KS matrix formulation when the wavefunction is expanded into a basis

System size \( \{N_{el}, M\}, P [M \times M], C [M \times N] \)

\[ \psi_i(\mathbf{r}) = \sum_{\alpha} C_{\alpha i} \phi_{\alpha}(\mathbf{r}) \]

\[ n(\mathbf{r}) = \sum_i \sum_{\alpha \beta} f_i C_{\alpha i} C_{\beta i} \phi_{\alpha}(\mathbf{r}) \phi_{\beta}(\mathbf{r}) = \sum_{\alpha \beta} P_{\alpha \beta} \phi_{\alpha}(\mathbf{r}) \phi_{\beta}(\mathbf{r}) \]

\[ P = PSP \]

KS total energy

\[ E[\{\psi_i\}] = T[\{\psi_i\}] + E^{\text{ext}}[n] + E^H[n] + E^{\text{XC}}[n] + E^{II} \]

Matrix formulation of the KS equations

\[ K(C)C = T(C) + V_{\text{ext}}(C) + E^H(C) + E^{\text{xc}}(C) = SC\varepsilon \]
Generate a starting density $\Rightarrow n^{\text{init}}$

Generate the KS potential $\Rightarrow V_{\text{KS}}^{\text{init}}$

Solve the KS equations $\Rightarrow \epsilon, \psi$

Calculate the new density $\Rightarrow n^1$

New KS potential $\Rightarrow V_{\text{KS}}^1$

New orbitals and energies $\Rightarrow \epsilon^1, \psi$

New density $\Rightarrow n^2$

.....

until self-consistency to required precision
Classes of Basis Sets

- Extended basis sets, $\text{PW}$: condensed matter
- Localised basis sets centred at atomic positions, $\text{GTO}$

Idea of $\text{GPW}$: auxiliary basis set to represent the density

- Mixed ($\text{GTO+PW}$) to take best of two worlds, $\text{GPW}$
- Augmented basis set, $\text{GAPW}$: separated hard and soft density domains
GPW Ingredients

**linear scaling KS matrix computation for GTO**

- **Gaussian basis sets (many terms analytic)**

\[ \psi_i(r) = \sum_\alpha C_{\alpha i} \phi_\alpha(r) \]

\[ \phi_\alpha(r) = \sum_m d_{m\alpha} g_m(r) \]

\[ g_m(r) = x^{m_x} y^{m_y} z^{m_z} e^{-\alpha_m r^2} \]

- **Pseudo potentials**

- **Plane waves auxiliary basis for Coulomb integrals**

- **Regular grids and FFT for the density**

- **Sparse matrices (KS and P)**

- **Efficient screening**

G. Lippert et al, Molecular Physics, 92, 477, 1997
J. VandeVondele et al, Comp. Phys. Comm., 167 (2), 103, 2005
Localised, atom-position dependent GTO basis

\[ \varphi_{\mu}(r) = \sum_{m} d_{m\mu} g_{m}(r) \]

Expansion of the density using the density matrix

\[ n(r) = \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu}(r) \varphi_{\nu}^{*}(r) \]

Operator matrices are sparse

\[ S_{\mu\nu} = \int \varphi_{\mu}(r) \varphi_{\nu}(r) dr \]
\[ H_{\mu\nu} = \int \varphi_{\mu}(r) V(r) \varphi_{\nu}(r) dr \]
Analytic Integrals

Cartesian Gaussian

\[ g(r, n, \eta, R) = (x - R_x)^{n_x} (y - R_y)^{n_y} (z - R_z)^{n_z} e^{-\eta (r-R)^2} \]

\[ l = n_x + n_y + n_z \quad (l + 1)(l + 2)/2 \]

Differential relations

\[ \frac{\partial}{\partial R_i} |n\rangle = 2\eta |n + 1_i\rangle - n_i |n - 1_i\rangle \]

\[ \frac{\partial}{\partial R_i} |n\rangle = -\frac{\partial}{\partial r_i} |n\rangle \]

