

Calculations on metallic systems with ONETEP

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Density matrix DFT

DFT energy with molecular orbitals

$$E_{\text{DFT}} = \sum_i f_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]$$

Density matrix

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

Density

$$n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$$

Molecular
orbitals

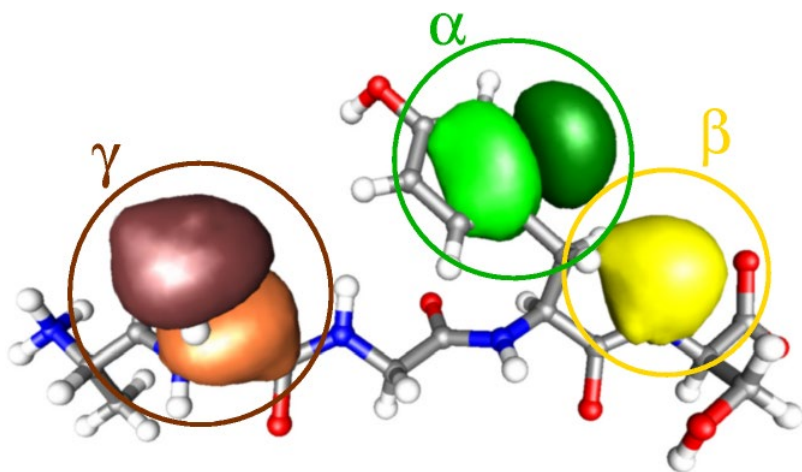
Localised
orbitals

DFT energy with density matrix

$$E_{\text{DFT}} = - \sum_{\alpha, \beta} K^{\alpha\beta} \int \phi_\beta^*(\mathbf{r}) \frac{1}{2} \nabla^2 \phi_\alpha(\mathbf{r}) d\mathbf{r} + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n]$$

The ONETEP linear-scaling approach

- Use a minimal number of $\{\phi_\alpha\}$ but optimise these, like **K**
- Linear-scaling DFT with the same level of basis set accuracy as conventional cubic-scaling DFT



$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta(\mathbf{r}')$$

Non-orthogonal
Generalised
Wannier Functions
(**NGWFs**)

**Density
kernel**

- NGWFs confined to spherical regions
- Density kernel **K** sparse by truncation

