Electronic energy optimisation in ONETEP

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Outline

1. Kohn-Sham calculations
   - Direct energy minimisation versus density mixing
2. ONETEP scheme: optimise both the density kernel and NGWFs
   - Conditions
3. Density matrix optimisation algorithms in ONETEP
   - Penalty, purification, LNV
   - Density kernel gradients, tensor properties
4. Optimisation of NGWFs
   - NGWF gradients, preconditioning schemes
   - The need for an orthogonal basis set
5. More detailed look at overall ONETEP scheme
   - Initialisation
   - Flowchart, input keywords

Density Functional Theory (DFT)

- Electronic density

$$n(\mathbf{r_1}) = N \int \cdots \int \Psi(\mathbf{r}_1 s_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) \Psi^*(\mathbf{r}_1 s_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) ds_1 d\mathbf{x}_2 \cdots \mathbf{x}_N$$

- Hohenberg-Kohn

$$E[n] = E_{\text{Kin}}[n] + E_{\text{ext}}[n] + E_{ee}[n]$$

- Kohn-Sham

$$E[n] = \sum_i \langle \psi_i | -\frac{1}{2}\nabla^2 | \psi_i \rangle + E_{\text{ext}}[n] + E_{\text{Coul}}[n] + E_{xc}[n]$$

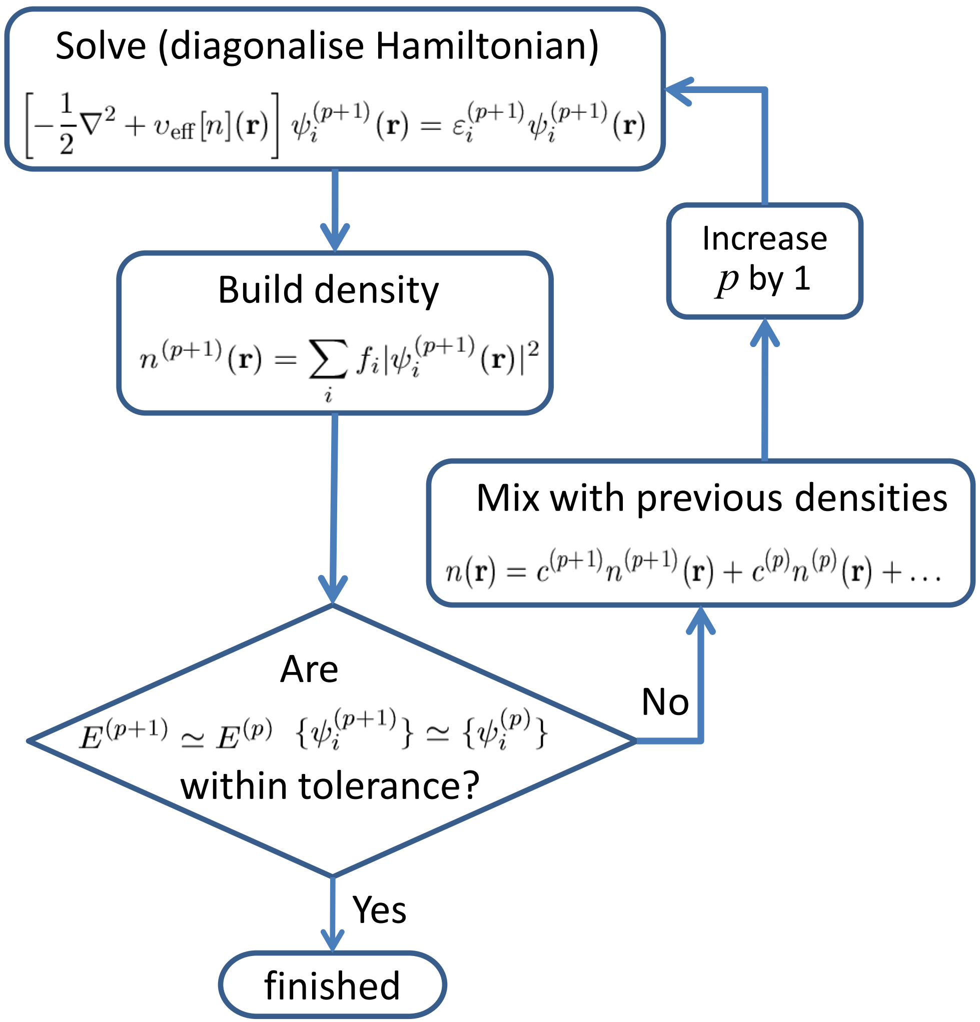
Non-interacting electrons

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Density of interacting electrons

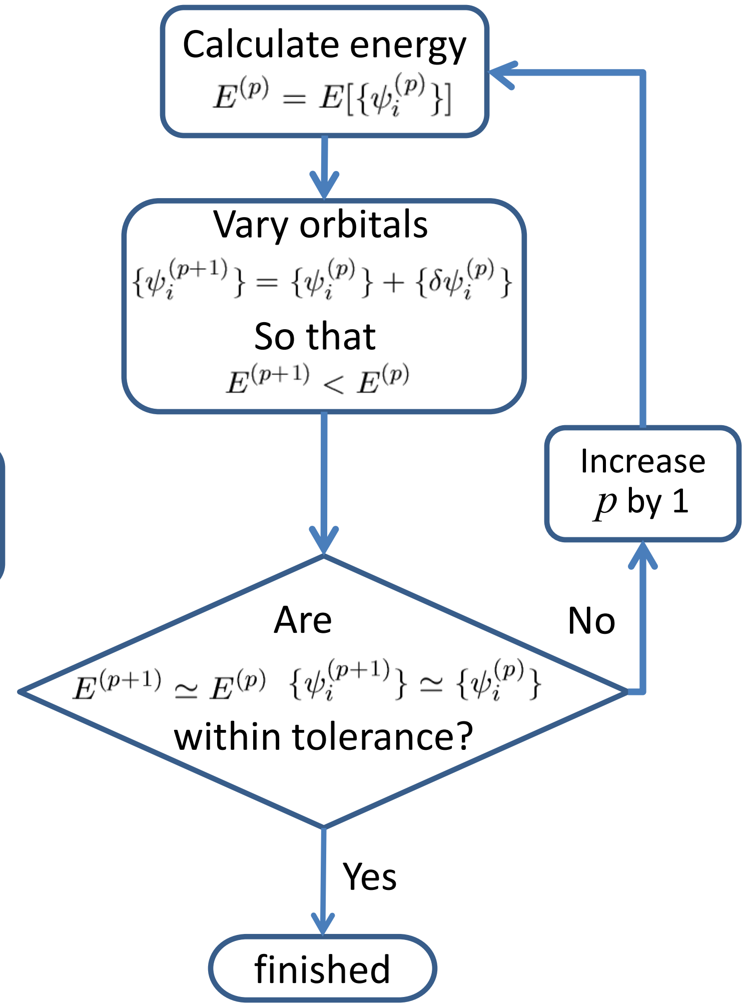
$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Density mixing



- Discontinuous changes
- Hamiltonian search (indirect)

