

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

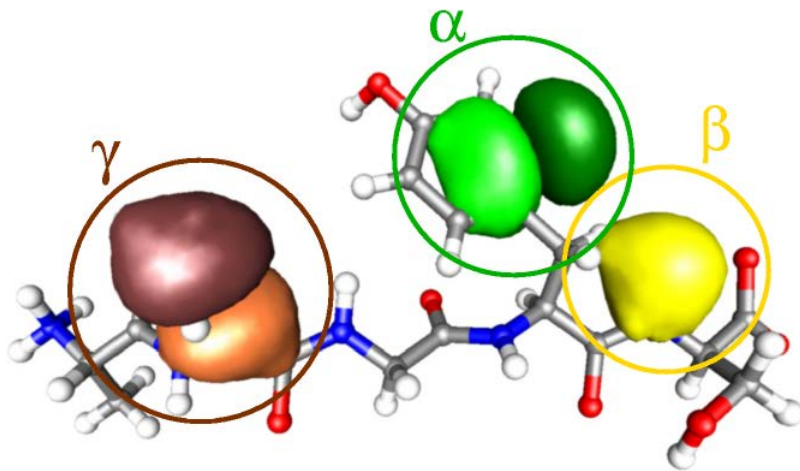
Localised
orbitals

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

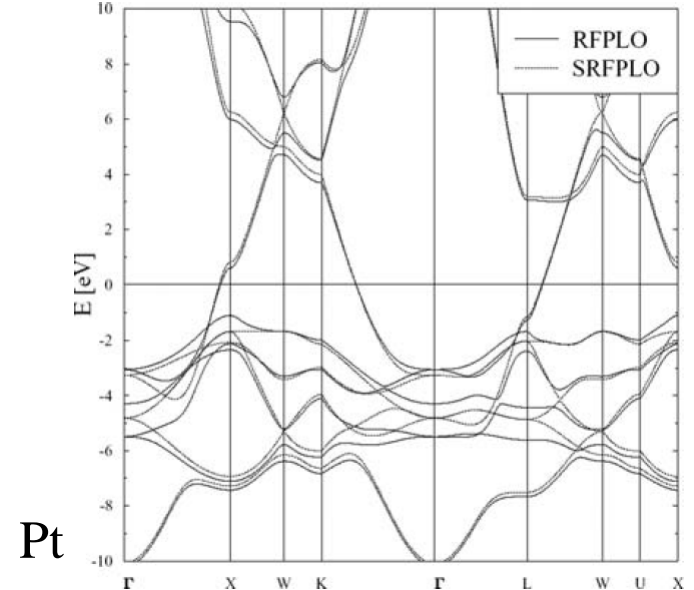
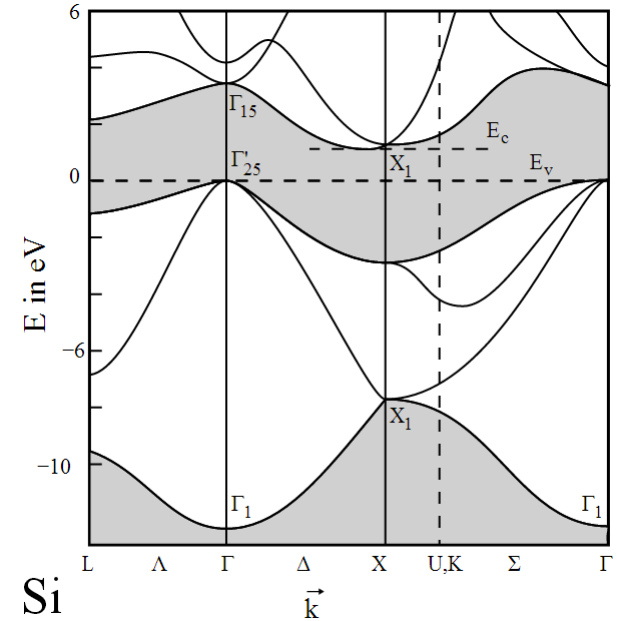
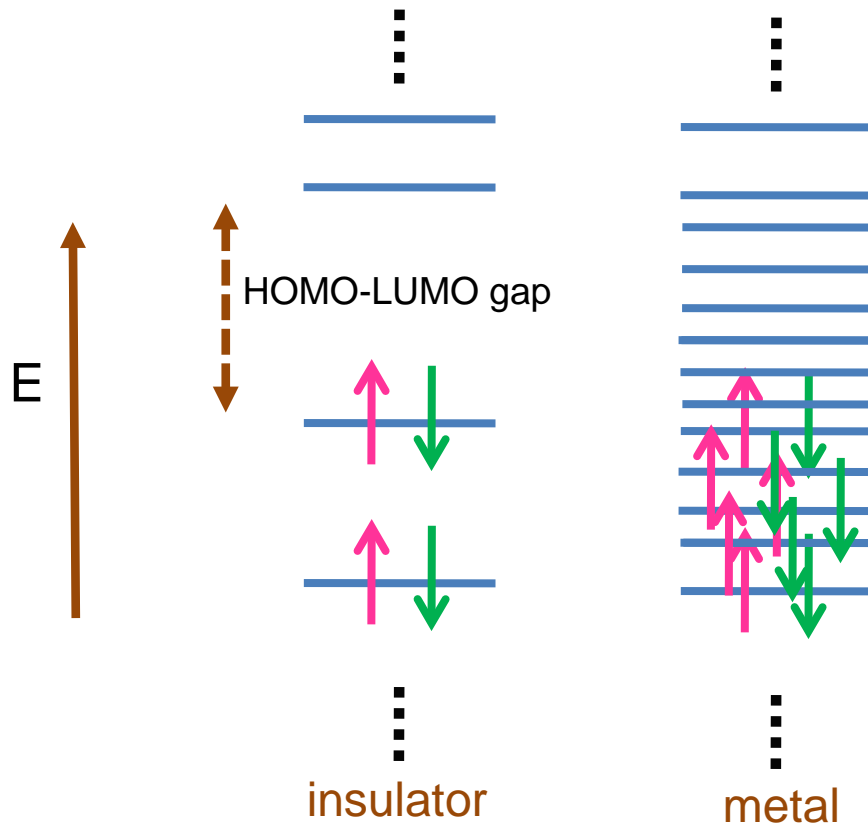
C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez, M. C. Payne, *Phys. Rev. B* **66**, 035119 (2002).

