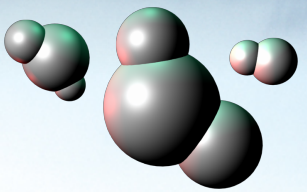
DFT+DMFT and non-periodic systems

Cedric Weber



Hartree Centre
Science & Technology Facilities Council

EPSRC

NVIDIA

ICAM : DIGITAL DESIGN OF MATERIALS

School of natural science
Department of Physics

THE THOMAS YOUNG CENTRE
TyC

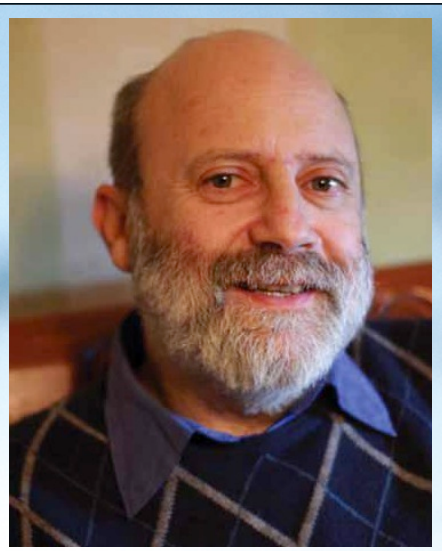
KING'S College LONDON

Peter B. Littlewood

Argonne NATIONAL LABORATORY

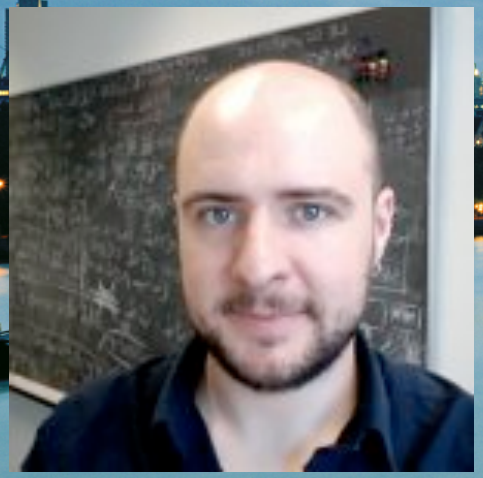
Mike C. Payne

UNIVERSITY OF CAMBRIDGE



Gabriel Kotliar

RUTGERS THE STATE UNIVERSITY OF NEW JERSEY

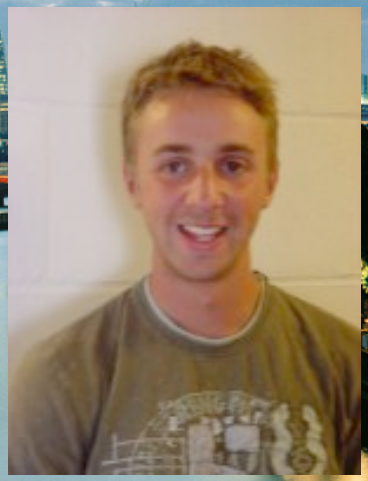


David D. O'Regan

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Nicholas D. M. Hine

UNIVERSITY OF CAMBRIDGE

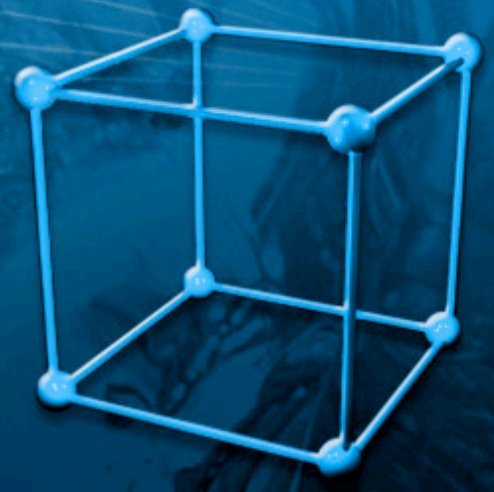


Daniel Cole

YALE

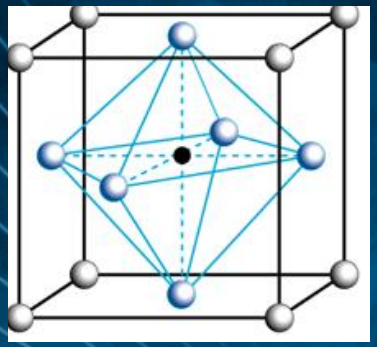
Outlines

- Strongly correlated systems
- Breakthrough in the last decades
- Promising directions
  - Nano-structuring & Drug design
- TOSCAM package
  - Myoglobin / Haemoglobin
  - Disordered oxide
  - Self-assembly
- Challenging Obstacles / Future progress
- Outlooks

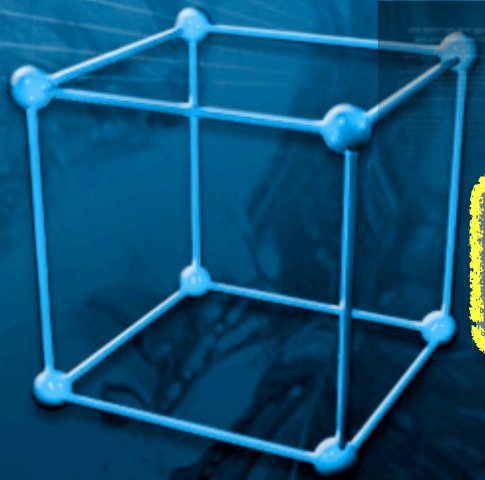


Strongly correlated systems

transition metal ions



ion+oxygen cage =transition metal oxide



V Cr Mn Fe Co Ni Cu

VO_2 Room temperature **MIT**

$La_{1-x}SrxMnO_3$
Colossal
Magnetoresistance

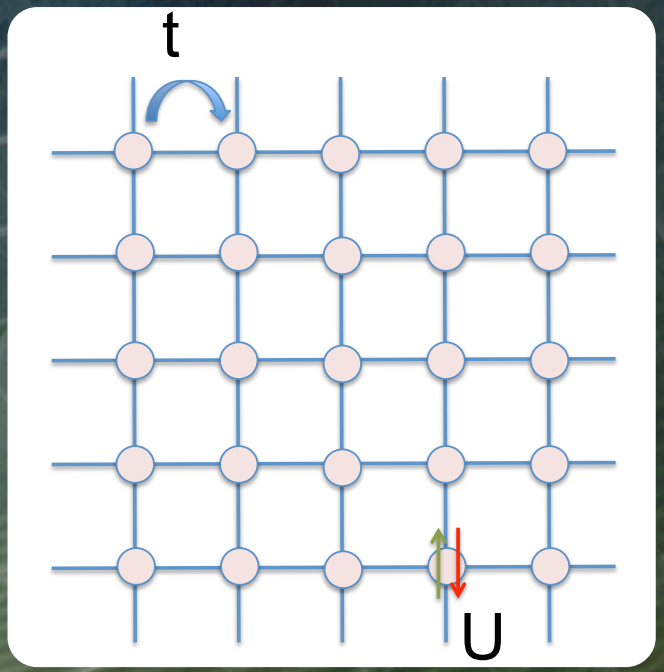
Li_xCoO_2, Na_xCoO_2
Battery materials
Thermoelectrics

$La_{1-x}Sr_xCuO_4$
High temperature
superconductor

Failure of band picture (DFT)

Material design for Strongly Correlated Compounds

$$H_{Hubbard} = -t \sum_{\langle i,j \rangle, \sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + h.c. \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$



U<<1: paramagnetic Metal

U>>1 : Mott insulator

- Metal to insulator transition
- Ordered phases (magnetism, superconductivity)
- Gives a good starting point to describe strongly correlated systems
- Numerical techniques available (Quantum Monte Carlo, variational Monte Carlo ...)
- Problem : not ab-initio

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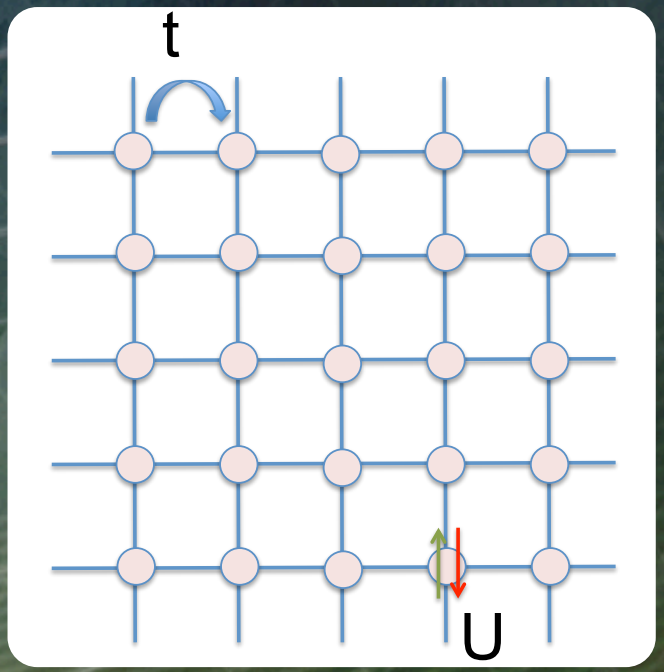

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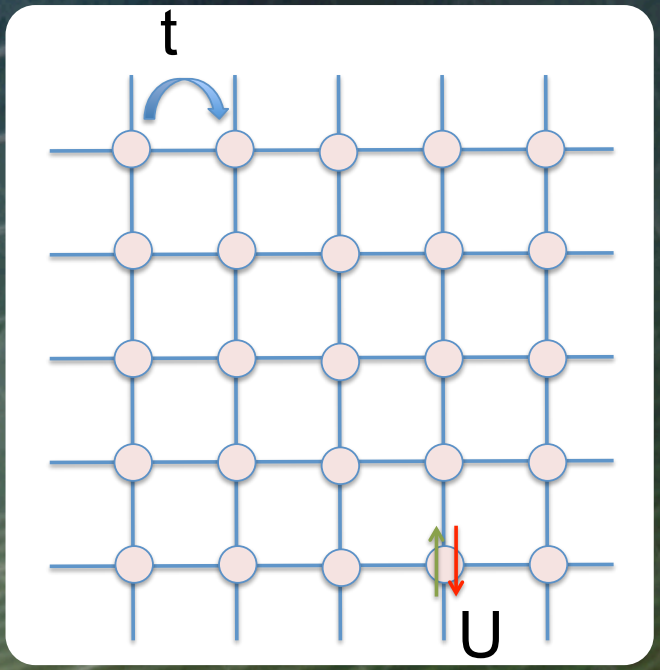

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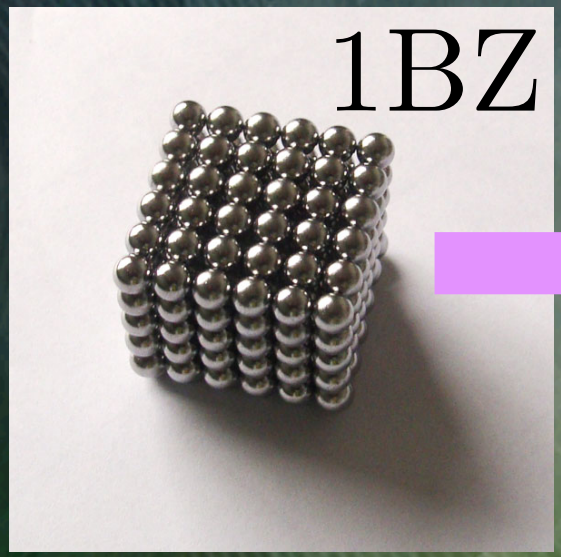
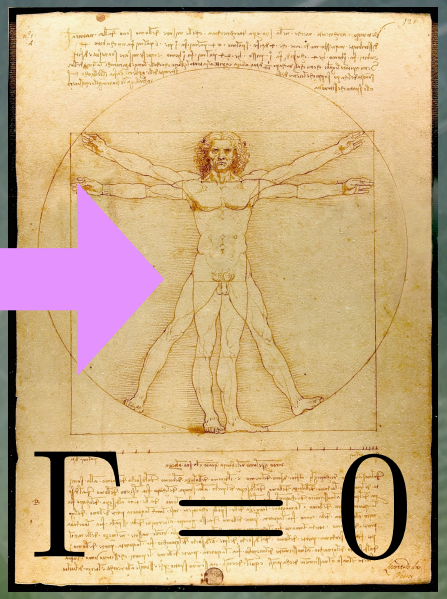
- **Break-through**:

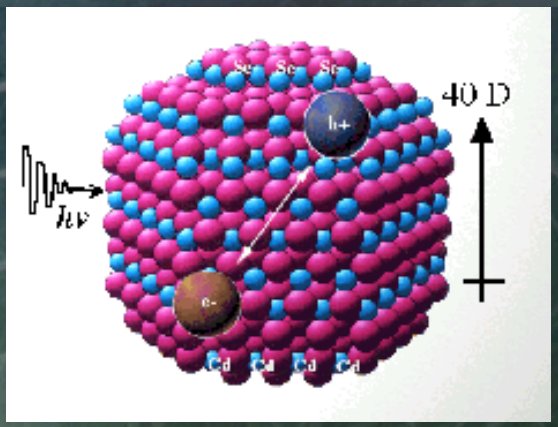
1) bridging strong correlations approaches with first-principle calculations in a consistent way

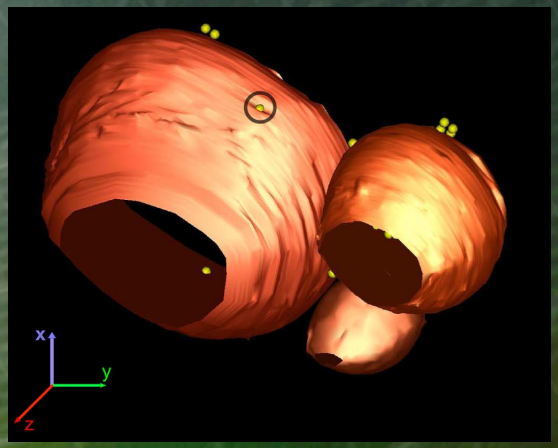
2) ***By using stable techniques with moderate computational costs*** : GW & DMFT

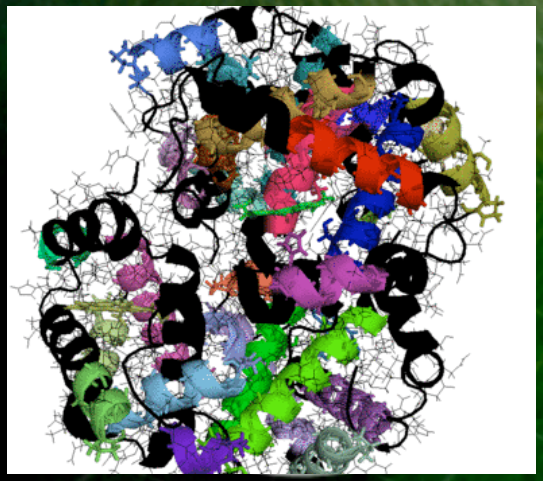
Promising directions : Non periodic systems

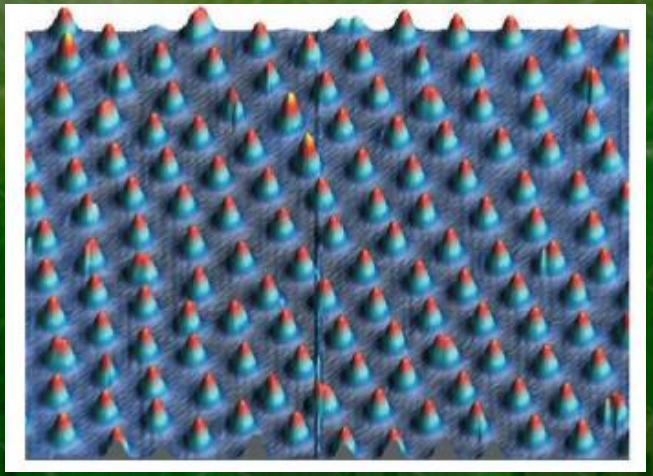


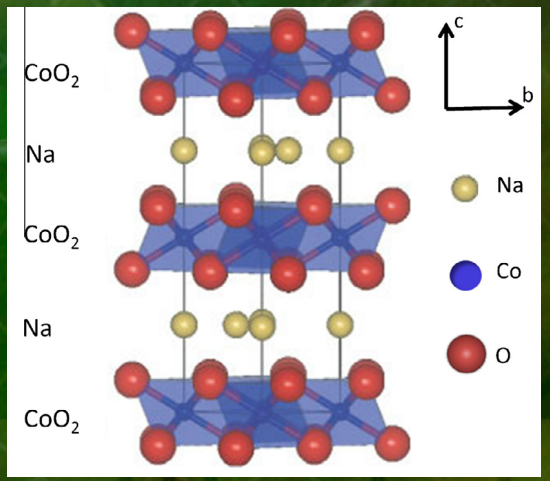




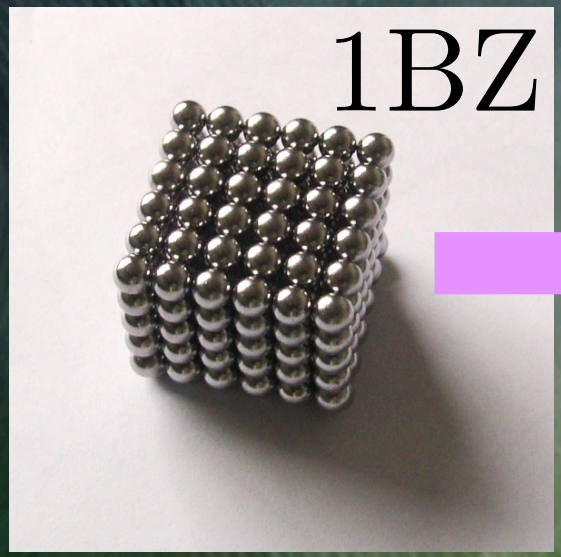


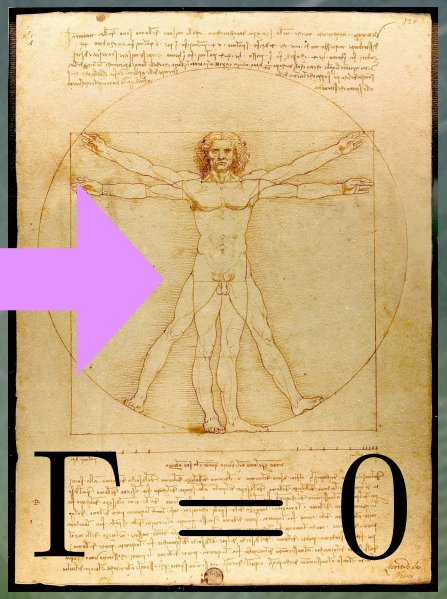




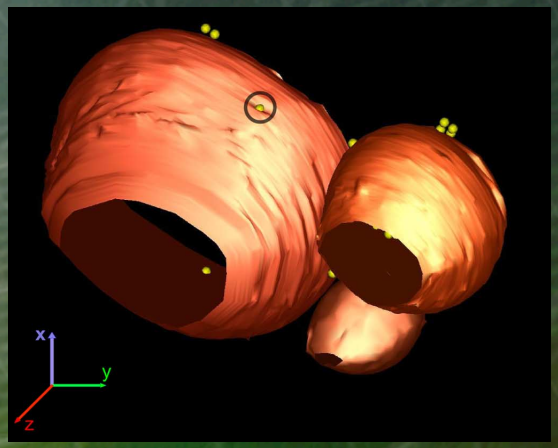


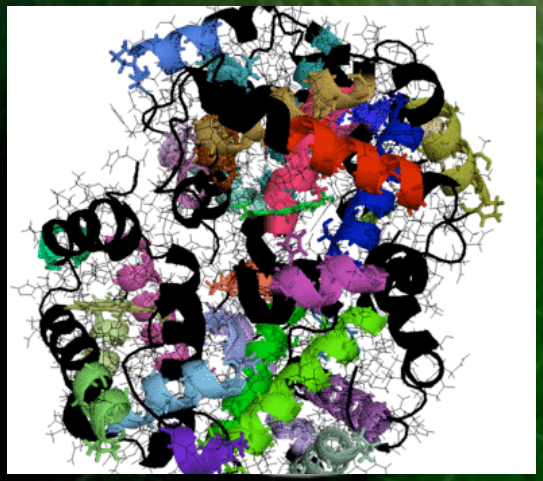
Promising directions :
Non periodic systems

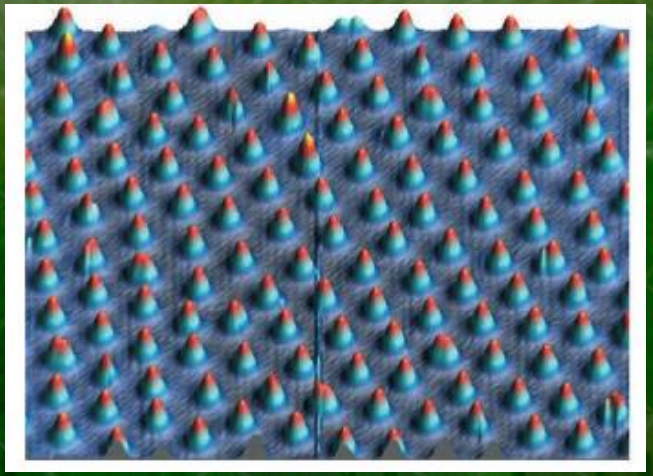


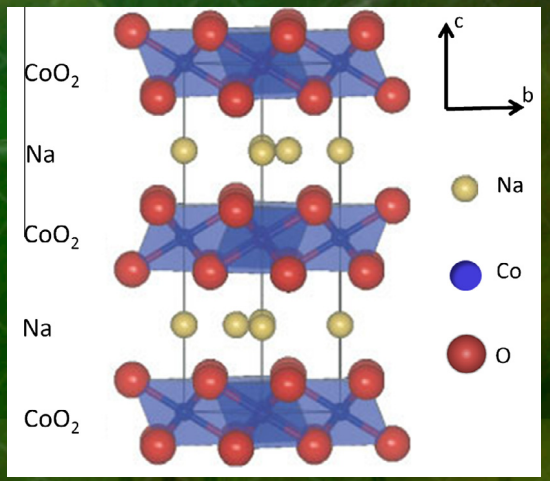


Nanocrystals
light harvesting









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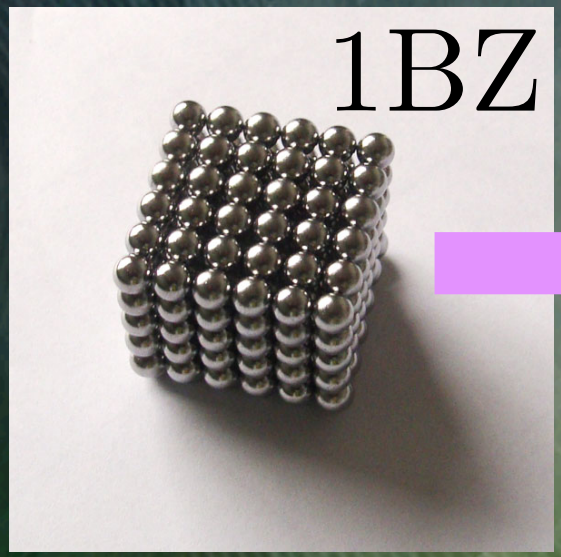
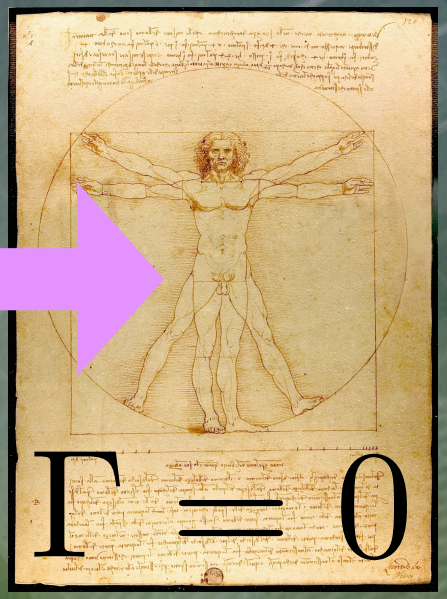
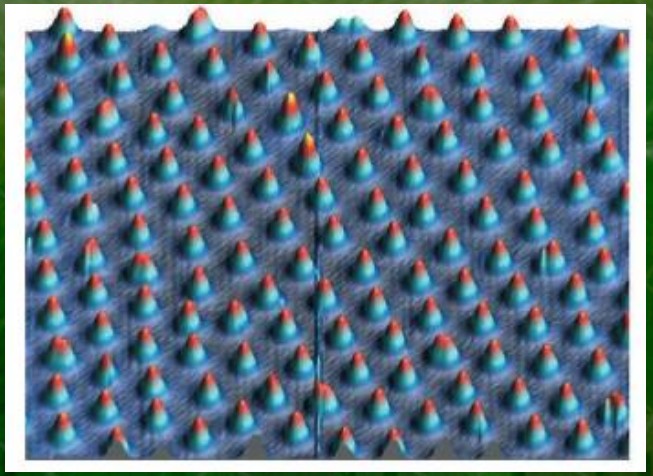
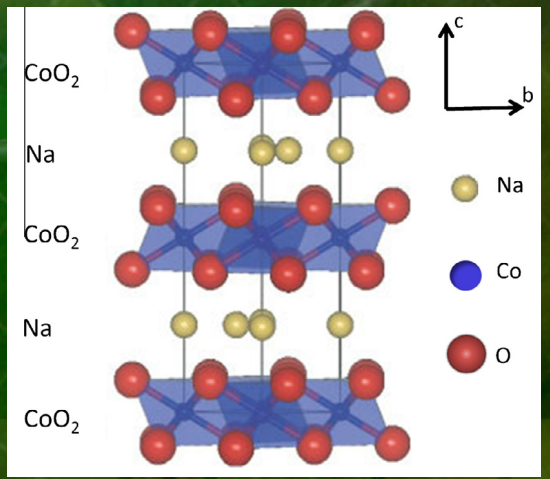