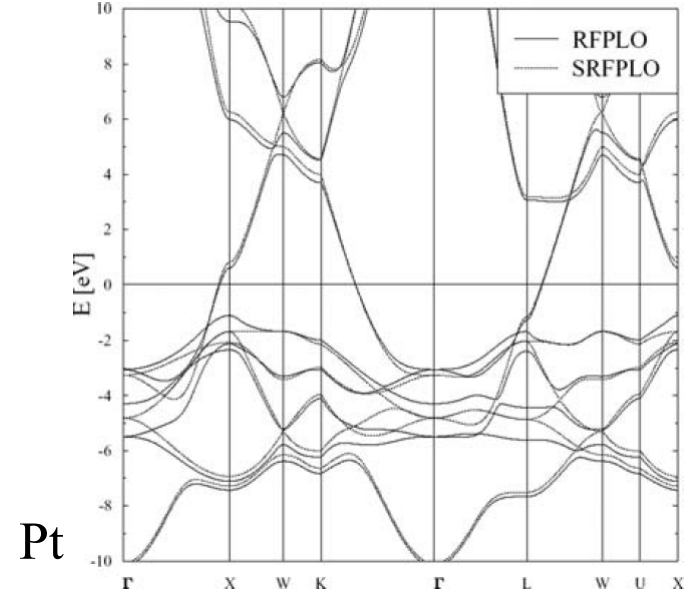
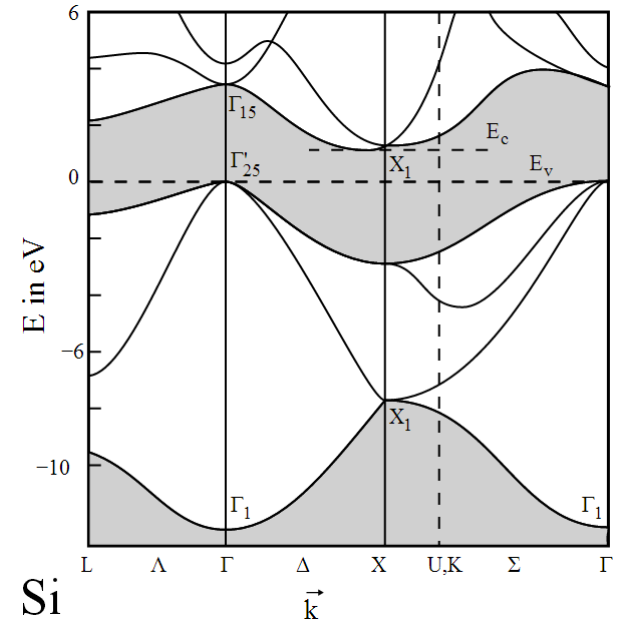
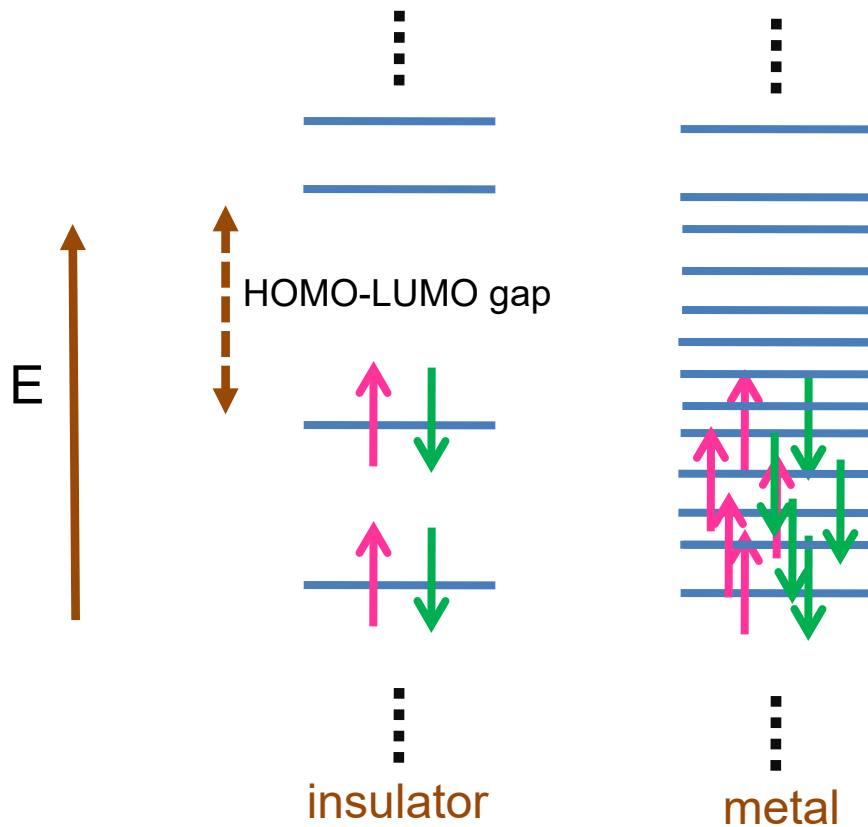
C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez, M. C. Payne, *Phys. Rev. B* **66**, 035119 (2002).

C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, *J. Chem. Phys.* **122**, 084119 (2005).

C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, *Phys. Stat. Sol. (b)* **243**, 973 (2006).

DFT for metals

- Conventional DFT not suitable for materials with small or no band gap
- Small electronic excitations due to finite temperature need to be accounted for



Canonical ensemble electronic theory

Pure state (isolated system at T=0)

- Wavefunction Density operator

$$|\Psi\rangle \quad \hat{\gamma}_N = |\Psi\rangle\langle\Psi|$$

- Energy (E)

$$\langle H \rangle = \langle \Psi | H | \Psi \rangle = \text{tr}(\hat{H} \hat{\gamma}_N)$$

- Variational principle

$$\text{tr}(\hat{H} \hat{\gamma}_N) \geq \text{tr}(\hat{H} \hat{\gamma}_N^0)$$

Mixed state (part of a larger system at finite T)

- Ensemble density operator

$$\hat{\Gamma}_N^0 = \sum_i w_i |\Psi_i\rangle\langle\Psi_i|$$

- Helmholtz Free Energy (A=E-TS)

$$A[\hat{\Gamma}_N] = \text{tr} \hat{\Gamma}_N \left(\frac{1}{\beta} \ln \hat{\Gamma}_N + \hat{H} \right)$$

