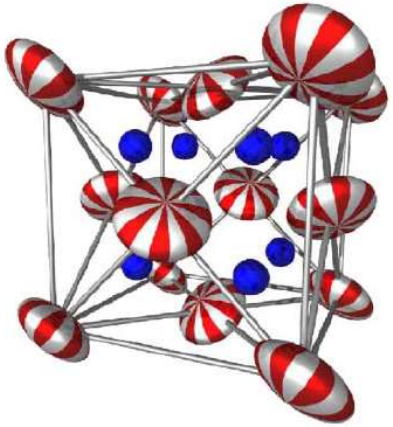
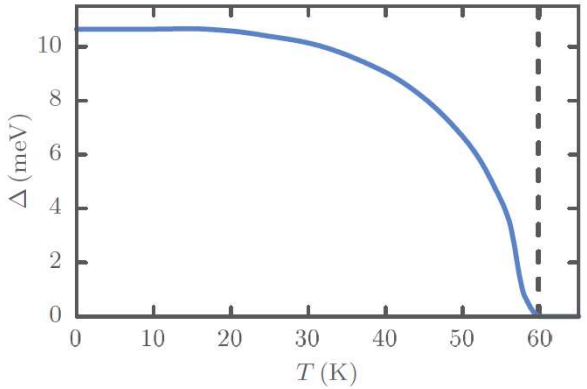
Ab initio theory of multipolar order and of superconductivity in selected compounds

Peter M. Oppeneer

Dept. of Physics and Astronomy, Uppsala University,
Box 516, S-751 20 Uppsala, Sweden

UPPSALA UNIVERSITET





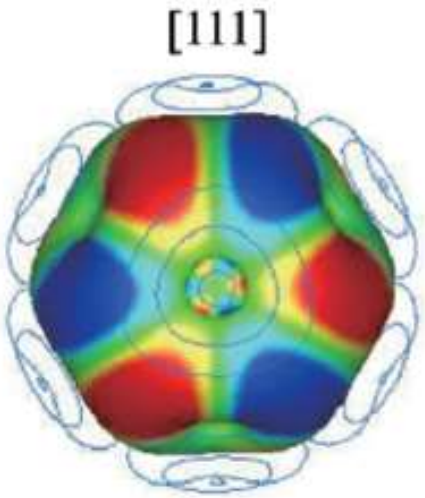
SPIN PHENOMENA
INTERDISCIPLINARY CENTER
SPICE

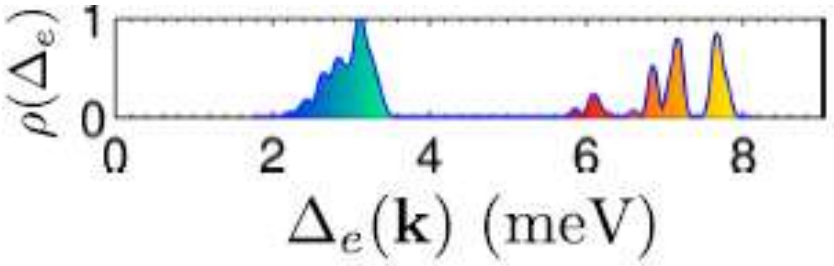
UPPSALA UNIVERSITET

Contents

Aim: Understand complex low-energy ordering phenomena using modern electronic structure calculations

- *Ab initio* theory for complex multipolar ordering in NpO_2, UO_2, AmO_2
- *Ab initio* DFT-based calculations of (un)conventional superconductivity – MgB_2 ($FeSe/SrTiO_3$)





Collaboration & Thanks To

Multipolar order

Michi-To Suzuki
(Tohoku U., Japan)

Nicola Magnani
(EU Science, JRC)

Ab initio superconductivity

Alex Aperis

Fabian Schrodi

Pablo Maldonado

Roberto Caciuffo, Gerry Lander

Review:

First-principles theory of magnetic multipoles in condensed matter systems.
M.-T. Suzuki, H. Ikeda, and P.M. Oppeneer,
J. Phys. Soc. Jpn. **87** (2018) 041008

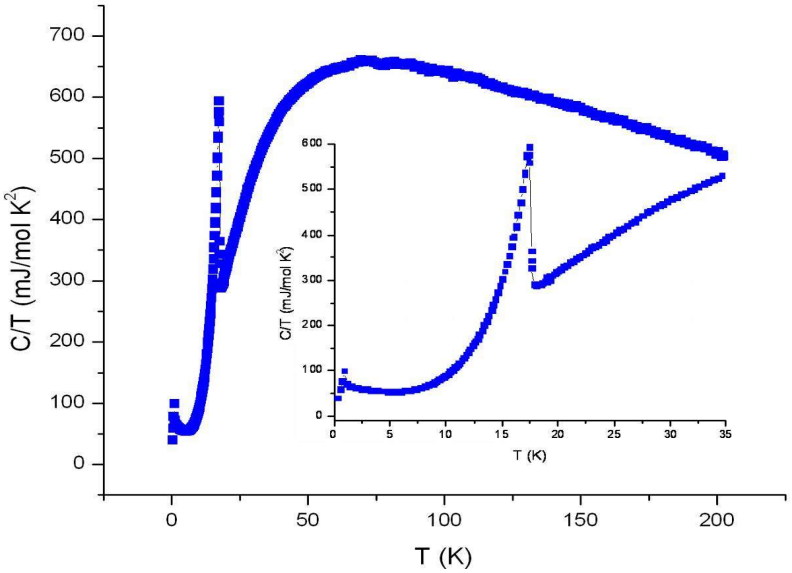
Uppsala Superconductivity (UppSC) code

Schrodi, Aperis & Oppeneer, PRB 99, 184508 (2019)
Bekaert et al, PRL 123, 077001 (2019)
Schrodi, Aperis & Oppeneer, PRB 98, 094509 (2018)
Aperis and Oppeneer, PRB 97, 060501(R) (2018)

UPPSALA UNIVERSITET

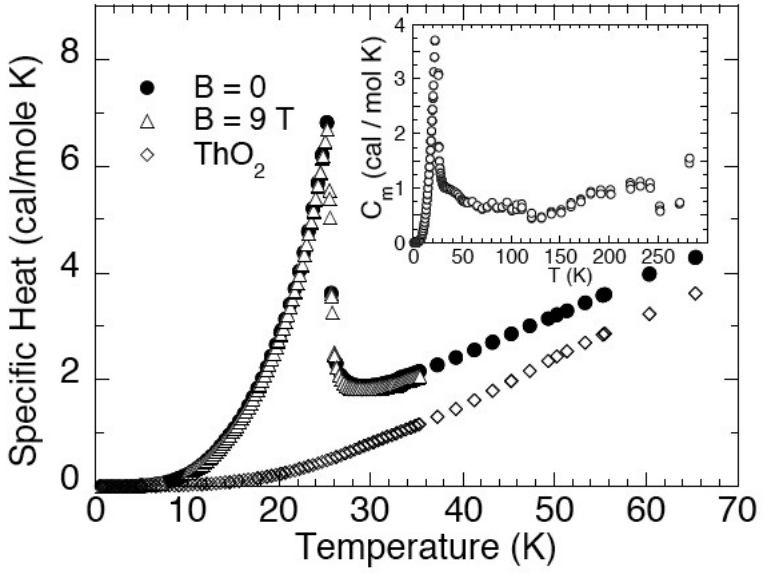
A major puzzle - Two "hidden" exotic phase transitions

URu_2Si_2 (heavy fermion SC)



Palstra et al, PRL **55** (1985)

NpO_2 (insulating oxide)



Westrum et al, J. Chem. Phys. **21** (1953)

After many years of research: no dipole magnetic ordering below T_0

Is the physical mechanism of the hidden orders the same ?

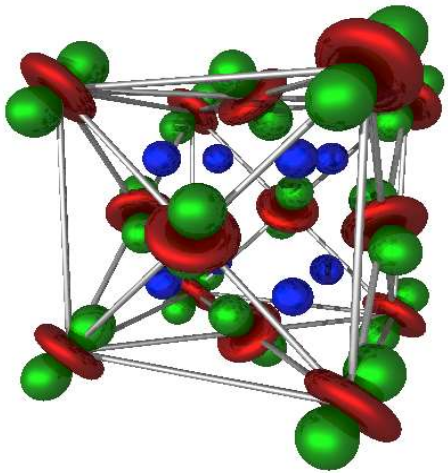
Many multipolar orders proposed (octupole, hexadecapole, triakontadipole?)

UPPSALA UNIVERSITET

Observed multipolar order in solid-state systems

Actinides: UO_2, NpO_2 and UPd_3

Lanthanides: CeB_6, $CePd_3S_4$, $PrPb_3$, $PrMg_3$, $DyPd_3S_4$, HoB_2C_2, DyB_2C_2, $PrRu_4P_{12}$, $PrOs_4Sb_{12}$, $SmRu_4P_{12}$, ...



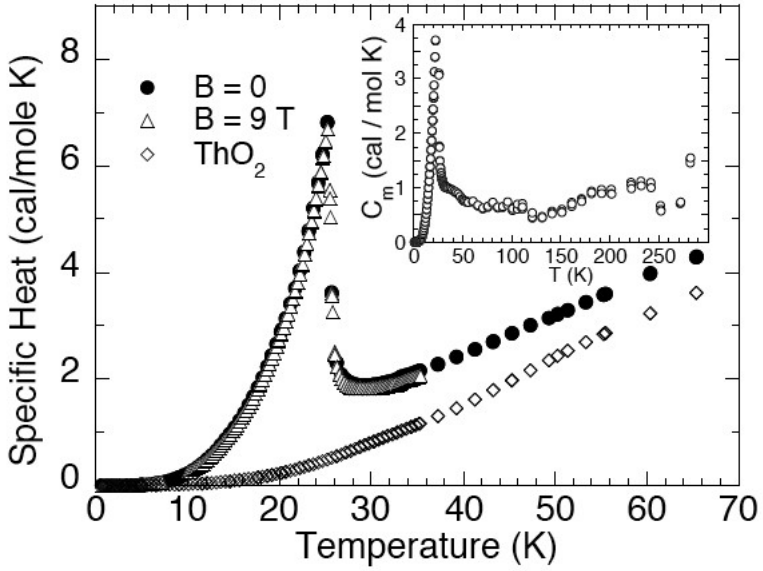
Reviews:

Santini et al, Rev. Mod. Phys. 81, 807 (2009)
Kusunose, J. Phys. Soc. Jpn. 77, 064710 (2008)
Kuramoto, Kusunose & Kiss, JPSJ 78, 072001 (2009)
Suzuki, Ikeda & Oppeneer, JPSJ 87, 041008 (2018)

UPPSALA UNIVERSITET

A puzzle: Multipolar ordering in NpO_2

Phase transition at 25 K



Westrum et al, J. Chem. Phys. **21**, 419 (1953)

