SCF Methods
— Diagonalisation & Orbital Transformation

Lianheng Tong
King’s College London, UK
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Self Consistent Field Calculation

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

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

\[ \rho(r) = \sum_n f_n \psi_n(r)\psi^*_n(r) \]

- 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:
  \[ A x = \lambda B x \]

- Find a way to rewrite back to the standard Eigen problem
  \[ A' x' = \lambda x' \]

- Cholesky decomposition based methods: \( B = U^T U \) must be positive definite:
  \[ (U^{-1})^T A U^{-1} U x = \lambda U x \]

  - REDUCE: \( A | U \Rightarrow A' | 1 \) followed by solving \( U x = x' \)
  - RESTORE: Same as Reduce, but with the single reduce step for \( A' \) replaced with two restore steps:
    - Solve \( x U = A \) \( \Rightarrow \) \( x = A U^{-1} \)
    - Solve \( U^T y = x \) \( \Rightarrow \) \( y = (U^T)^{-1} A U^{-1} \)
  - INVERSE: Same as Reduce, but calculate \( A' \) using the direct inverse of \( U \) (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 $B$: $B^{-\frac{1}{2}}$

\[
B = B^\frac{1}{2} \cdot B^\frac{1}{2} \\
B^{-\frac{1}{2}} AB^{-\frac{1}{2}} B^\frac{1}{2} x = B^\frac{1}{2} x \\
x' = B^\frac{1}{2} x \quad \Rightarrow \quad x = B^{-\frac{1}{2}} x'
\]

$B^{-\frac{1}{2}}$ is calculated by diagonalise $B$, 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:

\[ f(x_n) = f(x_{n-1}) + \alpha \nabla f(x_{n-1}) \]

- 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 \( x_0 \) 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:
  \[
  f(x) = f(x_0) + b^T(x - x_0) + (x - x_0)^T H(x - x_0) + O((x - x_0)^3)
  \]
  \[
  (H)_{ij} = \frac{1}{2} \left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_{x_0} \quad b = \nabla f \big|_{x_0}
  \]
  - We notice that \( x \) is the unique solution to \( \nabla f(x) = 0 \) if it is the solution of the equation
  \[
  \nabla f(x) = b + Hx = 0 \quad \Rightarrow Hx = -b
  \]
  - The Conjugate gradient method then tries to solve the above equation iteratively. Notice that \( H \) is always symmetric and when near a minimum, positive definite
  - We can express \( x \) in a basis set
  \[
  x = \sum_i \alpha_i P_i
  \]
  - Hence
  \[
  \sum_j P_i^T H P_j \alpha_j = -P_i^T b
  \]
Conjugate Gradient:

Now since $H$ is symmetric and positive definite, it can be diagonalised, and we can choose $P_i$ to be a set of conjugate vectors of $H$, then we can see that

$$
\alpha_i = \frac{-P_i^T b}{P_i^T H P_i} \quad P_i^T H P_j = 0 \quad (i \neq j)
$$

The conjugate gradient method then involves iteratively finding each $P_i$ using a Gram-Schmidt like process.

In other words: we take exactly $n = \dim H$ steps, starting from an initial guess $x_0$

$$
d_i = -b - Hx_i
$$

$$
P_1 = d_0
$$

$$
P_2 = d_1 - \frac{P_0^T H d_1}{P_0^T H P_0} P_0
$$

$$
P_3 = d_2 - \frac{P_0^T H d_2}{P_0^T H P_0} P_0 - \frac{P_1^T H d_2}{P_1^T H P_1} P_1
$$