Obara-Saika recursion relations

\[ (0_a \mid \mathcal{O}(r) \mid 0_b) \quad \rightarrow \quad (a + 1_i \mid \mathcal{O}(r) \mid b) \]

Obara and Saika JCP 84 (1986), 3963
## Basis Set library

### GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Basis Set Library</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>6-31G*</td>
<td>6-31G*</td>
</tr>
<tr>
<td></td>
<td>6-31G**</td>
<td>6-31G**</td>
</tr>
<tr>
<td></td>
<td>6-311++G3df3pd</td>
<td>6-311++G3df3pd</td>
</tr>
<tr>
<td></td>
<td>6-311++G(3df,3pd)</td>
<td>6-311++G(3df,3pd)</td>
</tr>
<tr>
<td></td>
<td>O 6-31Gx 6-31G*</td>
<td>O 6-31Gx 6-31G*</td>
</tr>
<tr>
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<td>O 6-31G**</td>
<td>O 6-31G**</td>
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<td></td>
<td>O 6-311++G3df3pd</td>
<td>O 6-311++G3df3pd</td>
</tr>
<tr>
<td></td>
<td>O 6-311++G(3df,3pd)</td>
<td>O 6-311++G(3df,3pd)</td>
</tr>
</tbody>
</table>

---

### Example:

**Basis Set Library**

- **6-31Gx 6-31G*:**
  - 6-31Gx
  - 6-31G*

- **6-31G**: 6-31G**

- **6-311++G3df3pd**: 6-311++G3df3pd

- **6-311++G(3df,3pd)**: 6-311++G(3df,3pd)

---

For more detailed information, refer to the basis set library documentation.
Tools for the optimisation of GTO basis sets are available in cp2k, based on atomic and molecular electronic structure calculations.
Core electrons are eliminated $Z_v = Z - Z_{\text{core}}$

Atomic 1s: $\exp\{-Z \ r\}$

Smooth nodeless pseudo-wfn close to nuclei

Bare Coulomb replaced by screened Coulomb

Inclusion of relativistic effects

Transferable

Angular dependent potentials:

$Pt \ p$ peaked at 3.9Å
$s$ peaked at 2.4Å
$d$ peaked at 1.3Å
GTH Pseudopotentials

- Norm-conserving, separable, dual-space
- Local PP: short-range and long-range terms

\[
V_{\text{loc}}^{\text{PP}}(r) = \sum_{i=1}^{4} C_i^{\text{PP}} \left( \sqrt{(2)} \alpha^{\text{PP}} r \right)^{(2i-2)} e^{-\left(\alpha^{\text{PP}} r\right)^2} - \frac{Z_{\text{ion}}}{r} \text{erf} \left( \alpha^{\text{PP}} r \right)
\]

analytically part of ES

- Non-Local PP with Gaussian type projectors

\[
V_{\text{nl}}^{\text{PP}}(r, r') = \sum_{lm} \sum_{ij} \langle r | p_{i}^{lm} \rangle h_{ij}^{l} \langle p_{j}^{lm} | r' \rangle
\]

\[
\langle r | p_{i}^{lm} \rangle = N_{i}^{l} Y^{lm}(\hat{r}) \ r^{(l+2i-2)} \ e^{-\frac{1}{2} \left( \frac{r}{r_{l}} \right)^{2}}
\]

Goedeker, Teter, Hutter, PRB 54 (1996), 1703;
Hartwigsen, Goedeker, Hutter, PRB 58 (1998) 3641
Periodic system

\[ E_{ES} = \int V_{pp}^{loc}(r)n(r)dr + 2\pi \Omega \sum_G \frac{\tilde{n}^*(G)\tilde{n}(G)}{G^2} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|} \]