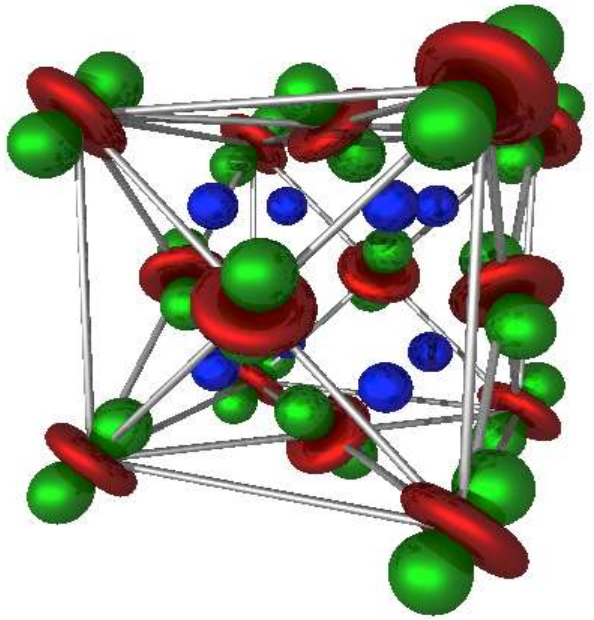
Ross and Lam, J. Appl. Phys. **38**, 1451 (1967)

Neutron exp.: No magnetic dipole order

Caciuffo et al, Solid State Commun. **64**, 149 (1987)

Muon spin relaxation: *magnetic signal*

Kopmann et al, J. Alloys Compd. **271-273**, 463 (1998)



RXS: 3***q*** electric quadrupole

Paixao et al, PRL **89** (2002) 187202

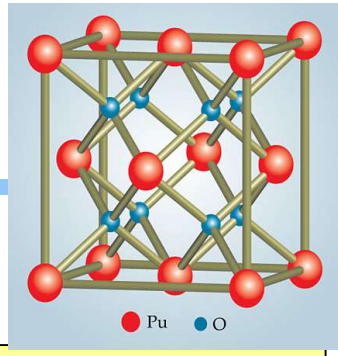
Santini et al, PRL **97** (2006) 207203 suggests 3***q***-triakontadipole (2^5) to explain observed properties

Support from INS

Magnani et al, PRB **78** (2008)104425

UPPSALA UNIVERSITET

Actinide dioxides



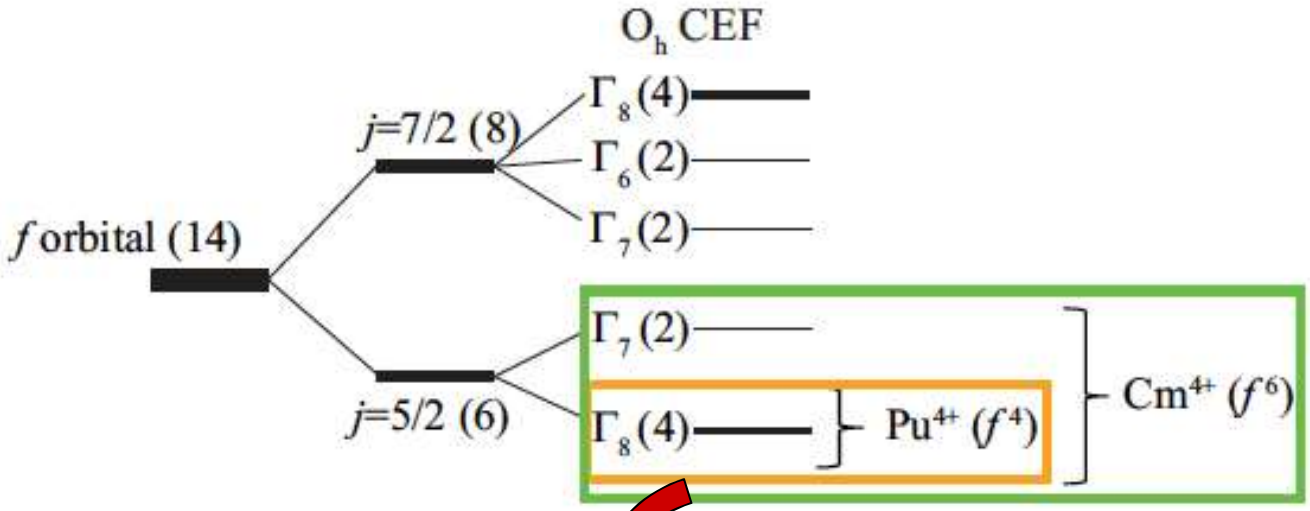
UO_2	NpO_2	PuO_2	AmO_2	CmO_2
Transverse 3*q*- noncollinear AFM with quadr. pole insulator	Long. 3*q*- noncollinear AF multipolar order insulator	Nonmagnetic insulator	Long. 3*q*- noncollinear AF multipolar order insulator (?)	Paramagnetic insulator
~$5f^2$				~$5f^6$

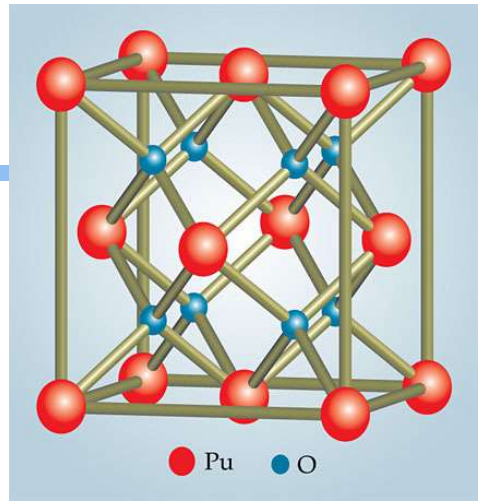
WHY ARE THEY SO DIFFERENT ?

- but all are insulators with fluorite structure !

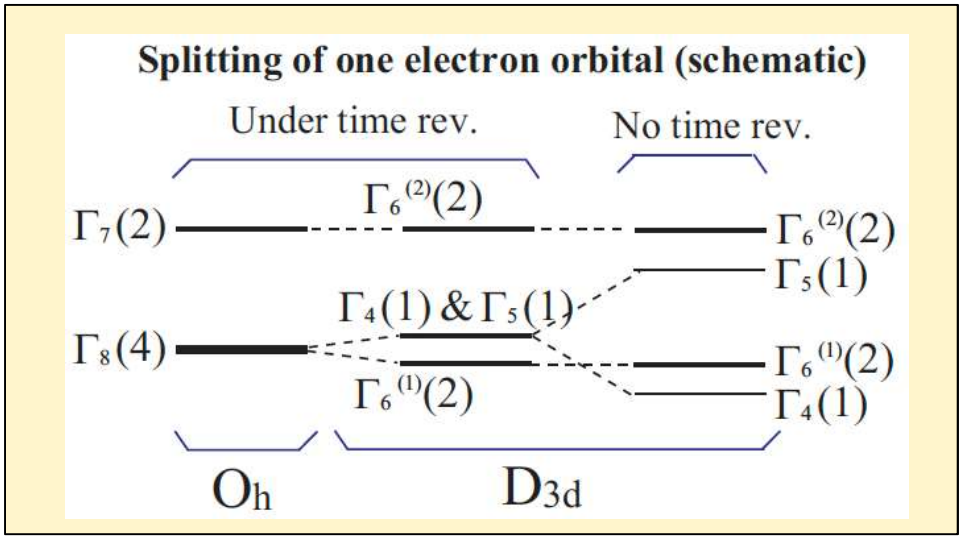
UPPSALA UNIVERSITET

Filling of 5f cubic CF levels





PuO_2 and CmO_2 can be nonmagnetic insulators, NpO_2 insulator only with Time Rev. Sym. breaking (D_{3d} with 4 fu, Pn3m group)



But: DFT & DFT+U make all AcO_2 5f-compounds antiferromagnetic!

UPPSALA UNIVERSITET

Need *ab initio* Theory for Multipoles

Electric multipoles:

$$\mathcal{Q}_{\ell m} \equiv \sqrt{\frac{4\pi}{2\ell+1}} \int d\boldsymbol{r}(r^{\ell} Y^{*}_{\ell m}(\theta,\phi))\rho_e(\boldsymbol{r})$$

Magnetic multipoles:

$$\mathcal{M}_{\ell m} = \sqrt{\frac{4\pi}{2\ell+1}} \int d\boldsymbol{r}\, \nabla(r^{\ell} Y^{*}_{\ell m}(\theta,\phi)) \cdot \boldsymbol{m}(\boldsymbol{r})$$

Rank: l =0 – monopole, l =1 – dipole, l =2 – quadrupole, l =3 – octupole,
l =4 –hexadecapole, l =5 – triakontadipole

Time reversal symmetry: electric MP – even , magnetic MP - odd
Spatial inversion symmetry: Nonzero even rank electric multipoles &
nonzero odd rank magnetic multipoles

In solids: classification according to IREP of the point group

UPPSALA UNIVERSITET

Active multipole moments in O_h Γ_8-quartet

Shiina et al., J. Phys. Soc. Jpn. **66** (1997) 1741

Dip. Γ_4^-

$$\frac{1}{\sqrt{2}}(-J_1^{(1)}+J_{-1}^{(1)})=J_x$$
$$\frac{\mathrm{i}}{\sqrt{2}}(J_1^{(1)}+J_{-1}^{(1)})=J_y$$
$$J_0^{(1)}=J_z$$

Quad. Γ_3^+

$$J_0^{(2)}=\tfrac{1}{2}(2J_z^2-J_x^2-J_y^2)\equiv O_2^0$$
$$\frac{1}{\sqrt{2}}(J_2^{(2)}+J_{-2}^{(2)})=\frac{\sqrt{3}}{2}(J_x^2-J_y^2)\equiv O_2^2$$

Quad. Γ_5^+

$$\frac{\mathrm{i}}{\sqrt{2}}(J_1^{(2)}+J_{-1}^{(2)})=\frac{\sqrt{3}}{2}\overline{J_yJ_z}\equiv O_{yz}$$
$$\frac{1}{\sqrt{2}}(-J_1^{(2)}+J_{-1}^{(2)})=\frac{\sqrt{3}}{2}\overline{J_zJ_x}\equiv O_{zx}$$
$$\frac{\mathrm{i}}{\sqrt{2}}(-J_2^{(2)}+J_{-2}^{(2)})=\frac{\sqrt{3}}{2}\overline{J_xJ_y}\equiv O_{xy}$$

Oct.

