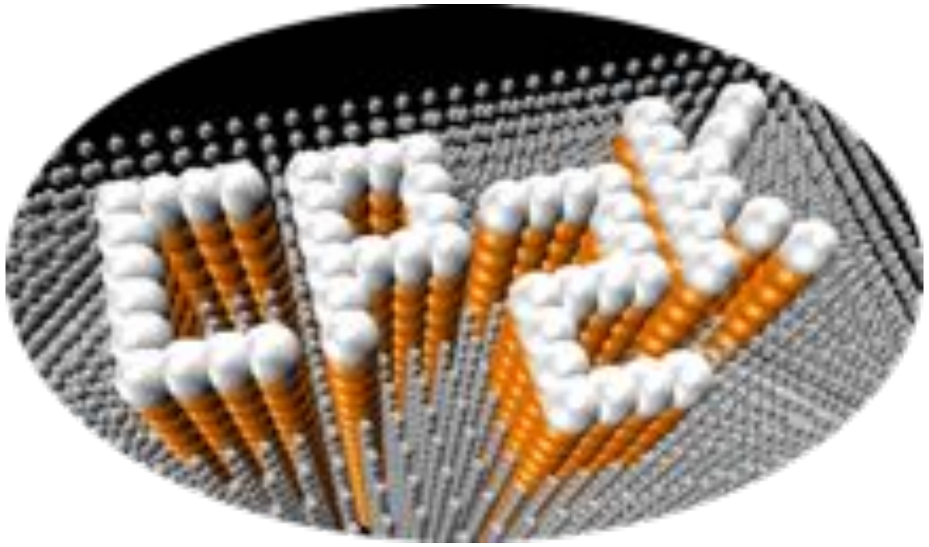
4th CP2K tutorial

August 31st -September 4th, Zurich

GPW (GAPW) electronic structure calculations

Marcella Iannuzzi

Department of Chemistry, University of Zurich



http://www.cp2k.org

Outline

- Density Functional Theory and the KS formalism
- Gaussian and Plane Wave method (GPW)
    - Basis sets and pseudo potentials
- Gaussian Augmented Plane Wave method (GAPW)

DFT

Why DFT?

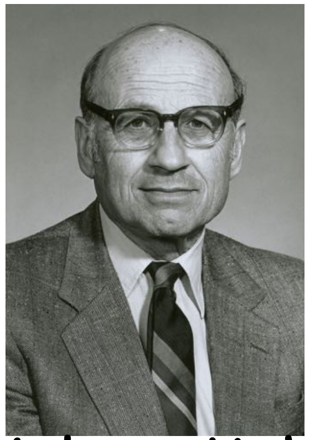
- Explicit inclusion of electronic structure
- Predicable accuracy (unlike empirical approaches, parameter free)
- Knowledge of electronic structure gives access to evaluation of many observables
- Better scaling compared to many quantum chemistry approaches
- Achievable improvements: development of algorithms and functionals

large systems, condensed matter, environment effects, first principle MD

Hohenberg-Kohn theorems

Theorem I

- Given a potential, one obtains the wave functions via Schrödinger equation



Walter Kohn

$$V_{\mathrm{ext}}(\mathbf{r},\mathbf{R}) \Rightarrow H(\mathbf{r},\mathbf{R}) = T(\mathbf{r}) + V_{\mathrm{ext}}(\mathbf{r},\mathbf{R}) + V_{\mathrm{ee}}(\mathbf{r})$$

$$H(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r},\mathbf{R})$$

- The density is the probability distribution of the wave functions

$$n(\mathbf{r}) \Leftrightarrow V_{\mathrm{ext}}(\mathbf{r},\mathbf{R})$$

the potential and hence also the total energy are unique functional of the electronic density n(r)

HK Total energy

Theorem II: The total energy is variational

$$E[n] \geq E[n_{\mathrm{GS}}]$$

$$E_{\mathrm{tot}}[n] = E_{\mathrm{kin}}[n] + E_{\mathrm{ext}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n]$$

- E_{kin} QM kinetic energy of electron (TF)
- E_{ext} energy due to external potential
- E_{H} classical Hartree repulsion
- E_{xc} non classical Coulomb energy: el. correlation

Kohn-Sham: non-interacting electrons

Electronic density

$$n(\mathbf{r}) = \sum_i f_i \left|\psi_i(\mathbf{r})\right|^2$$

no repulsion

Kinetic energy of non interacting electrons

$$T_{\mathrm{s}}[n] = \sum_i f_i \left\langle \psi_i(\mathbf{r}) \right| - \frac{1}{2}\nabla^2 \left| \psi_i(\mathbf{r}) \right\rangle$$

Electronic interaction with the external potential

$$E_{\mathrm{ext}}[n] = \int_r n(\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r}) d\mathbf{r} \qquad V_{\mathrm{ext}}(\mathbf{r}) = \sum_I -\frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

Exact solution

$$\Psi_s = \frac{1}{\sqrt{N!}} \det\left[\psi_1 \psi_2 \psi_3 \ldots \psi_N\right]$$

KS energy functional

Classical e-e repulsion

$$J[n] = \frac{1}{2}\int_{\mathbf{r}}\int_{\mathbf{r}'}\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' = \frac{1}{2}\int_{\mathbf{r}} n(\mathbf{r})V_{\mathrm{H}}(\mathbf{r})d\mathbf{r}$$

