Zurich, July 12th 2017

CP2K :
GPW and GAPW

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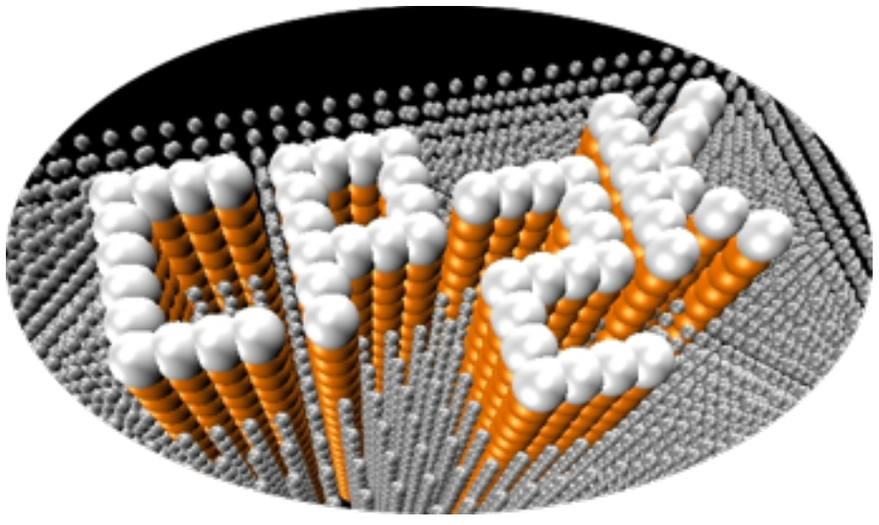


http://www.cp2k.org

Basis Set Representation

KS matrix formulation when the wavefunction is expanded into a basis

System size {N_{el}, M}, **P** [MxM], **C** [MxN]

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

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

$$\mathbf{P} = \mathbf{PSP}$$

Variational principle Constrained minimisation problem

KS total energy

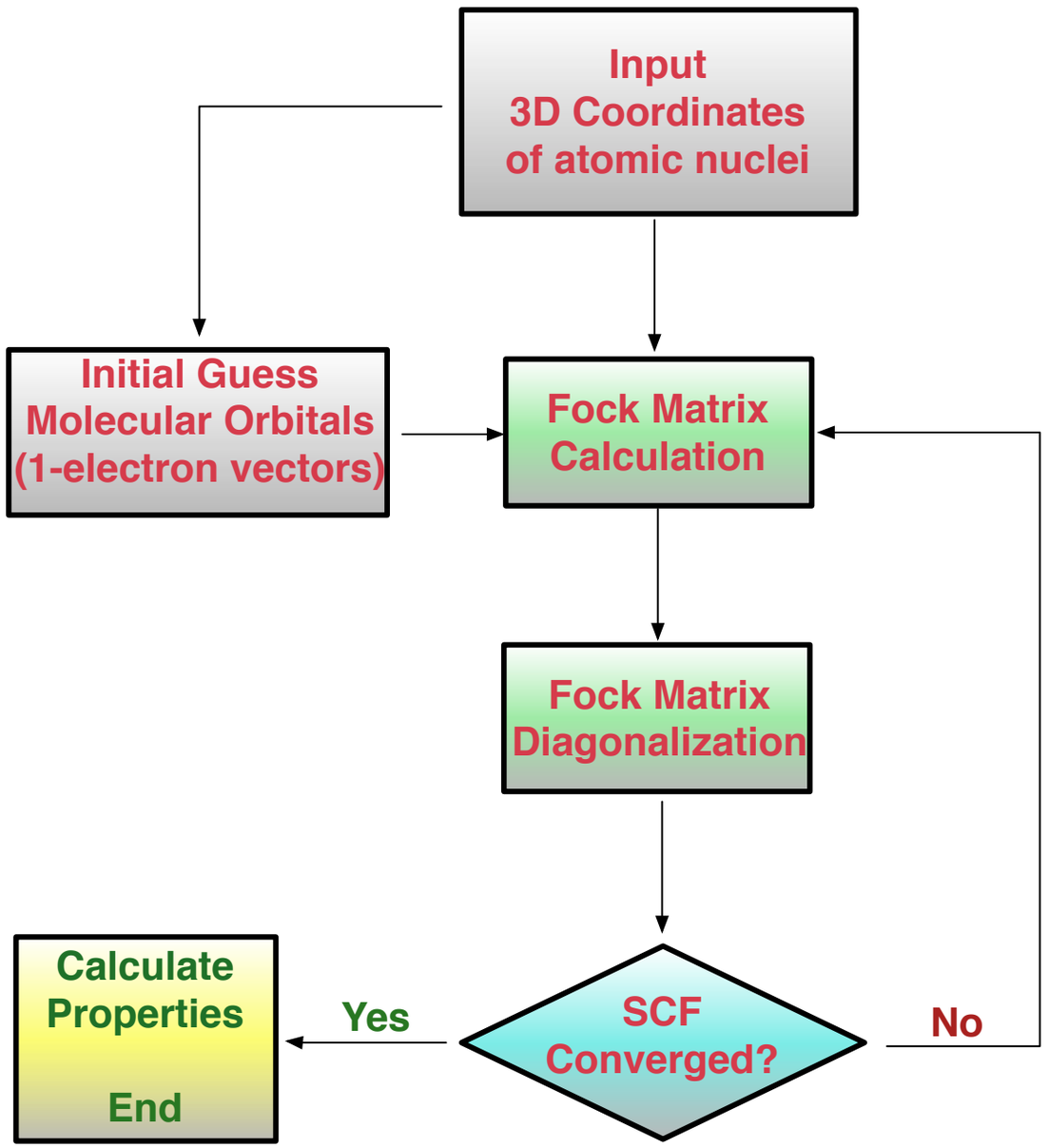
$$E[\{\psi_i\}] = T[\{\psi_i\}] + E^{\mathrm{ext}}[n] + E^{\mathrm{H}}[n] + E^{\mathrm{XC}}[n] + E^{II}$$

Matrix formulation of the KS equations

$$\mathbf{K}(C)\mathbf{C} = \mathbf{T}(C) + \mathbf{V}_{\mathrm{ext}}(C) + \mathbf{E}^{\mathrm{H}}(C) + \mathbf{E}^{\mathrm{xc}}(C) = \mathbf{SC}\varepsilon$$

Self-consistency

- Generate a starting density ⇒ n^{init}
- Generate the KS potential ⇒ V_{KS}^{init}
- Solve the KS equations ⇒ ϵ , ψ
- Calculate the new density ⇒ n^{1}
- New KS potential ⇒ V_{KS}^{1}
- New orbitals and energies ⇒ ϵ^{1} , ψ
- New density ⇒ n^{2}
- .....



until self-consistency to required precision

Classes of Basis Sets

- Extended basis sets, **PW** : condensed matter
- Localised basis sets centred at atomic positions, **GTO**

Idea of GPW: auxiliary basis set to represent the density

- Mixed (GTO+PW) to take best of two worlds, **GPW**
- Augmented basis set, **GAPW**: separated hard and soft density domains

GPW Ingredients

linear scaling KS matrix computation for GTO

- Gaussian basis sets (many terms analytic)

$$\psi_i(\mathbf{r}) = \sum_\alpha C_{\alpha i}\phi_\alpha(\mathbf{r}) \qquad \phi_\alpha(\mathbf{r}) = \sum_m d_{m\alpha} g_m(\mathbf{r}) \qquad g_m(\mathbf{r}) = x^{m_x} y^{m_y} z^{m_z} e^{-\alpha_m r^2}$$

- 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

Gaussian Basis Set

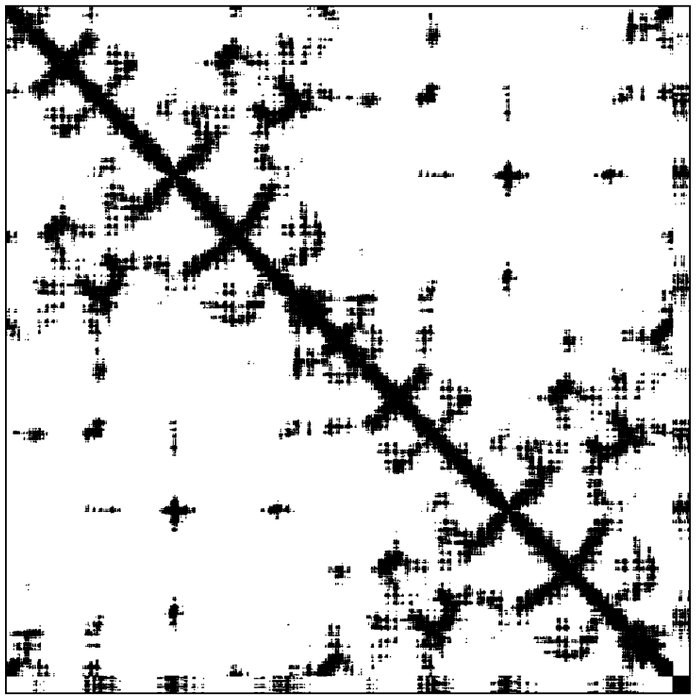
- Localised, atom-position dependent GTO basis

$$\varphi_\mu(\mathbf{r}) = \sum_m d_{m\mu} g_m(\mathbf{r})$$

- Expansion of the density using the density matrix

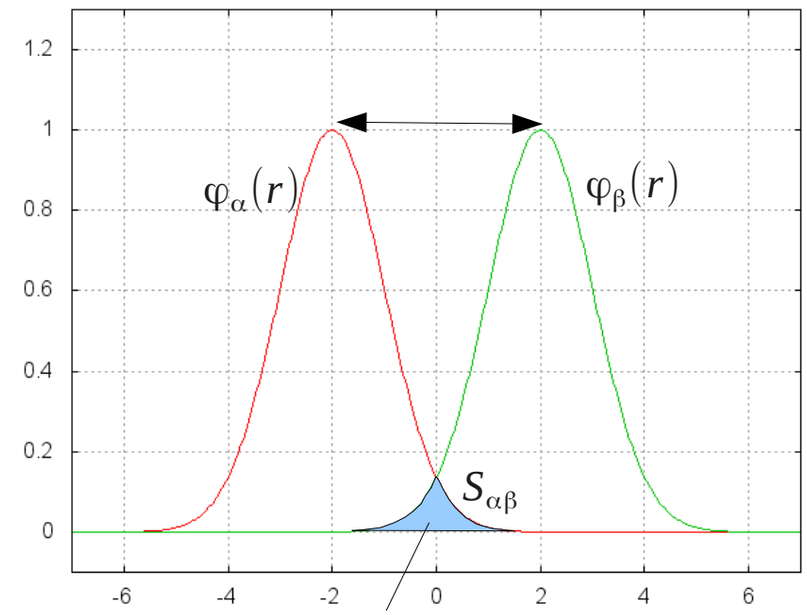
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu^*(\mathbf{r})$$

Operator matrices are sparse



$$S_{\mu\nu} = \int \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) d\mathbf{r}$$

$$H_{\mu\nu} = \int \varphi_\mu(\mathbf{r}) V(r) \varphi_\nu(\mathbf{r}) d\mathbf{r}$$



Analytic Integrals

Cartesian Gaussian

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

$$l = n_x + n_y + n_z \qquad (l+1)(l+2)/2$$

Differential relations

$$\frac{\partial}{\partial R_i}|\mathbf{n}) = 2\eta|\mathbf{n}+\mathbf{1}_i) - n_i|\mathbf{n}-\mathbf{1}_i)$$

$$\frac{\partial}{\partial R_i}|\mathbf{n}) = -\frac{\partial}{\partial r_i}|\mathbf{n})$$

Obara-Saika recursion relations

$$(\mathbf{0}_a|\mathcal{O}(\mathbf{r})|\mathbf{0}_b) \Rightarrow (\mathbf{a}+\mathbf{1}_i|\mathcal{O}(\mathbf{r})|\mathbf{b})$$

