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CHEMISTRY: MOLECULES TO MATERIALS

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Beyond regular DFT
Embedding and ensemble DFT illustrated on the Hubbard model

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Electronic Structure problem

- Electronic, time-independent non-relativistic Schrödinger equation: **Exponential Wall Problem**

$$\left(\hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ext}}\right)|\Psi_n\rangle = E_n\,|\Psi_n\rangle$$

Electronic Structure problem

- Electronic, time-independent non-relativistic Schrödinger equation: **Exponential Wall Problem**

$$\left(\hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ext}}\right)|\Psi_n\rangle = E_n |\Psi_n\rangle$$

- Kohn–Sham Density Functional Theory:

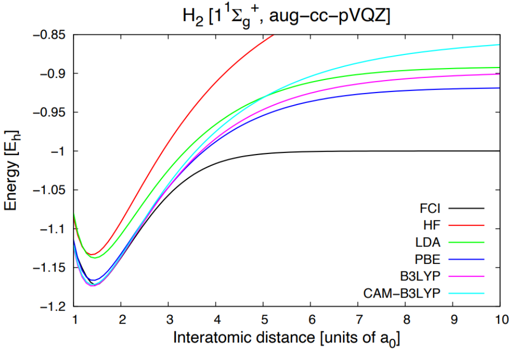
$$\left(\hat{T} + \hat{V}_{\mathrm{ext}} + \int \mathrm{d}\mathbf{r}\, \left.\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}\right|_{n=n^{\Phi_0^{\mathrm{KS}}}} \hat{n}(\mathbf{r})\right)|\Phi_0^{\mathrm{KS}}\rangle = \mathcal{E}_0^{\mathrm{KS}} |\Phi_0^{\mathrm{KS}}\rangle$$

- **(in-principle-exact)** Ground-state energy in $\mathcal{O}(N^3)$:

$$E_0 = \mathcal{E}_0^{\mathrm{KS}} + E_{\mathrm{Hxc}}[n^{\Phi_0^{\mathrm{KS}}}] - \int \mathrm{d}\mathbf{r}\, \left.\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}\right|_{n=n^{\Phi_0^{\mathrm{KS}}}} n^{\Phi_0^{\mathrm{KS}}}(\mathbf{r})$$

Limitations of regular KSDFT

Strongly correlated systems



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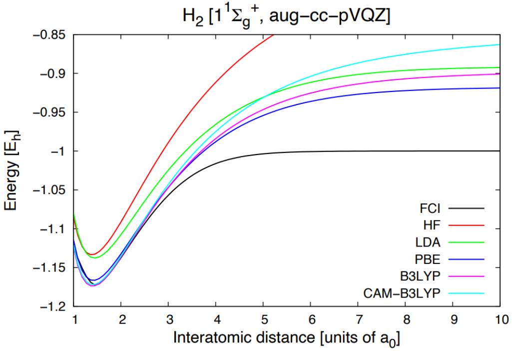
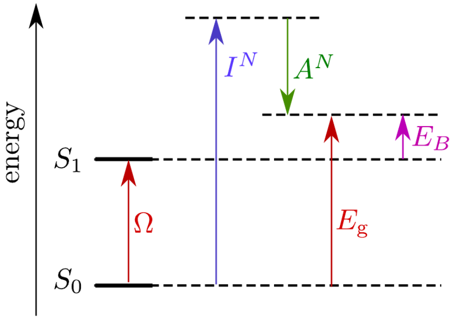


Charged and neutral excitation energies

$$E_g^N \neq \Omega^N \neq \varepsilon_L^N - \varepsilon_H^N$$



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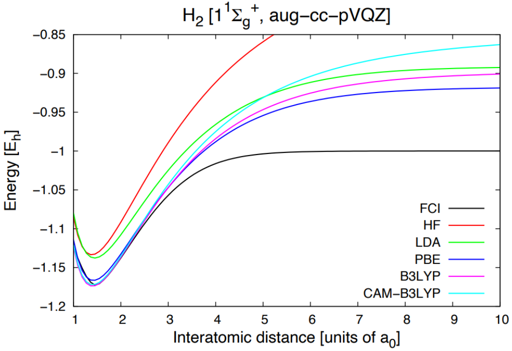

