SCF Methods
— Diagonalisation &Orbital Transformation

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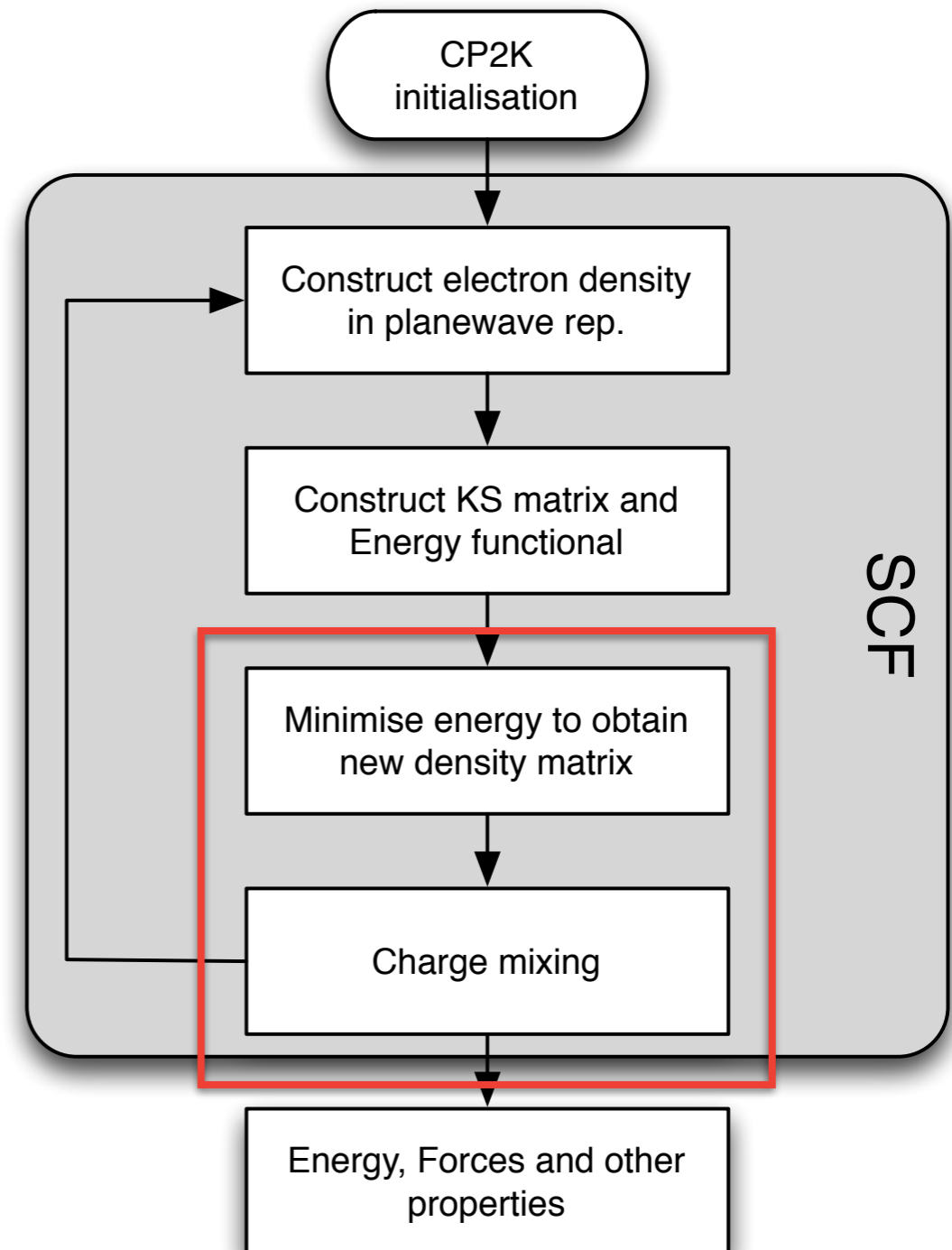
24 August 2016

Self Consistent Field Calculation

- Central to the QuickStep (DFT) calculation is the Self-Consistent-Field cycle

$$H[\rho]\psi_n = E_n\psi_n$$

$$\rho(\mathbf{r}) = \sum_n f_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r})$$

- Key to speed and stability of the calculation:
  - Energy minimisation
  - Charge mixing

- Common Methods In CP2K
  - Eigensolvers
  - Optimisers
- Orbital Transformation (OT)
  - Preconditions
- Charge Mixing for Diagonalisation Methods
  - Methods used in CP2K
  - Important parameters for convergence
- Examples

Eigensolvers In CP2K

- General Eigen problem:

$$\mathbf{Ax} = \lambda \mathbf{Bx}$$

- Find a way to rewrite back to the standard Eigen problem

$$\mathbf{A}'\mathbf{x}' = \lambda \mathbf{x}'$$

upper triangular

- Cholesky decomposition based methods: $\mathbf{B} = \mathbf{U}^\mathsf{T}\mathbf{U}$ must be positive definite:

$$(\mathbf{U}^{-1})^\mathsf{T}\mathbf{A}\mathbf{U}^{-1}\mathbf{U}\mathbf{x} = \lambda \mathbf{U}\mathbf{x}$$

- REDUCE: $\quad \mathbf{A}|\mathbf{U} \Rightarrow \mathbf{A}'|\mathbb{1} \quad$ followed by solving $\mathbf{U}\mathbf{x} = \mathbf{x}'$

- RESTORE: Same as Reduce, but with the single reduce step for $\mathbf{A}'$ replaced with two restore steps:
    - Solve $\mathbf{x}\mathbf{U} = \mathbf{A} \quad \Rightarrow \quad \mathbf{x} = \mathbf{A}\mathbf{U}^{-1}$
    - Solve $\mathbf{U}^\mathsf{T}\mathbf{y} = \mathbf{x} \quad \Rightarrow \quad \mathbf{y} = (\mathbf{U}^\mathsf{T})^{-1}\mathbf{A}\mathbf{U}^{-1}$

- INVERSE: Same as Reduce, but calculate $\mathbf{A}'$ using the direct inverse of $\mathbf{U}$ (involves one inversion of a triangular matrix plus two matrix multiplications)

- INVERSE_DBCSR: Same as inverse, but utilising sparse matrix algebra engine whenever possible (e.g. when doing matrix multiplication)

- **Without Cholesky decomposition:**

  - Useful if your basis set contains linearly dependent functions, i.e. B is non-positive definite

  - Slower, but more robust

- Find the inverse square root of $\mathbf{B}$: $\mathbf{B}^{-\frac{1}{2}}$

$$\mathbf{B} = \mathbf{B}^{\frac{1}{2}}\mathbf{B}^{\frac{1}{2}}$$

$$\mathbf{B}^{-\frac{1}{2}}\mathbf{A}\mathbf{B}^{-\frac{1}{2}}\mathbf{B}^{\frac{1}{2}}\mathbf{x} = \mathbf{B}^{\frac{1}{2}}\mathbf{x}$$

$$\mathbf{x}' = \mathbf{B}^{\frac{1}{2}}\mathbf{x} \qquad \Rightarrow \qquad \mathbf{x} = \mathbf{B}^{-\frac{1}{2}}\mathbf{x}'$$

- $\mathbf{B}^{-\frac{1}{2}}$ is calculated by diagonalise $\mathbf{B}$, invert the eigenvalues and then transform back.

