

# SCF Methods

## — Diagonalisation & Orbital Transformation

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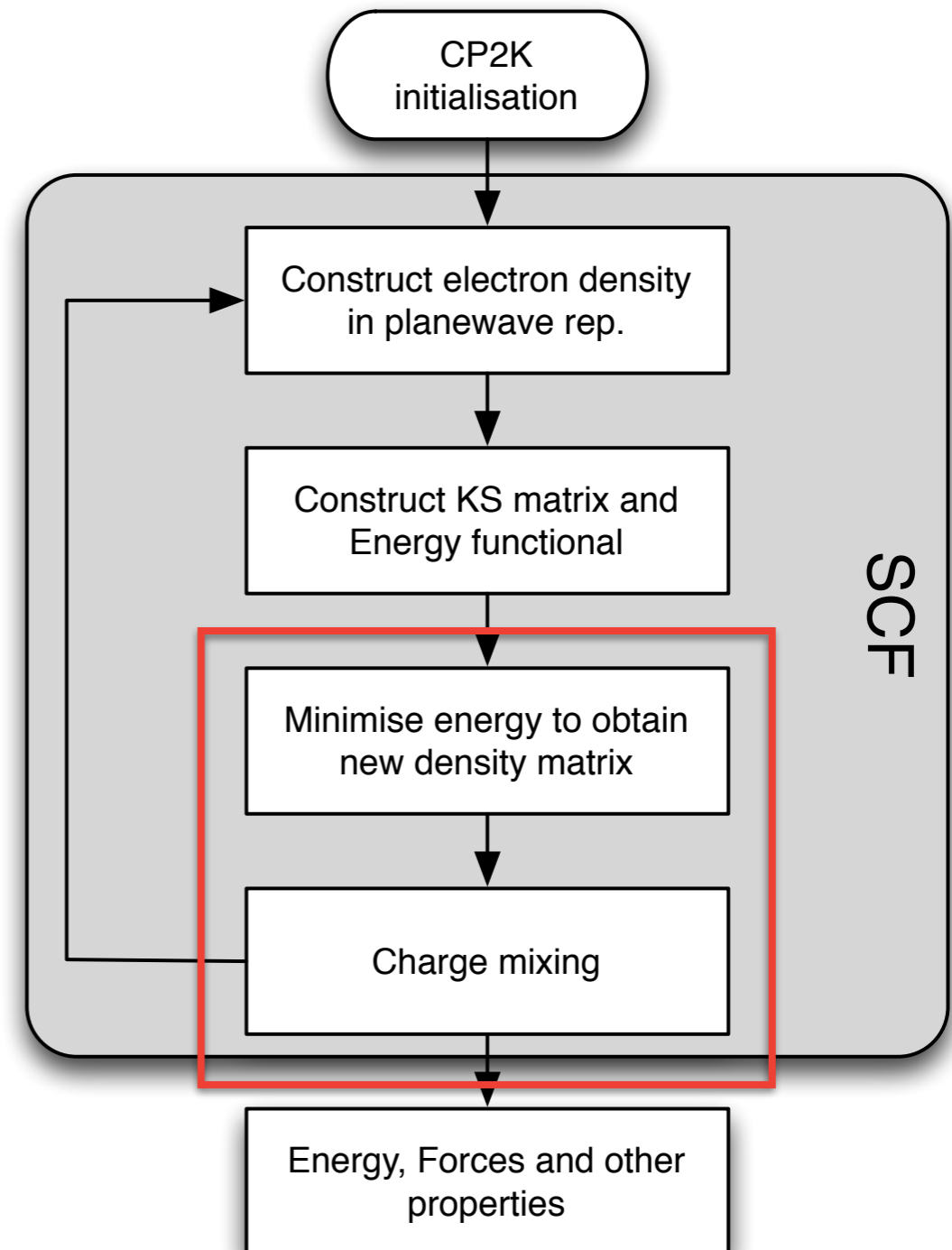
# Self Consistent Field Calculation

- 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

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- 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


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- General Eigen problem:

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

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

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

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

$$(\mathbf{U}^{-1})^T\mathbf{AU}^{-1}\mathbf{Ux} = \lambda\mathbf{Ux}$$

- **REDUCE**:  $\mathbf{A}|\mathbf{U} \Rightarrow \mathbf{A}'|\mathbf{1}$  followed by solving  $\mathbf{Ux} = \mathbf{x}'$
- **RESTORE**: Same as Reduce, but with the single reduce step for  $\mathbf{A}'$  replaced with two restore steps:
  - Solve  $\mathbf{xU} = \mathbf{A} \Rightarrow \mathbf{x} = \mathbf{AU}^{-1}$
  - Solve  $\mathbf{U}^T\mathbf{y} = \mathbf{x} \Rightarrow \mathbf{y} = (\mathbf{U}^T)^{-1}\mathbf{AU}^{-1}$
- **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

