Beyond DFT with ONETEP

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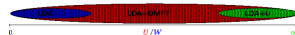Imperial College London

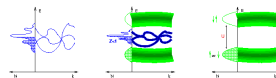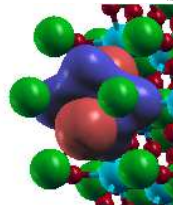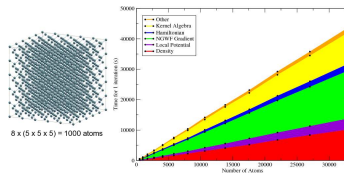16th April 2010

Outline

Beyond DFT with ONETEP

Beyond the scale of traditional DFT

- Already there!

Beyond DFT Accuracy

- NGWFs as a basis
- Correlated approaches
  - LDA+U
  - DMFT
  - MP2
  - ...?

What does a ONETEP Calculation Produce?

- Total Energy and Forces
  - Geometry Optimisation
  - Molecular Dynamics
  - Phonons

- Single Particle Density Matrix in an atom-centered basis
  - Polarisation, Localisation
  - LDOS
  - Population analysis

- In-Situ optimised, localised, minimal basis
  - DFT+U
  - Exact Exchange
  - Moller-Plesset Theory
  - Dynamical Mean Field Theory

Outline

NGWFs vs Wannier Functions

WFs well-known to describe many physical properties.
Is the term "Wannier Functions" appropriate to describe NGWFs?
Imagine Wannier Functions defined for a large cell at Γ:

$$|w_n\rangle = \sum_m U_{mn}|\psi_m\rangle \; ;$$

U_{mn} is a unitary matrix, so the Wannier functions are orthogonal:

$$\langle w_n|w_m\rangle = \delta_{nm}$$

which has many advantages.
NGWFs, on the other hand, are strictly localised:

$$\phi_\alpha(\mathbf{r}) = 0 \qquad \text{if} \qquad |\mathbf{r}| > R_\phi$$

and thus must be allowed to be nonorthogonal (hence *Generalised*)

$$\langle \phi_\alpha|\phi_\beta\rangle = S_{\alpha\beta} \; .$$

The matrix expressing Bloch states in NGWF basis therefore not unitary:

$$|\psi_n\rangle = \sum_\alpha M^\alpha{}_n|\phi_\alpha\rangle \; , \tag{1}$$

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NGWF Optimisation

NGWFs do have a lot in common with WFs!

Ba p   Ti d   O s
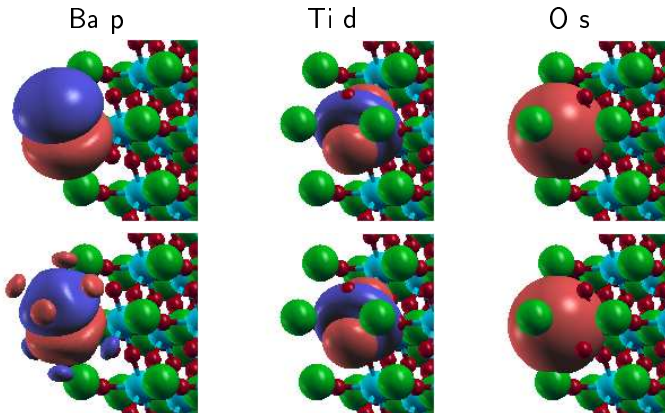
Given correct formalism adapted for nonorthogonal representation, can we use them to carry out the same tasks we do with WFs? Even use them as a basis for other methods?

Are NGWFs physically meaningful?

Exact connection to Bloch states broken by truncation:

$$\sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r})$$

($\phi_\alpha(\mathbf{r})$ strictly localised, $K^{\alpha\beta}$ may be truncated).

