Calculations with strictly localised Non-orthogonal Generalised Wannier Functions

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Overview

•Introduction to plane-wave peudopotential DFT for large systems.

•Reformulation in terms of strictly localised Non-orthogonal Generalised Wannier Functions, as implemented in the ONES code. The linear-scaling capability.

•Examples of calculations with the ONES method.

•How polarisation effects could be calculated within the ONES method.

Pseudopotential plane-wave density functional theory with periodic boundary conditions for large systems

- The simulation cell is large and equal to the crystal therefore the first Brillouin zone is (inversely proportional) small and is sampled by only one k-point.

- This is selected to be the Γ-point ($\mathbf{k} = 0$). With this choice the Kohn-Sham eigenfunctions:

$$\hat{H}_{KS}\psi_{n\mathbf{0}}(\mathbf{r}) = \epsilon_{n\mathbf{0}}\psi_{n\mathbf{0}}(\mathbf{r}), \qquad \langle \psi_{n\mathbf{0}}|\psi_{m\mathbf{0}} \rangle = \delta_{nm}$$

$$\psi_{n\mathbf{0}}(\mathbf{r}) = \psi_n(\mathbf{r}) = u_{n\mathbf{0}}(\mathbf{r}) = u_n(\mathbf{r}).$$

can be chosen to be real.

- Single-particle density matrix:

$$\hat{\rho} = \sum_n f_n |\psi_n\rangle\langle\psi_n|$$

$$\rho(\mathbf{r}, \mathbf{r}') = \langle\mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle = \sum_n f_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')$$

Here f_n is the occupation of ψ_n which we will assume it can take only the values 0 or 1 i.e. we will limit our discussion to insulators.

- The charge density $n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$ is the diagonal element in the position representation of the density matrix.

- Minimise total energy $E[\rho(\mathbf{r}, \mathbf{r}')]$ subject to constraints:

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \text{ and } \sum f_n = N_e$$

or equivalently:

$$\hat{\rho}^2 = \hat{\rho} \text{ and } \text{Tr}[\hat{\rho}] = N_e.$$

Non-orthogonal Generalised Wannier Functions

Wannier Functions (WFs): Unitary transformation of $\psi_{n\mathbf{k}}(\mathbf{r})$ in k-space to obtain an equivalent set of functions which are no longer Bloch-periodic but formally extend over all the crystal and are associated with particular simulation cells $w_n(\mathbf{r} - \mathbf{R})$. In our case, since our simulation cell is the crystal, our Wannier functions and "bands" are the same objects.

Generalised Wannier Functions (GWFs): Perform unitary transformations between groups of bands before the k-space transformation. This leads to more localised functions and/or functions that look more "meaningful" such as sp^3 hybrids, σ and π bonds, etc. In our case this means constructing another set of orthonormal orbitals which are no longer eigenfunctions of the Hamiltonian.

Non-orthogonal Generalised Wannier Functions (NGWFs): Perform a (non-singular) linear transformation between groups of bands before the k-space transformation that leads to a non-orthogonal set of functions. NGWFs are more localised than GWFs because they do not have "orthogonality tails".

In our case: mix occupied (and 0 or more unoccupied) eigenfunctions of Hamiltonian into an equivalent linearly independent set of non-orthogonal functions. NGWFs for Γ-point-only calculations (implicit summation convention for repeated Greek indices from now on):

$$\phi_\alpha(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) M_{na}, \; S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle \text{ and } \psi_n(\mathbf{r}) = \phi_\alpha(\mathbf{r})(M^{-1})^\alpha_{\ n}$$

The ONES method: Forget about delocalised "bands" $\{\psi_n\}$ and perform plane-wave pseudopotential DFT directly with NGWFs $\{\phi_\alpha\}$

- The density matrix becomes $\rho(\mathbf{r}, \mathbf{r}') = \sum_n \psi_n(\mathbf{r}) f_n \psi_n^*(\mathbf{r}') = \phi_a(\mathbf{r}) K^{\alpha\beta} \phi_\beta^*(\mathbf{r}')$

  where the *density kernel* is defined by $K^{\alpha\beta} = \sum_n (M^{-1})^\alpha_n f_n (M^{-\dagger})^\beta_n$

- The energy $E[\rho(\mathbf{r}, \mathbf{r}')] = E[\mathbf{K}, \{\phi\}]$

  has to be minimised w.r.t. both $\mathbf{K}$ and $\{\phi\}$. Subject to constraints:

  1. Idempotency (i.e. f_n equal to 1 or 0): $\mathbf{KSK} = \mathbf{K}$ $(\Rightarrow \hat{\rho}^2 = \hat{\rho})$
  2. Constant number of electrons: $\mathrm{Tr}[\mathbf{KS}] = N_e$ $(\Rightarrow \mathrm{Tr}[\hat{\rho}] = N_e)$