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 or 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

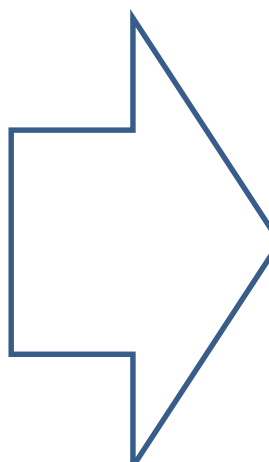
Entropy

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

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

where $\hat{\Gamma}_N^0$ 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

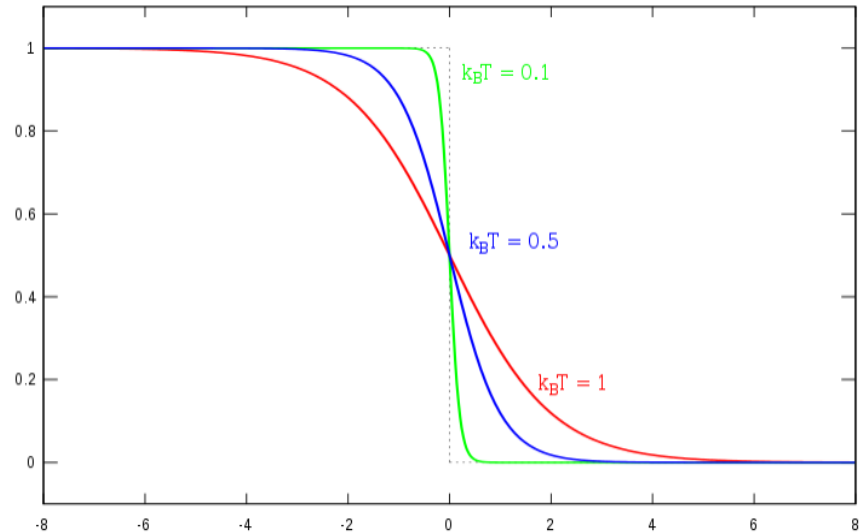
$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

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



ONETEP NGWFs
(non-orthogonal)

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

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

- Free energy

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

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

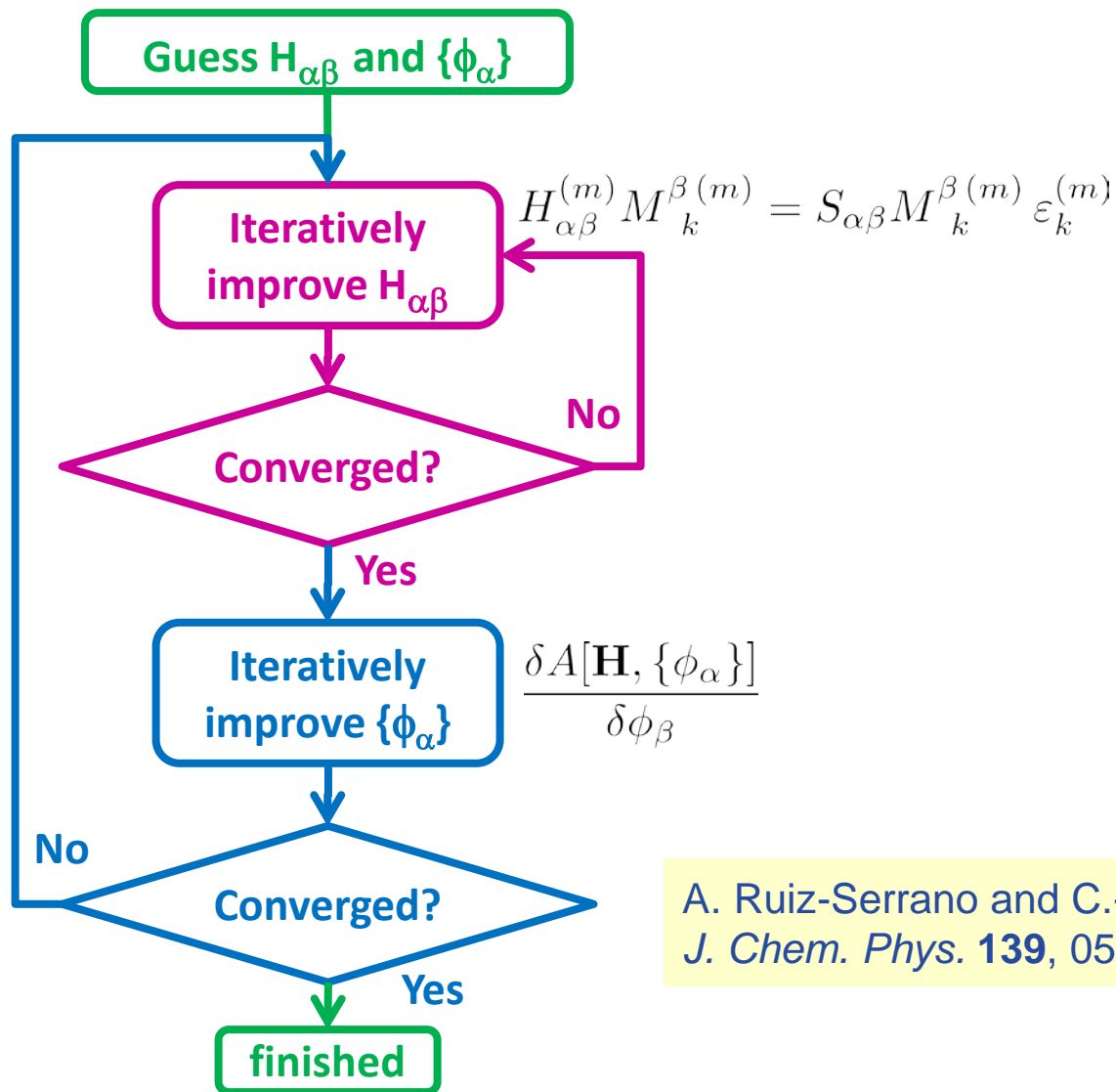
- Eigenvalue equation to solve for orbital energies (and occupancies)

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



$$\sum_\beta H_{\alpha\beta} M_k^\beta = \sum_\beta S_{\alpha\beta} M_k^\beta \varepsilon_k$$

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

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

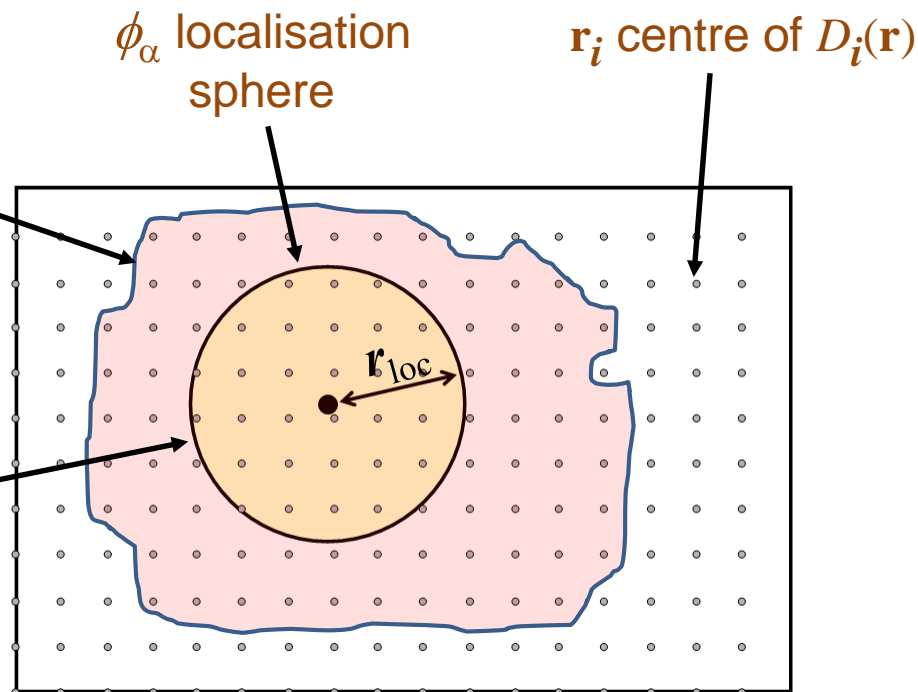
In the psinc basis set the gradient is delocalised