Obara and Saika JCP 84 (1986), 3963

Basis Set library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

```
O  6-31Gx 6-31G*
4
1  0  0  6  1
   5484.67170000      0.00183110
    825.23495000      0.01395010
    188.04696000      0.06844510
     52.96450000      0.23271430
     16.89757000      0.47019300
      5.79963530      0.35852090
1  0  1  3  1  1
     15.53961600     -0.11077750      0.07087430
      3.59993360     -0.14802630      0.33975280
      1.01376180      1.13076700      0.72715860
1  0  1  1  1  1
      0.27000580      1.00000000      1.00000000
1  2  2  1  1
      0.80000000      1.00000000
```

```
O  SZV-GTH
1
2 0 1 4 1 1
   8.3043855492   0.1510165999  -0.0995679273
   2.4579484191  -0.0393195364  -0.3011422449
   0.7597373434  -0.6971724029  -0.4750857083
   0.2136388632  -0.3841133622  -0.3798777957
#
O  DZVP-GTH
2
2 0 1 4 2 2
   8.3043855492   0.1510165999   0.0000000000  -0.0995679273   0.0000000000
   2.4579484191  -0.0393195364   0.0000000000  -0.3011422449   0.0000000000
   0.7597373434  -0.6971724029   0.0000000000  -0.4750857083   0.0000000000
   0.2136388632  -0.3841133622   1.0000000000  -0.3798777957   1.0000000000
3 2 2 1 1
   1.1850000000   1.0000000000
#
O  TZVP-GTH
2
2 0 1 4 3 3
  10.2674419938   0.2989598460   0.0000000000   0.0000000000  -0.0595856940   0.0000000000   0.0000000000
   3.7480495696   0.1941178339   0.0000000000   0.0000000000  -0.1875649045   0.0000000000   0.0000000000
   1.3308337704  -0.3808255700   0.0000000000   0.0000000000  -0.3700703718   0.0000000000   0.0000000000
   0.4556802254  -0.6232449802   1.0000000000   0.0000000000  -0.4204922615   1.0000000000   0.0000000000
   0.1462920596  -0.1677863491   0.0000000000   1.0000000000  -0.2313901687   0.0000000000   1.0000000000
3 2 2 1 1
   1.1850000000   1.0000000000
```

```
O  SZV-MOLOPT-GTH SZV-MOLOPT-GTH-q6
1
2 0 1 7 1 1
  12.015954705512 -0.060190841200  0.036543638800
   5.108150287385 -0.129597923300  0.120927648700
   2.048398039874  0.118175889400  0.251093670300
   0.832381575582  0.462964485000  0.352639910300
   0.352316246455  0.450353782600  0.294708645200
   0.142977330880  0.092715833600  0.173039869300
   0.046760918300 -0.000255945800  0.009726110600
#
O  DZVP-MOLOPT-GTH DZVP-MOLOPT-GTH-q6
1
2 0 2 7 2 2 1
  12.015954705512 -0.060190841200  0.065738617900  0.036543638800 -0.034210557400  0.014807054400
   5.108150287385 -0.129597923300  0.110885902200  0.120927648700 -0.120619770900  0.068186159300
   2.048398039874  0.118175889400 -0.053732406400  0.251093670300 -0.213719464600  0.290576499200
   0.832381575582  0.462964485000 -0.572670666200  0.352639910300 -0.473674858400  1.063344189500
   0.352316246455  0.450353782600  0.186760006700  0.294708645200  0.484848376400  0.307656114200
   0.142977330880  0.092715833600  0.387201458600  0.173039869300  0.717465919700  0.318346834400
   0.046760918300 -0.000255945800  0.003825849600  0.009726110600  0.032498979400 -0.005771736600
#
O  TZVP-MOLOPT-GTH TZVP-MOLOPT-GTH-q6
1
2 0 2 7 3 3 1
  12.015954705512 -0.060190841200  0.065738617900  0.041006765400  0.036543638800 -0.034210557400 -0.000592640200  0.014807054400
   5.108150287385 -0.129597923300  0.110885902200  0.080644802300  0.120927648700 -0.120619770900  0.009852349400  0.068186159300
   2.048398039874  0.118175889400 -0.053732406400 -0.067639801700  0.251093670300 -0.213719464600  0.001286509800  0.290576499200
   0.832381575582  0.462964485000 -0.572670666200 -0.435078312800  0.352639910300 -0.473674858400 -0.021872639500  1.063344189500
   0.352316246455  0.450353782600  0.186760006700  0.722792798300  0.294708645200  0.484848376400  0.530504764700  0.307656114200
   0.142977330880  0.092715833600  0.387201458600 -0.521378340700  0.173039869300  0.717465919700 -0.436184043700  0.318346834400
   0.046760918300 -0.000255945800  0.003825849600  0.175643142900  0.009726110600  0.032498979400  0.073329259500 -0.005771736600
```

```
O  6-31Gxx 6-31G**
4
1  0  0  6  1
   5484.67170000      0.00183110
    825.23495000      0.01395010
    188.04696000      0.06844510
     52.96450000      0.23271430
     16.89757000      0.47019300
      5.79963530      0.35852090
1  0  1  3  1  1
     15.53961600     -0.11077750      0.07087430
      3.59993360     -0.14802630      0.33975280
      1.01376180      1.13076700      0.72715860
1  0  1  1  1  1
      0.27000580      1.00000000      1.00000000
1  2  2  1  1
      0.80000000      1.00000000
```

```
O  6-311++G3df3pd    6-311++G(3df,3pd)
9
1  0  0  6  1
   8588.50000000       0.00189515
   1297.23000000       0.01438590
    299.29600000       0.07073200
     87.37710000       0.24000100
     25.67890000       0.59479700
      3.74004000       0.28080200
1  0  1  3  1  1
     42.11750000       0.11388900        0.03651140
      9.62837000       0.92081100        0.23715300
      2.85332000      -0.00327447        0.81970200
1  0  1  1  1  1
      0.90566100       1.00000000        1.00000000
1  0  1  1  1  1
      0.25561100       1.00000000        1.00000000
1  2  2  1  1
      5.16000000       1.00000000
1  2  2  1  1
      1.29200000       1.00000000
1  2  2  1  1
      0.32250000       1.00000000
1  0  1  1  1  1
      0.08450000       1.00000000        1.00000000
```

GTO in CP2K

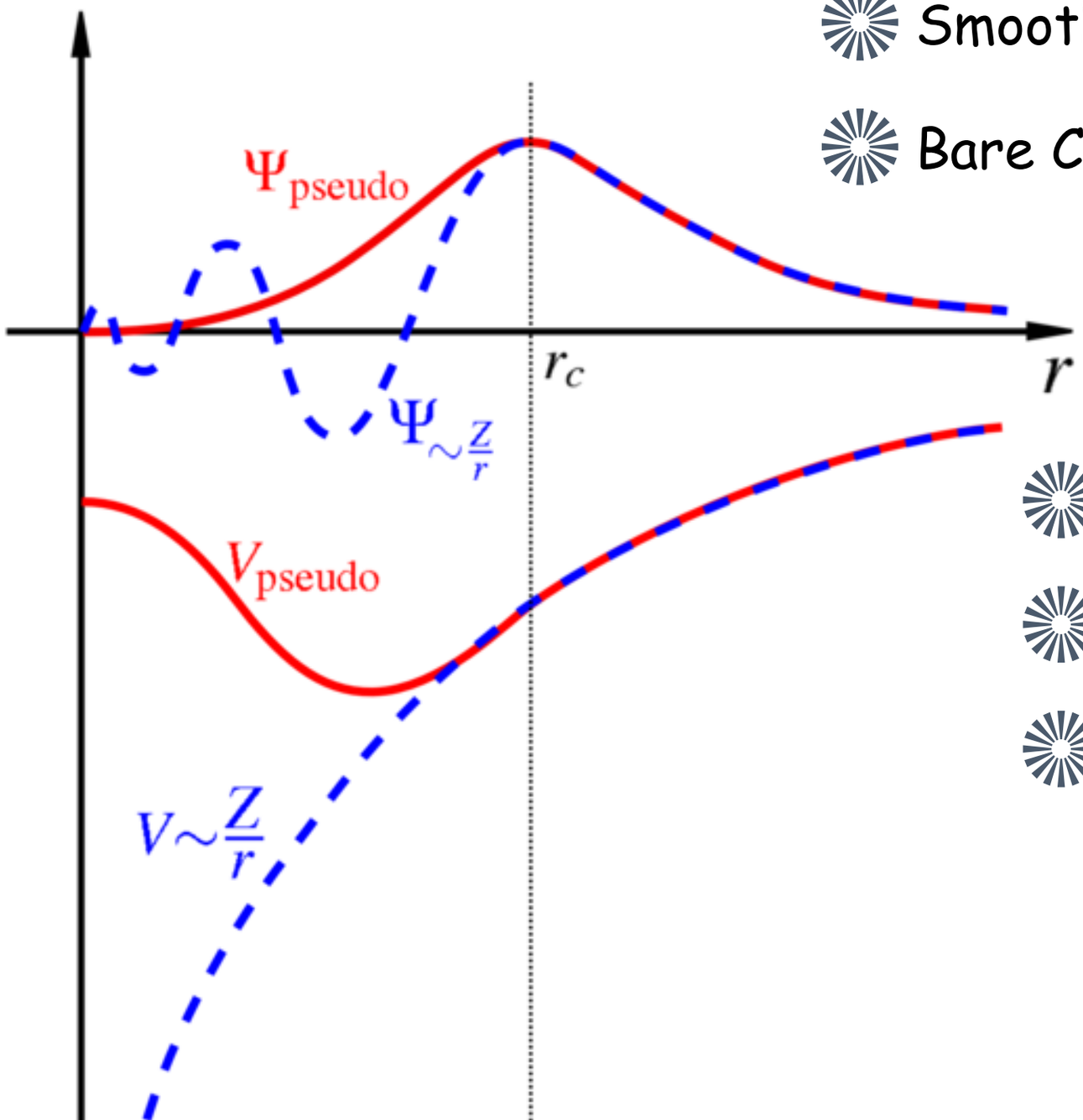
The repository contains several GTO libraries

cp2k/data/

ALL_BASIS_SETS	**BASIS_RI_cc-TZ**	GTH_POTENTIALS	dftd3.dat
ALL_POTENTIALS	**BASIS_SET**	**HFX_BASIS**	nm12_parameters.xml
BASIS_ADMM	**BASIS_ZIJLSTRA**	HF_POTENTIALS	rVV10_kernel_table.dat
BASIS_ADMM_MOLOPT	DFTB	MM_POTENTIAL	t_c_g.dat
BASIS_LRIGPW_AUXMOLOPT	ECP_POTENTIALS	NLCC_POTENTIALS	t_sh_p_s_c.dat
BASIS_MOLOPT	**EMSL_BASIS_SETS**	POTENTIAL	vdW_kernel_table.dat
BASIS_MOLOPT_UCL	GTH_BASIS_SETS	README	

Tools for the optimisation of GTO basis sets are available in cp2k, based on atomic and molecular electronic structure calculations

Pseudopotentials



- Core electrons are eliminated $Z_V=Z-Z_{core}$
- 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

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

analytically

part of ES

- Non-Local PP with Gaussian type projectors

$$V_{\rm nl}^{\rm PP}(\mathbf{r},\mathbf{r}') = \sum_{lm}\sum_{ij} \langle \mathbf{r}|p_i^{lm}\rangle h_{ij}^{l} \langle p_j^{lm}|\mathbf{r}'\rangle$$

$$\left\langle \mathbf{r} \mid p_i^{lm} \right\rangle = N_i^l \; Y^{lm}(\hat{r}) \; r^{(l+2i-2)} \; e^{-\frac{1}{2}\left(\frac{r}{r_l}\right)^2}$$

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

Accurate and Transferable

Scalar relativistic

Few parameters

Electrostatic Energy

Periodic system

$$E_{\rm ES} = \int V_{\rm loc}^{\rm PP}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + 2\pi\Omega \sum_{\mathbf{G}} \frac{\tilde{n}^*(\mathbf{G})\tilde{n}(\mathbf{G})}{G^2} + \frac{1}{2}\sum_{A\neq B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

total charge distribution including n(r) and Z

$$n_{\rm tot}(\mathbf{r}) = n(\mathbf{r}) + \sum_A n_A(\mathbf{r})$$

$$n_A(\mathbf{r}) = -\frac{Z_A}{(r_A^c)^3}\pi^{-3/2}\, e^{\left(\frac{\mathbf{r}-\mathbf{R}_A}{r_A^c}\right)}$$

$$V_{\rm core}^A(\mathbf{r}) = -\frac{Z_A}{|\mathbf{r}-\mathbf{R}_A|}\,{\rm erf}\left(\frac{|\mathbf{r}-\mathbf{R}_A|}{r_A^c}\right)$$

$$r_A^c = \sqrt{2}\, r_{{\rm loc}A}^{\rm PP}$$

cancels the long range term of local PP

$$E_{\rm ES} = \int V_{\rm loc}^{\rm SR}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2}\int\int \frac{n_{\rm tot}(\mathbf{r}) n_{\rm tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$E^H[n_{tot}]$ long range smooth

$$+ \frac{1}{2}\sum_{A\neq B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}\,{\rm erfc}\left[\frac{|\mathbf{R}_A - \mathbf{R}_B}{\sqrt{(r_A^c)^2 + (r_B^c)^2}}\right] - \sum_A \frac{1}{\sqrt{2\pi}}\frac{Z_A^2}{r_A^c}$$

