

The Towler Institute

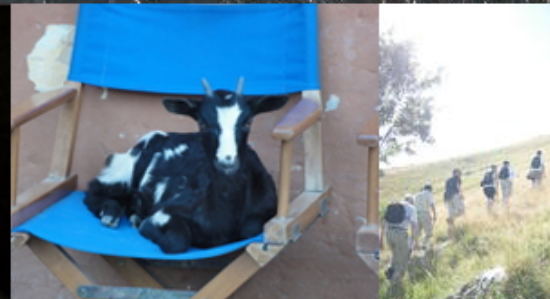
2016 International Summer School

Quantum Monte Carlo and the CASINO program X

Vallico Sotto, Tuscany, Italy 23rd - 30th July 2016

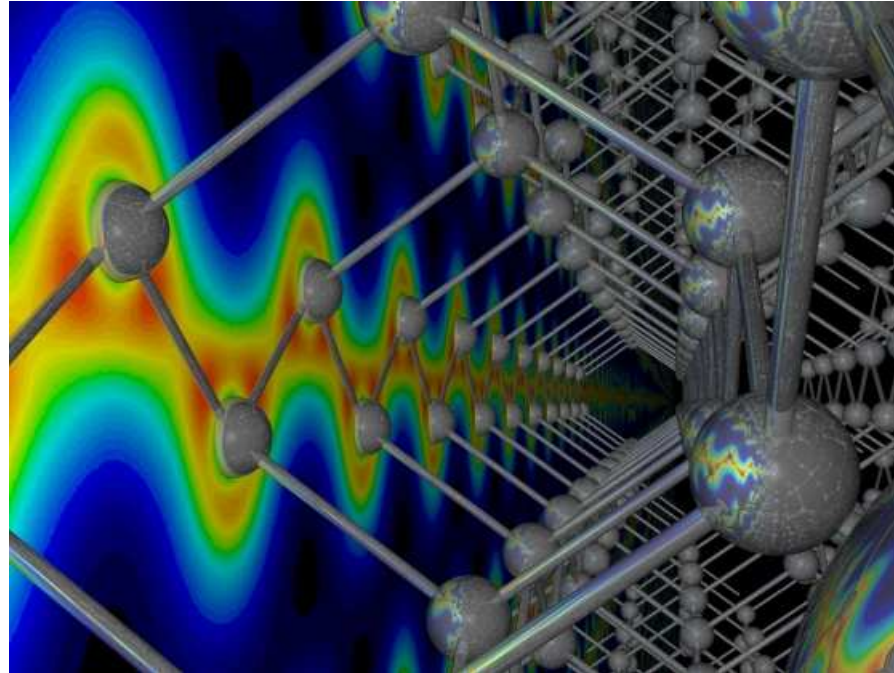
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Useful calculations for big, complicated systems

Quantum Monte Carlo at the research frontier



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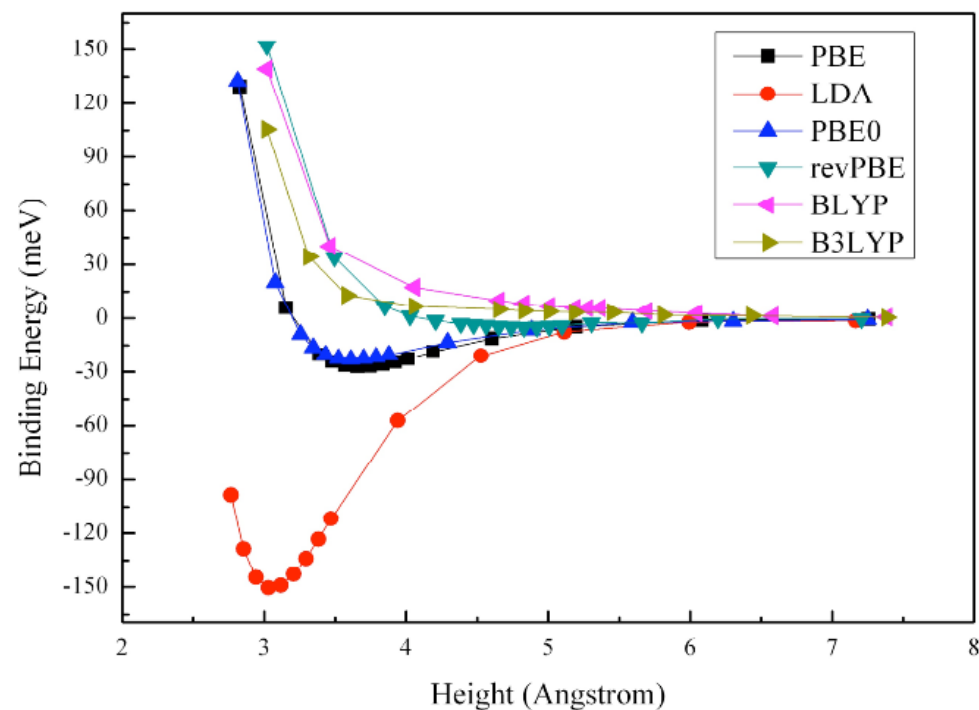
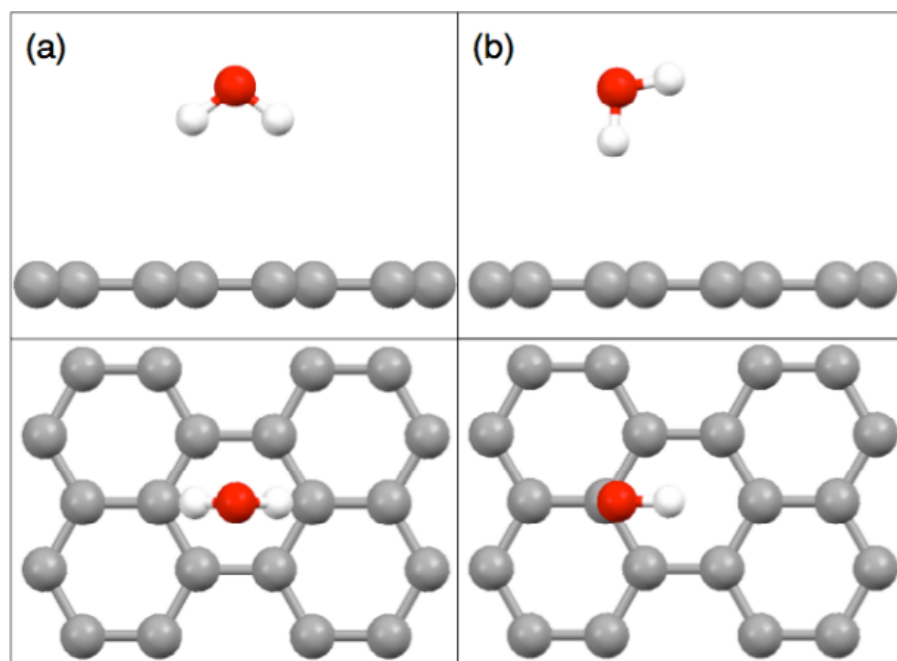
Some interesting applications of DMC..

See the original papers in the `summer_school/apps` folder..

Weak interactions

Simple question: does a water molecule stick to a graphene surface or not?

Water interacts with materials via van der Waals dispersion and hydrogen bonding - both weak interactions which DFT has a problem with. You can basically get any answer you like depending on which exchange-correlation functional you select.

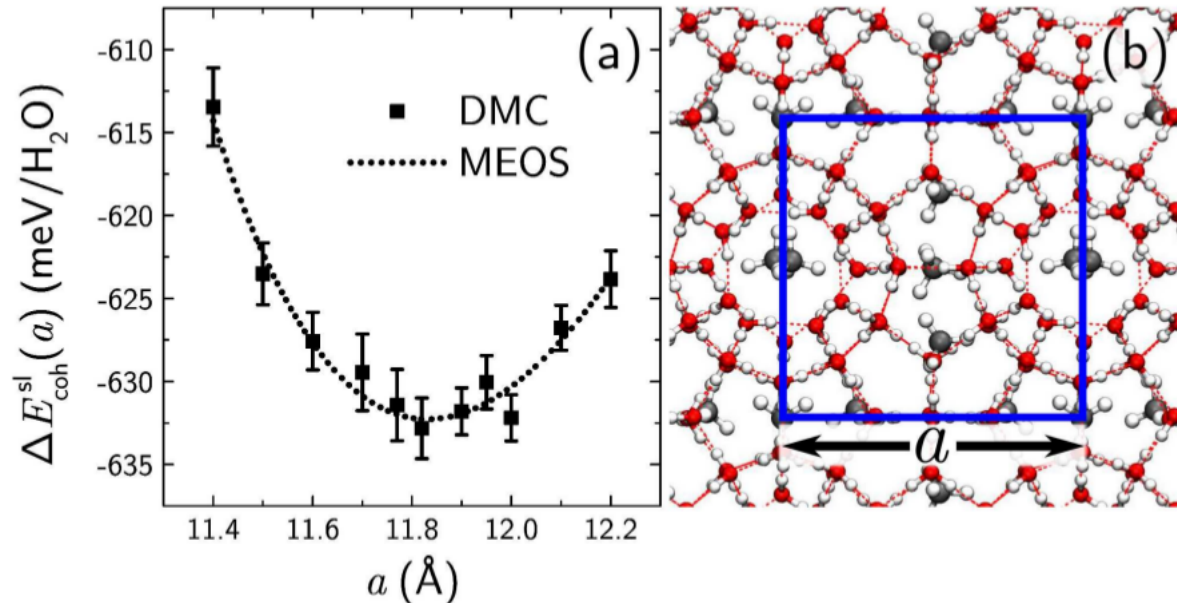


Which functional shall I choose? No real answer to this without comparing with a DMC benchmark..

The fashion nowadays would be to bring in one of the new functionals that supposedly incorporate empirical 'van der Waals corrections'. Do these work? Again - very difficult to say without comparison with DMC benchmarks. Let's try this with a complex material of current industrial interest..

Gas hydrates

Gas hydrates pose problems to the energy industry (their formation blocks gas lines) and they are a potential untapped energy resource (abundance of naturally occurring methane hydrate exceeding conventional gas reserves by at least an order of magnitude). Difficult for DFT since held together by hydrogen bonds and van der Waals. Our recent paper provides high-quality DMC reference data.

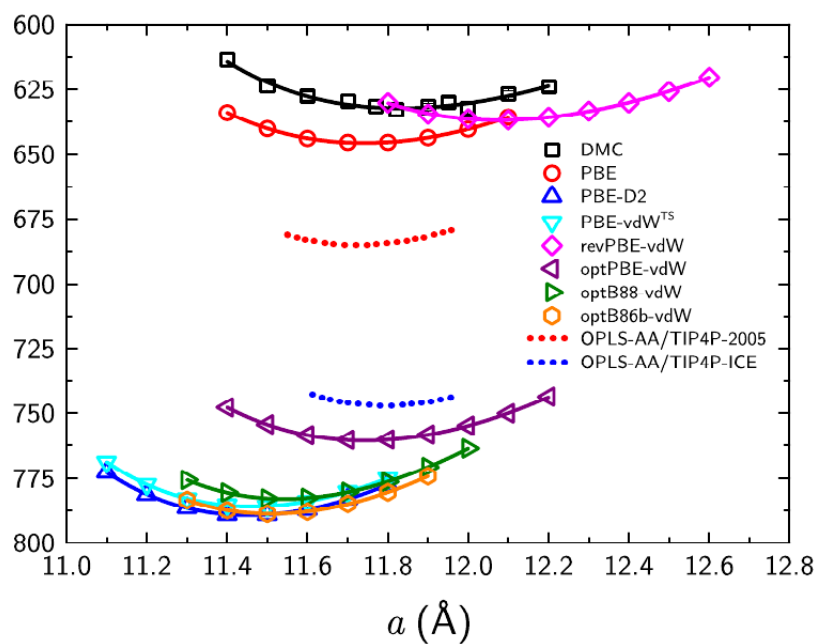


[Cox, Towler, Michaelides, Alfè, *J. Chem. Phys.* **140**, 174703 (2014)]

- Clathrate structures of gas hydrates are like ice (extended hydrogen bonded network of water molecules) but contain *cavities* - dodecahedrons and 14-sided tetrakaidecahedrons(!) in the sl structure considered here - that gas molecules like methane can occupy. Complex crystals with 178-atom simulation cells.
- I used CASINO to calculate (1) the lattice constant (11.83 ± 0.02 Å, cf. exp. 11.821 ± 0.001 Å), and (2) the cohesive energy for complete dissociation of the filled hydrate (into 46 water molecules and 8 methanes). In order to understand better the behaviour of DFT, we decompose this into two contributions by also calculating: (3) the cohesive energy of the empty hydrate (into 46 water molecules), and (4) the binding energy of methane to the empty hydrate..

My collaborator Stephen Cox did some DFT calculations as well.. How do they do?