Kohn-Sham functional

$$E_{\mathrm{KS}}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{ext}}[n] + J[n] + E_{\mathrm{XC}}[n]$$

$$E_{\mathrm{XC}}[n] = E_{\mathrm{kin}}[n] - T_{\mathrm{s}}[n] + \underbrace{E_{ee}[n] - J[n]}_{\text{non-classical part}}$$

KS Equations

Orthonormality constraint

$$\Omega_{\mathrm{KS}}[\psi_i] = E_{\mathrm{KS}}[n] - \underbrace{\sum_{ij} \epsilon_{ij} \int}_{\text{Lagrange multipliers}} \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}$$

Variational search in the space of orbitals

$$\frac{\delta\Omega_{\mathrm{KS}}[\psi_i]}{\delta\psi_i^*} = 0$$

$$H_{\mathrm{KS}}\psi_i = \left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}\right]\psi_i = \sum_{ij} \epsilon_{ij}\psi_j$$

$$V_{\mathrm{KS}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{XC}}(\mathbf{r})$$

KS Equations

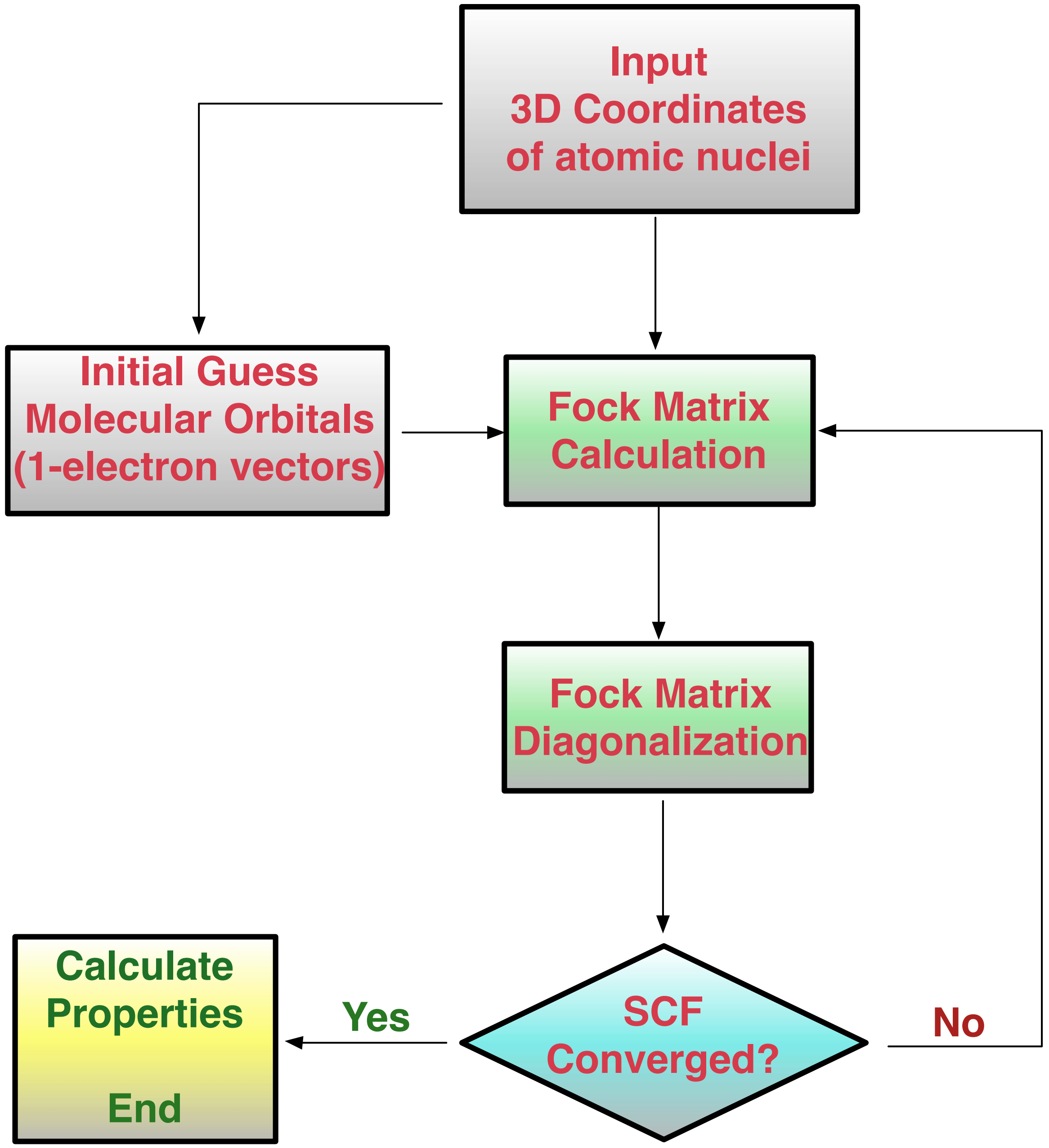
ϵ_{ij} diagonal

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

- KS equations looking like Schrödinger equations
- coupled and highly non linear
- Self consistent solution required
- ϵ and ψ are help variables
- KS scheme in principle exact (E_{xc}?)

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
- .....



Input
3D Coordinates
of atomic nuclei

Initial Guess
Molecular Orbitals
(1-electron vectors)

Fock Matrix
Calculation

Fock Matrix
Diagonalization

SCF
Converged?