E^{ov} short range, pair

E^{self}

Auxiliary Basis Set

- Long range term : Non-local Hartree potential

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

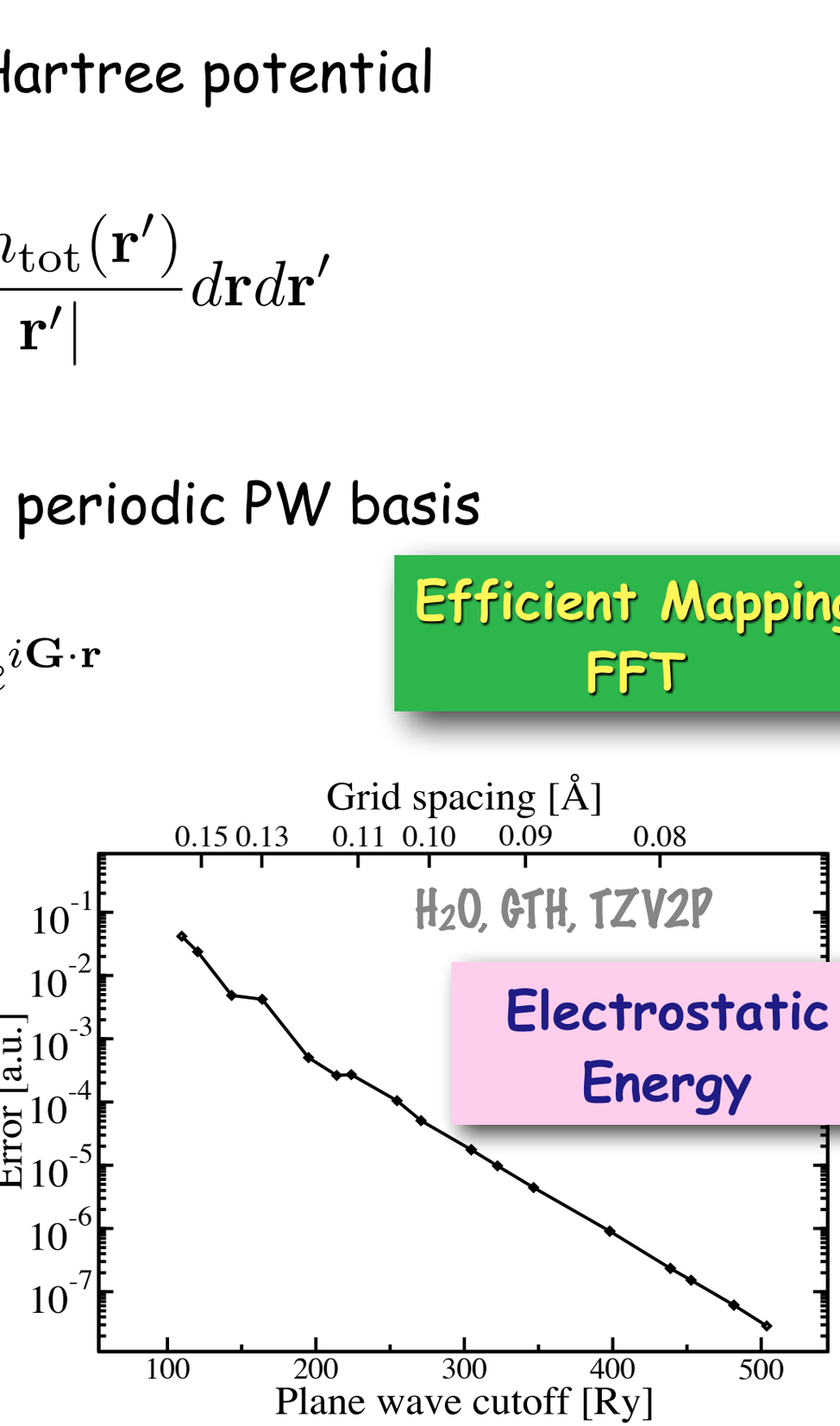
- Orthogonal, unbiased, naturally periodic PW basis

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

Efficient Mapping FFT

Linear scaling solution of the P

$$E^{\mathrm{H}}[n_{\mathrm{tot}}] = 2\pi\Omega\sum_{\mathbf{G}} \frac{\tilde{n}^{*}_{\mathrm{tot}}(\mathbf{G}}{(}$$



Electrostatic Energy

Real Space Integration

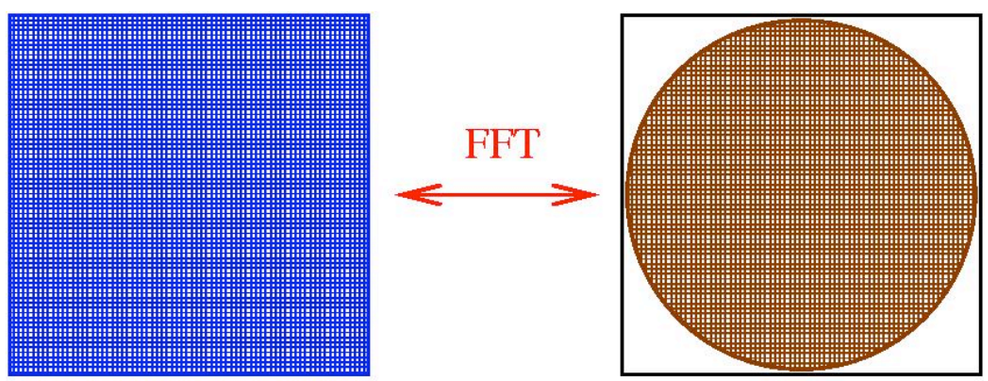
Finite cutoff and simulation box define a real space grid

- Density collocation

$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) \rightarrow \sum_{\mu\nu} P_{\mu\nu}\bar{\varphi}_{\mu\nu}(\mathbf{R}) = n(\mathbf{R})$$

Screening Truncation

$$\hat{n}(\mathbf{G}) \rightarrow V_H(\mathbf{G}) = \frac{\hat{n}(\mathbf{G})}{G^2} \rightarrow V_H(\mathbf{R})$$



- Numerical approximation of the gradient $n(\mathbf{R}) \rightarrow \nabla n(\mathbf{R})$
- ϵ_{XC} and derivatives evaluated on the grid $v_{XC}[n](\mathbf{r}) \rightarrow V_{XC}(\mathbf{R}) = \frac{\partial \epsilon_{xc}}{\partial n}(\mathbf{R})$
- Real space integration $H^{\mu\nu}_{HXC} = \langle\mu|V_{HXC}(\mathbf{r})|\nu\rangle \rightarrow \sum_R V_{HXC}(R)\varphi'_{\mu\nu}(R)$

G. Lippert et al, Molecular Physics, 92, 477, 1997
J. VandeVondele et al, Comp. Phys. Comm.,167 (2), 103, 2005

Multiple Grids

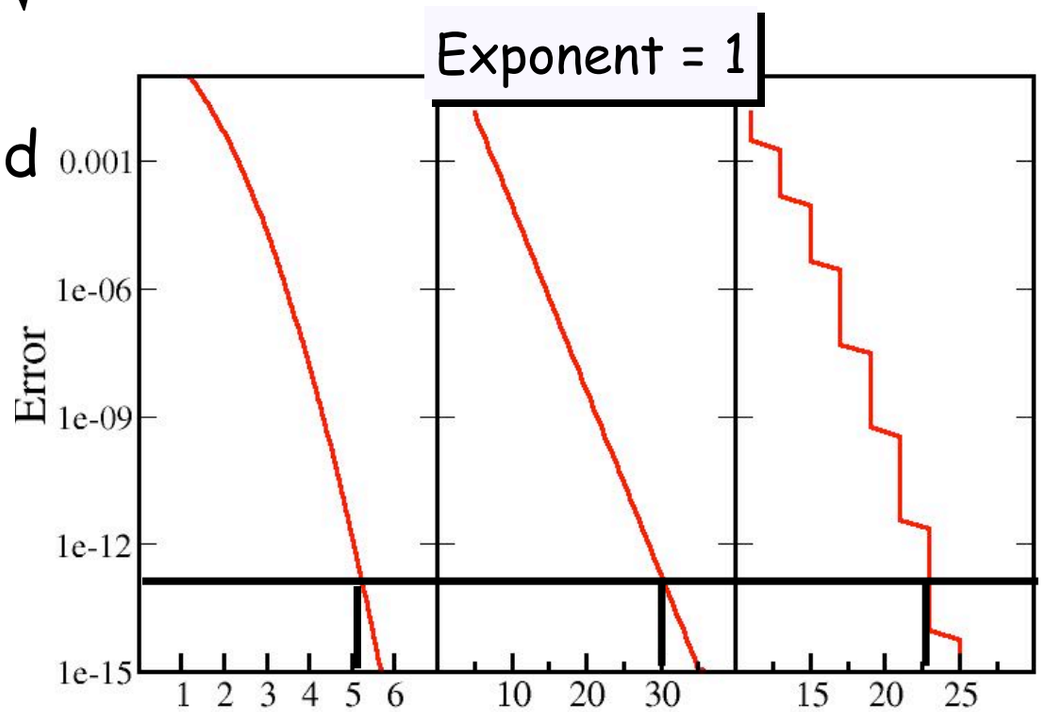
$$E^i_{\rm cut} = \frac{E^1_{\rm cut}}{\alpha^{(i-1)}}, \qquad i = 1..N$$

the exponent of Gaussian product selects the grid

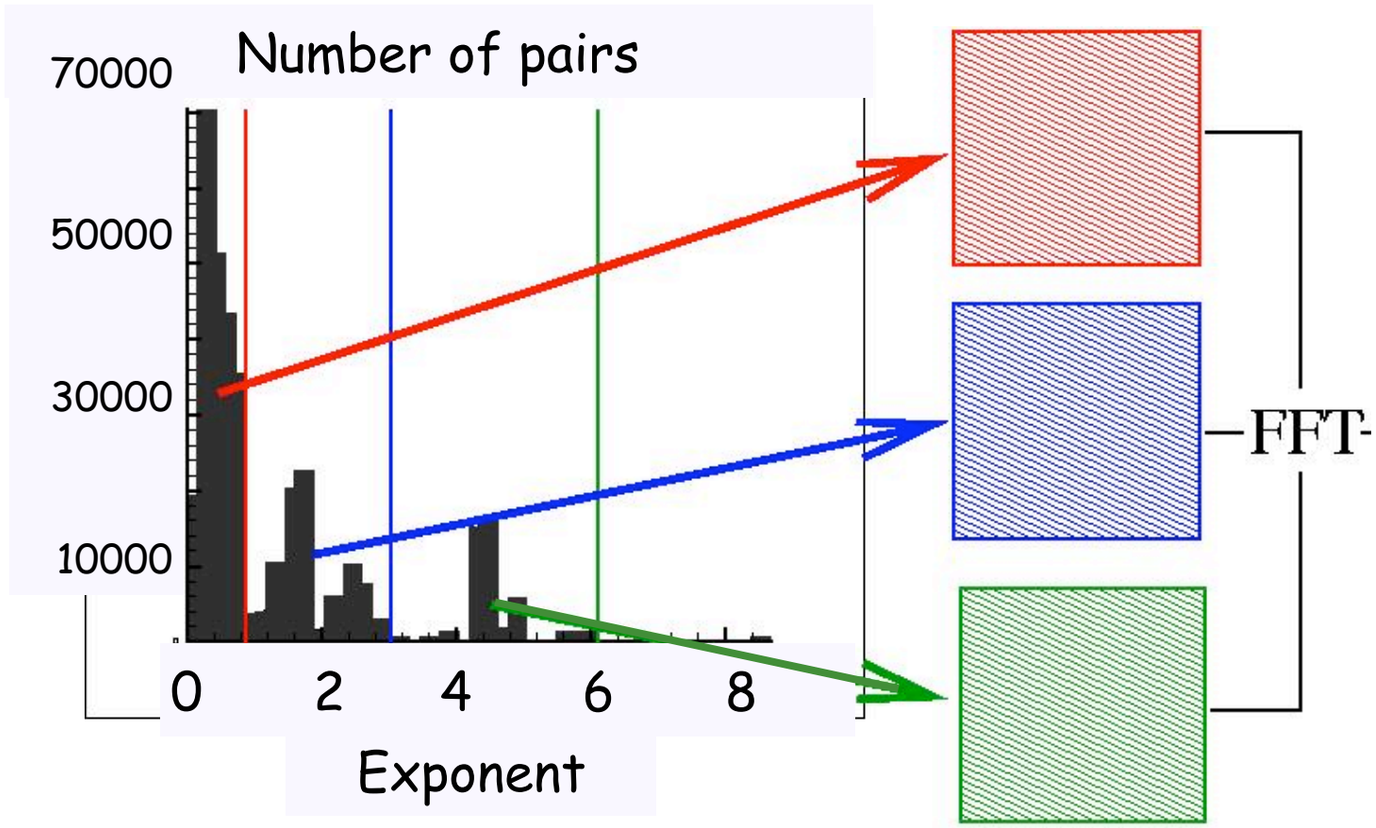
number of grid points is exponent-independent

$$\sigma_p^2 = 1/2\eta_p$$

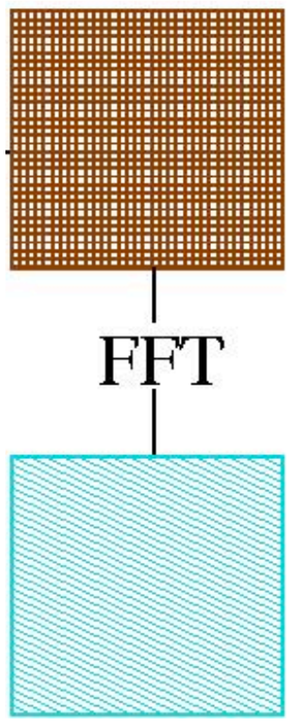
Accuracy
=> Relative Cutoff
~30 Ry



Integration range	Cutoff (Ry)	Integration Points



$$n_j^f = I_j(n_i^c)$$



Analysis of Multigrid

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

```
-------------------------------------------------------------------------------
----                          MULTIGRID INFO                                 ----
-------------------------------------------------------------------------------
count for grid        1:          2720          cutoff [a.u.]          50.00
count for grid        2:          5000          cutoff [a.u.]          16.67
count for grid        3:          2760          cutoff [a.u.]           5.56
count for grid        4:            16          cutoff [a.u.]           1.85
total gridlevel count  :         10496
```