- If B is non-positive definite: this normally corresponds to the basis set containing redundant linearly dependent vectors. This means the zero eigenvalues of B should not contribute to the linear problem.

  - This is equivalent to set inverse of the eigenvalues to zero

- Concerns with finding the local minimum of a function of many variables

- Steepest Decent:

$$f(\mathbf{x}_n) = f(\mathbf{x}_{n-1}) + \alpha \boldsymbol{\nabla} f(\mathbf{x}_{n-1})$$

  - How much we travel along the gradient is determined by a line search to find the minimum of the function along the path

- **Conjugate Gradient**:

    - If we start from a point $\mathbf{x}_0$ close to the minimum, we may Taylor expand around the point to the second order, and assume the minimum is within the radius of convergence:

    $$f(\mathbf{x}) = f(\mathbf{x}_0) + \mathbf{b}^\mathsf{T}(\mathbf{x} - \mathbf{x}_0) + (\mathbf{x} - \mathbf{x}_0)^\mathsf{T}\mathbf{H}(\mathbf{x} - \mathbf{x}_0) + \mathcal{O}((\mathbf{x} - \mathbf{x}_0)^3)$$

    $$(\mathbf{H})_{ij} = \frac{1}{2}\left.\frac{\partial^2 f}{\partial x_i \partial x_j}\right|_{\mathbf{x}_0} \qquad \mathbf{b} = \left.\boldsymbol{\nabla} f\right|_{\mathbf{x}_0}$$

    - We notice that $\mathbf{x}$ is the unique solution to $\nabla f(\mathbf{x}) = 0$ if it is the solution of the equation

    $$\boldsymbol{\nabla} f(\mathbf{x}) = \mathbf{b} + \mathbf{H}\mathbf{x} = 0 \quad \Rightarrow \mathbf{H}\mathbf{x} = -\mathbf{b}$$

    - The Conjugate gradient method then tries to solve the above equation iteratively. Notice that $\mathbf{H}$ is always symmetric and when near a minimum, positive definite

    - We can express $\mathbf{x}$ in a basis set

    $$\mathbf{x} = \sum_i \alpha_i \mathbf{P}_i$$

    - Hence

    $$\sum_j \mathbf{P}_i^\mathsf{T}\mathbf{H}\mathbf{P_j}\alpha_j = -\mathbf{P}_i^\mathsf{T}\mathbf{b}$$

- Conjugate Gradient:

  - Now since $\mathbf{H}$ is symmetric and positive definite, it can be diagonalised, and we can choose $\mathbf{P}_i$ to be a set of conjugate vectors of $\mathbf{H}$, then we can see that

$$\alpha_i = \frac{-\mathbf{P}_i^\mathsf{T}\mathbf{b}}{\mathbf{P}_i^\mathsf{T}\mathbf{H}\mathbf{P}_i} \qquad \mathbf{P}_i^\mathsf{T}\mathbf{H}\mathbf{P}_j = 0 \quad (i \neq j)$$

  - The conjugate gradient method then involves iteratively finding each $\mathbf{P}_i$ using a Gram-Schmidt like process

  - In other words: we take exactly $n = \dim \mathbf{H}$ steps, starting from an initial guess $\mathbf{x}_0$

$$\mathbf{d}_i = -\mathbf{b} - \mathbf{H}\mathbf{x}_i$$

$$\mathbf{P}_1 = \mathbf{d}_0$$

$$\mathbf{P}_2 = \mathbf{d}_1 - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_1}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0$$

$$\mathbf{x}_1 = \alpha_1\mathbf{P}_1$$

$$\mathbf{x}_2 = \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2$$

$$\mathbf{P}_3 = \mathbf{d}_2 - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_2}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0 - \frac{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{d}_2}{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{P}_1}\mathbf{P}_1$$

$$\mathbf{x}_3 = \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2 + \alpha_3\mathbf{P}_3$$

$$\vdots$$

$$\vdots$$

$$\mathbf{x}_n = \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2 + \alpha_3\mathbf{P}_3 + \cdots + \alpha_n\mathbf{P}_n \qquad \mathbf{P}_n = \mathbf{d}_{n-1} - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0 - \frac{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{P}_1}\mathbf{P}_1 - \cdots - \frac{\mathbf{P}_{n-1}^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_{n-1}^\mathsf{T}\mathbf{H}\mathbf{P}_{n-1}}\mathbf{P}_{n-1}$$

- Discrete Inversion in Iterative Space (DIIS), a.k.a. Pulay Method :

  - The new step is based on considerations over a list of previous steps:

  $$\mathbf{x}_{n+1} = \sum_i^n \alpha_i \mathbf{x}_i, \quad \sum_i^n \alpha_i = 1$$

  - Minimise by seeking the solution to $\nabla f(\mathbf{x}) = 0$

  - Assume when close enough to minimum, the gradient becomes a linear function:

  $$\nabla f(\mathbf{x}_{n+1}) = \sum_i^n \alpha_i \nabla f(\mathbf{x}_i) \qquad \mathbf{d}_i \equiv \nabla f(\mathbf{x}_i)$$

  - The new gradient (residual) is then a function of α_i, solve: $\dfrac{\partial \|\mathbf{d}_{n+1}\|}{\partial \alpha_i} = 0$ with constraints $\sum_i^n \alpha_i = 1$, we obtain:

  $$\alpha_i = \frac{\sum_i^n A_{ji}^{-1}}{\sum_{ij}^n A_{ji}^{-1}}, \quad A_{ij} = \mathbf{d}_i^\mathsf{T} \mathbf{d}_j$$
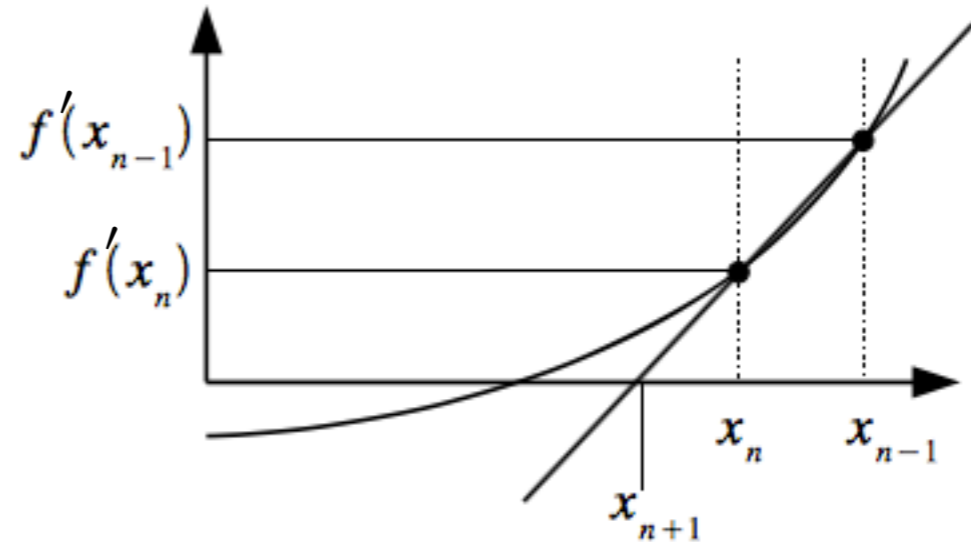
  - Can be over 50% faster than CG, but not as stable because bad history contribute to the next step.

  - Too many history included may not be beneficial.

