathbf{B} + \Pi_0 \mathbf{B}
ight\}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \operatorname{Tr} \{ \Pi_\alpha^{\text{d/x}} \mathbb{W}^{\text{I/II}} - \Pi_0 \mathbb{W}^{\text{I/II}} \}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^\infty \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1} \operatorname{Tr} \{ (\Pi_0 \mathbb{W}^{\text{d/x}})^{n-1} \Pi_0 \mathbb{W}^{\text{I/II}} \}$$

$$-\sum_{n=2} \frac{x^n}{n} = \operatorname{Log}(1-x) + x$$

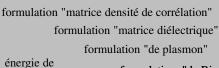
$$dRPA-I \qquad \text{and a degree } (K, K) \qquad Tr \{ (\Pi_0 \mathbb{W}^{\text{d/x}})^{n-1} \Pi_0 \mathbb{W}^{\text{I/II}} \}$$

$$E_c^{ ext{dRPA-IIa}} = rac{1}{2} \int_{-\infty}^{\infty} rac{d\omega}{2\pi} \operatorname{tr} \left\{ \operatorname{Log} \left(\mathbf{1} - \mathbf{\Pi}_0 \mathbf{K} \right) \mathbf{K}^{-1} \mathbf{B} + \mathbf{\Pi}_0 \mathbf{B}
ight\}$$

$$extstyle E_c^{\mathsf{RPAx ext{-}Ia}} = rac{1}{2} \int_{-\infty}^{\infty} rac{d\omega}{2\pi} \, \mathsf{tr} \left\{ \mathsf{Log} \left(\mathbf{1} - \mathbf{\Pi}_0 \mathbf{B}
ight) \mathbf{B}^{-1} \mathbf{K} + \mathbf{\Pi}_0 \mathbf{K}
ight\}$$

Conclusion

- différentes formulations pour écrire les équations RPA
 - formulation "matrice densité de corrélation"
 - formulation "matrice diélectrique"
 - formulation "de Riccati"
- des variantes émergent dans chacune de ces formulations
- comprendre les liens entre ces variantes
- systématiser les explorations (notamment "matrice diélectrique")



connexion

corrélation E_c

formulation "de Riccati"

problème adiabatique à *N*-corps HF **DFT** théorème de RSH fluctuationdissipation

Gradients

Lagrangien

Géométries

fonction de Unsöld réponse χ **EED**

espace réel

Adaptation de l'approximation du dénominateur effectif à l'espace réel

$$E_c^{ ext{dRPA-I}} = rac{1}{2} \int_{-\infty}^{\infty} rac{d\omega}{2\pi} \operatorname{tr} \left\{ \operatorname{Log} (\mathbf{1} - \mathbf{\Pi}_0 \mathbf{K}) + \mathbf{\Pi}_0 \mathbf{K}
ight\}$$

- éviter la double sommation occ/vir $(\chi_0 = \sum_{i=1}^{n} \dots)$
- éviter les états excités
- applications au calcul de :
 - polarisabilité dynamique
 - coefficients C₆
 - énergie RPA

$$\chi(\mathbf{r}_1, \mathbf{r}_2; i\omega) = 2 \operatorname{Re} \left(\sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_1) n_{\alpha}(\mathbf{r}_2)}{i\omega - \Omega_{\alpha}} \right) \doteq 2 \operatorname{Re} \left(\chi^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega) \right)$$

Approximation de Unsöld

$$\chi^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega) \approx \frac{\sum n_{\alpha}(\mathbf{r}_1) n_{\alpha}(\mathbf{r}_2)}{i\omega - \overline{\Omega}}$$

- résolution de l'identité
- $ightharpoonup \overline{\Omega}_{\mathbf{r}_1,\mathbf{r}_2,\omega}$ dépend de $(\mathbf{r}_1,\mathbf{r}_2,\omega)$

lpha états excités $\sum_{lpha} \left<0\right| \, \hat{n}(\mathbf{r}_1) \, |lpha ight> \left<lpha \right| \, \hat{n}(\mathbf{r}_2) \, |0 angle$ $\sum_{lpha} \left|lpha ight> \left<lpha \right| + \left|0 angle \left<0\right| = 1$

Approximation de l'EED

- généralisation où $\overline{\Omega}$ est une fonction
- moyennes sur l'état fondamental
- ▶ nouvelle énergie effective à approximer : $\Omega^{nn}(\mathbf{r}_1,\mathbf{r}_2;\omega)$
- hiérarchie d'équations

$$\chi(\mathbf{r}_1, \mathbf{r}_2; i\omega) = 2\operatorname{Re}\left(\sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)}{i\omega - \Omega_{\alpha}}\right) \doteq 2\operatorname{Re}\left(\chi^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega)\right)$$

$$\chi^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)}{i\omega - \Omega^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega)}$$

$$i\omega - \Omega^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega)$$

$$\Omega^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega) \chi^{nn}(\mathbf{r}_1, \mathbf{r}_2; i\omega) = \sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_1) n_{\alpha}(\mathbf{r}_2) \Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \chi^{nj}(\mathbf{r}_1, \mathbf{r}_2; i\omega)$$

$$\chi(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega) = 2\operatorname{Re}\left(\sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})}{i\omega - \Omega_{\alpha}}\right) \doteq 2\operatorname{Re}\left(\chi^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega)\right)$$

$$\chi^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})}{i\omega - \Omega^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega)}$$

$$\Omega^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega) \chi^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega) = \sum_{\alpha\neq 0} \frac{n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)\Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \chi^{nj}(\mathbf{r}_1,\mathbf{r}_2;i\omega)$$

$$\chi^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})\Omega_{\alpha}}{i\omega - \Omega^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)}$$

$$\Omega^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)\chi^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega) = \sum \frac{n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})\Omega_{\alpha}\Omega_{\alpha}}{i\omega} \doteq \chi^{ij}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)$$

$$\mathbf{\Omega}^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})\Omega_{\alpha}}{i\omega - \Omega^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)}$$

$$\mathbf{\Omega}^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)\chi^{nj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega) = \sum_{\alpha\neq0} \frac{n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})\Omega_{\alpha}\Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \chi^{jj}(\mathbf{r}_{1},\mathbf{r}_{2};i\omega)$$

$$\chi(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega) = 2\operatorname{Re}\left(\sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})}{i\omega - \Omega_{\alpha}}\right) \doteq 2\operatorname{Re}\left(\chi^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega)\right)$$

$$\chi^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_{1})n_{\alpha}(\mathbf{r}_{2})}{i\omega - \Omega^{nn}(\mathbf{r}_{1}, \mathbf{r}_{2}; i\omega)}$$