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

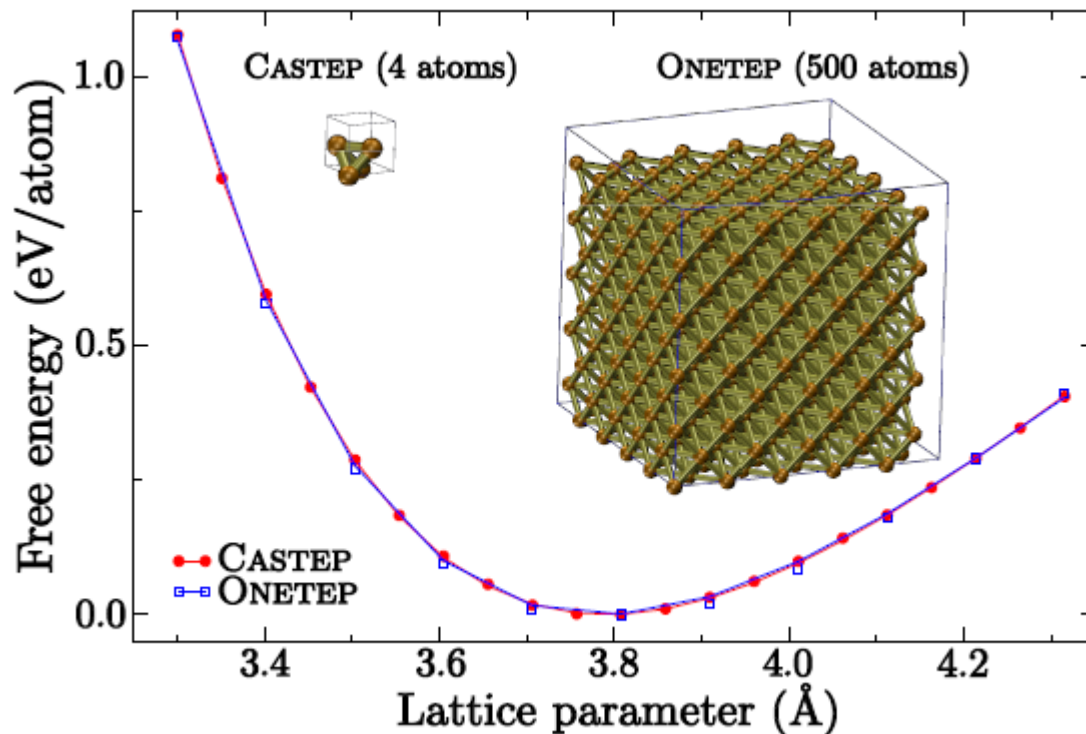
Re-localise by truncating outside localisation region of ϕ_{α}

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

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

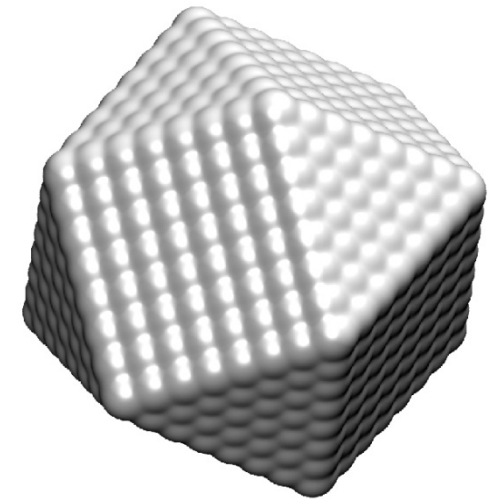
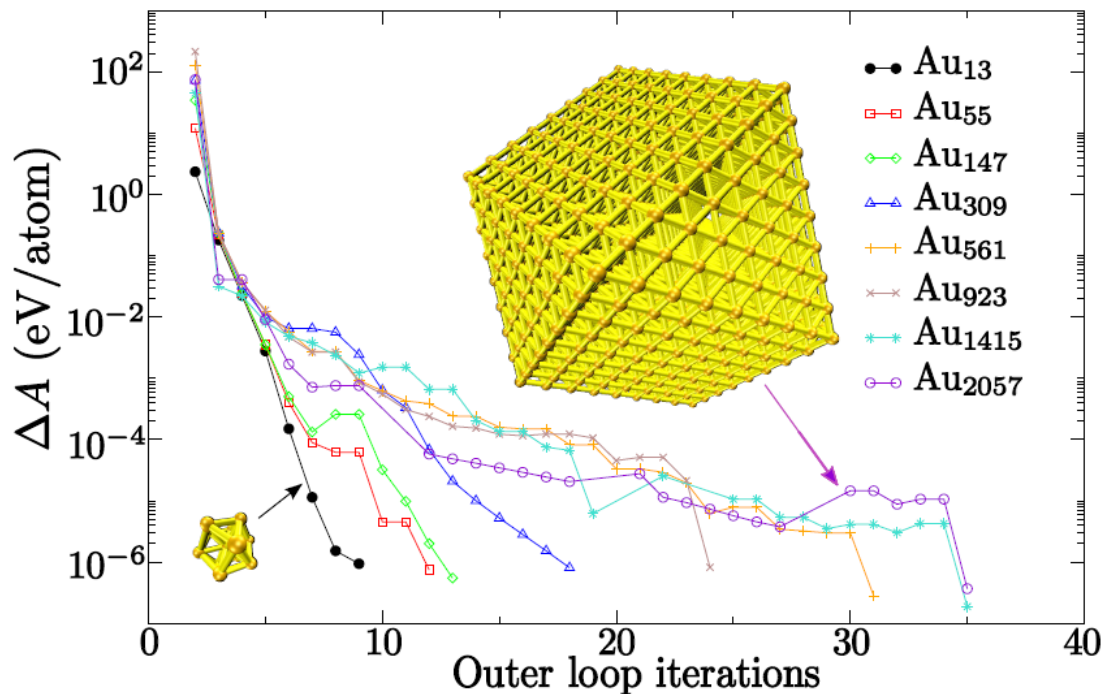
4500 energy levels (bands)