Γ_2^-

$$\frac{\mathrm{i}}{\sqrt{2}}(-J_2^{(3)}+J_{-2}^{(3)})=\frac{\sqrt{15}}{6}\overline{J_xJ_yJ_z}\equiv T_{xyz}$$

Γ_4^-

$$\tfrac{1}{4}[\sqrt{5}(-J_3^{(3)}+J_{-3}^{(3)})-\sqrt{3}(-J_1^{(3)}+J_{-1}^{(3)})]=\tfrac{1}{2}(2J_x^3-\overline{J_xJ_y^2}-\overline{J_z^2J_x})\equiv T_x^\alpha$$
$$-\tfrac{\mathrm{i}}{4}[\sqrt{5}(J_3^{(3)}+J_{-3}^{(3)})+\sqrt{3}(J_1^{(3)}+J_{-1}^{(3)})]=\tfrac{1}{2}(2J_y^3-\overline{J_yJ_z^2}-\overline{J_x^2J_y})\equiv T_y^\alpha$$
$$J_0^{(3)}=\tfrac{1}{2}(2J_z^3-\overline{J_zJ_x^2}-\overline{J_y^2J_z})\equiv T_z^\alpha$$

Γ_5^-

$$-\tfrac{1}{4}[\sqrt{3}(-J_3^{(3)}+J_{-3}^{(3)})+\sqrt{5}(-J_1^{(3)}+J_{-1}^{(3)})]=\frac{\sqrt{15}}{6}(\overline{J_xJ_y^2}-\overline{J_z^2J_x})\equiv T_x^\beta$$
$$\tfrac{\mathrm{i}}{4}[-\sqrt{3}(J_3^{(3)}+J_{-3}^{(3)})+\sqrt{5}(J_1^{(3)}+J_{-1}^{(3)})]=\frac{\sqrt{15}}{6}(\overline{J_yJ_z^2}-\overline{J_x^2J_y})\equiv T_y^\beta$$
$$\tfrac{1}{2}(J_2^{(3)}+J_{-2}^{(3)})=\frac{\sqrt{15}}{6}(\overline{J_zJ_x^2}-\overline{J_y^2J_z})\equiv T_z^\beta$$

- Santini and Amoretti (2000) [Phys. Rev. Lett. **85** (2000) 2188]

  Magnetic octupole T_{xyz} with Γ_2 symmetry suggested

- Paixão et al. (2002, Resonant x-ray) [Phys. Rev. Lett. **89** (2002) 187202]

  Triple-***q*** anti-ferro quadrupolar structure is suggested
  The quadrupole order could be driven by the magnetic octupoles of Γ_5 symmetry.

- Kiss and Fazekas (2003) [Phys. Rev. B **68** (2003) 174425]

  The Γ_5 octupoles $T_{111}{}^\beta=T_{x\beta}+T_{y\beta}+T_{z\beta}$ are the best candidates for octupolar order parameters

- Santini et al (2006) [Phys. Rev. Lett. **97** (2006) 207203]

  Γ_5 quadrupoles and Γ_5 triakontadipoles in the ordered state are suggested

Exp. status

UPPSALA UNIVERSITET

Methodology

- LSDA +U (FLL), with noncollinear atomic magnetization
- FPLAPW (Kansai – code, SOC) (isotropic) U = 4 – 5 eV, J = 0 – 0.5 eV

  anisotropic part: $F_4=41/297F_2$, $F_6=175/11583F_2$,
  $J=(286F_2+195F_4+250F_6)/6435$

- Choice of initial density matrix (e.g. NpO_2):

  $\mathrm{Tr}[n]=3$, $5f^3$ occupancy of states in D_{3d} irred. representation

multipole moments:

$$\langle O^{\tau\ell}\rangle = \sum_{kb\gamma\gamma'} \langle kb|\tau\ell\,\gamma\rangle O^{\tau\ell}_{\gamma\gamma'} \langle \tau\ell\,\gamma'|kb\rangle = \sum_{\gamma\gamma'} O^{\tau\ell}_{\gamma\gamma'} n^{\tau\ell}_{\gamma'\gamma}$$

Operator expressions

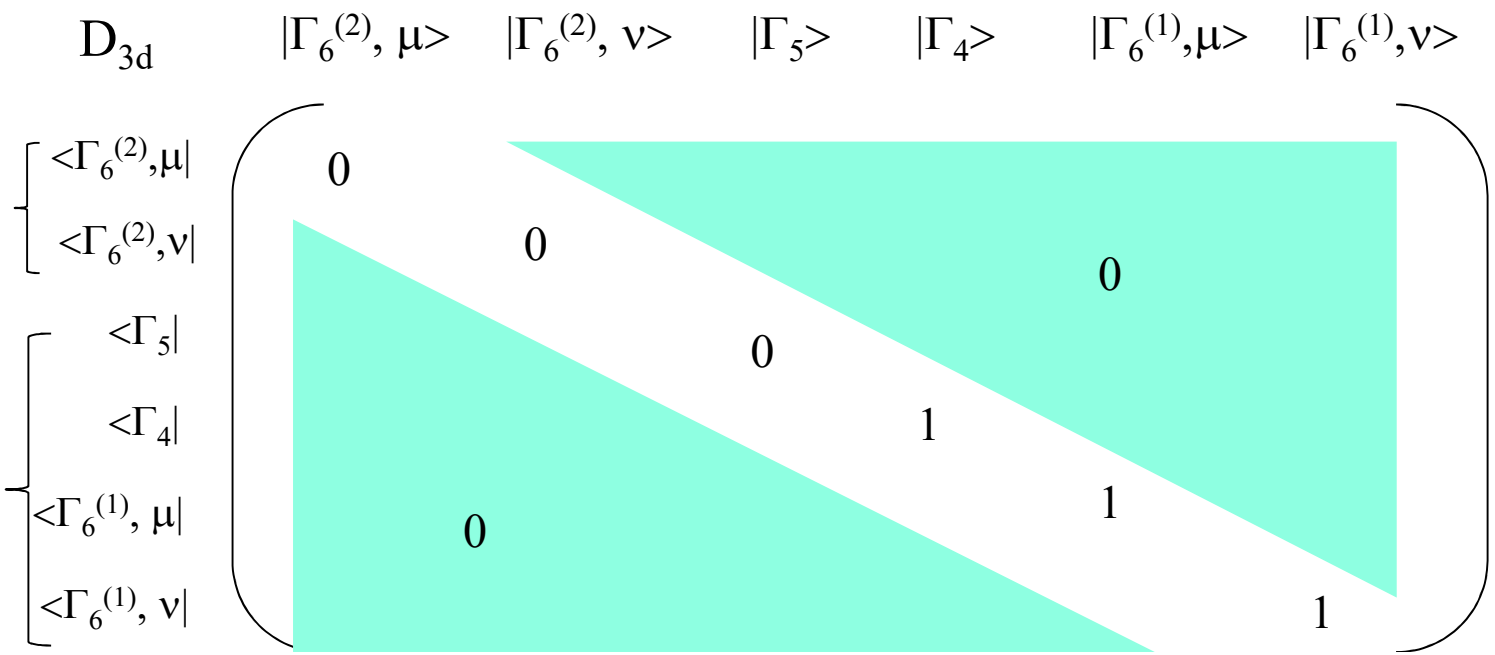
$|\tau\ l\ \gamma\rangle$ local basis in MT spheres

Methodology

- LSDA +U (FLL), with noncollinear atomic magnetization
- FPLAPW (Kansai – code) (isotropic) U = 4 – 5 eV, J = 0 – 0.5 eV

  anisotropic part: $F_4=41/297F_2$, $F_6=175/11583F_2$,
  $J=(286F_2+195F_4+250F_6)/6435$
- Choice of initial density matrix:

  E.g., Density matrix expressed by D_{3d} irreducible representation



UPPSALA UNIVERSITET

DFT+U methodology

$$h_{\mathrm{LDA}+U} = h_{\mathrm{LDA}} + \sum_{\tau} \sum_{\gamma\gamma'} |\tau\ell\gamma\rangle v^{\tau\ell}_{\gamma\gamma'} \langle\tau\ell\gamma'|$$

with local on-site 5f-Coulomb correction (FLL)

$$v^{\tau\ell}_{\{ms\}\{m's'\}} = \sum_{m''m'''} \Big[\delta_{ss'} \sum_{s''} n^{\tau\ell}_{\{m'''s''\}\{m''s''\}} \langle mm''|W|m'm'''\rangle - n^{\tau\ell}_{\{m'''s\}\{m''s'\}} \langle mm''|W|m'''m'\rangle \Big] - \delta_{mm'}\delta_{ss'} \Big[U(n-1/2) - \frac{J}{2}(n-1) \Big],$$

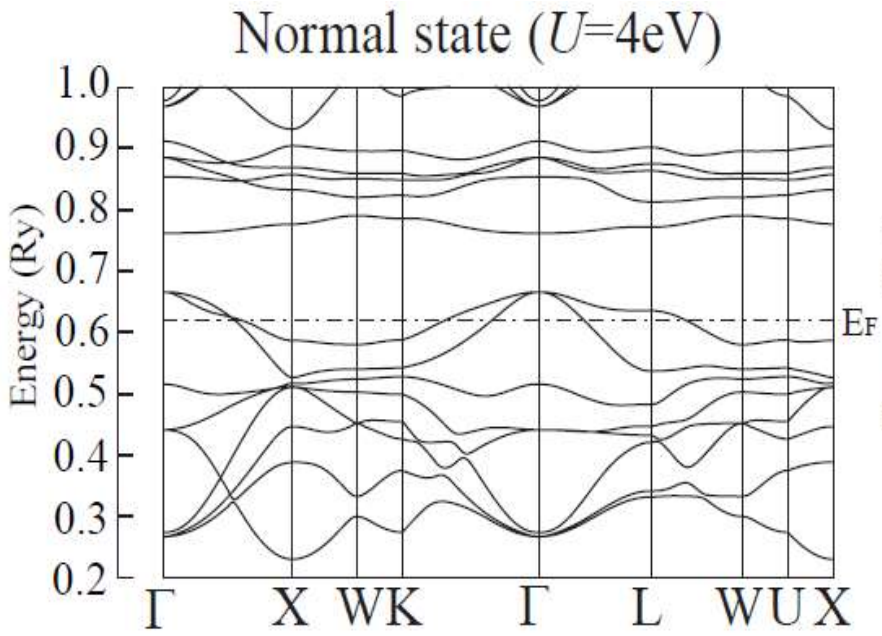
$$\langle m_1 m_2|W|m_3 m_4\rangle = \delta_{m_1+m_2,m_3+m_4} \sum_{k=0}^{6} c^k(\ell m_1;\ell m_3) \times c^k(\ell m_4;\ell m_2) F^k,$$

$(F_0=U,\ J= aF_2+bF_4+cF_6)$ $\quad F_4=41/297F_2,\ F_6=175/11583F_2\ ,$

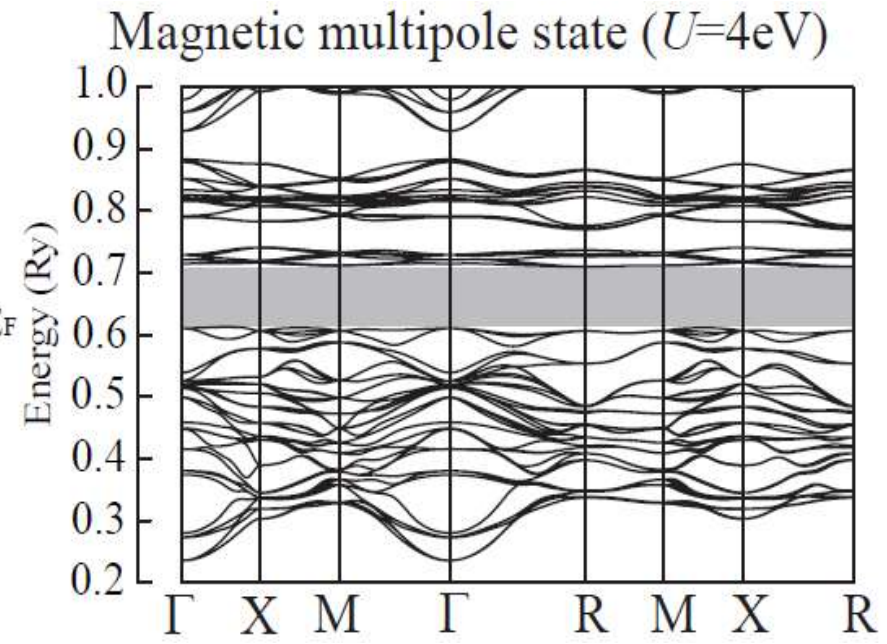
$J=(286F_2+195F_4+250F_6)/6435$

NpO_2 - LSDA+*U* calculations

Use appropriate symmetry: Not fluorite FCC (O_h) but D_{3d} local symmetry for Np $5f^3$ ions, with time-rev.symm. breaking, for 4-units NpO_2