$$\Omega^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega) \chi^{nn}(\mathbf{r}_1,\mathbf{r}_2;i\omega) = \sum_{\alpha\neq 0} \frac{n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)\Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \chi^{nj}(\mathbf{r}_1,\mathbf{r}_2;i\omega)$$

$$\chi^{nj}(\mathbf{r}_1, \mathbf{r}_2; i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_1) n_{\alpha}(\mathbf{r}_2) \Omega_{\alpha}}{i\omega - \Omega^{nj}(\mathbf{r}_1, \mathbf{r}_2; i\omega)}$$

$$\Omega^{nj}(\mathbf{r}_1, \mathbf{r}_2; i\omega)\chi^{nj}(\mathbf{r}_1, \mathbf{r}_2; i\omega) = \sum_{\alpha \neq 0} \frac{n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)\Omega_{\alpha}\Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \chi^{jj}(\mathbf{r}_1, \mathbf{r}_2; i\omega)$$

$$a_{lpha
eq 0} = i\omega - \Omega_{lpha}$$
 $a_{lpha
eq 0} = \frac{\sum n_{lpha}(\mathbf{r}_1)n_{lpha}(\mathbf{r}_2)\Omega_{lpha}\Omega_{lpha}}{i\omega}$

$$\chi^{jj}(\mathbf{r}_1, \mathbf{r}_2; i\omega) \doteq \frac{\sum n_{\alpha}(\mathbf{r}_1) n_{\alpha}(\mathbf{r}_2) \Omega_{\alpha} \Omega_{\alpha}}{i\omega - \Omega^{jj}(\mathbf{r}_1, \mathbf{r}_2; i\omega)}$$

 $\mathbf{\Omega}^{jj}(\mathbf{r}_1,\mathbf{r}_2;i\omega)\chi^{jj}(\mathbf{r}_1,\mathbf{r}_2;i\omega) = \sum_{\alpha\neq0} \frac{n_{\alpha}(\mathbf{r}_1)n_{\alpha}(\mathbf{r}_2)\Omega_{\alpha}\Omega_{\alpha}\Omega_{\alpha}}{i\omega - \Omega_{\alpha}} \doteq \dots$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$\begin{vmatrix} S^{nn} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \\ \chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}} \end{vmatrix} \begin{vmatrix} S^{nj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha} \\ \chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}} \end{vmatrix} \begin{vmatrix} S^{jj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha} \\ \chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}} \end{vmatrix} \begin{vmatrix} S^{jj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha} \\ \chi^{jj} = \frac{S^{jj}}{i\omega - \Omega^{jj}} \end{vmatrix}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$S^{nn} = \sum_{\substack{n \in S^{nn} \\ \chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}}} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2})$$

$$\chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$S^{nn} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2})$$

$$\chi^{nn} = \sum_{i\omega - \Omega^{nn}} n_{\alpha}$$

$$X^{nj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha}$$

$$\chi^{nj} = \sum_{i\omega - \Omega^{nj}} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}}{i\omega - \frac{S^{jj}}{S^{nj}} \frac{i\omega - \Omega^{nj}}{i\omega - \Omega^{jj}}}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$S^{nn} = \sum_{\substack{n \in S^{nn} \\ \chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}}} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2})$$

$$\chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}}{i\omega - \frac{S^{jj}}{S^{nj}} \frac{i\omega - \Omega^{nj}}{i\omega - \Omega^{jj}}}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$S^{nn} = \sum_{\substack{n \in S^{nn} \\ \chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}}} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2})$$

$$\chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}$$
 $\Omega^{nn(1)} = \frac{S^{nj}}{S^{nn}}$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}}{i\omega - \frac{S^{jj}}{S^{nj}} \frac{i\omega - \Omega^{nj}}{i\omega - \Omega^{jj}}}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$S^{nn} = \sum_{\substack{n \in S^{nn} \\ | \alpha \cap n| = \frac{S^{nn}}{|\alpha \cap n|}}} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2})$$

$$X^{nj} = \sum_{\substack{n \in S^{nj} \\ | \omega \cap \Omega^{nj}| = \frac{S^{nj}}{|\alpha \cup \Omega^{nj}|}}}$$

$$X^{nj} = \sum_{\substack{n \in S^{nj} \\ | \omega \cap \Omega^{nj}| = \frac{S^{nj}}{|\alpha \cap \Omega^{nj}|}}}$$

$$X^{nj} = \sum_{\substack{n \in S^{nj} \\ | \omega \cap \Omega^{nj}| = \frac{S^{nj}}{|\alpha \cup \Omega^{nj}|}}}$$

$$X^{nj} = \sum_{\substack{n \in S^{nj} \\ | \omega \cap \Omega^{nj}| = \frac{S^{nj}}{|\alpha \cup \Omega^{nj}|}}}$$

$$X^{nj} = \sum_{\substack{n \in S^{nj} \\ | \omega \cap \Omega^{nj}| = \frac{S^{nj}}{|\alpha \cup \Omega^{nj}|}}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}} \qquad \qquad \Omega^{nn(1)} = \frac{S^{nj}}{S^{nn}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}}{i\omega - \frac{S^{nj}}{S^{nj}} \frac{i\omega - \Omega^{nj}}{i\omega - \Omega^{nj}}}$$

$$\Omega^{nn(2)} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}}}{i\omega - \frac{S^{nj}}{S^{nj}}}$$

$$i\omega - \frac{S^{nj}}{S^{nj}} \frac{i\omega - \frac{S^{nj}}{S^{nn}}}{i\omega - \Omega^{nj}}$$

- les numérateurs sont des règles de sommes
- \triangleright on cherche une expression explicite de Ω^{nn}

$$\begin{vmatrix} S^{nn} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \\ \chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}} \end{vmatrix} \begin{vmatrix} S^{nj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha} \\ \chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}} \end{vmatrix} \begin{vmatrix} S^{jj} = \sum_{\alpha} n_{\alpha}(\mathbf{r}_{1}) n_{\alpha}(\mathbf{r}_{2}) \Omega_{\alpha} \\ \chi^{nj} = \frac{S^{jj}}{i\omega - \Omega^{jj}} \end{vmatrix}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}} \qquad \Omega^{nn(1)} = \frac{S^{nj}}{S^{nn}}$$

$$\Omega^{nn} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \Omega^{nn}}{i\omega - \Omega^{nj}}}{i\omega - \frac{S^{ij}}{S^{nj}} \frac{i\omega - \Omega^{nj}}{i\omega - \Omega^{jj}}} \qquad \Omega^{nn(2)} = \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}}}{i\omega - \frac{S^{jj}}{S^{nj}}}$$

