



Correcting the failings of DFT: DFT+ U , Koopmans spectral functionals, and dynamical mean field theory

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Quantum Fluids in Isolation Virtual Seminar Series, 10 Dec 2020

Outline

The general problem: many body electronic Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ - \sum_I \frac{1}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is $3N$ -dimensional

Outline

Density functional theory (DFT)

- Hohenberg-Kohn: $\rho(\mathbf{r})$ instead of $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$

$$E[\rho(\mathbf{r})] \geq E_{GS}; \quad E[\rho_{GS}(\mathbf{r})] = E_{GS}$$

- Kohn Sham: mapping to a tractable, single-particle problem BUT exchange and correlation must be approximated

$$E[\rho] = \underbrace{T_0[\rho]}_{\text{kinetic energy}} + \int d\mathbf{r} \rho(\mathbf{r}) [V_{ext}(\mathbf{r}) + \frac{1}{2} \underbrace{\Phi(\mathbf{r})}_{\text{Hartree potential}}] + \underbrace{E_{xc}[\rho]}_{\substack{\text{xc-functional} \\ (\text{approximated})}}$$

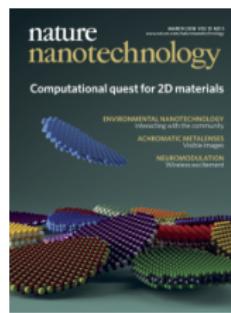
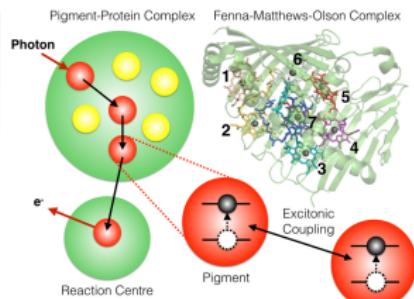
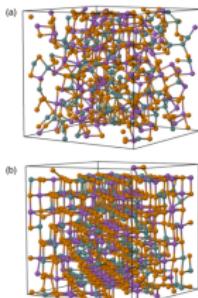
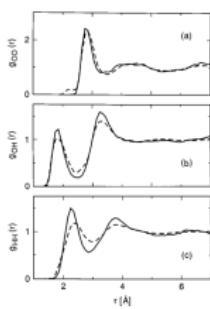
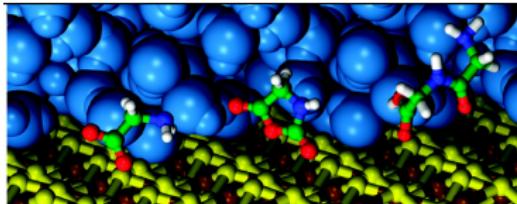
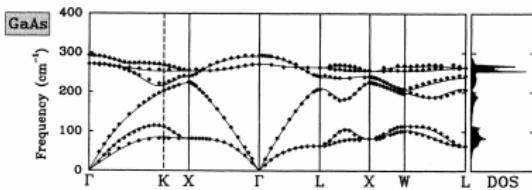
$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \Phi(\mathbf{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

End result: a non-interacting system which must be solved self-consistently

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}[\rho](\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}); \quad \rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2.$$

Outline

Works surprisingly well!



However...

P. Giannozzi et al. *Phys. Rev. B* 43.9 (15, 1991), 7231; E. Schreiner et al. *J. Am. Chem. Soc.* 130.9 (1, 2008), 2768; M. Sprik et al. *The Journal of Chemical Physics* 105.3 (15, 1996), 1142; R. O. Jones. *Rev. Mod. Phys.* 87.3 (25, 2015), 897; D. J. Cole et al. *J. Phys. Chem. Lett.* 4.24 (19, 2013), 4206; N. Mounet et al. *Nat. Nanotechnol.* 13.3 (3 2018), 246

Outline

Failures of DFT:

- band gap is almost universally too small (TMOs)
- problems with “strongly correlated” systems
- problems with vdW interactions
- eigenvalues are formally meaningless
- self-interaction error
- static correlation error

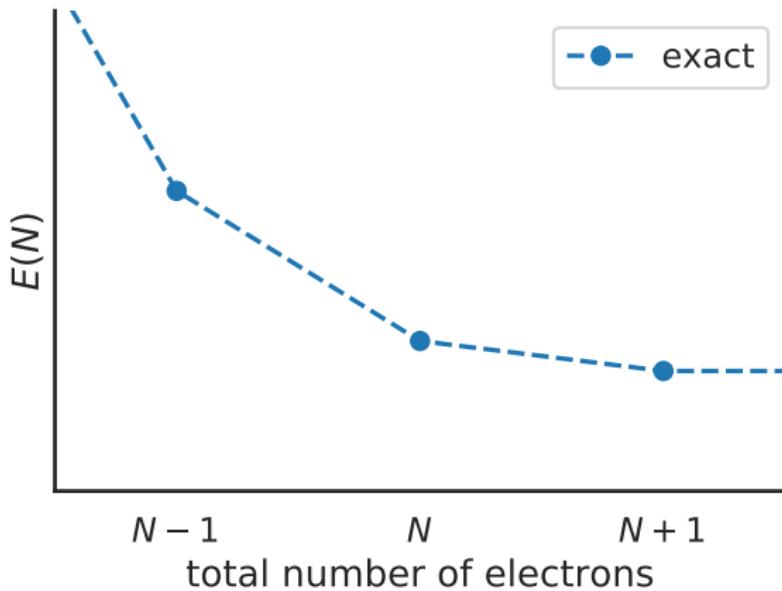
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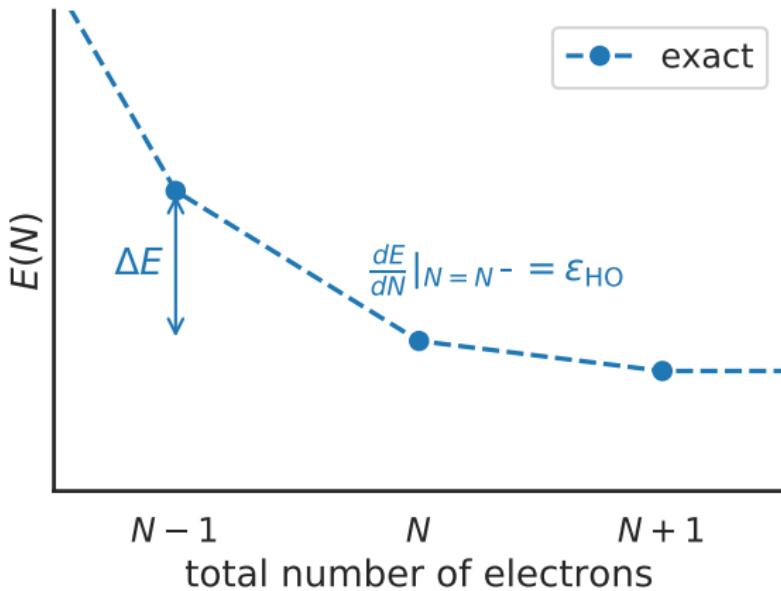
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$$\phi_i(\mathbf{r}) = \sum_{i \neq j} \int d\mathbf{r}' \frac{|\psi_{n_j}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \rightarrow \phi(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'}$$