Changing E_{cut} from 50 to 500 Ry

```
# REL_CUTOFF = 60
# Cutoff (Ry) | Total Energy (Ha) | NG on grid 1 | NG on grid 2 | NG on grid 3 | NG on grid 4
     50.00     -32.3795329864            5048         5432           16            0
    100.00     -32.3804557631            2720         5000         2760           16
    150.00     -32.3804554850            2032         3016         5432           16
    200.00     -32.3804554982            1880         2472         3384         2760
    250.00     -32.3804554859             264         4088         3384         2760
    300.00     -32.3804554843             264         2456         5000         2776
    350.00     -32.3804554846              56         1976         5688         2776
    400.00     -32.3804554851              56         1976         3016         5448
    450.00     -32.3804554851               0         2032         3016         5448
    500.00     -32.3804554850               0         2032         3016         5448
```

GPW Functional

$$
\begin{aligned}
E^{\mathrm{el}}[n] &= \sum_{\mu\nu} P_{\mu\nu} \left\langle \varphi_\mu \left| -\frac{1}{2}\nabla^2 + V_{\mathrm{loc}}^{\mathrm{SR}} + V_{\mathrm{nl}} \right| \varphi_\nu \right\rangle \\
&+ 2\pi\Omega \sum_{\mathbf{G}} \frac{\tilde{n}^*_{\mathrm{tot}}(\mathbf{G})\tilde{n}_{\mathrm{tot}}(\mathbf{G})}{\mathbf{G}^2} + \sum_{\mathbf{R}} \tilde{n}(\mathbf{R}) V^{\mathrm{XC}}(\mathbf{R}) \\
&= \sum_{\mu\nu} P_{\mu\nu} \left(\left\langle \varphi_\mu \left| -\frac{1}{2}\nabla^2 + V^{\mathrm{ext}} \right| \varphi_\nu \right\rangle + \sum_{\mathbf{R}} V_{\mu\nu}^{\mathrm{HXC}}(\mathbf{R}) \varphi'_{\mu\nu}(\mathbf{R}) \right)
\end{aligned}
$$

Linear scaling KS matrix construction

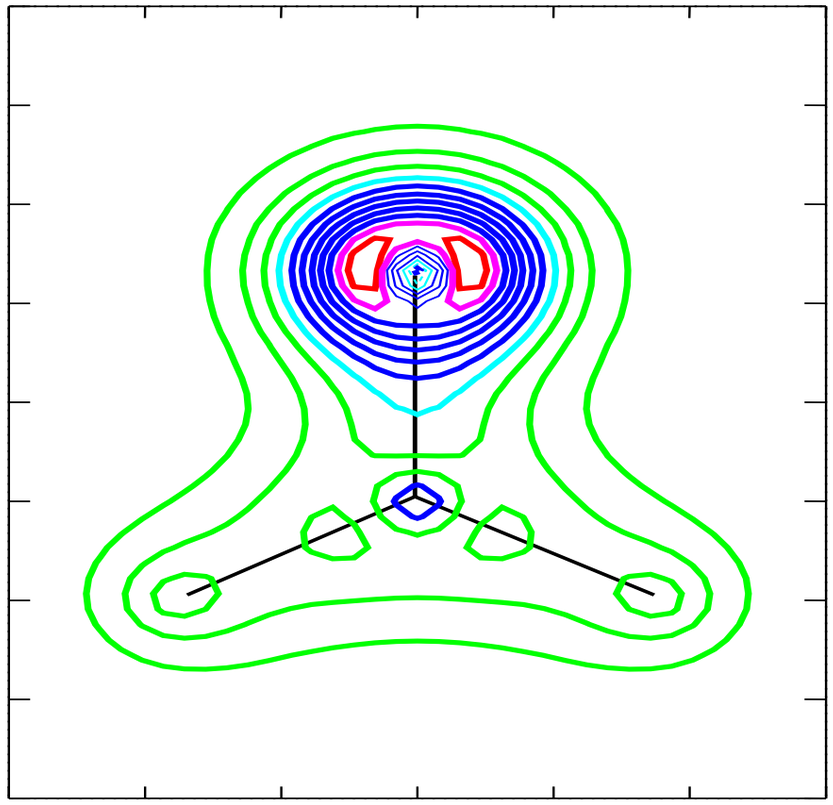
CP2K DFT input

```
&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
     O   0.000000    0.000000   -0.065587
     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
```

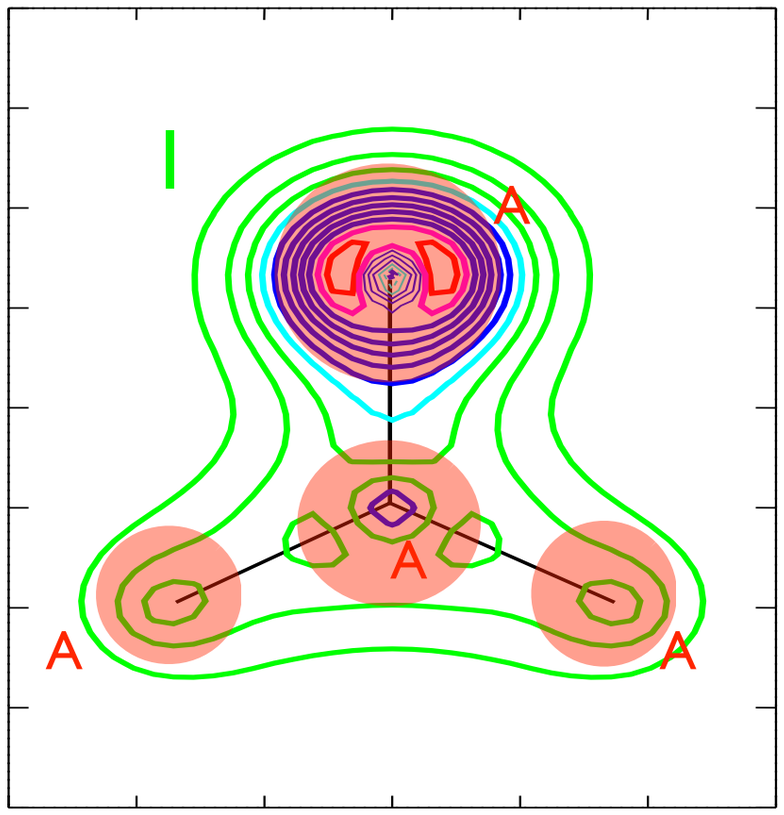
Hard and Soft Densities



Formaldehyde

- Pseudopotential ⇨ frozen core
- Augmented PW ⇨ separate regions (matching at edges)
  LAPW, LMTO (OK Andersen, PRB **12**, 3060 (1975)
- Dual representation ⇨ localized orbitals and PW
  PAW (PE Bloechl, PRB, **50**, 17953 (1994))

Partitioning of the Density



$$n = \tilde{n} + \sum_A n_A - \sum_A \tilde{n}_A$$

$$\left.\begin{array}{rcl} n(\mathbf{r}) & - & \tilde{n}(\mathbf{r}) = 0 \\ n_A(\mathbf{r}) & - & \tilde{n}_A(\mathbf{r}) = 0 \end{array}\right\} \mathbf{r} \in I$$

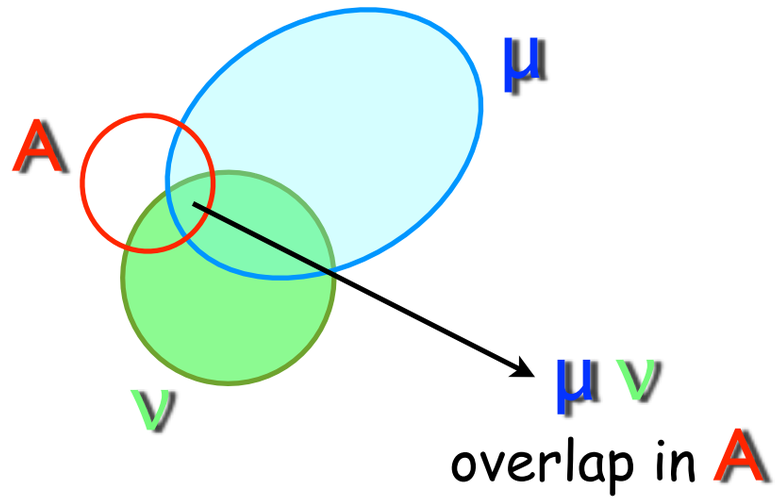
$$\left.\begin{array}{rcl} n(\mathbf{r}) & - & n_A(\mathbf{r}) = 0 \\ \tilde{n}(\mathbf{r}) & - & \tilde{n}_A(\mathbf{r}) = 0 \end{array}\right\} \mathbf{r} \in A$$

$$n_A(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi^A_\mu \chi^A_\nu \qquad \tilde{n}(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \tilde{\varphi}_\mu \tilde{\varphi}_\nu \rightarrow \sum_{\mathbf{G}} \hat{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{R}}$$

Gaussian Augmented Plane Waves

Local Densities

$$n_A(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_\mu^A \chi_\nu^A$$



X_μ projection of φ_μ in Ω_A
through atom-dependent d'

$$\chi_\mu = \sum_\alpha d'^A_{\mu\alpha} \; g_\alpha(\mathbf{r})$$

projector basis (same size)

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

$$n_A(\mathbf{r}) = \sum_{\alpha\beta} \left[\sum_{\mu\nu} P_{\mu\nu} d'^A_{\mu\alpha} d'^A_{\nu\beta} \right] g_\alpha(\mathbf{r}) g_\beta(\mathbf{r}) = \sum_{\alpha\beta} P'^A_{\alpha\beta} \; g_\alpha(\mathbf{r}) g_\beta(\mathbf{r})$$

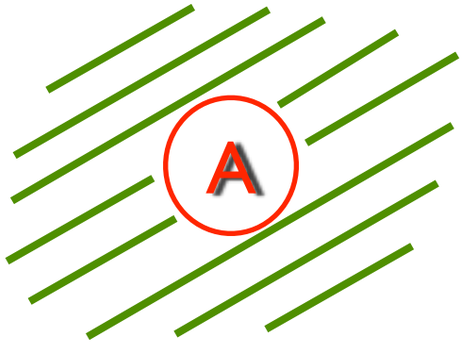
Density Dependent Terms: XC

Semi-local functionals like local density approximation, generalised gradient approximation or meta-functionals

Gradient:

$$\nabla n(\mathbf{r}) = \nabla \tilde{n}(\mathbf{r}) + \sum_A \nabla n_A(\mathbf{r}) - \sum_A \nabla \tilde{n}_A(\mathbf{r})$$

$$E[n] = \int V_{loc}(\mathbf{r}) n(\mathbf{r}) = \int \left\{ \tilde{V}_{loc}(\mathbf{r}) + \sum_A V^A_{loc}(\mathbf{r}) + \sum_A \tilde{V}^A_{loc}(\mathbf{r}) \right\}$$

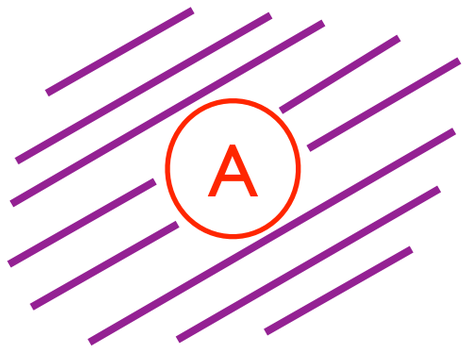


$$\times \left\{ \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \right\} d\mathbf{r}$$

$$= \int \left\{ \tilde{V}_{loc}(\mathbf{r}) \tilde{n}(\mathbf{r}) + \sum_A V^A_{loc}(\mathbf{r}) n_A(\mathbf{r}) - \sum_A \tilde{V}^A_{loc}(\mathbf{r}) \tilde{n}_A(\mathbf{r}) \right\}$$