- **Broyden's Method:**

  - Again, seeks the solution to $\nabla f(\mathbf{x}) = 0$, but using the secant method

  - The next step can be determined by the inverse of Jacobian:

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \mathbf{J}_n^{-1}\mathbf{d}_n$$

$$\mathbf{d}_n \equiv \nabla f(\mathbf{x}_n)$$

$$(\mathbf{J}_n)_{ij} = \frac{\partial(\mathbf{d}_n)_i}{\partial x_j}$$

  - But inverse of Jacobian too expensive, so instead approximate $\mathbf{J}_n^{-1}$ to be able to reproduce the changes in step (x) and residual (d) close to a set of previous results. In other words, minimise the weighted norm:

$$\sum_{i=1}^{n} w_i \|(\mathbf{x}_i - \mathbf{x}_{i-1}) - \mathbf{J}_n^{-1}(\mathbf{d}_i - \mathbf{d}_{i-1})\|^2$$

  - And at the same time the changes in $\mathbf{J}_n^{-1}$ should be the minimal possible from the initial step. So we find $\mathbf{J}_n^{-1}$ by minimise:

$$N = \sum_{i=1}^{n} w_i \|(\mathbf{x}_i - \mathbf{x}_{i-1}) - \mathbf{J}_n^{-1}(\mathbf{d}_i - \mathbf{d}_{i-1})\|^2 + w_0\|\mathbf{J}_n^{-1} - \mathbf{J}_0^{-1}\|$$

- Seeks to find the minimum of the energy functional with respect to the MO coefficients, with the constraint that MO are normalised.

- Optimisation problem on a M-dimensional spherical surface.

- Perform a variable transformation, from MO coefficients $\mathbf{C}$ to a set of auxiliary variables $\mathbf{X}$ such that the optimisation of E is now on a M-1 dimensional linear space w.r.t. $\mathbf{X}$

$$\mathbf{C}(\mathbf{X}) = \mathbf{C}_0 \cos(\mathbf{U}) + \mathbf{X}\mathbf{U}^{-1}\sin(\mathbf{U})$$

$$\mathbf{U} = (\mathbf{X}^\mathsf{T}\mathbf{S}\mathbf{X})^{\frac{1}{2}}$$

- With constraint (fixes the direction of the plane):

$$\mathbf{X}^\mathsf{T}\mathbf{S}\mathbf{C}_0 = 0$$

Direction of steepest decent on E surface tangent to manifold at n

correction

$\mathbf{C}_{n+1}$

$\mathbf{C}_n$ geodesic

Constraint manifold for $\mathbf{C}^\mathsf{T}\mathbf{S}\mathbf{C} = \mathbb{1}$

Direction of steepest decent on E surface tangent to manifold at n

$\mathbf{X}_{n+1}$

$\mathbf{X}_n$

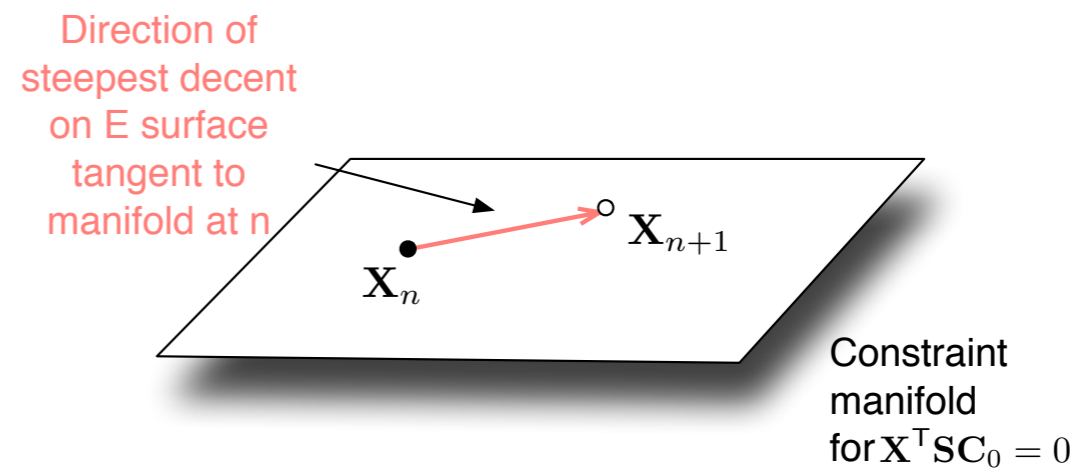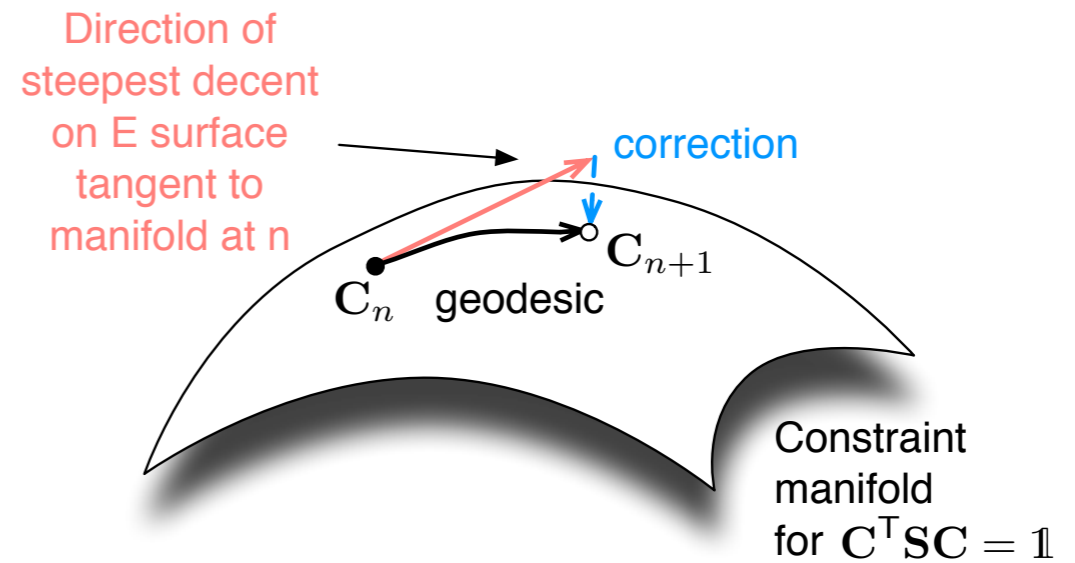Constraint manifold for $\mathbf{X}^\mathsf{T}\mathbf{S}\mathbf{C}_0 = 0$

- Seeks to find the minimum of the energy functional with respect to the MO coefficients, with the constraint that MO are normalised.