$$
\vdots
$$

$$
x_n = \alpha_1 P_1 + \alpha_2 P_2 + \alpha_3 P_3 + \cdots + \alpha_n P_n
$$

$$
P_n = d_{n-1} - \frac{P_0^T H d_{n-1}}{P_0^T H P_0} P_0 - \frac{P_1^T H d_{n-1}}{P_1^T H P_1} P_1 - \cdots - \frac{P_{n-1}^T H d_{n-1}}{P_{n-1}^T H P_{n-1}} P_{n-1}
$$
• **Discrete Inversion in Iterative Space (DIIS), a.k.a. Pulay Method:**
  - The new step is based on considerations over a list of previous steps:
    \[
    x_{n+1} = \sum_{i}^{n} \alpha_i x_i, \quad \sum_{i}^{n} \alpha_i = 1
    \]
  - Minimise by seeking the solution to \( \nabla f(x) = 0 \)
  - Assume when close enough to minimum, the gradient becomes a linear function:
    \[
    \nabla f(x_{n+1}) = \sum_{i}^{n} \alpha_i \nabla f(x_i) \quad d_i \equiv \nabla f(x_i)
    \]
  - The new gradient (residual) is then a function of \( \alpha_i \), solve:
    \[
    \frac{\partial \|d_{n+1}\|}{\partial \alpha_i} = 0
    \]
    with constraints \( \sum_{i}^{n} \alpha_i = 1 \), we obtain:
    \[
    \alpha_i = \frac{\sum_{i}^{n} A^{-1}_{ji}}{\sum_{ij}^{n} A^{-1}_{ji}}, \quad A_{ij} = d_i^T d_j
    \]
  - 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 $\nabla f(x) = 0$, but using the secant method.
- The next step can be determined by the inverse of Jacobian:

  \[
  x_{n+1} = x_n - J_n^{-1}d_n \\
  d_n \equiv \nabla f(x_n) \\
  (J_n)_{ij} = \frac{\partial (d_n)_i}{\partial x_j}
  \]

- But inverse of Jacobian too expensive, so instead approximate $J_n^{-1}$ 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:

  \[
  \sum_{i=1}^{n} w_i \| (x_i - x_{i-1}) - J_n^{-1}(d_i - d_{i-1}) \|^2
  \]

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

  \[
  N = \sum_{i=1}^{n} w_i \| (x_i - x_{i-1}) - J_n^{-1}(d_i - d_{i-1}) \|^2 + w_0 \| J_n^{-1} - J_0^{-1} \|
  \]
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 $C$ to a set of auxiliary variables $X$ such that the optimisation of $E$ is now on a $M-1$ dimensional linear space w.r.t. $X$

$$C(X) = C_0 \cos(U) + XU^{-1} \sin(U)$$

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

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

$$X^T SC_0 = 0$$
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 $C$ to a set of auxiliary variables $X$ such that the optimisation of $E$ is now on a M-1 dimensional linear space w.r.t. $X$

$$C(X) = C_0 \cos(U) + XU^{-1} \sin(U)$$

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

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

$$X^T S C_0 = 0$$

\[ C = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix} = C_0 \cos(\theta) + \hat{X} \sin(\theta) \]

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

$$\|X\| = \langle X, X \rangle^{\frac{1}{2}} = (X^T S X)^{\frac{1}{2}}$$
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 $U^{-1}$ as part of the Taylor expansion

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

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

- The function to be minimised:

\[ E(c(x)) = \text{tr}(c^T(x))H_{KS}c(x) + x^TSc_0\Lambda \]

- 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 \( c_0 \) are eigenstates of the initial KS hamiltonian, and we Taylor expand close by:

\[ E(x_0 + h) = E_{x_0} + \nabla_h E(x_0)^T h + \frac{1}{2} h^T E''(x_0) h + O(h^3) \]

- Then the Hessian of \( E \) close to minimum is:

\[ \frac{\partial^2 E}{\partial x_{i\mu} \partial x_{j\nu}} \bigg|_{x_0} = 2H_{ij}\delta_{\mu\nu} - 2S_{ij}\delta_{\mu\nu}\epsilon^0_\mu \]

- At minimum, we expect

\[ \frac{dE(x_0 + h)}{dh} = \nabla_h E(x_0) + E''(x_0) h + O(h^2) = 0 \]
Orbital Transform

Therefore, $h = -E''(x_0)^{-1} \nabla_h E(x_0)$, i.e.:

$$x_{n+1} = x_n - P_n \nabla E_n$$

The ideal preconditioner to the gradient is therefore:

$$P_n = (H_{KS} - S\epsilon_n)^{-1} \quad \epsilon_n = c_n^T H_{KS} c_n$$

- 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

- **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 $H_{KS} - S\epsilon_0$.
  - 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 $H_{KS} - S\epsilon_0$ 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 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

• Diagonalisation:
  - Solves the generalised eigen problem:
    \[ H_{KS} c = \lambda S c \]
  - Uses any one of the eigensolvers implemented in CP2K
  - Density matrix can be constructed from the MOs.
    \[ P_{ij} = \sum_n f_n c_i n c_j n \]
  - 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
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

