Density Functional Theory II

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Conclusions I

- For the ground state energy and density there is an exact mapping between the many body system and a fictitious non-interacting system.
  - DFT-people study the fictitious system !

- The fictitious system is subject to an unknown potential derived from the exchange-correlation functional

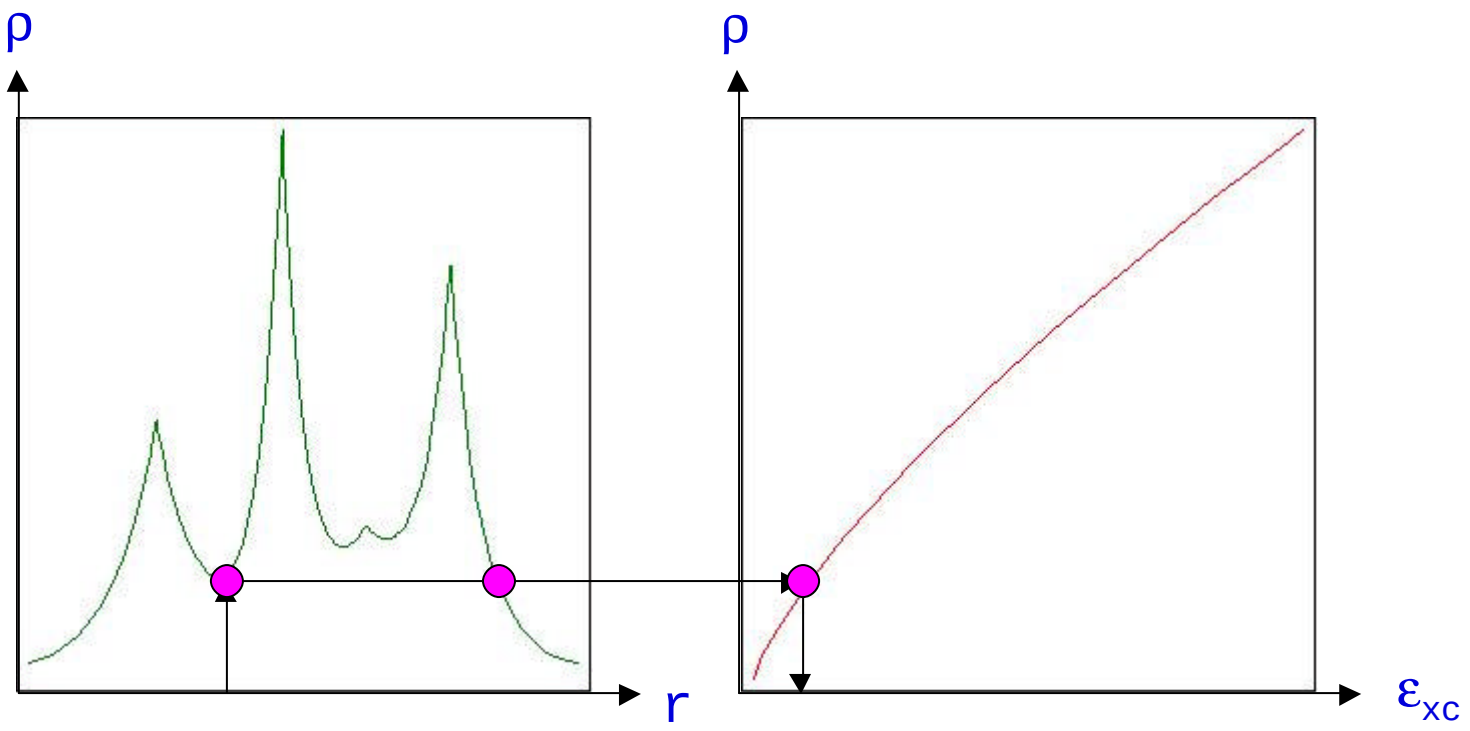
- The energy functional may be approximated as a local function of the density !

