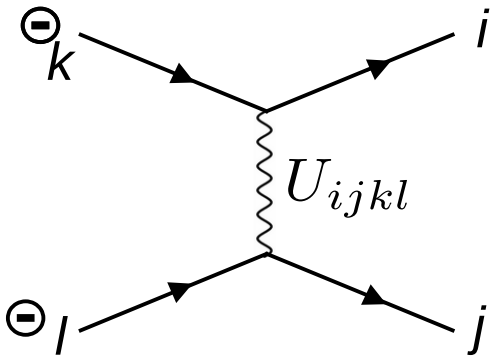

Symmetry properties of the Coulomb interaction tensor and their implications in correlated electron systems

NCTS-iTHEMS Joint Workshop on Matters to Spacetime: Symmetries and Geometry

August 26th, 2024

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Roser Valenti

Antoine Georges

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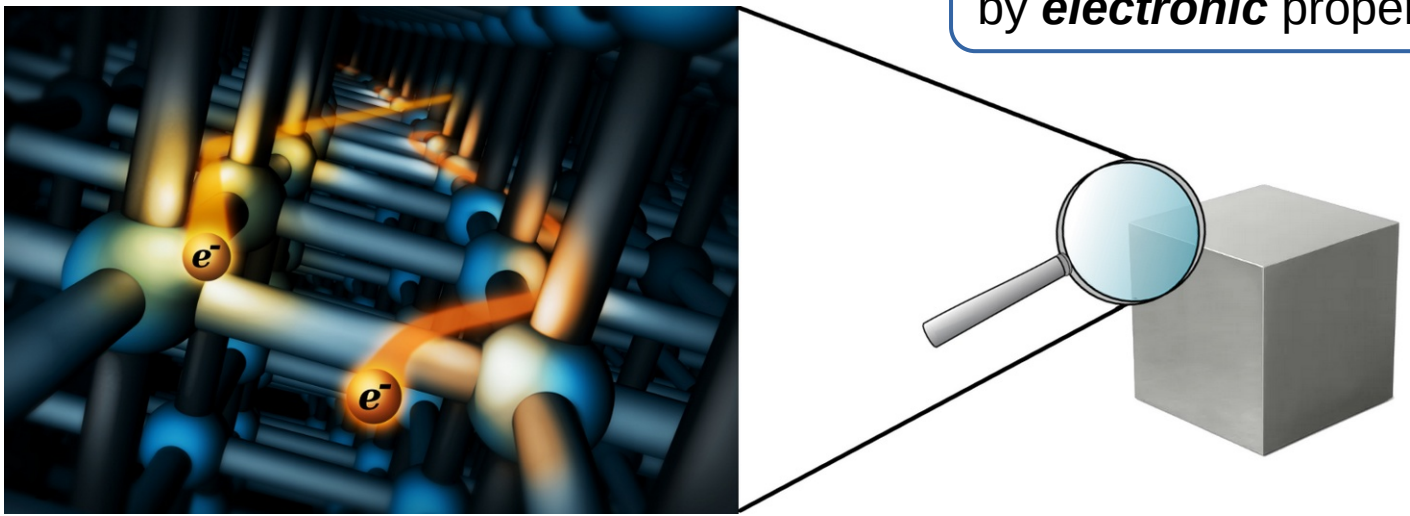
Ryotaro Arita

Problem of interest

Material properties:

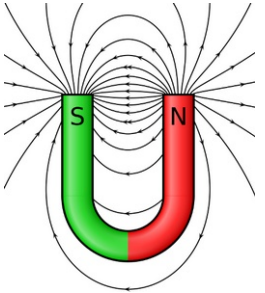
Considered to be governed by ***electronic*** properties!

Original image: P. Kim, Columbia Univ.



wikipedia.org/wiki/Horseshoe_magnet

Magnetism



Superconductivity

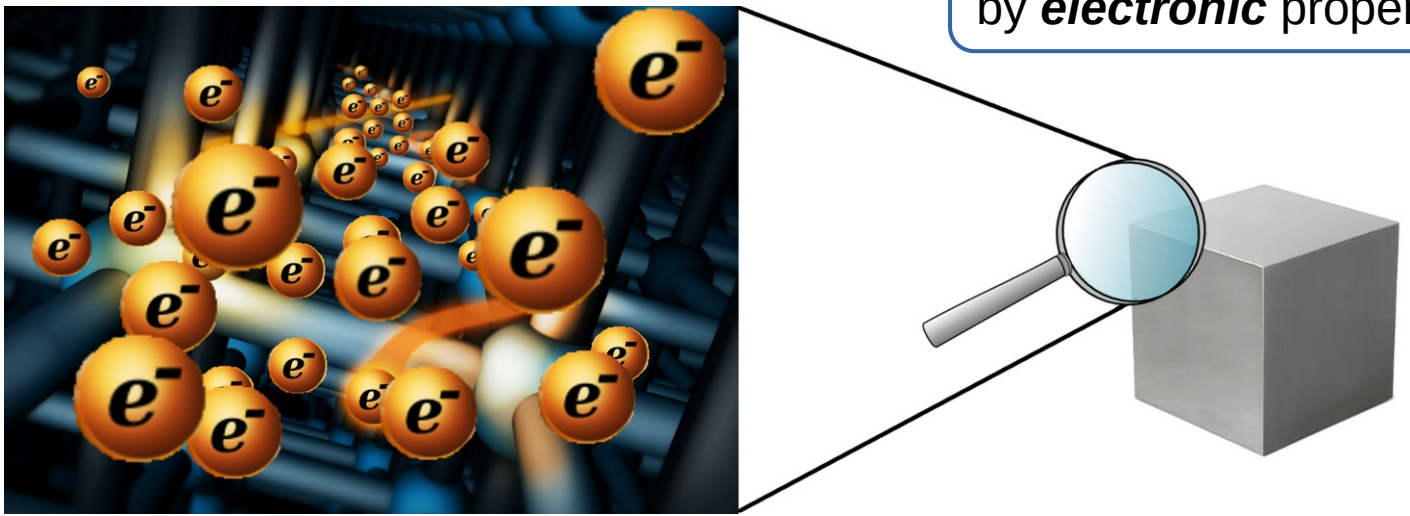
wikipedia.org/wiki/Meissner_effect

- Problem: Solid state materials are interacting many-electron systems
- Any study requires drastic but sensible approximations

⇒ Use simpler model systems and apply sophisticated solution techniques

Problem of interest

Original image: P. Kim, Columbia Univ.



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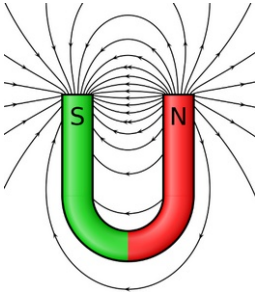
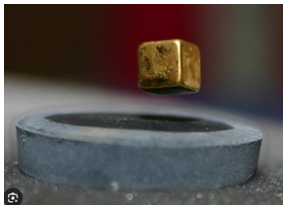
wikipedia.org/wiki/Horseshoe_magnet

Magnetism



Superconductivity

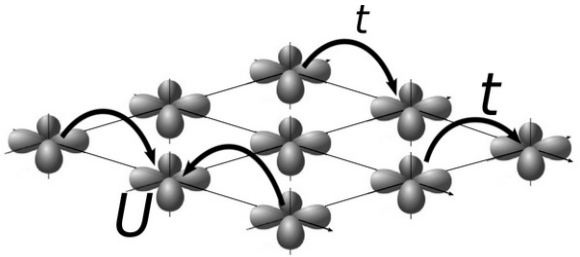


wikipedia.org/wiki/Meissner_effect

- Problem: Solid state materials are interacting <u>many</u>-electron systems
- Any study requires drastic but sensible approximations

➡ Use simpler model systems and apply sophisticated solution techniques

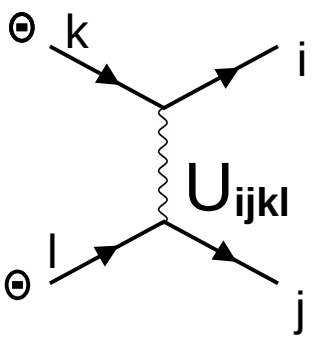
Hubbard model



- Project onto a low-energy space with a localized (Wannier) basis $|i\rangle$

$$H_{effective} = \sum_{ij,\sigma} \langle i|H_0|j\rangle c^{\dagger}_{i\sigma} c_{j\sigma} + \frac{1}{2} \sum_{ijkl,\sigma\sigma'} \langle ij|V_{Coul}|kl\rangle c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{l\sigma'} c_{k\sigma}$$

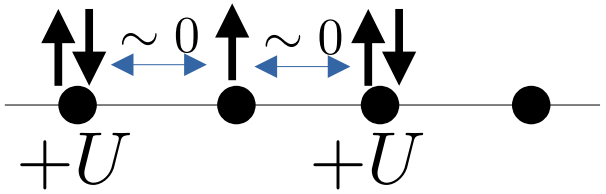
- All matrix elements can in principle be obtained (approximately) using ab-initio methods <u>specific for each model,</u> defined by the basis $|i\rangle$
- Solution not possible in general
  → Use approximations
  → (Dynamical) mean-field theory, etc.