 \blacktriangleright dépendance explicite à la fréquence ω

Approximations de χ^{nn}

- hierarchie d'expression pour χ^{nn}
- ▶ uniquement en fonction de moyennes sur l'état fondamental
- ► dépendance à la fréquence

$$\chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}$$

$$\chi^{nn(1)} = \frac{S^{nn}}{i\omega - \frac{S^{nj}}{S^{nn}}}$$

$$\chi^{nn(2)} = \frac{S^{nn}}{i\omega - \frac{S^{nj}}{S^{nn}}}$$

$$i\omega - \frac{S^{nj}}{S^{nn}} \frac{i\omega - \frac{S^{nj}}{S^{nn}}}{i\omega - \frac{S^{jj}}{S^{nj}}}$$

Polarisabilité

$$\alpha_{\alpha\beta}(i\omega) = 2\operatorname{Re}\sum_{ia} \frac{\langle i|\hat{r}_{\alpha}|a\rangle\langle a|\hat{r}_{\beta}|i\rangle}{i\omega - \Omega_{ia}} \quad \alpha/\beta = x, y, z$$

$$\beta = x, y, z$$

$$\sum_{i} \frac{S_{\alpha\beta,i}^{nn}}{i\omega - \frac{S_{\alpha\beta,i}^{nj}}{S_{\alpha\beta,i}^{nn}}}$$

$$\alpha_{\alpha\beta}(i\omega)^{(1)} = 2\operatorname{Re}\sum_{i} \frac{S_{\alpha\beta,i}^{nn}}{i\omega - \frac{S_{\alpha\beta,i}^{nj}}{S_{\alpha\beta,i}^{nn}}} \qquad S_{\alpha\beta,i}^{nn} = 4C_{i\mu}^{\mathsf{T}} (\mathbf{r}_{\alpha}\mathbf{Q}\mathbf{r}_{\beta})_{\mu\nu} C_{\nu i} S_{\alpha\beta,i}^{nj} = 4C_{i\mu}^{\mathsf{T}} (\mathbf{r}_{\alpha}\mathbf{S}^{-1}\mathbf{F}\mathbf{Q}\mathbf{r}_{\beta})_{\mu\nu} C_{\nu i} - 4C_{i\mu}^{\mathsf{T}} (\mathbf{r}_{\alpha}\mathbf{Q}\mathbf{r}_{\beta}\mathbf{S}^{-1}\mathbf{F})_{\mu\nu} C_{\nu i}$$

Polarisabilité

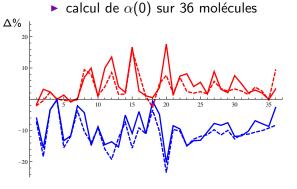
$$\alpha_{\alpha\beta}(i\omega) = 2\operatorname{Re} \sum_{ia} \frac{\langle i | \hat{r}_{\alpha} | a \rangle \langle a | \hat{r}_{\beta} | i \rangle}{i\omega - \Omega_{ia}} \quad \alpha/\beta = x, y, z$$

$$\sum_{\alpha\beta,i} \frac{S_{\alpha\beta,i}^{nn}}{S_{\alpha\beta,i}^{nn}} = 4C_{i\mu}^{\mathsf{T}} (\mathbf{r}_{\alpha} \mathbf{Q} \mathbf{r}_{\beta})_{\mu\nu} C_{\nu i}$$

$$\alpha_{\alpha\beta}(i\omega)^{(1)} = 2\operatorname{Re}\sum_{i} \frac{S_{\alpha\beta,i}^{nj}}{S_{\alpha\beta,i}^{nj}}$$

$$S_{\alpha\beta,i}^{nj} = 4C_{i\mu}^{\mathsf{T}} \left(\mathbf{r}_{\alpha} \mathbf{S}^{-1} \mathbf{F} \mathbf{Q} \mathbf{r}_{\beta} \right)_{\mu\nu} C_{\nu i}$$

 $-4C_{i\mu}^{\mathsf{T}}\left(\mathbf{r}_{\alpha}\mathbf{Q}\mathbf{r}_{\beta}\mathbf{S}^{-1}\mathbf{F}\right)_{\mu\nu}C_{\nu i}$



$$\alpha_{\text{moy}}^{\text{loc}}(1)$$

11.0 %

9.3 %

 $lpha_{
m mov}^{
m cano}$ (2) 4.6 % 3.7 %

$$\alpha_{\text{mov}}^{\text{loc}}(2)$$

24/40

Polarisabilité

$$\alpha_{\alpha\beta}(i\omega) = 2\operatorname{Re}\sum_{ia} \frac{\langle i|\hat{r}_{\alpha}|a\rangle \langle a|\hat{r}_{\beta}|i\rangle}{i\omega - \Omega_{ia}} \quad \alpha/\beta = x, y, z$$

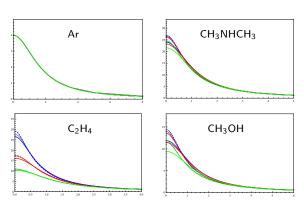
$$\beta = x, y, z$$

$$\alpha_{\alpha\beta}(i\omega)^{(1)} = 2\operatorname{Re}\sum_{i} \frac{S_{\alpha\beta,i}^{nn}}{i\omega - \frac{S_{\alpha\beta,i}^{nj}}{S_{\alpha\beta,i}^{nn}}} \qquad S_{\alpha\beta,i}^{nn} = 4C_{i\mu}^{\mathsf{T}} \left(\mathbf{r}_{\alpha}\mathbf{Q}\mathbf{r}_{\beta}\right)_{\mu\nu} C_{\nu i} S_{\alpha\beta,i}^{nj} = 4C_{i\mu}^{\mathsf{T}} \left(\mathbf{r}_{\alpha}\mathbf{S}^{-1}\mathbf{F}\mathbf{Q}\mathbf{r}_{\beta}\right)_{\mu\nu} C_{\nu i} - 4C_{i\mu}^{\mathsf{T}} \left(\mathbf{r}_{\alpha}\mathbf{Q}\mathbf{r}_{\beta}\mathbf{S}^{-1}\mathbf{F}\right)_{\mu\nu} C_{\nu i}$$

$$S_{\alpha\beta,i}^{nn} = 4C_{i\mu}^{\mathsf{I}} \left(\mathbf{r}_{\alpha} \mathbf{Q} \mathbf{r}_{\beta} \right)_{\mu\nu} C_{\nu i}$$

$$S_{\alpha\beta,i}^{nj} = 4C_{i\mu}^{\mathsf{T}} \left(\mathbf{r}_{\alpha} \mathbf{S}^{-1} \mathbf{F} \mathbf{Q} \mathbf{r}_{\beta} \right)_{\mu\nu} C_{\nu}$$

