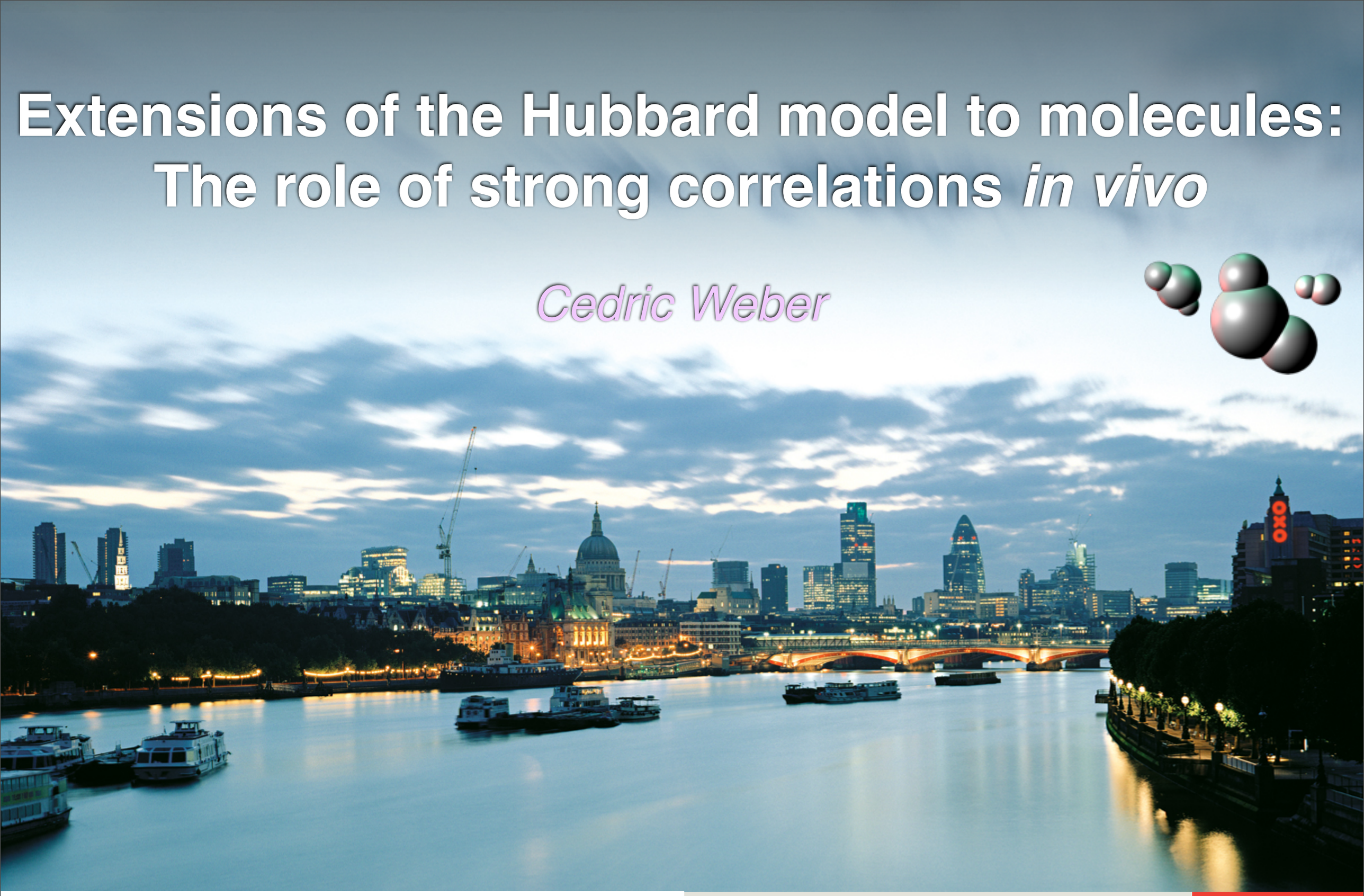
Extensions of the Hubbard model to molecules: The role of strong correlations *in vivo*

Cedric Weber



Condensed Matter Physics in the City 2013

Hubbard Theory Consortium

School of natural science
Department of Physics

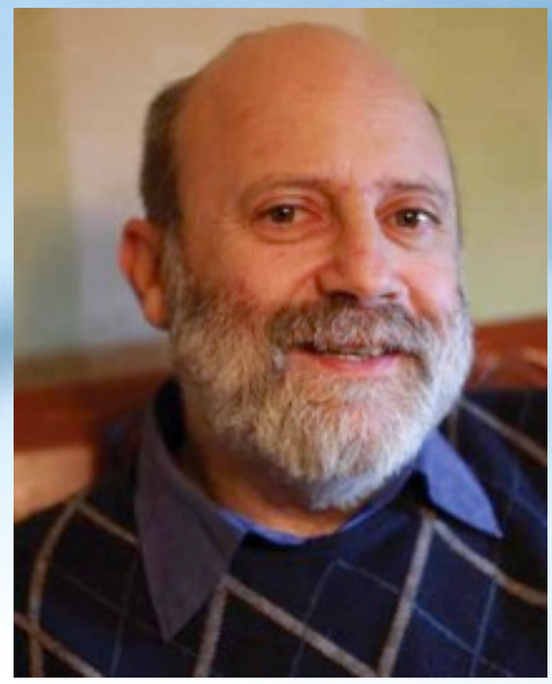
KING'S College LONDON

Peter B. Littlewood

Argonne NATIONAL LABORATORY

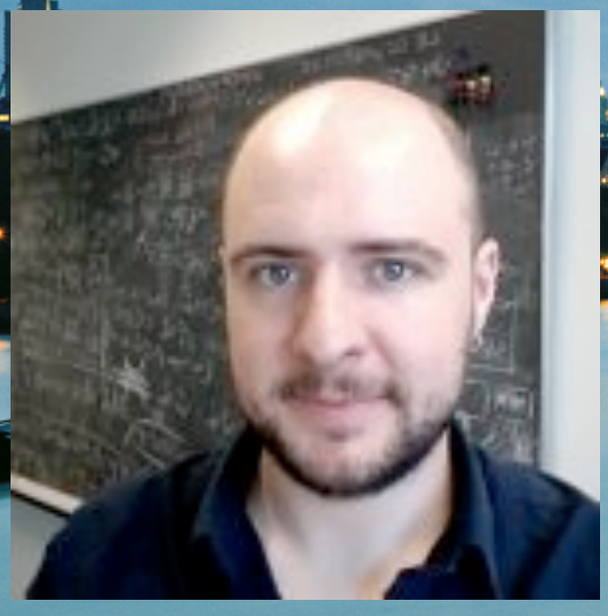
Mike C. Payne

UNIVERSITY OF CAMBRIDGE



Gabriel Kotliar

RUTGERS THE STATE UNIVERSITY OF NEW JERSEY

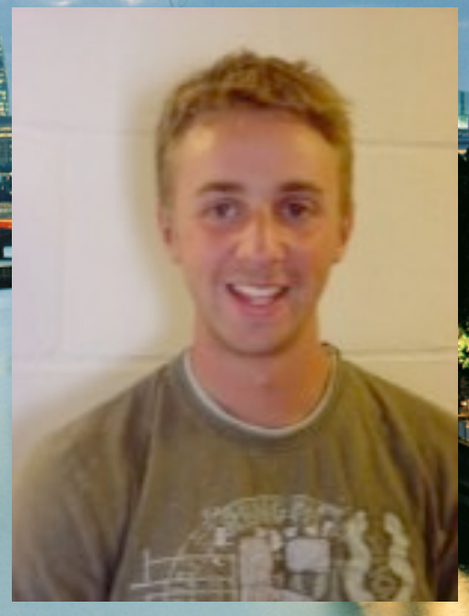


David D. O'Regan

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Nicholas D. M. Hine

UNIVERSITY OF CAMBRIDGE

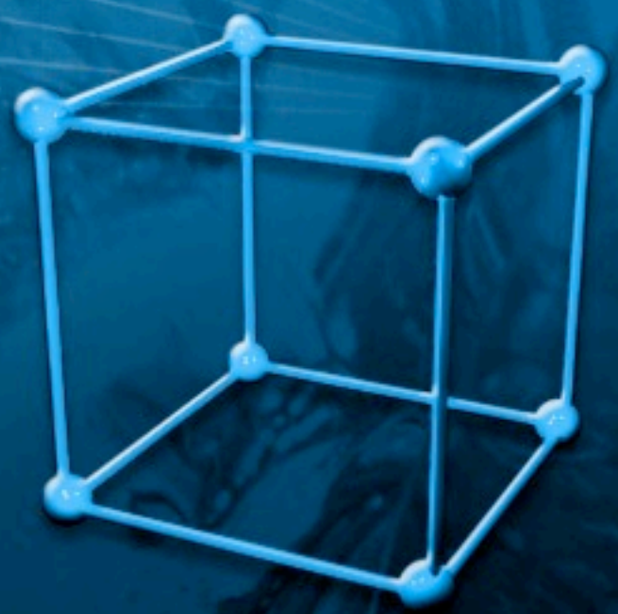


Daniel Cole

YALE

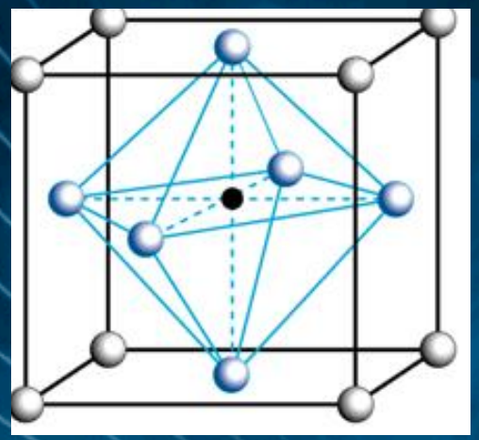
Outlines

- Introduction: strongly correlated systems
- Hubbard : the "*theory of everything*", model Hamiltonians
- Dynamical mean-field theory
- Moving from solids to molecules
- A DFT+DMFT toolbox to study molecules and nano-structures
- Application to haemoglobin
- Conclusion, outlooks

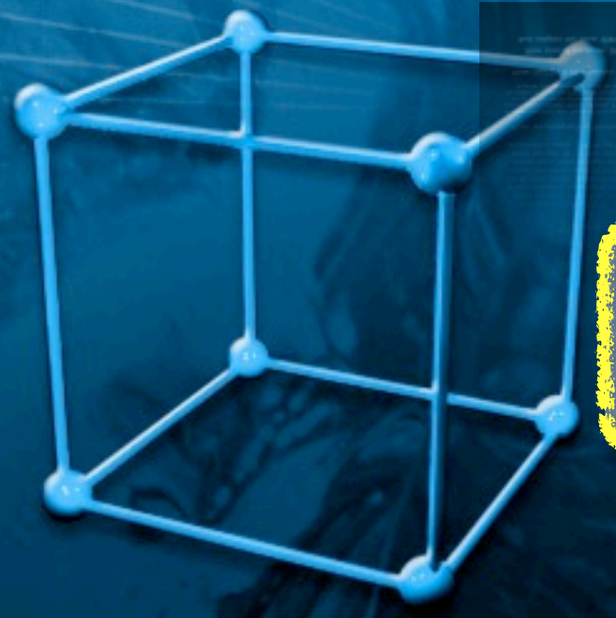


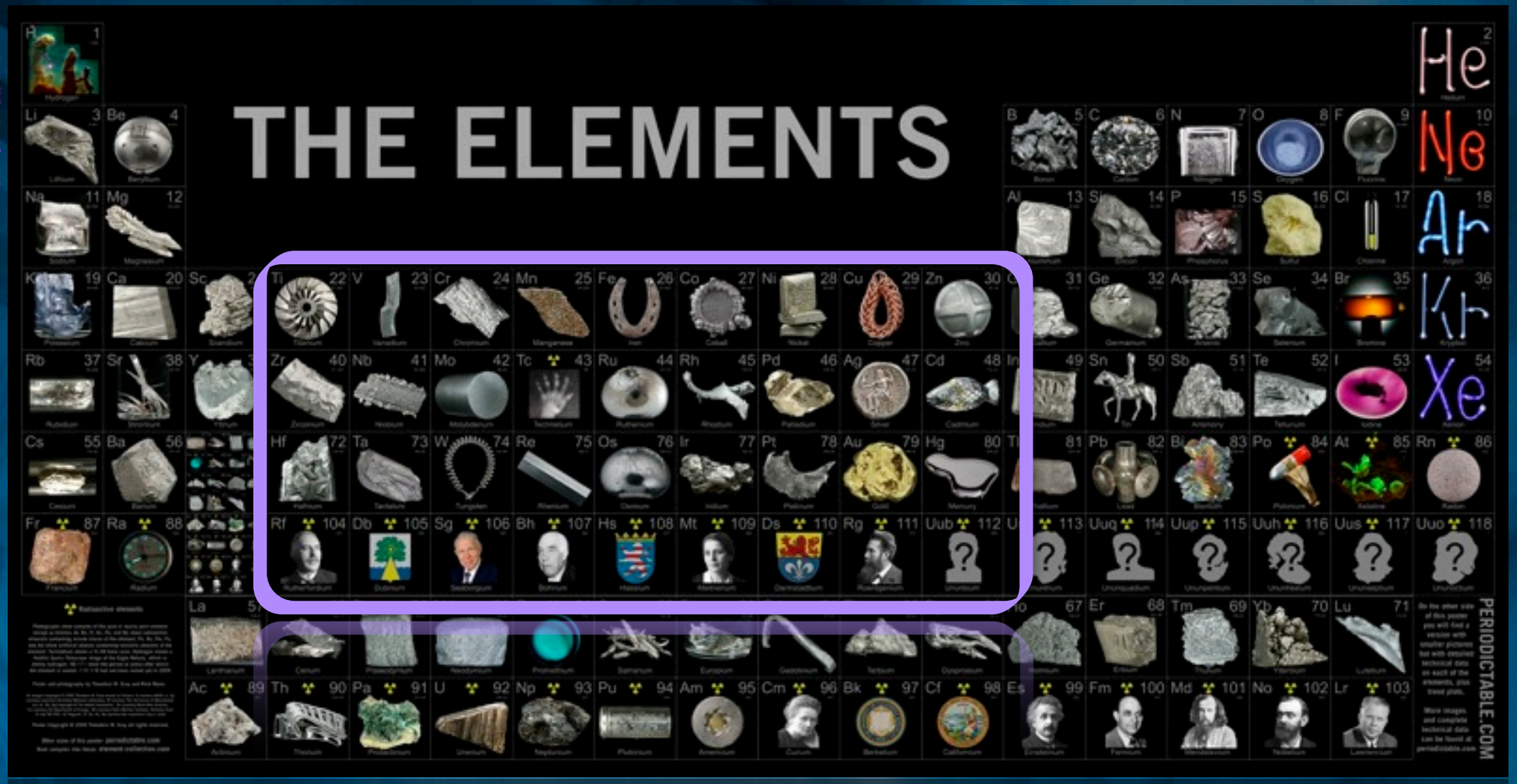
Strongly correlated systems

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)

Hubbard model : the theory of everything

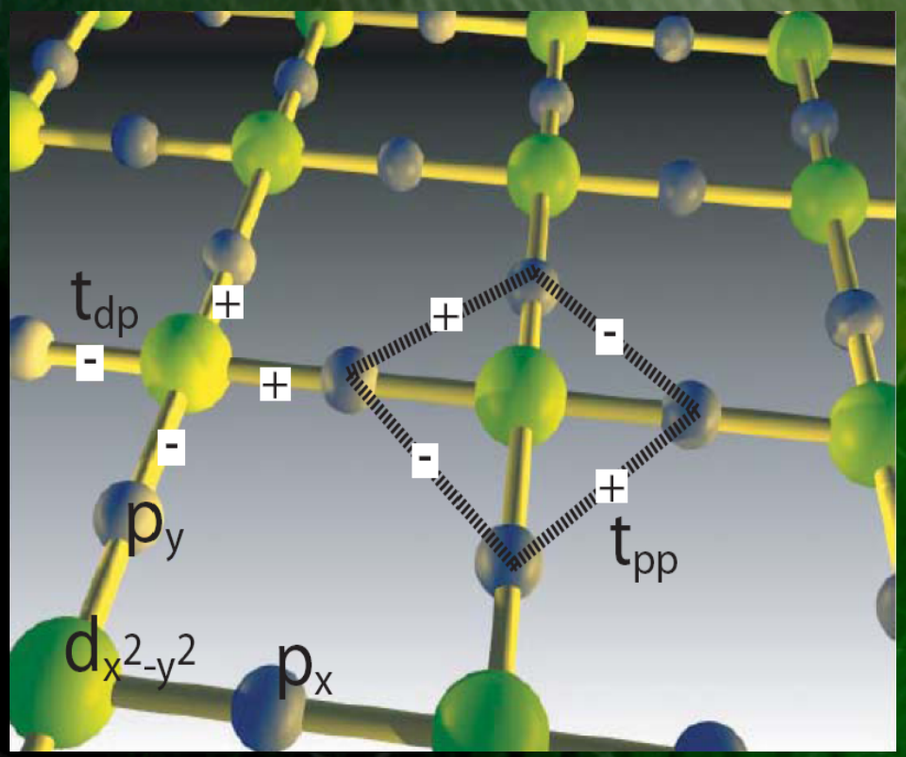
$$H_{Hubbard} = -t \sum_{\langle i,j \rangle,\sigma} \left(c^{\dagger}_{i\sigma} c_{j\sigma} + h.c. \right) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

- One band crossing the Fermi level, geometry of the lattice taken into account by the bandwidth "t" and the connectivity matrix <i,j>. Hilbert space 4^N, simple theory, but hard to solve.
- **Metal to insulator transition** (MIT) at integer filling:

