Strong-interaction limit of an adiabatic connection in Hartree-Fock theory

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28 gennaio 2019

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Outline

- HF theory: operators and energy
- HF adiabatic connection: definitions and local analysis
- DFT *vs* HF adiabatic connections (initial motivation)
- Conclusive remarks

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N-electron Hamiltonian

$$\hat{H} \equiv \hat{H}_N[v] = \underbrace{-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2}_{\hat{T}} + \underbrace{\sum_{i,j>i}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\hat{V}_{\mathrm{ee}}} + \underbrace{\sum_{i=1}^{N}v(\mathbf{r}_i)}_{\hat{V}_{\mathrm{ext}}} \quad (1)$$

- Minimize $\langle \hat{H} \rangle$, only in the N-electron states represented by Slater determinants, $\Phi(x_1, ..., x_N)$,

$$\Phi(x_1, ..., x_N) = \sum_P (-1)^P \psi_{P(1)}(x_1) \cdots \psi_{P(N)}(x_N), \quad (2)$$

with $\psi_n(x) \equiv \psi_n(\mathbf{r}\sigma) = \phi_n(\mathbf{r})\, s_n(\sigma)$,
enforcing orthonormality of $\{\psi_i(x)\}$ via Lagrange multipliers, ϵ_i, leads to the HF equations

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HF equations and GS

$$\left[-\tfrac{1}{2}\nabla^2 + \hat{v} + \hat{v}_{\rm H} + \hat{v}_{\rm F} \right] \psi_i(x) = \epsilon_i \, \psi_i(x) \qquad (i = 1, ..., N) \tag{3}$$

with

$$\hat{v}_{\rm H} = v_{\rm H}(\mathbf{r}) = \sum_{n=1}^{N} \int {\rm d}\mathbf{r}' \, \frac{|\phi_n(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \equiv \int {\rm d}\mathbf{r}' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{4}$$

and $\hat{v}_{\rm F}$ s.t.

$$\hat{v}_{\rm F} \, \psi_m(x) = -\sum_{n=1}^{N} \psi_n(x) \int {\rm d}\mathbf{r}' \, \frac{\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta_{s_m(\sigma')s_n(\sigma')} \tag{5}$$

- $|\Phi^{\rm HF}\rangle$ – built from the N $\{\psi_n\}$ with lowest ϵ_n– is the GS of

$$\hat{H}^{\rm HF} = \hat{T} + \hat{V}_{\rm ext} + \hat{J} + \hat{K}, \tag{6}$$

with $\hat{J} = \sum_{i=1}^{N} \hat{v}_i^{\rm H}$, and $\hat{K} = \sum_{i=1}^{N} \hat{v}_i^{\rm F}$

HF energies

- The GS energy of $\hat{H}^{\mathrm{HF}}$ is the sum of the lowest N HF eigenvalues,

$$E_0^{\mathrm{HF}} = \langle \Phi^{\mathrm{HF}} | \hat{H}^{\mathrm{HF}} | \Phi^{\mathrm{HF}} \rangle = \sum_{i=1}^{N} \epsilon_i \tag{7}$$

- However the HF approximation E^{HF} to $E_N[v]$ is

$$E^{\mathrm{HF}} = \langle \Phi^{\mathrm{HF}} | \hat{H} | \Phi^{\mathrm{HF}} \rangle = E_0^{\mathrm{HF}} - \left(U^{\mathrm{HF}} + E_x^{\mathrm{HF}} \right) \tag{8}$$

with

$$U^{\mathrm{HF}} = \frac{1}{2} \langle \Phi^{\mathrm{HF}} | \hat{J} | \Phi^{\mathrm{HF}} \rangle = U\left[\rho^{\mathrm{HF}}\right] \tag{9}$$

$$E_x^{\mathrm{HF}} = \frac{1}{2} \langle \Phi^{\mathrm{HF}} | \hat{K} | \Phi^{\mathrm{HF}} \rangle = E_x\left[\{\psi_1, ..., \psi_N\}\right] \tag{10}$$

- The difference $E_N[v] - E^{\mathrm{HF}} < 0$ is called the HF correlation energy, $E_{\mathrm{c}}^{\mathrm{HF}}$.