Density Functional Theory II

- Why does the LDA work ?
- The exchange correlation hole
- Comparison with exact exchange and correlation energy densities
- Generalised gradient approximations – GGA's
- Semi-local interactions: Meta-GGA's
- Hybrid-exchange functionals
- Performance in molecules and solids

The Local Density Approximation - LDA

$$E_{xc}^{LDA}[r] = \int r(\mathbf{r}) e_{xc}(r(\mathbf{r}))d\mathbf{r}$$



Picture courtesy of Andreas Savin

The Exchange-Correlation Hole

The pair density determines the total energy – does the LDA reproduce the pair density ?

The exchange correlation hole is the conditional probability – the probability of finding an electron at r_2 given that these is an electron at r_1

$$P_{xc}(\mathbf{r}_1,\mathbf{r}_2) = \frac{P_2(\mathbf{r}_1,\mathbf{r}_2)}{r(\mathbf{r}_1)} - r(\mathbf{r}_2)$$

It is the hole the electron at r_1 digs for itself in the surrounding density.

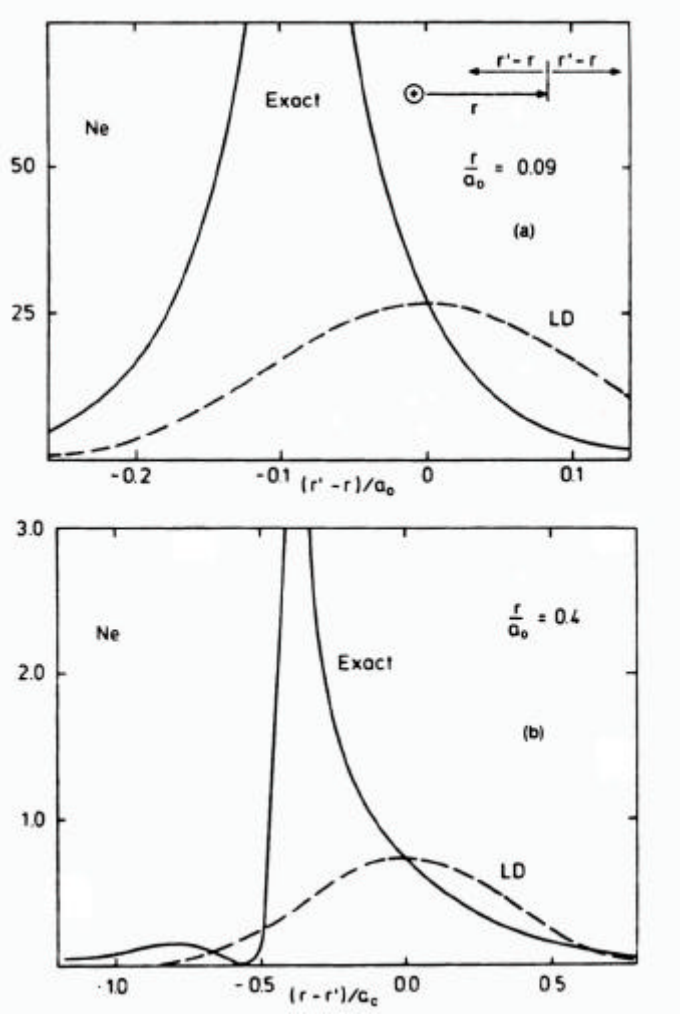
Exact Properties of P_{xc}

There are a number of properties which will be satisfied by the exact exchange correlation hole. For instance it should normalise to exactly one electron:

$$\int P_{xc}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$$

Both the LDA and Hartree-Fock theory satisfy this sum-rule.

P_{xc} is very poorly estimated in the LDA ?



