An introduction to core-level spectroscopy with hands-on exercises

x-ray absorption spectroscopy, x-ray photoemission spectroscopy and (non)-resonant inelastic x-ray scattering

Johan Schött

Division of Materials Theory
Department of Physics and Astronomy
Uppsala University

18th January, 2019

Outline

- Introduction: Many body to single particle physics
- Theoretical x-ray spectroscopy: DFT+MLFT
- XAS results for several TMOs
- Outlook

coffee break

- Hands-on tutorial: calculate core-level spectra (e.g. XAS, RIXS)

X-ray spectroscopies

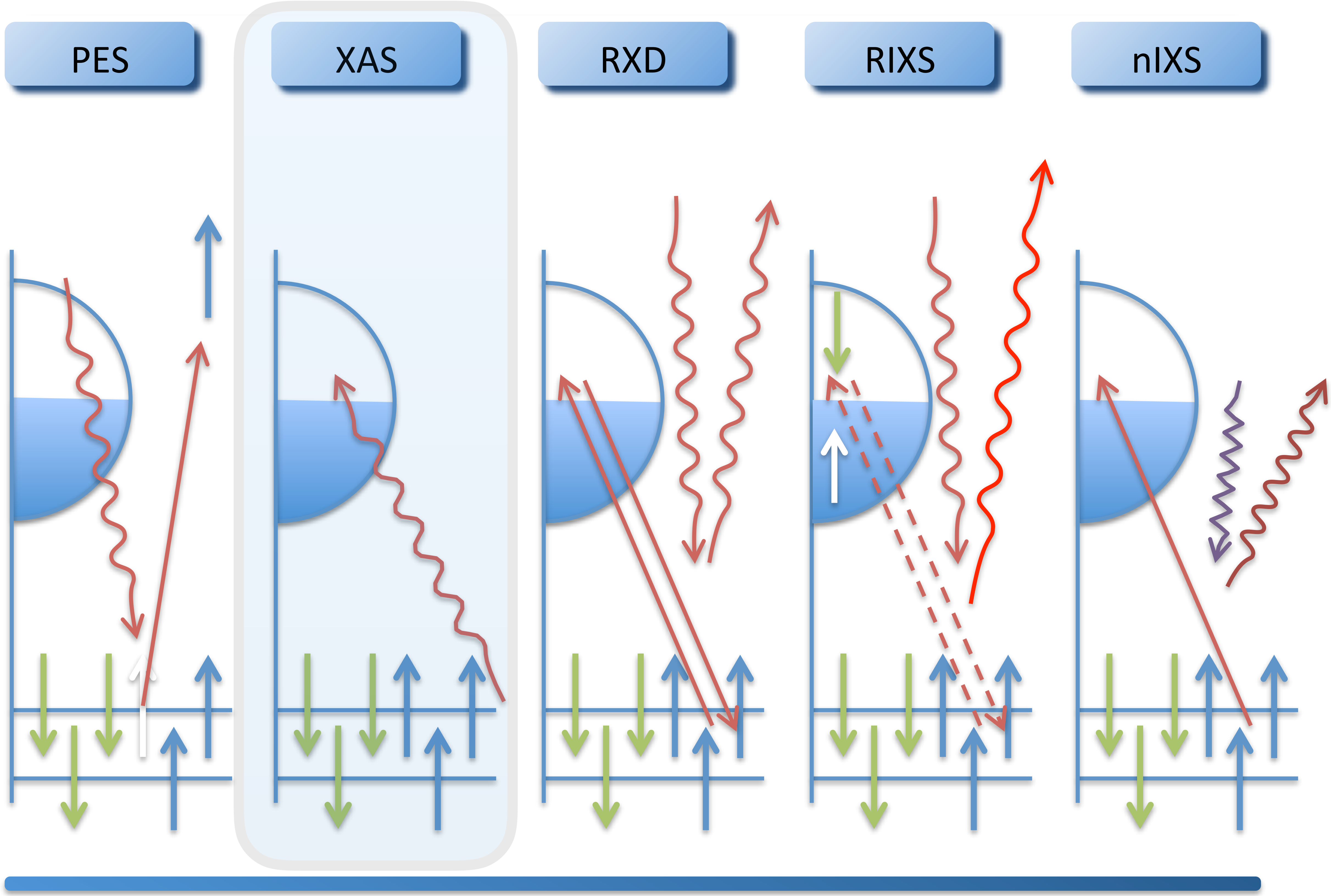


figure by M. Haverkort

Energy resolution

La_2CuO_4
Cu 2*p* → 3*d*
Photon energy ~ 931 eV

ΔE ~1.6 eV

K. Ichikawa *et al.*, J. Electron Spectrosc. Relat. Phenom.**78**, 183 (1996).

ΔE ~1.2 eV

L. C. Duda *et al.*, J. Electron Spectrosc. Relat. Phenom. **110–111**, 275 (2000).

ΔE ~0.8 eV

AXES @ ID08, 2003. G. Ghiringhelli *et al.*, Phys Rev Lett. **92**, 117406 (2004).

ΔE ~0.45 eV

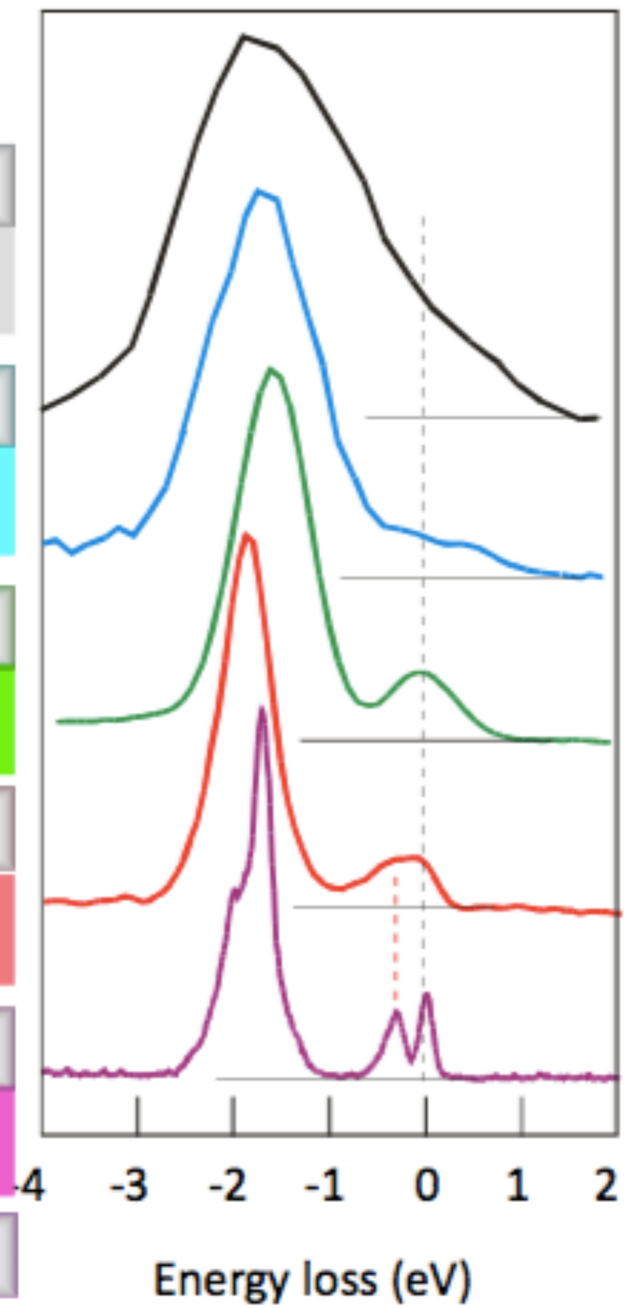
AXES @ ID08, 2007. L. Braicovich *et al.*, arXiv:0807:1140v1, (2008).

ΔE ~0.13 eV

SAXES @ SLS, 2008. G. Ghiringhelli, L. Braicovich, T. Schmit *et al.*, unpublished

ΔE ~0.050 eV

ΔE ~0.030 eV



2000	Uppsala
2003	ESRF + AXES
2007	ESRF + AXES
2008	SLS + SAXES
2015	ESRF + ERIXS
2016	ESRF + ERIXS

Increased resolution by a factor 30 in 20 years!

figure by G. Ghiringhelli

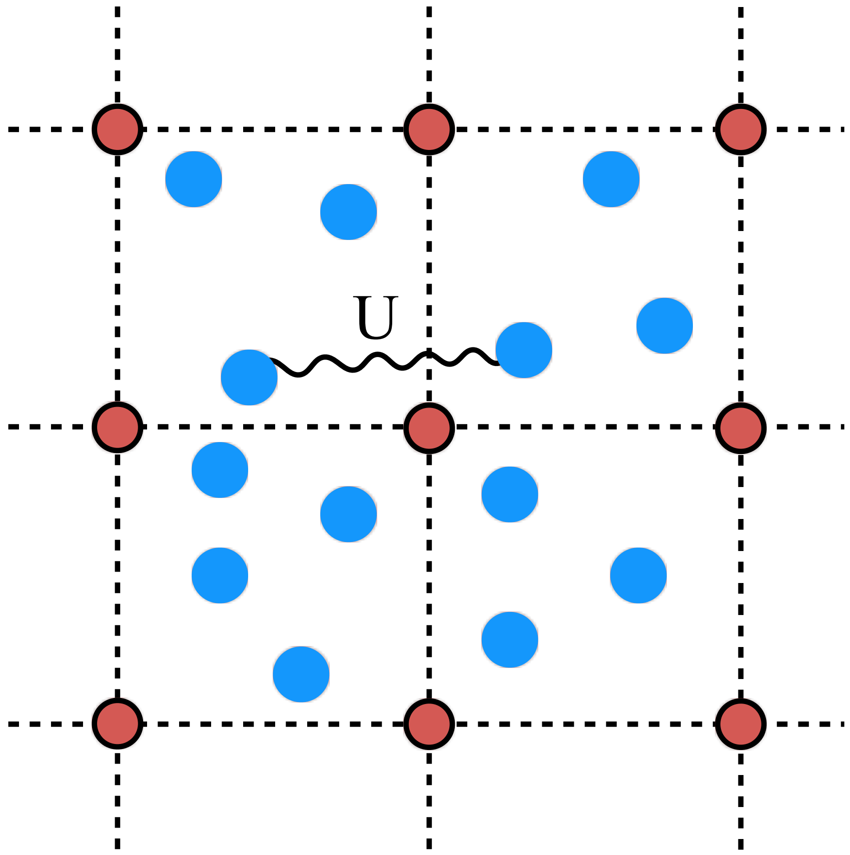
AXES: **2.2 m**
(2005)

SAXES, SLS: **5 m**
(2008)