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- Perform a variable transformation, from MO coefficients $\mathbf{C}$ to a set of auxiliary variables $\mathbf{X}$ such that the optimisation of E is now on a M-1 dimensional linear space w.r.t. $\mathbf{X}$

$$\mathbf{C}(\mathbf{X}) = \mathbf{C}_0 \cos(\mathbf{U}) + \mathbf{X}\mathbf{U}^{-1} \sin(\mathbf{U})$$

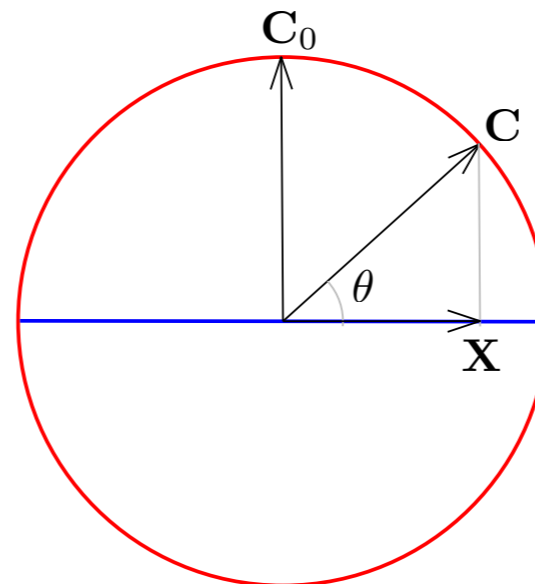$$\mathbf{U} = (\mathbf{X}^\mathsf{T}\mathbf{S}\mathbf{X})^{\frac{1}{2}}$$

- With constraint (fixes the direction of the plane):

$$\mathbf{X}^\mathsf{T}\mathbf{S}\mathbf{C}_0 = 0$$

$$\langle \mathbf{X}, \mathbf{C}_0 \rangle \equiv \mathbf{X}^T \mathbf{S} \mathbf{C}_0 = 0$$

$$\mathbf{C} = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} = \mathbf{C}_0 \cos(\theta) + \hat{\mathbf{X}} \sin(\theta)$$

$$\theta = \frac{\|\mathbf{x}\|}{\|\mathbf{C}\|} = \|\mathbf{X}\| \qquad \hat{\mathbf{X}} = \frac{\mathbf{x}}{\|\mathbf{X}\|}$$

$$\|\mathbf{X}\| = \langle \mathbf{X}, \mathbf{X} \rangle^{\frac{1}{2}} = \left(\mathbf{X}^T \mathbf{S} \mathbf{X}\right)^{\frac{1}{2}}$$

- Computation of SIN and COS terms

  - Can be calculated by diagonalisation: transforming to eigenspace, operate on eigenvalues, and then transform back. BUT too expensive.

  - Use Taylor expansion: 2 or 3 order expansion already give machine precision.

  - Calculate $\mathbf{U}^{-1}$ as part of the Taylor expansion

$$\cos(\mathbf{U}) = \sum_{i=0}^{K} \frac{(-1)}{(2i)!} (\mathbf{X}^\top \mathbf{S} \mathbf{X})^i$$

$$\mathbf{U}^{-1} \sin(\mathbf{U}) = \sum_{i=0}^{K} \frac{(-1)^i}{(2i+1)!} (\mathbf{X}^\top \mathbf{S} \mathbf{X})^i$$

- Preconditioners

  - The function to be minimised:

  $$E(\mathbf{c}(\mathbf{x})) = \operatorname{tr}(\mathbf{c}^{\mathsf{T}}(\mathbf{x}))\mathbf{H}_{KS}\mathbf{c}(\mathbf{x}) + \mathbf{x}^{\mathsf{T}}\mathbf{S}\mathbf{c}_0\mathbf{\Lambda})$$

  - While minimisation of E with respect to the OT variable is guaranteed to converge, it may do so very slowly.

  - Preconditioners can greatly speed up the convergence of an iterative optimisation process

  - Assuming $\mathbf{c}_0$ are eigenstates of the initial KS hamiltonian, and we Taylor expand close by:

  $$E(\mathbf{x}_0 + \mathbf{h}) = E_{\mathbf{x}_0} + \mathbf{\nabla}_{\mathbf{h}}E(\mathbf{x}_0)^{\mathsf{T}}\mathbf{h} + \frac{1}{2}\mathbf{h}^{\mathsf{T}}\mathbf{E}''(\mathbf{x}_0)\mathbf{h} + O(h^3)$$

  - Then the Hessian of E close to minimum is:

  $$\left.\frac{\partial^2 E}{\partial x_{i\mu}\partial x_{j\nu}}\right|_{\mathbf{x}_0} = 2H_{ij}\delta_{\mu\nu} - 2S_{ij}\delta_{\mu\nu}\epsilon_\mu^0$$

  - At minimum, we expect

  $$\frac{\mathrm{d}E(\mathbf{x}_0 + \mathbf{h})}{\mathrm{d}\mathbf{h}} = \mathbf{\nabla}_{\mathbf{h}}E(\mathbf{x}_0) + \mathbf{E}''(\mathbf{x}_0)\mathbf{h} + O(h^2) = 0$$

- Therefore, $\mathbf{h} = -\mathbf{E}''(\mathbf{x}_0)^{-1}\boldsymbol{\nabla}_{\mathbf{h}}E(\mathbf{x}_0)$, i.e.:

$$\mathbf{x}_{n+1} = \mathbf{x}_n - \mathbf{P}_n\boldsymbol{\nabla}E_n$$

- The ideal precondioner to the gradient is therefore:

$$\mathbf{P}_n = (\mathbf{H}_{KS} - \mathbf{S}\epsilon_n)^{-1} \qquad \epsilon_n = \mathbf{c}_n^{\mathsf{T}}\mathbf{H}_{KS}\mathbf{c}_n$$

- Practical Approximations to Preconditioner :
  - Ideal preconditioner requires:
    - Evaluation at *every* step
    - A different preconditioner matrix for every gradient vector
    - Matrix inversion
  - FULL_ALL:
    - Instead of calculating ϵ_n, replace it with a single scalar ϵ_0 that is similar to other energy levels. It is chosen to be the highest eigenvalue of the initial step/guess
    - Instead of evaluating at every step, do once at the beginning, and reuse the same preconditioner
    - Invert by diagonalisation, keep positive definite by truncating small eigenvalues

Orbital Transform

- **FULL_KINETIC**
  - Same as FULL_ALL, except only use kinetic energy part of KS matrix.
  - This gives sparse matrices, and can be taken advantage of using DBCSR based methods

- **FULL_SINGLE**
  - Same as FULL_ALL, however, only use the block diagonal parts of $\mathbf{H}_{KS} - \mathbf{S}\epsilon_0$
  - In other words, only on-site terms are considered by the preconditioner
  - Much faster, as each block can be calculated separately

- **FULL_SINGLE_INVERSE**
  - Same as FULL_SINGLE, but with the inversion process replaced by Cholesky process. Only works if $\mathbf{H}_{KS} - \mathbf{S}\epsilon_0$ is already positive definite.
  - Therefore less robust, but more efficient than FULL_SINGLE

- **FULL_S_INVERSE**
  - Ignore the KS matrix contribution all together, and utilise Cholesky decomposition of the full overlap matrix
  - Generally avoid

- **NONE**
  - Not recommended…

Orbital Transform

- Inner and Outer SCF/OT minimisation Loop :

  - Relevant only for OT:

  - KS matrix is updated at every OT minimisation step: minimisation and SCF happening at the same time

  - Inner Loop: Preconditioner is calculated at the begging of the loop, and remains constant throughout the inner loop

  - Outer Loop: Loops over the inner loop, this means the preconditioner is updated at every outer loop step

  - Tips for OT convergence:

    - If inner loop is converging slowly, try to reduce the number of allowed iterations in the inner loop, and increase the number of iterations allowed for the outer loop.