Nanocrystals
light harvesting

iron oxide NP
targeted
drug release





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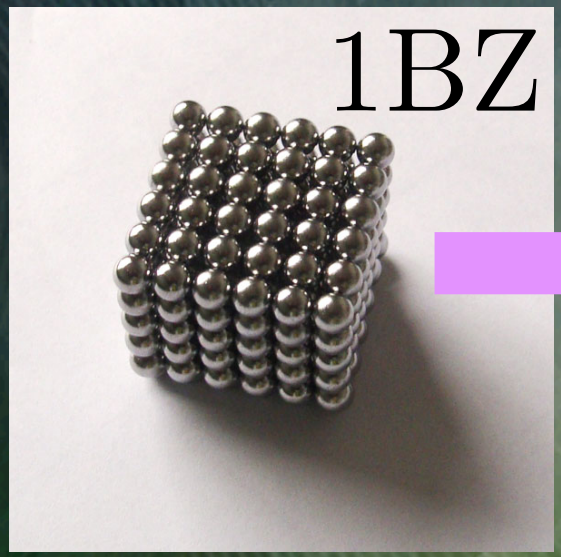

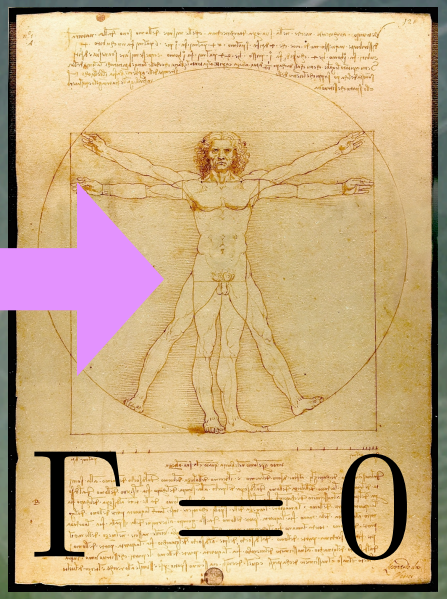

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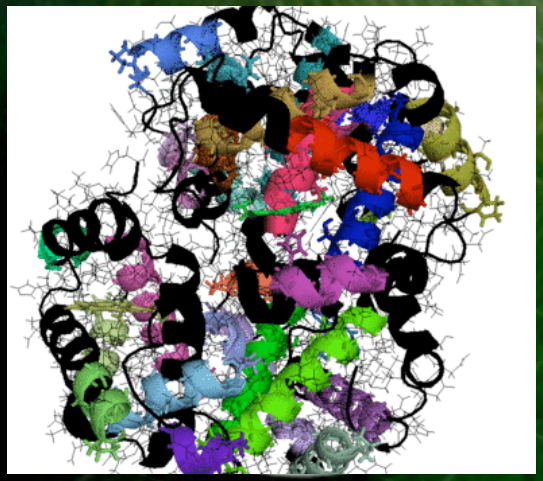
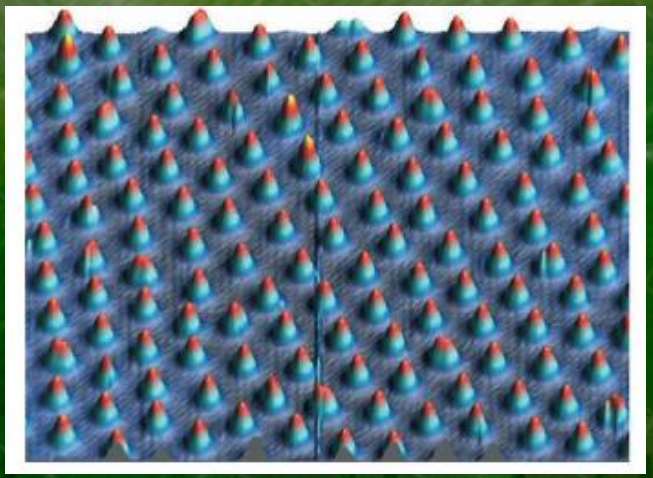
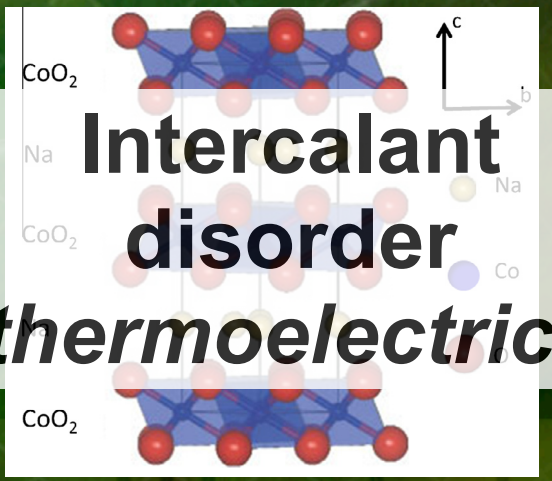
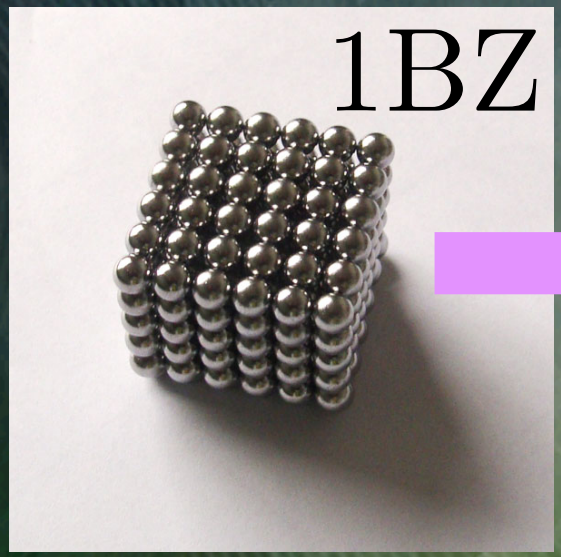


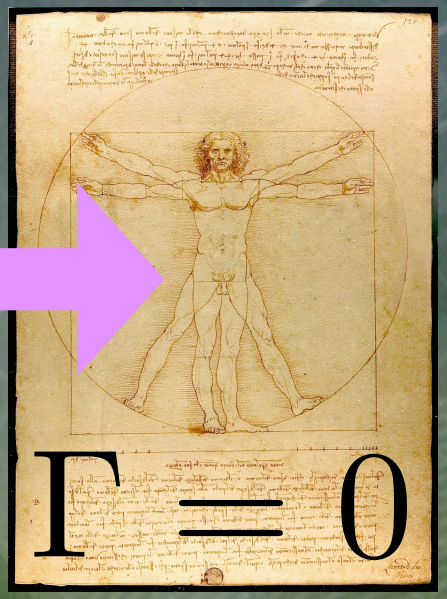




Intercalant
disorder
thermoelectrics

Promising directions :
Non periodic systems





Nanocrystals
light harvesting

iron oxide NP
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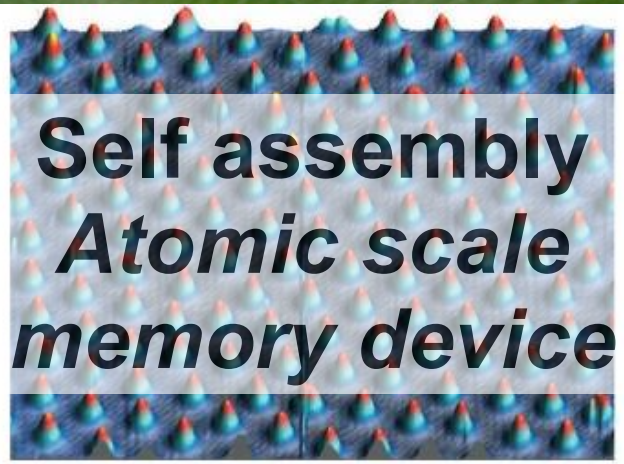
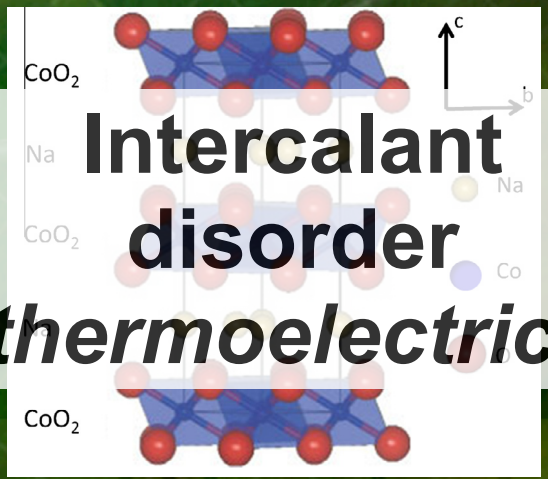


Self assembly
Atomic scale
memory device



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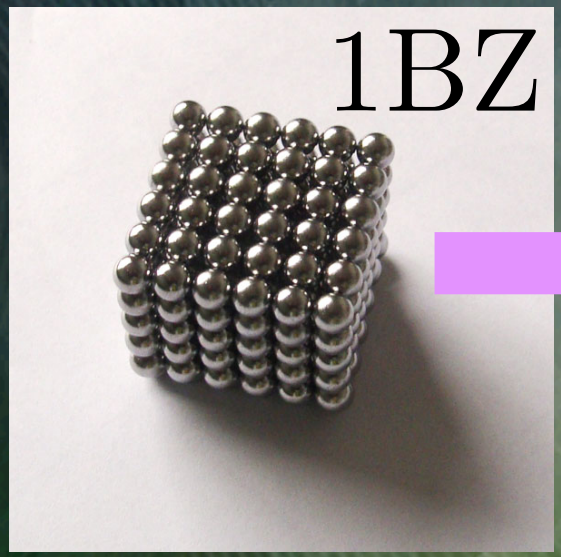
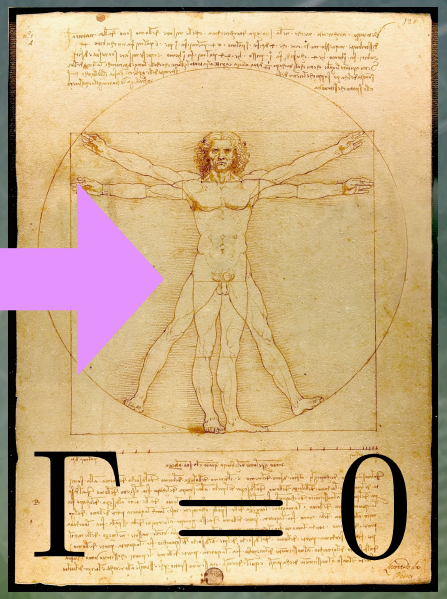
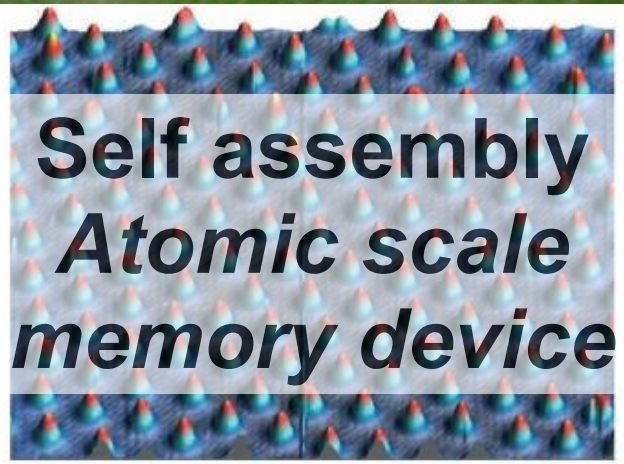




Nanocrystals
light harvesting

iron oxide NP
targeted
drug release

Metallo
porphyrin
systems
drug design



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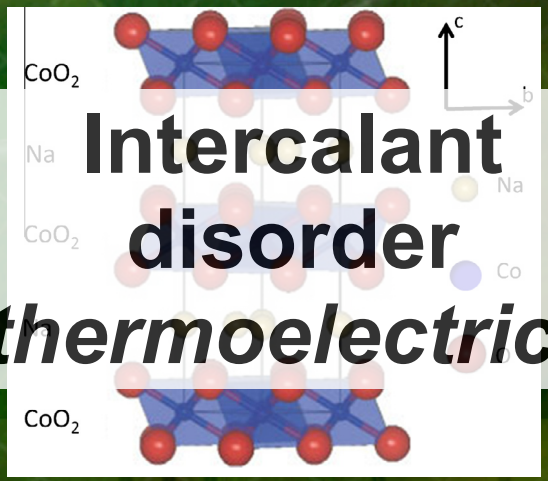

Intercalant
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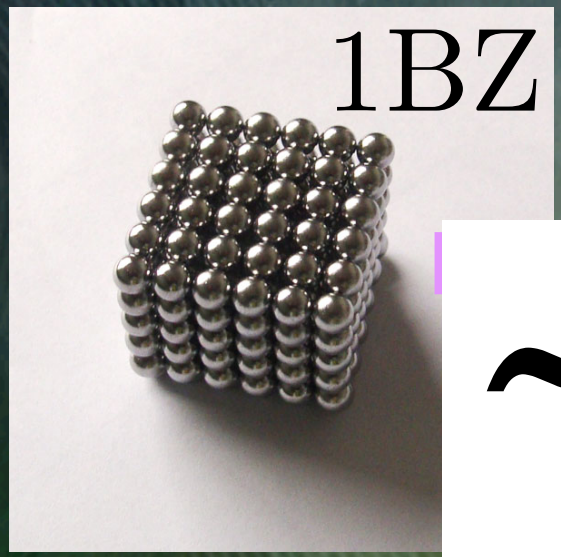
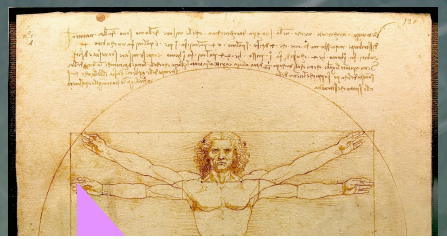


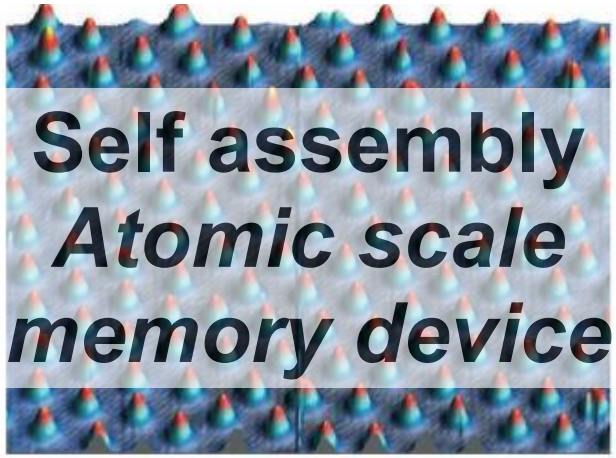


Nanocrystals
light harvesting

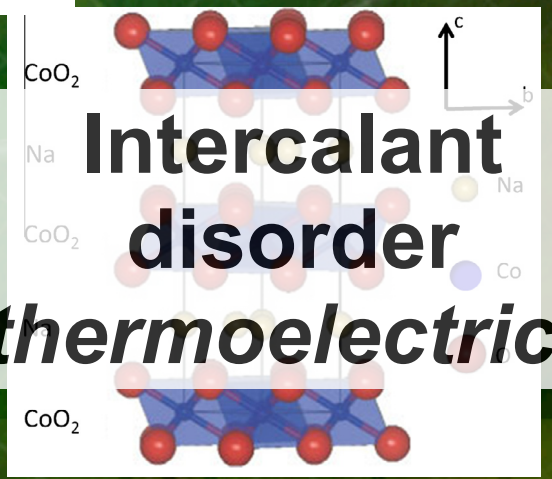
~2K-20K atoms

on oxide NP
targeted
rug release

Metallo porphyrin systems drug design

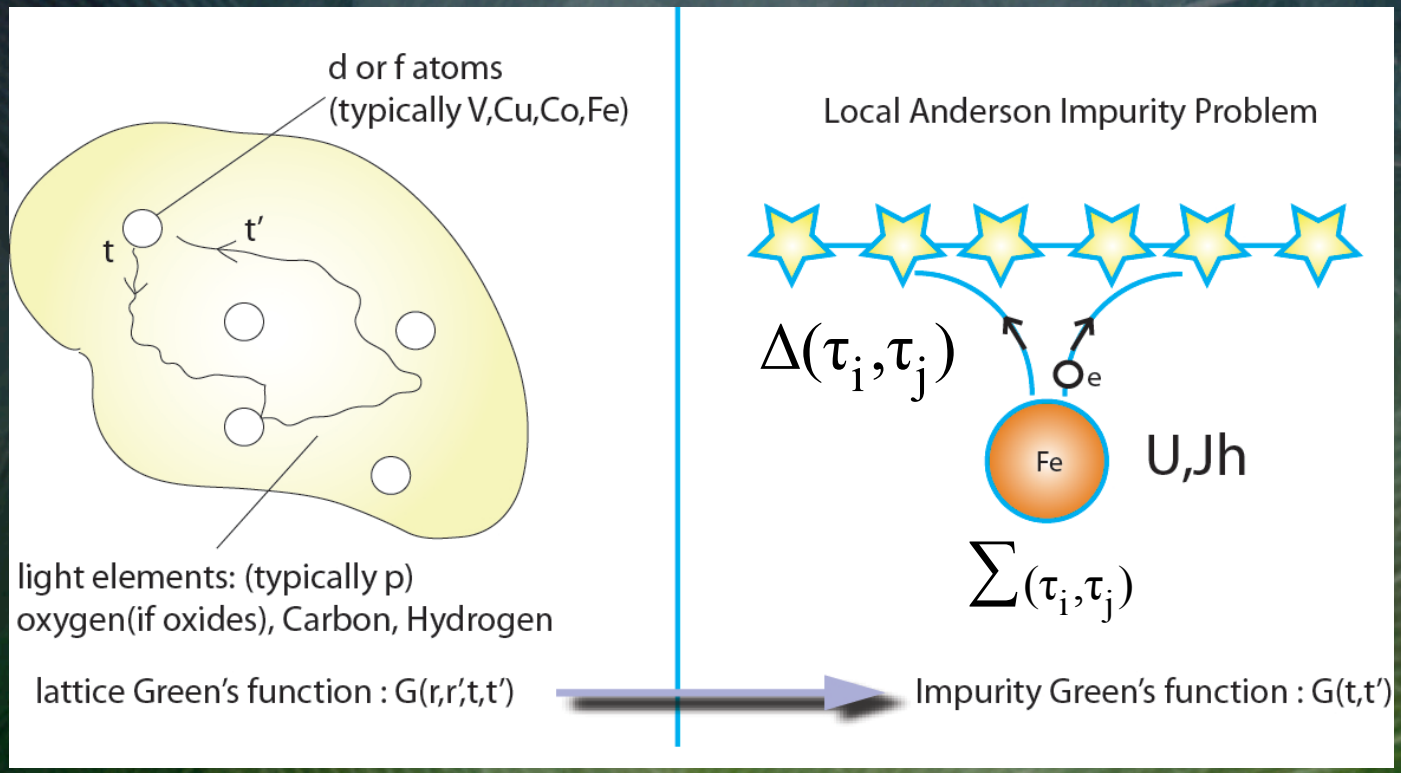


Self assembly
Atomic scale memory device



Intercalant disorder
thermoelectrics

Dynamical mean-field theory



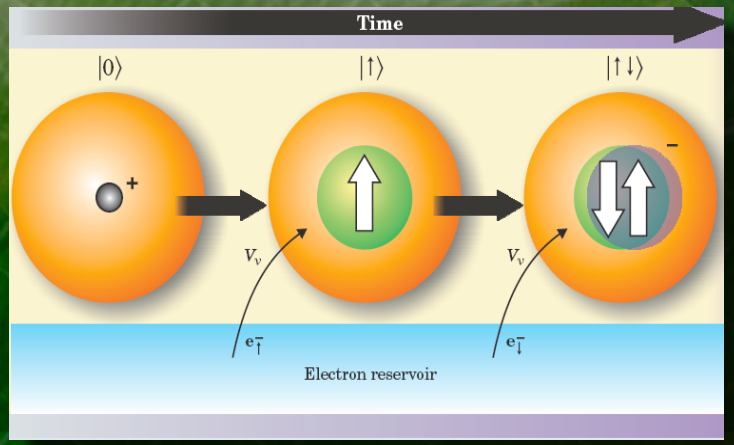
Approximation

The self energy is local in space

$$\sum(x,y) = \sum(x)$$

Projectors

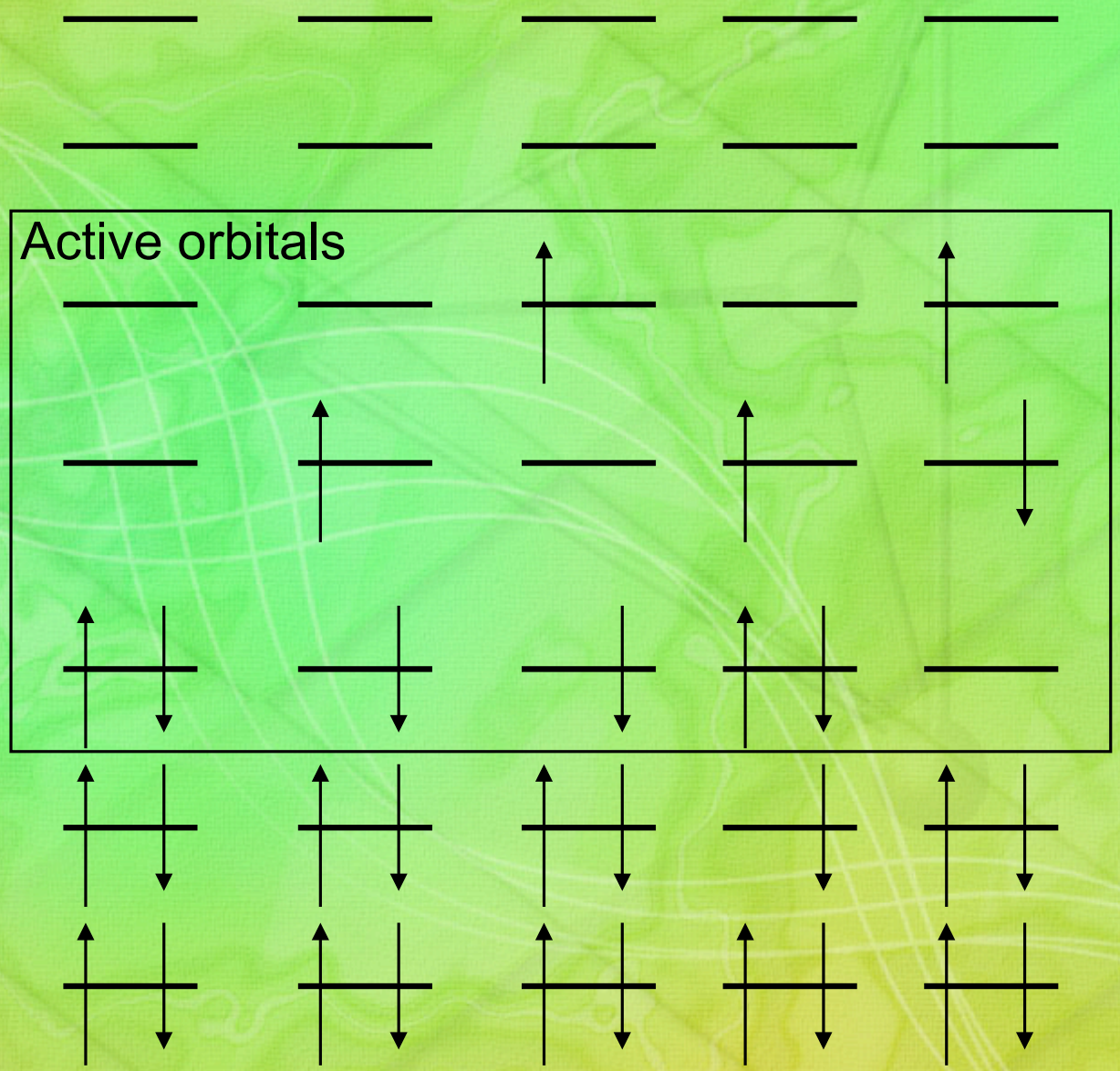
connect the Kohn-Sham orbitals to the local set of atomic orbitals



A. Georges and G. Kotliar PRB 45, 6479 (1992)

Quantum Chemistry Approaches

- **Partition of orbitals:**
  - **Core orbitals (filed, frozen)**
  - **active orbitals (occupied)**
  - **valence orbitals (unoccupied)**
  - **virtual orbitals (unoccupied, frozen)**



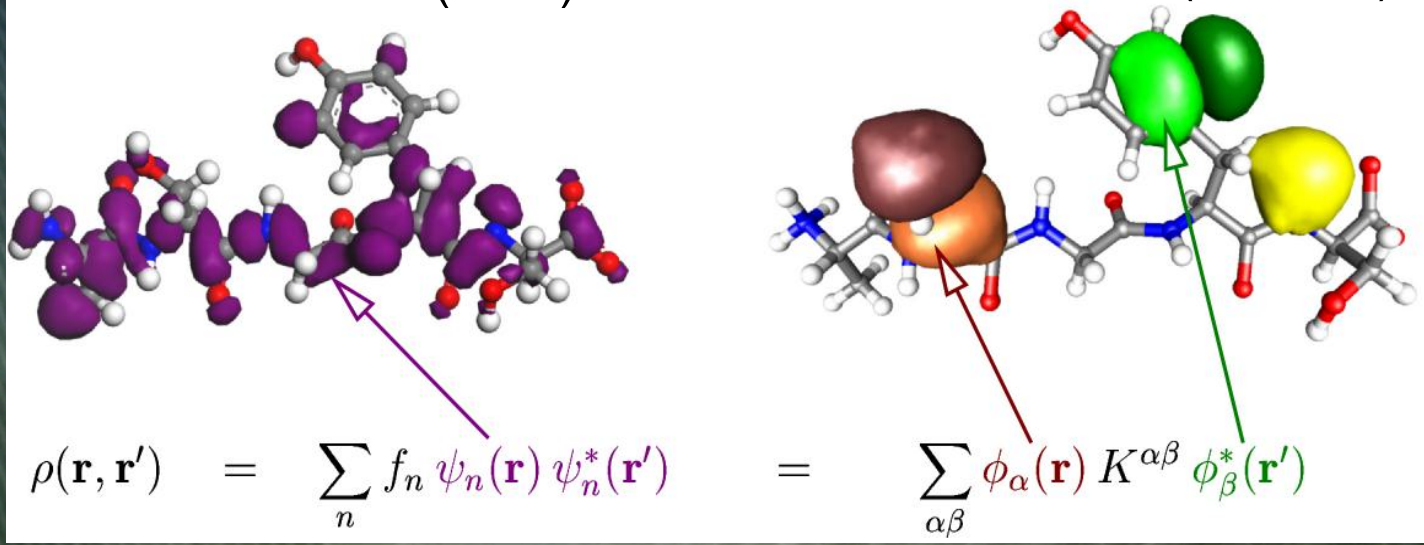
Challenges

- Cons : Large unit-cells - DFT scales with N^3
  - But : Modern architectures are faster than a decade ago
- Cons : Real space implementation - more difficult to access bulk properties
  - But : natural implementation of DMFT
- Cons : Requires a local basis, which however can also encodes the periodicity of the problem
  - But : Wannier functions are ideal candidates
- Cons : Most DFT tools are optimized for the band picture representation
- Cons : Chemists and Bio-Chemists already doing an outstanding job
  - But : We can bring our own view on this problem (Kohn-Sham instead of Hartree Fock, Green's functions, valence fluctuation ...)