NpO_2, FCC O_h

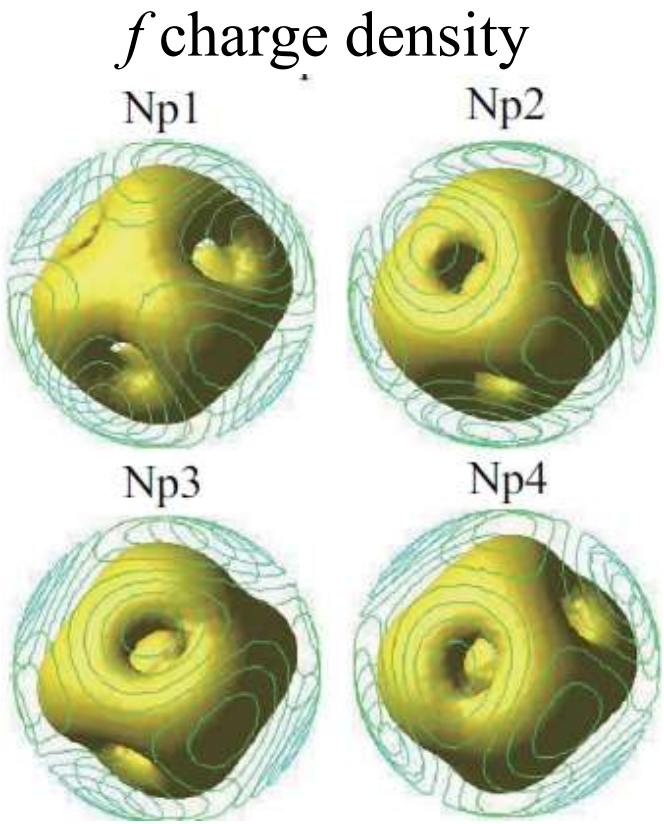


NpO_2, D_{3d} --> *insulator!*

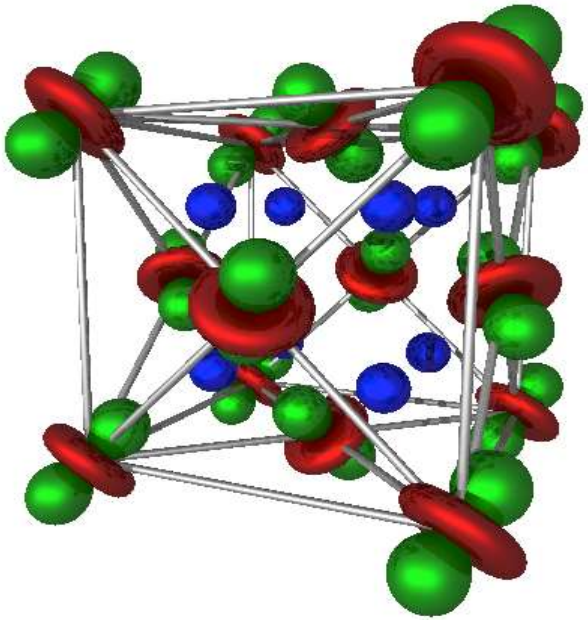
Converges to Non-Col. Multipol. ordered state with *lower* total energy

UPPSALA UNIVERSITET

Charge densities on Np ions



3***q*** structure with (111) axis



RXS: 3***q*** electric quadrupole
Paixao et al, PRL **89** (2002) 187202

UPPSALA UNIVERSITET

Paramagnetic vs. 3***q***-multipolar ordered state

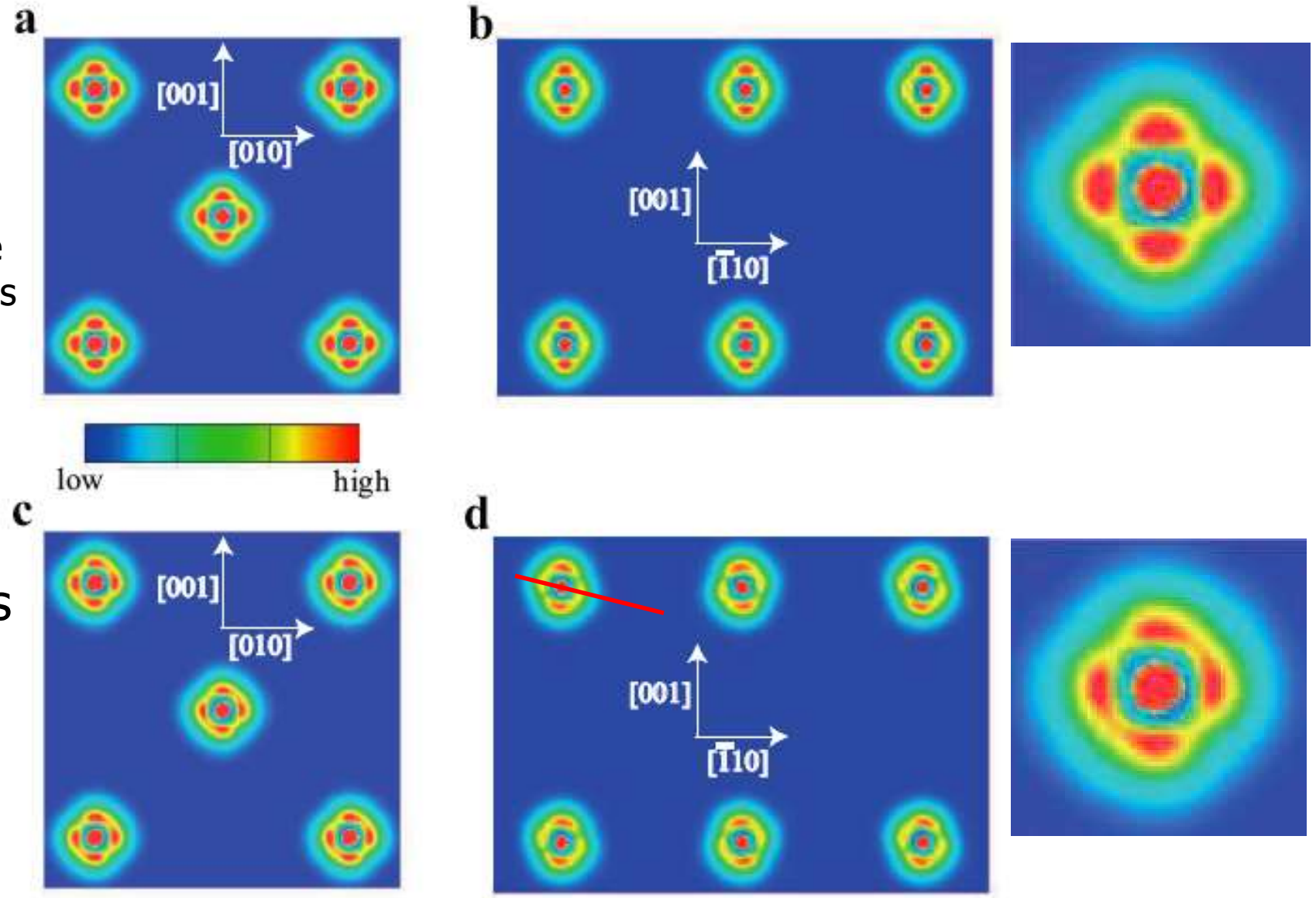
FCC

Charge densities

4-units

NpO_2

D_{3d}

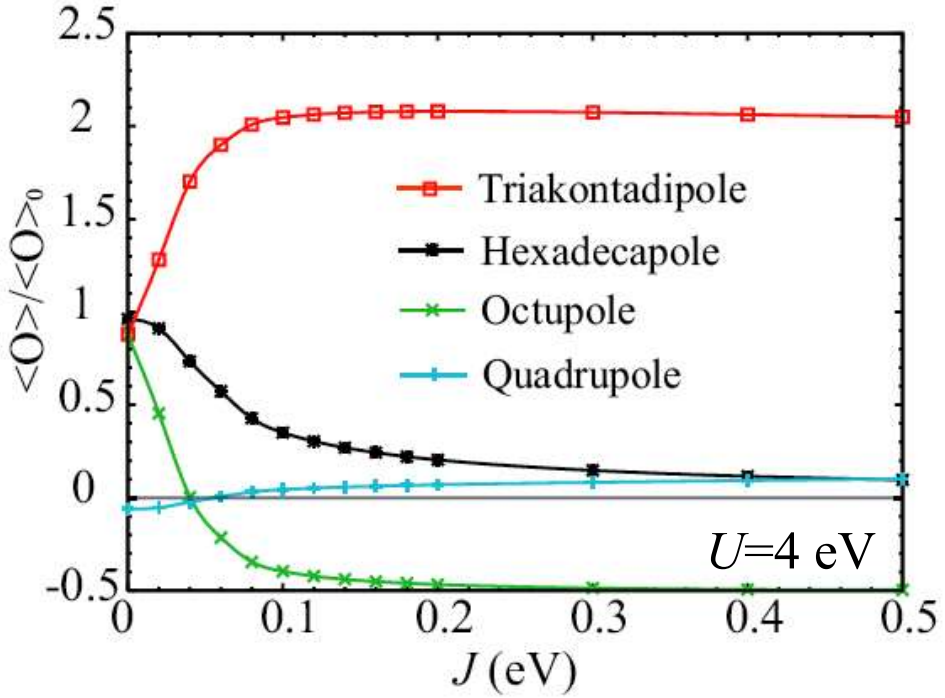


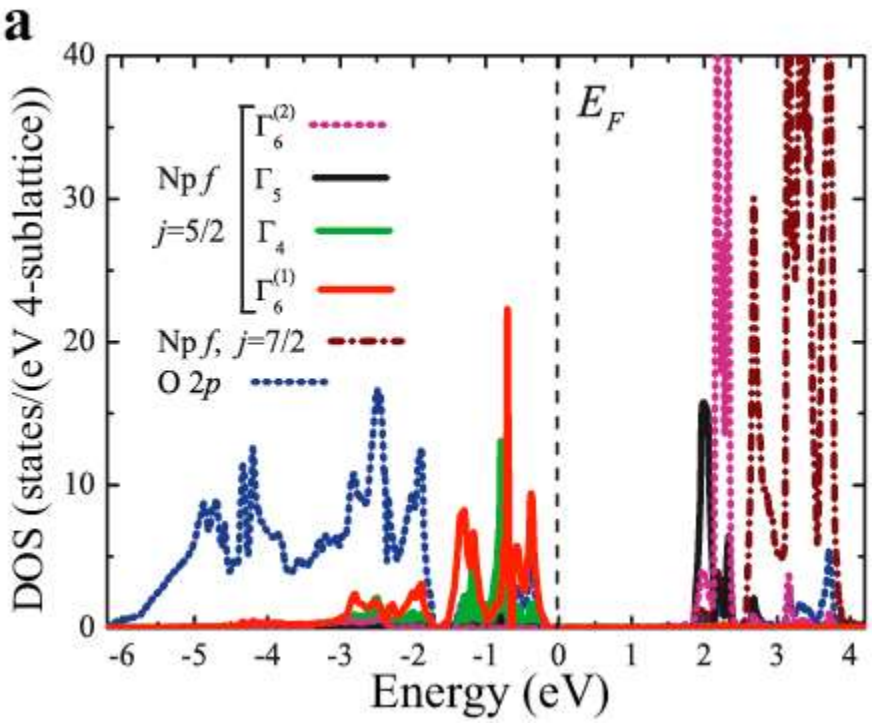
Which of the 3q-multipole order parameters ?