Gunnarsson *et. al.* 1979

How can V_{ee} be reasonable if P_{xc} is wrong ?

$$E_{ee} = \frac{1}{2}\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

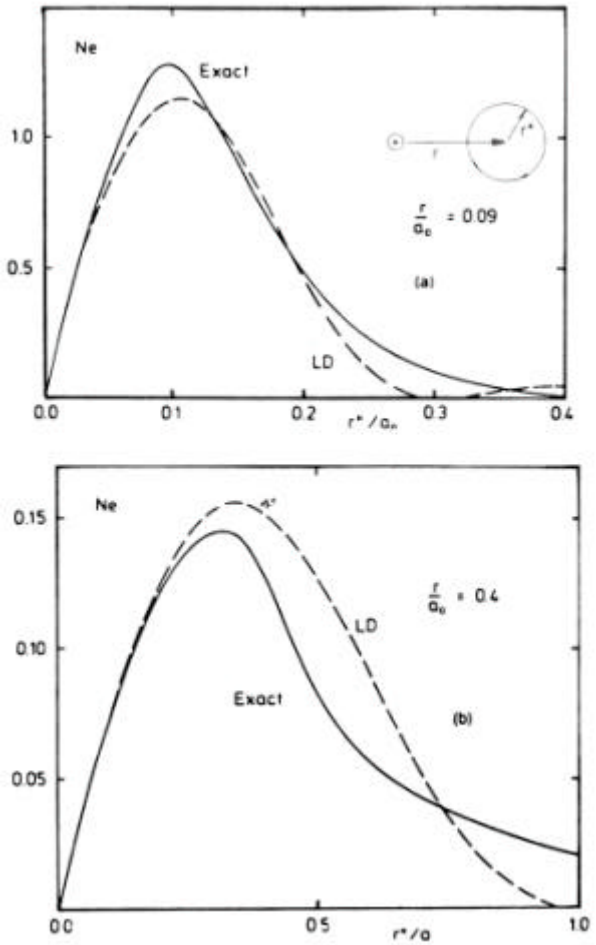
The Coulomb operator depends only on $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ ….

$$E_{ee} = \frac{1}{2}\int_0^\infty 4\pi u^2 . \left[\frac{\int P_2(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{u}) d\mathbf{r}_1}{u} \frac{d\Omega_u}{4\pi} \right] du$$

So V_{ee} depends only on the spherical average of the pair density, $P(u)$

$$.P(u) = \int P_2(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{u}) d\mathbf{r}_1 \frac{d\Omega_u}{4\pi}$$

The Spherical Average of P_{xc}



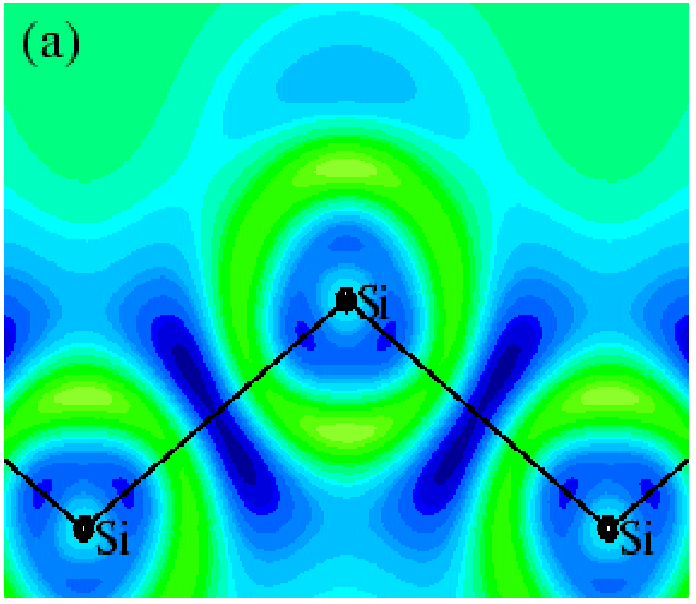
Gunnarsson *et. al.* 1979

The LDA works in part because it generates a reasonable estimate o the spherical average – despite being a poor approximation to the pair density

