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

Soutenance de thèse

Bastien Mussard

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CRM^2, 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 fluctuation-dissipation

Gradients

Lagrangien

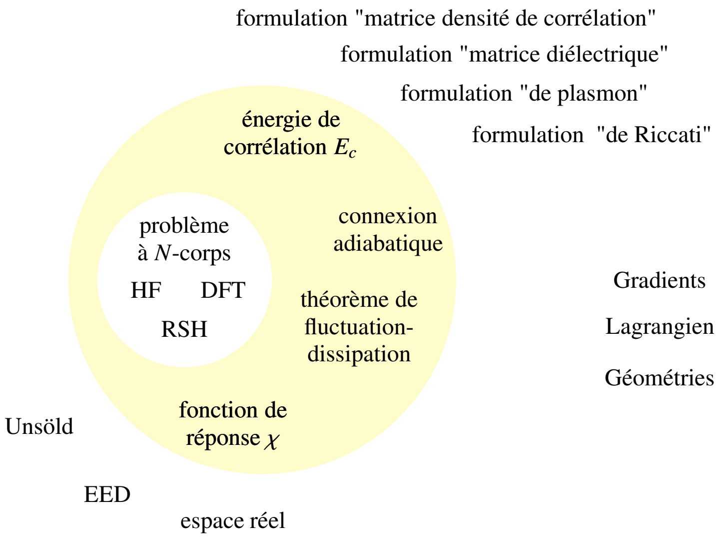
Géométries

Unsöld

fonction de réponse χ

EED

espace réel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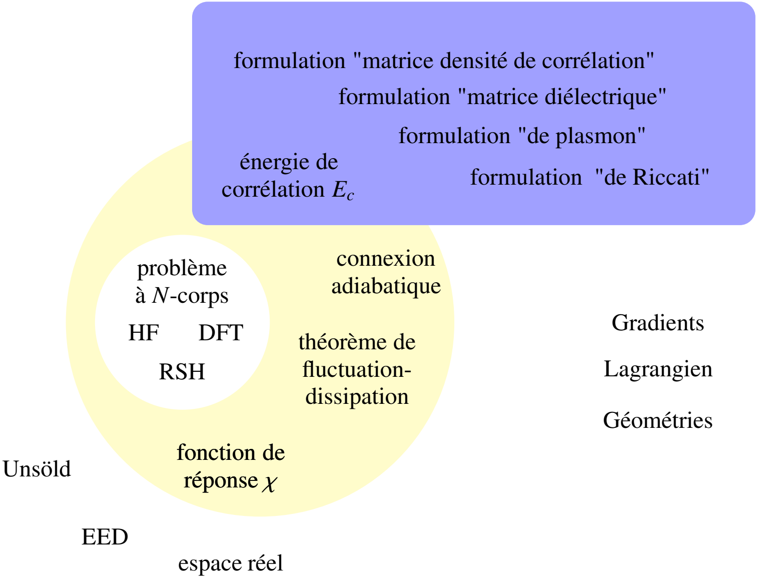
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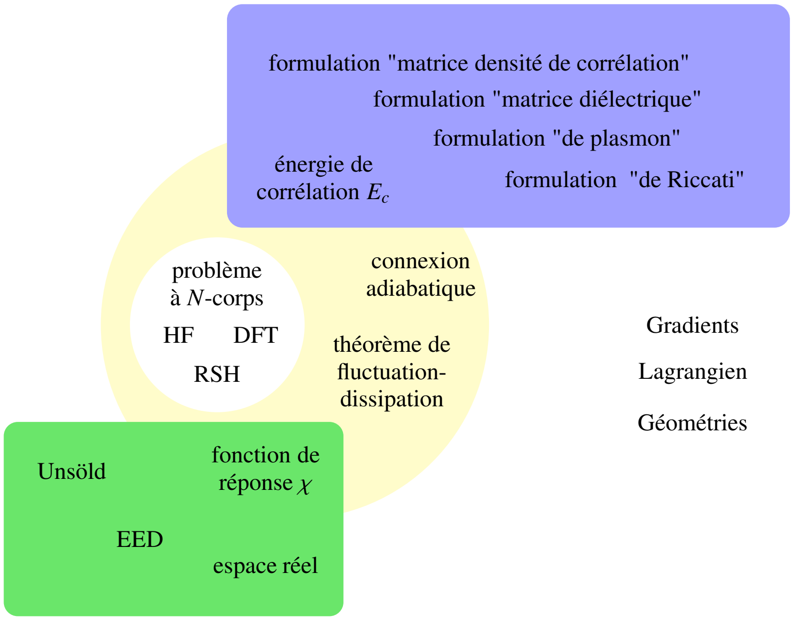
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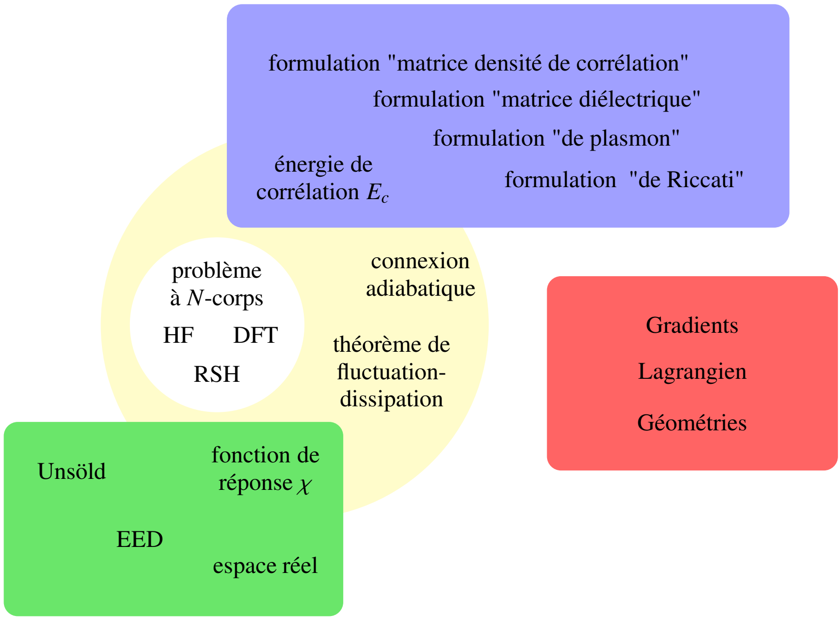

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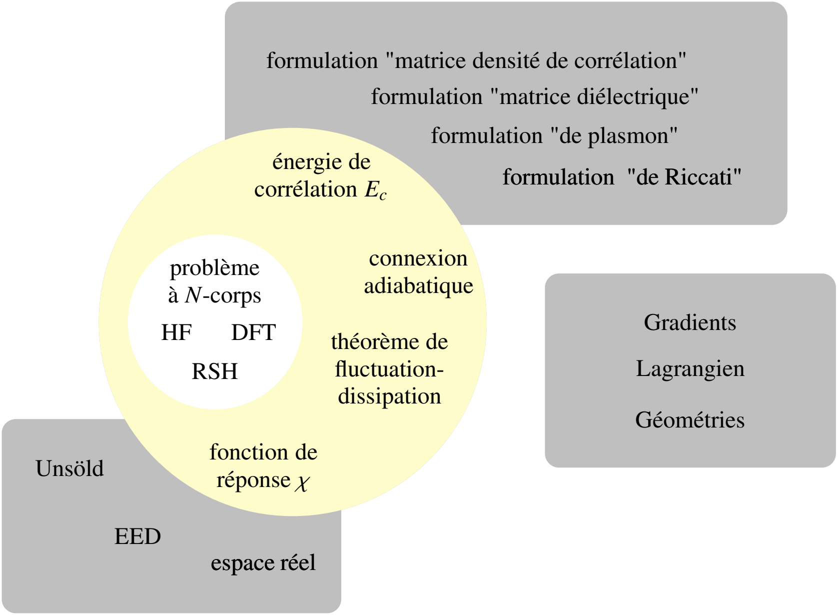
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Contexte théorique