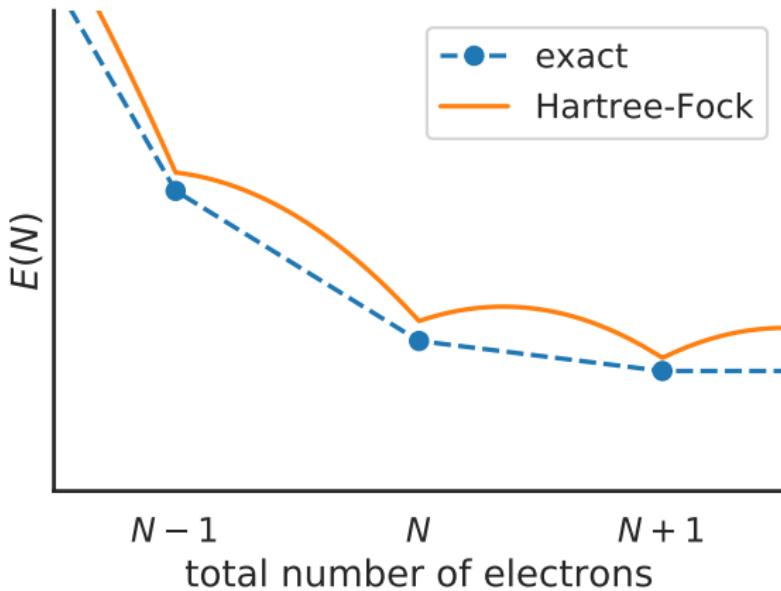
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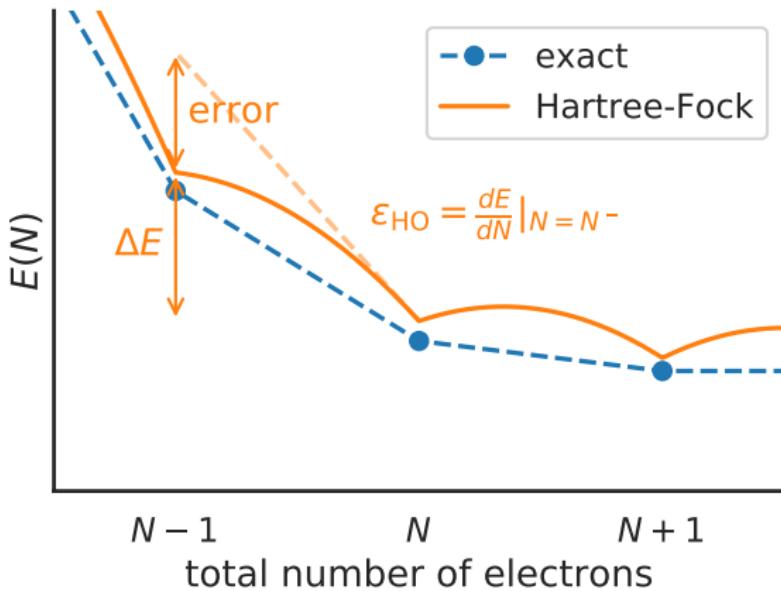
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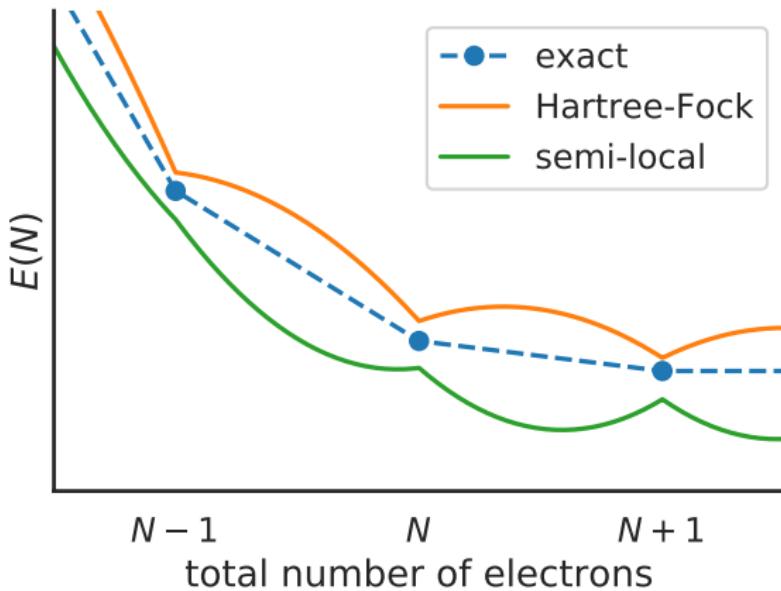
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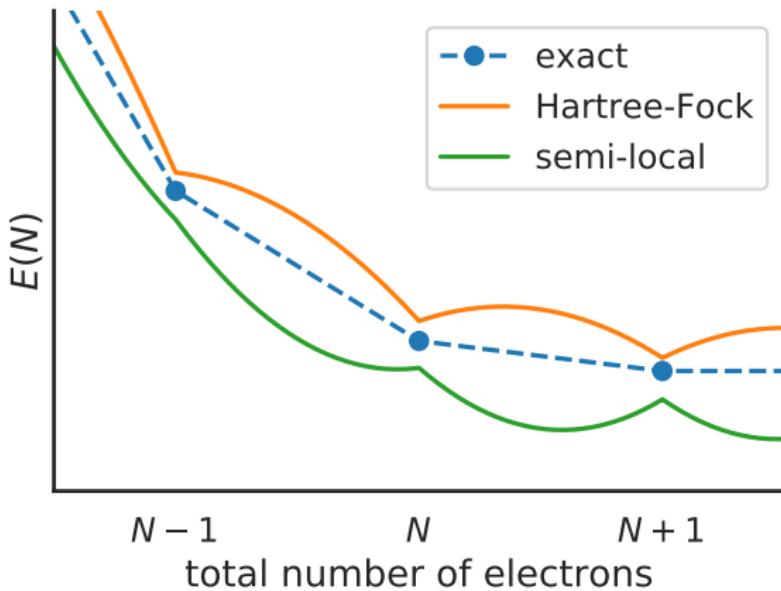
Outline



Outline



Outline



Consequences for band gaps, ionisation potentials, electron affinities...

Outline

Three methods

- DFT+ U
- Koopmans spectral functionals
- dynamical mean field theory

Method 1: DFT+ U

The historical derivation of DFT+ U : let's integrate the Hubbard model into the DFT framework!

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Start with an electron-electron interaction term...

$$\hat{U} = \sum_{mnm'n'} \sum_{\sigma\sigma'} U_{mnm'n'} c_{m\sigma}^\dagger c_{n\sigma'}^\dagger c_{m'\sigma'} c_{n'\sigma},$$

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We make various assumptions:

- ignore all but two-site interaction terms (à la Hubbard model)
- neglect terms between opposite spin (likewise)
- adopt a double-counting term
- assume single-Slater-determinant wavefunction

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... and finish with a correction term to DFT

$$E_{DFT+U}[\rho] = E_{DFT}[\rho] + E_U[\rho] = E_{DFT}[\rho] + \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})]$$

