SMR 1595 - 16

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Joint DEMOCRITOS - ICTP School on
CONTINUUM QUANTUM MONTE CARLO METHODS
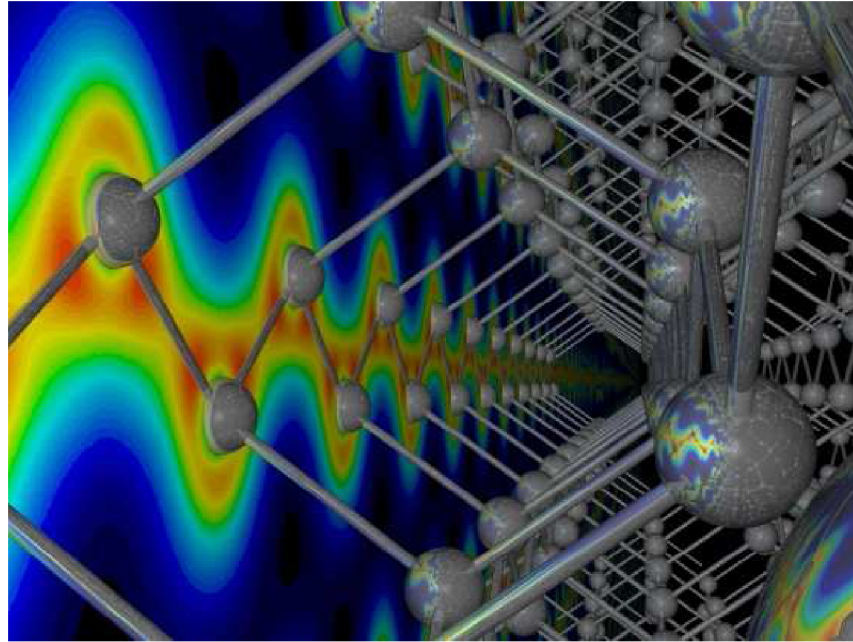**12 - 23 January 2004**

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(MOSTLY) SOLID-STATE APPLICATIONS

Mike TOWLER
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Cambridge CB3 OHE, U.K.

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These are preliminary lecture notes, intended only for distribution to participants.

(Mostly) Solid-state applications

What to do with your quantum Monte Carlo code

Mike Towler

Theory of Condensed Matter Group
Cavendish Laboratory
University of Cambridge

QMC web page: www.tcm.phy.cam.ac.uk/~mdt26/casino.html

Email: mdt26 at cam.ac.uk

What to talk about

- Cohesive energies

- The CASINO program

- Fullerenes

- Defects in semiconductors : self-diffusion in silicon

- Sample VMC calculation

- Exchange, correlation and density functional theory

- Sample variance minimization

- Excited states in diamond

- Sample DMC calculation

- Strongly correlated systems ; metals and insulators

- Sources of error and interesting current problems

[*references at end*]

Cohesive energies of tetrahedrally-bonded semiconductors (and NiO)

Method	Si	Ge	C	BN	NiO
LDA	5.28	4.59	8.61	15.07	10.96
VMC	4.48 ± 0.01	3.80 ± 0.02	7.36 ± 0.01	12.85 ± 0.09	8.57 ± 0.01
	4.38 ± 0.04		7.27 ± 0.07		
	4.82 ± 0.07				
DMC	4.63 ± 0.02	3.85 ± 0.02	7.346 ± 0.006	-	9.44 ± 0.01
Exp.	4.62 ± 0.08	3.85	7.37	12.9	9.45

Units: eV per atom Si/Ge/C and eV per 2 atoms BN/NiO

CASINÒ

The Cambridge Quantum Monte Carlo Code

R.J Needs, M.D. Towler, N.D. Drummond, P.R.C. Kent

casino m. **1** brothel, whorehouse **2** noise . . . **3** mess, $\langle volg \rangle$ screw-up

casinò m. casino

Basic CASINO capabilities

- VMC (+ variance minimization) and DMC (branching or with weights).

- Can treat atoms, molecules, polymers, slabs, solids, 2D/3D electron phases and 2D/3D electron-hole phases.

- Uses Slater-Jastrow wave functions where the Slater part may consist of (possibly spin-polarized) multiple determinants.

- Orbital expansions in plane-waves, blips, splines or atom-centred Gaussians (s, sp, p, d, f, g). Numerical orbitals on grids for atoms.

- Excited states from promotion, addition, or subtraction of electrons.

- Computation of distribution functions such as the pair correlation function.

- Written in strict Fortran 90 with some attempt at good software design. Parallelized using MPI . Tested in parallel on Hitachi SR2201, Cray T3E, SGI Origin, SGI Altix, Fujitsu Primepower, Sun Galaxy, IBM SP3, Linux clusters, and on single processor DEC Alpha, Linux PC, and SGI Octane.

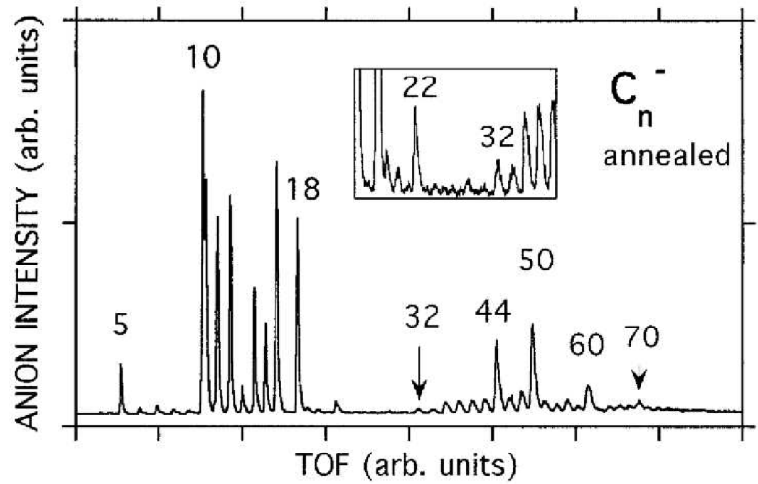- Quadratic scaling mode (otherwise known as 'linear' scaling).

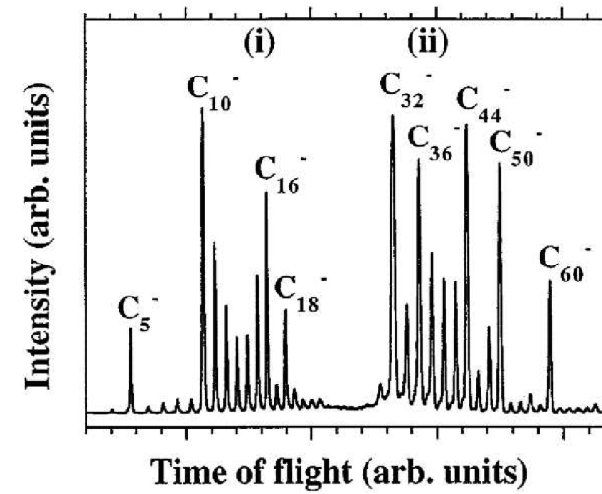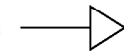www.tcm.phy.cam.ac.uk/~mdt26/casino.html

Interface to other packages
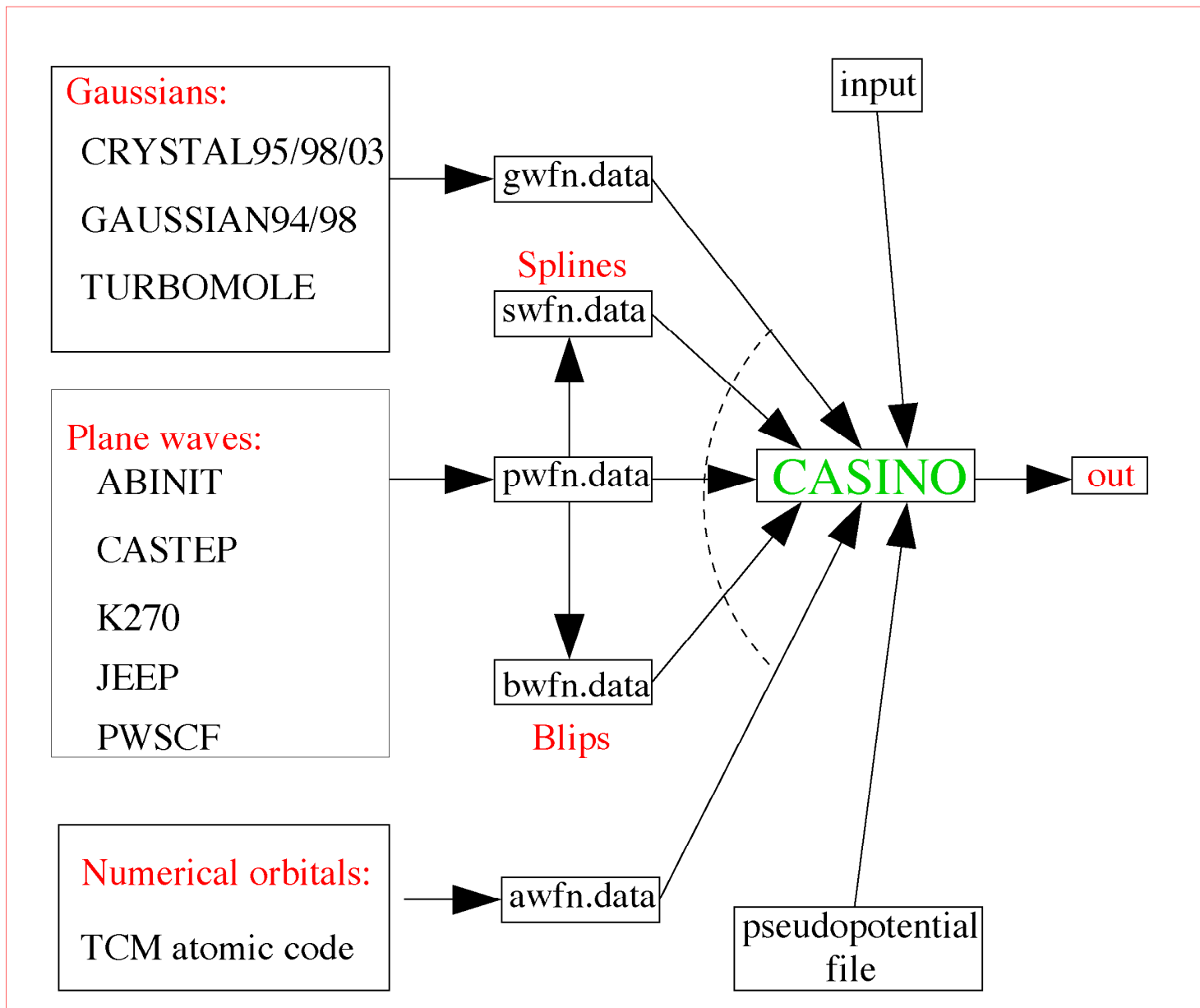
Carbon clusters near the crossover to fullerene stability

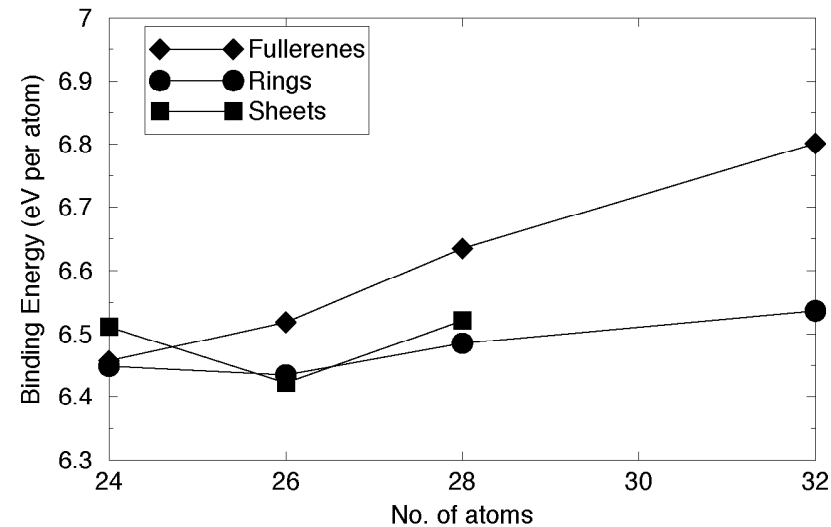Form clusters by laser vaporisation of graphite followed by annealing
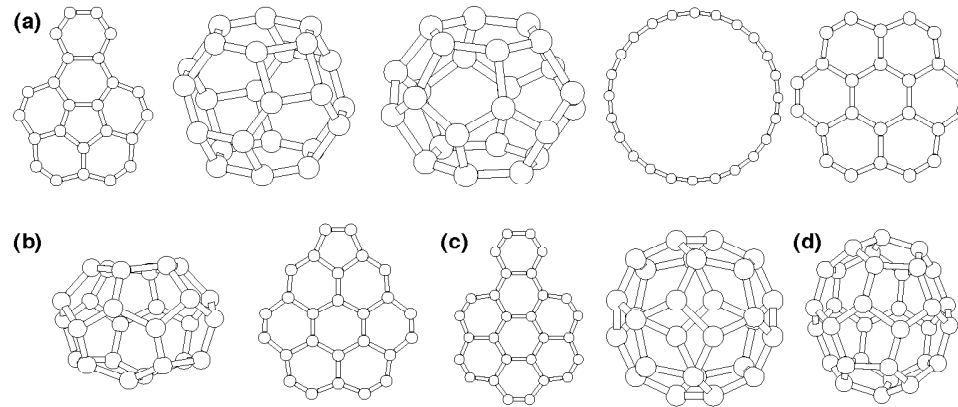

Handschuh *et al.*

Kietzmann *et al.*

Carbon clusters near the crossover to fullerene stability

Above DMC results sensible, but DFT/HF results show essentially arbitrary ordering depending on which functional is used. DFT *not good* for energy differences between very different systems (different coordination number/closed and open structures/metal-insulator etc..)