    - This effectively forces the preconditioner to be updated more frequently

Mixing Methods for Diagonalisation

- Diagonalisation:

  - Solves the generalised eigen problem:

$$\mathbf{H}_{KS}\mathbf{c} = \lambda\mathbf{S}\mathbf{c}$$

  - Uses any one of the eigensolvers implemented in CP2K

  - Density matrix can be constructed from the MOs.

$$P_{ij} = \sum_n f_n c_{in} c_{jn}$$

  - Occupy the MOs from the lowest energy up, until total number of electrons has reached.

    - This gives Fermi energy

    - Allows the opportunity to introduce smearing into the occupancy

  - From the density matrix, we can obtain electron charge, and this is then mixed back into the KS Hamiltonian, to complete the SCF loop

Mixing Methods for Diagonalisation

- **Smearing:**

  - Integer occupation numbers: discontinuity at Fermi energy.

  - If Fermi energy is close to a number of MOs, a small variation of MO energies can lead to a jump in total energy, due to the electrons either occupy or leave a particular orbital completely

    - This brings havoc to SCF optimisers, because all numerical optimisers work on the basis that functions they try to minimise is continuous and (at least once or twice) differentiable.

  - Not a problem if the Fermi energy is in a band gap. Is a problem for metals.

  - Smearing: replace the step function of occupancy with a smooth function of the similar shape, with smoothness controlled by a parametric temperature

  - The higher the smearing temperature, the less resolution (system size) required for the band structure, but also less accurate
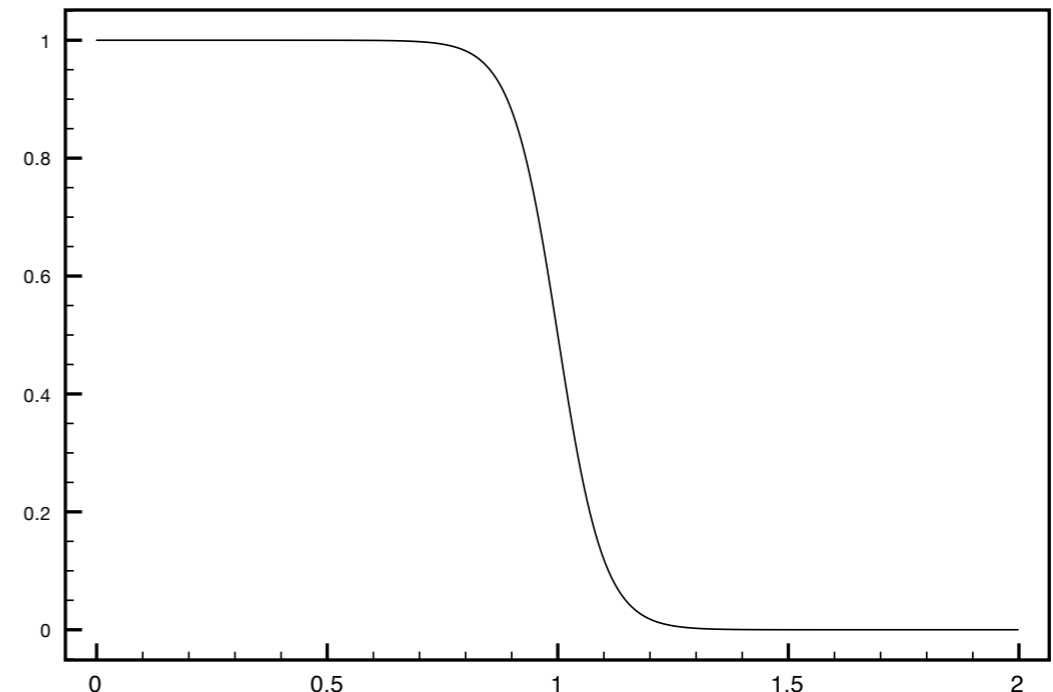
Mixing Methods for Diagonalisation

- Broyden / Pulay Mixing

  - The same as Broyden / DIIS optimisation method

  - Solving for $R[\rho^{\mathrm{in}}] = \rho^{\mathrm{out}} - \rho^{\mathrm{in}} = 0$

  - Broyden mixing is very similar to Pulay mixing, but slightly faster and somewhat more robust, as it does not involve matrix inversion

- Kerker Preconditioning (automatically turns on Pulay):

  - Solve SCF convergence issues caused by large changes in the Hartree energy due to the changes in charge density that are far apart at every iteration step.

  - The large change in Hartree energy then causes a corresponding reaction correction in the next output density, leading to a phenomenon referred to as "charge sloshing".

  - The problem can be solved by performing charge mixing in reciprocal space, and change the mixing parameter A to a preconditioner:

$$A \rightarrow A \frac{q^2}{q^2 + B^2}$$
  Long range change correspond to small q, and its contribution goes to 0

If you have a restart file, use RESTART

```
&SCF
   SCF_GUESS ATOMIC
   EPS_SCF 1.0E-06
   MAX_SCF 200
   &OT ON
      MINIMIZER DIIS
      PRECONDITIONER FULL_SINGLE_INVERSE
   &END OT
   &OUTER_SCF
      MAX_SCF 10
   &END OUTER_SCF
   &PRINT
      &RESTART  OFF
      &END RESTART
   &END PRINT
&END SCF
```

64 water box

```
SCF WAVEFUNCTION OPTIMIZATION

-------------------------------- OT --------------------------------
Minimizer    : DIIS            : direct inversion
                                 in the iterative subspace
                                 using   7 DIIS vectors
                                 safer DIIS on
Preconditioner : FULL_SINGLE_INVERSE : inversion of
                                 H + eS - 2*(Sc)(c^T*H*c+const)(Sc)^T
Precond_solver : DEFAULT
stepsize     :    0.08000000         energy_gap  :    0.08000000
eps_taylor   :    0.10000E-15        max_taylor  :           4
-------------------------------- OT --------------------------------

Step    Update method      Time   Convergence        Total energy   Change
--------------------------------------------------------------------------

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000014959     -0.0000014959
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000014914
Total charge density g-space grids:         -0.0000014914

    1 OT DIIS    0.80E-01   1.9    0.02242151    -1059.3825079557 -1.06E+03

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000017437     -0.0000017437
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000017392
Total charge density g-space grids:         -0.0000017392

    2 OT DIIS    0.80E-01   1.2    0.01583191    -1079.2016155971 -1.98E+01

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015128     -0.0000015128
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015083
Total charge density g-space grids:         -0.0000015083
```

```
Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015457     -0.0000015457
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015412
Total charge density g-space grids:         -0.0000015412

  149 OT DIIS    0.80E-01   1.2    0.00000102    -1101.0377081868 -3.67E-07

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015457     -0.0000015457
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015412
Total charge density g-space grids:         -0.0000015412

  150 OT DIIS    0.80E-01   1.2    0.00000101    -1101.0377086068 -4.20E-07

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015457     -0.0000015457
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015412
Total charge density g-space grids:         -0.0000015412

  151 OT DIIS    0.80E-01   1.2    0.00000101    -1101.0377089336 -3.27E-07

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015457     -0.0000015457
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015412
Total charge density g-space grids:         -0.0000015412

  152 OT DIIS    0.80E-01   1.2    0.00000100    -1101.0377093306 -3.97E-07

Trace(PS):                                 512.0000000000
Electronic density on regular grids:      -512.0000015457     -0.0000015457
Core density on regular grids:             512.0000000045      0.0000000045
Total charge density on r-space grids:      -0.0000015412
Total charge density g-space grids:         -0.0000015412

  153 OT DIIS    0.80E-01   1.2    0.00000100    -1101.0377096545 -3.24E-07

*** SCF run converged in   153 steps ***
```