$$\langle O^{\tau\ell}\rangle = \sum_{kb\gamma\gamma'} \langle kb|\tau\ell\,\gamma\rangle O^{\tau\ell}_{\gamma\gamma'} \langle \tau\ell\,\gamma'|kb\rangle = \sum_{\gamma\gamma'} O^{\tau\ell}_{\gamma\gamma'} n^{\tau\ell}_{\gamma'\gamma}$$

$|\tau\ l\ \gamma\rangle$ local basis in MT spheres

Operator expressions



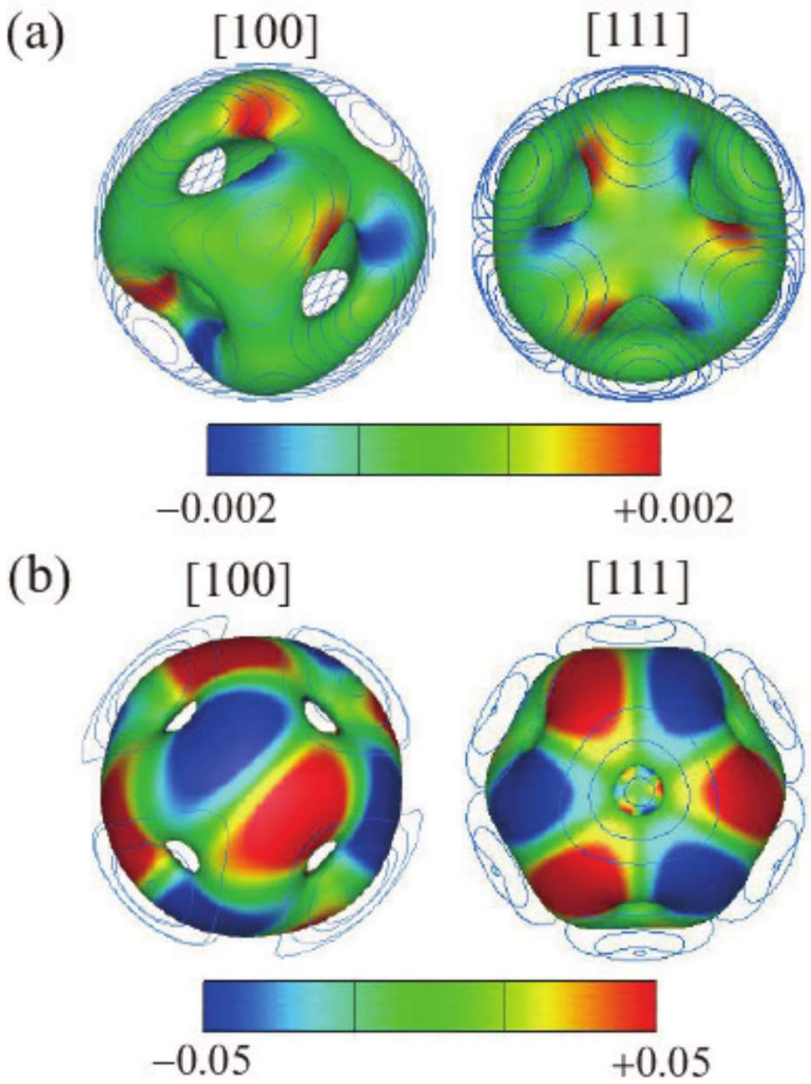


Magn. (Γ_5) triakontadipole leading OP (zero dipole moment)

Suzuki, Magnani & Oppeneer, PRB **82**, 241103 (2010)

Complex (tot.) magnetic distribution on Np in NpO_2

5f charge density isosurface with magnetization as color

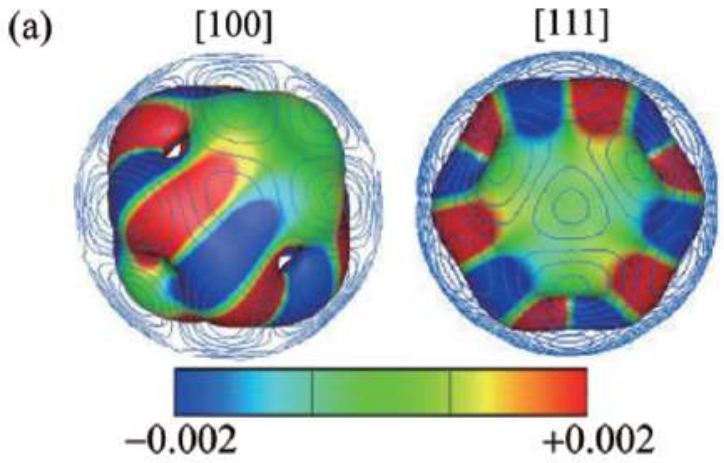


U=4 eV, J=0 eV
MMP

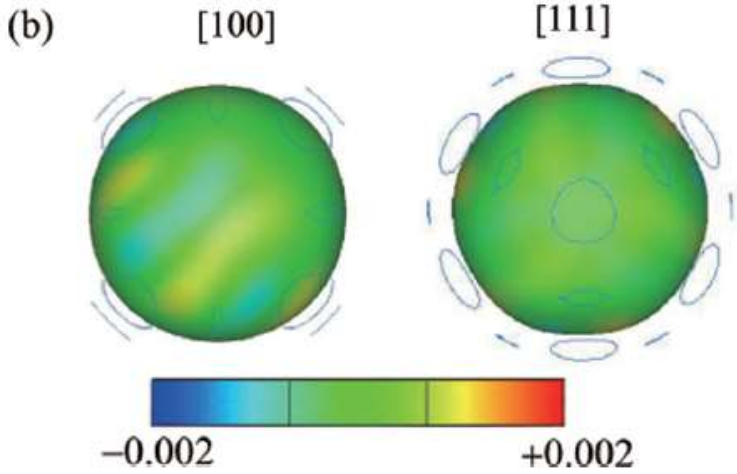
U=4 eV, J=0.5 eV
MMP

Zero dipole moment

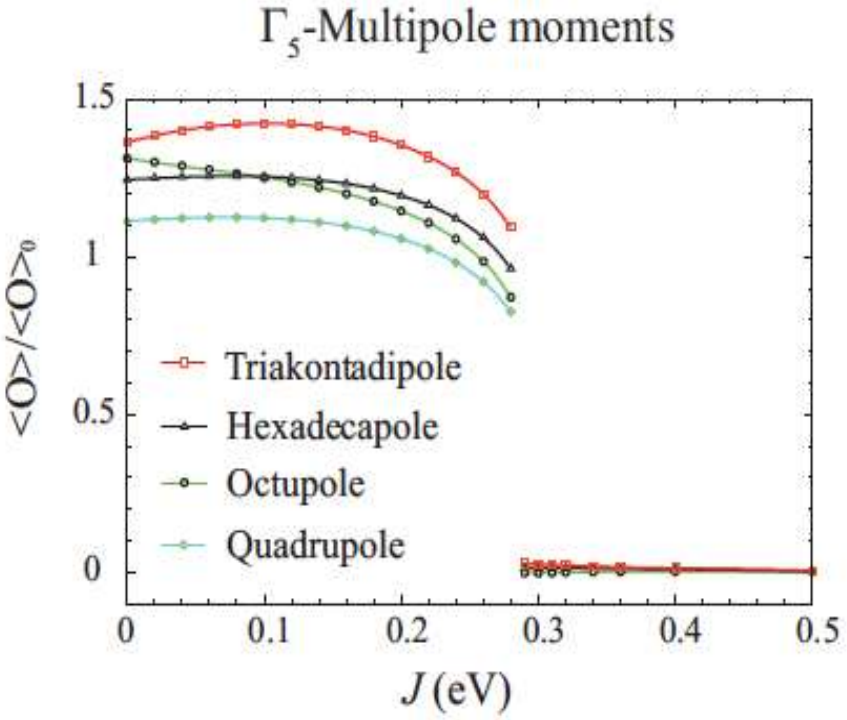
Multipole order on AmO_2

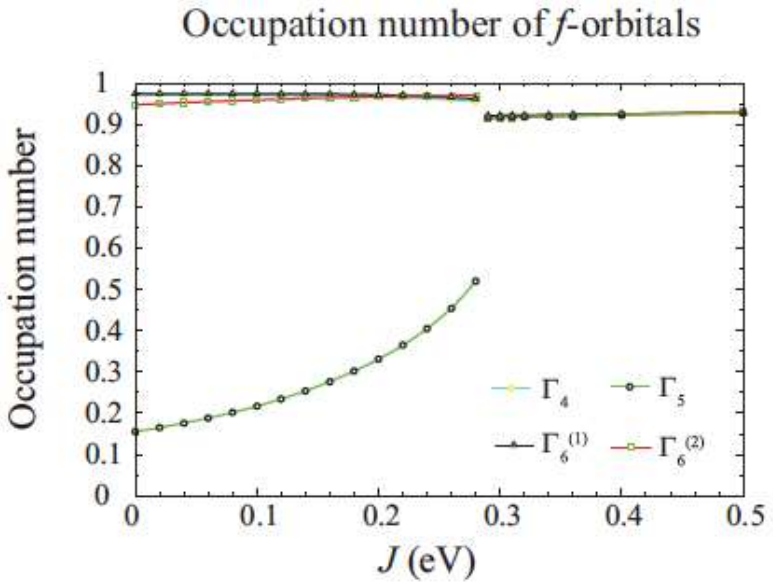


U=4 eV,
J=0 eV
MMP
insulator
1.3 eV gap



U=4 eV,
J=0.5 eV
NM
metal

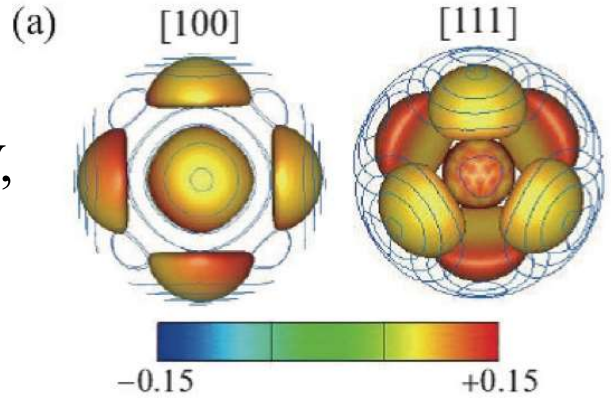




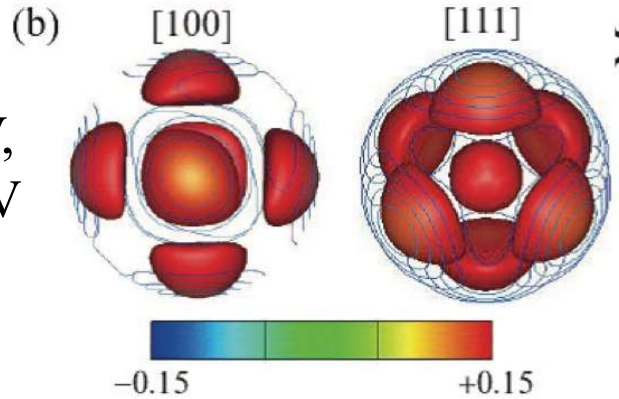
Collapse of MMP as the j_z=5/2, Γ_7 (2) almost fully occupied

