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DFT+U and DMFT and their implementation in ONETEP

Edward Linscott

Theory of Condensed Matter, Department of Physics, University of Cambridge

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Outline

- the motivation for DFT+U and DMFT
- the DFT+U formalism
- the DMFT formalism
- its implementation in ONETEP

Failures of DFT

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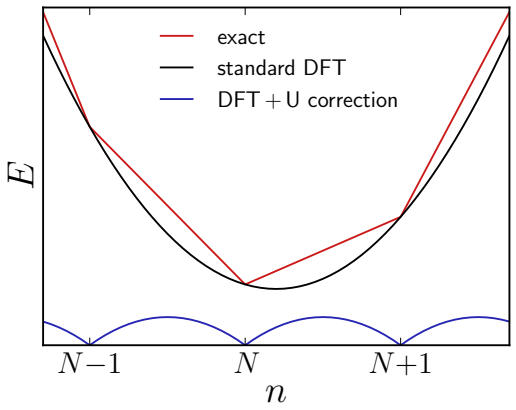
- d/f orbitals tend to overbind since these orbitals are delocalised and wrongly participate in bonding (elemental Plutonium in its delta phase: cell volumes off by 30%)
- we need to appeal to a less approximate theory to treat these electrons

Delocalisation error; DFT + U



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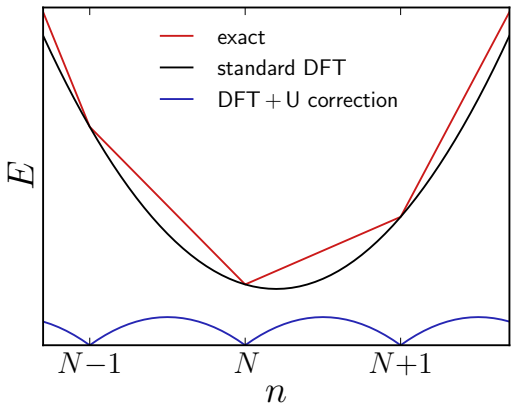

DFT+U (Anisimov *et al.*, 1991 & 1993)

$$E_{DFT+U} = E_{DFT} + \frac{U}{2} \sum_{\sigma} \mathrm{Tr}[\mathbf{n}^{\sigma}(1 - \mathbf{n}^{\sigma})]$$

where $\mathbf{n}^{\sigma}$ is the density-matrix of some correlated subspace

- Inclusion of Hubbard-model-like term to DFT
- identify correlated subspaces that require special treatment ($\hat{P} = \sum_i |\varphi_i\rangle\langle\varphi_i|$)
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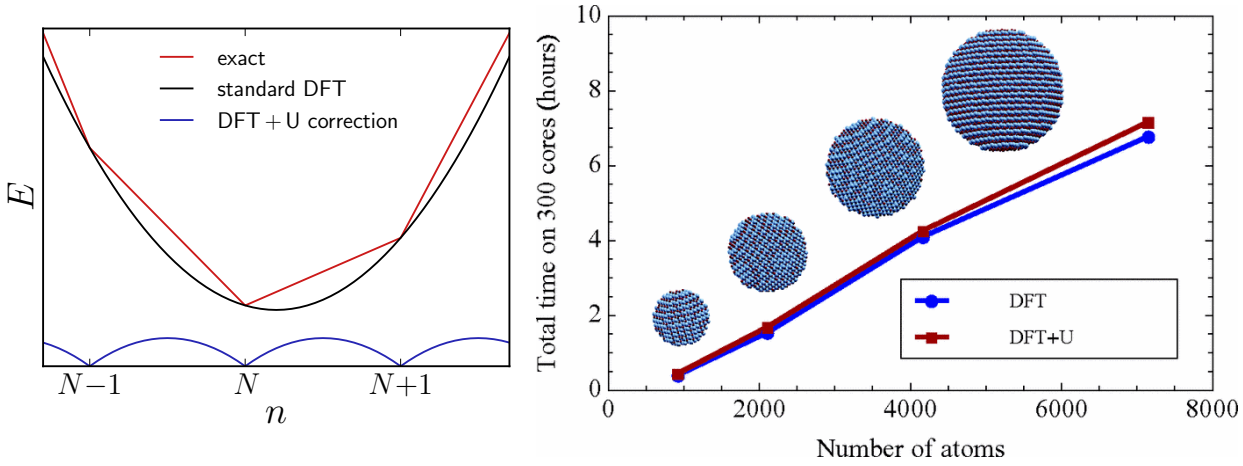

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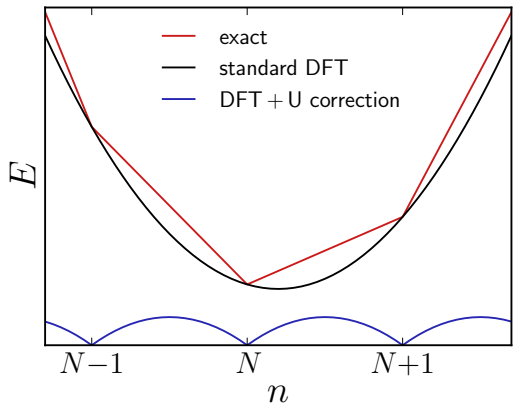

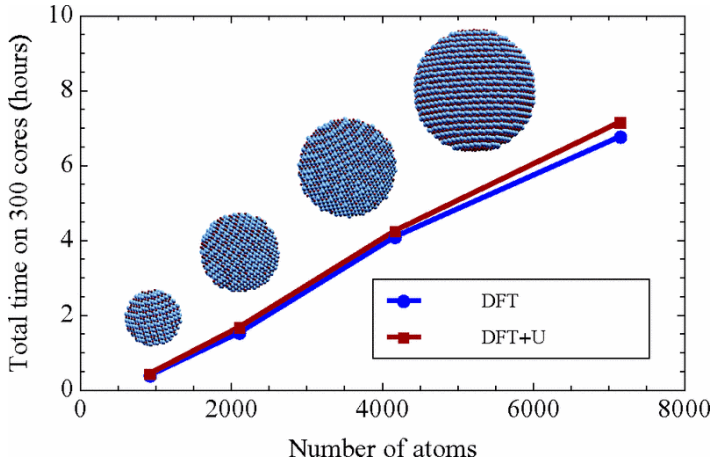

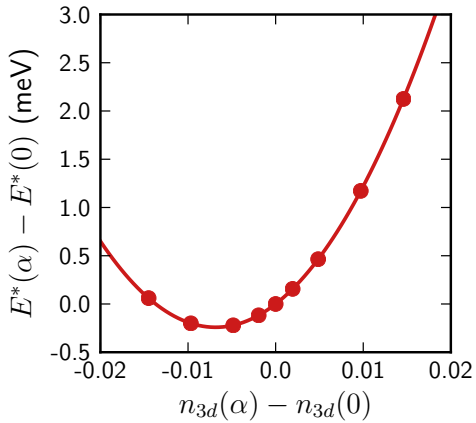

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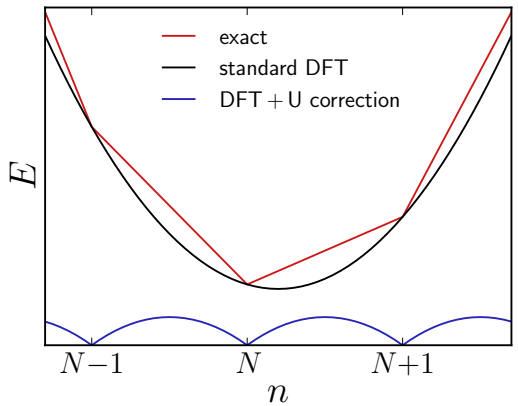