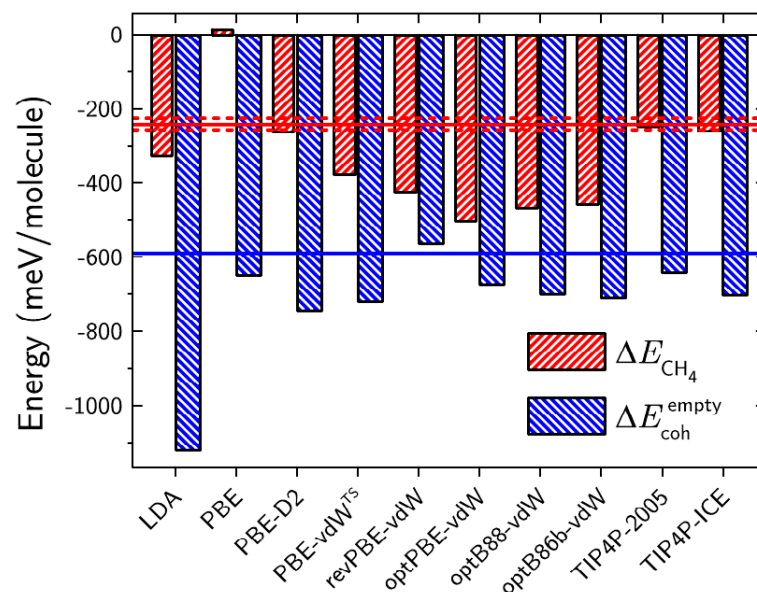
DFT vdW corrections don't work for gas hydrates



Variation of full cohesive energy with lattice constant

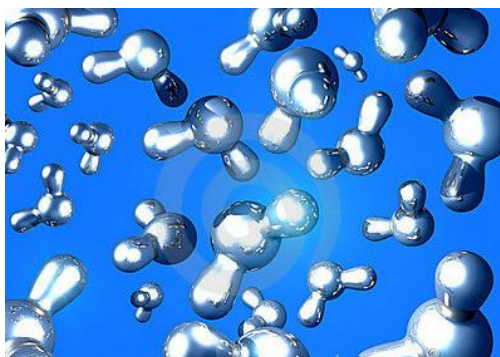
- All DFT functionals overbind the filled hydrate, most of them significantly. Only PBE gets more or less the right cohesive energy and lattice constant - even though it doesn't account for vdW interaction at all (note that correcting for it totally stuffs up the answer!).
- If no vdW how come PBE *overbinds* at all then? VdW is an attractive force isn't it?
- Answer (see below): Lack of vdW in PBE means there is *no binding at all* between the methane and the water, but this is compensated for by an overbinding of the hydrogen-bonded water framework.
- Although overbinding of water framework is small per molecule, water and methane exist in a ratio of 23:4 in the stoichiometric hydrate - so small errors in describing water-water interactions are much amplified compared to apparently larger errors in the methane binding energy.

- With exception of PBE-D2, the vdW-corrected functionals all *overcorrect*: methane binding energies too strong by 83-130 meV/H₂O. Similar analyses can be made for the other functionals.
- All results assume H₂O/CH₄ vapour phases as reference state. More important to gas hydrate phase equilibria is relative energy of hydrate to CH₄ gas and either liquid water or ice. For case of ice I_h DMC predicts endothermic dissociation costing 155±34 meV/CH₄.
- Experimental dissociation enthalpy 188±3 meV/CH₄. DMC value reasonable - though total ΔE s not enthalpies; expect difference due to neglect of T, P and also from non-stoichiometry (methane occupancy 96% in this study - configurational entropy effects?). Alternative analysis of experimental data sets using Clapeyron equation exists suggesting dissociation enthalpy 157±6 meV/CH₄.
- PBE disastrous: predicts sl methane hydrate will explode.
- Best functional for agreement with DMC in this case is PBE-D2, closely followed by er.. LDA and PBE-vdW.



Binding energy of methane to the empty hydrate (red) and formation energy of empty hydrate (blue). Horizontal lines are DMC.

Other work on water chemistry



'Energy benchmarking with QMC for water nanodroplets and bulk liquid water, Alfè, Bartók, Csányi, Gillan, J. Chem. Phys. 138, 221102 (2013).

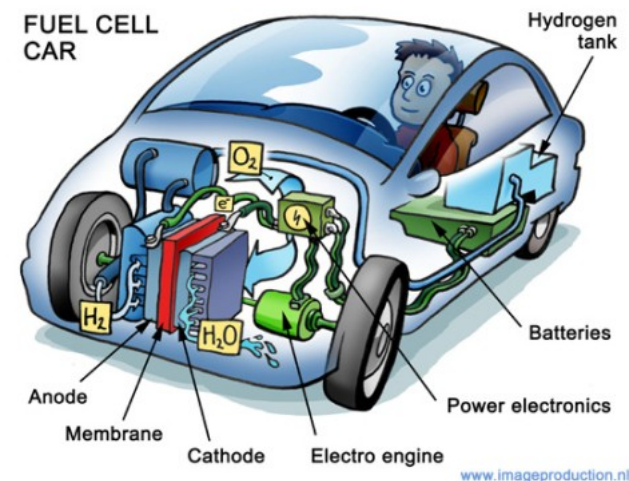
- Shows feasibility of using DMC to compute benchmark energies for configuration samples of thermal equilibrium water clusters and the bulk liquid containing up to 64 molecules.
- Accuracy of benchmarks checked using coupled cluster calculations in complete basis set limit.
- Illustrates the usefulness of such benchmarks by using them to analyze the errors of DFT exchange-correlation functionals - similar to what we saw for the gas hydrates but including a proper treatment of many-body effects (partitioned into one-body, two-body, and 'beyond two-body').
- Gabor Csanyi (Cambridge) GAP potential stuff of great use in doing this analysis.

'Framework for solvation in quantum Monte Carlo - Schwarz, Sundararaman, Letchworth, Arias, Hennig, Phys. Rev. B 85, 201102 (2012)

- Show that the framework of *joint density functional theory* provides a rigorous and efficient method for solvation in QMC, without need for phase space sampling of the fluid.
- Allows calculation of free energies and thermodynamic averages of solvated systems.
- They have a special procedure allowing self-consistency of the joint calculation to be obtained (along with estimate of the remaining errors) to within chemical accuracy, all at the cost of only a single QMC total-energy calculation carried out in a fixed external potential.
- Can be applied to molecules and surfaces, and e.g. surface reactions in liquid environments.

Hydrogen storage

Desirable to replace petrol as a fuel with portable form of hydrogen (since plenty of it, high energy density, and used efficiently by fuel cells). Use materials-based H storage - trade some of high energy/mass performance to improve low energy/volume performance.



- Requires very particular material with desorption enthalpy ΔH^0 in precise 20 kJ/mol range (to allow recharging under moderate pressure and desorption under moderate temp). Difficult to achieve since chemical bounds normally too strong and hydrogen bonds usually too weak..
- *Metal hydrides* (where the metal is e.g. Li, Na, Mg, Al) good candidates: high H content, thermodynamically stable relative to physisorption materials.
- However most metal hydrides bind with H very strongly - high T required to release it ($\longrightarrow$ low equilibrium vapour pressure). Can improve this by using alloys which consists of 'strong' hydride and 'weak' one e.g. LiNH_2 , LiBH_4 and NaBH_4 . These are able to form weaker bonds, thereby requiring less energy input to release stored hydrogen. Also: using *nanoscale* particles could help: surface energy then additional lever to adjust ΔH^0 .

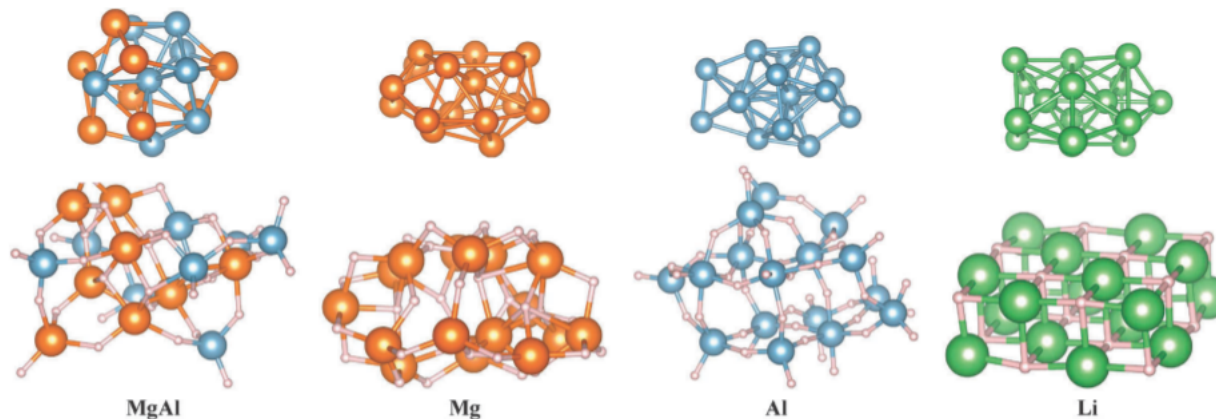
Basic questions

- (1) To what extent can we use size and composition to control ΔH^0 in metal hydrides?
- (2) How much can we rely on DFT in such cases?

Hydrogen storage

Wagner *et al.* used DMC to compute change in energy in the reaction $(MH_m)_n \longrightarrow M_n + \frac{mn}{2}H_2$ for $M = \text{Li, Mg, Al}$, and two alloys of MgAl. Motivation: MgH_2 is too stable, but AlH_3 is too unstable - attempt to 'interpolate between them'.

DMC shows that mixed Mg-Al nanoclusters are predicted to have intermediate stability, and that their size composition can be tuned to obtain H_2 desorption thermodynamics within the desired range for onboard H storage.

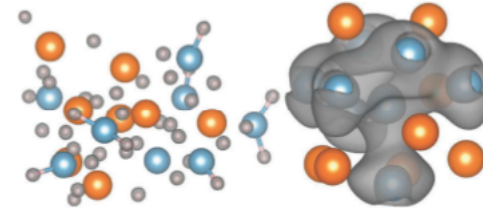


Calculations

- Generate minimum energy structures of metal hydride and pure metal clusters with number of metal atoms up to 20 (c. 1 nm regime, where most atoms reside at the surface). They use something like Pickard/Needs random structure searching.
- Evaluate hydrogen desorption energies ΔE with both DFT and DMC (good approximation to enthalpy ΔH^0 since standard pressure v. small compared to internal energy in these nanostructures).
- Do some test calculations with CCSD(T) extrapolated to complete basis set limit for the small clusters where this is feasible to check it agrees with DMC (it does).
- Calculate zero-point energy in the usual way when comparing to experimental numbers.

Hydrogen storage

- DFT results all over the place: functional-dependent spread of 30-40 kJ/mol. Not good enough to predict what kind of alloy/cluster will have a ΔH in some 20kJ/mol range.
- Generally, hydride nanoparticles are ionic (H acts as charge acceptor) but pure metal clusters increase metallic character with size. DFT not capable of reliably calculating difference between such qualitatively different electronic states.