Yes

No

Calculate
Properties

End

until self-consistency to required precision

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

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

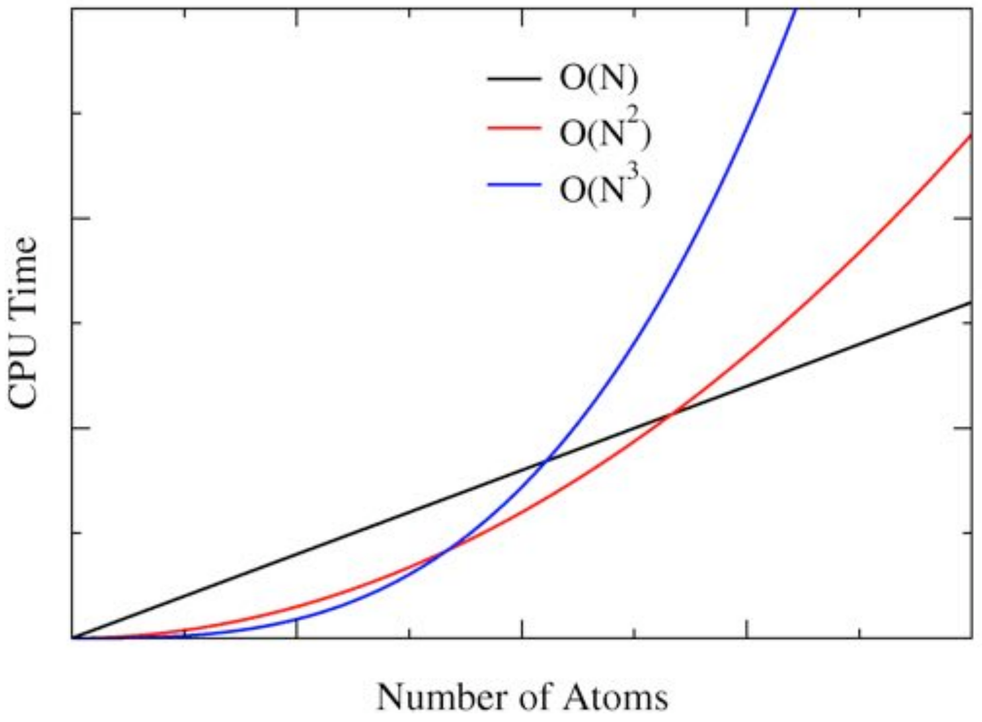
Critical Tasks

- Construction of the Kohn-Sham matrix
  - Hartree potential
  - XC potential
  - HF/exact exchange
- Fast and robust minimisation of the energy functional
- Efficient calculation of the density matrix and construction of the MOs (C)

O(N) scaling in basis set size

Big systems: biomolecules, interfaces, material science
1000+ atoms

Long time scale: 1 ps = 1000 MD steps, processes
several ps a day



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**: over-completeness
- 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

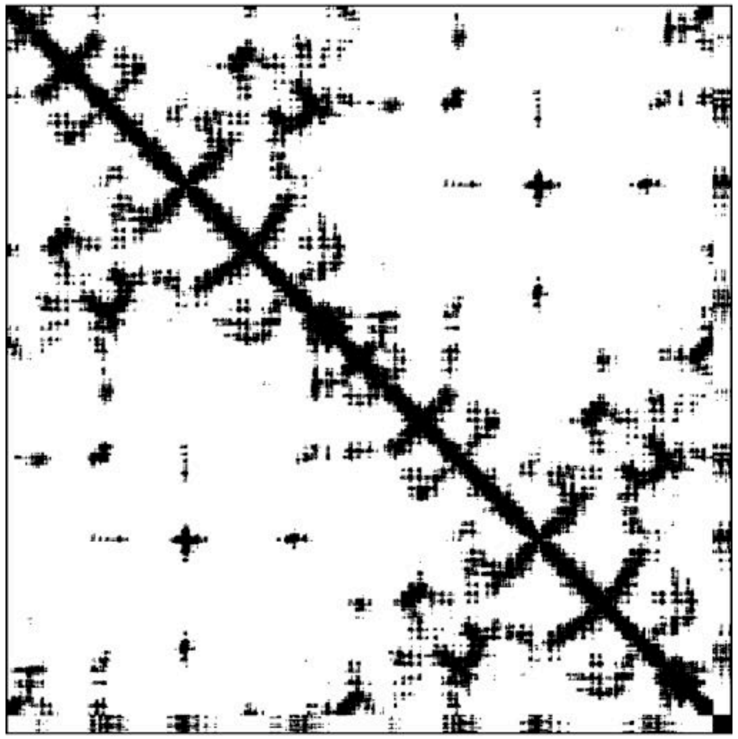
- Localised, atom-position dependent GTO basis