Density Dependent Terms: ES

Non local Coulomb operator



$$\mathbf{n^0(r)} = \sum_A \mathbf{n_A^0(r)} = \sum_A \left\{ \sum_L Q_A^L \; g_A^L(\mathbf{r}) \right\}$$

Compensation charge

Same multipole expansion as the local densities

$$\mathcal{Q}_A^L = \int \left\{ n_A(\mathbf{r}) - \tilde{n}_A(\mathbf{r}) + n_A^Z(\mathbf{r}) \right\} r^l \mathcal{Y}_{lm}(\theta\phi) r^2 dr \sin(\theta) d\theta d\phi$$

$$V[\tilde{n} + \mathbf{n}^0] + \sum_A V[n_A + n_A^Z] - \sum_A V[\tilde{n}_A + \mathbf{n}_A^0]$$

Interstitial region

Atomic region

GAPW Functionals

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

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

on global grids
via collocation + FFT

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

Analytic integrals
Local Spherical Grids

Iannuzzi, Chassaing, Hutter, Chimia (2005);
VandeVondele , Iannuzzi, Hutter, CSCM2005 proceedings

GAPW Input

```
&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


&END DFT
```

```
&SUBSYS
  ...
    &KIND O
      BASIS_SET DZVP-MOLOPT-GTH-q6
      POTENTIAL GTH-BLYP-q6
      LEBEDEV_GRID 80
      RADIAL_GRID 200
    &END KIND
    &KIND O1
      ELEMENT O
#       BASIS_SET 6-311++G2d2p
        BASIS_SET 6-311G**
        POTENTIAL ALL
        LEBEDEV_GRID 80
        RADIAL_GRID 200
      &END KIND


&END SUBSYS
```

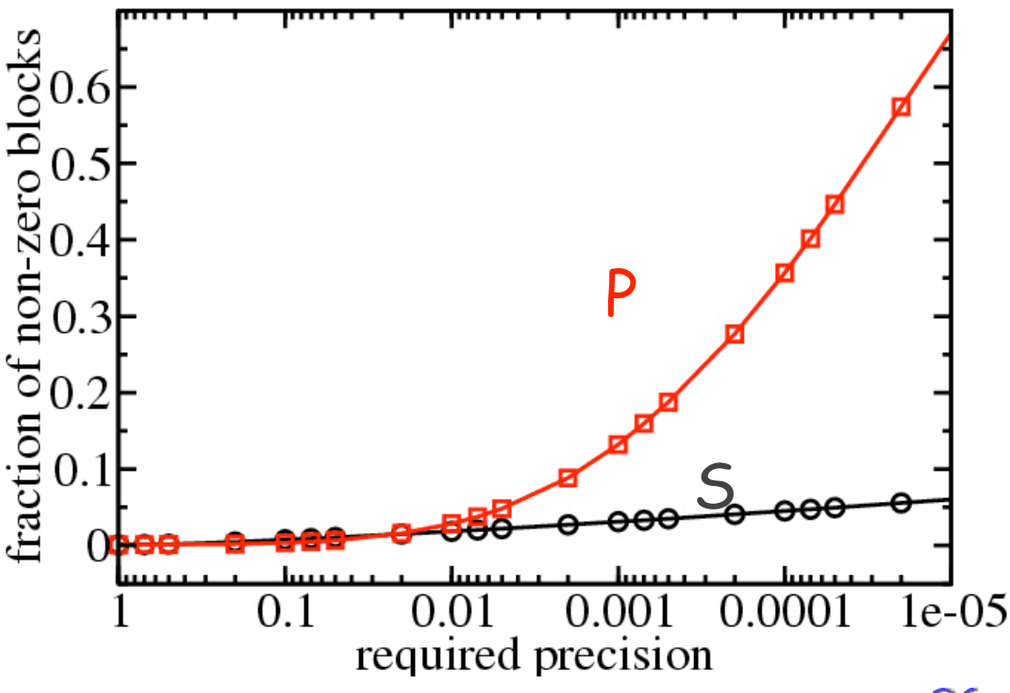
Energy Functional Minimisation

$$C^* = \arg\min_C \left\{ E(C) \ : \ C^T S C = 1 \right\}$$

- Standard: Diagonalisation + mixing (DIIS, Pulay, J. Comput. Chem. 3, 556,(1982); iterative diag. Kresse G. et al, PRB, 54(16), 11169, (1996))
- 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))

$$\mathbf{P}(\mathbf{r},\mathbf{r}') \propto e^{-c\sqrt{E_{\mathrm{gap}}}|\mathbf{r}-\mathbf{r}'|}$$

$$\mathbf{P}_{\mu\nu} = \sum_{pq} \mathbf{S}^{-1}_{\mu p} \mathbf{S}^{-1}_{q\nu} \iint \varphi_p(\mathbf{r}) \mathbf{P}(\mathbf{r},\mathbf{r}\prime) \varphi_q(\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$



Traditional Diagonalisation

Eigensolver from standard parallel program library: SCALAPACK

$$\mathbf{KC} = \mathbf{SC}\varepsilon$$

Transformation into a standard eigenvalues problem

Cholesky decomposition $\quad \mathbf{S} = U^T U \qquad \mathbf{C}' = U\mathbf{C}$

$$\mathbf{KC} = U^T U \mathbf{C}\varepsilon \quad \Rightarrow \quad \left[(U^T)^{-1}\mathbf{K}U^{-1}\right]\mathbf{C}' = \mathbf{C}'\varepsilon$$

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

DIIS for SCF convergence acceleration: few iterations

error matrix

$$\mathbf{e} = \mathbf{KPS} - \mathbf{SPK}$$

scaling ($O(M^3)$) and stability problems

Orbital Transformation Method

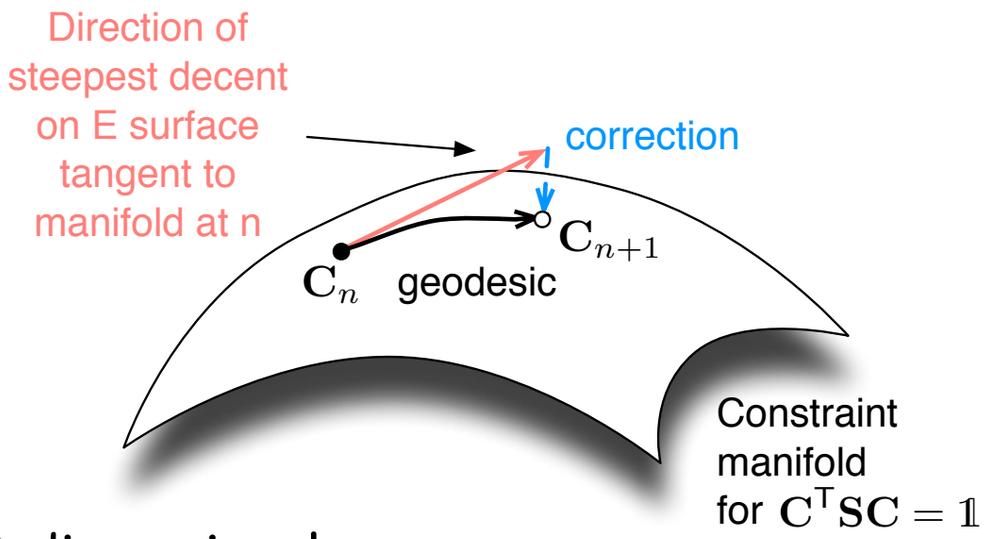
Auxiliary **X**, linearly constrained variables to parametrise the occupied subspace

not linear orthonormality constraint

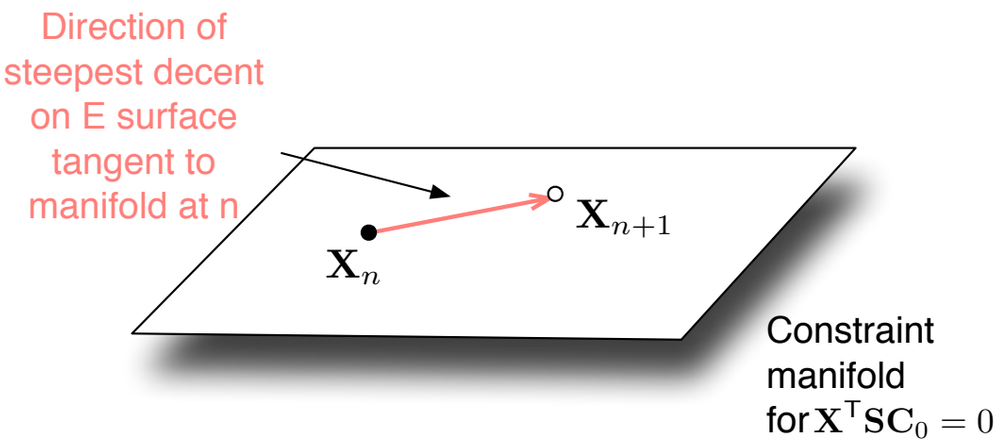
$$\mathbf{C}^T\mathbf{S}\mathbf{C} = \mathbf{I}$$

Linear constraint

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



M dimensional

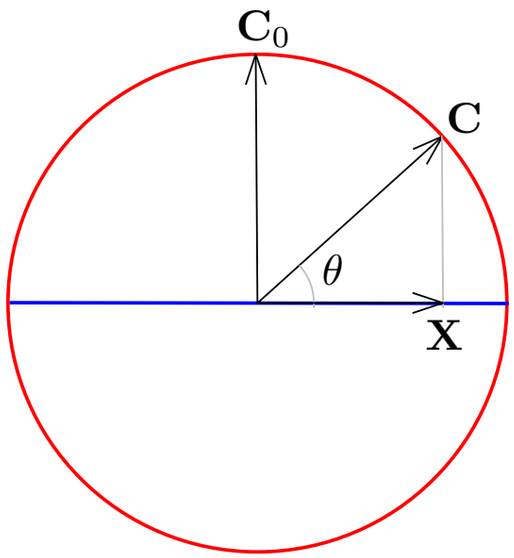


M-1 dimensional

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

$$\mathbf{U} = \left(\mathbf{X}^T\mathbf{S}\mathbf{X}\right)^{1/2}$$

matrix functionals by Taylor expansions in X^TSX



Preconditioned OT

minimisation in the auxiliary tangent space, idempotency verified

$$\frac{\partial E(\mathbf{C}(\mathbf{X})) + \mathrm{Tr}(\mathbf{X}^\dagger \mathbf{S}\mathbf{C}_0\Lambda)}{\partial \mathbf{X}} = \frac{\partial E}{\partial C}\frac{\partial \mathbf{C}}{\partial \mathbf{X}} + \mathbf{S}\mathbf{C}_0\Lambda$$

HC and SX dominated O(MN)

CG(LS) or DIIS

Preconditioned gradients

$$\mathbf{P}(\mathbf{H} - \mathbf{S}\epsilon)\mathbf{X} - \mathbf{X} \approx 0 \qquad \mathbf{X} \rightarrow \sqrt{\mathbf{P}}\mathbf{X}$$

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

ideal preconditioner $\mathbf{P}_n = (\mathbf{H} - \mathbf{S}\varepsilon_n)^{-1}$ $\varepsilon_n = \mathbf{C}_n^T \mathbf{H}\mathbf{C}_n$