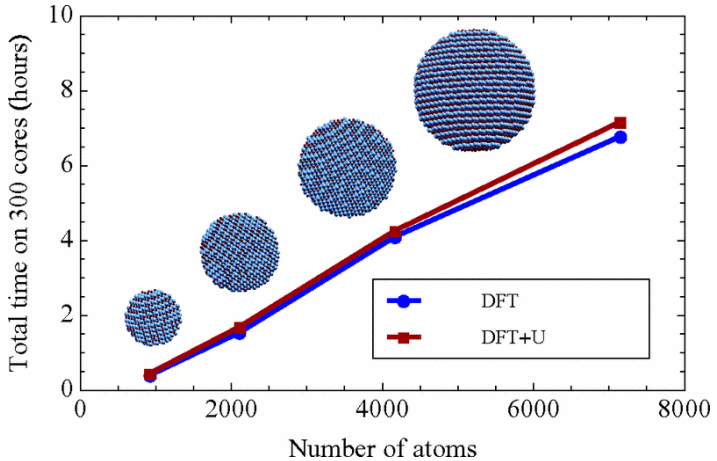

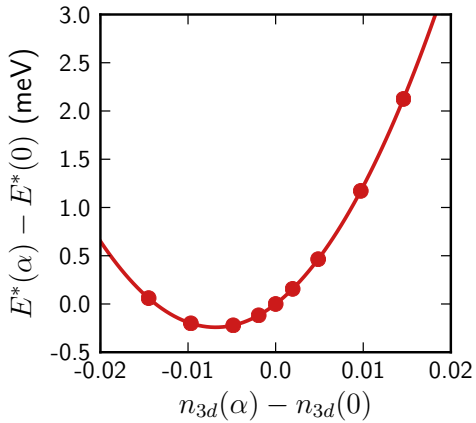

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Green's functions

DMFT (Metzner *et al.* (1989), Georges *et al.* (1992) and Anisimov *et al.* (1997)); incorporation of Green function formalism into DFT

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

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

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$$\hat{X}, \hat{Y} \to \hat{c}^\dagger_\alpha, \hat{c}_\beta \qquad G^+_{XY}(t) \qquad \to G^+_{\alpha\beta}(t) = -i\Theta(t)\langle\{c_\alpha(t), c^\dagger_\beta(0)\}\rangle$$

For non-interacting systems

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

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

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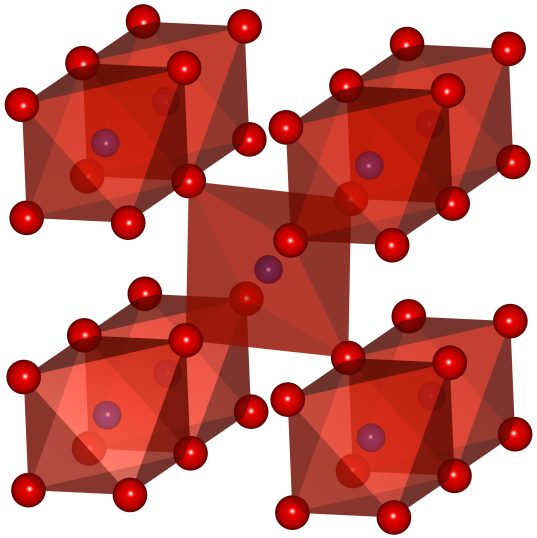
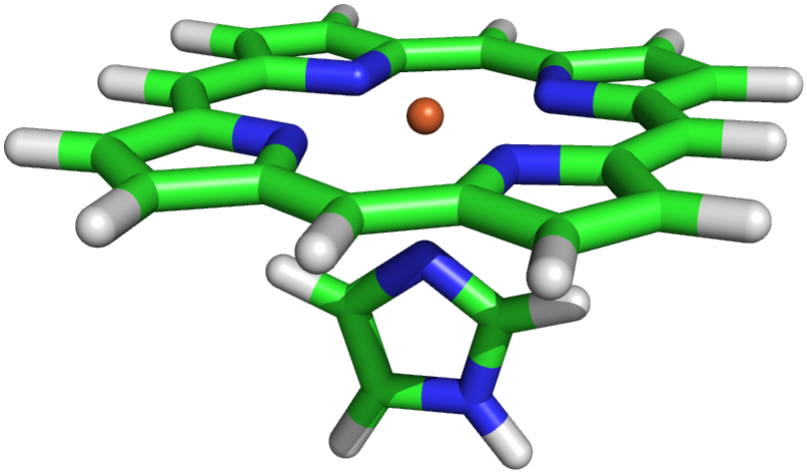
The principle of DMFT





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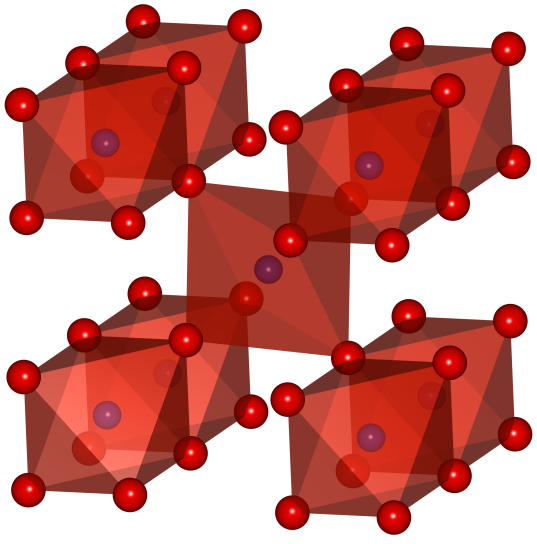

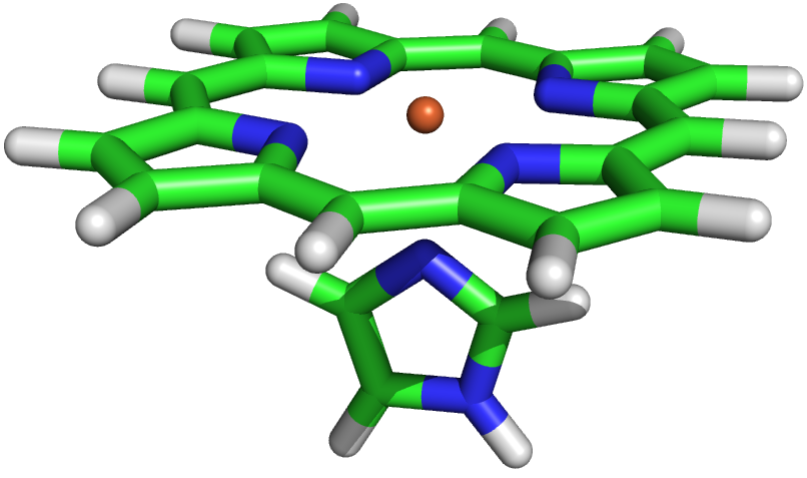

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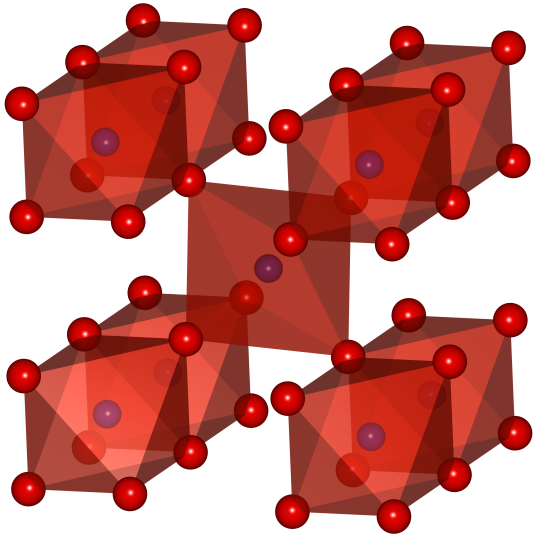

