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CP2K Summer School 2016

SCF Methods

— Diagonalisation &Orbital Transformation

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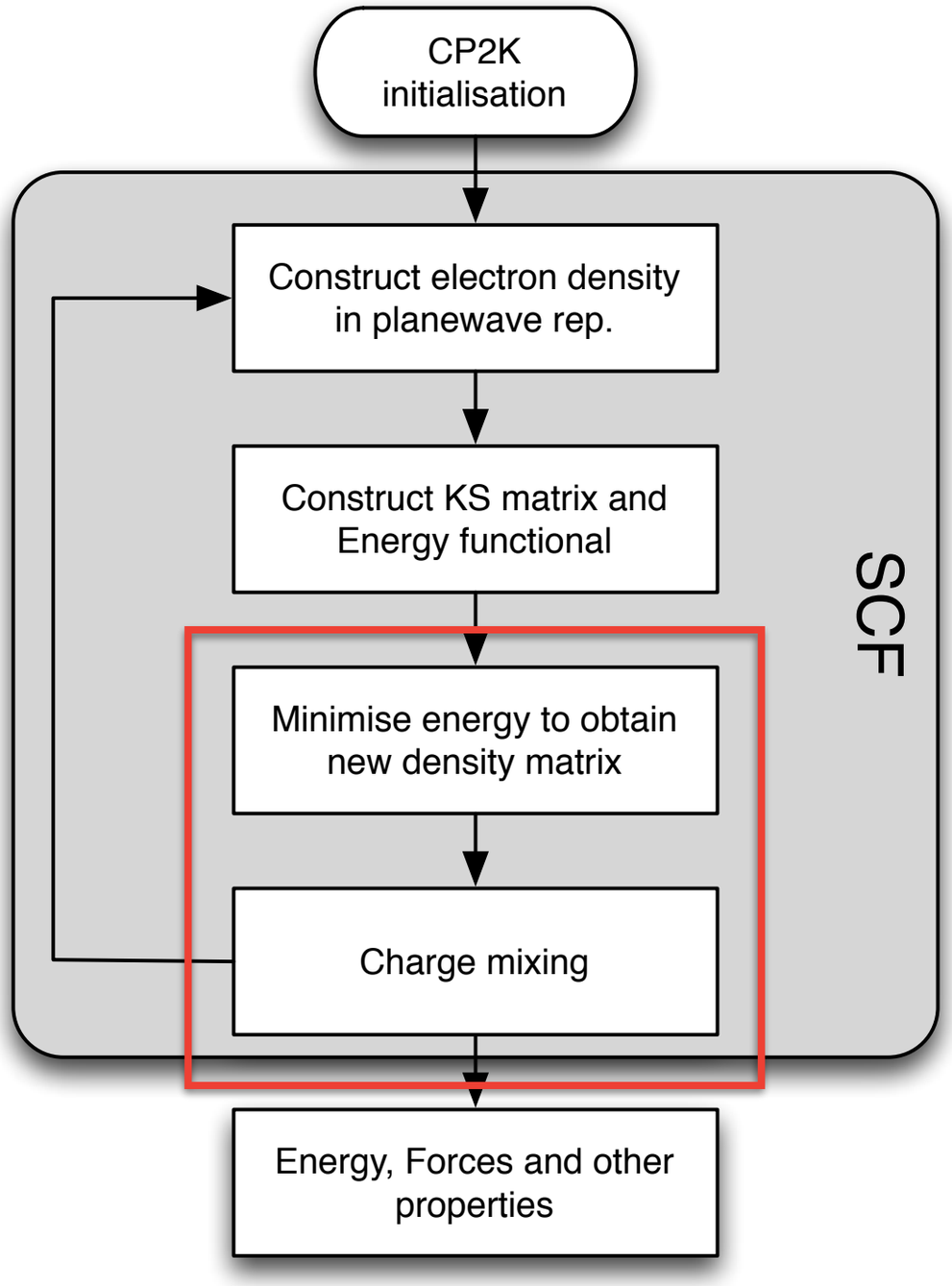
Self Consistent Field Calculation

- 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

Topics In This Talk

- 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:

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

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

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

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

upper triangular

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

  - `REDUCE`: $\mathbf{A}|\mathbf{U} \Rightarrow \mathbf{A}'|\mathbb{1}$ 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)

Eigensolvers In CP2K

- 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

Optimisers In CP2K

- 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

Optimisers In CP2K

- 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:

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

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

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

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

Optimisers In CP2K

- 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 $\mathbf{x}_0$

$$\begin{aligned}
\mathbf{x}_1 &= \alpha_1\mathbf{P}_1 \\
\mathbf{x}_2 &= \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2 \\
\mathbf{x}_3 &= \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2 + \alpha_3\mathbf{P}_3 \\
&\vdots \\
\mathbf{x}_n &= \alpha_1\mathbf{P}_1 + \alpha_2\mathbf{P}_2 + \alpha_3\mathbf{P}_3 + \cdots + \alpha_n\mathbf{P}_n
\end{aligned}$$

$$\begin{aligned}
\mathbf{d}_i &= -\mathbf{b} - \mathbf{H}\mathbf{x}_i \\
\mathbf{P}_1 &= \mathbf{d}_0 \\
\mathbf{P}_2 &= \mathbf{d}_1 - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_1}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0 \\
\mathbf{P}_3 &= \mathbf{d}_2 - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_2}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0 - \frac{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{d}_2}{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{P}_1}\mathbf{P}_1 \\
&\vdots \\
\mathbf{P}_n &= \mathbf{d}_{n-1} - \frac{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_0^\mathsf{T}\mathbf{H}\mathbf{P}_0}\mathbf{P}_0 - \frac{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_1^\mathsf{T}\mathbf{H}\mathbf{P}_1}\mathbf{P}_1 - \cdots - \frac{\mathbf{P}_{n-1}^\mathsf{T}\mathbf{H}\mathbf{d}_{n-1}}{\mathbf{P}_{n-1}^\mathsf{T}\mathbf{H}\mathbf{P}_{n-1}}\mathbf{P}_{n-1}
\end{aligned}$$

Optimisers In CP2K

- 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: $\frac{\partial \|\mathbf{d}_{n+1}\|}{\partial \alpha_i} = 0$ with constraints $\sum_i^n \alpha_i = 1$, we obtain:

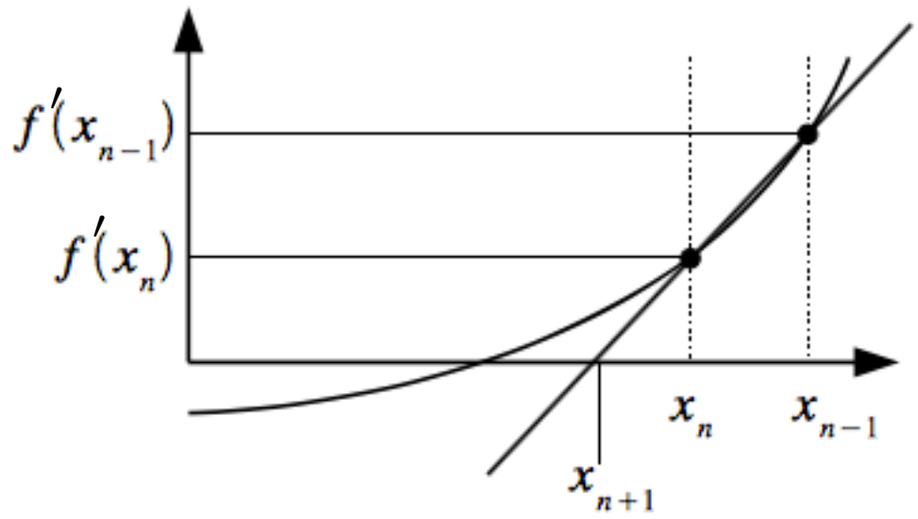
$$\alpha_i = \frac{\sum_i^n A_{ji}^{-1}}{\sum_{ij}^n A_{ji}^{-1}}, \quad A_{ij} = \mathbf{d}_i^{\mathsf{T}} \mathbf{d}_j$$

  - 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.