- 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)

$$\Big(\underbrace{\hat{T}_e + \hat{V}_{ne}}_{\sum_i \hat{h}_i} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\Big)|\Psi\rangle = E\,|\Psi\rangle$$

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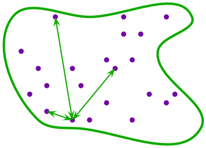
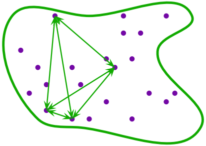


$$\Big(\underbrace{\hat{T}_e + \hat{V}_{ne}}_{\sum_i \hat{h}_i} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\Big)|\Psi\rangle = E\,|\Psi\rangle$$



Approche "fonction d'onde"

$$\Big(\underbrace{\hat{T}_e + \hat{V}_{ne}}_{\sum_i \hat{h}_i} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\Big)|\Psi\rangle = E\,|\Psi\rangle$$

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

$$E_{\mathrm{HF}} = \langle\Phi_{\mathrm{HF}}|\,\textstyle\sum_i \hat{h}_i + \sum_{ij}\hat{g}_{ij}\,|\Phi_{\mathrm{HF}}\rangle = \sum \langle\phi_i|\,\hat{h}_i + \boxed{\hat{v}_{\mathrm{Hx},i}}\,|\phi_i\rangle$$

$$\frac{\mathbf{1}}{\mathbf{r}}$$

$$E = E_{\mathrm{HF}} + \boxed{E_c}$$

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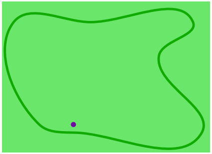
$$\frac{1}{\mathbf{r}}$$

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

Approche "fonctionnelle de la densité"

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

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



Approche “fonction d’onde”

$$\Big(\underbrace{\hat{T}_e + \hat{V}_{ne}}_{\sum_i \hat{h}_i} + \underbrace{\hat{V}_{ee}}_{\sum_{ij} \hat{g}_{ij}}\Big)|\Psi\rangle = E\,|\Psi\rangle$$

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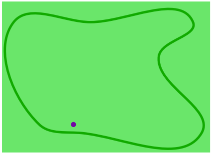
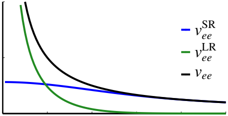


Séparation de portée

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

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



énergie totale $\quad E = E_{\mathrm{RSH}} + E_c^{\mathrm{lr}}$

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

Connexion adiabatique

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

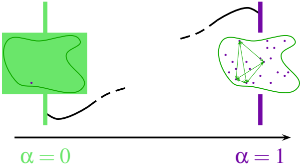
Connexion adiabatique

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

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

$$\hat{H}_{\alpha}=\hat{T}+\hat{V}_{ne}+(1-\alpha)\hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}+\alpha\hat{V}_{ee}^{\mathrm{lr}}+\hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[\Psi_{\alpha}]$$

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



Connexion adiabatique

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

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$$\hat{H}_\alpha = \hat{T}+\hat{V}_{ne}+(1-\alpha)\hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}+\alpha\hat{V}_{ee}^{\mathrm{lr}}+\hat{V}_{\mathrm{Hxc}}^{\mathrm{sr}}[\Psi_\alpha]$$

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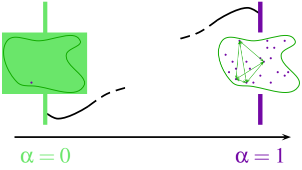

Énergie de corrélation

$$\frac{\mathrm{d}E_\alpha}{\mathrm{d}\alpha} = \langle\Psi_\alpha|\,\hat{W}_{ee}^{\mathrm{lr}}\,|\Psi_\alpha\rangle \quad ; \quad \hat{W}_{ee}^{\mathrm{lr}} = \frac{\mathrm{d}\hat{H}_\alpha}{\mathrm{d}\alpha} = \hat{V}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hx,HF}}^{\mathrm{lr}}$$

Connexion adiabatique

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

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

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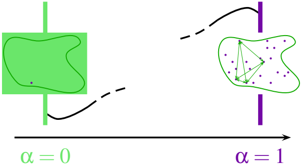

Énergie de corrélation

$$\int_0^1 d\alpha\ \frac{\mathrm{d}E_\alpha}{\mathrm{d}\alpha} = \int_0^1 d\alpha\ \langle\Psi_\alpha|\ \hat{W}_{ee}^{\text{lr}}\,|\Psi_\alpha\rangle \qquad ; \qquad \hat{W}_{ee}^{\text{lr}} = \frac{\mathrm{d}\hat{H}_\alpha}{\mathrm{d}\alpha} = \hat{V}_{ee}^{\text{lr}} - \hat{V}_{\text{Hx,HF}}^{\text{lr}}$$

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

Théorème de Fluctuation-Dissipation

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

$$\begin{aligned} P_{c,\alpha}(1,2) &= n_{2,\alpha}(1,2) - n_{2,0}(1,2) \\ &= \langle \Psi_\alpha | \delta\hat{n}_1(2)\delta\hat{n}_1(1) | \Psi_\alpha \rangle \\ &\quad - \langle \Psi_0 | \delta\hat{n}_1(2)\delta\hat{n}_1(1) | \Psi_0 \rangle + \Delta n_\alpha \end{aligned}$$

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Fluctuations

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

Théorème de Fluctuation-Dissipation

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

$$P_{c,\alpha}(1,2) = n_{2,\alpha}(1,2) - n_{2,0}(1,2)$$
$$= \langle \Psi_\alpha | \delta\hat{n}_1(2)\delta\hat{n}_1(1) | \Psi_\alpha \rangle$$
$$- \langle \Psi_0 | \delta\hat{n}_1(2)\delta\hat{n}_1(1) | \Psi_0 \rangle + \Delta n_\alpha$$

Fluctuations

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

Réponse du système

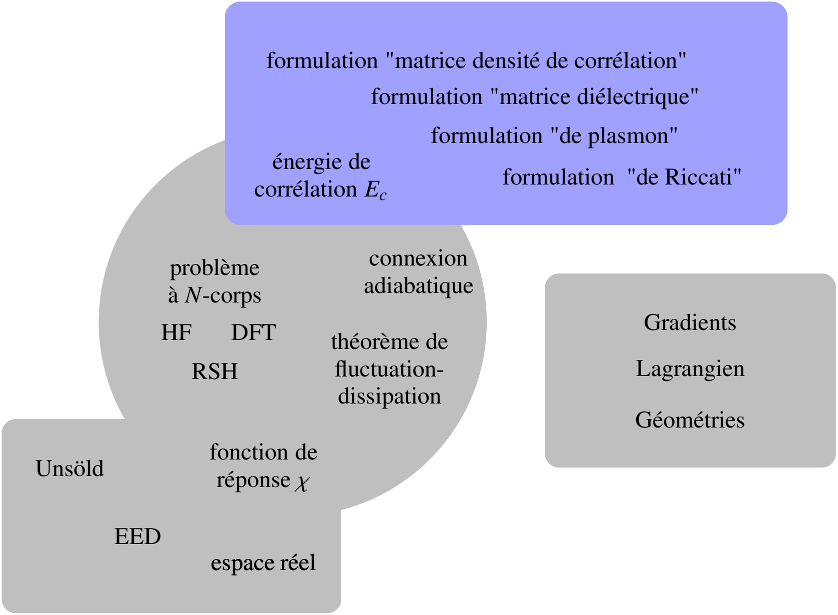
$$\langle \Psi_\alpha | \, \delta\hat{n}(1)\delta\hat{n}(2) \, | \Psi_\alpha \rangle = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \ \chi_\alpha(1,2;\omega)$$

