Large-scale DFT calculations on metallic systems

Chris-Kriton Skylaris

UNIVERSITY OF Southampton
School of Chemistry

Outline

- Theory
  - Canonical ensemble electronic systems
  - Finite temperature DFT
  - Kohn-Sham
  - Direct energy minimisation approaches for Kohn-Sham calculations at finite T
  - Implementation in ONETEP
- Validation
- Performance tests
- Scaling
- Conclusions

Canonical ensemble electronic theory

Pure state (isolated system at T=0)

- Wavefunction or density operator

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

- Energy (E)

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

- Variational principle

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

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)

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

- Variational principle

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

where Γ_N^0 is the equilibrium canonical ensemble density operator

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

Finite temperature DFT

- The zero temperature formulation of DFT is not suited to materials with small or no band gap
- Small excitations due to finite temperature become significant and need to be accounted for
- Mermin's finite temperature formulation 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

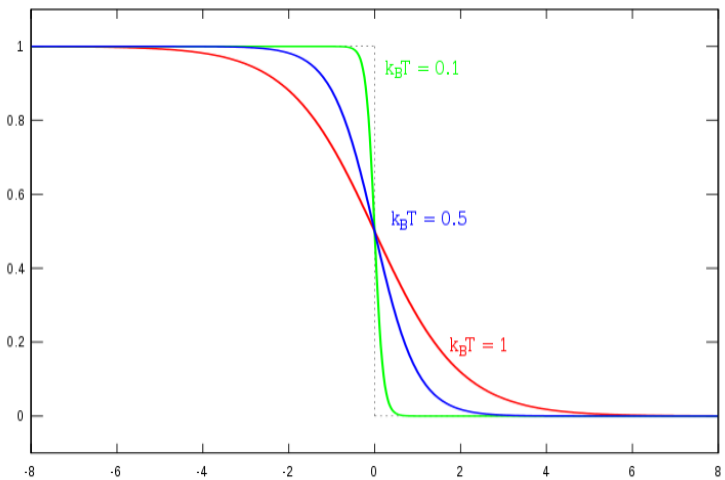
- Kohn-Sham Helmholtz free energy functional

$$A[T;\{\psi_i\},\{f_i\}] = \sum_i f_i \langle \psi_i | \hat{T} + V_{\text{ext}} | \psi_i \rangle + E_{\text{Hxc}}[n] - TS[\{f_i\}]$$

- **Non-integer molecular orbital occupancies** which obey the Fermi-Dirac distribution

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

for molecular orbital ψ_i with energy ε_i



- Electronic density

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

- Electronic entropy

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

Finite temperature DFT calculations by energy minimisation

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r})\, U^\dagger_{ji}$$

canonical orbitals

non-canonical orbitals

- Non-diagonal occupancies (density kernel)

$$\mathrm{f}_{ij} = \sum_k U_{ik}\, f_k\, U^\dagger_{kj}$$

- Eigenvalue equation for energies

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

- Helmholtz free energy

$$A_T[n_0] = \min_{\{\chi_j\}} \left(\min_{\{f_{ij}\}} A_T[\{f_{ij}\}, \{\chi_j\}] \right)$$

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

$$A_T[n_0] = \min_{\{\chi_j\}\{H_{ij}\}} A_T[\{H_{ij}\}, \{\chi_j\}]$$

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

Finite temperature DFT calculations

Molecular orbitals

$$\psi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r})\, U^{\dagger}_{ji}$$

