

School of Chemistry

Electronic energy minimization methods in the ONETEP program

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Computational bottlenecks in DFT





Linear-scaling DFT

Physical principle: Nearsightedness of electronic matter W. Kohn, *Phys. Rev. Lett.* **76**, 3168 (1996)

- Localised orbitals
- No diagonalisation
- Energy minimisation
- Sparse matrices and algorithms – O(N) memory and CPU cost





The ONETEP linear-scaling approach

To achieve linear-scaling DFT with large basis set accuracy we use two levels of resolution:

- Fine: self-consistently optimise local orbitals $\{\phi_{\alpha}\}$
- Coarse: self-consistently optimise K (coefficients)





• 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).



Linear-scaling with the same accuracy as cubic-scaling DFT





ONETEP linear-scaling DFT

NGWF radii (Å)	# NGWFs	BE (kcal/mol)
2.9	166	-11.93
3.2	166	-12.86
3.7	166	-8.25
4.2	166	-7.06
4.8	166	-7.04

C.-K. Skylaris, O. Dieguez, P. D. Haynes and M. C. Payne, *Phys. Rev. B* **66**, 073103 (2002).

Cubic-scaling DFT

Basis set	# AOs	BE + BSSE (kcal/mol)
3-21G	361	-12.55
6-31G*	535	-8.95
6-311++G**	1017	-7.39
cc-pVTZ	1765	-7.04

P. D. Haynes, C.-K. Skylaris, A. A. Mostofi and M. C. Payne, *Chem. Phys. Lett.* **422** 345 (2006).

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Linear-scaling with the number of atoms Example: ONETEP calculations on amyloid fibril proteins





Density matrix

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{n=1}^{N_{\rm MO}} f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \quad \Longrightarrow \quad \rho(\mathbf{r},\mathbf{r}') = \sum_{\alpha,\beta} \phi_\alpha(\mathbf{r}) K^{\alpha\beta} \phi_\beta^*(\mathbf{r}')$$

$$\psi_n(\mathbf{r}) = \sum_{\alpha} \phi_{\alpha}(\mathbf{r}) M^{\alpha}_{\ n}$$
Localised orbitals

Density kernel

$$K^{\alpha\beta} = \sum_{n} M^{\alpha}_{\ n} f_{n} M^{\dagger \ \beta}_{n}$$

Molecular Orbitals (MO)

Idempotency condition



$$\rho(\mathbf{r},\mathbf{r}'')
ho(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''=
ho(\mathbf{r},\mathbf{r}')$$

 $\mathbf{KSK}=\mathbf{K}$



Maintaining idempotency: Purification transformation

 $f_{new} = 3f_{old}^2 - 2f_{old}^3 \qquad \text{R. McWeeny, Rev. Mod. Phys. 32, 335 (1960)}$

- Improves the idempotency of a nearly idempotent density matrix
- Forces occupancies in interval [0,1] ("weak" idempotency)
- Quadratic convergence. Example:
 - > $f^{(1)} = 1.1$
 - > $f^{(2)} = 3 \times 1.1^3 2 \times 1.1^2 = 0.968$
 - > $f^{(3)} = 3 \times 0.968^3 2 \times 0.968^2 = 0.997$
 - ➤ Etc..
- But, diverges if the initial occupancies are not within certain bounds



Linear-scaling functional which maintains idempotency

$$L_2[\sigma] = E\left[\frac{N_e}{\mathrm{tr}[\rho]}\rho\right] = E\left[\frac{N_e}{\mathrm{tr}[3\sigma^2 - 2\sigma^3]}(3\sigma^2 - 2\sigma^3)\right]$$

P. D. Haynes, C.-K. Skylaris, A. A. Mostofi, and M. C. Payne, *J. Phys.: Condens. Matter* **20**, 294207 (2008)

- Direct minimisation of interacting energy –no need for density mixing
- Purification never allowed to break down
 - Occupancy maxima and minima tracked
 - Occupancies restored by penalty functional if out of safe range
- Electron number conserved without need to know the chemical potential



Conjugate gradients energy minimisation in ONETEP



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





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

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

• 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



• Electronic entropy

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

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

$$N_e = \sum_i f_i$$



Free energy with non-orthogonal orbitals



- $A[T; \{H_{ij}\}, \{\chi_i\}] \qquad \qquad A[T; \{H_{\alpha\beta}\}, \{\phi_\alpha\}]$
- Eigenvalue equation to solve for orbital energies (and occupancies)

$$\sum_{j} H_{ij} U_{jk} = U_{ik} \varepsilon_k \qquad \qquad \sum_{\beta} H_{\alpha\beta} M^{\beta}_{\ k} = \sum_{\beta} S_{\alpha\beta} M^{\beta}_{\ k} \varepsilon_k$$

Efficient methods to minimise the free energy using non-canonical orthogonal 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).

Electronic free energy optimisation in ONETEP



Inner loop: Hamiltonian matrix optimisation

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

At iteration m

$$\begin{array}{l} \bigstar \text{ MO energies } H^{(m)}_{\alpha\beta}M^{\beta\,(m)}_{\ k} = S_{\alpha\beta}M^{\beta\,(m)}_{\ k}\varepsilon^{(m)}_k \\ \\ \text{F-D occupancies } f^{(m)}_i = f(\varepsilon^{(m)}_i) \\ \\ \text{Density } n^{(m)}(\mathbf{r}) = \phi_{\alpha}(\mathbf{r})K^{\alpha\beta(m)}\phi^*_{\beta}(\mathbf{r}) \quad K^{\alpha\beta} = \sum_k M^{\alpha}_k f_k M^{\dagger\beta}_k \\ \\ \text{F-D Hamiltonian } \tilde{H}^{(m)}_{\alpha\beta} = H_{\alpha\beta}[n^{(m)}] \\ \\ \text{Search direction } \Delta^{(m)}_{\alpha\beta} = \tilde{H}^{(m)}_{\alpha\beta} - H^{(m)}_{\alpha\beta} \\ \\ \text{Energy minimisation } H^{(m+1)}_{\alpha\beta} = H^{(m)}_{\alpha\beta} + \lambda\Delta^{(m)}_{\alpha\beta} \end{array}$$



