Analytical Gradient for Random Phase Approximation Using a Lagrangian Framework

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[a] CRM^2, Université de Lorraine, Nancy, France
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Molecular Physics

$$\Psi(r_{1\to N}; \underbrace{R_{1\to M}}_{\text{atomic coordinates}}) \to E(R_{1\to M})$$

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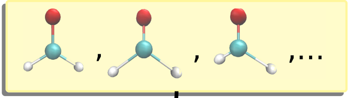

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Geometry : a collection of atomic coordinates

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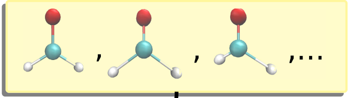

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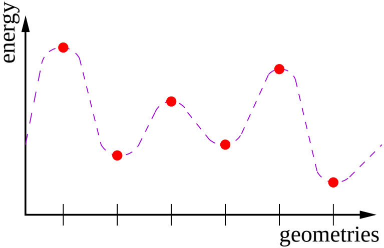

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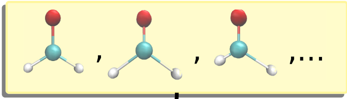

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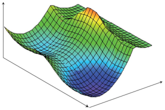

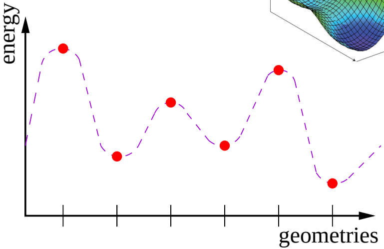

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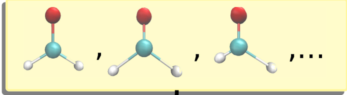

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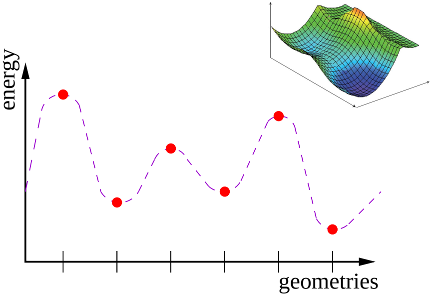
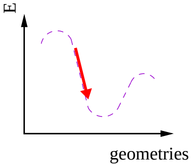


Gradients



$$\frac{\partial E}{\partial \kappa}$$

Analytical Gradient

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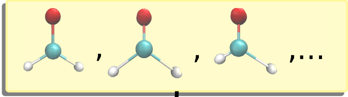

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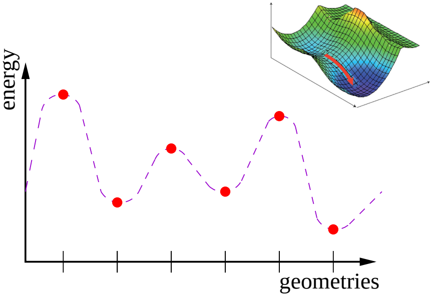

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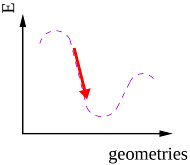

$$\frac{\partial E}{\partial \kappa}$$

The gradient of the energy $\frac{\partial E}{\partial \kappa}$ allows one to find optimum geometries

Random Phase Approximation

Random Phase Approximation

Hartree-Fock

- a good first approximation

$$\hat{H} = S^{-1}_{\mu\alpha} h_{\alpha\beta} S^{-1}_{\nu\beta} \chi^{\dagger}_{\mu} \chi_{\nu} + \frac{1}{2} S^{-1}_{\mu\alpha} S^{-1}_{\nu\beta} (\alpha\beta|\gamma\delta) S^{-1}_{\gamma\sigma} S^{-1}_{\delta\lambda} \chi^{\dagger}_{\mu} \chi^{\dagger}_{\nu} \chi_{\sigma} \chi_{\lambda}$$

$$E_{HF} = \langle HF|\hat{H}|HF\rangle$$

- still missing the **correlation energy**...