Optimisers In CP2K

- 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:

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

Orbital Transform

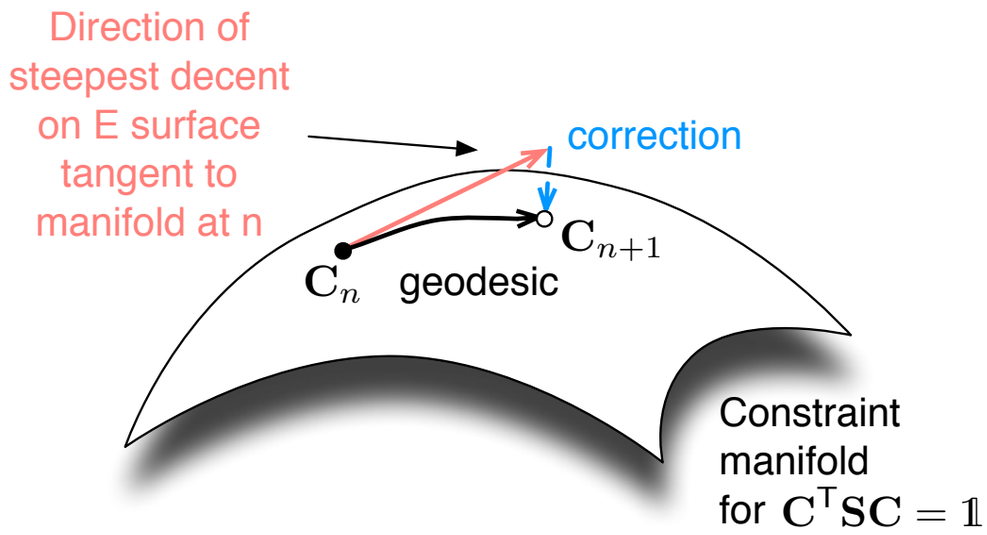
- Seeks to find the minimum of the energy functional with respect to the MO coefficients, with the constraint that MO are normalised.
- Optimisation problem on a M-dimensional spherical surface.
- Perform a variable transformation, from MO coefficients $\mathbf{C}$ to a set of auxiliary variables $\mathbf{X}$ such that the optimisation of E is now on a M-1 dimensional linear space w.r.t. $\mathbf{X}$

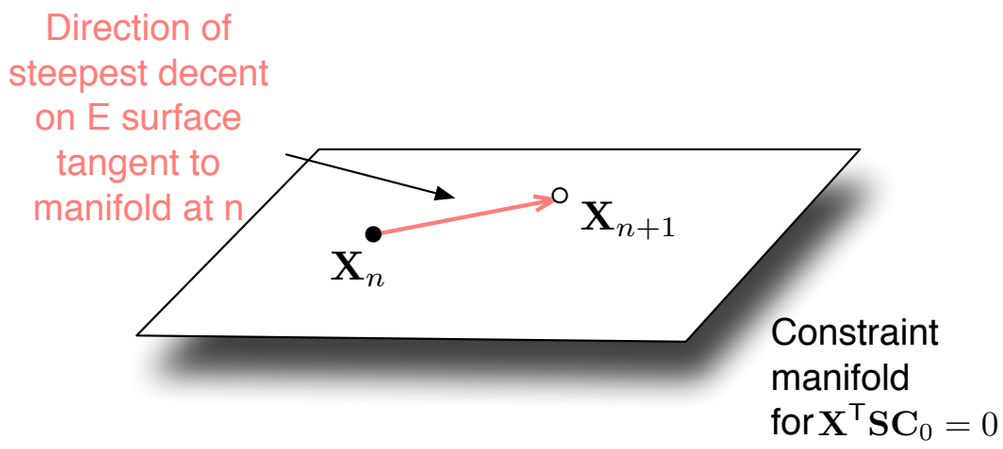
$$\mathbf{C}(\mathbf{X}) = \mathbf{C}_0 \cos(\mathbf{U}) + \mathbf{X}\mathbf{U}^{-1} \sin(\mathbf{U})$$