What about the interaction?

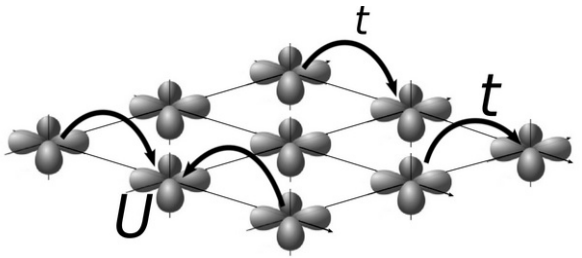
Interaction term U_{ijkl}

- Coulomb interaction $\sim \frac{1}{r}$
- Screening effects outside of the low-energy space reduce effective interaction further
- Often reasonable approximation: local U_{ijkl} !
  ($ijkl$ on same atomic site)



- Starting point for many methods:
  Local density approximation+U, dynamical mean-field theory (DMFT), random-phase approximation (RPA), ...

Multi-orbital Hubbard model

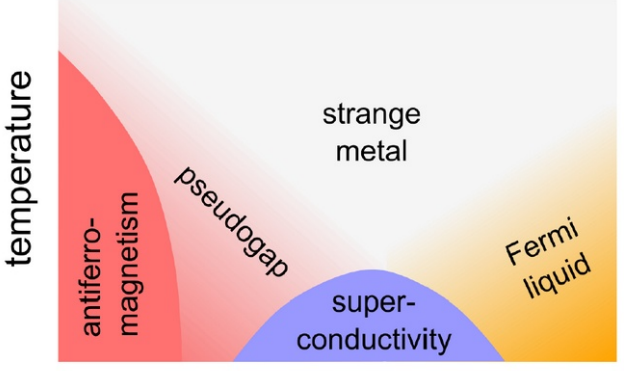


Hubbard,, Proc. R. Soc. London, Ser. A 276, 1365 (1963)
Kanamori, Progress of Theoretical Physics 30(3), 275, (1963)

$$H = \sum_{rr',\sigma} t_{rr'} c^{\dagger}_{r\sigma} c_{r'\sigma}$$ } "electron hopping"

$$+\frac{1}{2} \sum_{ijkl,\sigma\sigma'} \underbrace{\langle ij|V_{Coul}|kl\rangle c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{l\sigma'} c_{k\sigma}}$$

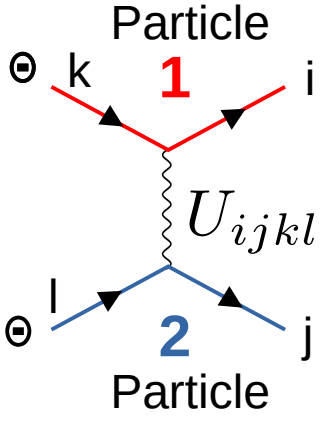
Model for correlated electron systems (cuprates, perovskites, nickelates, ...)



Qin et al., Annual Review of Condensed Matter Physics, 13, 275-302 (2022)

On-site orbital indices i, j, k, l

Electron-Electron Interaction:



Convention:

$$U_{ijkl} = \langle ij|V_{Coul}|kl\rangle$$

$$= \int \psi^*_i(r_1)\psi^*_j(r_2)V_{Coul}(r_1,r_2)\psi_k(r_1)\psi_l(r_2)\mathrm{d}r_1\mathrm{d}r_2$$

Standard Interaction Terms

Common definition:

$U_{ii} \equiv U_{iiii}$ (intra)
$U'_{ij} \equiv U_{ijij}$ (inter)
$J_{ij} \equiv U_{ijji}$ (Hund)

$$H_{int} = \sum_i U_{ii} n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j,\sigma} U'_{ij} n_{i\sigma} n_{j\sigma'}$$

intra-orbital

inter-orbital

Density-Density type (Hartree)

Hund's type (Fock)

$$+ \frac{1}{2} \sum_{i \neq j,\sigma} J_{ij} \left(-n_{i\sigma} n_{j\sigma} + \underbrace{c^\dagger_{i\sigma} c^\dagger_{j\bar{\sigma}} c_{i\bar{\sigma}} c_{j\sigma}}_{spin-flip} \right)$$

High-spin Hund's rule

$$+ \frac{1}{2} \sum_{i \neq j,\sigma} J_{ij} \underbrace{c^\dagger_{i\sigma} c^\dagger_{i\bar{\sigma}} c_{j\bar{\sigma}} c_{j\sigma}}_{pair-hopping}$$

$+?$

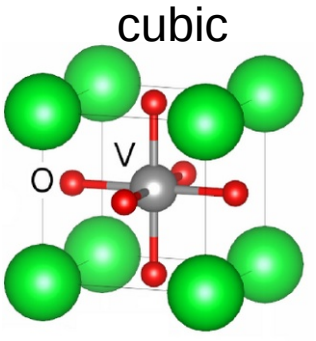
Questions:

- Which of the N^4_{orb} terms vanish due to symmetry? $(3d : 5^4 = 625)$
- What about real materials?
- What is the effect of U_{ijkl} on electronic properties?

See also:
Ribic, Assmann, Tóth, Held, *PRB* **90**, 165105 (2014)
Zhang et al., *PRL* **116**, 106402 (2016)
Hausoel, et al., *Nat.Comm.* **8**, 16062 (2017)

Symmetry of the Coulomb Tensor

- Coulomb tensor must obey the symmetry of the atoms' environment



$$T_g \psi_i(r) = \sum_j \Gamma^g_{ij} \psi_j(r)$$

T_g Point-group operation g

Γ^g_{ij} Matrix-representation of irreducible representation

$$U_{ijkl} \overset{!}{=} \sum_{abcd} \Gamma^g_{ia} \Gamma^g_{jb} U_{abcd} \Gamma^g_{kc} \Gamma^g_{ld}$$

Invariant under symmetry transformation!

- Symmetry properties restrict the form of U_{ijkl}

E.g. t_{2g} manifold (cubic)

$$U_{iiii} = U_{jjjj} \ \forall i, j$$

Coulomb matrix elements in multi-orbital Hubbard models,
J. Bünemann, F. Gebhard
J. Phys.: Condens. Matter 29, 165601 (2017)

Symmetry of the Coulomb Tensor

Rewrite as:

$$U_\alpha = \sum_\beta \Omega^g_{\alpha\beta} U_\beta$$

where $\alpha = (ijkl)$ combined index

$$\Omega^g_{\alpha\beta} = \Gamma^g_{ia} \otimes \Gamma^g_{jb} \otimes \Gamma^g_{kc} \otimes \Gamma^g_{ld}$$

- U is an Eigenvector with Eigenvalue $\lambda = 1$ of Ω^g
- Physical operators (such as U) live in : $M = \bigcap_g \mathrm{Eig}_{\lambda=1}[\Omega^g]$
- Idea: Construct basis of M !

Due to symmetry: $\dim[M] \ll \dim[\Omega^g]$ ⇒ U can be parametrized by $\dim[M]$ parameters!

