Dynamical mean-field theory and strong correlations in <u>solids</u> and molecules



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Outlines

Introduction: strongly correlated systems Hubbard: the "theory of everything", model Hamiltonians Dynamical mean-field theory ONETEP+DMFT, implementation Example 1 : Large scale DFT+DMFT, vanadium dioxide



Example 2 : DMFT for molecules, Iron porphyrin

Conclusion, outlooks

Strongly correlated systems



Recipe : take a transition metal (open shell d electron) Build crystal with this building block or build layers separated by lanthanides (spacers)

<u>V Cr Mn Fe Co Ni Cu</u>

VO2 Room temperature <u>MIT</u>

La_{1-x}SrxMnO₃ Colossal <u>Magnetoresistance</u>

Li_xCoO₂, Na_xCoO₂ Battery materials <u>Thermoelectrics</u> La_{1-x}Sr_xCuO₄ High temperature superconductor

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Hubbard model : the theory of everything

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

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 (Uc₂), simple argument (PRB 2, 4302 '70) and confirmed by single site DMFT (G. Kotliar, EPB 11,27'99)

For oxides, a simple generalization is obtained with a three-band model Hamiltonian



$$H_{t} = \sum_{\langle i,j \rangle} \left(t_{ij} d_{i}^{\dagger} p_{j} + hc \right) + \sum_{\langle i,j \rangle} \left(t_{ij} p_{i}^{\dagger} p_{j} + hc \right) + \sum_{i} \epsilon_{p} p_{i}^{\dagger} p_{i} + \sum_{i} \epsilon_{d} d_{i}^{\dagger} d_{i}$$
$$H_{cor} = U_{d} \sum n_{i\uparrow} n_{i\downarrow}$$

Competition between charge transfer energy and local U repulsion, Zanen-Sawatzky-Allen milestone (ZSA) paper (*PRL* 55, 418'85).

Ud large (charge transfer insulator):

small charge transfer energy (Mott insulator) :

 $U \rightarrow \varepsilon_d - \varepsilon_p$

 $U \rightarrow U_A$

Dynamical mean-field theory



Linear scaling O(N) DFT (ONETEP) combined with DMFT

 $\tilde{\Sigma}^{(I)(J)} = 0$

 $(I \neq J)$



This defines the local AIM, we can solve it by using numerical techniques (Lanczos, continuous time quantum Monte Carlo,...), we obtain the projected self energy, and we upfold back to the large NGWF space:

$$\Sigma_{\alpha\beta} = \sum_{IJ} V_{\alpha m}^{(I)} \left(\tilde{\Sigma}_{mm'}^{(I)(J)} - E_{\rm dc} \delta_{mm'}^{(I)(J)} \right) W_{m'\beta}^{(J)}$$

Beowulf cluster, Rutgers



8xGPU units, Tesla c2050

cluster DMFT 6

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Workflow



Example 1 : Vanadium dioxide, open questions



Monoclinic M1 phase, rutile axis along "a" axis



 chains along the rutile axis
T=290K : structural phase transition (dimerization).



Goodenough (Progr. Solid. State Chem.3'71): Simple ionic picture : V⁴⁺, O²⁻. single d electron.

- Peierls distortion at low T splits the d₁ into bonding/anti-bonding => insulator
- LDA fails to reproduce the insulator (Terakura, PRB 30'84)
- model Hamiltonian calculations for a d₁ configuration finds a band insulator, but no Mott instability <u>(Biermann,PRL 94'05).</u>
- Transition is observed also under the presence of disorder, points toward a Mott instability (Chudnovskii, J.Solid.State.Chem 98'92).
- Evidence for strong correlations in metallic (rutile) phase points to Mott physics (Belozerov, JETP Letters, 93'11)
 - Cr-doped VO₂ shows Heisenberg-like magnetic moments, hinting towards Mott correlations (Pouget, PRB 10'74).