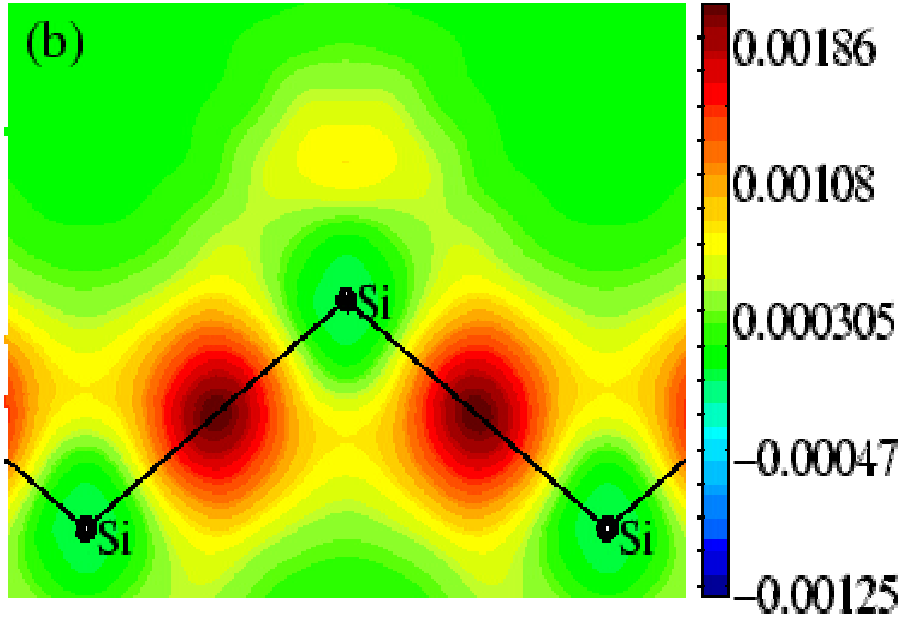
The LDA energy densities in direct space ?

The difference between the exact (V-QMC) and LDA energy density in bulk silicon (au)

Exchange



Correlation



Hood et al PRB 57 8972 ’98

Why does the LDA work ?

- Exact properties of the xc-hole maintained
- The electron-electron interaction depends only on the spherical average of the xc-hole – this is reasonably well reproduced
- The errors in the exchange and correlation energy densities tend to cancel

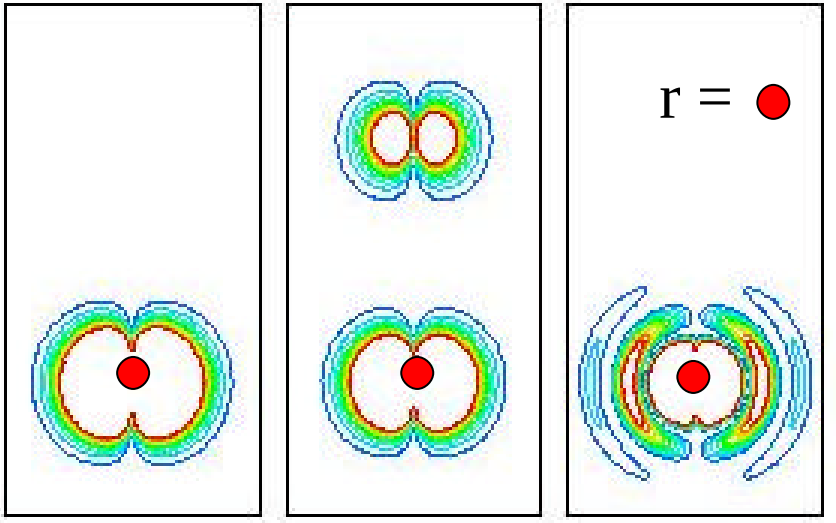
Improving on the LDA is non-trivial.

Why not Hartree Fock Exchange + $E_c[r]$?

The xc-hole in H_2 at a large bond length

$P(r_1,r_2)/ \rho(r_1)\rho(r_2)$

$E_c < E_x$; error less important?



The semi-local component of HF-exchange is excellent.

The non-local part is often very poor (eg: metals).