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

- Expansion of the density using the density matrix

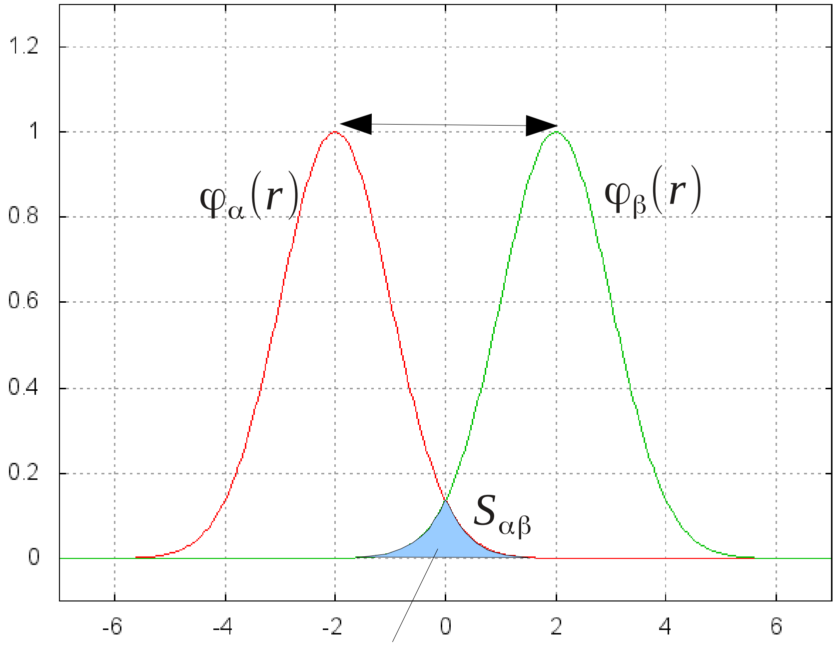
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu^*(\mathbf{r})$$

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

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

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

OS Recursion relations

Invariance of integrals

$$\frac{\partial}{\partial r_i}(\mathbf{a}|\mathcal{O}(r)|\mathbf{b}) = 0$$

Shift of angular momentum

$$(\mathbf{a}|\mathcal{O}(r)|\mathbf{b}+\mathbf{1}_i) = (\mathbf{a}+\mathbf{1}_i|\mathcal{O}(r)|\mathbf{b}) + (A_i - B_i)(\mathbf{a}|\mathcal{O}(r)|\mathbf{b})$$

Overlap

$$(\mathbf{0}_a|\mathbf{0}_b) = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} \exp[-\xi(\mathbf{A}-\mathbf{B})^2] \qquad \xi = \frac{\alpha\beta}{\alpha+\beta}$$

$$(\mathbf{a}+\mathbf{1}_i|\mathbf{b}) = (P_i - A_i)\,(\mathbf{a}|\mathbf{b}) + \frac{1}{2(\alpha+\beta)}\,[n_{ia}(\mathbf{a}-\mathbf{1}_i|\mathbf{b}) + n_{ib}(\mathbf{a}|\mathbf{b}-\mathbf{1}_i)]$$

$$\mathbf{P} = \frac{\alpha\mathbf{A}+\beta\mathbf{B}}{\alpha+\beta}$$

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  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-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  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  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  TZVP-GTH
2
2 0 1 5 3 3
  10.2674419938   0.0989598460   0.0000000000   0.0000000000  -0.0595856940   0.0000000000   0.0000000000
   3.7480495696   0.1041178339   0.0000000000   0.0000000000  -0.1875649045   0.0000000000   0.0000000000
   1.3308337704  -0.3808255700   0.0000000000   0.0000000000  -0.3700707718   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  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  6-311++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  3  3  1  1
       1.40000000          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
ALL_POTENTIALS
BASIS_ADMM
BASIS_ADMM_MOLOPT
BASIS_MOLOPT
BASIS_RI_cc-TZ
BASIS_SET
BASIS_ZIJLSTRA
DFTB
EMSL_BASIS_SETS
GTH_BASIS_SETS
GTH_POTENTIALS
HFX_BASIS
HF_POTENTIALS
MM_POTENTIAL
NLCC_POTENTIALS
POTENTIAL
README
dftd3.dat
nm12_parameters.xml
rVV10_kernel_table.dat
t_c_g.dat
t_sh_p_s_c.dat
vdW_kernel_table.dat