Total charge distribution including n(r) and Z

\[ n_{tot}(r) = n(r) + \sum_A n_A(r) \]

\[ n_A(r) = -\frac{Z_A}{(r_A^c)^3} \pi^{-3/2} e \left( \frac{r - R_A}{r_A^c} \right) \]

\[ r_A^c = \sqrt{2} r_{locA} \]

cancels the long range term of local PP

\[ V_A^{core}(r) = -\frac{Z_A}{|r - R_A|} \text{erf} \left( \frac{|r - R_A|}{r_A^c} \right) \]

\[ E_{ES} = \int V_{loc}^{SR}(r)n(r) + \frac{1}{2} \int \int \frac{n_{tot}(r)n_{tot}(r')}{|r - r'|} drdr' \]

\[ + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|} \text{erfc} \left[ \frac{|R_A - R_B|}{\sqrt{(r_A^c)^2 + (r_B^c)^2}} \right] - \sum_A \frac{1}{\sqrt{2\pi}} \frac{Z_A^2}{r_A^c} \]

\[ E^{ov} \text{ short range, pair} \quad E^{self} \]
Orthogonal, unbiased, naturally periodic PW basis

Long range term: Non-local Hartree potential

$$E^H[n_{tot}] = \frac{1}{2} \int \int \frac{n_{tot}(r)n_{tot}(r')}{|r - r'|} dr dr'$$

Orthogonal, unbiased, naturally periodic PW basis

$$\tilde{n}(\mathbf{r}) = \frac{1}{\Omega} \sum_G \tilde{n}(G) e^{i\mathbf{G} \cdot \mathbf{r}}$$

Linear scaling solution of the Poisson equation

$$E^H[n_{tot}] = 2\pi \Omega \sum_G \tilde{n}^*(G) e^{i\mathbf{G} \cdot \mathbf{r}}$$
Finite cutoff and simulation box define a real space grid

Density collocation

\[ n(r) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(r) \varphi_\nu(r) \rightarrow \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu\nu}(R) = n(R) \]

\[ \hat{n}(G) \rightarrow V_H(G) = \frac{\hat{n}(G)}{G^2} \rightarrow V_H(R) \]

Numerical approximation of the gradient

\[ n(R) \rightarrow \nabla n(R) \]

\( \epsilon_{xc} \) and derivatives evaluated on the grid

\[ v_{xc}[n](r) \rightarrow V_{xc}(R) = \frac{\partial \epsilon_{xc}}{\partial n}(R) \]

Real space integration

\[ H^{\mu\nu}_{Hxc} = \langle \mu | V_{Hxc}(r) | \nu \rangle \rightarrow \sum_{R} V_{Hxc}(R) \varphi'_{\mu\nu}(R) \]
Multiple Grids

\[ E_{\text{cut}}^i = \frac{E_{\text{cut}}^1}{\alpha(i-1)}, \quad i = 1..N \]

The exponent of Gaussian product selects the grid number of grid points is exponent-independent.

\[ \sigma_p^2 = 1/2\eta_p \]

Accuracy => Relative Cutoff ~30 Ry

\[ n_j^f = I_j(n_i^c) \]
Analysis of Multigrid

Bulk Si, 8 atoms, $a=5.43\,\text{Å}, E_{\text{cut}}=100\,\text{Ry}, E_{\text{rel}}=60\,\text{Ry}$

---

<table>
<thead>
<tr>
<th>count for grid</th>
<th>cutoff [a.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:</td>
<td>50.00</td>
</tr>
<tr>
<td>2:</td>
<td>16.67</td>
</tr>
<tr>
<td>3:</td>
<td>5.56</td>
</tr>
<tr>
<td>4:</td>
<td>1.85</td>
</tr>
<tr>
<td>total gridlevel count</td>
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</tr>
</tbody>
</table>

Changing $E_{\text{cut}}$ from 50 to 500 Ry

# REL_CUTOFF = 60

<table>
<thead>
<tr>
<th>Cutoff (Ry)</th>
<th>Total Energy (Ha)</th>
<th>NG on grid 1</th>
<th>NG on grid 2</th>
<th>NG on grid 3</th>
<th>NG on grid 4</th>
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<tr>
<td>500.00</td>
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<td>0</td>
<td>2032</td>
<td>3016</td>
<td>5448</td>
</tr>
</tbody>
</table>
\[ E^{\text{el}}[n] = \sum_{\mu\nu} P_{\mu\nu} \left< \varphi_{\mu} \left| -\frac{1}{2} \nabla^2 + V_{\text{loc}}^{\text{SR}} + V_{\text{nl}} \right| \varphi_{\nu} \right> \]