- Variational principle Entropy
 $S = -k_B \text{tr}(\hat{\Gamma}_N \ln \hat{\Gamma}_N)$

$$A[\hat{\Gamma}_N] \geq A[\hat{\Gamma}_N^0]$$

where Γ_N^0 is the equilibrium canonical ensemble density operator

$$\hat{\Gamma}_N^0 = \sum_i \frac{e^{-\beta \hat{E}_i}}{\text{tr}(e^{-\beta \hat{H}})} |\Psi_i\rangle\langle\Psi_i|$$

Finite temperature DFT

- Finite temperature formulation by Mermin combines canonical ensemble statistical mechanics with DFT
- Mermin-Hohenberg-Kohn Helmholtz free energy functional

N. D. Mermin, *Phys. Rev.* **137**, A1441 (1965)

$$A_V[n] = F_T[n] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

Kohn-Sham finite temperature DFT

- We can develop a Kohn-Sham approach based on Mermin's finite temperature DFT
- Helmholtz Kohn-Sham free energy functional

$$A[T; \{\psi_i\}, \{f_i\}] = \sum_i f_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} + \int V_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] - TS[\{f_i\}]$$

- Electronic density

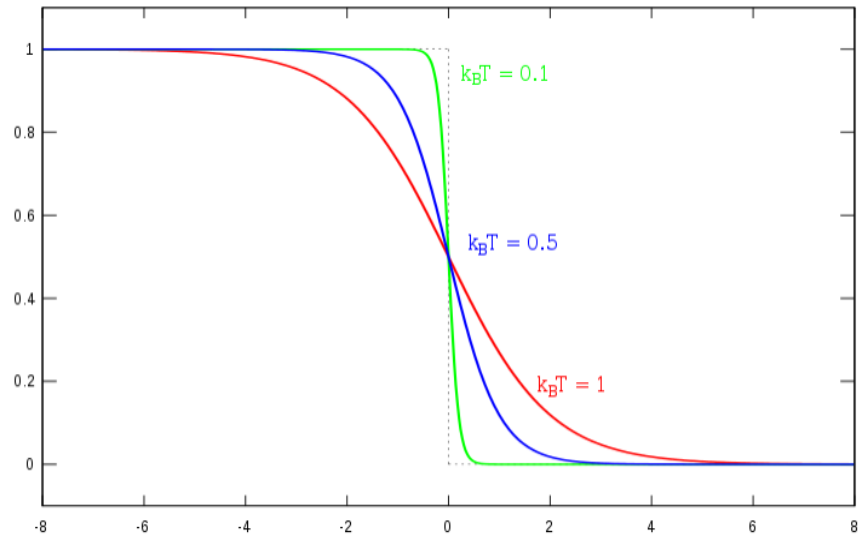
$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

Kohn-Sham finite temperature DFT

- Molecular orbital occupancies follow Fermi-Dirac distribution

$$f_i = f\left(\frac{\varepsilon_i - \mu}{k_B T}\right) = \frac{1}{1 + \exp\left(\frac{\varepsilon_i - \mu}{k_B T}\right)}$$

for molecular orbital ψ_i with energy ε_i



- Electronic entropy

$$S[\{f_i\}] = -k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]$$

- In the canonical ensemble μ is determined by conserving the number of electrons

$$N_e = \sum_i f_i$$

Free energy with orthogonal orbitals

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) U_{ji}^\dagger$$

canonical orbitals \nearrow $\psi_i(\mathbf{r})$ \nwarrow non-canonical orbitals $\chi_j(\mathbf{r})$

- Non-diagonal occupancies

$$f_{ij} = \sum_k U_{ik} f_k U_{kj}^\dagger$$

The Helmholtz free energy

$$A[T; \{\varepsilon_i\}, \{\psi_i\}]$$

becomes

$$A[T; \{H_{ij}\}, \{\chi_i\}]$$

- Eigenvalue equation for energies

$$\sum_j H_{ij} U_{jk} = U_{ik} \varepsilon_k$$

Efficient methods to minimise the free energy using non-canonical orbitals

• N. Marzari, D. Vanderbilt and M. C. Payne, *Phys. Rev. Lett.* **79**, 1337 (1997)

• C. Freysoldt, S. Boeck, and J. Neugebauer, *Phys. Rev. B*, **79**, 241103(R) (2009).