- ‘More sophisticated’ functionals (M06, B3LYP) no better than LDA and PBE.
- Idea of ‘interpolation’ really does work:

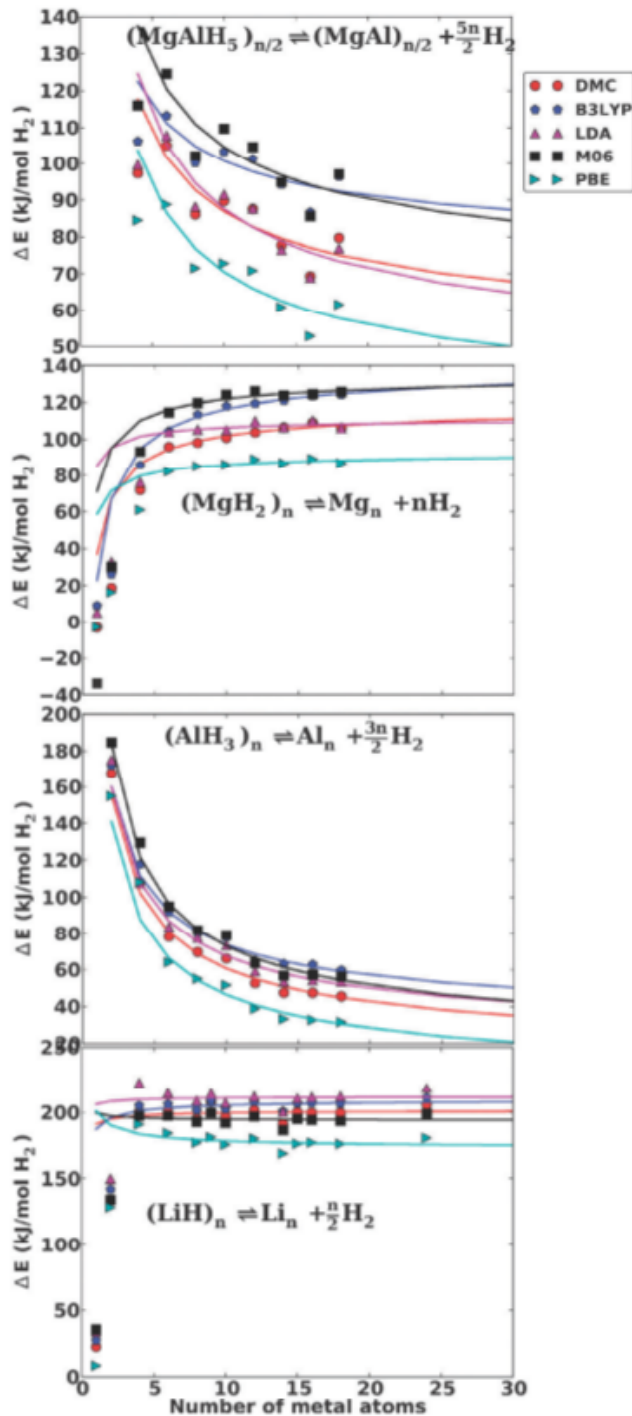
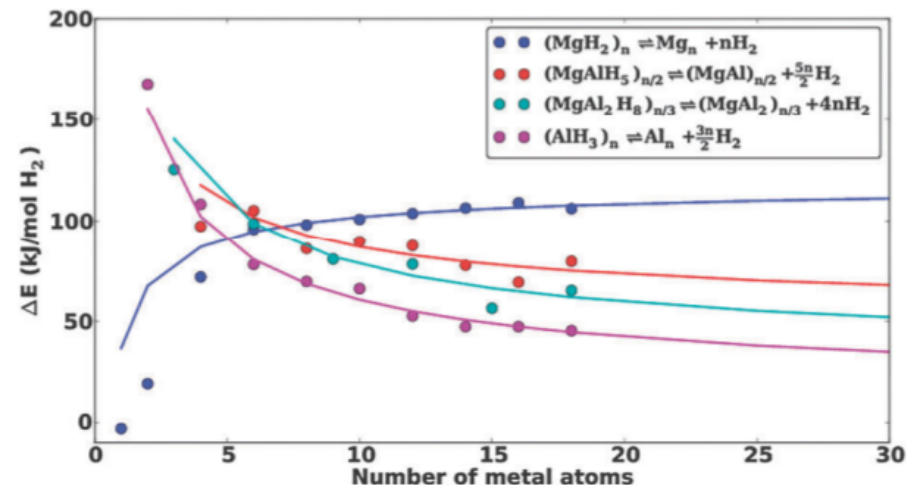
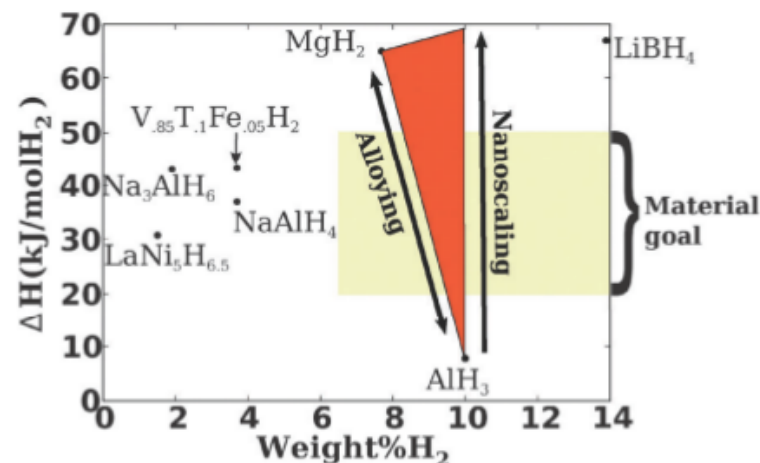


Fig. 3 The trends of the reaction energy for various methods, along with fits to $\Delta E(n) = \alpha/n^{2/3} + \beta$ (solid lines). The stochastic errors of the DMC data are smaller than the symbol sizes. The CCSD(T) result are indistinguishable from the DMC results on these scales.



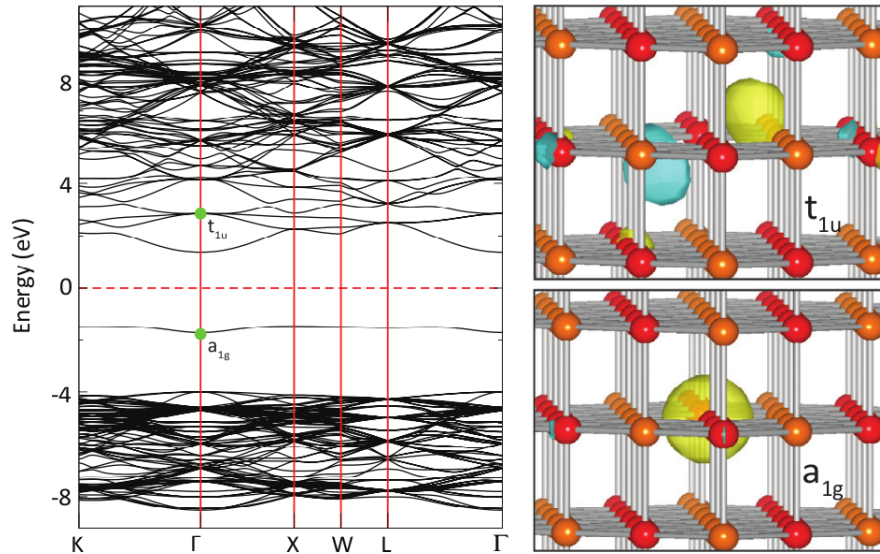
Hydrogen storage: conclusions

- High-accuracy DMC scaling curves for the hydrogen desorption energy of several different intermetallic alloys were computed as a function of nanoparticle size. Strong size dependence in the scaling of ΔE as the nanoparticle size becomes close to 1 nm. Specific predictions for nanoparticle sizes with ΔE in the correct range were made (see paper). Occurs for MgAl and Al clusters only, not Mg or Li.
- Similar predictions with DFT depend hugely on the chosen functional, and are simply not reliable.
- The computational cost of the several hundred required DMC calculations was not prohibitive (about the same as the relaxation of the atomic coordinates in DFT). Future calculations should therefore use DMC energetics to correct the DFT ones.
- Alloying can significantly alter the size range in which the nanoparticles have the desired desorption energies. The alloys are generally *stabilized* by nanoscale effects.
- So here we have a suggestion for a **tunable hydrogen storage system** that uses alloys of Mg and Al. Either the alloy composition or particle size can be tuned to optimize the ease of making and storing the nanoparticles, while the other variable can be tuned to obtain the correct desorption energy. Kinetics at the nanoscale will likely be much improved over the bulk systems.



Defect energetics

'Point-defect optical transitions and thermal ionization energies from quantum Monte Carlo methods: application to the F -center defect in MgO, Ertekin, Wagner, Grossman, *Phys. Rev. B* **87**, 155210 (2013).



DFT-PBE band structure for 64-atom MgO cell containing single oxygen vacancy. Introduces localized midgap defect level of symmetry a_{1g}

- Application of QMC to F -center defect (oxygen vacancy) in MgO: defect formation energies, thermal ionization levels, optical ionization energies.
- Experimental properties ambiguous. Different charge states apparently have near-identical optical absorption energies. GW and now DMC disagree. Time for reassessment of experiment?
- DFT band gap severely underestimated - problem for midgap defect states, defect energetics, defect-induced optical adsorption/emission energies!
- DMC treatment of pure MgO: calculate ground state E_0 , Γ -point optically excited state $E_{\Gamma \rightarrow \Gamma}$, and the positively and negatively charged states E_+ and E_- . Then ionization potential $IP = E_0 - E_+$, electron affinity $EA = E_- - E_0$, quasiparticle gap $QP = EA - IP$, optical gap $E_{\Gamma \rightarrow \Gamma} - E_0$. Good agreement with experiment where possible to compare; DFT not.

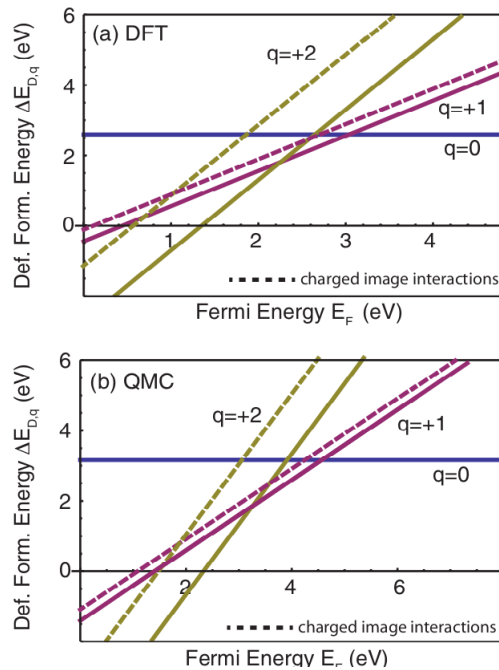
Compute defect formation energies:

$$\Delta E_{D,q} = (E_{D,q} - E_{\text{perf}}) - \sum_i n_i \mu_i + q(E_V + E_F)$$

Here $E_{D,q}$ is the (computed) total energy of the supercell containing a defect D in the charge state q , and E_{perf} is the (computed) total energy of the perfect supercell. The n_i is the number of atoms of species i added to create the defect (can be negative). The μ_i are the set of chemical potentials to represent different environmental conditions. E_V is energy of valence band maximum (ionization potential in DMC), and E_F is the Fermi energy referenced to E_V so that $0 \leq E_F \leq E_g$ where E_g is the band gap.

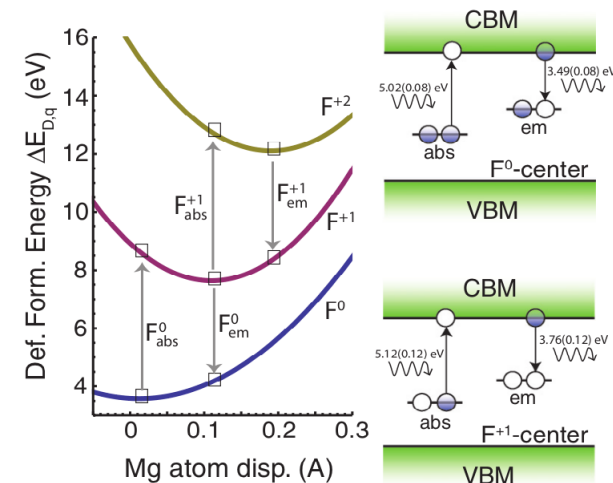
Charged defects introduce electrostatic image interactions between neighbouring supercells which manifest as finite size errors. These can be estimated using an extrapolation approach. For simplicity the authors use the DFT extrapolation; even though expensive this can also be done in QMC in principle, and probably should be since differences in electron localization and screening in the two approaches should lead to different answers..

Defect energetics



- Thermal ionization energies correspond to the Fermi energies at which the energetically most-favoured charge state of the defect changes.
- Creation of an F^0 centre results in formation of filled midgap defect level. Very little lattice relaxation on removal of O.
- When electron is removed to form F^{+1} centre, there is large lattice relaxation - positive Mg ions move outward away from and negative O ions move inward towards, the positively charged vacancy in conjunction with a 0.55 eV drop in energy (DFT). Further ionization to form F^{+2} centre gives further lattice relaxation and energy recovery of 1.18 eV.
- Defect formation energies and thermal ionization energies plotted on left as function of Fermi energy. Note domain of Fermi energy (length of x -axis) determined by the band gap of the method in question (which is much better for DMC).
- DMC modifies somewhat the absolute values of the defect formation energies (by 0.5eV for F^0), but maintains thermal ionization levels near midgap. DMC shows that DFT underestimates formation energies in the case of occupied midgap levels.

- QMC description of optical ionization energies (which correspond to vertical Franck-Condon transitions).
- Optical transition occurs when photon absorbed or emitted by defect - takes place essentially instantaneously at fixed atomic coordinates. Therefore compute these transition using the relaxed coords of the *initial state*. Implies difference between absorption and emission.
- DMC absorption energies in excellent agreement with experiment and GW calculations. DMC emission energies agree with GW, but disagree with experiment. GW authors suggest experimental people have misinterpreted their results (something to do with electrons in the defect level recombine with holes in the valence band). Our QMC people agree with this.



	F^0_{abs}	F^0_{em}	F^{+1}_{abs}	F^{+1}_{em}
QMC	5.0(1)	3.8(1)	5.1(1)	3.5(1)
GW ⁸	4.95	3.6	4.92	3.4
Exp	5.00	3.1-3.2	4.95	2.3-2.4

Application of QMC to point defects still relatively new field, but lots of fascinating possibilities!