U<<1: paramagnetic Metal U>>1 : Mott insulator

- T=0, Brinkman-Rice QCP (Uc_2), simple argument (**PRB** 2, 4302 '70) and confirmed by single site DMFT (G. Kotliar, **EPB** 11,27'99)

For <u>oxides</u>, a simple generalization is obtained with a three-band model Hamiltonian



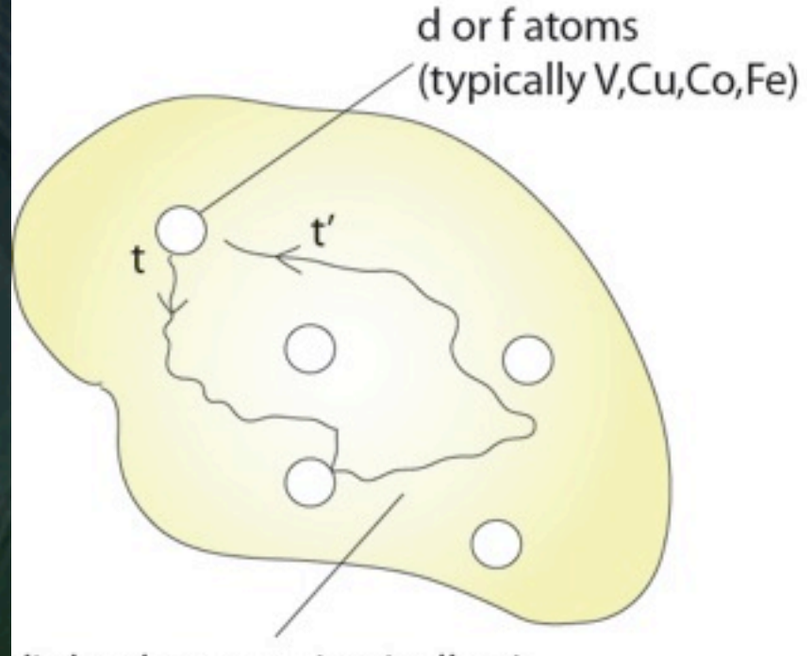
$$H_t = \sum_{\langle i,j \rangle} \left(t_{ij} d^{\dagger}_i p_j + hc \right) + \sum_{\langle i,j \rangle} \left(t_{ij} p^{\dagger}_i p_j + hc \right) + \sum_i \epsilon_p p^{\dagger}_i p_i + \sum_i \epsilon_d d^{\dagger}_i d_i$$

$$H_{cor} = U_d \sum_i n_{i\uparrow} n_{i\downarrow}$$

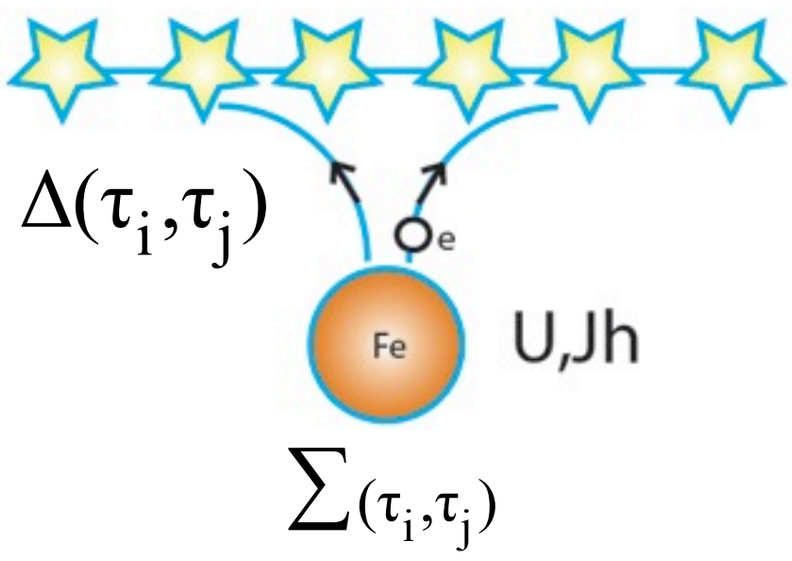
Electronic correlation due to both charge transfer energy and local U repulsion, **Zanen-Sawatzky-Allen** milestone (ZSA) paper (*PRL* 55, 418 ' 85).

charge transfer insulator : $U \rightarrow \varepsilon_d - \varepsilon_P$

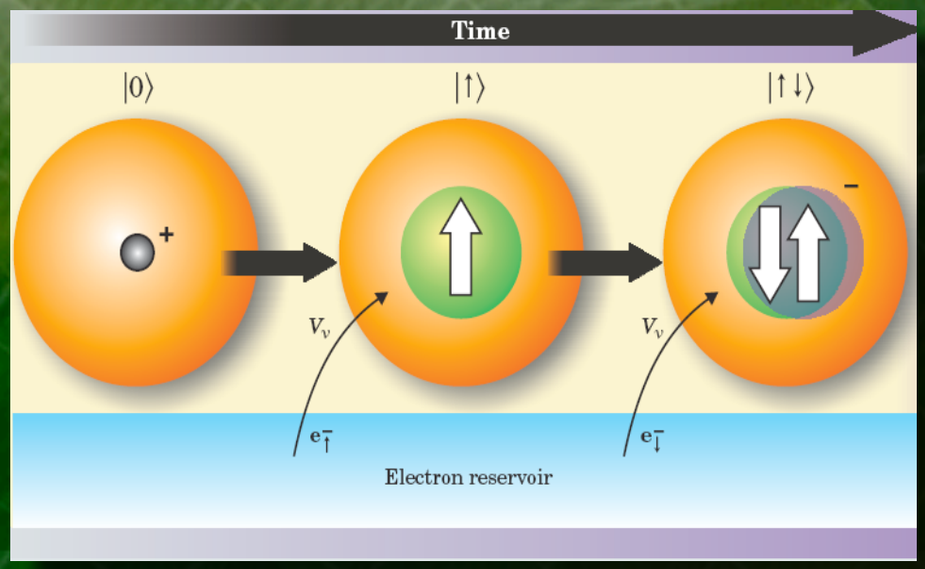
Dynamical mean-field theory



lattice Green's function : G(r,r',t,t')



Impurity Green's function : G(t,t')



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)

DMFT : a success story

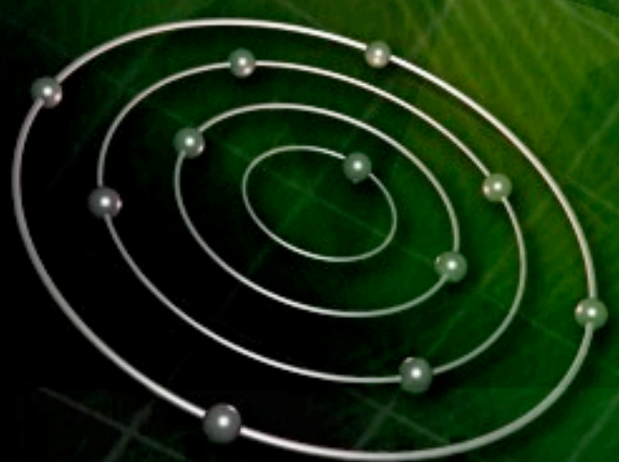
Captures the transition from localised quantum states to delocalized band electrons

Bridges many body theory with density functional theory in a consistent way (DFT-DMFT)

Quantum concepts such as entanglement, quantum supersition, valence fluctuations, are captured within this theory

- Mott transition
  - Sordi et al, PRL 104, 226402 ’ 10
- High T-c superconductors
  - E. Gull et al, arXiv 1304.6406
- Chalcogenides
  - Z. Pin et al, PRB 86, 195141
- Plutonium
  - Savrasov et al, Nature 410, 793, ‘ 01
- Cold atoms
  - L. De Leo et al, PRL 101, 210403 ’08
- Vanadates
  - Biermann et al, PRL 94, 26404, ‘ 05
- Nano contacts
  - D. Jacob et al, PRL 103,16803 ‘ 09

1BZ

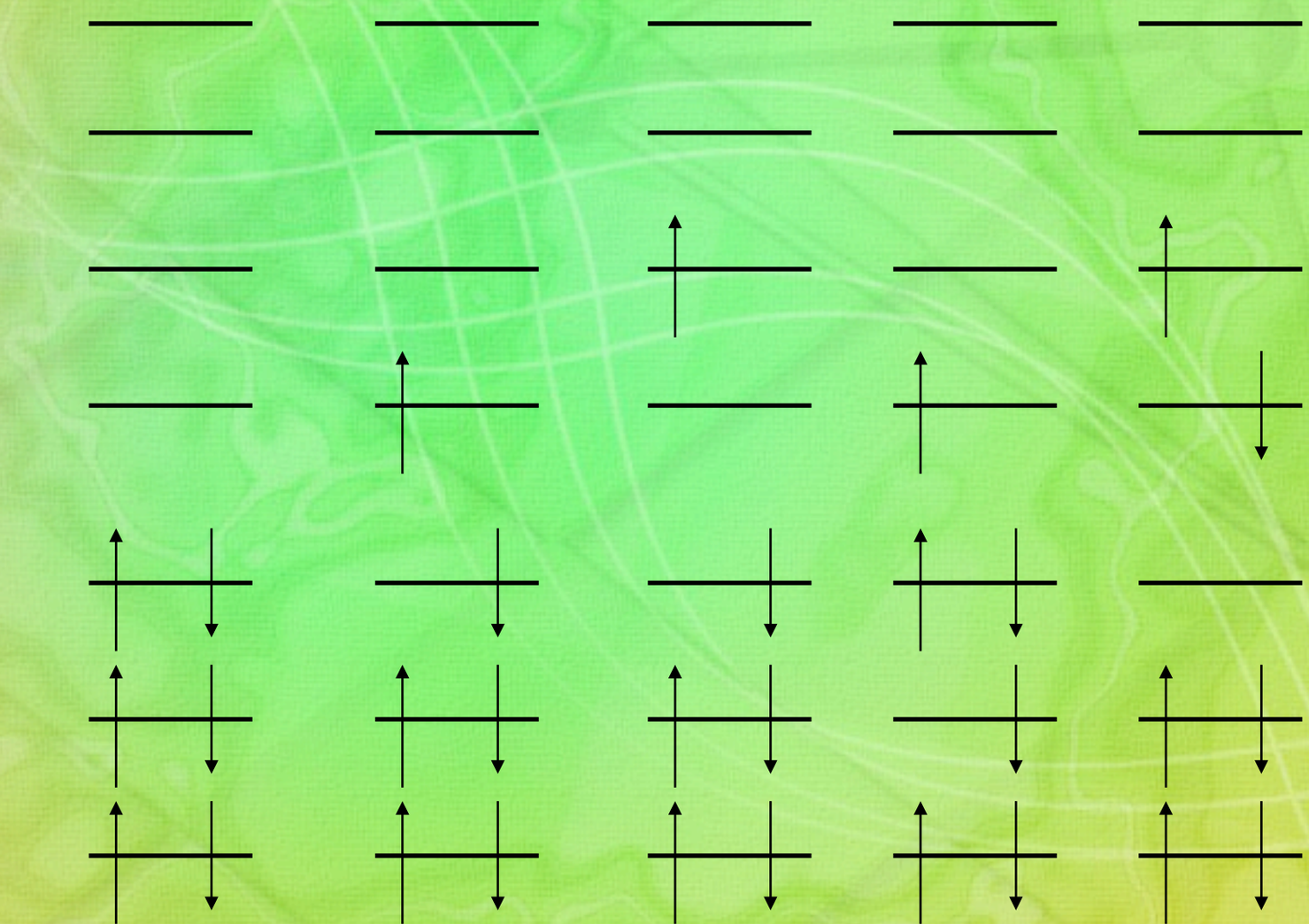


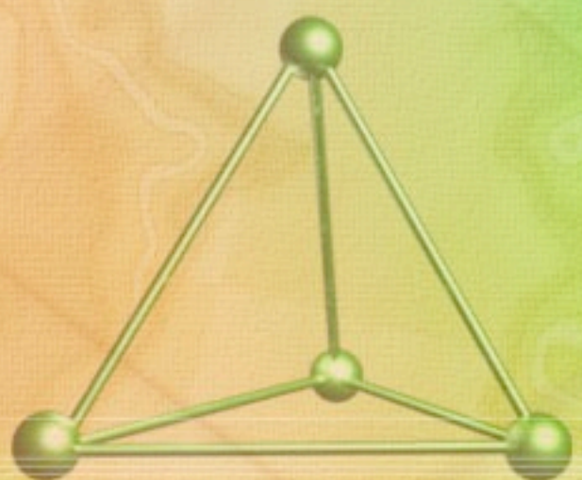
$\Gamma = 0$

Quantum Chemistry Approaches

- **Configuration Interaction (CI) - expand the wave-funciton in terms of Slater determinants :**

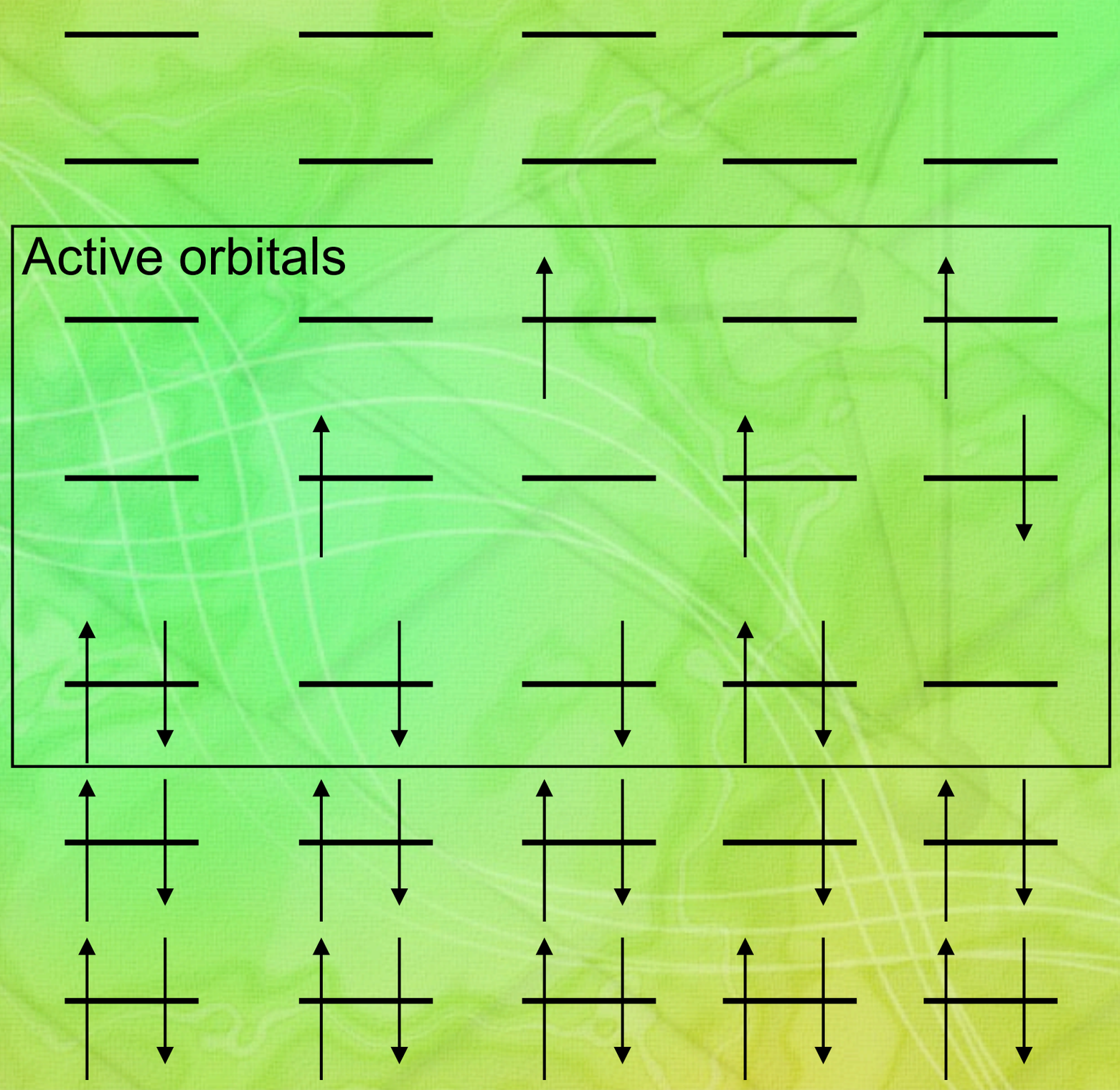
$$\Psi_{CI} = \sum_{m=1}^{N^{CSF}} c_m \Psi_m$$