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RPA

- especially useful for dispersion energies (vdW forces)

$$\boxed{\begin{cases} E_c^{\text{RPA}} &= \frac{1}{2}\langle \mathbf{KT} \rangle \\ 0 &= \mathbf{K} + \mathbf{AT} + \mathbf{TA} + \mathbf{TKT} \end{cases}}$$

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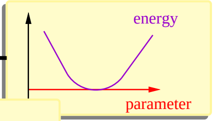
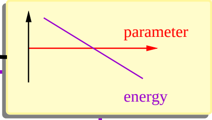
- still missing the **correlation energy**...
- a variational method



RPA

- especially useful for dispersion energies (vdW forces)
- a non-variational method



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A Simple Gradient : HF

Hellmann-Feynman theorem

- valid for **variational** wavefunctions

$$\boxed{\frac{\partial E}{\partial \kappa} = \langle \Psi | \frac{\partial \hat{H}}{\partial \kappa} | \Psi \rangle}$$

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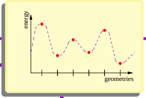

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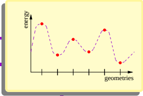

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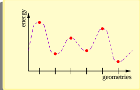

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- HF gradient *straightforwardly* found by the Hellman-Feynman theorem

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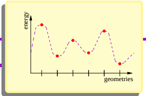

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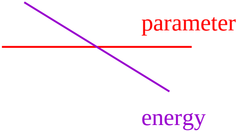
For non-variational wavefunctions... (RPA)



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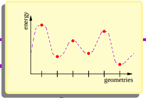

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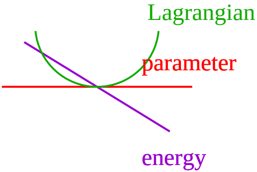

Work with an alternative object that **is** variational

Lagrangian Framework

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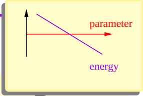
Remember : for a non-variational method :

Lagrangian Framework

Remember : for a non-variational method : energy
$E(\mathbf{P})$

Lagrangian Framework



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	energy	rules for $\mathbf{P}$
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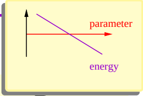
Lagrangian Framework



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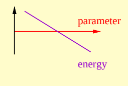
Lagrangian Framework



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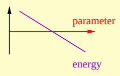
Lagrangian Framework



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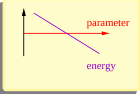

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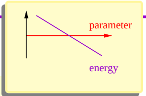
Lagrangian Framework



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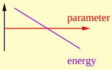
non zero !

Lagrangian Framework



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non zero !

RPA case

- parameters : $E(\mathbf{T}, \mathbf{C})$
- three constraints : $\mathbf{R} = 0$, $\mathbf{F} = 0$ and $\mathbf{O} = 0$
- three Lagrangian multipliers : $\boldsymbol{\lambda}$, $\mathbf{z}$ and $\mathbf{x}$

$$\mathcal{L}(\mathbf{T}, \boldsymbol{\lambda}, \mathbf{C}, \mathbf{z}, \mathbf{x}) = E(\mathbf{T}, \mathbf{C}) + \langle \boldsymbol{\lambda} \mathbf{R} \rangle + \langle \mathbf{z} \mathbf{F} \rangle + \langle \mathbf{x} \mathbf{O} \rangle$$

Computing Lagrangian multipliers

RPA Gradient

$\mathcal{L}(\mathbf{T},\boldsymbol{\lambda},\mathbf{C},\mathbf{z},\mathbf{x})=\frac{1}{2}\langle\mathbf{KT}\rangle+\langle\boldsymbol{\lambda}\mathbf{R}\rangle+\langle\mathbf{zF}\rangle+\langle\mathbf{xO}\rangle$

Computing Lagrangian multipliers

- $\boldsymbol{\lambda}$ multiplier : $\frac{\partial\mathcal{L}}{\partial\mathbf{T}} = \frac{1}{2}\mathbf{K} + \boldsymbol{\lambda}(\mathbf{A}+\mathbf{TK}) + (\mathbf{A}+\mathbf{KT})\boldsymbol{\lambda} = 0$