Self-diffusion in silicon

- Diffusion of impurity atoms critically influenced by self-interstitials and vacancies.

- Self-diffusion can be measured at high T using radioactive isotopes of silicon as tracers

$$
\begin{aligned}
D^{\mathrm{SD}} &= D_0^{\mathrm{SD}} \exp\left[-(4.1\!\rightarrow\!5.1 \text{ eV})/kT\right] \\
&\approx \sum_{\mathrm{mechanisms}\ i} C_i D_i
\end{aligned}
$$

Concentrations C_i and diffusivities D_i

- Somewhat indirect estimates give:

$$
\begin{aligned}
C_{\mathrm{I}} D_{\mathrm{I}} &= 914 \exp\left[-(4.84 \text{ eV})/kT\right] \\
C_{\mathrm{V}} D_{\mathrm{V}} &= 0.6 \exp\left[-(4.03 \text{ eV})/kT\right]
\end{aligned}
$$

- Can use electronic structure calculations to work out activation energy barriers from defect formation and migration energies.

# Silicon Defect Formation Energies

Defect	LDA	GGA	DMC
Split–$\langle 110 \rangle$	3.31	3.84	4.96(28)
Hexagonal	3.31	3.80	4.82(28)
Tetrahedral	3.43	4.07	5.40(28)
Concerted Exchange	4.45	4.80	5.78(27)

LDA, GGA and DMC formation energies in eV of the self-interstitial defects and the saddle point of the concerted–exchange mechanism.

- Activation energy from self-interstitial diffusion deduced from experimental measurements is 4.84 eV, compared with 3.5 and 4.0 eV for LDA and GGA respectively. Such energy differences have large effect on self-diffusion constant since it depends exponentially on the defect formation energy and the migration energy barrier.

- DFT results thus do not provide a satisfactory explanation of the experimental temperature dependence of the self-diffusivity. This appears to be essentially because LDA and GGA functionals are not reliable for calculating energy differences between structures with very different interatomic bonding.

- DMC estimate of activation energy is 5 eV. Appears to be in agreement with the experimental number.

Sample VMC calculation

Hydrogen atom
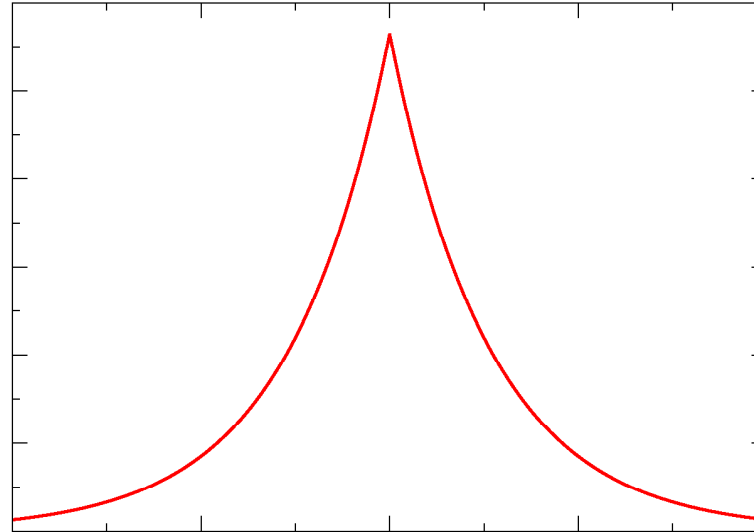
Let's compute the total energy with variational Monte Carlo!

Move an electron on a random walk around a proton using the Metropolis algorithm such that it samples a probability distribution equal to the square of the above wave function. Calculate the total energy every time it moves. Average the numbers at the end. We should get -0.5 Hartree.
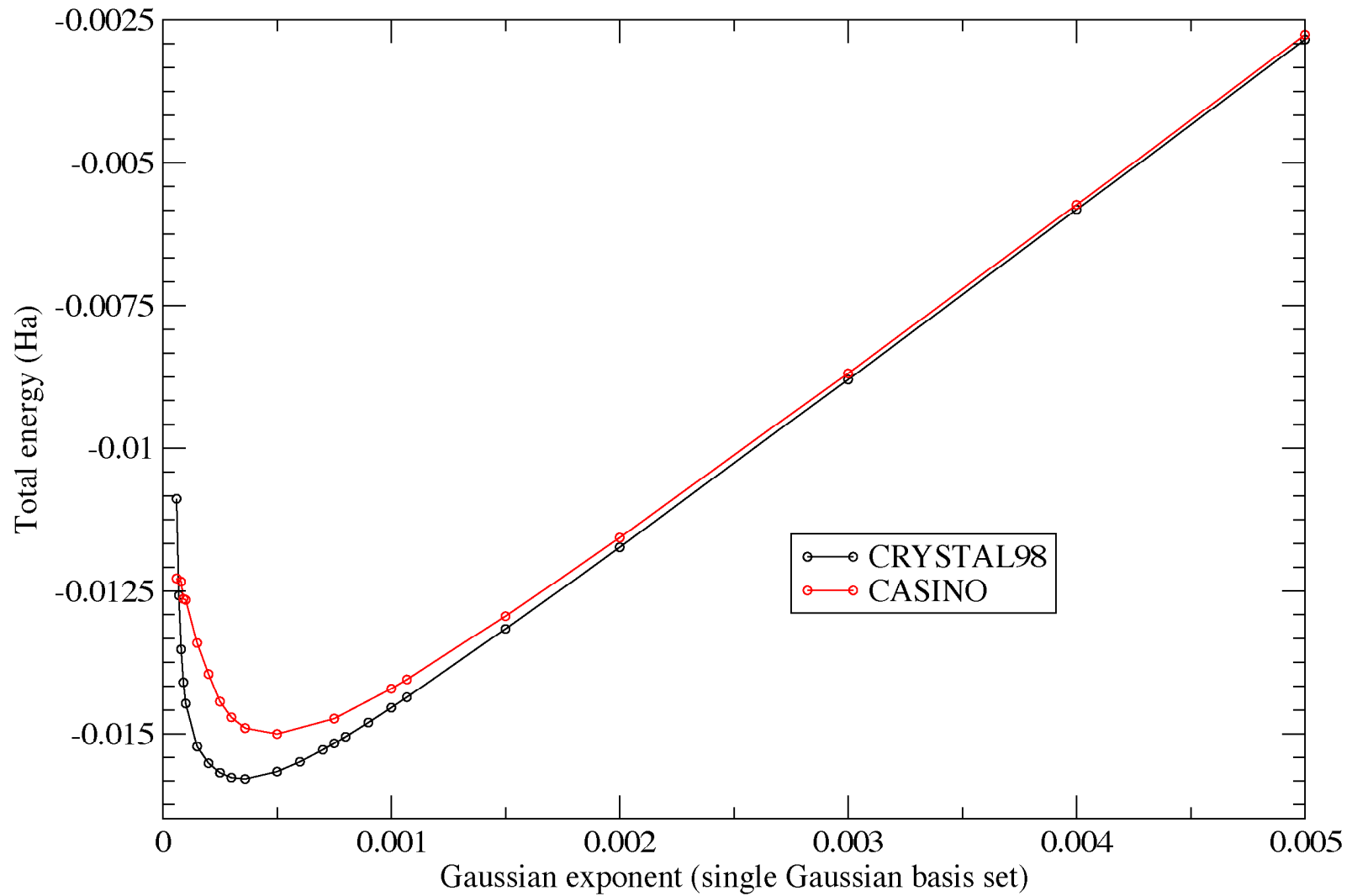
CRYSTAL Hartree-Fock   : -0.4999286

CASINO Hartree-Fock   : -0.50000767 ± 0.000075 (with cusp corrections).

But it's not as if the correlation energy in H atom is difficult to calculate!
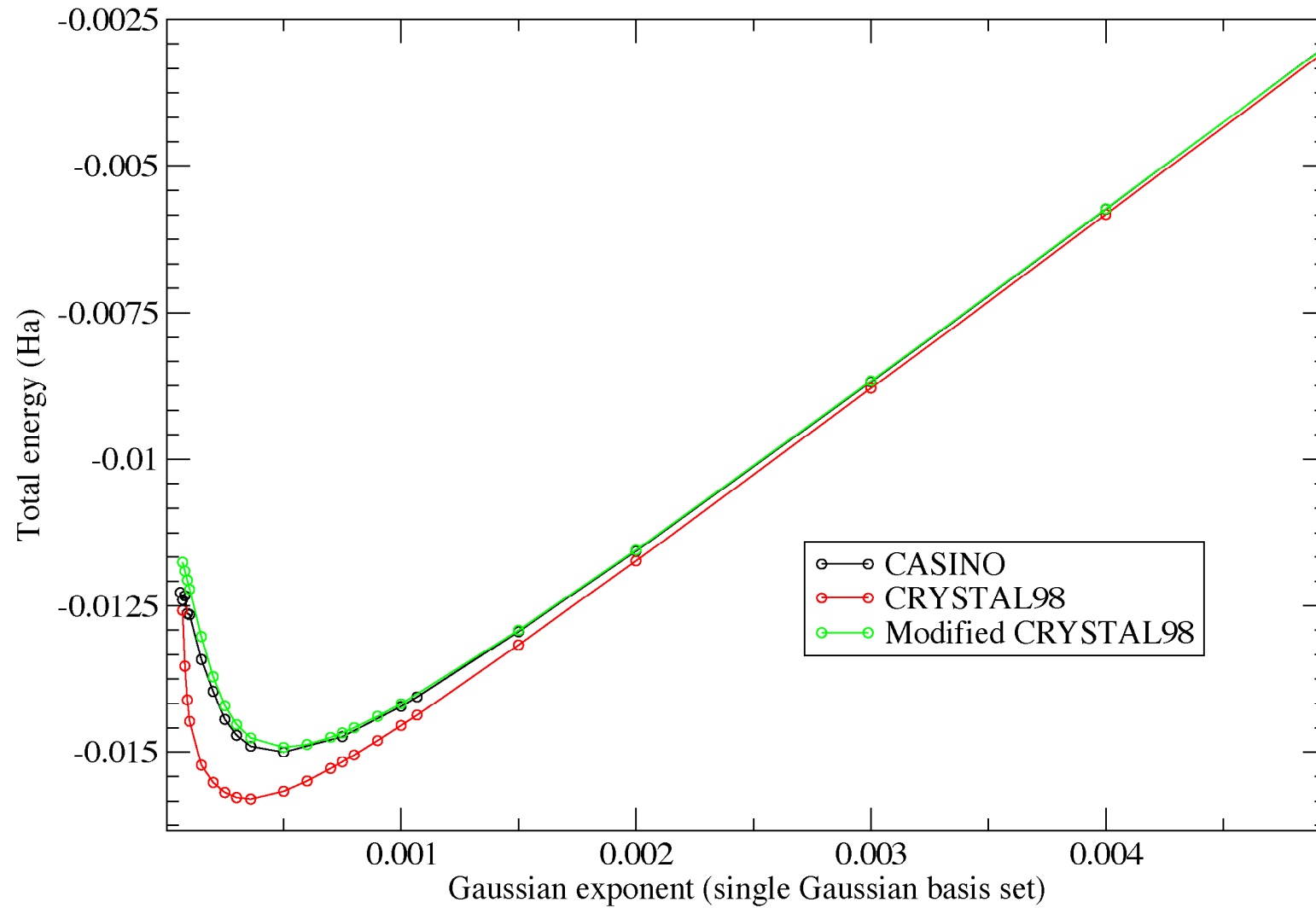Unless you use DFT! ('self-interaction' - try it..).

CRYSTAL and CASINO disagree!

Hartree-Fock energy of Wigner crystal ($r_s = 100$)
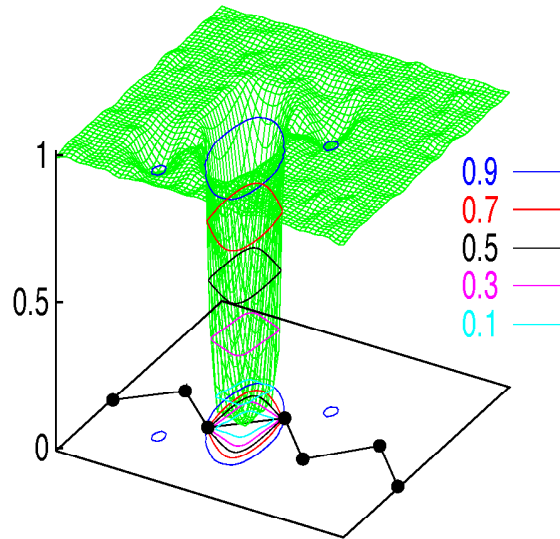
CRYSTAL and CASINO disagree!