On the other hand, VO₂ was shown to have a large charge transfer energy, points to a charge transfer insulator (Bocquet, PRB 53'96).

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Results : Anderson localization

- trapping of electrons due to lo imperfections of the lattice could also drive the system towards an insulator
- we introduce a random displacement of the atomic positions (Gaussian distribution)
- Z_d=m/m* quantífication of correlations, 1=metal,0=insulator



localization as disorder increases





enhance mass renormalization

Results : Non-local correlations

- Peierls physics: distortion of the lattice creates V-V dimers, we introduce a non-local self-energy between the V atoms belonging to these V-V pairs
- The non-local self energy induces a splitting of the local orbitals in bonding and antibonding combinations

orbital occupations (rutile axis along x direction)

	d _{yz}	d _{xz}	d _{xy}	Deierde plancies in duese que exhited
single-site	0.57	0.57	0.76	selection, now 2e in 2 orbitals, half-filled!
cluster	0	1	1	

Pole in the local self-energy of the d_{xy} orbital => Mott insulator
Gap in the spectral function ~0.5eV, good agreement with Exp.
signature of Mott physics: in-gap localized state if O-vacancies



Results : Test of the theory

optical conductivity:

Linear response (Kubo formalism)

Transition from occupied to un-occupied states

ONETEP+DMFT is in very good agreement with Exp. data.



Conclusions

Several orthogonal views on VO2 in the literature: Charge transfer / Mott / Peierls

our pícture is merging all the three above:

<u>charge transfer hybridizes strongly the eg, leaving 2e in the t2g</u>
(2e in 3 orbitals)

subtle interplay captured by DFT +DMFT only.

- <u>Peierls distortions</u> induce an orbital selection (the orbital in the perpendicular plane to the distortion is now empty), leaving 2e in 20rbitals
- <u>Mott correlations</u> in this half-filled system induces a pole in the imaginary part of the self energy (dynamical correlations), leading to a Mott insulator, stable against perturbation, such as disorder.

<u>Signature of this process</u> can be observed by an in-gap localized state when O-vacancies are introduced.

"Peierls-assisted orbital selective Mott transition"

Example 2 : DMFT in molecules

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.



(pictures obtained from PDB database)

With DMFT: capture the quantum entanglement (singlet ,triplet) and describe excited states not captured by DFT.

Iron porphyrin topology



Heme binding to O₂ dimer (planar shape) FeP(O₂) From X-ray data (PDB database)



HemeB in solvent, dome shape, FeP. Fe is out of the nitrogen plane by 0.35Angstrom

Heme -----> AIM



Link between topology/Binding and electronic states (charge/spin)?

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Hund's rule

- 1) spin in the paramagnetic state by the spin correlator (A finite quantum system does not spontaneously break the spin symmetry, this is true only for solids).
- 2) Physical J~0.8eV places Heme at the transition between low- to high-spin



Quantum entanglement

Reduced density matrix



Relaxation, femto dynamics





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

> out of equilibrum quantum formalism (Keldysh formalism)

Different geometries have different response against perturbations, applications for Timeresolved resonance Raman measurements, spot 18 molecules according to their magnetic response.

Optical absorption



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Conclusion

- We presented two simple case of study where DFT was combined with DMFT
- DMFT refines ONETEP by treating the strong correlations (opens a gap where DFT was finding a metallic ground state)
- DMFT captures the interplay of competing types of physics (Mott, charge transfer, Peierls,...)
- Hund's coupling in molecules, not taken into account in most DFT or DFT+U approaches for molecules
- ONETEP provides an ideal set of localized orbitals, optimized during the energy minimization, which we can use as projectors for the local atomic problems. Linear scaling allows to tackle large unit-cells, ideal to study disorder effects or the effect of dislocations/vacancies

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Thanks for your attention! For more details:

- Vanadium dioxide : A Peierls-Mott insulator stable against disorder (arXiv/1202.1423)

- Binding of iron porphyrin driven by valence fluctuations (to be submitted soon)