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

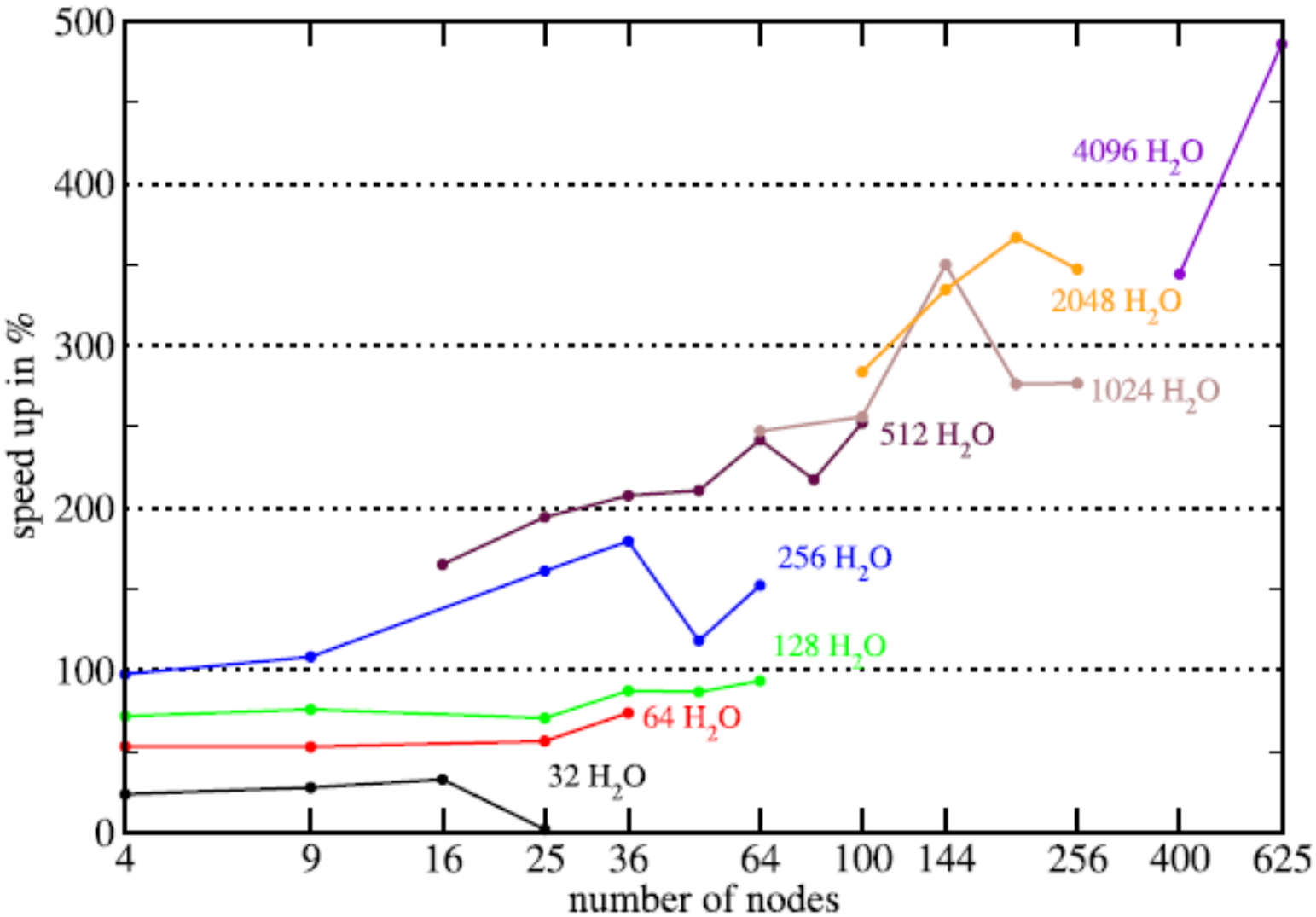
VandeVondele et al, JCP, 118, 4365 (2003)

OT Performance

- 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

OT Performance

Refined preconditioner, most effective during MD of large systems with well conditioned basis sets



on Daint (XC30)

3844 nodes

(8 cores + 1 GPU)

Schiffmann, VandeVondele, JCP 142 244117 (2015)

OT input

```
&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
```

Linear Scaling SCF

- Based on sparse matrix matrix multiplications (iterative proc.)

$$P = \frac{1}{2}\left(I - \mathrm{sign}\left(S^{-1}H - \mu I\right)\right) S^{-1}$$

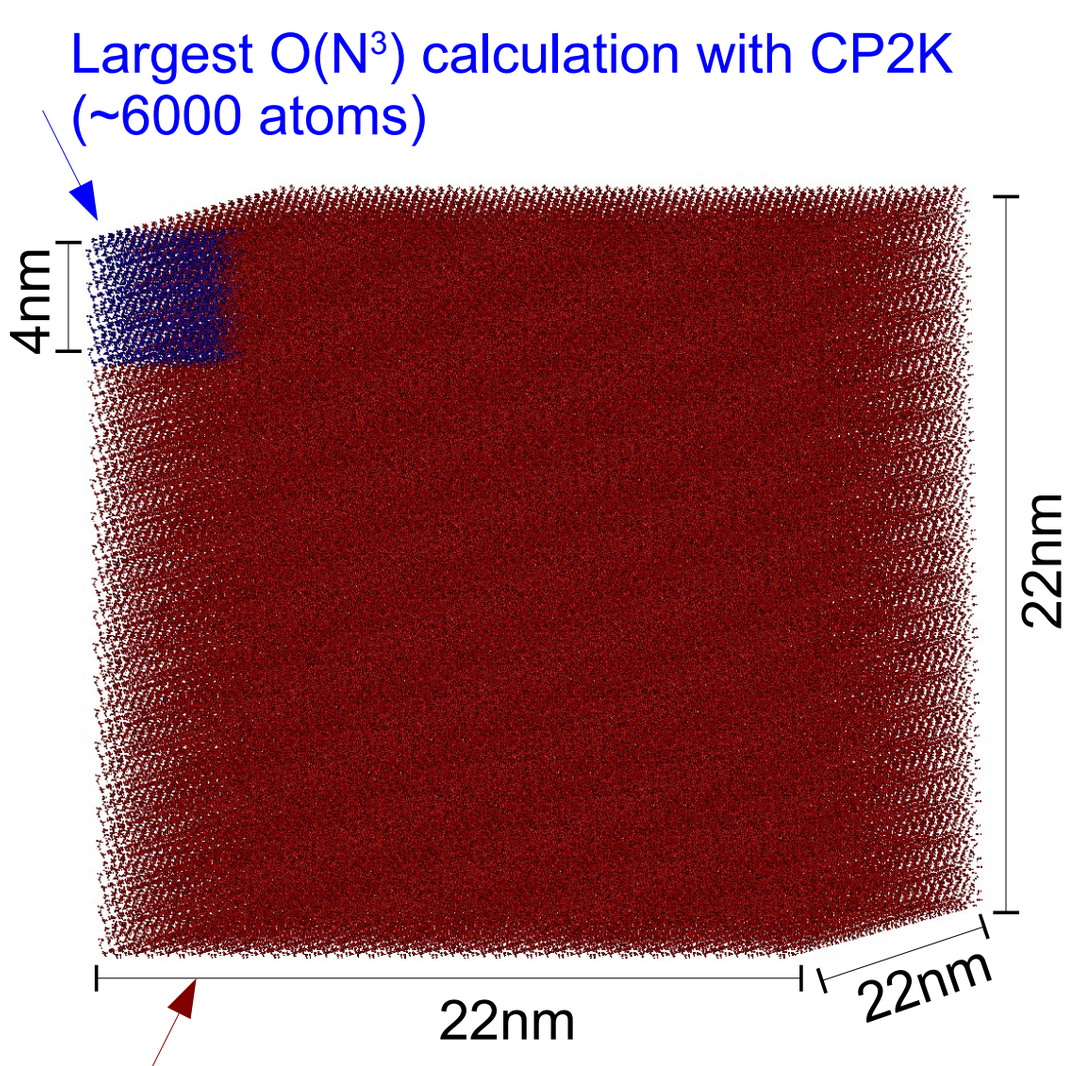
- Self consistent solution by mixing

$$H_{n+1}(P_{n+1})$$

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

- Chemical potential by bisecting until

$$\mu_{n+1}: \qquad |\mathrm{trace}(P_{n+1}S) - N_{el}| < 1/2$$

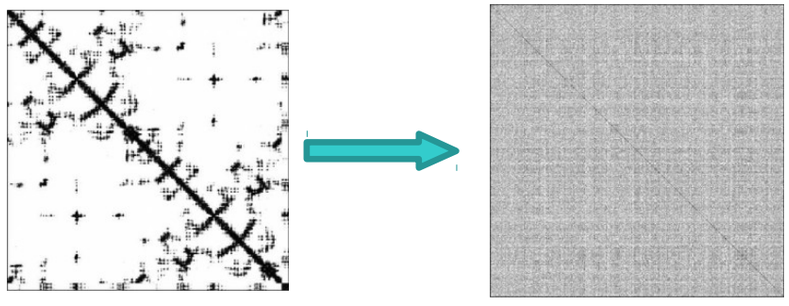


VandeVondele, Borstnik, Hutter; JCTC 10, 3566 (2012)

Sparse Matrix Library

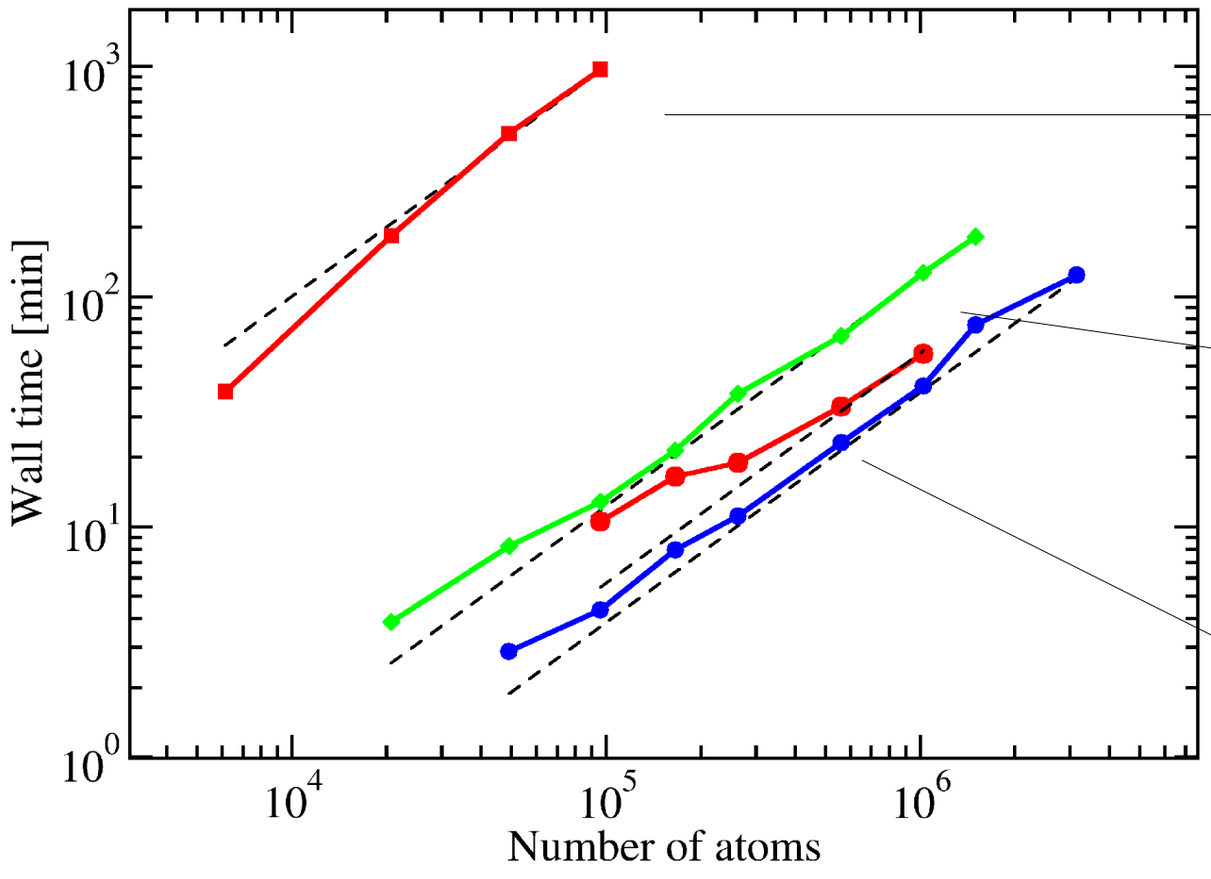
DBCSR: Distributed Blocked Compressed Sparse Row

- 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 number of processors increases

Millions of atoms



Accurate basis sets, DFT
46656 cores

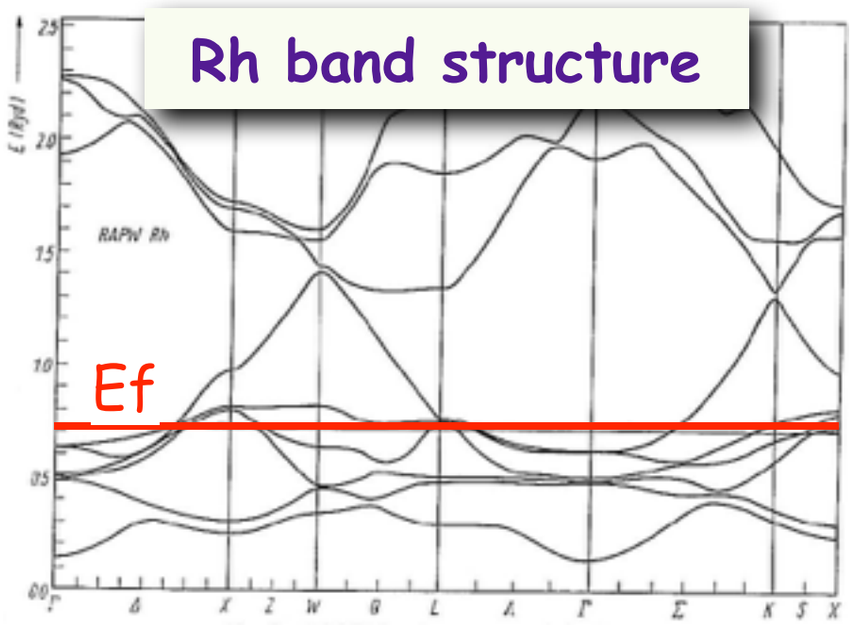
The electronic structure
O(10^6) atoms in < 2 hours