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

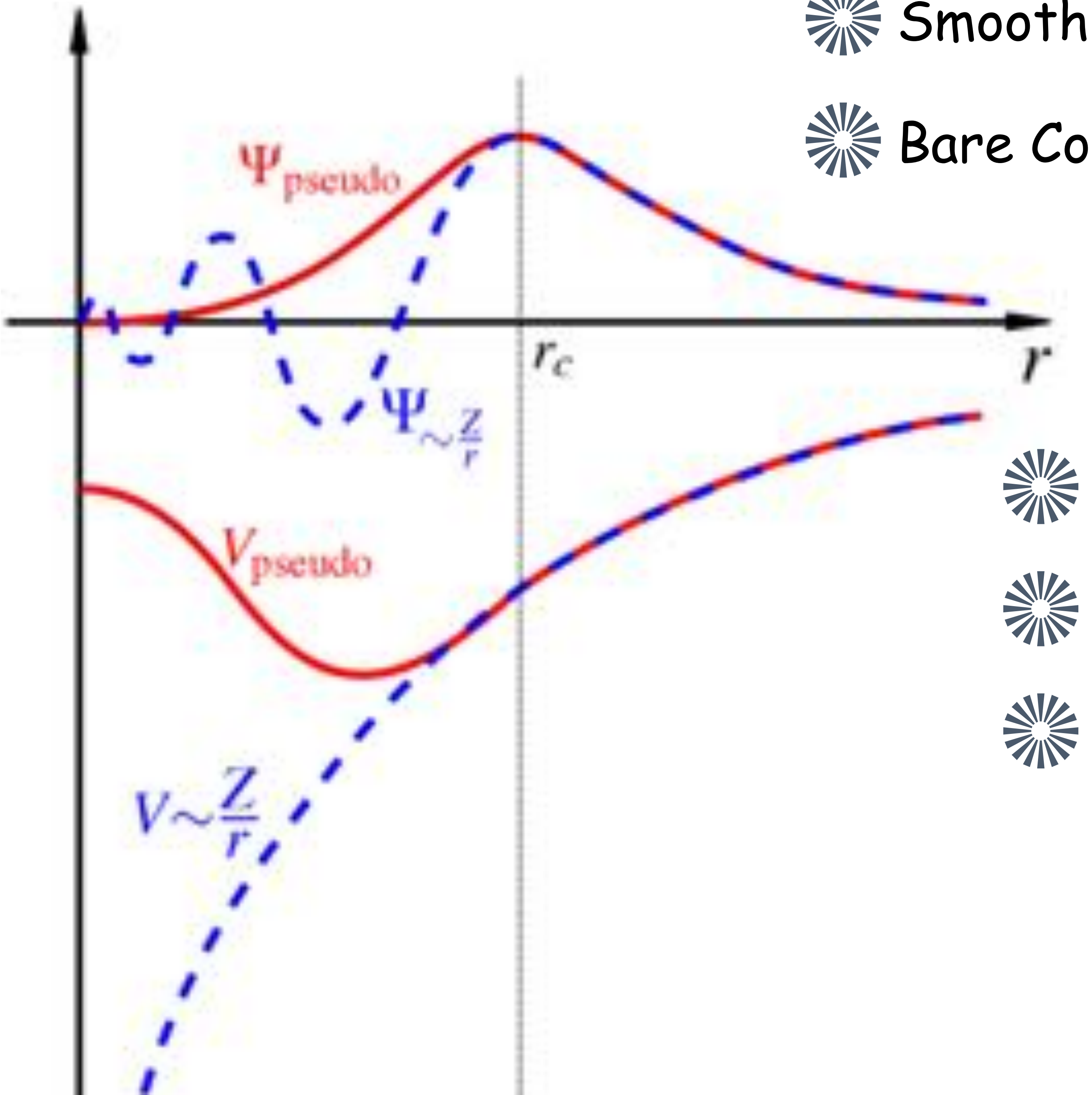
Generate GTO basis set

```
&ATOM
  ELEMENT Ru
  RUN_TYPE BASIS_OPTIMIZATION
  ELECTRON_CONFIGURATION  CORE 4d7 5s1
  CORE [Kr]
  MAX_ANGULAR_MOMENTUM 2
  &METHOD
     METHOD_TYPE  KOHN-SHAM
     &XC
       &XC_FUNCTIONAL
         &PBE
         &END
       &END XC_FUNCTIONAL
     &END XC
  &END METHOD
  &OPTIMIZATION
    EPS_SCF 1.e-8
  &END OPTIMIZATION
  &PP_BASIS
   NUM_GTO  6 6 6
   S_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
   P_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
   D_EXPONENTS 3.73260 1.83419 0.80906 0.34515
0.13836 0.04967
   EPS_EIGENVALUE 1.E-14
  &END PP_BASIS
```

```
  &POTENTIAL
    PSEUDO_TYPE GTH
    &GTH_POTENTIAL
   1     0    7
    0.61211332  1  5.04489332
   3
    0.6421504 2 4.625563 -1.8033490
                          2.32811359
    0.6793665 2 3.233952 -2.42101064
                          2.86457842
    0.3805972 2 -15.5316  13.58045054
                         -15.39878349
    &END GTH_POTENTIAL
    CONFINEMENT   0.5  20.00  4.5
  &END POTENTIAL
  &POWELL
     ACCURACY   1.e-8
     STEP_SIZE  1.0
  &END POWELL
&END ATOM
```

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

Generate PP

Reference

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{H}}[n](r) + V_{\mathrm{xc}}[n](r) + V_{\mathrm{nuc}}(r)\right)\psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$

PP

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{H}}[n_{\mathrm{val}}](r) + V_{\mathrm{xc}}[n_{\mathrm{val}}](r) + V_{\mathrm{pp}}^{l}(r)\right)\tilde{\psi}_l(\mathbf{r}) = \epsilon_l \tilde{\psi}_l(\mathbf{r})$$

Normconserving

$$\int \left|\tilde{\psi}_l(\mathbf{r})\right|^2 d\mathbf{r} = 1$$

Separable: local, nonlocal

$$V_{\mathrm{pp}}(\mathbf{r}) = V_{\mathrm{loc}}(|\mathbf{r}|) + \sum_{lm}^{L_{\max}} |p_{lm}\rangle \nu_l \langle p_{lm}|$$