	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: $9.45 a_0$



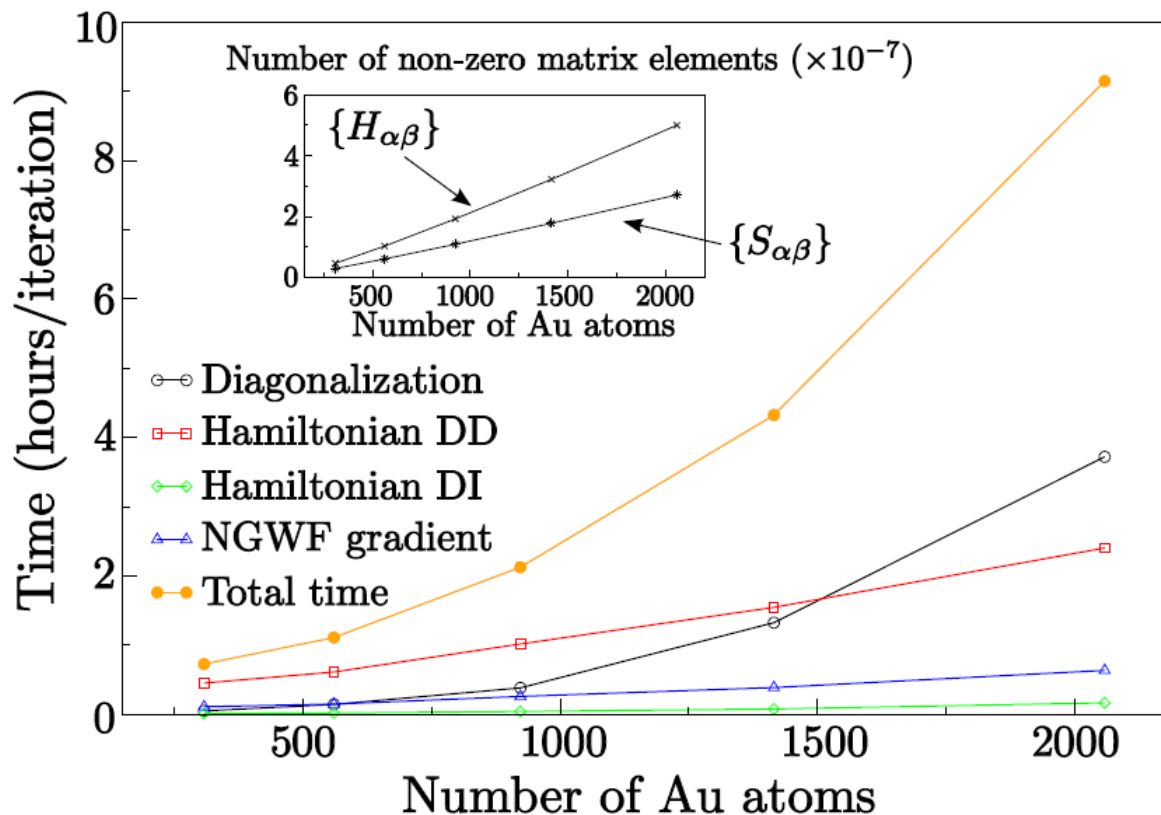
Electron density isosurface of Au_{1415} (run on 192 cores)

Reference: Au_{13} to Au_{1415} , run on 32768 cores

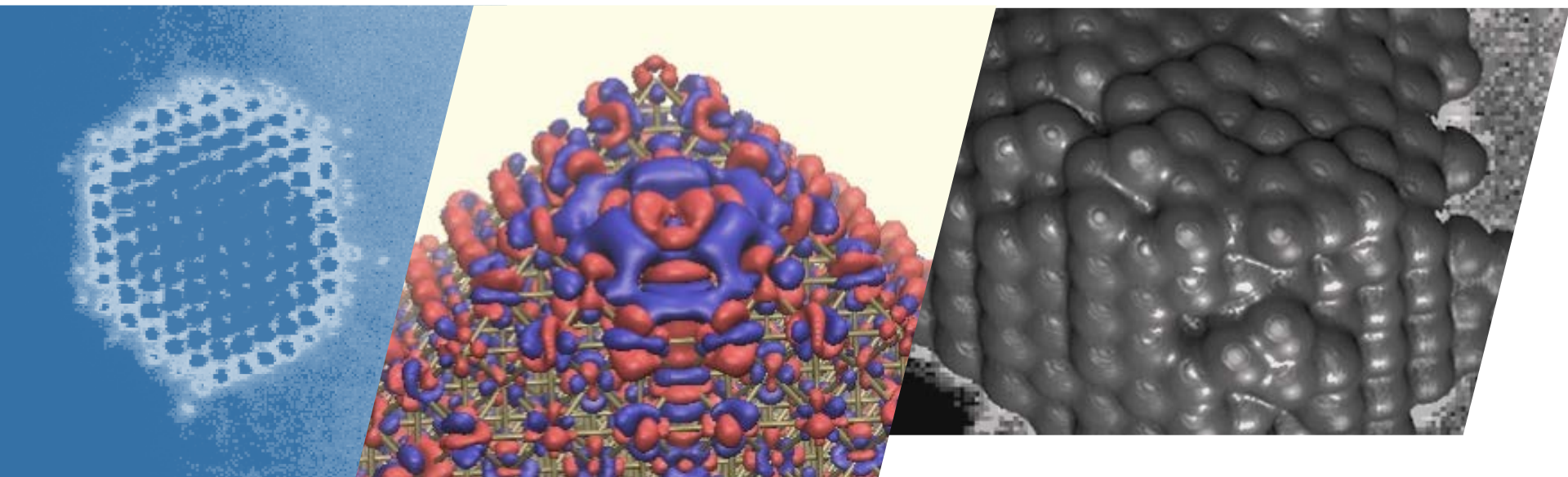
J. Kleis, ..., J. K. Nørskov, et al, *Catal. Lett.* **141**, 1067 (2011)

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



NANO LETTERS

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Predicting the Oxygen-Binding Properties of Platinum Nanoparticle Ensembles by Combining High-Precision Electron Microscopy and Density Functional Theory