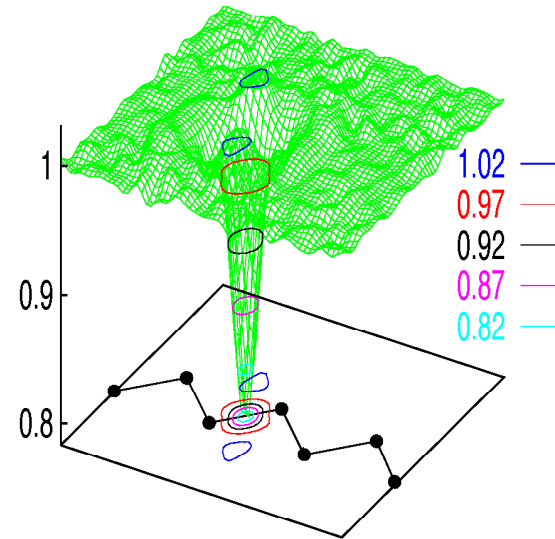## Hartree-Fock energy of Wigner crystal (r_s=100)

Exchange and correlation

$\bar{g}_{\uparrow\uparrow}(\mathbf{r}, \mathbf{r}'; [n])$

r at bond center

$\mathbf{r}'$ in (110) plane

$\bar{g}_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}'; [n])$

r at bond center

$\mathbf{r}'$ in (110) plane

electron density

$$n(\mathbf{r}) = \ N \int \Psi(\mathbf{r}, \mathbf{r_2}, \mathbf{r}_3 \ldots \mathbf{r}_N)^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

pair correlation function

$$g(\mathbf{r}, \mathbf{r}') \ = \ \frac{N(N-1)}{n(\mathbf{r})n(\mathbf{r}')} \int \Psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3 \ldots \mathbf{r}_N)^2 \, d\mathbf{r}_3 \ldots d\mathbf{r}_N$$

14

Density functional theory

$$E[n(\mathbf{r})] = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})d\mathbf{r} + \int n(\mathbf{r})V_{\text{ion}}(\mathbf{r})d\mathbf{r}$$

$$+\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[n(\mathbf{r})]$$

The Adiabatic connection

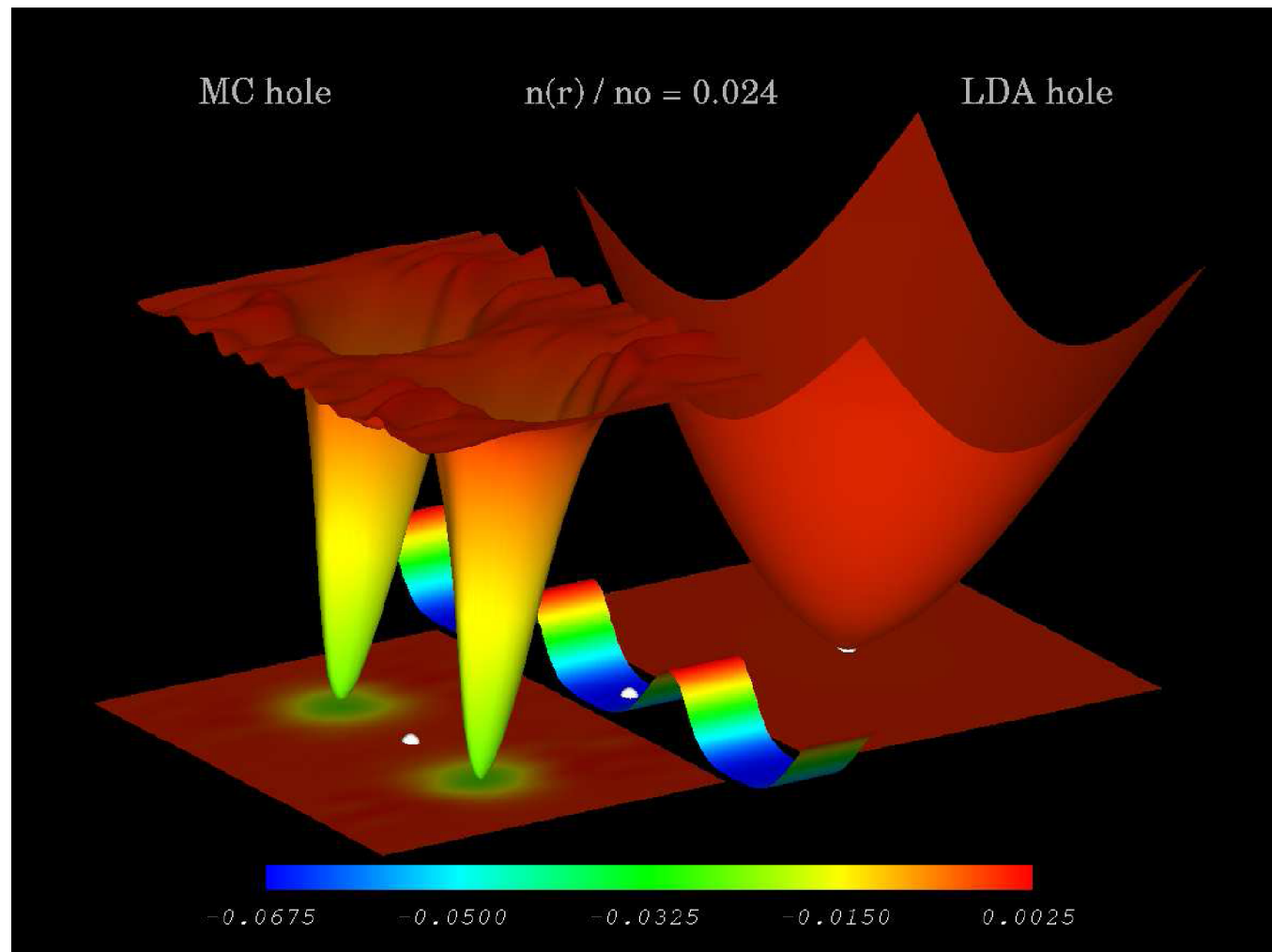|	
E_{xc}	exchange$-$correlation energy
e_{xc}	exchange$-$correlation energy density
$\rho_{\text{xc}}(\mathbf{r},\mathbf{r}')$	exchange$-$correlation hole
$\bar{g}(\mathbf{r},\mathbf{r}')$	$\lambda-$integrated pair correlation function
λ	Coulomb coupling constant

$$\bar{g}(\mathbf{r},\mathbf{r}') = \frac{N(N-1)}{n(\mathbf{r})n(\mathbf{r}')}\int_0^1 d\lambda \int \Psi_\lambda(\mathbf{r},\mathbf{r}',\mathbf{r}_3..\mathbf{r}_N)^2\, d\mathbf{r}_3..d\mathbf{r}_N$$

$$\rho_{\text{xc}}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\left(\bar{g}(\mathbf{r},\mathbf{r}')-1\right)$$

$$e_{\text{xc}}(\mathbf{r}) = \frac{n(\mathbf{r})}{2}\int\frac{\rho_{\text{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

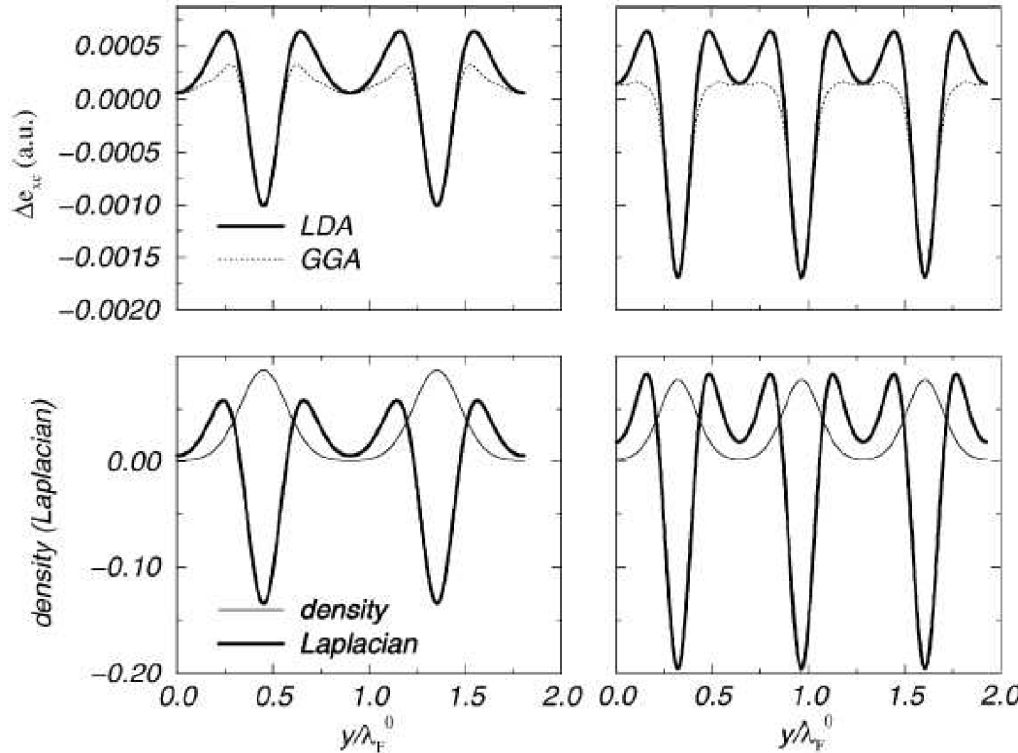$$E_{\text{xc}} = \int e_{\text{xc}}(\mathbf{r})\,d\mathbf{r}$$

Exchange and correlation in
the inhomogeneous electron gas

Towards improved density functionals

$$E_{\text{xc}}^{\text{LDA}} = \int e_{\text{xc}}^{\text{hom}}(n(\mathbf{r}))d\mathbf{r} \qquad\qquad E_{\text{xc}}^{\text{GGA}} = \int e_{\text{xc}}^{\text{GGA}}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$$

Error $e_{\text{xc}}^{\text{LDA}} - e_{\text{xc}}^{\text{VMC}}$ and $e_{\text{xc}}^{\text{GGA}} - e_{\text{xc}}^{\text{VMC}}$ along direction parallel to density oscillation in two different strongly inhomogeneous electron gases, with corresponding densities and Laplacians.

- Shape, magnitude and sign of LDA errors in e_{xc} closely follow $\nabla^2 n(\mathbf{r})$.
- GGA correction always negative - can't correct near density maximum where LDA underestimates e_{xc}.
- $\nabla^2 n(\mathbf{r})$ provides means to distinguish between physically different regions around density maxima and density minima which is lacking in GGAs.
- Offers important clues for designing new functionals.

Sample variance minimization
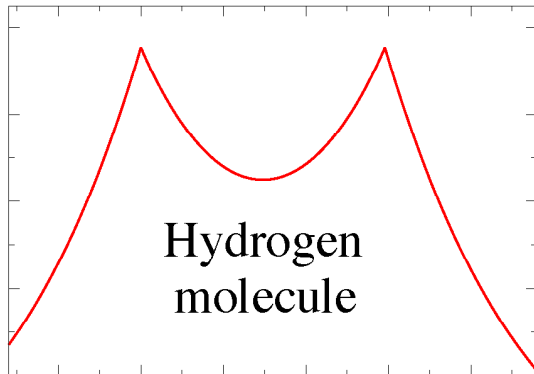
Hydrogen molecule

Let's optimize the Jastrow factor!

$$\Psi_{\mathcal{J}} = \exp(\mathcal{J}),$$

$$\mathcal{J} = \sum_{i \neq j}^{N_e} \left[-U_0(r_{ij}) - U(r_{ij}) + \sum_n^{N_n} S^n(\mathbf{r}_i, \mathbf{r}_j, r_{ij}) \right],$$

and $U_0(r_{ij}) = \frac{A}{r_{ij}} \left(1 - \exp\left(-\frac{r_{ij}}{F}\right) \right).$

History of the hydrogen molecule

Wave function	Total Energy (Ha)	R_e
Minimal basis M.O.	-1.0990	0.850
Minimal basis M.O. (scaled)	-1.1288	0.730
Best M.O. calculation	-1.1330	0.743
Minimal basis C.I.	-1.1187	0.884
Minimal basis C.I. (scaled)	-1.1480	0.757
Best C.I. (no r_{12} terms)	-1.1731	(exp R_e)
"Exact"	-1.1744757	(exp R_e)

CRYSTAL HF   : -1.128852

CASINO HF   : -1.128032 ± 0.00071 (short run with cusps)

CASINO VMC   : -1.157280 ± 0.00047 (with 5 minute Jastrow factor)

62.3% of correlation energy! (Can probably do better with more effort.)