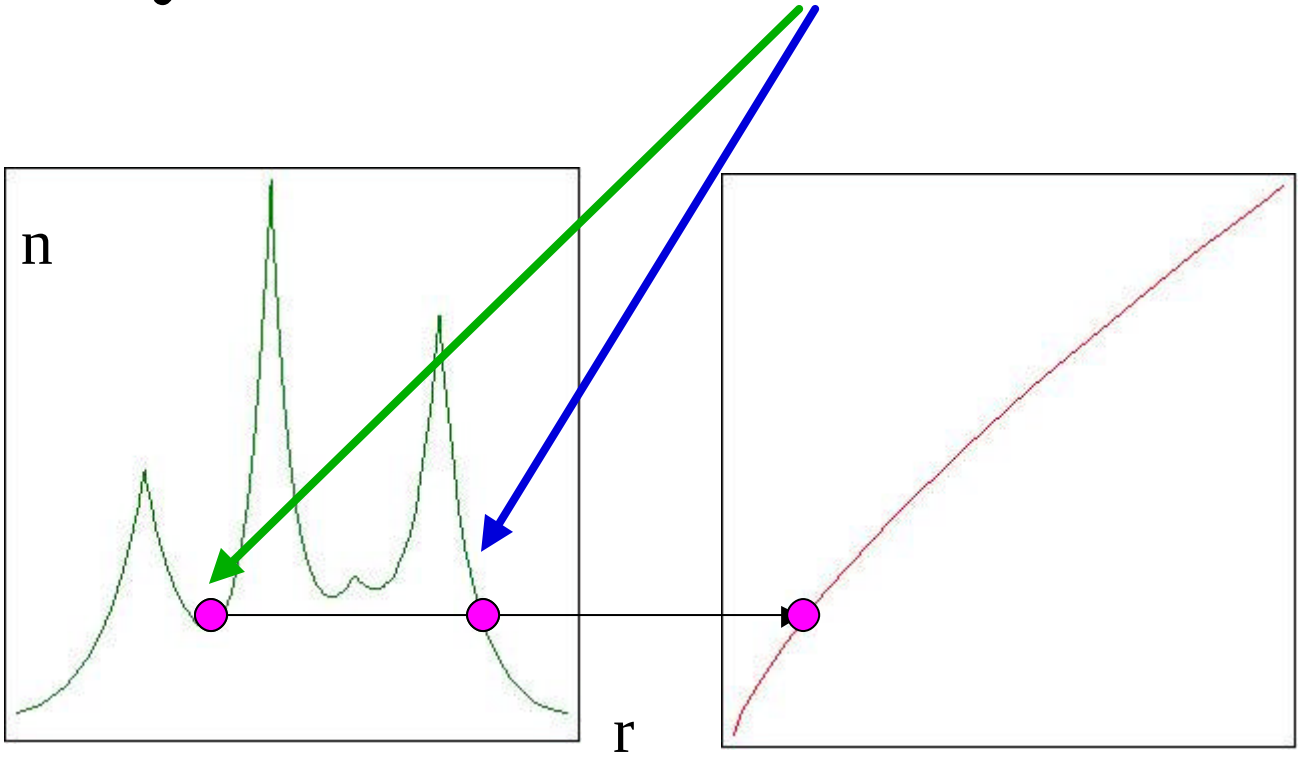
The correlation correction to HF is mostly trying to fix this.

So, Treat XC together, locally = > LDA

Picture courtesy of Andreas Savin

Role of GGA

$$E_{xc}^{GGA}[\,r\,] = \int r(\mathbf{r}) e_{xc}(\,r(\mathbf{r}), |\nabla r(\mathbf{r})|) d\mathbf{r}$$



Families of Approximations to $E_{xc}[r]$

$$E_{XC}(r) = \int r(\mathbf{r}) e_{XC}(\mathbf{r}) d\mathbf{r}$$

LDA

$$e_{xc} = e_{xc}(r(\mathbf{r}))$$

GGA (generalized gradient approximation)

$$e_{xc} = e_{xc}(r(\mathbf{r}), |\nabla r(\mathbf{r})|)$$

meta-GGA

$$e_{xc} = e_{xc}(r(\mathbf{r}), |\nabla r(\mathbf{r})|, \nabla^2 r(\mathbf{r}), \sum_i |\nabla j_i|^2$$

Hybrid Functionals – the best of both worlds !!