Free energy with non-orthogonal orbitals

Molecular orbitals
(orthogonal)

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) U_{ji}^\dagger$$

canonical orbitals \nearrow $\chi_j(\mathbf{r})$ non-canonical orbitals \nwarrow



ONETEP NGWFs
(non-orthogonal)

$$\psi_i(\mathbf{r}) = \sum_\alpha \phi_\alpha(\mathbf{r}) M_i^\alpha$$

canonical orbitals \nearrow $\phi_\alpha(\mathbf{r})$ NGWFs \nwarrow

- Free energy

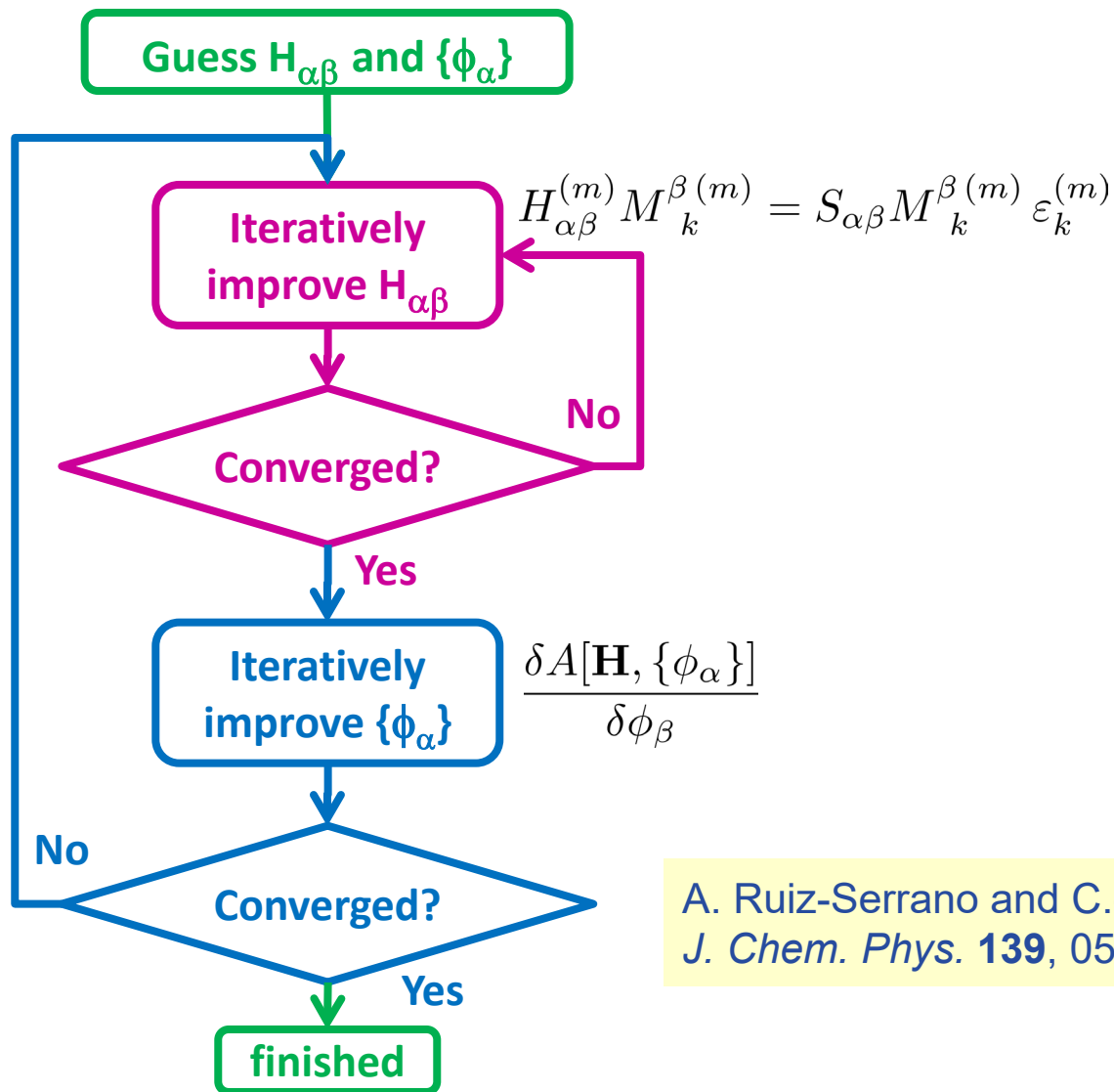
$$A[T; \{H_{ij}\}, \{\chi_i\}]$$

$$A[T; \{H_{\alpha\beta}\}, \{\phi_\alpha\}]$$

- Eigenvalue equation to solve for orbital energies (and occupancies)

$$\sum_j H_{ij} U_{jk} = U_{ik} \varepsilon_k \quad \longrightarrow \quad \sum_\beta H_{\alpha\beta} M_k^\beta = \sum_\beta S_{\alpha\beta} M_k^\beta \varepsilon_k$$