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- $\mathbf{x}$ and $\mathbf{z}$ multipliers : $\frac{\partial\mathcal{L}}{\partial\mathbf{C}} = \cdots = \boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z}) + 2\mathbf{x} = 0$

RPA Gradient

$\mathcal{L}(\mathbf{T},\boldsymbol{\lambda},\mathbf{C},\mathbf{z},\mathbf{x})=\frac{1}{2}\langle\mathbf{KT}\rangle+\langle\boldsymbol{\lambda}\mathbf{R}\rangle+\langle\mathbf{zF}\rangle+\langle\mathbf{xO}\rangle$

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  - yields a set of two equations, solved for $\mathbf{z}$ and $\mathbf{x}$:

$$\begin{cases} \left(\boldsymbol{\Theta} - \tilde{\boldsymbol{\Theta}}^\dagger + \mathbf{Fz} - \mathbf{zF} + \mathbf{4g}(\mathbf{z})\right)_{ai} & = 0 \\ (1+\tau_{pq})\left(\boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z})\right)_{pq} & = -2(\mathbf{x})_{pq} \end{cases}$$

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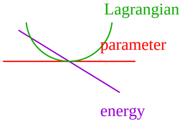

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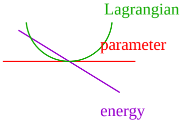
$\mathcal{L}(\mathbf{T},\boldsymbol{\lambda},\mathbf{C},\mathbf{z},\mathbf{x})=\frac{1}{2}\langle\mathbf{KT}\rangle+\langle\boldsymbol{\lambda}\mathbf{R}\rangle+\langle\mathbf{zF}\rangle+\langle\mathbf{xO}\rangle$

Computing Lagrangian multipliers

- $\boldsymbol{\lambda}$ multiplier : $\frac{\partial\mathcal{L}}{\partial\mathbf{T}} = \frac{1}{2}\mathbf{K} + \boldsymbol{\lambda}(\mathbf{A}+\mathbf{TK}) + (\mathbf{A}+\mathbf{KT})\boldsymbol{\lambda} = 0$
- $\mathbf{x}$ and $\mathbf{z}$ multipliers : $\frac{\partial\mathcal{L}}{\partial\mathbf{C}} = \cdots = \boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z}) + 2\mathbf{x} = 0$
  - yields a set of two equations, solved for $\mathbf{z}$ and $\mathbf{x}$:

$$\begin{cases} \left(\boldsymbol{\Theta} - \tilde{\boldsymbol{\Theta}}^\dagger + \mathbf{Fz} - \mathbf{zF} + 4\mathbf{g}(\mathbf{z})\right)_{ai} & = 0 \\ (1+\tau_{pq})\left(\boldsymbol{\Theta} + \tilde{\boldsymbol{\Theta}}(\mathbf{z})\right)_{pq} & = -2(\mathbf{x})_{pq} \end{cases}$$



(at last) RPA gradient

once multipliers are known : gradients obtained from **derivatives of $\mathcal{L}$**

$$\frac{\partial\mathcal{L}}{\partial\boldsymbol{\kappa}} = \frac{\partial E}{\partial\boldsymbol{\kappa}} = \langle\mathbf{D}^{①}\delta\mathbf{H}\rangle + \langle\mathbf{X}^{①}\delta\mathbf{S}\rangle + \left(\mathbf{D}^{②} + \boldsymbol{\Gamma}^{②}\right)_{\mu\nu,\rho\sigma}\delta(\mu\nu|\rho\sigma)$$

Conclusion & Outlook

The **Lagrangian framework** has successfully been applied to derive the **RPA gradient**

Outlook

- Implementation is in progress
- Useful (but not yet fully understood) parallel with **MP2 gradients**
- Gradients of "mixed" RPA energy expressions need further derivation (e.g. Szabo-Ostlund variant)
- Extension to **density fitting** seems straighforward