UO_2 – antiferromagnetic insulator

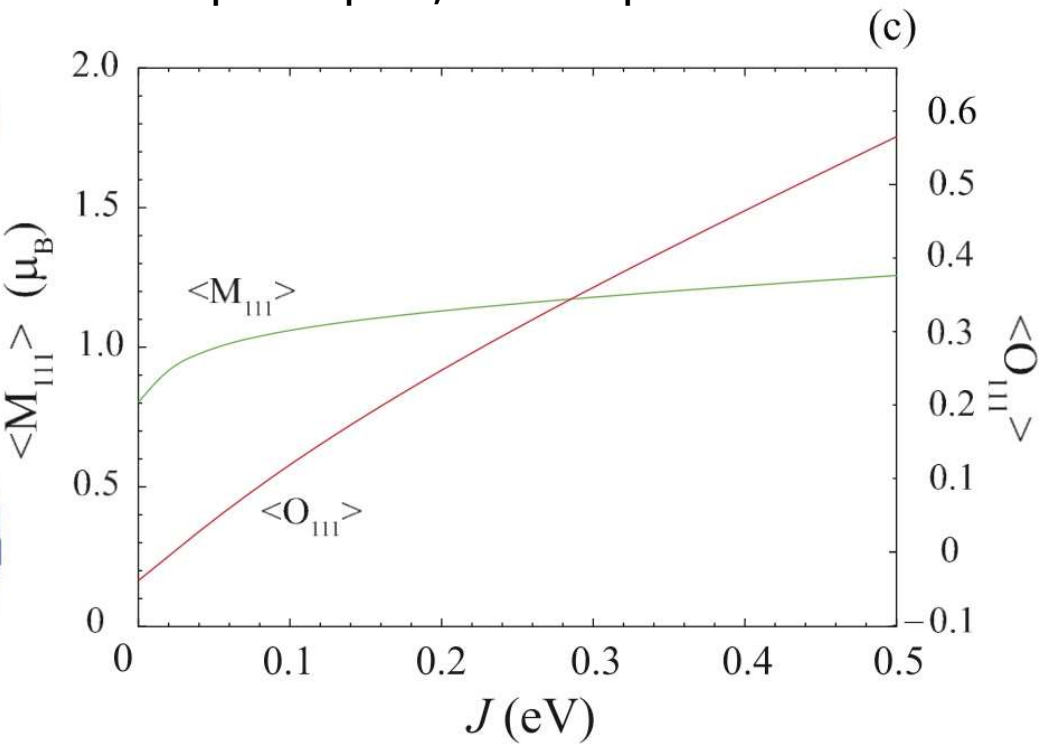
U=4 eV,
J=0 eV



U=4 eV,
J=0.5 eV



<O> quadrupole, <M> dipole moment

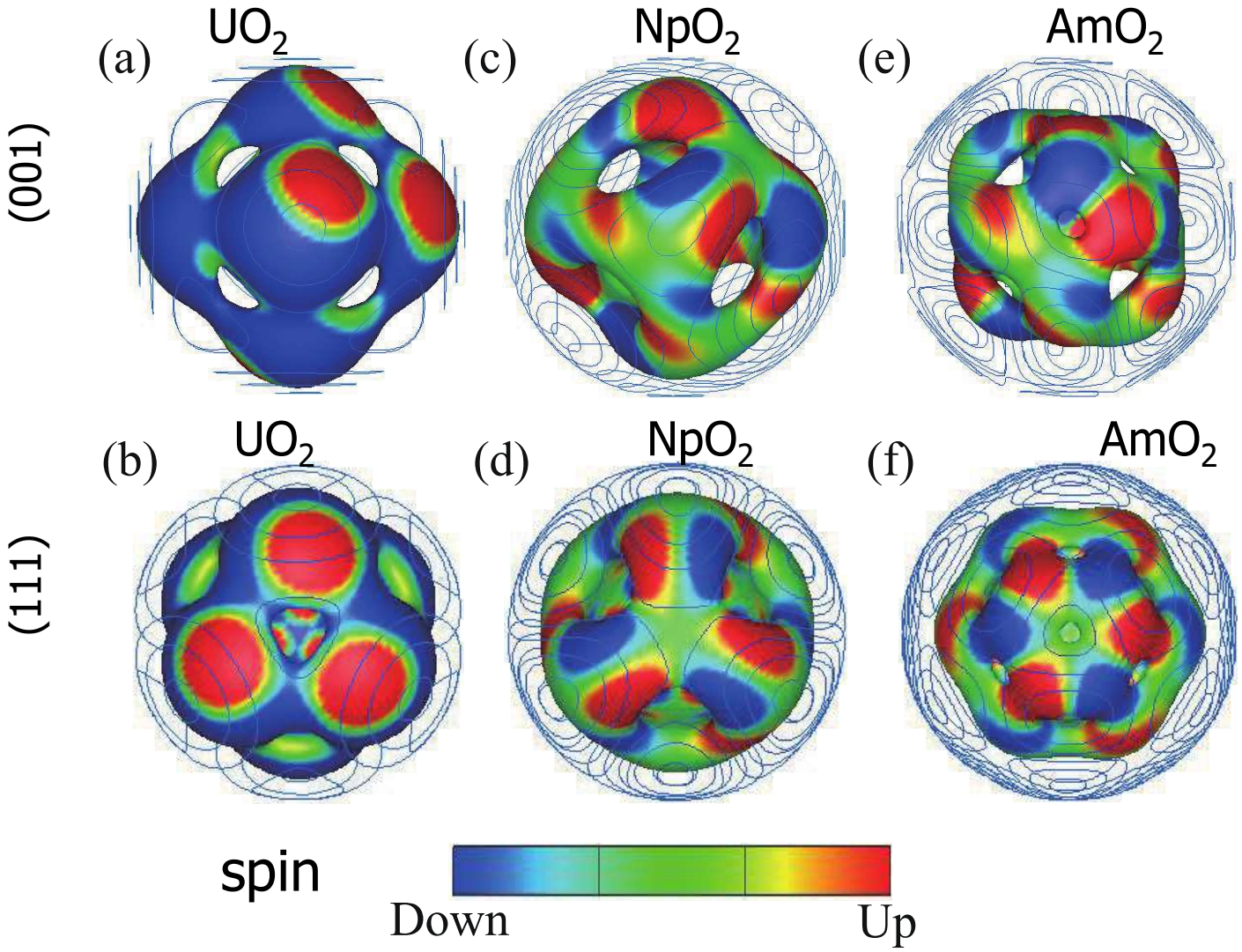


Transverse 3**q** antiferromagnet with quadrupole moment
(computed without lattice distortion)

Suzuki, Magnani & Oppeneer, PRB **88,** 195146 (2013)
Magnani, Suzuki & Oppeneer, Comp. Rend. Phys. **15** (2015)