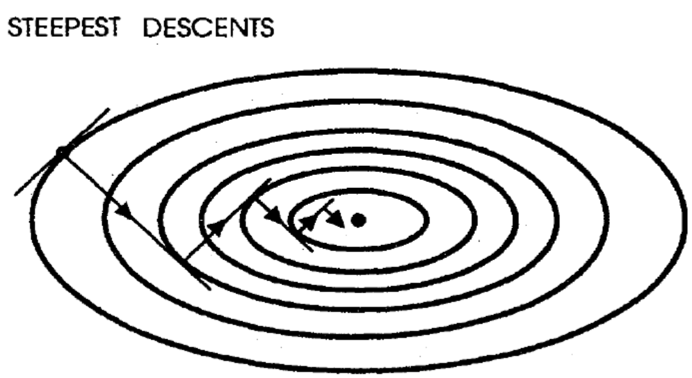
Direct energy minimisation

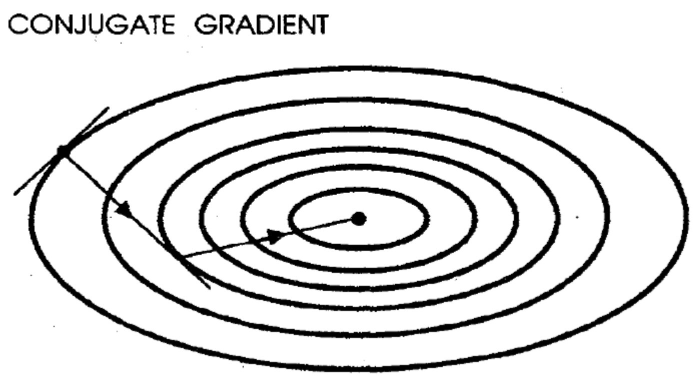


- Direct search for well-defined minimum

Function minimisation

- Iterative procedures
- Need the value of the function and its gradient at each step
- Converge to local minima





- Moves always downhill
- Robust but may need very large number of iterations

- Converges in N steps for N-dimensional quadratic function
- In practice very efficient even for non-quadratic functions

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Kohn-Sham DFT calculations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

Minimise *E* w.r.t.:

Orbitals

$$\{\psi_i\}$$

Density matrix

$$\rho(\mathbf{r},\mathbf{r}') = \sum_i f_i\, \psi_i(\mathbf{r})\, \psi_i^*(\mathbf{r}')$$

Computational bottlenecks

Build

$$E[n]$$

> O(N^2)

Orthogonality / solve Hamiltonian

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

O(N^3)

Idempotency

$$\hat{\rho}^2 = \hat{\rho}$$

O(N^3)

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

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

Density matrix localisation

Nearsightedness of electronic matter

W. Kohn, *Phys. Rev. Lett*. **76**, 3168 (1996); E. Prodan and W. Kohn, *P.N.A.S.* **102** 11635 (2005)

In systems with a band gap:

$$\rho(\mathbf{r},\mathbf{r}') \sim e^{-\gamma|\mathbf{r}-\mathbf{r}'|} \to 0 \quad \text{as} \quad |\mathbf{r}-\mathbf{r}'| \to \infty$$

Linear-scaling approaches:

Truncate exponential "tail", impose:

$$\rho(\mathbf{r},\mathbf{r}') = 0 \quad \text{when} \quad |\mathbf{r}-\mathbf{r}'| > r_{\text{cut}}$$

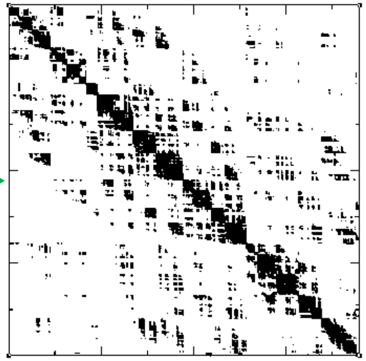
Non-orthogonal localised functions

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

- **K** matrix made sparse by truncation
- **S** and **H** in terms of $\{\phi_\alpha\}$ also sparse

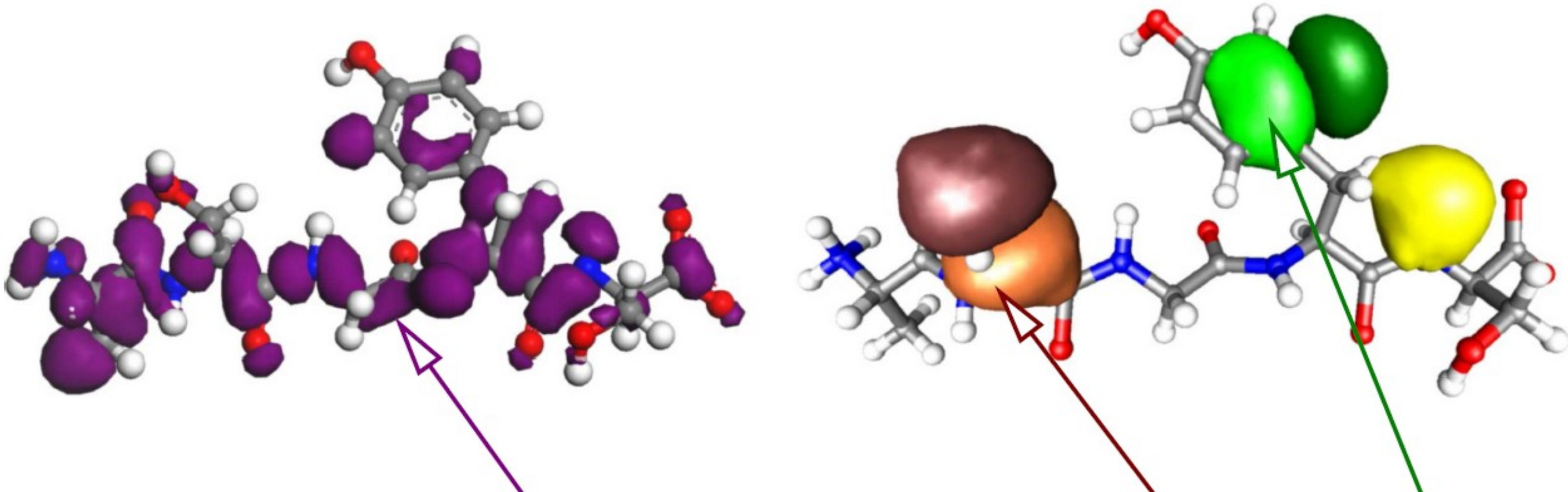
Optimise energy with respect to **K**

sparse matrix



ONETEP aims for high accuracy

Use only a minimal number of $\{\phi_\alpha\}$ but also optimise these *in situ*, (in addition to **K)**



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

Molecular orbitals (MOs)

Non-orthogonal Generalised Wannier Functions (NGWFs)

Density matrix

- Operator

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

- Position representation

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

$$\rho^2(\mathbf{r},\mathbf{r}') = \int \rho(\mathbf{r},\mathbf{r}'')\,\rho(\mathbf{r}'',\mathbf{r}')\,d\mathbf{r}'' = \sum_n f_n^2\, \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')$$

$$\mathrm{tr}[\rho] = \int \rho(\mathbf{r},\mathbf{r})d\mathbf{r} = \int \sum_n f_n\, \psi_n(\mathbf{r})\psi_n^*(\mathbf{r})\,d\mathbf{r} = \sum_n f_n \int |\psi_n(\mathbf{r})|^2 d\mathbf{r} = \sum_n f_n$$