Nevertheless, NGWFs can perform many of the same roles as WF's:

- Polarisation
- Band structure interpolation
- Model Hamiltonians
- Projectors for correlated methods (DFT+U, DMFT)

Polarisation

Wannier function centres describe dipole moment of isolated system:

$$\mathbf{d}_{el} = \sum_{i \text{ occ}} \langle \psi_i | \mathbf{r} | \psi_i \rangle = \sum_{n} \langle w_n | \mathbf{r} | w_n \rangle$$

Wannier functions defined for the occupied subspace $\rightarrow$ polarisation of same

$$\begin{aligned}
\mathbf{d}_{el} &= \sum_{i} f_i \langle \psi_i | \mathbf{r} | \psi_i \rangle \\
&= \sum_{i} (M^{\dagger})_i{}^{\beta} f_i M^{\alpha}{}_i \langle \phi_{\alpha} | \mathbf{r} | \phi_{\beta} \rangle \\
&= K^{\alpha\beta} \mathbf{R}_{\alpha\beta}
\end{aligned}$$

Polarisabilities

Gives good description of polarisability of small molecules:

Atomic units	Mean		Anisotropy	
	NGWF	MLWF	NGWF	MLWF
H_2O	10.58	10.48	0.15	0.16
NH_3	15.27	15.23	2.4	2.6
CH_4	17.70	17.49	-	-
C_2H_4	28.50	28.39	12.18	12.03
CO	13.64	13.53	3.52	3.53
CO_2	18.00	17.85	13.88	13.95
N_2	11.99	11.87	4.50	4.55

O'Regan *et al.*, in preparation   3% rms error

NGWFs as a Localised Basis

Advantages compared to a large set of fixed functions (eg Gaussians, NAOs):

- Minimal basis size (eg 4 NGWFs to represent sp^3).
- *In-situ* optimisation
- Controllable accuracy tunable via E_{cut}, R_ϕ.

Several advantages to NGWFs as opposed even to WFs:

- No orthogonality constraint means greater localisation possible.
- Strict localisation imposed:

$$\phi_\alpha(\mathbf{r}) = \begin{cases} \phi_\alpha(\mathbf{r}) & |\mathbf{r} - \mathbf{R}_\alpha| \le R_\phi \\ 0 & |\mathbf{r} - \mathbf{R}_\alpha| > R_\phi \end{cases}$$

- NGWFs are a pre-existing part of the calculation, rather than a post-processing step

Outline

DFT+U

DFT+U: Augment description of on-site Coulomb interactions: cancel spurious self-interaction and promote integer occupancy of localised orbitals

$$E_U = E_{Hubbard} - E_{double-counting}$$
$$= \sum_{I\sigma} \frac{U^I}{2} \text{Tr}(\mathbf{n}^{I\sigma} - \mathbf{n}^{I\sigma}\mathbf{n}^{I\sigma})$$
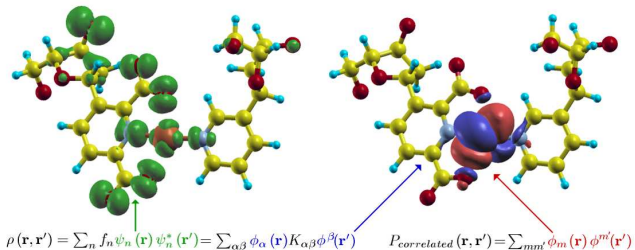
where

$$n^{I\sigma}{}_{mm'} = \sum_i \langle \varphi^I_m | \psi^\sigma_i \rangle f_i \langle \psi^\sigma_i | \varphi^I_{m'} \rangle .$$

Ambiguity over what to use as projectors $\varphi^I_m(\mathbf{r})$... common choices include hydrogenic wavefunctions, valence pseudo-orbitals, LCAO basis functions, and MLWFs. (NB: MLWFs maximise on-site Coulomb repulsion).

DFT+U with NGWFs as Projectors

Providing one can overcome the complications introduced by non-orthogonality, NGWFs provide a resolution of this ambiguity as they emerge naturally from a calculation.