HF adiabatic connection

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}_{\mathrm{ext}} + \hat{J} + \hat{K} + \lambda(\hat{V}_{ee} - \hat{J} - \hat{K}) \qquad \begin{cases} \hat{H}_{\lambda=0}^{\mathrm{HF}} = \hat{H}^{\mathrm{HF}}, \\ \hat{H}_{\lambda=1}^{\mathrm{HF}} = \hat{H}, \end{cases} \tag{11}$$

with $|\Psi_\lambda^{\mathrm{HF}}\rangle$ its GS and E_λ^{HF} its GS energy

Defining

$$W_\lambda^{\mathrm{HF}} \equiv \langle \Psi_\lambda^{\mathrm{HF}} | \hat{V}_{ee} - \hat{J} - \hat{K} | \Psi_\lambda^{\mathrm{HF}} \rangle + U[\rho^{\mathrm{HF}}] + 2E_x^{\mathrm{HF}}. \tag{12}$$

we find, via $\frac{\mathrm{d}}{\mathrm{d}\lambda} E_\lambda^{\mathrm{HF}}$, the exact formula

$$E_x^{\mathrm{HF}} + E_c^{\mathrm{HF}} = \int_0^1 W_\lambda^{\mathrm{HF}} \, \mathrm{d}\lambda = E_{xc}^{\mathrm{HF}} \tag{13}$$

for the XC energy in terms of the HF adiabatic connection integrand, W_λ^{HF}.

Local analysis

- $W^{\mathrm{HF}}_{\lambda\to 0} = E_x^{\mathrm{HF}} + \sum_{n=2}^{\infty} n\, E_c^{\mathrm{MP}n}\, \lambda^{n-1}$,

- Assume $\langle \Psi^{\mathrm{HF}}_\lambda | \hat{K} | \Psi^{\mathrm{HF}}_\lambda \rangle = O(\lambda^{-1/2}) \qquad (\lambda \to \infty)$,

$$\Rightarrow \hat{\mathcal{H}}^{\mathrm{HF}}_\infty = \hat{V}_{ee} - \hat{J}[\rho^{\mathrm{HF}}], \tag{14}$$

$$\Rightarrow \lim_{\lambda\to\infty} \Psi^{\mathrm{HF}}_\lambda = \operatorname*{argmin}_{\Psi} \langle \Psi | \hat{V}_{ee} - \hat{J} | \Psi \rangle = \Psi^{\mathrm{HF}}_\infty[\rho^{\mathrm{HF}}], \tag{15}$$

$$\Rightarrow \lim_{\lambda\to\infty} W^{\mathrm{HF}}_\lambda = \underbrace{\min_{\{\mathbf{r}_1 \ldots \mathbf{r}_N\}} \left\{ \sum_{\substack{i,j=1 \\ j>i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} v_{\mathrm{H}}(\mathbf{r}_i; [\rho]) + U[\rho] \right\}}_{E_{\mathrm{el}}[\rho^{\mathrm{HF}}]} + 2E_x^{\mathrm{HF}} + O(\lambda^{-\frac{1}{2}})$$

Subleading term: variational argument

Consider the simple trial wavefunction

$$\Psi_\lambda^T(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \prod_{i=1}^{N} G_{\alpha(\lambda)}(\mathbf{r}_i - \mathbf{r}_i^{\min}), \tag{17}$$

where $\underline{R}^{\min} \equiv \{\mathbf{r}_i^{\min}\}$ is the global minimum of $\hat{\mathcal{H}}_\infty^{\mathrm{HF}}$ and $G_\alpha(\mathbf{r}) = \frac{\alpha^{3/4}}{\pi^{3/4}} e^{-\frac{\alpha}{2}|\mathbf{r}|^2}$ with $\alpha(\lambda) \sim \lambda^q$ with $q > 0$, s.t.

$$\lim_{\lambda\to\infty} |\Psi_\lambda^T[\rho^{\mathrm{HF}}]|^2 = |\Psi_\infty^{\mathrm{HF}}[\rho^{\mathrm{HF}}]|^2 \tag{18}$$

- Evaluating $\langle\Psi_\lambda^T|\hat{\mathcal{H}}_\lambda^{\mathrm{HF}}|\Psi_\lambda^T\rangle \to \ldots$