Method 1: DFT+ U

The DFT + U correction in detail:

$$E_U = \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})]$$

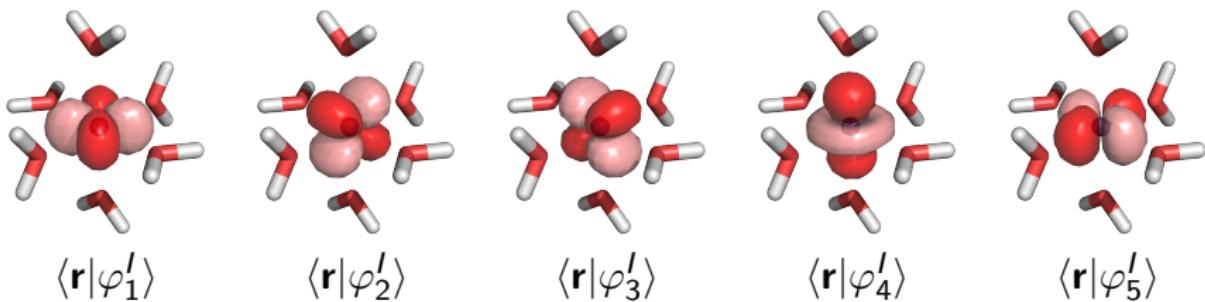
$$\hat{n}^{I\sigma} = \hat{P}^I \hat{\rho}^\sigma \hat{P}^I = \sum_{i,j} |\varphi_i^I\rangle\langle\varphi_i^I| \hat{\rho}^\sigma |\varphi_j^I\rangle\langle\varphi_j^I|$$

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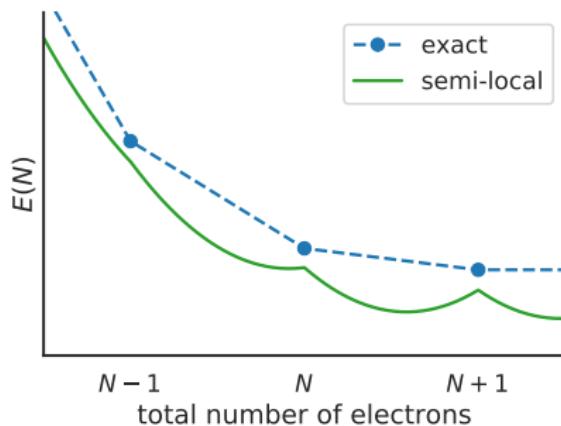
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$$\hat{V}_U = \sum_{I\sigma ij} U^I |\varphi_i^I\rangle \left(\frac{1}{2} - n_{ij}^{I\sigma} \right) \langle \varphi_j^I |$$

Creates gap of U between filled and empty states

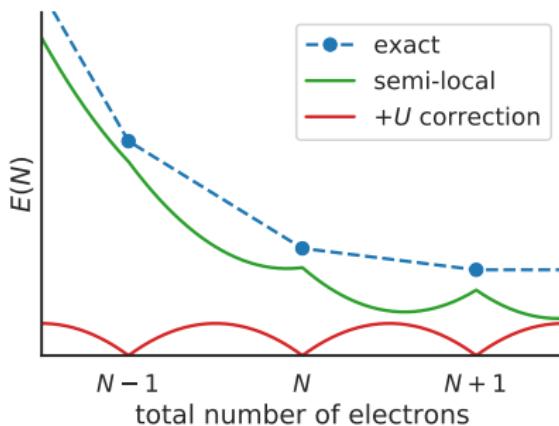
Method 1: DFT+U



A modern interpretation: in a basis such that $\hat{n}^{l\sigma} = \text{diag}(\lambda_1^{l\sigma}, \dots, \lambda_n^{l\sigma})$

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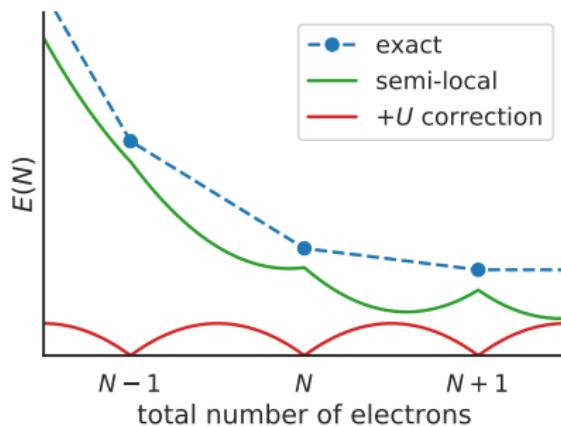
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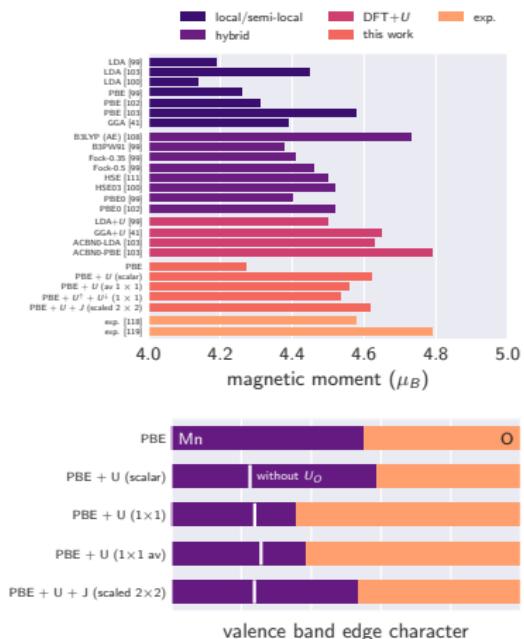
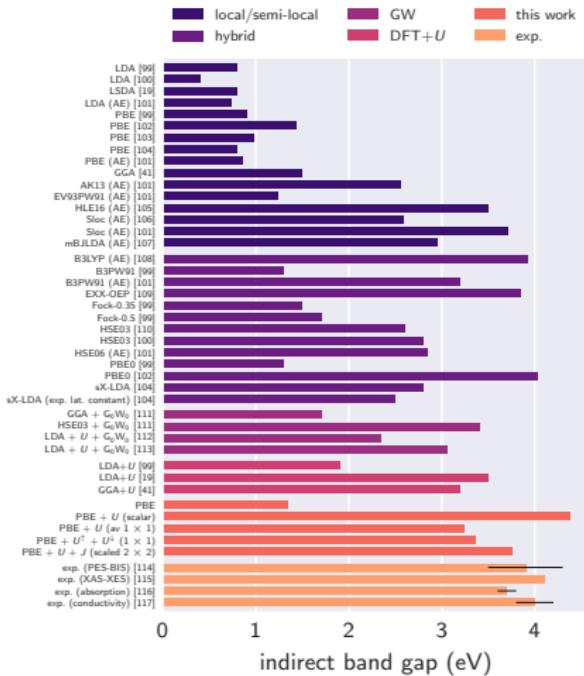
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We can calculate U via linear response \rightarrow “self-correcting” DFT

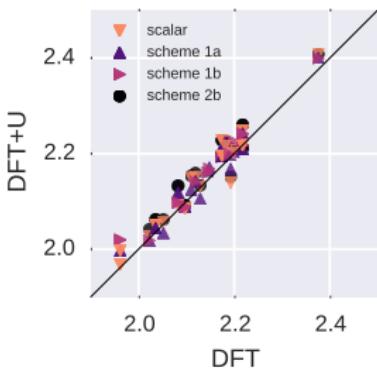
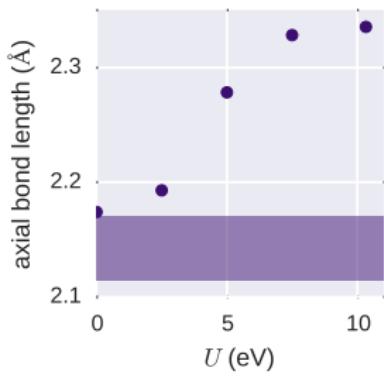
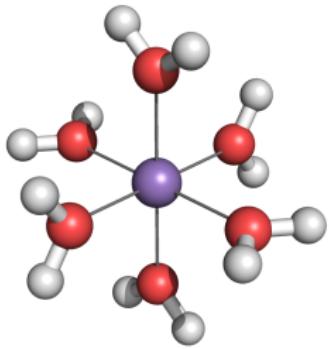
Method 1: DFT+ U