Electronic free energy optimisation in ONETEP



A. Ruiz-Serrano and C.-K. Skylaris,
J. Chem. Phys. **139**, 054017 (2013)

Inner loop: Hamiltonian matrix optimisation

$$A'[T; \{\phi_\alpha\}] = \min_{\{H_{\alpha\beta}\}} A[T; \{H_{\alpha\beta}\}, \{\phi_\alpha\}]$$

At iteration m

MO energies $H_{\alpha\beta}^{(m)} M_k^{\beta(m)} = S_{\alpha\beta} M_k^{\beta(m)} \varepsilon_k^{(m)}$

F-D occupancies $f_i^{(m)} = f(\varepsilon_i^{(m)})$

Density $n^{(m)}(\mathbf{r}) = \phi_\alpha(\mathbf{r}) K^{\alpha\beta(m)} \phi_\beta^*(\mathbf{r}) \quad K^{\alpha\beta} = \sum_k M_k^\alpha f_k M_k^{\dagger\beta}$

F-D Hamiltonian $\tilde{H}_{\alpha\beta}^{(m)} = H_{\alpha\beta}[n^{(m)}]$

Search direction $\Delta_{\alpha\beta}^{(m)} = \tilde{H}_{\alpha\beta}^{(m)} - H_{\alpha\beta}^{(m)}$

Energy minimisation $H_{\alpha\beta}^{(m+1)} = H_{\alpha\beta}^{(m)} + \lambda \Delta_{\alpha\beta}^{(m)}$

$m \leftarrow m+1$

Outer loop: NGWF optimisation

$$\min_{\{\phi_\alpha\}} A'[T; \{\phi_\alpha\}]$$

Conjugate gradients approach. Computation of gradient at iteration l :

- 1) Gradient
$$g^{\beta(l)}(\mathbf{r}) = \left(\frac{\delta A'}{\delta \phi_\beta^*} \right)^{(l)} = \hat{H}^{(l)} \phi_\gamma^{(l)}(\mathbf{r}) K^{\gamma\beta}$$
- 2) MO orthonormality constraint
$$g^{\beta(l)}(\mathbf{r}) = \hat{H}^{(l)} \phi_\gamma^{(l)}(\mathbf{r}) K^{\gamma\beta} - \phi_\gamma^{(l)}(\mathbf{r}) K^{\gamma\delta} H_{\delta\nu}^{(l)} S^{\nu\beta(l)}$$
- 3) Make covariant
$$g_\alpha^{(l)}(\mathbf{r}) = \hat{H}^{(l)} \phi_\gamma^{(l)}(\mathbf{r}) K^{\gamma\beta} S_{\beta\alpha}^{(l)} - \phi_\gamma^{(l)}(\mathbf{r}) K^{\gamma\delta} H_{\delta\alpha}^{(l)}$$
- 4) Occupancy preconditioning
$$g_\alpha^{(l)}(\mathbf{r}) = \hat{H}^{(l)} \phi_\alpha^{(l)}(\mathbf{r}) - \phi_\gamma^{(l)}(\mathbf{r}) S^{\gamma\delta(l)} H_{\delta\alpha}^{(l)}$$
- 5) Kinetic energy preconditioning
$$g_\alpha^{(l)}(\mathbf{r}) = \hat{P} \left[\hat{H}^{(l)} \phi_\alpha^{(l)}(\mathbf{r}) - \phi_\gamma^{(l)}(\mathbf{r}) S^{\gamma\delta(l)} H_{\delta\alpha}^{(l)} \right]$$

Outer loop: NGWF optimisation

$$g_{\alpha}^{(l)}(\mathbf{r}) = \hat{P} \left[\hat{H}^{(l)} \phi_{\alpha}^{(l)}(\mathbf{r}) - \phi_{\gamma}^{(l)}(\mathbf{r}) S^{\gamma\delta(l)} H_{\delta\alpha}^{(l)} \right]$$