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- Without Cholesky decomposition:
  - Useful if your basis set contains linearly dependent functions, i.e.  $\mathbf{B}$  is non-positive definite
  - Slower, but more robust
- Find the inverse square root of  $\mathbf{B}$ :  $\mathbf{B}^{-\frac{1}{2}}$

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

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

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

- $\mathbf{B}^{-\frac{1}{2}}$  is calculated by diagonalise  $\mathbf{B}$ , invert the eigenvalues and then transform back.
- If  $\mathbf{B}$  is non-positive definite: this normally corresponds to the basis set containing redundant linearly dependent vectors. This means the zero eigenvalues of  $\mathbf{B}$  should not contribute to the linear problem.
  - This is equivalent to set inverse of the eigenvalues to zero

# Optimisers In CP2K

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- Concerns with finding the local minimum of a function of many variables
- **Steepest Decent:**

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

- 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

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- **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:

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

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

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

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

- The Conjugate gradient method then tries to solve the above equation linearly. 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

$$\sum_j \mathbf{P}_i^\top \mathbf{H} \mathbf{P}_j \alpha_j = -\mathbf{P}_i^\top \mathbf{b}$$

# 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

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

- 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  $\mathbf{x}_0$

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

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

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

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

⋮

$$\mathbf{P}_n = \mathbf{d}_{n-1} - \frac{\mathbf{P}_0^\top \mathbf{H} \mathbf{d}_{n-1}}{\mathbf{P}_0^\top \mathbf{H} \mathbf{P}_0} \mathbf{P}_0 - \frac{\mathbf{P}_1^\top \mathbf{H} \mathbf{d}_{n-1}}{\mathbf{P}_1^\top \mathbf{H} \mathbf{P}_1} \mathbf{P}_1 - \dots - \frac{\mathbf{P}_{n-1}^\top \mathbf{H} \mathbf{d}_{n-1}}{\mathbf{P}_{n-1}^\top \mathbf{H} \mathbf{P}_{n-1}} \mathbf{P}_{n-1}$$

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

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

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

⋮

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



# Optimisers In CP2K

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- 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:

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

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

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

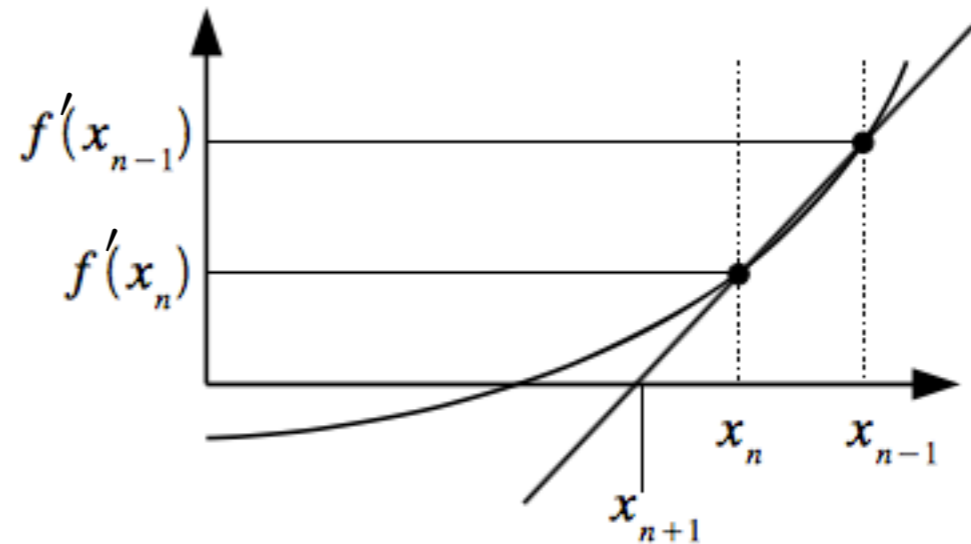
- Can be over 50% faster than CG, but not as stable because bad history contribute to the next step.
- Too many history included may not be beneficial.