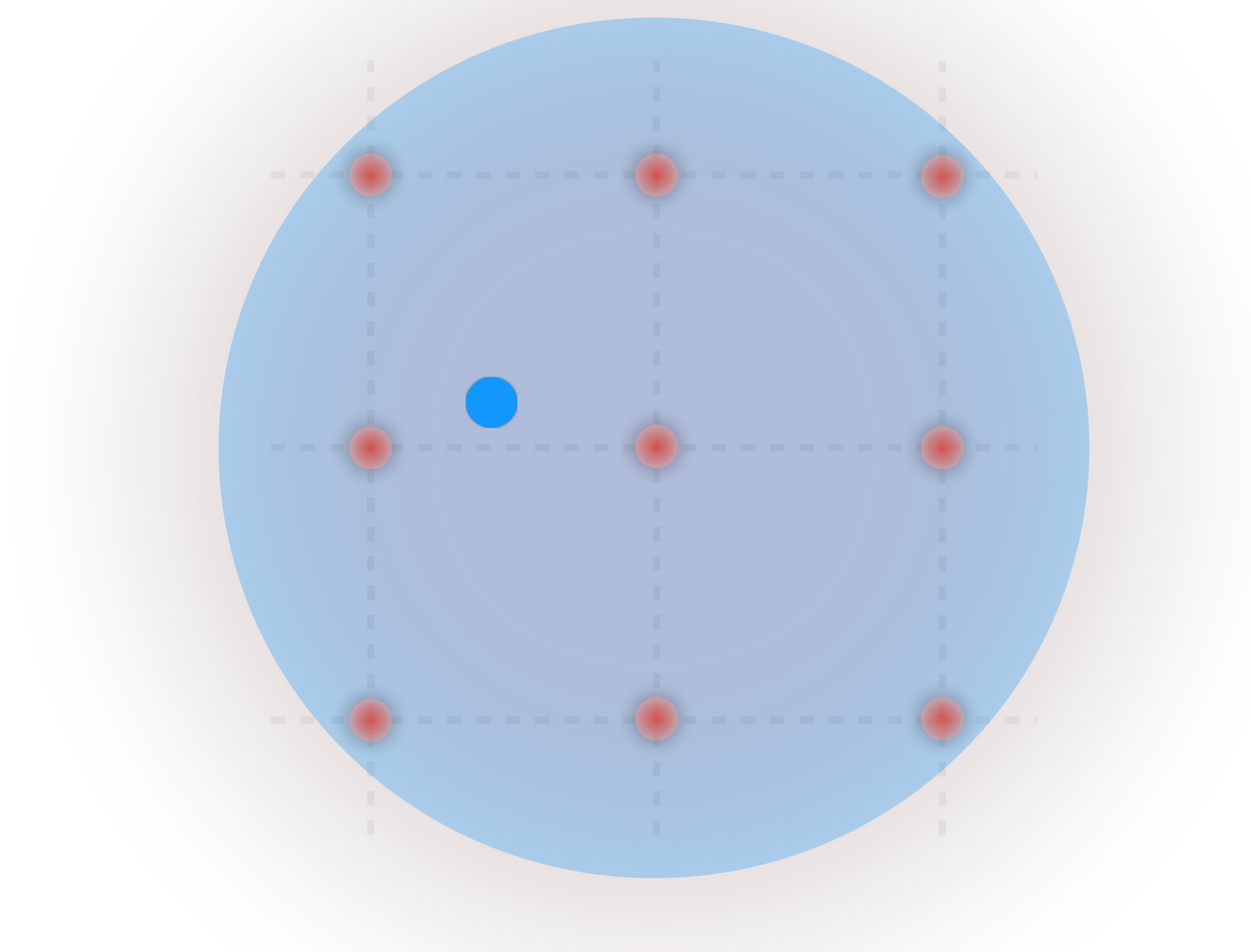
(2015)
ERIXS, ID32: **10 m**

Introduction: From many-body to single particle

Many-Body perspective



Density perspective



$$\hat{H} = \sum_{ij,\sigma} t_{ij} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + \frac{1}{2} \sum_{ijkl,\sigma\sigma'} U_{ijkl} \hat{c}^{\dagger}_{i,\sigma} \hat{c}^{\dagger}_{j,\sigma'} \hat{c}_{k,\sigma'} \hat{c}_{l,\sigma}$$

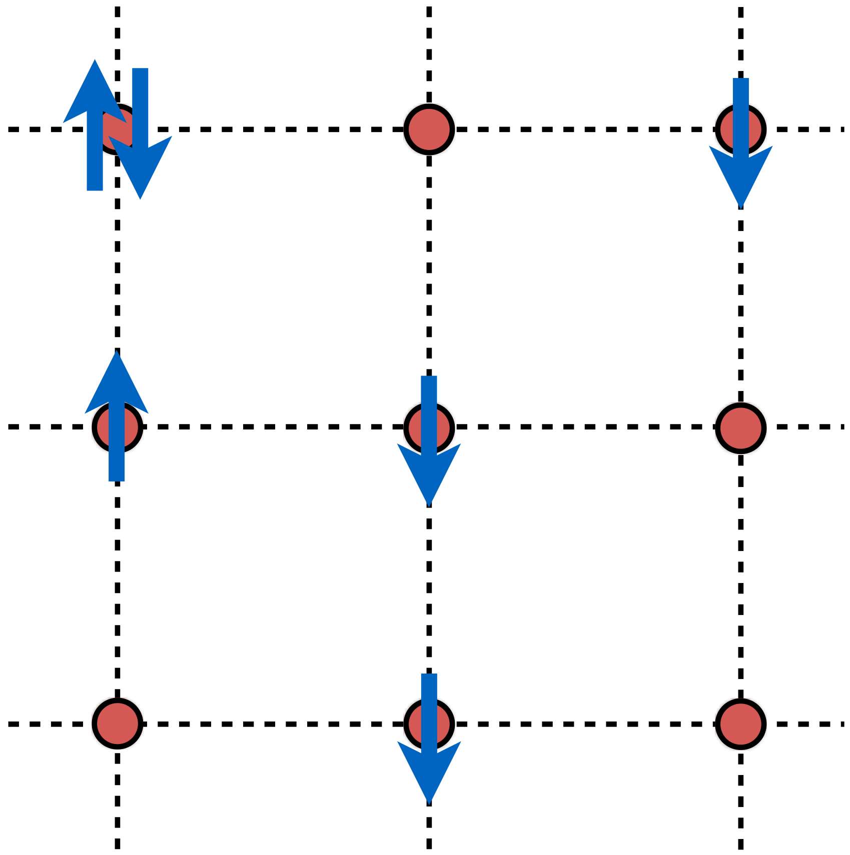
$$\hat{H}^{\mathrm{KS}} = \sum_{ij,\sigma} t^{\mathrm{KS}}_{ij} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma}$$

$$t_{ij} = \int d^3 r \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + V_{\mathrm{ext.}}(\mathbf{r}) \right) \psi_j(\mathbf{r})$$

$$t^{\mathrm{KS}}_{ij} = \int d^3 r \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 + V_{\mathrm{eff.}}(\mathbf{r}) \right) \psi_j(\mathbf{r})$$

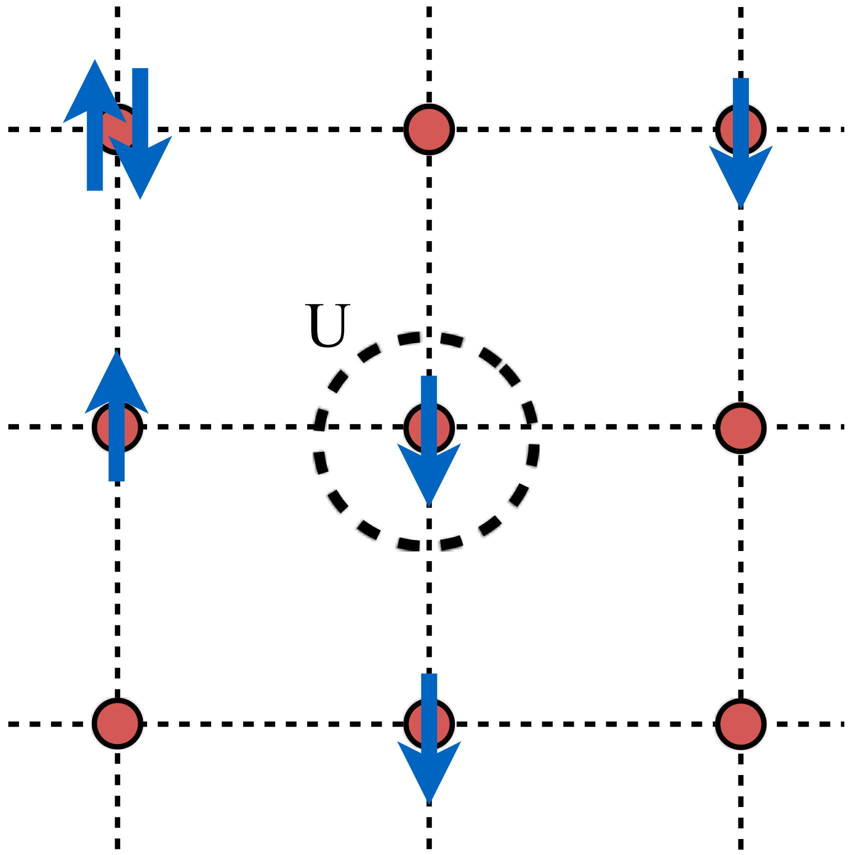
Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT}$$