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

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

- expression *exacte* de l' énergie de corrélation

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

"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)
- intégrale analytique sur la constante de couplage $\left(\int_0^1 d\alpha\right)$
  formulation "matrice diélectrique" $\boldsymbol{\varepsilon} = \mathbf{1} - \boldsymbol{\Pi}_0 \mathbf{K}$

Comprendre et Unifier

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

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

Représentation de Lehmann

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

Équation de Bethe-Salpeter

$$\chi_\alpha \quad (1,2;1',2';\omega)^{-1} = \chi_0(1,2;1',2';\omega)^{-1} - f_\alpha(1,2;1',2';\omega)$$

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

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

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

Représentation de Lehmann

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

Équation de Bethe-Salpeter

$$\chi_\alpha\quad(1,2;1',2';\omega)^{-1}=\chi_0(1,2;1',2';\omega)^{-1}-f_\alpha(1,2;1',2';\omega)$$

$$\begin{aligned}f_\alpha(1,2;1',2';\omega)&=\frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2}+f_{x,\alpha}(1,2;1',2';\omega)+f_{c,\alpha}(1,2;1',2';\omega)\\&=\alpha f^{\mathrm{RPA}}(1,2;1',2')=\alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2}+f_x(1,2;1',2')\right)\end{aligned}$$

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

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

Représentation de Lehmann

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

Équation de Bethe-Salpeter

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

$$\begin{aligned} f_\alpha(1,2;1',2';\omega) &= \frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega) \\ &= \alpha f^{\text{RPA}}(1,2;1',2') = \alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2} + f_x(1,2;1',2')\right) \end{aligned}$$

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

$$P_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)-\chi_0(1,2;1',2';\omega)+\cancel{\Delta n_{\alpha}}\right] \qquad \mathbb{P}_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\mathbb{\Pi}_{\alpha}^{\text{RPA}}-\mathbb{\Pi}_0\right]$$

Représentation de Lehmann

$$\chi_0(1,2;1',2',\omega)=\sum_{ia}\frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega-(\varepsilon_a-\varepsilon_i)+i\eta^+}+\frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega-(\varepsilon_a-\varepsilon_i)+i\eta^+} \qquad (\mathbb{\Pi}_0)^{-1}=\omega\mathbb{\Delta}-\mathbb{\Lambda}_0$$

Équation de Bethe-Salpeter

$$\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1}=\chi_0(1,2;1',2';\omega)^{-1}-\alpha f^{\text{RPA}}(1,2;1',2') \qquad (\mathbb{\Pi}_{\alpha}^{\text{RPA}})^{-1}=(\mathbb{\Pi}_0)^{-1}-\alpha\mathbb{F}^{\text{RPA}}$$

$$\begin{aligned} f_{\alpha}(1,2;1',2';\omega)&=\frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2}+f_{x,\alpha}(1,2;1',2';\omega)+f_{c,\alpha}(1,2;1',2';\omega)\\ &=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2}+f_x(1,2;1',2')\right)\end{aligned}$$

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

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

$$\mathbb{P}_{c,\alpha}^{\text{RPA}} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \left[\Pi_\alpha^{\text{RPA}} - \Pi_0\right]$$

Représentation de Lehmann

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

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

Équation de Bethe-Salpeter

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

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

$$\begin{aligned} f_\alpha(1,2;1',2';\omega) &= \frac{\alpha}{\mathbf{r}_1 - \mathbf{r}_2} + f_{x,\alpha}(1,2;1',2';\omega) + f_{c,\alpha}(1,2;1',2';\omega) \\ &= \alpha f^{\text{RPA}}(1,2;1',2') = \alpha\left(\frac{1}{\mathbf{r}_1 - \mathbf{r}_2} + f_x(1,2;1',2')\right) \end{aligned}$$

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

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

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

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

$$\mathbb{P}_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\mathbb{\Pi}_{\alpha}^{\text{RPA}}-\mathbb{\Pi}_0\right]$$

Représentation de Lehmann

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

$$(\mathbb{\Pi}_0)^{-1}=\omega\mathbb{\Delta}-\mathbb{\Lambda}_0$$

Équation de Bethe-Salpeter

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

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

$$\begin{aligned}f_{\alpha}(1,2;1',2';\omega)&=\frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2}+f_{x,\alpha}(1,2;1',2';\omega)+f_{c,\alpha}(1,2;1',2';\omega)\\&=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2}+f_x(1,2;1',2')\right)\end{aligned}$$

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

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

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

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

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

$$P_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)-\chi_0(1,2;1',2';\omega)+\cancel{\Delta n_\alpha}\right] \qquad \mathbb{P}_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\Pi_{\alpha}^{\text{RPA}}-\Pi_0\right]$$

Représentation de Lehmann

$$\chi_0(1,2;1',2',\omega)=\sum_{ia}\frac{\psi_i^*(1')\psi_a(1)\psi_a^*(2')\psi_i(2)}{\omega-(\varepsilon_a-\varepsilon_i)+i\eta^+}+\frac{\psi_i^*(2')\psi_a(2)\psi_a^*(1')\psi_i(1)}{-\omega-(\varepsilon_a-\varepsilon_i)+i\eta^+} \qquad (\Pi_0)^{-1}=\omega\Delta-\Lambda_0$$

Équation de Bethe-Salpeter

$$\chi_{\alpha}^{\text{RPA}}(1,2;1',2';\omega)^{-1}=\chi_0(1,2;1',2';\omega)^{-1}-\alpha f^{\text{RPA}}(1,2;1',2') \qquad (\Pi_{\alpha}^{\text{RPA}})^{-1}=(\Pi_0)^{-1}-\alpha\mathbb{F}^{\text{RPA}}$$

$$\begin{aligned}f_\alpha(1,2;1',2';\omega)&=\frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2}+f_{x,\alpha}(1,2;1',2';\omega)+f_{c,\alpha}(1,2;1',2';\omega)\\&=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2}+f_x(1,2;1',2')\right)\end{aligned}$$

$$f^{\text{dRPA}}=w(1,2)[\delta(1,1')\delta(2,2')] \qquad \mathbb{F}^{\text{dRPA}}=\begin{pmatrix}\mathbf{K}&\mathbf{K}\\\mathbf{K}&\mathbf{K}\end{pmatrix}$$

$$f^{\text{RPAx}}=w(1,2)[\delta(1,1')\delta(2,2')-\delta(1,2')\delta(2,1')] \qquad \mathbb{F}^{\text{RPAx}}=\begin{pmatrix}\mathbf{A}'&\mathbf{B}\\\mathbf{B}&\mathbf{A}'\end{pmatrix}$$

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

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

$$E_c^{\text{RPAx-II}}=\frac{1}{4}\int_0^1 d\alpha\;\text{Tr}\left(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{RPAx}}\right) \qquad E_c^{\text{dRPA-II}}=\frac{1}{2}\int_0^1 d\alpha\;\text{Tr}\left(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{dRPA}}\right)$$

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

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

$$\mathbb{P}_{c,\alpha}^{\text{RPA}}=\int_{-\infty}^{\infty}\frac{-d\omega}{2\pi i}\left[\mathbb{\Pi}_\alpha^{\text{RPA}}-\mathbb{\Pi}_0\right]$$

Représentation de Lehmann

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

$$(\mathbb{\Pi}_0)^{-1}=\omega\mathbb{\Delta}-\mathbb{\Lambda}_0$$

Équation de Bethe-Salpeter

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

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

$$\begin{aligned}f_\alpha(1,2;1',2';\omega)&=\frac{\alpha}{\mathbf{r}_1-\mathbf{r}_2}+f_{x,\alpha}(1,2;1',2';\omega)+f_{c,\alpha}(1,2;1',2';\omega)\\&=\alpha f^{\text{RPA}}(1,2;1',2')=\alpha\left(\frac{1}{\mathbf{r}_1-\mathbf{r}_2}+f_x(1,2;1',2')\right)\end{aligned}$$