\[ + 2\pi\Omega \sum_G \frac{\tilde{n}_{\text{tot}}^*(G)\tilde{n}_{\text{tot}}(G)}{G^2} + \sum_R \tilde{n}(R)V^{\text{XC}}(R) \]

\[ = \sum_{\mu\nu} P_{\mu\nu} \left( \left< \varphi_{\mu} \left| -\frac{1}{2} \nabla^2 + V^{\text{ext}} \right| \varphi_{\nu} \right> + \sum_R V^{\text{HXC}}_{\mu\nu}(R)\varphi'_{\mu\nu}(R) \right) \]

**Linear scaling KS matrix construction**
&FORCE_EVAL
 METHOD Quickstep

&DFT
 BASIS_SET_FILE_NAME  GTH_BASIS_SETS
 POTENTIAL_FILE_NAME  GTH_POTENTIALS
 LSD  F
 MULTIPlicity 1
 CHARGE 0
 &MGRID
     CUTOFF 300
     REL_CUTOFF 50
 &END MGRID
 &QS
     EPS_DEFAULT 1.0E-10
 &END QS
 &SCF
     MAX_SCF 50
     EPS_SCF 2.00E-06
     SCF_GUESS  ATOMIC
 &END SCF
 &XC
     &XC_FUNCTIONAL
      &PBE
      &END PBE
     &END XC_FUNCTIONAL
     &XC_GRID
      XC_DERIV SPLINE2_smooth
      XC_SMOOTH_RHO NN10
     &END XC_GRID
     &END XC
     &END DFT

&SUBSYS
 &CELL
      PERIODIC XYZ
      ABC 8. 8. 8.
 &END CELL
 &COORD
      H 0.000000 -0.757136 0.520545
      H 0.000000  0.757136 0.520545
 &END COORD
 &KIND H
      BASIS_SET DZVP-GTH-PBE
      POTENTIAL GTH-PBE-q1
 &END KIND
 &KIND O
      BASIS_SET DZVP-GTH-PBE
      POTENTIAL GTH-PBE-q6
 &END KIND
 &END SUBSYS
 &END FORCE_EVAL
Hard and Soft Densities

- Pseudopotential $\Rightarrow$ frozen core
- Augmented PW $\Rightarrow$ separate regions (matching at edges)
  LAPW, LMTO (OK Andersen, PRB 12, 3060 (1975))
- Dual representation $\Rightarrow$ localized orbitals and PW
  PAW (PE Bloechl, PRB, 50, 17953 (1994))
Partitioning of the Density

\[ n = \tilde{n} + \sum_A n_A - \sum_A \tilde{n}_A \]

\[ n(r) - \tilde{n}(r) = 0 \quad r \in I \]

\[ n_A(r) - \tilde{n}_A(r) = 0 \quad r \in I \]

\[ n_A(r) = \sum_{\mu\nu} P_{\mu\nu} \chi^A_\mu \chi^A_\nu \]

\[ \tilde{n}(r) = \sum_{\mu\nu} P_{\mu\nu} \tilde{\phi}_\mu \tilde{\phi}_\nu \rightarrow \sum_G \hat{n}(G) e^{iG\cdot R} \]

Gaussian Augmented Plane Waves
$n_A(r) = \sum_{\mu \nu} P_{\mu \nu} \chi^A_\mu \chi^A_\nu$

$\chi_\mu$ projection of $\varphi_\mu$ in $\Omega_A$ through atom-dependent $d'$

$\chi_\mu = \sum_{\alpha} d'_{\mu \alpha} g_\alpha(r)$

projector basis (same size)

$\{p_\alpha\} \quad \lambda_\alpha = k^\alpha \lambda_{min} \quad \langle p_\alpha | \varphi_\mu \rangle = \sum_{\beta} d'_{\mu \beta} \langle p_\alpha | g_\beta \rangle$