Breakthrough : Linear scaling density (ONETEP)

Molecular orbitals (MOs)

Non-orthogonal Generalised Wannier Functions (NGWFs)



$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n\,\psi_n(\mathbf{r})\,\psi_n^*(\mathbf{r}') = \sum_{\alpha\beta}\phi_\alpha(\mathbf{r})\,K^{\alpha\beta}\,\phi_\beta^*(\mathbf{r}')$$

- NGWFs, non-orthogonal localised basis set optimised during the DFT iterations
- Near-sighted approximation: truncation of density kernel. Efficient for solids near the localized/delocalized transition or molecules.
- Same accuracy as plane-wave methods (J.Chem. Phys 119, 8842 ’03)
- Linear scaling with number of atoms, stable convergence
- Scales near linearly with the number of processors

Molecular DMFT+DFT : TOSCAM

TOlbox for **S**trongly **C**orrelated **A**pproaches to **M**olecules
Green's function written in the basis of a set of NGWFs :

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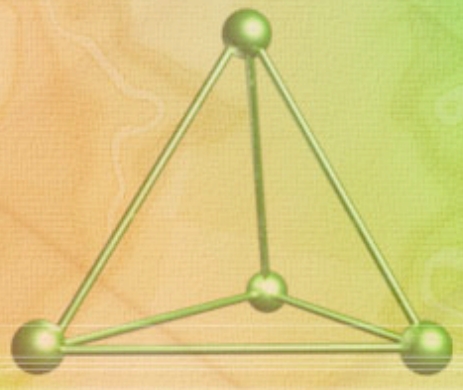

5K atoms ~1h

Molecular DMFT+DFT : TOSCAM

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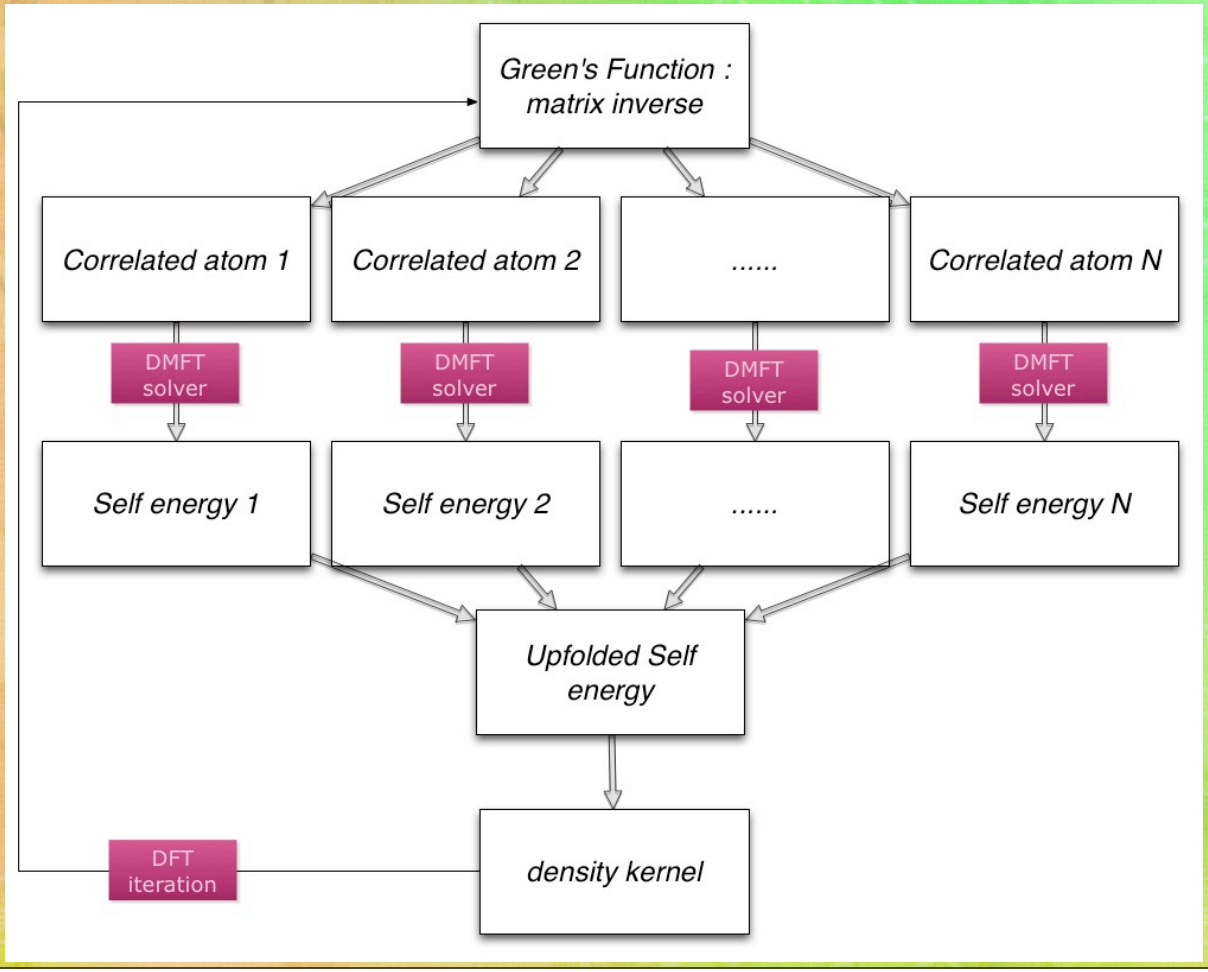

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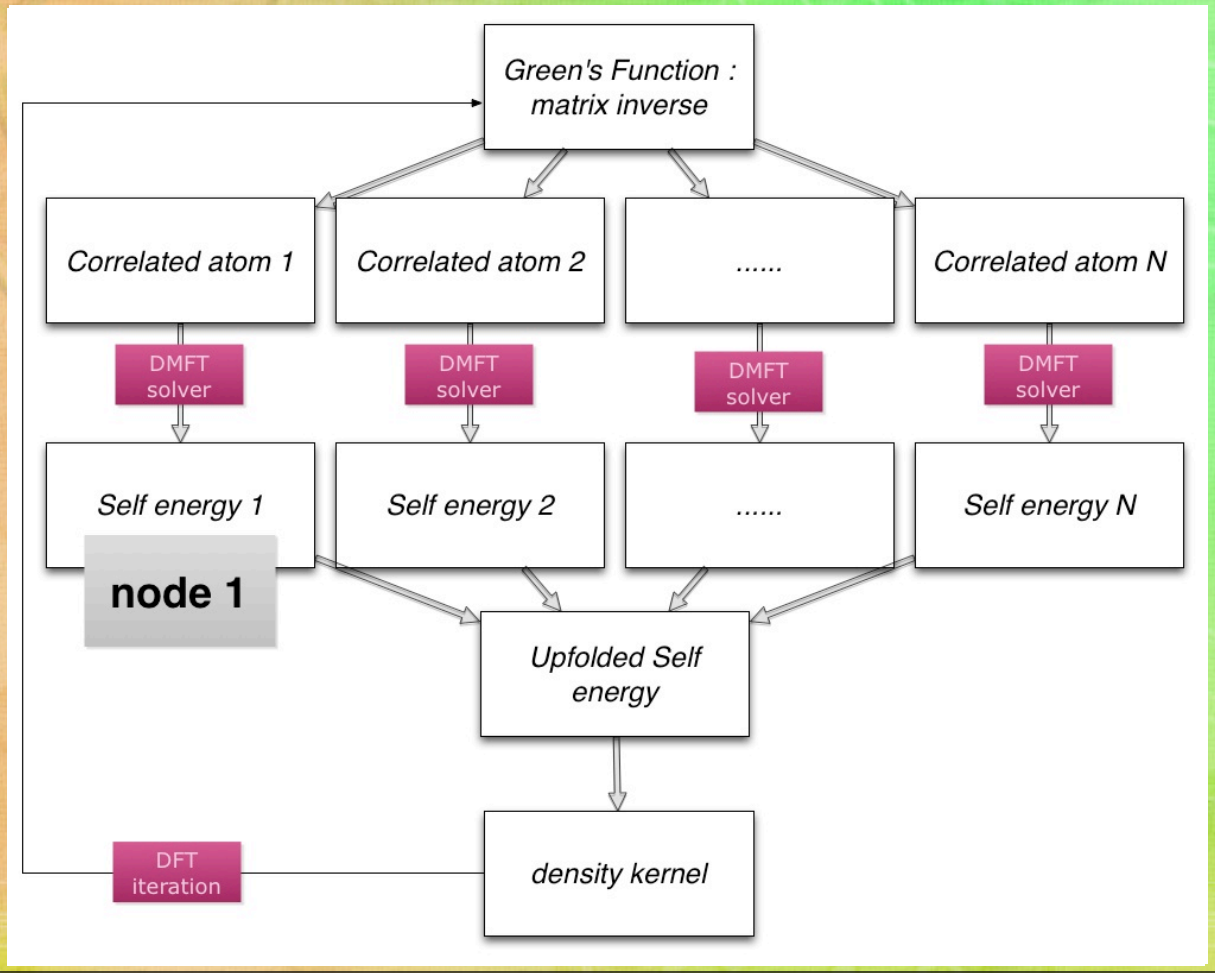

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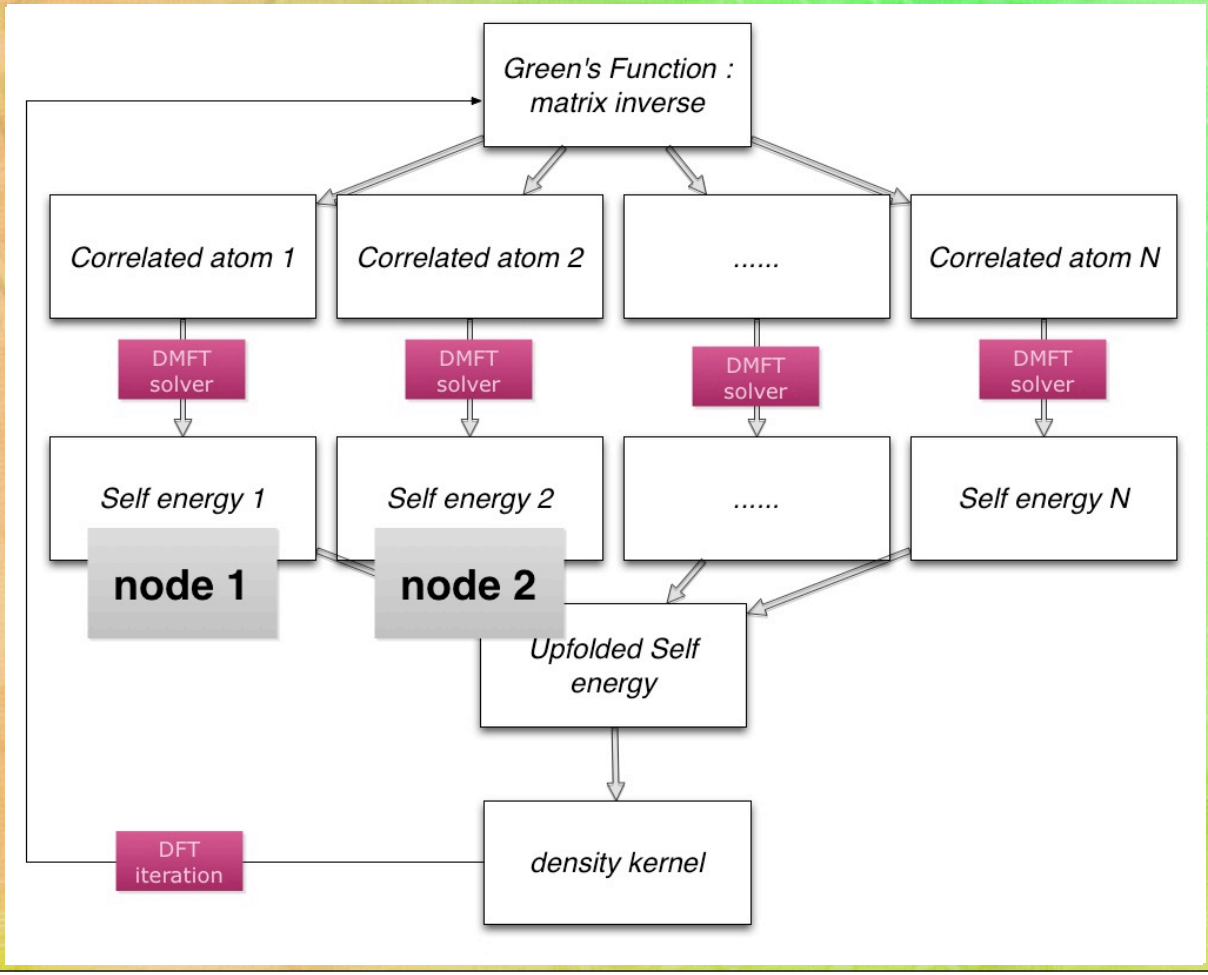

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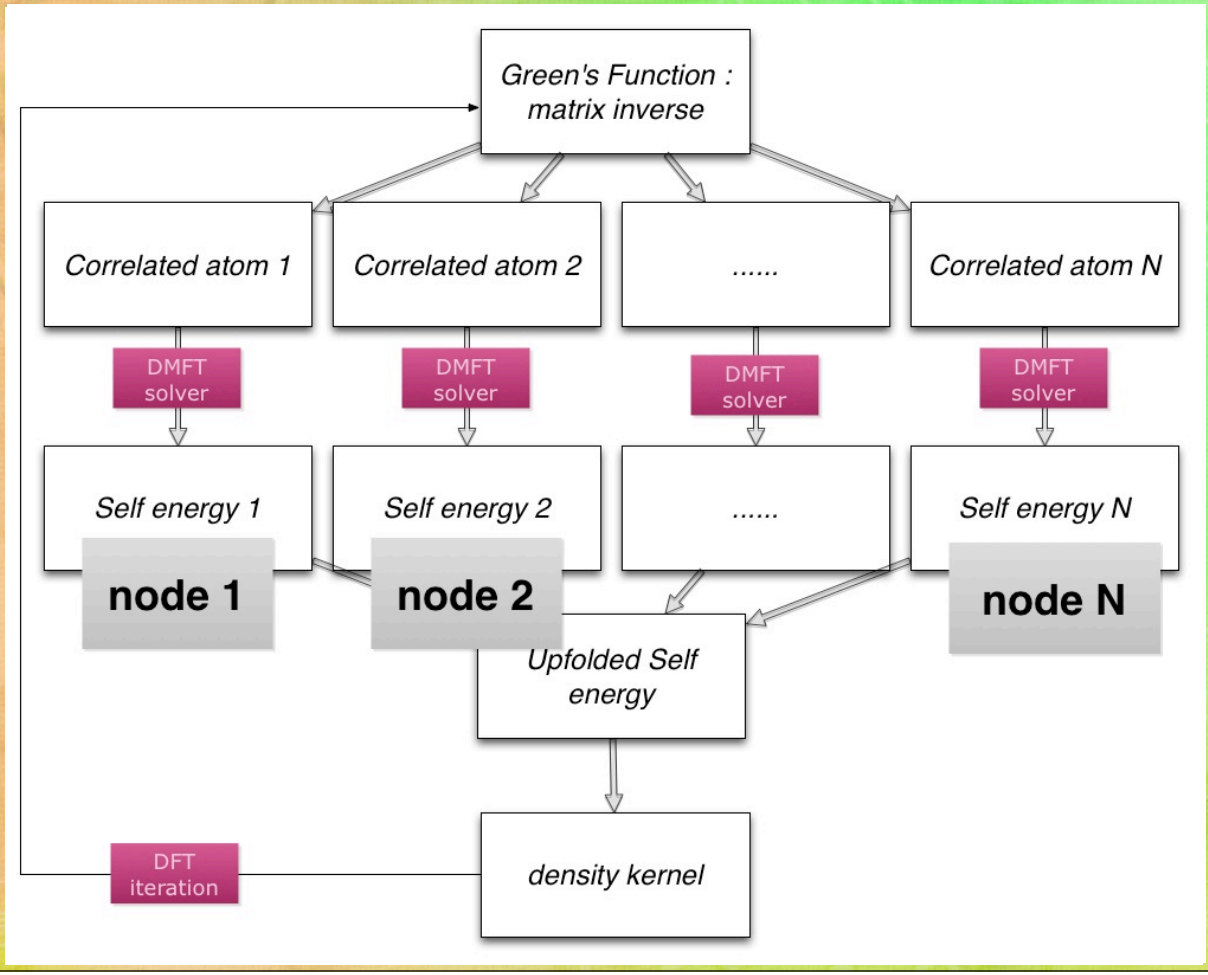

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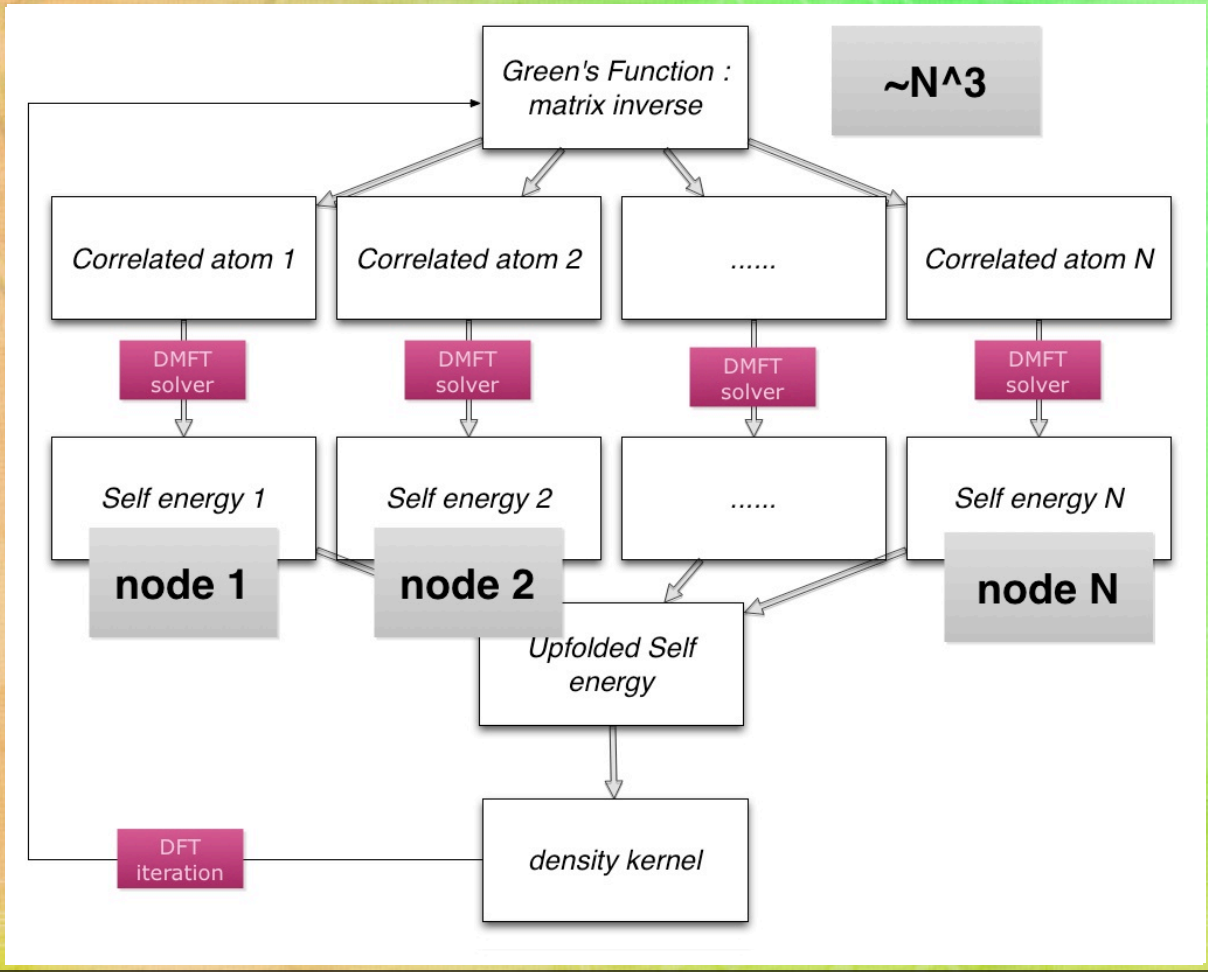

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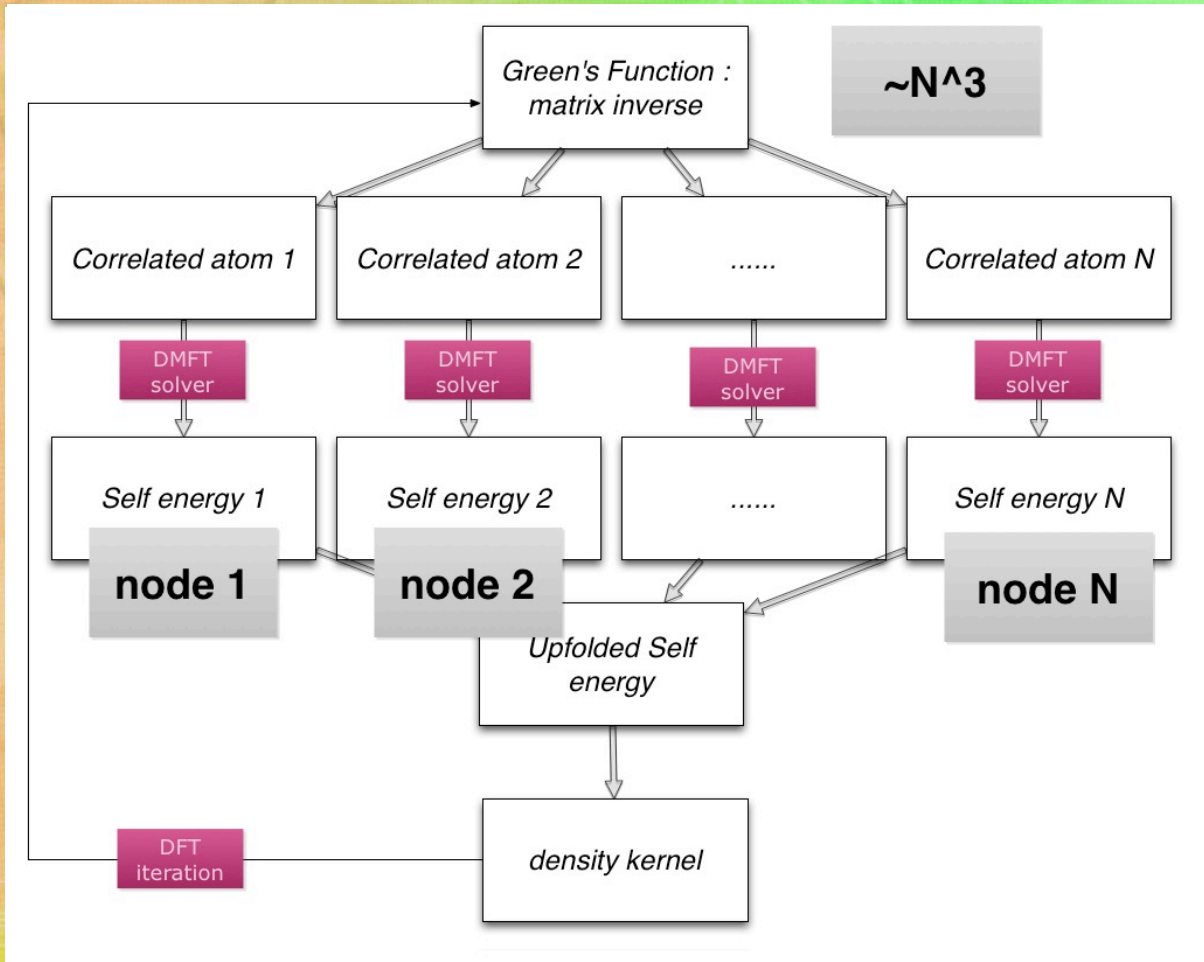