Excited states

VMC/DMC designed to study ground states but can provide some information about excited states. Usually work with particular excited states containing one or two quasiparticles.

How can DMC treat excited states if the wave function always evolves towards the ground state?

• Generalized variational principle : the DMC energy obtained using nodes of a trial function of symmetry Γ is always greater than or equal to the lowest energy eigenvalue of that symmetry (providing the state transforms as a one-dimensional irreducible representation of the symmetry group of the Hamiltonian i.e. it's not degenerate or has only accidental degeneracies).

• Fixed-node constraint ensures convergence to the lowest energy state compatible with the imposed nodal surface (can show if nodal surface of Ψ_T is same as that of exact eigenstate, then FN-DMC gives exact energy of eigenstate). Also seems to work in practice even if not lowest energy state of a particular symmetry. Very strong constraint!

Diamond band structure
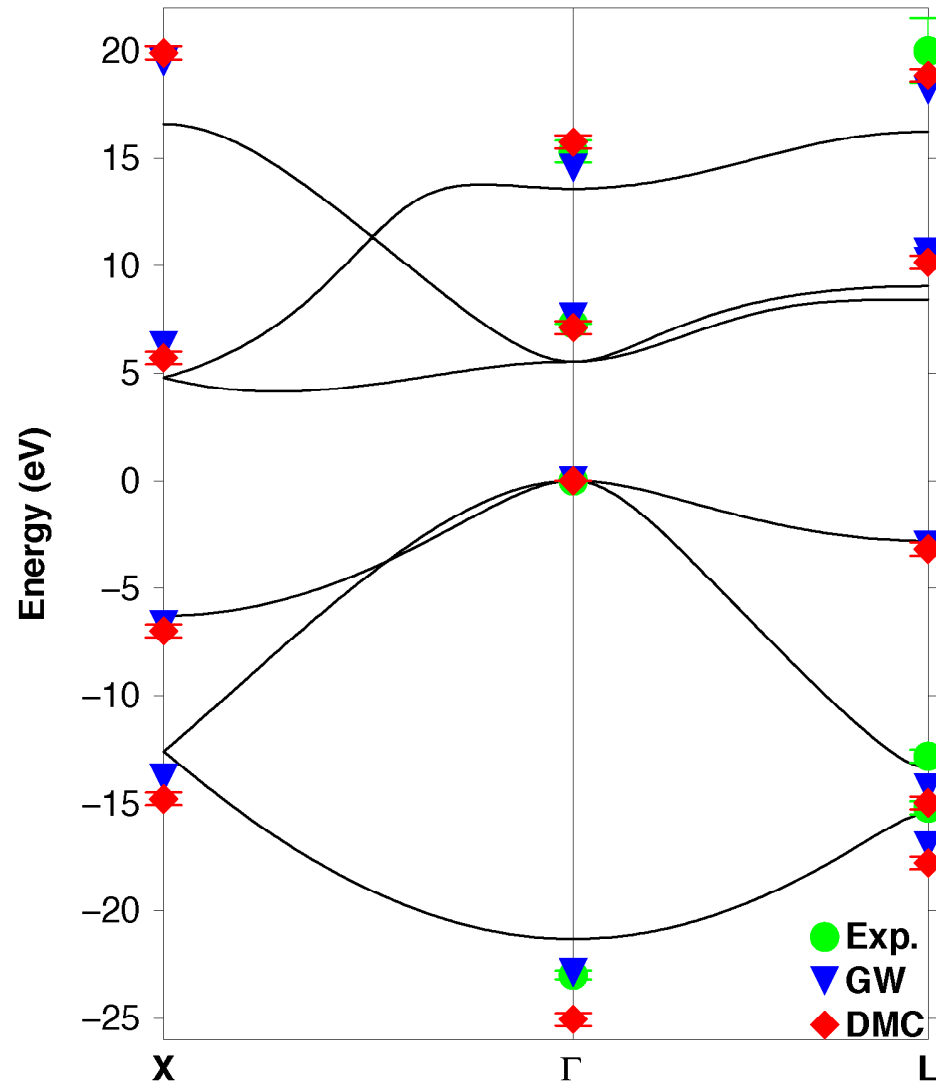
LDA band structure overlaid on DMC quasiparticle energies from electron-hole pair excitations (and GW results). DMC energy of state at top of valence band is zero by definition, but rest of energies are meaningful.

Low-lying quasiparticle energies very accurate, but calculated energies of hole lying deeper in the valence band significantly overstimated. Probably because fixed-node approximation recovers larger fraction of the correlation energy of ground state than highly excited state.

Vacancy in diamond

First QMC calculation of the multiplet structure of a defect.

$^1A_1$ ——————— 2.69 +− 0.33

$^1T_2$ ——————— 1.51 +− 0.34

$^3T_1$ ——————— 0.45 +− 0.32

^1E ———————
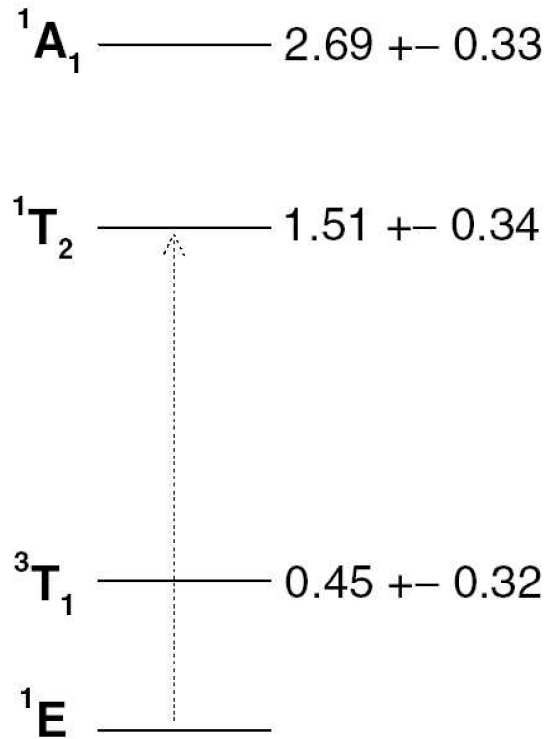
Best known optical transition - GR1 at 1.673 eV - long associated with neutral vacancy, although first principles approaches have not been able to demonstrate this.

The figure shows the computed DMC energies in eV with statistical errors of the four lowest symmetry states of the neutral diamond vacancy (Hood/Needs *et al.*). Arrow shows lowest spin and orbitally dipole-allowed transition from ground state.

• The calculation used symmetrized multideterminant trial wave functions (different degenerate orbitals occupied in each determinant).

• In an LDA calculation, with a fixed ground state charge density, these four states would all have the same energy.

Sample DMC calculation
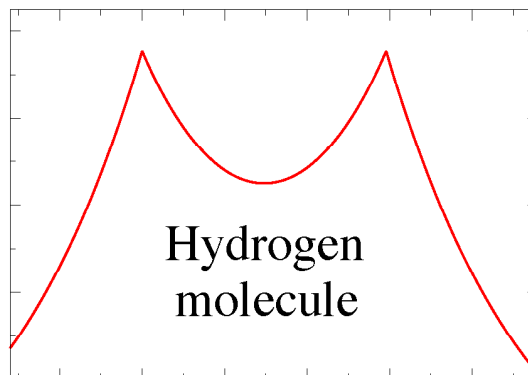
Hydrogen molecule

History of the hydrogen molecule

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Minimal basis M.O.	-1.0990	0.850
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Best C.I. (no r_{12} terms)	-1.1731	(exp R_e)
"Exact"	-1.1744757	(exp R_e)

CASINO HF : -1.1280326 ± 0.000713

CASINO VMC : -1.1569247 ± 0.00057

CASINO DMC : -1.1744731 ± 0.00056 (Gaussian basis, cusp corrections)

We recover around 100% of the correlation energy!

Strongly correlated systems

Definitions from strongly correlated physicists

- "A material which cannot be described by one-electron band theory." (not really!).

- "Pair correlation functions for electrons of same spin and electrons of opposite spin are comparable in size" (?).

- "Electron interaction larger than kinetic energy." (virial theorem? OK - they mean in restricted band models.).

- "Strong correlations (=strong on-site Coulomb interactions), which are not contained in band theory (they are), are important."

- "Localized electrons $\Longrightarrow$ atomic character important." (Fair enough..).

Practicalities

However, simpler forms of density functional theory (LDA/GGA) often fail to predict the correct ground state in materials with complicated eigenvalue spectra such as transition metal oxides (difficult to introduce a splitting between states with e.g. different atomic 'd' character..). But a band theory where the eigenvalue spectrum has a well-defined meaning (e.g. Hartree-Fock) will usually give the correct ground state, or even a density functional theory with an orbitally dependent potential (e.g. B3LYP hybrid functional). Implications for QMC?
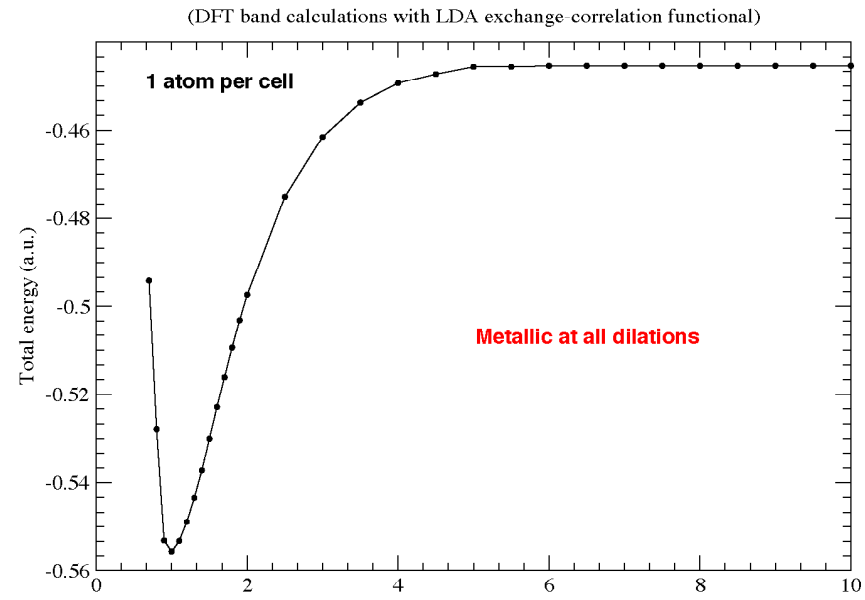
Linear chain of hydrogen atoms
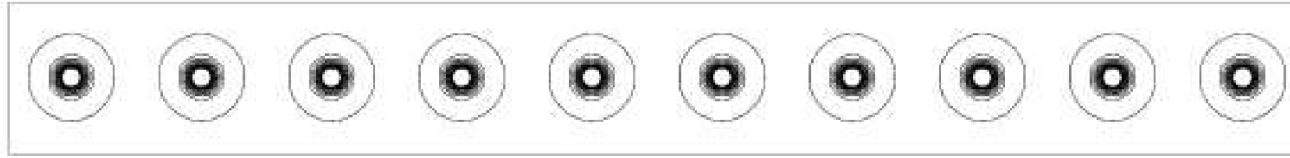
"Consider a linear chain of hydrogen atoms with a lattice constant of 1 Å. This has one electron per atom in the conduction band and is therefore metallic. Imagine we now dilate the lattice parameter of the crystal to 1 metre. We would agree that at some point in this dilation process the crystal must become an insulator because certainly when the atoms are 1 metre apart they are not interacting. But band theory says 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 in another way. Why is the crystal with a 1 metre lattice parameter 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 a neutral H atom. The energy cost in this process is $U = I - A$. Band theory ignores terms such as these." (Sutton, Electronic Structure of Materials)