NGWFs are strictly localised in real space by being constrained inside spherical regions of fixed radius.
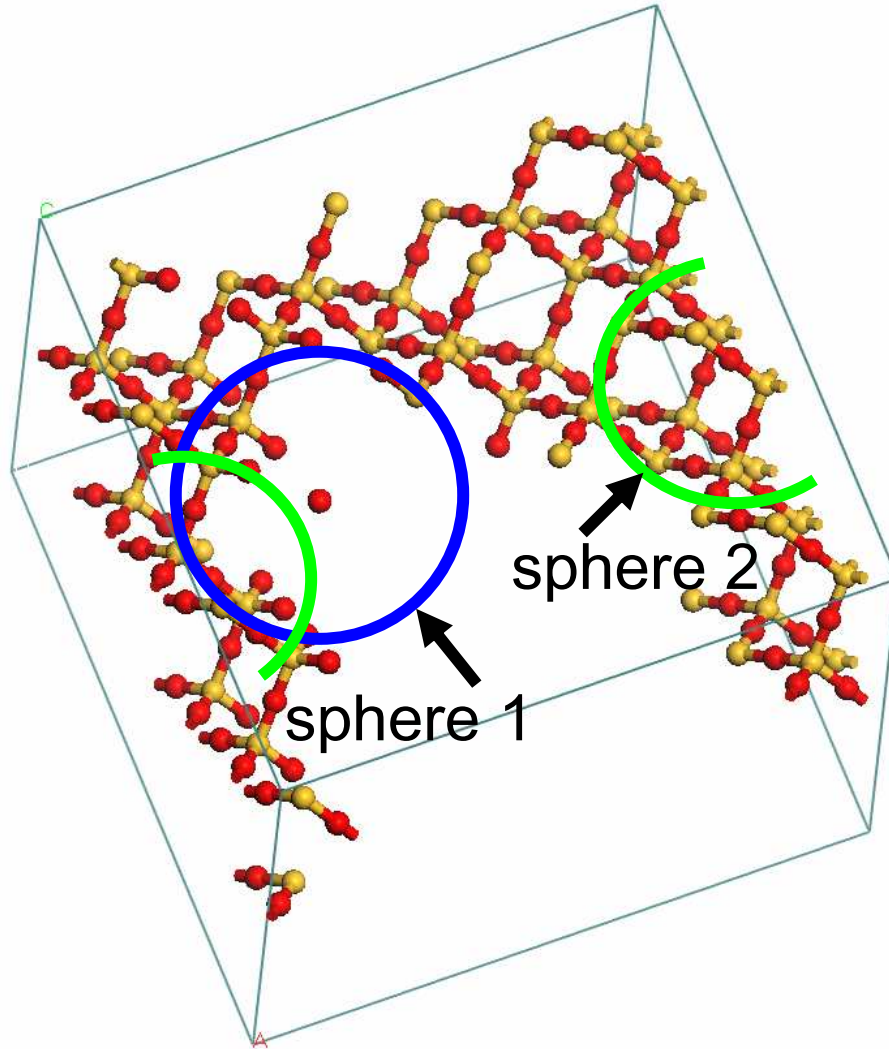
Currently the spherical regions are centred on atoms (and move with them)

Example:

ϕ_α, ϕ_β, ϕ_γ, ϕ_δ are limited to sphere 1.

ϕ_ε, ϕ_ζ, ϕ_η are limited to sphere 2. Etc…

Benefits from using NGWFs: Sparse matrices

• The elements ($S_{\alpha\beta}$) of the NGWF overlap matrix are nonzero only for pairs of functions whose spheres overlap. Their number scales linearly with system size. The same is true for all operators in the NGWF representation (e.g. the Hamiltonian matrix elements $H_{\alpha\beta}$).

•The sparsity pattern of the matrices is therefore fixed during energy minimisation iterations and the energy is variational because no *ad hoc* truncation of the matrices is needed.

Strict localisation in real space means strict delocalisation in reciprocal space!
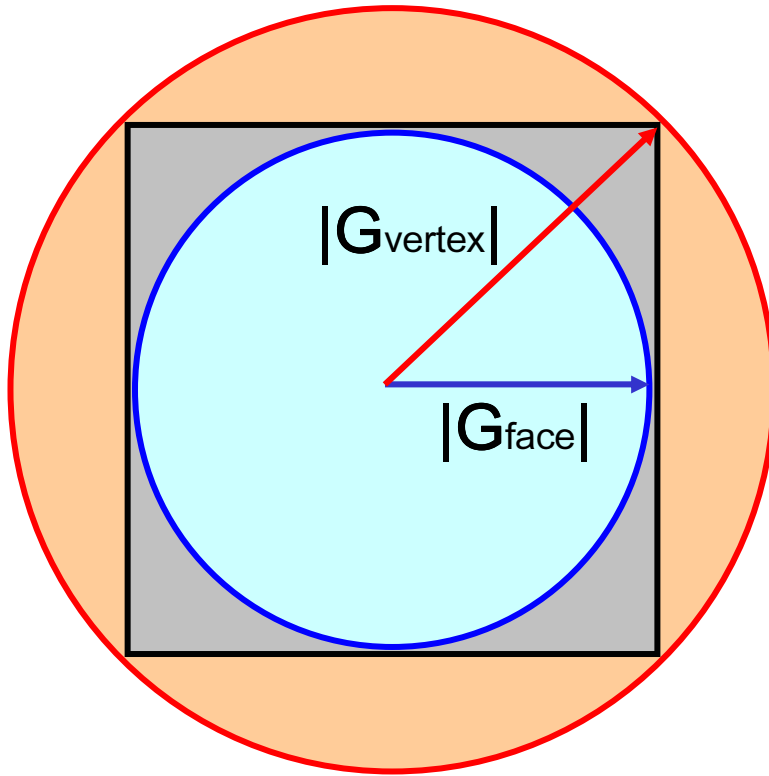
Expand NGWFs in plane-waves of reciprocal lattice vectors **G** of cube with edge 2x$|G_{face}|$.