Manganese oxide



Method 1: DFT+ U

Hexahydrated transition metals



Method 1: DFT+ U

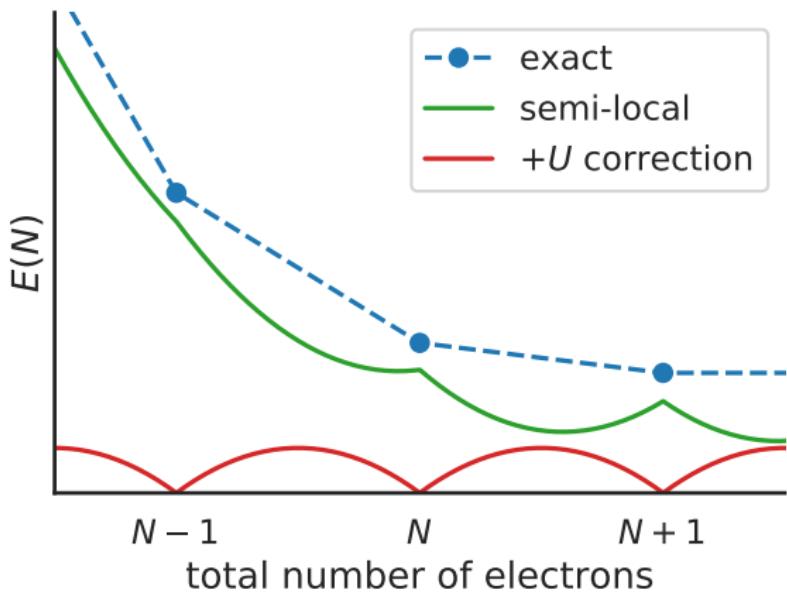
Strengths

- “self-correcting”
- computationally inexpensive

Weaknesses

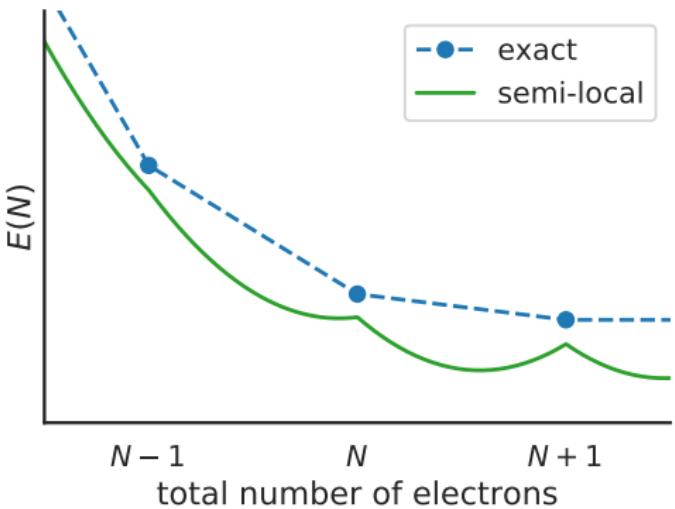
- arbitrary subspaces (both in shape and number)
- complications due to self-consistency
- it's always going to increase the bandgap
- nothing more than Hartree-Fock
- local vs global curvature (I lied earlier...)

Method 1: DFT+U

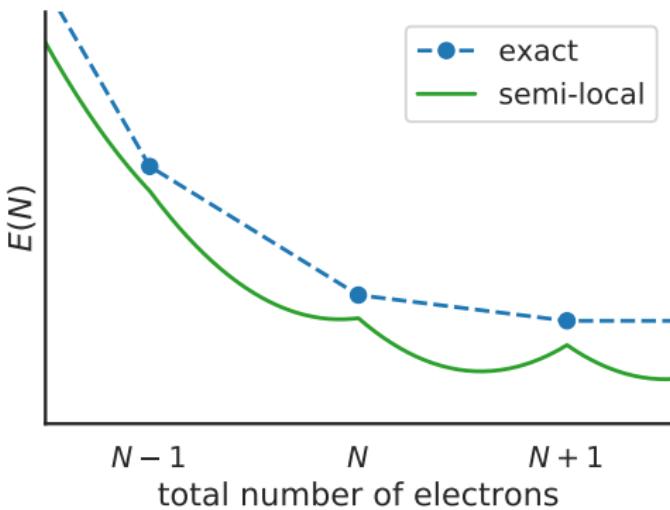


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Method 2: Koopmans spectral functionals

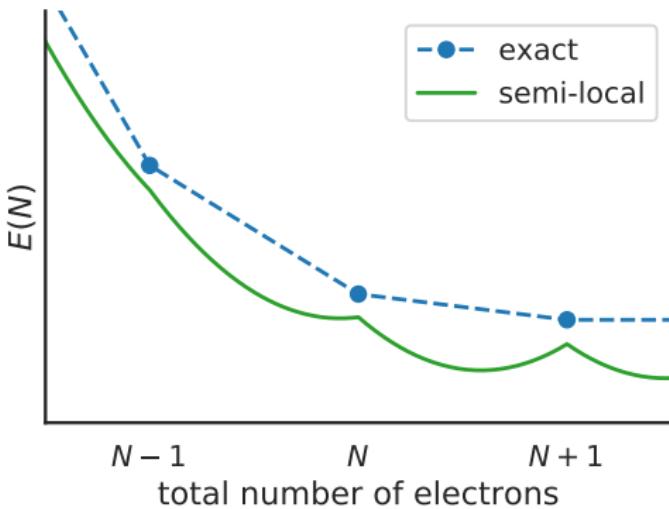


Method 2: Koopmans spectral functionals



KC functionals: assert that $\varepsilon_i = \langle \varphi_i | H | \varphi_i \rangle = \partial E / \partial f_i$ is independent of f_i

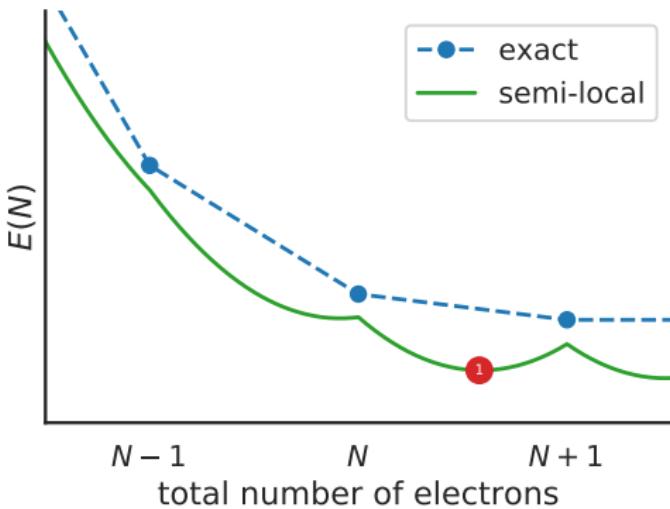
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$$E_{KC}[\rho, \{f_i\}] = E_{DFT}[\rho] + \sum_i \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \int_0^1 \varepsilon_i(f) df \right)$$