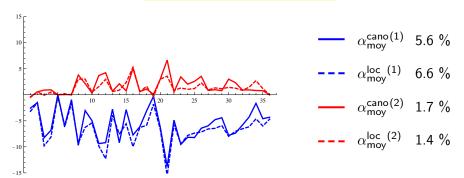
$$-4C_{i\mu}^{\mathsf{T}}\left(\mathsf{r}_{\alpha}\mathsf{Q}\mathsf{r}_{\beta}\mathsf{S}^{-1}\mathsf{F}\right)_{\mu\nu}C_{\nu i}$$





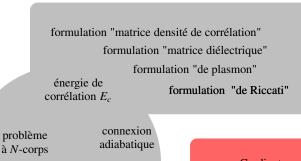
 $\alpha_{zz}^{(2)}$

$$C_6^{ij} = \frac{3}{\pi} \int_0^\infty d\omega \ \overline{\alpha}^i(i\omega) \overline{\alpha}^j(i\omega)$$



- ► comme précédemment, ordre 1(2) sous-estime(sur-estime) systématiquement les C₆
- ▶ comportement orbitales canoniques/localisées pas systématique
- nette amélioration dans la description des coefficients à l'ordre 2

- généralisation de l'approximation de Unsöld
- ▶ hierarchie d'expressions | pour approximer χ^{nn}
- ▶ application au calcul de polarisabilité dynamique et de coefficients C₆
- perspective du calcul de l'énergie de corrélation



à *N*-corps

HF DFT théorème de fluctuation-dissipation

fonction de réponse χ

Gradients

Lagrangien

Géométries

EED espace réel

Unsöld

Gradients analytiques d'énergies de type hybride à séparation de portée électronique (RSH) mélant théorie de la fonctionnelle de la densité (DFT) et approximation de la phase aléatoire (RPA)

On dérive ici les gradients analytiques d'énergies RSH+RPA

nouveau: gradients analytiques RPA

depuis: gradients analytiques HF+RPA

Rekkedal, Coriani, Iozzi, Teale, Helgaker, Pedersen; J. Chem. Phys. (2013)

et : gradients analytiques PBE+dRPA(DF)

Burow, Bates, Furche, Eshuis; J.C.T.C. (Just Accepted Manuscript)

nouveau: gradients analytiques d'énergies sr+lr

en fait : gradients RSH+MP2

Chabbal, Stoll, Werner, Leininger; Mol. Phys. (2010)

ici : dérivation "tout-en-un"

Péter G. Szalay
 Institute of Chemistry, Eötvös Loránd University
 Budapest, Hongrie

Motivation

- ▶ obtenir forces sur les noyaux $\frac{\partial E}{\partial \kappa}$ (géométries, états de transition)
- ▶ obtenir des constantes de forces $\frac{\partial^2 E}{\partial \kappa_1 \partial \kappa_2}$ (fréquence de vibration)
- ▶ toute propriété monoélectronique définie comme $\frac{\partial E}{\partial x}$ (dipôles,...)

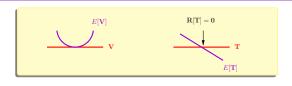
gradients numériques (inefficaces, imprécis)

Gradients analytiques

Gradients analytiques

Paramètres

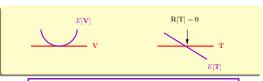
$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$



Gradients analytiques

Paramètres

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

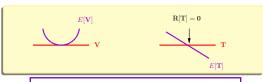


Gradients

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

Paramètres

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



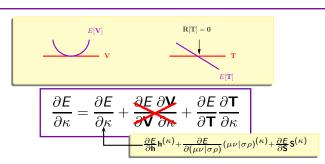
Gradients

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

Paramètres

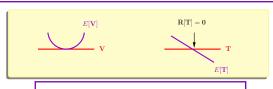
$$E \doteq E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$$





Paramètres

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



Gradients

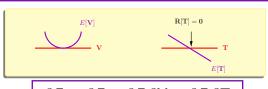
$$\frac{\partial E}{\partial \kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \lambda} \frac{\partial V}{\partial \kappa} + \frac{\partial V}{\partial \lambda} \frac{\partial V}{\partial \lambda} + \frac{\partial V}{\partial \lambda} \frac{$$

Méthodes variationnelles

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

Paramètres

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



Gradients

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

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

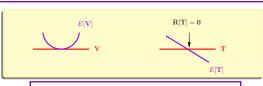
Méthodes variationnelles

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

Méthodes non-variationnelles

Paramètres

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



Gradients

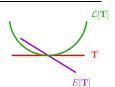
$$\frac{\partial E}{\partial \kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{T}} \frac{\partial \mathbf{T}}{\partial \kappa}$$
$$-\frac{\partial E}{\partial \mathbf{h}} \mathbf{h}^{(\kappa)}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

Méthodes variationnelles

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

Méthodes non-variationnelles





Travailler avec un objet alternatif qui est variationnel

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

Rappel: pour non-variationnelle E[V,T] R[T] = 0

énergie règle pour T

Rappel: énergie règle pour T pour non-variationnelle E[V,T] R[T]=0

R[T] = 0 E[T]

on introduit le Lagrangien

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

Rappel: pour non-variationnelle

énergie règle pour **T** E[V,T] R[T]=0



on introduit le Lagrangien

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

conditions stationnaires pour
$${\cal L}$$

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

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

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

Rappel: énergie règle pour **T** pour non-variationnelle $E[\mathbf{V}, \mathbf{T}] = 0$



on introduit le Lagrangien

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

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

conditions stationnaires pour $\ensuremath{\mathcal{L}}$

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

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

Rappel: pour non-variationnelle

énergie règle pour **T** E[V,T] R[T]=0



on introduit le Lagrangien

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

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

conditions stationnaires pour $\mathcal L$

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

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

Rappel:

pour non-variationnelle

énergie règle pour T E[V,T] R[T]=0

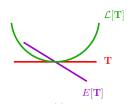


on introduit le Lagrangien

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

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

conditions stationnaires pour $\mathcal L$



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

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

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

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

Notation avec fockiennes

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

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

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

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

Notation avec fockiennes

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

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

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

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

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

Notation avec fockiennes

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

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

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

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

$$E_{Hxc}^{\text{sr}}[n] = \int dr \ F[\xi] \\ g_{ab}^{\text{sr}} = \int dr \ \sum_{A} \frac{\partial F}{\partial \xi_{A}} \frac{\partial \xi_{A}}{\partial g_{ab}^{(0)}}$$

$$\xi = \{\xi_{A}\} = \{n, n_{\alpha}, \nabla n_{\alpha}, \dots \}$$

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

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

Notation avec fockiennes

$$\begin{split} E &= \left\langle \mathbf{d}^{(0)} \mathbf{f} \right\rangle + \Delta_{\text{DC}} + E_c^{\text{lr}} \\ &= \left\langle \mathbf{d}^{(0)} \mathbf{f}^{\text{lr}} \right\rangle + \Delta_{\text{DC}}^{\text{lr}} + E_c^{\text{lr}} \\ &+ \left\langle \mathbf{d}^{(0)} \mathbf{g}^{\text{sr}} \right\rangle + \Delta_{\text{DC}}^{\text{sr}} \end{split}$$