64 water box

```
&SCF
  SCF_GUESS ATOMIC
  EPS_SCF 1.0E-06
  MAX_SCF 200
  &OT ON
    MINIMIZER DIIS
    PRECONDITIONER FULL_ALL
  &END OT
  &OUTER_SCF
    MAX_SCF 10
  &END OUTER_SCF
  &PRINT
    &RESTART  OFF
    &END RESTART
  &END PRINT
&END SCF
```

```
SCF WAVEFUNCTION OPTIMIZATION

-------------------------------- OT --------------------------------------
Minimizer      : DIIS           : direct inversion
                                  in the iterative subspace
                                  using   7 DIIS vectors
                                  safer DIIS on
Preconditioner : FULL_ALL       : diagonalization, state selective
Precond_solver : DEFAULT
stepsize       :    0.15000000          energy_gap     :    0.08000000
eps_taylor     :    0.10000E-15         max_taylor     :             4
-------------------------------- OT --------------------------------------

Step     Update method      Time    Convergence         Total energy   Change
--------------------------------------------------------------------------

Trace(PS):                            512.0000000000
Electronic density on regular grids:  -512.0000014959      -0.0000014959
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000014914
Total charge density g-space grids:      -0.0000014914

   1 OT DIIS    0.15E+00    4.2    0.02500388    -1059.3825079557 -1.06E+03

Trace(PS):                            512.0000000000
Electronic density on regular grids:  -512.0000020917      -0.0000020917
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000020873
Total charge density g-space grids:      -0.0000020873

   2 OT DIIS    0.15E+00    1.3    0.01405947    -1091.5303639854 -3.21E+01

Trace(PS):                            512.0000000000
Electronic density on regular grids:  -512.0000011239      -0.0000011239
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000011194
Total charge density g-space grids:      -0.0000011194
```

```
 108 OT DIIS    0.15E+00    1.3    0.00000105    -1101.0377126778 -3.05E-07

Trace(PS):                            511.9999999999
Electronic density on regular grids:  -512.0000015456      -0.0000015456
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000015411
Total charge density g-space grids:      -0.0000015411

 109 OT DIIS    0.15E+00    1.3    0.00000104    -1101.0377130143 -3.37E-07

Trace(PS):                            511.9999999999
Electronic density on regular grids:  -512.0000015456      -0.0000015456
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000015411
Total charge density g-space grids:      -0.0000015411

 110 OT DIIS    0.15E+00    1.3    0.00000103    -1101.0377133249 -3.11E-07

Trace(PS):                            511.9999999999
Electronic density on regular grids:  -512.0000015456      -0.0000015456
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000015411
Total charge density g-space grids:      -0.0000015411

 111 OT DIIS    0.15E+00    1.3    0.00000102    -1101.0377136686 -3.44E-07

Trace(PS):                            511.9999999999
Electronic density on regular grids:  -512.0000015456      -0.0000015456
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000015411
Total charge density g-space grids:      -0.0000015411

 112 OT DIIS    0.15E+00    1.3    0.00000101    -1101.0377140259 -3.57E-07

Trace(PS):                            511.9999999999
Electronic density on regular grids:  -512.0000015456      -0.0000015456
Core density on regular grids:        512.0000000045        0.0000000045
Total charge density on r-space grids:   -0.0000015411
Total charge density g-space grids:      -0.0000015411

 113 OT DIIS    0.15E+00    1.3    0.00000100    -1101.0377143737 -3.48E-07

*** SCF run converged in    113 steps ***
```

64 water box

```
&SCF
  SCF_GUESS ATOMIC
  EPS_SCF 1.0E-06
  MAX_SCF 20
  &OT ON
    MINIMIZER DIIS
    PRECONDITIONER FULL_ALL
  &END OT
  &OUTER_SCF
    MAX_SCF 100
  &END OUTER_SCF
  &PRINT
    &RESTART  OFF
    &END RESTART
  &END PRINT
&END SCF
```

Examples

```
   18 OT DIIS    0.15E+00    1.3     0.00010381     -1101.0333773217 -3.82E-03

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015462        -0.0000015462
Core density on regular grids:               512.0000000045         0.0000000045
Total charge density on r-space grids:        -0.0000015417
Total charge density g-space grids:           -0.0000015417

   19 OT DIIS    0.15E+00    1.3     0.00009753     -1101.0345262445 -1.15E-03

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015467        -0.0000015467
Core density on regular grids:               512.0000000045         0.0000000045
Total charge density on r-space grids:        -0.0000015422
Total charge density g-space grids:           -0.0000015422

   20 OT DIIS    0.15E+00    1.3     0.00006603     -1101.0350962104 -5.70E-04

*** SCF run NOT converged ***


Electronic density on regular grids:        -512.0000015467        -0.0000015467
Core density on regular grids:               512.0000000045         0.0000000045
Total charge density on r-space grids:        -0.0000015422
Total charge density g-space grids:           -0.0000015422

Overlap energy of the core charge distribution:        0.00000562599749
Self energy of the core charge distribution:       -2805.30499493854950
Core Hamiltonian energy:                             825.30614501411810
Hartree energy:                                     1145.24847973284727
Exchange-correlation energy:                        -266.28473164478658

Total energy:                                      -1101.03509621037347

outer SCF iter =     1 RMS gradient =    0.66E-04 energy =       -1101.0350962104
```

```
Step     Update method      Time    Convergence        Total energy     Change
-----------------------------------------------------------------------------------

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015467         -0.0000015467
Core density on regular grids:               512.0000000045          0.0000000045
Total charge density on r-space grids:        -0.0000015422
Total charge density g-space grids:           -0.0000015422

    1 OT DIIS    0.15E+00    5.9     0.00016580     -1101.0355385583 -4.42E-04

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015454         -0.0000015454
Core density on regular grids:               512.0000000045          0.0000000045
Total charge density on r-space grids:        -0.0000015409
Total charge density g-space grids:           -0.0000015409

    2 OT DIIS    0.15E+00    1.2     0.00006738     -1101.0374081725 -1.87E-03

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015475         -0.0000015475
Core density on regular grids:               512.0000000045          0.0000000045
Total charge density on r-space grids:        -0.0000015430
Total charge density g-space grids:           -0.0000015430

    3 OT DIIS    0.15E+00    1.2     0.00003004     -1101.0377417272 -3.34E-04

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015459         -0.0000015459
Core density on regular grids:               512.0000000045          0.0000000045
Total charge density on r-space grids:        -0.0000015415
Total charge density g-space grids:           -0.0000015415

    4 OT DIIS    0.15E+00    1.2     0.00000106     -1101.0377661454 -2.44E-05

Trace(PS):                                   512.0000000000
Electronic density on regular grids:        -512.0000015460         -0.0000015460
Core density on regular grids:               512.0000000045          0.0000000045
Total charge density on r-space grids:        -0.0000015415
Total charge density g-space grids:           -0.0000015415

    5 OT DIIS    0.15E+00    1.2     0.00000062     -1101.0377661763 -3.09E-08

*** SCF run converged in     5 steps ***
```