# 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:

$$\begin{aligned}\mathbf{x}_{n+1} &= \mathbf{x}_n - \mathbf{J}_n^{-1} \mathbf{d}_n \\ \mathbf{d}_n &\equiv \nabla f(\mathbf{x}_n) \\ (\mathbf{J}_n)_{ij} &= \frac{\partial (\mathbf{d}_n)_i}{\partial x_j}\end{aligned}$$



- But inverse of Jacobian too expensive, so instead approximate  $\mathbf{J}_n^{-1}$  to be able to reproduce the changes in step ( $\mathbf{x}$ ) and residual ( $\mathbf{d}$ ) 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

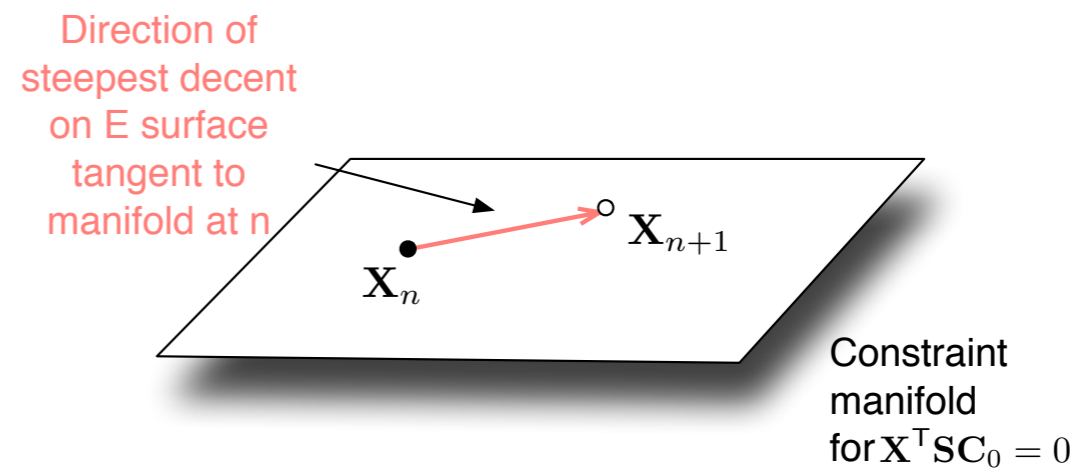
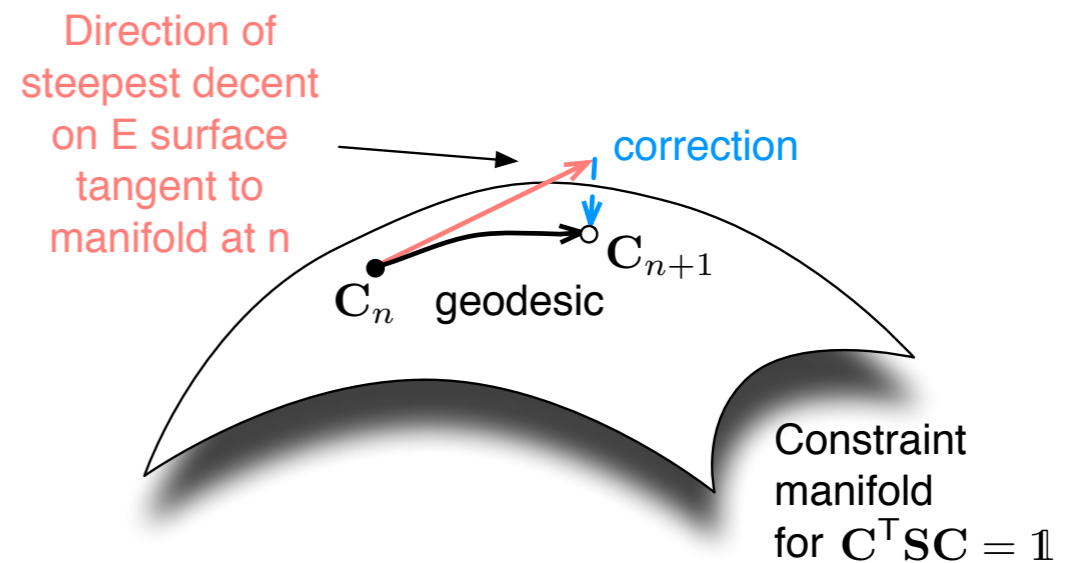
- Seeks to find the minimum of the energy functional with respect to the MO coefficients, with the constraint that MO are normalised.
- Optimisation problem on a M-dimensional spherical surface.
- Perform a variable transformation, from MO coefficients  $\mathbf{C}$  to a set of auxiliary variables 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