$\sum_{\alpha \beta} \left[ \sum_{\mu \nu} P_{\mu \nu} d'_{\mu \alpha} d'_{\nu \beta} \right] g_\alpha(r) g_\beta(r) = \sum_{\alpha \beta} P'_{\alpha \beta} g_\alpha(r) g_\beta(r)$
Semi-local functionals like local density approximation, generalised gradient approximation or meta-functionals

\[ \nabla n(r) = \nabla \tilde{n}(r) + \sum_A \nabla n_A(r) - \sum_A \nabla \tilde{n}_A(r) \]

\[ E[n] = \int \tilde{V}_{loc}(r)n(r) = \int \left\{ \tilde{V}_{loc}(r) + \sum_A V_{loc}^A(r) + \sum_A \tilde{V}_{loc}^A(r) \right\} \times \left\{ \tilde{n}(r) + \sum_A n_A(r) - \sum_A \tilde{n}_A(r) \right\} dr \]

\[ = \int \left\{ \tilde{V}_{loc}(r)\tilde{n}(r) + \sum_A V_{loc}^A(r)n_A(r) - \sum_A \tilde{V}_{loc}^A(r)\tilde{n}_A(r) \right\} \]
Density Dependent Terms: ES

Non local Coulomb operator

\[ n^0(r) = \sum_A n^0_A(r) = \sum_A \left\{ \sum_L Q^L_A g^L_A(r) \right\} \]

<table>
<thead>
<tr>
<th>Compensation</th>
<th>charge</th>
</tr>
</thead>
</table>

Same multipole expansion as the local densities

\[ Q^L_A = \int \left\{ n_A(r) - \tilde{n}_A(r) + n^Z_A(r) \right\} r^l Y_{lm}(\theta \phi) r^2 dr \sin(\theta) d\theta d\phi \]

\[ V[\tilde{n} + n^0] + \sum_A V[n_A + n^Z_A] - \sum_A V[\tilde{n}_A + n^0_A] \]

| Interstitial region | Atomic region |
\[ E_{xc}[n] = E_{xc}[\tilde{n}] + \sum_A E_{xc}[n_A] - \sum_A E_{xc}[\tilde{n}_A] \]

\[ E_H[n + n^Z] = E_H[\tilde{n} + n^0] + \sum_A E_H[n_A + n^Z_A] - \sum_A E_H[\tilde{n}_A + n^0_A] \]

on global grids via collocation + FFT

Analytic integrals
Local Spherical Grids

Lippert et al., Theor. Chem. Acc. 103, 124 (1999); Krack et al, PCCP, 2, 2105 (2000)

Iannuzzi, Chassaing, Hutter, Chimia (2005); VandeVondele, Iannuzzi, Hutter, CSCM2005 proceedings
&DFT
    ...
&QS
    EXTRAPOLATION ASPC
    EXTRAPOLATION_ORDER 4
    EPS_DEFAULT 1.0E-12
    METHOD GAPW
    EPS_DEFAULT 1.0E-12
    QUADRATURE GC_LOG
    EPSFIT 1.E-4
    EPSISO 1.0E-12
    EPSRHO0 1.E-8
    LMAXN0 4
    LMAXN1 6
    ALPHA0_H 10
&END QS
&SUBSYS
    ...
&KIND 0
    BASIS_SET DZVP-MOLOPT-GTH-q6
    POTENTIAL GTH-BLYP-q6
    LEBEDEV_GRID 80
    RADIAL_GRID 200
&END KIND
&KIND 01
    ELEMENT 0
    BASIS_SET 6-311++G2d2p
    BASIS_SET 6-311G**
    POTENTIAL ALL
    LEBEDEV_GRID 80
    RADIAL_GRID 200
&END KIND
&END DFT
&END SUBSYS
Energy Functional Minimisation

\[ C^* = \arg \min_C \{ E(C) : C^T SC = 1 \} \]


- Direct optimisation: Orbital rotations (maximally localised Wannier functions)