Hubbard model

$$H = \sum_{i,j} t_{ij} a_{i\sigma} a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$
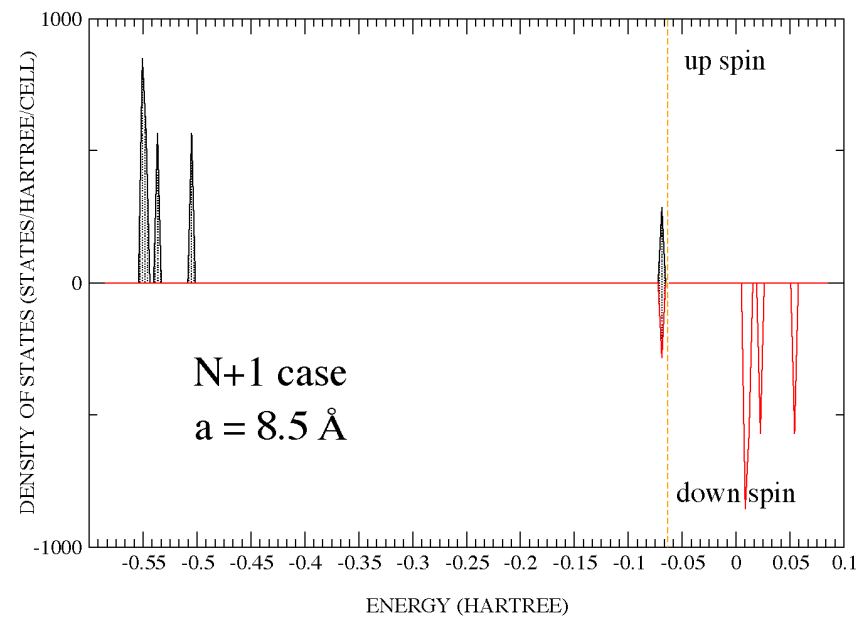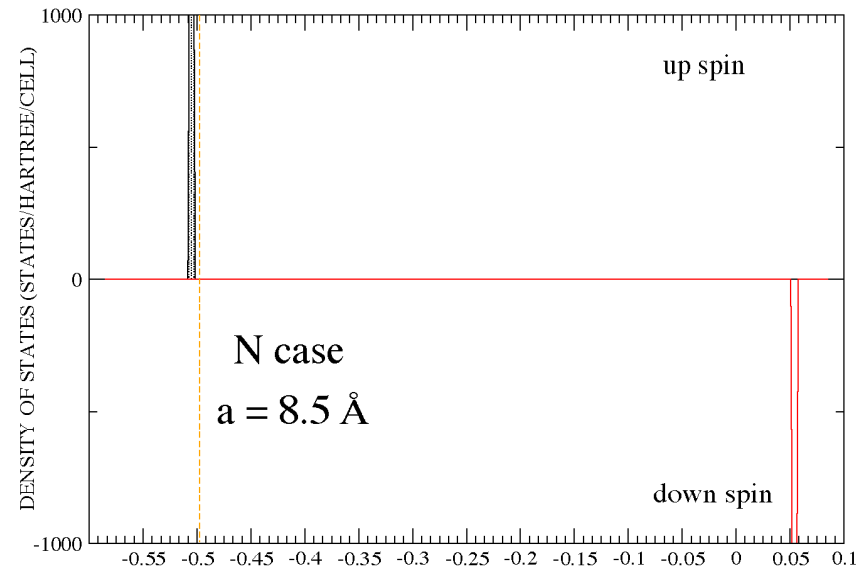
Band theory of linear hydrogen chain

(DFT band calculations with LDA exchange-correlation functional)

1 atom per cell

Metallic at all dilations

a = 3Å
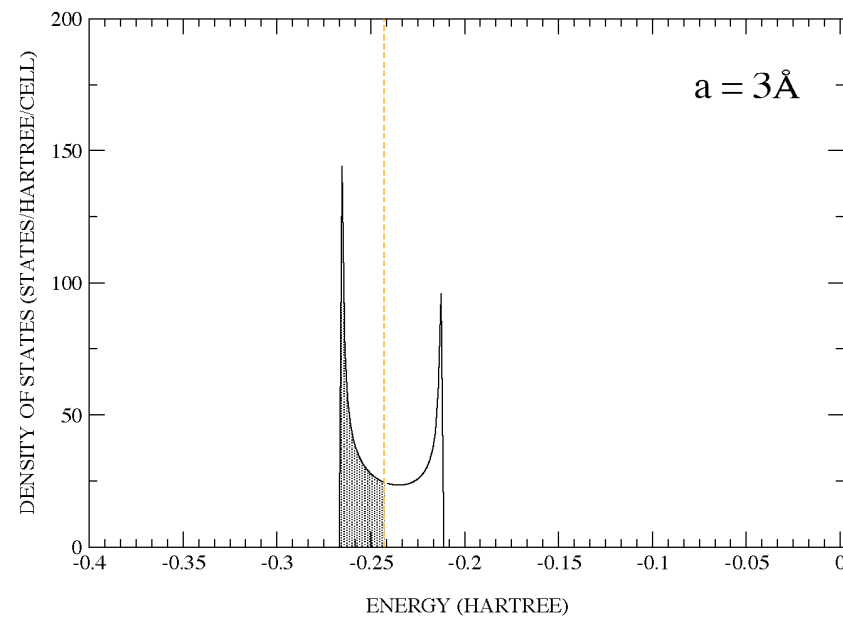
Spin-unrestricted band theory of linear hydrogen chain

(LSDA functional)

1 atom per cell

- ferromagnetic
- spin-unpolarized

METAL   INSULATOR

Hydrogen linear chain

Density of states

ENERGY (HARTREE)
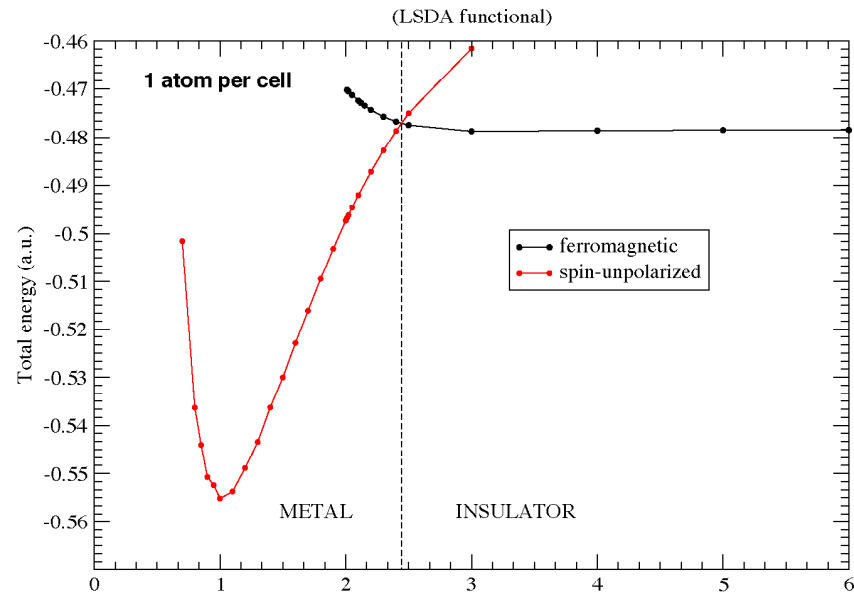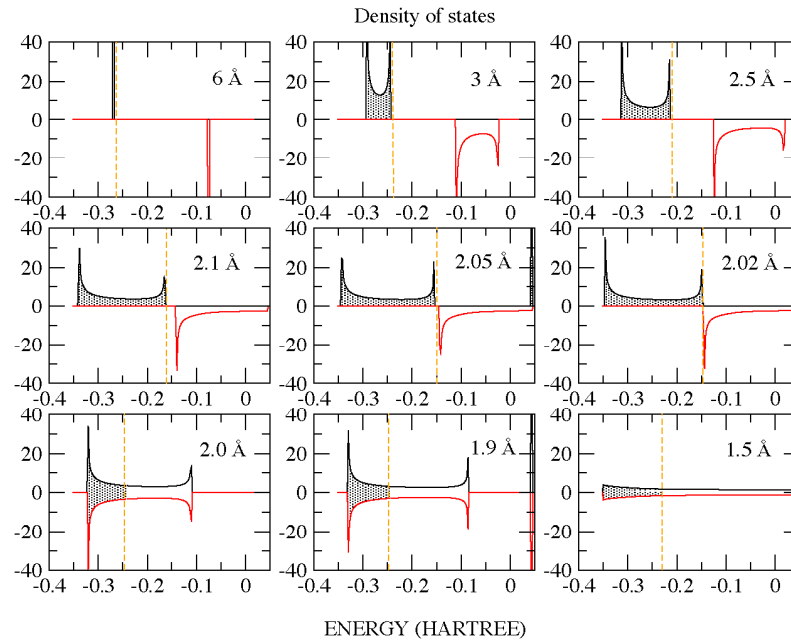
N+1 system

N+1/N-1 system

$$U = \quad + \quad -2$$
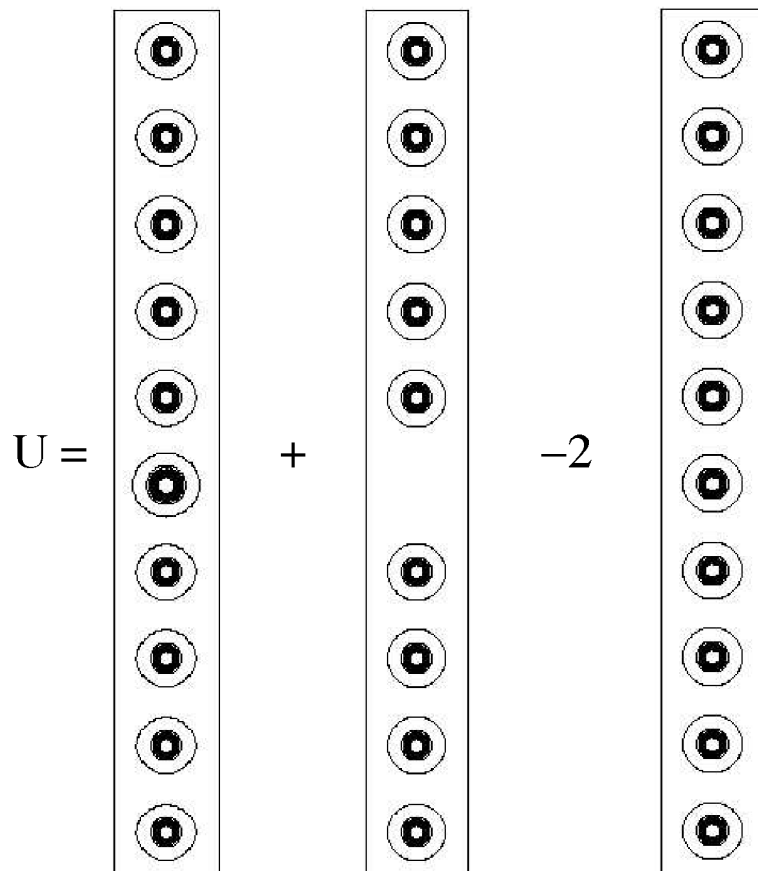
	LSDA (eV)	UHF (eV)	B3LYP (eV)
U (as above)	11.44	13.03	12.01
U (Band gap)	5.30	11.99	8.56

Should be around 13 eV.

Localization

Insulating state of matter is characterized by gap to low-lying excitations, but also by qualitative features of the ground state - which sustains macroscopic polarization and is localized. Kohn 1964

Localization is a property of the many-electron wave function: insulating behaviour arises whenever the ground state wave function of an extended system breaks up into a sum of functions Ψ_M which are localized in essentially disconnected regions R_M of configuration space i.e.

$$\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \sum_{M=-\infty}^{+\infty} \Psi_M(\mathbf{x}_1, \ldots, \mathbf{x}_N)$$

where for a large supercell Ψ_M and $\Psi_{M'}$ have an exponentially small overlap for $M' \neq M$. Under such a hypothesis, Kohn proved that the dc conductivity vanishes.

Hence, electronic localization in insulators does not occur in real space (charge density) but in configuration space (wave function).

Many-body phase operators

- Both macroscopic polarization and electron localization are expectation values of 'many-body phase operators' $z_N^{(\alpha)}$, where

$$z_N^{(x)} = \langle \Psi | e^{i\frac{2\pi}{L}\sum_{i=1}^{N} x_i} | \Psi \rangle$$

These quantities are zero for metals!

- Ground state expectation value of the position operator in periodic boundary conditions

$$\langle X \rangle = \frac{L}{2\pi} \mathsf{Im} \ln z_N$$

- Phase of $z_N^{(\alpha)}$ used to define the macroscopic polarization of an insulator.

- Modulus of $z_N^{(\alpha)}$ used to define the localization tensor $\langle r_\alpha r_\beta \rangle$ (finite in insulators, diverges in metals).

# Localization tensor
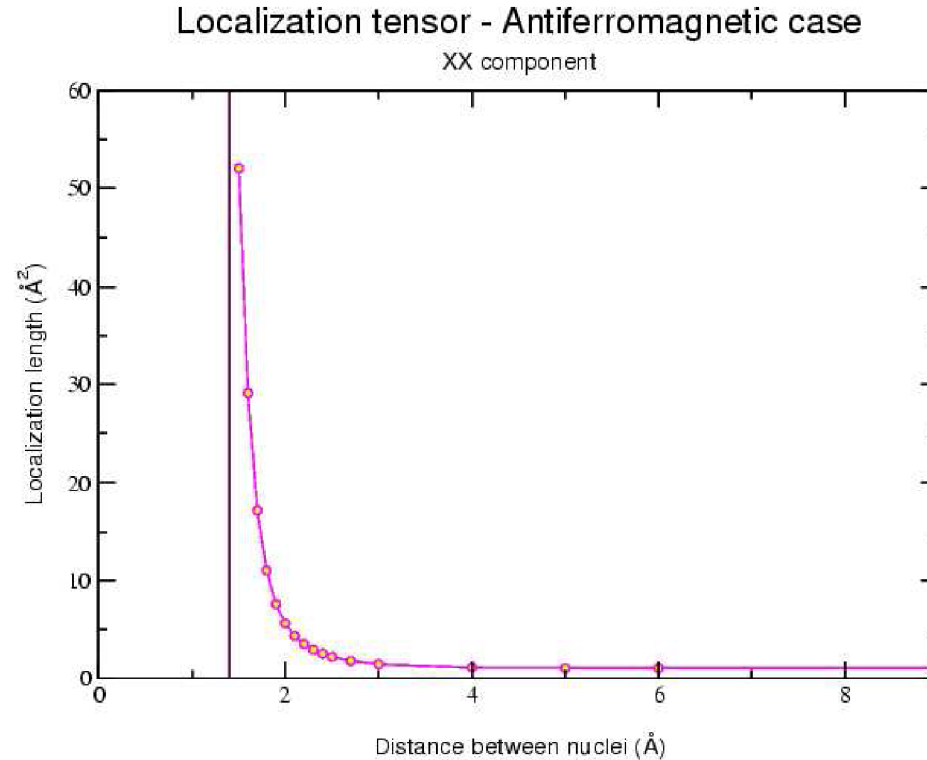
Simone Chiesa's thesis :

The aim of this study is understanding the influence that electron correlation plays in determining this transition. The introduction of correlation can be easily performed in the framework of QMC methods. This thesis unfortunately does not contain this interesting part which represents the natural conclusion of the work done so far.