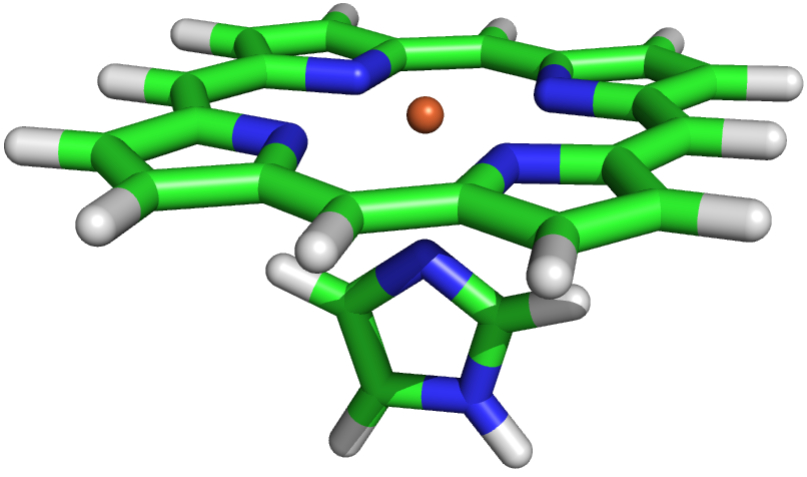

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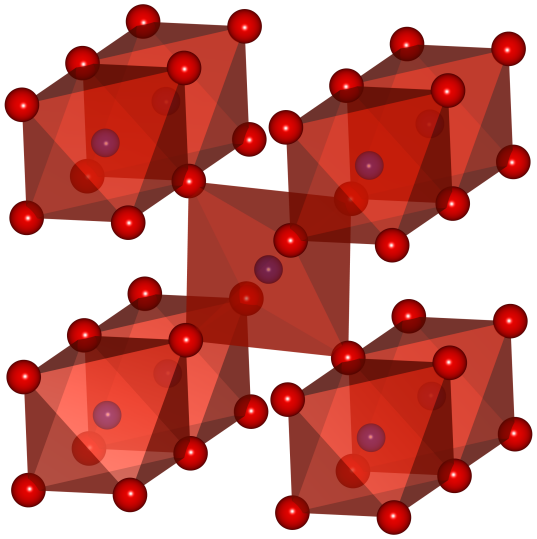

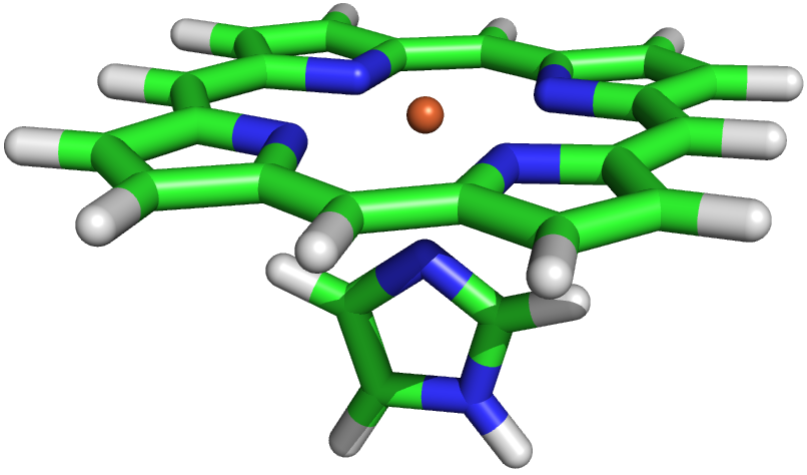

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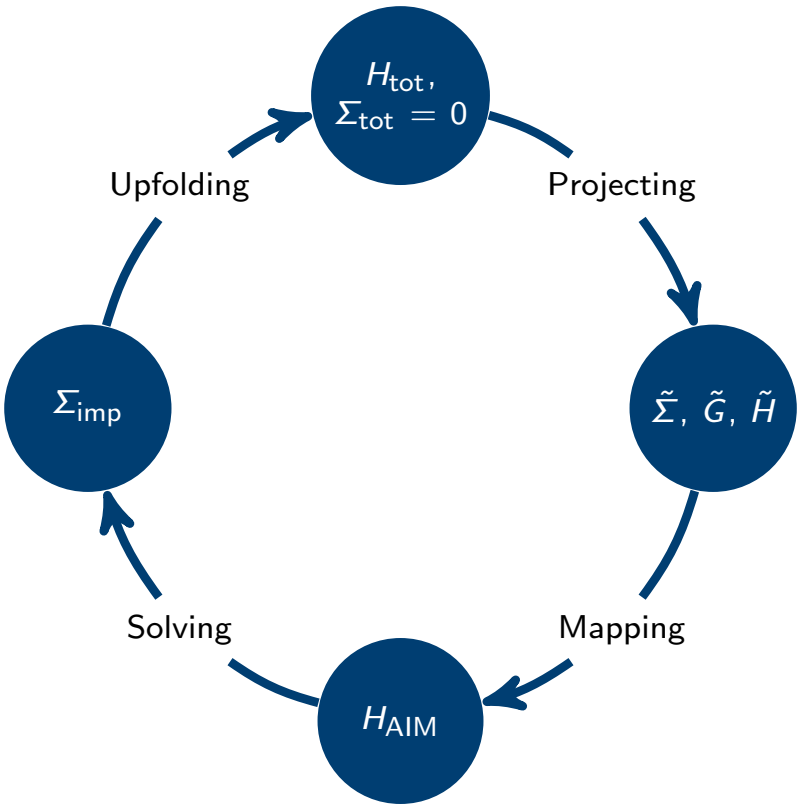
The DMFT loop