Exact Exchange	$V_{HF}(r_1, r_2)$
LDA	$V_{LDA}(\rho(r))$
GGA	$V_{GGA}(\rho(r), \nabla\rho\ (r))$
B3LYP(exchange)	$20\%\ V_{HF} + \ 58\%\ V_{LDA} + \ 22\%\ V_{GGA}$

Becke 1993

Producing functionals

LDA from uniform electron gas calculations

Two broad philosophies:

Fit to known experimental data

- Examples: Becke, Pople, Scuseria, …: ansatz(even polynomial)+ parameters
  - —‘training’ set of molecules (some problems with transition metal elements)

Use of exact properties

- Examples, Levy, Perdew,…
  - —not free of arbitrariness: ansatz

Performance of several functionals

From recent publications making comparisons between LDA, GGAs, m-GGAs, and B3LYP:

- S. Kurth, J. P. Perdew, P. Blaha,
  Int. J. Quantum. Chem 75 (1999) 889: atoms, molecules, crystals

- C. Adamo, M. Ernzerhof, G.E. Scuseria,
  J. Chem. Phys. 112 (2000) 2643: larger set of molecules

Mnemonics !

	family	parameterisation
LDA	local	-
BLYP	GGA	light
PBE	GGA	-
HCTH	GGA	heavy – 18
VS98	mGGA	heavy – 21
PKZB	mGGA	light – 1
Hybrid	hybrid	light – 3

Atomisation Energies

	Kurth - m.r.e % 20 molecules	Adamo m.a.e (max) kcal/mol G2 set of 148 molecules
LDA	22%	
BLYP	5%	
PBE	7%	17 (51)
HCTH	3%	-
VS98	2%	3 (12)
PKZB	3%	5 (38)
Hybrid	-	3 (20)

Structures

	Kurth - m.r.e % Unit cell volumes 12 crystals (incl. T-metals)	Adamo m.a.e (Max) – Ang. Bond lengths 23 molecules
LDA	5%	
BLYP	8%	
PBE	4%	0.011 (0.064)
HCTH	6%	
VS98	8%	0.008 (0.08)
PKZB	3%	0.019 (0.111)
hybrid	-	0.007 (0.062)

Is the molecular fit a good guide to performance in the solid ?

Vibrations – E”

	Kurth Bulk Moduli - m.r.e % 12 crystals (incl. T-metals)	Adamo – Harmonic frequencies m.a.e (cm^{-1}) (Max) 55 molecules
LDA	19%	
BLYP	22%	
PBE	10%	65 cm^{-1} (-194)
HCTH	20%	
VS98	29%	33 cm^{-1} (-109)
PKZB	9%	72 cm^{-1} (+ 144)
Hybrid	-	40 cm^{-1} (-209)