NiO

Questions

- Are UHF/B3LYP orbitals good enough for DMC of (a) ground and (b) excited states of NiO? What about LSDA/GGA orbitals, even though they give the wrong ground state?

- Can we cope with the expected high variance?

- Furthermore, can we grind down the variance enough to look e.g. at the very small energy differences between magnetic states? Probably not with current technology, but let's try.

'Crystal field' splitting of d orbitals (octahedral coordination)
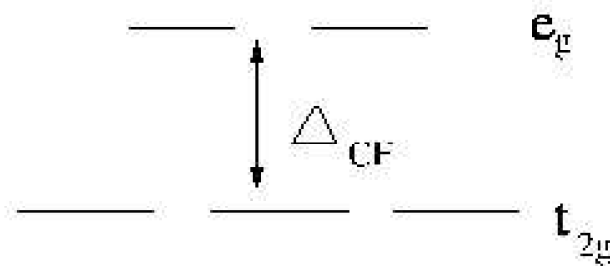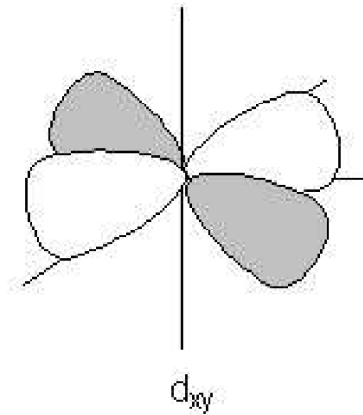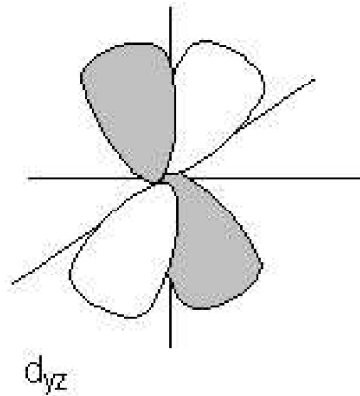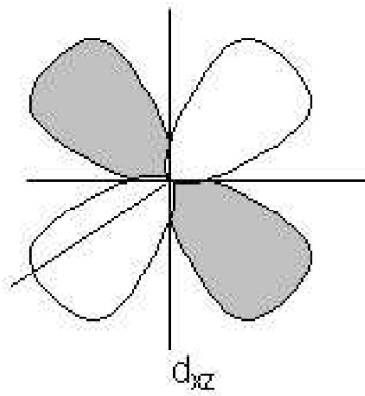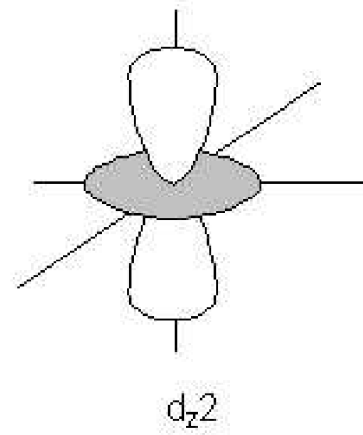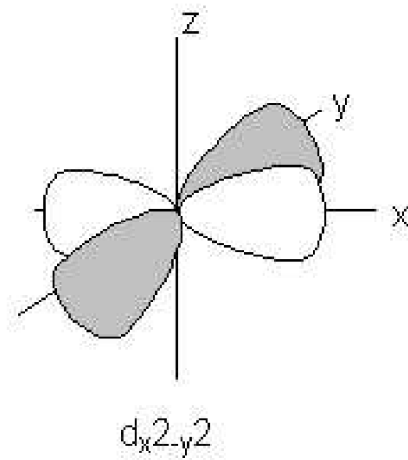
Electronic states in NiO

Interactions:

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.
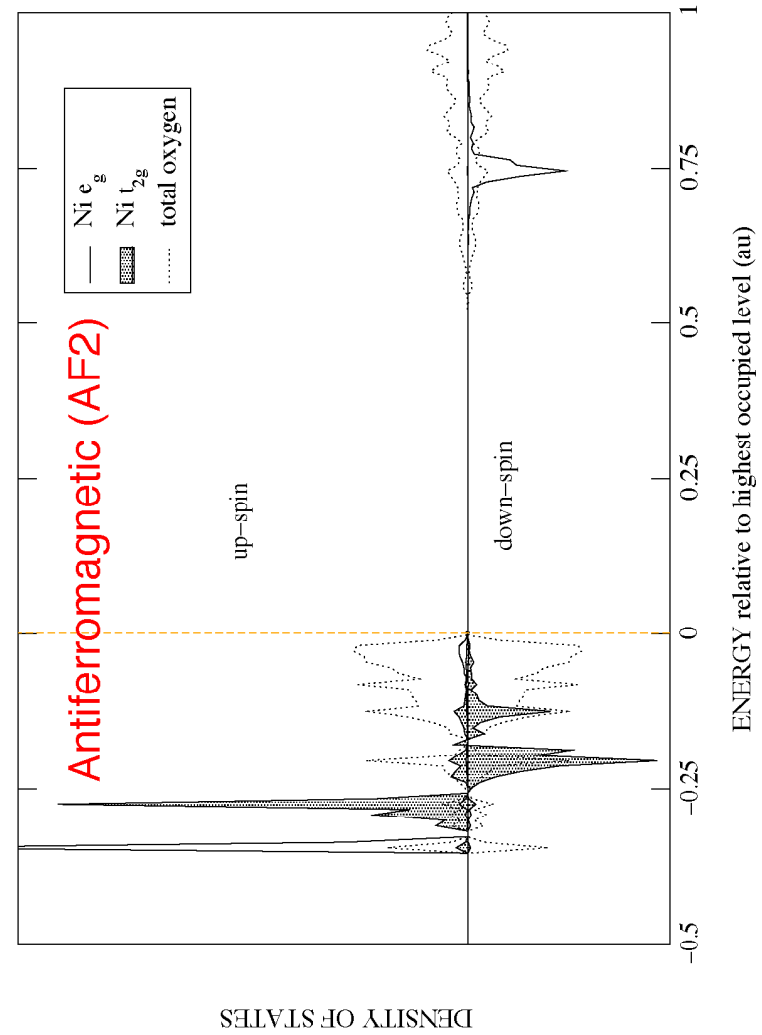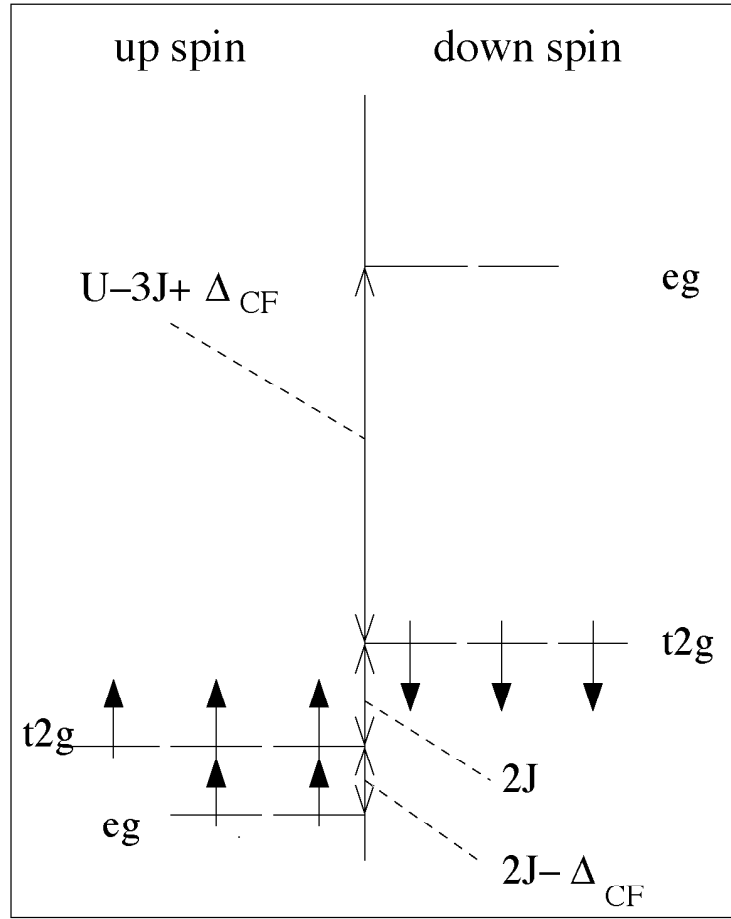
On a Ni site in NiO:

$\uparrow$-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=5.8eV, J=0.67eV, U'=4.5eV, Δ_{CF}=1.1eV
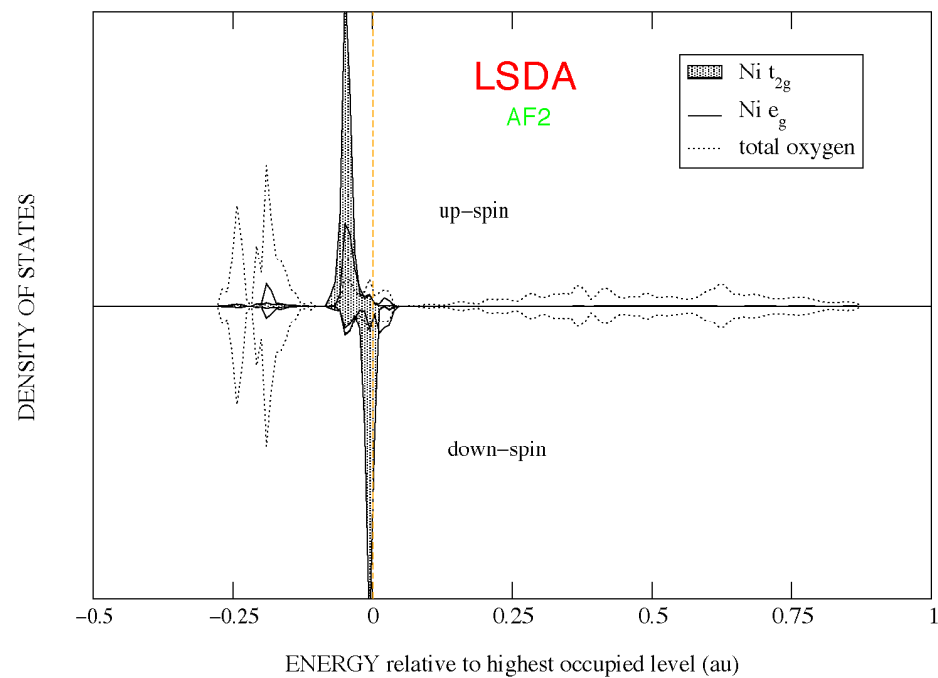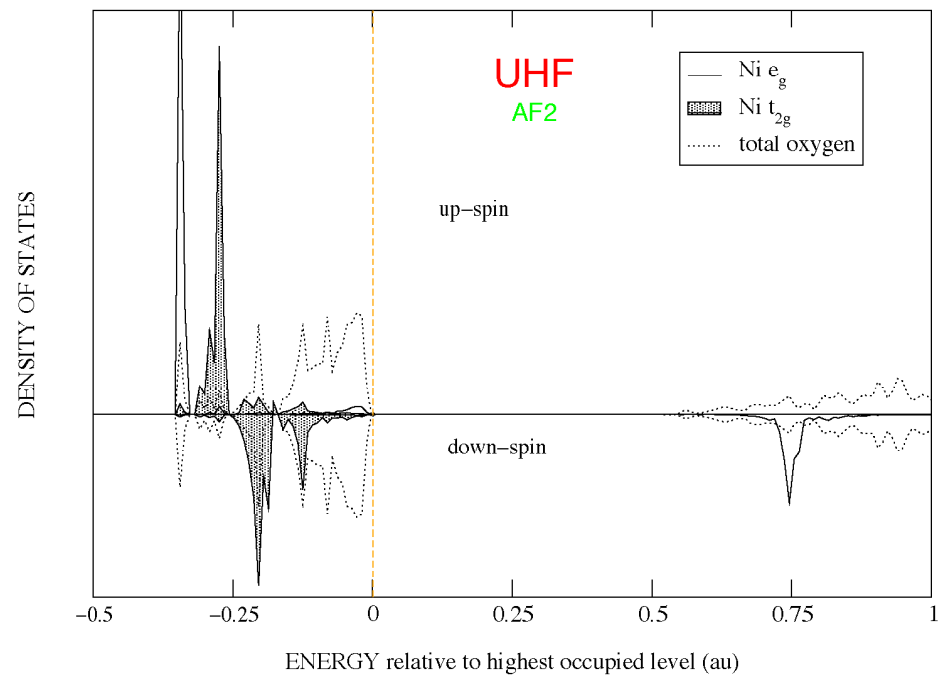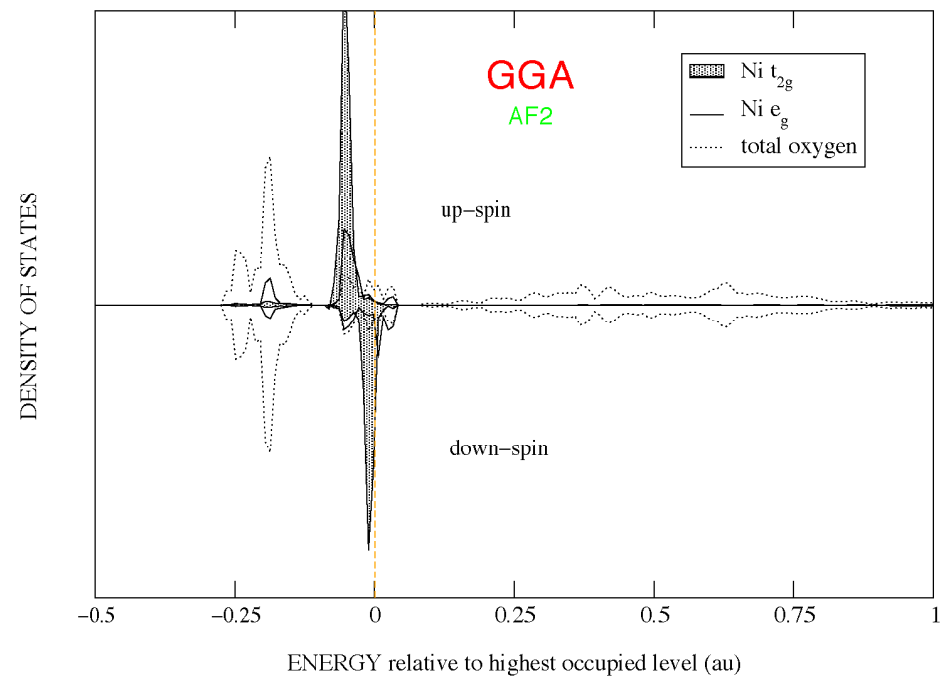