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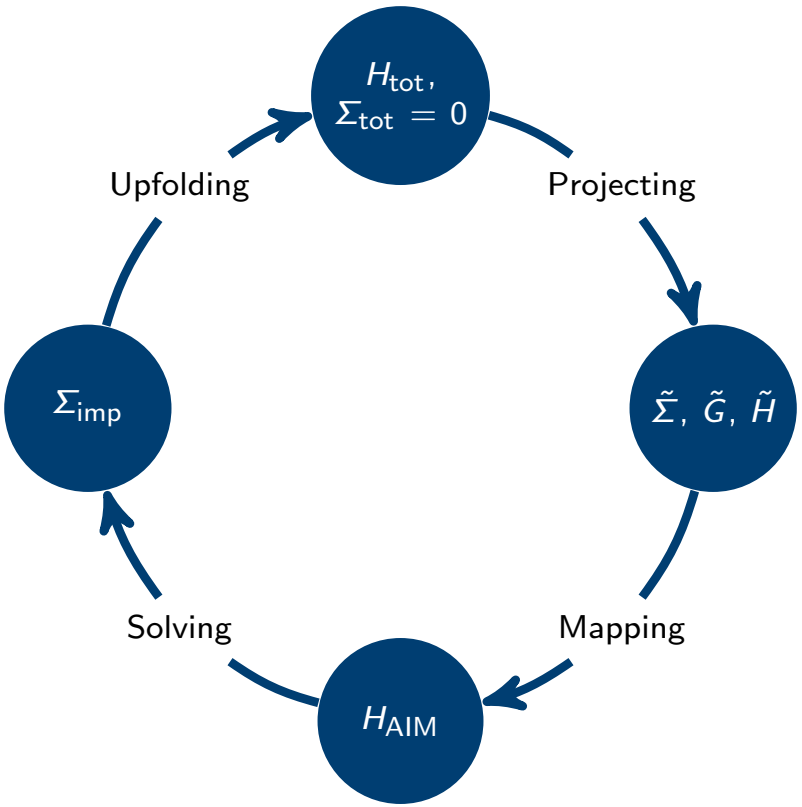
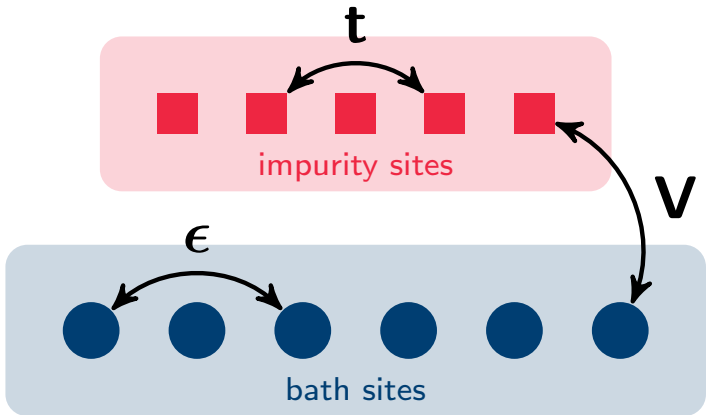
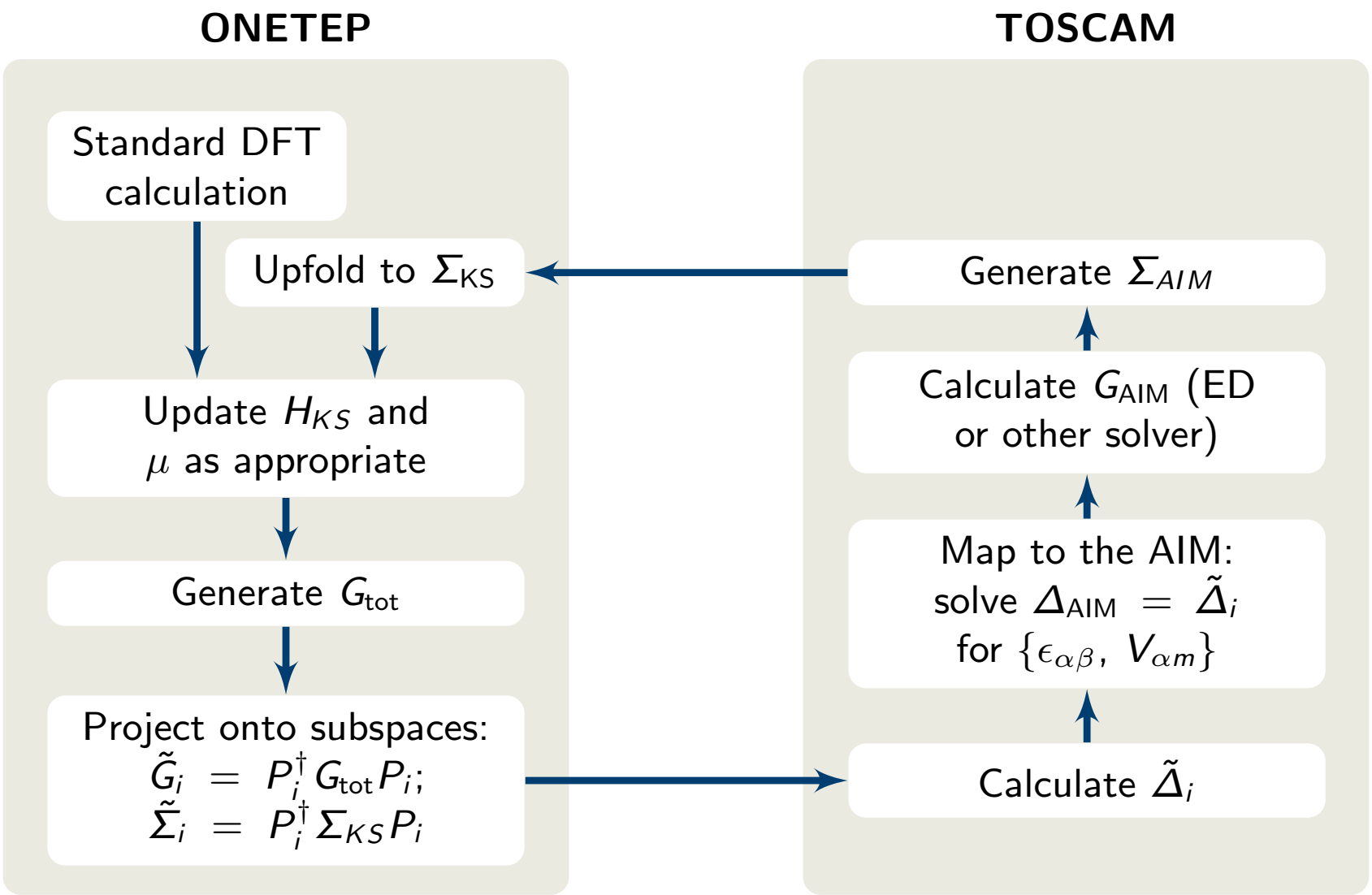




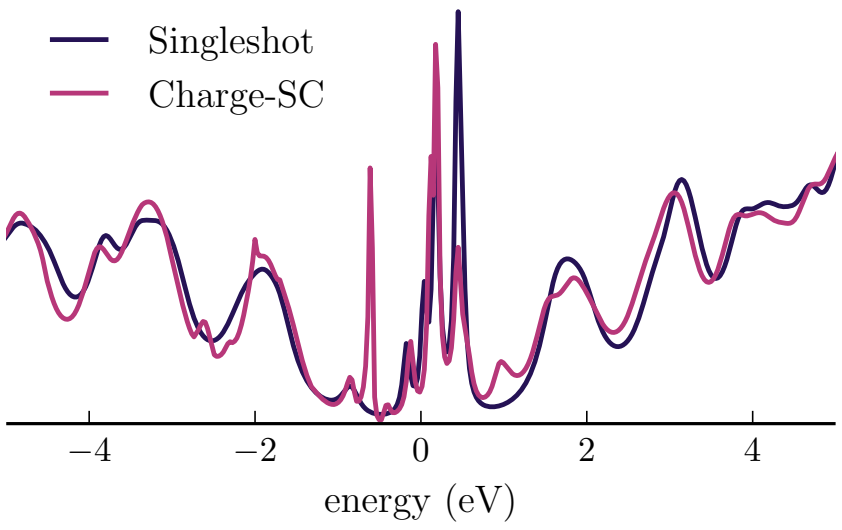
$$\hat{H}_{AIM} = \sum_{ij\sigma} (\epsilon_{ij} - \mu) c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i\alpha\sigma} \left(V_{\alpha i} f^{\dagger}_{\alpha\sigma} c_{i\sigma} + h.c. \right) + \sum_{\alpha\beta\sigma} (t_{\alpha\beta} - \mu) f^{\dagger}_{\alpha\sigma} f_{\beta\sigma} + \hat{H}_U$$