Site-Occupation Embedding Theory

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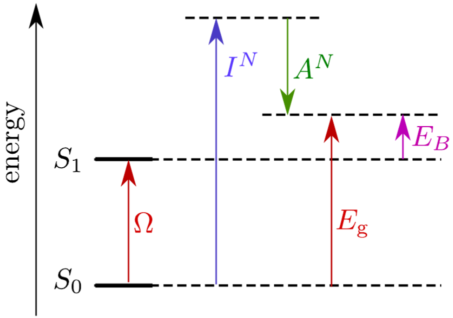

Ensemble Density Functional Theory

From ab-initio Hamiltonian to the Hubbard model

- **Second quantized** electronic Hamiltonian projected onto N **basis functions** $\{\phi_i(\mathbf{r})\}$:

$$
\begin{aligned}
\hat{H} &= \sum_{ij}^{N}\sum_{\sigma} t_{ij}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + \frac{1}{2}\sum_{ijkl}^{N}\sum_{\sigma\overline{\sigma}} \langle ij|kl\rangle \hat{c}^{\dagger}_{i\sigma}\hat{c}^{\dagger}_{j\overline{\sigma}}\hat{c}_{l\overline{\sigma}}\hat{c}_{k\sigma}, \\
t_{ij} &= \int \mathrm{d}\mathbf{r}\phi_i^*(\mathbf{r})\left(-\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\right)\phi_j(\mathbf{r}) \\
\langle ij|kl\rangle &= \iint \mathrm{d}\mathbf{r}_1\mathbf{r}_2 \frac{\phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_k(\mathbf{r}_1)\phi_l(\mathbf{r}_2)}{\mathbf{r}_{12}}
\end{aligned}
$$

From ab-initio Hamiltonian to the Hubbard model

- **Second quantized** electronic Hamiltonian projected onto N **basis functions** $\{\phi_i(\mathbf{r})\}$:

$$\hat{H} = \sum_{ij}^{N} \sum_{\sigma} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + \frac{1}{2} \sum_{ijkl}^{N} \sum_{\sigma\overline{\sigma}} \langle ij|kl \rangle \hat{c}^{\dagger}_{i\sigma} \hat{c}^{\dagger}_{j\overline{\sigma}} \hat{c}_{l\overline{\sigma}} \hat{c}_{k\sigma},$$

- $\{\phi_i(\mathbf{r})\}$ (centered on the atomic positions) form an atomic shell with **smaller radius** than $\mathbf{r}_{ij}$

$$t_{ij} \longrightarrow -t(\delta_{j(i+1)} + \delta_{j(i-1)}), \qquad \langle ij|kl \rangle \longrightarrow U = \langle ii|ii \rangle$$

From ab-initio Hamiltonian to the Hubbard model

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$$t_{ij} \longrightarrow -t(\delta_{j(i+1)} + \delta_{j(i-1)}), \qquad \langle ij|kl\rangle \longrightarrow U = \langle ii|ii\rangle$$

- Hubbard model:

$$\hat{H} = -t \sum_{\langle ij\rangle} \sum_{\sigma} (\hat{c}^{\dagger}_{i\sigma} \hat{c}_{j\sigma} + \text{h.c.}) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \mu \sum_{i} \hat{n}_i$$

- **Bethe Ansatz**: **analytical** (and numerical) solution in 1D (Lieb & Wu 1968)

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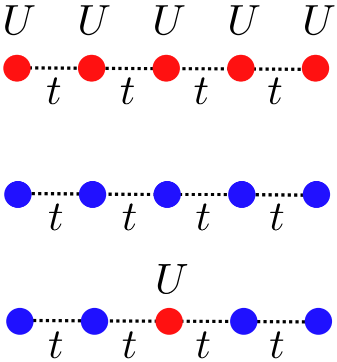
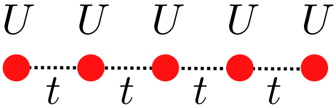
Embedding methods