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

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

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

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

Énergie de corrélation

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

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

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

$$E_c^{\text{RPAx-II}}=\frac{1}{4}\int_0^1 d\alpha\ \text{Tr}\left(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{RPAx}}\right)\qquad E_c^{\text{dRPA-II}}=\frac{1}{2}\int_0^1 d\alpha\ \text{Tr}\left(\mathbb{W}^{\text{II}}.\mathbb{P}_{c,\alpha}^{\text{dRPA}}\right)$$

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

Formulation "de plasmon" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

$\mathbb{\Pi}_\alpha^{-1} = \omega\mathbb{\Delta} - \mathbb{\Lambda}_0 - \alpha\mathbb{F}$

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

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

$\mathbb{\Pi}_\alpha^{-1} = \omega\mathbb{\Delta} - \mathbb{\Lambda}_0 - \alpha\mathbb{F}$

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

Formulation "de plasmon" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

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

Formulation "de Riccati" $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

$$\begin{pmatrix} \varepsilon + \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \varepsilon + \mathbf{A}' \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ -\mathbf{Y} \end{pmatrix} \qquad \mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$$

$$\mathbf{R}[\mathbf{T}] = \mathbf{B} + \left[\mathbf{A}', \mathbf{T}\right]_+ + \mathbf{T}\mathbf{B}\mathbf{T} + [\varepsilon, \mathbf{T}]_+ = \mathbf{0}$$

$$E_c^{\mathrm{dRPA\text{-}I}} = \frac{1}{2} \, \mathrm{tr}\left\{\mathbf{B}^{\mathrm{dRPA}}\mathbf{T}^{\mathrm{dRPA}}\right\}$$

$$E_c^{\mathrm{RPAx\text{-}II}} = \frac{1}{4} \, \mathrm{tr}\left\{\mathbf{B}^{\mathrm{RPAx}}\mathbf{T}^{\mathrm{RPAx}}\right\}$$

équivalent à (d)rCCD

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

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

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

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

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

$$E_c^{\text{d/x-II}} \rightsquigarrow E_c^{\text{d/x-IIa}} = \int_0^1 d\alpha \; \text{tr}\left\{\mathbf{P}_\alpha^{\text{d/x}} \mathbf{B}\right\}$$

$$(\mathbf{1} + \mathbf{P}_\alpha)^{-1} \approx (\mathbf{1} - \mathbf{P}_\alpha)$$

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

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

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

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

$$\int_0^1 d\alpha \; \mathbf{P}_\alpha \text{ et } \mathbf{T} \text{ ?}$$

Jansen, Liu, Ángyán; *J. Chem. Phys.* (2010)

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

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

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

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

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

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

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

$$\int_0^1 d\alpha \, \mathbf{P}_\alpha \text{ et } \mathbf{T} \; ?$$

Jansen, Liu, Ángyán; *J. Chem. Phys.* (2010)

Hesselmann; *Phys. Rev. A* (2012)

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

$$E_c^{\text{RPAX2}} = \text{tr}\{\mathbf{KT}\}$$

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

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

$$E_c^{\text{d/x-II}} \rightsquigarrow E_c^{\text{d/x-IIa}} = \int_0^1 d\alpha \; \text{tr}\left\{\mathbf{P}_\alpha^{\text{d/x}} \mathbf{B}\right\}$$

$$(\mathbf{1} + \mathbf{P}_\alpha)^{-1} \approx (\mathbf{1} - \mathbf{P}_\alpha)$$

Variantes (formulation "de Riccati") $\left(\int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\right)$ et $\left(\int_0^1 d\alpha\right)$

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

$$E_c^{\text{dRPA-I}} = \text{tr}\left\{\mathbf{KT}\right\}$$

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

$$\int_0^1 d\alpha \; \mathbf{P}_\alpha \text{ et } \mathbf{T} \;?$$

Jansen, Liu, Ángyán; *J. Chem. Phys.* (2010)

Hesselmann; *Phys. Rev. A* (2012)

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

$$E_c^{\text{RPAX2}} = \text{tr}\left\{\mathbf{KT}\right\}$$

Comprendre et Unifier

Ángyán, Liu, Toulouse, Jansen; *J.C.T.C.* (2011)

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

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\, \mathrm{Tr}\{\mathbb{\Pi}_\alpha^{\mathrm{d/x}}\mathbb{W}^{\mathrm{I/II}} - \mathbb{\Pi}_0\mathbb{W}^{\mathrm{I/II}}\}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1}\, \mathrm{Tr}\{\left(\mathbb{\Pi}_0\mathbb{W}^{\mathrm{d/x}}\right)^{n-1}\mathbb{\Pi}_0\mathbb{W}^{\mathrm{I/II}}\}$$

$$\mathbb{\Pi}_\alpha^{\mathrm{d/x}} = \left(\mathbb{1} - \alpha\mathbb{\Pi}_0\mathbb{W}^{\mathrm{d/x}}\right)^{-1}\mathbb{\Pi}_0$$

$$(1-\alpha x)^{-1} = 1 + \sum_{n=2} \alpha^{n-1}x^{n-1}$$

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

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

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\ \mathrm{Tr}\{\mathbb{\Pi}_\alpha^{\mathrm{d/x}}\mathbb{W}^{\mathrm{I/II}} - \mathbb{\Pi}_0\mathbb{W}^{\mathrm{I/II}}\}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1}\ \mathrm{Tr}\{\left(\mathbb{\Pi}_0\mathbb{W}^{\mathrm{d/x}}\right)^{n-1}\mathbb{\Pi}_0\mathbb{W}^{\mathrm{I/II}}\}$$

$$\mathbb{\Pi}_\alpha^{\mathrm{d/x}} = \left(\mathbb{1} - \alpha\mathbb{\Pi}_0\mathbb{W}^{\mathrm{d/x}}\right)^{-1}\mathbb{\Pi}_0$$

$$(1-\alpha x)^{-1} = 1 + \sum_{n=2}\alpha^{n-1}x^{n-1}$$

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

<u>dRPA-I</u>

$$\mathbb{W}^{\mathrm{d}} = \mathbb{W}^{\mathrm{I}} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathrm{Tr}\left\{(\mathbb{\Pi}_0\mathbb{W}^{\mathrm{d}})^n\right\} = \mathrm{tr}\{(\mathbf{\Pi}_0\mathbf{K})^n\}$$

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ \mathrm{tr}\left\{\mathrm{Log}(\mathbf{1} - \mathbf{\Pi}_0\mathbf{K}) + \mathbf{\Pi}_0\mathbf{K}\right\}$$

$$\boldsymbol{\epsilon} = \mathbf{1} - \mathbf{\Pi}_0\mathbf{K}$$

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

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i}\ \mathrm{Tr}\{\mathbb{\Pi}_\alpha^{d/x}\mathbb{W}^{I/II} - \mathbb{\Pi}_0\mathbb{W}^{I/II}\}$$

$$E_c^{\text{AC-FDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi i} \sum_{n=2} \alpha^{n-1}\ \mathrm{Tr}\{\left(\mathbb{\Pi}_0\mathbb{W}^{d/x}\right)^{n-1}\mathbb{\Pi}_0\mathbb{W}^{I/II}\}$$

$$\mathbb{\Pi}_\alpha^{d/x} = \left(\mathbb{1} - \alpha\mathbb{\Pi}_0\mathbb{W}^{d/x}\right)^{-1}\mathbb{\Pi}_0$$

$$(1-\alpha x)^{-1} = 1 + \sum_{n=2} \alpha^{n-1}x^{n-1}$$

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

<u>dRPA-I</u>

$$\mathbb{W}^{d} = \mathbb{W}^{I} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathrm{Tr}\left\{(\mathbb{\Pi}_0\mathbb{W}^{d})^n\right\} = \mathrm{tr}\{(\mathbf{\Pi}_0\mathbf{K})^n\}$$