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

$$E_{Hxc}^{\text{sr}}[n] = \int dr \ F[\xi] \\ g_{ab}^{\text{sr}} = \int dr \ \sum_{A} \frac{\partial F}{\partial \xi_{A}} \frac{\partial \xi_{A}}{\partial g_{\alpha b}^{(0)}}$$

$$\xi = \{\xi_{A}\} = \{n, n_{\alpha}, \nabla n_{\alpha}, \dots \}$$

Lagrangien RSH+RPA (sr+Ir)

▶ 2 paramètres non-varia. : amplitudes **T**, coefficients orbitalaires **C**

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

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

Rappel: $E=E_{RSH}+E_c^{lr}=\langle \Phi | \hat{T}+\hat{V}_{ne}+\hat{V}_{ee}^{lr} | \Phi \rangle +E_{Loc}^{sr}[n_{\Phi}]+E_c^{lr}$

 $=\left\langle \mathbf{d}^{(0)}\mathbf{f}^{\mathsf{lr}}\right
angle + \Delta_{\mathsf{DC}}^{\mathsf{lr}} + E_{c}^{\mathsf{lr}}$

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

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

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

 $g_{ab}^{sr} = \int dr \sum_{\Delta} \frac{\partial F}{\partial \xi_A} \frac{\partial \xi_A}{\partial d_{c}^{(0)}}$

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

 $g^{\text{lr}}[\mathbf{d}^{(0)}]_{rs} = d_{rs}^{(0)}((pq|rs)^{\text{lr}} - \frac{1}{2}(pr|qs)^{\text{lr}})$ $E_{Hxc}^{sr}[n] = \int dr \ F[\xi]$ $\xi = \{\xi_A\} = \{n, n_\alpha, \nabla n_\alpha, \dots\}$

Lagrangien RSH+RPA (sr+Ir)

2 paramètres non-varia. : amplitudes T, coefficients orbitalaires C

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

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

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

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

$$\begin{array}{ll} \text{par rapport à T} & \frac{\partial}{\partial T} \Big(\langle \mathsf{KT} \rangle + \left\langle \lambda \Big(\mathsf{K} + [\mathsf{K},\mathsf{T}]_+ + \mathsf{TKT} + [\varepsilon,\mathsf{T}]_+ \Big) \right\rangle \Big) = 0 \\ & - \mathsf{P} = \mathbf{Q} [\mathsf{T}] \frac{\lambda}{\lambda} + \frac{\lambda}{\lambda} \mathbf{Q} [\mathsf{T}]^\mathsf{T} \end{array}$$

$$\begin{split} \mathcal{L} &= \left\langle \mathbf{d^{(0)}f} \right\rangle + \Delta_{DC} + \underline{F_c^{lr}} + \left\langle \lambda \mathbf{R}[\mathbf{T},\mathbf{C}] \right\rangle + \left\langle \mathbf{x}(\mathbf{C}^\mathsf{T}\mathbf{S}\mathbf{C} - \mathbf{1}) \right\rangle + \left\langle \mathbf{z}\mathbf{f} \right\rangle \\ \text{par rapport à T} & \frac{\frac{\partial}{\partial T} \left(\left\langle \mathsf{K}\mathsf{T} \right\rangle + \left\langle \lambda \left(\mathsf{K} + [\mathsf{K},\mathsf{T}]_+ + \mathsf{T}\mathsf{K}\mathsf{T} + [\varepsilon,\mathsf{T}]_+ \right) \right\rangle \right) = 0 \\ & - \mathbf{P} &= \mathbf{Q}[\mathbf{T}] \boldsymbol{\lambda} + \lambda \mathbf{Q}[\mathbf{T}]^\mathsf{T} \\ \text{par rapport à C} & \left\langle \mathsf{K} \left(\mathsf{T} + \lambda + [\lambda,\mathsf{T}]_+ + \mathsf{T}\lambda \mathsf{T} \right) \right\rangle + \left\langle \varepsilon[\lambda,\mathsf{T}]_+ \right\rangle \dot{=} \left\langle \mathsf{K}\mathsf{M}_\lambda \right\rangle + \left\langle \mathbf{d}_\lambda^{(2)} \mathbf{f} \right\rangle \end{split}$$

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

$$\begin{split} \text{par rapport à T} & \quad \frac{\frac{\partial}{\partial T} \left(\langle \mathsf{KT} \rangle + \left\langle \lambda \left(\mathsf{K} + [\mathsf{K},\mathsf{T}]_+ + \mathsf{TKT} + [\varepsilon,\mathsf{T}]_+ \right) \right\rangle \right) = 0}{-\mathsf{P} = \mathsf{Q}[\mathsf{T}] \boldsymbol{\lambda} + \lambda \mathsf{Q}[\mathsf{T}]^\mathsf{T}} \\ \text{par rapport à C} & \quad \left\langle \mathsf{K} \big(\mathsf{T} + \lambda + [\lambda,\mathsf{T}]_+ + \mathsf{T} \lambda \mathsf{T} \big) \right\rangle + \left\langle \varepsilon[\lambda,\mathsf{T}]_+ \right\rangle \dot{=} \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{d}_{\lambda}^{(2)} f \right\rangle \\ \mathcal{L} = & \quad \left\langle \left(\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z} \right) \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle \\ & \quad \left\langle \mathsf{K} \right\rangle + \left\langle \mathsf{K} \right\rangle \left\langle \mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1} \right\rangle \end{split}$$