- NGWF representation

$$\psi_n(\mathbf{r}) = \phi_\alpha(\mathbf{r})M^\alpha{}_n \qquad S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$$

$$\rho(\mathbf{r},\mathbf{r}') = \sum_n f_n\, \psi_n(\mathbf{r})\,\psi_n^*(\mathbf{r}') = \phi_\alpha(\mathbf{r})\left(\sum_n M^\alpha{}_n f_n M_n^{\dagger\,\beta}\right)\phi_\beta^*(\mathbf{r}') = \phi_\alpha(\mathbf{r})K^{\alpha\beta}\phi_\beta^*(\mathbf{r}')$$

$$K^{\alpha\beta} = \sum_n M^\alpha{}_n f_n M_n^{\dagger\,\beta}$$

$$\rho^2(\mathbf{r},\mathbf{r}') = \phi_\alpha(\mathbf{r})K^{\alpha\gamma}S_{\gamma\epsilon}K^{\epsilon\beta}\phi_\beta^*(\mathbf{r}')$$

$$\mathrm{tr}[\rho] = K^{\alpha\beta}S_{\beta\alpha} = \mathrm{tr}[\mathbf{KS}]$$

Conditions

- Self-consistency

$$\hat{H}[\{\psi_i^{(p)}\}]\,|\psi_n^{(p+1)}\rangle = \varepsilon_n^{(p+1)}|\psi_n^{(p+1)}\rangle$$ therefore $$\hat{H}[\{\psi_i^{(p)}\}] = \sum_n \varepsilon_n^{(p+1)}|\psi_n^{(p+1)}\rangle\langle\psi_n^{(p+1)}|$$

$$\hat{\rho}[\{\psi_i^{(p)}\}] = \sum_n f_n\,|\psi_n^{(p)}\rangle\langle\psi_n^{(p)}|$$

When $|\psi_n^{(p)}\rangle = |\psi_n^{(p+1)}\rangle$ the operators commute $\left[\hat{H}[\{\psi_i^{(p)}\}],\, \hat{\rho}[\{\psi_i^{(p)}\}]\right] = 0$

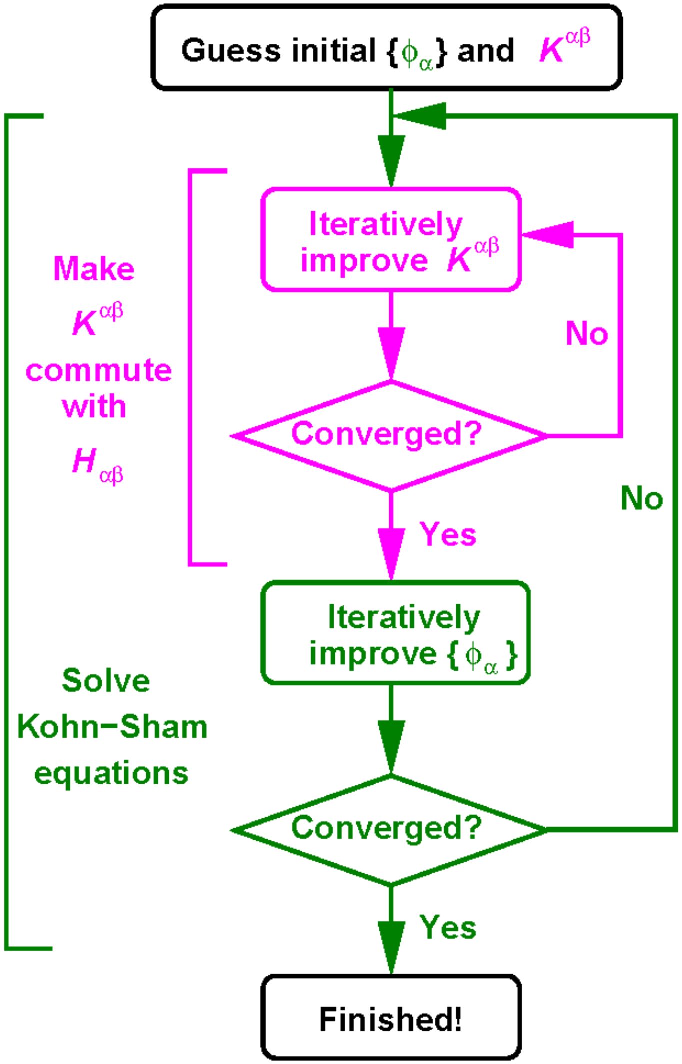
- Idempotency

$$\hat{\rho}^2 = \hat{\rho} \;\Leftrightarrow\; f_n = 0 \text{ or } 1$$

- Normalisation

$$N_e = 2\,\mathrm{tr}[\rho] = 2\sum_n f_n$$ (spin-unpolarised case)

Density matrix optimisation in ONETEP



$$E = E[\mathbf{K}, \{\phi_\alpha\}]$$

- **Inner loop**: **Self-consistently** optimise total (interacting) energy *E* w.r.t **K** for fixed $\{\phi_\alpha\}$ while imposing "weak" **idempotency** and **normalisation** constraints

- **Outer loop**: **Self-consistently** optimise total (interacting) energy *E* w.r.t. $\{\phi_\alpha\}$

Equivalent to solving Kohn-Sham equations in psinc basis

$$\hat{H}\psi_i = \varepsilon_i \psi_i$$

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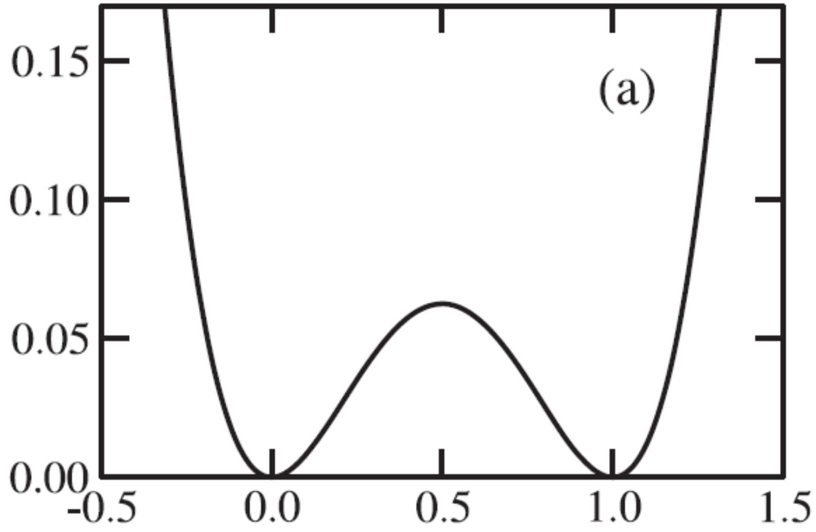
P. D. Haynes, C.-K. Skylaris, A. A. Mostofi and M. C. Payne,
J. Phys.: Condens. Matter **20**, 294207 (2008)