canonical orbitals

non-canonical orbitals

ONETEP NGWFs

$$\psi_i(\mathbf{r}) = \sum_\alpha \phi_\alpha(\mathbf{r}) M^{\alpha}_{\ i}$$

canonical orbitals

NGWFs

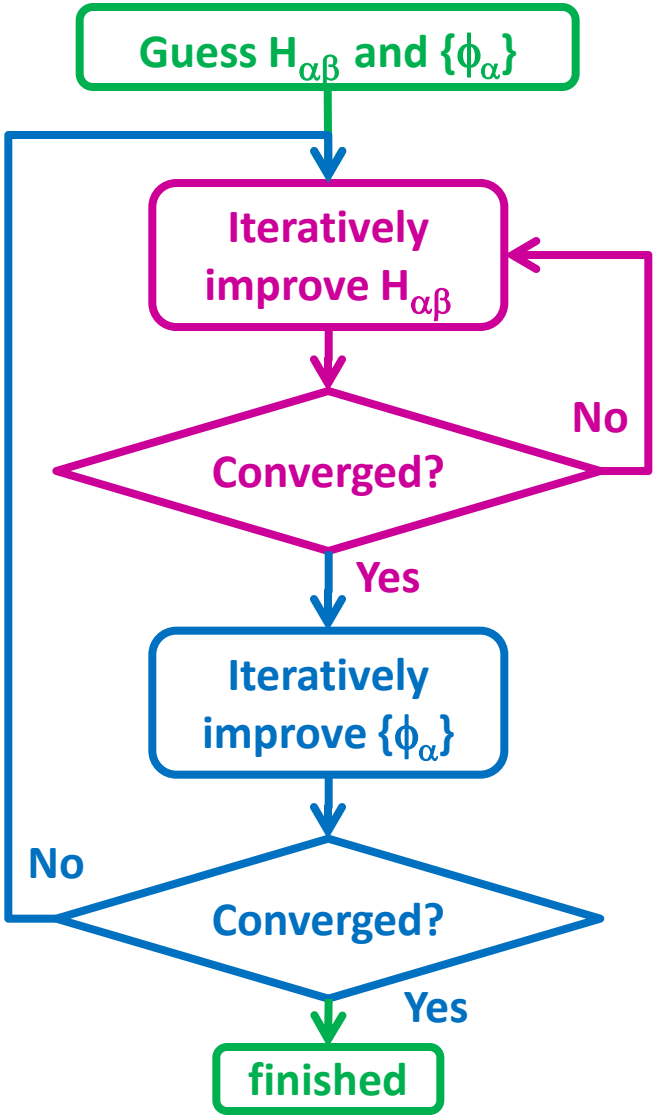
- Non-diagonal occupancies (density kernel)

$$\mathrm{f}_{ij} = \sum_k U_{ik}\, f_k\, U^{\dagger}_{kj} \quad \Longrightarrow \quad K^{\alpha\beta} = \sum_k M^{\alpha}_{\ k} f_k M^{\dagger\beta}_{k}$$

- Orbital eigenvalue equation to solve for energies (and occupancies)

$$\sum_j H_{ij} U_{jk} = U_{ik}\varepsilon_k \quad \Longrightarrow \quad \sum_\beta H_{\alpha\beta} M^{\beta}_{\ k} = \sum_\beta S_{\alpha\beta} M^{\beta}_{\ k}\, \varepsilon_k$$

Finite temperature energy optimisation in ONETEP



$$A[\mathbf{K}, \{\phi_\alpha\}] \Rightarrow A[\mathbf{H}, \{\phi_\alpha\}]$$

Use Hamiltonian matrix instead of density kernel (molecular orbital occupancies) as independent variable

- **Inner loop**: Optimise total (interacting) energy *E* w.r.t **H** for fixed $\{\phi_\alpha\}$ while imposing **fractional occupancies**
- **Outer loop:** Optimise total (interacting) energy *E* w.r.t. $\{\phi_\alpha\}$

Finite temperature energy optimisation in ONETEP

- Inner loop (Hamiltonian matrix optimisation):

$$H^{(m)}_{\alpha\beta} M^{\beta\,(m)}_{k} = S_{\alpha\beta} M^{\beta\,(m)}_{k}\, \varepsilon^{(m)}_{k}$$

→ F-D occupancies → density

→ F-D Hamiltonian

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

Line search $H^{(m+1)}_{\alpha\beta} = H^{(m)}_{\alpha\beta} + \lambda \Delta^{(m)}_{\alpha\beta}$

- Outer loop (NGWF optimisation):