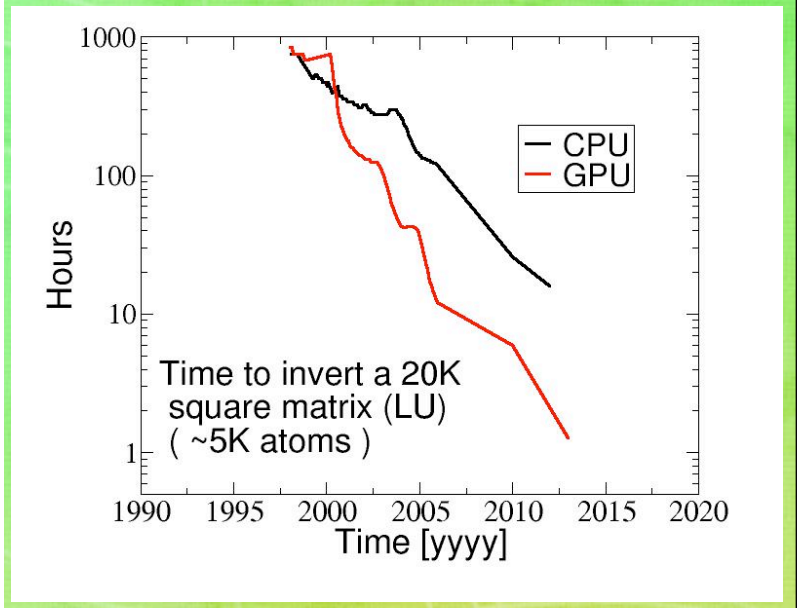

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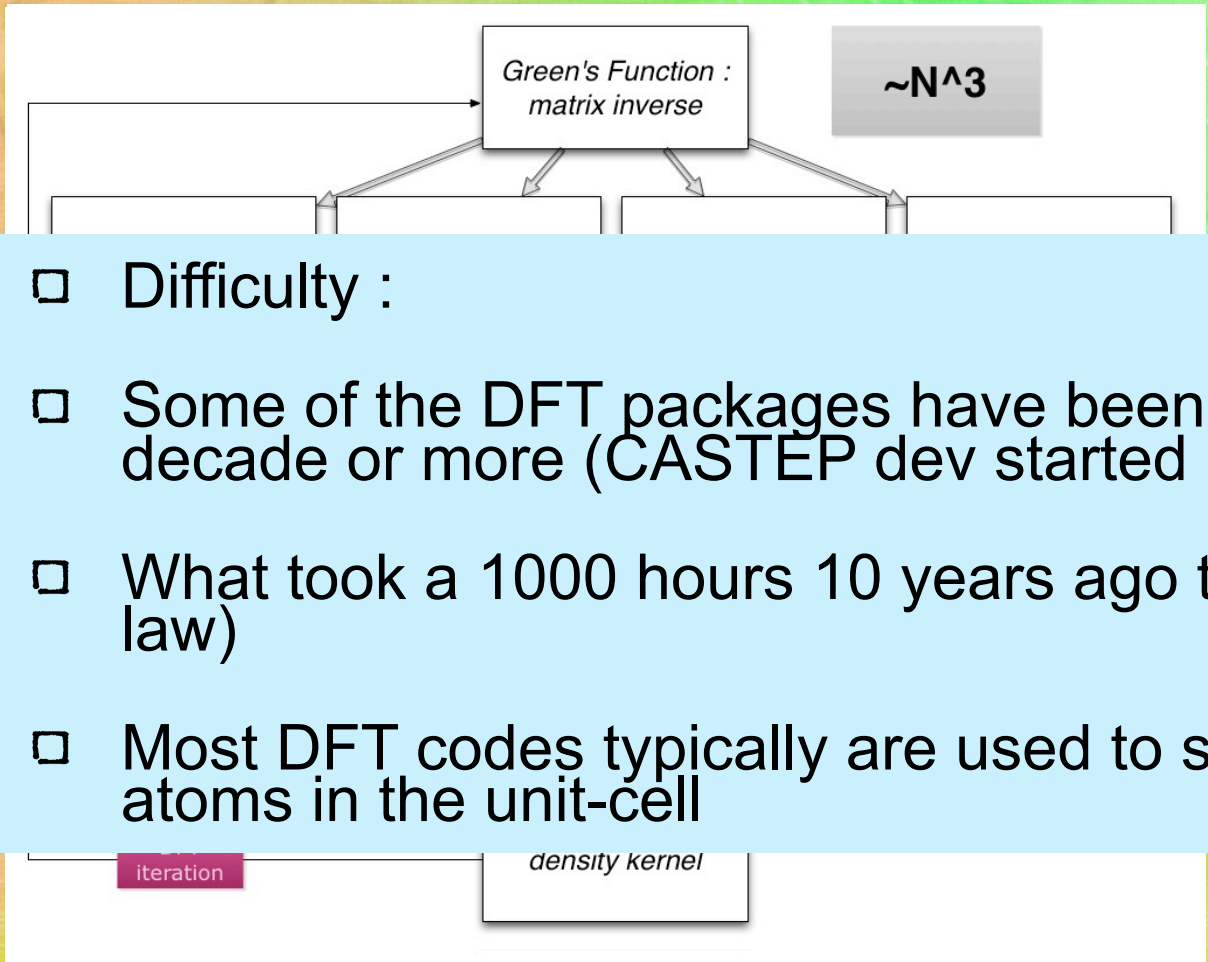
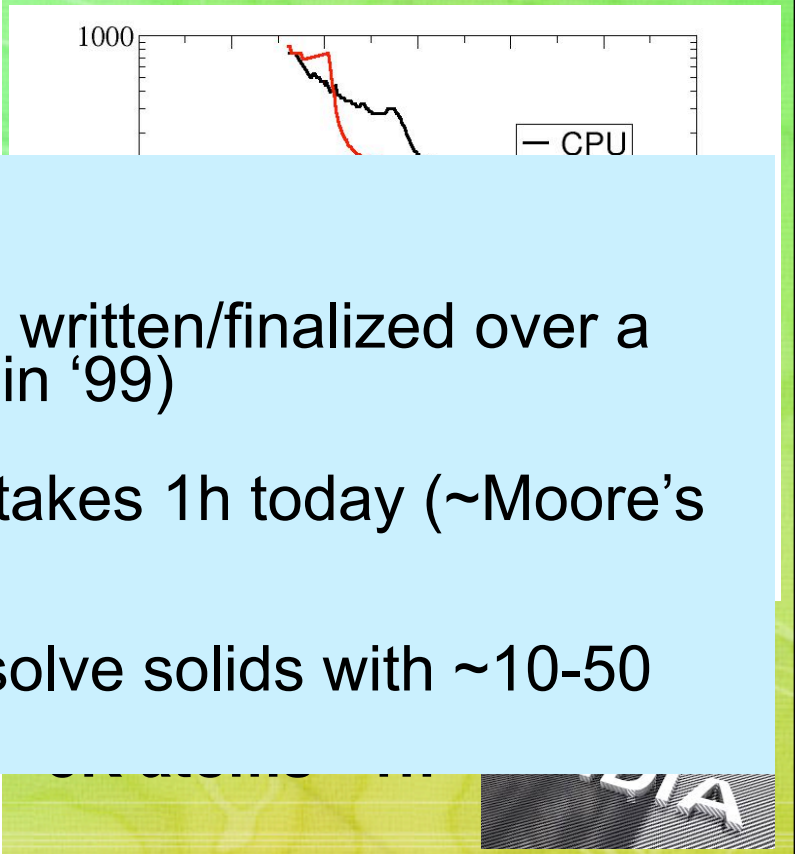
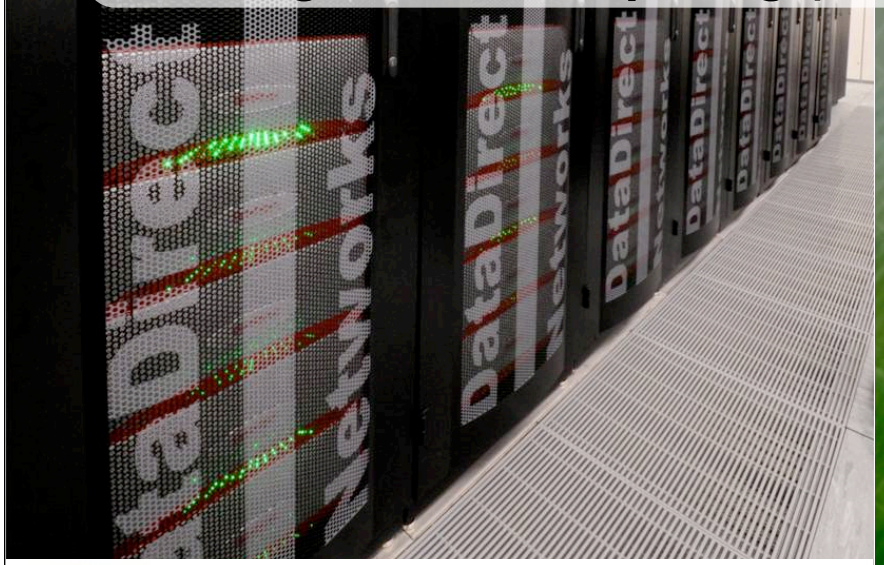


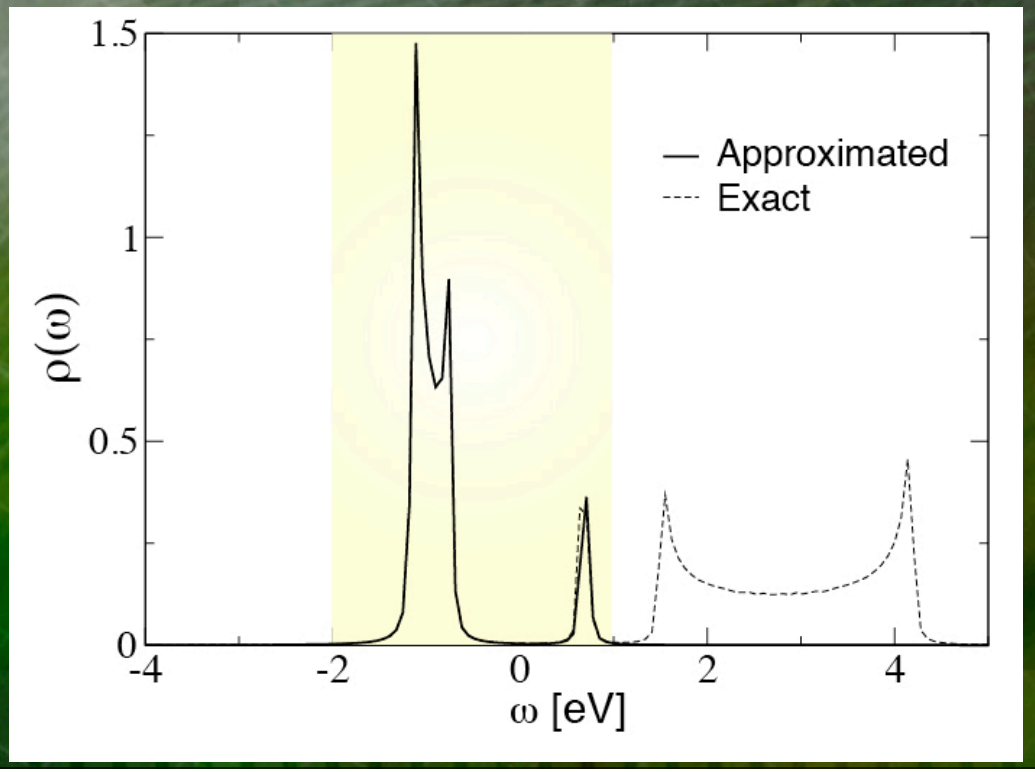


- Difficulty :
- Some of the DFT packages have been written/finalized over a decade or more (CASTEP dev started in '99)
- What took a 1000 hours 10 years ago takes 1h today (~Moore's law)
- Most DFT codes typically are used to solve solids with ~10-50 atoms in the unit-cell

Large scale computing

- Beyond direct inverse, impose energy window (restart Arnoldi method, Lanczos) and obtain spectral properties
- Uncorrelated Green's function
- Correlations added via updates of the Green's function (~N^2), fast if a large number of uncorrelated orbitals
- Large scale computing (Bluegene/Q)





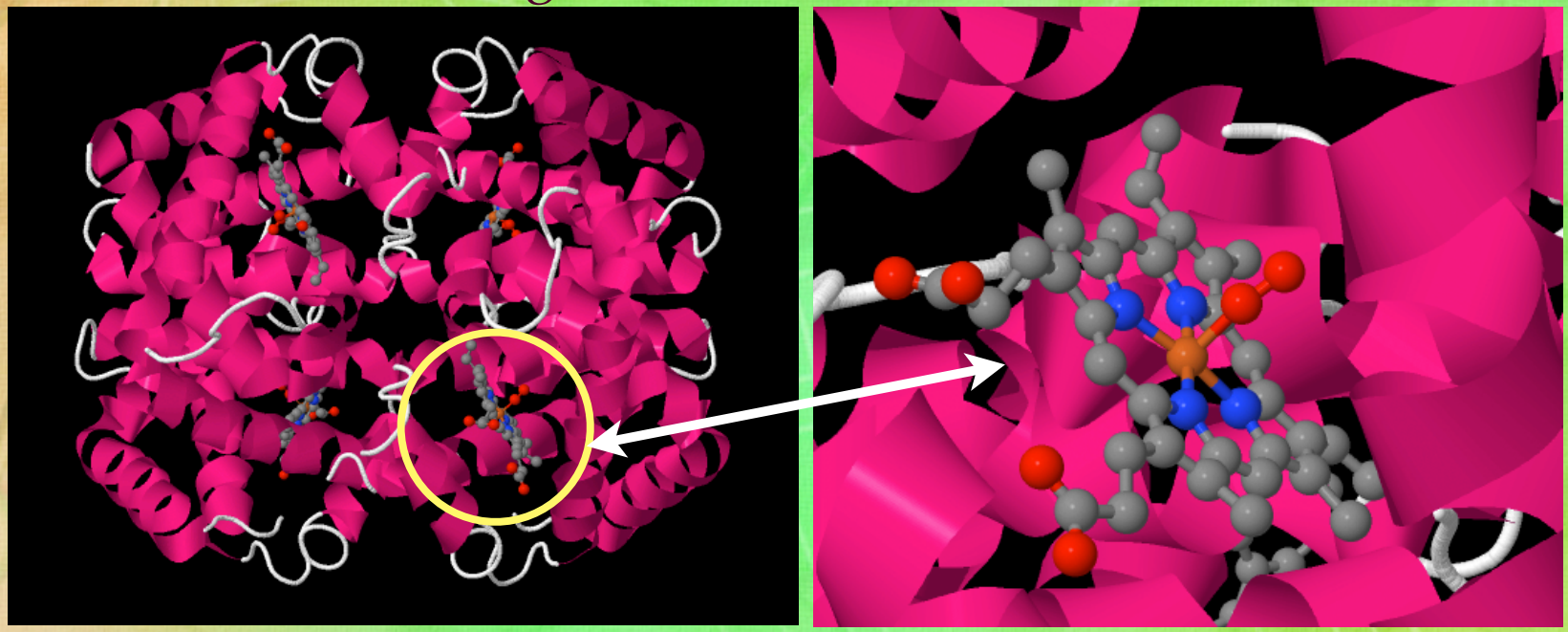
Hartree Centre
Science & Technology Facilities Council

Ligand Binding : haemoglobin

Biological Molecules typically consist of large uncorrelated structures (C,H,O) surrounding a functional kernel with a correlated ion, such as iron porphyrin in haemoglobin.

Human haemoglobin

heme (kernel) binding to O_2



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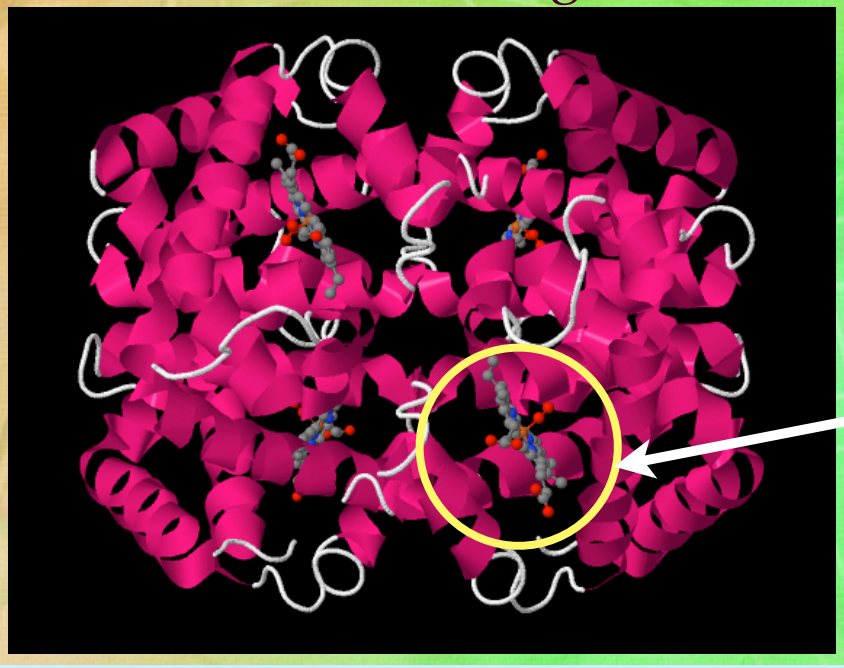

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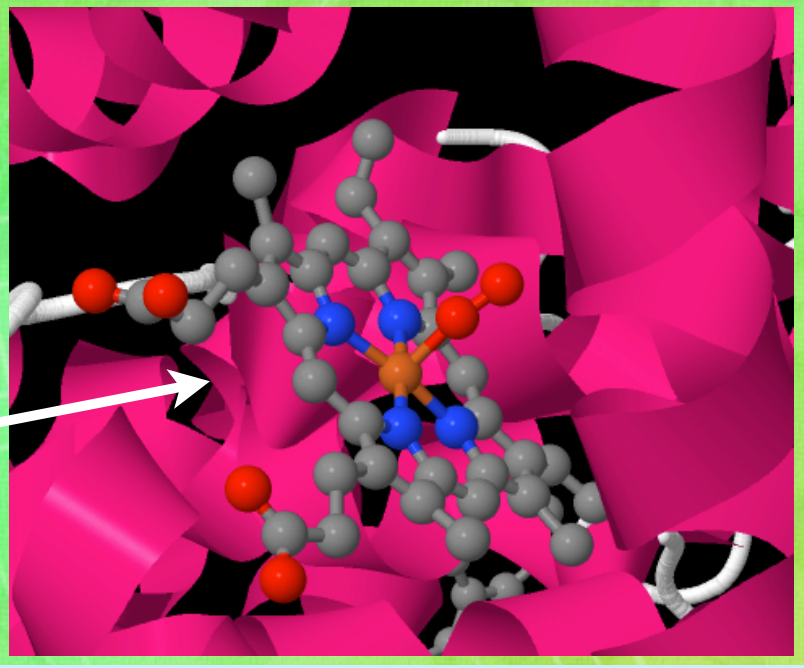

- quantum/thermal fluctuations
- multi-determinantal effects and entropy
- fluctuating magnetic moment (no spin contamination)
- ligand energetics: we need a good estimate of the orbital dependent hybridization and crystal field
- Beyond energy crossings = dynamical effects

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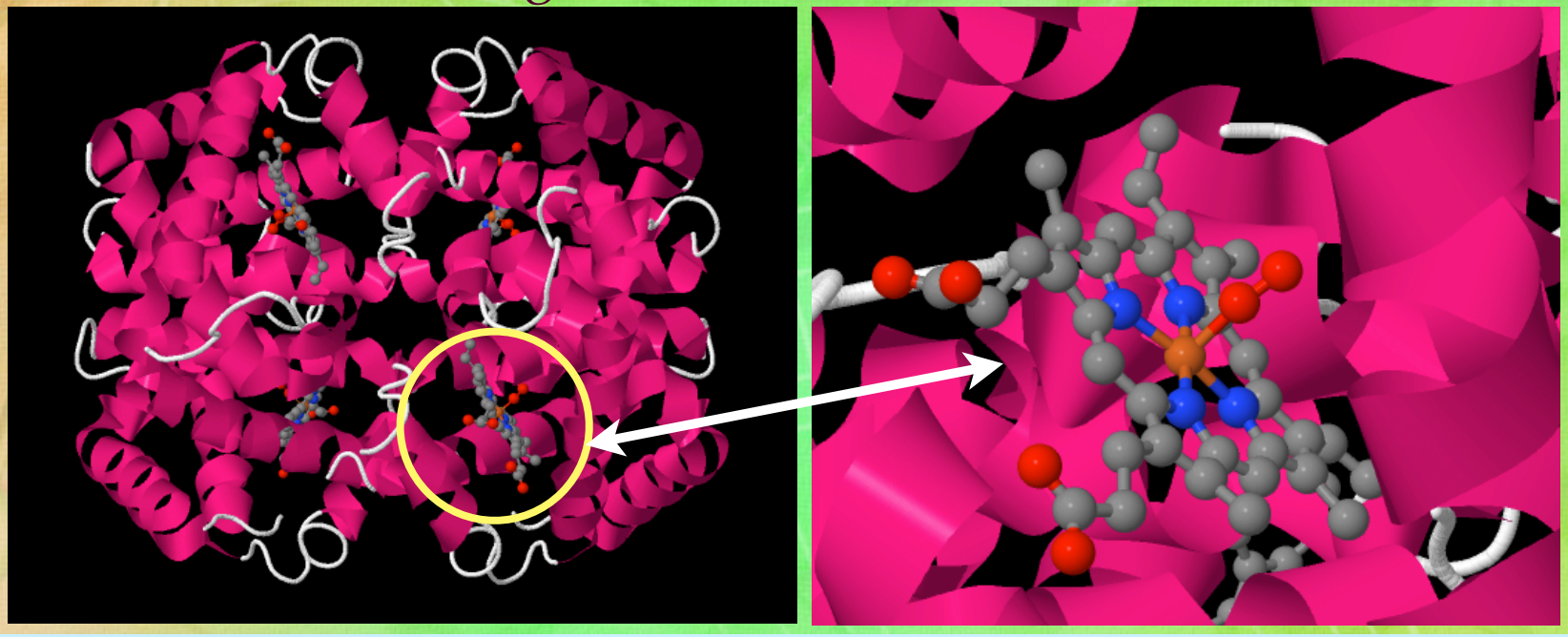

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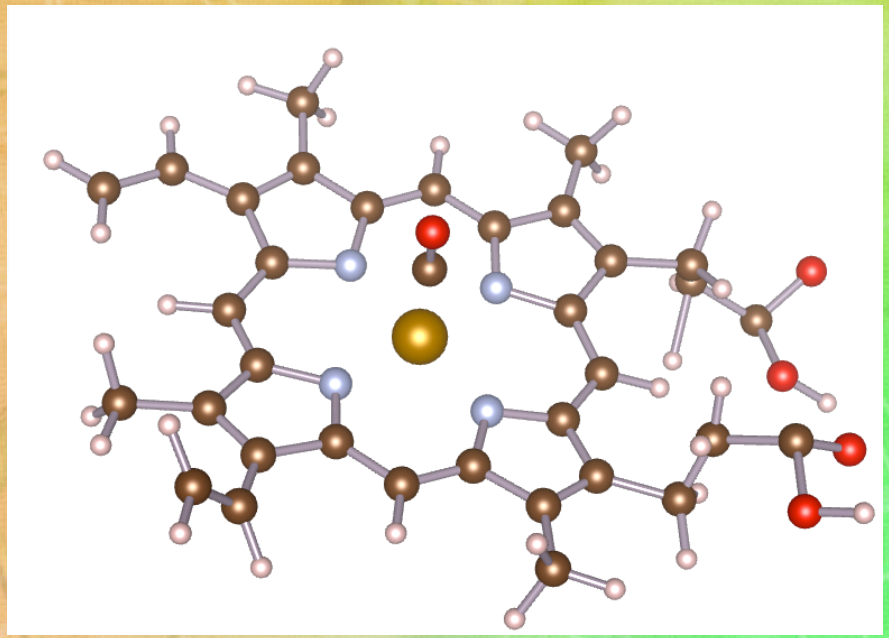
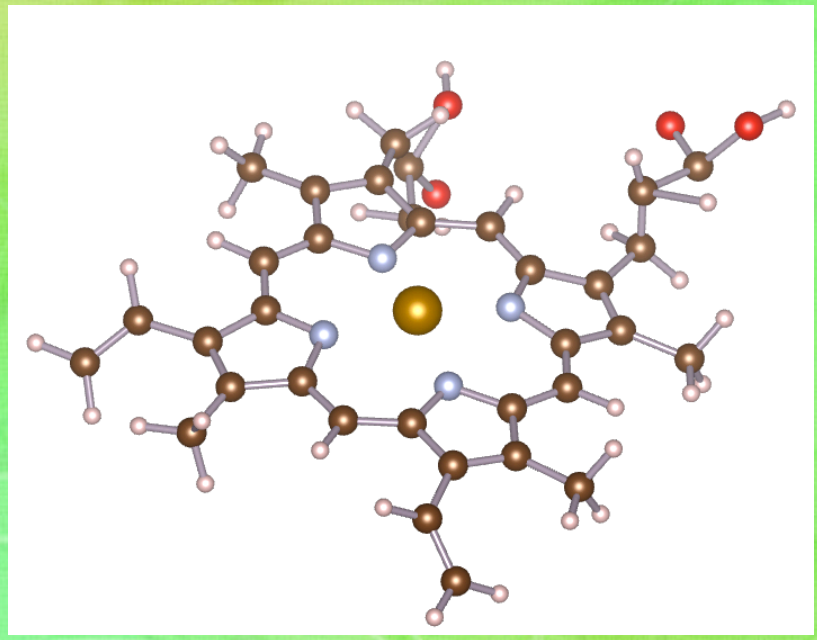
DMFT

Heme : Kernel Conformation



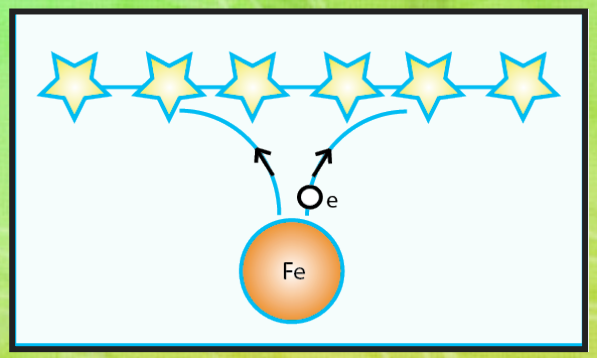


oxy-Heme ($FeP(O_2)$) - planar shape

desoxy-heme (FeP) - domed shape.
Fe out of the nitrogen plane by 0.35A

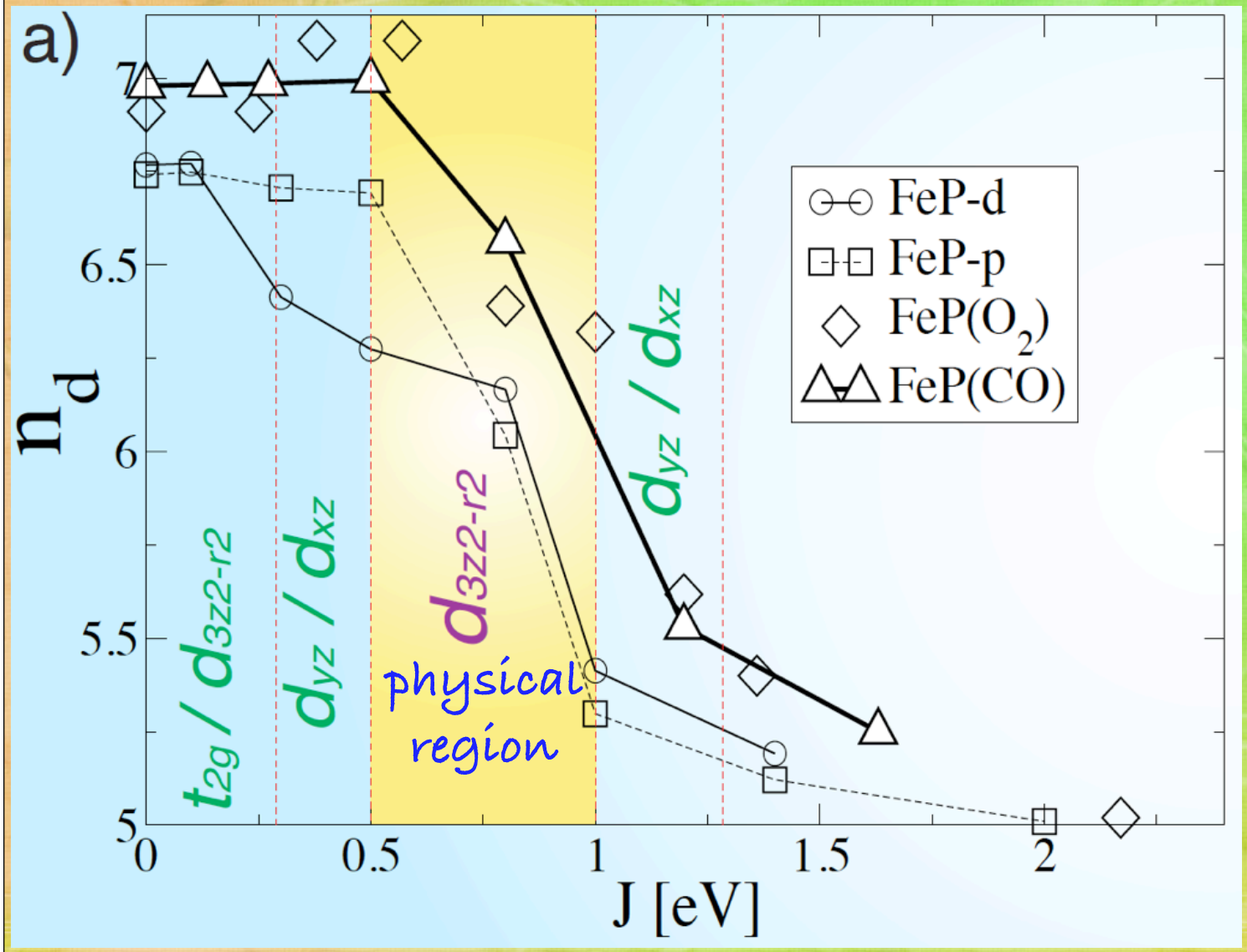
Heme
(~240 orbitals)

AIM
5d orbitals
+bath



What is the link between topology/Binding and electronic states (charge/spin)?