Symmetry of the Coulomb interaction

- We construct basis of $M = \bigcap_g \mathrm{Eig}_{\lambda=1}[\Omega^g]$

$$v \in V,\ \dim[V] = n < d$$ e.g. $d = 625$ for 5 orbitals

- And basis of complement space

$$w \in W : \langle w|v\rangle = 0,\ \dim[W] = d - n$$

- Then

$$u_i = \langle v_i|U\rangle, \quad n$$ independent Coulomb parameters

$$0 = \langle w_i|U\rangle\ \forall w_i \in W$$

Symmetry of the Coulomb interaction

$$\begin{pmatrix} \cdots v_1^* \cdots \\ \cdots v_2^* \cdots \\ \vdots \\ \cdots w_{d-n} \cdots \end{pmatrix} U = MU = \begin{pmatrix} u_1 \\ \vdots \\ u_n \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

M full rank $\Rightarrow M^{-1}u = U$

- Full U reconstructed from minimal set u_i
- u_i in general arbitrary linear combinations of U_{ijkl}
- Physical intuitive parameters U_{iiii}, U_{ijij} etc., can be chosen as *n* indep. parameters by partial transform & back-transform
- $U_{\mathbf{i}jk\mathbf{l}} = U_{\mathbf{k}j\mathbf{i}l}$ etc. can be implemented in the same way

Symmetry of the Coulomb interaction

- Symmetries independent of crystal structure?

$$
\begin{aligned}
U_{ijkl} &= \langle ij|V_{Coul}|kl\rangle \\
&= \int \psi_i^*(r_1)\psi_j^*(r_2)V_{Coul}(r_1,r_2)\psi_k(r_1)\psi_l(r_2)\mathrm{d}r_1\mathrm{d}r_2 \\
&= \langle ji|V_{Coul}|lk\rangle = U_{jilk} \\
&= \langle kl|V_{Coul}|ij\rangle^* = U^*_{klij} \\
&= \ldots
\end{aligned}
$$

$$V_{Coul}(r_1,r_2) \sim \frac{1}{|r_1 - r_2|}$$

- $U_{\mathbf{i}j\mathbf{k}l} = U_{\mathbf{k}j\mathbf{i}l}$ can be exploited by $U_{(kjil)} = \Omega^g U_{(ijkl)}$

Minimal set of parameters for *d* shell

when using Slater form with $F^2/F^4 = 8/5$ → only U_{avg}, J_{avg}

- Spherical symmetry (free atom): **3** (#129/625 nonzero)
- Cubic O_h (Sr**V**O_3, **Ni**O): **10** (#129/625 nonzero)
- Tetragonal D_{4h} (Sr_2**Ru**O_4) : **23** (#129/625 nonzero)
- Tetragonal D_{2d} (**Fe**Se, Ba**Fe**$_2As_2$) : **23** (#129/625 nonzero)
- Tetragonal C_{2h} (La_2**Cu**O_4) : **66** (#313/625 nonzero)

Same form of Coulomb tensor (except lifting of degeneracies)

Nonzero Elements (except C_{2h}):

Density U, U' Hund J

$iiii,\ ijij,$ $ijji,\ iijj,$ ~~$ijjj$~~ 2-index

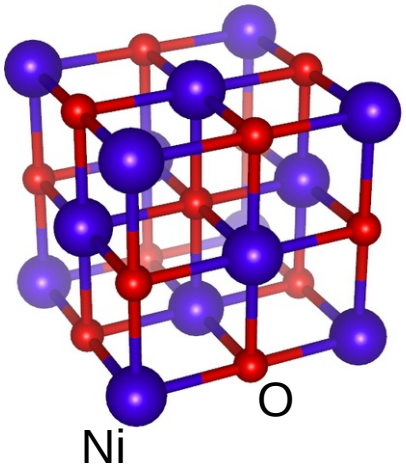
$\sim (c_i^\dagger c_k + c_k^\dagger c_i) n_j$ ← 3-index $ijkj,\ ijkk$ $ijkl$ 4-index } only between e_g-t_{2g}

"correlated" inter-orbital hopping

(Using constrained RPA: Aryasetiawan et al., PRB 70, 195104 (2004))

Interaction term for real materials (*3d*)

NiO (cubic)



$U_{ij} \sim 4 - 6\text{eV}$

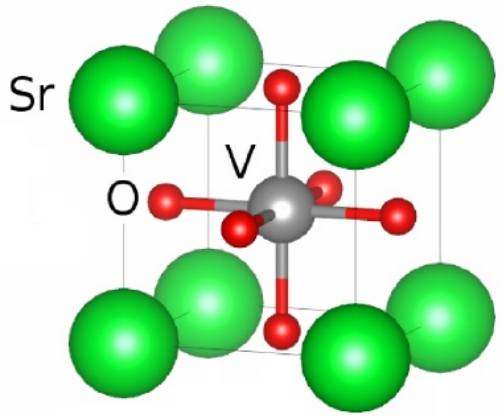
$J_{ij} \sim 0.5 - 0.8\text{eV}$

$U_{ikjk} \sim 0.3\text{eV}$

$U_{ijkk} \sim 0.2\text{eV}$

$U_{ijkl} \sim 0.2 - 0.3\text{eV}$

$SrVO_3$ (cubic)



$U_{ij} \sim 2.5 - 3.5\text{eV}$

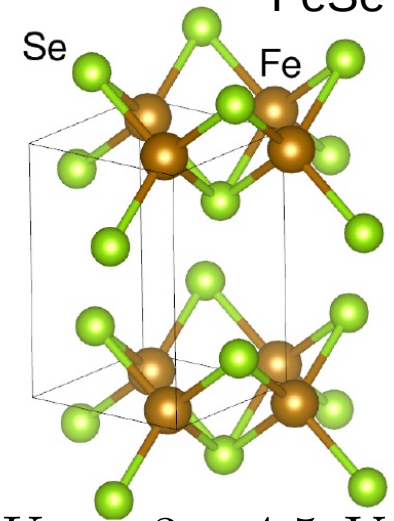
$J_{ij} \sim 0.4\text{eV}$

$U_{ikjk} \sim 0.2\text{eV}$

$U_{ijkk} \sim 0.1\text{eV}$

$U_{ijkl} \sim 0.1 - 0.2\text{eV}$

FeSe (tetr.)