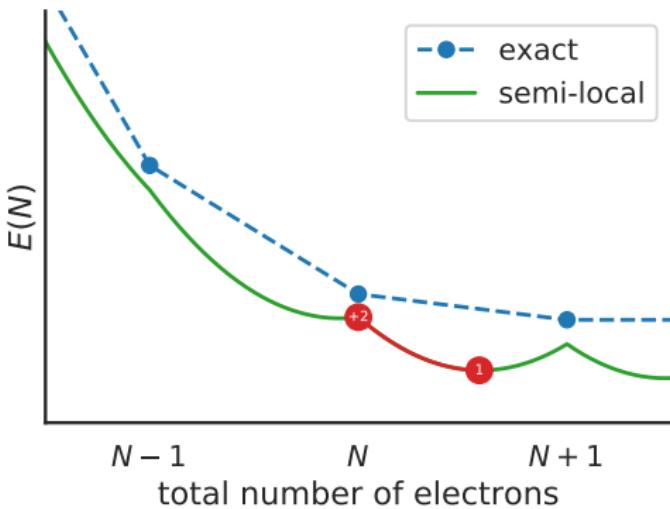
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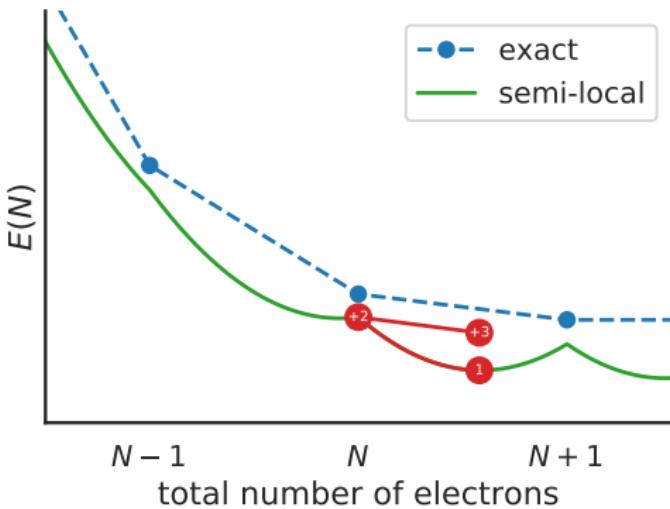
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- orbital density dependence

Method 2: Koopmans spectral functionals

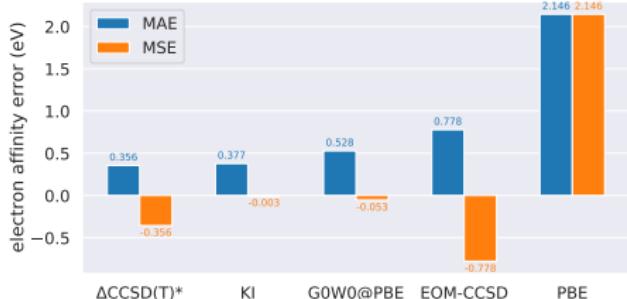
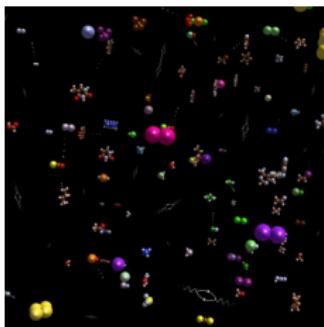
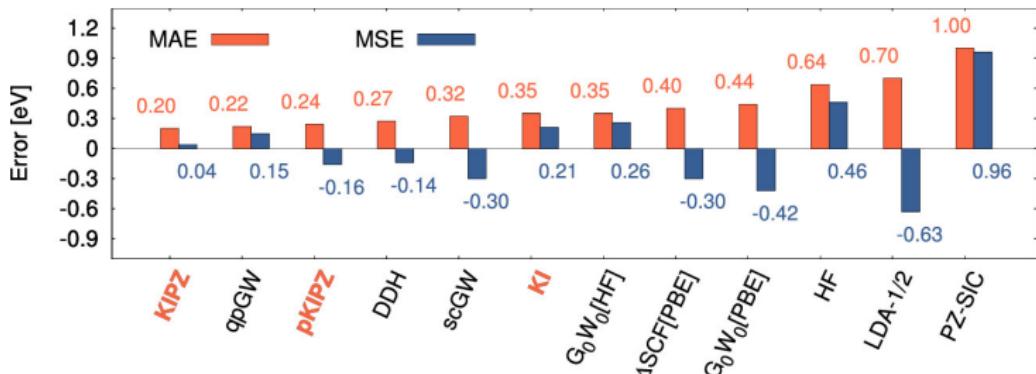
$$E_{KC}[\rho, \{f_i\}, \{\alpha_i\}] = E_{DFT}[\rho] + \sum_i \textcolor{red}{\alpha_i} \left(- \int_0^{f_i} \varepsilon_i(f) df + f_i \int_0^1 \varepsilon_i(f) df \right)$$

- orbital density dependence
- screening

$$\alpha_i = \alpha^0 \frac{E^{KC}(N) - E_i^{KC}(N-1) - \lambda_{ii}^0(1)}{\lambda_{ii}^{\alpha^0}(1) - \lambda_{ii}^0(1)}$$

$$\lambda_{ii}^\alpha(f) = \langle \varphi_i | H^{\text{DFT}} + \alpha_i v_i^{\text{KC}} | \varphi_i \rangle \Big|_{f_i=f}$$

Method 2: Koopmans spectral functionals



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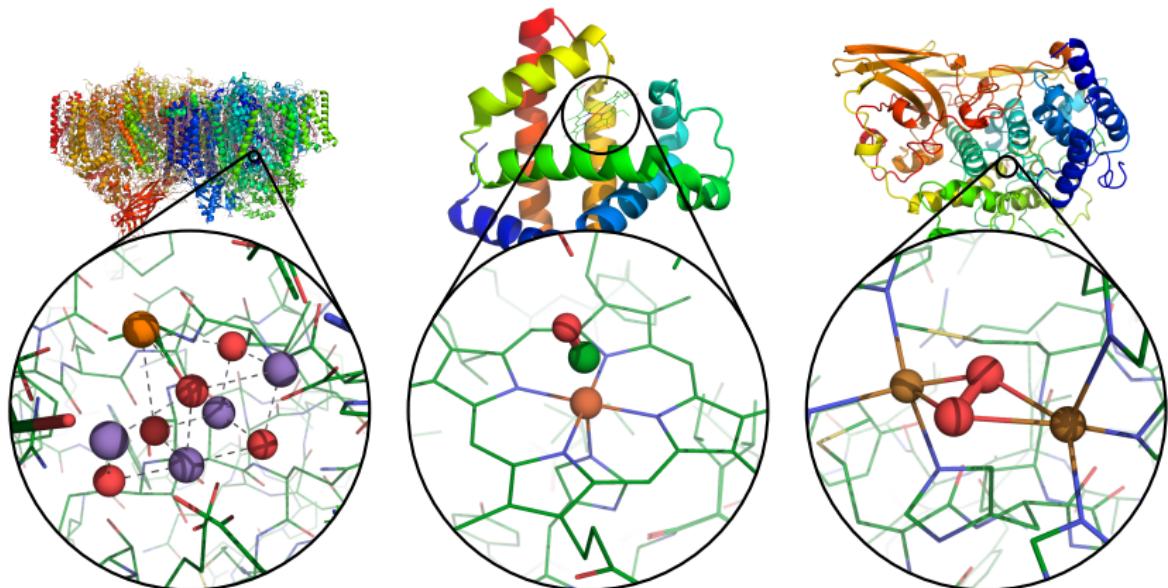
Strengths

- systematic
- orbital dependent
- great results!