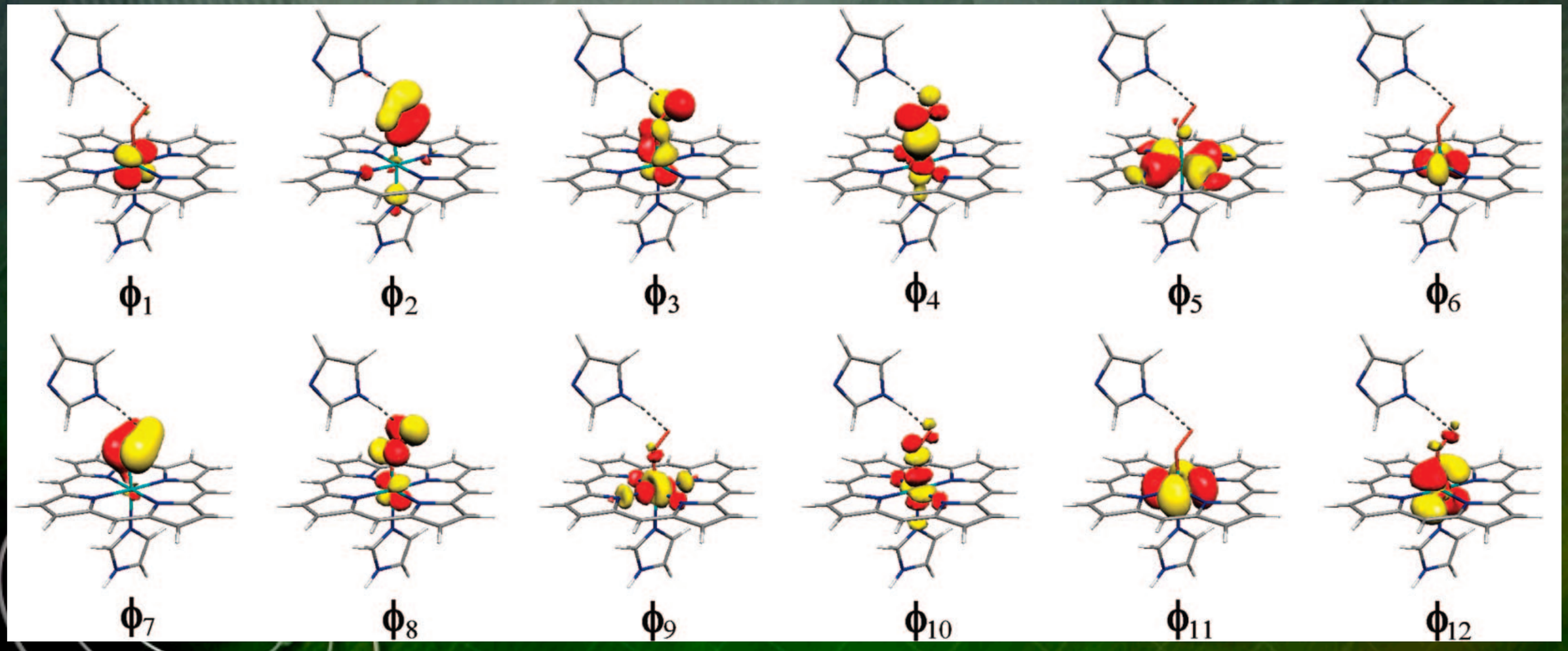
Quantum Chemistry Approaches

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



Quantum Chemistry Approaches

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



- JACS, 130, 14778 ’ 08

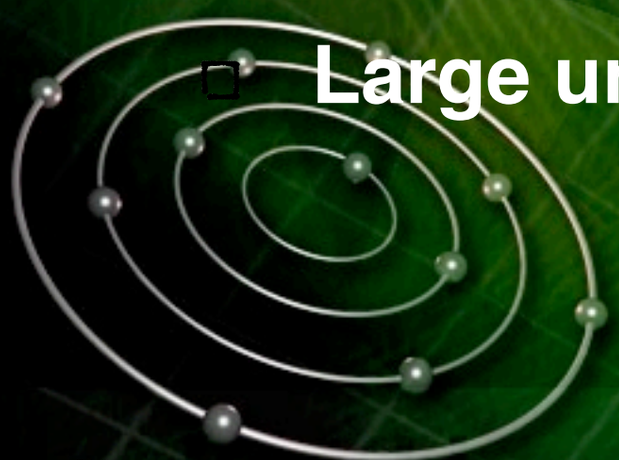
Convergence of DMFT and CI

- 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

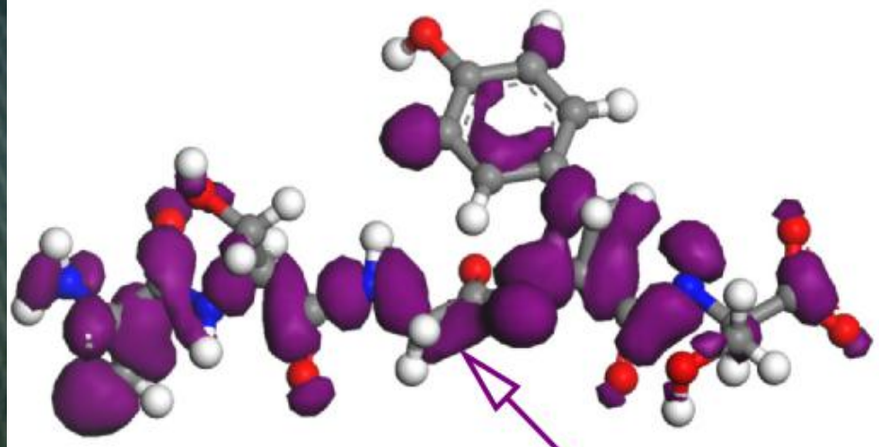


Can DMFT improve CI or DFT approaches to molecules?

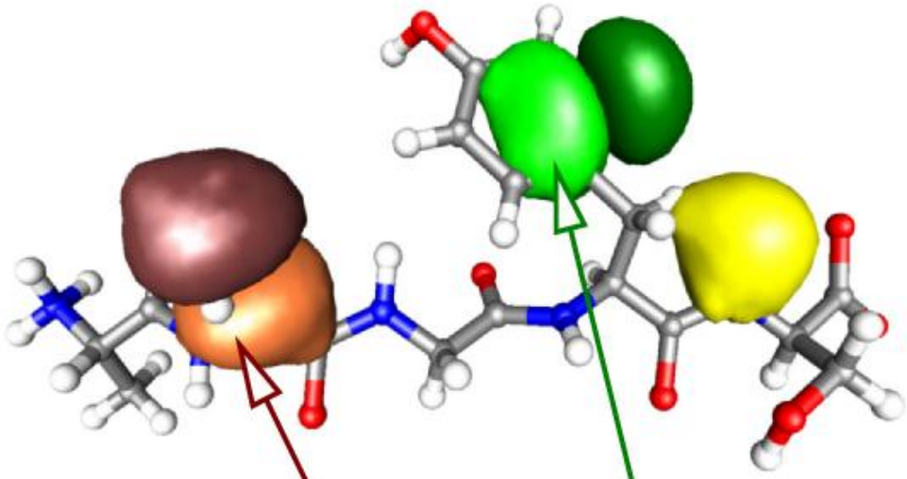
- DMFT treats all impurity-bath excited configurations
- Quantum entanglement: multi-determinantal effects contained in the theory
- Fluctuating magnetic moment, rather than symmetry broken states
- valence fluctuations
- Finite temperature properties (most experiments done on liquid phases)
- Self-consistent DMFT : corrects back the DFT
- Catch : hard to implement, expensive numerically, impurity solver on real axis

ONETEP : Linear scaling density matrix DFT

Molecular orbitals (MOs)



Non-orthogonal Generalised Wannier Functions (NGWFs)



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

- Optimise the NGWFs, the non-orthogonal localised functions {Φ}
- instead of orthogonal extended wave-functions {ψ}
- With the same accuracy as plane-wave methods (J.Chem. Phys 119, 8842 ’03)
- Linear scaling (truncation of the density kernel)

DMFT in the NGWFs basis set

Lattice 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}:

$$W^{(I)}_{m\alpha} = \langle \varphi^{(I)}_m | \phi_\alpha \rangle \qquad V^{(I)}_{\alpha m} = \langle \phi_\alpha | \varphi^{(I)}_m \rangle$$

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.

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:

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

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 solver

Finite temperature Lanczos solver

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

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

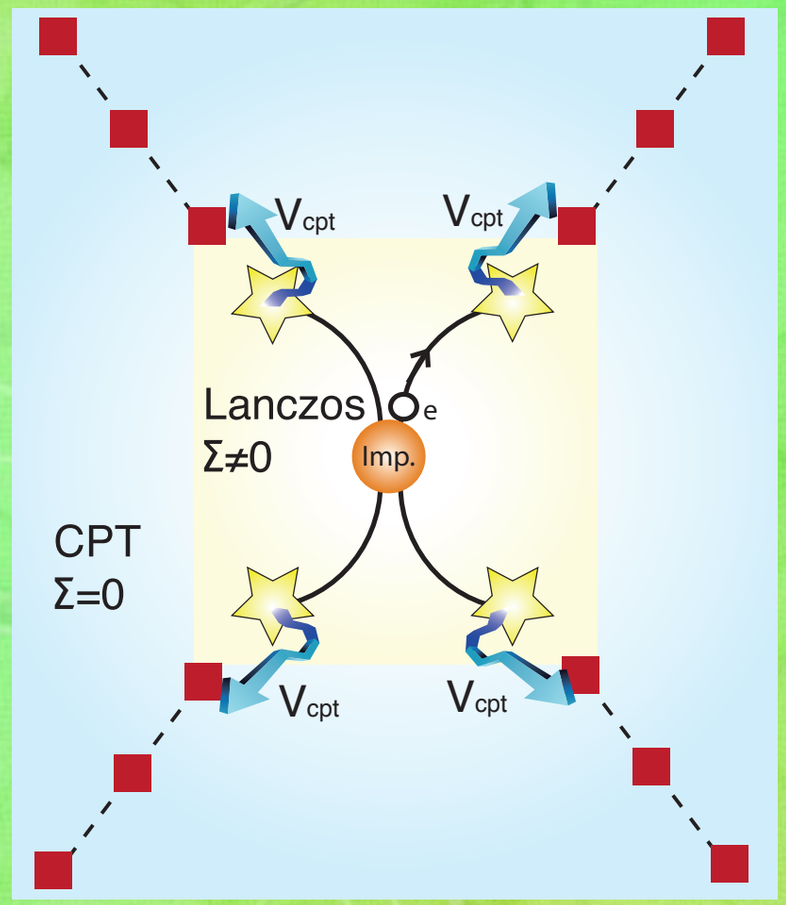
This hamiltonian yield the hybridization function:

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

We enforce that Himp reproduces the DMFT hybridization:

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

Hybrid Lanczos solver

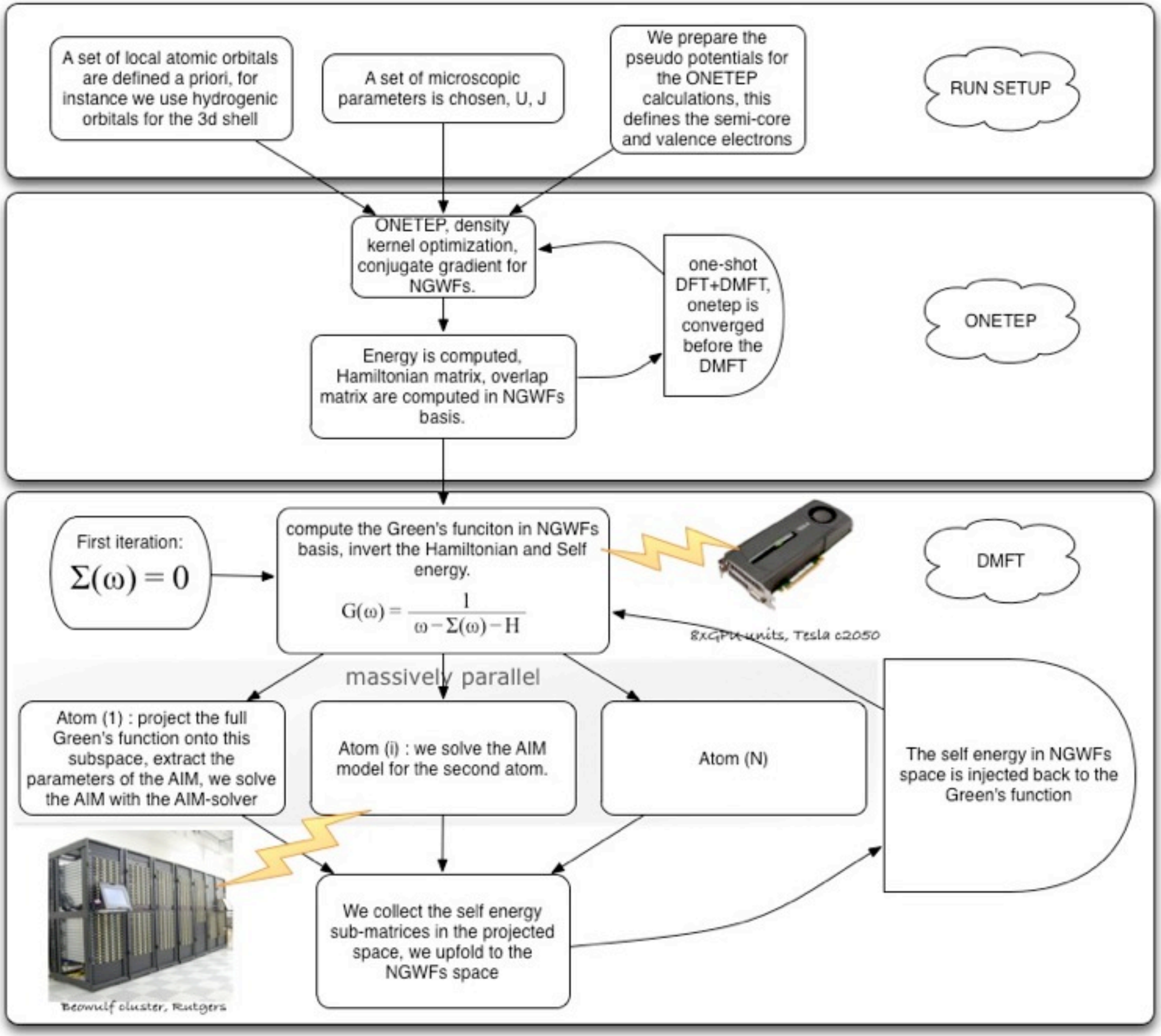


cluster perturbation theory (CPT) :

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

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

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.

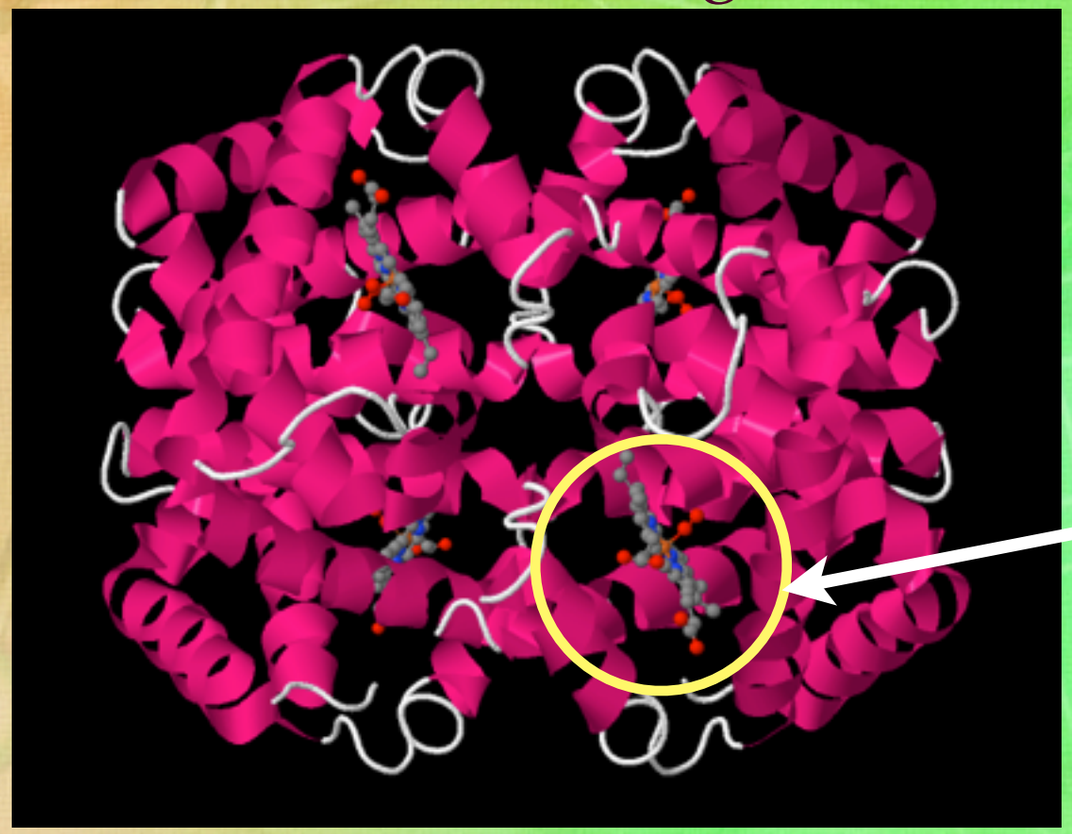
5) Solve the AIM local problems in parallel (MPI+OPENMP).