- Linear scaling methods: Efficiency depends on sparsity of \( P \) ( S. Goedecker, Rev. Mod. Phys. 71, 1085,(1999))

\[
P(r, r') \propto e^{-c \sqrt{E_{\text{gap}} |r-r'|}}
\]

\[
P_{\mu \nu} = \sum_{pq} S_{\mu \mu}^{-1} S_{\nu \nu}^{-1} \int \int \varphi_p(r) P(r, r') \varphi_q(r') \, dr \, dr'
\]
Traditional Diagonalisation

Eigen solver from standard parallel program library: SCALAPACK

\[ KC = SC\epsilon \]

**Transformation into a standard eigenvalues problem**

Cholesky decomposition

\[ S = U^T U \quad C' = UC \]

\[ KC = U^T UC\epsilon \quad \Rightarrow \quad [(U^T)^{-1}KU^{-1}] C' = C'\epsilon \]

Diagonalisation of \( K' \) and back transformation of MO coefficients (occupied only (20%))

DIIS for SCF convergence acceleration: few iterations

Error matrix

\[ e = KPS - SPK \]

Scaling (\( O(M^3) \)) and stability problems
Orbital Transformation Method

**Auxiliary** $X$, linearly constrained variables to parametrise the occupied subspace

- **not linear orthonormality constraint**
  \[ C^T S C = I \]

- **Linear constraint**
  \[ X S C_0 = 0 \]

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

**$M$ dimensional**

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

\[ U = (X^T S X)^{1/2} \]

**Matrix functionals by Taylor expansions in $X^T S X$**

**$M-1$ dimensional**

Direction of geodesic correction

Constraint manifold for $C^T S C = 1$

Constraint manifold for $X^T S C_0 = 0$
Preconditioned OT

minimisation in the auxiliary tangent space, idempotency verified

\[ \frac{\partial E(C(X)) + \text{Tr}(X^\dagger SC_0 \Lambda)}{\partial X} = \frac{\partial E}{\partial C} \frac{\partial C}{\partial X} + SC_0 \Lambda \]

\[ \text{HC and SX dominated O(MN)} \]

**CG(LS) or DIIS**

Preconditioned gradients

\[ P(H - S\varepsilon)X - X \approx 0 \quad X \rightarrow \sqrt{P}X \]

\[ X_{n+1} = X_n - P_n \nabla E_n \]

ideal preconditioner

\[ P_n = (H - S\varepsilon_n)^{-1} \quad \varepsilon_n = C_n^T HC_n \]

- Full All
- Full Kinetic
- Full Single
- Full Single Inverse
- Full S Inverse

Use Inner and Outer loop

Guaranteed convergence with CG + line search

Various choices of preconditioners

Limited number of SCF iterations

KS diagonalisation avoided

Sparsity of S and H can be exploited

Based on matrix-matrix and matrix-vector products

Scaling $O(N^2M)$ in cpu and $O(NM)$ in memory

Optimal for large system, high quality basis set
Refined preconditioner, most effective during MD of large systems with well conditioned basis sets

OT Performance

Schiffmann, VandeVondele, JCP 142 244117 (2015)

on Daint (XC30)
3844 nodes
(8 cores + 1 GPU)
&SCF
  EPS_SCF  1.01E-07
&OUTER_SCF
  MAX_SCF 20
  EPS_SCF  1.01E-07
&END  OUTER_SCF
SCF_GUESS RESTART
MAX_SCF 20
&OT
  MINIMIZER DIIS
  PRECONDITIONER FULL_ALL
&END  OT
&END  SCF
Based on sparse matrix matrix multiplications (iterative proc.)

\[ P = \frac{1}{2} \left( I - \text{sign} \left( S^{-1} H - \mu I \right) \right) S^{-1} \]

Self consistent solution by mixing

\[ \hat{H}_{n+1}(P_{n+1}) \]

\[ \hat{H}_{n+1} = (1 - \alpha)\hat{H}_n - \alpha H_{n+1} \]

Chemical potential by bisecting until

\[ \mu_{n+1} : \quad |\text{trace}(P_{n+1}S) - N_{el}| < 1/2 \]
DBCSR: Distributed Blocked Compressed Sparse Row

- For massively parallel architectures
- Optimised for 10000s of non-zeros per row (dense limit)
- Stored in block form: atoms or molecules
- Cannons algorithm: 2D layout (rows/columns) and 2D distribution of data
- Homogenised for load balance

Given processor communicates only with nearest neighbours. Transferred data decreases as the number of processors increases.
Millions of atoms

Millions of atoms in the condensed phase Bulk liquid water. Dashed lines represent ideal linear scaling.