$|G_{face}| = \pi/a$ where:
a=real space grid spacing.

Provided the NGWFs are converged with respect to sphere size:

$$E_{CASTEP}(|G_{max}| = |G_{vertex}|) \leq E_{ONES} \leq E_{CASTEP}(|G_{max}| = |G_{face}|)$$

- No waste of resources to simulate "empty" space! NGWFs are stored in their real-space representation which is independent of system size. Storage (memory) requirements scale linearly.

- However, for operations in reciprocal space the number of plane-waves per NGWF is proportional to the system size – a situation that leads to quadratic scaling! ☹

- It turns out that the NGWFs are smooth in reciprocal space and can be represented with a small number of plane-waves which is independent of system size:

Linear-scaling restored by the "FFT box" technique! ☺

A linear-scaling pseudopotential plane-wave code

- Sparse matrices with O(N) non-zero elements.

- O(N) storage requirements in real and in reciprocal space for all NGWFs together.

- O(N) energy minimisation algorithms.

- The density matrix decreases exponentially in insulators, so it should also be O(N) sparse.

$$\rho(\mathbf{r}, \mathbf{r}') = \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta^*(\mathbf{r}') \quad \text{and} \quad \lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} \rho(\mathbf{r}, \mathbf{r}') = 0$$

The $\{\phi\}$ are localised by construction. What remains is to make $\mathbf{K}$ sparse by truncating its elements that correspond to spheres separated by more than some cutoff threshold distance.

Silane (40a0)^3 cell

Legend:
- ONES 5a0
- ONES 6a0
- ONES 7a0
- ONES 8a0
- ONES 9a0
- ONES 10a0
- CASTEP E_face
- CASTEP E_vertex