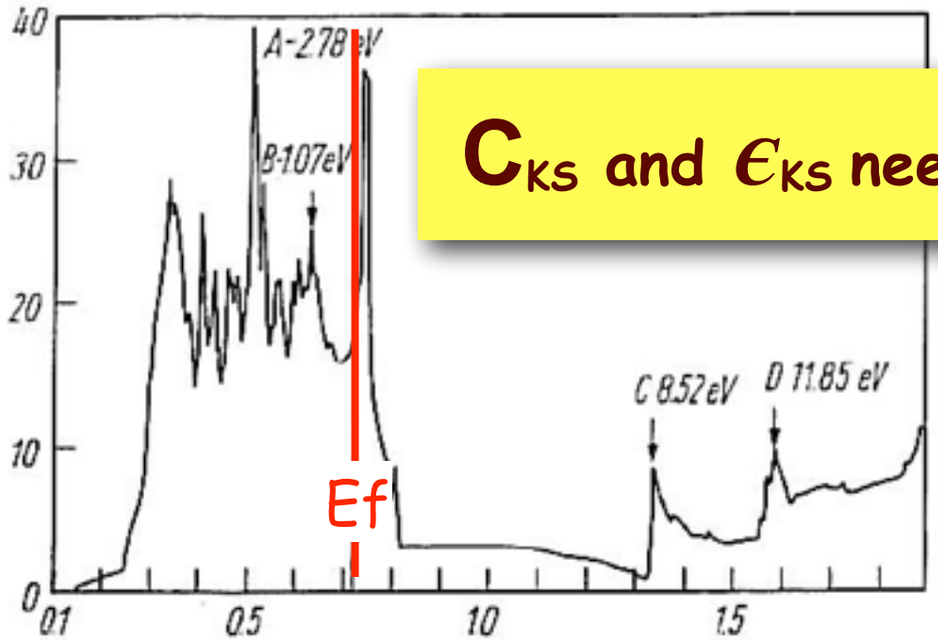
Minimal basis sets:
DFT, NDDO, DFTB
9216 cores

Bulk liquid water. Dashed lines represent ideal linear scaling.

Metallic Electronic Structure

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





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

Smearing & Mixing in G-space

Mermin functional: minimise the free energy

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

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

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

Fermi-Dirac

Trial density mixed with previous densities: damping oscillations

$$n^{\text{inp}}_{m+1} = n^{\text{inp}}_m + \mathbf{G}^I \mathcal{R}[n^{\text{inp}}_m] + \sum_{i=1}^{m-1} \alpha_i \left(\Delta n_i + \mathbf{G}^I \Delta \mathcal{R}_i\right)$$

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 the n(r)

Input density matrix

$$\mathbf{P}^{\mathrm{in}}_{\alpha\beta} \rightarrow n^{\mathrm{in}}(\mathbf{r})$$

Update of KS Hamiltonian

diagonalization plus iterative refinement $\mathbf{C}_n \ \varepsilon_n$

Calculation of Fermi energy and occupations $E_f \ f_n$

New density matrix

$$\mathbf{P}^{\mathrm{out}}_{\alpha\beta} \rightarrow n^{\mathrm{out}}(\mathbf{r})$$

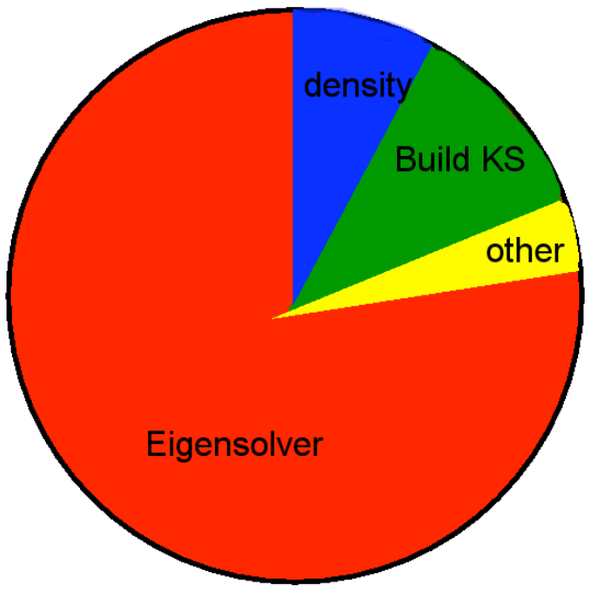
Check convergence

$$\max\left\{\mathbf{P}^{\mathrm{out}}_{\alpha\beta} - \mathbf{P}^{\mathrm{in}}_{\alpha\beta}\right\}$$

Density mixing

$$n^{\mathrm{out}} \ n^{\mathrm{in}} \ n^{\mathrm{h}} \ \ldots \rightarrow n^{\mathrm{new}}$$

$\mathbf{P}^{\mathrm{out}}_{\alpha\beta} \ n^{\mathrm{new}}(\mathbf{r})$

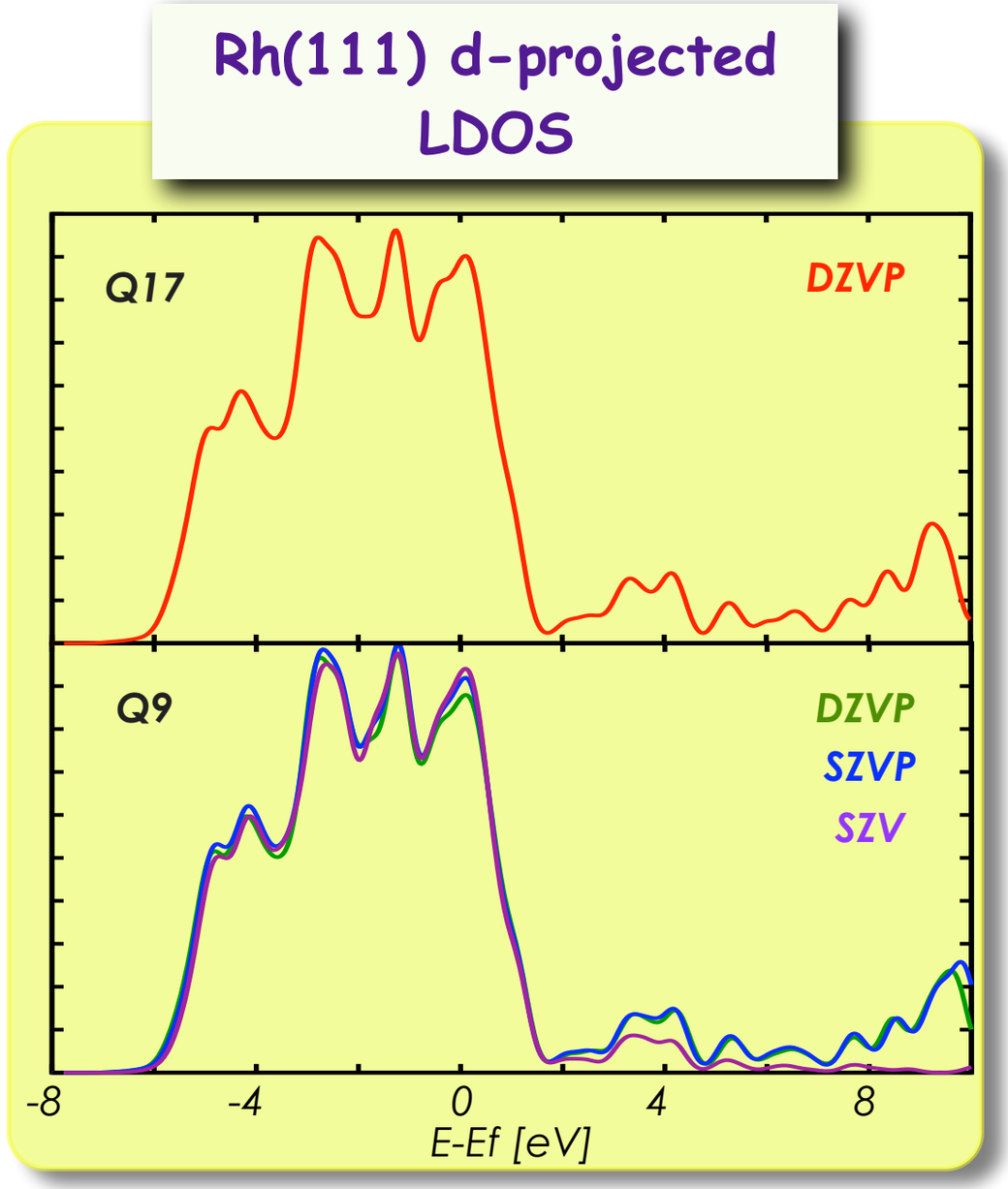


Rhodium: Bulk and Surface

Bulk: 4x4x4

Surface: 6x6 7 layers

Basis	PP	a_0 [Å]	B[GPa]	E_s[eV/Å^2]	W_f[eV]
3s2p2df	17e	3.80	258.3	0.186	5.11
2s2p2df	9e	3.83	242.6	0.172	5.14
2sp2d	9e	3.85	230.2	0.167	5.20
spd	9e	3.87	224.4	0.164	5.15

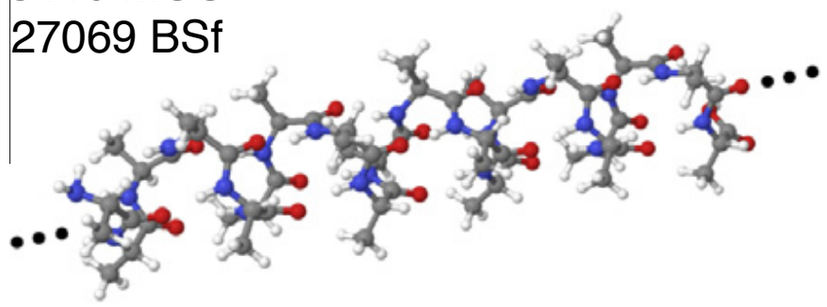


ScaLAPACK for diagonlisation

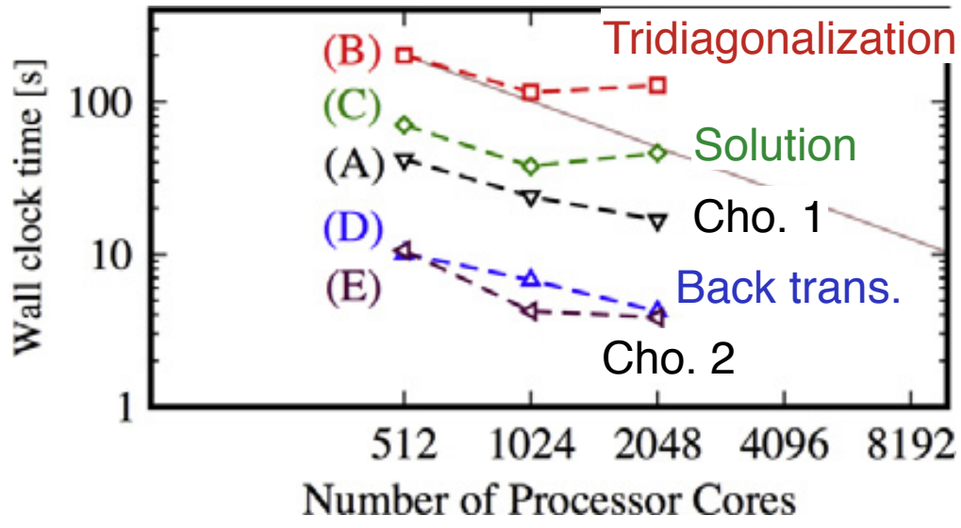
$$A \xrightarrow[\text{reduction to tridiagonal form}]{} T \xrightarrow[\text{compute eigenvalues and –vectors of T}]{} (\lambda, q_T) \xrightarrow[\text{transform eigenvectors}]{} q_A$$

1003 atoms
3410 MOS
27069 BSf

Polyalanine peptide



pdsyevd (ESSL) on IBM BGP



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

nprocs	syevd	syevr	Cholesky
32	106 (49%)	72 (40%)	38 (21%)
64	69 (46%)	48 (37%)	34 (26%)
128	41 (41%)	29 (34%)	23 (28%)
256	35 (41%)	26 (34%)	24 (32%)