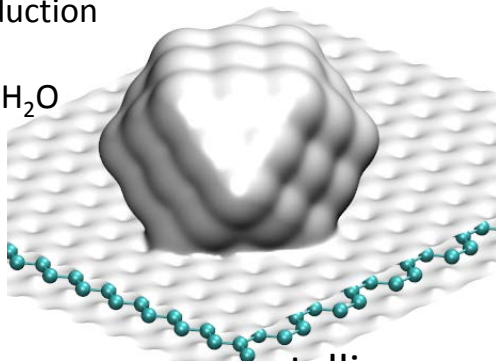
Jolyon Aarons, 

JM 

Johnson Matthey

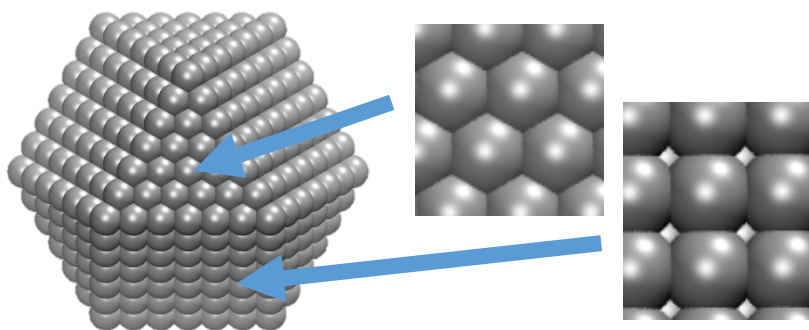
Nanoparticles in Catalysis

Oxygen Reduction
Reaction:
 $O_2 + 2H_2 \rightarrow 2H_2O$



Real nanoparticles are not so strongly faceted

Catalysis occurs on metallic nanoparticles that are supported e.g. on an oxide



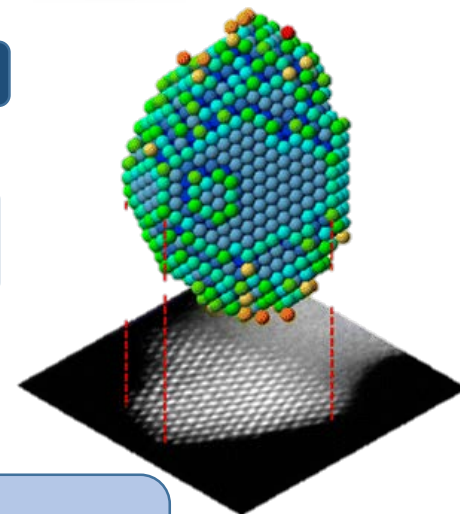
Conventionally, different facets are modelled individually using a slab model

ADF STEM: 2 D atomic coordinates

Z coordinates approximated by optimising force field model in 1D

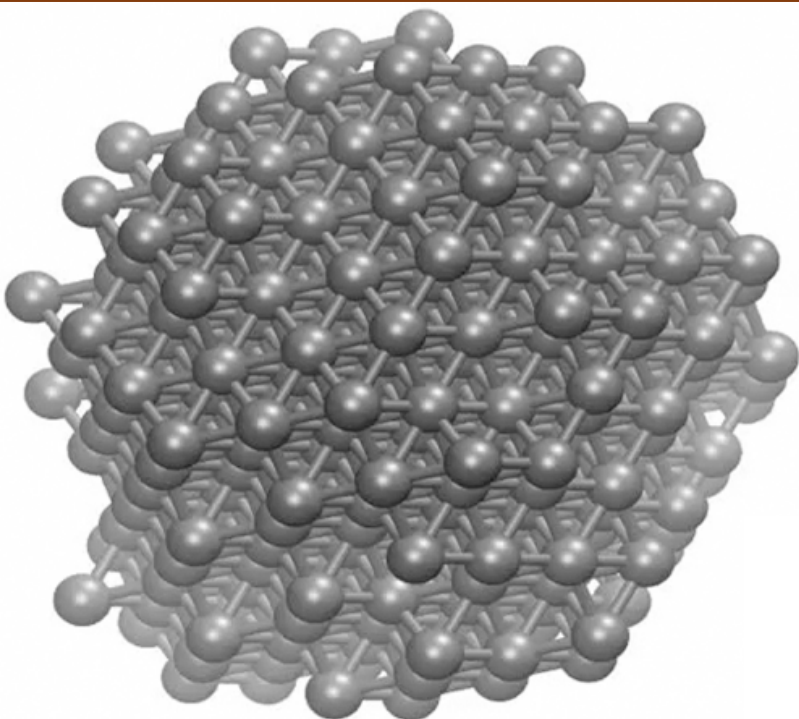
Investigate NP using Molecular Dynamics simulations and annealing approach

These datasets are then passed to us for analysis in ONETEP



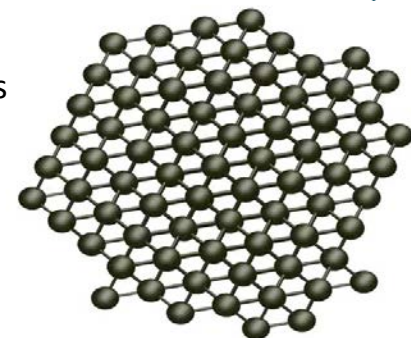
Lewys Jones, Katherine E. MacArthur, Vidar T. Fauske, Antonius T. J. van Helvoort, and Peter D. Nellist
Nano Letters **2014** 14 (11), 6336-6341

Optimisation of an Experimental Pt Nanoparticle

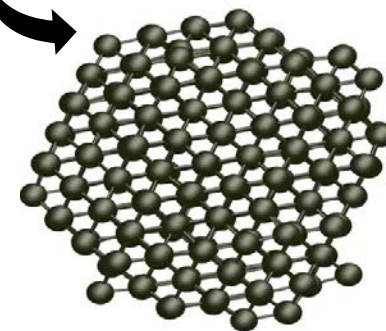


BFGS Structural Optimisation Process

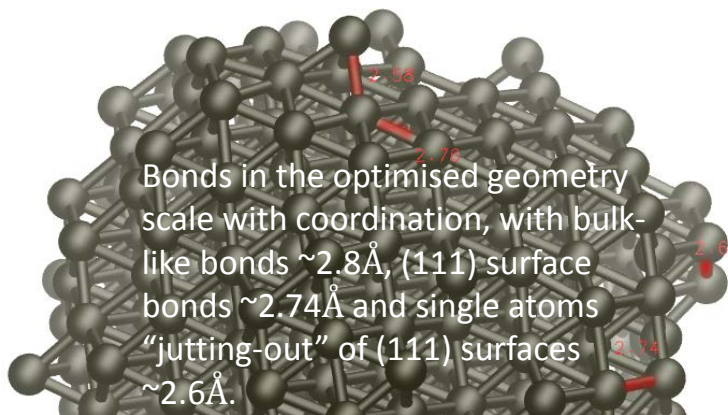
- Coordinates for several Pt nanoparticles determined by the Nellist group (Oxford) [1]
- DFT (RPBE, 850eV plane-wave cutoff energy, PAW – GBRV and Coulomb cutoff) structure optimisation performed with ONETEP
- Huge number of potential oxygen binding sites



