Exchange and Correlation – cause and effects

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Overview of lecture

- What is Exchange? And correlation?
- LDA and GGA
- Van der Waals bonding
- Beyond GGA
- CASTEP details
- Examples
The problem with DFT

- Difficulty comes from mapping the N-body QM problem onto Nx 1-body QM problem
  - Mapping interacting electrons onto quasi-p
- “DFT cannot do...” :
  - This statement is usually wrong
- Should instead say:
  - “DFT using the ??? XC-functional can be used to calculate ???, but that particular functional introduces an error of ??? because of ???”
In KS-DFT we put all the unknown physics into the XC functional.

Hence: \( E_{xc} = T - T_{KS} + E_{ee} - E_H \)

- \( T \) = exact many-body KE
- \( T_{KS} \) = Kohn-Sham KE of KS orbitals
- \( E_{ee} \) = exact electron-electron interaction
- \( E_H \) = Hartree electron-electron interaction
What is Exchange?
Electrons are Fermions and hence obey Pauli Exclusion Principle

- If exchange the coordinates of 2 identical particles then total wavefunction (space*spin) changes sign = antisymmetric

- This gives rise to the Exchange Energy:

\[ E_X = -\int\int \psi_i(r_1)\psi_j(r_2) \frac{1}{r_{12}} \psi_i(r_2)\psi_j(r_1) dr_1 dr_2 \]
In DFT we want to eliminate wavefunctions

Can we derive a suitable approximation from something we can solve analytically?

Preferably using a density?

Homogenous Electron Gas (HEG)

Put N electrons into a volume V with a uniform positive background charge

No PE, just KE and exchange-correlation

Exchange energy density $\varepsilon_{xc}[n(r)] \sim n^{1/3}$
HEG results

- Analytic result for exchange in HEG

\[
E_{x}^{LDA}[n] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n(r) \frac{4}{3} dr
\]

- Can then use this as an approximation for the exchange energy in any system of the same density – the Local Density Approximation (LDA)

- But not for correlation …
What is Correlation?
Correlation

- Much harder to define!
- Usually defined as difference between exact many-body QM and Hartree-Fock answer:

\[ E_x = E_{tot}^{HF} - T^{HF} - E_{ee}^{HF} - E_{eN}^{HF} \]

- Cannot derive analytically even for HEG except in certain limits
- Use of QMC (Ceperly-Alder 1981) to derive values of \( E_{xc} \) for varying densities
  - Different authors then fit to produce LDA
Formally, we can write

$$E_{xc}[n] = \frac{1}{2} \iiint n(r) \frac{n_{xc}(r, r')}{|r - r'|} drdr'$$

But we do not know $n_{xc}$!

This is the Coulomb energy of an electron at $r$ interacting with its XC hole at $r'$

The XC hole is the displaced charge around an electron – should integrate to 1 e⁻
- We know from the Pauli Exclusion Principle that
  \[ \int n_{xc} (r, r') dr' = -1 \]

- This is known as the *sum rule*

- But we do not know the shape of the hole!
LDA and GGA
The simplest approximation, the LDA, assumes that the hole is spherical:

- DOES obey the sum rule
- Reasonably effective
- Good for many simple systems
- Tends to over-bind atoms – makes the bonds too short and strong, lattice parameters too small, etc.

\[
E_{xc}^{LDA} [n(r)] = \int n(r) \varepsilon_{xc}^{\text{hom}} [n(r)] dr
\]
Generalized Gradient Approximation

- Include value of density AND its derivative
- A *semi-local* approximation so still very quick to calculate
- Parameterized from QMC calculations of HEG + cosine perturbation
- Tends to under-bind – makes bonds too weak – but better for surfaces etc.

\[
E_{xc}^{GGA} [n(r)] = \int n(r) \varepsilon_{xc}^{GGA} [n(r), \nabla n(r)] dr
\]
How good is the GGA?