Minimal basis sets: DFT, NDDO, DFTB

Accurate basis sets, DFT
46656 cores

The electronic structure
O(10^6) atoms in < 2 hours

Minimal basis sets: DFT, NDDO, DFTB
9216 cores

Bulk liquid water. Dashed lines represent ideal linear scaling.
Metallic Electronic Structure

\[ E_{\text{band}} = \sum_n \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} \varepsilon_{n\mathbf{k}} \Theta(\varepsilon_{n\mathbf{k}} - E_f) d^3\mathbf{k} \rightarrow \sum_n \sum_k w_k \varepsilon_{n\mathbf{k}} \Theta(\varepsilon_{n\mathbf{k}} - E_f) d^3\mathbf{k} \]

Rh band structure

\textbf{\textit{C}}_{\text{KS}} \text{ and } \varepsilon_{\text{KS}} \text{ needed}

- Charge sloshing and exceedingly slow convergence
- Wavefunction must be orthogonal to unoccupied bands close in energy
- Discontinuous occupancies generate instability (large variations in \( n(r) \))
- Integration over \( k \)-points and iterative diagonalisation schemes
Mermin functional: minimise the free energy

$$F(T) = E - \sum_n k_B T S(f_n) \quad S(f_n) = -[f_n \ln f_n + (1 - f_n) \ln(1 - f_n)]$$

Any smooth operator that allows accurate $S(f_n)$ to recover the $T=0$ result

$$f_n \left( \frac{\varepsilon_n - E_f}{kT} \right) = \frac{1}{\exp \left( \frac{\varepsilon_n - E_f}{k_B T} \right) + 1} \quad \text{Fermi-Dirac}$$

Trial density mixed with previous densities: damping oscillations

$$n_{m+1}^{\text{inp}} = n_m^{\text{inp}} + G^I \mathcal{R}[n_m^{\text{inp}}] + \sum_{i=1}^{m-1} \alpha_i (\Delta n_i + G^I \Delta \mathcal{R}_i)$$

residual

$$\mathcal{R}[n^{\text{inp}}] = n^{\text{out}}[n^{\text{inp}}] - n^{\text{inp}}$$

minimise the residual

$G$ preconditioning matrix damping low $G$
Iterative Improvement of the Density $n(r)$

**Input density matrix**

\[ \mathbf{P}_{\alpha\beta}^{\text{in}} \rightarrow n_{\text{in}}^{\text{in}}(r) \]

**Update of KS Hamiltonian**

**Diagonalization plus iterative refinement**

\[ C_n \in_n \]

**Calculation of Fermi energy and occupations**

\[ E_f f_n \]

**New density matrix**

\[ \mathbf{P}_{\alpha\beta}^{\text{out}} \rightarrow n_{\text{out}}^{\text{out}}(r) \]

**Check convergence**

\[ \max \left\{ \mathbf{P}_{\alpha\beta}^{\text{out}} - \mathbf{P}_{\alpha\beta}^{\text{in}} \right\} \]

**Density mixing**

\[ n_{\text{out}}^{\text{out}} n_{\text{in}}^{\text{in}} n_{\text{h}} \ldots \rightarrow n^{\text{new}} \]
Rhodium: Bulk and Surface

Bulk: 4x4x4
Surface: 6x6 7 layers

<table>
<thead>
<tr>
<th>Basis</th>
<th>PP</th>
<th>$a_0$ [Å]</th>
<th>$B$ [GPa]</th>
<th>$E_s$ [eV/Å²]</th>
<th>$W_f$ [eV]</th>
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<tr>
<td>3s2p2df</td>
<td>17e</td>
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<td>spd</td>
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<td>3.87</td>
<td>224.4</td>
<td>0.164</td>
<td>5.15</td>
</tr>
</tbody>
</table>