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

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

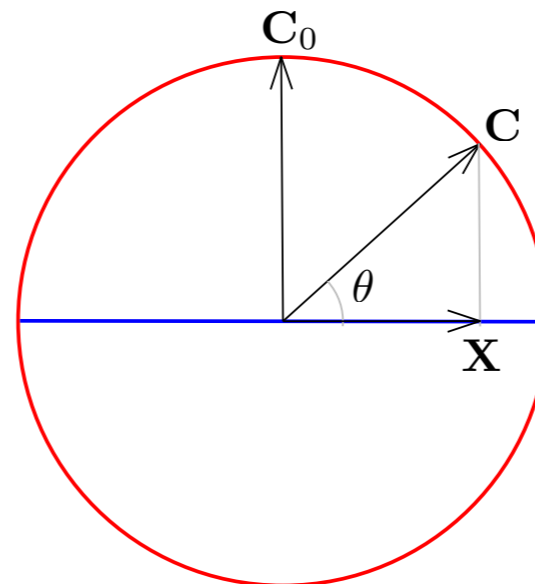
- With constraint (fixes the direction of the plane):

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



# 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.  $\mathbf{X}$



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

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

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

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

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

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

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

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

# Orbital Transform

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- 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

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

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

# Orbital Transform

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- **Preconditioners**

- The function to be minimised:

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

- 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:

$$E(\mathbf{x}_0 + \mathbf{h}) = E_{\mathbf{x}_0} + \nabla_{\mathbf{h}}E(\mathbf{x}_0)^\top\mathbf{h} + \frac{1}{2}\mathbf{h}^\top\mathbf{E}''(\mathbf{x}_0)\mathbf{h} + O(h^3)$$

- 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

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

# Orbital Transform

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- 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 preconditioner to the gradient is therefore:

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

- **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  $\epsilon_n$ , replace it with a single scalar  $\epsilon_0$  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

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## - 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

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- 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 beginning 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

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- Diagonalisation:
  - Solves the generalised eigen problem:

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

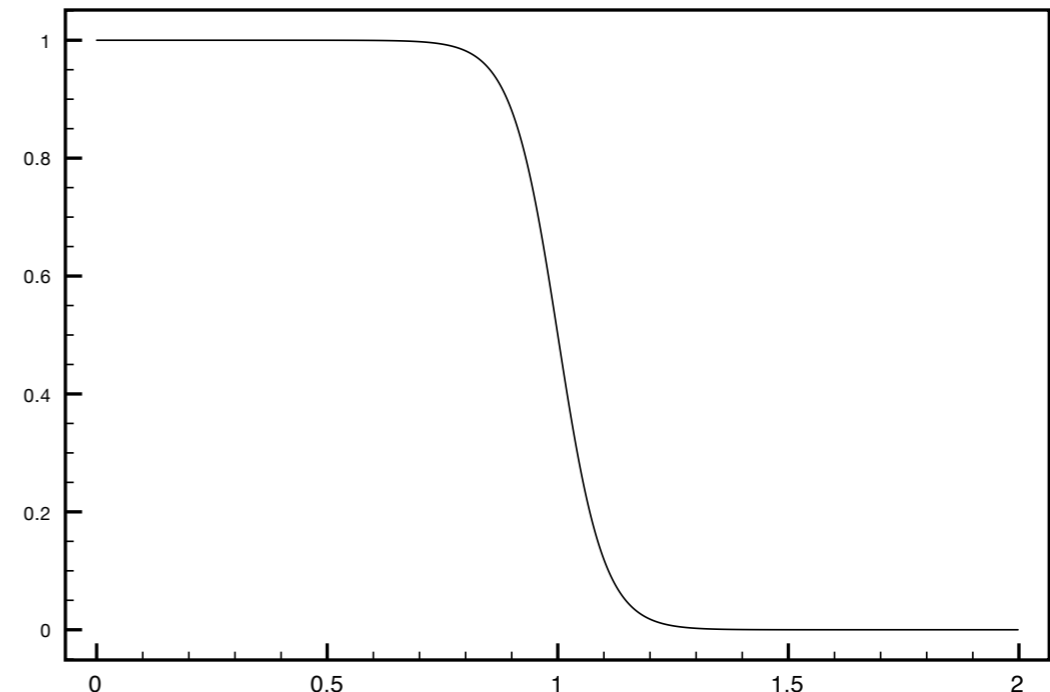
- Uses any one of the eigensolvers implemented in CP2K
- Density matrix can be constructed from the MOs.

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

- 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:

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

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

# Examples

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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

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## 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

## 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 \*\*\*



# 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

---

## Au 128 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

---

## Au 128 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

---

## Au 128 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 \*\*\*