Initial Geometry



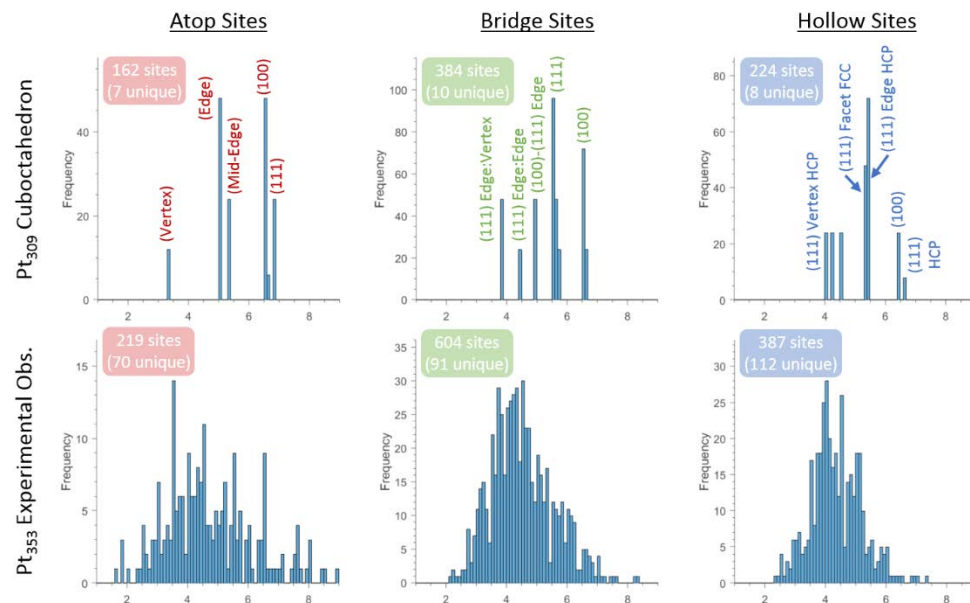
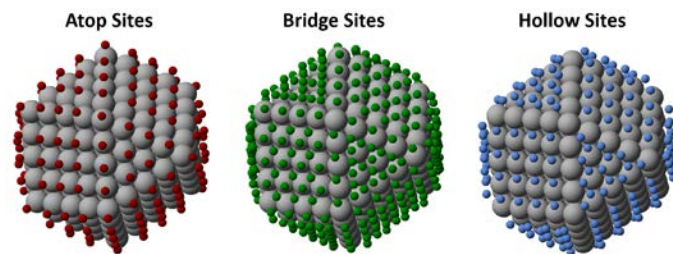
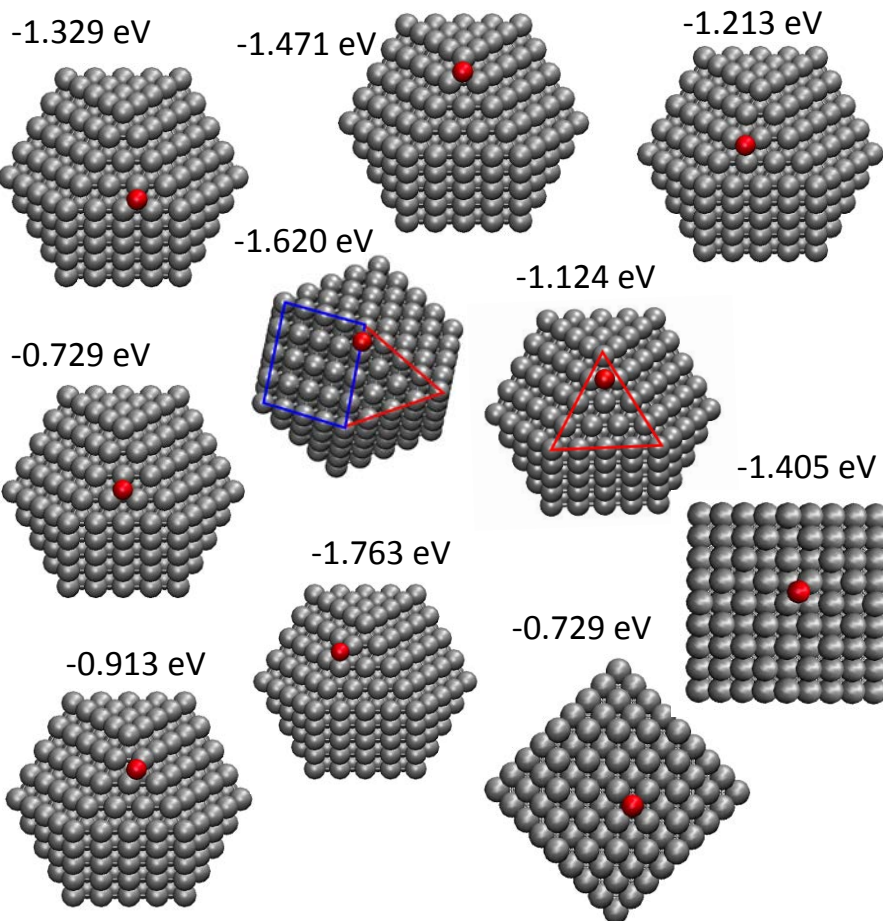
Optimised Geometry



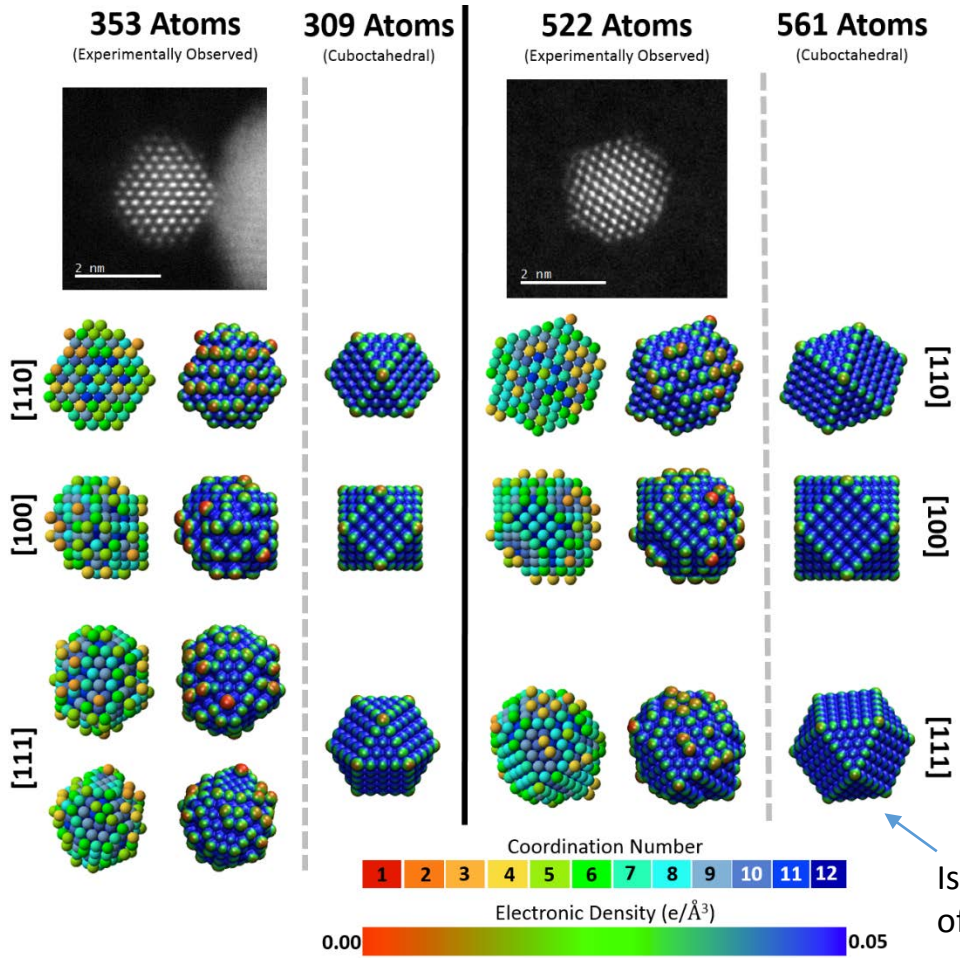
Bonds in the optimised geometry scale with coordination, with bulk-like bonds $\sim 2.8\text{\AA}$, (111) surface bonds $\sim 2.74\text{\AA}$ and single atoms "jutting-out" of (111) surfaces $\sim 2.6\text{\AA}$.