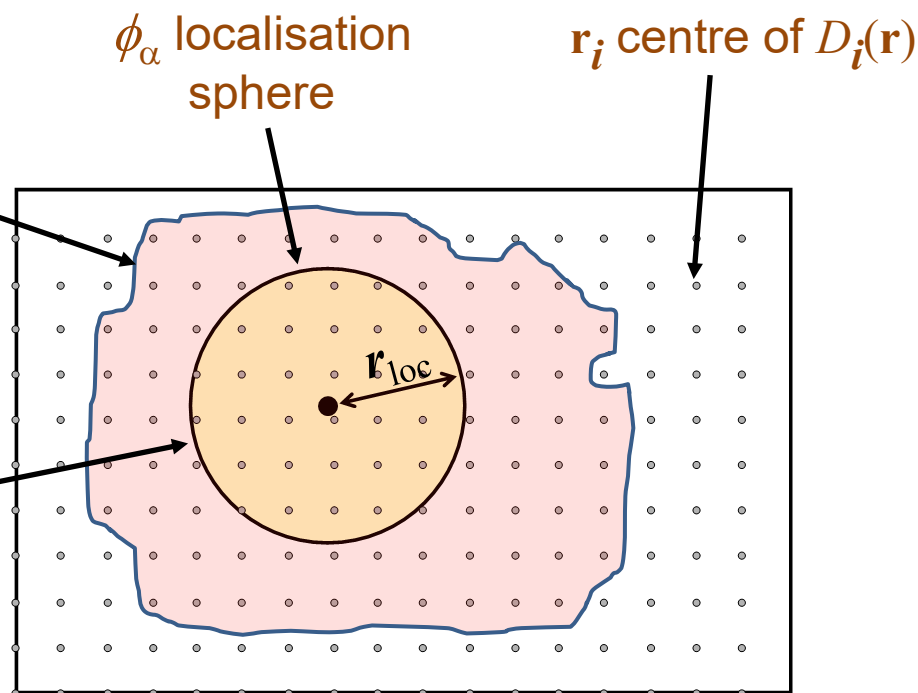
In the psinc basis set the gradient is delocalised

$$g_{\alpha}^{(l)}(\mathbf{r}) = \sum_i D_i(\mathbf{r}) g_{\alpha,i}^{(l)}$$

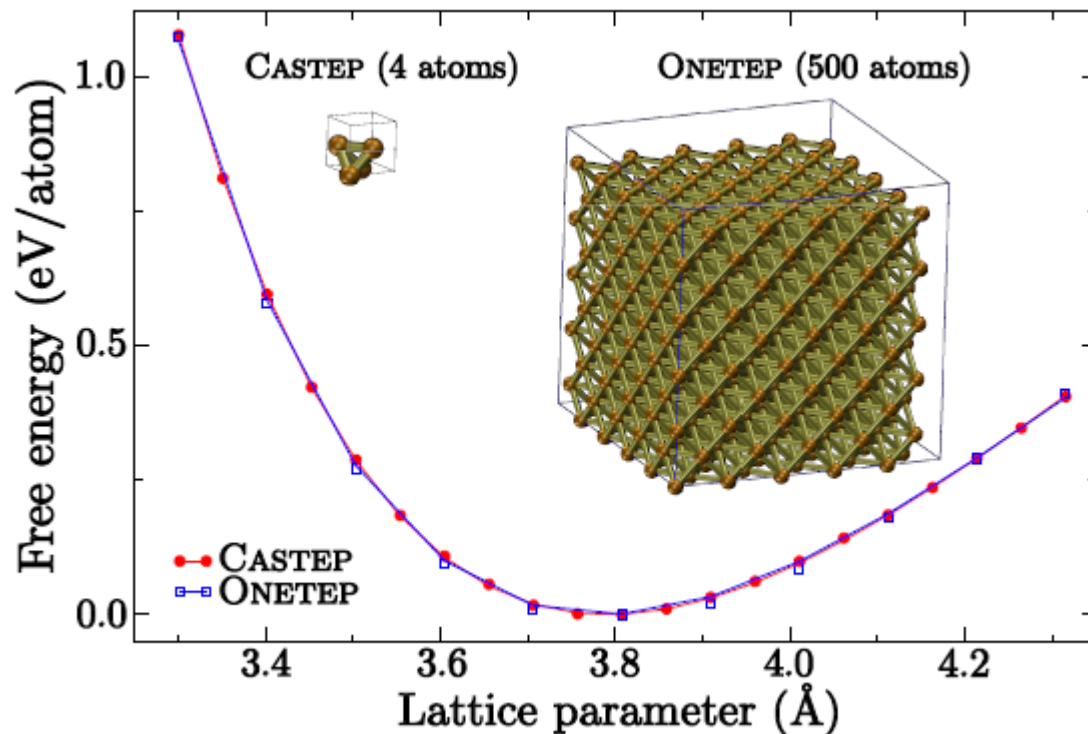
Re-localise by truncating outside localisation region of ϕ_{α}

$$g_{\alpha,\text{loc}}^{(l)}(\mathbf{r}) = \sum_{i \in \text{LR}_{\alpha}} D_i(\mathbf{r}) g_{\alpha,i}^{(l)}$$