Hund's rule J in Heme



J drives a **transition between low- to high-spin**

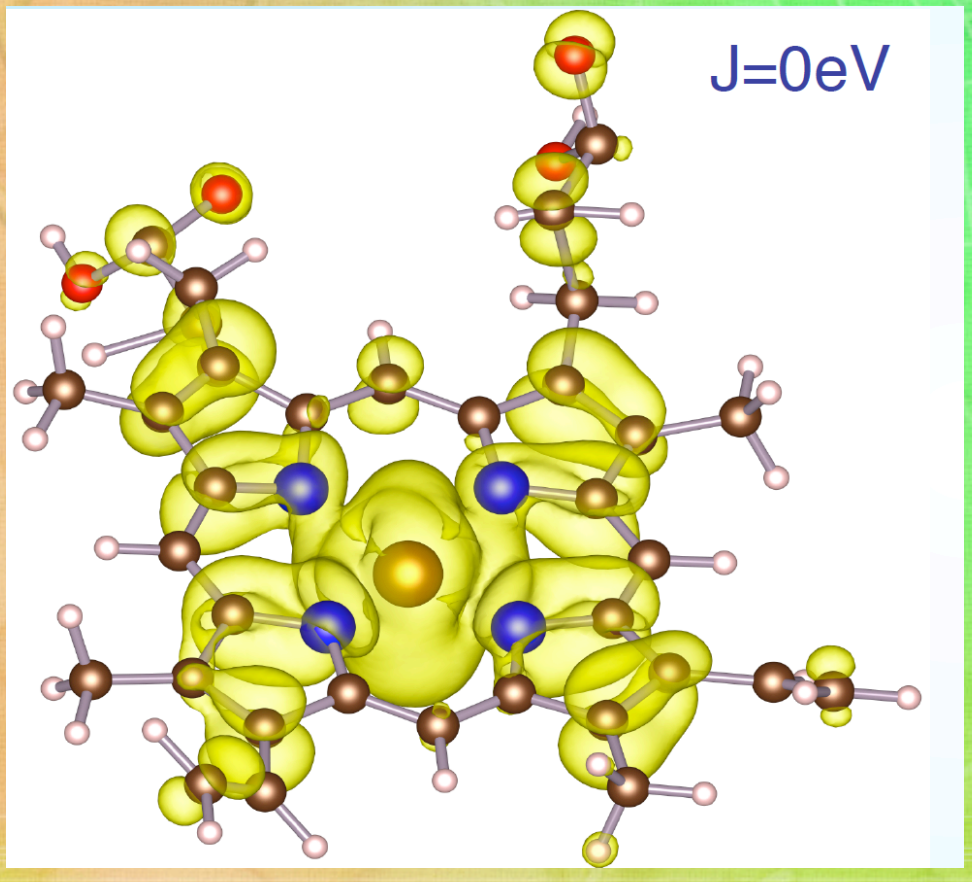
Fully polarised state has 5 electrons (d-shell)

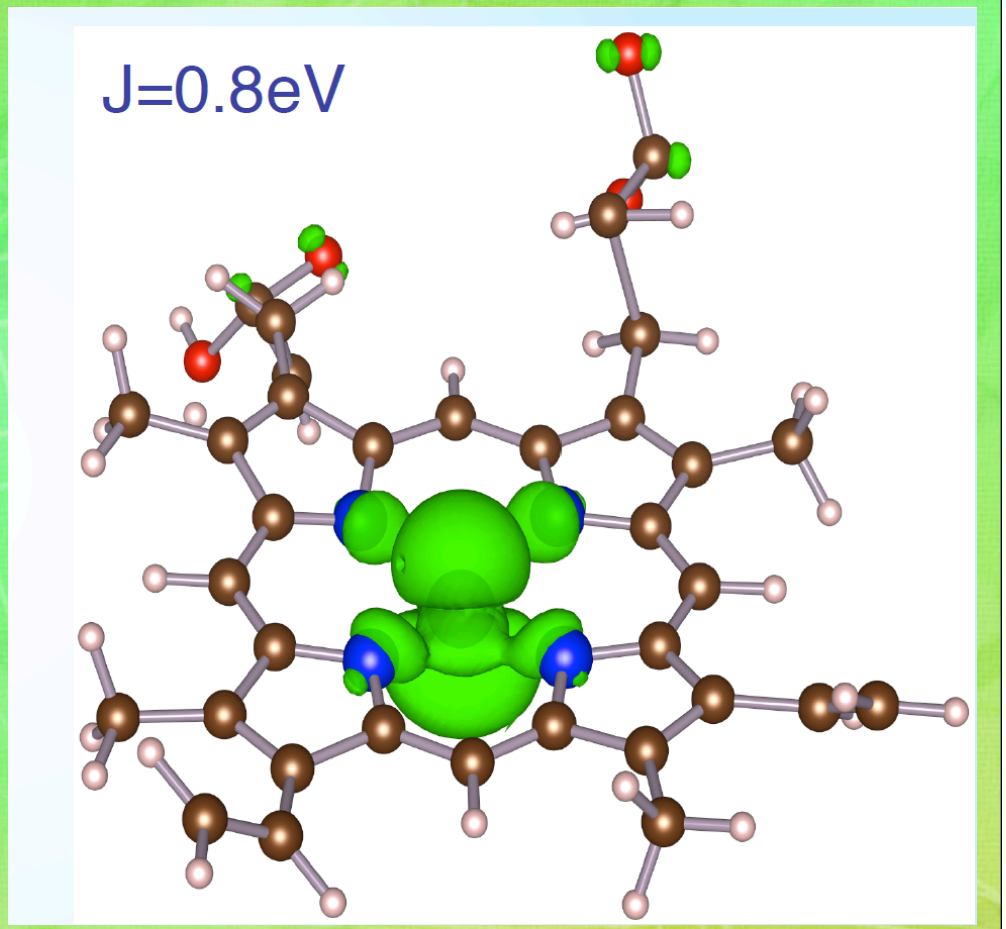
Change of **orbital polarization** across the phase diagram

Sharp drop of the iron density at J~0.7 eV

HOMO Orbital character in desoxy-heme

J affects strongly the symmetry of the HOMO





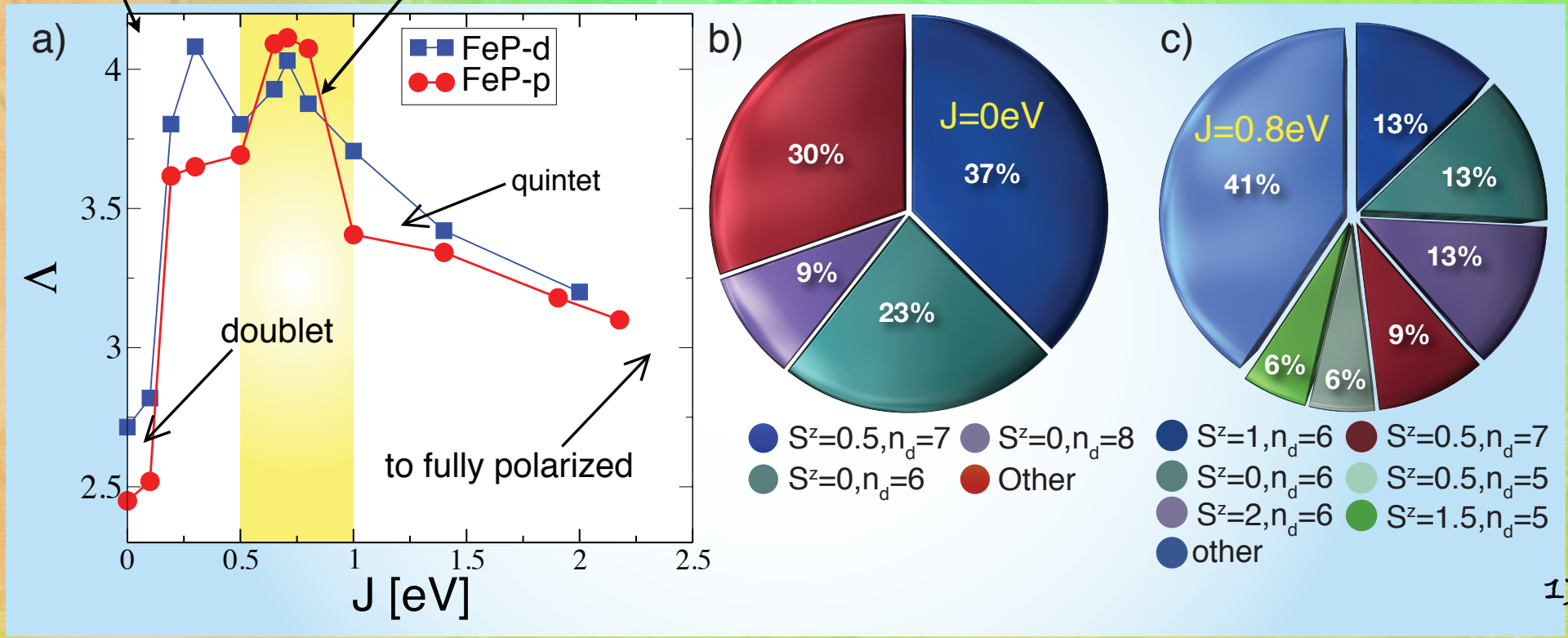
Multi-determinantal effects (unligated heme)

d-shell reduced density matrix (bath degrees of freedom are integrated out)

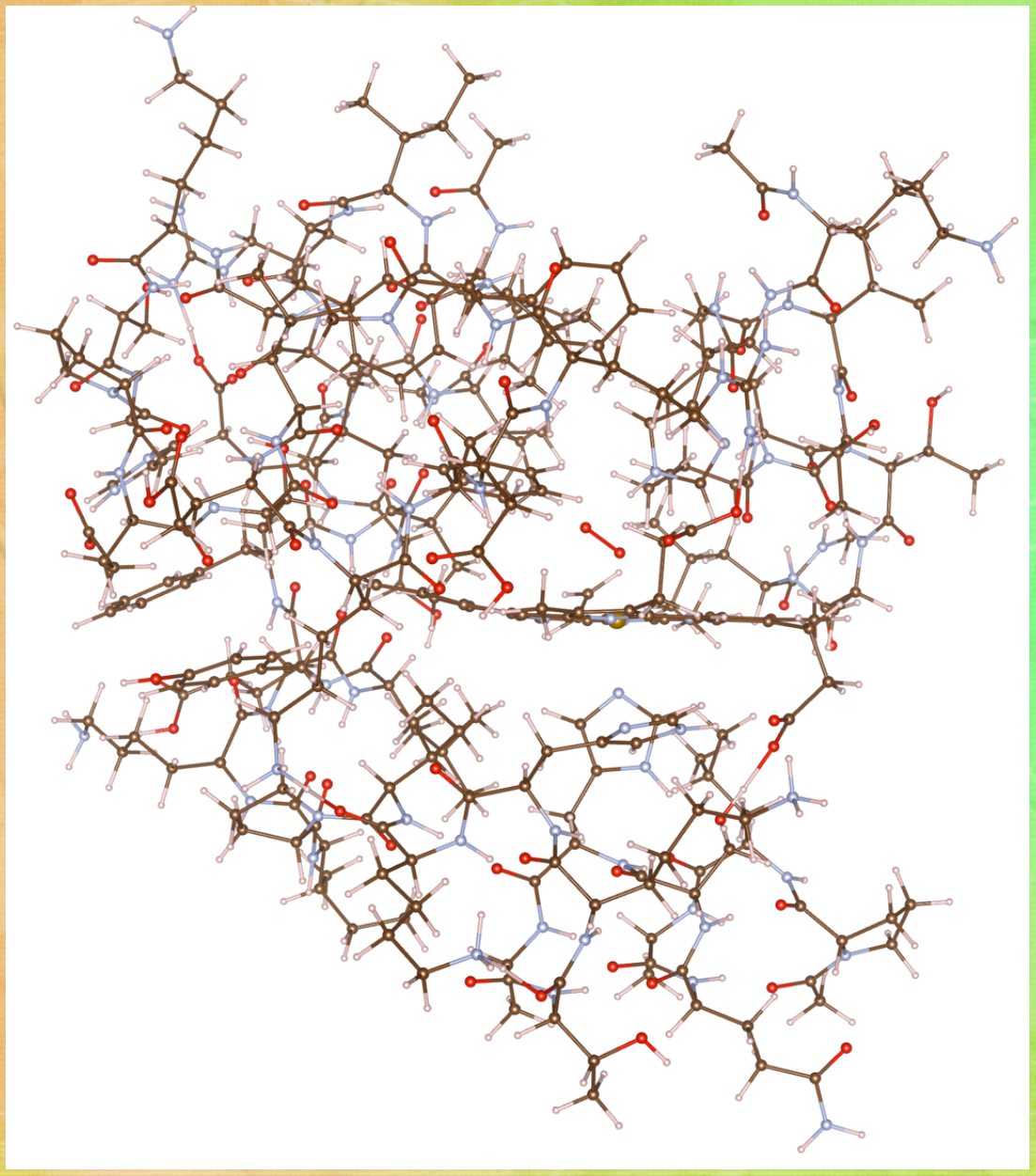
low spin Fe state, low entropy, classical valence

physical region, high entropy, valence fluctuation

"valence fluctuations"



DFT+DMFT : Myoglobin



DFT calculations : binding energy to CO is 1eV greater than to O_2

Problem : CO is toxic ! (Biophys. Journ. 65, 1942 ‘ 93)

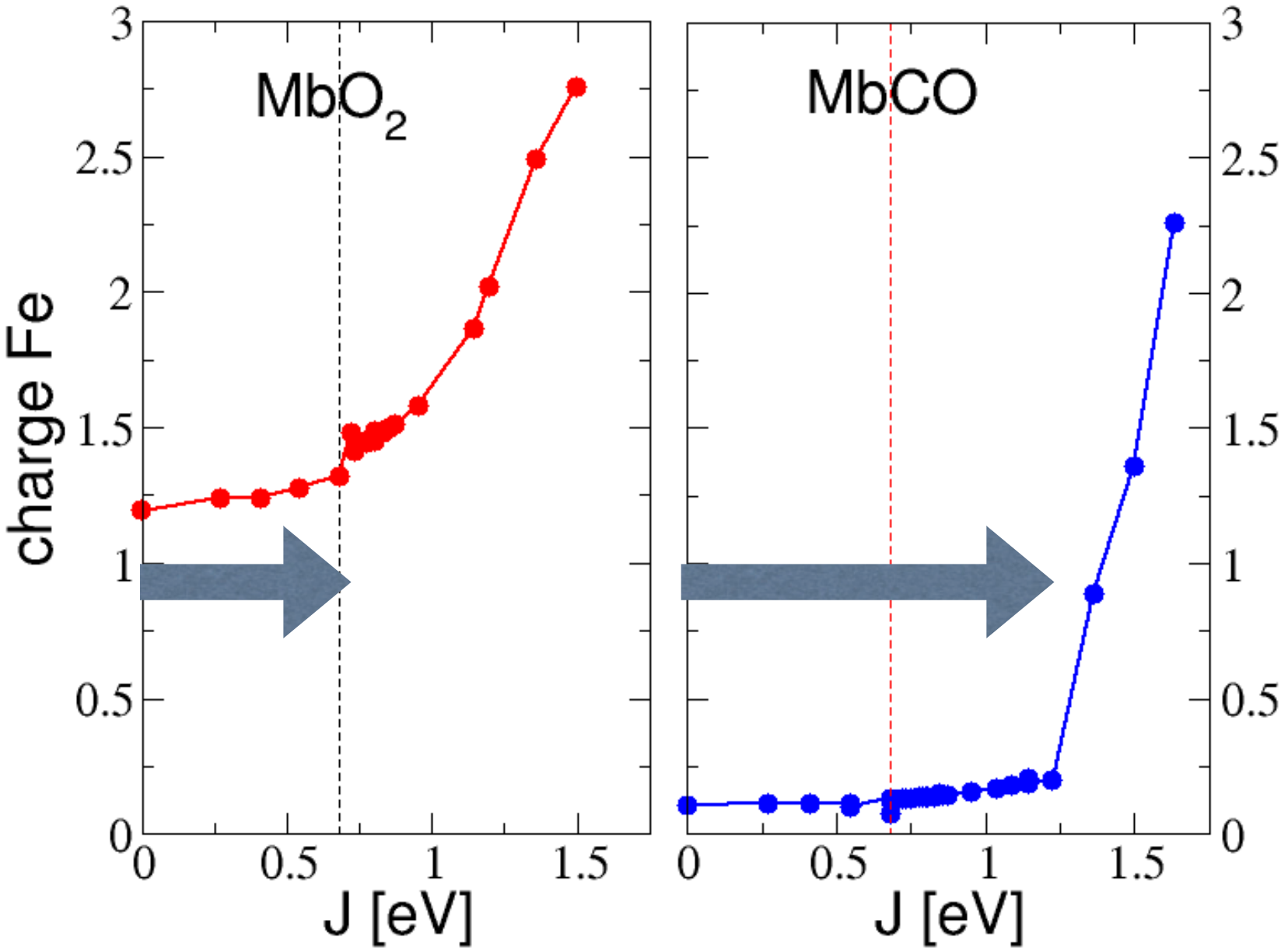
DFT

Treatment of correlations ?