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ \mathrm{tr}\left\{\mathrm{Log}(\mathbf{1} - \mathbf{\Pi}_0\mathbf{K}) + \mathbf{\Pi}_0\mathbf{K}\right\}$$

$$\epsilon = \mathbf{1} - \mathbf{\Pi}_0\mathbf{K}$$

<u>dRPA-II</u>

$$\mathbb{W}^{d} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathbb{W}^{II} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix} = \begin{pmatrix} \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{B} \end{pmatrix} + \begin{pmatrix} \mathbf{A}'-\mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}'-\mathbf{B} \end{pmatrix}$$

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

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

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

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

$$\Pi_\alpha^{d/x} = \left(\mathbb{1} - \alpha\Pi_0\mathbb{W}^{d/x}\right)^{-1}\Pi_0$$

$$(1-\alpha x)^{-1} = 1 + \sum_{n=2} \alpha^{n-1}x^{n-1}$$

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

<u>dRPA-I</u>

$$\mathbb{W}^{d} = \mathbb{W}^{I} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathrm{Tr}\left\{(\Pi_0\mathbb{W}^d)^n\right\} = \mathrm{tr}\{(\mathbf{\Pi}_0\mathbf{K})^n\}$$

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \mathrm{tr}\left\{\mathrm{Log}(\mathbf{1} - \mathbf{\Pi}_0\mathbf{K}) + \mathbf{\Pi}_0\mathbf{K}\right\}$$

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

<u>dRPA-II</u>

$$\mathbb{W}^{d} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix} \quad ; \quad \mathbb{W}^{II} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix} = \begin{pmatrix} \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{B} \end{pmatrix} + \begin{pmatrix} \mathbf{A}'-\mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}'-\mathbf{B} \end{pmatrix}$$

$$E_c^{\text{dRPA-IIa}} = \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \mathrm{tr}\left\{\mathrm{Log}\left(\mathbf{1} - \mathbf{\Pi}_0\mathbf{K}\right)\mathbf{K}^{-1}\mathbf{B} + \mathbf{\Pi}_0\mathbf{B}\right\}$$

<u>RPAx-I</u>

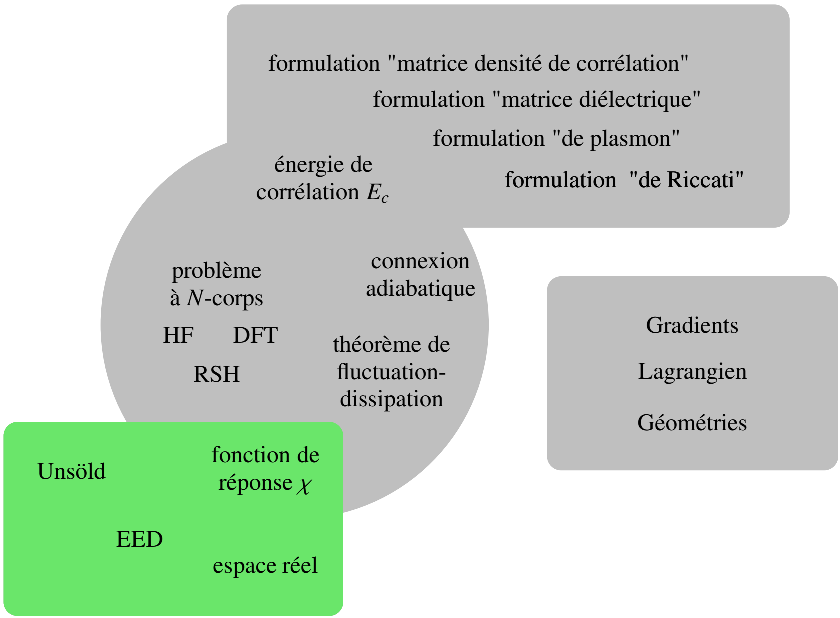
$$\mathbb{W}^{x} = \begin{pmatrix} \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & \mathbf{A}' \end{pmatrix} = \begin{pmatrix} \mathbf{B} & \mathbf{B} \\ \mathbf{B} & \mathbf{B} \end{pmatrix} + \begin{pmatrix} \mathbf{A}'-\mathbf{B} & \mathbf{0} \\ \mathbf{0} & \mathbf{A}'-\mathbf{B} \end{pmatrix} \quad ; \quad \mathbb{W}^{II} = \begin{pmatrix} \mathbf{K} & \mathbf{K} \\ \mathbf{K} & \mathbf{K} \end{pmatrix}$$

$$E_c^{\text{RPAx-Ia}} = \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \mathrm{tr}\left\{\mathrm{Log}\left(\mathbf{1} - \mathbf{\Pi}_0\mathbf{B}\right)\mathbf{B}^{-1}\mathbf{K} + \mathbf{\Pi}_0\mathbf{K}\right\}$$

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”)



formulation "matrice densité de corrélation"
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énergie de corrélation E_c
problème à N-corps
HF
DFT
RSH
connexion adiabatique
théorème de fluctuation-dissipation
Gradients
Lagrangien
Géométries
Unsöld
fonction de réponse χ
EED
espace réel

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

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\mathrm{tr}\left\{\mathrm{Log}(\mathbf{1} - \mathbf{\Pi}_0\mathbf{K}) + \mathbf{\Pi}_0\mathbf{K}\right\}$$

- éviter la double sommation occ/vir ($\chi_0 = \sum_{ia} \dots$)
- éviter les états excités
- applications au calcul de :
  - polarisabilité dynamique
  - coefficients C_6
  - énergie RPA

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

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
- $\overline{\Omega}_{\mathbf{r}_1,\mathbf{r}_2,\omega}$ dépend de $(\mathbf{r}_1,\mathbf{r}_2,\omega)$

α états excités

$$\sum_\alpha \langle 0| \hat{n}(\mathbf{r}_1) |\alpha\rangle \langle\alpha| \hat{n}(\mathbf{r}_2) |0\rangle$$

$$\sum_\alpha |\alpha\rangle \langle\alpha| + |0\rangle \langle 0| = 1$$

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

Berger, Reining, Sottile; *Phys. Rev. B* (2010)

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

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

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

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

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

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

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

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Approximations de Ω^{nn}

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

$S^{nn} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2)$ $\chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}$ $\Omega^{nn} = \frac{\chi^{nj}}{\chi^{nn}}$	$S^{nj} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2) \Omega_\alpha$ $\chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}}$ $\Omega^{nj} = \frac{\chi^{jj}}{\chi^{nj}}$	$S^{jj} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2) \Omega_\alpha \Omega_\alpha$ $\chi^{jj} = \frac{S^{jj}}{i\omega - \Omega^{jj}}$

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$\ldots$

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$\dots$

Approximations de Ω^{nn}

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$S^{nn} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2)$	$S^{nj} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2)\Omega_\alpha$	$S^{jj} = \sum n_\alpha(\mathbf{r}_1) n_\alpha(\mathbf{r}_2)\Omega_\alpha\Omega_\alpha$
$\chi^{nn} = \frac{S^{nn}}{i\omega - \Omega^{nn}}$	$\chi^{nj} = \frac{S^{nj}}{i\omega - \Omega^{nj}}$	$\chi^{jj} = \frac{S^{jj}}{i\omega - \Omega^{jj}}$
$\Omega^{nn} = \frac{\chi^{nj}}{\chi^{nn}}$	$\Omega^{nj} = \frac{\chi^{jj}}{\chi^{nj}}$	

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

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$$\dots \qquad \dots$$

- 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

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

$$\boxed{\begin{aligned} \chi^{nn(1)} &= \frac{S^{nn}}{i\omega - \dfrac{S^{nj}}{S^{nn}}} \\[2em] \chi^{nn(2)} &= \frac{S^{nn}}{i\omega - \dfrac{S^{nj}}{S^{nn}} \dfrac{i\omega - \dfrac{S^{nj}}{S^{nn}}}{i\omega - \dfrac{S^{jj}}{S^{nj}}}} \end{aligned}}$$