$U_{ij} \sim 3 - 4.5\text{eV}$

$J_{ij} \sim 0.4 - 0.6\text{eV}$

$U_{ikjk} \sim 0.2\text{eV}$

$U_{ijkk} \sim 0.1\text{eV}$

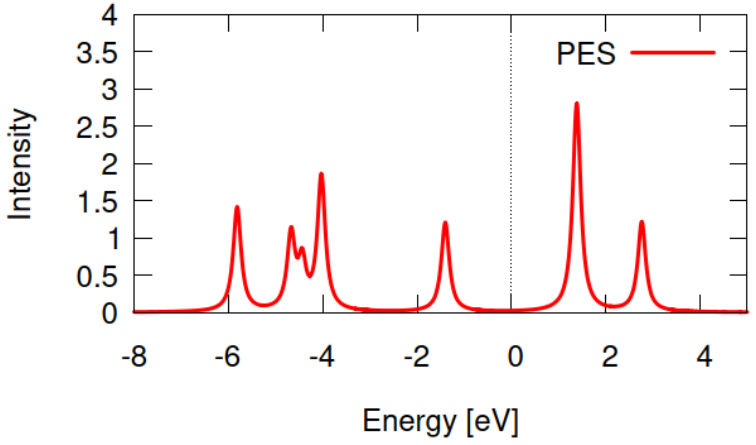
$U_{ijkl} \sim 0.1 - 0.2\text{eV}$

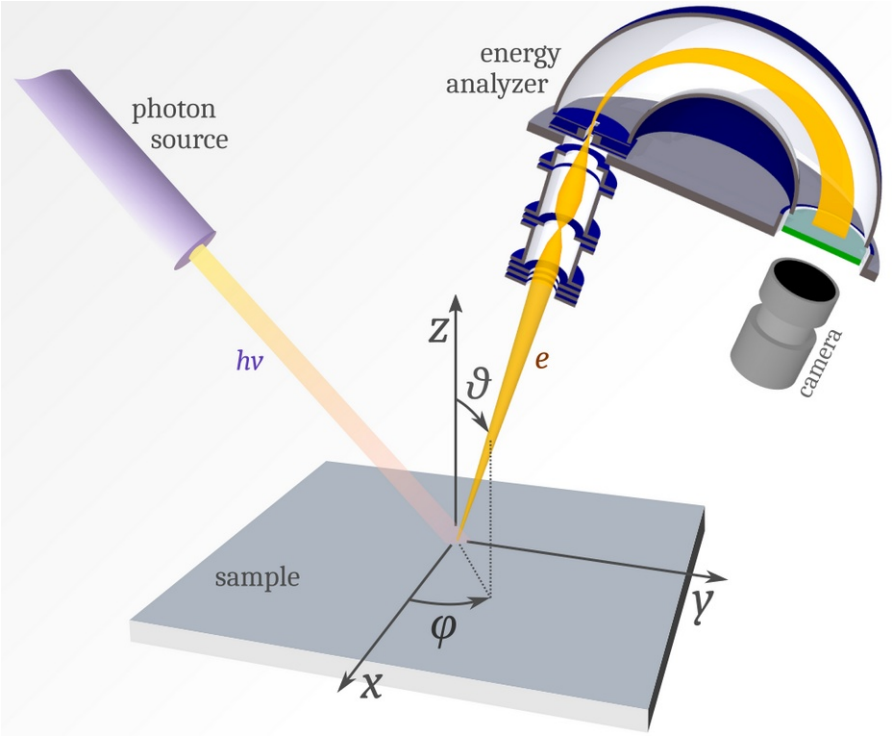
Some actual examples

- **Photoemission spectroscopy (PES)**
- Accessible via Green's function:

$$A(\omega) = \mathrm{Im} \sum_n \frac{|\langle \mathrm{Ex}_n | c | \mathrm{GS} \rangle|^2}{\omega + i0^+ - (E_N - E_{GS})} + \ldots$$

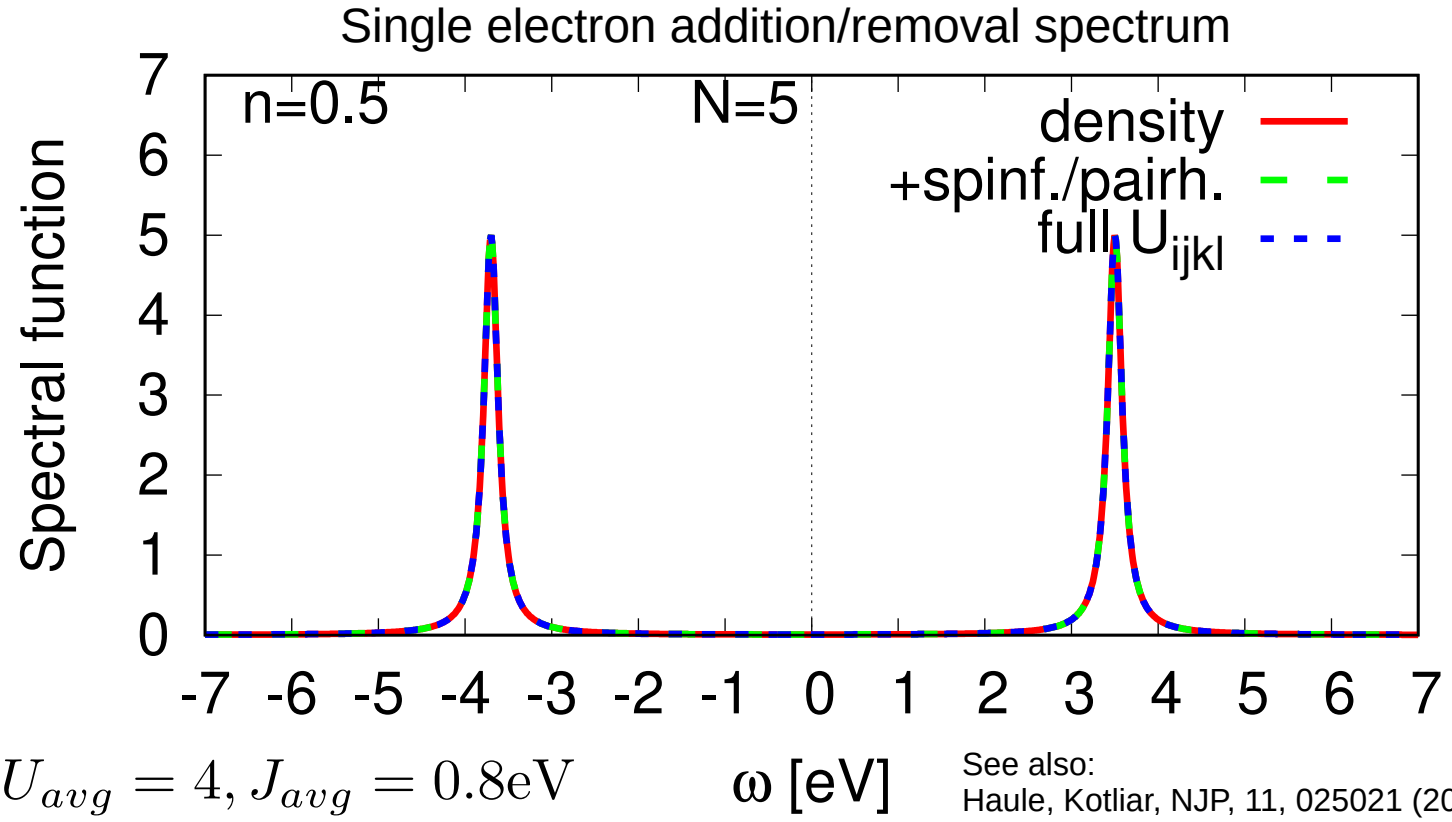
- Typical spectrum:





https://en.wikipedia.org/wiki/Photoemission_spectroscopy

3d shell, N_{el}=5, isolated atom toy model



$U_{avg} = 4, J_{avg} = 0.8\text{eV}$

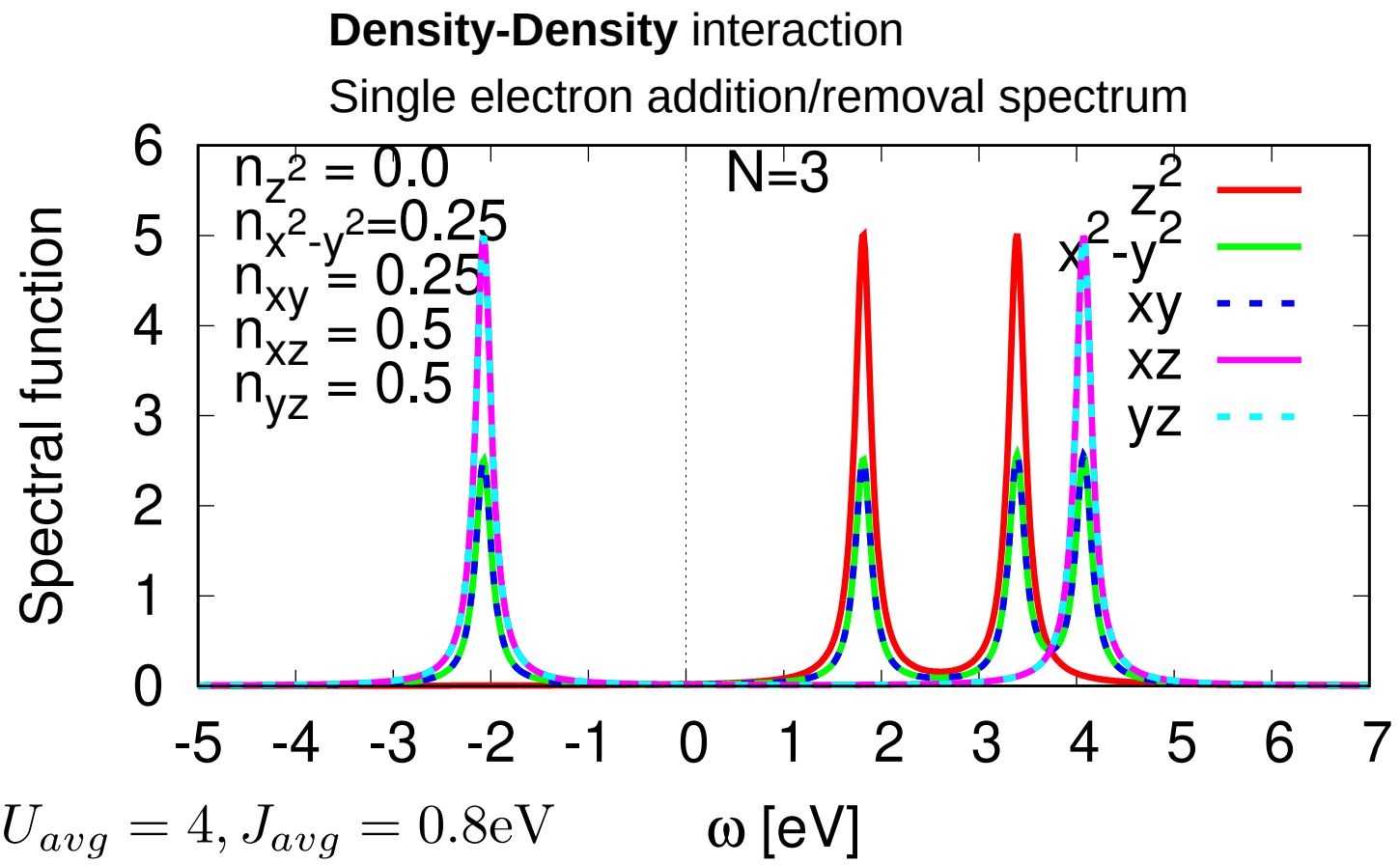
See also:
Haule, Kotliar, NJP, 11, 025021 (2009)