Use this gradient to iteratively optimise the NGWFs with a conjugate gradients approach



Calculations on bulk Cu



ONETEP settings

K.E. cutoff: 900 eV

$K_B T$: 0.1 eV

xc: RPBE

NGWF radius: 4 Å

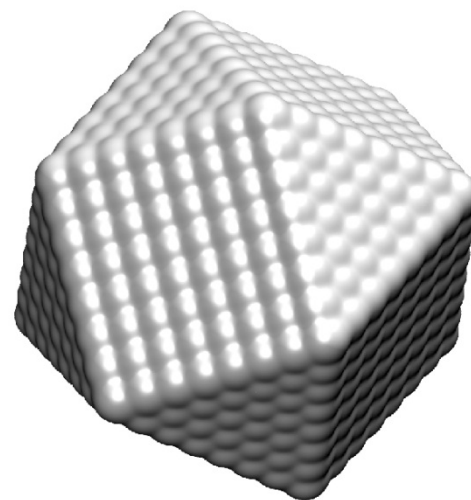
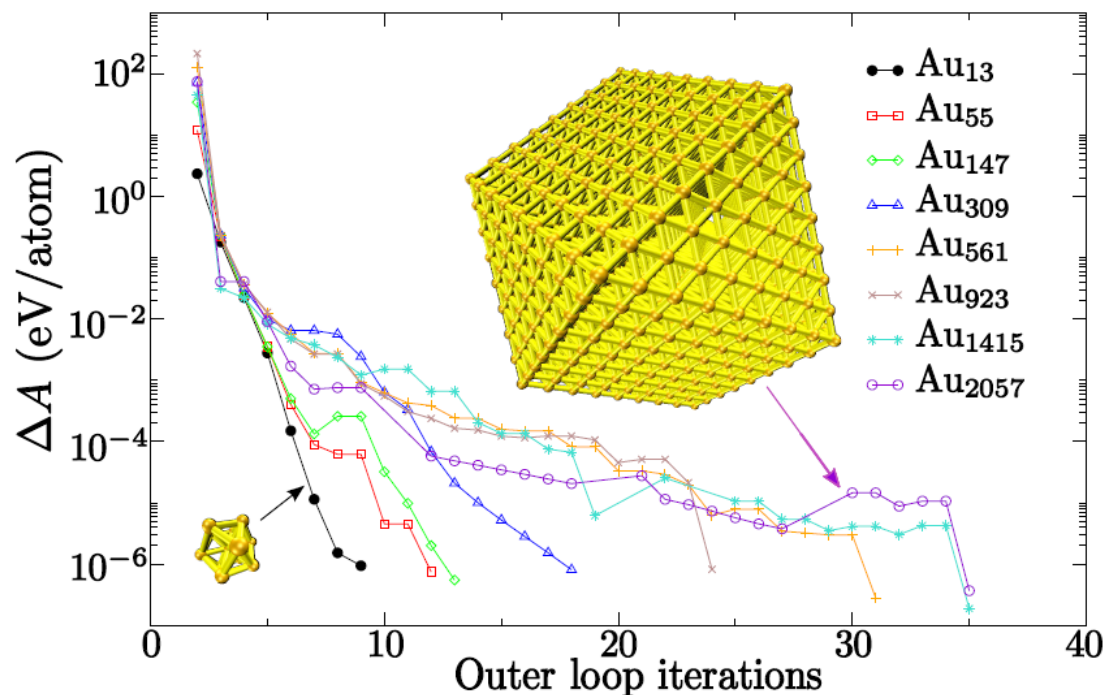
4500 energy levels (bands)

	B (GPa)	L_0 (Å)
CASTEP	93.57	3.79
ONETEP	93.51	3.79

Au cubo-octahedral nanoparticles

- Optimisation of NGWFs
- Convergence

- Psinc kinetic energy cut-off: 950 eV
- XC functional: RPBE
- NGWF radii: $9.45 a_0$