Projectors chosen as $2l+1$ NGWFs with maximal projection onto hydrogenic functions. Accurate description of hybridisation of localised orbitals with neighbours.

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_n f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K_{\alpha\beta} \phi^\beta(\mathbf{r}')$$ $$P_{correlated}(\mathbf{r}, \mathbf{r}') = \sum_{mm'} \phi_m(\mathbf{r}) \phi^{m'}(\mathbf{r}')$$
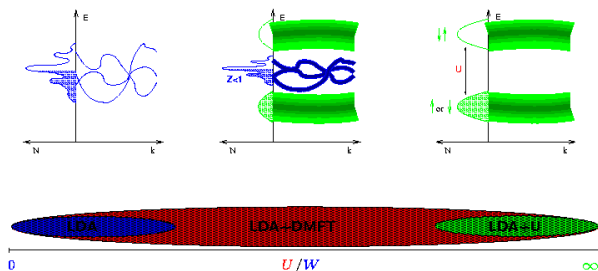
Alleviates the empirical nature of DFT+U somewhat, especially if we can calculate *ab initio* U parameters.

See upcoming talk by David O'Regan.

DFT+DMFT

Dynamical Mean Field Theory

Different regimes of on-site Coulomb U vs bandwidth W:

LDA: works well for $U \ll W$.
No Hubbard bands.
Weakly correlated metal.

LDA+DMFT
$U \sim W$, so we have
Hubbard bands *and*
quasiparticle peaks
Strongly correlated metal

LDA+U: works well for
$U \gg W$.
Hubbard bands split.
Mott Insulator.

DFT+DMFT

Outline

- Perform a standard DFT calculation
- Identify a subspace $\mathscr{C}$ of localised, 'correlated' orbitals.
- Extract $G_{mm'}^{\mathrm{imp}}(i\omega)$ of an effective 'impurity' coupled to a '*dynamical* mean field' representing the rest of the system
- Solve this local problem (the hard work!) for $\Delta\Sigma_{mm'}^{\mathrm{imp}}(i\omega)$
- Promote this back to the full system

DFT+DMFT with NGWF basis

DMFT formalism already expressed in a localised basis. Project out correlated subspace:

$$\hat{P}^{(\mathscr{C})} = \sum_{m \in \mathscr{C}} |\varphi_m\rangle\langle\varphi_m|$$

Transform Greens function between full system and correlated subspace:

$$G_{\alpha\beta}^{-1}(i\omega) = (i\omega + \mu_e)S_{\alpha\beta} - H_{\alpha\beta} - \Sigma_{\alpha\beta}(i\omega)$$

$$G_{mm'}^{\mathrm{imp}}(i\omega) = \langle\varphi_m|\phi_\alpha\rangle G^{\alpha\beta}(i\omega)\langle\phi_\beta|\varphi_{m'}\rangle$$

Becomes a matter of interfacing matrices from ONETEP with a suitable DMFT solver!

In principle, should do self-consistency over charge density, but this is much harder

Outline

Exact Exchange

Calculate the Hartree-Fock exchange energy in terms of eigenstates:

$$E_X = -\sum_{ij} \int \int \frac{\psi_i^*(\mathbf{r}_1) f_i \psi_i(\mathbf{r}_2) \psi_j^*(\mathbf{r}_2) f_j \psi_j(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \ .$$

Can use $\psi_i(\mathbf{r}) = \phi_\alpha(\mathbf{r}) M^\alpha_{\ n}$, $\psi_i^*(\mathbf{r}) = \phi_\beta^*(\mathbf{r}) M_n^{\dagger\beta}$ and $K^{\alpha\beta} = \sum_i M^\alpha_{\ n} f_n M_n^{\dagger\beta}$ to re-write this as

$$E_X = -\sum_{\alpha\beta\gamma\delta} \int \int \frac{\phi_\alpha^*(\mathbf{r}_1) K^{\alpha\beta} \phi_\beta(\mathbf{r}_2) \phi_\gamma^*(\mathbf{r}_2) K^{\gamma\delta} \phi_\delta^*(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \ .$$