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

$$\begin{split} \text{par rapport à T} & \quad \frac{\partial}{\partial T} \left(\langle \mathsf{KT} \rangle + \left\langle \lambda \left(\mathsf{K} + [\mathsf{K},\mathsf{T}]_+ + \mathsf{TKT} + [\varepsilon,\mathsf{T}]_+ \right) \right\rangle \right) = 0 \\ & \quad - \mathsf{P} = \mathsf{Q}[\mathsf{T}] \boldsymbol{\lambda} + \lambda \mathsf{Q}[\mathsf{T}]^\mathsf{T} \\ \\ \text{par rapport à C} & \quad \left\langle \mathsf{K} \big(\mathsf{T} + \lambda + [\lambda,\mathsf{T}]_+ + \mathsf{T} \lambda \mathsf{T} \big) \right\rangle + \left\langle \varepsilon[\lambda,\mathsf{T}]_+ \right\rangle \dot{=} \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{d}_{\lambda}^{(2)} f \right\rangle \\ & \quad \mathcal{L} = & \quad \left\langle \left(\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathsf{z} \right) \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} + \underbrace{\left\langle \mathsf{KM}_{\lambda} \right\rangle}_{\mathsf{C},jb} + \left\langle \mathsf{x} \big(\mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1} \big) \right\rangle \\ & \quad \sum_{kc,b} (ib|kc)(\mathsf{M}_{\lambda})_{kc,jb} \\ & \quad \sum_{kc,j} (ij|kc)(\mathsf{M}_{\lambda})_{kc,jb} \\ & \quad \sum_{kc,j} (aj|kc)(\mathsf{M}_{\lambda})_{kc,jb} \\ & \quad \sum_{kc,j} (aj|kc)(\mathsf{M}_{\lambda})_{kc,jb} \end{split}$$

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

 $\frac{\partial}{\partial T} (\langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + [\mathsf{K}, \mathsf{T}]_{+} + \mathsf{TKT} + [\varepsilon, \mathsf{T}]_{+}) \rangle) = 0$ par rapport à T $-P = Q[T] \lambda + \lambda Q[T]^T$

$$\begin{array}{c|c} \text{par rapport à C} & \left\langle \mathsf{K} \big(\mathsf{T} + \lambda + [\lambda, \mathsf{T}]_+ + \mathsf{T} \lambda \mathsf{T} \big) \right\rangle + \left\langle \varepsilon [\lambda, \mathsf{T}]_+ \right\rangle \dot{=} \left\langle \mathsf{K} \mathsf{M}_{\lambda} \right\rangle + \left\langle \mathsf{d}_{\lambda}^{(2)} \mathsf{f} \right\rangle \\ & \mathcal{L} = \left\langle \left(\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathsf{z} \right) \mathsf{f} \right\rangle + \Delta_{\mathsf{DC}} + \left\langle \mathsf{K} \mathsf{M}_{\lambda} \right\rangle + \left\langle \mathsf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1}) \right\rangle \\ & \mathsf{dh} \rightarrow \mathsf{dh} \\ & \mathsf{df}^\mathsf{lr} + \\ & \begin{array}{c} \sum\limits_{kc,b} (ib|kc) (\mathsf{M}_{\lambda})_{kc,jk} \\ & \end{array}$$

 $\mathcal{L} = \left. \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} \right. + \left. \left\langle \mathsf{KM}_{\lambda} \right\rangle \right. + \left\langle \mathsf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle$ $\sum_{kc,b} (ib|kc) (\mathbf{M}_{\lambda})_{kc,jb}$ $\mathbf{d} \quad \mathbf{g}^{lr}[\mathbf{d}^{(0)}] \rightarrow \quad \mathbf{d} \quad \mathbf{g}^{lr}[\mathbf{d}^{(0)}] + \quad \mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}]$ $\sum_{kc,b} (ab|kc) (\mathbf{M}_{\lambda})_{kc,jb}$ $\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(2)}+\mathbf{z}]$ $-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}]$ $\sum_{kc,j} (ij|kc) (\mathbf{M_{\lambda}})_{kc,jb}$

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

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

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

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

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

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

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

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

$$\mathbf{d}^\mathsf{lr} + \quad \mathbf{d}^\mathsf{log}(\mathbf{g}^\mathsf{lr}[\mathbf{d}^{(2)}] + \mathbf{z}]$$

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

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

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

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

par rapport à T
$$\begin{array}{c} -\mathbf{P} = \mathbf{Q}[\mathbf{T}] \frac{\lambda}{\lambda} + \lambda \mathbf{Q}[\mathbf{T}]^{\mathsf{T}} \\ -\mathbf{P} = \mathbf{Q}[\mathbf{T}] \frac{\lambda}{\lambda} + \lambda \mathbf{Q}[\mathbf{T}]^{\mathsf{T}} \\ \end{array}$$
 par rapport à C
$$\langle \mathsf{K}(\mathsf{T} + \lambda + [\lambda, \mathsf{T}]_+ + \mathsf{T} \lambda \mathsf{T}) \rangle + \langle \varepsilon[\lambda, \mathsf{T}]_+ \rangle \dot{=} \langle \mathsf{KM}_{\lambda} \rangle + \langle \mathsf{d}_{\lambda}^{(2)} \mathsf{f} \rangle \\ \mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathsf{f} \right\rangle + \Delta_{\mathsf{DC}} + \langle \mathsf{KM}_{\lambda} \rangle + \langle \mathsf{x}(\mathbf{C}^{\mathsf{T}} \mathsf{SC} - \mathbf{1}) \rangle$$

 $\frac{\partial}{\partial T} (\langle \mathsf{KT} \rangle + \langle \lambda (\mathsf{K} + [\mathsf{K}, \mathsf{T}]_{+} + \mathsf{TKT} + [\varepsilon, \mathsf{T}]_{+}) \rangle) = 0$

```
dh \rightarrow dh
                                                                                                                                                                                         df<sup>lr</sup>+
 \textbf{d} \quad \textbf{g}^{\text{lr}}[\textbf{d}^{(0)}] \rightarrow \quad \textbf{d} \quad \textbf{g}^{\text{lr}}[\textbf{d}^{(0)}] + \quad \textbf{d}^{(0)}\textbf{g}^{\text{lr}}[\textbf{d}]
```

 $\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(2)}+\mathbf{z}]$ $-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathsf{lr}}[\mathbf{d}^{(0)}]$ $\mathbf{dg}^{sr}{\rightarrow} \mathbf{dg}^{sr}{+}\mathbf{d}^{(0)}\mathbf{W}^{sr}[\mathbf{d}]$ $dg^{sr}+$ $\Delta_{DC}^{sr} \rightarrow -\mathbf{d}^{(0)}\mathbf{W}^{sr}[\mathbf{d}^{(0)}]$ $d^{(0)}W^{sr}[d^{(2)}+z]$