Penalty functional

$$P[\rho] = \mathrm{tr}[(\rho^2 - \rho)^2] = \sum_n (f_n^2 - f_n)^2$$



- Minimum (P=0) for idempotent density matrices
- Will always converge, regardless how non-idempotent the initial guess
- Constraints to preserve the total number of electrons are needed

Penalty functional derivatives

$$P[\rho] = \mathrm{tr}[(\rho^2 - \rho)^2] = \sum_n (f_n^2 - f_n)^2$$

- Assume a steepest descents "step" to update f_k

$$\frac{\partial P}{\partial f_k} = 4f_k^3 - 6f_k^2 + 2f_k$$

$$f_k^{(p+1)} = f_k^{(p)} + \lambda d_k^{(p)} \qquad f_k^{(p+1)} = f_k^{(p)} - \lambda \frac{\partial P}{\partial f_k}^{(p)}$$

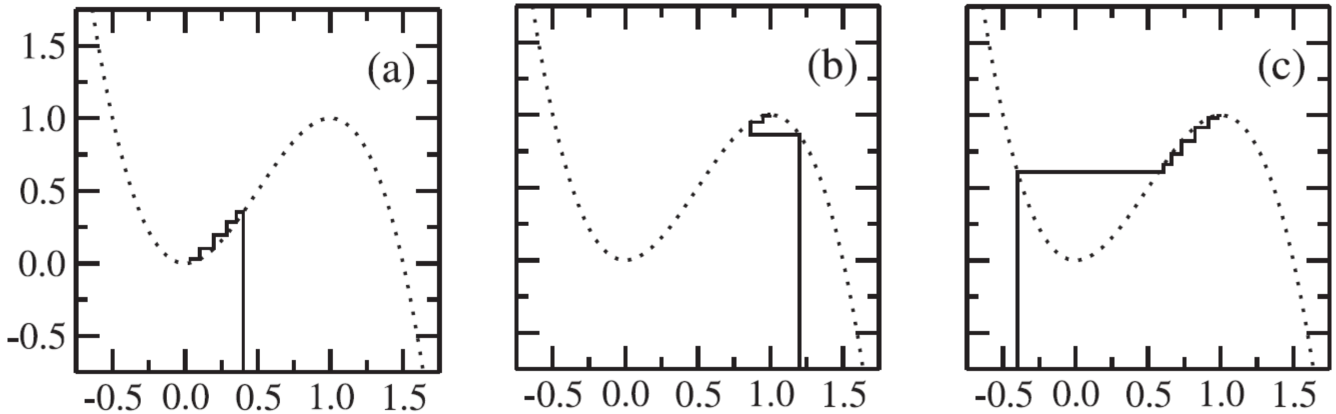
- If we apply a quadratic approximation (near the minimum):

$$f_{new} = f_{old} - \frac{1}{2}(4f_{old}^3 - 6f_{old}^2 + 2f_{old}) = 3f_{old}^2 - 2f_{old}^3$$

Purification transformation

R. McWeeny, *Rev. Mod. Phys.* **32**(2), 335(1960)

Purification transformation



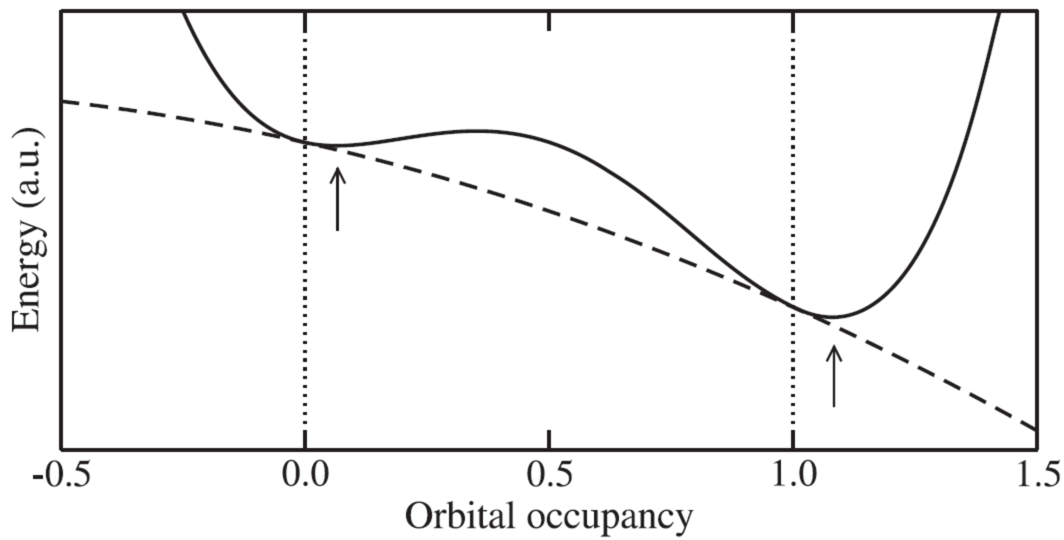
$$f_{new} = 3f_{old}^2 - 2f_{old}^3$$

- Improves the idempotency of a nearly idempotent density matrix
- Forces occupancies in interval [0,1] ("weak" idempotency)
- Quadratic convergence. Example:
  - $f^{(1)} = 1.1$
  - $f^{(2)} = 3\times1.1^3 - 2\times1.1^2 = 0.968$
  - $f^{(3)} = 3\times0.968^3 - 2\times0.968^2 = 0.997$
  - Etc..
- But, diverges if the initial occupancies are not within certain bounds

Energy with penalty functional

P. D. Haynes and M. C. Payne, *Phys. Rev. B* **59**, 12173 (1999)

$$Q[\rho] = E[\rho] + \alpha P[\rho]$$



- Balance between minimum energy and minimum penalty
- Near-idempotency, depending on value of α
- Correction expression available for the energy

Li-Nunes-Vanderbilt (LNV) functionals

$$\rho = 3\sigma^2 - 2\sigma^3$$

X.-P. Li., R. W. Nunes and D. Vanderbilt, *Phys. Rev. B* **47**, 10891 (1993),
M. S. Daw, *Phys. Rev. B* **47**,10895 (1993)

$$\Omega_1[\sigma] = \mathrm{tr}[\rho(H - \mu)]$$

J. M. Millam and G. E. Scuseria, *J. Chem. Phys.* **106**, 5569 (1997)

$$\Omega_2[\sigma] = \mathrm{tr}[\rho H] + \mu'(\mathrm{tr}[\sigma] - N_e)$$

- Energy expressions containing a purification transformation of an "auxiliary" density matrix
- Implicitly enforce idempotency
- Break down if purification transformation breaks
- Minimisation of band structure energy (equivalent to diagonalisation)
- But H also depends on ρ: Self-consistency by density mixing