Polarisabilité

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

$$\alpha_{\alpha\beta}(i\omega)^{(1)} = 2\mathrm{Re}\sum_{i} \frac{S^{nn}_{\alpha\beta,i}}{i\omega - \frac{S^{nj}_{\alpha\beta,i}}{S^{nn}_{\alpha\beta,i}}}$$

$$S^{nn}_{\alpha\beta,i} = 4C^{\mathrm{T}}_{i\mu}\left(\mathbf{r}_\alpha \mathbf{Q} \mathbf{r}_\beta\right)_{\mu\nu} C_{\nu i}$$

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

Polarisabilité

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

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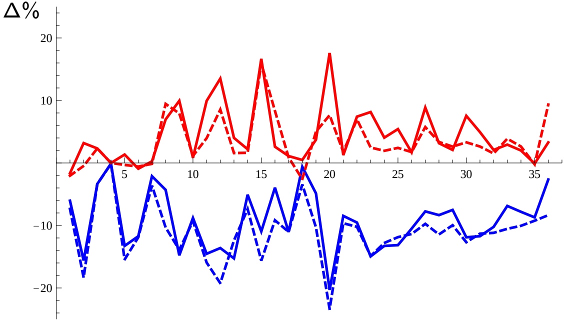
- calcul de $\alpha(0)$ sur 36 molécules



$\alpha^{\text{cano}\,(1)}_{\text{moy}}$	9.3 %
$\alpha^{\text{loc}\,(1)}_{\text{moy}}$	11.0 %
$\alpha^{\text{cano}\,(2)}_{\text{moy}}$	4.6 %
$\alpha^{\text{loc}\,(2)}_{\text{moy}}$	3.7 %

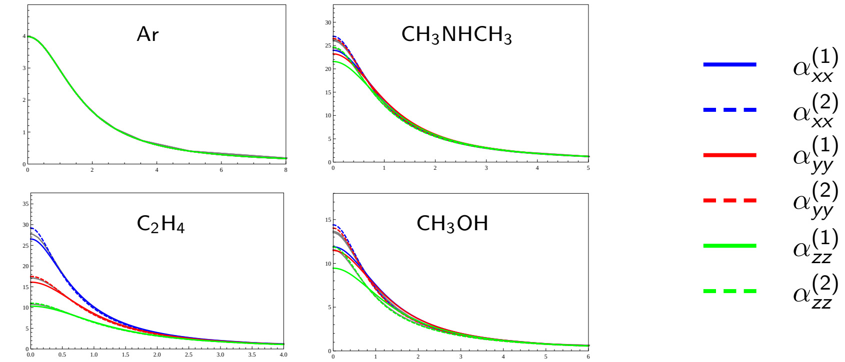
Polarisabilité

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

$$\alpha_{\alpha\beta}(i\omega)^{(1)} = 2\mathrm{Re} \sum_{i} \frac{S^{nn}_{\alpha\beta,i}}{i\omega - \dfrac{S^{nj}_{\alpha\beta,i}}{S^{nn}_{\alpha\beta,i}}}$$

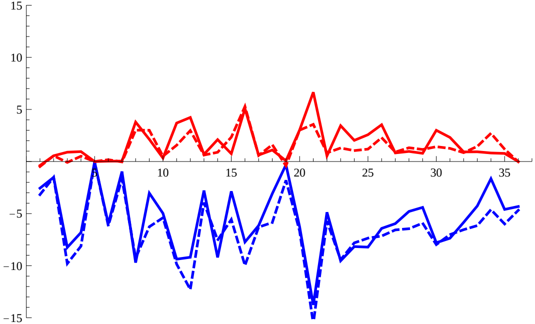
$$S^{nn}_{\alpha\beta,i} = 4 C^{\mathrm{T}}_{i\mu} \left(\mathbf{r}_\alpha \mathbf{Q} \mathbf{r}_\beta\right)_{\mu\nu} C_{\nu i}$$

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



Coefficients C_6

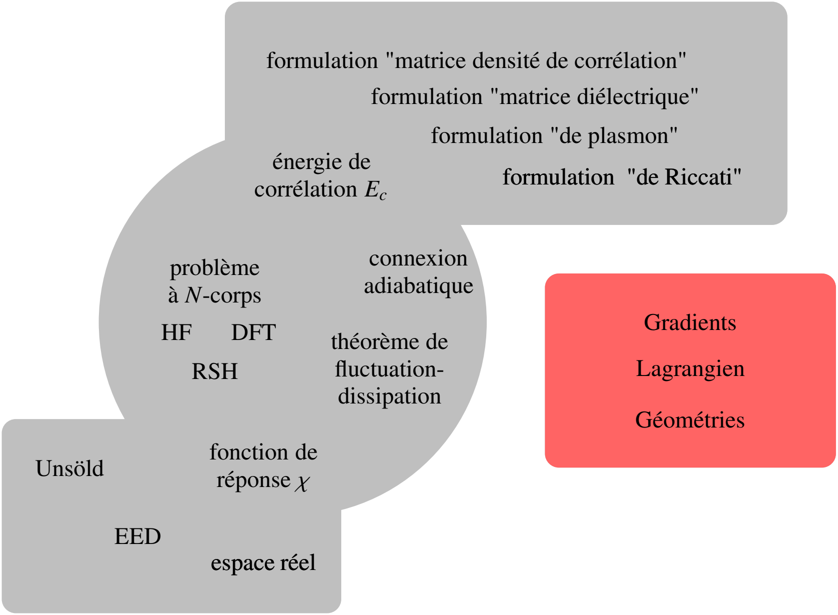
$$C_6^{ij} = \frac{3}{\pi} \int_0^\infty d\omega \, \overline{\alpha}^i(i\omega)\overline{\alpha}^j(i\omega)$$



———	$\alpha_{\text{moy}}^{\text{cano}\,(1)}$	5.6 %
- - -	$\alpha_{\text{moy}}^{\text{loc}\,(1)}$	6.6 %
———	$\alpha_{\text{moy}}^{\text{cano}\,(2)}$	1.7 %
- - -	$\alpha_{\text{moy}}^{\text{loc}\,(2)}$	1.4 %

- comme précédemment, ordre 1(2) sous-estime(sur-estime) systématiquement les C_6
- 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 C_6
- perspective du calcul de l'énergie de corrélation



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fonction de réponse χ
EED
espace réel

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,. . .)

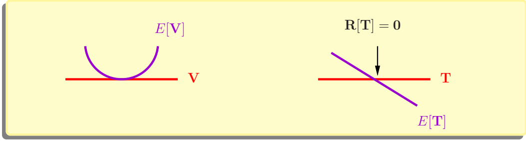
- gradients numériques (inefficaces, imprécis)

Gradients analytiques

Gradients analytiques

Paramètres

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



Gradients analytiques

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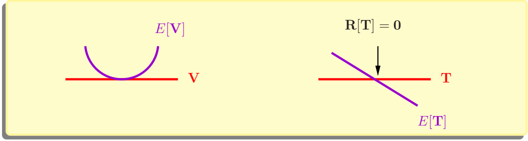


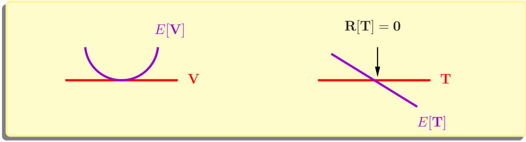
Gradients

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

Gradients analytiques

Paramètres

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



Gradients

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

Gradients analytiques

Paramètres

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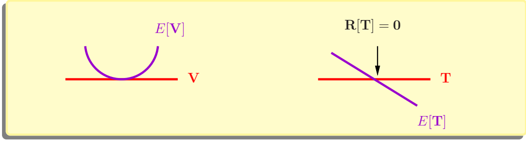