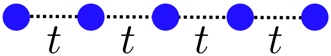
- WFT-in-DFT
- Dynamical Mean-Field Theory, Self-energy Embedding Theory
- Density-Matrix Embedding Theory and related (Householder)

Challenge: **in-principle-exact** and **practical** embedding

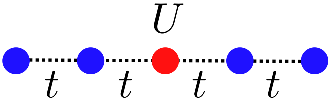
Site-Occupation Embedding Theory (SOET)



$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle \right\}$$



$$E_0 = \min_{\mathbf{n}} \left\{ T_s(\mathbf{n}) + E_{\text{Hxc}}(\mathbf{n}) \right\}$$



$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{U}_{\text{imp}} | \Psi \rangle + \overline{E}_{\text{Hxc}}^{\text{bath}}(\mathbf{n}^{\Psi}) \right\}$$

Extracting local quantities (impurity: $i = 0$)

- **Uniform** model ⟶ **LDA is exact**

$$\overline{E}_{\rm c}^{\rm bath}(\mathbf{n}) = E_{\rm c}(\mathbf{n}) - E_{\rm c}^{\rm imp}(\mathbf{n}) \xrightarrow{\rm LDA} \sum_i e_{\rm c}(n_i) - E_{\rm c}^{\rm imp}(\mathbf{n}) = \sum_{i \neq 0} e_{\rm c}(n_i) + \overline{e}_{\rm c}^{\rm bath}(\mathbf{n})$$

where

$$\boxed{\overline{e}_{\rm c}^{\rm bath}(\mathbf{n}) = e_{\rm c}(n_0) - E_{\rm c}^{\rm imp}(\mathbf{n})}$$

[1]**BS**, N. Nakatani, M. Tsuchiizu, E. Fromager, *Phys. Rev. B* **97**, 235105 (2018).

Extracting local quantities (impurity: $i = 0$)

- **Uniform** model $\longrightarrow$ **LDA is exact**

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where

$$\boxed{\overline{e}_{\rm c}^{\rm bath}(\mathbf{n}) = e_{\rm c}(n_0) - E_{\rm c}^{\rm imp}(\mathbf{n})}$$

- Extraction of the exact **double occupation** and **per-site energy**[1]:

$$d = \langle \hat{n}_{0\uparrow}\hat{n}_{0\downarrow}\rangle_{\Psi^{\rm imp}} + \frac{\partial \overline{e}_{\rm c}^{\rm bath}(\mathbf{n}^{\Psi^{\rm imp}})}{\partial U}$$

$$e = U\langle \hat{n}_{0\uparrow}\hat{n}_{0\downarrow}\rangle_{\Psi^{\rm imp}} + t_{\rm s}(n_0^{\Psi^{\rm imp}}) + t\frac{\partial e_{\rm c}(n_0^{\Psi^{\rm imp}})}{\partial t} + U\frac{\partial \overline{e}_{\rm c}^{\rm bath}(\mathbf{n}^{\Psi^{\rm imp}})}{\partial U}$$

[1] **BS**, N. Nakatani, M. Tsuchiizu, E. Fromager, *Phys. Rev. B* **97**, 235105 (2018).

Correlation functionals [2]

$L \to +\infty,\ e_c(n) \to \boxed{e_c^{\mathrm{BALDA}}(n)}$

iBALDA(M)

$E_c^{\mathrm{imp}}(\mathbf{n}) \longrightarrow e_c^{\mathrm{BALDA}}(n_0)$

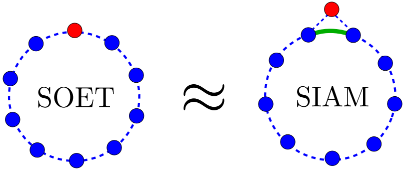
$\overline{e}_c^{\mathrm{bath}}(\mathbf{n}) = 0$