Conjugate gradients minimisation using $\dfrac{\delta A[\mathbf{H}, \{\phi_\alpha\}]}{\delta \phi_\beta}$

Subject to MO orthonormality corrections and KE and occupancy preconditioning

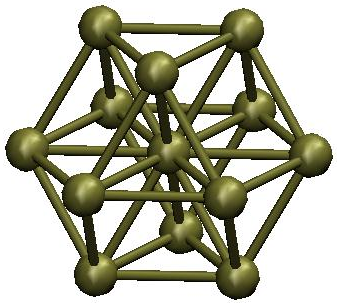
Express kernel in new NGWFs before going back to inner loop, using

$$K^{\alpha\beta} = \sum_k M^{\alpha}_{\ k} f_k M^{\dagger\beta}_{k}$$

$$\tilde{M}^{\alpha}_{\ i} = S^{\alpha\beta(l+1)} \langle \phi^{(l+1)}_{\alpha} | \phi^{(l)}_{\gamma} \rangle M^{\gamma}_{\ i}$$

UNIVERSITY OF Southampton
School of Chemistry

Validation: calculations on Pt_{13}



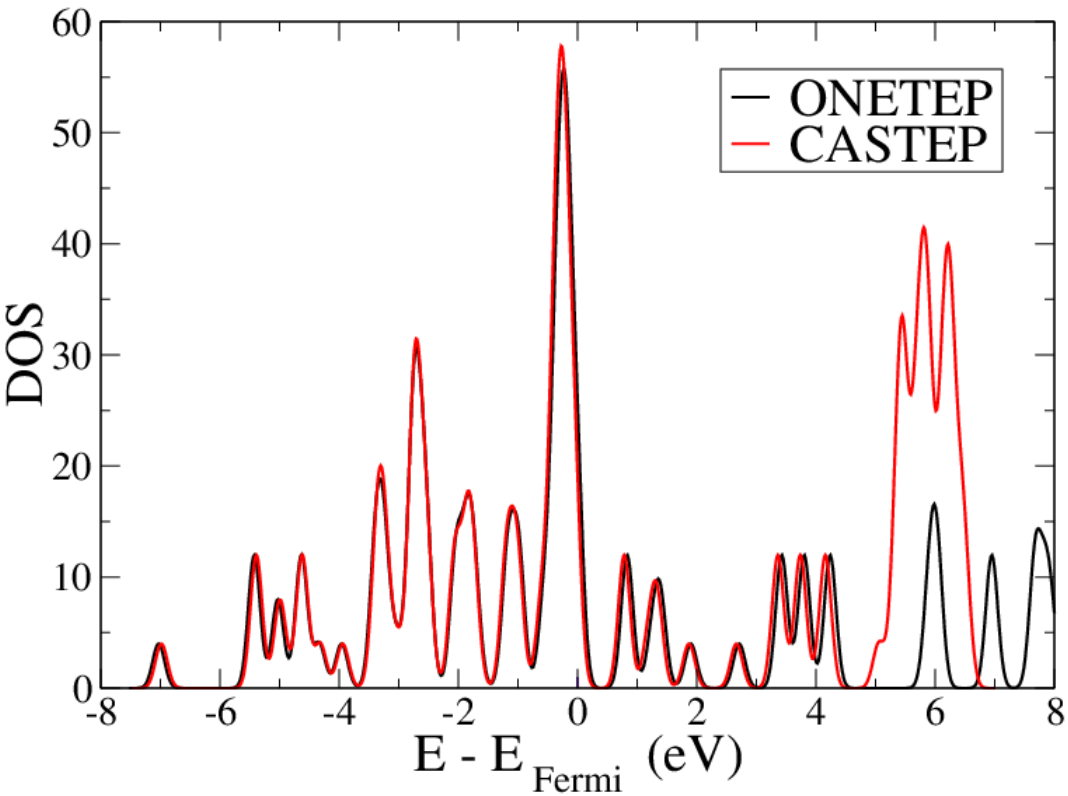
- Psinc kinetic energy cut-off: 950 eV
- XC functional: RPBE
- NGWF radii: 9.0 a_0