Au128 bulk

```
&SCF
  SCF_GUESS ATOMIC
  EPS_SCF 1.0E-6
  MAX_SCF 500
  ADDED_MOS 200
  CHOLESKY INVERSE
  &SMEAR ON
    METHOD FERMI_DIRAC
    ELECTRONIC_TEMPERATURE [K] 300
  &END SMEAR
  &DIAGONALIZATION
    ALGORITHM STANDARD
  &END DIAGONALIZATION
  &MIXING
    METHOD DIRECT_P_MIXING
    ALPHA 0.5
  &END MIXING
  &OUTER_SCF
    EPS_SCF 1.0E-6
    MAX_SCF 1
  &END OUTER_SCF
&END SCF
```

Examples

```
Step      Update method    Time    Convergence    Total energy       Change
--------------------------------------------------------------------------
  1 P_Mix/Diag. 0.50E+00    2.1     0.41056021   -2133.4408435676  -2.13E+03
  2 P_Mix/Diag. 0.50E+00    3.2     0.20432922   -2132.0776002852   1.36E+00
  3 P_Mix/Diag. 0.50E+00    3.2     0.10741372   -2131.3677551799   7.10E-01
  4 P_Mix/Diag. 0.50E+00    3.2     0.05420394   -2131.0080867703   3.60E-01
  5 DIIS/Diag.  0.39E-03    3.2     0.02722180   -2130.8276990683   1.80E-01
  6 DIIS/Diag.  0.19E-03    3.1     0.00062404   -2130.6473761946   1.80E-01
  7 DIIS/Diag.  0.84E-04    3.2     0.00050993   -2130.6473778175  -1.62E-06
  8 DIIS/Diag.  0.63E-04    3.2     0.00021250   -2130.6473781683  -3.51E-07
  9 DIIS/Diag.  0.11E-03    3.2     0.00019003   -2130.6473780859   8.24E-08
 10 DIIS/Diag.  0.29E-03    3.1     0.00037131   -2130.6473764995   1.59E-06
 11 DIIS/Diag.  0.34E-03    3.2     0.00045761   -2130.6473757354   7.64E-07
 12 DIIS/Diag.  0.10E-02    3.2     0.00121294   -2130.6473574307   1.83E-05
 13 DIIS/Diag.  0.47E-03    3.1     0.00355236   -2130.6473668667  -9.44E-06
 14 DIIS/Diag.  0.74E-02    3.1     0.00485367   -2130.6464389964   9.28E-04
 15 DIIS/Diag.  0.80E-02    3.1     0.01204111   -2130.6462412097   1.98E-04
 16 DIIS/Diag.  0.10E-01    3.1     0.00709698   -2130.6441536117   2.09E-03
 17 DIIS/Diag.  0.73E-02    3.1     0.06036011   -2130.6454804871  -1.33E-03
 18 DIIS/Diag.  0.32E-01    3.1     0.07606048   -2130.6085108701   3.70E-02
 19 P_Mix/Diag. 0.50E+00    3.1     1.20934863   -2130.4320575334   1.76E-01
 20 P_Mix/Diag. 0.50E+00    3.1   164.38141403   -2083.0458429170   4.74E+01
 21 P_Mix/Diag. 0.50E+00    3.1   484.77129296     642.3682176809   2.73E+03
 22 P_Mix/Diag. 0.50E+00    3.1   242.49533726     680.0967740982   3.77E+01
 23 P_Mix/Diag. 0.50E+00    3.1   108.28073503     713.7098573905   3.36E+01
 24 P_Mix/Diag. 0.50E+00    3.1   133.38323194     -83.2160327233  -7.97E+02
 25 P_Mix/Diag. 0.50E+00    3.1   243.65162842     257.9355830764   3.41E+02
 26 P_Mix/Diag. 0.50E+00    3.1   360.75338107     804.4210109712   5.46E+02
 27 P_Mix/Diag. 0.50E+00    3.2   423.28363111     790.1670568787  -1.43E+01
 28 P_Mix/Diag. 0.50E+00    3.1   527.98757101    1358.0740107382   5.68E+02
 29 P_Mix/Diag. 0.50E+00    3.1   467.44558067    1279.1848521006  -7.89E+01
 30 P_Mix/Diag. 0.50E+00    3.1   511.11190255    1700.0469627750   4.21E+02
 31 P_Mix/Diag. 0.50E+00    3.1   531.81962633    1488.0293045448  -2.12E+02
 32 P_Mix/Diag. 0.50E+00    3.1   469.22980247    1449.5252473273  -3.85E+01
```

```
274 P_Mix/Diag. 0.50E+00    3.1    496.18271982    1433.1258409018  -2.52E+02
275 P_Mix/Diag. 0.50E+00    3.1    465.21950527    1708.0865674753   2.75E+02
276 P_Mix/Diag. 0.50E+00    3.2    526.35992000    1701.9896437225  -6.10E+00
277 P_Mix/Diag. 0.50E+00    3.1    500.55201331    1429.0695309273  -2.73E+02
278 P_Mix/Diag. 0.50E+00    3.1    452.47323777    1685.6997235986   2.57E+02
279 P_Mix/Diag. 0.50E+00    3.1    525.66284299    1726.0727258188   4.04E+01
280 P_Mix/Diag. 0.50E+00    3.1    504.85174061    1437.1005594299  -2.89E+02
281 P_Mix/Diag. 0.50E+00    3.1    452.73958110    1626.9128568615   1.90E+02
282 P_Mix/Diag. 0.50E+00    3.2    524.88774970    1767.5496813722   1.41E+02
283 P_Mix/Diag. 0.50E+00    3.1    509.84684807    1454.1863412940  -3.13E+02
284 P_Mix/Diag. 0.50E+00    3.1    424.76338293    1583.5008811158   1.29E+02
285 P_Mix/Diag. 0.50E+00    3.1    516.88135732    1784.1133181315   2.01E+02
286 P_Mix/Diag. 0.50E+00    3.1    514.48307366    1475.1702369153  -3.09E+02
287 P_Mix/Diag. 0.50E+00    3.1    429.02575267    1494.4059971253   1.92E+01
288 P_Mix/Diag. 0.50E+00    3.2    505.84474236    1762.0172683978   2.68E+02
289 P_Mix/Diag. 0.50E+00    3.1    521.09854796    1519.1104495575  -2.43E+02
290 P_Mix/Diag. 0.50E+00    3.2    460.28042402    1463.1850194878  -5.59E+01
291 P_Mix/Diag. 0.50E+00    3.1    494.65034012    1736.5367974686   2.73E+02
292 P_Mix/Diag. 0.50E+00    3.1    523.62795354    1561.0634325581  -1.75E+02
293 P_Mix/Diag. 0.50E+00    3.1    470.92963686    1458.4095785993  -1.03E+02
294 P_Mix/Diag. 0.50E+00    3.1    489.94822751    1740.7536880093   2.82E+02
295 P_Mix/Diag. 0.50E+00    3.1    527.88371821    1586.4713619002  -1.54E+02
296 P_Mix/Diag. 0.50E+00    3.1    477.46948475    1461.2599044466  -1.25E+02
297 P_Mix/Diag. 0.50E+00    3.1    481.52741519    1744.2498516733   2.83E+02
298 P_Mix/Diag. 0.50E+00    3.1    528.64978975    1631.2670959487  -1.13E+02
299 P_Mix/Diag. 0.50E+00    3.1    483.01432540    1447.7674793116  -1.83E+02
300 P_Mix/Diag. 0.50E+00    3.1    475.21476950    1734.9217161865   2.87E+02
301 P_Mix/Diag. 0.50E+00    3.1    527.70245328    1640.9047892819  -9.40E+01
302 P_Mix/Diag. 0.50E+00    3.1    485.65879289    1448.0327123002  -1.93E+02
303 P_Mix/Diag. 0.50E+00    3.1    474.33206574    1735.1993514743   2.87E+02
304 P_Mix/Diag. 0.50E+00    3.1    528.41442815    1652.4630012861  -8.27E+01
305 P_Mix/Diag. 0.50E+00    3.1    487.89310966    1441.5618979731  -2.11E+02
306 P_Mix/Diag. 0.50E+00    3.1    472.80773473    1735.6753322017   2.94E+02
307 P_Mix/Diag. 0.50E+00    3.1    528.03454596    1664.1188498883  -7.16E+01
308 P_Mix/Diag. 0.50E+00    3.1    489.55606395    1439.4935858980  -2.25E+02
309 P_Mix/Diag. 0.50E+00    3.2    471.87729366    1733.8307029231   2.94E+02
310 P_Mix/Diag. 0.50E+00    3.1    527.88042982    1669.9038337698  -6.39E+01
```