[1] Lewys Jones, Katherine E. MacArthur, Vidar T. Fauske, Antonius T. J. van Helvoort, and Peter D. Nellist
Nano Letters **2014** 14 (11), 6336-6341

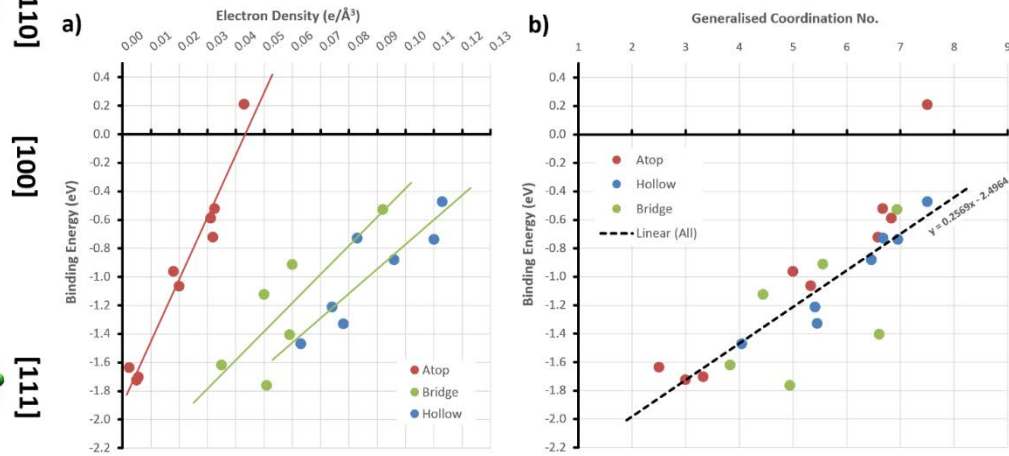
Models for Atomic Oxygen Binding



Electronic and geometric descriptors of regular & experimental nanoparticles



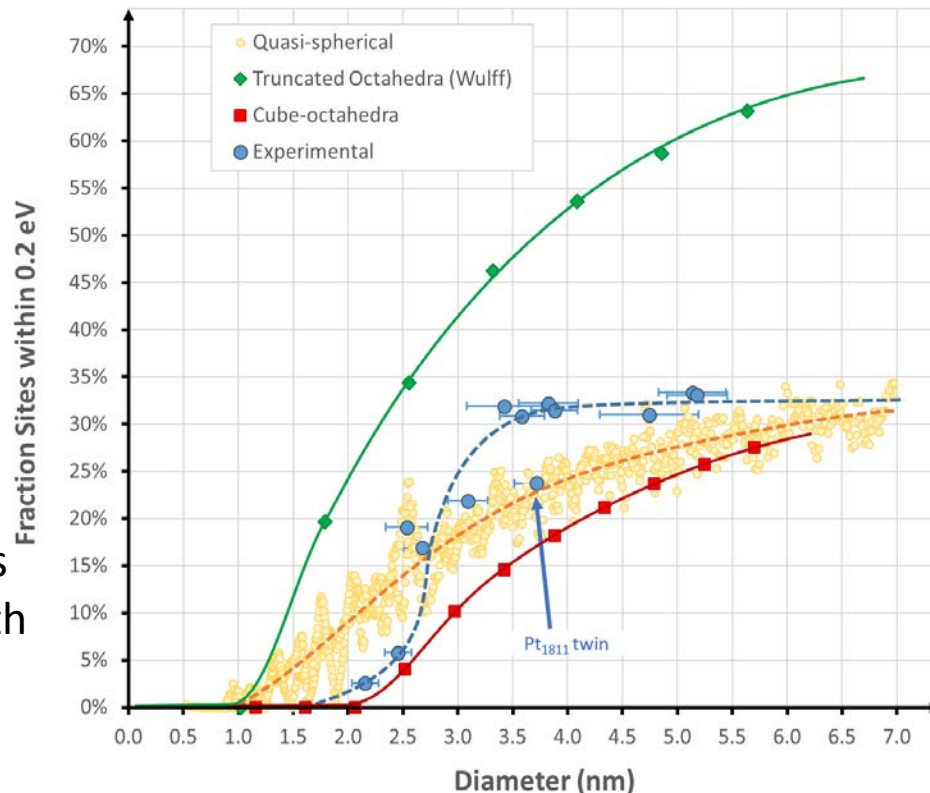
The value of electron density plotted on an isosurface of the electrostatic potential is well correlated with on-site oxygen binding affinity (a) and works when GCN (b) breaks down, i.e. multi-species systems



Isosurface of the Electrostatic Potentials of each Nanoparticle at $0.0 E_H$

Electron Density Distributions of Regular & Experimental

- Formed a model parameterised from binding energies on 22 distinct sites calculated using ONETEP on idealised cuboctahedral particles
- The model maps through the generalised coordination number or electron density values on the electrostatic potential isosurface and allows us to characterise huge numbers of large experimental nanoparticles with a high throughput



New developments: Linear-scaling DFT for metallic systems

Electronic annealing Fermi Operator Expansion for DFT calculations on metallic systems

Jolyon Aarons and Chris-Kriton Skylaris*
Department of Chemistry, University of Southampton,
Highfield, Southampton SO17 1BJ, UK