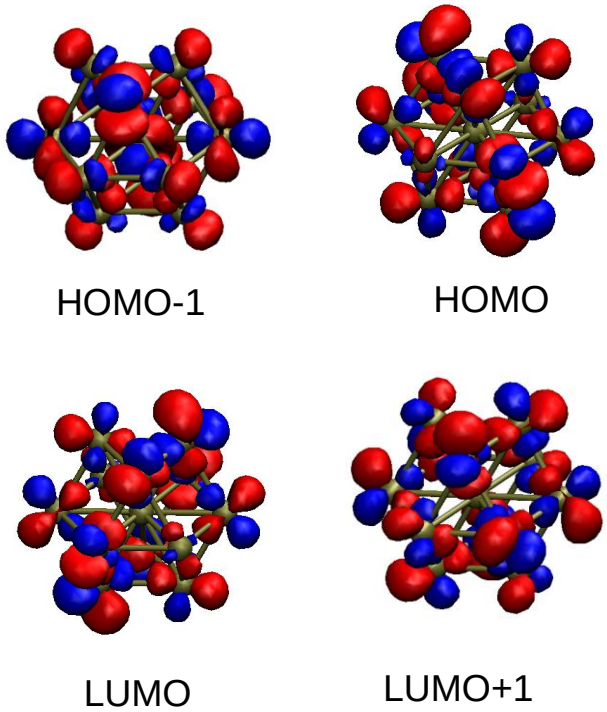
Geometry optimisation

Pt-Pt bond length:

CASTEP: 2.708 Å

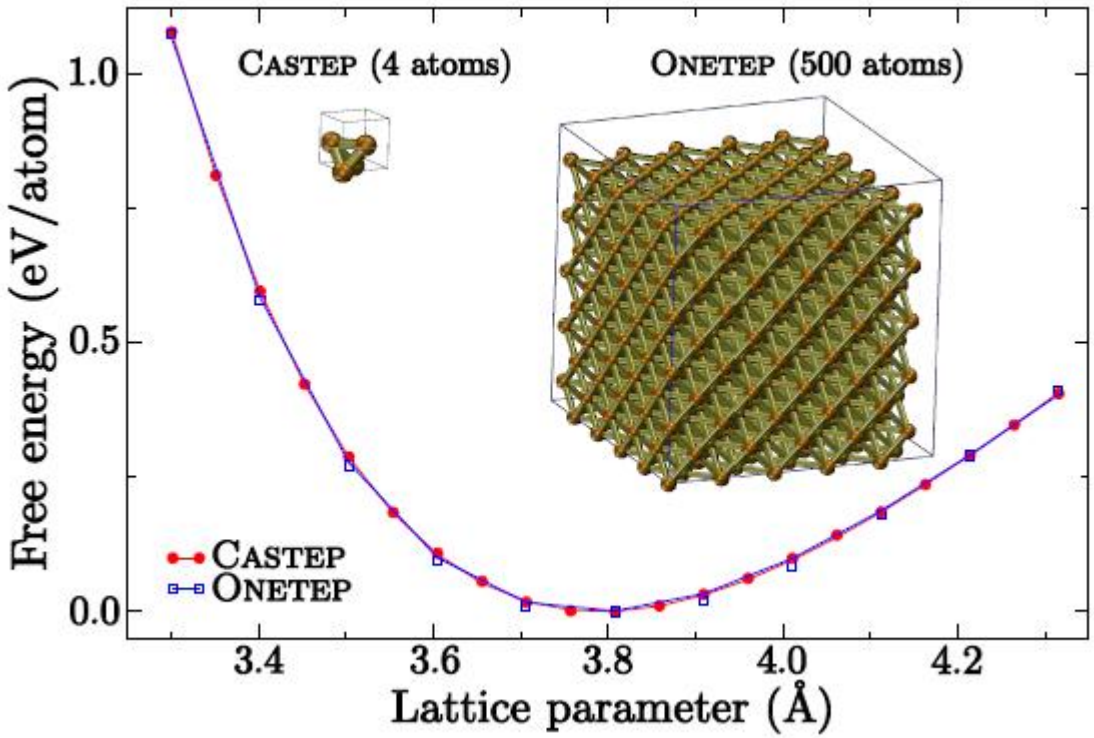
ONETEP: 2.701 Å





UNIVERSITY OF Southampton School of Chemistry

Validation: calculations on bulk Cu



ONETEP settings
K.E. cutoff: 900 eV
K_BT: 0.1 eV
xc: RPBE
NGWF radius: 4 Å
4500 energy levels (bands)