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**Minimizer**: DIIS

- diis
- in the iterative subspace

**Preconditioner**: FULL_SINGLE_INVERSE

- inverse of
- $H + eS - 2(S(c^T H c + \text{const})(S c)^T)$

**Precond_solver**: DEFAULT

---

**Step** | **Update method** | **Time** | **Convergence** | **Total energy** | **Change**
---|---|---|---|---|---
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014957$ | | | | |
Total charge density on r-space grids: | $-0.0000014959$ | | | | |
Total charge density g-space grids: | $-0.0000014959$ | | | | |
1 OT DIIS | $0.80E-01$ | $1.9$ | $0.02242151$ | $-1059.3825079557$ | $-1.06E+03$ |
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014959$ | | | | |
Total charge density on r-space grids: | $-0.0000014914$ | | | | |
Total charge density g-space grids: | $-0.0000014914$ | | | | |
149 OT DIIS | $0.80E-01$ | $1.2$ | $0.00000102$ | $-1101.0377081868$ | $-3.67E-07$ |
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014957$ | | | | |
Total charge density on r-space grids: | $-0.0000014912$ | | | | |
Total charge density g-space grids: | $-0.0000014912$ | | | | |
150 OT DIIS | $0.80E-01$ | $1.2$ | $0.00000101$ | $-1101.0377093306$ | $-3.27E-07$ |
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014957$ | | | | |
Total charge density on r-space grids: | $-0.0000014912$ | | | | |
Total charge density g-space grids: | $-0.0000014912$ | | | | |
151 OT DIIS | $0.80E-01$ | $1.2$ | $0.00000100$ | $-1101.0377096545$ | $-3.24E-07$ |
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014957$ | | | | |
Total charge density on r-space grids: | $-0.0000014912$ | | | | |
Total charge density g-space grids: | $-0.0000014912$ | | | | |
152 OT DIIS | $0.80E-01$ | $1.2$ | $0.00000100$ | $-1101.0377099336$ | $-3.97E-07$ |
Trace(PS): | | | | | |
Electronic density on regular grids: | $512.0000000000$ | | | | |
Core density on regular grids: | $-512.0000014957$ | | | | |
Total charge density on r-space grids: | $-0.0000014912$ | | | | |
Total charge density g-space grids: | $-0.0000014912$ | | | | |
153 OT DIIS | $0.80E-01$ | $1.2$ | $0.00000100$ | $-1101.0377102545$ | $-3.24E-07$ |

*** 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
SCF WAVEFUNCTION OPTIMIZATION

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

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):                                  511.9999999999
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     -1101.0377126778 -3.21E+01
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     0.00000102     -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     0.00000100     -1101.0377136686 -3.48E-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 ***

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Examples

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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 ***
&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

64 water box
18 OT DIIS  0.15E+00  1.3   0.00010381  -1101.033773217 -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
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

3 OT DIIS     0.15E+00    5.9    0.00016580    -1101.0355385583 -4.42E-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    0.00006738    -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

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

*** SCF run converged in     5 steps ***
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&SMEAR ON
  METHOD FERMI_DIRAC
  ELECTRONIC_TEMPERATURE [K] 300
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&DIAOGNALIZATION
  ALGORITHM STANDARD
&END DIAOGNALIZATION
&MIXING
  METHOD DIRECT_P_MIXING
  ALPHA 0.5
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&OUTER_SCF
  EPS_SCF 1.0E-6
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&END OUTER_SCF
&END SCF
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<th>Change</th>
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   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

Au128 bulk
### SCF WAVEFUNCTION OPTIMIZATION

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<th>Update method</th>
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<th>Convergence</th>
<th>Total energy</th>
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*** SCF run converged in 17 steps ***
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      ELECTRONIC_TEMPERATURE [K] 300
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      NBUFFER 5
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   &OUTER_SCF
      EPS_SCF 1.0E-6
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   &END OUTER_SCF
&END SCF

Au128 bulk
### SCF WAVEFUNCTION OPTIMIZATION

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<th>Convergence</th>
<th>Total energy</th>
<th>Change</th>
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*** SCF run converged in 21 steps ***