X-axis: Grid spacing (a0)
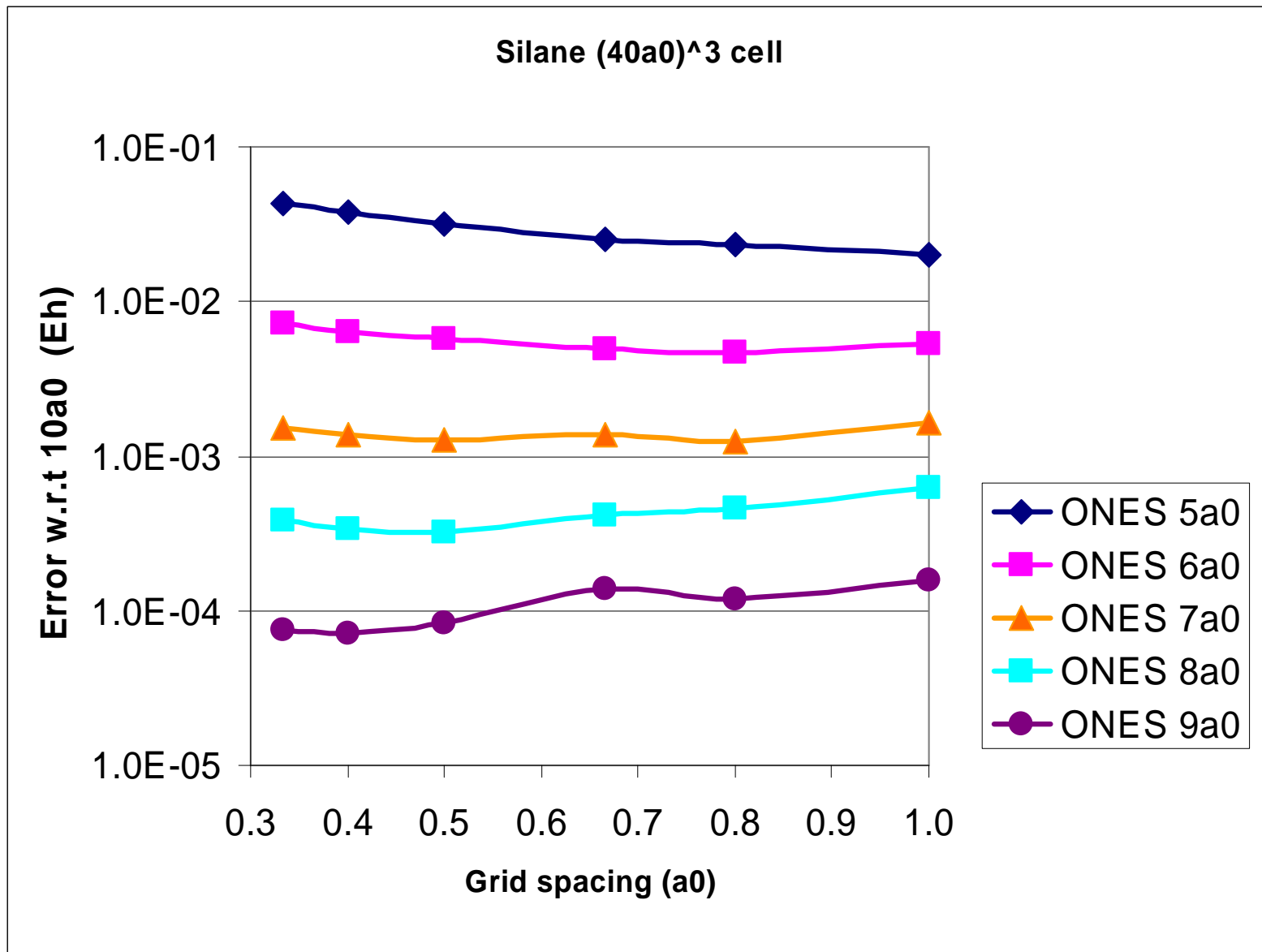Y-axis: Total energy (Eh)
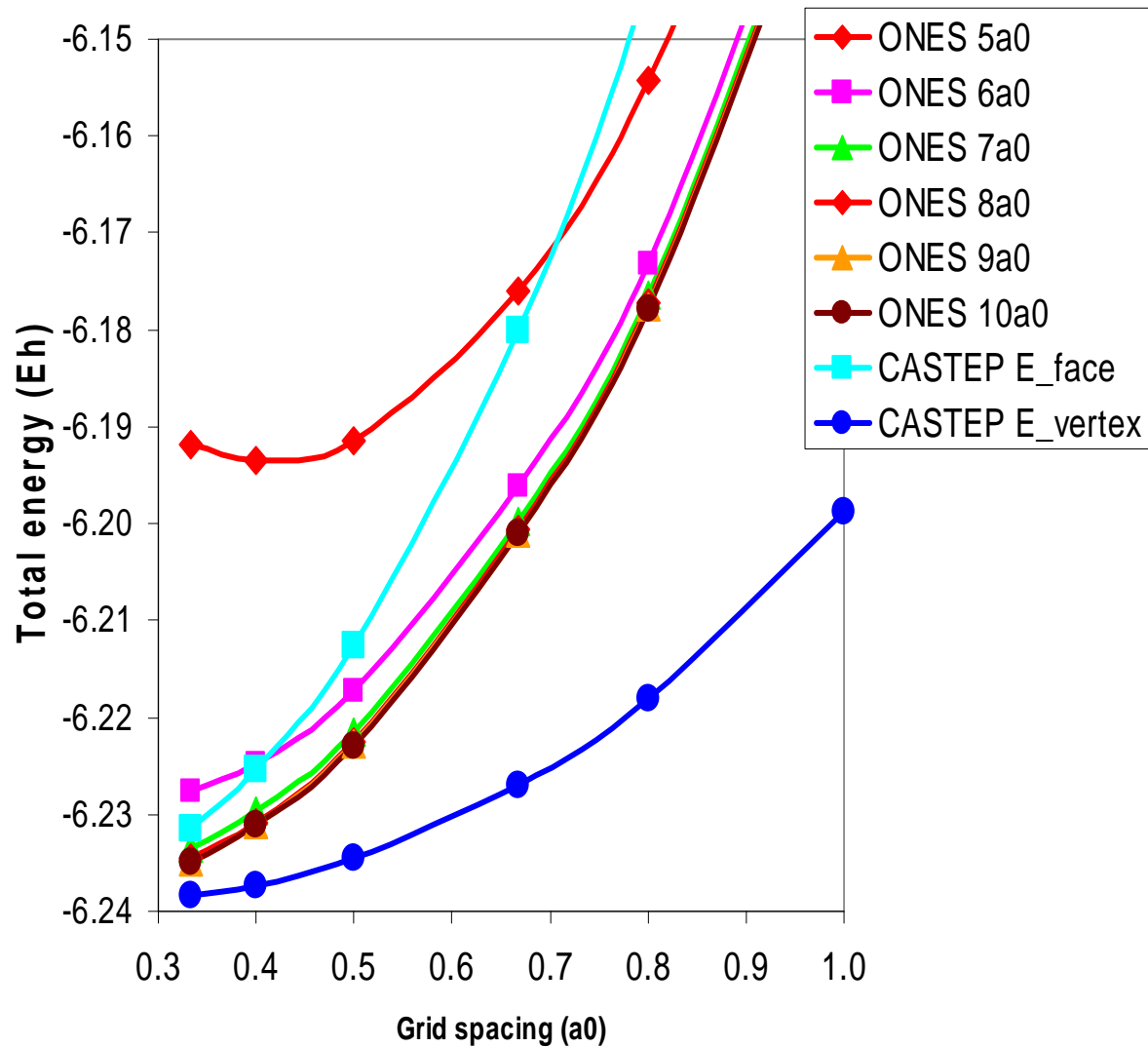
Examples:

Silane molecule, SiH_4.