Submitted for publication,
August 2017

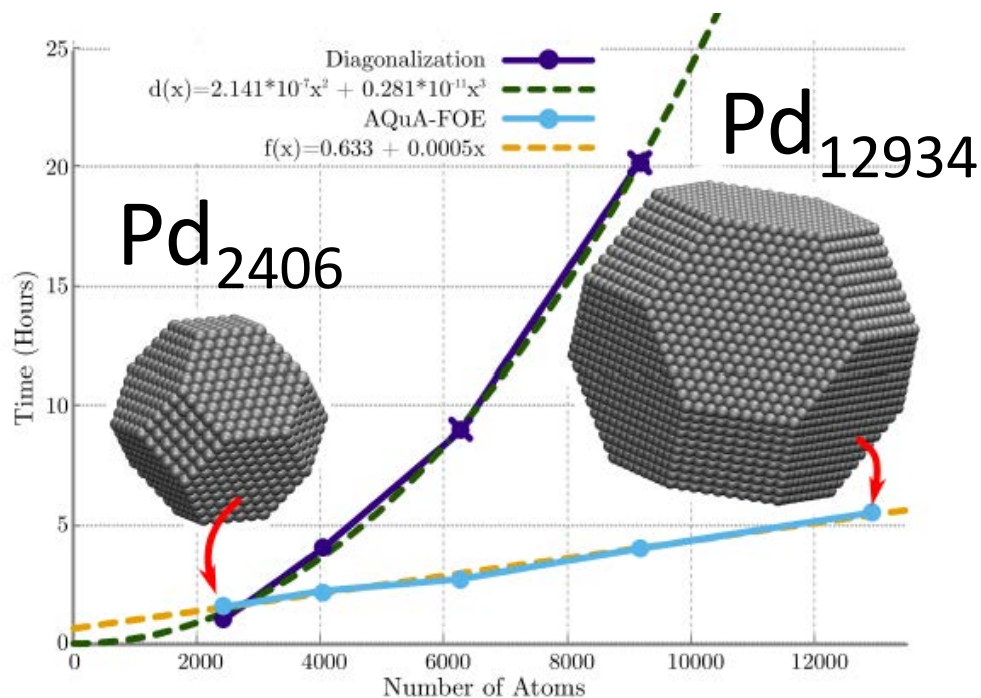
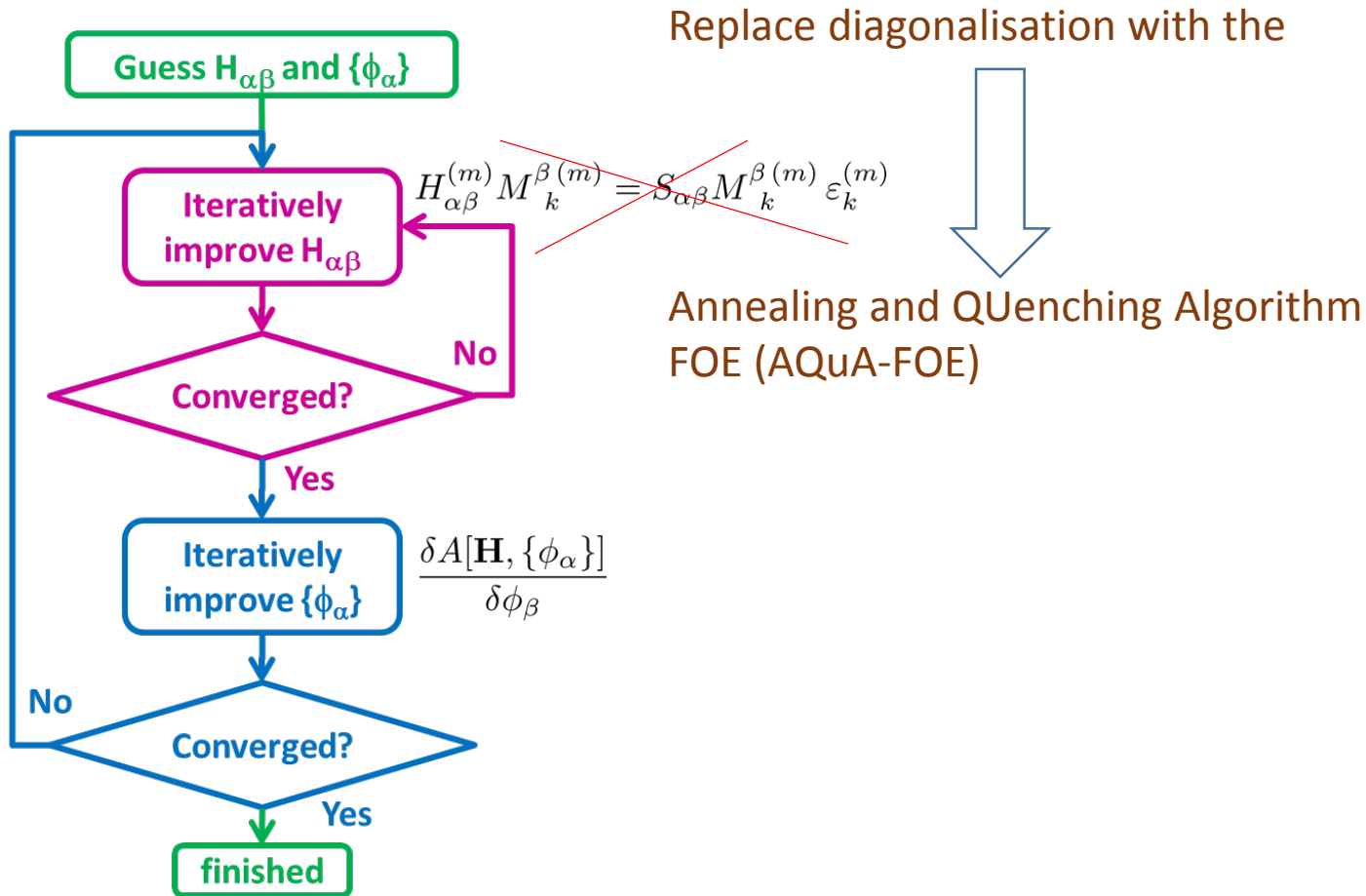


FIG. 3: A comparison of EDFT in ONETEP using both Diagonalization with Scalapack (deep purple) and AQuA-FOE

New developments: Linear-scaling DFT for metallic systems



Annealing and Quenching Algorithm FOE (AQuA-FOE)

- Fermi Operator Expansion (FOE) techniques: Computing the density matrix as a matrix series expansion of the Hamiltonian matrix

$$\mathbf{K} \simeq \sum_{j=1}^{N_{pl}} c_j \mathbf{H}^j$$

AQuA-FOE

- Apply the FOE to a constant interval where the number of terms is independent of the number of atoms. This is achieved by using a raised temperature
- Determine the chemical potential by modifying directly the density kernel using identities from hyperbolic trigonometric functions.
- Quench the resulting Hamiltonian and density kernel to the desired electronic temperature by successive application of an exact scaling function which is written as a Chebyshev expansion with a constant number of terms.
- Compute the electronic entropy directly from the density kernel using a Pade approximant:

$$\mathcal{S} = \text{tr}[\mathbf{K} \ln(\mathbf{K}) + [\mathbf{I} - \mathbf{K}] \ln(\mathbf{I} - \mathbf{K})]$$

ONETEP papers with developments or applications on metallic systems

- A variational method for density functional theory calculations on metallic systems with thousands of atoms. A. Ruiz-Serrano, and C.-K. Skylaris. *J. Chem. Phys.* **139** (2013) 054107
- Effect of Graphene Support on Large Pt Nanoparticles. L. G. Verga, J. Aarons, M. Sarwar, D. Thompsett, A. E. Russell and C.-K. Skylaris. *Phys. Chem. Chem. Phys.* **18** (2016) 32713
- Perspective: Methods for Large-Scale Density Functional Calculations on Metallic Systems. J. Aarons, M. Sarwar, D. Thompsett and C.-K. Skylaris. *J. Chem. Phys.* **145** (2016) 220901
- Predicting the Oxygen-Binding Properties of Platinum Nanoparticle Ensembles by Combining High-Precision Electron Microscopy and Density Functional Theory. J. Aarons, L. Jones, A. Varambhia, K. E. MacArthur, D. Ozkaya, M. Sarwar, C.-K. Skylaris, and P. D. Nellist. *Nano Lett.*, **17** (7) (2017) 4003.

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Johnson Matthey



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