LNV functionals in ONETEP

`exact_lnv = F`

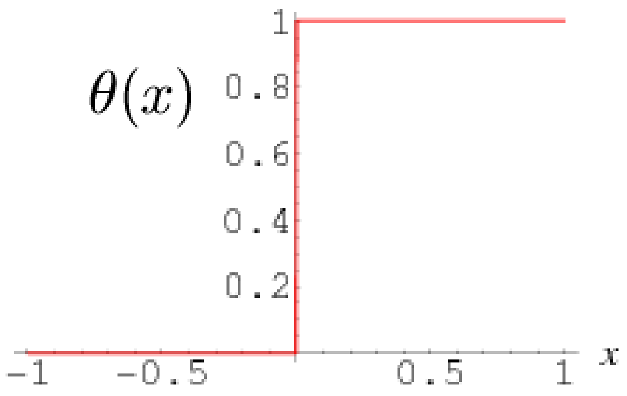
$$L_1[\sigma] = E[\rho] + \mu' \left(\mathrm{tr}[\sigma] - N_e\right) = E[3\sigma^2 - 2\sigma^3] + \mu' \left(\mathrm{tr}[\sigma] - N_e\right)$$

`exact_lnv = T (default)`

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

- No density mixing, just direct minimisation of interacting energy
- Purification never allowed to break down
    - Occupancy maxima and minima tracked
    - Restored by penalty functional if out of safe range
- Electron number conserved without need to know the chemical potential

Canonical purification



$$\hat{\rho} = \theta(\mu \hat{I} - \hat{H})$$

$$H(\mathbf{r}, \mathbf{r}') = \sum_i \varepsilon_i \, \psi_i(\mathbf{r}) \psi_i(\mathbf{r}')$$

$$\theta(\mu \hat{I} - \hat{H})(\mathbf{r}, \mathbf{r}') = \ldots = \sum_i \theta(\mu - \varepsilon_i) \psi_i(\mathbf{r}) \psi_i(\mathbf{r}') = \sum_i f_i \, \psi_i(\mathbf{r}) \psi_i(\mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}')$$

$$f_i = \begin{cases} 1, & \text{if } \varepsilon_i < \mu \\ 0, & \text{if } \varepsilon_i > \mu \end{cases}$$

- One can approximate ρ as a polynomial expansion of *H*
- Can do this iteratively with a formula that resembles the purification transformation:
  - A. H. Palser and D. E. Manolopoulos, *Phys. Rev. B* **58**, 12704 (1998)
- Always converges
- No need to know μ

Derivatives with respect to the density kernel

Relationship between canonical Kohn-Sham orbitals and NGWFs

$$\psi_n(\mathbf{r}) = \phi_\alpha(\mathbf{r}) M^\alpha_{\ n} \quad \Leftrightarrow \quad \phi_\alpha(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) (M^\dagger)_{n\alpha}$$

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \qquad \langle \phi_\alpha | \phi_\beta \rangle = S_{\alpha\beta} \ , \quad (S^{-1})^{\alpha\beta}$$

$$K^{\alpha\beta} = \sum_n M^\alpha_{\ n} f_n (M^\dagger)_n^{\ \beta}$$

When varying K:

- Occupancies change
- Kohn-Sham orbitals change
- NGWFs do not change

Example: Gradient of penalty functional with respect to K

$$P[\rho] = \mathrm{tr}[(\rho^2 - \rho)^2] = \sum_n (f_n^2 - f_n)^2 = \mathrm{tr}[(\mathbf{KSKS} - \mathbf{KS})^2]$$

Differentiate with respect to the elements of K

$$\frac{\partial P}{\partial K^{\alpha\beta}} = \sum_n \frac{\partial P}{\partial f_n} \frac{\partial f_n}{\partial K^{\alpha\beta}} = \ldots = (4SKSKSKS - 6SKSKS + 2SKS)_{\beta\alpha} = G_{\beta\alpha}$$

Tensor correction

- To obtain search directions (in steepest descents or conjugate gradients) a contravariant gradient is needed

$$G^{\alpha\beta} = S_-^{\alpha\gamma} G_{\gamma\epsilon} S_-^{\epsilon\beta} = (4KSKSK - 6KSK + 2K)^{\alpha\beta}$$

E. Artacho and L. M. del Bosch, *Phys. Rev. A* **43**, 5770 (1991).

C. A. White, P. Maslen, M. S. Lee and M. Head-Gordon, *Chem. Phys. Lett*. **276**, 133 (1997).

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Optimisation of NGWFs

$$\phi_\alpha(\mathbf{r}) = \sum_m D_m(\mathbf{r})\, C_{m\alpha}$$

Gradient of LNV functional with respect to psinc expansin coefficents of NGWFs

$$g_m^{\ \alpha} = \frac{\partial L}{\partial C^*_{m\alpha}} = 2w\left[(\hat{H}\phi_\beta)(\mathbf{r})K^{\beta\alpha} + \phi_\beta(\mathbf{r})Q^{\beta\alpha}\right]_{\mathbf{r}=\mathbf{r_m}}$$

Tensor-corrected covariant gradient

$$g_{m\alpha} = g_m^{\ \beta} S_{\beta\alpha} = 2w\left[(\hat{H}\phi_\beta)(\mathbf{r})K^{\beta\gamma}S_{\gamma\alpha} + \phi_\beta(\mathbf{r})Q^{\beta\gamma}S_{\gamma\alpha}\right]_{\mathbf{r}=\mathbf{r_m}}$$

Linear-scaling calculation of gradient with:

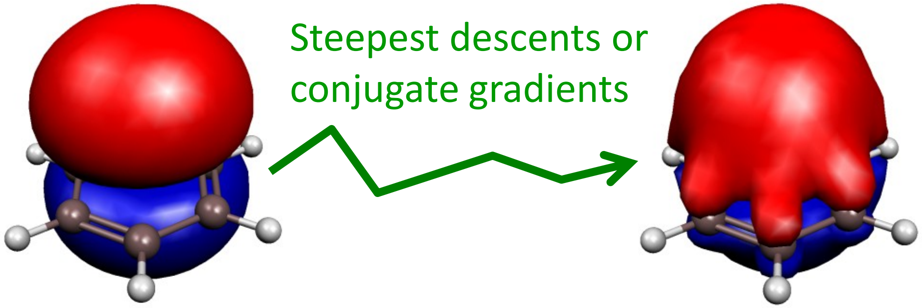
- FFT box technique
- Sparse Hamiltonian and overlap matrices
- Sparse density kernel