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

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

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

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

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

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

par rapport à T
$$\frac{\frac{\partial}{\partial T} \left(\langle KT \rangle + \left\langle \lambda \left(K + [K,T]_{+} + TKT + [\varepsilon,T]_{+} \right) \right\rangle \right) = 0}{-P = \mathbf{Q}[\mathbf{T}] \frac{\boldsymbol{\lambda}}{\boldsymbol{\lambda}} + \frac{\boldsymbol{\lambda} \mathbf{Q}[\mathbf{T}]^{\mathsf{T}}}{}$$

 $\langle \mathsf{K} \big(\mathsf{T} + \lambda + [\lambda, \mathsf{T}]_+ + \mathsf{T} \lambda \mathsf{T} \big) \rangle + \langle \varepsilon [\lambda, \mathsf{T}]_+ \rangle \dot{=} \langle \mathsf{K} \mathsf{M}_{\lambda} \rangle + \langle \mathsf{d}_{\lambda}^{(2)} \mathsf{f} \rangle$ par rapport à C $\mathcal{L} = \left| \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f} \right\rangle + \Delta_{\mathsf{DC}} \right| + \left| \left\langle \mathsf{KM}_{\lambda} \right\rangle \right| + \left\langle \mathsf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - 1) \right\rangle$

 $\sum_{kc,b} (ib|kc) (\mathbf{M_{\lambda}})_{kc,jb}$ $\textbf{d} \quad \textbf{g}^{\text{lr}}[\textbf{d}^{(0)}] \rightarrow \quad \textbf{d} \quad \textbf{g}^{\text{lr}}[\textbf{d}^{(0)}] + \quad \textbf{d}^{(0)}\textbf{g}^{\text{lr}}[\textbf{d}]$ $\sum_{kc,b} (ab|kc) (\mathbf{M}_{\lambda})_{kc,jb}$ $-\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{lr}[\mathbf{d}^{(0)}]$ $\textbf{dg}^{\text{sr}}{\rightarrow} \textbf{dg}^{\text{sr}}{+}\textbf{d}^{(0)}\textbf{W}^{\text{sr}}[\textbf{d}]$ $dg^{sr}+$

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

$$\begin{array}{lll} \mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \rightarrow -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] + -\frac{1}{2}\mathbf{d}^{(0)}\mathbf{g}^{\mathrm{lr}}[\mathbf{d}^{(0)}] \\ \mathbf{d}\mathbf{g}^{\mathrm{sr}} \rightarrow \mathbf{d}\mathbf{g}^{\mathrm{sr}} + \mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}] \\ \Delta^{\mathrm{sr}}_{\mathrm{DC}} \rightarrow -\mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(0)}] \end{array} \qquad \begin{array}{ll} \mathbf{d}\mathbf{d}\mathbf{g}^{\mathrm{sr}} + \mathbf{z} \\ \mathbf{d}\mathbf{g}^{\mathrm{sr}} + \mathbf{z} \\ \mathbf{d}^{(0)}\mathbf{W}^{\mathrm{sr}}[\mathbf{d}^{(2)} + \mathbf{z}] \end{array}$$

$$\begin{array}{ll} \mathbf{dg^{sr}} \rightarrow \mathbf{dg^{sr}} + \mathbf{d^{(0)}W^{sr}[d]} & \mathbf{dg^{sr}} + \\ \Delta_{DC}^{sr} \rightarrow -\mathbf{d^{(0)}W^{sr}[d^{(0)}]} & \mathbf{d^{(0)}W^{sr}[d^{(2)} + \mathbf{z}]} \end{array}$$

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

$$\Delta_{\mathrm{DC}}^{\mathrm{sr}} \rightarrow -\mathbf{d}^{(0)} \mathbf{W}^{\mathrm{sr}} [\mathbf{d}^{(0)}] \qquad \qquad \mathbf{d}^{(0)} \mathbf{W}^{\mathrm{sr}} [\mathbf{d}^{(2)} + \mathbf{z}] \qquad \qquad \sum_{k \in J} (aj|kc) (\mathbf{M}_{\lambda})_{kc,jl}$$

$$\Delta_{\mathsf{DC}}^{\mathsf{sr}} o - \mathbf{d}^{(0)} \mathbf{W}^{\mathsf{sr}} [\mathbf{d}^{(0)}]$$
 $\mathbf{d}^{(0)} \mathbf{W}^{\mathsf{sr}} [\mathbf{d}^{(2)} + \mathbf{z}]$ $\sum_{kc,j} (aj|kc) (\mathsf{M}_{\lambda})_{kc,j}$

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

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

(CP-RPA)

34/40

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

$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f}^{\mathsf{sr} + \mathsf{lr}} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{sr} + \mathsf{lr}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x} (\mathbf{C}^{\mathsf{T}} \mathbf{SC} - \mathbf{1}) \right\rangle$$
 simplement la dérivée d'un objet variationnel



$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f}^{\mathsf{sr} + \mathsf{lr}} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{sr} + \mathsf{lr}} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x} (\mathsf{C}^\mathsf{T} \mathsf{SC} - \mathbf{1}) \right\rangle$$
 simplement la dérivée d'un objet variationnel





$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z})\mathbf{f}^{\mathsf{Sr}} + \mathbf{r} \right\rangle + \Delta_{\mathsf{DC}}^{\mathsf{Sr}} + \mathbf{r} + \left\langle \mathsf{KM}_{\lambda} \right\rangle + \left\langle \mathsf{x}(\mathsf{C}^{\mathsf{T}}\mathsf{SC} - \mathbf{1}) \right\rangle$$
simplement la dérivée d'un objet variationnel

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

$$\begin{split} &(\mathbf{D}^{1})_{\mu\nu} \! = \! C_{\mu\rho} \bigg(\mathbf{d}^{(0)} \! + \! \mathbf{d}_{\lambda}^{(2)} \! + \! \mathbf{z} \bigg)_{\rho q} C_{q\nu}^{\dagger} \! = \! \bigg(\mathbf{D}^{(0)} \! + \! \mathbf{D}_{\lambda}^{(2)} \! + \! \mathbf{Z} \bigg)_{\mu\nu} \\ &(\mathbf{D}^{2})_{\mu\nu,\sigma\rho} \! = \! \bigg(\frac{1}{2} \mathbf{D}^{(0)} \! + \! \mathbf{D}_{\lambda}^{(2)} \! + \! \mathbf{Z} \bigg)_{\mu\nu} D_{\rho\sigma}^{(0)} \! - \! \frac{1}{2} \bigg(\frac{1}{2} \mathbf{D}^{(0)} \! + \! \mathbf{D}_{\lambda}^{(2)} \! + \! \mathbf{Z} \bigg)_{\mu\rho} D_{\nu\sigma}^{(0)} \end{split}$$