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

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

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





Orbital Transform

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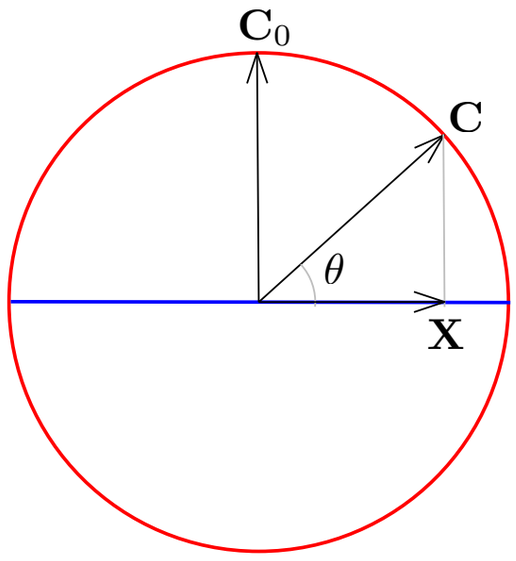


$$\langle \mathbf{X}, \mathbf{C}_0 \rangle \equiv \mathbf{X}^T\mathbf{S}\mathbf{C}_0 = 0$$

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

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

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

Orbital Transform

- 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

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

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

Orbital Transform

- Preconditioners
  - The function to be minimised:

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

  - 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:

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

  - Then the Hessian of E close to minimum is:

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

  - At minimum, we expect

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

Orbital Transform

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

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

- 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.

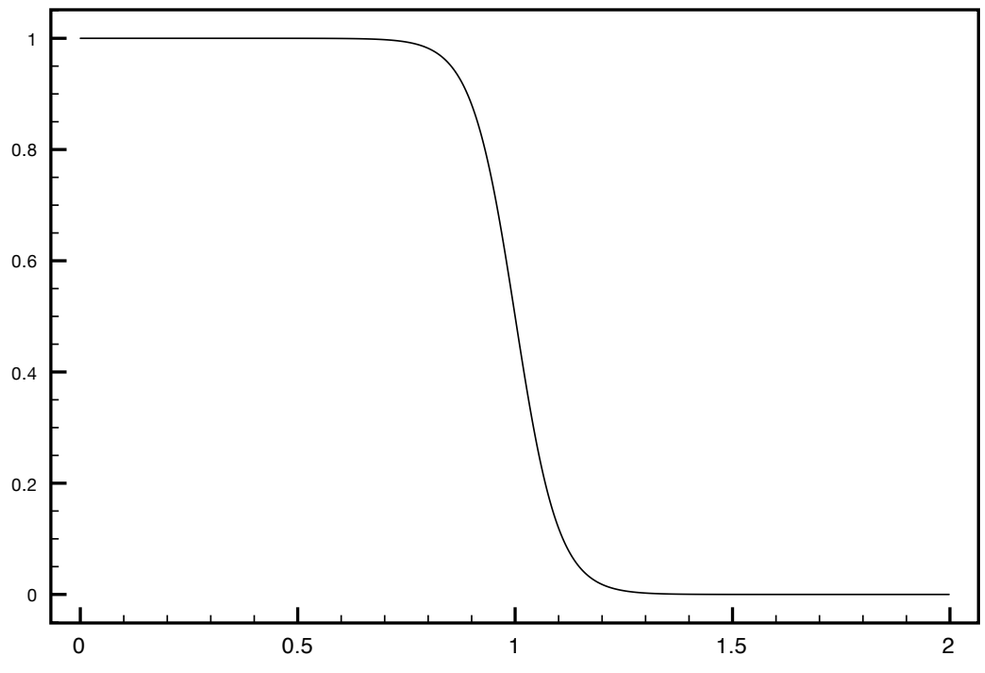
$$P_{ij} = \sum_n f_n c_{in} c_{jn}$$

  - 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 $R[\rho^{\text{in}}] = \rho^{\text{out}} - \rho^{\text{in}} = 0$
  - 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:

$$A \to A\frac{q^2}{q^2 + B^2}$$

Long range change correspond to small q, and its contribution goes to 0

Examples

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

Examples

```
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 ***
```

Examples

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
```

Examples

```
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 ---------------------------------- 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 ***
```

Examples

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 ***
```

Examples

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

Examples

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
```

Examples

```
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 ***
```

Examples

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
```

Examples

```
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 ***
```