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

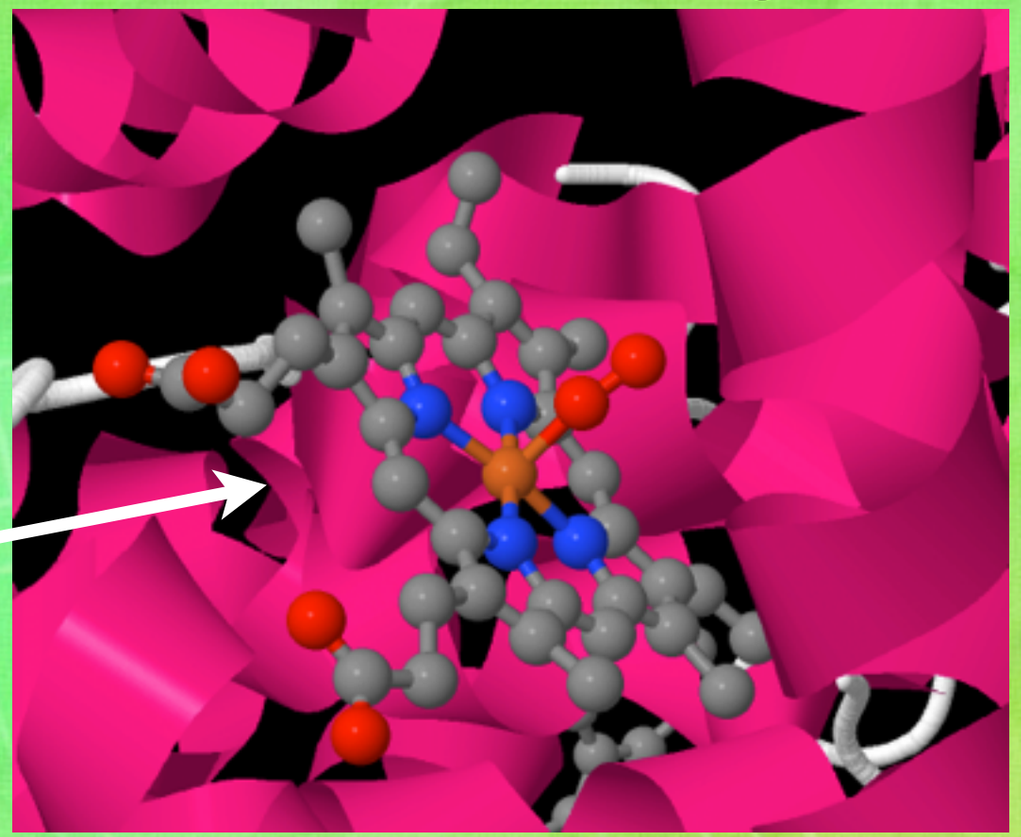
Ligand Binding : haemoglobin

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



(pictures obtained from PDB database)

With DMFT: i) capture the quantum and thermal fluctuations not present at the DFT level, ii) capture subtle multi-determinantal effects (entanglement)

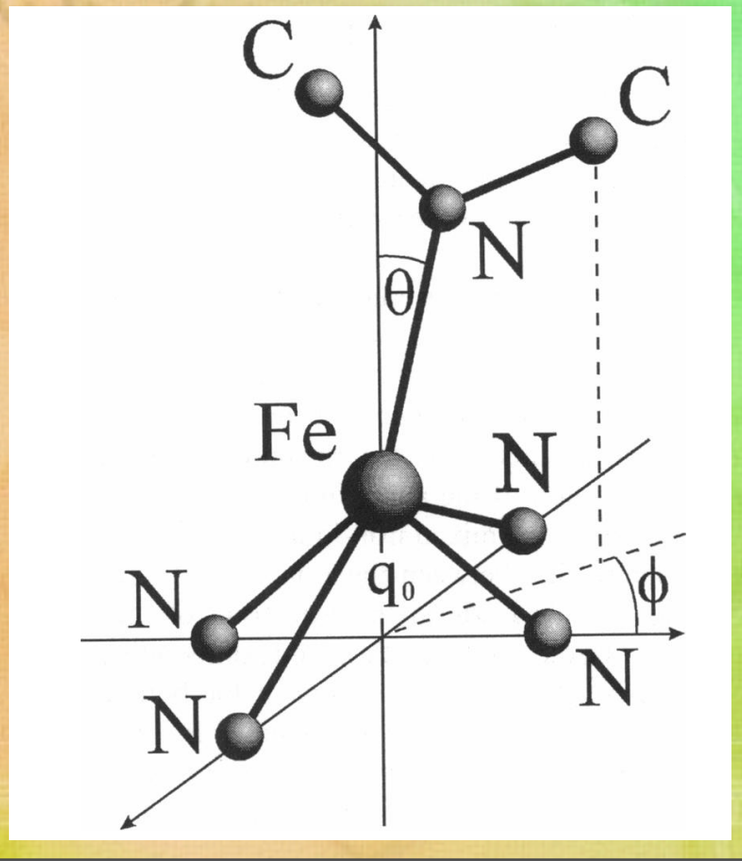
Earlier work, DFT+U calculations :
D. A. Scherlis, M. Cococcion, P. Sit, and N. Marzari. J. Phys. Chem. B, 111 '07.

Haemoglobin : common wisdom

Patent Pending

desoxy-haemoglobin is magnetic (and blue)
Depending on configuration : singlet, triplet, or open-shell singlet

oxy-haemoglobin is non-magnetic (and red)
Depending on configuration: triplet, quintet

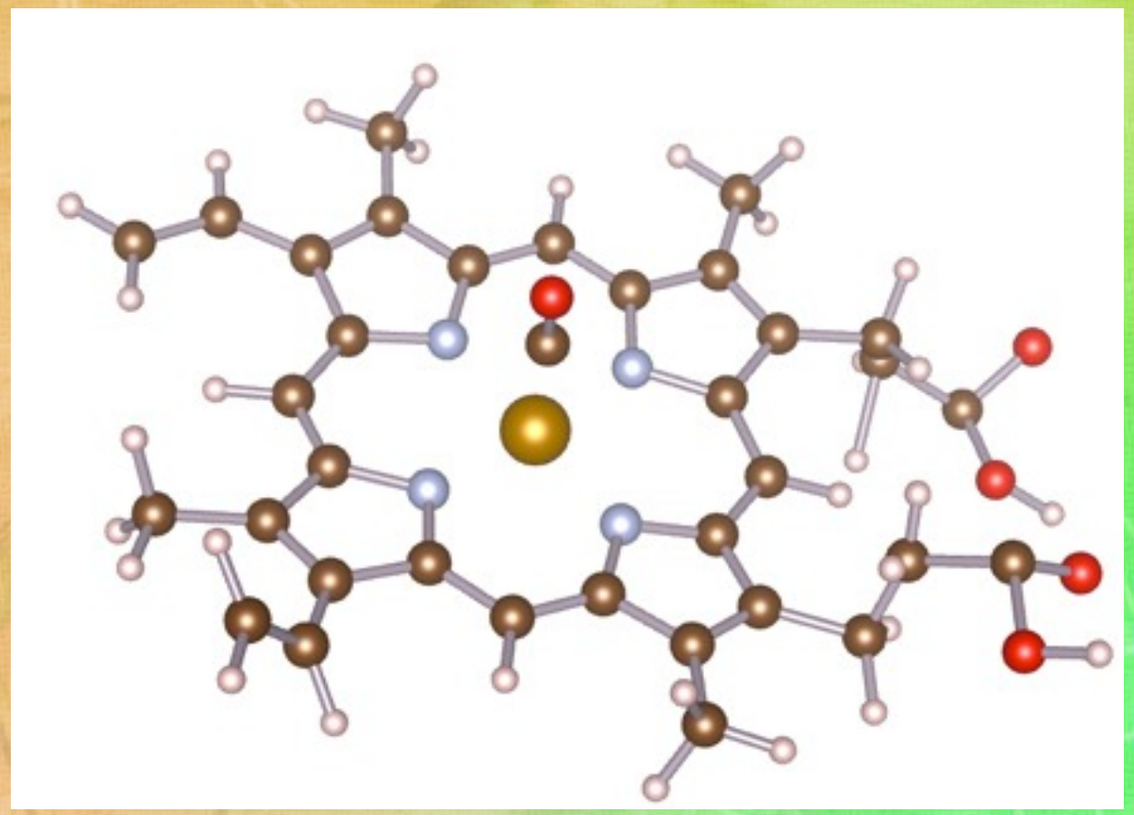


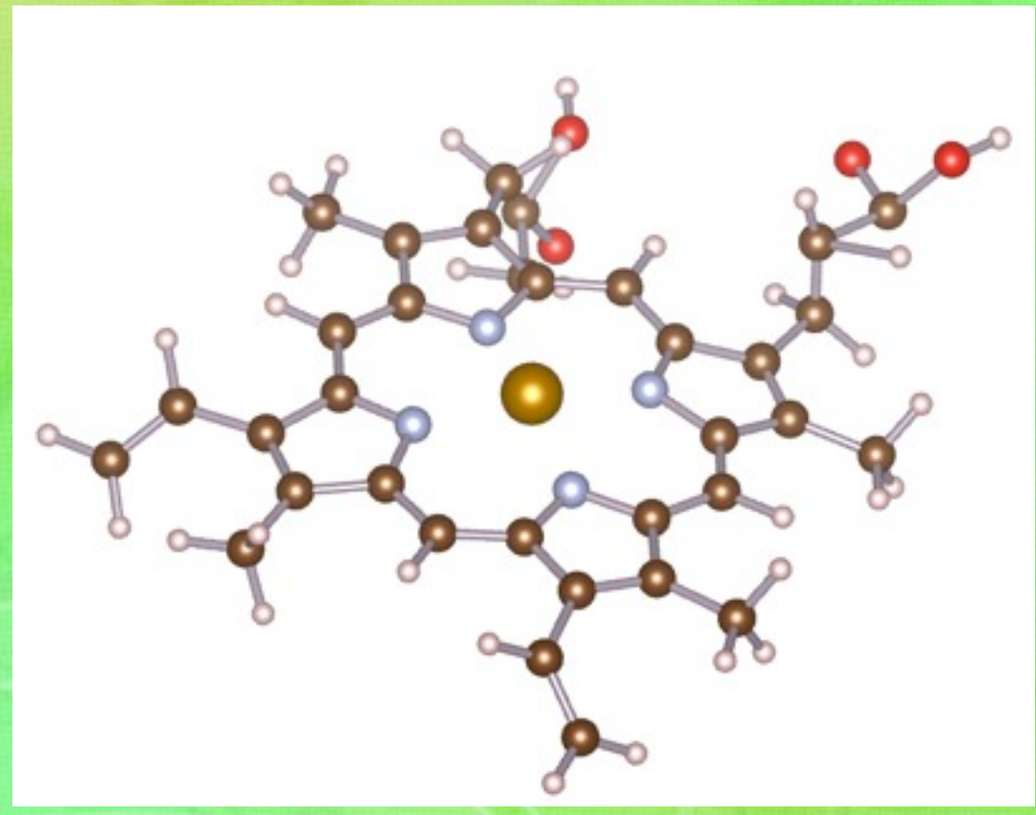
DFT calculations: energetics is affected by the conformation

problem: binding energy to CO is 1eV greater than to O_2. CO is toxic !
(Biophys. Journ. 65, 1942 ‘ 93)

Iron atom: J~0.8eV, U~4eV

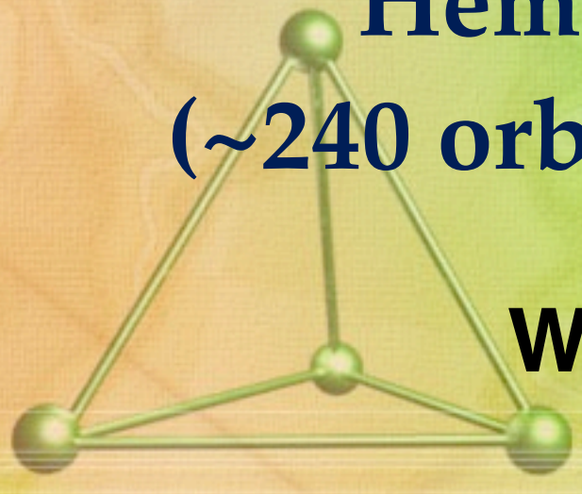
Heme topology





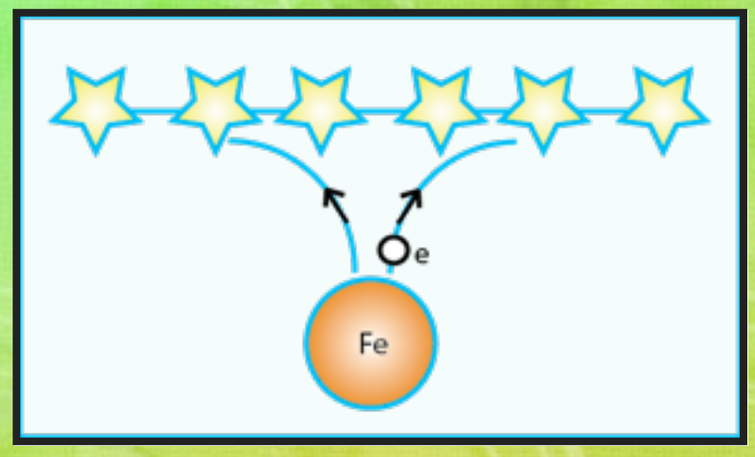
<u>oxy-Heme (FeP(O_2))</u> - planar shape
X-ray data (PDB database)

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



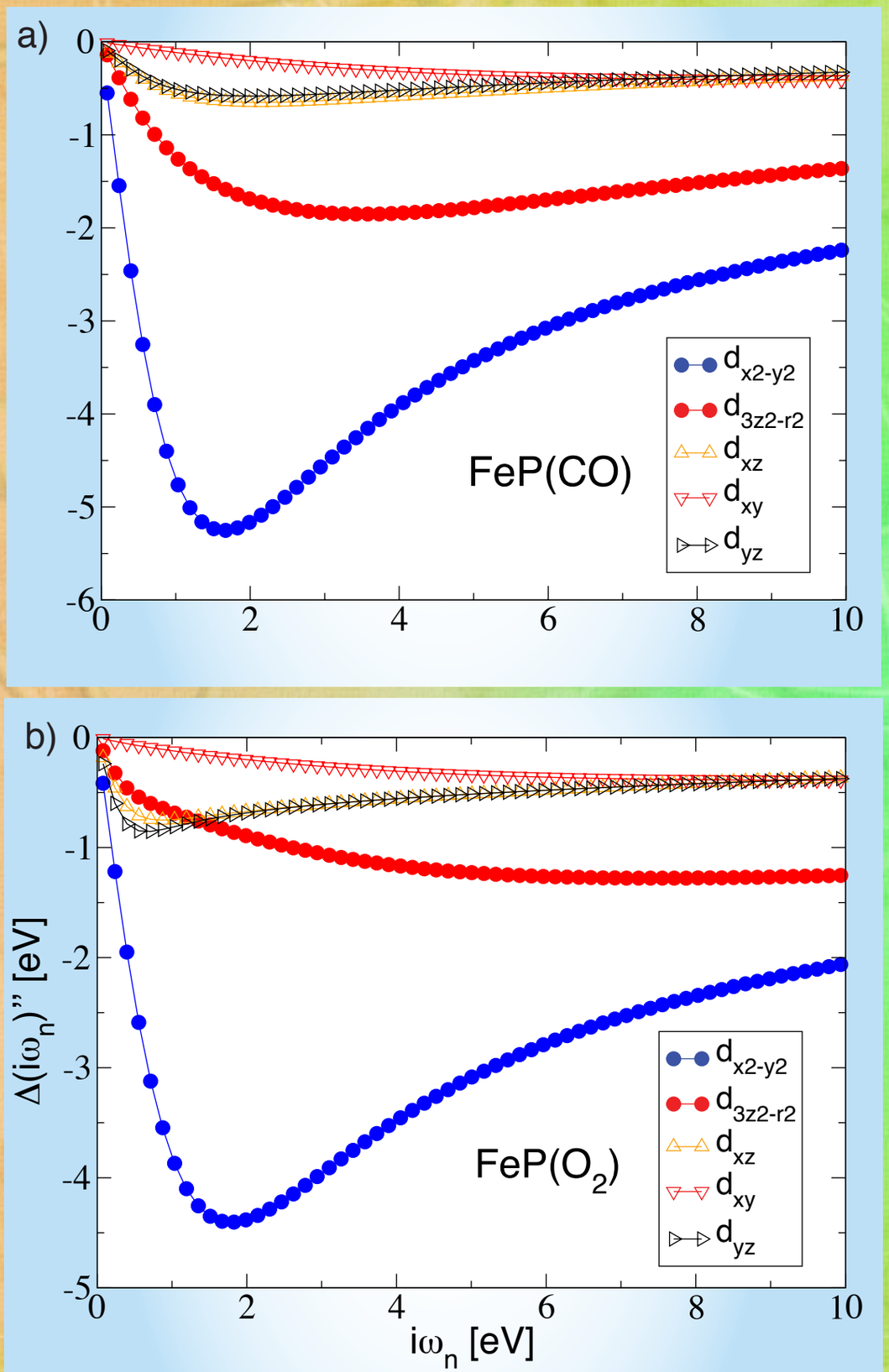
Heme
(~240 orbitals)