- Dens.-dens. ground state: high spin ↑ ↑ ↑ ↑ ↑
- Full 4-index ground state: high/low spin degenerate

  ↓ ↑ ↑ ↑ ↑ , ↓ ↑ ↓ ↑ ↑

  $+4J$ Hund's coupling
  $-4J$ spin-flip
  } $\Delta E = 0$
- U_{ijkl}: restores symmetry e.g. $\langle S_i^z S_j^z \rangle = \langle S_i^x S_j^x \rangle$
- GS degeneracy enhanced, but spectrum identical

3d shell, N_{el}=3, isolated atom toy model



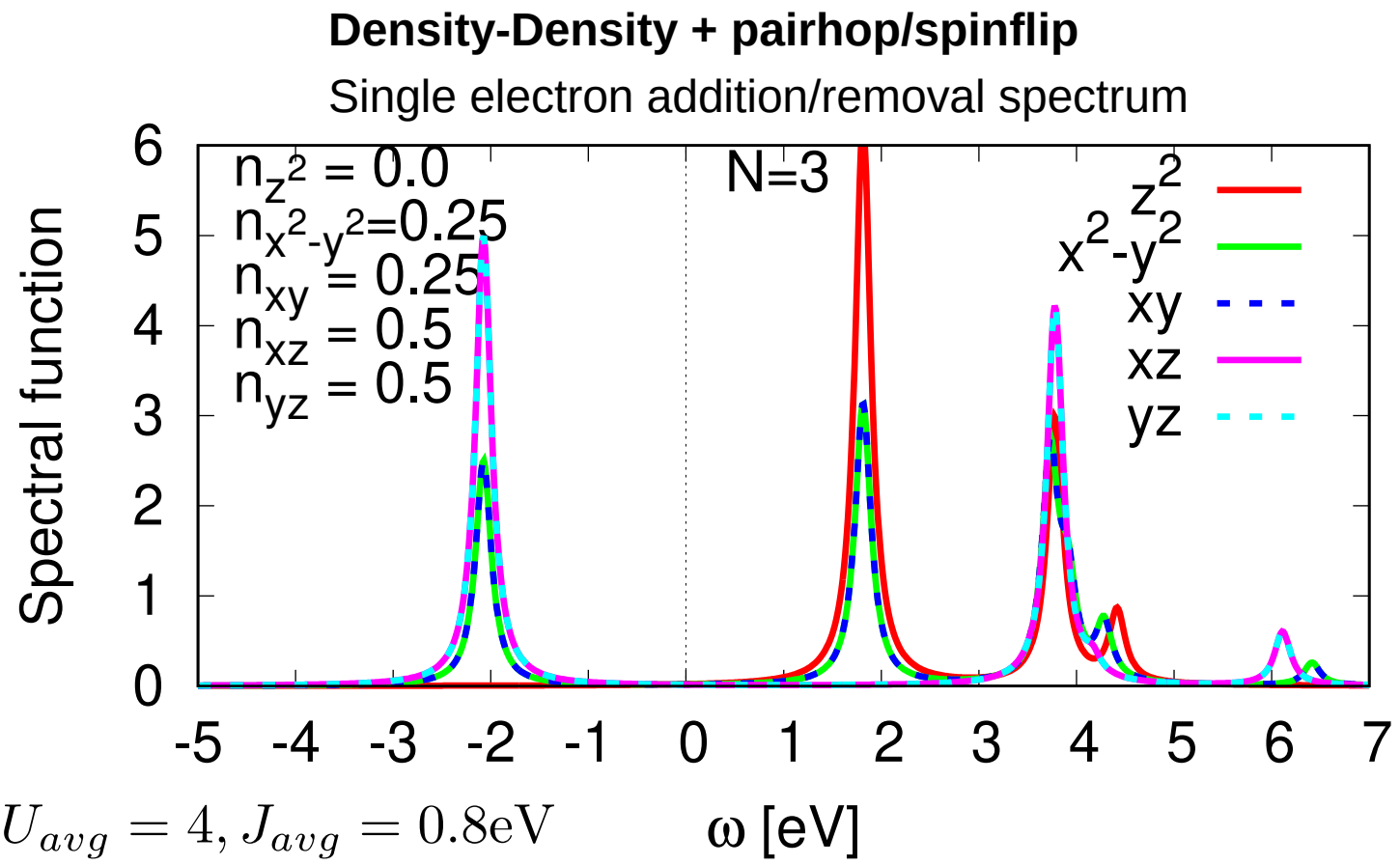
- Dens.-dens. ground state breaks spin-rotational invariance & orbital sym.

$$U_{ij} =$$

z^2	x^2-y^2	xy	xz	yz	
4.9	3.5	3.5	4.0	4.0	z^2
3.5	4.9	4.2	3.7	3.7	x^2-y^2
3.5	4.2	4.9	3.7	3.7	xy
4.0	3.7	3.7	4.9	3.7	xz
4.0	3.7	3.7	3.7	4.9	yz

- pairhop/spinflip + 3-index terms still break orbital symmetry
- Full U_{ijkl} restores sym.

3d shell, N_{el}=3, isolated atom toy model



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$$U_{ij} =$$

	z^2	x^2-y^2	xy	xz	yz
z^2	4.9	3.5	3.5	4.0	4.0
x^2-y^2	3.5	4.9	4.2	3.7	3.7
xy	3.5	4.2	4.9	3.7	3.7
xz	4.0	3.7	3.7	4.9	3.7
yz	4.0	3.7	3.7	3.7	4.9