Weaknesses

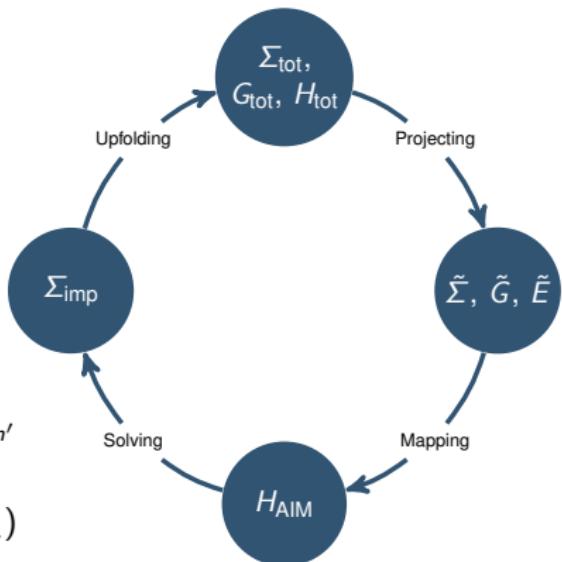
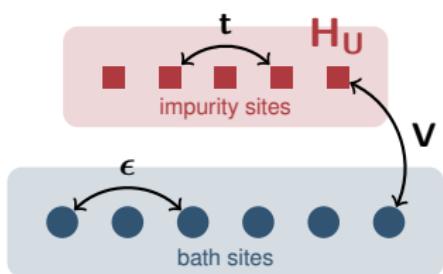
- orbital dependent
- complicated workflow
- only for insulators
- untested on “strongly correlated” systems

Method 3: dynamical mean field theory



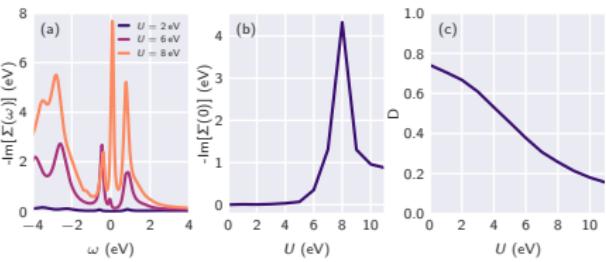
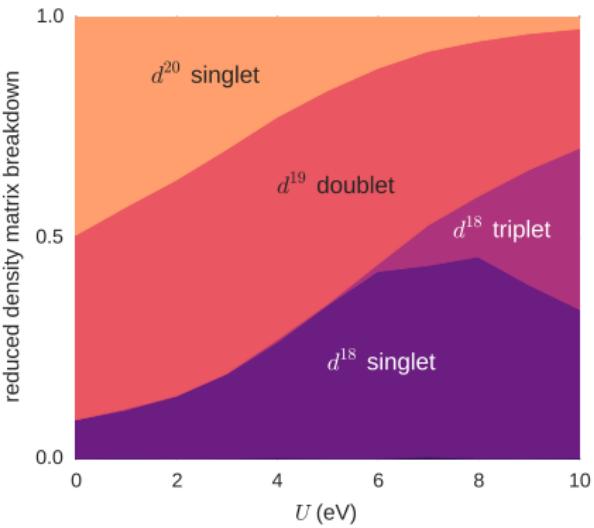
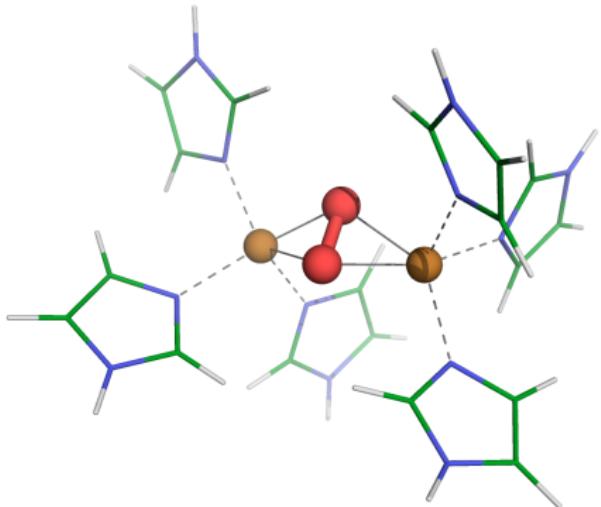
Method 3: dynamical mean field theory

$$\hat{H} = \underbrace{\sum_{ij\sigma} (\varepsilon_{ij} - \mu) \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}}_{\hat{H}_{\text{bath}}} + \underbrace{\sum_{im\sigma} (V_{mi} \hat{f}_{m\sigma}^\dagger \hat{c}_{i\sigma} + h.c.)}_{\hat{H}_{\text{mix}}} + \underbrace{\sum_{mm'\sigma} (t_{mm'} - \mu) \hat{f}_{m\sigma}^\dagger \hat{f}_{m'\sigma}}_{\hat{H}_{\text{loc}}} + \hat{H}_U$$



$$H_U = U \sum_m n_{m\uparrow} n_{m\downarrow} + \left(U' - \frac{J}{2} \right) \sum_{m > m'} n_m n_{m'} - J \sum_{m > m'} (2 \mathbf{S}_m \cdot \mathbf{S}_{m'} + f_{m\uparrow}^\dagger f_{m\downarrow}^\dagger f_{m'\uparrow} f_{m'\downarrow})$$

Method 3: dynamical mean field theory



Method 3: dynamical mean field theory

Strengths

- accurate
- truly many-body

Weaknesses

- arbitrary
- expensive
- difficult convergence

Conclusions

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- DFT+ U : “self-correcting”, cheap, somewhat arbitrary
- Koopmans spectral functionals: systematic but only for insulators
- dynamical mean field theory: difficult but truly many-body physics

Acknowledgements



Danny Cole



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Marzari



Nicola
Colonna



Riccardo
De Gennaro



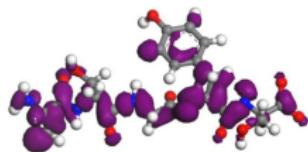
Cedric Weber



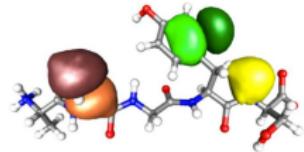
Mohamed Ali
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An accurate and linear-scaling DFT code

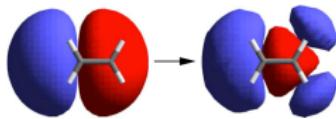
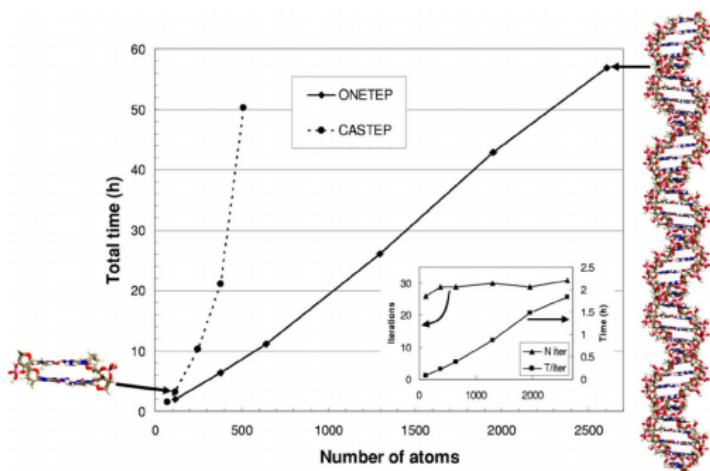