Au128 bulk

```
&SCF
  SCF_GUESS ATOMIC
  EPS_SCF 1.0E-6
  MAX_SCF 500
  ADDED_MOS 200
  CHOLESKY INVERSE
  &SMEAR ON
    METHOD FERMI_DIRAC
    ELECTRONIC_TEMPERATURE [K] 300
  &END SMEAR
  &DIAGONALIZATION
    ALGORITHM STANDARD
  &END DIAGONALIZATION
  &MIXING
    METHOD PULAY_MIXING
    ALPHA 0.2
    NBUFFER 5
  &END MIXING
  &OUTER_SCF
    EPS_SCF 1.0E-6
    MAX_SCF 1
  &END OUTER_SCF
&END SCF
```

```
SCF WAVEFUNCTION OPTIMIZATION

Step     Update method    Time   Convergence      Total energy      Change
--------------------------------------------------------------------------------
    1 NoMix/Diag. 0.20E+00   2.1   0.41056021   -2133.4408435676 -2.13E+03
    2 Pulay/Diag. 0.20E+00   3.0   0.09203127   -2201.3765392945 -6.79E+01
    3 Pulay/Diag. 0.20E+00   3.0   0.16880309   -2158.2415807244  4.31E+01
    4 Pulay/Diag. 0.20E+00   3.1   0.00518342   -2130.6192970241  2.76E+01
    5 Pulay/Diag. 0.20E+00   3.0   0.00047075   -2130.6728564565 -5.36E-02
    6 Pulay/Diag. 0.20E+00   3.0   0.00158949   -2130.6457378471  2.71E-02
    7 Pulay/Diag. 0.20E+00   3.1   0.00183981   -2130.6474323880 -1.69E-03
    8 Pulay/Diag. 0.20E+00   3.0   0.00070883   -2130.6475388056 -1.06E-04
    9 Pulay/Diag. 0.20E+00   3.1   0.00008650   -2130.6474330363  1.06E-04
   10 Pulay/Diag. 0.20E+00   3.1   0.00006343   -2130.6473426916  9.03E-05
   11 Pulay/Diag. 0.20E+00   3.1   0.00001087   -2130.6473443079 -1.62E-06
   12 Pulay/Diag. 0.20E+00   3.0   0.00001251   -2130.6473829189 -3.86E-05
   13 Pulay/Diag. 0.20E+00   3.0   0.00000690   -2130.6474093517 -2.64E-05
   14 Pulay/Diag. 0.20E+00   3.1   0.00000588   -2130.6474056927  3.66E-06
   15 Pulay/Diag. 0.20E+00   3.0   0.00000429   -2130.6473907798  1.49E-05
   16 Pulay/Diag. 0.20E+00   3.0   0.00000128   -2130.6473708497  1.99E-05
   17 Pulay/Diag. 0.20E+00   3.0   0.00000069   -2130.6473700587  7.91E-07

 *** SCF run converged in    17 steps ***
```

Au128 bulk

```
&SCF
  SCF_GUESS ATOMIC
  EPS_SCF 1.0E-6
  MAX_SCF 500
  ADDED_MOS 200
  CHOLESKY INVERSE
  &SMEAR ON
    METHOD FERMI_DIRAC
    ELECTRONIC_TEMPERATURE [K] 300
  &END SMEAR
  &DIAGONALIZATION
    ALGORITHM STANDARD
  &END DIAGONALIZATION
  &MIXING
    METHOD BRYODEN_MIXING
    ALPHA 0.2
    NBUFFER 5
  &END MIXING
  &OUTER_SCF
    EPS_SCF 1.0E-6
    MAX_SCF 1
  &END OUTER_SCF
&END SCF
```

```
SCF WAVEFUNCTION OPTIMIZATION

 Step     Update method    Time   Convergence        Total energy      Change
 --------------------------------------------------------------------------------
    1 NoMix/Diag. 0.20E+00   2.1    0.41056021   -2133.4408435676 -2.13E+03
    2 Broy./Diag. 0.20E+00   3.0    0.09203127   -2201.3765392945 -6.79E+01
    3 Broy./Diag. 0.20E+00   3.0    0.16796900   -2158.0252203875  4.34E+01
    4 Broy./Diag. 0.20E+00   3.0    0.00119322   -2130.7623431374  2.73E+01
    5 Broy./Diag. 0.20E+00   3.0    0.00354041   -2130.8401320934 -7.78E-02
    6 Broy./Diag. 0.20E+00   3.0    0.00027721   -2130.6310148769  2.09E-01
    7 Broy./Diag. 0.20E+00   3.0    0.00021364   -2130.6341596109 -3.14E-03
    8 Broy./Diag. 0.20E+00   3.0    0.00096927   -2130.6425441433 -8.38E-03
    9 Broy./Diag. 0.20E+00   3.0    0.00061032   -2130.6368211911  5.72E-03
   10 Broy./Diag. 0.20E+00   3.0    0.00008199   -2130.6405099448 -3.69E-03
   11 Broy./Diag. 0.20E+00   3.1    0.00004376   -2130.6475333293 -7.02E-03
   12 Broy./Diag. 0.20E+00   3.1    0.00001638   -2130.6493205024 -1.79E-03
   13 Broy./Diag. 0.20E+00   3.1    0.00001451   -2130.6486762850  6.44E-04
   14 Broy./Diag. 0.20E+00   3.2    0.00001432   -2130.6482674682  4.09E-04
   15 Broy./Diag. 0.20E+00   3.1    0.00001122   -2130.6476512837  6.16E-04
   16 Broy./Diag. 0.20E+00   3.1    0.00000112   -2130.6472295415  4.22E-04
   17 Broy./Diag. 0.20E+00   3.1    0.00000103   -2130.6472635676 -3.40E-05
   18 Broy./Diag. 0.20E+00   3.1    0.00000112   -2130.6472999859 -3.64E-05
   19 Broy./Diag. 0.20E+00   3.0    0.00000168   -2130.6473550000 -5.50E-05
   20 Broy./Diag. 0.20E+00   3.0    0.00000144   -2130.6473964425 -4.14E-05
   21 Broy./Diag. 0.20E+00   3.1    0.00000009   -2130.6474004989 -4.06E-06

 *** SCF run converged in    21 steps ***
```