4 NGWFs on Si, 1NGWF per H. Same radii on both atoms.

Convergence of total energy with:
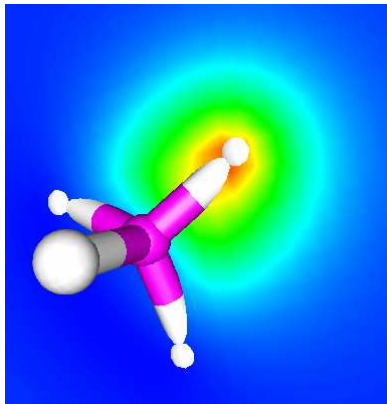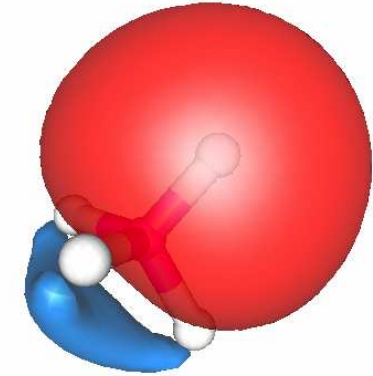
- Grid spacing
- NGWF radius
- Comparisons with CASTEP

Error in total energy with respect to NGWF spheres of radius 10a0
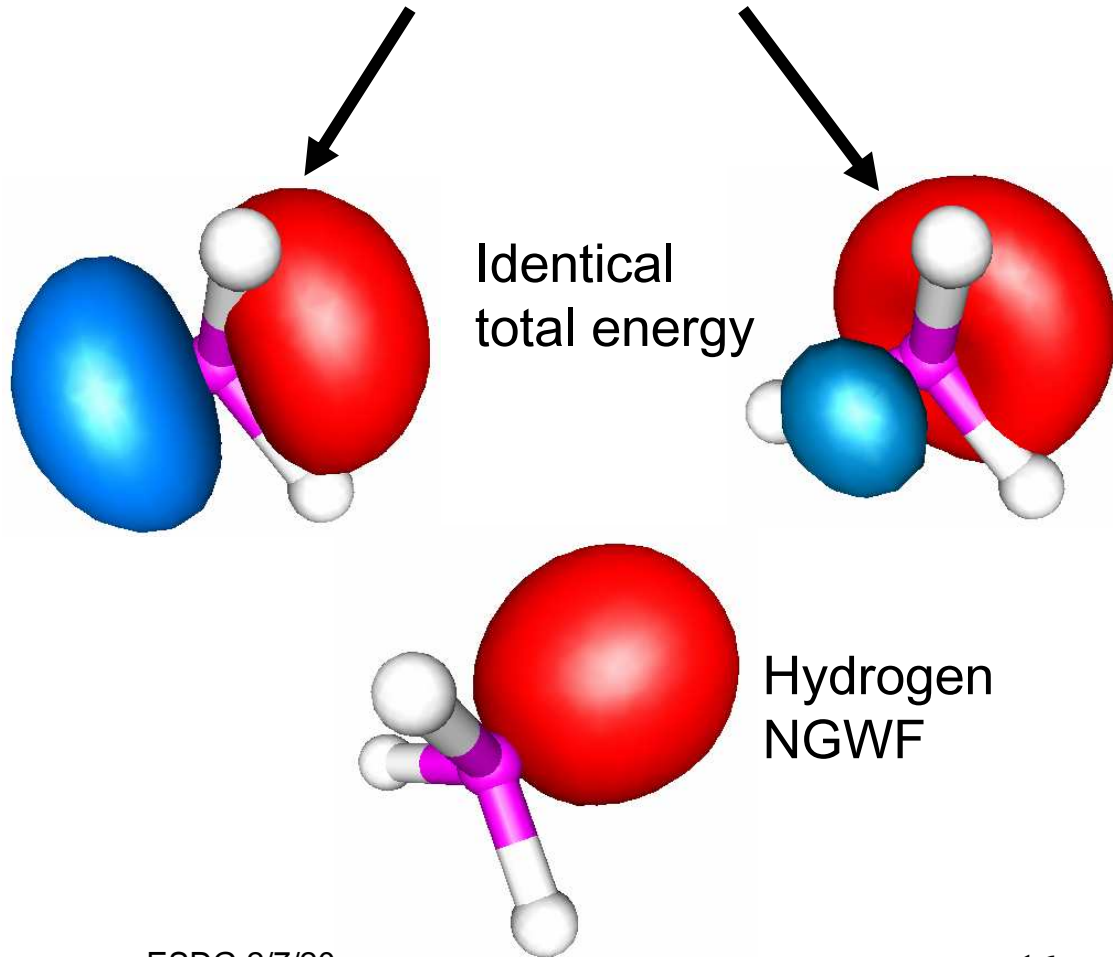
Description in terms of NGWFs is not unique