GTH Pseudopotentials

- Norm-conserving, separable, dual-space

- Local PP : short-range and long-range terms

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

analytically

part of ES

- Non-Local PP with Gaussian type projectors

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

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

Accurate and Transferable

Scalar relativistic

Few parameters

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

Pseudopotential integrals

Local PP (SR): 3-center terms

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i|\mathbf{c}|\mathbf{b}) &= H_i(\mathbf{a}|\mathbf{c}|\mathbf{b}) \\ &+ \frac{1}{2(\alpha+\beta+\gamma)}\left[n_{ia}(\mathbf{a}-\mathbf{1}_i|\mathbf{c}|\mathbf{b}) + n_{ib}(\mathbf{a}|\mathbf{c}|\mathbf{b}-\mathbf{1}_i)\right. \\ &+ \left. n_{ic}\left[(\mathbf{a}+\mathbf{1}_i|\mathbf{c}-\mathbf{2}_i|\mathbf{b}) + (A_i - C_i)(\mathbf{a}|\mathbf{c}-\mathbf{2}_i|\mathbf{b})\right]\right]\end{aligned}$$

$$\mathbf{H} = \frac{\beta\mathbf{B}+\gamma\mathbf{C}-(\beta+\gamma)\mathbf{A}}{\alpha+\beta+\gamma}$$

$$(\mathbf{0}_a|\mathbf{0}_c|\mathbf{0}_b) = \left(\frac{\alpha+\beta}{\alpha+\beta+\gamma}\right)^{3/2} \exp\left[-\gamma\frac{\alpha+\beta}{\alpha+\beta+\gamma}(\mathbf{P}-\mathbf{C})^2\right](\mathbf{a}|\mathbf{b})$$

GTH PP for O: 6 val. el.

```
&ATOM

  ELEMENT O
  RUN_TYPE  PSEUDOPOTENTIAL_OPTIMIZATION

  ELECTRON_CONFIGURATION  [He] 2s2 2p4
  CORE [He]
  MAX_ANGULAR_MOMENTUM 2

  COULOMB_INTEGRALS ANALYTIC
  EXCHANGE_INTEGRALS ANALYTIC

  &METHOD
     METHOD_TYPE  KOHN-SHAM
     RELATIVISTIC DKH(2)
     &XC
       &XC_FUNCTIONAL PBE0
       &END XC_FUNCTIONAL
     &END XC
  &END METHOD
  &OPTIMIZATION
    EPS_SCF 1.e-10
  &END
  &PRINT
    &BASIS_SET
    &END
  &END
```

```
  &AE_BASIS
     BASIS_TYPE GEOMETRICAL_GTO
  &END AE_BASIS
  &PP_BASIS
     BASIS_TYPE GEOMETRICAL_GTO
  &END PP_BASIS
  &POTENTIAL
    PSEUDO_TYPE GTH
    &GTH_POTENTIAL
     2    4
     0.24455430  2 -16.66721480 2.48731132
     2
     0.22095592  1  18.33745811
     0.21133247  0
    &END GTH_POTENTIAL
  &END POTENTIAL

  &POWELL
     ACCURACY   1.e-10
     STEP_SIZE  0.5
     WEIGHT_PSIR0 0.1
  &END

&END ATOM
```

PP Library

GTH_POTENTIALS

$$N_{\text{el}}(s) \qquad N_{\text{el}}(p) \qquad N_{\text{el}}(d) \qquad \ldots$$

$$r_{\text{loc}}^{\text{PP}} \qquad N_C \qquad C_1^{\text{PP}} \quad \ldots \quad C_{N_C}^{\text{PP}}$$

$$N_p$$

$$r_1 \qquad n_{\text{nl}}^1 \qquad \{h_{ij}^1\}_{ij=1\ldots n^1}$$

$$r_2 \qquad n^2 \qquad \{h_{ij}^2\}_{ij=1\ldots n^2}$$

Few parameters

```
C GTH-BLYP-q4
    2    2
     0.33806609    2    -9.13626871      1.42925956
    2
     0.30232223    1     9.66551228
     0.28637912    0
#
N GTH-BLYP-q5
    2    3
     0.28287094    2   -12.73646720      1.95107926
    2
     0.25523449    1    13.67893172
     0.24313253    0
```

```
#
Al GTH-PBE-q3
    2    1
     0.45000000    1    -7.55476126
    2
     0.48743529    2     6.95993832    -1.88883584
                                        2.43847659
     0.56218949    1     1.86529857
```

Electrostatic Energy

Periodic system

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

total charge distribution
including n(r) and Z

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

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

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

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

cancels the long range term of local PP

$$\begin{aligned} E_{\mathrm{ES}} &= \int V_{\mathrm{loc}}^{\mathrm{SR}}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\int\int\frac{n_{\mathrm{tot}}(\mathbf{r})n_{\mathrm{tot}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \\ &+ \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|}\mathrm{erfc}\left[\frac{|\mathbf{R}_A-\mathbf{R}_B|}{\sqrt{(r_A^c)^2+(r_B^c)^2}}\right] - \sum_A\frac{1}{\sqrt{2\pi}}\frac{Z_A^2}{r_A^c} \end{aligned}$$