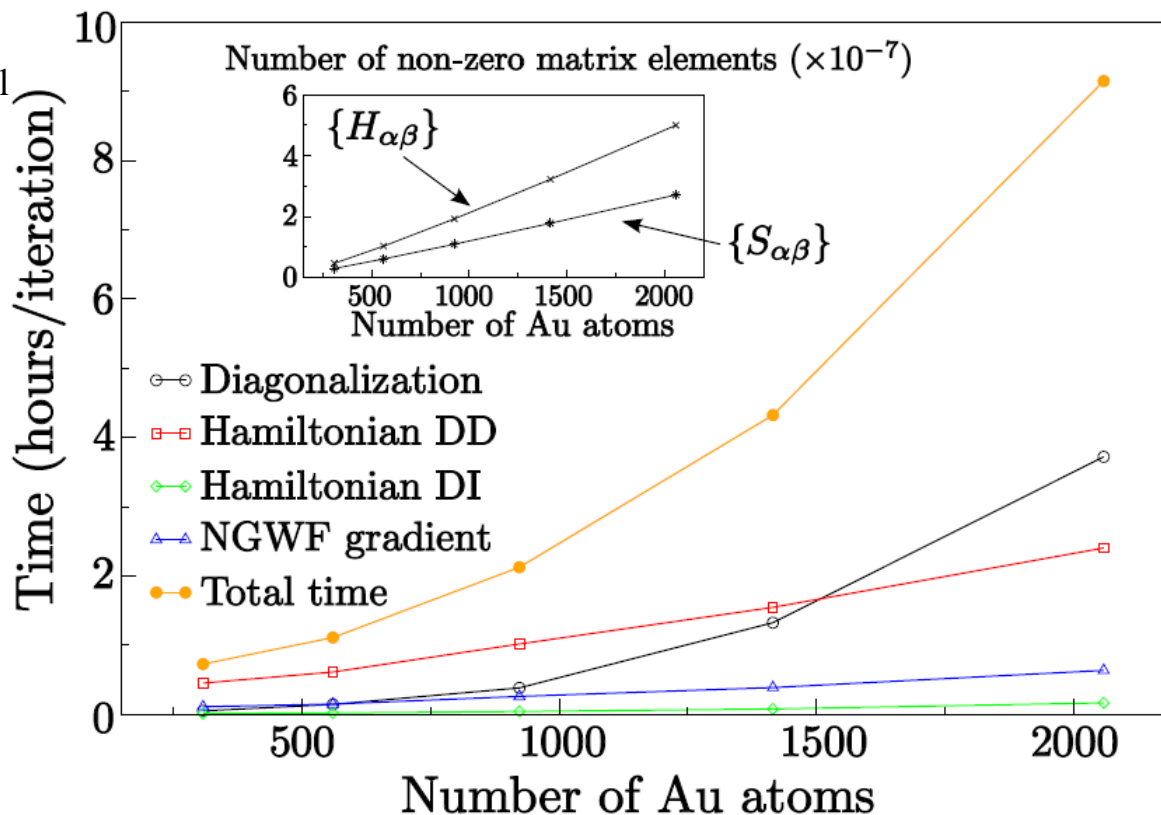
Electron density isosurface of Au₁₄₁₅ (run on 192 cores)

Reference: Au₁₃ to Au₁₄₁₅, run on 32768 cores

J. Kleis, ..., J. K. Nørskov, et al, *Catal. Lett.* **141**, 1067 (2011)

Performance and scaling with the number of atoms

- 120 cores (2.4 GHz Intel Westmere)
- ScaLAPACK parallel eigensolver



- Most operations are linear-scaling operations such as the construction of the (sparse) Hamiltonian matrix
- But diagonalisation of the Hamiltonian is a cubic-scaling operation
- Calculations with thousands of atoms are possible due to the minimal size of matrices in ONETEP and the use of parallel eigensolvers

EDFT in ONETEP: main keywords

EDFT T ---- activate EDFT

EDFT_SMEARING_SCHEME ---- occupancies smearing scheme, Fermi-Dirac (default), Methfessel-Paxton, or Gaussian

EDFT_MAXIT ----- max number of iterations in the inner loop, usually between 10 to 25

EDFT_SMEARING_WIDTH ----- the electronic temperature, typically a value like 0.1 eV which is close to 1000 K

EDFT_SPIN_FIX ----- spin relaxation, for example a value of 2 means that spin is held fixed in the first 2 NGWF iterations and then it is relaxed

EDFT_FERMI_TRESH --- more «expert» parameter for controlling convergence of the Fermi level, for example 1E-8 Ha would provide very tight convergence

All keywords can be found in the documentation for EDFT:

https://docs.onetep.org/onetep_edft_documentation.html