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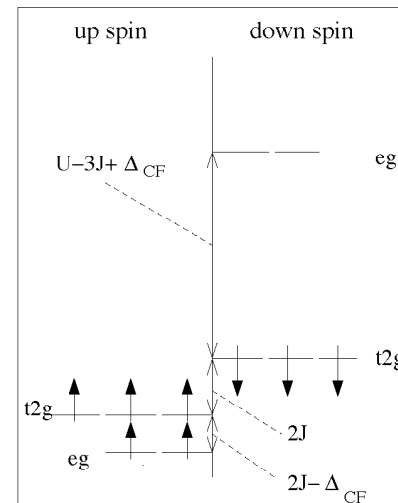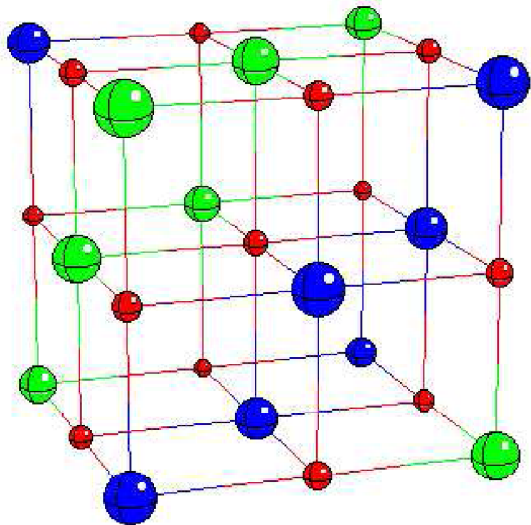
Compare model with NiO UHF DOS

UHF : effect of magnetic ordering
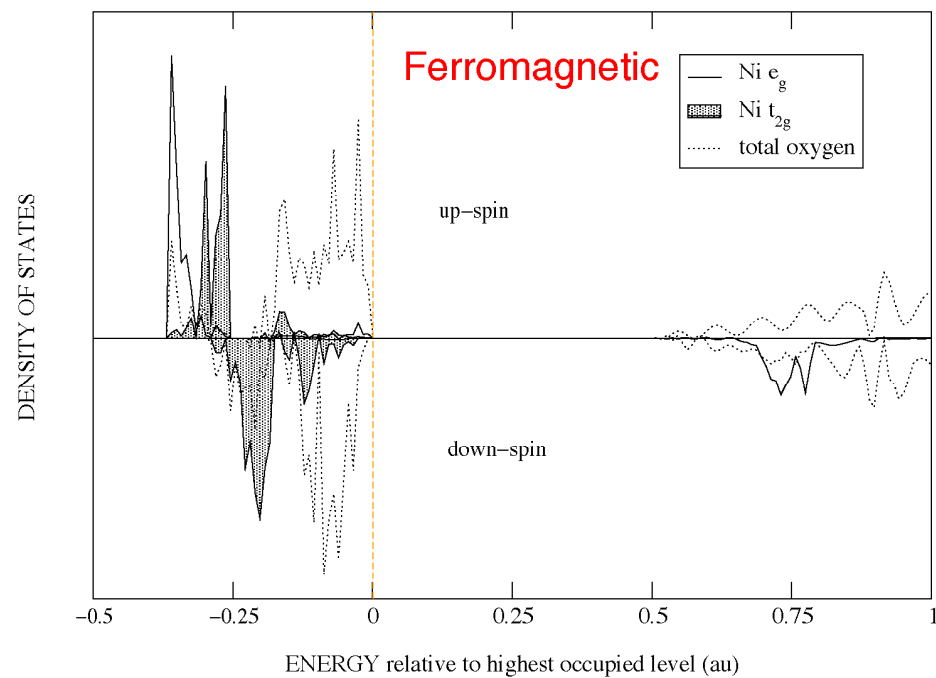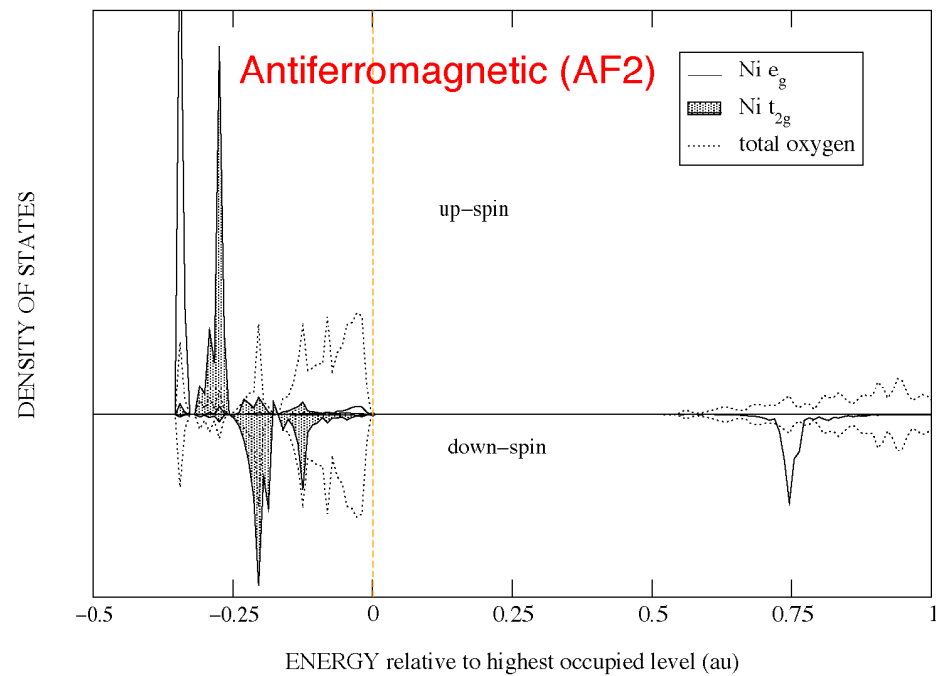
UHF vs. LDA

UHF vs. GGA

UHF vs. B3LYP

UHF

AF2

Ni e_g

Ni t_{2g}

total oxygen

up–spin

down–spin

DENSITY OF STATES

ENERGY relative to highest occupied level (au)

B3LYP

AF2

Ni t_{2g}

Ni e_g

total oxygen

up–spin

down–spin

DENSITY OF STATES

ENERGY relative to highest occupied level (au)