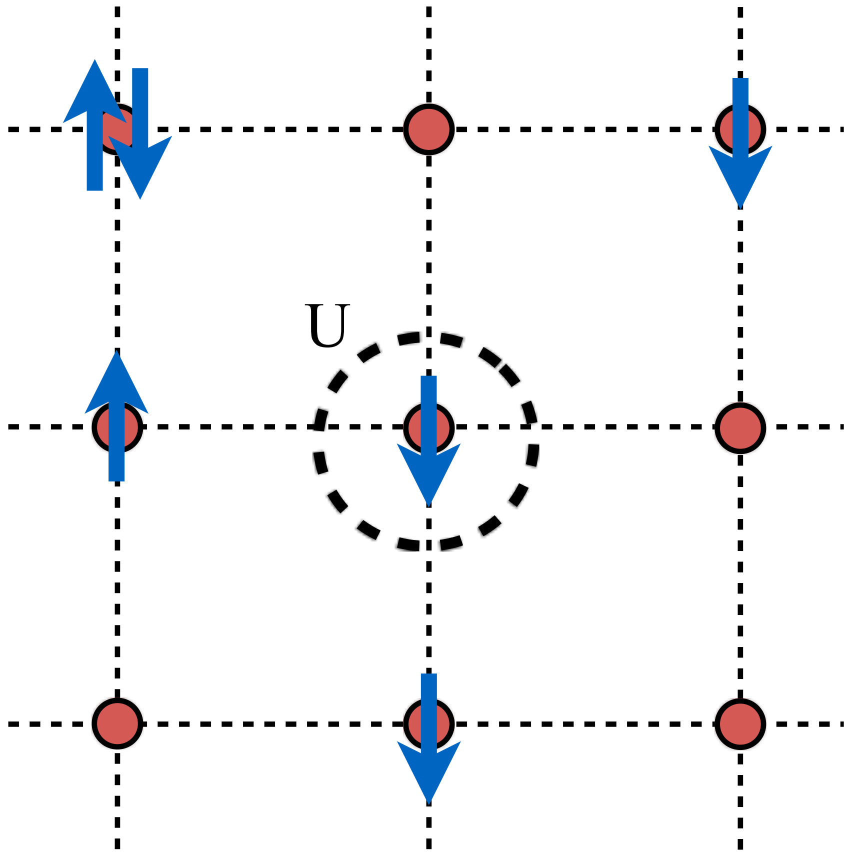
Introduction: Beyond DFT using DFT+MLFT

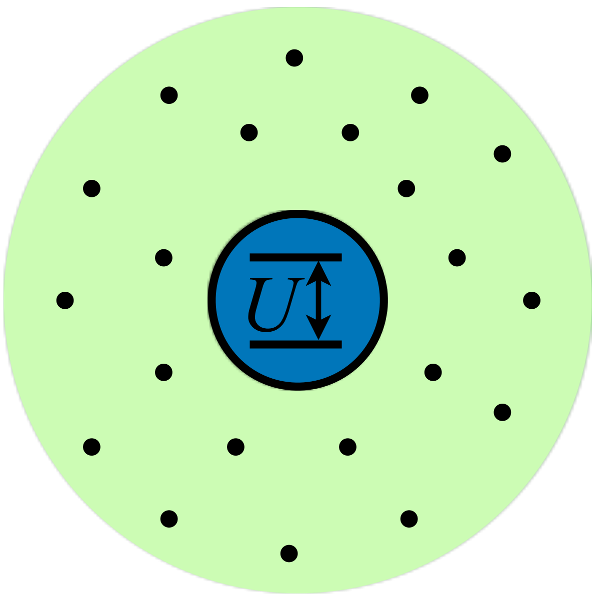
$$H = H_{DFT} + H_U - H_{DC}$$



Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT} + H_U - H_{DC}$$

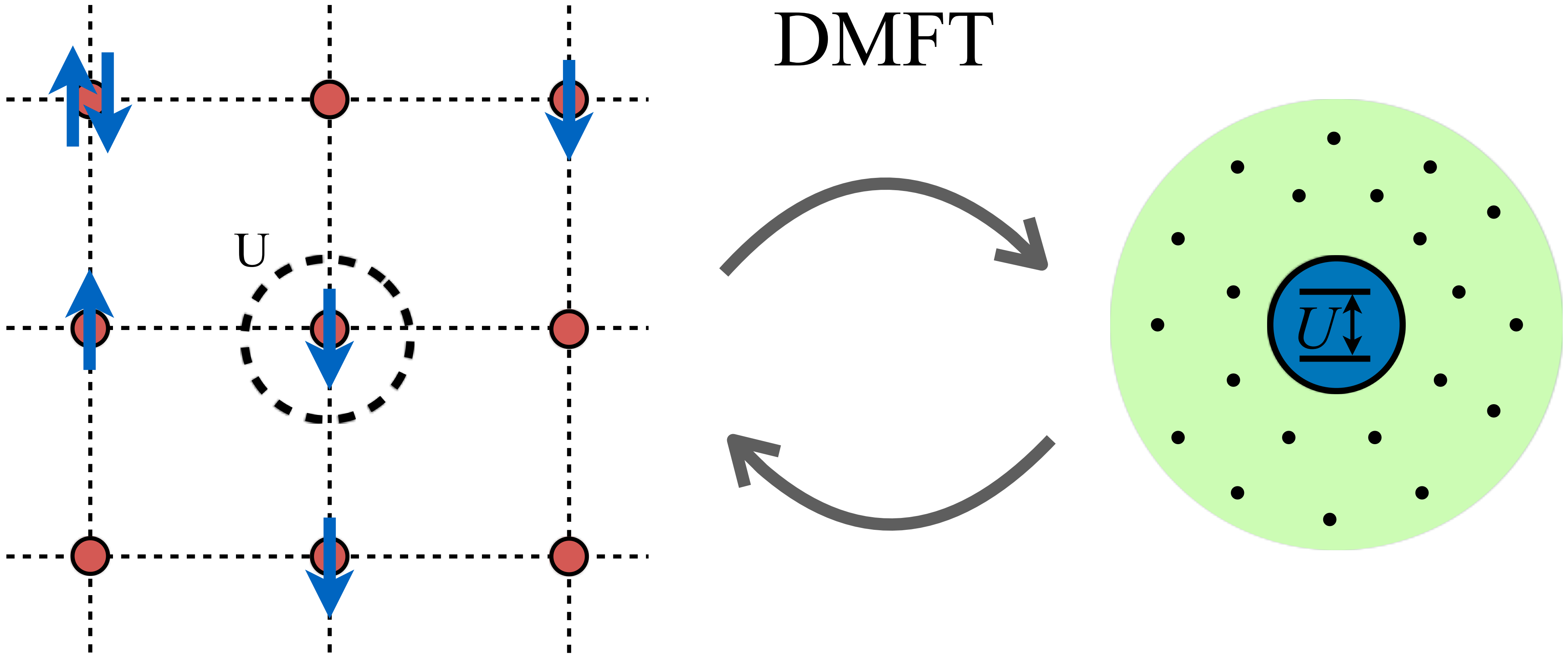




Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT} + H_U - H_{DC}$$

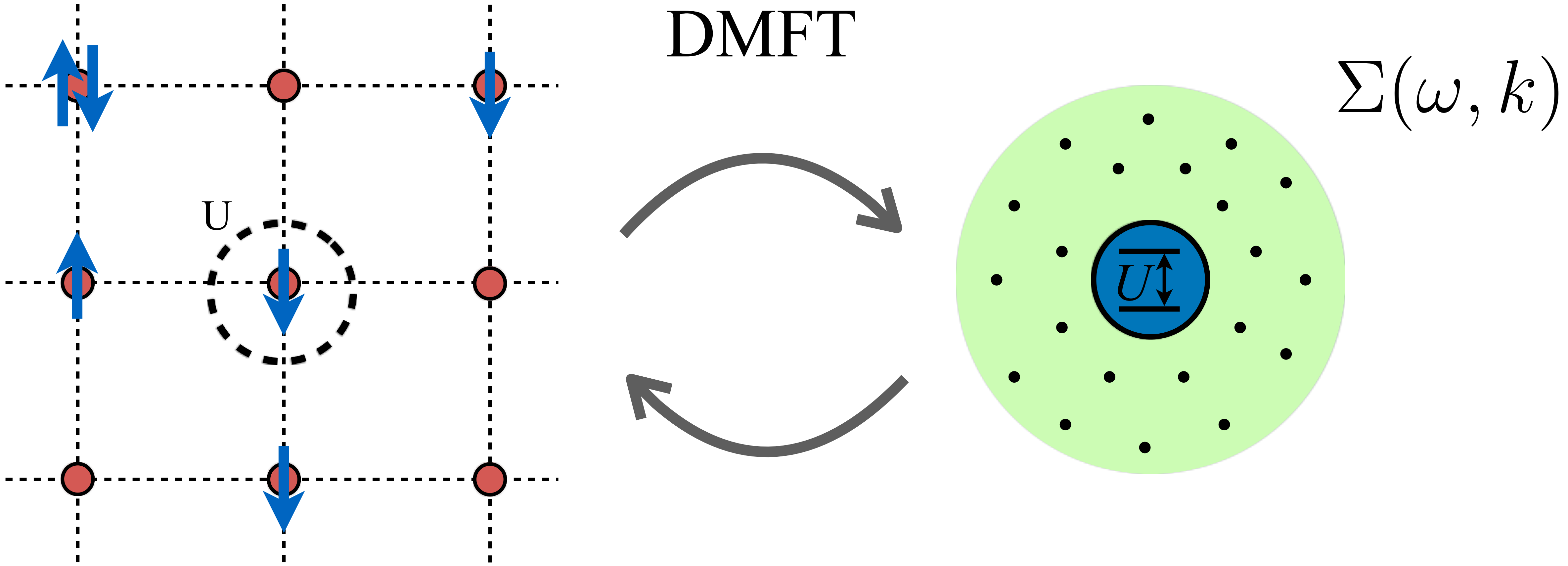
DMFT



Introduction: Beyond DFT using DFT+MLFT

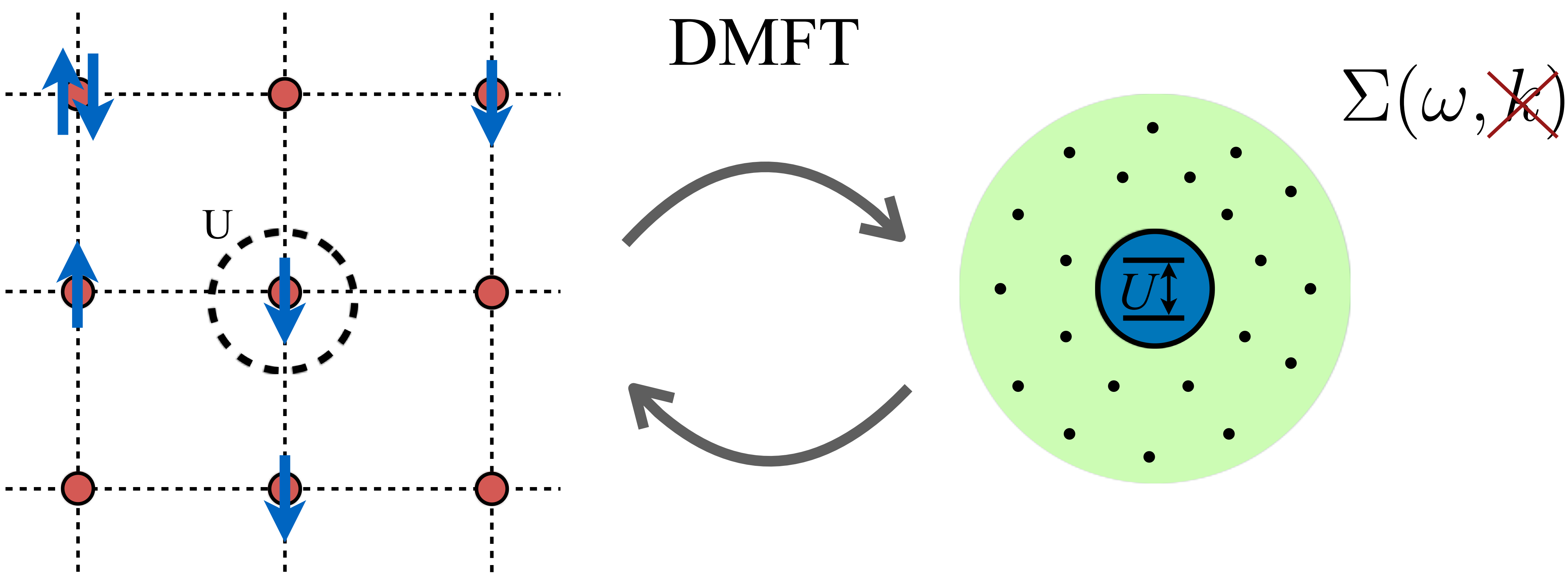
$$H = H_{DFT} + H_U - H_{DC}$$

DMFT



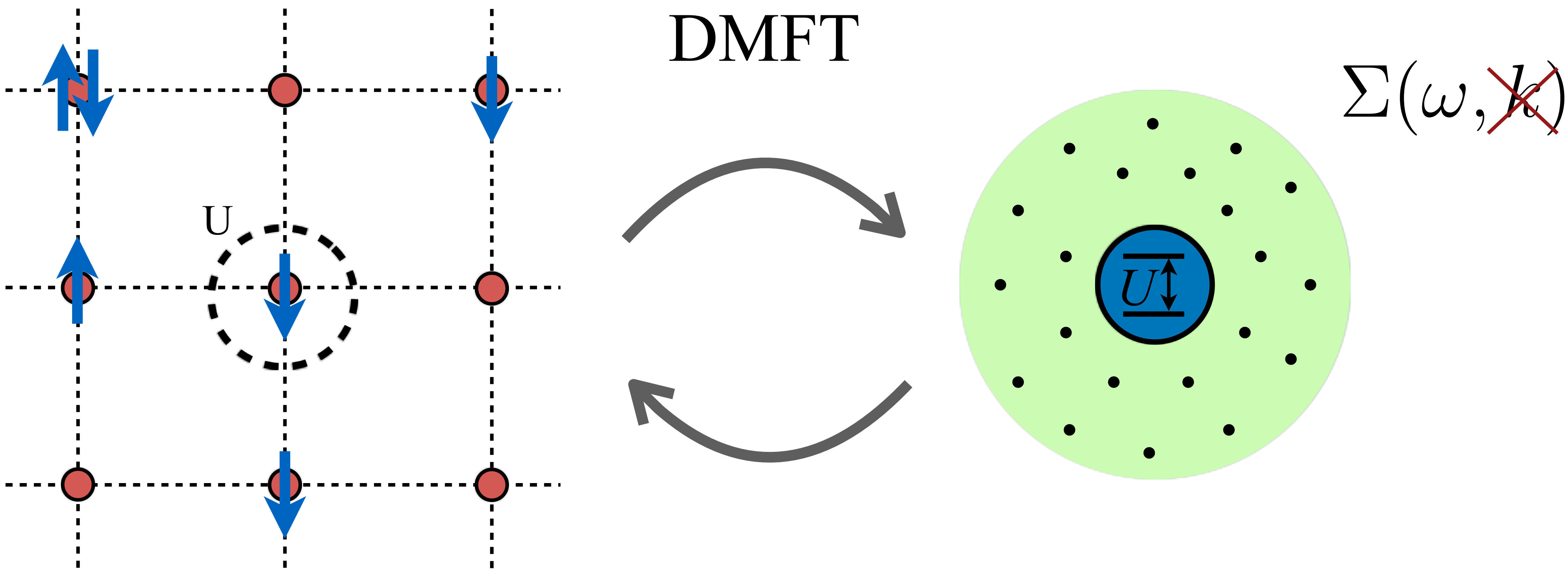
Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT} + H_U - H_{DC}$$



Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT} + H_U - H_{DC}$$

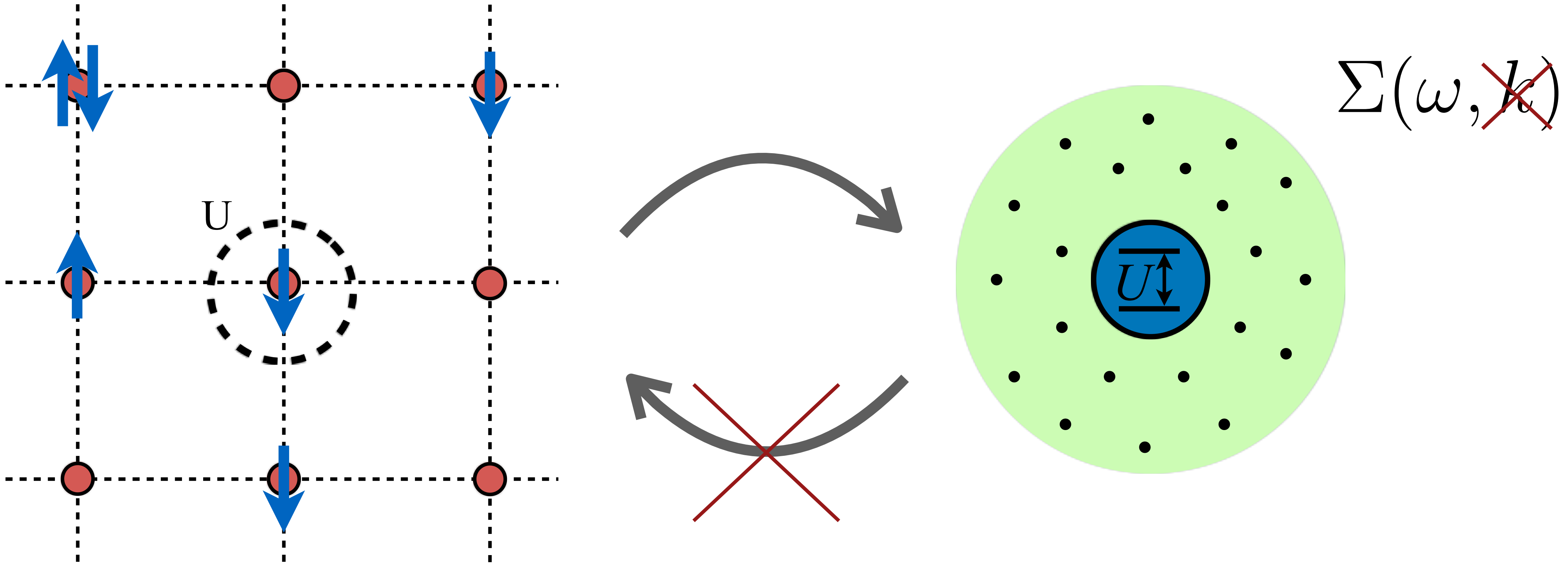


Impurity solvers:

- Exact diagonalization (ED)
- QMC
- “Hartree-Fock”

Introduction: Beyond DFT using DFT+MLFT

$$H = H_{DFT} + H_U - H_{DC}$$

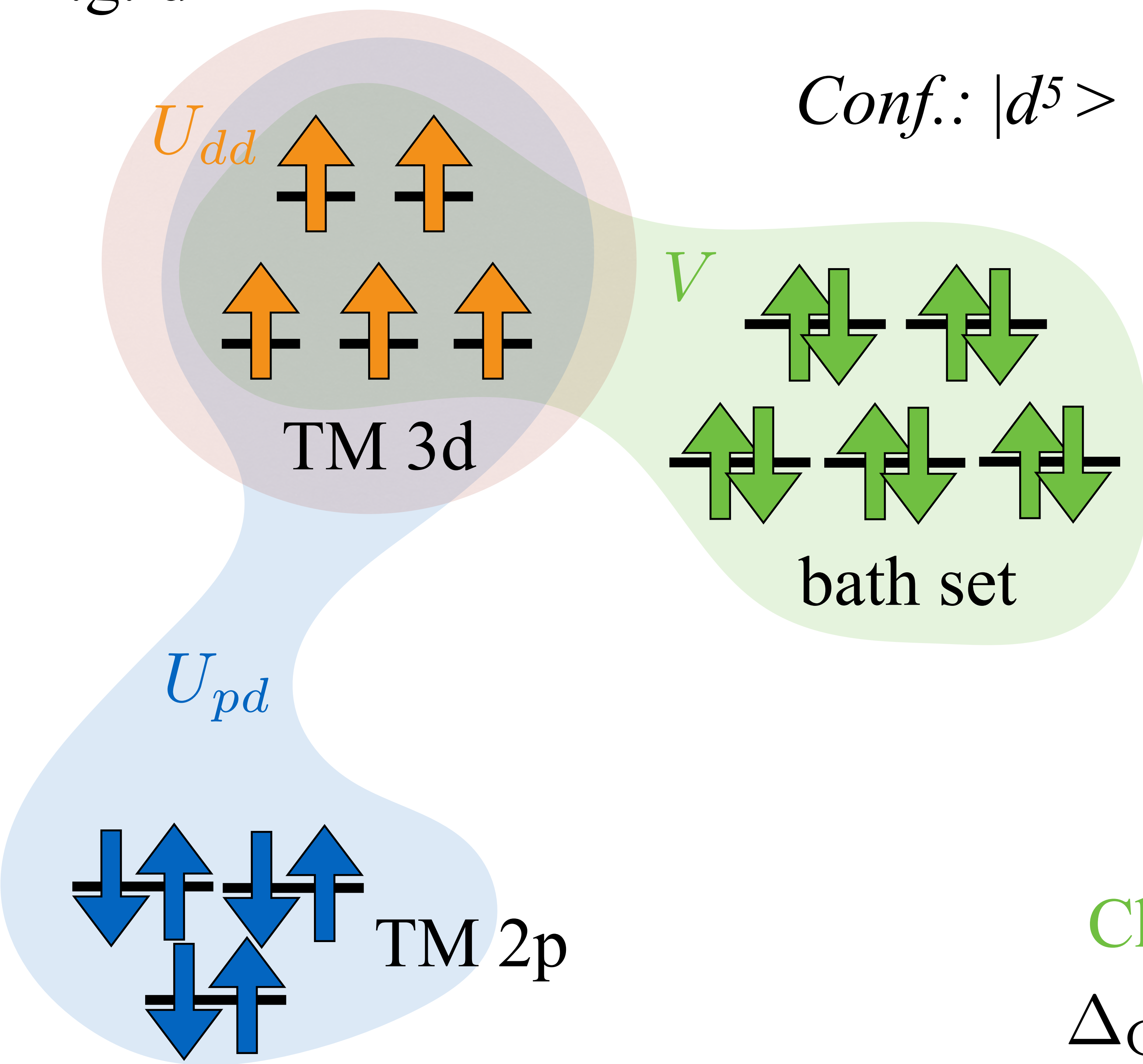


Impurity solvers:
- Exact diagonalization (ED)
- QMC
- "Hartree-Fock"

Multiplet Ligand Field Theory

E.g. d^5

$Conf.: |d^5> \quad + \quad |d^6 \underline{L}> \quad + \quad |d^7 \underline{L}^2>$



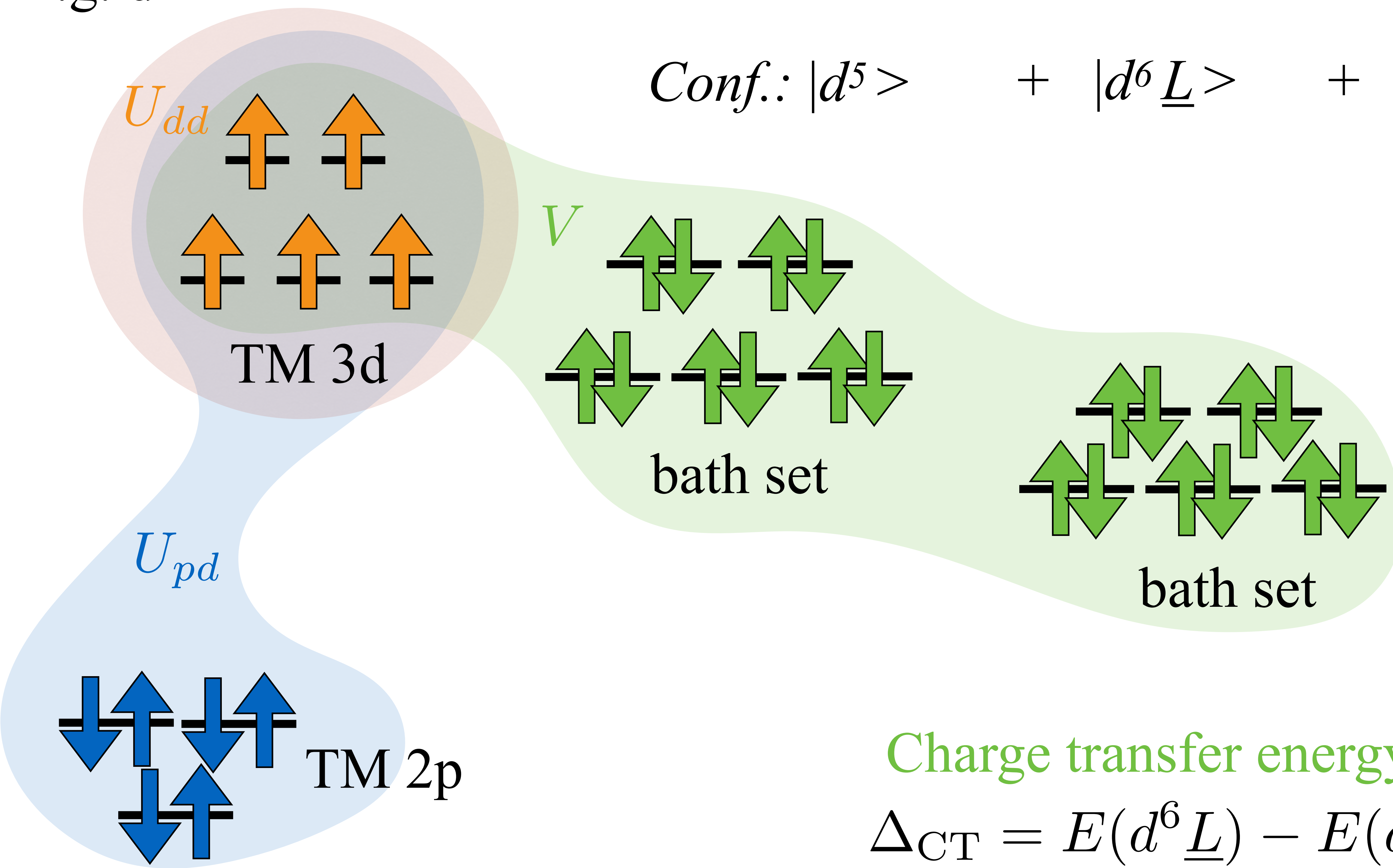
Charge transfer energy:

$$\Delta_{\mathrm{CT}} = E(d^6 \underline{L}) - E(d^5)$$

Multiplet Ligand Field Theory

E.g. d^5

$Conf.: |d^5> \quad + \quad |d^6\,\underline{L}> \quad + \quad |d^7\,\underline{L}^2>$