Syevd: D&C

Syevr: MRRR

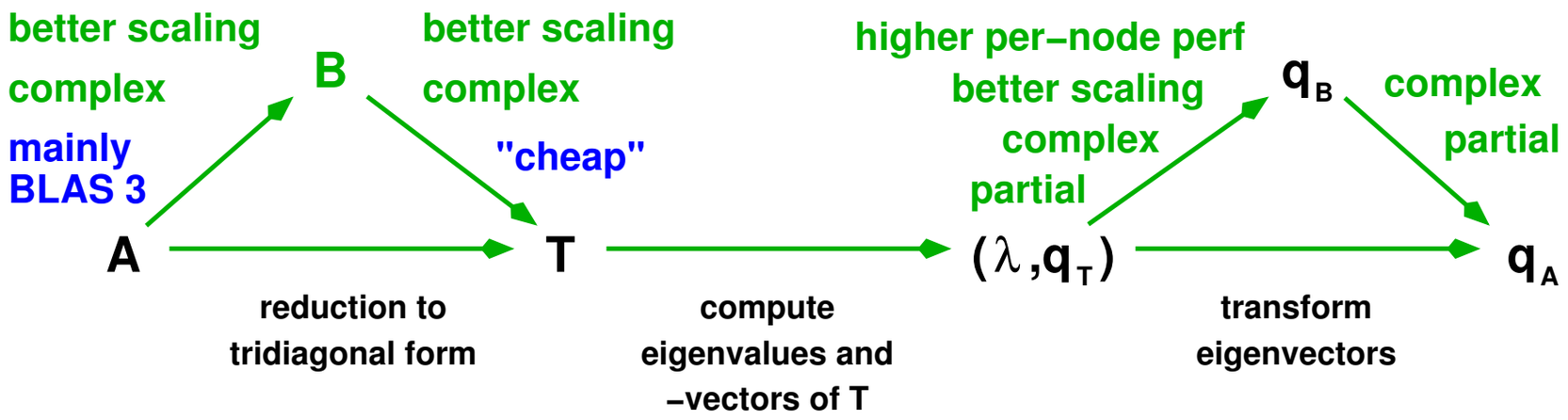
time x SCF, on CRAY XE6

>70% in eigenvalue solver

poor scaling

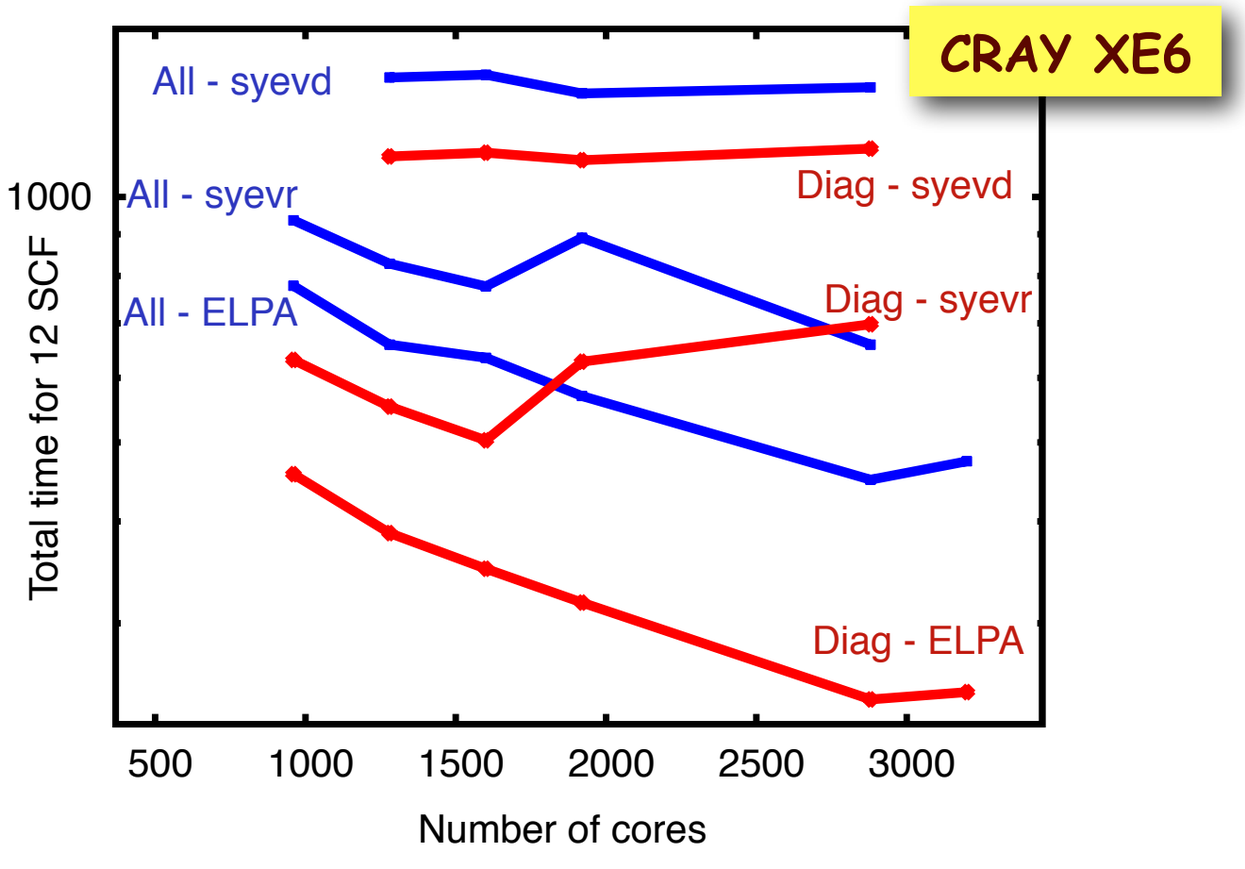
ELPA (http://elpa.rzg.mpg.de)

Improved efficiency by a two-step transformation and back transformation

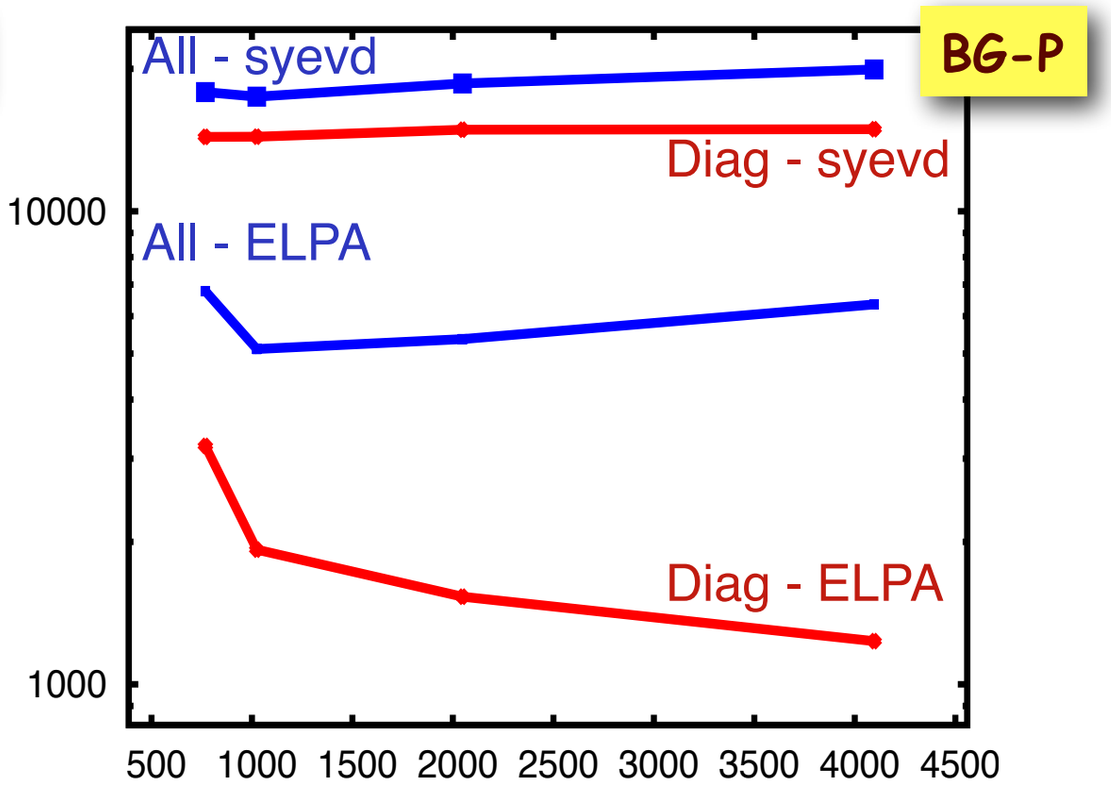


band form by blocked orthogonal transformations

N atom= 2116; Nel = 16928;
nmo = 10964; nao = 31740

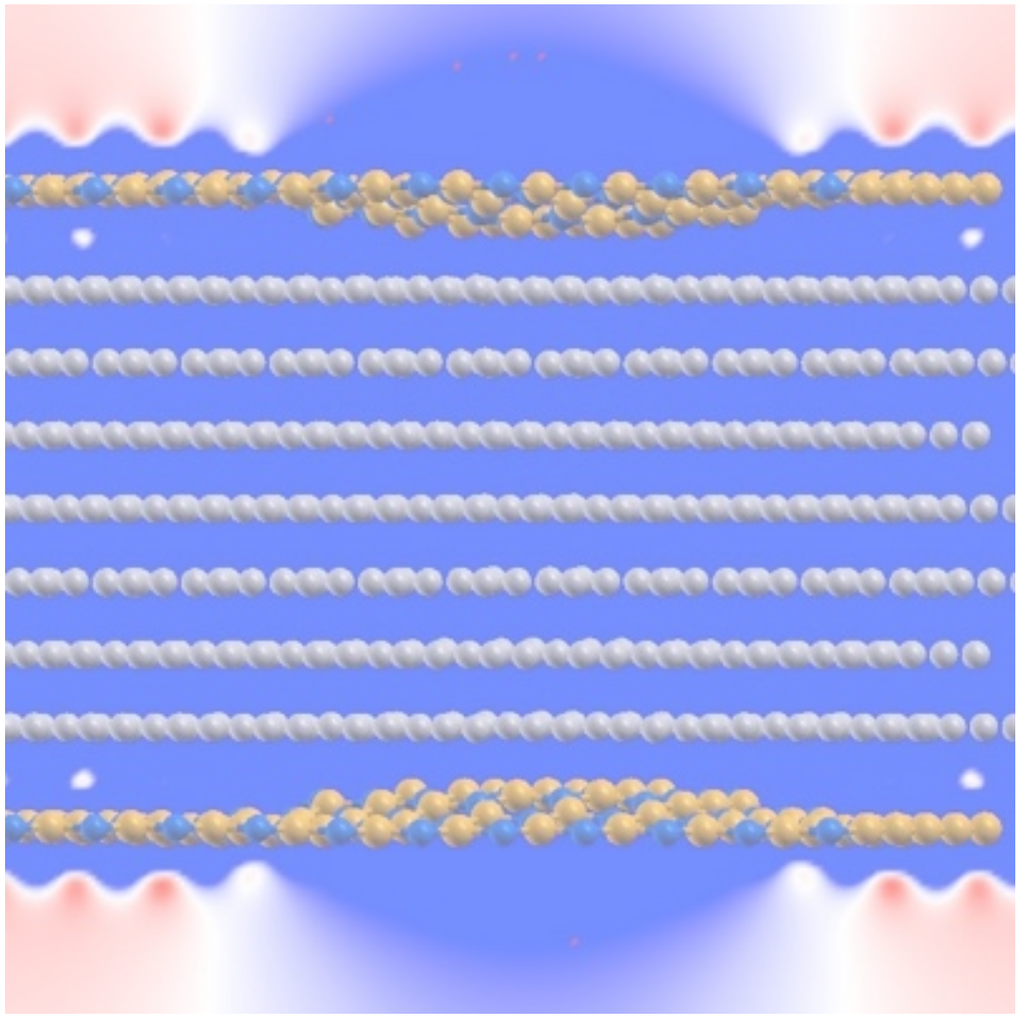


N atom= 480; Nel = 6000;
nmo = 7400; nao = 14240



Large metallic systems

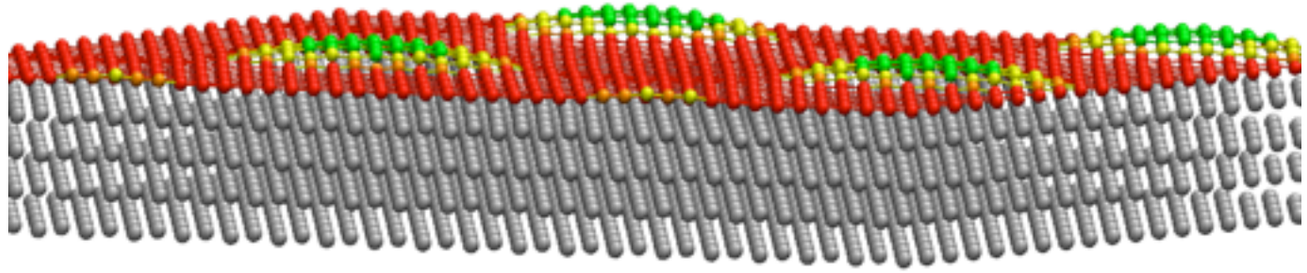
hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab



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

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

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



2116 Ru atoms (8 valence el.) + 1250 C atoms,
Nel=21928, Nao=47990 ;

~ 25 days per structure optimisation, on 1024 cpus

SCF for Metals

```
&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
  &XC_FUNCTIONAL PBE
  &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
```