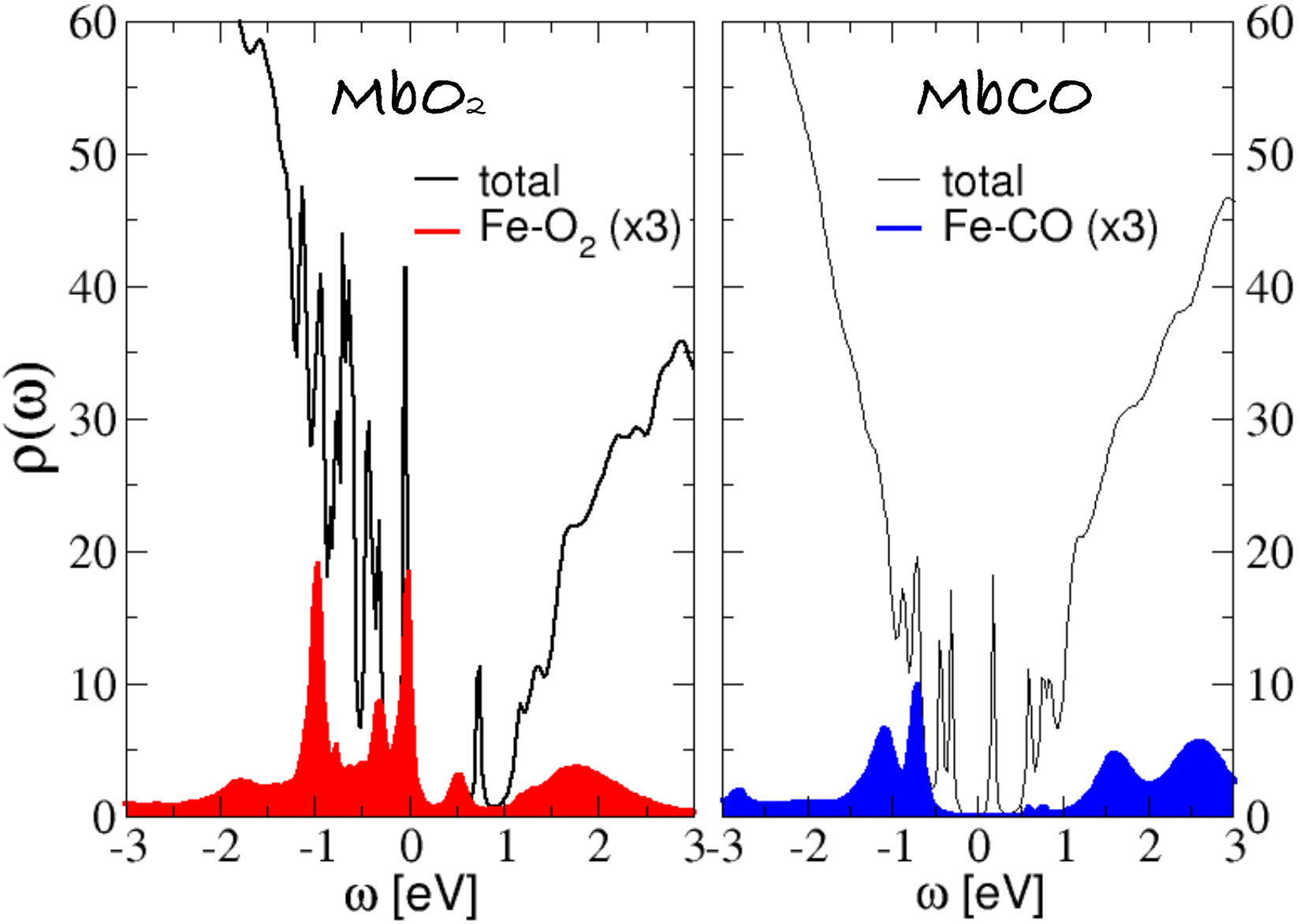
U and J

Iron atom: J~0.68eV, U~4eV

Fe charge



Binding discrimination



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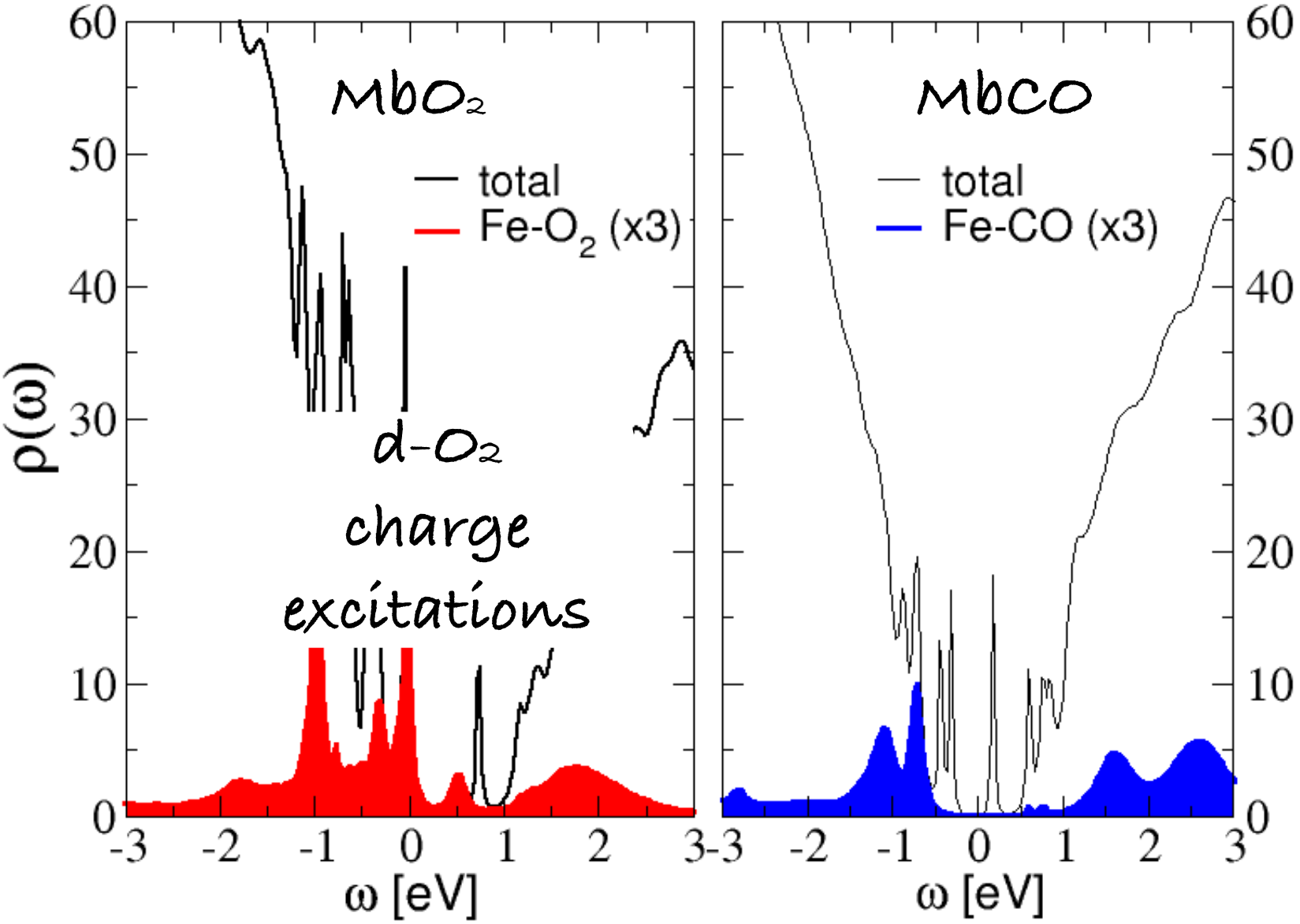
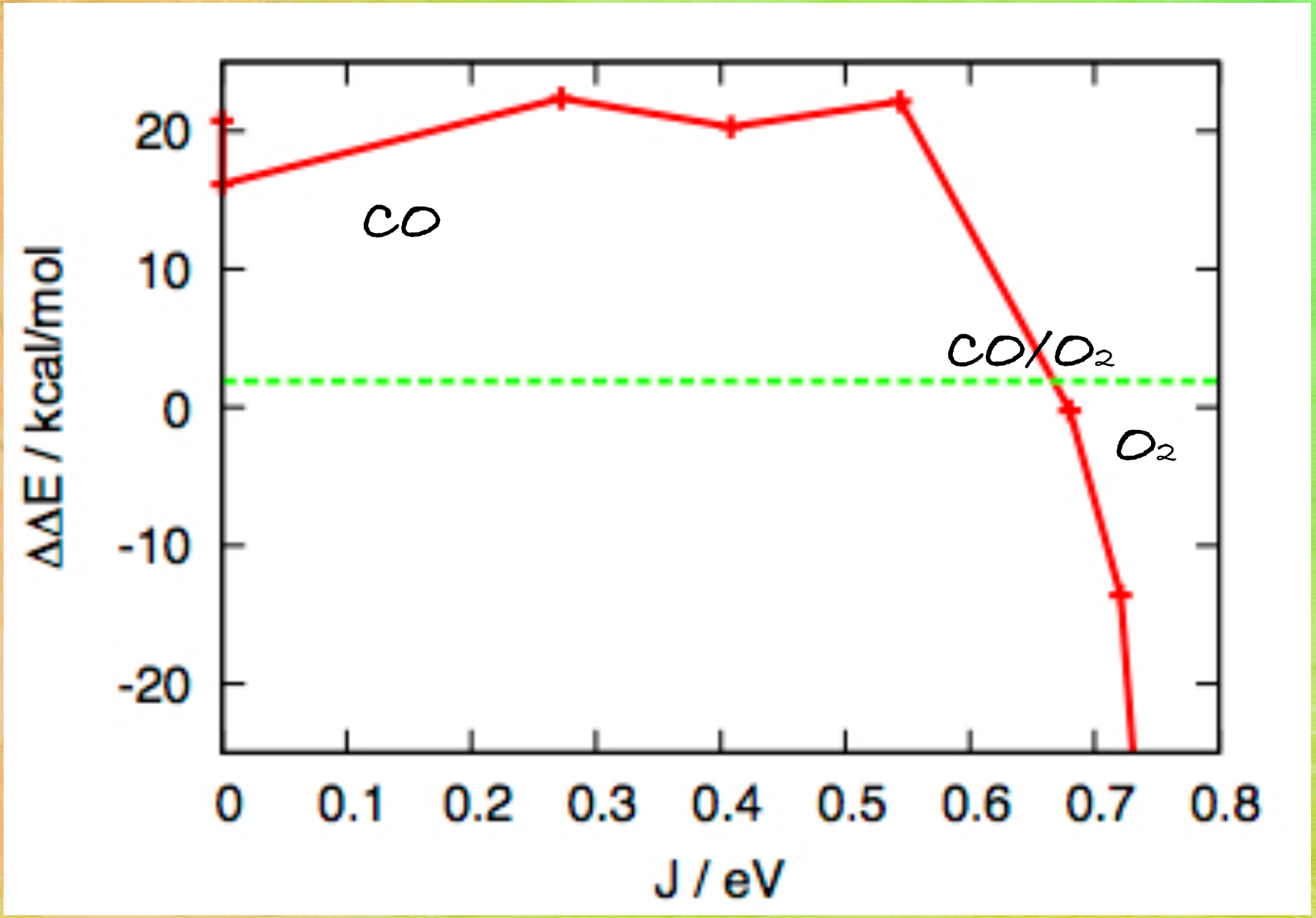


Energetics



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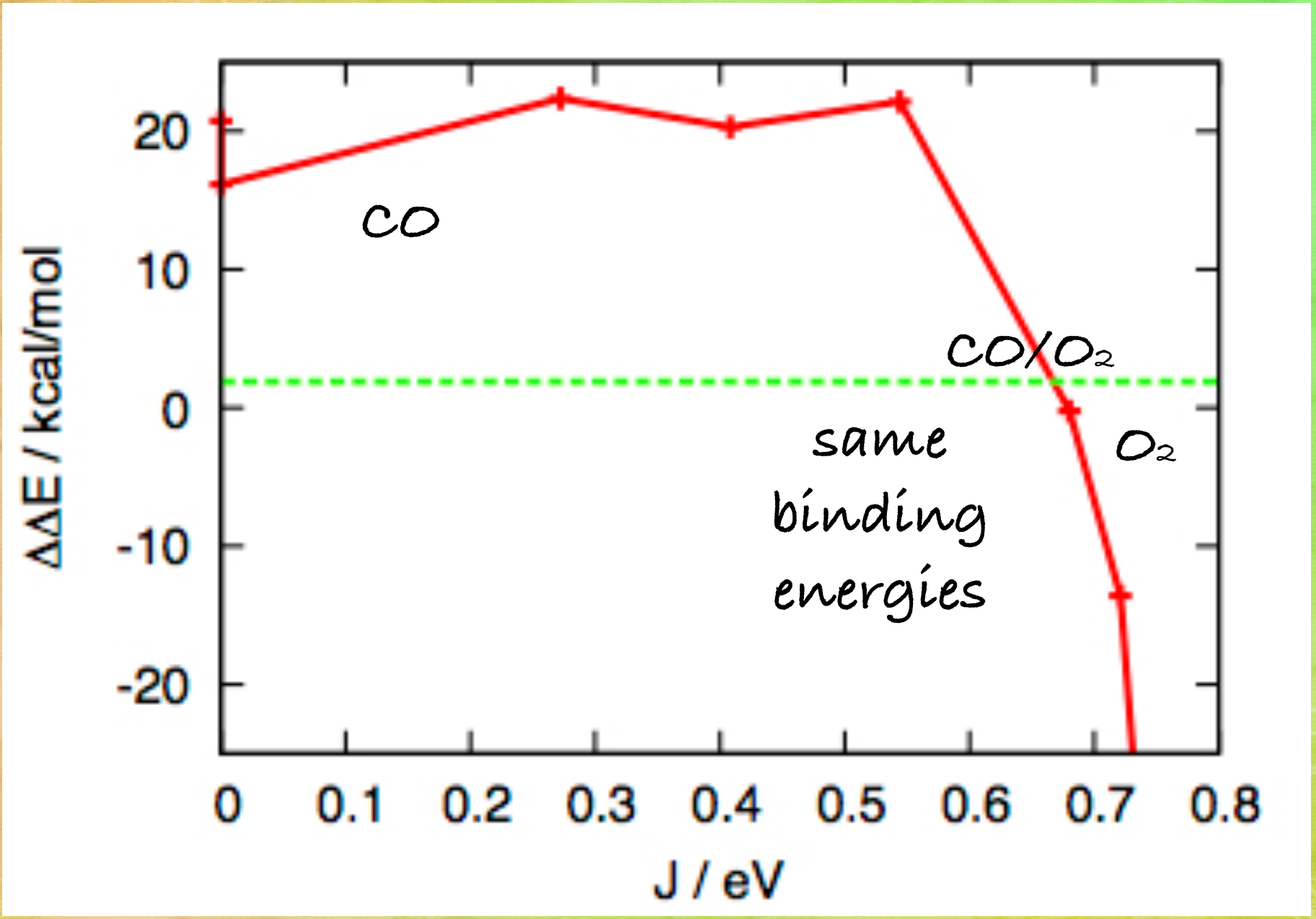
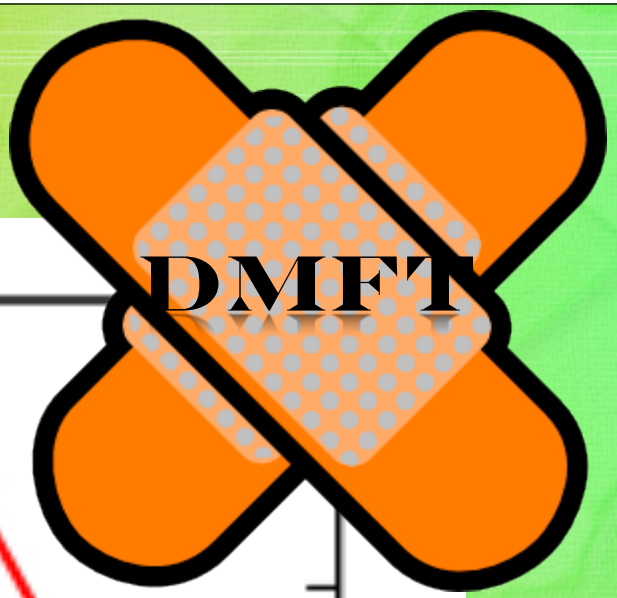
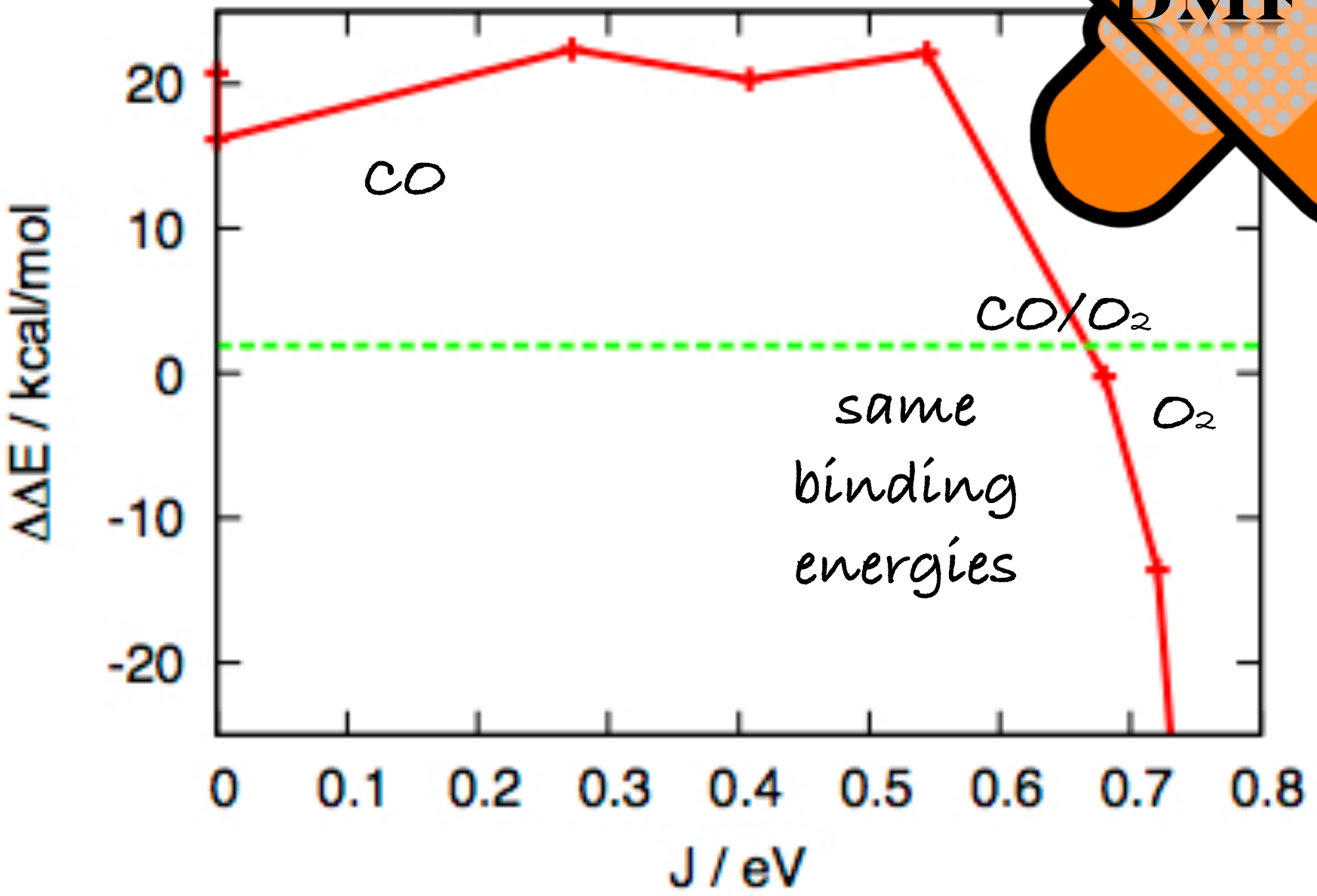
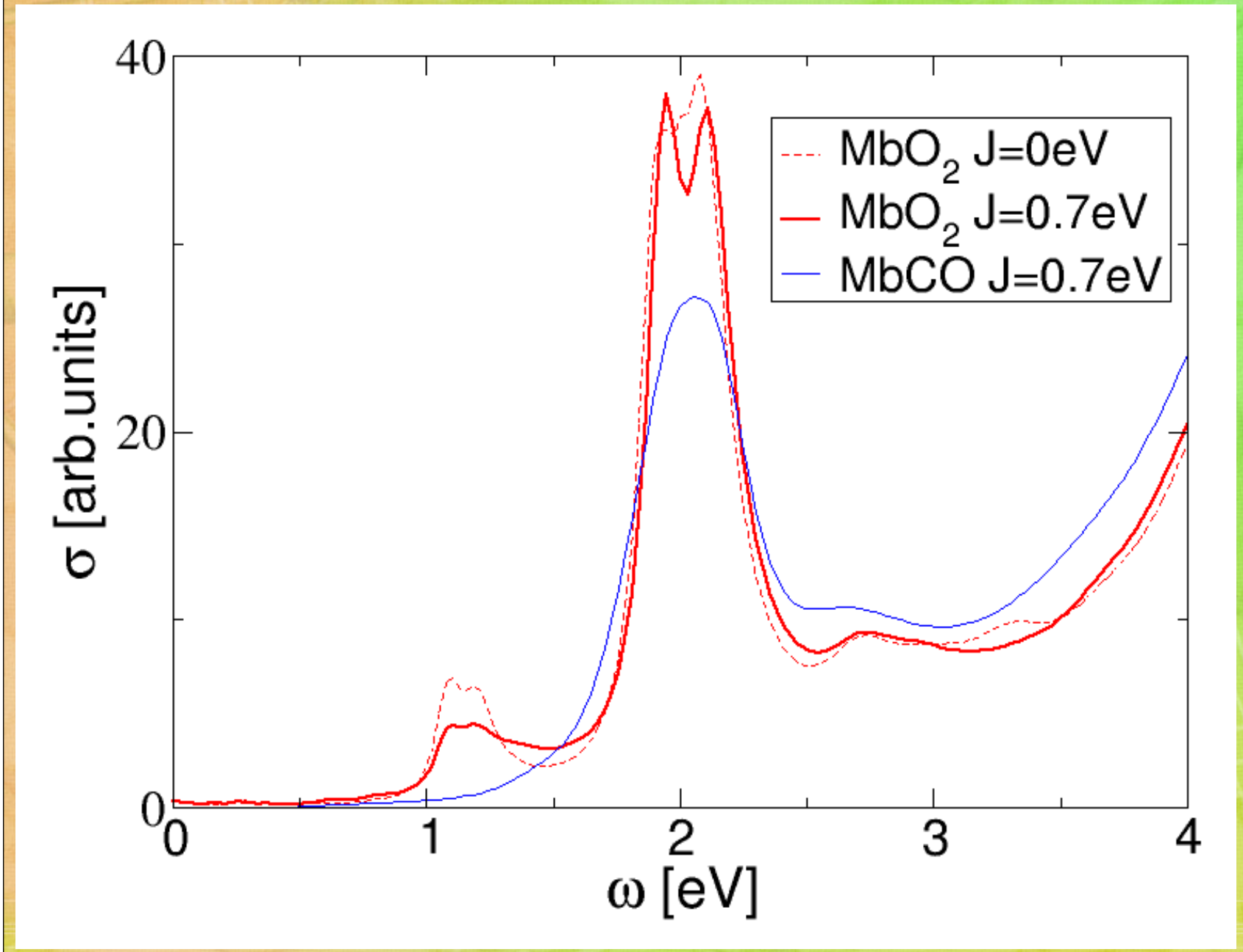

20
10
0
-10
-20
ΔΔE / kcal/mol
CO
CO/O2
same
binding
energies
O2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
J / eV

Energetics


DMFT


ΔΔE / kcal/mol
20
10
0
-10
-20
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
J / eV
CO
CO/O2
O2
same
binding
energies

Optical absorption



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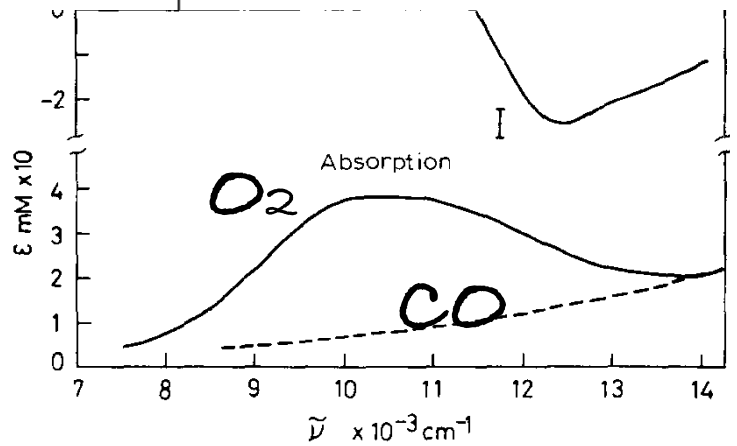
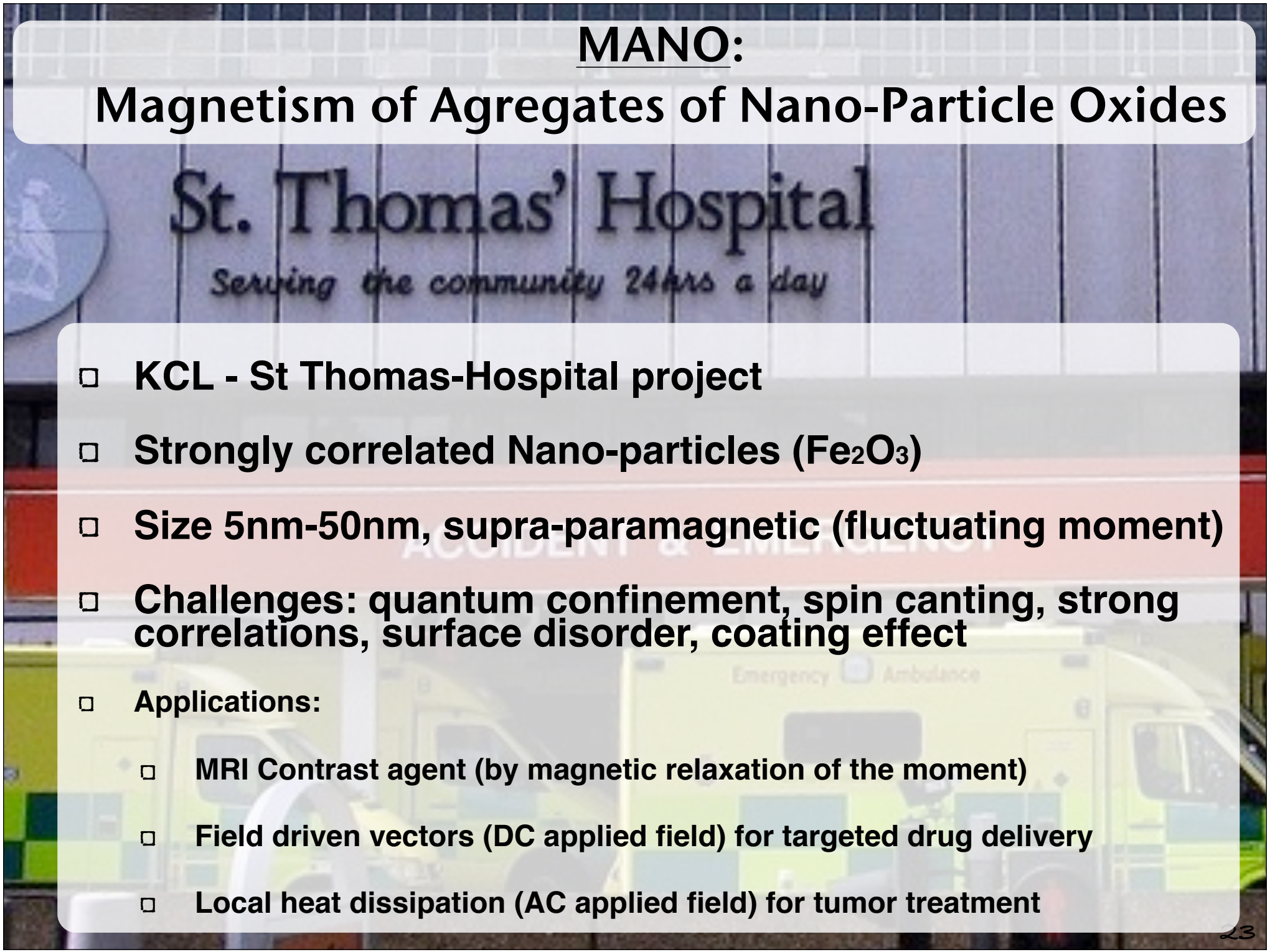


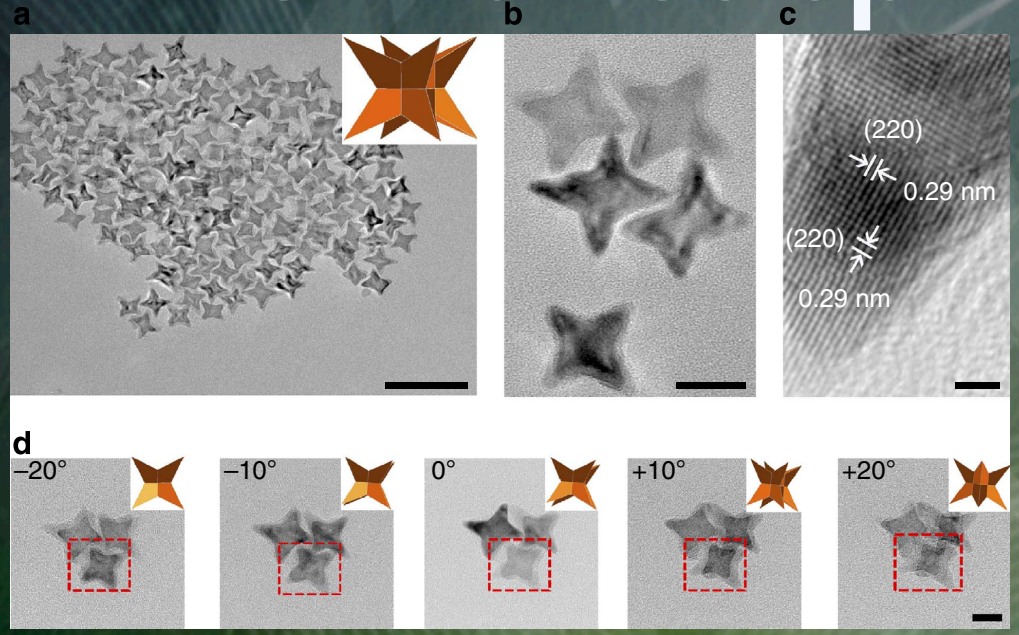
Nozawa et al,
Bio. Bio. Acta, 427, 28 '76

MANO:
Magnetism of Agregates of Nano-Particle Oxides

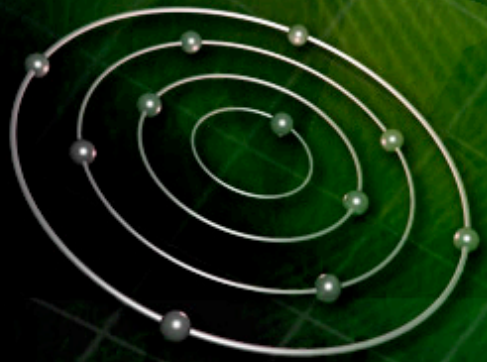


- KCL - St Thomas-Hospital project
- Strongly correlated Nano-particles (Fe_2O_3)
- Size 5nm-50nm, supra-paramagnetic (fluctuating moment)
- Challenges: quantum confinement, spin canting, strong correlations, surface disorder, coating effect
- Applications:
  - MRI Contrast agent (by magnetic relaxation of the moment)
  - Field driven vectors (DC applied field) for targeted drug delivery
  - Local heat dissipation (AC applied field) for tumor treatment

Nano-particle: doping to enhance *spin* relaxation



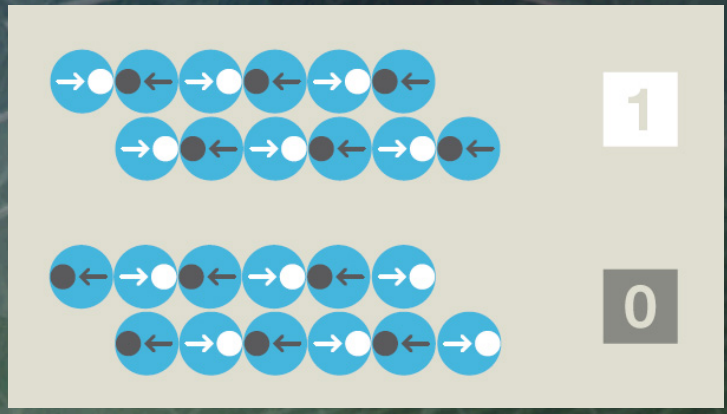
Zhao et al, Ncomms 4:2266 ’13



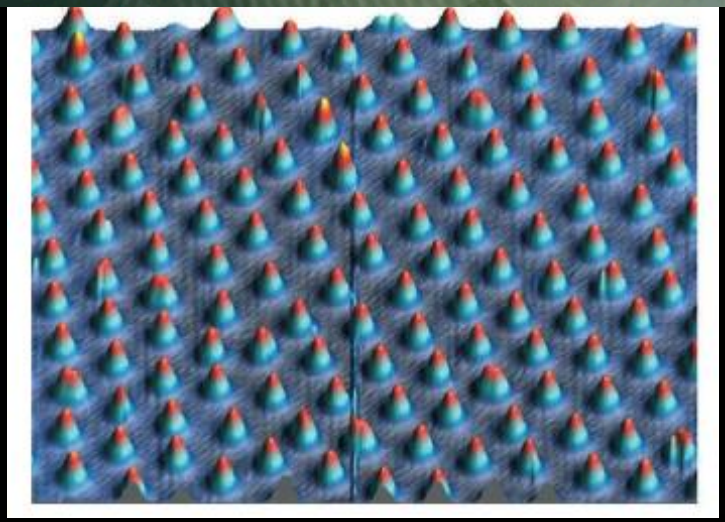
- Doping NP Fe_3O_4 with NaCl
- Unexpected effect: change of symmetry of the NP, it forms an octapod
- Enhances the effective radius, which gives better MRI contrast
- Unexpected: doping affects both magnetism AND structural properties
- Need for predictions and microscopic understanding of the chemical substitution