Databases/high-throughput QMC

Various efforts are ongoing to create standard benchmarks and databases of DMC results for large numbers of material with different types of binding.

Requires development of consistent, automated procedures to achieve high throughput. See, for example:

'Quantum Monte Carlo applied to solids', Shulenburger, Mattsson,
Phys. Rev. B **88**, 245117 (2013)

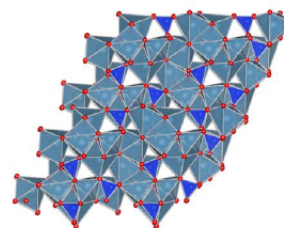
'Quantum Monte Carlo for materials design', Mueller,
http://vallico.net/talk_archive/mueller_tti2013.pdf

The Long-Term Goal

1. Material designer dreams up new material for some technology. Calculated material properties look promising.

2. Designer runs QMC on hypothetical material and checks stability against database of known free energies.

3. Designer determines whether it is worth synthesizing the material, and under what conditions it might be synthesized.



"By 2016-ish, we should be able to calculate QMC energies for every known inorganic material on a single supercomputer in about a week (roughly)." [Tim Mueller, Vallico Sotto, August 2013]

Other work on photovoltaics

Band alignment: 'Quantum Monte Carlo simulation of nanoscale MgH_2 cluster thermodynamics', Wu, Allendorf, Grossman *J. Am. Chem. Soc.* **131**, 13918 (2009); see also 'Charge separation in nanoscale photovoltaic materials: recent insights from first-principles electronic structure theory', Kanai, Wu, Grossman *J. Mater. Chem. Soc.* **20**, 1053 (2010).

- Problem of 'band alignment' - critical for designing new solar cell materials and for surface physics. Requires accurate ΔE between systems with very different electronic character ($\longrightarrow$ no DFT!).
- For case considered by Wu, DFT predicted Type II junction suitable for heterojunctions; DMC predicted unsuitable Type I junction ($\longrightarrow$ elimination from consideration for solar materials..).

Se-doped silicon: 'Insulator to metal transition in selenium hyperdoped-silicon: observation and origin', Ertekin, Winkler, Recht, Said, Azia, Buonassisi, Grossman, *Phys. Rev. Lett.* **108**, 026401 (2012).

- DMC calculations aided significantly in interpretation of experimental attempt to produce intermediate band defect states.
- Experiment detected large increase in light absorption in Se-hyperdoped silicon. Metal insulator transition? Intermediate bands?
- Difficult to distinguish with DFT because of band gap problems. Metal-insulator transition seen in DMC - provided confidence that the light absorption was not due to an intermediate band.

Amorphous silicon: 'Microscopic description of light-induced defects in amorphous silicon solar cells', Wagner, Grossman, *Phys. Rev. Lett.* **101**, 265501 (2008).

- Studied hydrogenated amorphous Si (well-established thin-film technology used in e.g. flat panel displays). Requires simultaneous accurate barrier heights, excited states, defect energy estimation.
- Disadvantage: hole transport very slow, and degrades further upon exposure to light.
- Helped by accurate large scale DMC calculations, W+G found new degradation channel that involves bond rotations to create stressed regions of silicon bonds that can trap holes.

Strongly correlated materials

From Wikipedia, the free encyclopedia

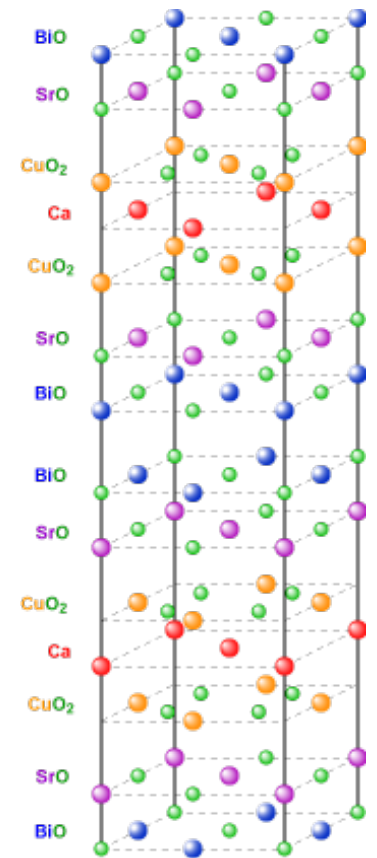
"Strongly correlated materials are a wide class of electronic materials that show unusual (often technologically useful) electronic and magnetic properties, such as metal-insulator transitions or half-metallicity. The essential feature that defines these materials is that the behavior of their electrons cannot be described effectively in terms of non-interacting entities. Theoretical models of the electronic structure of strongly correlated materials must include **electronic correlation** to be accurate.

Many transition metal oxides belong into this class which may be subdivided according to their behavior, e.g. high- T_c , spintronic materials, Mott insulators, spin Peierls materials, heavy fermion materials, quasi-low-dimensional materials, etc. The single most intensively studied effect is probably **high-temperature superconductivity in doped cuprates**, e.g. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Other ordering or magnetic phenomena and temperature-induced phase transitions in many transition-metal oxides are also gathered under the term 'strongly correlated materials'.

Typically, strongly correlated materials have *incompletely filled d - or f -electron shells* with narrow energy bands. One can no longer consider any electron in the material as being in a 'sea' of the averaged motion of the others (also known as mean field theory). Each single electron has a complex influence on its neighbors.

The term strong correlation refers to behavior of electrons in solids that is **not well-described** (often not even in a qualitatively correct manner) by simple one-electron theories such as the local-density approximation (LDA) of density-functional theory or Hartree-Fock theory. For instance, the seemingly simple material NiO has a partially filled $3d$ -band (the Ni atom has 8 of 10 possible $3d$ -electrons) and therefore would be expected to be a good conductor. However, strong Coulomb repulsion (a correlation effect) between d -electrons makes NiO instead a wide-band gap insulator. Thus, strongly correlated materials have electronic structures that are neither simply free-electron-like nor completely ionic, but a mixture of both.

Extensions to the LDA (LDA+U, GGA, SIC, GW, etc.) as well as simplified models Hamiltonians (e.g. Hubbard-like models) have been proposed and developed in order to describe phenomena that are due to strong electron correlation. Among them, Dynamical Mean Field Theory successfully captures the main features of correlated materials. Schemes that use both LDA and DMFT explain many experimental results in the field of correlated electrons."



The perovskite structure of BSCCO, a high-temperature superconductor and a strongly correlated material

NB: must understand what the above means when translated to our language - not the same thing. In general 'strongly correlated electron physicists' misunderstand what we do. QMC actually very promising approach to accurately computing everything required with no parameters - a fact not generally appreciated..

Some background: linear chain of hydrogen atoms



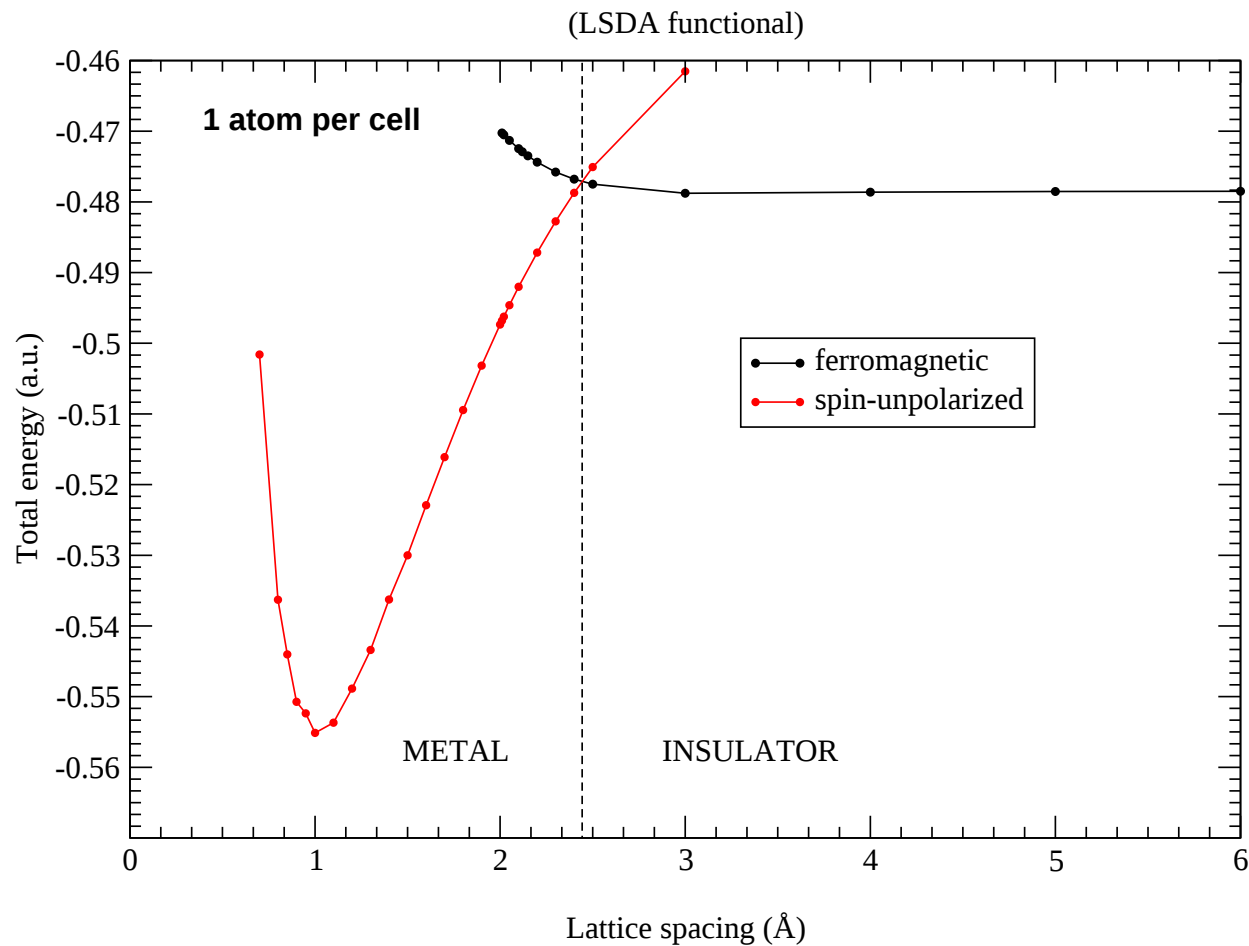
“Consider a linear chain of hydrogen atoms with a lattice constant of 1 Å. This has one electron per atom in the conduction band and is therefore metallic. Imagine we now dilate the lattice parameter of the crystal to 1 metre. We would agree that at some point in this dilation process the crystal must become an insulator because certainly when the atoms are 1 metre apart they are not interacting. But band theory says that the crystal remains a metal because at all dilations the energy difference between occupied and unoccupied states remains vanishingly small. Now look at this thought experiment from the other way. Why is the crystal with a lattice parameter of 1 metre an insulator? Because to transfer an electron from one atom to another we have to supply an ionization energy, I to remove the electron and then we recover the electron affinity, A , when we add the electron to the neutral H atom. The energy cost in this process is $U = I - A$. Band theory ignores terms such as these.”

[From recent solid-state textbook.. Not true, of course!]