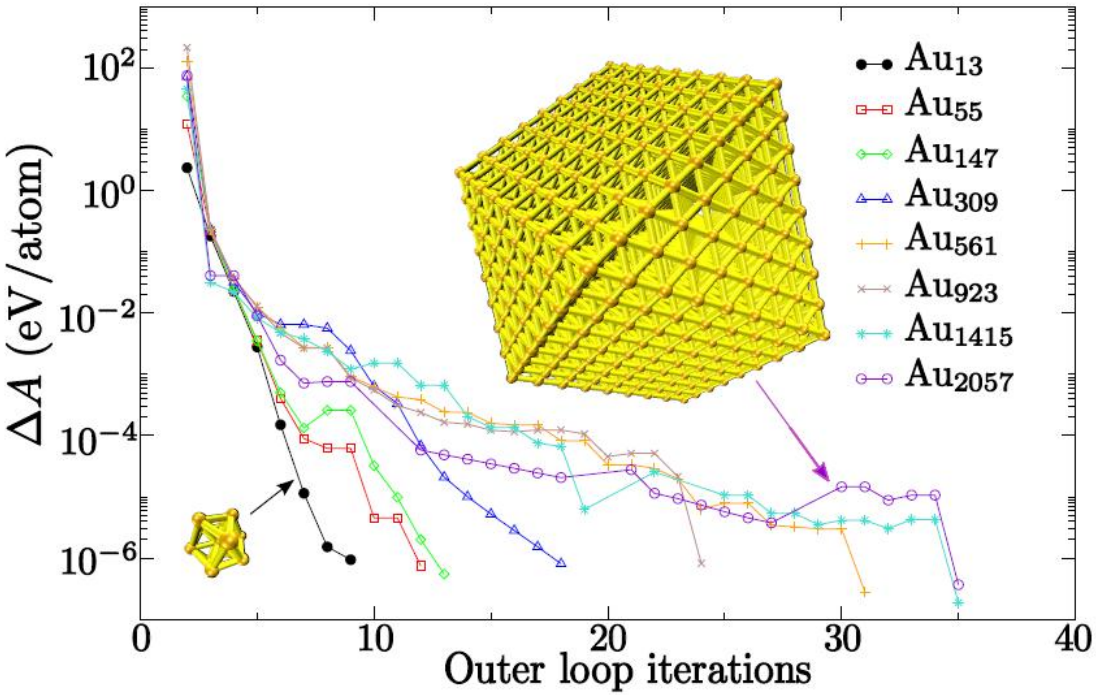
	B (GPa)	L_0 (Å)
CASTEP	93.57	3.79
ONETEP	93.51	3.79

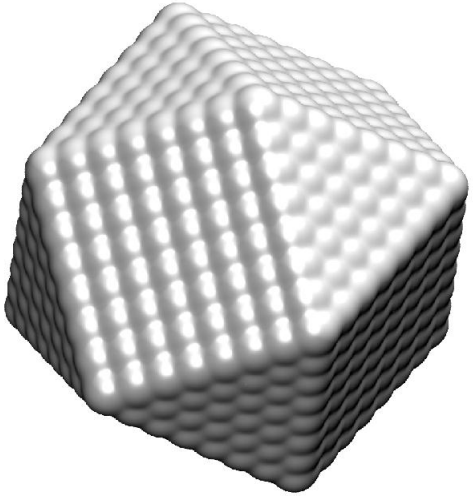
UNIVERSITY OF Southampton
School of Chemistry