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

E^{ov} short range, pair

E^{self}

Auxiliary Basis Set

- Long range term : Non-local Hartree potential

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

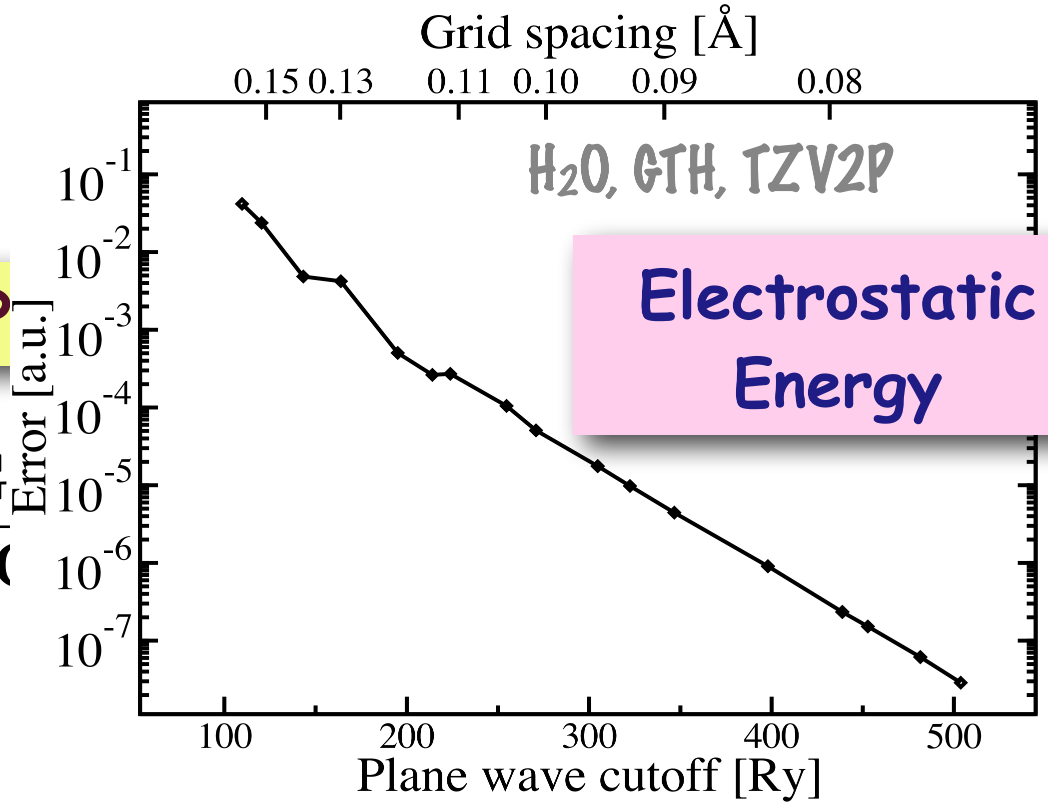
- Orthogonal, unbiased, naturally periodic PW basis

Efficient Mapping FFT

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

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

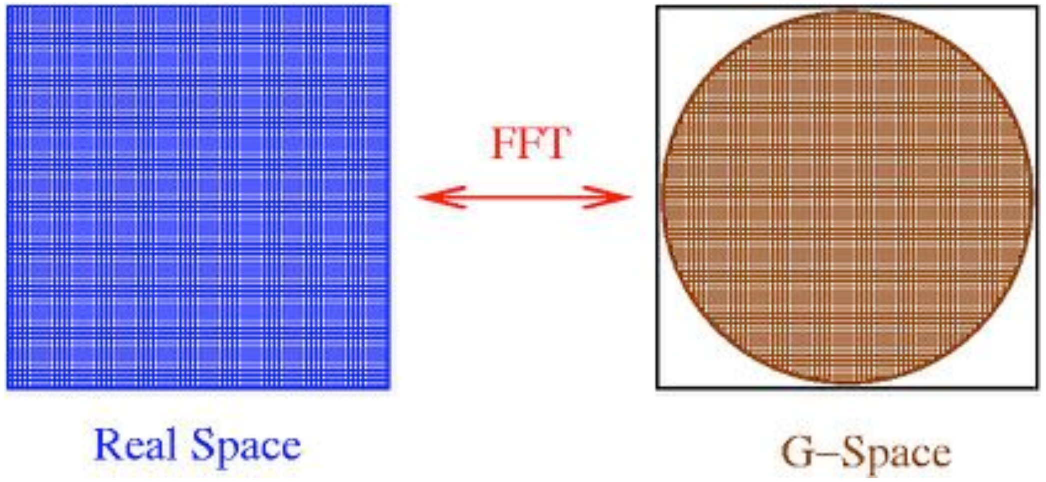
Finite cutoff and simulation box define a real space grid

Screening
Truncation

- Density collocation

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

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



- 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

$$H^{\mu\nu}_{HXC} = \langle \mu | V_{HXC}(\mathbf{r}) | \nu \rangle \rightarrow \sum_R V_{HXC}(R)\varphi'_{\mu\nu}(R)$$