Subleading term: variational argument

$$\langle\Psi_\lambda^T|\hat{\mathcal{H}}_\lambda^{\mathrm{HF}}|\Psi_\lambda^T\rangle \begin{cases} \langle\Psi_\lambda^T|\hat{T}|\Psi_\lambda^T\rangle = t\,\alpha, \\ \langle\Psi_\lambda^T|\lambda(\hat{V}_{ee}-\hat{J})|\Psi_\lambda^T\rangle = \lambda(E_{el}-U)+\lambda\left(\frac{h}{\alpha}+o(\alpha^{-1})\right) \\ \langle\Psi_\lambda^T|-\lambda\,\hat{K}|\Psi_\lambda^T\rangle = \lambda\left(\frac{k}{\alpha}+o(\alpha^{-1})\right) \\ \langle\Psi_\lambda^T|\hat{V}_{\mathrm{ext}}+\hat{J}+\hat{K}|\Psi_\lambda^T\rangle \sim O(\alpha^0), \end{cases}$$

$$\langle\Psi_\lambda^T|\hat{H}_\lambda^{\mathrm{HF}}|\Psi_\lambda^T\rangle = \lambda(E_{el}-U)+t\lambda^q+(h+k)\lambda^{1-q}+o(\lambda^{1-q}) \qquad (19)$$

- t, h, and k are all *positive* numbers

$$q = 1/2$$

DFT vs HF ACs

$$\hat{H}_\lambda^{\mathrm{DFT}} = \hat{T} + \hat{V}_{\mathrm{ext}} + \lambda \hat{V}_{ee} + \hat{V}^\lambda[\rho]$$

$$W_\lambda^{\mathrm{DFT}} \equiv \langle \Psi_\lambda^{\mathrm{DFT}} | \hat{V}_{ee} | \Psi_\lambda^{\mathrm{DFT}} \rangle - U[\rho]$$

$$E_{xc}^{\mathrm{DFT}} = \int_0^1 W_\lambda^{\mathrm{DFT}} \, \mathrm{d}\lambda$$

$$\lambda \ll 1 \quad W_\lambda^{\mathrm{DFT}} \to E_x^{\mathrm{DFT}} + \lambda 2E_c^{\mathrm{GL2}} + \cdots$$

$$\lambda \gg 1 \quad W_\lambda^{\mathrm{DFT}} \to W_\infty^{\mathrm{DFT}} + \frac{W'^{\mathrm{DFT}}_\infty}{\sqrt{\lambda}} + \cdots$$

P. Gori-Giorgi *et al. J. Chem. Theory Comput.* **5**, 743-753 (2009)

J. Grossi *et al. J. Chem. Theory Comput.* **13**, 6089-6100 (2017)

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}_{\mathrm{ext}} + \hat{J} + \hat{K} + \lambda(\hat{V}_{ee} - \hat{J} - \hat{K})$$

$$W_\lambda^{\mathrm{HF}} \equiv \langle \Psi_\lambda^{\mathrm{HF}} | \hat{V}_{ee} - \hat{J} - \hat{K} | \Psi_\lambda^{\mathrm{HF}} \rangle + U[\rho_{\lambda=0}^{\mathrm{HF}}] + 2E_x^{\mathrm{HF}}$$

$$E_{xc}^{\mathrm{HF}} = \int_0^1 W_\lambda^{\mathrm{HF}} \, \mathrm{d}\lambda$$

$$\lambda \ll 1 \quad W_\lambda^{\mathrm{HF}} \to E_x^{\mathrm{HF}} + \lambda 2E_c^{\mathrm{MP2}} + \cdots$$

$$\lambda \gg 1 \quad W_\lambda^{\mathrm{HF}} \to W_\infty^{\mathrm{HF}} + \frac{W'^{\mathrm{HF}}_\infty}{\sqrt{\lambda}} + \cdots$$