- pairhop/spinflip + 3-index terms still break orbital symmetry
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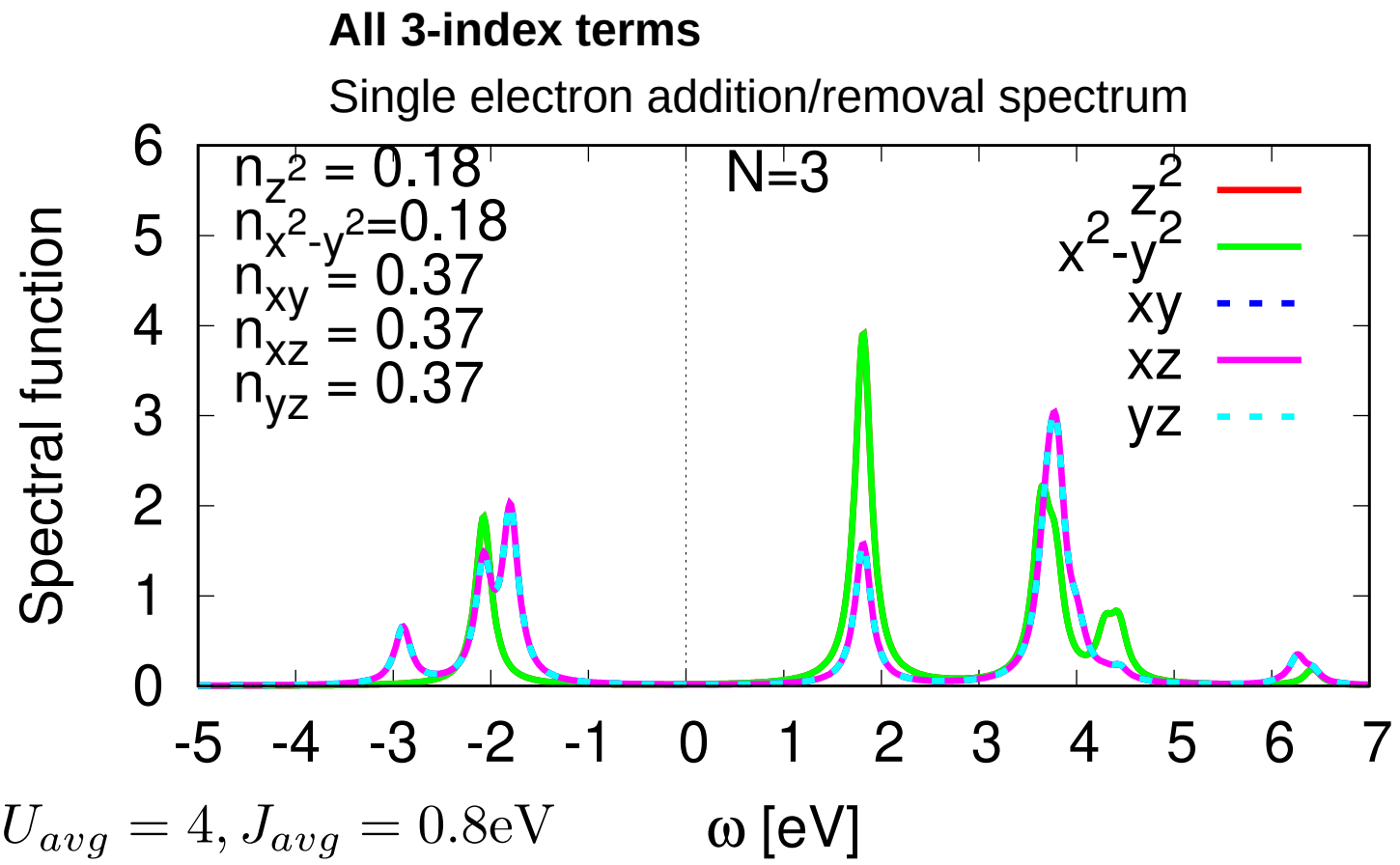
3d shell, N_{el}=3, isolated atom toy model



$U_{avg} = 4, J_{avg} = 0.8\text{eV}$

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$$U_{ij} =$$

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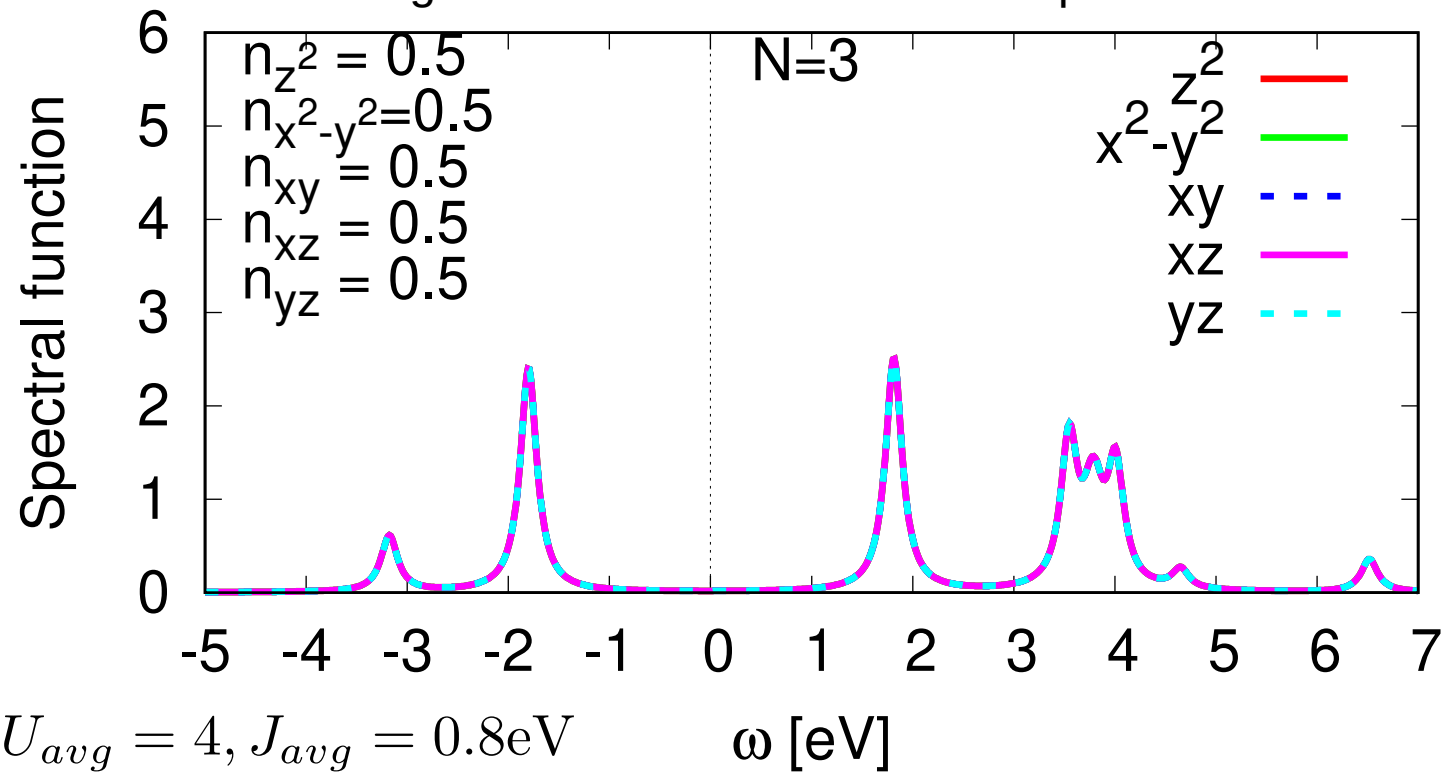
x^2-y^2	3.5	4.9	4.2	3.7	3.7
xy	3.5	4.2	4.9	3.7	3.7
xz	4.0	3.7	3.7	4.9	3.7
yz	4.0	3.7	3.7	3.7	4.9

- pairhop/spinflip + 3-index terms still break orbital symmetry
- Full U_{ijkl} restores sym.

3d shell, N_{el}=3, isolated atom toy model

Full 4-index U_{ijkl}

Single electron addition/removal spectrum



$U_{avg} = 4, J_{avg} = 0.8\text{eV}$

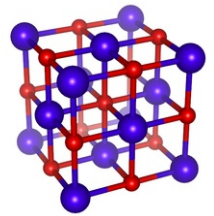
- Dens.-dens. ground state breaks spin-rotational invariance & orbital sym.