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

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

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

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

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



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

$$c / (1(0) + 1(2) + 3)c sr + |r| + A sr + |r|$$

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

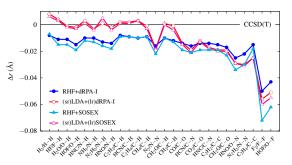
$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}_{\lambda}^{(2)} + \mathbf{z}) \mathbf{f}^{\mathbf{Sr} + \mathbf{lr}} \right\rangle + \Delta_{\mathsf{DC}}^{\mathbf{Sr} + \mathbf{lr}} + \left\langle \mathbf{KM}_{\lambda} \right\rangle + \left\langle \mathbf{x} (\mathbf{C}^\mathsf{T} \mathbf{SC} - \mathbf{1}) \right\rangle$$
 simplement la dérivée d'un objet variationnel

$$\begin{split} (\mathbf{D}^{2})_{\mu\nu,\sigma\rho} &= \left(\frac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}_{\lambda}^{(2)} + \mathbf{Z}\right)_{\mu\nu} D_{\rho\sigma}^{(0)} - \frac{1}{2} \left(\frac{1}{2}\mathbf{D}^{(0)} + \mathbf{D}_{\lambda}^{(2)} + \mathbf{Z}\right)_{\mu\rho} D_{\nu\sigma}^{(0)} \\ (\mathbf{\Gamma}^{2})_{\mu\nu,\sigma\rho} &= C_{\mu k} C_{\nu j} C_{c\rho}^{\dagger} C_{b\sigma}^{\dagger} (\mathbf{M}_{\lambda})_{ia,kc} \\ \\ \mathbf{SR}^{(\kappa)} &= \omega_{\lambda}^{(\kappa)} \left(F(\xi_{A}) + \frac{\partial F}{\partial \xi_{A}} \left(\xi_{A}^{\mathbf{d}^{(2)}} + \xi_{A}^{\mathbf{z}}\right)\right) \\ &+ \omega_{\lambda} \frac{\partial F}{\partial \xi_{B}} \left(\xi_{B}^{\mathbf{d}^{(0)}(x)} + \xi_{B}^{\mathbf{d}^{(2)}(x)} + \xi_{B}^{\mathbf{z}(x)}\right) + \omega_{\lambda} \frac{\partial^{2} F}{\partial \xi_{B} \partial \xi_{A}} \left(\xi_{A}^{\mathbf{d}^{(2)}} + \xi_{A}^{\mathbf{z}}\right) \xi_{B}^{(\kappa)} \end{split}$$

Implémentation

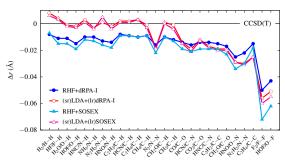
- ▶ implémenté dans MOLPRO , dans le "coeur"
- ▶ utilise un parallèle avec les gradients RSH+MP2
- validation par la correspondance aux gradients numériques
- temps de calcul est double du calcul d'une énergie
- ► croissance en N⁶
- optimisation de géométrie
- densité corrélée
- dipôles
- de manière générale : meilleure convergence avec la base

Longueurs de liaisons de simples molécules



RHF+dRPA-I : 0.016 (sr)LDA+(Ir)dRPA-I : 0.013 RHF+SOSEX : 0.021 (sr)LDA+(Ir)SOSEX : 0.014

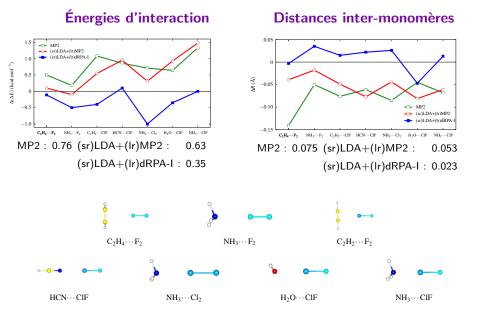
Longueurs de liaisons de simples molécules



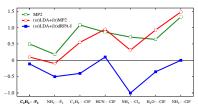
RHF+dRPA-I: 0.016 (sr)LDA+(lr)dRPA-I: 0.013 RHF+SOSEX: 0.021 (sr)LDA+(lr)SOSEX: 0.014

- ightharpoonup à la limite $\mu=0$, résultats sans séparation de portée sont bien reproduits
- convergence avec la base utilisée meilleure avec séparation de portée
- ▶ RSH attenue les différences de performances entre MP2, dRPA et SOSEX

- erreurs sont inférieures à 0.1 Å
- déviations moyennes sont meilleures avec la séparation de portée
- ▶ gain surtout sur les liaisons X−H
- ► F—X sont pathologiques



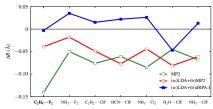
Énergies d'interaction



 $\Delta(\Delta E)$ (kcal.mol⁻¹)

MP2: 0.76 (sr)LDA+(Ir)MP2: 0.63 (sr)LDA+(Ir)dRPA-I: 0.35

Distances inter-monomères



MP2: 0.075 (sr)LDA+(Ir)MP2: 0.053 (sr)LDA+(Ir)dRPA-I: 0.023

- après optimisation sans correction counterpoise
- $ightharpoonup NH_3\cdots F_2$: faible magnitudes des valeurs pas un cas problématique
- ► H₂O···CIF : bonne énergie d'interaction, longueur inter-monomère moyenne
- ► NH₃ · · · Cl₂ : bonne longueur inter-monomère, énergie d'interaction moyenne liaisons plus déformées lors de la dimérisation (sr)LDA+(Ir)dRPA-I

Perspectives

Formulations RPA

- intégration numérique sur la fréquence (formulation "matrice diélectrique")
- ▶ implémentation du Density Fitting

EED

- clarifier question des orbitales
- calculs de l'énergie de corrélation

Gradients analytiques

- ▶ implémentation additionnelle de variantes telles que SO1 et SO2 difficile pour des raisons techniques (contraction de JM_{λ})
- ▶ applications supplémentaires (densité corrélée, dipôle, ...)
- Density Fitting

Remerciements

- membres du jury
- ► toute l'équipe du CRM²
- ▶ le laboratoire de chimie théorique de Eötvös Loránd University
- Virginie Pichon, Faculté de Pharmacie
- ► Sébastien Lebègue
- ▶ János Ángyán