Self-assembly

- Realization of d- and f- diluted super-lattices with different inter-ad-atom distance (Ag/Ce(111) and Fe/Cu(111)).
- Atomic scale memory device
- Not science fiction : IBM 12-Fe bit

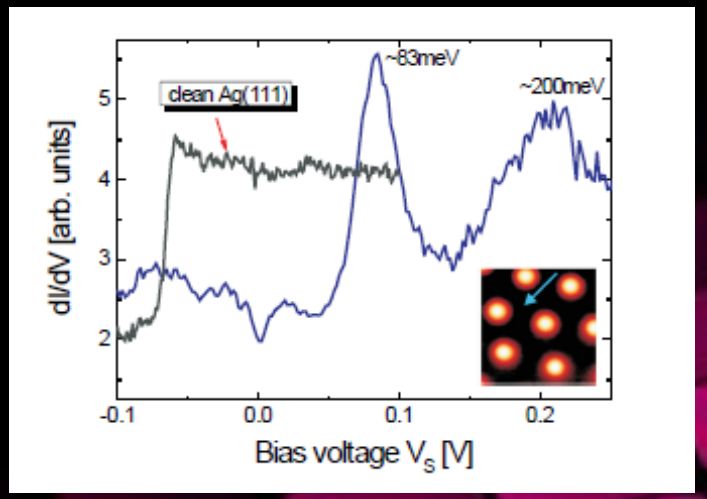


Andreas J Heinrich's group, Science, 335, 196 '12



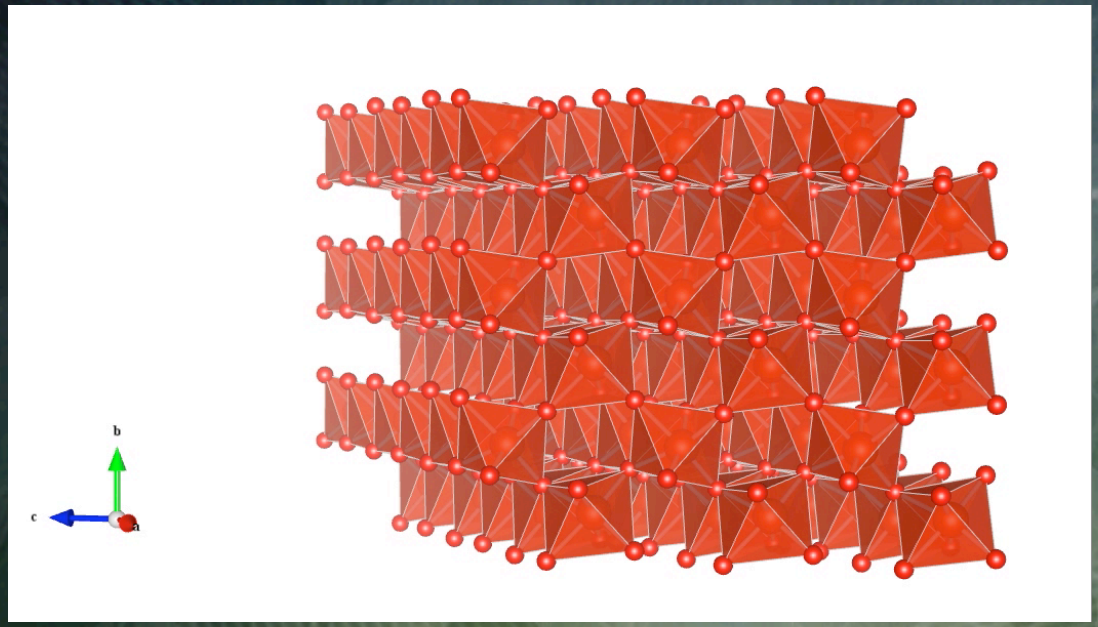
a) STM image of Ce (red) on Ag(111)

W-D Scheider's group, PRL 92, 16101 '04

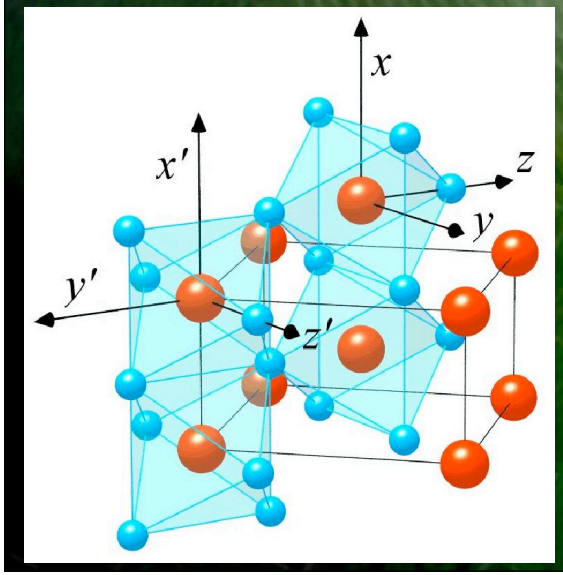


b) Spectra of clean Ag(111) and with Ce superlattice

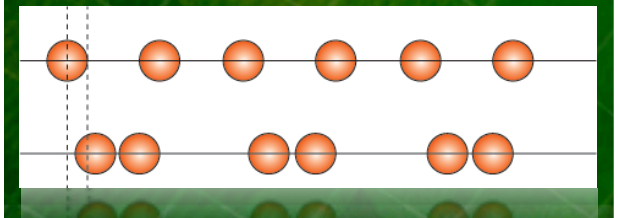
Disorder in Vanadium dioxide



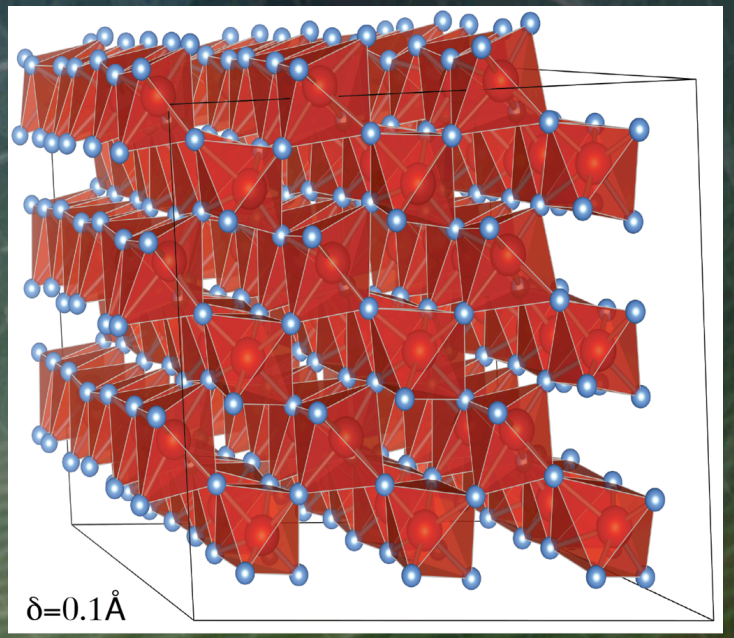
Monoclinic M_1 phase, rutile axis along “a” axis

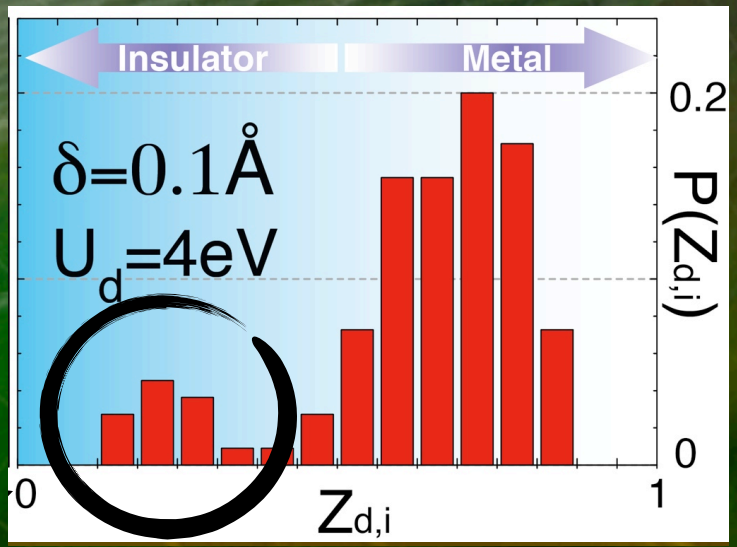


T=290K : structural phase transition



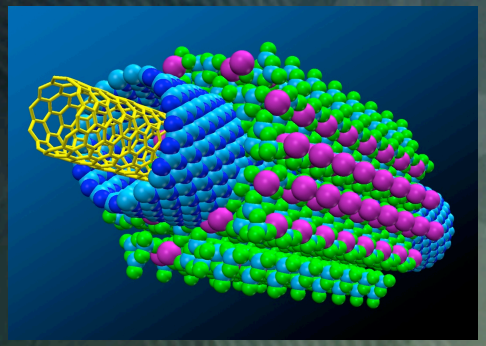
Static disorder





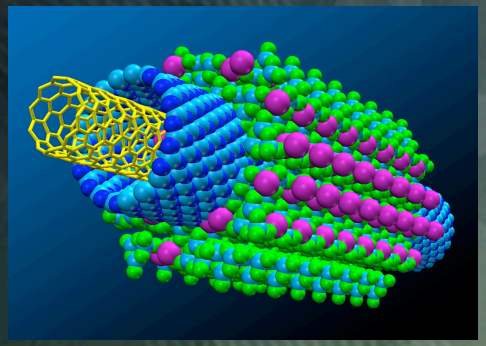
Insulator-like pockets

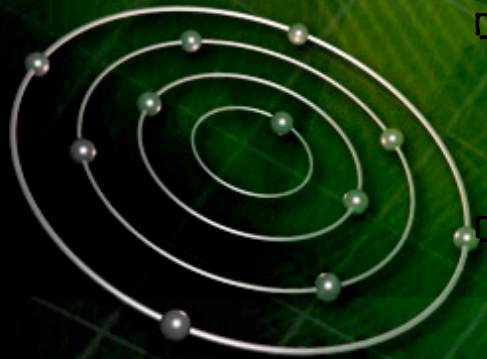
Obstacles



- professional integration : **bringing the new tools to the community. Coding is professional, Delivery is very poor (tutorials, graphical interfaces, ...)**
- **Onetep/Castep : Part of Material Studio (Accelrys). Range of users significant, professional data pipeline.**
- Range of users **is small, but** potential for significant advances is large**, we need to make a case !**
- engage better with industries**, pharmaceuticals, material driven rather then method-driven**
- **Hub with upfront range of expertise (TYC example in London)**
- **Interdisciplinary science : hard to deliver, hard to review (funding agencies). On paper attractive.**

Obstacles





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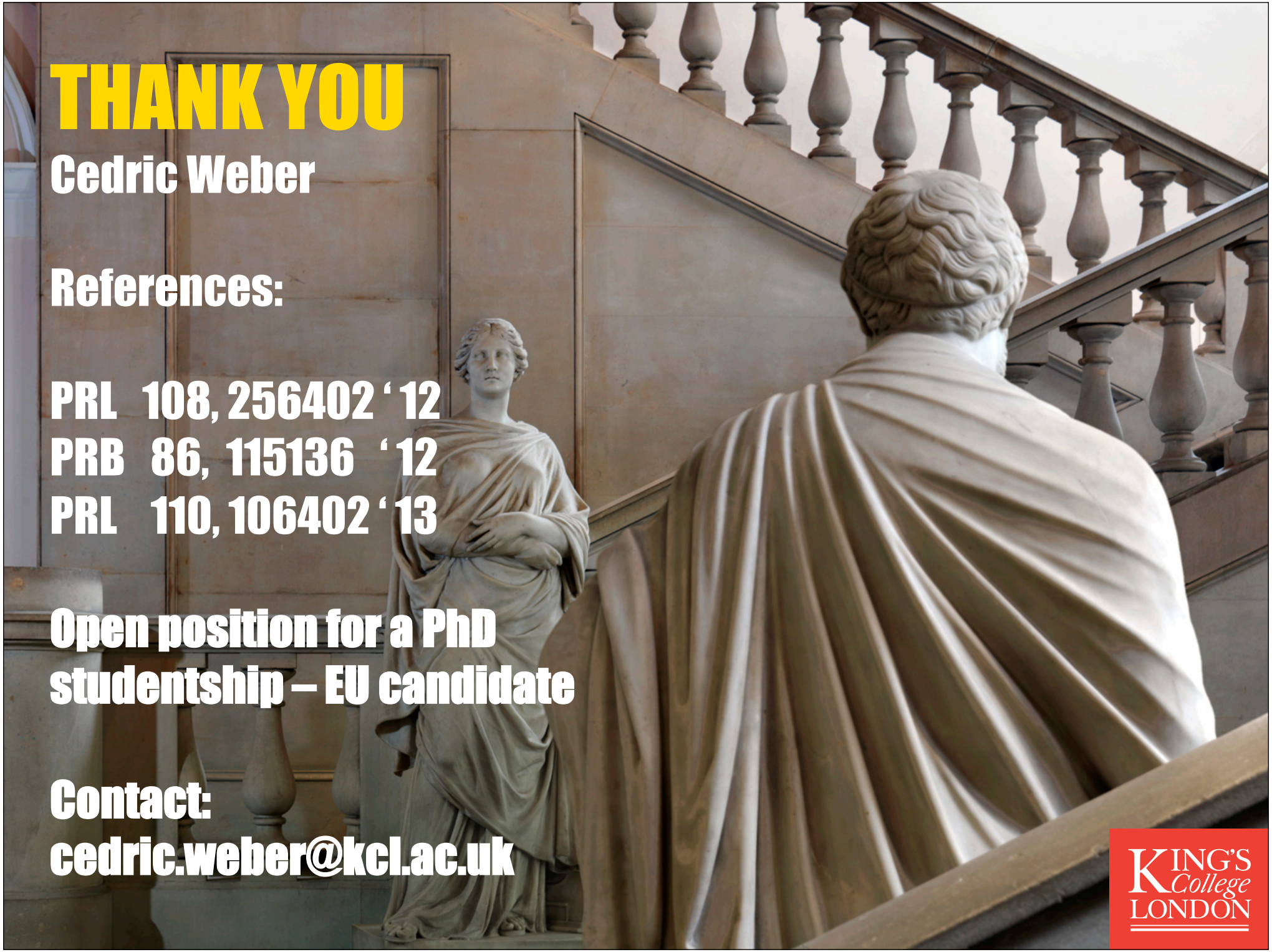
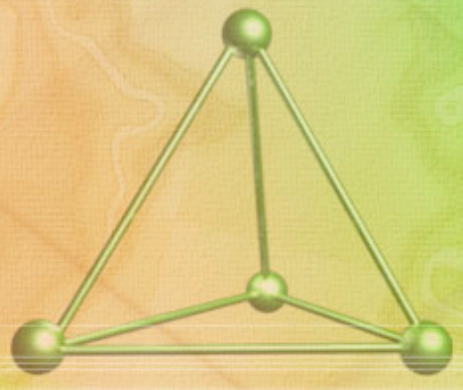
Conclusion / Roadmap to drug design

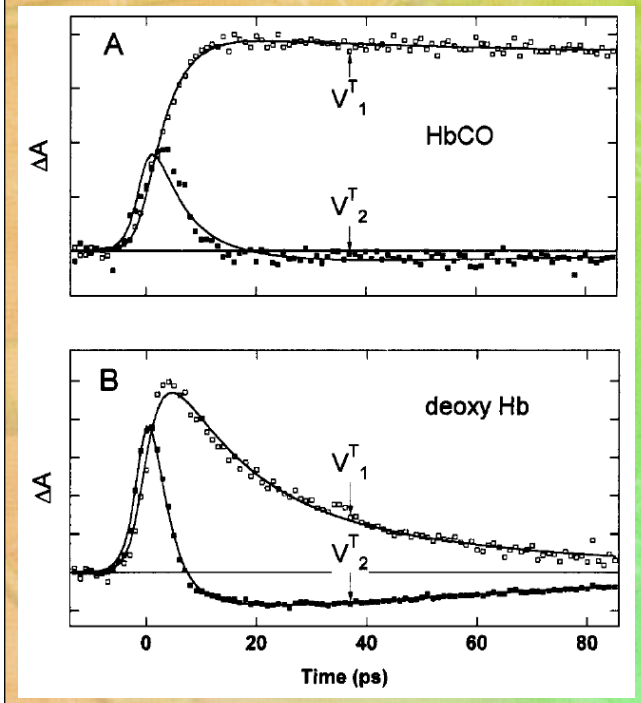
- Promising direction : extensions to non-periodic systems (nano-crystals, molecules, self-assembly ...)
- nano-structure tailoring / drug design - Roadmap
  - Geometry optimization (now only ONETEP/DFT+U)
  - DMFT treatment restricted in energy or spatial range, need more
  - DMFT + Molecular dynamic (Forces , ...), we have energies, but we need better “value/money” algorithms
  - GW and DMFT+GW in real space for molecules
  - Data mining
  - Multi-scale approaches (effective Kohn-Sham potential ...)
  - Beyond linear response : DMFT+Boltzman equation (Nicola Bonini-KCL, transport)


THANK YOU
Cedric Weber
References:
PRL 108, 256402 ‘12
PRB 86, 115136 ‘12
PRL 110, 106402 ‘13
Open position for a PhD studentship – EU candidate
Contact:
cedric.weber@kcl.ac.uk
KING’S College LONDON

THE END

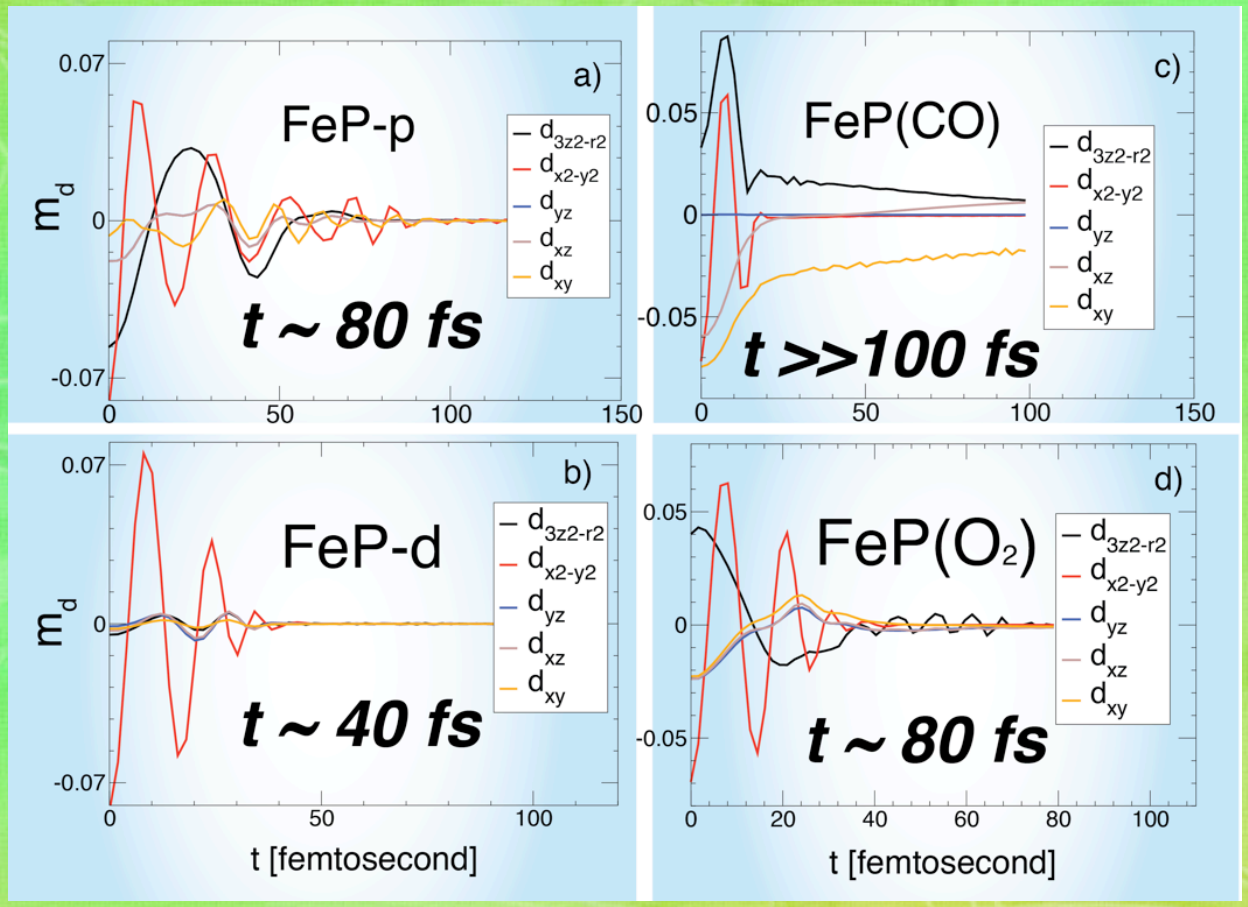


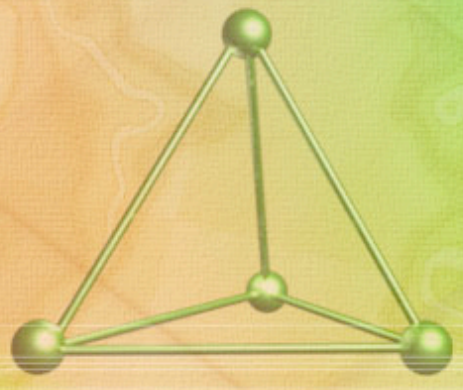
Relaxation, femto dynamics



Photolysis excitation, shift in Raman spectra versus time,
(Franzen, Biophys. Journal 80'01)

T=0 polarization, relaxation





Topology / response dependence
Protein characterization by time dependence

AIM - Entanglement - bath/impurity

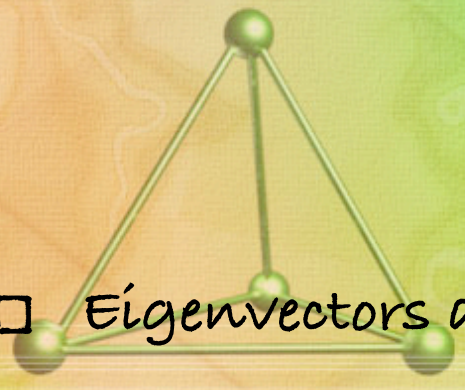
- Decomposition of the ground state (and excited states) in impurity and bath parts

- Reduced density matrix of the impurity **ρ**

$$\hat{\rho} = \sum_i e^{-\beta E_i} Tr_B |i\rangle\langle i|$$

- Diagonalization of **ρ** yields the Von Neuman entropy:

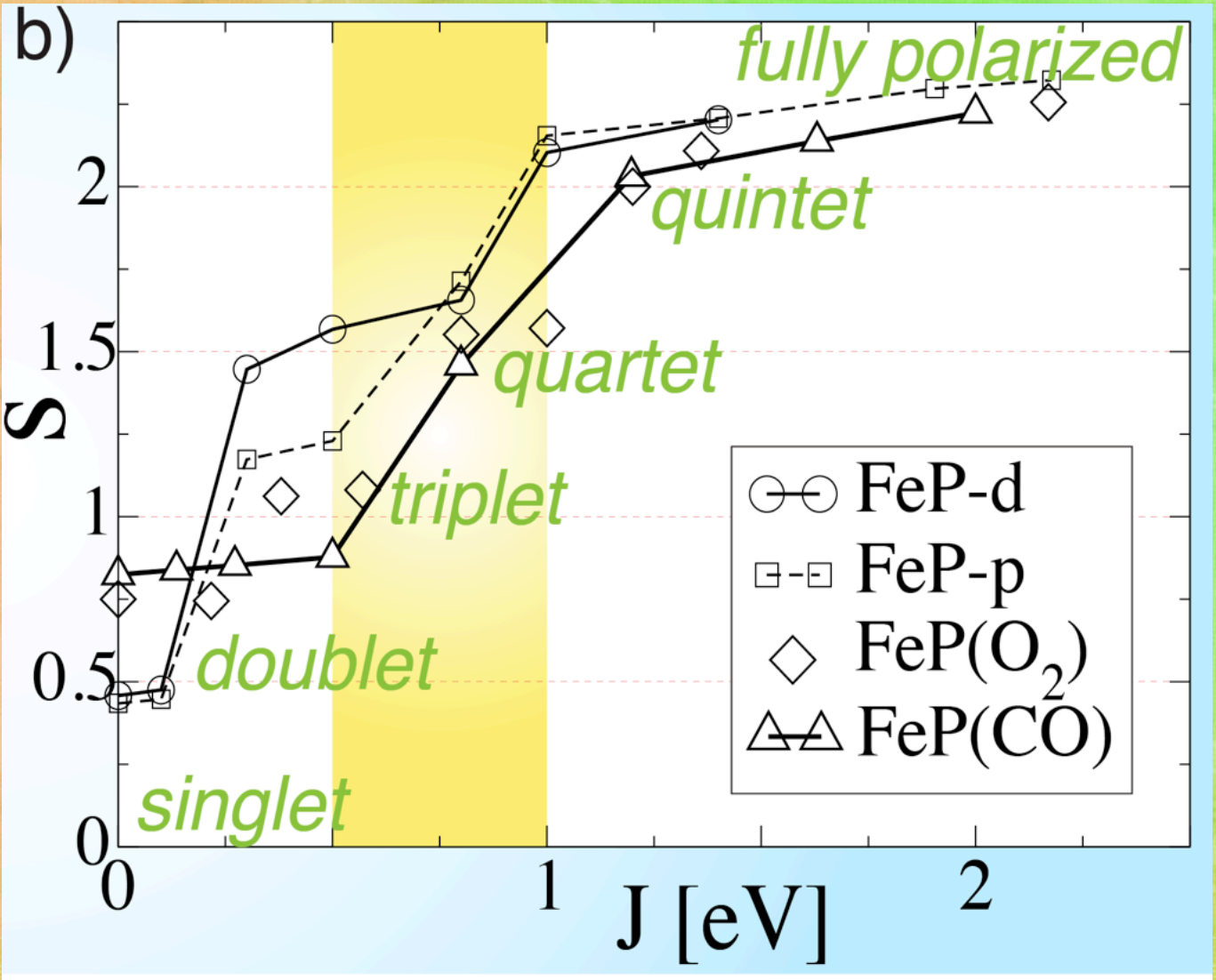
$$\Lambda = -k_B \sum_k \lambda_k \ln(\lambda_k)$$