Implementation of DMFT in ONETEP

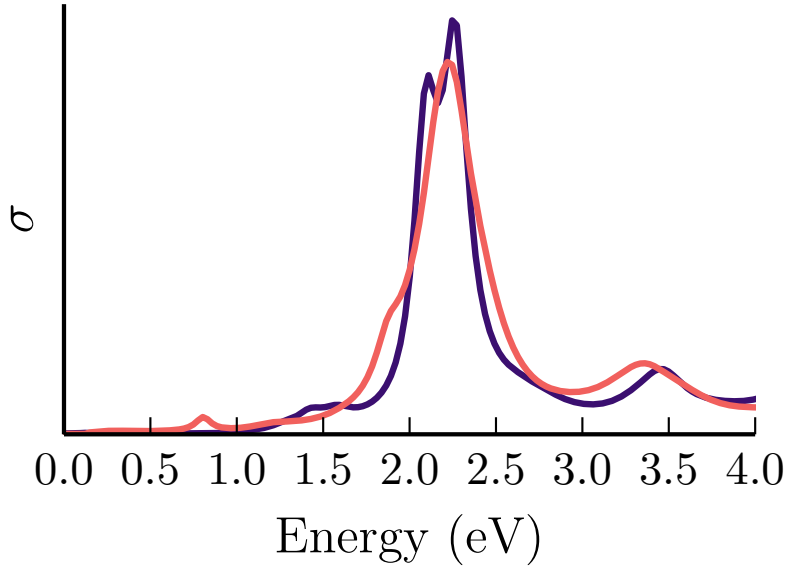


Example results

DOS



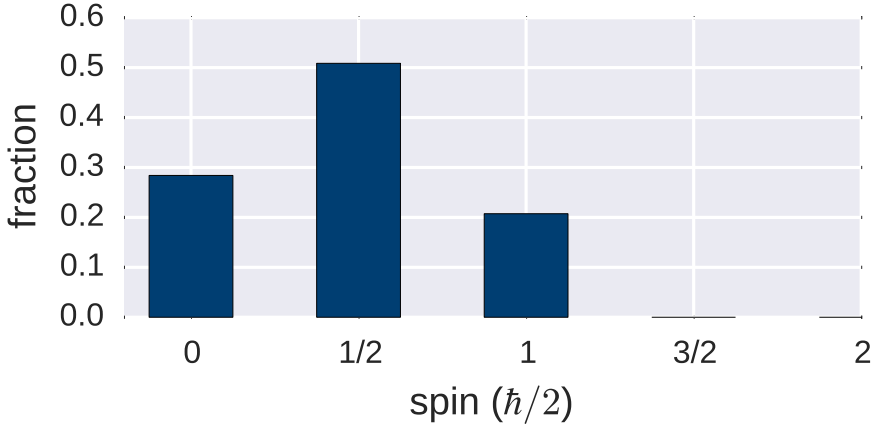
Optical spectra



Reduced density matrix

$$\hat{\rho} = \sum_i e^{-\beta E_i} \mathrm{Tr}_{\mathrm{bath}} \left[|i\rangle\langle i| \right]$$

yields spin distributions, entropies
(we are in a mixed quantum state)



Outlook

- Functionality is about to be committed to devel version
- TOSCAM to become available under LGPL (freely accessible via a git repository)
- Get in touch if interested! (`ebl27@cam.ac.uk` or `cedric.weber@kcl.ac.uk`)

Acknowledgements and References

Thanks to Cédric Weber, Daniel Cole, Nicholas Hine, and Mike Payne

CAMBRIDGE COMMONWEALTH EUROPEAN AND INTERNATIONAL TRUST

the Royal Society of New Zealand RUTHERFORD FOUNDATION

EPSRC Engineering and Physical Sciences Research Council

[1] V. I. Anisimov et al. *Phys. Rev. B* 44.3 (1991).

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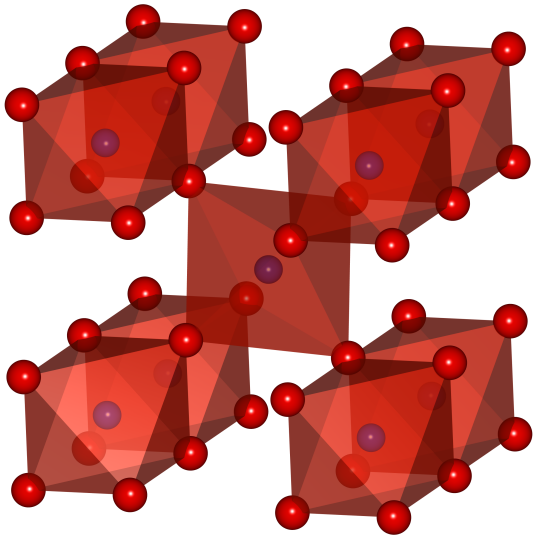

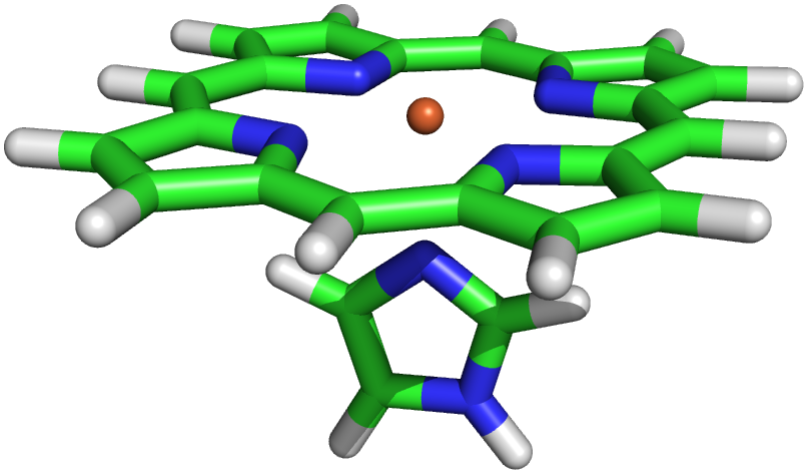

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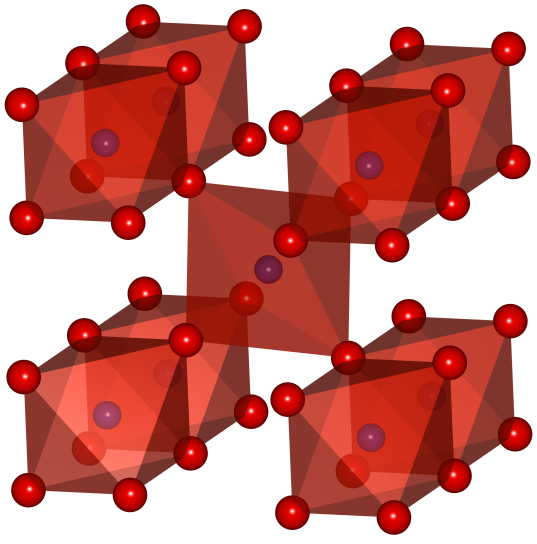

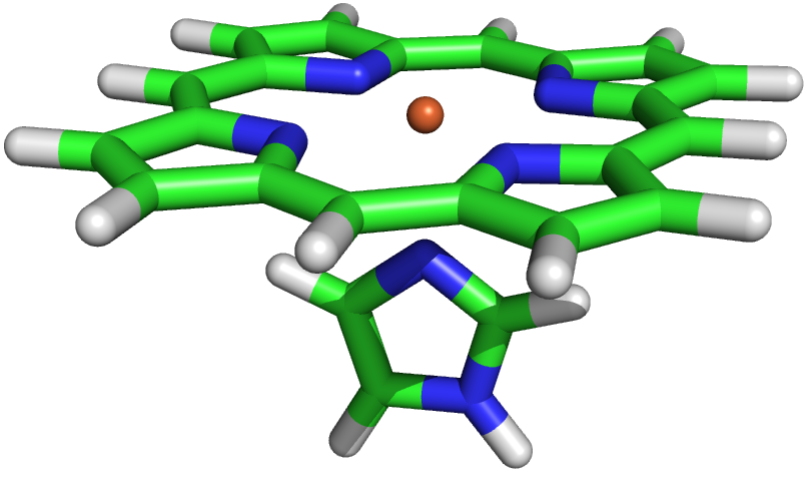

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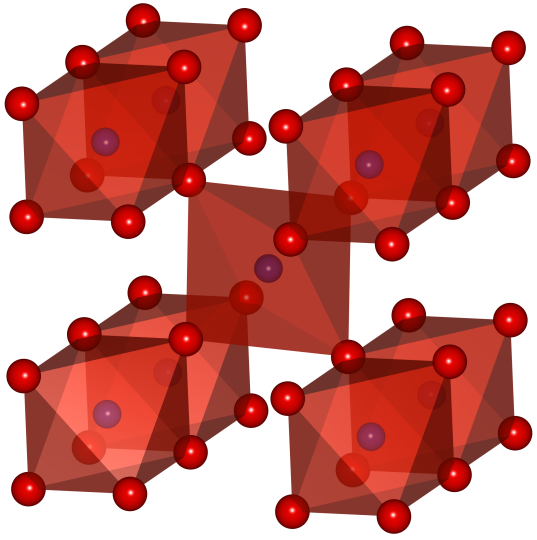