Hubbard model (for reference)

$$H = \sum_{i,j} t_{ij} a_{i\sigma} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

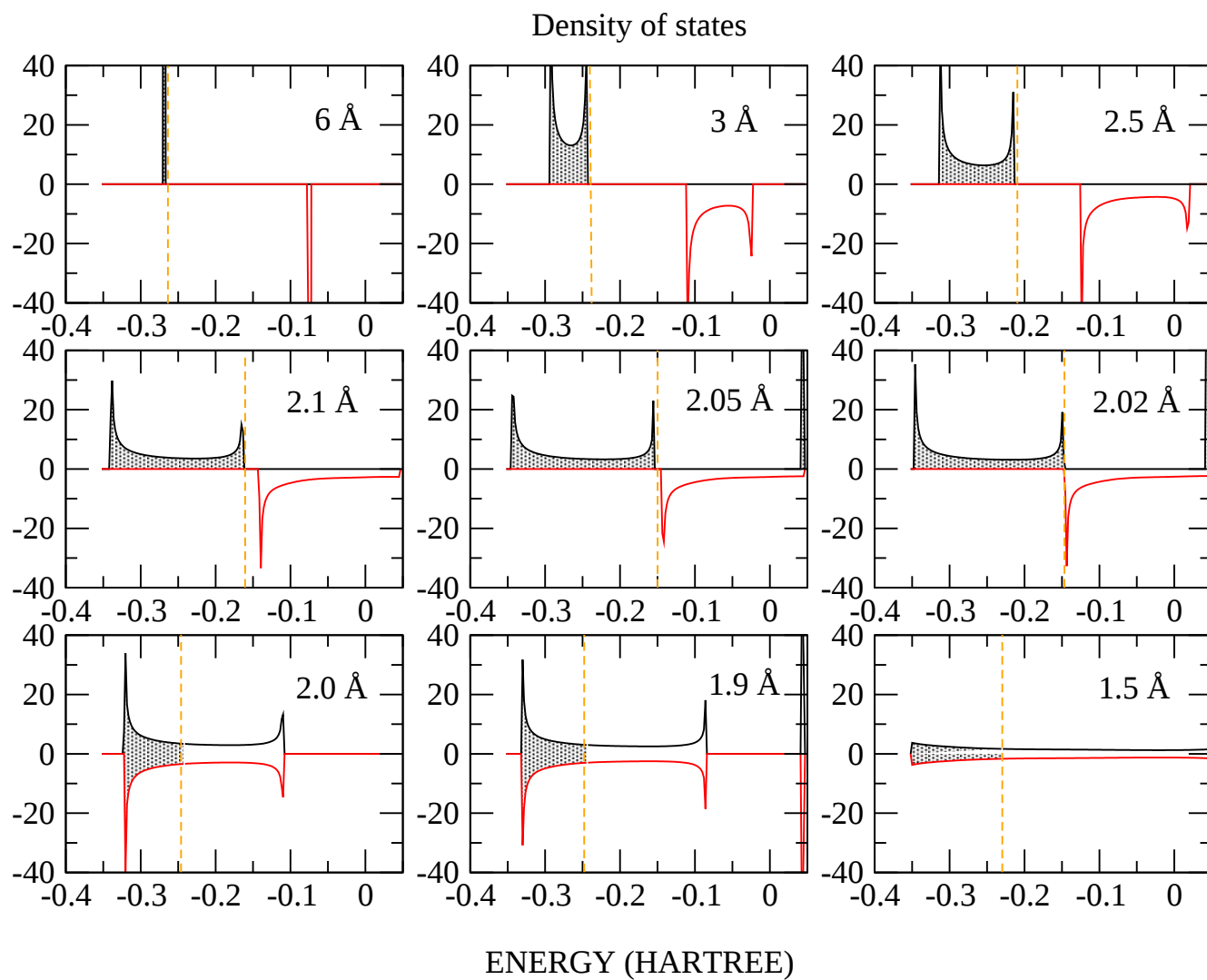
Spin-unrestricted band treatment of linear hydrogen chain



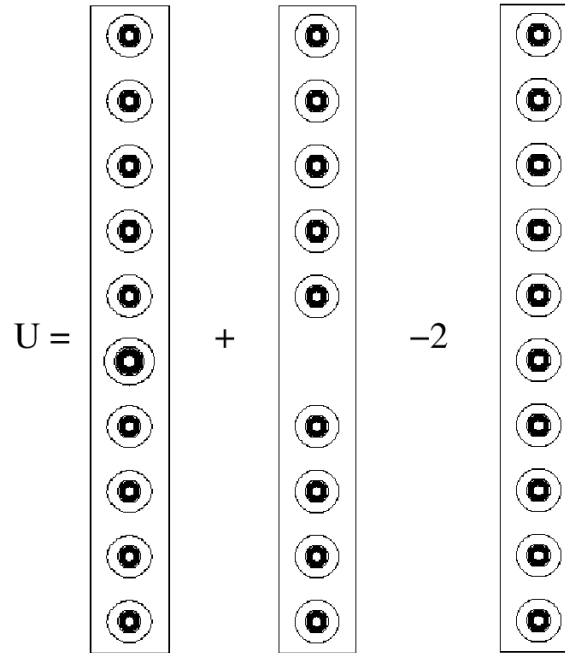
There's your metal-insulator transition. So it actually works fine using DFT-LDA (and, for that matter, Hartree-Fock), so long as you remember to allow spin polarization! As who wouldn't..

Spin-unrestricted band treatment of linear hydrogen chain

Hydrogen linear chain



N+1/N-1 system



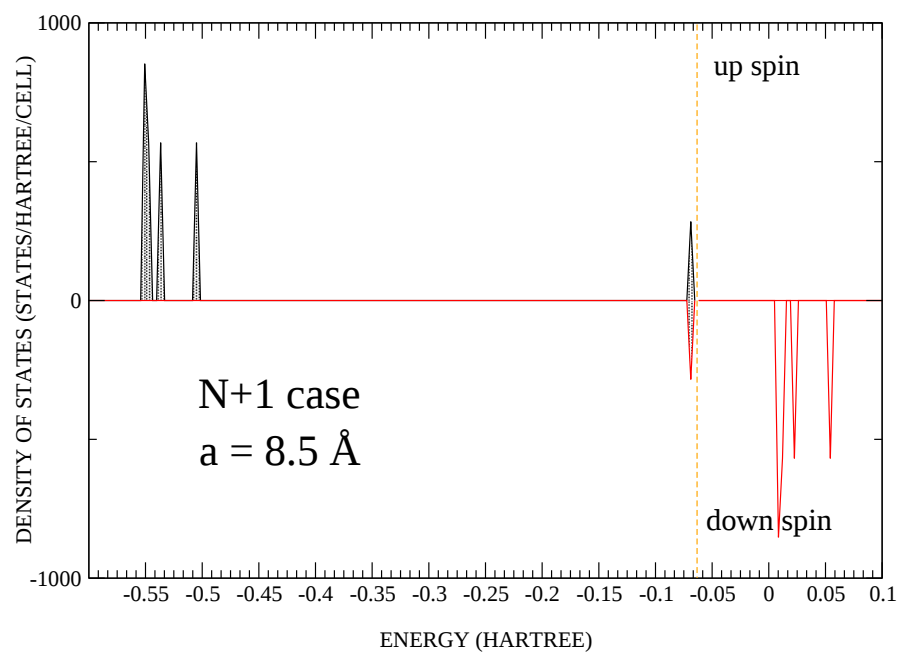
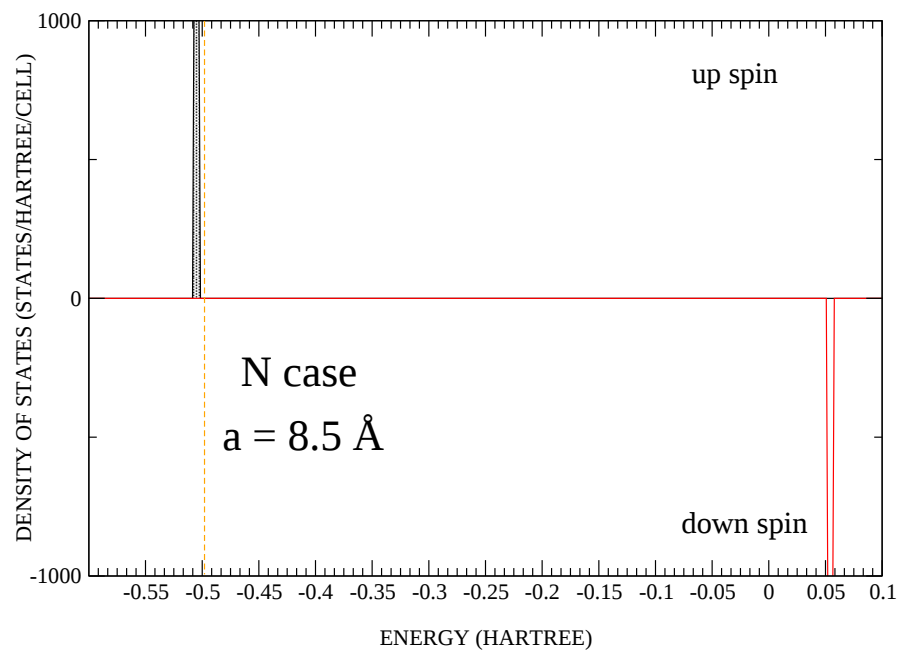
U = ionization energy [$E(N + 1) - E(N)$] minus electron affinity [$E(N) - E(N - 1)$]

	LSDA (eV)	UHF (eV)	B3LYP (eV)
U (as above)	11.44	13.03	12.01
U (Band gap)	5.30	11.99	8.56

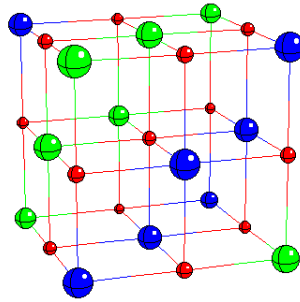
Should be around 13 eV

So subtract electron affinity from ionization potential (using calculations where you explicitly have an extra electron or a hole) and you can calculate U pretty much exactly in Hartree-Fock theory! LDA and GGA calculations give a reasonable approximation to that (with self-interaction errors). Taking U from the one-electron energies (band gap) is a further approximation which ignores relaxation (like Koopmans). Here this is good in Hartree-Fock and much worse in DFT-LSDA etc..

Effect of extra electron on the density of states



Wikipedia prototypical strongly-correlated system: NiO



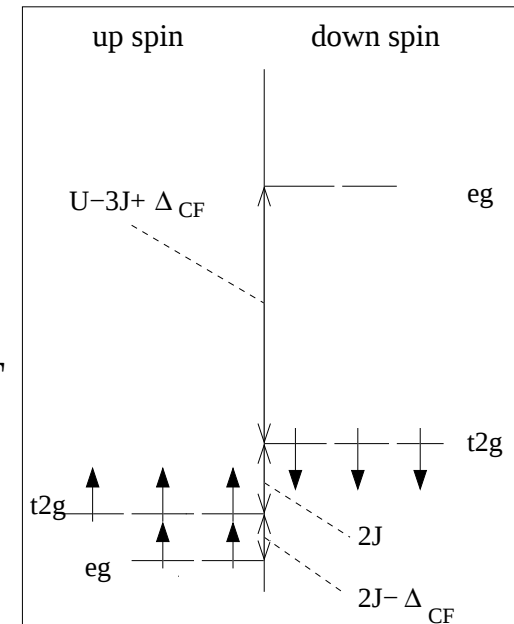
Interactions

'Mott insulator'. Parameterize on-site interactions in terms of U and U' (Coulomb interactions between electrons in same (U) or different (U') d orbitals) and J (exchange interaction between same spin electrons). Augment with Δ_{CF} i.e. crystal-field splitting energy due to neighbours.

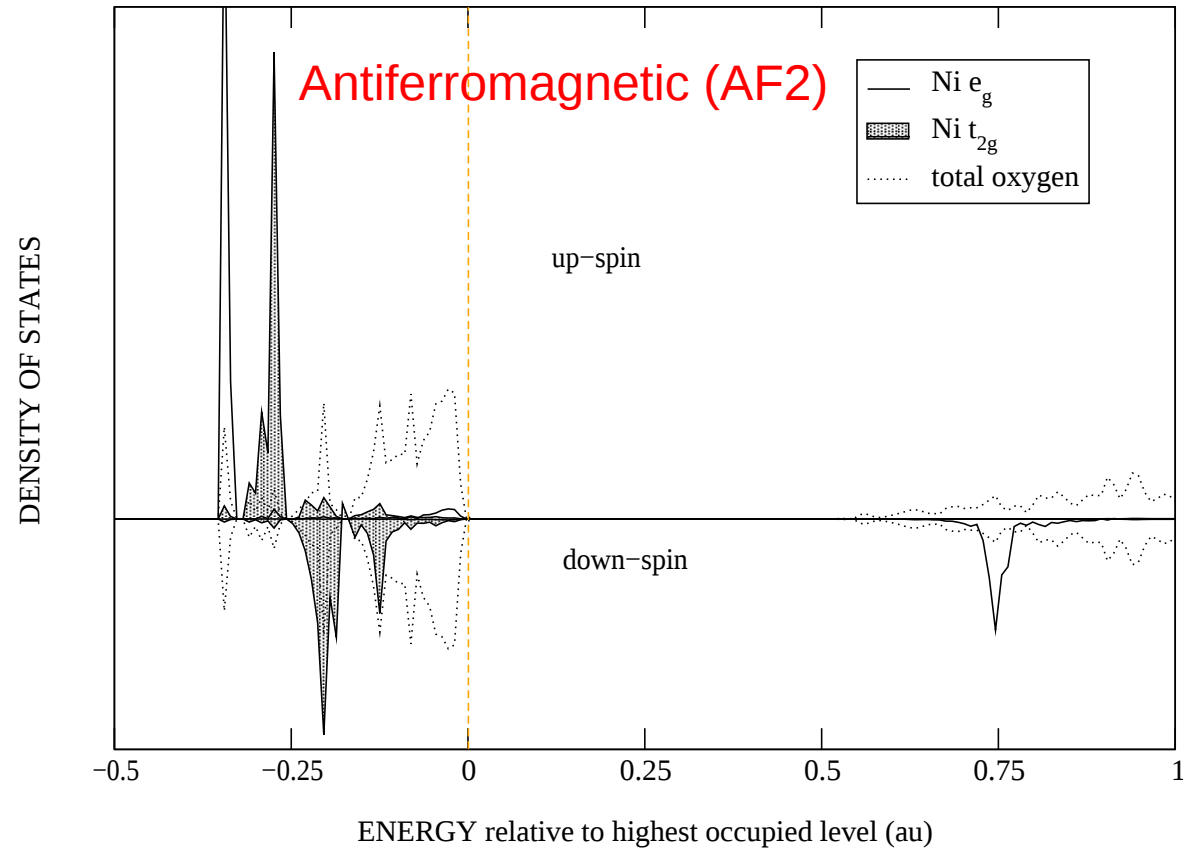
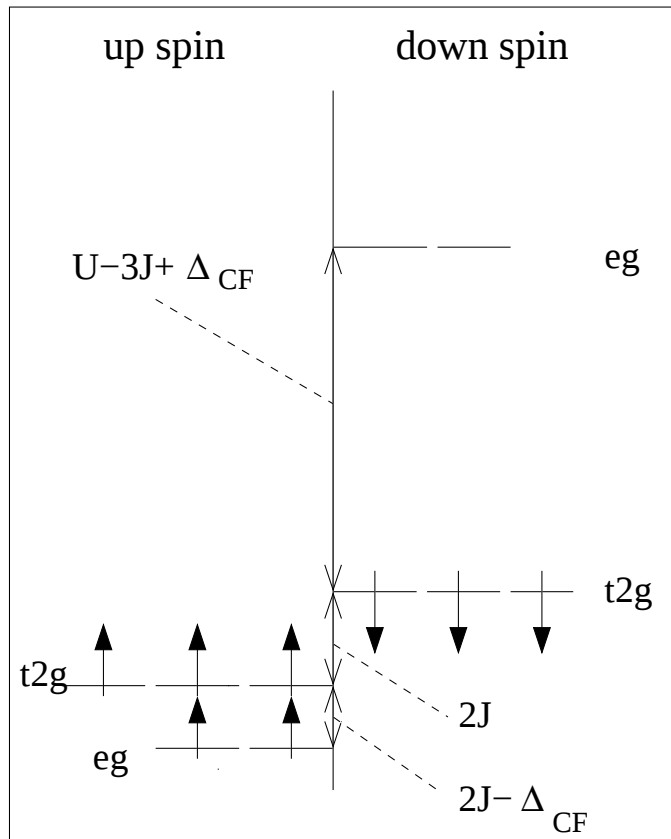
On a Ni site in NiO:

$\uparrow$ -spin e_g electron feels:	$7U' - 4J + \Delta_{CF}$
$\uparrow$ -spin t_{2g} electron feels:	$U + 6U' - 4J$
$\downarrow$ -spin e_g electron feels:	$U + 7U' - 3J + \Delta_{CF}$
$\downarrow$ -spin t_{2g} electron feels:	$U + 6U' - 2J$

Expt: $U=5.8\text{eV}$, $J=0.67\text{eV}$, $U'=4.5\text{eV}$, $\Delta_{CF}=1.1\text{eV}$



Model vs. unrestricted Hartree-Fock

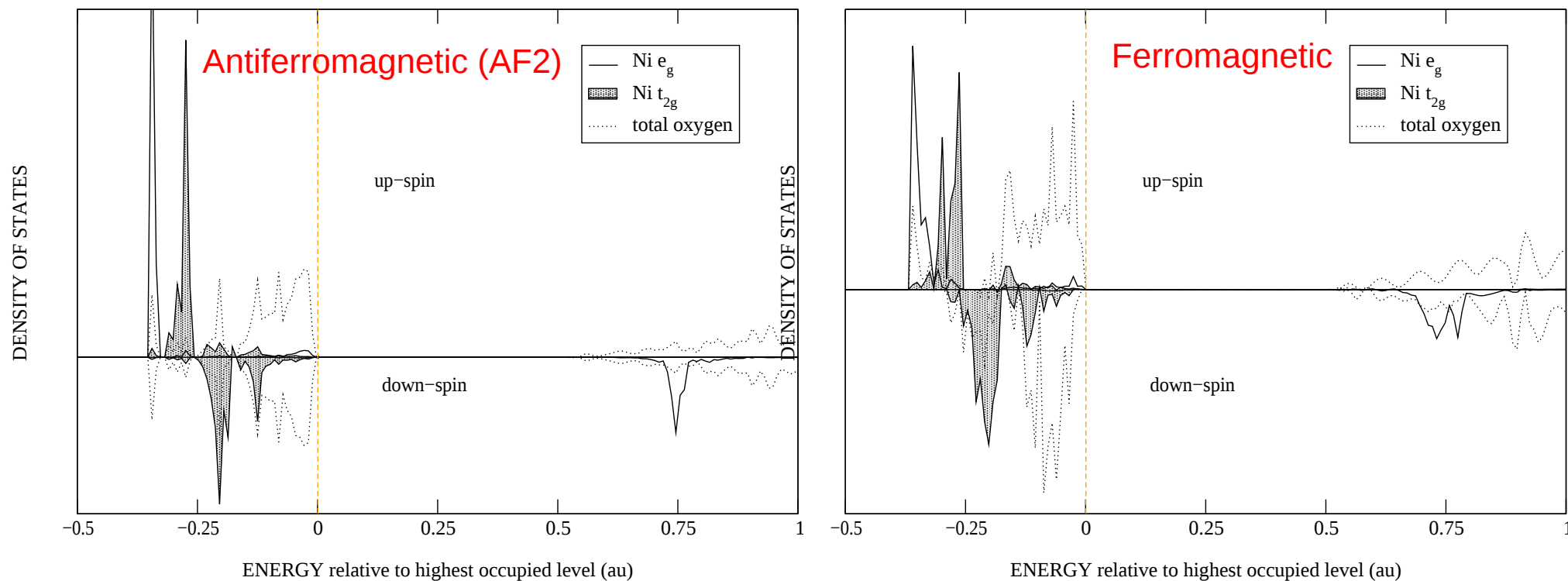


UHF gives a wide band gap insulator with the states exactly where a 'multi-orbital Hubbard model' says they should be, i.e., qualitatively the right answer!

But Wikipedia said 'simple one-electron theories' like Hartree-Fock theory are 'not even qualitatively correct'.. ['ganz falsch' - not even wrong..]

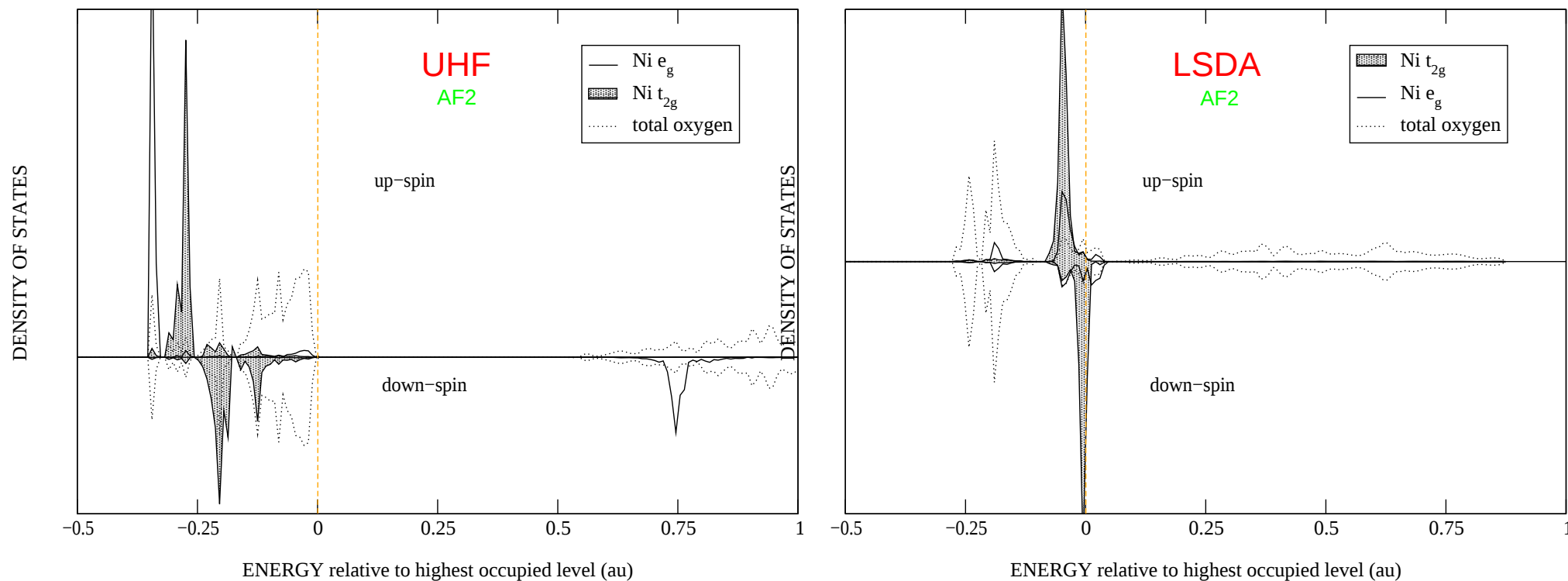
Something is very wrong with the 'standard view' - but you will find that nobody cares. Reminds me of trying to persuade people that de Broglie-Bohm theory isn't complete nonsense.

Hartree-Fock: effect of magnetic ordering



Not much!

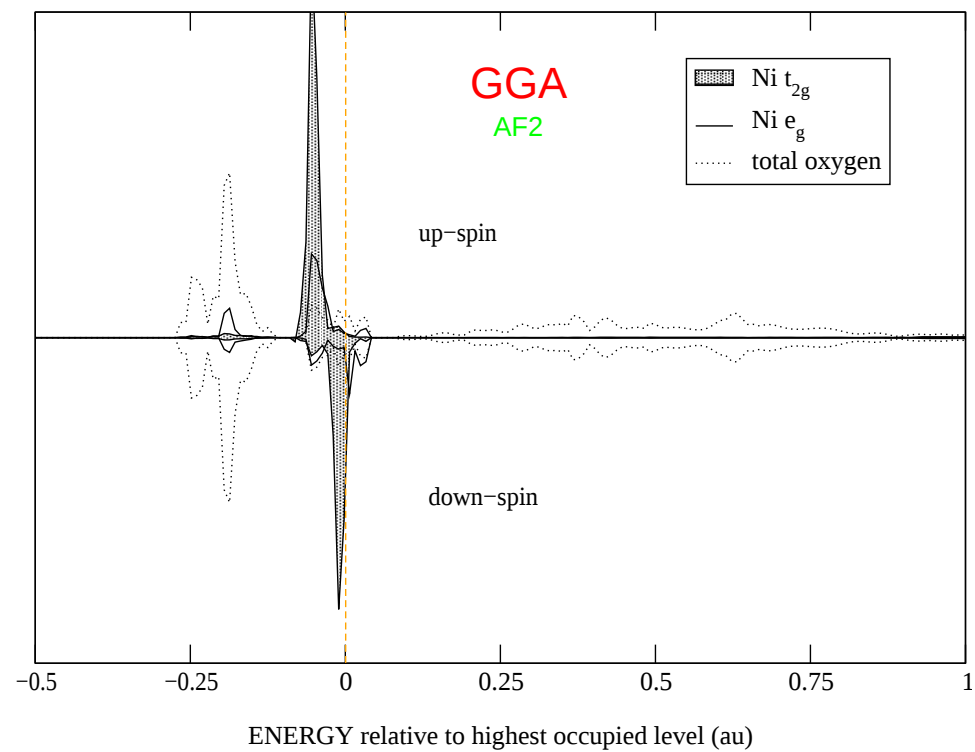
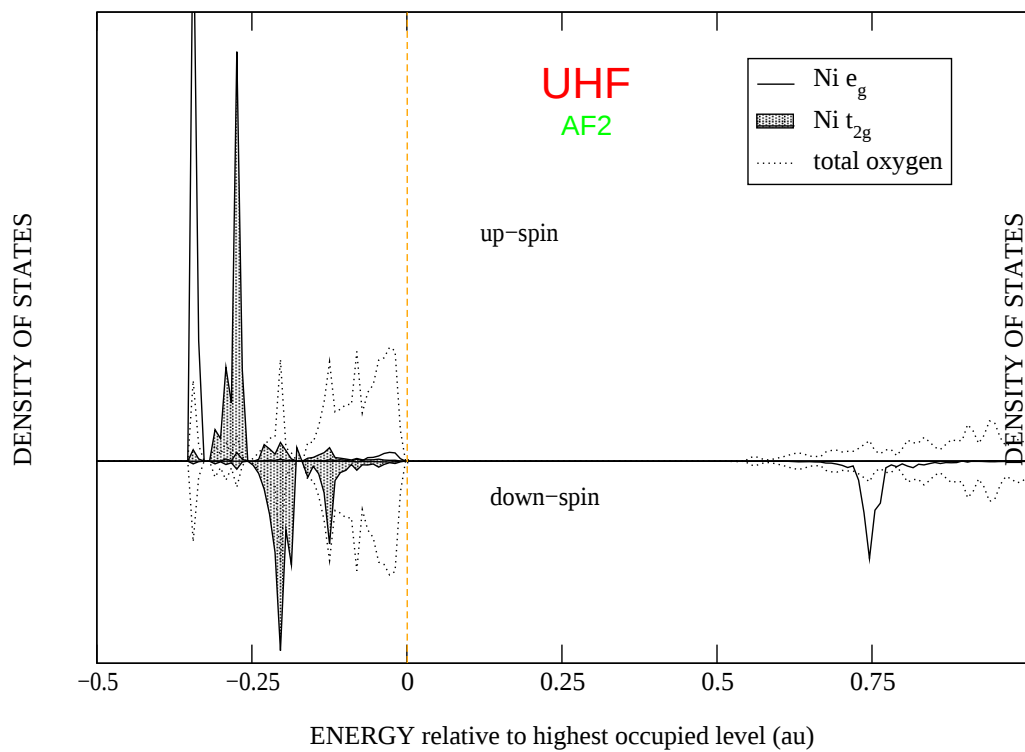
Hartree-Fock vs. DFT-LSDA



Metallic. Ah!