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 $g^{\beta(l)}(\mathbf{r}) = \hat{H}^{(l)}\phi_{\gamma}^{(l)}(\mathbf{r})K^{\gamma\beta} - \phi_{\gamma}^{(l)}(\mathbf{r})K^{\gamma\delta}H^{(l)}_{\delta\nu}S^{\nu\beta(l)}$

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

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



Outer loop: NGWF optimisation

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



conjugate gradients approach



Validation: calculations on bulk Cu



Performance and scaling with the number of atoms



- Most operations are linear-scaling 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





Fermi Operator Expansion (FOE) instead of Diagonalisation

- Write
$$f(\varepsilon,\mu,\beta) = \frac{1}{1+e^{(\varepsilon-\mu)\beta}}$$
 in terms of matrices, not eigs

• To obtain:

$$\mathbf{K} = \left(\mathbf{I} + e^{(\mathbf{H} - \mu \mathbf{I})\beta}\right)^{-1}$$

- ill-conditioned if we were to do this directly with a matrix exponential technique and an inversion.
- Instead, expand the Fermi-Dirac function as a polynomial expansion, with Chebyshevs:

$$f(\mathbf{X}) = \sum_{i=0} a_i \mathbf{T}_i(\mathbf{X})$$
$$\mathbf{T}_0(\mathbf{X}) = \mathbf{I}$$
$$\mathbf{T}_1(\mathbf{X}) = \mathbf{X}$$
$$\mathbf{T}_{n+1}(\mathbf{X}) = 2\mathbf{X}\mathbf{T}_n(\mathbf{X}) - \mathbf{T}_{n-1}(\mathbf{X})$$



Annealing and Quenching algorithm FOE (AQUA-FOE)

1) Anneal: Create the scaled and shifted Hamiltonian **H**' (note that $\beta = 1/k_BT$)

$$\mathbf{H}' = (\mathbf{H} - \mu \mathbf{I})\beta$$

Then downscale by 2^n where n is determined so that its eigenvalues are within the interval of convergence of the FOE Chebyshev expansion with a constant number of terms, i.e. create a Hamiltonian **H**_{hot} that corresponds to a much "hotter" temperature to obtain **K**_{hot}

$$\mathbf{H'}_{hot} = \mathbf{H'}/2^n$$

2) Quench: The resulting "hot" density kernel \mathbf{K}_{hot} needs to be reduced to the initial "cold" electronic temperature. To do this we use the relation of the Fermi function with the tanh function and apply the tanh double angle formula n times to "cool" the kernel **K**

$$f(x) = \frac{1}{1+e^x} = \frac{1}{2} \left(1 + \tanh\left(\frac{x}{2}\right) \right) \quad x = (\varepsilon - \mu)\beta \quad x_{\text{hot}} = (\varepsilon - \mu)\beta/2^n = x/2^n$$

$$\tanh(x_{i+1}) = \tanh(2x_i) = \frac{2\tanh(x_i)}{1+\tanh^2(x_i)} \quad \mathbf{R}_{i+1} = \frac{2\mathbf{R}_i}{1+\mathbf{R}_i^2} \quad \mathbf{R} = 2\mathbf{K} - 1$$



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AQUA-FOE method

Other parts that need to be computed in linear-scaling cost:

- Electronic entropy is computed via Chebyshev expansion
- The chemical potential is computed via a combination of hyperbolic trigonometric identities and more Chebyshev expansions

Density Kernel Sparsity

- · Need kernel sparsity for linear-scaling, finite temperature metals
- Pattern derived from truncated polynomial expansion → a power of H, whose sparsity pattern is obtained from the localisation of the NGWFs
- We used \mathbf{H}^2 in our tests



Example of density kernel sparsity with 2406 Al atoms

AQUA-FOE scaling tests

- Comparison of AQUA-FOE with EDFT (diagonalization based) within ONETEP
- Calculations run on ~5000 cores on ARCHER



Annealing and QUenching Algorithm FOE (AQuA-FOE) J. Aarons and C.-K. Skylaris, *J. Chem. Phys.* **148**, 074107 (2018)



Application: Pt nanoparticle catalysts

Ideal geometry



Conventionally, different facets are modelled individually using a slab model



L. Jones, Katherine E. MacArthur, V. T. Fauske, A. T. J. van Helvoort, and P. D. Nellist. *Nano Letters* **2014** *14* (11), 6336-6341



ONETEP geometry relaxation of Pt nanoparticle from Electron Microscopy





Electronic and geometric descriptors for O adsorption





Predicting the catalytic activity of Pt nanoparticles

- Model parameterised from binding energies calculated with ONETEP on Pt nanoparticles
- Using the electronic or geometric descriptors allows us to characterise huge numbers of nanoparticles
- We assess their performance as catalysts for the Oxygen Reduction Reaction (rate determining step in fuel cells): O₂+2H₂→ 2H₂O from their fraction of sites with the "right" adsorption energy





J. Aarons, L. Jones, A. Varambhia, K. E. MacArthur, D. Ozkaya, M. Sarwar, C.-K. Skylaris, and P. D. Nellist. *Nano Lett.* **17** (2017) 4003-4012

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Iridis