AIM
5d orbitals
+bath



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

HEME = AIM



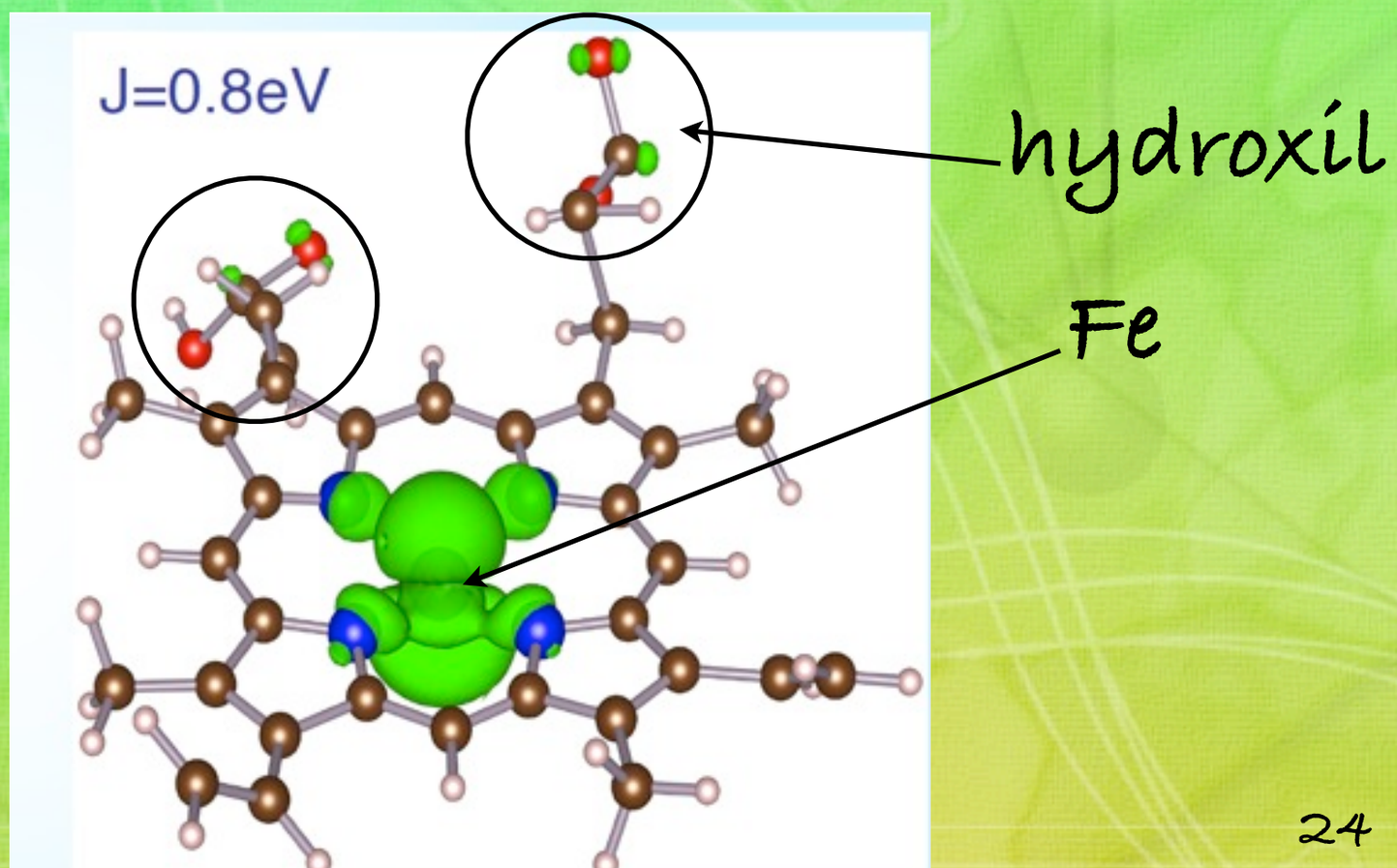
o) DMFT converge after 1 iteration, no mean-field here (1 correlated atom)

o) hybridization depends on the structure

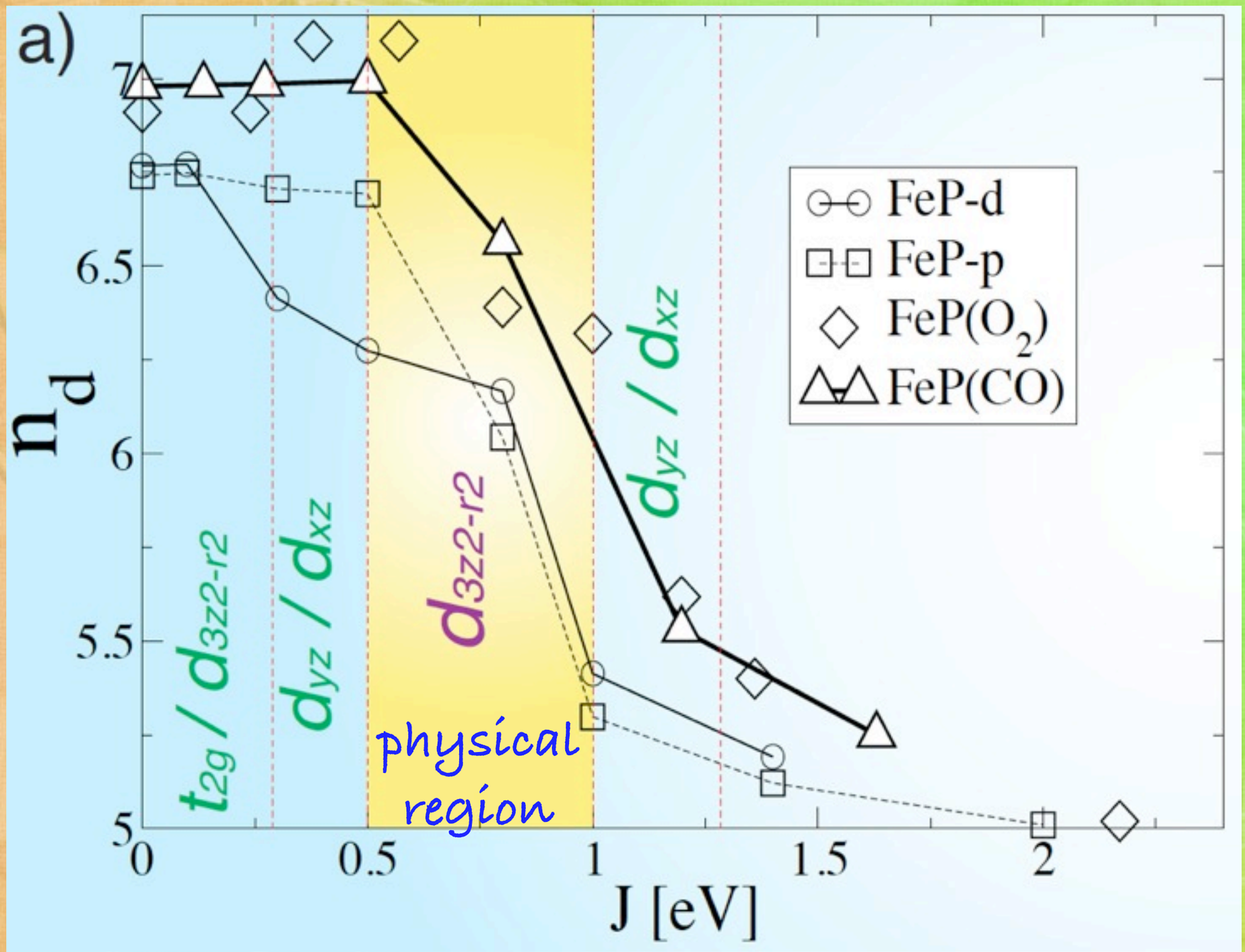
o) electronegative hydroxil group

o) Nitrogen ring around Fe atom

o) Strong hybridization of the d_{x2-y2} orbital



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~0.5-0.8eV

nd is a **local observable**, does not commute with the Hamiltonian (not a conserved quantity), e.g. fluctuate strongly

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

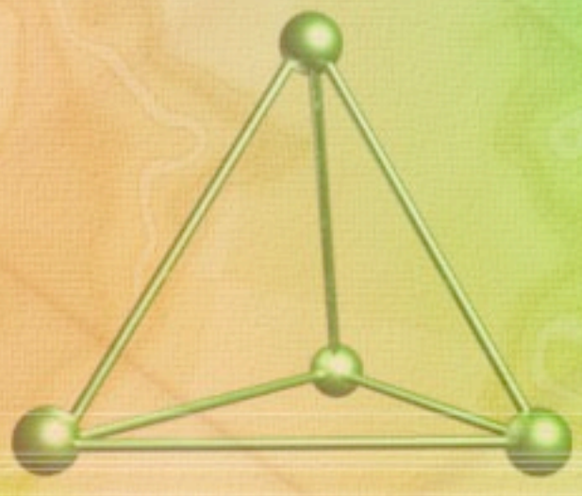
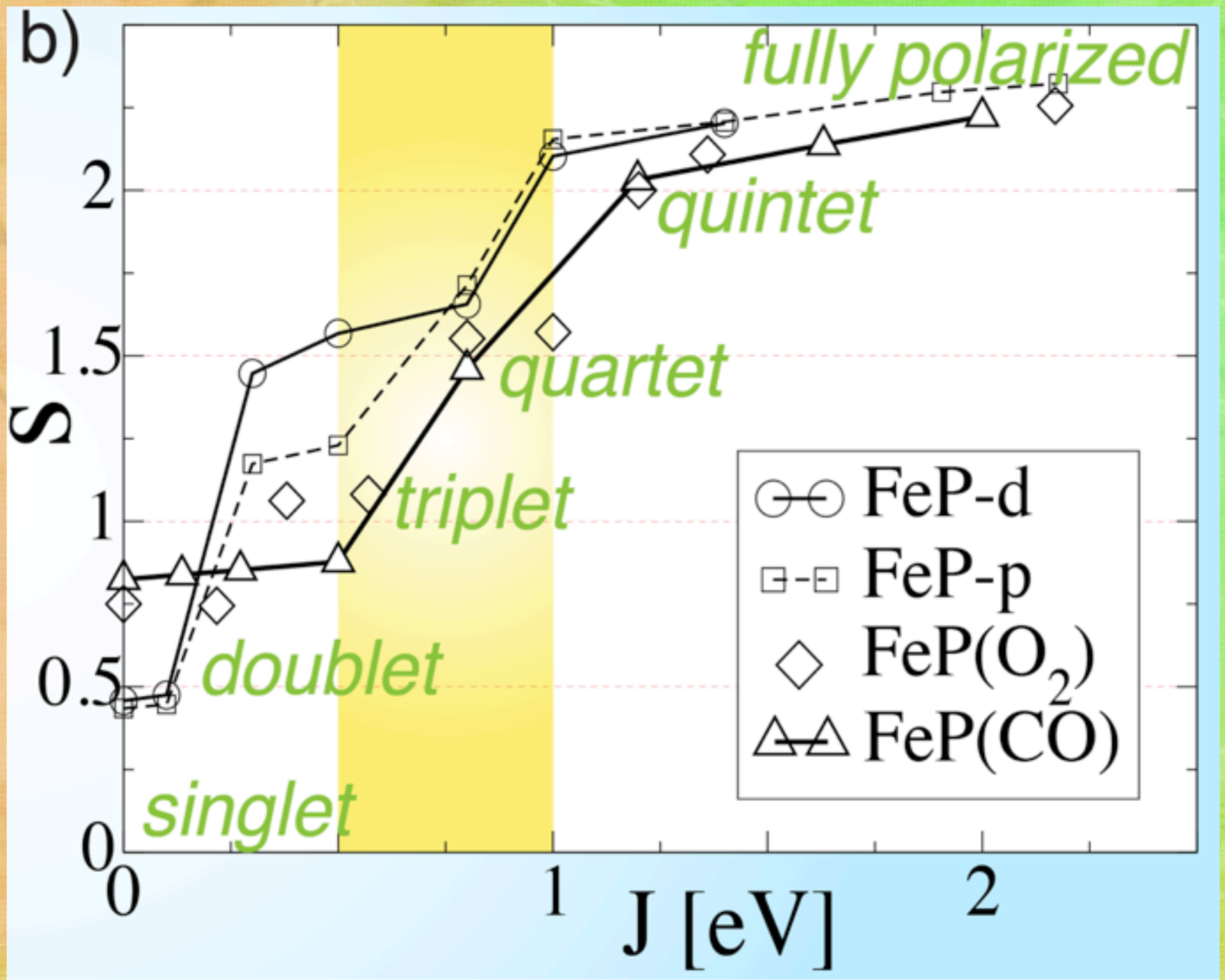


TABLE I: Average occupations n_d^α of the iron d orbitals for FeP, FeP(CO) and $FeP(O_2)$, for J=0 and J=0.8.

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

AIM - Entanglement - bath/impurity

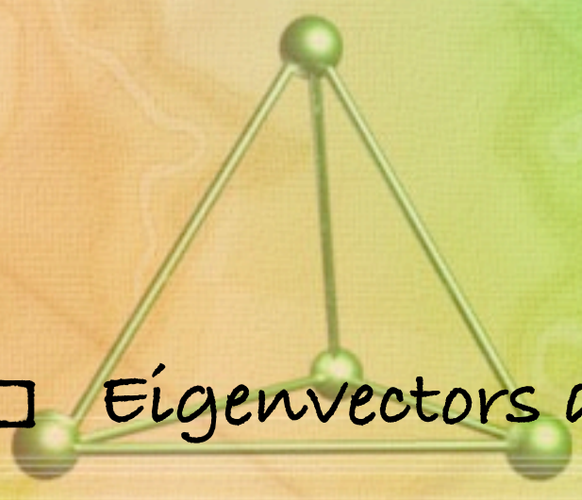
- Decomposition of the ground state (and excited states) in impurity and bath parts

- 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

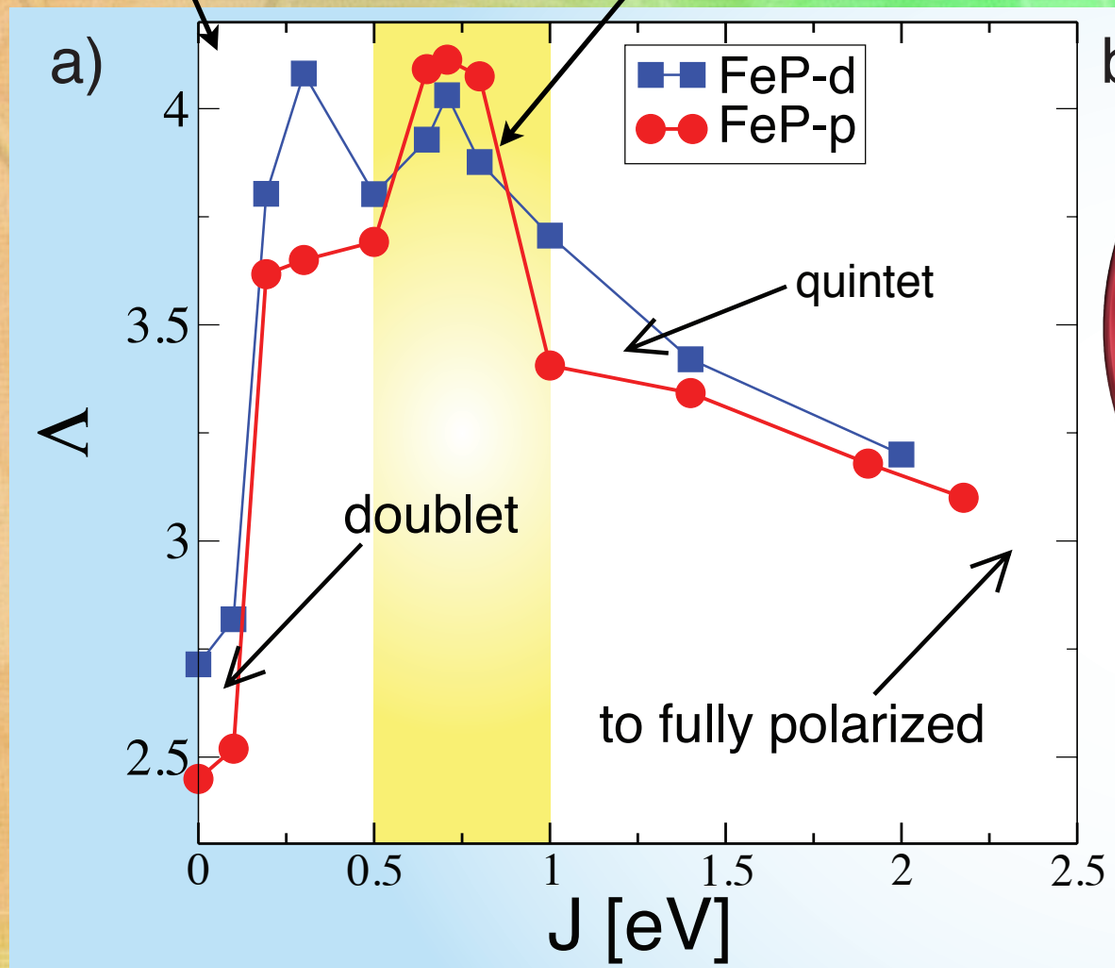
Quantum entanglement (unligated heme)

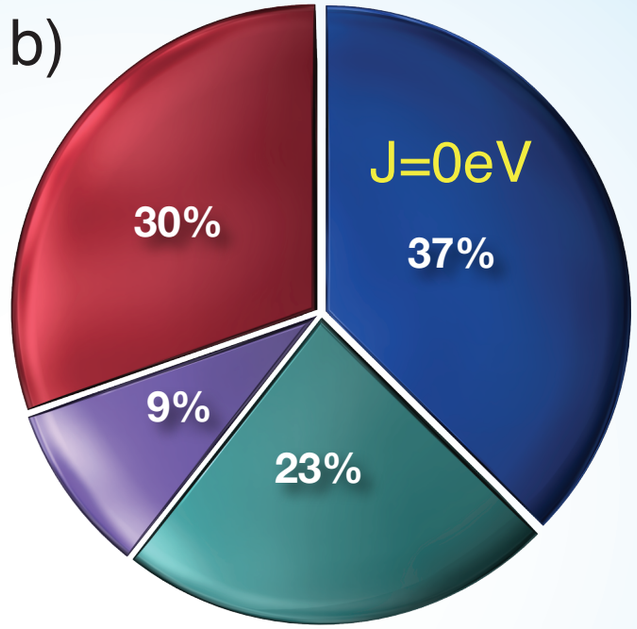
d-shell reduced density matrix (bath degrees of freedom are integrated out)

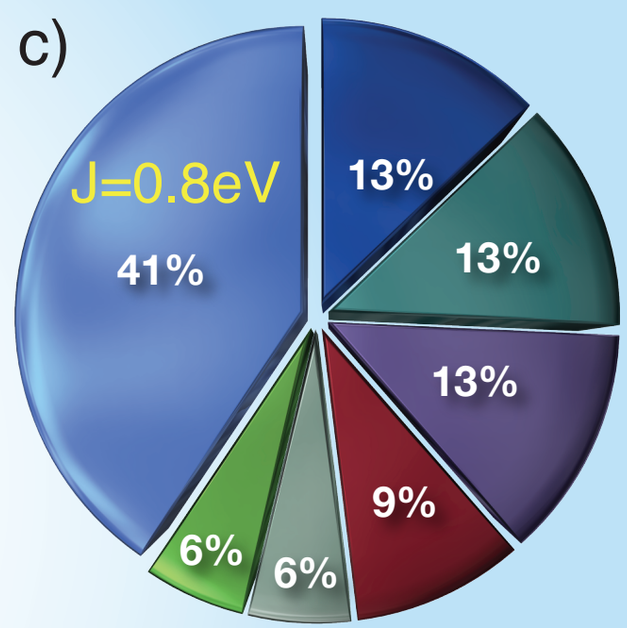
low spin Fe state, low entropy, classical valence

physical region, high entropy, valence fluctuation

"valence fluctuations"