Dimer(2L) — DFT — SOET

DFT: $E_c^{\mathrm{2L}}(U, n_0)$ — SOET: $E_c^{\mathrm{2L}}(U/2, n_0)$

2L-BALDA

$E_c^{\mathrm{imp}}(\mathbf{n}) \longrightarrow E_c^{\mathrm{2L}}(U/2, n_0)$



SIAM-BALDA

$E_c^{\mathrm{imp}}(\mathbf{n}) \longrightarrow E_c^{\mathrm{SIAM}}(n_0)$

[2] Lima *et al.* PRL 2003 ; Carrascal *et al.* *J. Phys. Condens. Matter* 2015 ; K. Yamada, Prog. Theo. Phys. 1975 ;

Illustration on the 1D Hubbard model

$$d = \langle \hat{n}_{\uparrow} \hat{n}_{\downarrow} \rangle$$

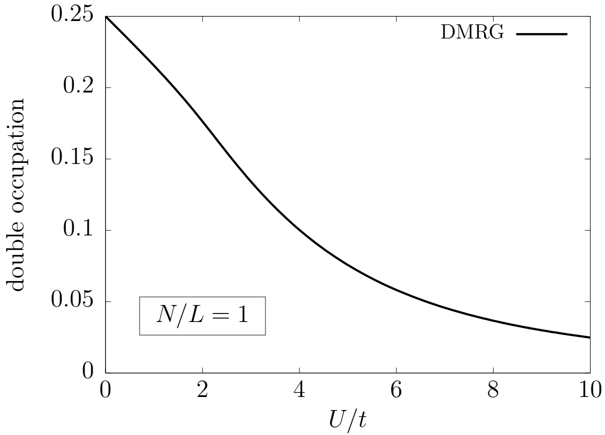


Illustration on the 1D Hubbard model

$$d \approx \langle \hat{n}_{0\uparrow}\hat{n}_{0\downarrow} \rangle_{\Psi^{\text{imp}}}$$

Typically what is obtained in DMET

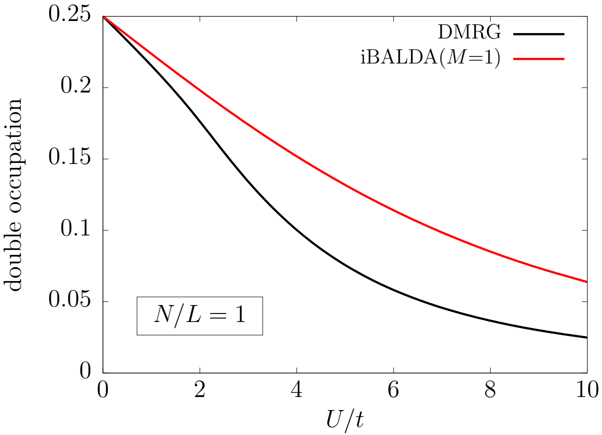


Illustration on the 1D Hubbard model

$$d \approx \langle (\hat{n}_{0\uparrow}\hat{n}_{0\downarrow} + \hat{n}_{1\uparrow}\hat{n}_{1\downarrow})/2 \rangle_{\Psi^{\text{imp}}}$$

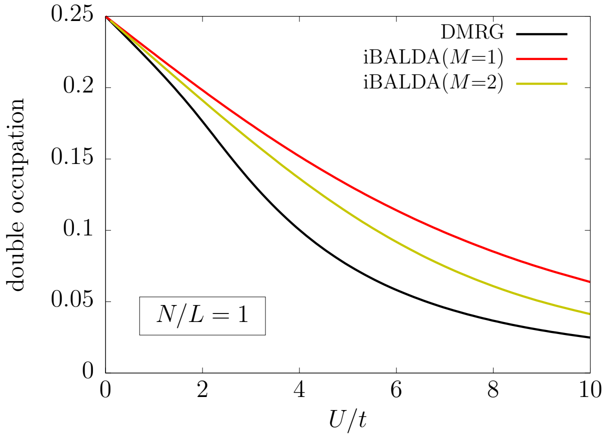


Illustration on the 1D Hubbard model

$$d \approx \langle (\hat{n}_{0\uparrow}\hat{n}_{0\downarrow} + \hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\hat{n}_{2\downarrow})/3 \rangle_{\Psi^{\text{imp}}}$$