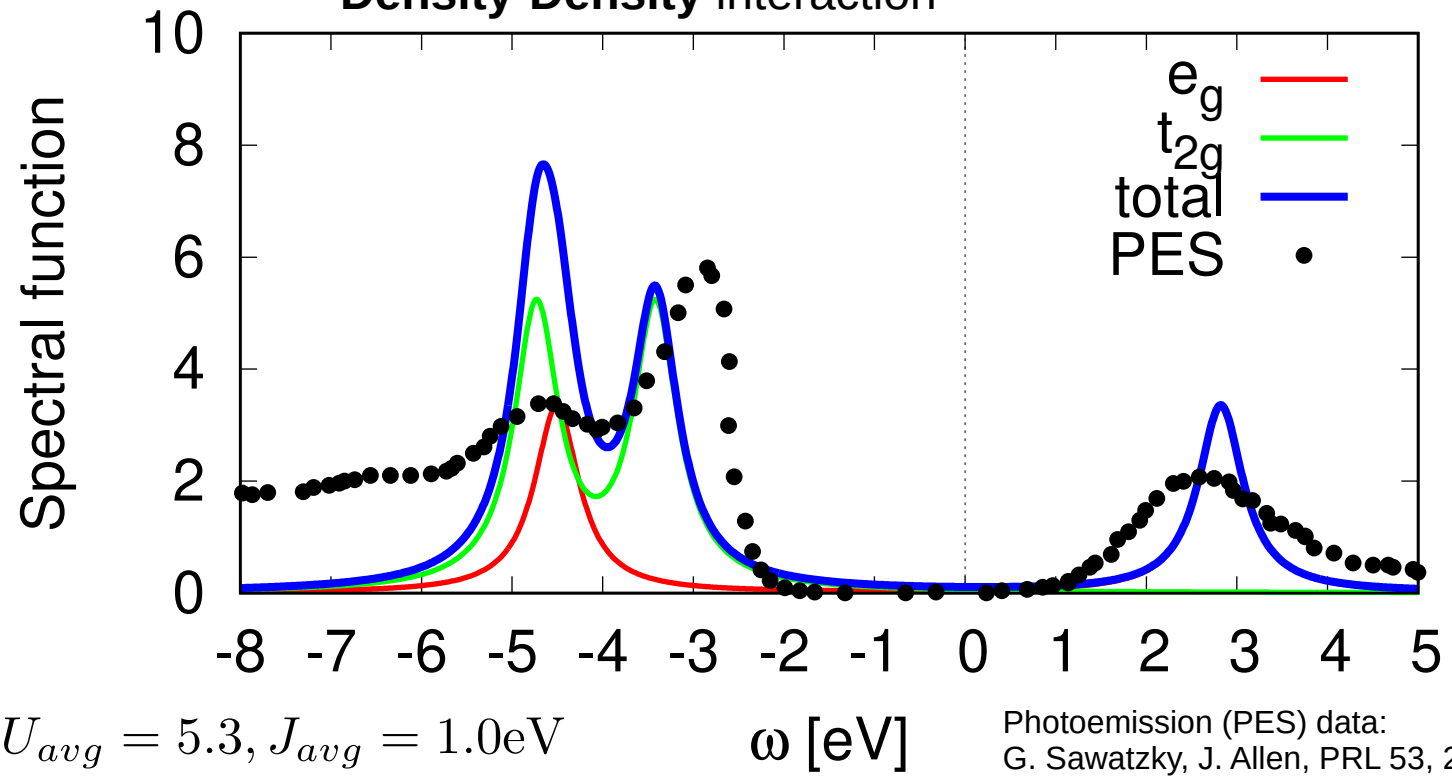
$U_{ij} =$

	z^2	x^2-y^2	xy	xz	yz
z^2	4.9	3.5	3.5	4.0	4.0
x^2-y^2	3.5	4.9	4.2	3.7	3.7
xy	3.5	4.2	4.9	3.7	3.7
xz	4.0	3.7	3.7	4.9	3.7
yz	4.0	3.7	3.7	3.7	4.9

- pairhop/spinflip + 3-index terms still break orbital symmetry
- Full U_{ijkl} restores sym.

NiO: Ni *3d*, N_{el}=8, atom toy model





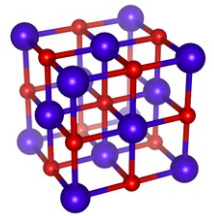
$U_{avg} = 5.3, J_{avg} = 1.0\text{eV}$

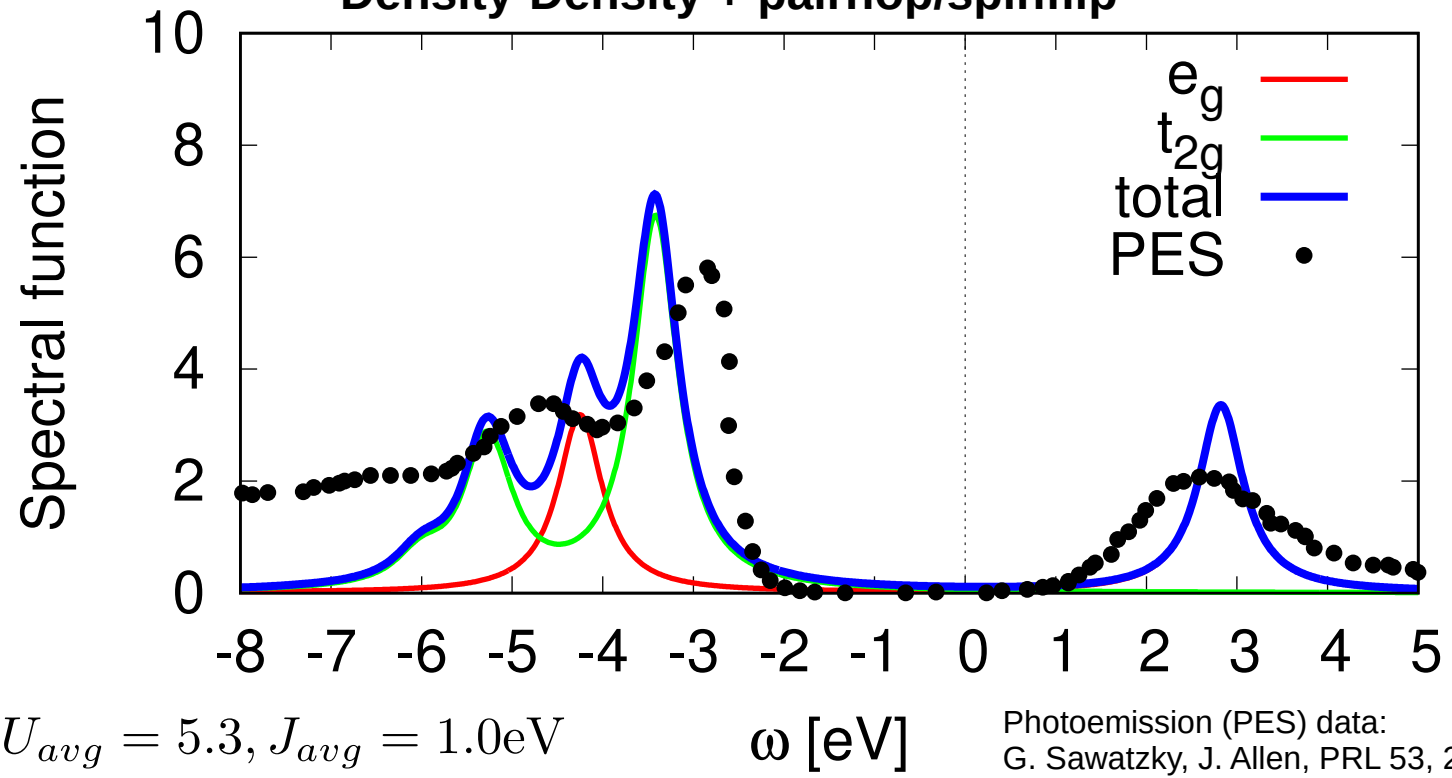
- Half-filled e_g, full t_{2g}
- Dens.-dens. interaction reproduces e_g gap but wrong spectral weights
- spin-flip/pair-hopping improves t_{2g} weight (e_g symmetry broken)
- 4-index interaction terms induce ~0.1-0.2eV shifts

Photoemission (PES) data:
G. Sawatzky, J. Allen, PRL 53, 24 (1984)

For charge-transfer discussion, see: (and refs therein)
Zaanen, et al., PRL 55, 418 (1985)
Schuler, et al., PRB 71, 115113 (2005)

NiO: Ni *3d*, N_{el}=8, atom toy model





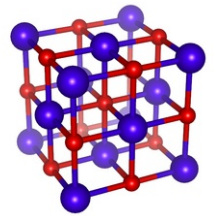
- Half-filled e_g, full t_{2g}
- Dens.-dens. interaction reproduces e_g gap but wrong spectral weights
- spin-flip/pair-hopping improves t_{2g} weight (e_g symmetry broken)
- 4-index interaction terms induce ~0.1-0.2eV shifts