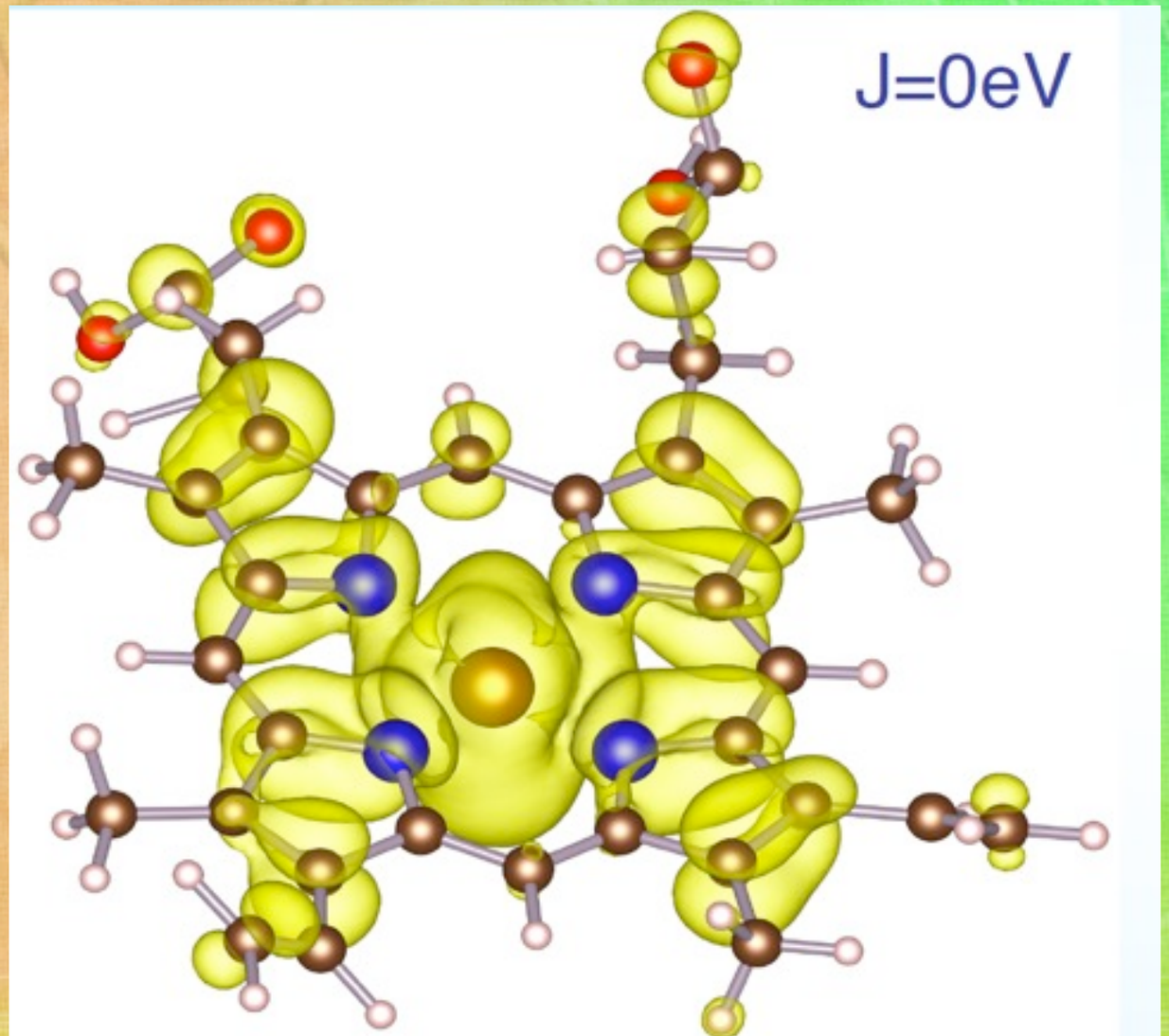


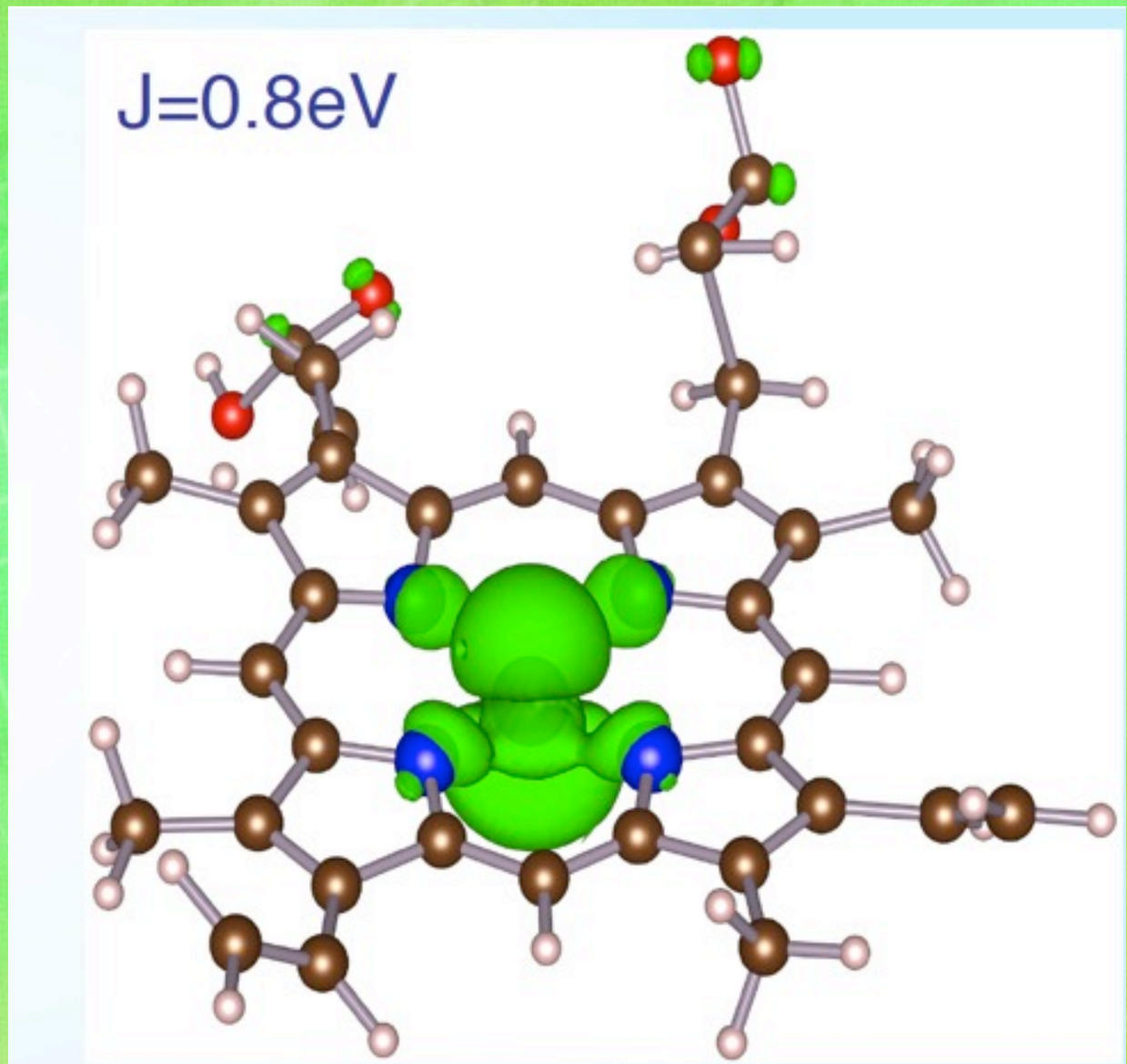


Orbital selection in desoxy-heme

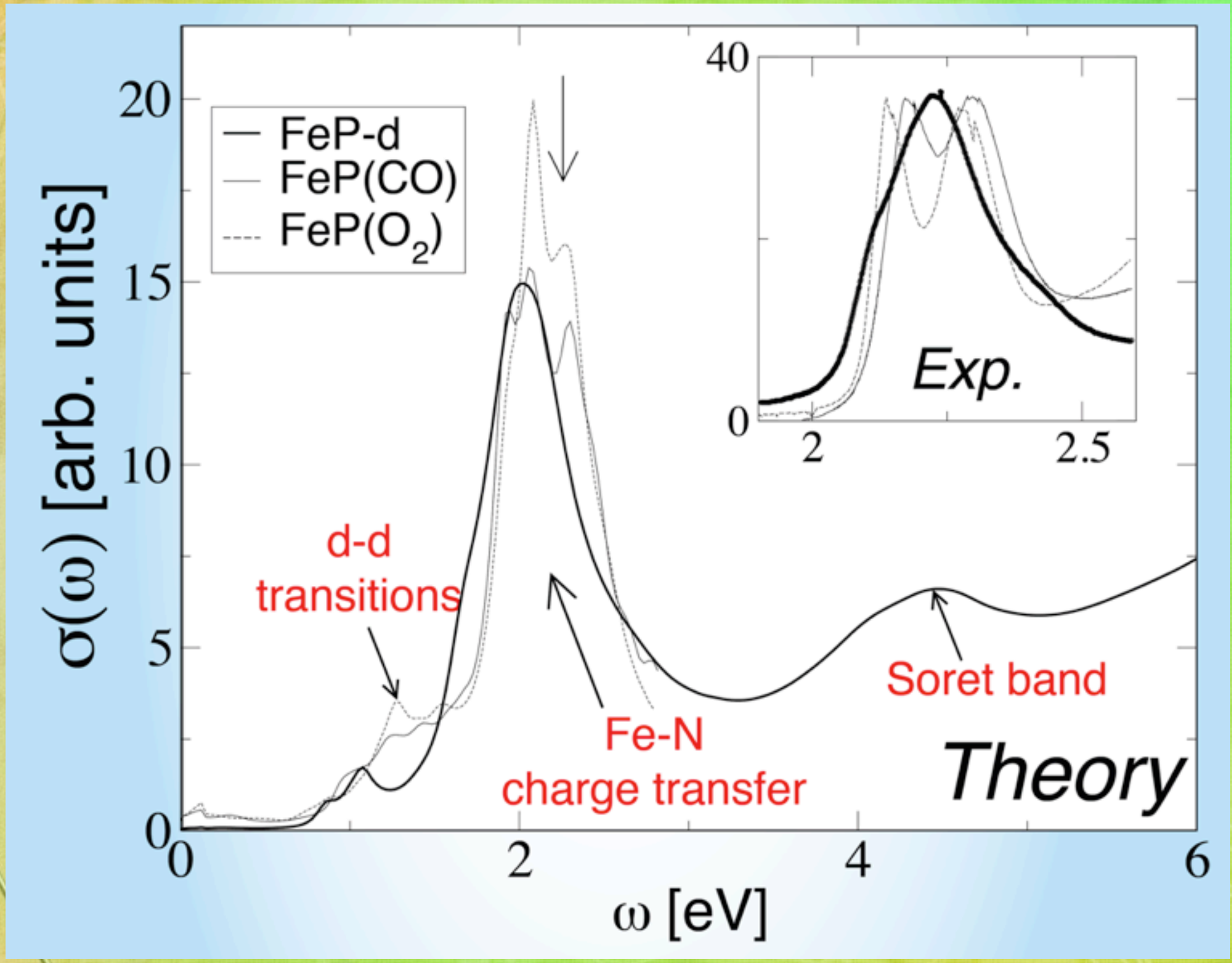
o) charge density of HOMO (highest occupied orbital)

o) J pins the charge at the Fe site, +orbital along out-of-plane axis, orbital selection



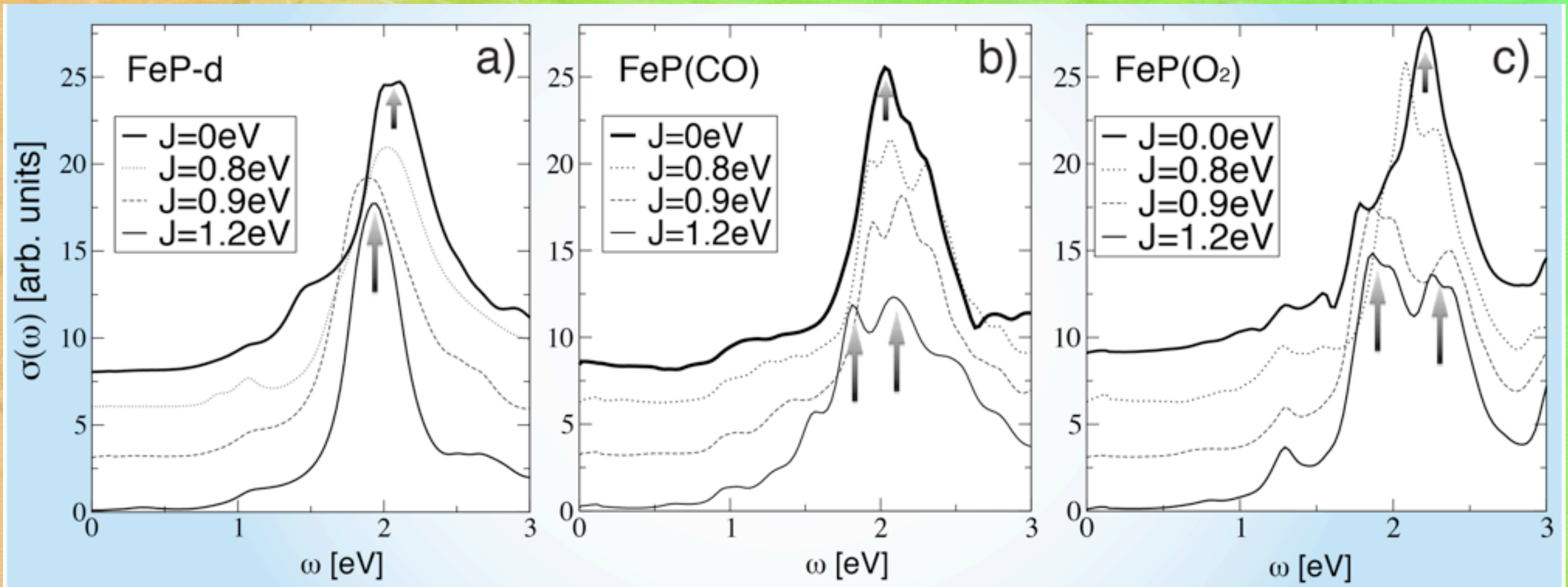


Optical absorption J=0.8eV



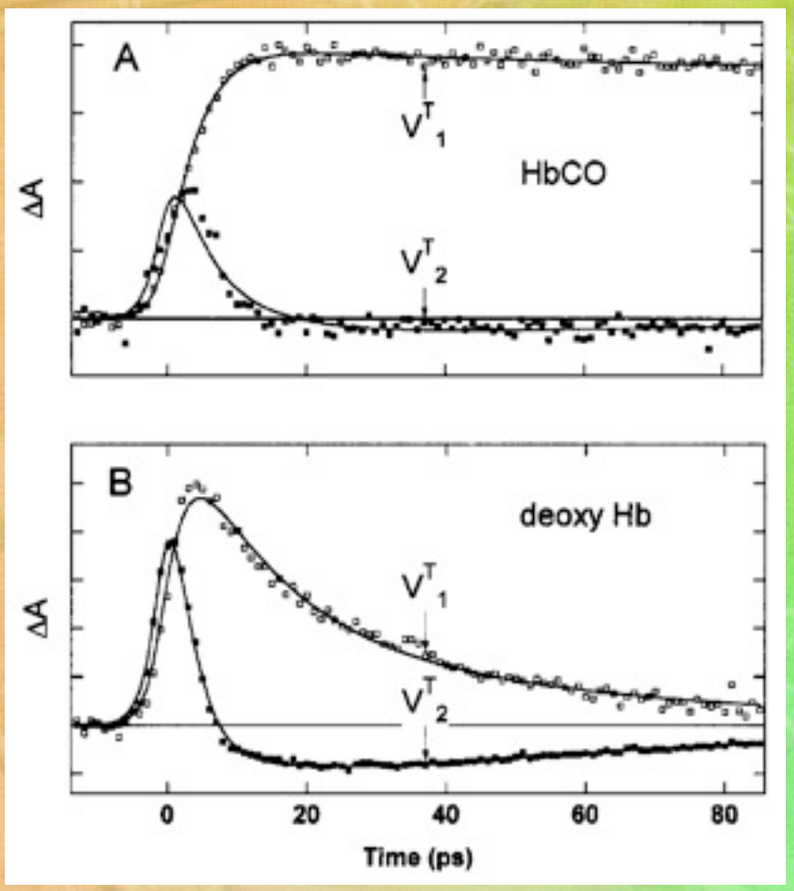
Exp. data : Steinke, Clin. Chem., 38'92.