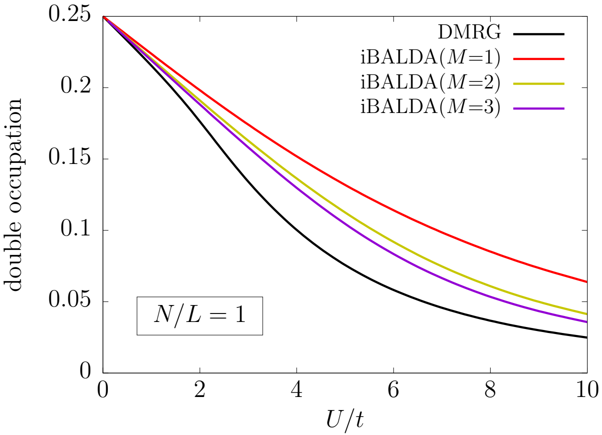


Illustration on the 1D Hubbard model

$$d \approx \langle \hat{n}_{0\uparrow}\hat{n}_{0\downarrow}\rangle_{\Psi^{\mathrm{imp}}} + \frac{\partial \overline{e}_{\mathrm{c}}^{\mathrm{bath,2L}}(n_0^{\Psi^{\mathrm{imp}}})}{\partial U}$$

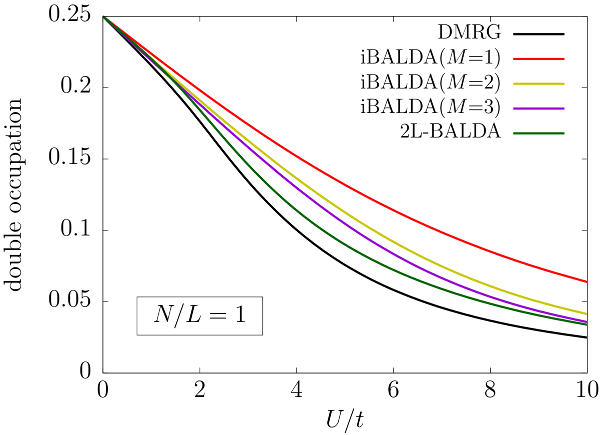
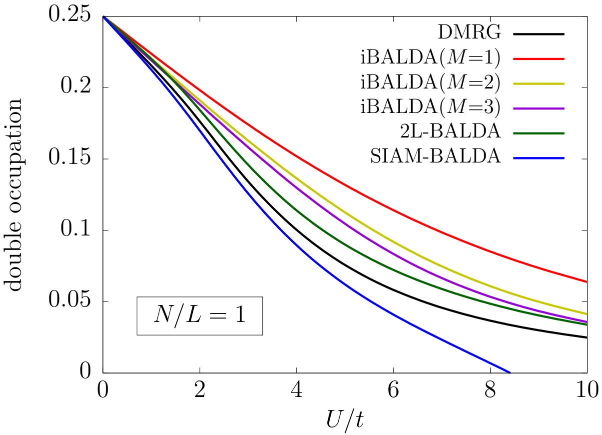


Illustration on the 1D Hubbard model

$$d \approx \langle \hat{n}_{0\uparrow}\hat{n}_{0\downarrow}\rangle_{\Psi^{\mathrm{imp}}} + \frac{\partial \overline{e}_{\mathrm{c}}^{\mathrm{bath,SIAM}}(n_0^{\Psi^{\mathrm{imp}}})}{\partial U}$$



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Exact versus KS gap

Fundamental Gap

$$E_g^N = I^N - A^N = \varepsilon_L^N - \varepsilon_H^N + \Delta_{\text{xc}}^{\text{fun.}}$$