$U_{avg} = 5.3, J_{avg} = 1.0\text{eV}$

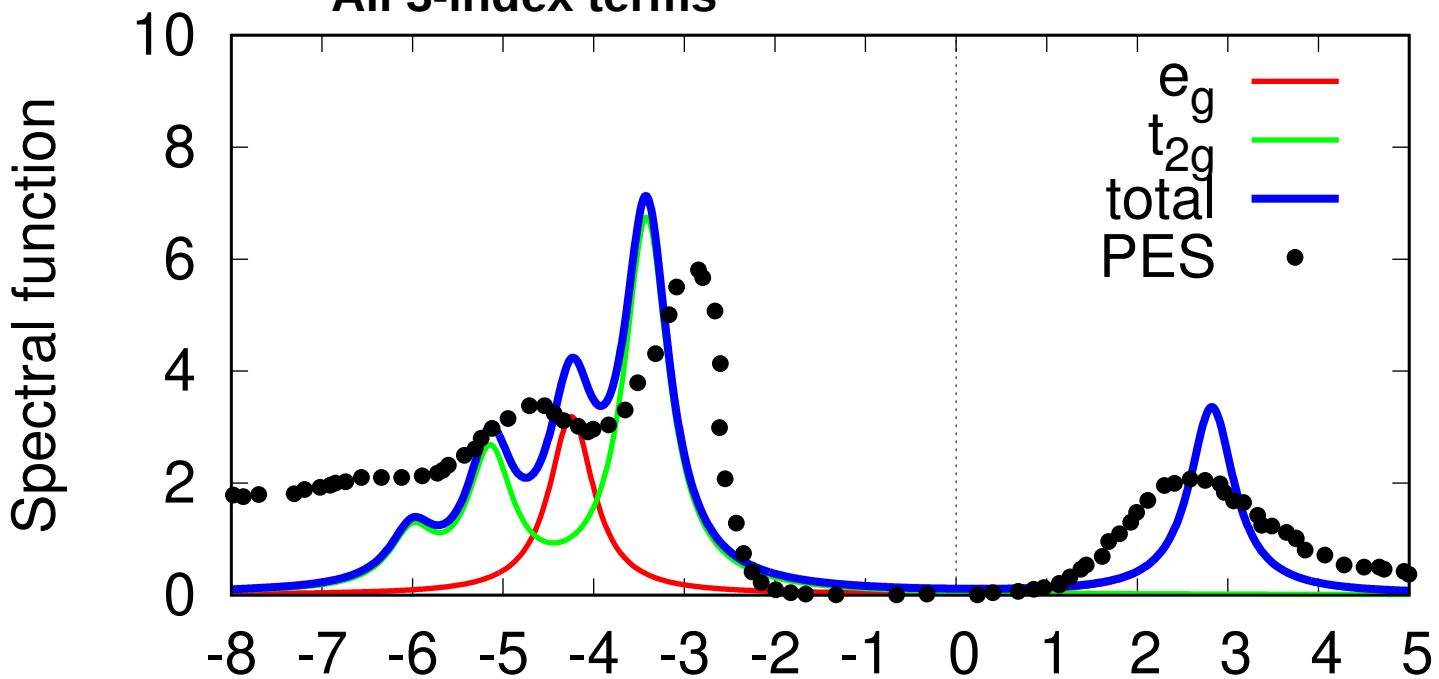
Photoemission (PES) data:
G. Sawatzky, J. Allen, PRL 53, 24 (1984)

For charge-transfer discussion, see: (and refs therein)
Zaanen, et al., PRL 55, 418 (1985)
Schuler, et al., PRB 71, 115113 (2005)

NiO: Ni *3d*, N_{el}=8, atom toy model



NiO *d-d* atomic model with crystal field splitting
No oxygen *p* included
All 3-index terms



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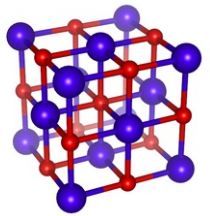
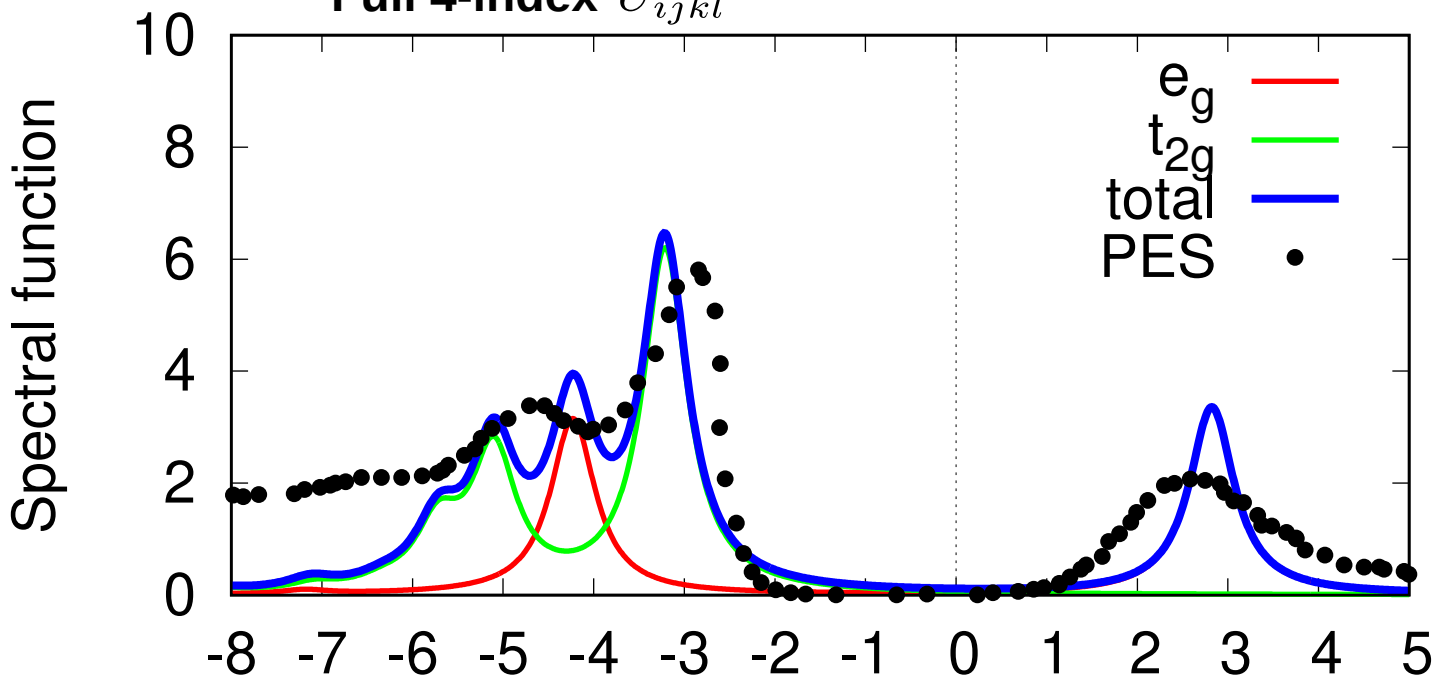


NiO *d-d* atomic model with crystal field splitting
No oxygen *p* included
Full 4-index U_{ijkl}



$U_{avg} = 5.3, J_{avg} = 1.0\text{eV}$

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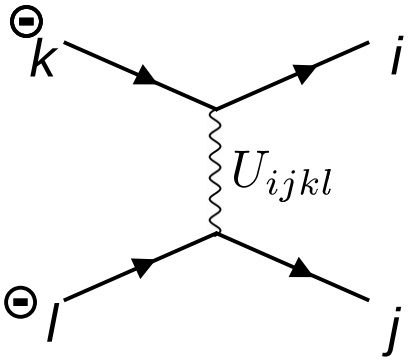
Further applications

- Projection provides efficient compression of data onto minimal set according to the symmetry of the system (Storage)

$$MU = u \quad \text{compression}$$
$$U = M^{-1}u \quad \text{decompression}$$

- Applies to any local two-particle quantity in orbital representation:
  → Only the independent parameters need to be calculated
  (Susceptibility, Vertex functions, etc.)
- Explicit symmetrization matrices available for restoring symmetry (Numerical errors, identify effect of symmetry breaking)

Conclusion



- Symmetry of the crystal environment restricts the form of the Coulomb interaction (sparse)
- Symmetry allows parametrization of full U_{ijkl} with a minimal parameter set
- Without full U_{ijkl}: Artificial breaking of symmetries, artificial ordered states, wrong multiplet positions
- Strongly correlated materials: spin-flip/pair hopping considered, but 3(4)-index terms hardly studied

Thank you very much for your attention!