Optics : J dependence



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

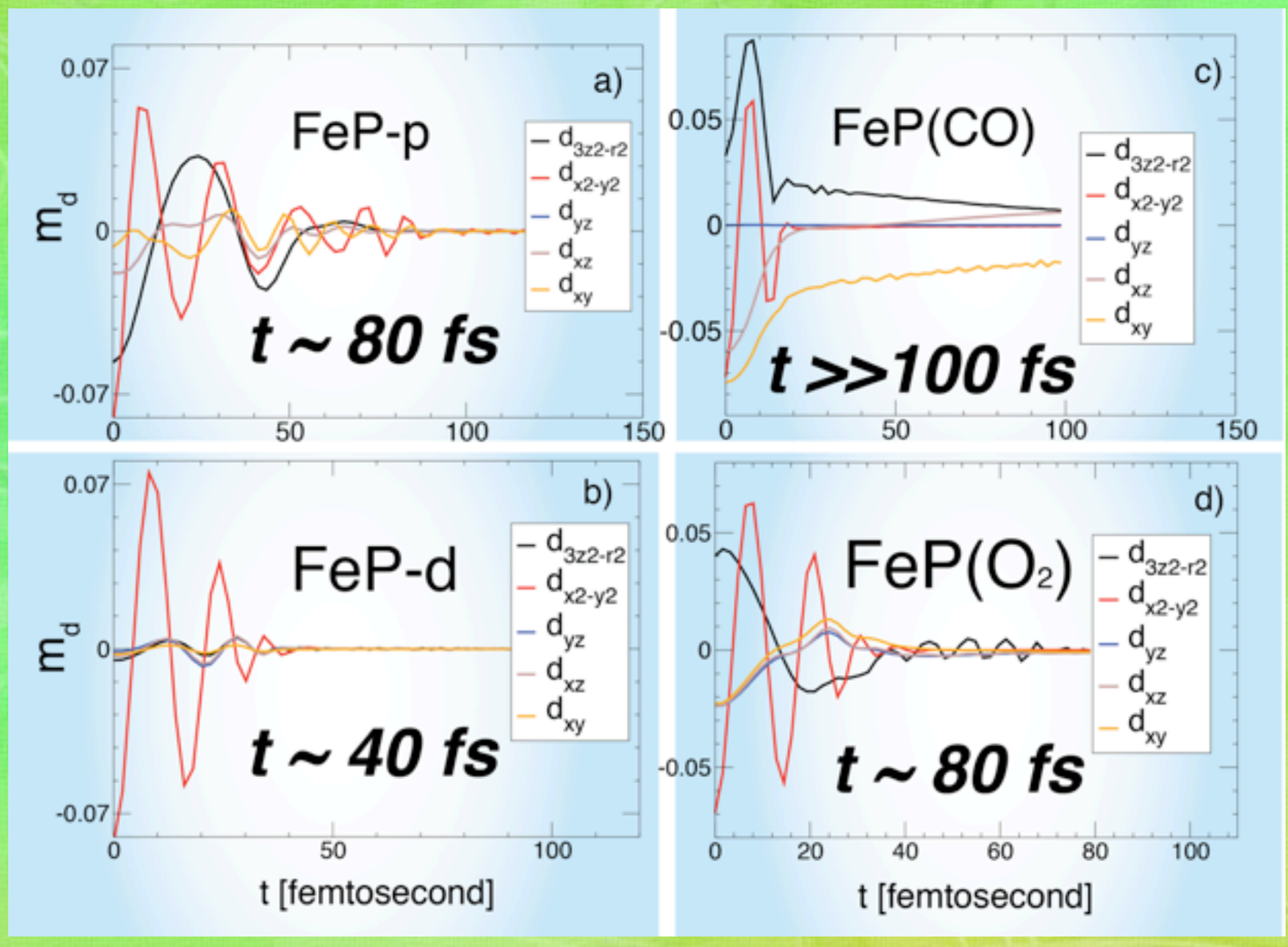
Relaxation, femto dynamics

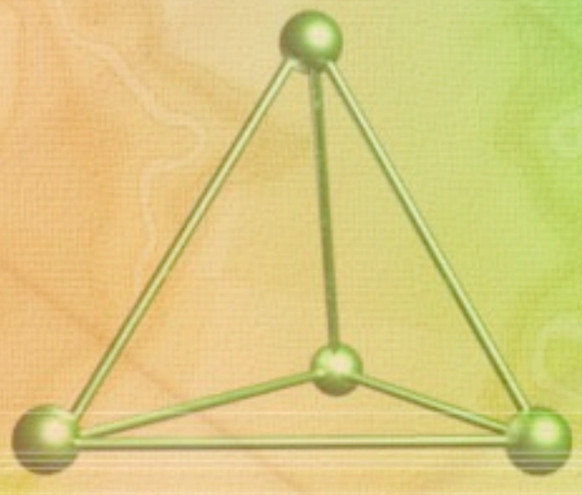


Photolysis excitation, shift in Raman spectra versus time, (Franzen, Biophys. Journal 80'01)

i) at t=0 we polarize Fe, and we let the system relax to equilibrum

ii) out of equilibrum quantum formalism (Keldysh formalism)





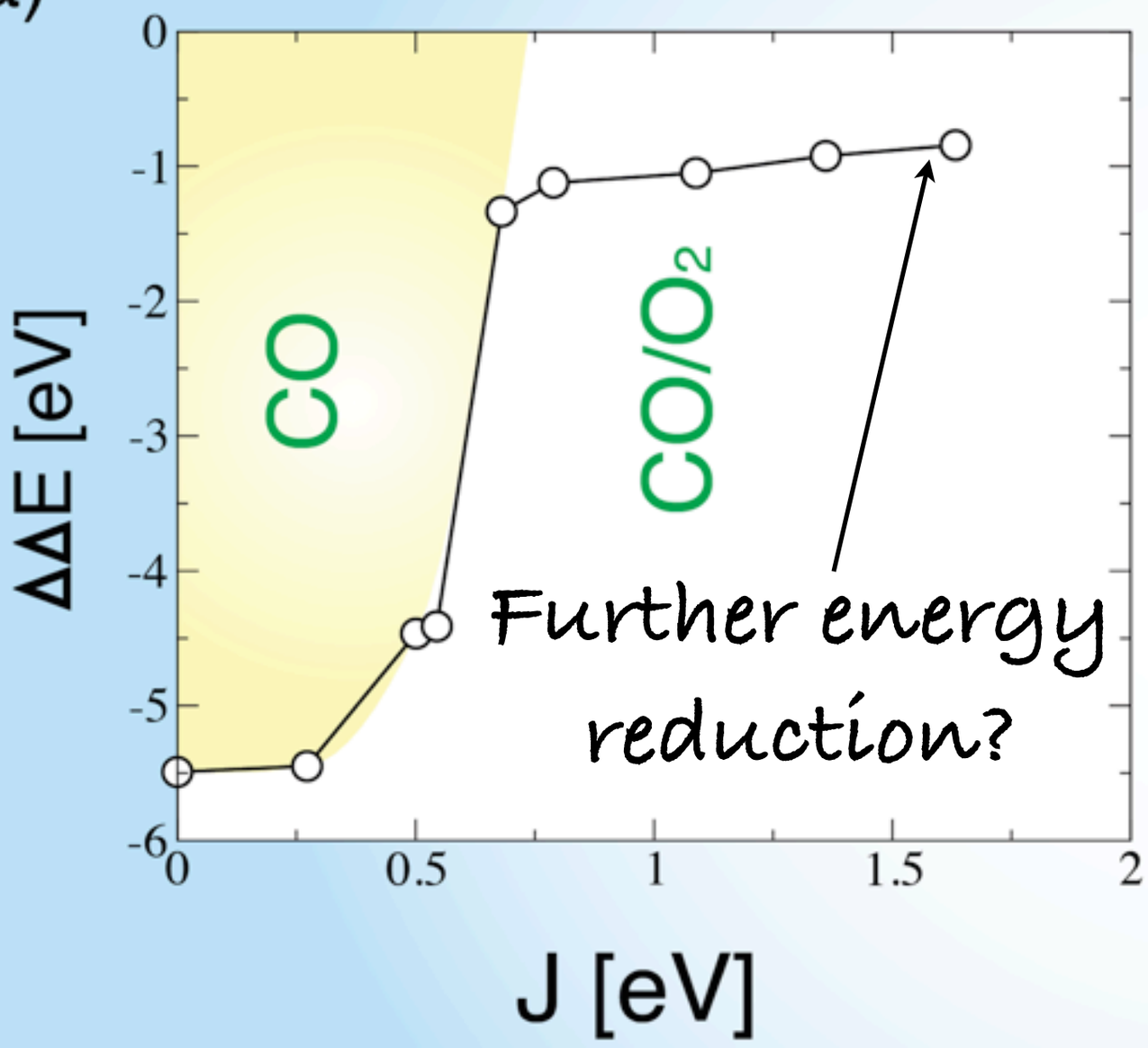
Different geometries have different response against perturbations, spot molecules according to their magnetic response.

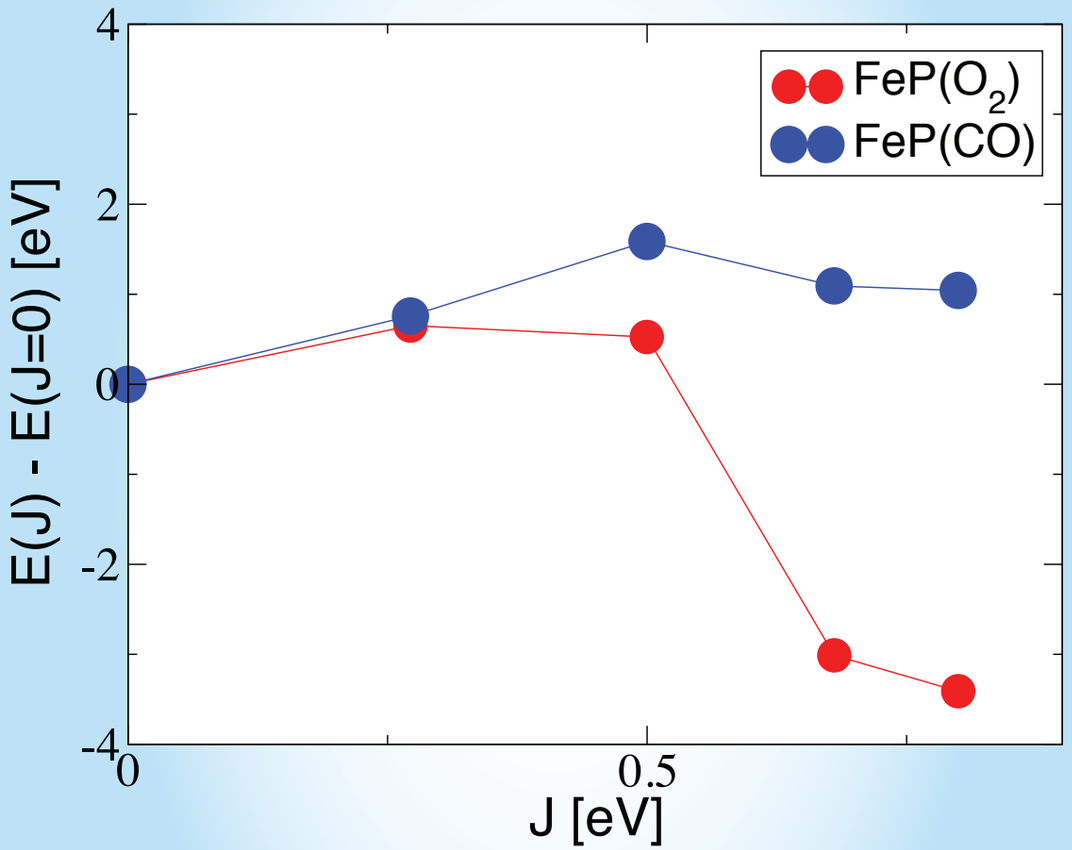
Energetics

$$\Delta E = E(FeP(X)) - (E(FeP) + E(X))$$

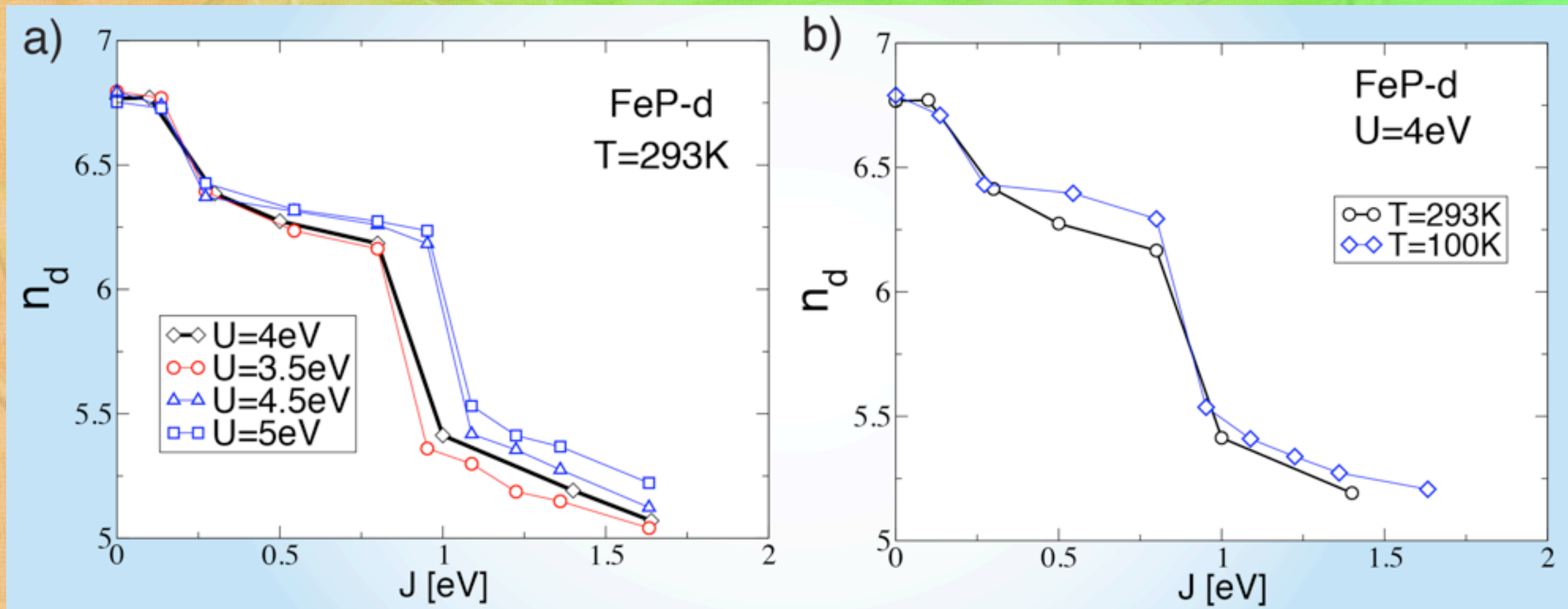
$$\Delta\Delta E = \Delta E_{CO} - \Delta E_{O_2}$$

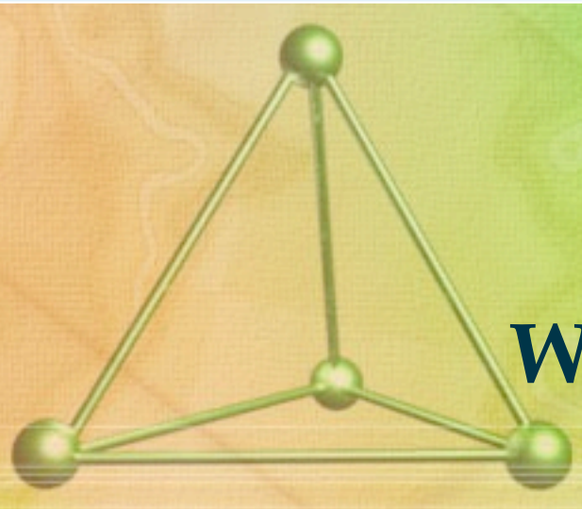
a)