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

Maintaining localisation: Advantages of orthogonal basis set

Localisation by truncation of basis set expansion

$$\phi(\mathbf{r}) = \sum_i D_i(\mathbf{r}) c^i$$



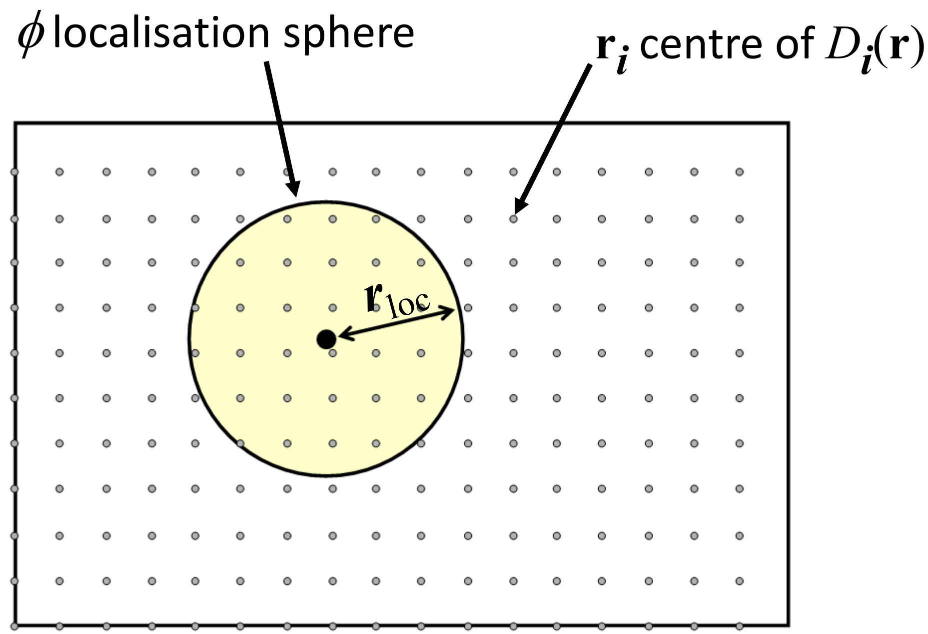
What happens with a non-orthogonal basis:

$$\frac{\partial E}{\partial c^{*i}} = g_i$$

$$S_{ij} = \langle D_i(\mathbf{r}) | D_j(\mathbf{r}) \rangle$$

$$c^i{}_{\text{new}} = c^i_{\text{old}} - \lambda \sum_j (S^{-1})^{ij} g_j$$

Iterative update contains gradients from outside of localisation region



Occupancy preconditioning

- Derivative of E w.r.t. K-S orbitals

$$\frac{\delta E}{\delta \psi_n^*(\mathbf{r})} = 2 f_n [\hat{H}\psi_n(\mathbf{r}) - \epsilon_n \psi_n(\mathbf{r})]$$

- Derivative of E w.r.t. NGWFs

$$\frac{\delta E}{\delta \psi_n^*(\mathbf{r})} = \int \frac{\delta E}{\delta \phi_\alpha^*(\mathbf{r}')} \left(\frac{\partial \phi_\alpha(\mathbf{r}')}{\partial \psi_n(\mathbf{r})} \right)^* d\mathbf{r}' = \frac{\delta E}{\delta \phi_\alpha^*(\mathbf{r})} M_{\alpha n}$$

$$\frac{\delta E}{\delta \phi_\alpha^*(\mathbf{r})} = \frac{\delta E}{\delta \psi_n^*(\mathbf{r})} (M^\dagger)_{n\beta} (S^{-1})^{\beta\alpha}$$

Relations between Kohn-Sham orbitals and NGWFs

$$\phi_\alpha(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) (M^\dagger)_{n\alpha}$$

$$\psi_n(\mathbf{r}) = \phi_\alpha(\mathbf{r}) M^\alpha{}_n \qquad \langle \psi_n | \psi_m \rangle = \delta_{nm}$$

$$\langle \phi_\alpha | \phi_\beta \rangle = S_{\alpha\beta} \ , \quad (S^{-1})^{\alpha\beta}$$

$$K^{\alpha\beta} = \sum_n M^\alpha{}_n f_n (M^\dagger)_n{}^\beta$$

Remove ill-conditioning of f_n ~0

$$\frac{\delta E}{\delta \phi_\alpha^*(\mathbf{r})}$$

f_n in [0,1] →

$$2[\hat{H}\phi_\beta(\mathbf{r}) K^{\beta\alpha} - \phi_\beta(\mathbf{r}) K^{\beta\gamma} H_{\gamma\eta} (S^{-1})^{\eta\alpha}]$$

make all f_n =1 `occ_mix = 1.0` ↓

$$2[\hat{H}\phi_\beta(\mathbf{r}) (S^{-1})^{\beta\alpha} - \phi_\beta(\mathbf{r}) (S^{-1})^{\beta\gamma} H_{\gamma\eta} (S^{-1})^{\eta\alpha}]$$

Covariant →

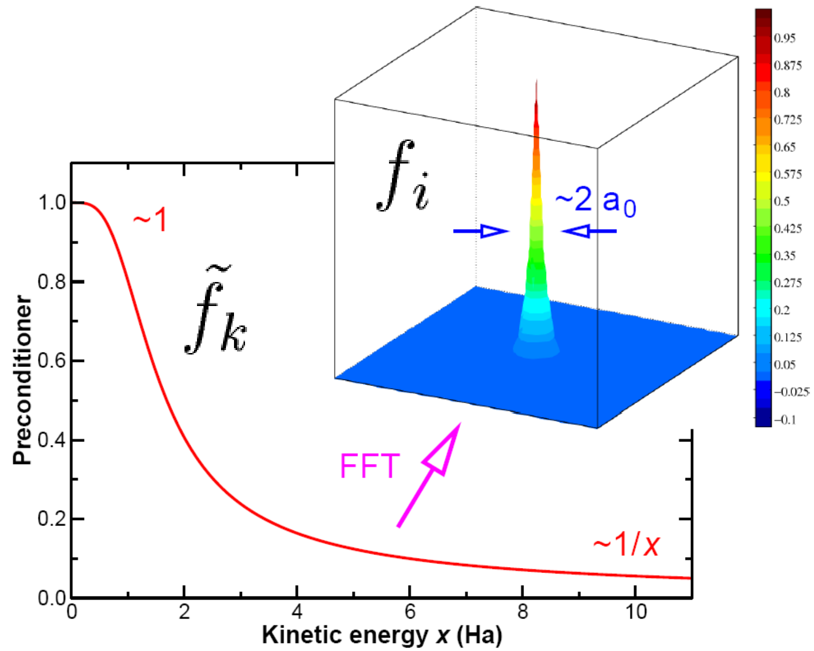
$$2[\hat{H}\phi_\alpha(\mathbf{r}) - \phi_\beta(\mathbf{r}) (S^{-1})^{\beta\gamma} H_{\gamma\alpha}]$$

Use for search directions

Kinetic energy preconditioning

Length scale ill-conditioning

- Convergence rate falls with increasing ratio of max/min eigenvalues of the Hamiltonian
- High energy eigenstates are dominated by kinetic energy
- Need to reduce the contribution of kinetic energy in the NGWF gradient



- Pre-multiply NGWF gradient in reciprocal space with a function that behaves as the inverse of the kinetic energy at high wave vectors and approaches 1 at low wavevectors:

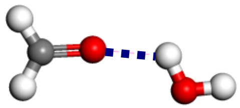
$$\tilde{g}_{k\alpha} \longrightarrow \tilde{f}_k \tilde{g}_{k\alpha}$$

Example: $$\tilde{f}_k = \frac{k_0^2}{k_0^2 + \mathbf{k}^2}$$ `k_zero`

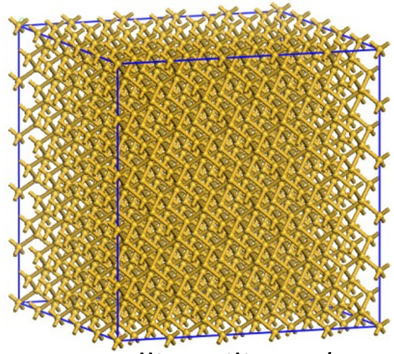
A. A. Mostofi, P. D. Haynes, C.-K. Skylaris and M. C. Payne, *J. Chem. Phys.* **119**, 8842 (2003)