- Which GGA?
  - There are many! Different ways of parameterizing the same data
  - Not possible to obey all the known analytical limits with any given functional form
  - Discretion in choosing which rules to obey and which functional form to choose
  - NOT a silver bullet – does NOT improve all the things that LDA does not do well – and does some things worse!
Common GGAs


Although exact form of XC functional is not known, we DO know certain rules/limits:

- **Sum rule**: hole integrates to -1
- **Self-interaction correction**:
  - The Hartree energy is Coulomb interaction of classical charge and so contains interactions between electron and itself!
  - True XC functional should correct this.
- **Long-range decay**:
  - Should decay as $r^{-1}$ at long distances
And it is non-analytic:

- There should be a discontinuous jump when add an infinitesimal charge to an integer number of electrons.
How well do the LDA, GGA and HF do?

- Why not use HF? VERY poor band gaps and vibrational properties, more expensive

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<th>Property</th>
<th>LDA</th>
<th>GGA</th>
<th>HF</th>
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<td>Self-interaction correction</td>
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<td>Y*</td>
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<td>$r^{-1}$ long-range decay</td>
<td>N</td>
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<td>Derivative discontinuity</td>
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* Only for occupied orbitals
## Lattice Parameters

### Semiconductor lattice parameters (in Å)

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### Bulk Modulus

#### Bulk modulus (in GPa)

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- Bulk Si: $\rho(\text{LDA}) - \rho(\text{GGA})$
General comments

- **LDA**
  - Nice covalent systems & simple metals

- **GGA:**
  - Molecules, surfaces, H-bonded materials
  - Highly varying densities (d and f states)
  - Some nasty metals
  - Most magnetic systems

- **Missing?**
  - Van der Waals bonded materials, localized electrons, strongly correlated materials …
Van der Waals bonding
VdW (or dispersion bonding) is a non-local effect

- A fluctuation in the electron density on atom 1 causes a temporary electric dipole
- This dipole causes an electric field which decays as $r^{-3}$
- E-field induces dipole on atom 2
- Dipole on atom 2 causes interaction with atom 1 as $r^{-6}$
- Long range, non-local, NOT in any local or semi-local XC functional
A special-purpose functional

- E.g. Dion functional – lacking theoretical foundation and not very good in practice

Semi-empirical dispersion correction (SEDC)

- All based on simple $r^{-6}$ form with pair-wise interaction:

$$E_{vdW} = C_{ij} \frac{f_{damp}(r_{ij})}{r_{ij}^6}$$

- Different schemes have different forms for interaction strength $C_{ij}$ and short-range damping
Beyond GGA
- LDA – only depends on $n(r)$
- GGA – depends on $n(r), \nabla n(r)$
- Meta-GGA – depends on $n(r), \nabla n(r), \nabla^2 n(r)$
- … could continue to higher derivatives BUT always semi-local and more expensive and diminishing returns

- Alternative – go non-local …
- XC hole in simple cosine potential

Accurate XC hole

LDA vs QMC?

Some pictures: XC hole for a simple cosine potential

LDA
XC hole in silicon

Change density of Si in the [111] plane.

The XC-hole associated with an electron at the interstitial site.
- Non-local functionals
  - Screened exchange, WDA etc

- Can go beyond DFT:
  - DFT+U
    - A way of treating very localized (e.g. f electrons) with a Hubbard U parameter
  - Hybrid functionals – mix HF and DFT
  - GW theory, RPA, etc.

- See next week for more details!
CASTEP details
CASTEP

- **LDA**: \texttt{xc\_functional} = LDA
- **GGA**: \texttt{xc\_functional} = PW91/ PBE/ RPBE/ WC/ PBEsol ...
  - All functionality supported by LDA and GGA
- **SEDC**: \texttt{sedc\_scheme} = G06/ OBS/ JCHS/ TS ...
  - Not all elements supported and not all GGA
  - No dispersion corrected phonons (yet)
- **Non-local**: \texttt{xc\_functional} = sX/ PBE/ PBE0/ B3LYP/ HSE03/ HSE06 ...
Examples
Silicon with LDA and sX
AFM FeO with PBE and LDA+U
AFM FeO with PBE0 and sX
Summary
Summary

- DFT is formally exact but in practice has one key approximation – XC functional
  - LDA is quick & simple, tends to over-bind
  - GGA is almost as fast, tends to under-bind
- Both leave out vdW – a non-local interaction
  - SEDC is quick & simple fix for vdW BUT is empirical and not universal
- Non-local XC is expensive
  - See next week for sX and hybrids etc
References