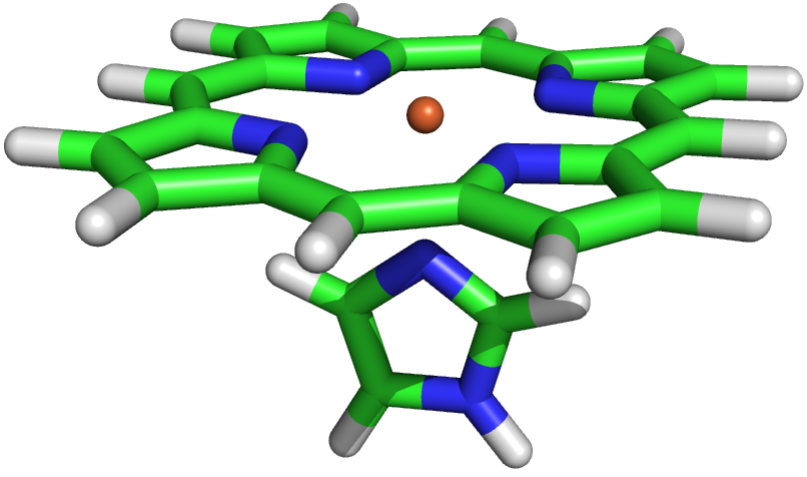

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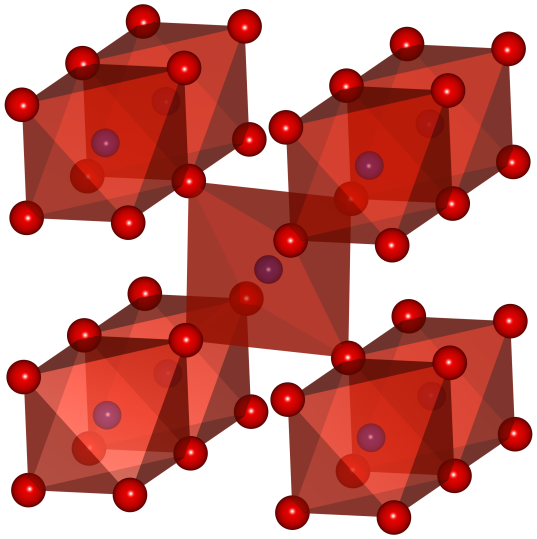

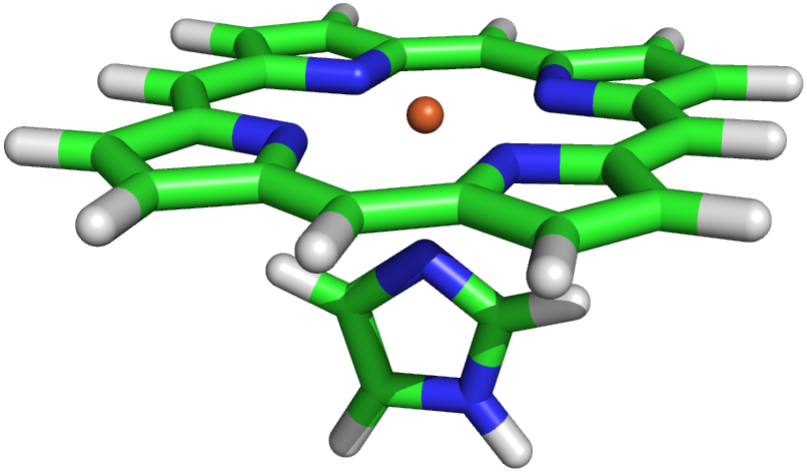

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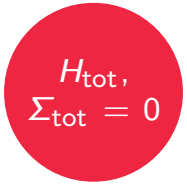

We start with the Hamiltonian of a DFT calculation:

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

and as a starting guess for the Green's function

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

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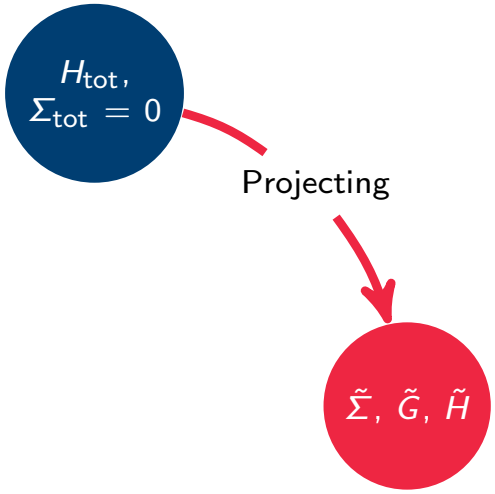

Projection onto Hubbard subspaces:

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

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

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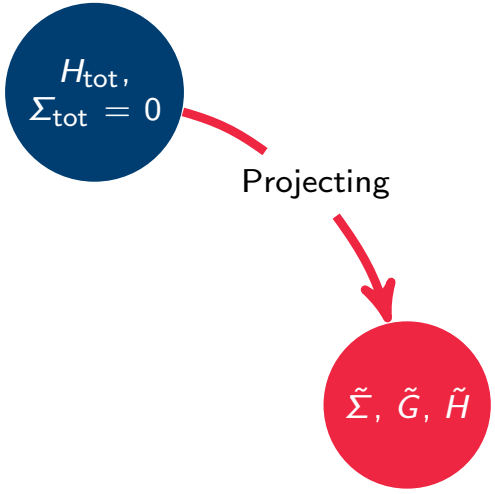

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How to consider these projected quantities while not disregarding interaction with the rest of the system? The trick: map to an Anderson Impurity Model (AIM)