Fast convergence

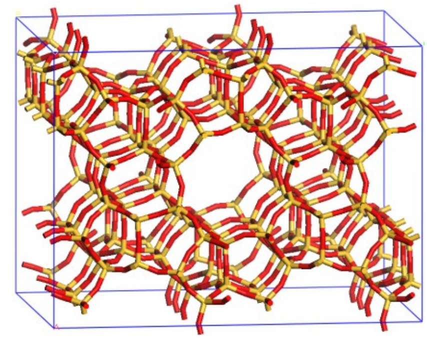
True linear-scaling



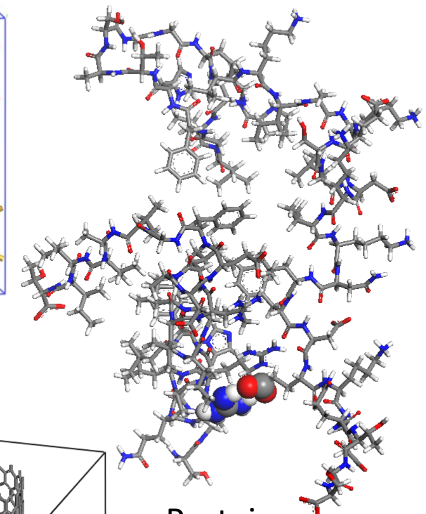
H-bond (7 atoms)



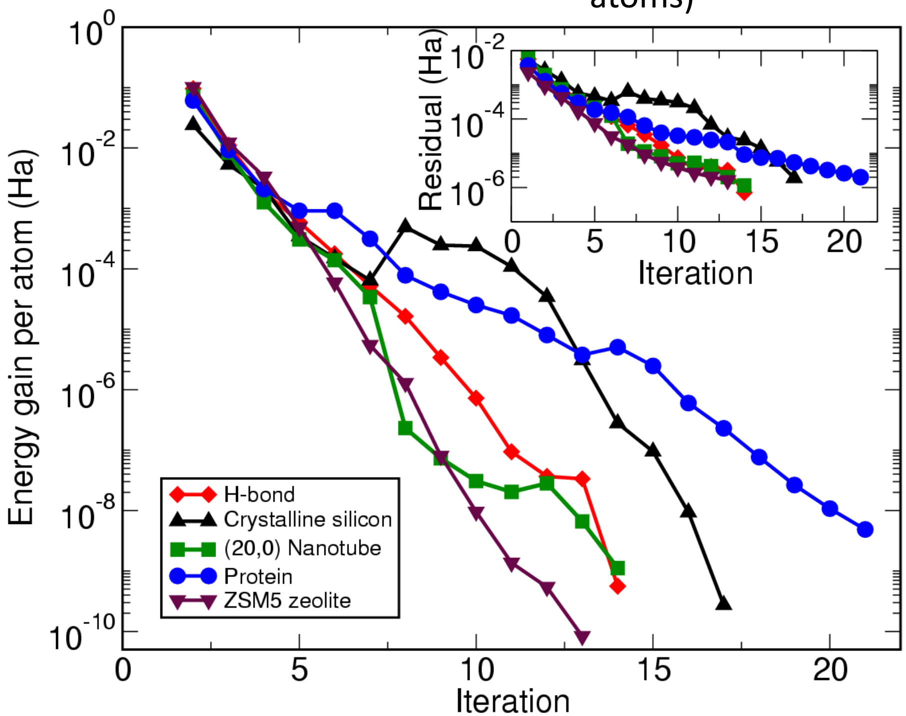
Crystalline silicon (1000 atoms)

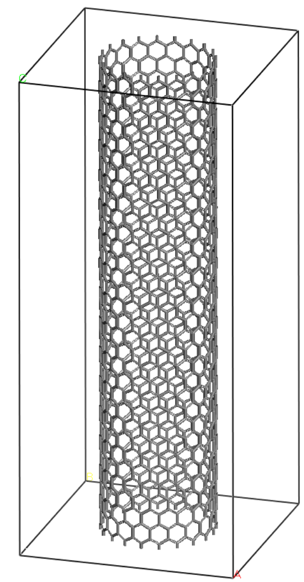


ZSM5 zeolite (576 atoms)



Protein (988 atoms)





(20, 0) Nanotube (1280 atoms)

C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, *Phys. Stat. Sol. (b)* **243**(5), 973 (2006)

Calculation of S^{-1}

Inverse of $S_{\alpha\beta} = \langle \phi_\alpha | \phi_\beta \rangle$

Is a contravariant tensor, like the density kernel

Can be iteratively generated with the Hotelling formula

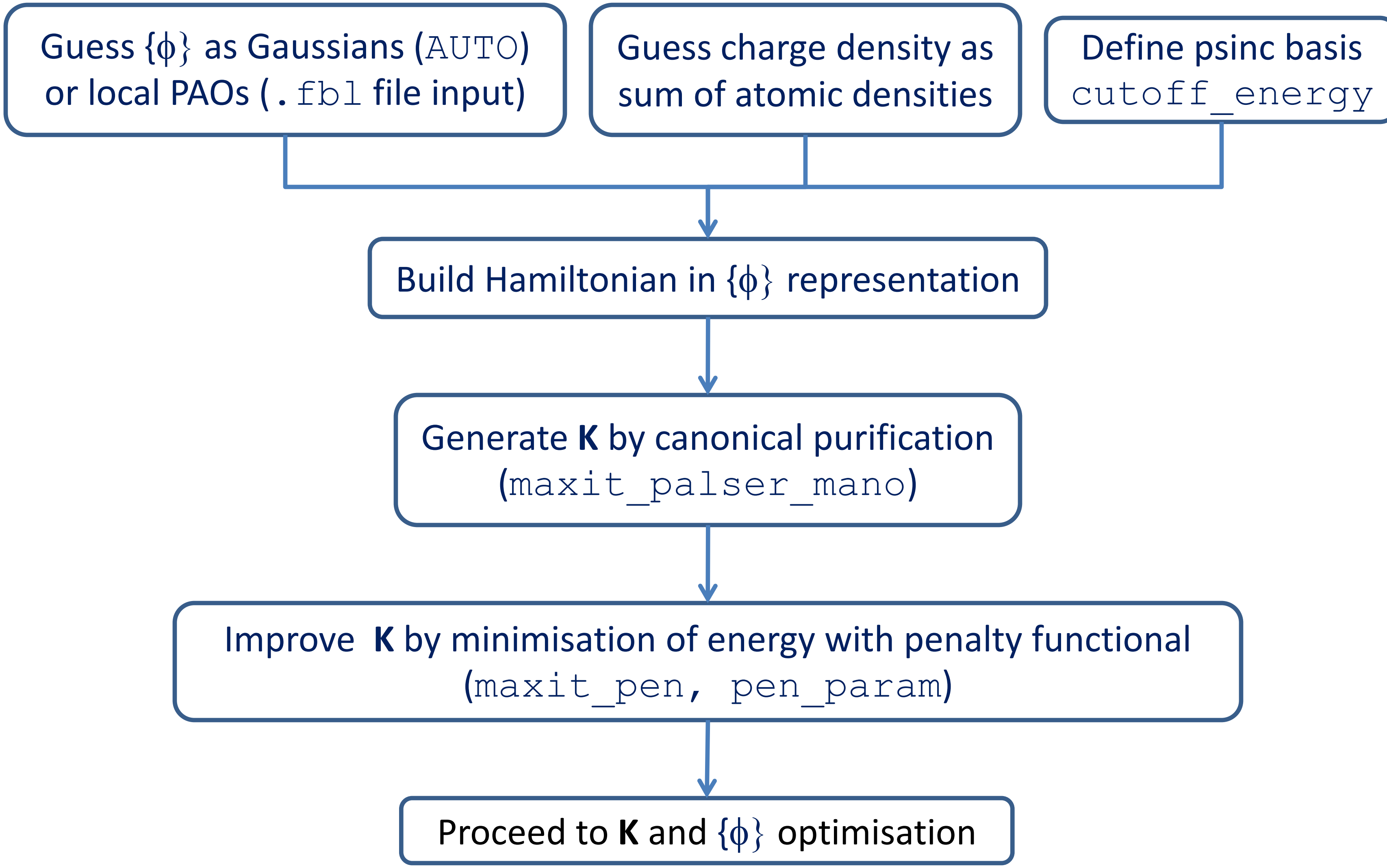
$$\mathbf{S}^{-1}_{\text{new}} = 2\mathbf{S}^{-1}_{\text{old}} - \mathbf{S}^{-1}_{\text{old}}\,\mathbf{S}\,\mathbf{S}^{-1}_{\text{old}}$$