Kohn-Sham orbital



NGWFs

Basis of NGWFs and cut-offs
→ sparse matrix algebra
→ linear scaling



NGWFs are optimised in situ
→ accurate, minimal, and systematically extendible basis
→ equivalent to plane-wave codes

DFT+U: Linear-response via projected potentials

$$U^I = (\chi_0^{-1} - \chi^{-1})_{II}$$

If we work in terms of projected potentials $v^I = \text{Tr}[\hat{P}^I \hat{v}] / \text{Tr}[\hat{P}]$ then the Dyson equation

$$f_{Hxc} = \chi_0^{-1} - \chi^{-1}$$

falls out, with the response matrices

$$\chi_{IJ} = \frac{dn^I}{d\nu_{\text{ext}}^J};$$

$$(\chi_0)_{IJ} = \left[\frac{dn}{d\nu_{\text{ext}}} \left(\frac{d\nu_{\text{KS}}}{d\nu_{\text{ext}}} \right)^{-1} \right]_{IJ}$$

“Minimum-tracking LR”; suited to direct-minimisation codes

DFT+U: resolving spin

Removing coarse-graining

$$\chi = \begin{pmatrix} \chi_{11}^{\uparrow\uparrow} & \chi_{11}^{\uparrow\downarrow} & \chi_{12}^{\uparrow\uparrow} & \chi_{12}^{\uparrow\downarrow} \\ \chi_{11}^{\downarrow\uparrow} & \chi_{11}^{\downarrow\downarrow} & \chi_{12}^{\downarrow\uparrow} & \chi_{12}^{\downarrow\downarrow} \\ \chi_{21}^{\uparrow\uparrow} & \chi_{21}^{\uparrow\downarrow} & \chi_{22}^{\uparrow\uparrow} & \chi_{22}^{\uparrow\downarrow} \\ \chi_{21}^{\downarrow\uparrow} & \chi_{21}^{\downarrow\downarrow} & \chi_{22}^{\downarrow\uparrow} & \chi_{22}^{\downarrow\downarrow} \end{pmatrix} = \begin{pmatrix} (\chi^{\sigma\sigma'})_{11} & (\chi^{\sigma\sigma'})_{12} \\ (\chi^{\sigma\sigma'})_{21} & (\chi^{\sigma\sigma'})_{22} \end{pmatrix}.$$

c.f. Hubbard functional

$$E_{+U} = \sum_{I\sigma} \frac{U^I}{2} \text{Tr}[\hat{n}^{I\sigma}(1 - \hat{n}^{I\sigma})] \rightarrow \sum_S \frac{U^S}{2} \text{Tr}[\hat{n}^S(1 - \hat{n}^S)]$$

Results:

- by including/removing off-diagonal components we can construct new equations for U , J selectively excluding/including screening by different subspaces (parallels with work on olivines)
- conventional “scalar” linear response corresponds to a weighted-averaging of the spin-indexed f_{Hxc} to obtain U

Green's functions

If $\hat{H} = \hat{H}_0 + F(t)\hat{Y}$ then

$$\langle \hat{X}(t) \rangle = \int dt' G_{XY}^+(t) F(0)$$

We are interested in excitations/holes:

$$\hat{X}, \hat{Y} \rightarrow \hat{c}_\alpha^\dagger, \hat{c}_\beta \quad G_{XY}^+(t) \rightarrow G_{\alpha\beta}^+(t) = -i\Theta(t)\langle\{c_\alpha(t), c_\beta^\dagger(0)\}\rangle$$

For non-interacting systems

$$G^0(\omega) = \frac{1}{\omega + \mu - H}$$

Extend to interacting systems by introducing the *self energy* Σ :

$$G(\omega) = \frac{1}{\omega + \mu - H - \Sigma(\omega)} \implies \mathbf{G} = \mathbf{G}^0 + \mathbf{G}^0 \Sigma \mathbf{G}$$

System properties are then accessed via the Green's function

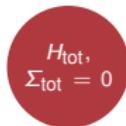
$$\text{e.g. } \rho^{\alpha\beta} = \frac{1}{2i\pi} \left(G(\omega) - G^\dagger(\omega) \right)^{\alpha\beta}$$

The principle of DMFT

We want to solve for the Green's function and the self-energy

- we can't (nor do we want to) explicitly solve for the Green's function of the entire system
- identify correlated subspaces that require special treatment
 $(\hat{P} = \sum_i |\varphi_i\rangle\langle\varphi_i|)$
- trust DFT to adequately describe the rest of the system

The DMFT loop


$$H_{\text{tot}}, \\ \Sigma_{\text{tot}} = 0$$

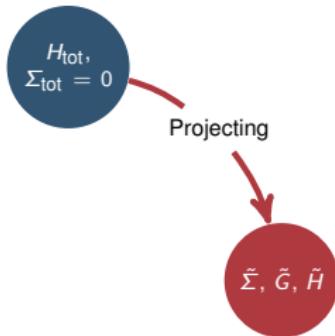
We start with the Hamiltonian of a DFT calculation:

$$H_{\text{tot}}$$

and as a starting guess for the Green's function

$$G_{tot} = G_{tot}^0 = \frac{1}{\omega + \mu - H}$$

The DMFT loop

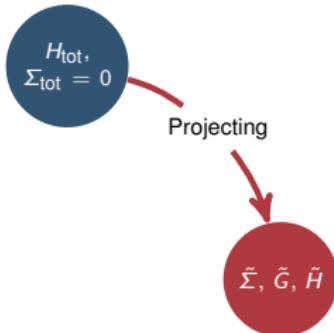


Projection onto Hubbard sub-spaces:

$$\tilde{G}_{mm'} = \langle \varphi_m | \phi_\alpha \rangle G_{\text{tot}}^{\alpha\beta} \langle \phi_\beta | \varphi_{m'} \rangle$$

(Likewise for $\tilde{H}, \tilde{\Sigma}$)