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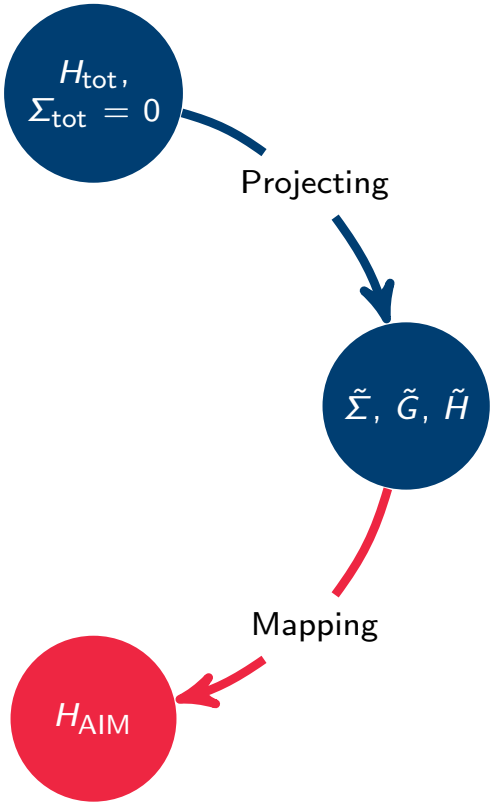
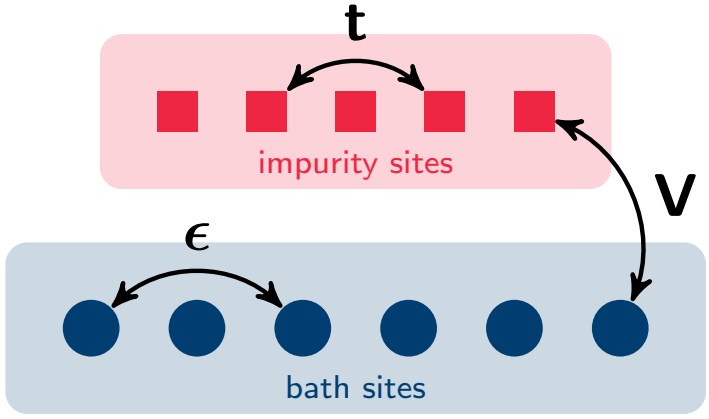
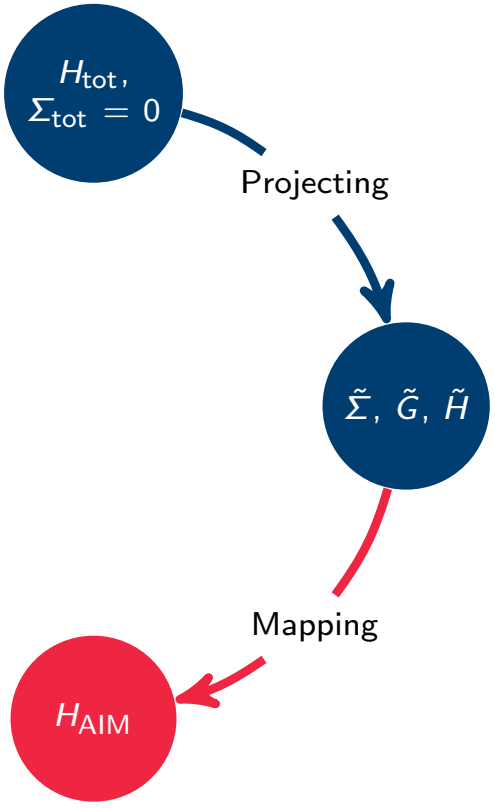
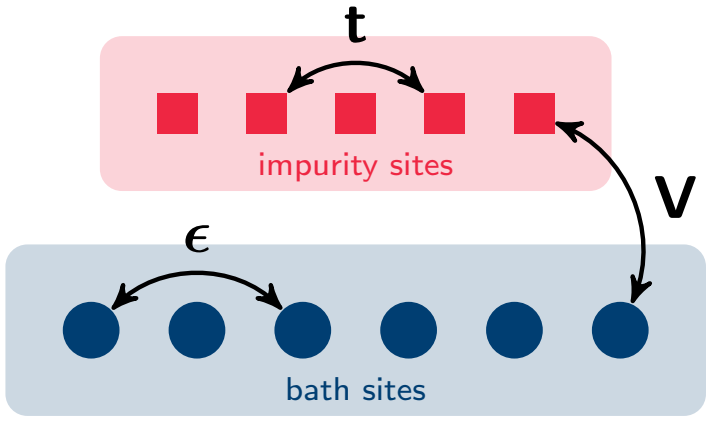




$$\hat{H}_{AIM} = \sum_{ij\sigma} (\epsilon_{ij} - \mu) c^{\dagger}_{i\sigma} c_{j\sigma}$$
$$+ \sum_{i\alpha\sigma} \left(V_{\alpha i} f^{\dagger}_{\alpha\sigma} c_{i\sigma} + h.c. \right)$$
$$+ \sum_{\alpha\beta\sigma} (t_{\alpha\beta} - \mu) f^{\dagger}_{\alpha\sigma} f_{\beta\sigma} + \hat{H}_U$$

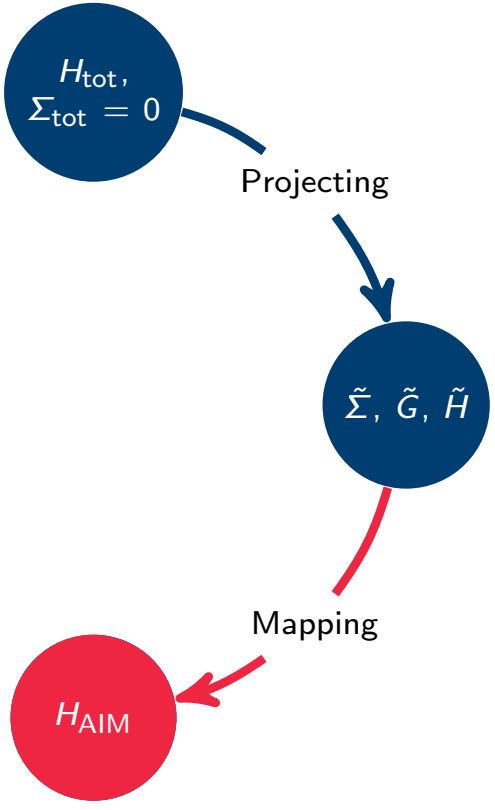
The DMFT loop

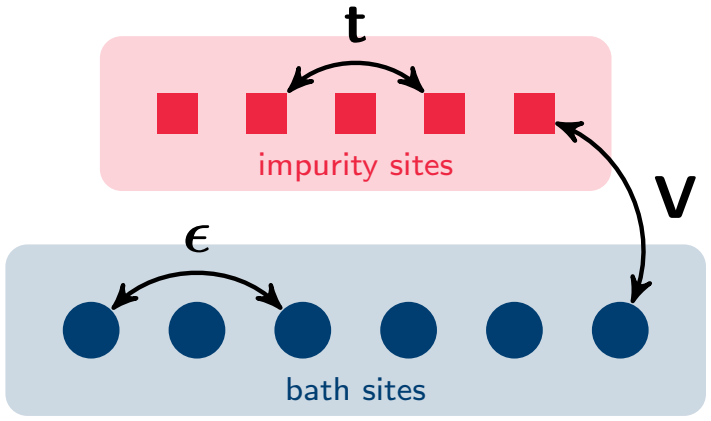




$$G_{\text{imp}}(\omega)^{-1} = \omega + \mu - \mathbf{t} - \Sigma_{\text{imp}}(\omega) \underbrace{- \mathbf{V} \frac{1}{\omega + \mu - \epsilon} \mathbf{V}^{\dagger}}_{\Delta_{\text{imp}}(\omega)}$$

The DMFT loop



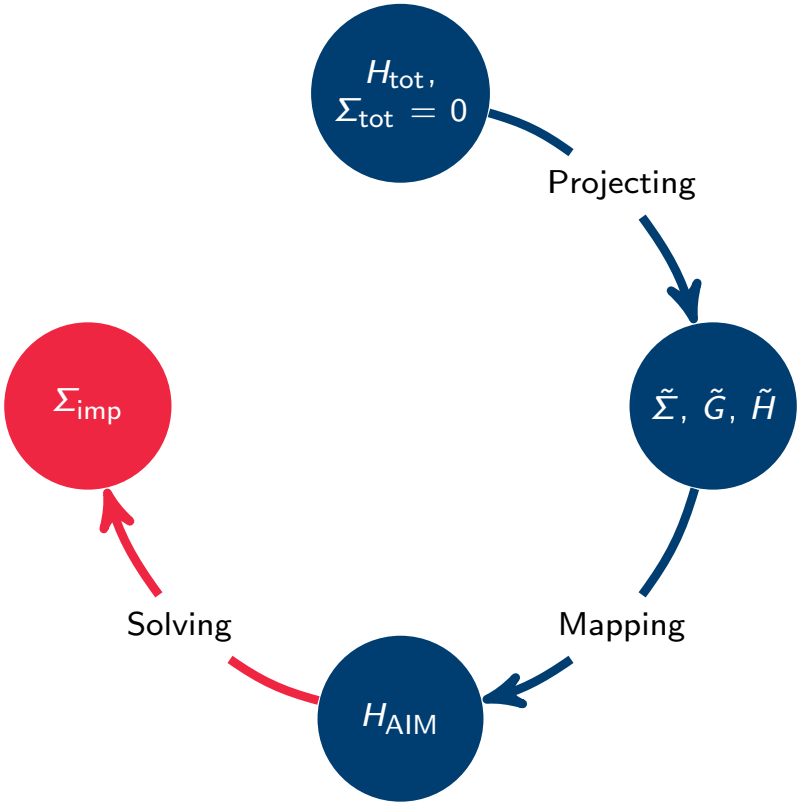


$$G_{\text{imp}}(\omega)^{-1} = \omega + \mu - \mathbf{t} - \Sigma_{\text{imp}}(\omega) \underbrace{- \mathbf{V} \frac{1}{\omega + \mu - \epsilon} \mathbf{V}^{\dagger}}_{\Delta_{\text{imp}}(\omega)}$$