- DFT+U, GW
- **Derivative discontinuity**: $\Delta_{\text{xc}}^{\text{fun.}} = \Delta_{\text{xc}}^{\text{fun.}}[n]$ (PPLB 1982, Perdew Levy 1983)
- **Jump in the xc potential** when crossing an integer number of electrons

Optical gap

$$\Omega^N = E_1^N - E_0^N = \varepsilon_L^N - \varepsilon_H^N + \Delta_{\text{xc}}^{\text{opt.}}$$

- TDDFT, BSE
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- **Jump in the xc potential** when moving from N-electron ground state to an ensemble of N-electron ground and excited states

Challenge: **Time- and frequency-independent** single DFT calculation able to **reproduce the DD**

Optical gap: GOKDFT

- Consider a **weighted** **ensemble** of the **ground**- and **first-excited** states:

$$E^w = (1 - w) E_0^N + w \, E_1^N ,$$

with the ensemble density as a basic variable

$$n^w(\mathbf{r}) = (1 - w) n_0(\mathbf{r}) + w \, n_1(\mathbf{r})$$

- Interestingly:

$$\boxed{\frac{\mathrm{d}E^w}{\mathrm{d}w} = E_1^N - E_0^N = \Omega^N}$$

Optical gap: GOKDFT

- GOKDFT **variational principle**:

$$E^w = \min_{\hat{\gamma}^w} \left\{ \mathrm{Tr}\left[\hat{\gamma}^w \hat{T}\right] + E^w_{\mathrm{Hxc}}[n_{\hat{\gamma}^w}] + \int d\mathbf{r}\; v(\mathbf{r}) n_{\hat{\gamma}^w}(\mathbf{r}) \right\}$$

- The **minimizing KS ensemble density matrix**

$$\hat{\gamma}^w_{\mathrm{s}} = (1-w)\hat{\gamma}^w_0 + w\hat{\gamma}^w_1, \qquad \hat{\gamma}^w_i = \left|\Phi_i^{\mathrm{KS},w}\right\rangle\left\langle\Phi_i^{\mathrm{KS},w}\right|$$

reproduces the **exact interacting ensemble density** and fulfils **ensemble analog SCE**

$$\boxed{\left(\hat{T} + \hat{V}_{\mathrm{ext}} + \int d\mathbf{r} + \frac{\delta E^w_{\mathrm{Hxc}}[n_{\hat{\gamma}^w_{\mathrm{s}}}]}{\delta n(\mathbf{r})}\hat{n}(\mathbf{r})\right)\left|\Phi_i^{\mathrm{KS},w}\right\rangle = \mathcal{E}_i^{\mathrm{KS},w}\left|\Phi_i^{\mathrm{KS},w}\right\rangle}$$

Derivative discontinuity: weight-derivative

- Expressing $\dfrac{\mathrm{d}E^w}{\mathrm{d}w} = \Omega^N$ within GOKDFT:

$$\Omega^N[n] = \varepsilon_L^{\mathrm{KS},w}[n] - \varepsilon_H^{\mathrm{KS},w}[n] + \frac{\partial E_{\mathrm{xc}}^w[n]}{\partial w} \xrightarrow{w=0} \boxed{\left.\frac{\partial E_{\mathrm{xc}}^w[n_{\Psi_0^N}]}{\partial w}\right|_{w=0} = \Delta_{\mathrm{xc}}^{\mathrm{opt.}}}$$

- Infamous DD is nothing but the **weight-derivative** of the xc energy in GOKDFT

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- Infamous DD is nothing but the **weight-derivative** of the xc energy in GOKDFT

- Designing weight-dependent functionals: **Generalized Adiabatic Connection for Ensembles** (Franck, Fromager 2014)

$$\begin{aligned} E_{\mathrm{Hxc}}^w[n] &= E_{\mathrm{Hxc}}[n] + \left(E_{\mathrm{xc}}^w[n] - E_{\mathrm{xc}}[n]\right) \\ &= E_{\mathrm{Hxc}}[n] + \int_0^w \mathrm{d}\xi \frac{\partial E_{\mathrm{xc}}^\xi[n]}{\partial \xi} = E_{\mathrm{Hxc}}[n] + \int_0^w \mathrm{d}\xi \Delta_{\mathrm{xc}}^\xi[n] \end{aligned}$$