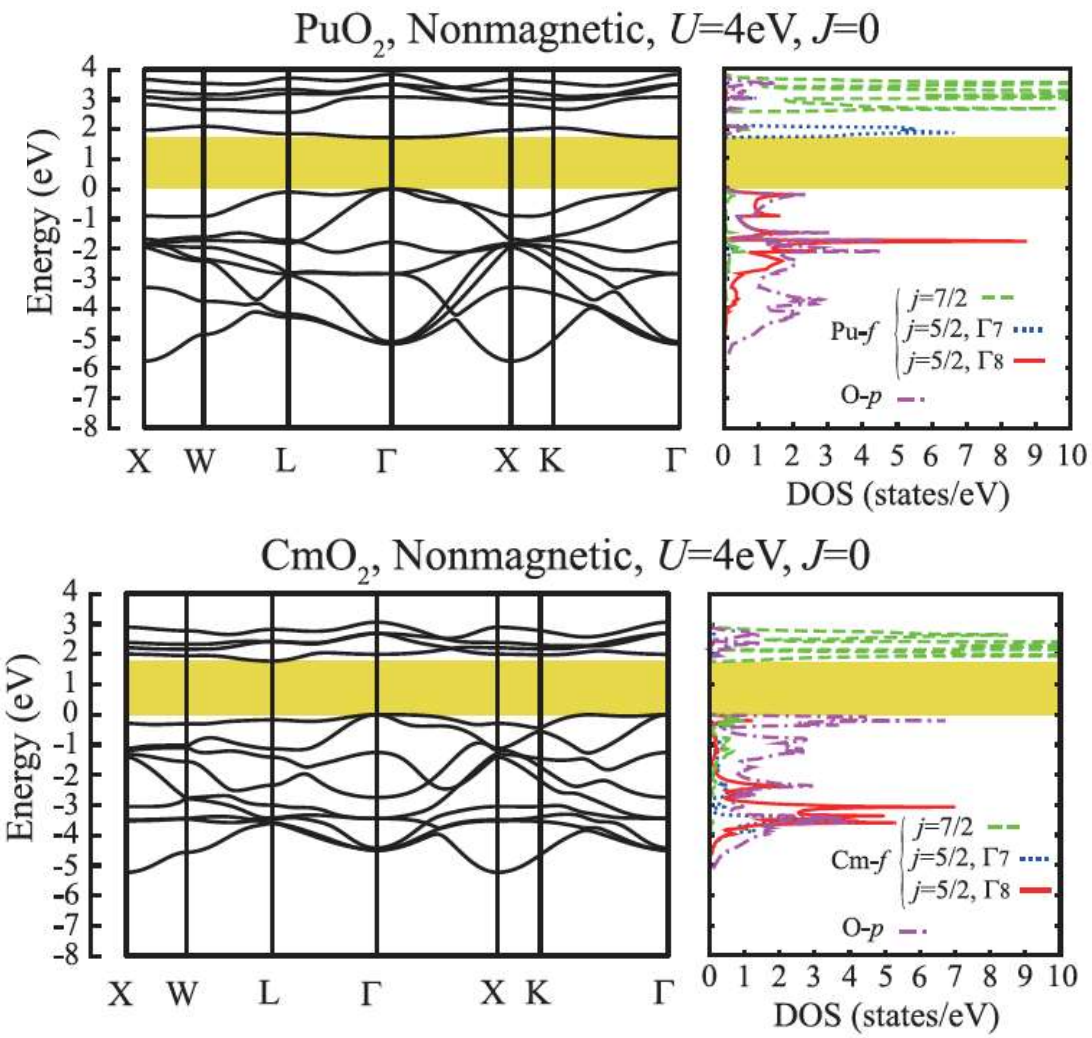
UPPSALA UNIVERSITET

Spin & charge distributions at the Ac side

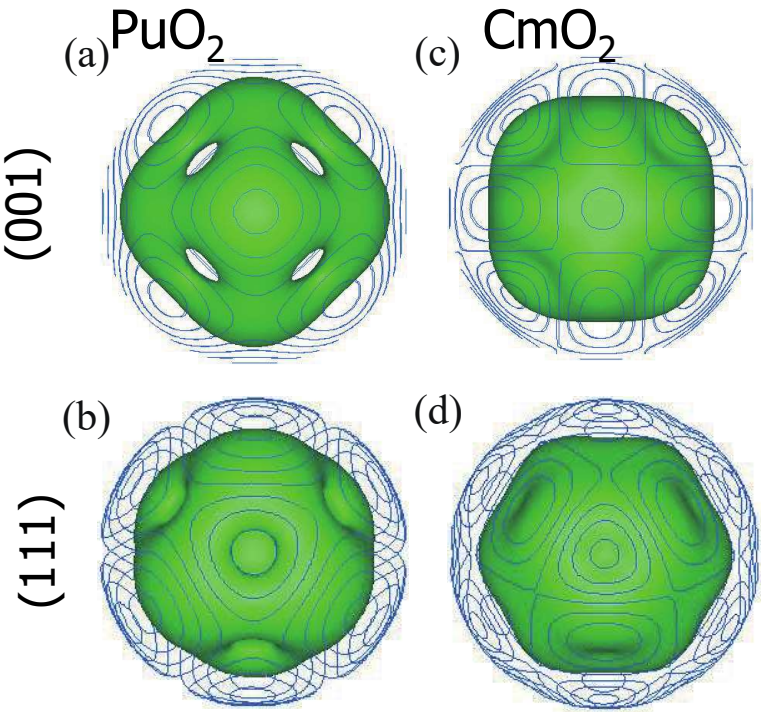


UPPSALA UNIVERSITET

Nonmagnetic AcO_2 compounds



(but smaller gaps for larger *J*)



Charge distributions of the Ac 5f electrons in PuO_2 and CmO_2

UPPSALA UNIVERSITET

Ab initio theory of 'unconventional' superconductivity

- No definite *identification* of unconvent. pairing mechanism
- Not much *ab initio* theory of SC (e.g., phononic SC in MgB_2 *)
- *Multiband, anisotropic* Eliashberg theory with *ab initio* DFT input (Uppsala Superconductivity code)
- Search for unconventional superconductivity in MgB_2
  - Magnetic-field induced odd-frequency pairing
  - MgB_2 is good test case for calculations (anisotropic, two-band SC)

<u>UppSC:</u>

- full bandwidth
- even- and odd-frequency pairing
- phonon and SF mediated SC
- Adiabatic & non-adiabatic SC

*Choi et al, Nature 418 (2002)

UPPSALA UNIVERSITET

Fully anisotropic Eliashberg equations

Eliashberg equations with Zeeman field and even & odd-freq. gap

$$Z_{\mathbf{k},n} = 1 + \frac{1}{2\omega_n}\pi T \sum_{n',\pm} \left\langle \lambda(\mathbf{k}\,\mathbf{k}', n\,n') \frac{\omega_{n'} \pm i\tilde{\mathrm{H}}_{\mathbf{k}',n'}}{\left[\left(\omega_{n'} \pm i\tilde{\mathrm{H}}_{\mathbf{k}',n'}\right)^2 + \left(-\Delta^e_{\mathbf{k}',n'} \pm i\Delta^o_{\mathbf{k}',n'}\right)^2\right]^{\frac{1}{2}}} \right\rangle_{\mathbf{k}'}$$

$$\Sigma^h_{\mathbf{k},n} = \frac{1}{2}\pi T \sum_{n',\pm} \left\langle \lambda(\mathbf{k}\,\mathbf{k}', n\,n') \frac{\tilde{\mathrm{H}}_{\mathbf{k}',n'} \mp i\omega_{n'}}{\left[\left(\omega_{n'} \pm i\tilde{\mathrm{H}}_{\mathbf{k}',n'}\right)^2 + \left(-\Delta^e_{\mathbf{k}',n'} \pm i\Delta^o_{\mathbf{k}',n'}\right)^2\right]^{\frac{1}{2}}} \right\rangle_{\mathbf{k}'}$$

$$Z_{\mathbf{k},n}\Delta^e_{\mathbf{k},n} = \frac{1}{2}\pi T \sum_{n',\pm} \left\langle [\lambda(\mathbf{k}\,\mathbf{k}', n\,n') - \mu^*] \frac{\Delta^e_{\mathbf{k}',n'} \mp i\Delta^o_{\mathbf{k}',n'}}{\left[\left(\omega_{n'} \pm i\tilde{\mathrm{H}}_{\mathbf{k}',n'}\right)^2 + \left(-\Delta^e_{\mathbf{k}',n'} \pm i\Delta^o_{\mathbf{k}',n'}\right)^2\right]^{\frac{1}{2}}} \right\rangle_{\mathbf{k}'}$$

$$Z_{\mathbf{k},n}\Delta^o_{\mathbf{k},n} = \frac{1}{2}\pi T \sum_{n',\pm} \left\langle [\lambda(\mathbf{k}\,\mathbf{k}', n\,n') - \mu^*] \frac{\Delta^o_{\mathbf{k}',n'} \pm i\Delta^e_{\mathbf{k}',n'}}{\left[\left(\omega_{n'} \pm i\tilde{\mathrm{H}}_{\mathbf{k}',n'}\right)^2 + \left(-\Delta^e_{\mathbf{k}',n'} \pm i\Delta^o_{\mathbf{k}',n'}\right)^2\right]^{\frac{1}{2}}} \right\rangle_{\mathbf{k}'}$$

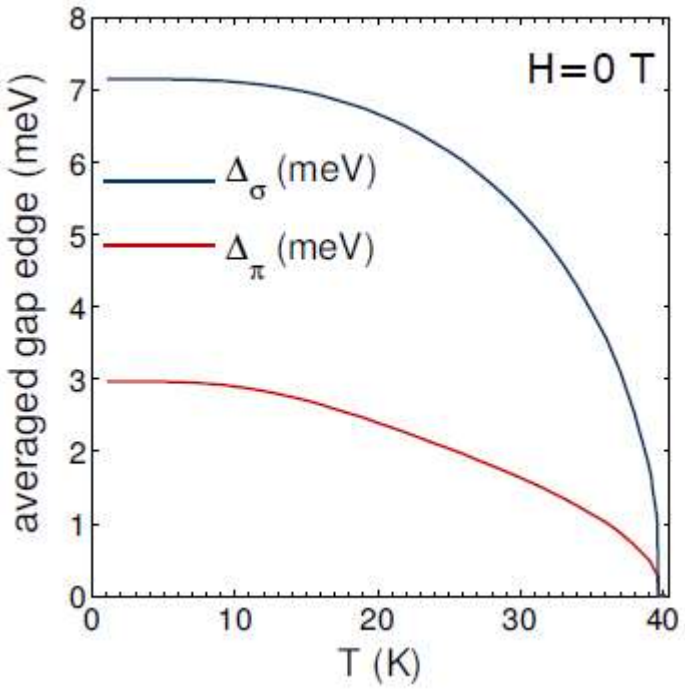
$$\langle \cdots \rangle_{\mathbf{k}} = \sum_{\mathbf{k}} \frac{\delta(\xi_{\mathbf{k}})}{N_F} \qquad \mathrm{H}(\mathbf{k}',n') = \Sigma_h(\mathbf{k}',n') + \mu_B h$$

We solve the above self-consistently with *ab initio* input!

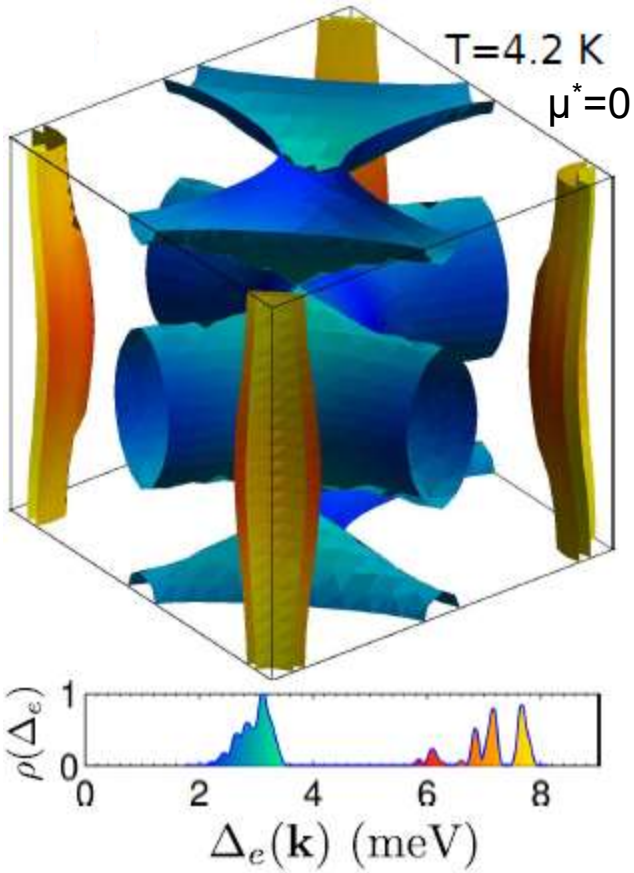
$$\lambda(\mathbf{k},\mathbf{k}';n,n') = \int_0^\infty d\Omega \alpha^2 F(\mathbf{k},\mathbf{k}';\Omega) \frac{2\Omega}{(\omega_n - \omega_{n'})^2 + \Omega^2}$$

$\omega_n = (2n+1)\pi k_B T$, Matsubara frequency

MgB_2: Calculated two anisotropic gaps in zero field



Calculated Tc = 39.8 K



σ-FS

Superconducting gap edge

Aperis, Maldonado & Oppeneer, PRB **92**, 054516 (2015)

Odd-frequency SC

Not possible in BCS Δ not $\Delta(\omega)$

Cooper pair wave function is **odd**

$$\Psi_{\alpha\beta}(\mathrm{k},\omega) \sim g(\mathrm{k}) \otimes \chi(\alpha\beta) \otimes f(\omega)$$