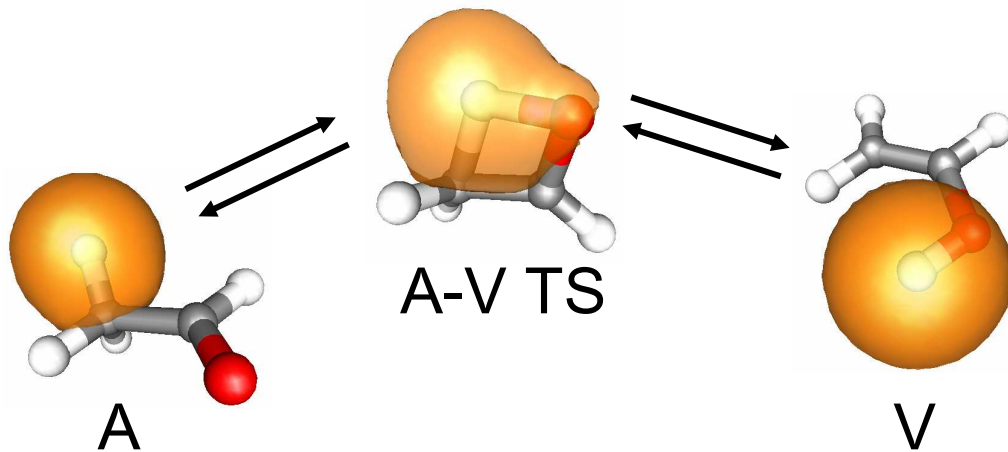One NGWF per H, none on Si:

"Traditional" Generalised Wannier functions

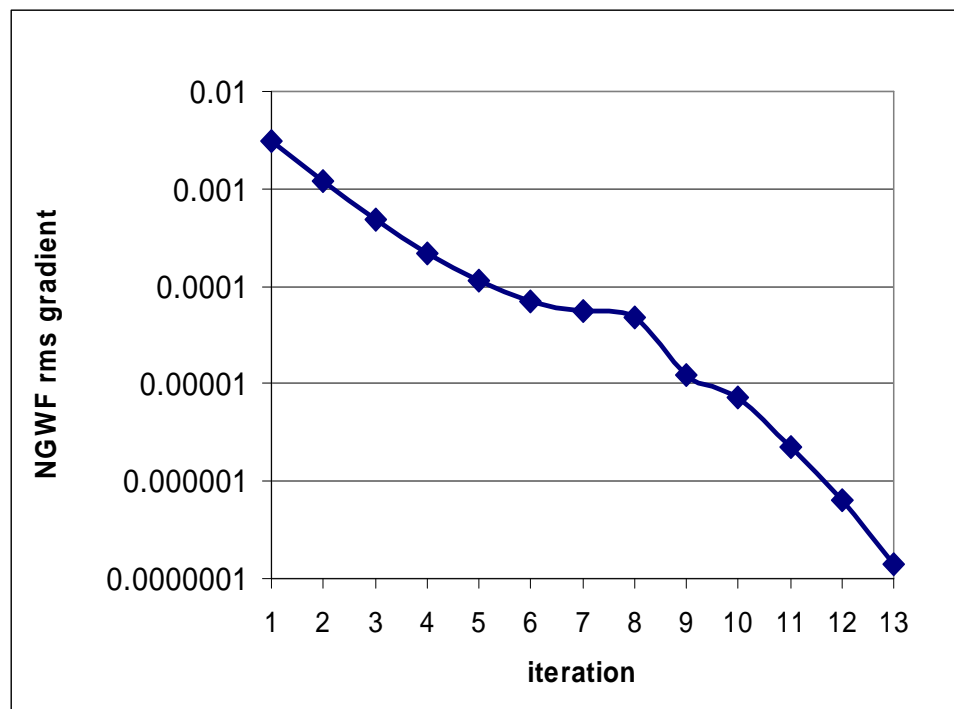Four NGWFs on Si, one per H:

Si NGWFs "atomic" or "sp³ hybrids".