Gradients

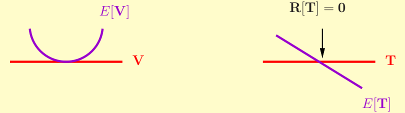
$$\boxed{\frac{\partial E}{\partial \kappa} = \frac{\partial E}{\partial \kappa} + \cancel{\frac{\partial E}{\partial \mathbf{V}}\frac{\partial \mathbf{V}}{\partial \kappa}} + \frac{\partial E}{\partial \mathbf{T}}\frac{\partial \mathbf{T}}{\partial \kappa}}$$

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

Gradients analytiques

Paramètres

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



Gradients

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

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

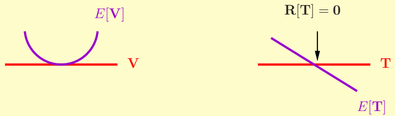
Méthodes variationnelles

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

Gradients analytiques

Paramètres

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



Gradients

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

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

<u>Méthodes variationnelles</u>

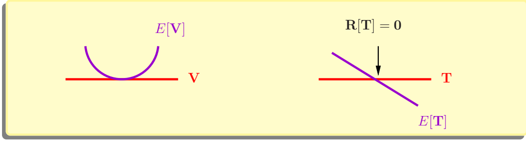
$$\frac{\partial E_{HF}}{\partial \kappa} = \underline{\delta h_{\alpha\beta}} P_{\alpha\beta} + \frac{1}{2}\underline{\delta(\mu\lambda|\nu\sigma)}(P_{\mu\lambda}P_{\nu\sigma} - P_{\mu\sigma}P_{\nu\lambda}) + \underline{\delta S_{\mu\nu}} S^{-1}_{\nu\lambda} F_{\lambda\sigma} P_{\sigma\mu}$$

<u>Méthodes non-variationnelles</u>

Gradients analytiques

Paramètres

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



Gradients

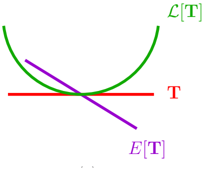
$$\boxed{\frac{\partial E}{\partial \kappa} = \frac{\partial E}{\partial \kappa} + \cancel{\frac{\partial E}{\partial \mathbf{V}}\frac{\partial \mathbf{V}}{\partial \kappa}} + \frac{\partial E}{\partial \mathbf{T}}\frac{\partial \mathbf{T}}{\partial \kappa}}$$

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

<u>Méthodes variationnelles</u>

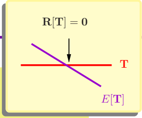
$$\frac{\partial E_{HF}}{\partial \kappa} = \underline{\delta h_{\alpha\beta}} P_{\alpha\beta} + \frac{1}{2}\underline{\delta(\mu\lambda|\nu\sigma)}(P_{\mu\lambda}P_{\nu\sigma} - P_{\mu\sigma}P_{\nu\lambda}) + \underline{\delta S_{\mu\nu}} S^{-1}_{\nu\lambda} F_{\lambda\sigma} P_{\sigma\mu}$$

<u>Méthodes non-variationnelles</u>



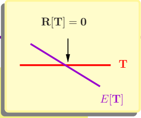
$$\boxed{\text{Travailler avec un objet alternatif qui \textbf{est} variationnel}}$$

Technique du Lagrangien



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

Technique du Lagrangien

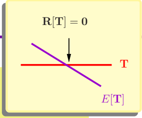


Rappel :	énergie	règle pour $\mathbf{T}$
pour non-variationnelle	$E[\mathbf{V},\mathbf{T}]$	$\mathbf{R}[\mathbf{T}]=0$

on introduit le Lagrangien

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

Technique du Lagrangien



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

on introduit le Lagrangien

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

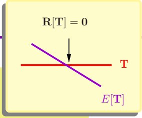
conditions stationnaires pour $\mathcal{L}$

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

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

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

Technique du Lagrangien



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

on introduit le Lagrangien

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

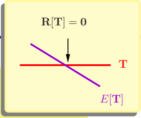
conditions stationnaires pour $\mathcal{L}$

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

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

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

Technique du Lagrangien



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

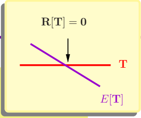
on introduit le Lagrangien
$$\boxed{\mathcal{L}[\mathbf{V},\mathbf{T},\boldsymbol{\lambda}] = E[\mathbf{V},\mathbf{T}] + \langle \boldsymbol{\lambda}\mathbf{R}[\mathbf{T}]\rangle}$$

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

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

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

Technique du Lagrangien



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

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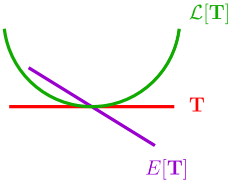

Énergie et Lagrangien RSH+RPA

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

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Notation avec fockiennes

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

Énergie et Lagrangien RSH+RPA

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

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&\quad + \left\langle \mathbf{d}^{(0)}\mathbf{g}^{\text{sr}} \right\rangle + \Delta_{\text{DC}}^{\text{sr}}
\end{aligned}
$$

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

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

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

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

Notation avec fockiennes

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

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

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

$$E_{Hxc}^{\text{sr}}[n] = \int dr\ F[\xi]$$

$$\boldsymbol{\xi} = \{\xi_A\} = \{n, n_\alpha, \nabla n_\alpha, \ldots\}$$

$$g_{ab}^{\text{sr}} = \int dr\ \sum_A \frac{\partial F}{\partial \xi_A} \frac{\partial \xi_A}{\partial d_{ab}^{(0)}}$$

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

Énergie et Lagrangien RSH+RPA

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Notation avec fockiennes

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

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

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

Lagrangien RSH+RPA (sr+lr)

- 2 paramètres non-varia. : amplitudes $\mathbf{T}$, coefficients orbitalaires $\mathbf{C}$
- 3 contraintes: $\mathbf{R}[\mathbf{T},\mathbf{C}] = 0$, $(\mathbf{f})_{ai} = 0$, $\left(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}\right) = 0$

Énergie et Lagrangien RSH+RPA

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

Notation avec fockiennes

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

$$\Delta_{\mathrm{DC}}^{\mathrm{lr}} = -\tfrac{1}{2}\left\langle \mathbf{d}^{(0)} \mathbf{g}^{\mathrm{lr}}\left[\mathbf{d}^{(0)}\right]\right\rangle$$

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

$$E_{Hxc}^{\mathrm{sr}}[n] = \int dr\ F[\xi] \qquad \xi = \{\xi_A\} = \{n, n_\alpha, \nabla n_\alpha, \dots\}$$

$$g_{ab}^{\mathrm{sr}} = \int dr \sum_A \frac{\partial F}{\partial \xi_A} \frac{\partial \xi_A}{\partial d_{ab}^{(0)}}$$

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

Lagrangien RSH+RPA (sr+lr)

- 2 paramètres non-varia. : amplitudes $\mathbf{T}$, coefficients orbitalaires $\mathbf{C}$
- 3 contraintes: $\mathbf{R}[\mathbf{T},\mathbf{C}] = 0$, $(\mathbf{f})_{ai} = 0$, $\left(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C} - \mathbf{1}\right) = 0$

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

Conditions Stationnaires

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T}\rangle + \Big\langle \boldsymbol{\lambda}\Big(\mathbf{K} + [\mathbf{K},\mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon},\mathbf{T}]_+\Big)\Big\rangle\Big) = 0$$

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T} \rangle + \Big\langle \boldsymbol{\lambda}\Big(\mathbf{K} + [\mathbf{K}, \mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon}, \mathbf{T}]_+ \Big)\Big\rangle \Big) = 0$$

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

par rapport à C

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T} \rangle + \Big\langle \boldsymbol{\lambda}\Big(\mathbf{K} + [\mathbf{K},\mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon},\mathbf{T}]_+\Big)\Big\rangle\Big) = 0$$

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

par rapport à C

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

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T}\rangle + \big\langle \boldsymbol{\lambda}\big(\mathbf{K}+[\mathbf{K},\mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon},\mathbf{T}]_+\big)\big\rangle\Big) = 0$$