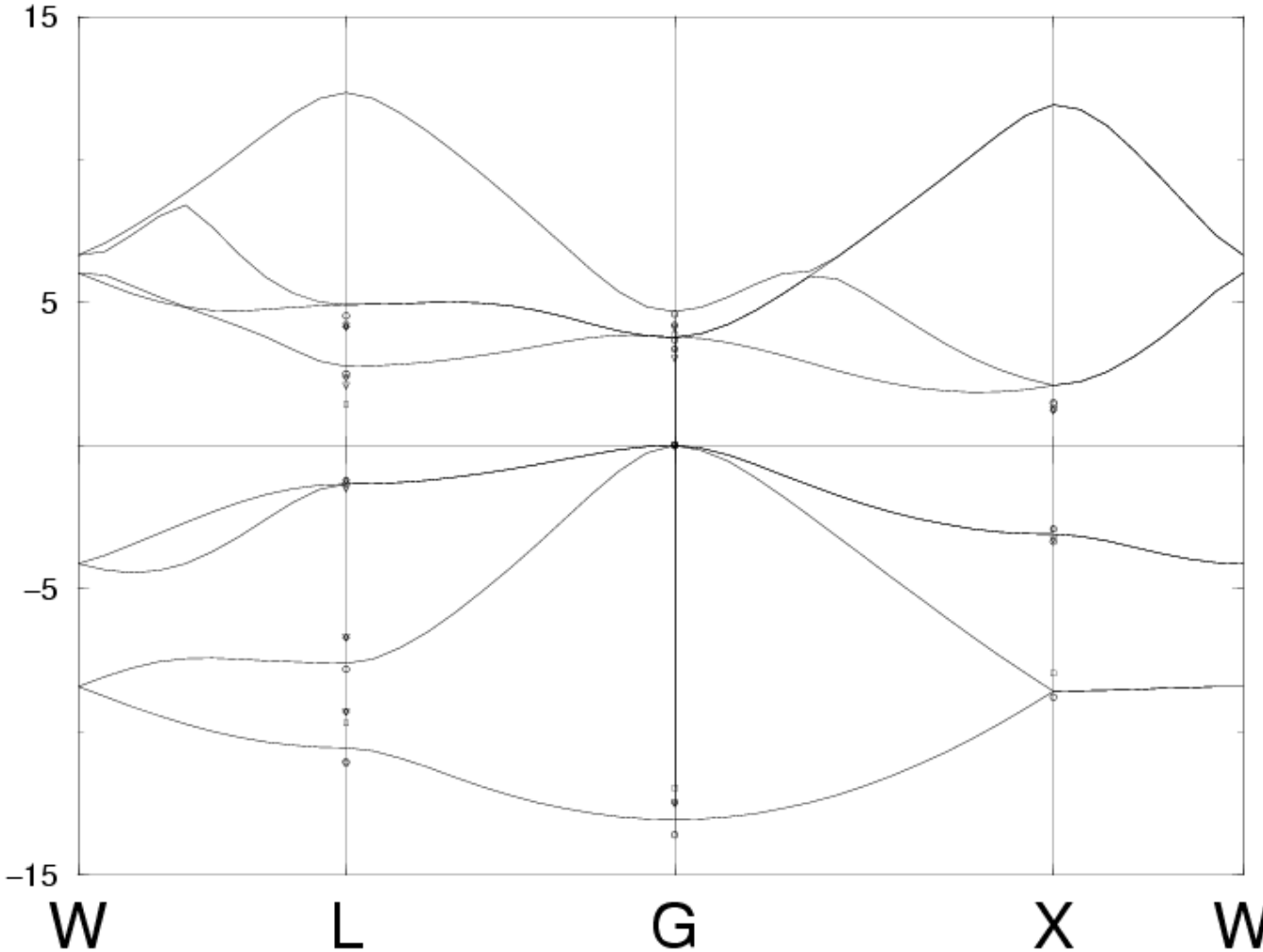
Conclusions II

- Approximations to DFT are currently the state of the art for materials simulation but do not provide a systematic approach to the exact result.
- With a judicious choice of functional atomisation energies are *typically* accurate to 3-5 kcal/mol, structures to 0.01 Ang., frequencies to 40-60 cm^{-1}
- Much larger errors are possible in ‘difficult’ systems
- Heavily parameterised functionals gain a little for the training set but appear to be less transferable
- Hybrid and meta-GGA look very promising.

Hybrid Functionals and Band Gaps

	Expt (eV)	Hybrid (eV)
Si	~ 3.5	3.8
Diamond	5.5	5.8
GaAs	1.4	1.5
ZnO	3.4	3.2
Al_2O_3	~ 9.0	8.5
Cr_2O_3	3.3	3.4
MgO	7.8	7.3
MnO	3.6	3.8
NiO	3.8	3.9
TiO_2	3.0	3.4
FeS_2	1.0	2.0
ZnS	3.7	3.5

The Band Structure of Silicon



Hybrid-DFT lines

GW theory □

QMC ○

Expt Ñ

J. Muscat, A. Wander, N.M. Harrison *Chem. Phys. Lett 2001.*