Identical total energy

Hydrogen NGWF

Acetaldehyde – Vinyl alcohol reaction

A-V TS

A

V

NGWFs:

Four on each C,O
with spheres of 6a0.
One on each H with
spheres of 5a0

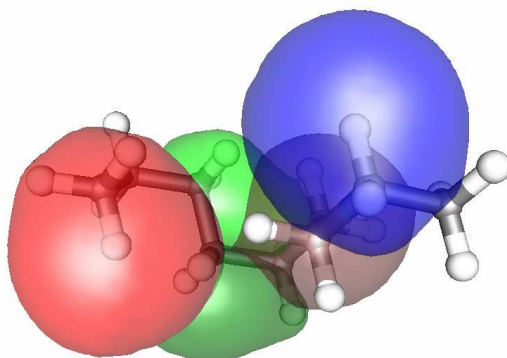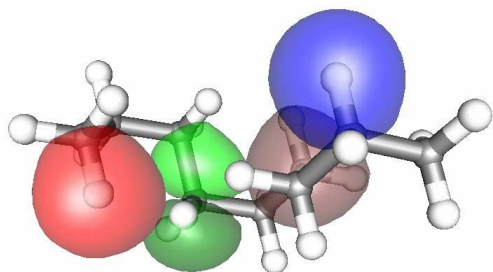NGWF rms gradient vs iteration

Relative energies in kJ/mol

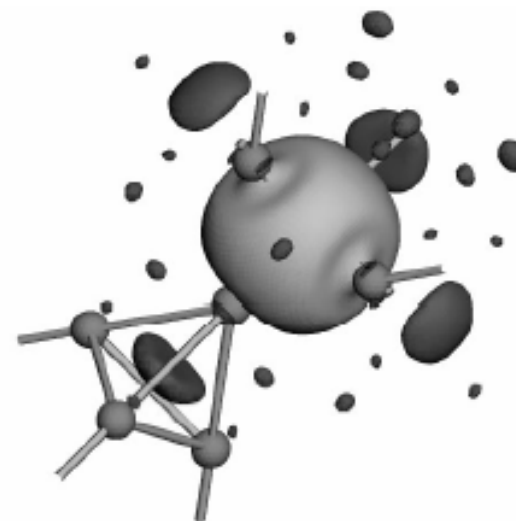|	ONES (0.5 a0)	CASTEP (600 eV)	NWChem (pTZV)
A	0	0	0
A-V TS	224	227	235
V	27	45	31

Nonane: C_9H_{20}

56 NGWFs, 4 on each C atom and 1 one each H atom.

Isosurfaces of NGWFs.
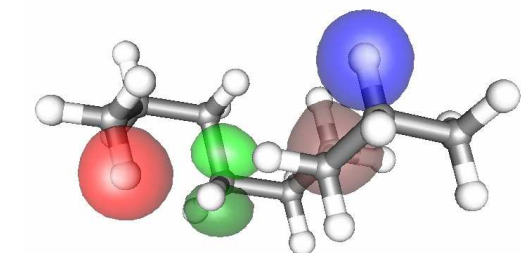
Strict localisation,
no "orthogonality
tails"!

# Calculation of polarisation effects in large systems with periodic boundary conditions

•Finite system, no periodicity: Polarisation is defined as dipole moment per unit volume. Surface contribution must be taken into account as it does not vanish in the thermodynamic limit.

•Periodic system: No surface!
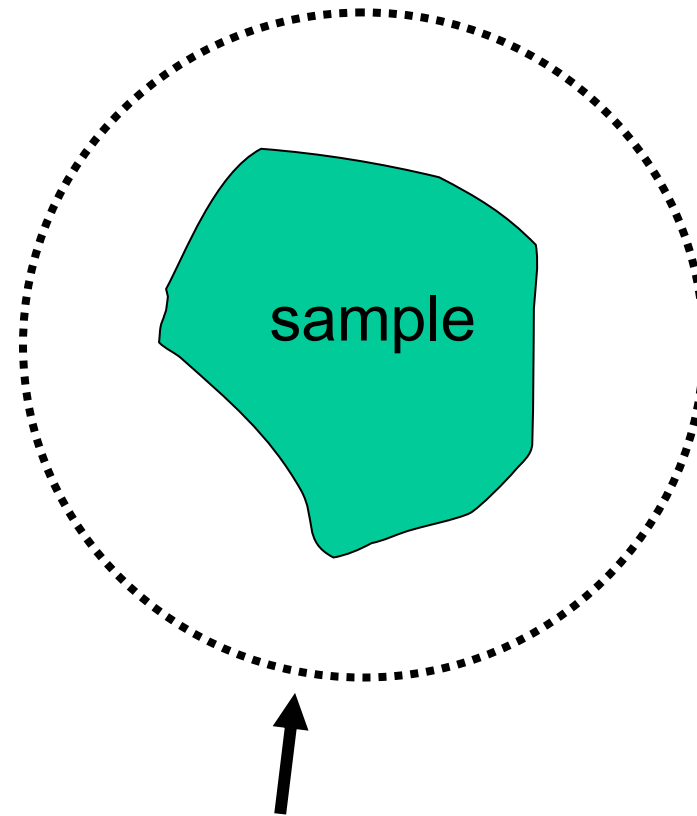
sample

Bounding surface enclosing whole sample and surface charge can always be chosen.