M. Seidl, S.G, S. Vuckovic, E. Fabiano, P. Gori-Giorgi *J. Chem. Phys.* **149**, 241101 (2018)

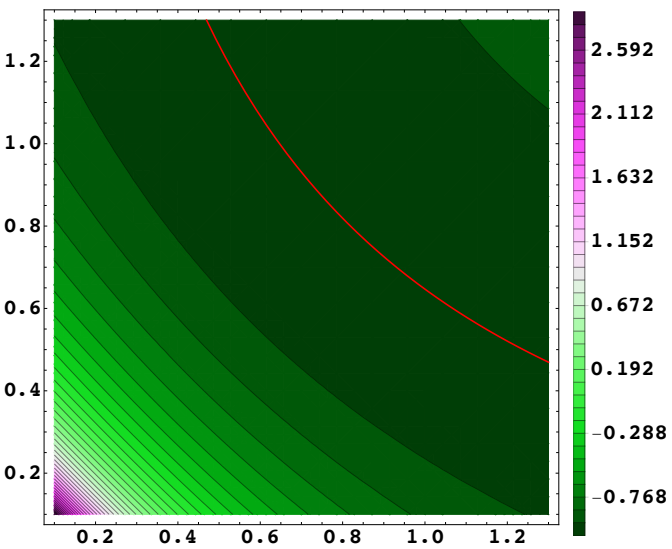
DFT vs HF ACs

$$|\Psi_{SCE}(1,...,N)|^2 = \frac{\rho(\mathbf{r})}{N}\,\delta(\mathbf{r}_2 - \mathbf{f}_2(\mathbf{r}))...\delta(\mathbf{r}_N - \mathbf{f}_N(\mathbf{r})) + \cdots$$

$$|\Psi_{\infty}^{\mathrm{HF}}(1,...,N)|^2 = \prod_{i=1}^{N} \int \delta(\mathbf{r}_i^{\min} - \mathbf{s})\,\mathrm{d}\mathbf{s}$$

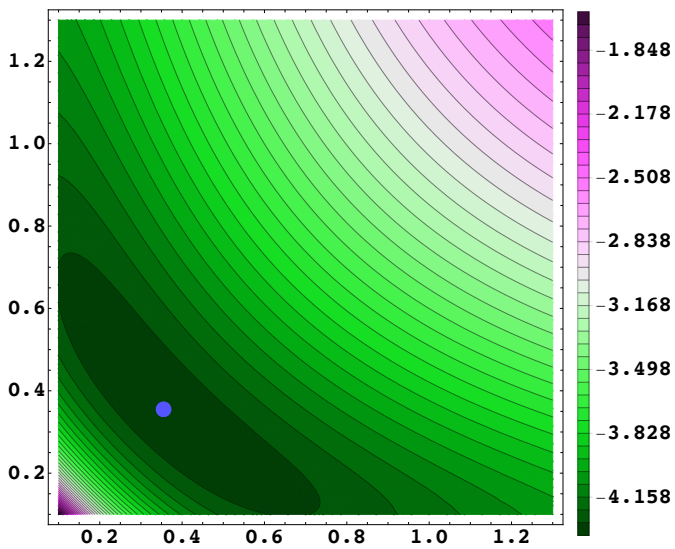
- **He**:

$W_{\infty}^{\mathrm{DFT}} \simeq -1.50\mathrm{E_h}$



$\hat{\mathcal{H}}_{\infty}^{\mathrm{DFT}}(r_1, r_2, \pi)$

$W_{\infty}^{\mathrm{HF}} \simeq -4.34\mathrm{E_h}$

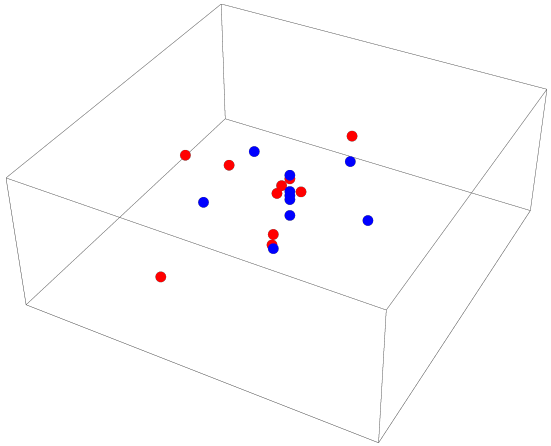


$\hat{\mathcal{H}}_{\infty}^{\mathrm{HF}}(r_1, r_2, \pi)$

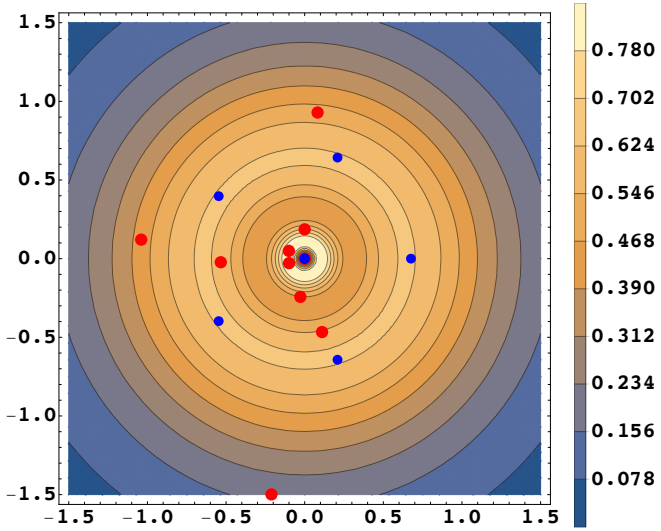
DFT vs HF ACs

$$|\Psi_{SCE}(1,...,N)|^2 = \frac{\rho(\mathbf{r})}{N}\,\delta(\mathbf{r}_2 - \mathbf{f}_2(\mathbf{r}))...\delta(\mathbf{r}_N - \mathbf{f}_N(\mathbf{r})) + \cdots$$

$$|\Psi_{\infty}^{\mathrm{HF}}(1,...,N)|^2 = \prod_{i=1}^{N} \int \delta(\mathbf{r}_i^{\min} - \mathbf{s})\,\mathrm{d}\mathbf{s}$$



- **Ne**:
  $W_{\infty}^{\mathrm{DFT}} \simeq -20.04\mathrm{E_h}$; $W_{\infty}^{\mathrm{HF}} \simeq -49.90\mathrm{E_h}$



Upper panel: HF crystal (strong interaction HF "density") compared to one SCE configurations (the superposition of all infinite configurations delivers the physical density)

Lower panel: 2D projection of the HF crystal and the SCE configuration on the Ne probability density.

Conclusive remarks

Initial motivation

- DFAs that model W_λ^{DFT} consistently give much more accurate results for binding/interaction energies (energy differences) – usually better than MPn, with $n = 2, 3, 4$ methods – when ρ^{HF} and $\{\psi_i^{\mathrm{HF}}\}$ are used

E. Fabiano, P. Gori-Giorgi, M. Seidl, F. Della Sala, *J. Chem. Theory Comput.* **12**, 4885 (2016)

S. Vuckovic, P.Gori-Giorgi, F. Della Sala, E. Fabiano,*J. Phys. Chem. Lett.* **9**, 3137 (2018)

S.G., P. Gori-Giorgi, F. Della Sala, E. Fabiano, *J. Chem. Phys.* **148**, 134106 (2018)

Outcomes

- an all orders resummation of the MP series might be constructed from an interpolation along the HF adiabatic connection
- the leading term of the strong interaction limit of the HF adiabatic connection can be fully determined from a functional of ρ^{HF} and $\{\psi_i^{\mathrm{HF}}\}$, which are known exactly.

Some outlooks

- Study the rather novel term $W'^{\mathrm{HF}}_{K,\infty}$ in the expansion large λ of $W^{\mathrm{HF}}_{\lambda}$,

$$W'^{\mathrm{HF}}_{\infty} = \underbrace{\frac{1}{2}\sum_{\alpha=1}^{3N}\frac{\omega_\alpha[\rho^{\mathrm{HF}}]}{2}}_{\langle \hat{T}+\lambda(\hat{V}_{ee}+\hat{J})\rangle_{min},\ O(\lambda^{\frac{1}{2}})} + W'^{\mathrm{HF}}_{K,\infty} \tag{20}$$

- Sistematic numerical exploration of the HF adiabatic connection
- Study the related adiabatic connection that connects HF and KS system (missing link)

$$\hat{H}^{HFKS}_{\lambda} = \hat{T} + \hat{V}_{ext} + \hat{J} + \hat{K} + \lambda(\hat{V}_R - \hat{J} - \hat{K}) \tag{21}$$

where $\hat{V}_R = \hat{V}_s - \hat{V}_{ext}$ and $\hat{V}_s$ is the N-electron equivalent of the (augmented) KS potential operator

- ...

Thanks to my collaborators

M. Seidl
S. Vuckovic
E. Fabiano
P. Gori-Giorgi

European Research Council

Established by the European Commission

Thank you for your attention!