U and temperature variations

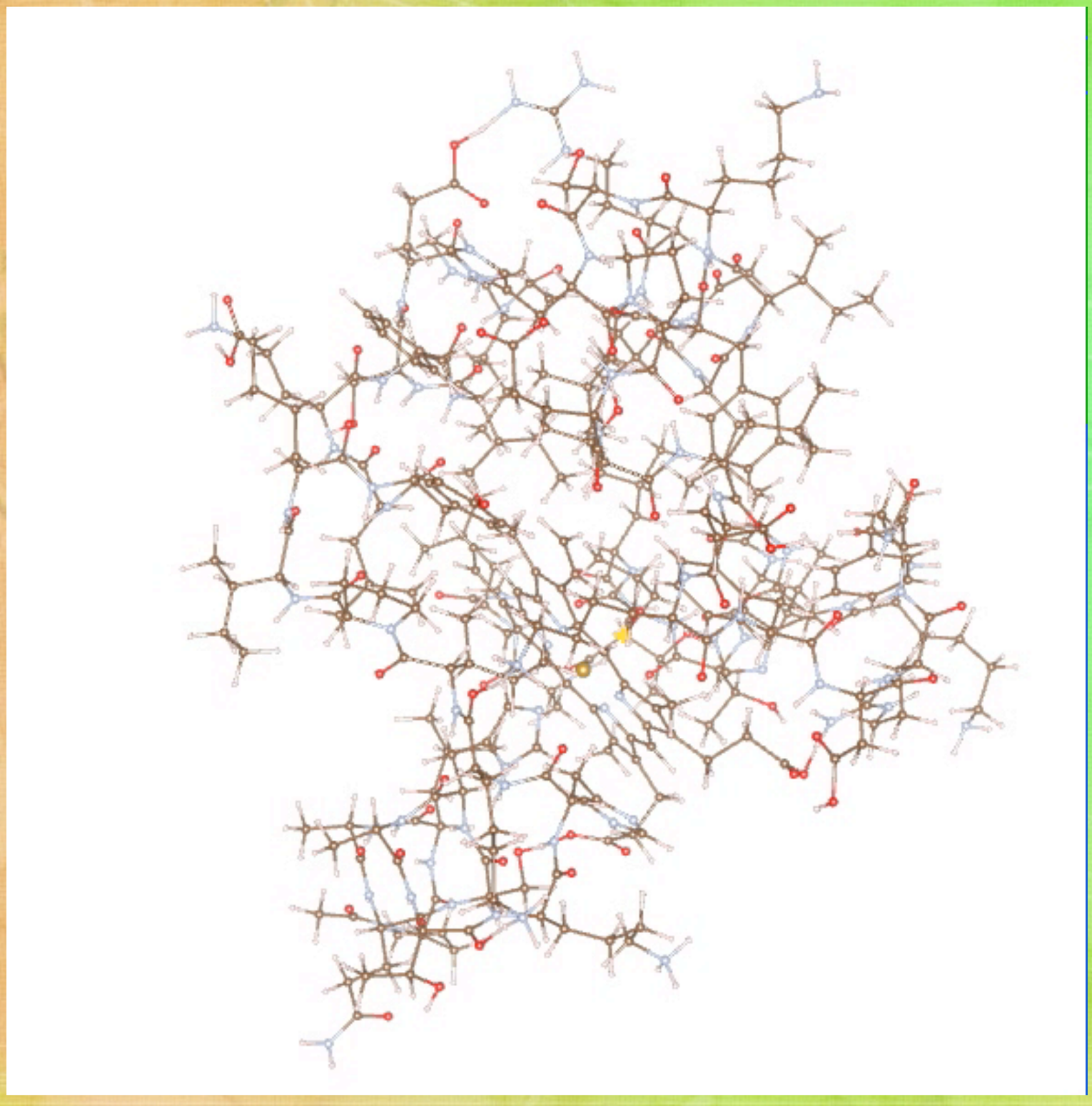




Weak U and temperature dependence

Weak variation of the charge with U for J=0

Myoglobin, 53 residues



oxy-myoglobin

Geometry optimization, by first principle calculations by Daniel Cole

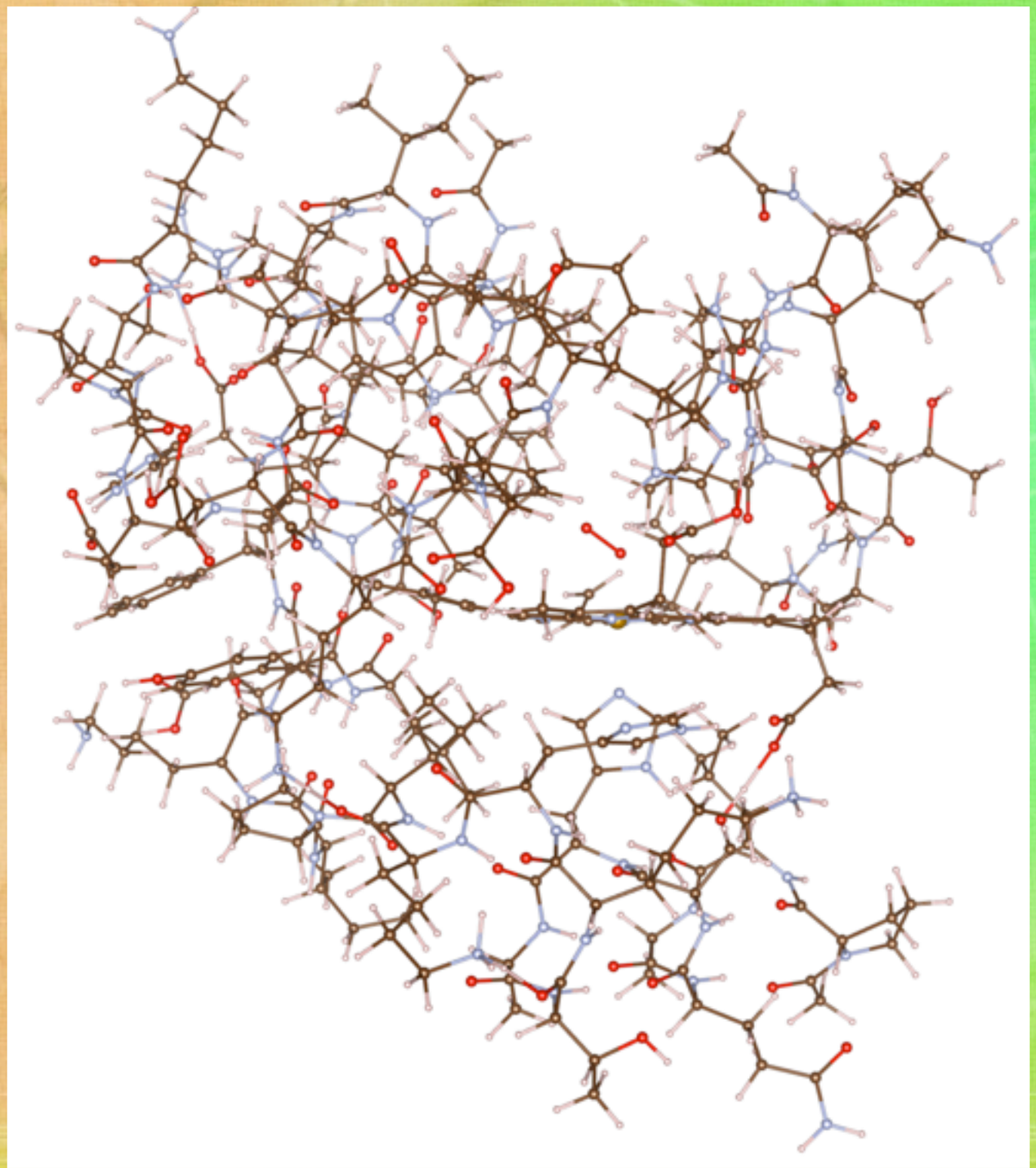
i) 5th ligand

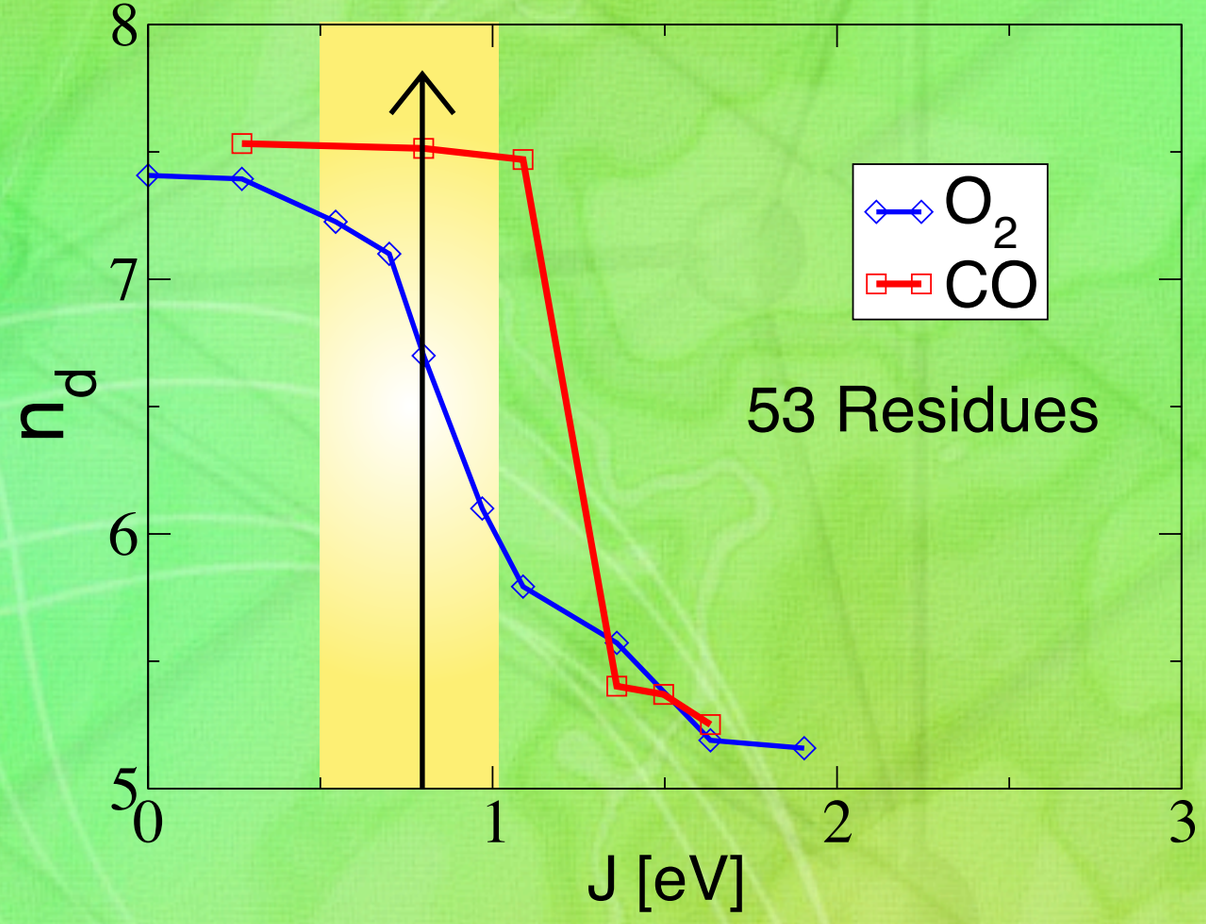
ii) bending of the Fe-O angle

iii) strain induced by the protein (protein effect)

D. Cole et al, J. Phys. Chem. Lett., 3, 1448 ’ 12

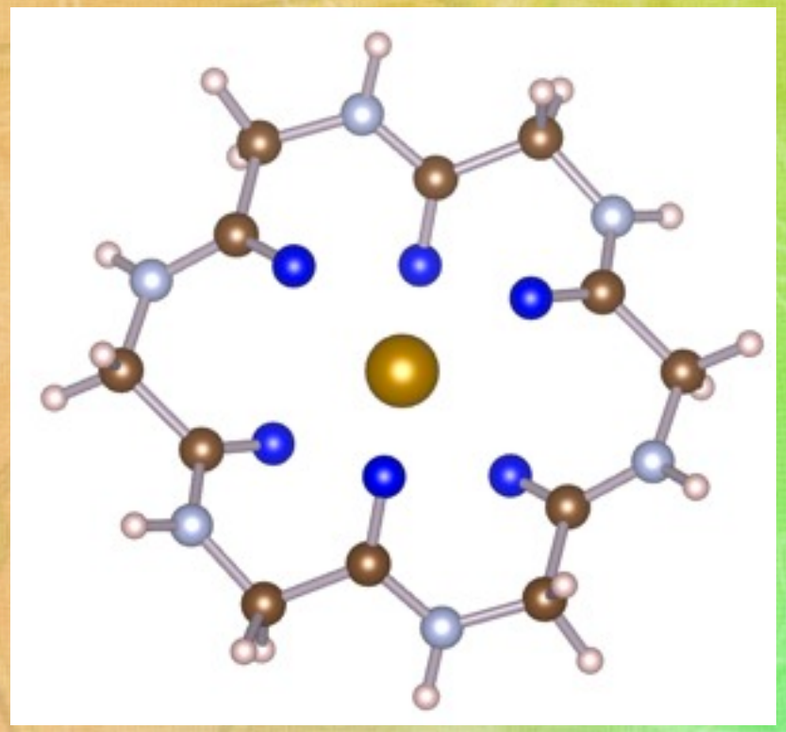
DFT+DMFT: myoglobin



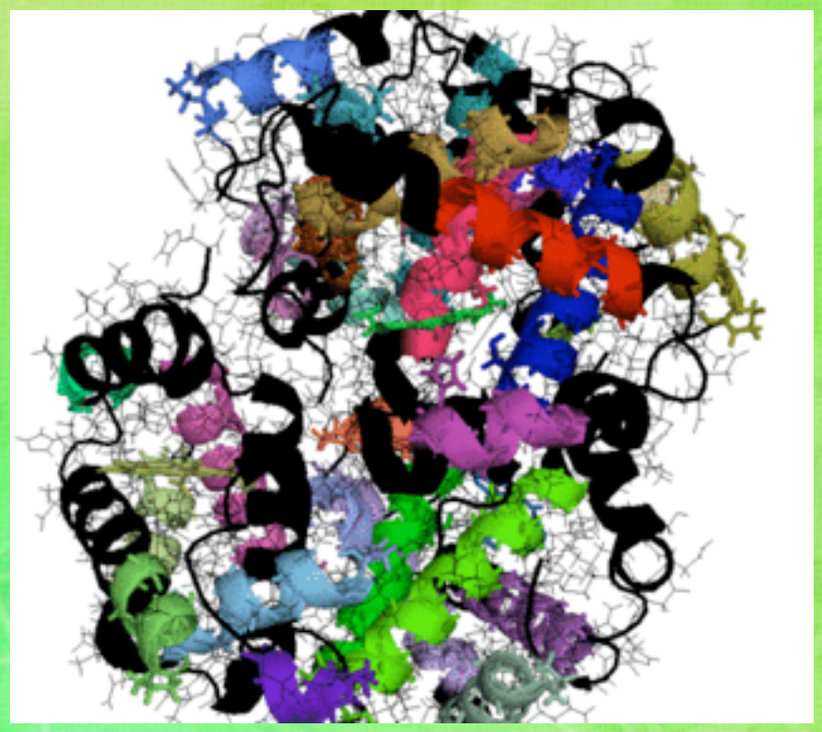


ΔΔE ~ 0 for J=0.8eV

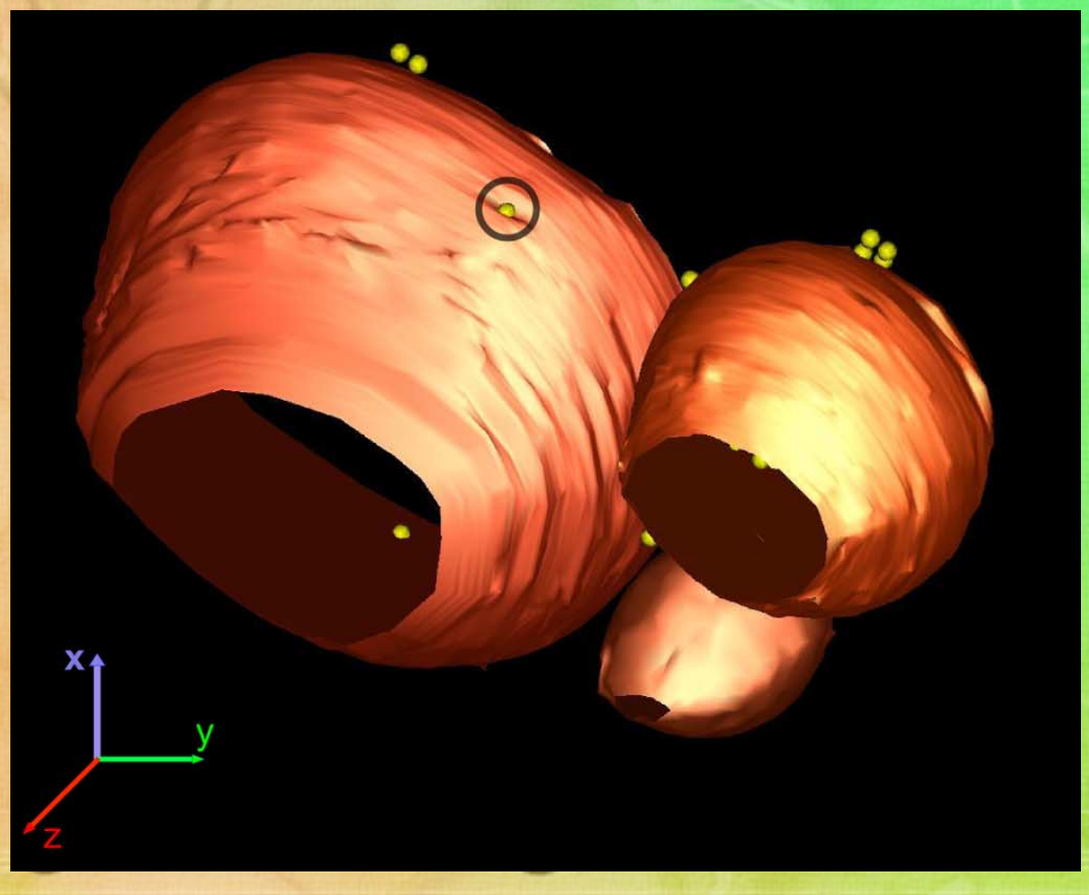
Outlooks



Iron peptides, applications for drug design



DMFT along conformal trajectory (change of structure of the molecule)

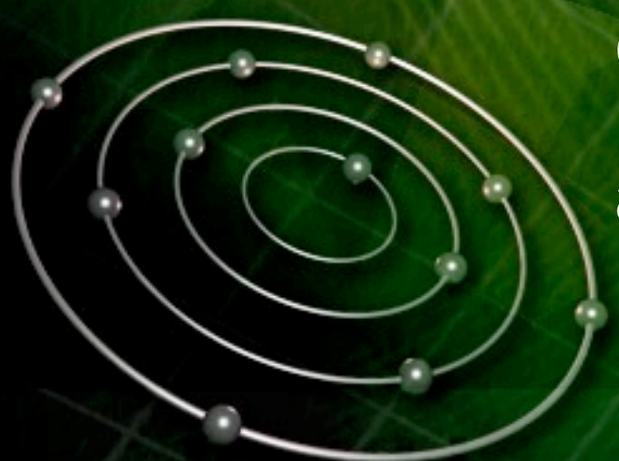


**Supra-paramagnetic iron oxide (SPION) molecules,
applications for targeted drug delivery, MRI contrast agents, ...**

**left : Spion diffusion in a liposome surface
C. Bonnaud et al, TMAG, 49, 2219040 ’ 12**

Conclusion

- DMFT refines ONETEP by treating the strong correlations in the atomic d shell
- We presented an implementation of *molecular dynamical mean-field theory*
- Hund's coupling in molecules, not taken into account in most DFT or DFT+U, a new approach for molecules
- Energetics are corrected by the DMFT
- A view on ligand binding from the strong correlation perspective, convergence and interdisciplinary work with Quantum Chemistry approaches



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