Exact Exchange

Or in terms of a non-local potential $X_{\alpha\beta}$ dependent on the kernel:

$$E_X = \sum_{\alpha\beta} K^{\alpha\beta} X_{\alpha\beta} \,,$$

where $\quad X_{\alpha\beta} = \sum_{\gamma\delta} \int \phi_\alpha(\mathbf{r}_1)\phi_\delta(\mathbf{r}_1) \int \frac{\phi_\beta(\mathbf{r}_2)K^{\gamma\delta}\,\phi_\gamma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$

Exact Exchange

Ability to calculate the exchange matrix allows us to use hybrid functionals (eg PBE0, B3LYP) combining some fraction of exact exchange with some fraction of GGA exchange.

PBE0:

$$E_{xc}^{PBE0} = E_{xc}^{PBE} + 0.25(E_x^{HF} - E_x^{PBE})$$

B3LYP:

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} - a_0(E_x^{HF} - E_x^{LDA}) + a_x\Delta E_x^{Becke88} + a_c(E_c^{LYP} - E_c^{LDA})$$

with $a_0 = 0.20$, $a_x = 0.72$ and $a_c = 0.81$.

Good reproduction of quantities such as bandgaps
(is this a good thing?).

Møller-Plesset Perturbation Theory

Møller-Plesset Perturbation Theory: Rayleigh-Schrödinger perturbation theory with the perturbation:

$$\hat{V} = \hat{H} - \hat{F} - \langle \Phi_0 | \hat{H} - \hat{F} | \Phi_0 \rangle$$

where $|\Phi_0\rangle$ is the ground state of the Fock operator, hence $\hat{F}|\Phi_0\rangle = 2\sum_i \varepsilon_i |\Phi_0\rangle$. The unperturbed zeroth-order operator is written

$$\hat{H}_0 = \hat{F} - \langle \Phi_0 | \hat{H} - \hat{F} | \Phi_0 \rangle$$

so the zeroth order energy is just the Hartree-Fock energy:

$$E_{MP0} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$

and the first order correction due to the correlation potential $\hat{V}$ is clearly zero:

$$E_{MP1} = \langle \Phi_0 | \hat{V} | \Phi_0 \rangle$$

Møller-Plesset Perturbation Theory

Only doubly-excited Slater determinants contribute to E_{MP2}.
Applying Slater-Condon rules, second order correction is

$$E_{MP2} = \sum_{i,j,a,b} \langle \psi_i(1)\psi_j(2)|r_{12}^{-1}|\psi_a(1)\psi_b(2)\rangle .$$

$$\frac{2\langle \psi_a(1)\psi_b(2)|r_{12}^{-1}|\psi_i(1)\psi_j(2)\rangle - \langle \psi_a(1)\psi_b(2)|r_{12}^{-1}|\psi_j(1)\psi_i(2)\rangle}{\varepsilon_i - \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

So we can write

$$E \simeq E_{HF} + E_{MP2}$$

However, this scales as $O(N^5)$!

Further terms can be evaluated (MP3, MP4...) with even worse scaling!

Linear-Scaling MP2

Re-write E_{MP2} in terms of local orbitals, transform energy denominators through Laplace transform

Sufficient truncation allows $O(N)$ MP2 calculations.

Will require accurate description of unnoccupied subspace! See upcoming talk by Laura Ratcliff .

Conclusion

- Re-formulate correlated approaches in terms of NGWFs
- NGWFs provide a localised, minimal, *in-situ* optimised basis these calculations
- Good prospects for $O(N)$ correlated methods:
  - DFT+U
  - DMFT
  - MP2 and other QC approaches