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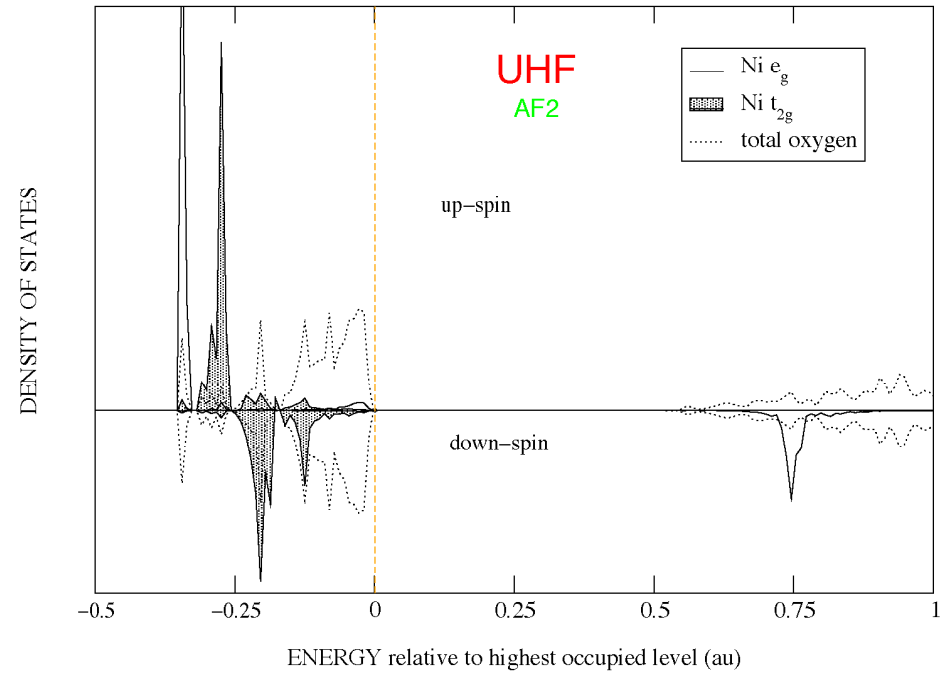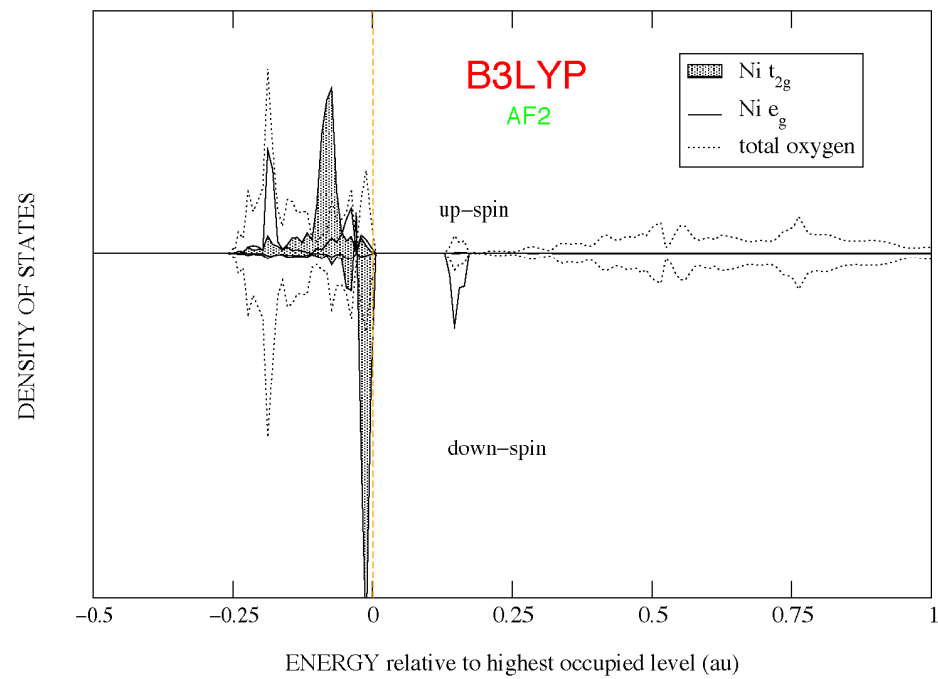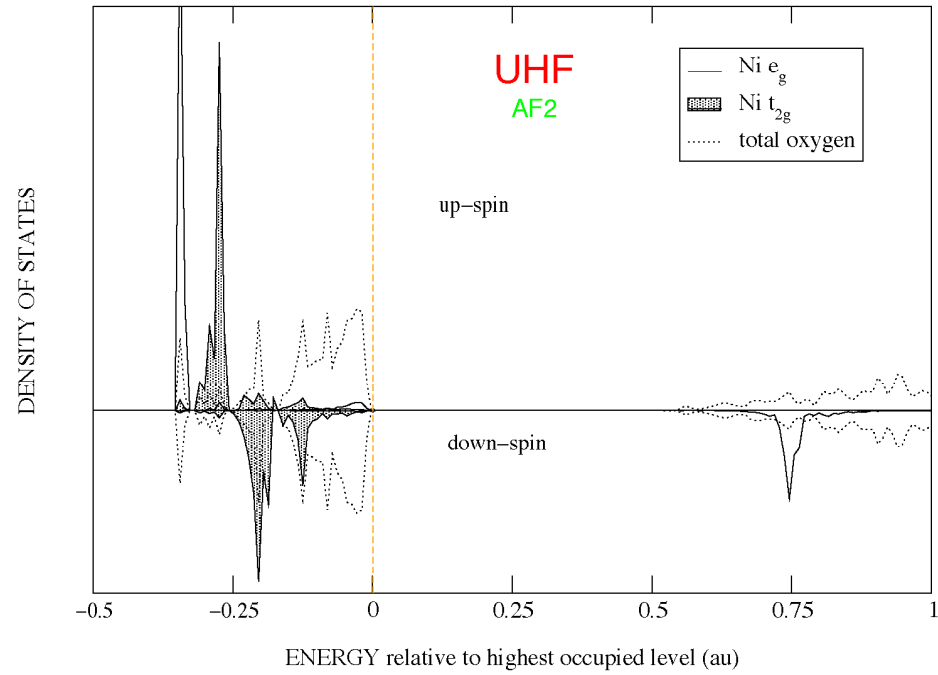
DMC data for ground state of NiO
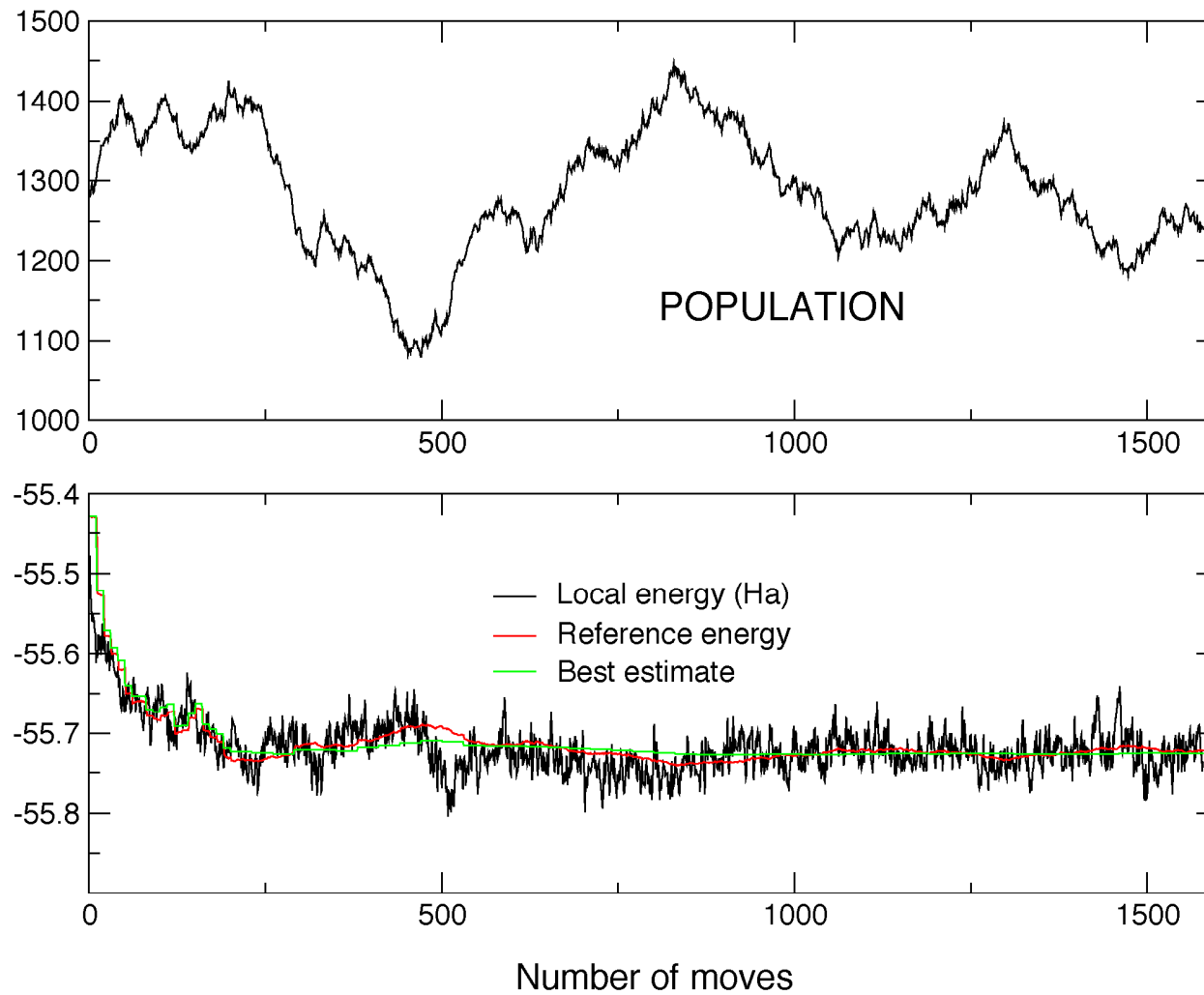
NiO lattice constant
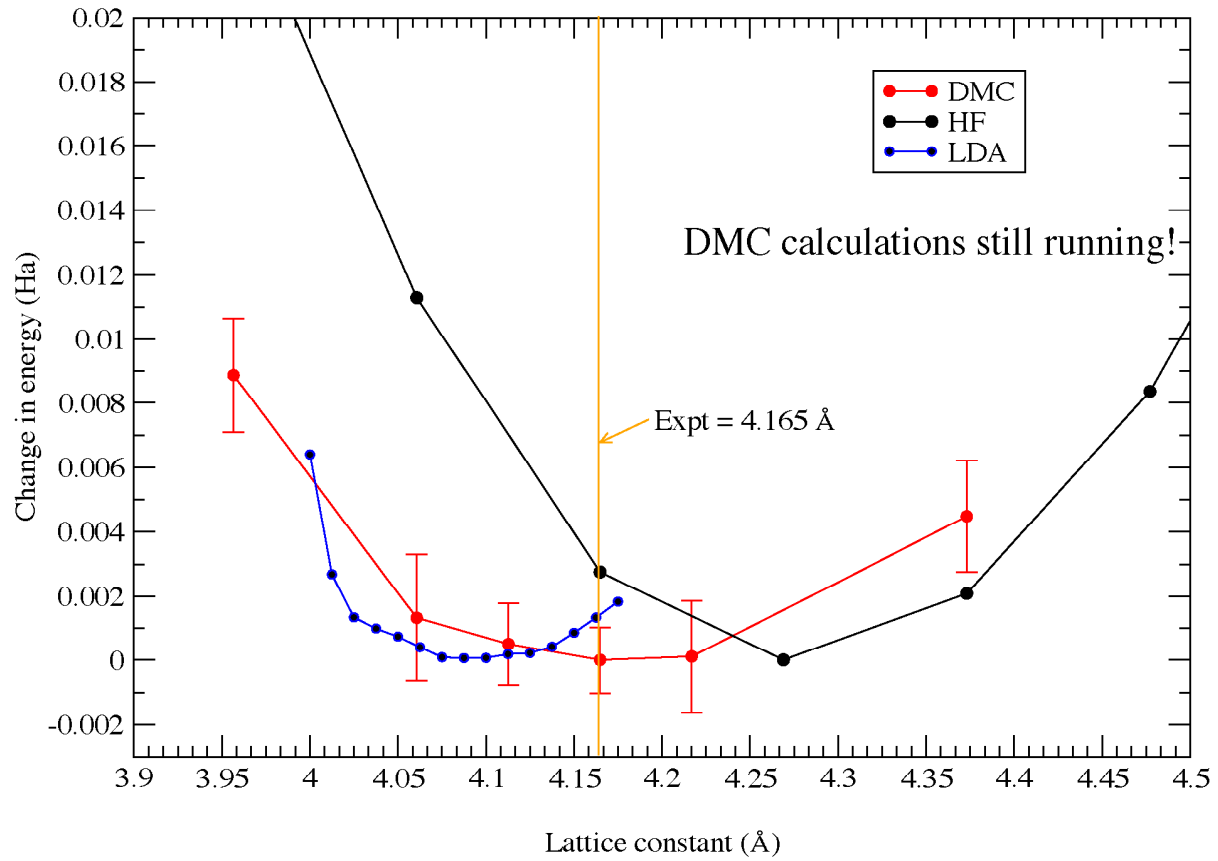
Table of results

	a (Å)	E_C (eV)	E_g (eV)
UHF	4.26	6.2	14.2
LSDA	4.09	10.96	0
GGA	4.22	8.35	0
B3LYP	4.22	7.8	3.9
DMC(UHF)	(4.16ish?)	9.44(13)	
DMC(B3LYP)		9.19(14)	4.3(2)
Exp.	4.165	9.45($\pm$?)	4.0–4.3

Lattice constant, a, cohesive energy, E_C, and band gap, E_g, of NiO.

Sources of error in DMC

- Statistical error.

- Born-Oppenheimer approximation. Using geometries from band theory. (forces difficult to calculate directly in QMC).

- Fixed-node error.

- Time step error.

- Pseudopotentials in general.

- Localization approximation (non-local integration of pseudopotentials)

- Possible 'spin contamination'.

Conclusions

- VMC using Slater-Jastrow wave functions with $\sim$30 variational parameters can recover between 60 and 85% of the valence correlation energy, and DMC calculations can recover roughly 95% plus. The remaining 5% is largely due to fixed-node error.

- In solids, QMC is the *only* practical method based on many-body correlated wave functions, the variational principle, and the many-electron Schrödinger equation. It is now the method of choice for tackling large quantum many-body problems.

- Efficient implentations of VMC and DMC for finite and periodic systems have been made in our computer program CASINO. Much remains to be done to make QMC as flexible and easy to use as traditional methods.

- With its emphasis on many-electron wave functions and probabilities, QMC has shown that it is possible to study interacting electrons in real solids using very direct computational techniques; there is no need to resort to perturbation theory or mean-field approximations.

CASINO : www.tcm.phy.cam.ac.uk/$\sim$mdt26/casino.html

References

Selected references for applications mentioned in this talk

- *Quantum Monte Carlo simulations of solids*, W.M.C. Foulkes, L. Mitas, R.J. Needs and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).

- *Carbon clusters near the crossover to fullerene stability*, P.R.C. Kent, M.D. Towler, R.J. Needs and G. Rajagopal, Phys. Rev. B 62, 15394 (2000).

- *Calculations of silicon self-interstitial defects*, W.K. Leung, R.J. Needs, G. Rajagopal, S. Itoh and S. Ihara, Phys. Rev. Lett. **83**, 2351 (1999).

- *Minimum principles and level splitting in quantum Monte Carlo excitation spectra: application to diamond*, M.D. Towler, R.Q. Hood and R.J. Needs, Phys. Rev. B **62**, 2330-2337 (2000).

- *Quantum Monte Carlo analysis of exchange and correlation in the strongly inhomogeneous electron gas*, M. Nekovee, W.M.C. Foulkes, and R.J. Needs, Phys. Rev. Lett. **87**, 036401 (2001).

- *Quantum Monte Carlo study of the optical and diffusive properties of the vacancy defect in diamond*, R. Q. Hood, P. R. C. Kent, R. J. Needs, and P. R. Briddon, Phys. Rev. Lett. **91**, 076403 (2003).

Job advertisement

Ph.D. studentships

Department of Physics, University of Cambridge, UK

Ph.D. positions are available on or after 1st October 2004
to work on ab initio electronic structure calculations in
the groups of Dr. Richard Needs or Dr. Mike Towler. We
use quantum Monte Carlo methods and density-functional methods
to study problems in condensed matter physics.

For those wishing to look around the department, and to chat
to students and members of staff of the TCM Group, an Open Day
will be held on Wednesday 4 February 2004 at 2.15 pm.

Interviews of candidates for PhD studentships will be held
on Monday 16th February and Monday 1st March.

For further information about formal application procedures
contact Tracey Ingham by email: ti201 at cam.ac.uk
For further information about available projects contact:
rn11 at cam.ac.uk or mdt26 at cam.ac.uk