Charge transfer energy:

$$\Delta_{\mathrm{CT}} = E(d^6\underline{L}) - E(d^5)$$

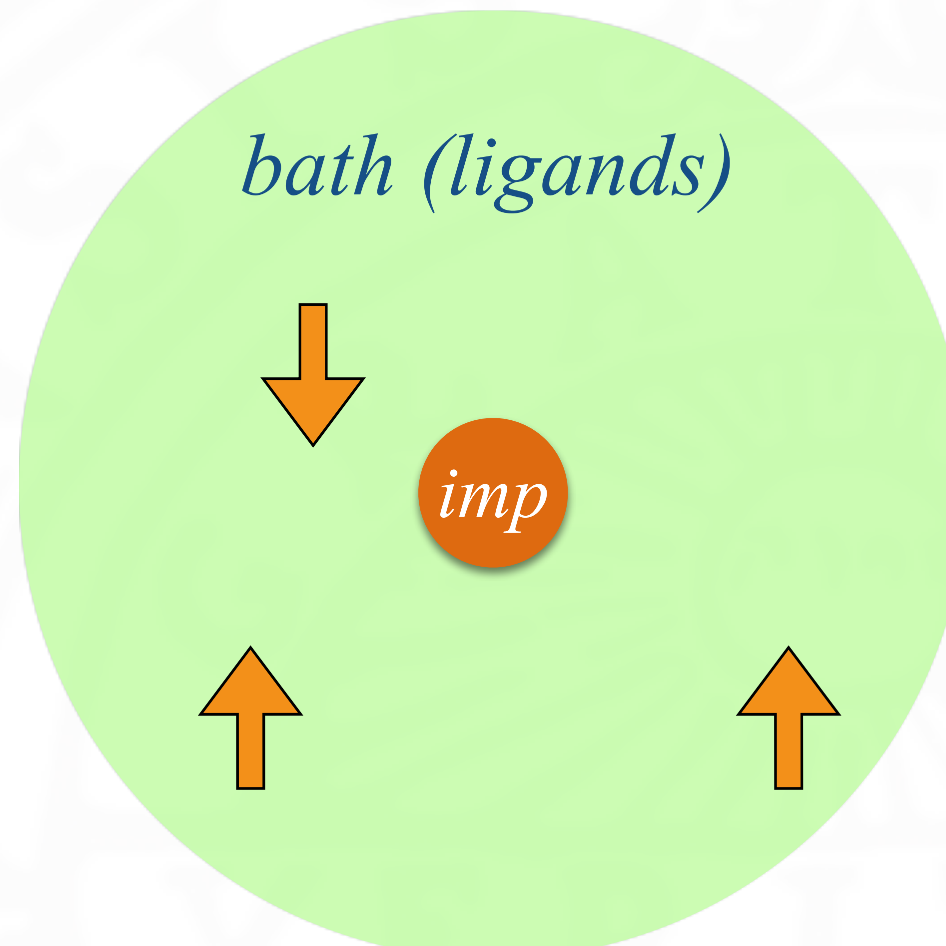
Anderson Impurity Model

Use DFT to parameterize Hamiltonian

$$\left.\begin{aligned}\hat{H} = \sum_{i,j} t_{i,j}\hat{d}_i^\dagger \hat{d}_j + \sum_i \epsilon_{b_i}\hat{b}_i^\dagger \hat{b}_i + \sum_{i,j} \epsilon_{p_{i,j}}\hat{p}_i^\dagger \hat{p}_j \\ + \sum_{i,j} V_{i,j}(\hat{d}_i^\dagger \hat{b}_j + \text{h.c.})\end{aligned}\right\} \hat{H}_0$$

$$+\hat{H}_U^{dd} + \hat{H}_U^{pd}$$

$$\hat{H}|n\rangle = E_n|n\rangle$$

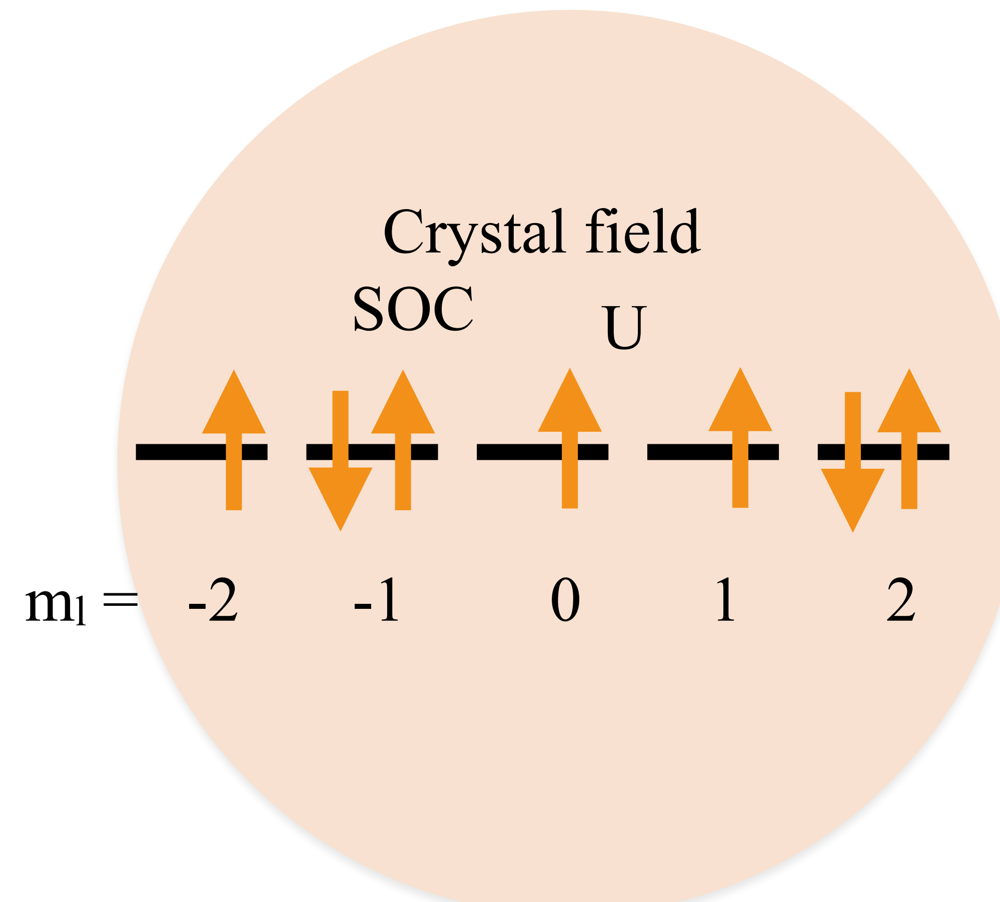


Anderson Impurity Model

Use DFT to parameterize Hamiltonian

$$\left.\begin{aligned}\hat{H} = &\sum_{i,j} t_{i,j}\hat{d}_i^\dagger \hat{d}_j + \sum_i \epsilon_{b_i}\hat{b}_i^\dagger \hat{b}_i + \sum_{i,j}\epsilon_{p_{i,j}}\hat{p}_i^\dagger \hat{p}_j \\ &+ \sum_{i,j} V_{i,j}(\hat{d}_i^\dagger \hat{b}_j + \text{h.c.})\end{aligned}\right\} \hat{H}_0$$

$$+\hat{H}_U^{dd} + \hat{H}_U^{pd}$$



$$\hat{H}|n\rangle = E_n|n\rangle$$

$$I(\omega) = \frac{1}{Z}\sum_n -\frac{1}{\pi}\text{Im}\, G^{(n)}(\omega + i\delta) \times \exp(-\beta E_n)$$

$$G^{(n)}(\omega + i\delta) = \langle n|\hat{T}^\dagger \frac{1}{\tilde{\omega}\hat{1} - \hat{H}}\hat{T}|n\rangle \quad \text{with} \quad \tilde{\omega} = \omega + i\delta + E_n$$

Calculate core-level spectroscopy

Many body basis: product states (PS)

E.g. $$|\mathrm{PS}_j\rangle = |\underbrace{0\ 1\ 2\ 3\ 4\ 5}_{\mathrm{TM2p}}, \underbrace{6\ 9\ 10\ 11\ 12}_{\mathrm{TM3d}}, \underbrace{16\ 17\ 18 \ldots 25}_{\mathrm{bath}}\rangle$$

$$\hat{H}|\mathrm{PS}_j\rangle = \sum_n \hat{H}_n |\mathrm{PS}_j\rangle = \sum_i H_{i,j} |\mathrm{PS}_i\rangle$$

$$H = \begin{array}{cc} & j=0 \\ \begin{array}{r} \\ \\ \\ \\ i=324 \\ \\ \\ \end{array} & \left[\begin{array}{c|c|c} H_{0,0} & & \\ 0 & & \\ \vdots & & \\ 0 & \cdots & \\ H_{324,0} & & \\ 0 & & \\ \vdots & & \end{array}\right]_{d \times d} \end{array}$$

extremely sparse

$d = \#\mathrm{PS}$

Calculate core-level spectroscopy

Computational aspects: Hamiltonian **basis size** (of ground state)

NiO using **one** bath set (1 bath orbital per impurity orbital):

$$d = \binom{10}{8}\binom{10}{10} + \binom{10}{9}\binom{10}{9} + \binom{10}{10}\binom{10}{8} = 45 \cdot 1 + 10 \cdot 10 + 1 \cdot 45 = 190$$

CoO using **one** bath set (1 bath orbital per impurity orbital):

$$d = \binom{10}{7}\binom{10}{10} + \binom{10}{8}\binom{10}{9} + \binom{10}{9}\binom{10}{8} = 120 \cdot 1 + 45 \cdot 10 + 10 \cdot 45 = 1020$$

CoO using **10** bath sets (10 bath orbital per impurity orbital):

$$d = \binom{10}{7}\binom{100}{100} + \binom{10}{8}\binom{100}{99} + \binom{10}{9}\binom{100}{98} = 120 \cdot 1 + 45 \cdot 100 + 10 \cdot 4950 = 54120$$

Calculate core-level spectroscopy

Lanczos iterative algorithm

$$H_{\text{krylov}} = \begin{bmatrix} \alpha_0 & \beta_0 & 0 & 0 & 0 \\ \beta_0 & \alpha_1 & \beta_1 & 0 & 0 \\ 0 & \beta_1 & \alpha_2 & \ddots & 0 \\ 0 & 0 & \ddots & \ddots & \beta_{m-2} \\ 0 & 0 & 0 & \beta_{m-2} & \alpha_{m-1} \end{bmatrix}_{m \times m} \qquad m \ll d$$

Diagonalize tridiagonal matrix

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$I(\omega) = \frac{1}{Z}\sum_n -\frac{1}{\pi}\mathrm{Im}\, G^{(n)}(\omega + i\delta) \times \exp(-\beta E_n)$$

$$G^{(n)}(\omega + i\delta) = \langle n|\hat{T}^\dagger \frac{1}{\tilde{\omega}\hat{1} - \hat{H}}\hat{T}|n\rangle \quad \text{with} \quad \tilde{\omega} = \omega + i\delta + E_n$$

Calculate core-level spectroscopy

Lanczos iterative algorithm

$$H_{\text{krylov}} = \begin{bmatrix} \alpha_0 & \beta_0 & 0 & 0 & 0 \\ \beta_0 & \alpha_1 & \beta_1 & 0 & 0 \\ 0 & \beta_1 & \alpha_2 & \ddots & 0 \\ 0 & 0 & \ddots & \ddots & \beta_{m-2} \\ 0 & 0 & 0 & \beta_{m-2} & \alpha_{m-1} \end{bmatrix}_{m \times m} \qquad m \ll d$$