Momentum **x** ***Spin*** **x** ***Frequency***

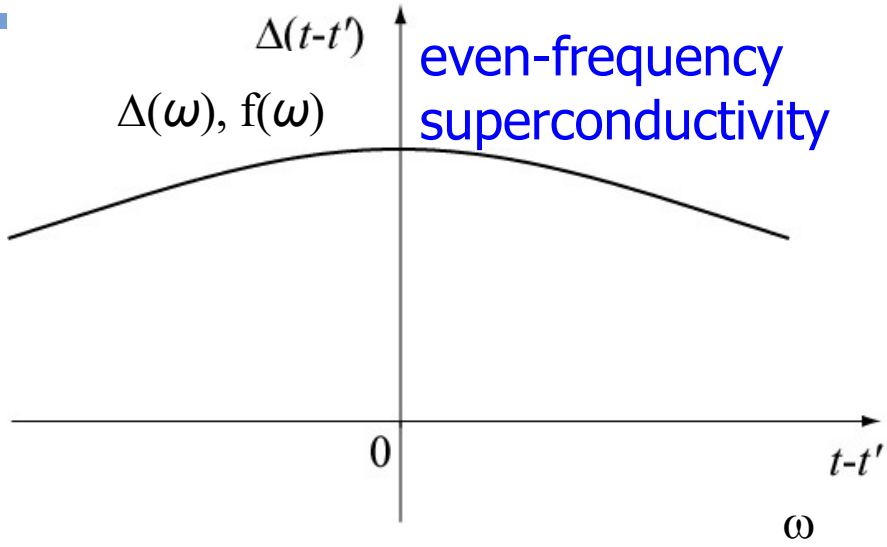
What if.. $f(-\omega) = -f(\omega)$

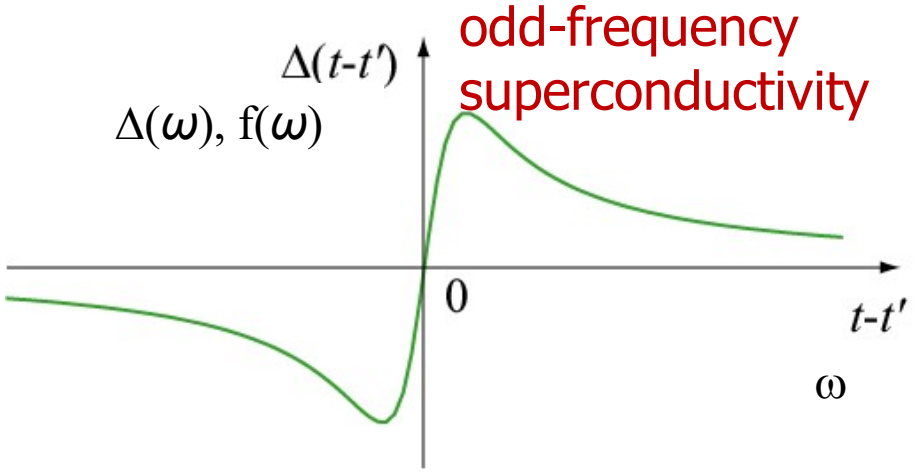
Berezinskii (1974):

Spin-triplet s-wave

Balatsky & Abrahams (1992):

Spin-singlet p-wave





ω, Matsubara frequency

No conclusive experimental evidence!

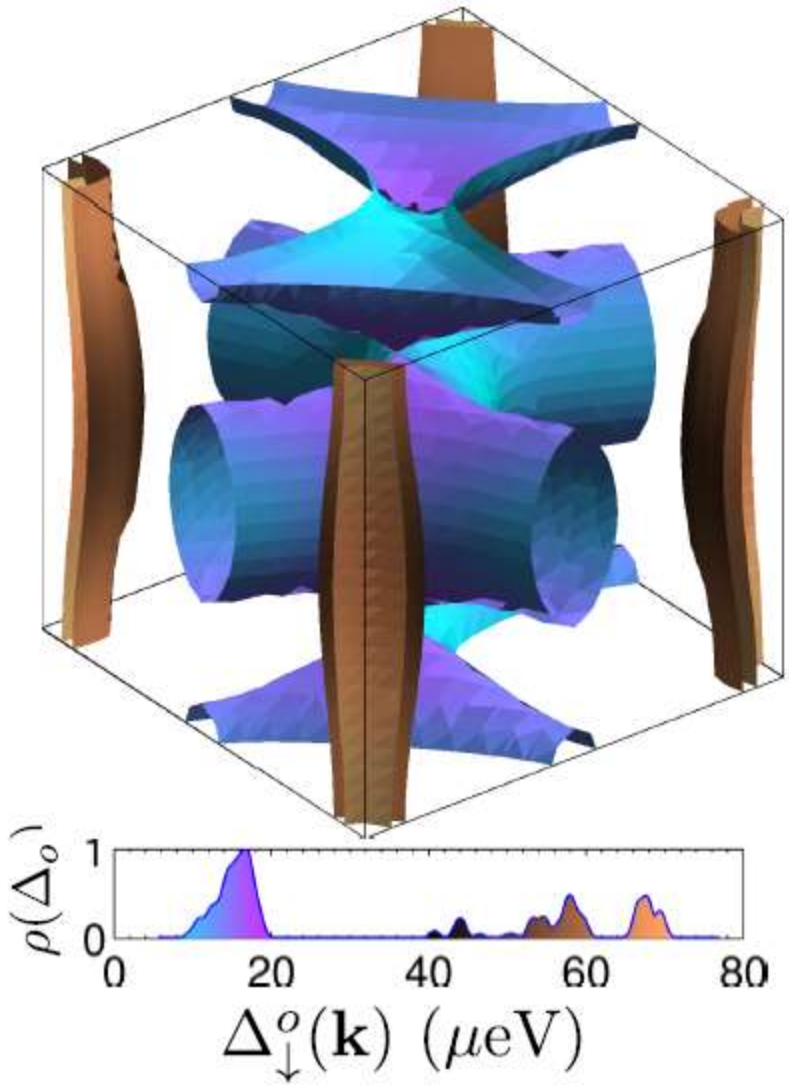
Predicted odd-frequency gap edge at 40 T, 4.2 K

Introduce the gap edges

$$\Delta^{e(o)}_{\uparrow(\downarrow)}(\mathbf{k}) = \Delta_{e(o)}(\mathbf{k}, \omega_{\mathbf{k},\uparrow(\downarrow)})$$

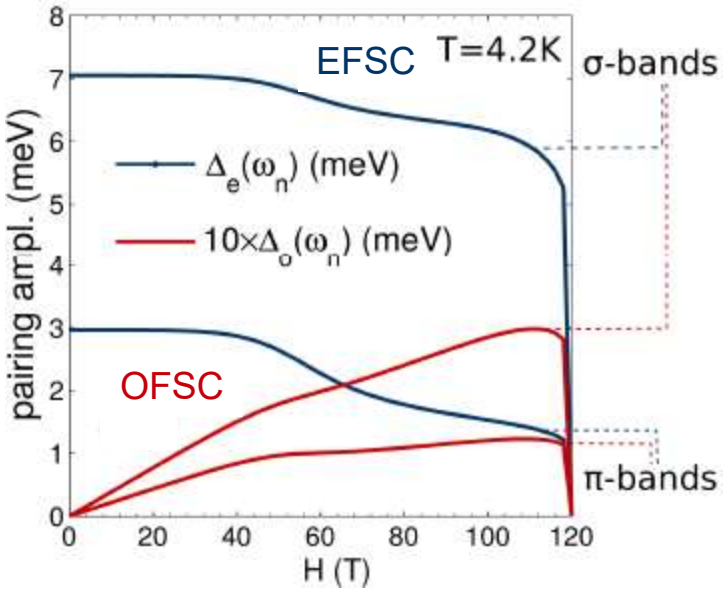
field-induced odd-freq. SC gap edge

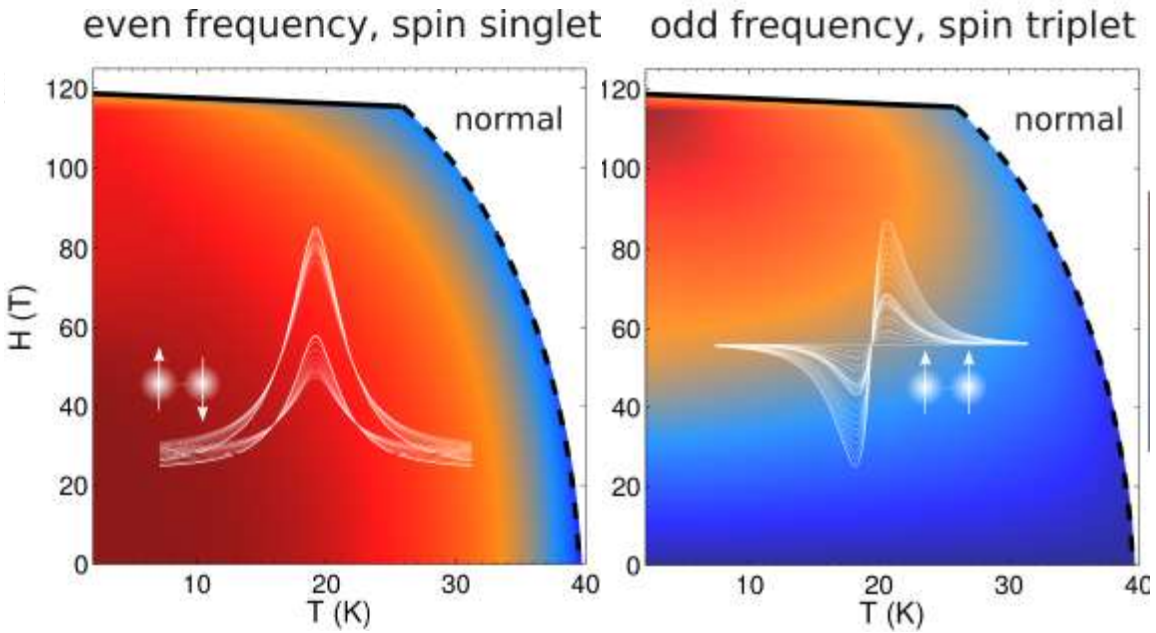
Small gap, "by-product" only present due to even-freq. SC



Aperis, Maldonado & Oppeneer, PRB **92**, 054516 (2015)

Magnetic-field induced odd-frequency SC in MgB_2





Prediction of field induced, Two-band odd-freq. spin-triplet, s-wave SC

Calculated Tc = 39.8 K

Calculated H-T phase diagram

Ab initio estimation of the Pauli limiting field $H_p = 119\ \mathrm{T}$

Aperis, Maldonado & Oppeneer, PRB **92**, 054516 (2015)

UPPSALA UNIVERSITET

Conclusions ...

- LSDA+U theory predicts 3***q***-multipolar order in NpO_2 & AmO_2
- Largest contribution from triakontadipole term in NpO_2
- Superexchange coupled MMP induces insulator state
- Dipolar 3***q*** AFM order with quadrupole predicted for UO_2
- Nonmagnetic insulator state obtained for PuO_2 and CmO_2

- Prediction of field-induced multiband odd-freq. SC in MgB_2
- Roadmap for ab initio materials' specific description of SC

THANK YOU !!