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

par rapport à C

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

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

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

Conditions Stationnaires

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

par rapport à T

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

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

par rapport à C

$$\big\langle \mathbf{K}\big(\mathbf{T} + \boldsymbol{\lambda} + [\boldsymbol{\lambda},\mathbf{T}]_+ + \mathbf{T}\boldsymbol{\lambda}\mathbf{T}\big)\big\rangle + \big\langle \boldsymbol{\varepsilon}[\boldsymbol{\lambda},\mathbf{T}]_+ \big\rangle \doteq \langle \mathbf{KM}_{\boldsymbol{\lambda}}\rangle + \langle \mathbf{d}_{\boldsymbol{\lambda}}^{(2)}\mathbf{f}\rangle$$

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

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

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

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

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

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

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

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

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T}\rangle + \big\langle \boldsymbol{\lambda}\big(\mathbf{K} + [\mathbf{K},\mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon},\mathbf{T}]_+\big)\big\rangle\Big) = 0$$

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

par rapport à C

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

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

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

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

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

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

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

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

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

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

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

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

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

Conditions Stationnaires

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

par rapport à T

$$\frac{\partial}{\partial T}\Big(\langle \mathbf{K}\mathbf{T}\rangle + \big\langle \boldsymbol{\lambda}\big(\mathbf{K} + [\mathbf{K},\mathbf{T}]_+ + \mathbf{T}\mathbf{K}\mathbf{T} + [\boldsymbol{\varepsilon},\mathbf{T}]_+\big)\big\rangle\Big) = 0$$

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

par rapport à C

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

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

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

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

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

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

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

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

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

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

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

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

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

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

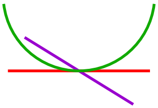
Expression du gradient

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

Expression du gradient

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

simplement la dérivée d'un objet variationnel

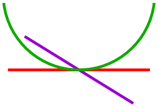


Expression du gradient

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

simplement la dérivée d'un objet variationnel

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



Expression du gradient

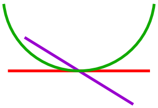
$$\mathcal{L} = \left\langle (\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z})\mathbf{f}^{\text{ sr } + \text{ lr}} \right\rangle + \Delta_{\text{DC}}^{\text{sr } + \text{ lr}} + \langle \mathbf{K}\mathbf{M}_{\boldsymbol{\lambda}} \rangle + \left\langle \mathbf{x}(\mathbf{C}^{\mathsf{T}}\mathbf{S}\mathbf{C}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

simplement la dérivée d'un objet variationnel

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

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

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



Expression du gradient

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

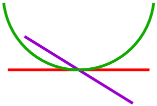
simplement la dérivée d'un objet variationnel

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

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

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

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



Expression du gradient

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

simplement la dérivée d'un objet variationnel

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

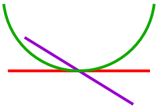
$$(\mathbf{D}^1)_{\mu\nu} = C_{\mu p} \left(\mathbf{d}^{(0)} + \mathbf{d}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{z} \right)_{pq} C^{\dagger}_{q\nu} = \left(\mathbf{D}^{(0)} + \mathbf{D}^{(2)}_{\boldsymbol{\lambda}} + \mathbf{Z} \right)_{\mu\nu}$$

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

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

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

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



Implémentation

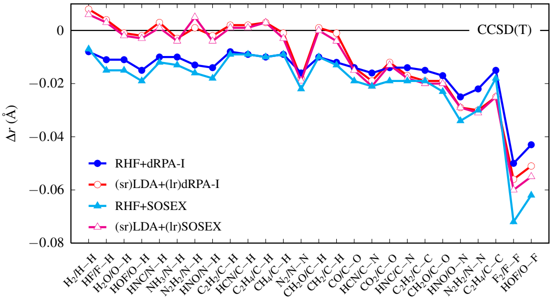
- implémenté dans MOLPRO , dans le "coeur"
- utilise un parallèle avec les gradients RSH+MP2

- validation par la correspondance aux gradients numériques
- temps de calcul est double du calcul d'une énergie
- croissance en N^6

- optimisation de géométrie
- densité corrélée
- dipôles

- de manière générale : meilleure convergence avec la base

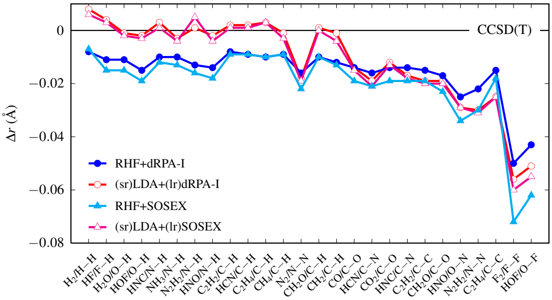
Longueurs de liaisons de simples molécules



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

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

Longueurs de liaisons de simples molécules



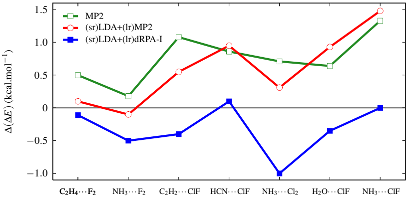
RHF+dRPA-I :	0.016
(sr)LDA+(lr)dRPA-I :	0.013
RHF+SOSEX :	0.021
(sr)LDA+(lr)SOSEX :	0.014

- 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

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

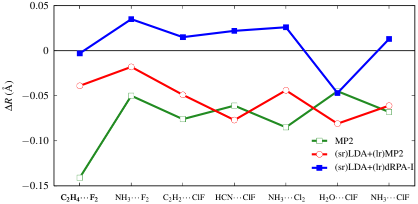
Énergies d'interaction



MP2 : 0.76 (sr)LDA+(lr)MP2 : 0.63

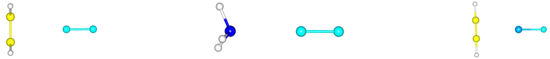
(sr)LDA+(lr)dRPA-I : 0.35

Distances inter-monomères



MP2 : 0.075 (sr)LDA+(lr)MP2 : 0.053

(sr)LDA+(lr)dRPA-I : 0.023

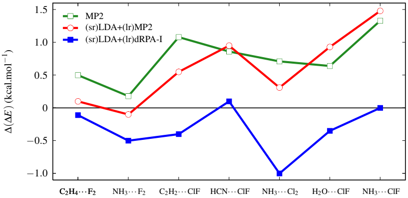


$C_2H_4\cdots F_2$ $NH_3\cdots F_2$ $C_2H_2\cdots F_2$

$HCN\cdots ClF$ $NH_3\cdots Cl_2$ $H_2O\cdots ClF$ $NH_3\cdots ClF$

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

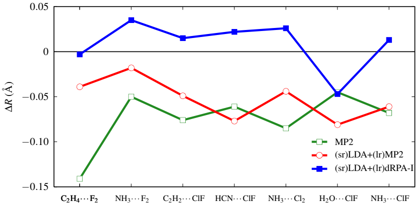
Énergies d'interaction



MP2 : 0.76 (sr)LDA+(lr)MP2 : 0.63

(sr)LDA+(lr)dRPA-I : 0.35

Distances inter-monomères



MP2 : 0.075 (sr)LDA+(lr)MP2 : 0.053

(sr)LDA+(lr)dRPA-I : 0.023

- après optimisation sans correction *counterpoise*
- $NH_3 \cdots F_2$: faible magnitudes des valeurs
  pas un cas problématique
- $H_2O \cdots ClF$: bonne énergie d'interaction, longueur inter-monomère moyenne
- $NH_3 \cdots Cl_2$: bonne longueur inter-monomère, énergie d'interaction moyenne
  liaisons plus déformées lors de la dimérisation (sr)LDA+(lr)dRPA-I

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

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 $\mathbf{JM}_\lambda$)
- applications supplémentaires (densité corrélée, dipôle, . . .)
- *Density Fitting*

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