Diagonalize tridiagonal matrix

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$I(\omega) = \frac{1}{Z}\sum_n -\frac{1}{\pi}\text{Im}\, G^{(n)}(\omega + i\delta) \times \exp(-\beta E_n)$$

$$G^{(n)}(\omega + i\delta) = \langle n'|\frac{1}{\tilde{\omega}\hat{1} - \hat{H}}|n'\rangle \qquad \text{with} \qquad \tilde{\omega} = \omega + i\delta + E_n$$

$$|n'\rangle = \hat{T}|n\rangle$$

Calculate core-level spectroscopy

Lanczos iterative algorithm

$$H_{\text{krylov}} = \begin{bmatrix} \alpha_0 & \beta_0 & 0 & 0 & 0 \\ \beta_0 & \alpha_1 & \beta_1 & 0 & 0 \\ 0 & \beta_1 & \alpha_2 & \ddots & 0 \\ 0 & 0 & \ddots & \ddots & \beta_{m-2} \\ 0 & 0 & 0 & \beta_{m-2} & \alpha_{m-1} \end{bmatrix}_{m \times m}$$

$$m \ll d$$

Diagonalize tridiagonal matrix

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$I(\omega) = \frac{1}{Z}\sum_n -\frac{1}{\pi}\mathrm{Im}\, G^{(n)}(\omega + i\delta) \times \exp(-\beta E_n)$$

$$G^{(n)}(\omega + i\delta) = \langle n'|\frac{1}{\tilde{\omega}\hat{1} - \hat{H}}|n'\rangle$$

with $\tilde{\omega} = \omega + i\delta + E_n$

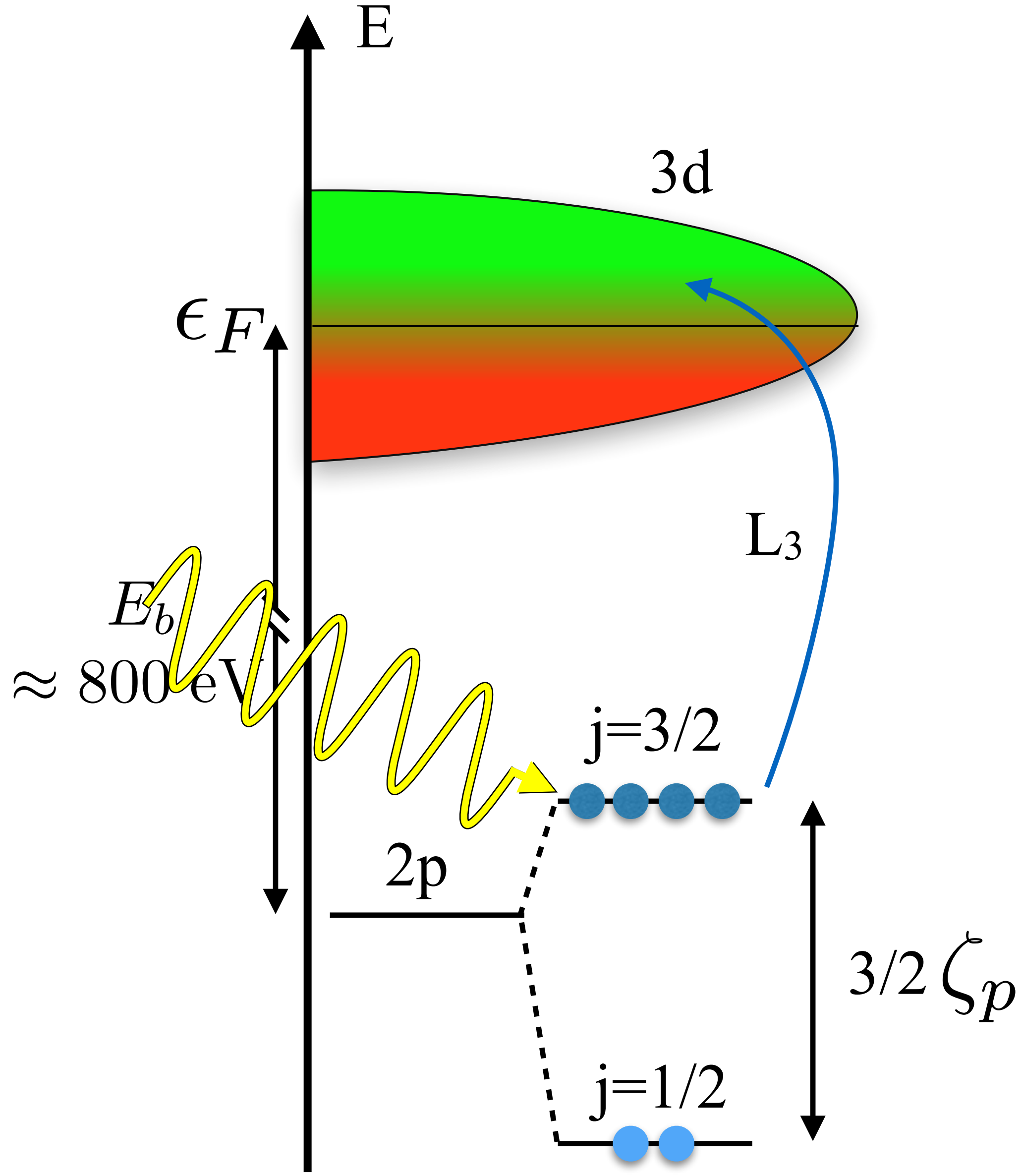
$|n'\rangle = \hat{T}|n\rangle$

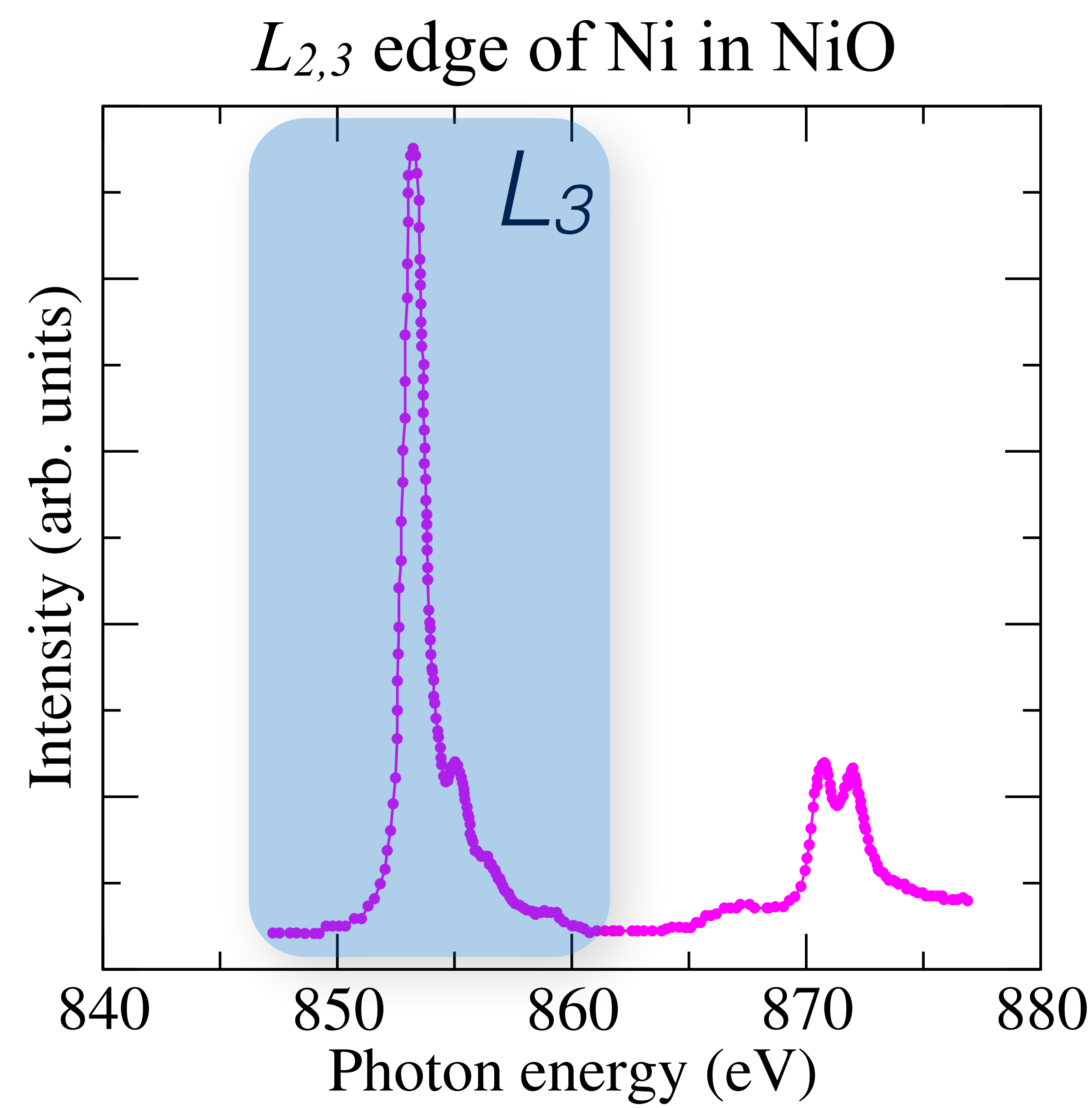
Continued fraction:

$$G^{(n)}(\omega + i\delta) \propto \frac{1}{\tilde{\omega} - \alpha_0 - \frac{\beta_0^2}{\tilde{\omega} - \alpha_1 - \frac{\beta_1^2}{\tilde{\omega} - \alpha_2 \cdots}}}.$$