`maxit_hotelling`

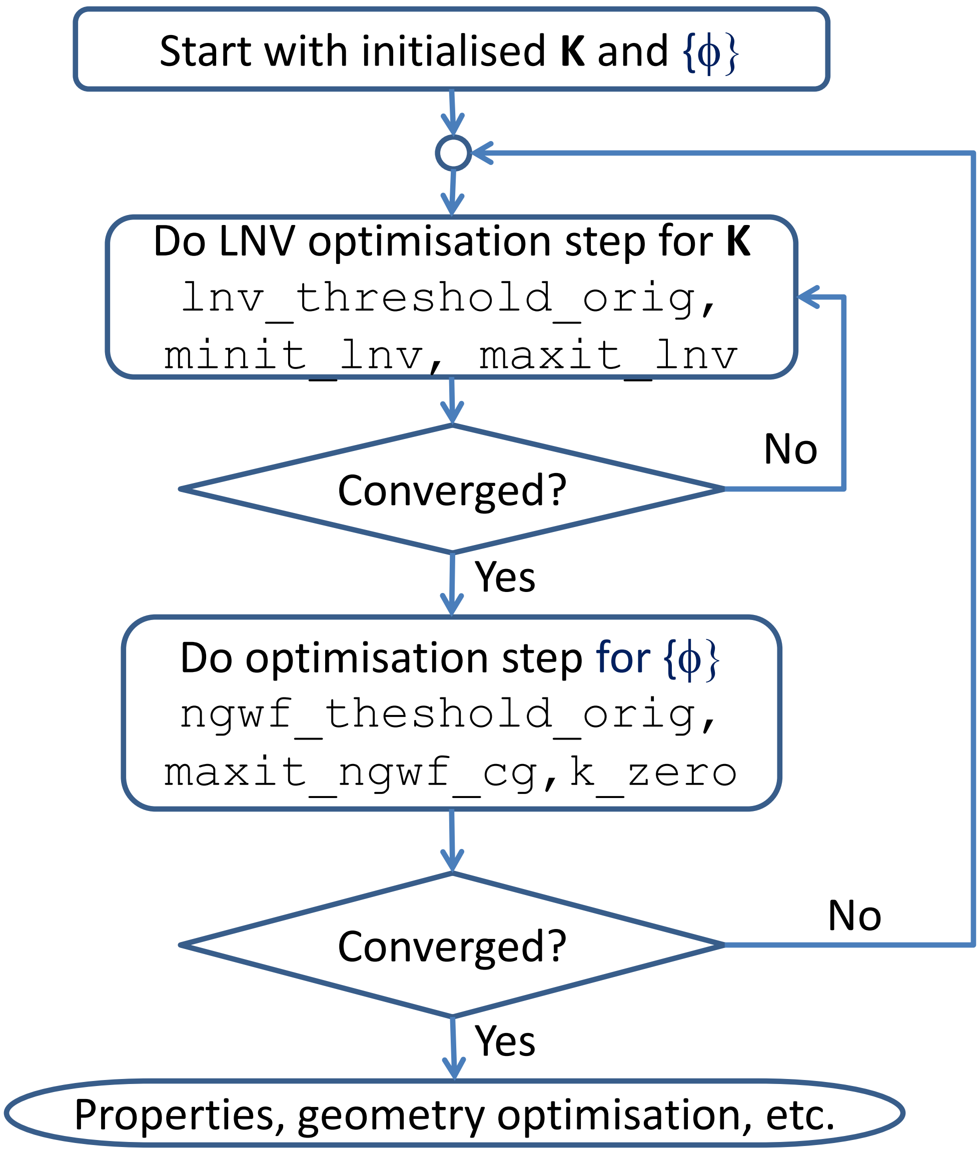
- Similar to purification transformation
- Converges rapidly
- Can generate S^{-1} with linear-scaling cost from the beginning
- Can be used to update S^{-1} when NGWFs are updated with minimal computational effort
- Takes advantage of kernel truncation

1. Kohn-Sham calculations
    - Direct energy minimisation versus density mixing
2. ONETEP scheme: optimise both the density kernel and NGWFs
    - Conditions
3. Density matrix optimisation algorithms in ONETEP
    - Penalty, purification, LVN
    - Density kernel gradients, tensor properties
4. Optimisation of NGWFs
    - NGWF gradients, preconditioning schemes
    - The need for an orthogonal
5. More detailed look at overall ONETEP scheme
    - Initialisation
    - Flowchart, input keywords

Initialisation of density kernel and NGWFs



NGWF and density kernel optimisation



Key points

- Direct energy minimisation, no density mixing
- All quantities (Hamiltonian, energy, gradients) built with linear-scaling cost
  - NGWF localisation in real space, FFT-box technique in reciprocal space
  - Sparse Hamiltonian and overlap matrixes
  - Sparse density kernel (`kernel_cutoff`)
- Linear-scaling iterative algorithms using sparse-matrix algebra
- Matrix products preserve sparsity patterns, e.g. **KSK** is less sparse than **K**
- Tensorially correct gradients
- Preconditioned NGWF optimisation

The ONETEP program

Wiki http://www2.tcm.phy.cam.ac.uk/onetep/

J. Chem. Phys. **122,** 084119 (2005)

EPSRC Engineering and Physical Sciences Research Council

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