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

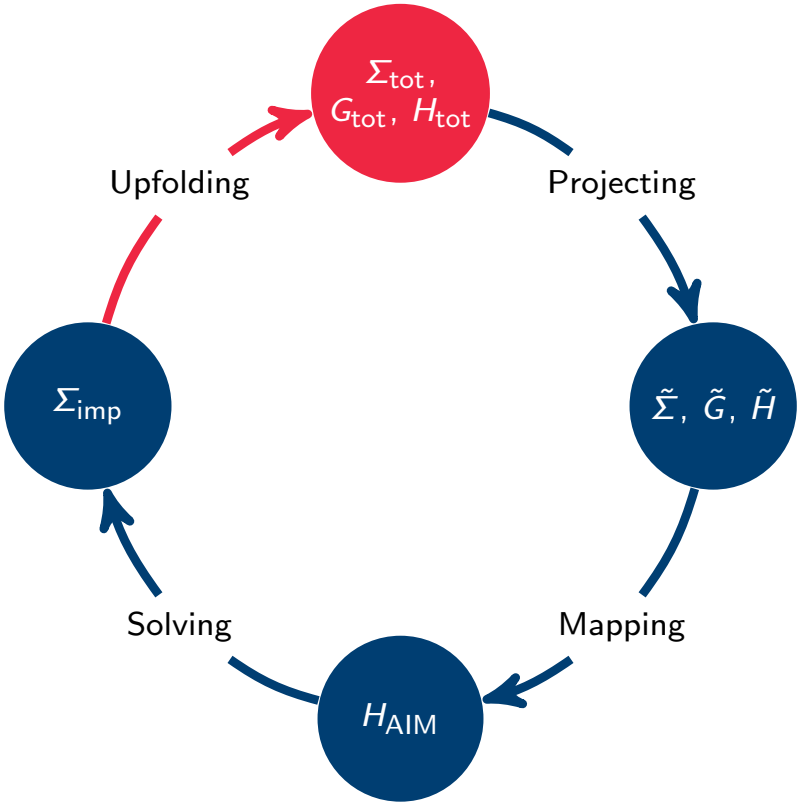
$$d(\mathbf{V}, \epsilon) = \int d\omega \left(\Delta_{imp}(\omega) - \tilde{\Delta}(\omega) \right)$$

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



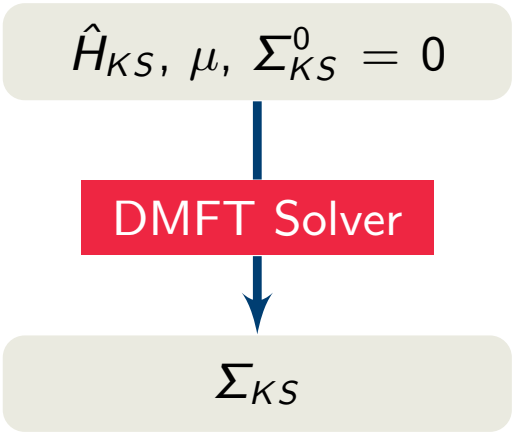
Upfolding the self-energy

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

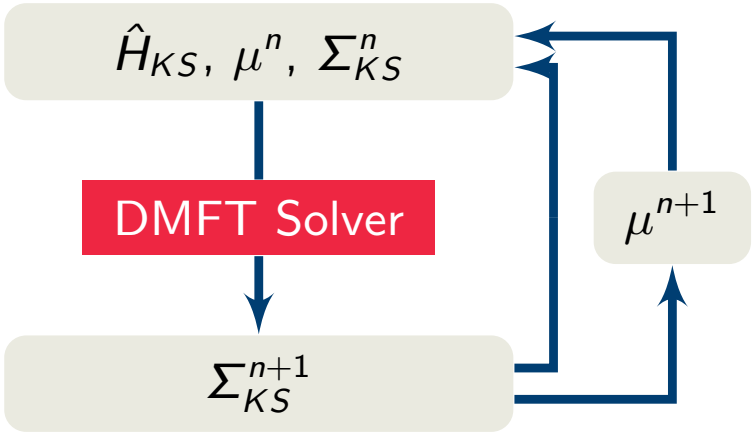
and update the Green's function

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

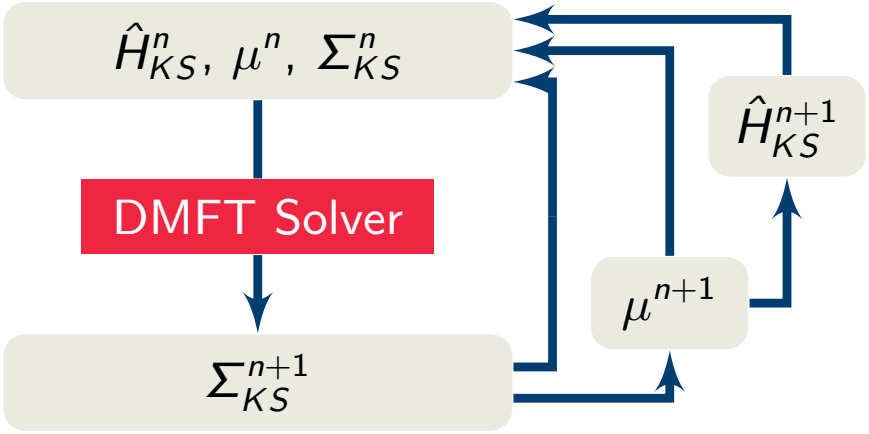
Self-consistency schemes



(a) single-shot



(b) charge self-consistent



(c) fully self-consistent

Three SC schemes, in increasing order of accuracy (and computational cost)

The interaction Hamiltonian

In the auxiliary AIM system, H_U is chosen to be of the Slater-Kanamori form:

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

where $U' = U - 2J$; $\mathbf{S}_m$ is the spin of orbital m, given by

$$(\mathbf{S}_m)_i = \frac{1}{2} \sum_{\sigma\sigma'} f^\dagger_{m\sigma} (\mathbf{s}_i)_{\sigma\sigma'} f_{m\sigma'},$$

with $\{\mathbf{s}_i\}$ being the Pauli spin matrices. U and J are user-specified parameters that in principle could be obtained via linear response.

Double-counting correction

The double-counting term (used when upfolding) is given by

$$E_{dc} = \frac{U^{av}}{2} n\,(n-1) - \frac{J}{2} \sum_{\sigma} n_{\sigma}(n_{\sigma}-1)$$

where n is the total occupancy of the subspace, and

$$U^{av} = \frac{U + 2(N-1)U'}{2N-1}$$

with N being the number of orbitals and $U' = U - 2J$. This double-counting is derived by attempting to subtract the DFT contributions in an average way; U^{av} is the average of the intra- and inter-orbital Coulomb parameters.

$$E_D^{mm'} C = E_d c O^{mm'}$$

where $O^{mm'} = \langle \varphi^m | \phi^{\alpha} \rangle S_{\alpha\beta} \langle \phi^{\beta} | \varphi^{m'} \rangle$ is the overlap matrix of the subspace NGWFs

Mixed quantum spin states

The reduced density matrix is defined as

$$\hat{\rho} = \sum_i e^{-\beta E_i} \mathrm{Tr}_{\mathrm{bath}} \left[|i\rangle\langle i| \right]$$

The eigenvectors of $\hat{\rho}$ provide a description of the many-body states of the impurity subspace
The eigenvalues λ_k are normalised weights ($\sum_k \lambda_k = 1$), and the von Neumann entropy is

$$\Lambda = -k_B \sum_k \lambda_k ln(\lambda_k)$$