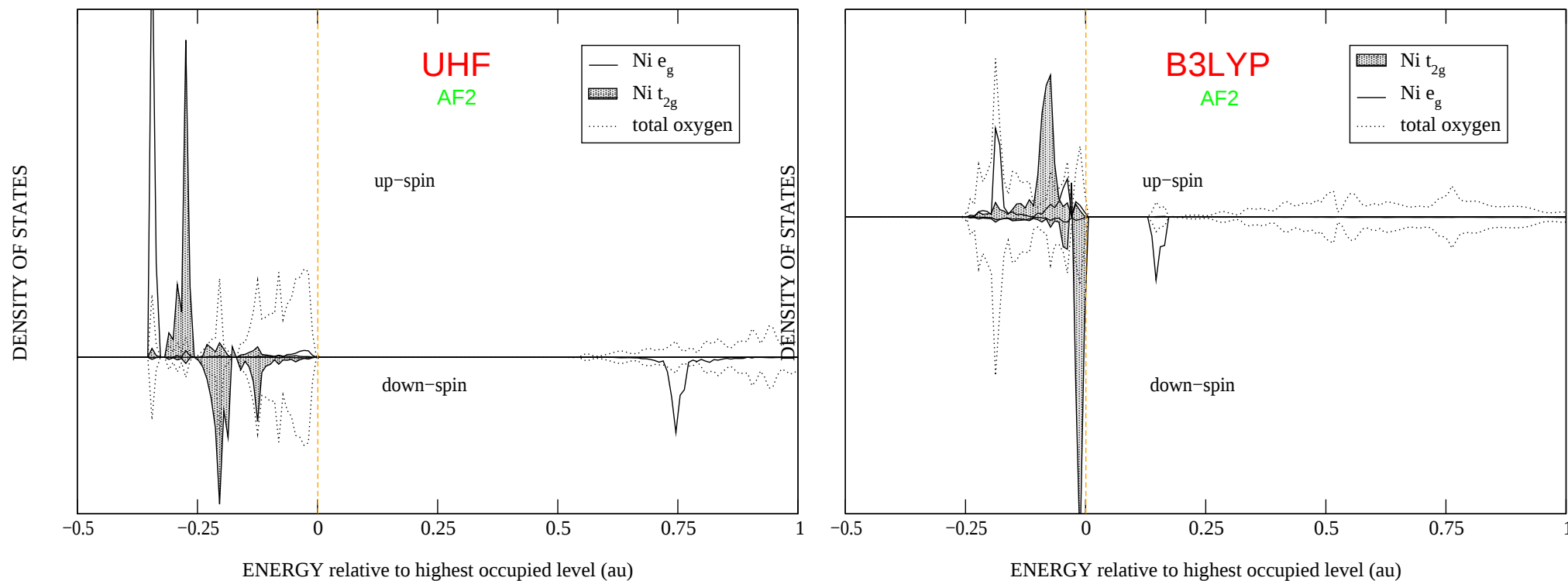
LSDA doesn't 'split the states' correctly; only effect is that up-spin Ni states are slightly lower in energy than down-spin Ni states. This is simply because there are more up-spin electrons and the energy lowering effect of exchange is proportional to the number of electrons of that spin (i.e. each up-spin electron 'keeps out of the way' of the other 7 electrons more effectively than do the down-spin ones).

Hartree-Fock vs. DFT-GGA



Same as DFT-LSDA

Hartree-Fock vs. DFT-B3LYP



Now we get a gap. Looks a lot better.

B3LYP is hybrid functional which mixes in a proportion of Hartree-Fock non-local exchange. Introduces appropriate 'orbital-dependent potential' to drive formation of a 'strongly-correlated' state.

Self-interaction - Hartree-Fock case

- Label orbitals occupied ($a, b, \dots$) or virtual ($i, j, \dots$).

What is the expression for the orbital energy?

$$\epsilon_a = \langle \phi_a | \hat{h} | \phi_a \rangle + \sum_{b=1}^N \text{Occupied} (\langle \phi_a \phi_a || \phi_b \phi_b \rangle - \langle \phi_a \phi_b || \phi_b \phi_a \rangle)$$

$$\epsilon_i = \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{b=1}^N \text{Virtual} (\langle \phi_i \phi_i || \phi_b \phi_b \rangle - \langle \phi_i \phi_b || \phi_b \phi_i \rangle)$$

- Sum over b is over occupied orbitals only. Therefore for the first expression only, one of the terms will cancel when $b=a$:

$$\langle \phi_a \phi_a || \phi_a \phi_a \rangle - \langle \phi_a \phi_a || \phi_a \phi_a \rangle = 0$$

- Therefore in the HF approximation an electron does not feel its own field, since the self-interaction is cancelled by an equivalent term in the exchange energy.

Self-interaction - LSDA case

- LSDA exchange energy $E_{exchange} = \int d^3\mathbf{r} \epsilon_x [\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})]$ and, since the mean-field contains all the electrons, then e.g. the LSDA energy of H atom is incorrectly -0.47 (or whatever) instead of -0.5 due to 'self-interaction'.

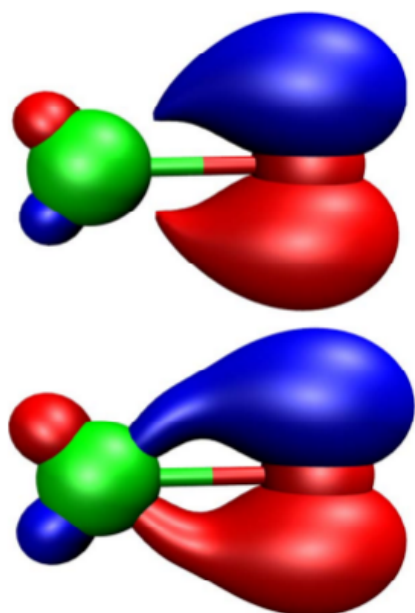
Implications:

- U (interpreted as the 'self-exchange' term) equals J (the 'different orbital' exchange term).
- But U and J differ by an order of magnitude in NiO. LSDA effectively *averages* these quantities.
- Therefore additional potential U felt by unoccupied orbitals disappears, and instead all the states are shoved up in energy by something like the average of U and J .
- Local density theory lumps all these exchange interactions together and thus dilutes the effect of self-exchange and underestimates the driving force for the formation of a correlated state. This is the root of the difficulty of contemporary calculations in describing strongly-correlated systems.

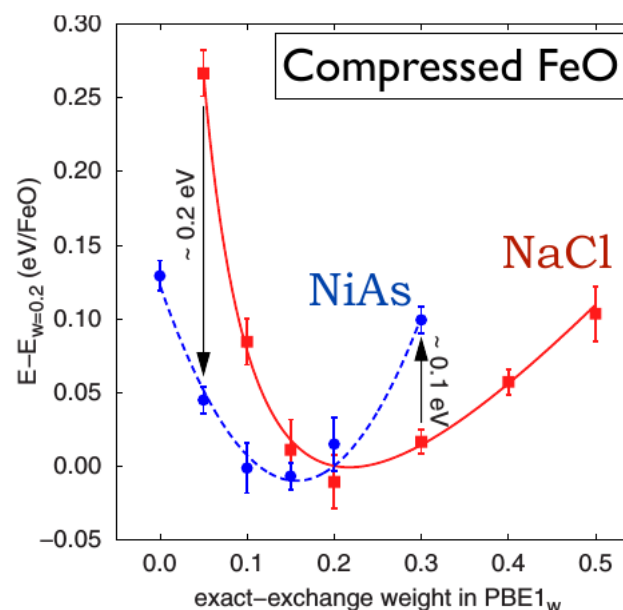
Note this is nothing to do with 'naive band theory' or 'simple one-electron theories' not containing the U term (©large numbers of people) - to a first approximation U is just a basic onsite Coulomb repulsion present even in Hartree theory! So this isn't physics, more of a 'convergence problem' with the simpler DFT exchange-correlation functionals. Suggests that we can get pretty good trial wave functions for such systems for use in QMC calculations - just use UHF or hybrid functionals instead!

Optimizing the nodal surface in strongly-correlated system

An excellent practical way to do this - exploiting the variational nature of the DMC method - is to treat the percentage of HF exchange in a hybrid DFT functional such as B3LYP as a variable parameter (effectively varying the amount of d - p hybridization). (Could also optimize orbitals directly; this is more difficult but not impossible. Multireference trial functions could also be useful in some circumstances.). This is not usually thought to be necessary for 'normal' compounds without transition elements where the nodal surface is usually 'good enough'.



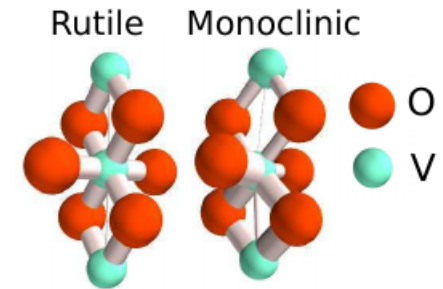
Above left is an isosurface of the d - p hybridization orbital for the TiO molecule, calculated in Hartree-Fock (above) and DFT-B3LYP (below). Oxygen atom in red on the right. Titanium in green on the left. UHF solution overionizes the p orbital and causes large fixed-node errors. See Wagner, *J. Phys.: Cond. Mat.* **19**, 343201 (2007).



Above right is graph showing variation in DMC energy as the nodal surface is varied with the exchange weight for two structures (NiAs and NaCl) of FeO.

Mechanism of vanadium dioxide (VO_2) metal-insulator transition

VO_2 undergoes metal-insulator transition at $T=340$ K, with accompanying decrease in conductivity of more than 4 orders of magnitude and change in structure from rutile (high T , V at centre of O octahedra, equidistant V) to monoclinic (low T , zigzag of V dimers).



Zheng and Wagner, arXiv:1310.1066 (Oct 2013)

Long-standing debate for 50 years whether transition is primarily caused by structural change that doubles the unit cell (Peierls distortion) or by 'strong correlation effects' that drive the system to become insulating.

Predictions of traditional theoretical methods

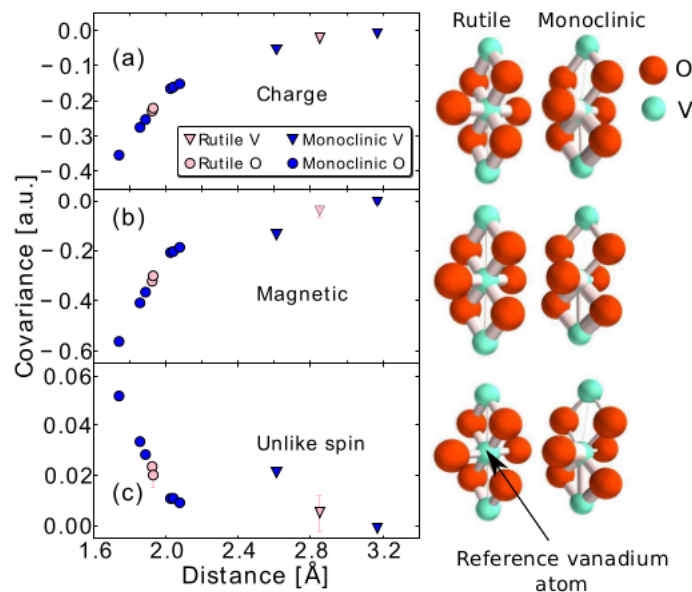
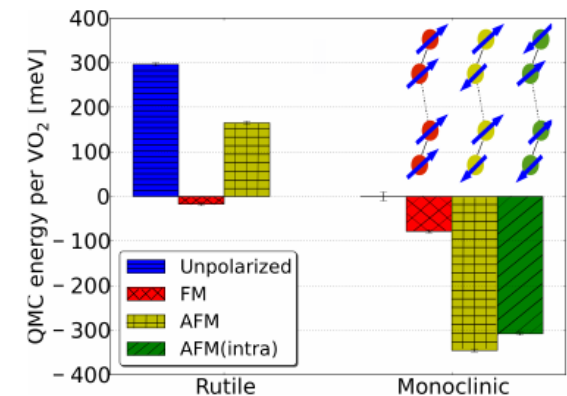
- **DFT(LDA), DFT(GGA)**: monoclinic VO_2 metallic (**wrong**)
- **DFT(hybrid functional)**: rutile metallic, monoclinic insulating (**yes!**); rutile lower in energy (**wrong**).
- **DFT+U**: monoclinic VO_2 insulating (**yes!**); rutile VO_2 insulating (**wrong**); incorrect magnetic GS for monoclinic VO_2 (**wrong**); depends on parameter; no total energy.
- **cluster DMFT**: correct gaps, but depends on parameters; no total energy.
- **GW**: correct gap; does not address magnetic properties; no total energy.