Fundamental Gap: Grand canonical ensemble

- PPLB 1982, Perdew Levy 1983 (DFT fractional e^- number, DD $\longrightarrow$ jump in the xc potential)

$$I^N - A^N = \varepsilon_L^N - \varepsilon_H^N + \left.\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\right|_{N+\delta} - \left.\frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\right|_{N-\delta}$$

- In principle sufficient to extend the domain of definition of $E_{\mathrm{xc}}[n]$ to **fractional** electron numbers

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- In principle sufficient to extend the domain of definition of $E_{\mathrm{xc}}[n]$ to **fractional** electron numbers

- Far from trivial, and maybe **not the correct route to pursue** (Baerends)

- Grand canonical ensemble (Kraisler, Kronik 2013)

$$n^\alpha(\mathbf{r}) = (1-\alpha)n_{\Psi_0^{N-1}} + \alpha n_{\Psi_0^N}(\mathbf{r})$$

$\longrightarrow \mathcal{N} = \alpha + N - 1$ (analogy with GOK-DFT can **only be partial**, and **no GACE**!)

N-centered ensemble DFT

- Ensemble containing the **anionic**, **cationic** and **neutral** species (Senjean, Fromager 2018)

$$E^{N,\xi} = \xi E_0^{N-1} + \xi E_0^{N+1} + (1-2\xi) E_0^{N}$$

- Interestingly:

$$\boxed{\frac{\mathrm{d}E^{N,\xi}}{\mathrm{d}\xi} = E_{\mathrm{g}}^{N}}$$

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- Interestingly:

$$\boxed{\frac{\mathrm{d}E^{N,\xi}}{\mathrm{d}\xi} = E_{\mathrm{g}}^N}$$

- By construction, the **ensemble density integrates to N**

- **In exact analogy with GOKDFT**:

$$\boxed{\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}^{N,\xi}[n_{\hat{\Gamma}_{\mathrm{s}}^{N,\xi}}]}{\delta n(\mathbf{r})}\right)\varphi_i^{N,\xi}(\mathbf{r}) = \varepsilon_i^{N,\xi}\varphi_i^{N,\xi}(\mathbf{r}).}$$

Derivative discontinuity: weight-derivative

- Expressing $\dfrac{\mathrm{d}E^{N,\xi}}{\mathrm{d}\xi} = E_g^N$ within N-centered ensemble DFT:

$$E_g^N[n] = \varepsilon_L^{N,\xi}[n] - \varepsilon_H^{N,\xi}[n] + \frac{\partial E_{\mathrm{xc}}^{N,\xi}[n]}{\partial \xi} \xrightarrow{\xi=0} \boxed{\left.\frac{\partial E_{\mathrm{xc}}^{N,\xi}[n_{\Psi_0^N}]}{\partial \xi}\right|_{\xi=0} = \Delta_{\mathrm{xc}}^{\mathrm{fun.}}}$$

- Infamous DD is nothing but the **weight-derivative** of the xc energy in N-centered ensemble DFT
- Design of **weight-dependent** functionals → GACE
- **Same formalism**: advances in GOKDFT will benefit N-centered ensemble DFT

Illustration on the Hubbard dimer

- Asymmetric Hubbard dimer, the ensemble kinetic energy and ensemble KS potential can be obtained **analytically**

$$T_s^{N,\xi}(n) = -2t\sqrt{(\xi-1)^2-(n-1)^2}$$
$$\Delta v_{KS}^{N,\xi}(n) = \frac{2t(n-1)}{\sqrt{(\xi-1)^2-(n-1)^2}}$$

- The ensemble **noninteracting representability** condition holds:

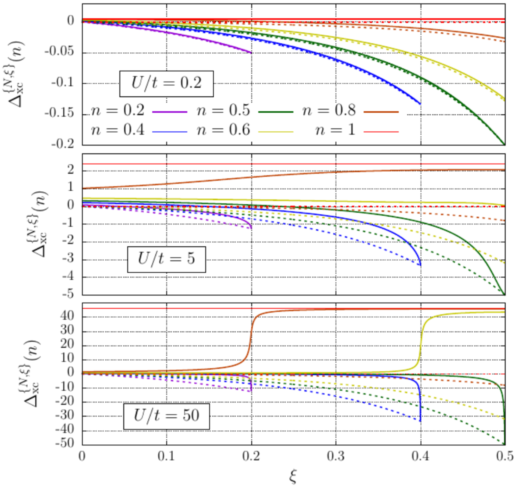
$$\xi \leq n^{N,\xi} \leq 2-\xi$$

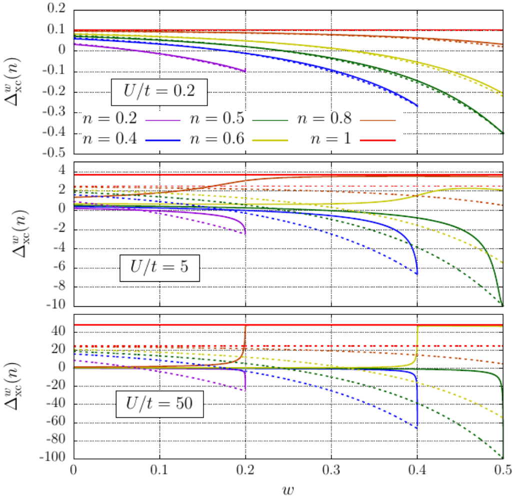
- As well as the analytical expression for the ensemble Hx energy:

$$E_{Hx}^{N,\xi}[n] = \frac{U}{2}\left[1+(1-2\xi)\left(\frac{n-1}{\xi-1}\right)^2\right]$$

- Access to everything **analytically**, except $F^{N,\xi}[n]$, $\Delta v^{N,\xi}[n]$ and $E_c^{N,\xi}[n]$

$$E_{\mathrm{Hxc}}^{N,\xi}(n) = E_{\mathrm{Hxc}}(n) + \int_0^{\xi} d\alpha \Delta_{\mathrm{xc}}^{N,\alpha}(n), \qquad \Delta_{\mathrm{xc}}^{N,\alpha}(n) = \frac{\partial E_{\mathrm{Hxc}}^{N,\alpha}(n)}{\partial \alpha}$$





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Extensions and Perspectives

- Projected-SOET: opening of the band gap with a single impurity (Senjean 2019)
- Generalization to quantum chemical Hamiltonian (Senjean, Yalouz, Nakatani, Fromager 2022)
- Weight-dependent functionals for quantum chemistry based on the finite uniform electron gas (Loos, Fromager 2020)
- Neutral charged excitations described simultaneously with ensemble DFT (Filip, Loos, Senjean, Fromager 2024)

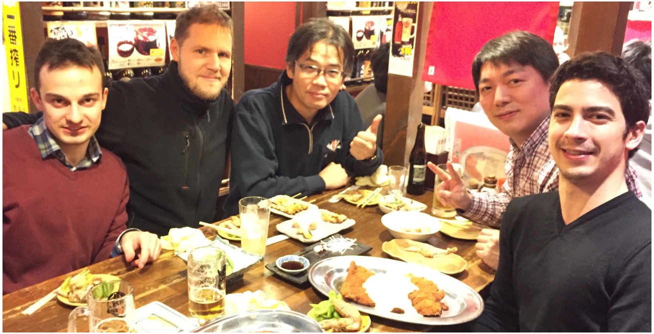
Acknowledgments

Ensemble DFT

Filip Cernatic LCQS

Emmanuel Fromager LCQS

Pierre-François Loos LCPQ



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CHEMISTRY: MOLECULES TO MATERIALS