Rh(111) d-projected LDOS
**ScalAPACK for diagonalisation**

A → T → \((\lambda, q_T)\) → \(q_A\)

- **A** → **T**
  - Reduction to tridiagonal form
  - Compute eigenvalues and eigenvectors of T
  - Transform eigenvectors

**Polypeptide peptide**

- 1003 atoms
- 3410 MOS
- 27069 BSf

![Polyalanine peptide](image)

**Pdsyevd (ESSL) on IBM BGP**

- **(B)** Tridiagonalization
- **(C)** Solution
- **(A)** Cholesky 1
- **(D)** Back trans.
- **(E)** Cho. 2

**Wall clock time [s]**

![Graph showing wall clock time vs. number of processor cores]

- **576 Cu, nao=14400, Nelect.=6336, k of eigen-pairs=3768**

<table>
<thead>
<tr>
<th>nprocs</th>
<th>syevd</th>
<th>syevr</th>
<th>Cholesky</th>
</tr>
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<tr>
<td>32</td>
<td>106 (49%)</td>
<td>72 (40%)</td>
<td>38 (21%)</td>
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<tr>
<td>64</td>
<td>69 (46%)</td>
<td>48 (37%)</td>
<td>34 (26%)</td>
</tr>
<tr>
<td>128</td>
<td>41 (41%)</td>
<td>29 (34%)</td>
<td>23 (28%)</td>
</tr>
<tr>
<td>256</td>
<td>35 (41%)</td>
<td>26 (34%)</td>
<td>24 (32%)</td>
</tr>
</tbody>
</table>

**Syevd**: D&C
**Syevr**: MRRR

**Time x SCF, on CRAY XE6**

- >70% in eigenvalue solver
- Poor scaling
Improved efficiency by a two-step transformation and back transformation

![Diagram showing the two-step strategy and its components](image)

**Two-step Strategy**

1. **Reduction to tridiagonal form**
2. **Compute eigenvalues and eigenvectors of T**
3. **Transform eigenvectors**

**Algorithmic paths for eigenproblems**

- **Improved with ELPA**
  - Efficient tridiagonalization
  - Better scaling
  - Complex, mainly BLAS 3, "cheap"
  - Two-step variant with better scaling and improved robustness

**Benchmark results**

- **CRAY XE6**
  - N atom = 2116; Nel = 16928; nmo = 10964; nao = 31740
  - Total time for 12 SCF

- **BG-P**
  - N atom = 480; Nel = 6000; nmo = 7400; nao = 14240
  - Total time for 12 SCF
Large metallic systems

hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab

graph./Ru(0001) Superstructure
25x25 g on 23x23 Ru

Slab 12x12 Rh(111) slab, \( a_0 = 3.801 \text{ Å} \), 1 layer hBN 13x13
- 4L: 576Rh + 169BN: \( \text{Nao}=19370 \); \( \text{ Nel}=11144 \)
- 7L: 1008Rh + 338BN: \( \text{Nao}=34996 \); \( \text{ Nel}=19840 \)

Structure opt. > 300 iterations => 1÷2 week on 512 cores

~ 25 days per structure optimisation, on 1024 cpus
&SCF
  SCF_GUESS ATOMIC
  MAX_SCF  50
  EPS_SCF  1.0e-7
  EPS_DIIS  1.0e-7
&SMEAR
  METHOD FERMI_DIRAC
    ELECTRONIC_TEMPERATURE  500.
&END SMEAR
&MIXING
  METHOD BROYDEN_MIXING
    ALPHA  0.6
    BETA  1.0
    NBROYDEN  15
&END MIXING
  ADDED_MOS  20 20
&END SCF

&XC
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  &END
  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
    &PAIR_POTENTIAL
      TYPE DFTD3
      PARAMETER_FILE_NAME dftd3.dat
      REFERENCE_FUNCTIONAL PBE
    &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
  &END XC