• In experiments, changes (infinitesimal or finite) in polarisation are measured and these appear to be bulk properties.
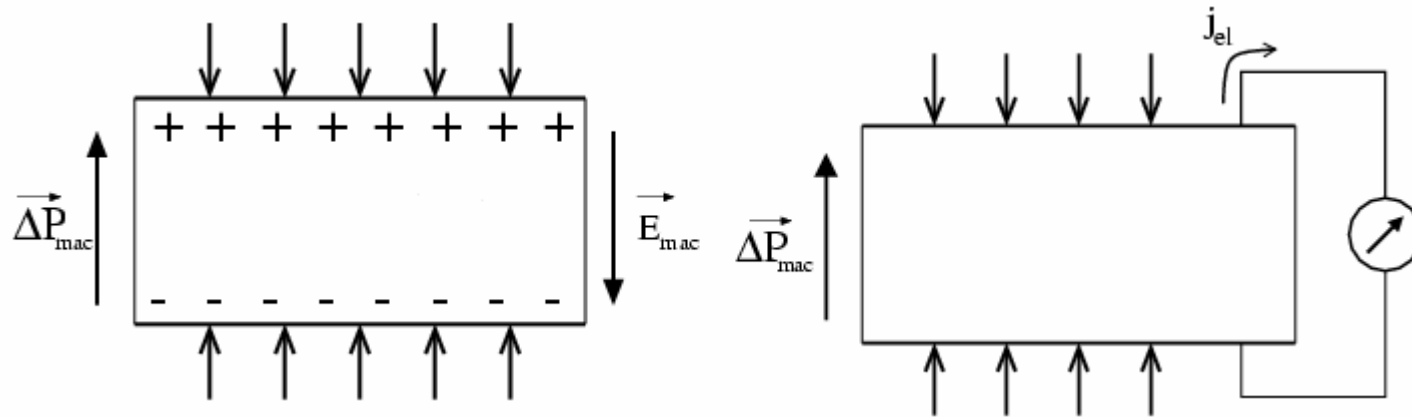
• Changes in polarisation result in changes to surface charge – equivalent to current flow through the solid. Current flow is a bulk property and can be calculated as a phase of the wavefunction, hence it can be applied to solids with periodic boundary conditions and no surfaces!

- Assume electronic current density flowing through system $J_x(t) = \frac{e}{L^3}\frac{d}{dt}\langle\hat{X}\rangle$ where slow (adiabatic approximation) change of system in time is assumed.

- Change in electronic polarisation is defined as:

$$\Delta P_x = \int_0^{\Delta t} dt\, J_x(t) = \frac{e}{L^3}(\langle\hat{X}\rangle^{(\Delta t)} - \langle\hat{X}\rangle^{(0)}) = P^{(\Delta t)} - P^{(0)}$$

- However, the position operator $\hat{X} = \sum_{n=1}^{n_{occ}} x_n$ can not be used in a Hilbert space of periodic functions since when it acts on the functions they are no longer periodic.

- Fix this difficulty by defining:

$$\langle \hat{X} \rangle = \frac{L}{2\pi} \, \text{Im} \ln \langle \Psi | e^{i\frac{2\pi}{L}\hat{X}} | \Psi \rangle$$

where Ψ is the many-body wave function.

- In the mean field case, the change in polarisation can (apparently) be written as:

$$\Delta P_x = \frac{i2e}{(2\pi)^3} \sum_{n=1}^{n_{occ}} \int_{1BZ} d\mathbf{k} \left(\langle u_{n\mathbf{k}}^{(\Delta t)} | \frac{\partial}{\partial k_x} u_{n\mathbf{k}}^{(\Delta t)} \rangle - \langle u_{n\mathbf{k}}^{(0)} | \frac{\partial}{\partial k_x} u_{n\mathbf{k}}^{(0)} \rangle \right)$$

or in terms of Wannier functions:

$$\Delta P_x = \frac{2e}{\Omega} \sum_{n=1}^{n_{occ}} \int_\Omega x \left(|w_n^{(\Delta t)}(\mathbf{r})|^2 - |w_n^{(0)}(\mathbf{r})|^2 \right) d\mathbf{r}$$

and this expression is *invariant* to the various choices of Wannier (or generalised Wannier) functions.

- Indinvidual Wannier (but not generalised Wannier) function centres can be thought of as classical "positions" of the electrons. The conventional multiplicative position operator re-emerged in the above formula as the Wannier functions are no longer periodic (in the ideal case of infinitely extended systems, continuous Brillouin zone sampling).

- The change in polarisation is defined however only modulo $(2e/\Omega)\mathbf{R}$ (="the quantum of polarisation") which corrsponds to charge transport through cells. For small perturbations it should not be observed.

- How can we calculate polarisation changes with ONES? Express Wannier function formula for change in polarisation in NGWF representation:

$$\Delta P_x = \frac{2e}{\Omega}\left(K^{\alpha\beta(\Delta t)}\langle\phi_\alpha^{(\Delta t)}|x|\phi_\beta^{(\Delta t)}\rangle - K^{\alpha\beta(0)}\langle\phi_\alpha^{(0)}|x|\phi_\beta^{(0)}\rangle\right)$$

THE END

Not as elegant as in the case of the (orthogonal) Wannier functions, but it may still be that diagonal position operator elements $\langle\phi_\alpha|x|\phi_\alpha\rangle$ between NGWFs have some meaning. To be continued...