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)

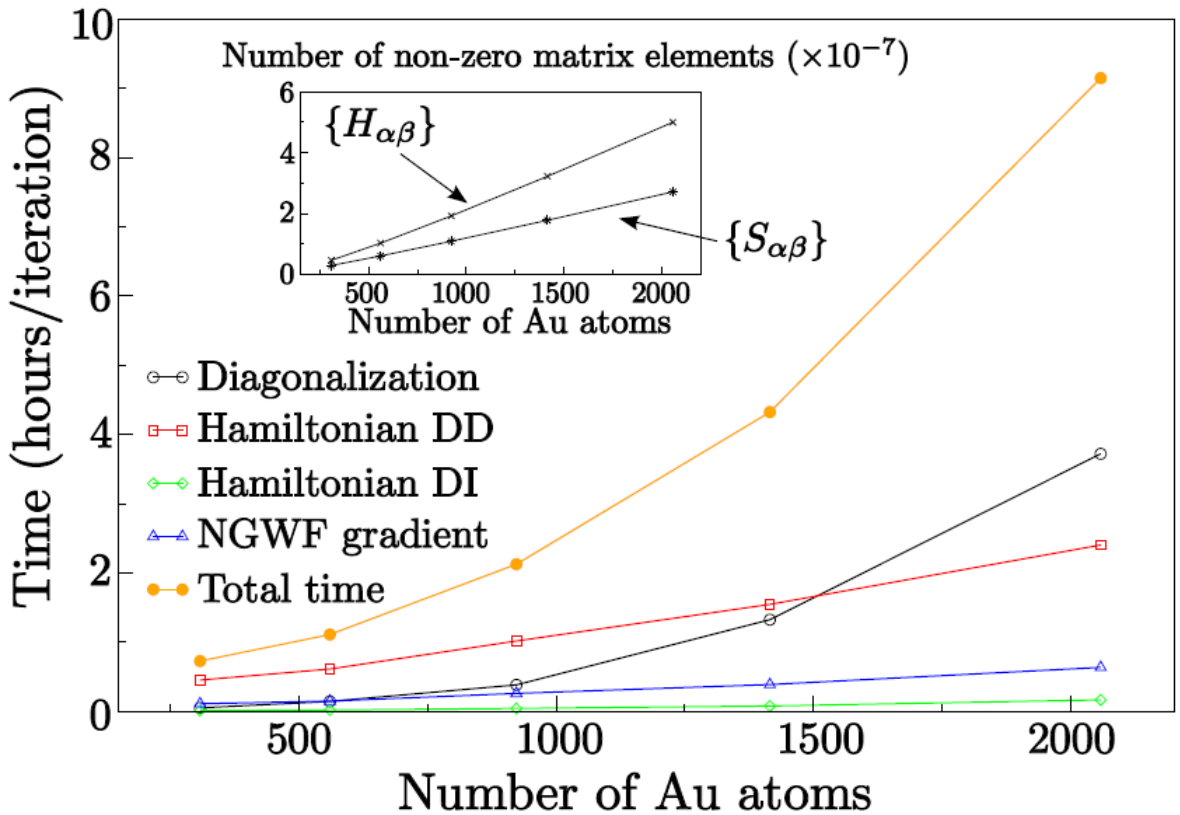
Reference: Au_{13} to Au_{1415}, run on 32768 cores

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

UNIVERSITY OF Southampton
School of Chemistry

Performance and scaling with 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 diagonalisers

Conclusions

- DFT calculations on metallic systems with thousands of atoms, with the ONETEP program
- Energy and forces. Can be combined with other functionalities available in ONETEP
- Finite electronic temperature DFT
- Non-linear scaling
- Linear-scaling formulation will be a future development based on approaches such as the Fermi Operator Expansion (FOE)
- Method described here has been published in:

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

- Documentation is available in www.onetep.org
http://www2.tcm.phy.cam.ac.uk/onetep/pmwiki/uploads/Main/Documentation/Finite-temperature%20Ensemble-DFT%20calculations