- Eigenvectors are "cartoon"representation of the dominant states

Fluctuating magnetic moment

$$S = \sqrt{\langle \hat{\mathbf{S}}\hat{\mathbf{S}} \rangle - (\langle \hat{\mathbf{S}} \rangle)^2} = \sqrt{\langle \hat{\mathbf{S}}\hat{\mathbf{S}} \rangle} \qquad S = s\,(s+1)$$

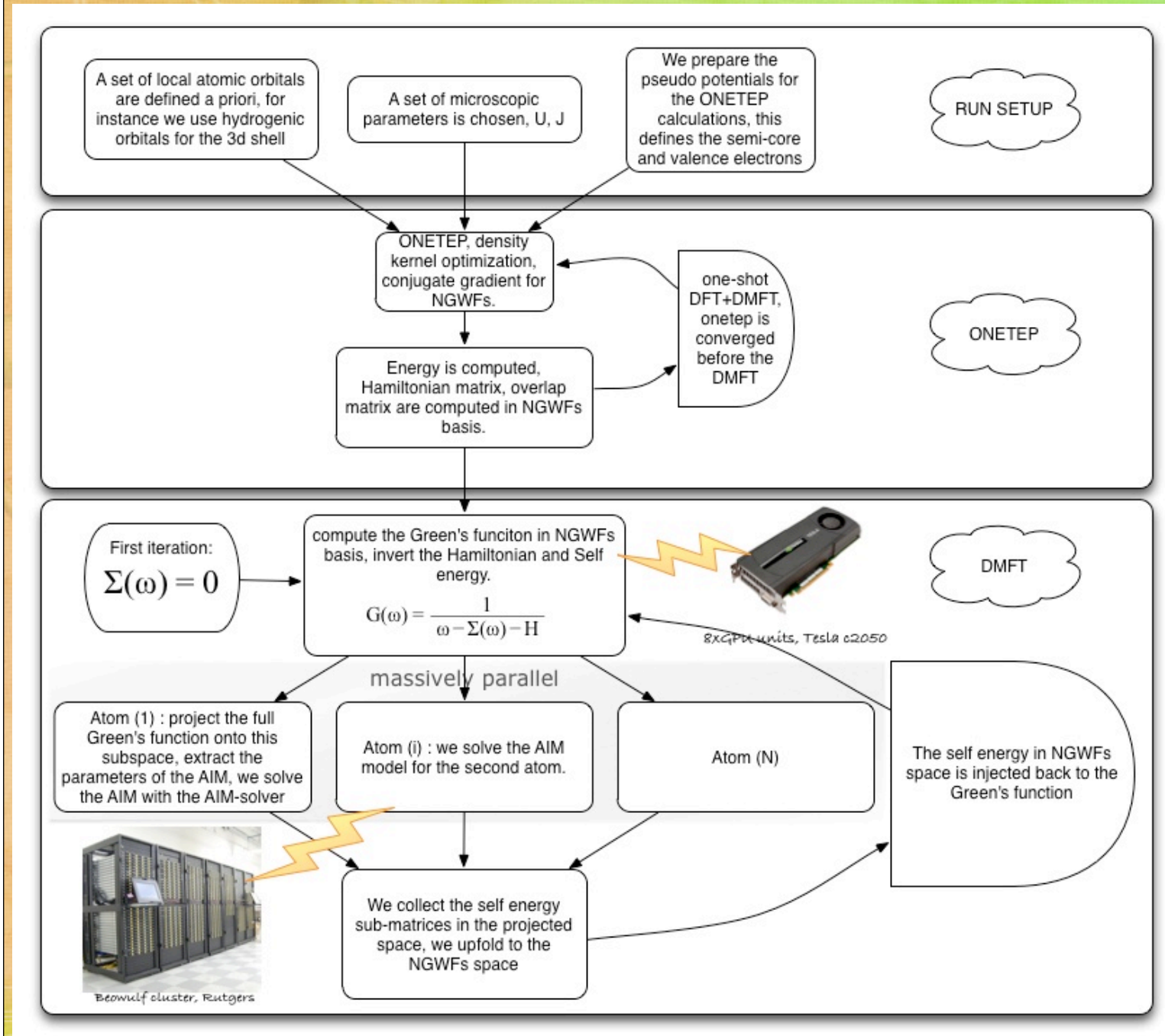


no-symmetry breaking (paramagnetic solution)

not in a classical representation of a triplet state for J~0.8eV

Experimentally : strong dependence of the spin state with respect to small modifications in the structure

Workflow



1) Setup the problem (pseudo-potentials, crystallographic structure, screened interactions)

2) Converge the DFT calculations

3) Invert the Self-energy and hamiltonian (GPU)

4) Project the Green's function on many atomic local problems.

5) Solve the AIM local problems in parallel (MPI+OPENMP).

6) Upfold back the projected Self-energy to the large Kohn-Sham Hilbert space

Where do the electron go?

J transfers charge to hydroxyl groups

atom	$\Delta n(r)$
Iron d orbitals	-0.52
Nitrogen ring	-0.25
hydroxyl groups	+0.77

TABLE III: Variation of the charge $\Delta n(r) = n(r, J = 0.8) - n(r, J = 0)$ in FeP induced by the Hund's coupling.

	J	$d_{x^2-y^2}$	$d_{3z^2-r^2}$	d_{xz}	d_{xy}	d_{yz}
FeP	0	0.85	1.86	1.24	1.98	0.82
FeP	0.8	1.10	1.75	1.08	1.14	1.08
FeP(CO)	0	1.06	0.86	1.99	1.06	1.99
FeP(CO)	0.8	1.14	1.33	1.16	1.05	1.85
$FeP(O_2)$	0	0.72	1.82	1.25	1.87	1.28
$FeP(O_2)$	0.8	1.03	1.07	1.18	1.97	1.09

increase J : empties doublets

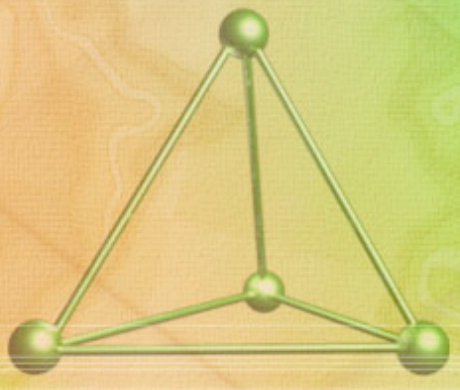
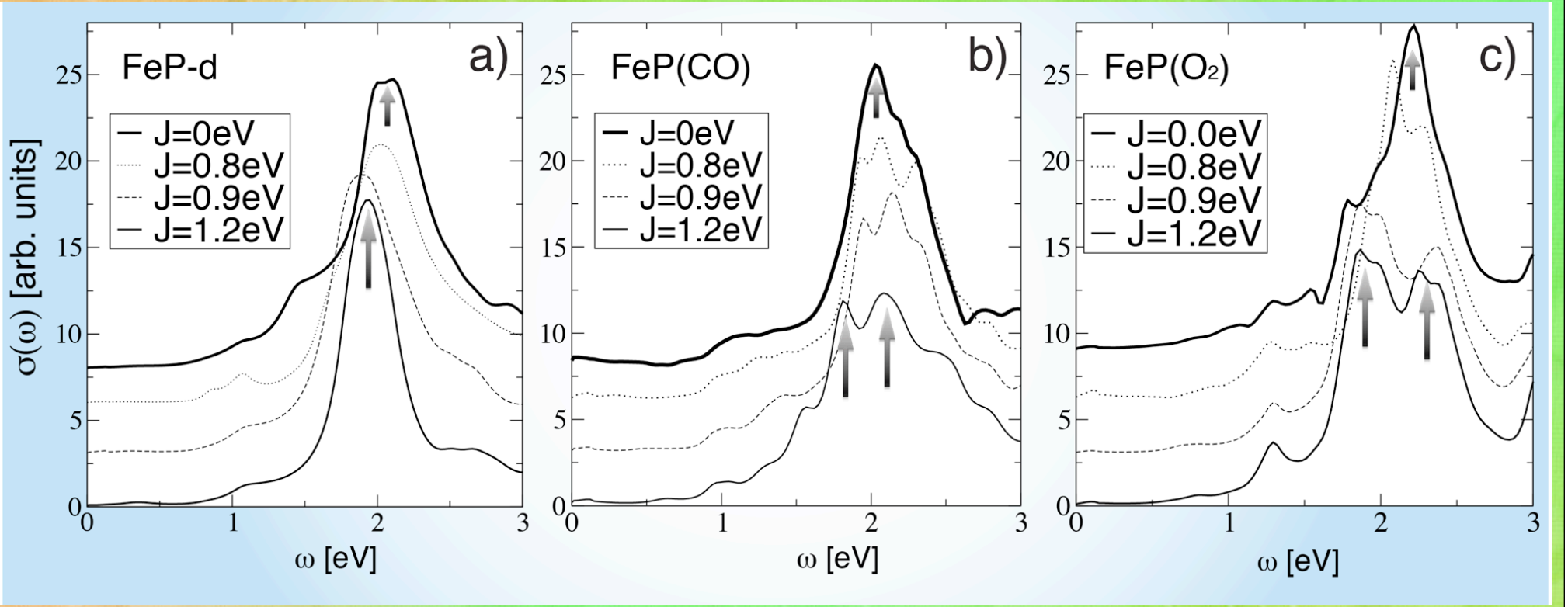


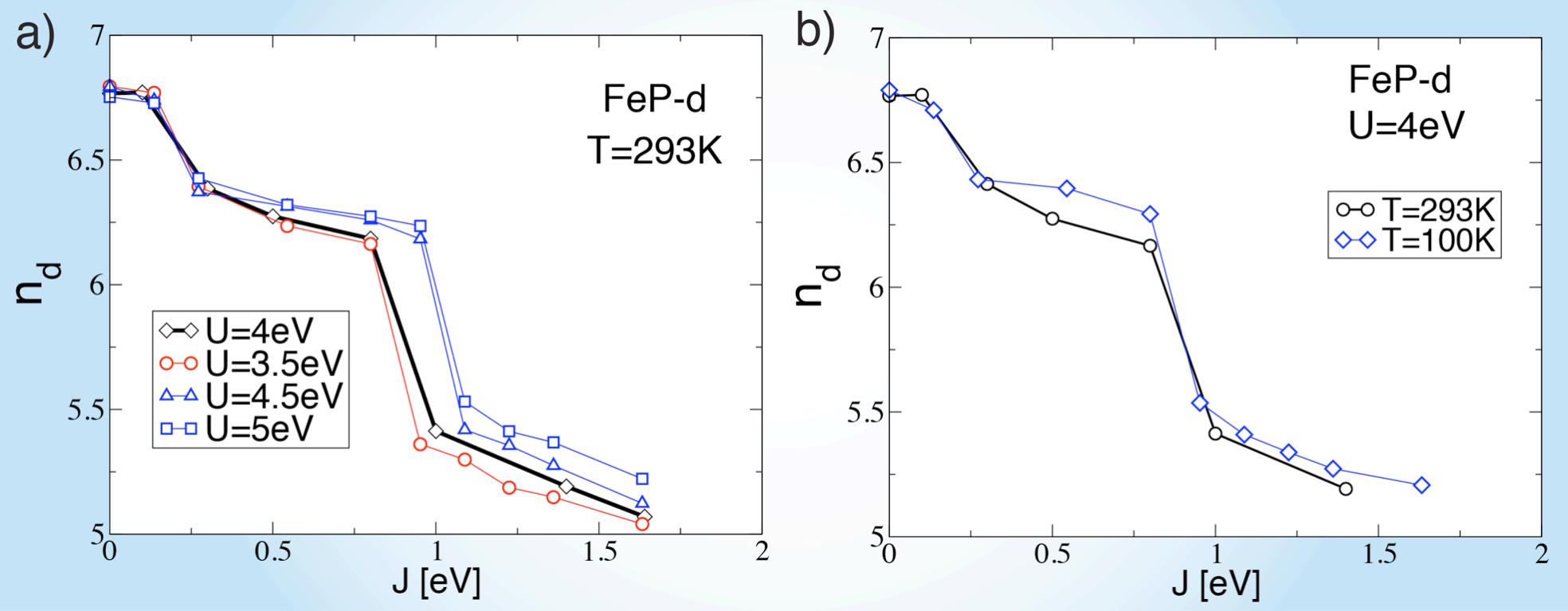
TABLE I: Average occupations n_d^α of the iron d orbitals for FeP, FeP(CO) and $FeP(O_2)$, for J=0 and J=0.8.

Optics : J dependence



double peak structure (present in experiments) in oxy-heme emerges as J increases

U and temperature variations

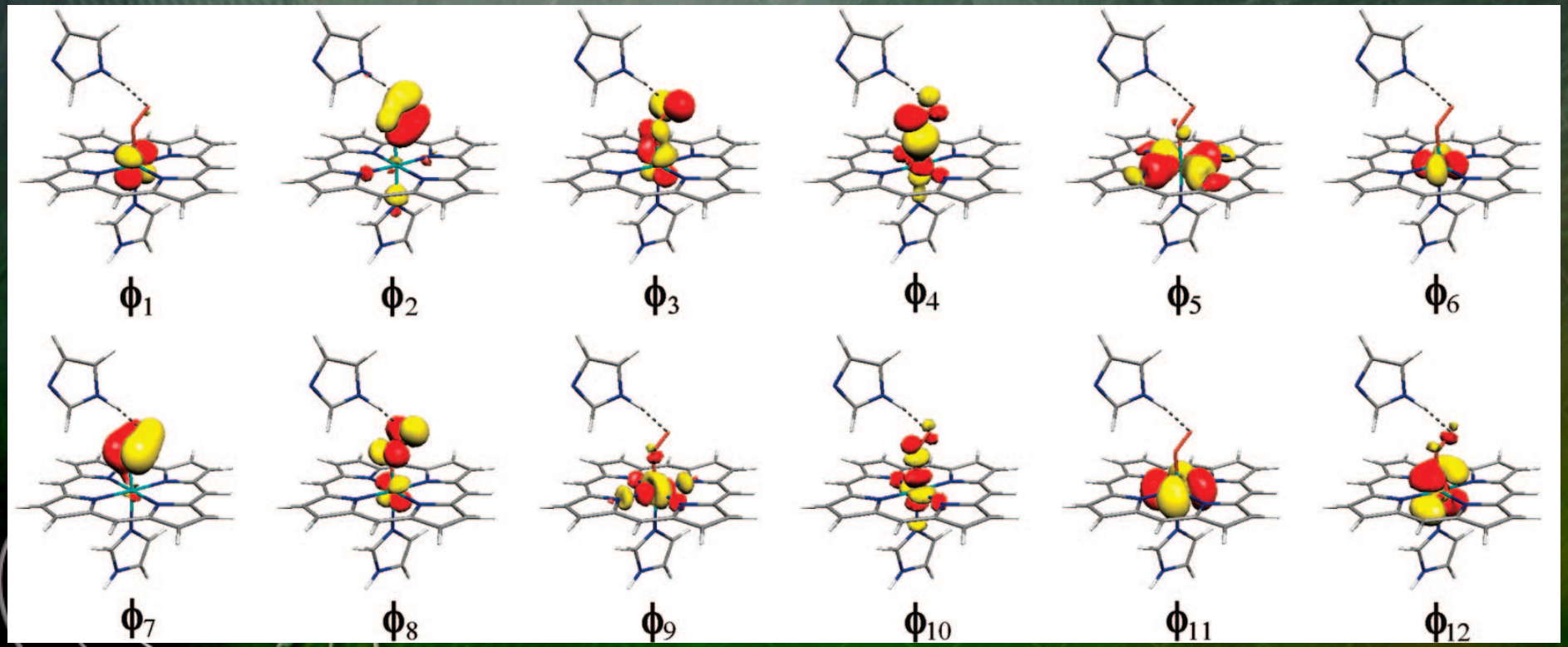


Weak U and temperature dependence

Weak variation of the charge with U for J=0

Quantum Chemistry Approaches

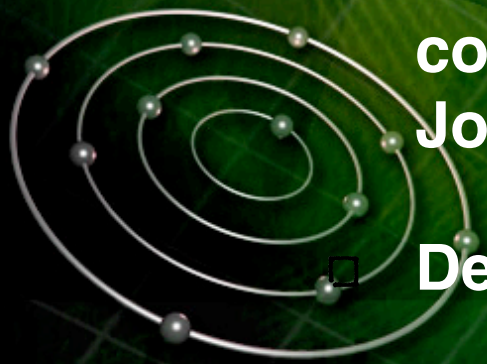
- Important to choose carefully orbitals
- Example : set of active orbitals for heme :



- JACS, 130, 14778 ' 08

Convergence of DMFT and CI

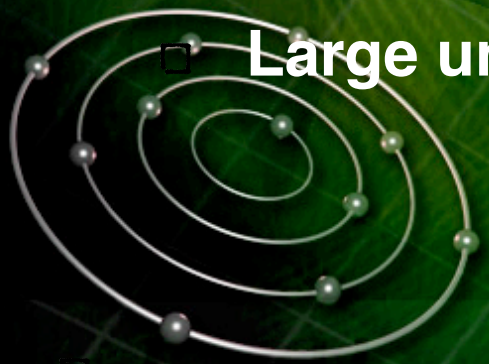
- Hartree Fock type approaches used as solver for DMFT
- "Dynamical mean-field theory from a quantum chemical perspective
- D. Zgid and G. Chan J. Chem. Phys., 134, 094115 (2011)
- Quantum Monte Carlo to sample CI configurations, see e.g. Booth GH, Chan GKL, Journal of Chemical Physics, 138, 029901 (2013)
- Decoupling of correlated atom from system



DFT+DMFT

- Extensive set DFT+DMFT packages in the plane wave basis
  - Wien2K+DMFT (K.Haule)
  - Wien2K+TRIQS (M. Aichhorn, M.Ferrero, O. Parcollet)
  - DFT+DMFT in LMTO basis (A.I. Lichtenstein)
  - DFT+DMFT in Abinit (B. Amadon) ... and others ...

- Γ=0 approach, requirements :
  - DMFT in localized basis set
  - Real space approach
  - Large unit-cells
    - The catch (problematic to some extent ...) :
      - non-orthogonal basis set



DMFT solver

Finite temperature Lanczos solver

AIM defined by a set of local basis of atomic orbitals (c operator) connected to a bath (a operator) :

$$H_{imp} = \sum_{\sigma=\uparrow\downarrow,ij=1}^{m} \epsilon_{ij\sigma}(a^{\dagger}_{i\sigma}a_{j\sigma} + h.c.)$$
$$+ \sum_{\sigma=\uparrow\downarrow,i=1}^{m} V_{i\sigma}(a^{\dagger}_{i\sigma}c_{\sigma} + h.c.) + U\hat{n}_{\uparrow}\hat{n}_{\downarrow} - \mu\hat{n}$$

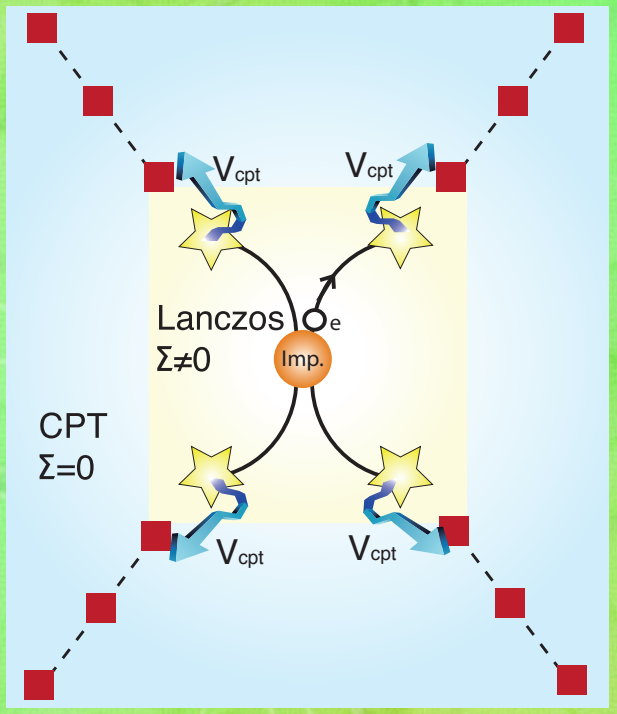
This hamiltonian yield the hybridization function:

$$\mathbf{\Delta}^{\mathrm{ED}}(i\omega_n) = \mathbf{V}^{\dagger}\left(i\omega_n - \epsilon\right)^{-1}\mathbf{V}$$

We enforce that Himp reproduces the DMFT hybridization:

$$d = \sum_{\omega<\omega_0} \frac{\left|\Delta^{\mathrm{ED}}(i\omega_n) - \Delta(i\omega_n)\right|^2}{\omega_n}$$

Hybrid Lanczos solver



cluster perturbation theory (CPT) :

$$\lambda\left(\sum_i |V^i_{CPT}|^2\right)$$

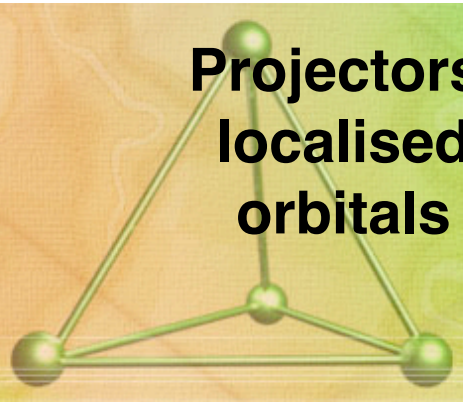
$$\mathbf{G}^{CPT}(i\omega_n) = \frac{1}{\mathbf{G}^{V_0}(i\omega_n)^{-1} - \mathbf{V_{CPT}}}$$

Molecular dynamical mean-fiel theory

Lattice Dyson equation: $$G_{i\sigma l;j\sigma' m}(\omega) = G^{0}_{i\sigma l;j\sigma' m}(\omega) + \left[G^{(0)}(\omega)\Sigma(\omega)G(\omega)\right]_{i\sigma l;j\sigma' m}$$

GF Matrix reprensentation:

$$\hat{G}^{-1}(\omega) = \begin{pmatrix} \omega+\mu-\Sigma_1(\omega) & t_{12} & t_{13} & \dots & t_{1N} \\ t_{21} & \omega+\mu-\Sigma_2(\omega) & t_{23} & \dots & t_{2N} \\ t_{31} & t_{32} & \omega+\mu-\Sigma_3(\omega) & \dots & t_{3N} \\ \dots & \dots & \dots & \dots & \dots \\ t_{N1} & t_{N2} & t_{N3} & \dots & \omega+\mu-\Sigma_N(\omega) \end{pmatrix}$$



Projectors, localised orbitals

Local projected Green's function:

$$G^{-1}_{ii}(\omega) = \mathcal{G}^{-1}_{ii}(\omega) - \Sigma_i(\omega)$$

DMFT solver

D. Zgid & G. Chan, J.Chem.Phys 134, 094115 ' 11

DMFT density kernel

Green's function written in the basis of a set of NGWFs :

$$G^{\alpha\beta}\left(i\omega_n\right) = \left(\left(i\omega_n + \mu\right)S_{\alpha\beta} - H_{\alpha\beta} - \Sigma_{\alpha\beta}\right)^{-1}$$

DMFT - **projection** on a set of atomic wave-function {φ}:

$$W_{m\alpha}^{(I)} = \langle \varphi_m^{(I)} | \phi_\alpha \rangle \qquad V_{\alpha m}^{(I)} = \langle \phi_\alpha | \varphi_m^{(I)} \rangle$$

Projected Green's function:

$$\tilde{G}_{0mm'}\left(i\omega_n\right) = W_{m\alpha} G^{\alpha\beta}\left(i\omega_n\right) V_{\beta m'}$$

Projected Self energy:

$$\tilde{\Sigma}_{mm'}\left(i\omega_n\right) = W_{m\alpha} \Sigma^{\alpha\beta}\left(i\omega_n\right) V_{\beta m'}$$

Anderson Impurity Model

DMFT AIM local problem Hybridization of the AIM is given by:

$$\mathbf{\Delta}(i\omega_n) = (i\omega_n + \mu)\,\tilde{\mathbf{O}} - \tilde{\mathbf{\Sigma}} - \mathbf{E^{imp}} - \tilde{\mathbf{G}}^{-1}$$

with :

$$\tilde{\mathbf{O}} = \left(\mathbf{W}\mathbf{S}^{-1}\mathbf{V}\right)^{-1} \qquad E^{imp} = \tilde{\mathbf{O}}\mathbf{W}\left(\mathbf{S}^{-1}\mathbf{H}\mathbf{S}^{-1}\right)\mathbf{V}\tilde{\mathbf{O}}$$

Obtain the self-energy from the local problem, and upfold back to NGWF space. How can we upfold ? It should be the inverse operation :

$$\tilde{\Sigma}(\omega = \infty) = \tilde{\mathbf{O}}\mathbf{W}\left(\mathbf{S}^{-1}\Sigma_{upfolded}(\omega = \infty)\mathbf{S}^{-1}\right)\mathbf{V}\tilde{\mathbf{O}}$$

$$\mathbf{\Sigma}_{upfolded} = \mathbf{V}\tilde{\mathbf{\Sigma}}\mathbf{W}$$

$$\left(\tilde{\mathbf{o}}\mathbf{W}\mathbf{S}^{-1}\right)\mathbf{V} = 1$$

$$\mathbf{W}\left(\mathbf{S}^{-1}\mathbf{V}\tilde{\mathbf{o}}\right) = 1$$

Causal ! But this simplication is only for Γ=0 ! The k dependence of the overlap matrix complicates everyting.