The DMFT loop



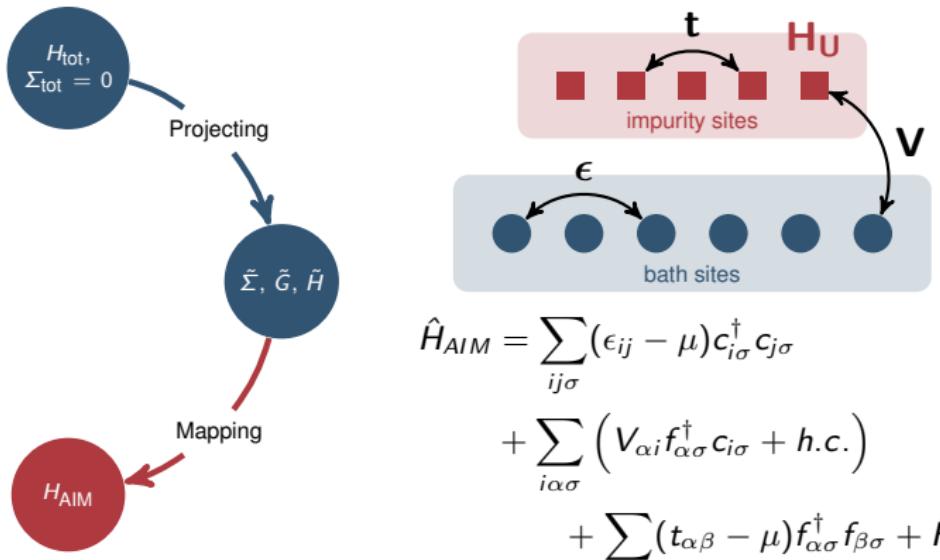
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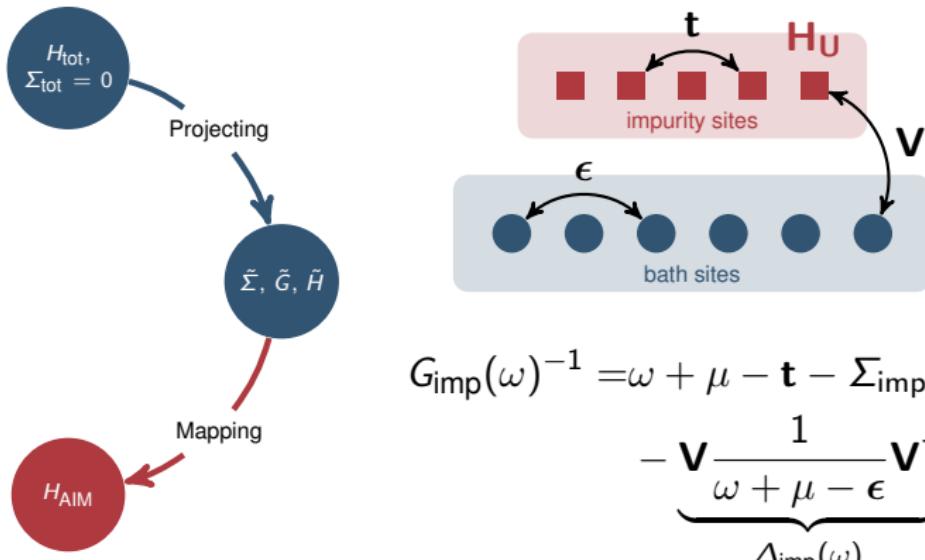
(Likewise for $\tilde{H}, \tilde{\Sigma}$)

How to consider these projected quantities while not disregarding interaction with the rest of the system? The trick: map to an Anderson Impurity Model (AIM)

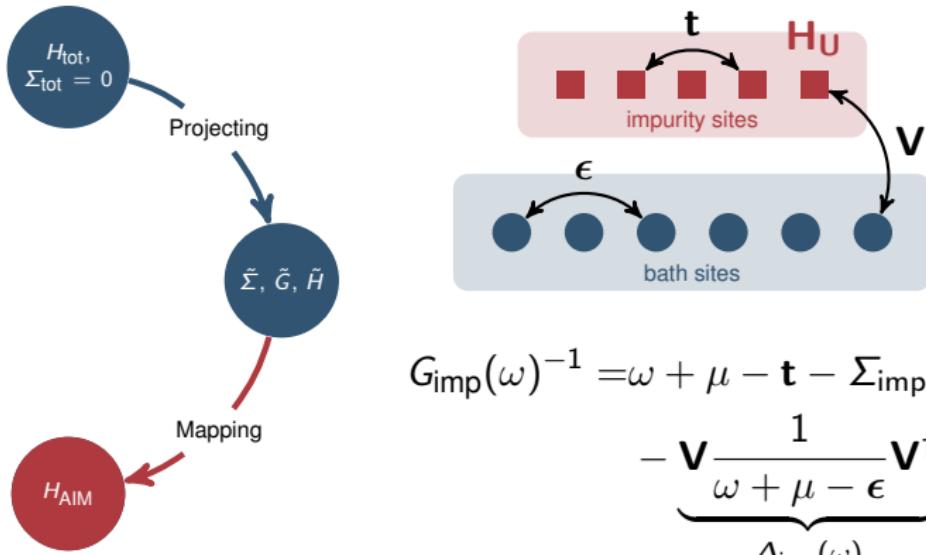
The DMFT loop



The DMFT loop



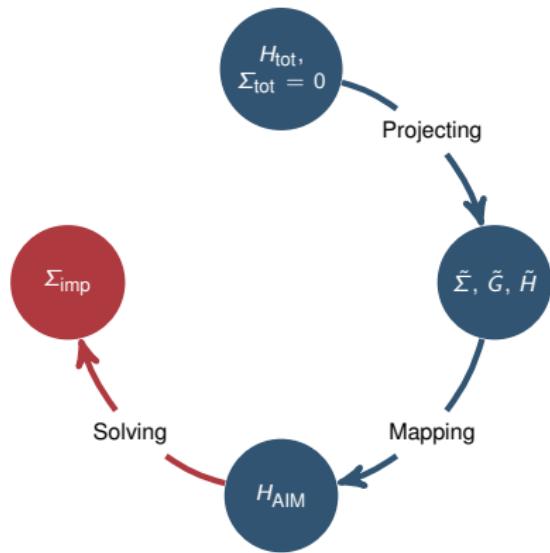
The DMFT loop



For the original system define analogously a hybridisation function $\tilde{\Delta}(\omega) = \omega + \mu - \tilde{H} - \tilde{G}^{-1}(\omega) - \tilde{\Sigma}(\omega)$ and then minimise the difference

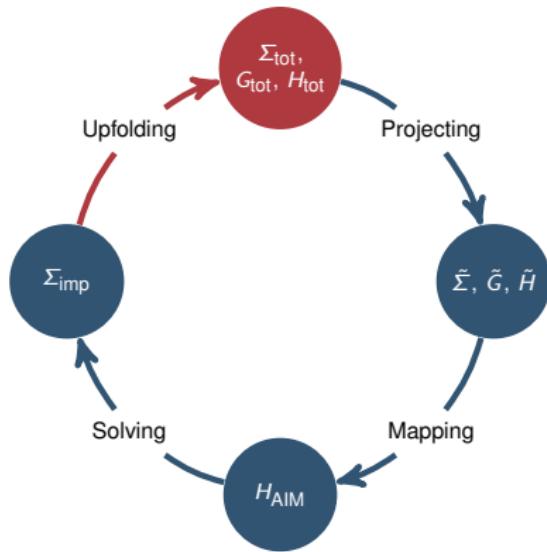
$$d(\mathbf{V}, \epsilon) = \int d\omega (\Delta_{\text{imp}}(\omega) - \tilde{\Delta}(\omega))$$

The DMFT loop



We now have H_{AIM} which we solve can explicitly via exact diagonalisation (Lanczos), CTQMC, ... This is the most expensive step of the calculation (empty, \uparrow , \downarrow , and $\uparrow\downarrow$ on each site)

The DMFT loop



Upfolding the self-energy

$$(\Sigma_{tot})_{\alpha\beta} = \langle \phi_\alpha | \varphi_m \rangle (\Sigma^{mm'} - E_{DC}^{mm'}) \langle \varphi_{m'} | \phi_\beta \rangle$$

and update the Green's function

$$G_{tot} = \frac{1}{\omega + \mu - H_{tot} - \Sigma_{tot}}$$