XAS $L_{2,3}$-edges of 3d metal systems

- ☑ Element selective
- ☑ Direct information about 3d states

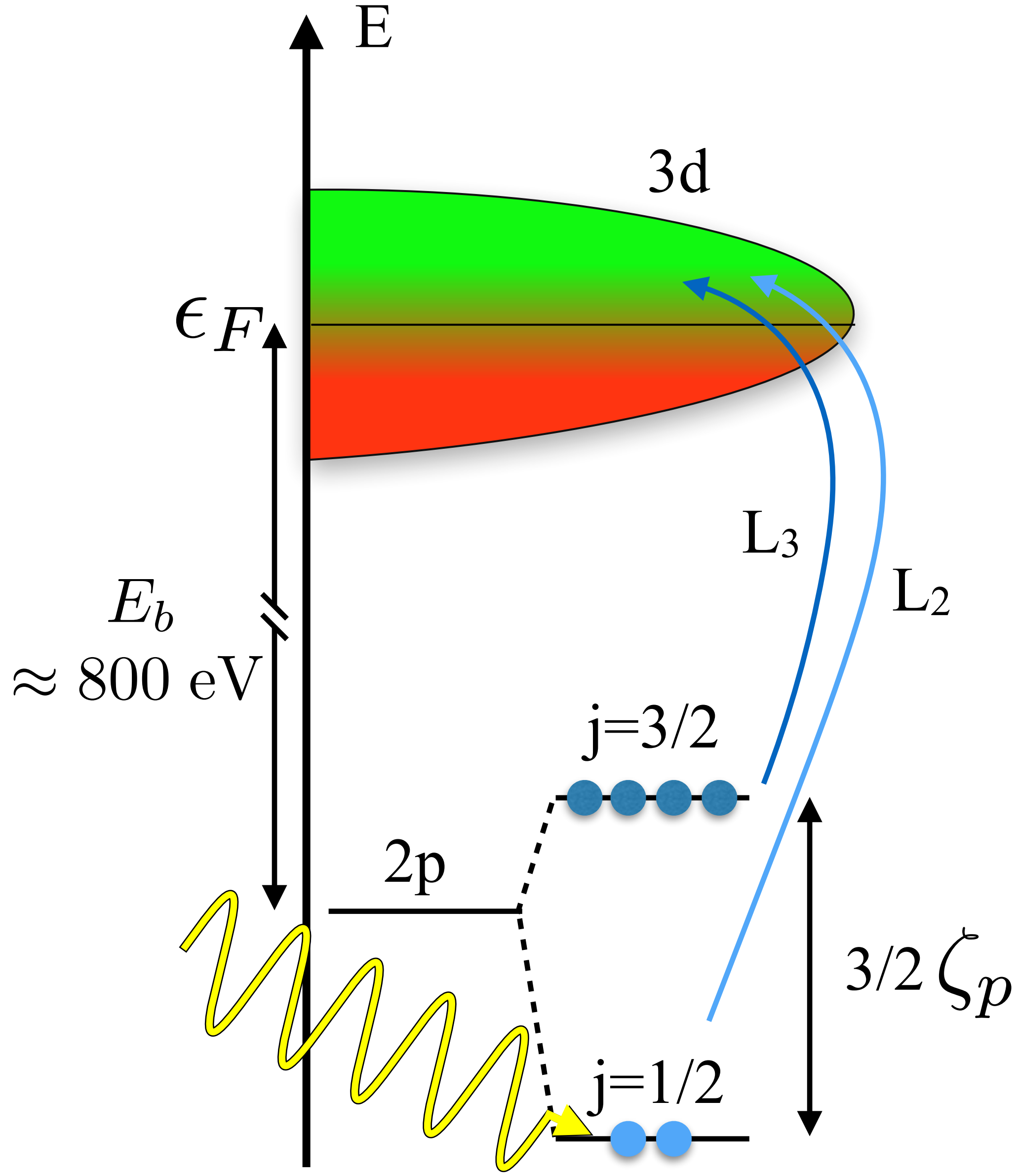


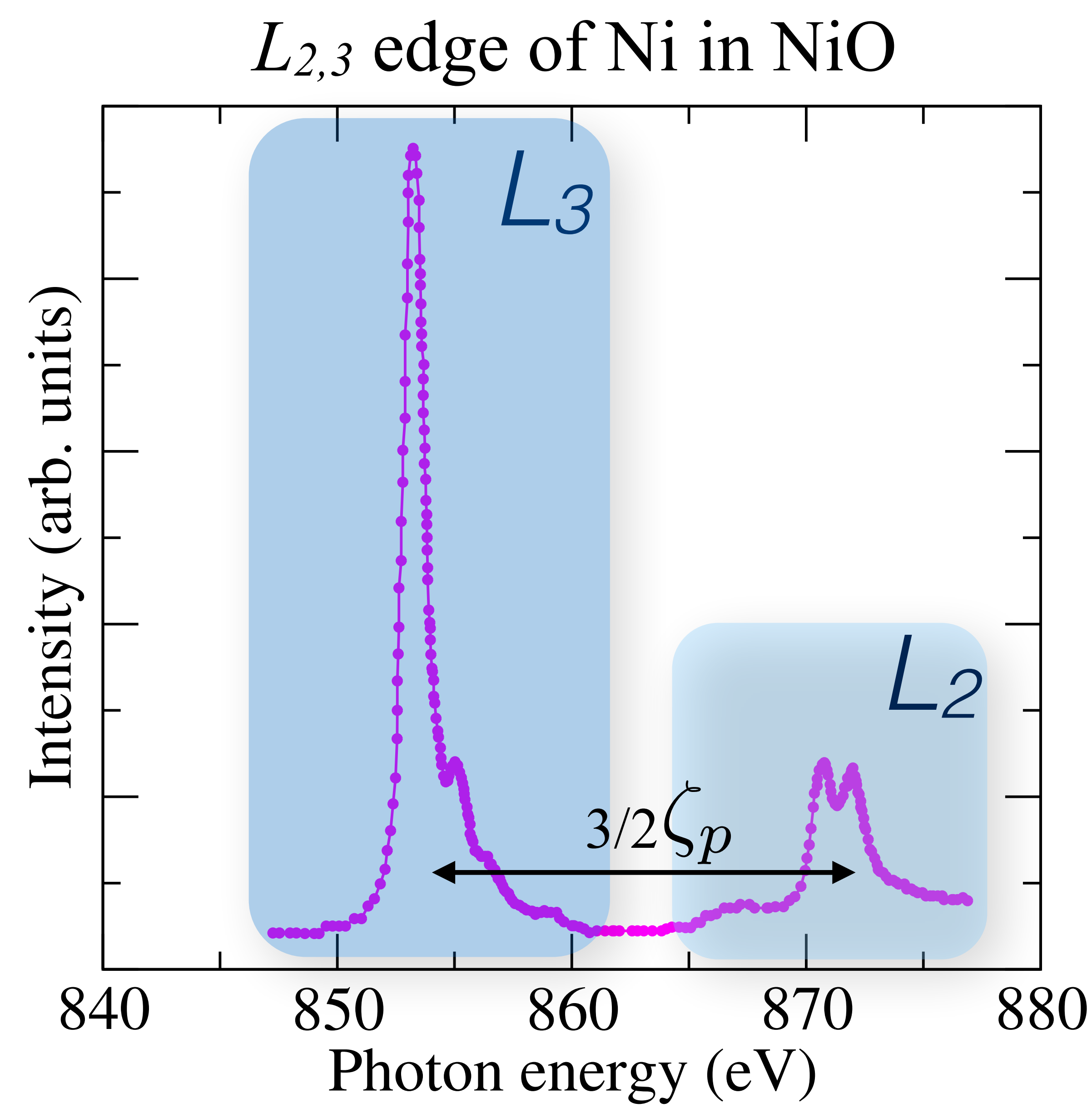


exp. data: PRB **57** 11623 (1998)

XAS $L_{2,3}$-edges of 3d metal systems

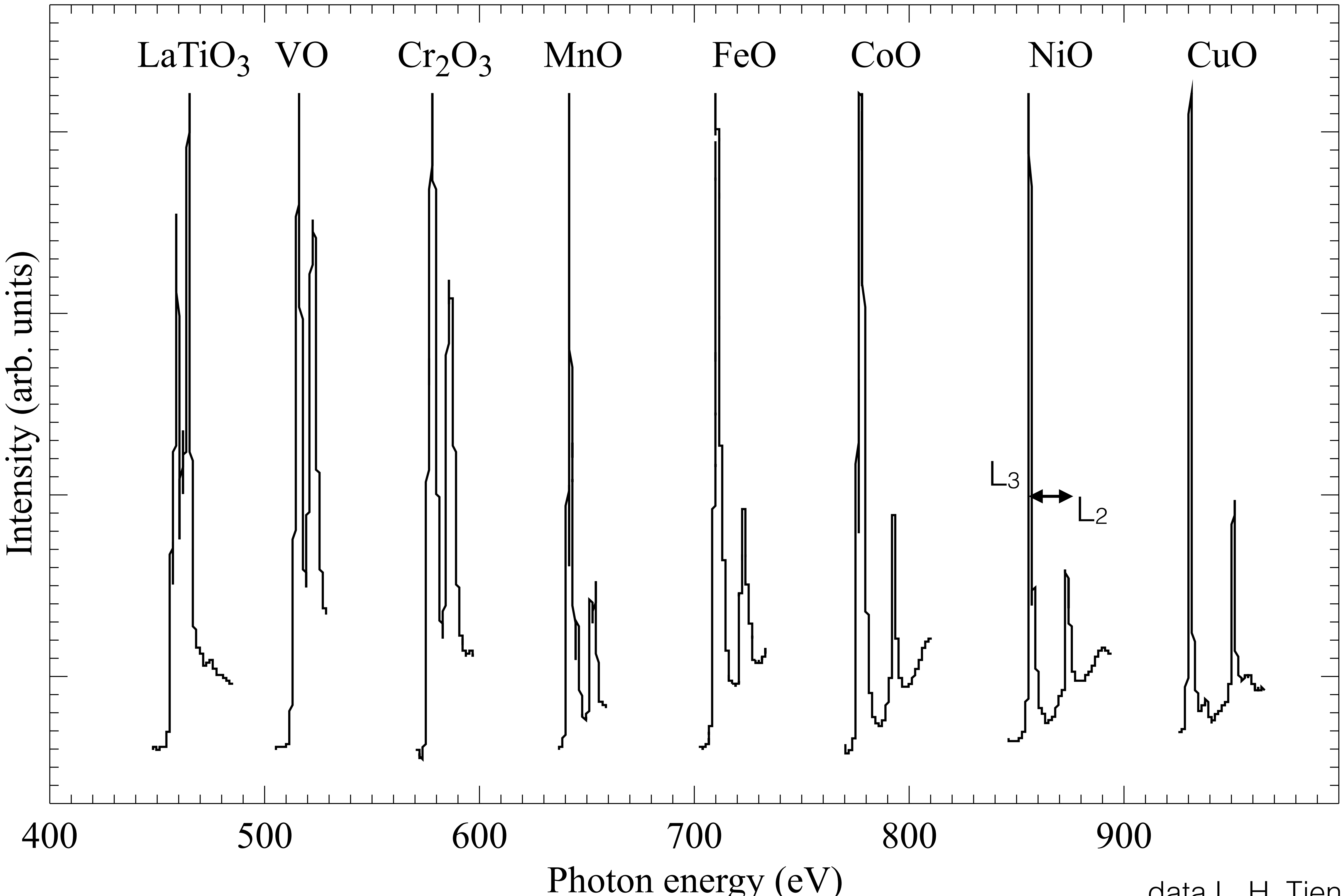
☑ Element selective
☑ Direct information about 3d states





exp. data: PRB **57** 11623 (1998)

XAS $L_{2,3}$-edges of 3d metal systems

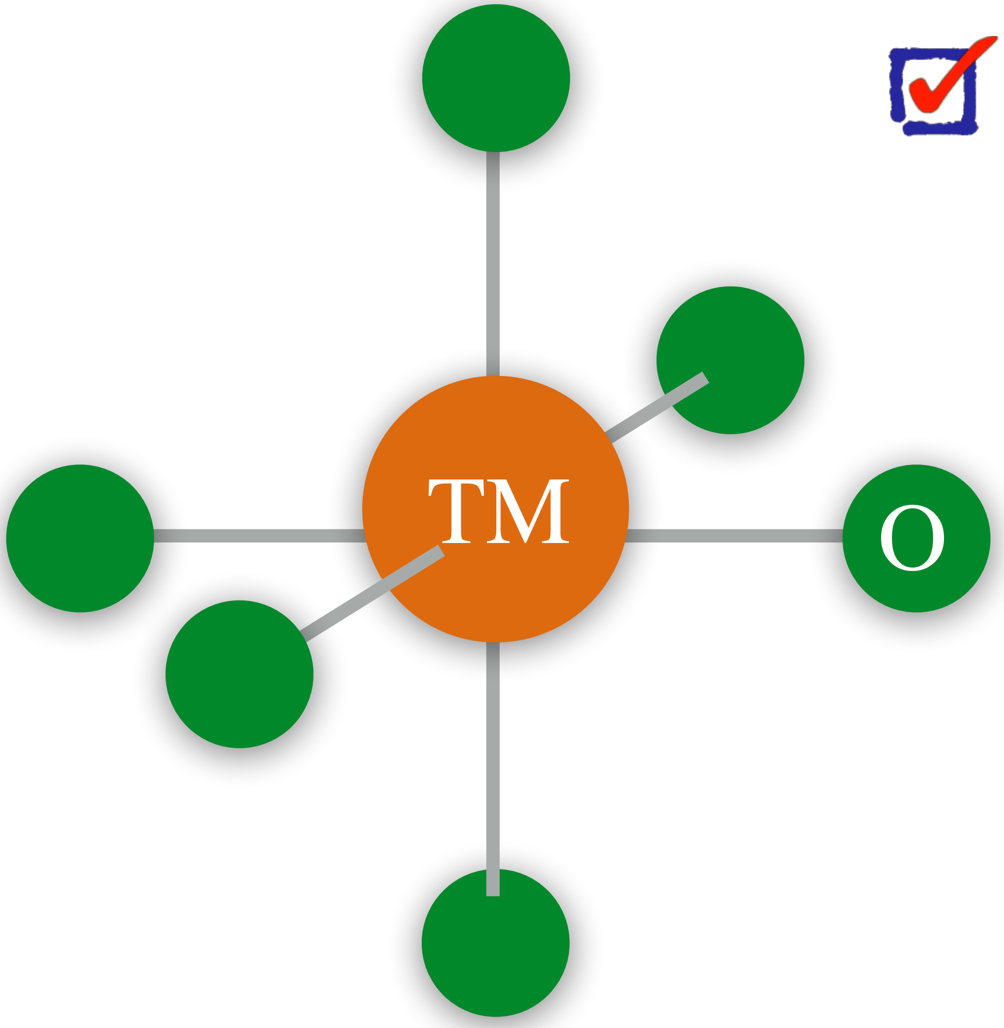


data L. H. Tjeng et al.

Transition metal oxides: MnO, FeO, CoO, NiO

What's in common ?