Predictions of DMC

Zheng and Wagner's DMC calculations (using PBE, PBE0, UHF trial wave functions from CRYSTAL09): correct low energy monoclinic structure for VO_2 ; correct energy gap and characterization of magnetic states for both phases, all in agreement with experiment (**yes!**)

What is the mechanism of the transition in VO₂ in DMC?

Structural distortion changes orbital hybridization and results in strong charge localization within V dimers - rearranges crystalline orbitals near Fermi surface, leading to strong magneto-structural coupling. In particular, get strong intra-dimer antiferromagnetic coupling in monoclinic VO₂ which drives system to a state made of spin-singlet dimers.



Clever bit: Calculate atomic charges $\langle n_i \rangle$, spins $\langle n_i^\uparrow \rangle$ and $\langle n_i^\downarrow \rangle$, and magnetic moments $\langle n_i^\uparrow - n_i^\downarrow \rangle$ (by counting electrons of a given spin in Voronoi polyhedra around each nucleus). Calculate fluctuations such as $\langle n_i^\uparrow - \langle n_i^\uparrow \rangle \rangle^2$ (zero in the atomic limit; large for metallic systems), and spatial correlations through covariances such as $\langle O_i O_j \rangle - \langle O_i \rangle \langle O_j \rangle$. (Can also associate such quantities with U and hopping t).

Intersite charge, magnetic moment, and unlike-spin covariance plotted on left. All decay with distance. Because of change in interatomic distances in monoclinic structure, intra-dimer V-V covariance $2\times$ that of rutile, inter-dimer V-V almost zero (dramatic decrease in charge mobility $\rightarrow$ insulator!). Magneto-structural coupling associated with substantial enhancement of intra-dimer charge fluctuations at expense of inter-dimer charge fluctuations. Monoclinic VO₂ forms weakly coupled spin-singlet V-V dimers rather than long-range AFM order (confirmed by intersite magnetic covariance).

MIT in VO₂ more complex than Peierls distortion (which just opens gap near Fermi surface). Strong correlations resulting in different magnetic couplings in rutile/monoclinic phases important. Both mechanisms will drive structural distortion, but amount of energy reduction due to intra-dimer singlet formation of same order as Peierls distortion with no magnetic ordering. Electron correlations provide crucial role in lowering E and opening large gap.

DMC provides high accuracy with no parameters.. can solve 50-year old problems. Good!

High- T_c cuprates with DMC

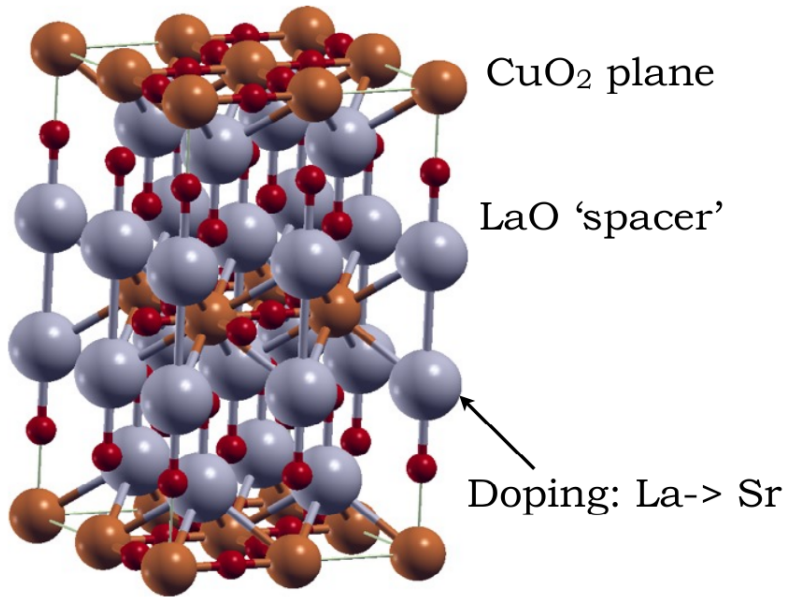


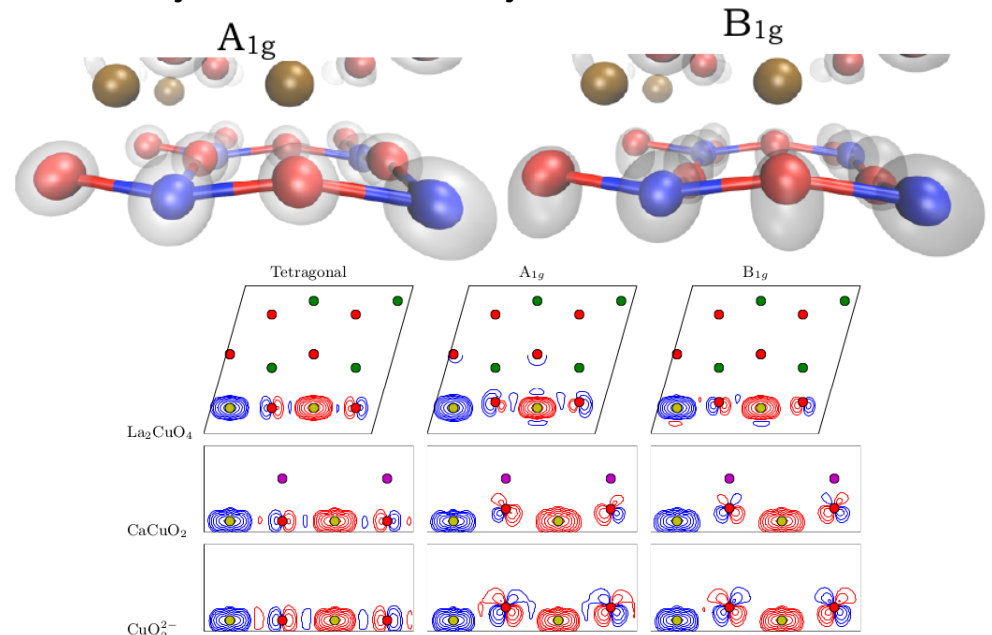
TABLE I: Validation of the first-principles FN-DMC calculation for La₂CuO₄. The B_{1g} and A_{1g} modes refer to the oxygen buckling modes in the tetragonal symmetry labeling. The hypothetical A_{1g} mode used for comparison here is not an eigenmode of the dynamical matrix, and thus does not have an experimental value.

Quantity	PBE ^a	PBE0	FN-DMC	Experiment
J (eV)	0.34	0.16	0.160(13)	0.14
Mag moment of Cu (Bohr)	0.36	0.69	0.6	0.6
Quasiparticle gap (eV)	0.33	3.86	2.0(3)	2.2
AFM B _{1g} freq (meV)	30	30	32(1)	33 12
FM B _{1g} freq (meV)	24	25	25(1)	
AFM A _{1g} freq (meV)	42.8	45.1	45(1)	
FM A _{1g} freq (meV)	39.9	43.7	43(1)	

Proper understanding of these materials still lacking after decades of research; clear that spin, charge, and lattice degrees of freedom are active in the phase space near the superconducting state, but precise roles still controversial. Difficult to probe experimentally and theoretically.

Wagner and Abbamonte did DMC calculations of undoped La₂CuO₄, CaCuO₄, and a hypothetical unsupported CuO₂²⁻ plane. *Very accurate results with no parameters* for all basic properties: spin coupling J , correlated gap, Cu magnetic moment, and s -wave A_{1g} and d -wave B_{1g} phonon frequencies.

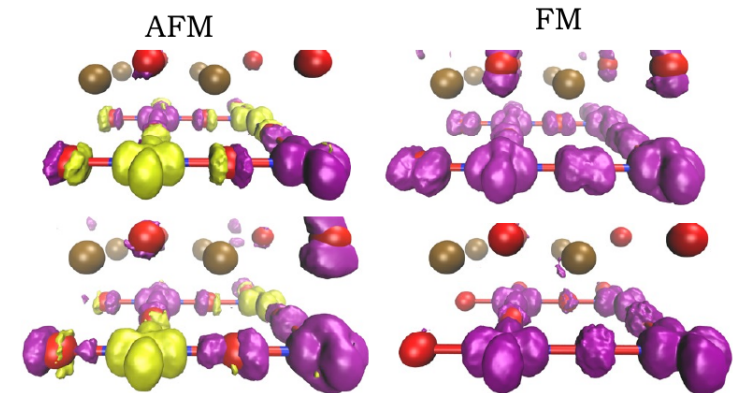
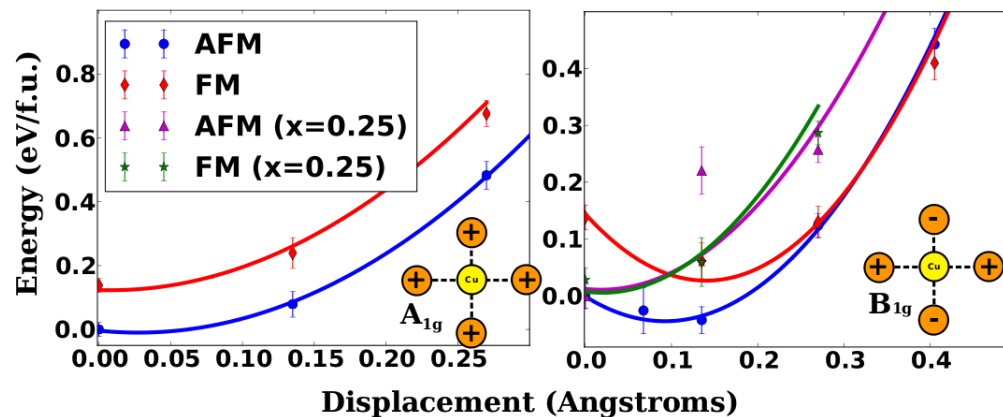
arXiv:1402.4680 (2014)



Superconductivity in cuprates with QMC

Experimentally B_{1g} mode shifts and broadens on entering the superconducting state, while A_{1g} does not. Wagner-Abbamonte DMC showed modes differ through interaction with interlayer - comparing La_2CuO_4 (apical O), CaCuO_4 (no apical O), and the pure CuO_2^{2-} plane (no interlayer at all). In A_{1g} mode interlayer prevents magneto-elastic coupling, mainly by shifting phonon frequency up. Plot bottom right of previous slide shows Cu-O bonding/superexchange clearly affected by interlayer once phonon mode is activated. Thus DMC results show magneto-elastic coupling highly dependent on supposedly inert plane layers - may help explain why different cuprates have very different T_c :

Doping



Some lattice degrees of freedom depend strongly on the magnetic state!

However - spin lattice coupling removed with 25% doping.

This is because hole introduced by doping sits on *oxygen* (which mediates the AFM ‘superexchange’ interaction). Upper valence band mainly O states for later 3d oxides (Ni, Cu, etc.).

[See my previous ESDG talks and various papers on manganites, KCuF_3 , Li-doped NiO, La_2CuO_4 etc.. This ancient one from 16 years ago is v. interesting: www.tcm.phy.cam.ac.uk/~mdt26/tmo/scm_talk.html. Glad someone has finally done what I suggested! I’ve been far too lazy..]

“Despite all these years, the mechanism of high- T_c superconductivity is still highly controversial, mostly due to the lack of exact theoretical computations on such strongly interacting electron systems”

[Wikipedia, ‘High-temperature superconductivity’, 2014] *Is that really all they need? Cool..*

Quantum Monte Carlo in 2016



- Quantum Monte Carlo is in good health, with groups from all over the world engaged in pushing the boundaries of what can be done with this technique.
- Computers are now fast enough that the application of QMC to proper, genuine scientific and technical problems is becoming routine.
- For many of these problems, QMC is the *only* known method which can normally be relied on to get the answer right without an unreasonable amount of computing effort.
- Much work remains to be done - in code development as much as in running applications. Get in touch if you're interested..

Engage with the QMC community:

<https://vallico.net/casinoqmc/>

<https://vallico.net/casino-forum/>