- ☑ Insulators (Mott or charge-transfer)
- ☑ antiferromagnetic (super-exchange)
- ☑ rocksalt structure

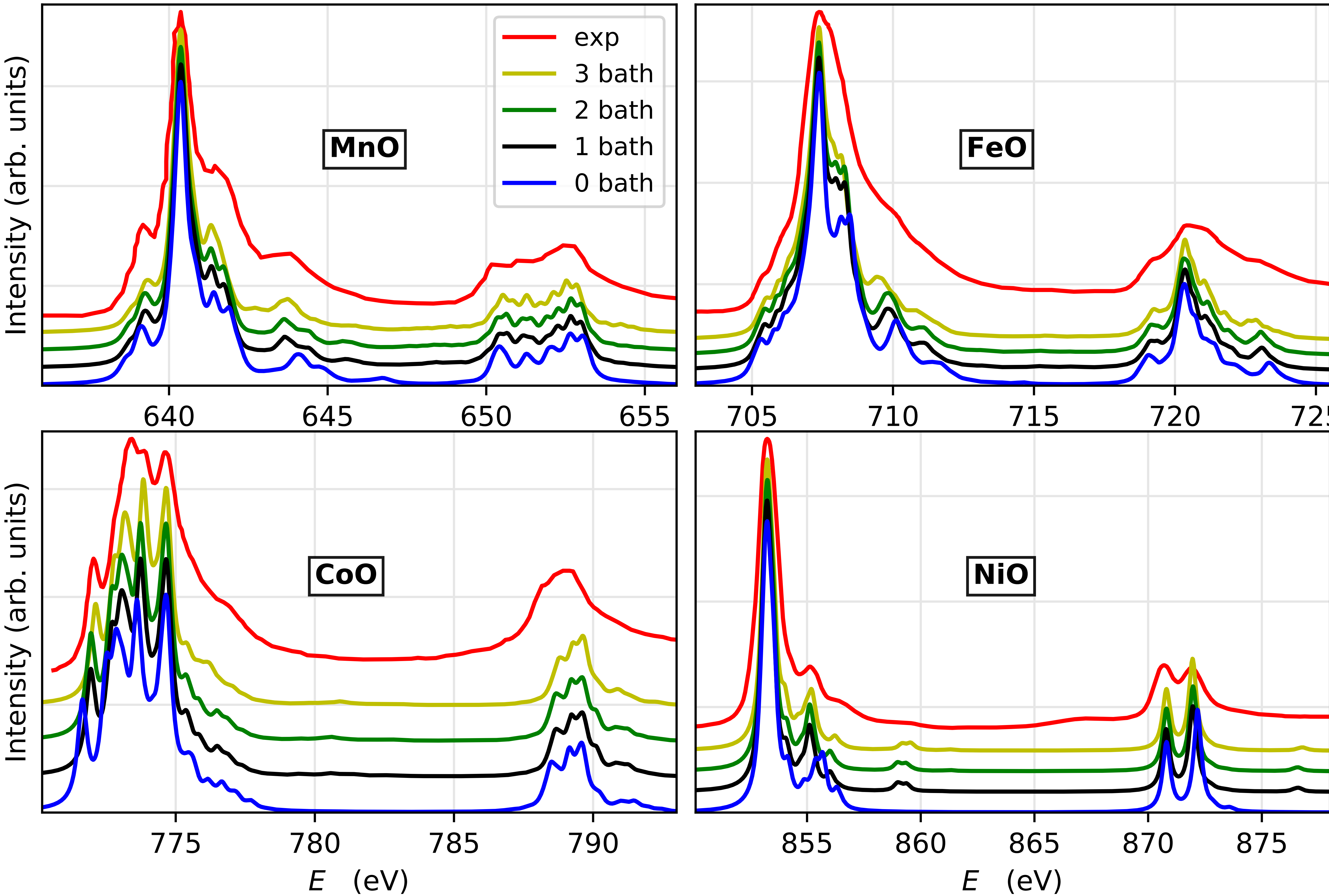


Symmetry of TM site : $\boldsymbol{O_h}$

$\rightarrow$ e_g and t_{2g} orbitals

XAS $L_{2,3}$-edges

PRB **96** 245131 (2017)



Computational scheme summary

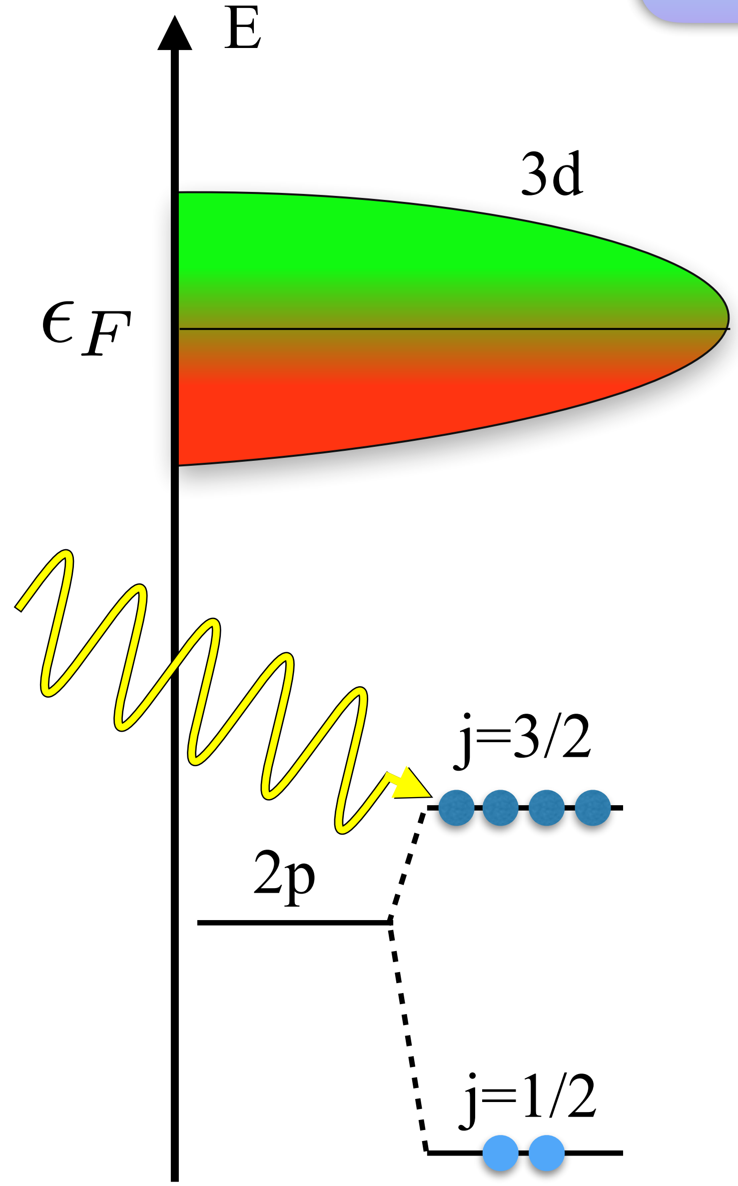
- Use DFT to parameterize Hamiltonian

$$\hat{H} = \sum_{i,j} t_{i,j} \hat{d}_i^\dagger \hat{d}_j + \sum_i \epsilon_{b_i} \hat{b}_i^\dagger \hat{b}_i + \sum_{i,j} \epsilon_{p_{i,j}} \hat{p}_i^\dagger \hat{p}_j$$
$$+ \sum_{i,j} V_{i,j} (\hat{d}_i^\dagger \hat{b}_j + \text{h.c.}) + \hat{H}_U^{dd} + \hat{H}_U^{pd}$$

- $\hat{H}|n\rangle = E_n|n\rangle$

- $G^{(n)}(\omega + i\delta) = \langle n|\hat{T}^\dagger \frac{1}{\tilde{\omega}\hat{1} - \hat{H}} \hat{T}|n\rangle$ with $\tilde{\omega} = \omega + i\delta + E_n$

Calculate core-level spectroscopy



Light matter interaction

$$H_{\text{int}} \propto \boxed{\mathbf{A}^2} + \boxed{\mathbf{p}\cdot\mathbf{A}}$$

Transition operators $\hat{T}$

$$|n'\rangle = \hat{T}|n\rangle$$

XAS: $\epsilon \cdot \hat{r}$

NIXS: $\exp(i\mathbf{q}\cdot\hat{r})$

XPS: $\hat{c}_{a,\sigma}$

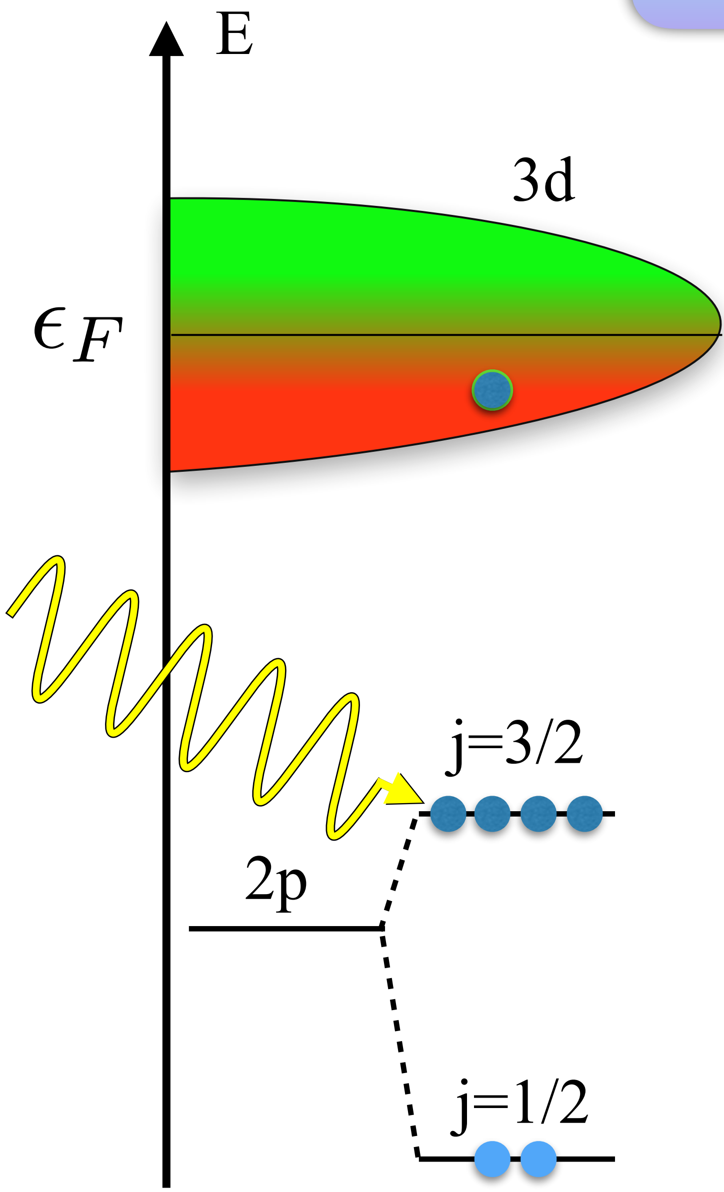
$|n\rangle$

Green's function

$$G^{(n)}(\omega + i\delta) = \langle n|\hat{T}^{\dagger}\frac{1}{\tilde{\omega}\hat{1} - \hat{H}}\hat{T}|n\rangle \quad \text{with} \quad \tilde{\omega} = \omega + i\delta + E_n$$

$$= \langle n'|\frac{1}{\tilde{\omega}\hat{1} - \hat{H}}|n'\rangle$$

Calculate core-level spectroscopy



RIXS

$|n'\rangle = \hat{T}|n\rangle$

$$|m'\rangle = \frac{1}{\tilde{\omega}_{\text{in}}\hat{1} - \hat{H}}|n'\rangle$$

$|n\rangle$

$|m\rangle = \hat{T}^\dagger|m'\rangle$

$$G(\omega_{\text{in}}, \omega_{\text{loss}}) = \langle n|\hat{R}^\dagger \frac{1}{\tilde{\omega}_{\text{loss}}\hat{1} - \hat{H}}\hat{R}|n\rangle \quad \text{with} \quad \tilde{\omega}_{\text{loss}} = \omega_{\text{loss}} + E_n + i\delta$$

$$\hat{R} = \hat{T}^\dagger \frac{1}{\tilde{\omega}_{\text{in}}\hat{1} - \hat{H}}\hat{T} \quad \text{with} \quad \tilde{\omega}_{\text{in}} = \omega_{\text{in}} + E_n + i\delta$$

Conclusions

✓ L-edge spectra are dominated by atomic physics. Multiplets important.

✓ XAS in good agreement with experiments.

Outlook

✓ Compare XPS, RIXS and NIXS with experiments

✓ Use DFT+DMFT


Thank you for your attention

Spectroscopy tutorial

https://github.com/JohanSchott/impurityModelTutorial

https://github.com/JohanSchott/impurityModel