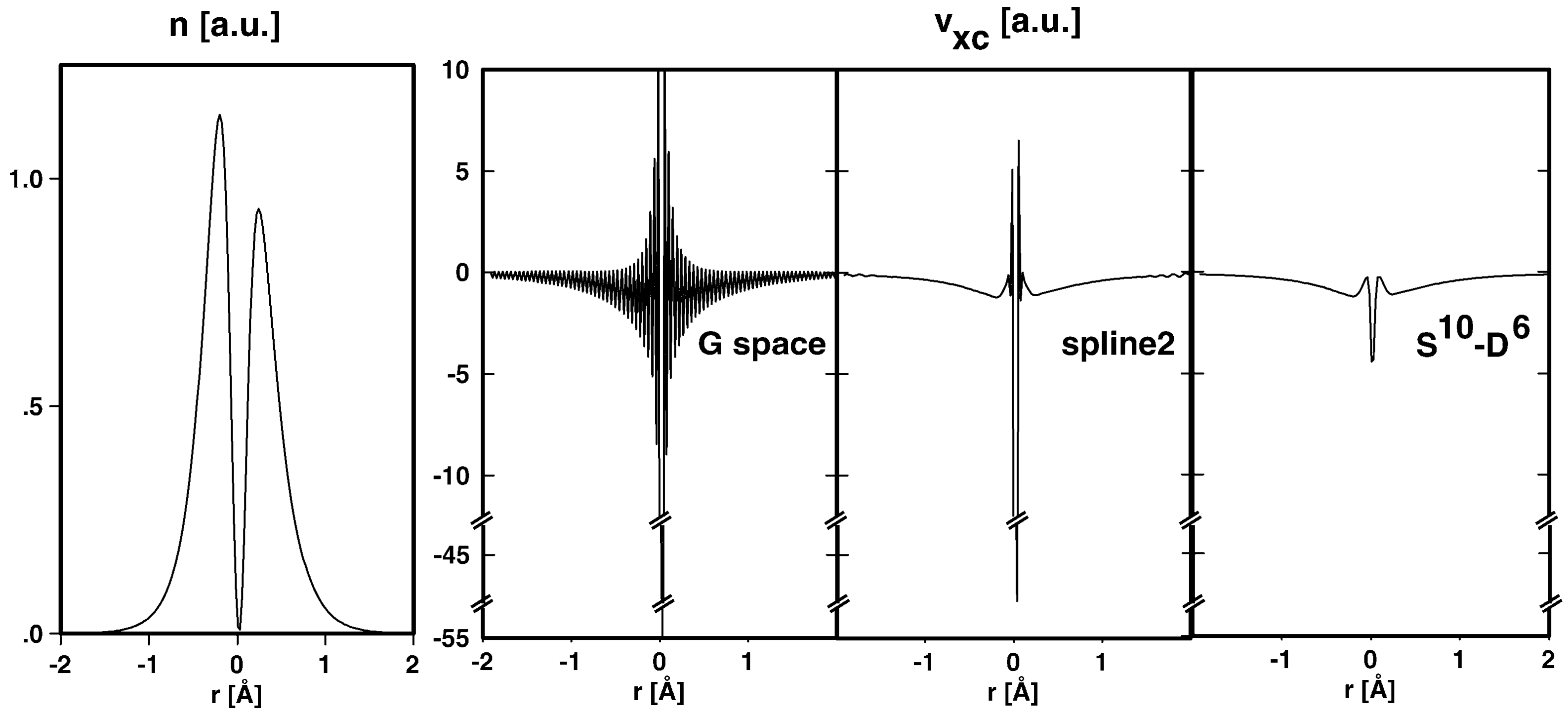
G. Lippert et al, Molecular Physics, 92, 477, 1997
J. VandeVondele et al, Comp. Phys. Comm.,167 (2), 103, 2005

Energy Ripples

Low density region can induce unphysical behaviour of terms such $\frac{|\nabla n|^2}{n^\alpha}$

H_2O, BLYP
close to O along
HOH bisector

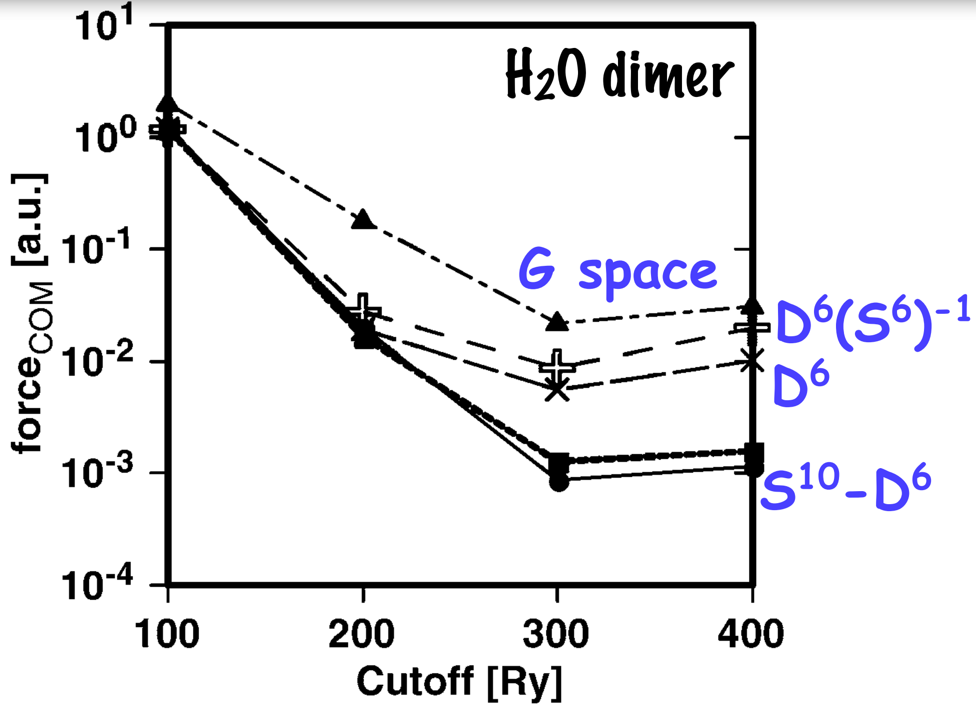
with PP
low density
at core



locally averaged n (neigh. q points S^q)

smoothed finite differences (D^q)

Spikes in v_{xc} ⇒ small variations of the total energy as atoms move relative to the grid



alternatively:
Non-linear core corrected PP
GAPW

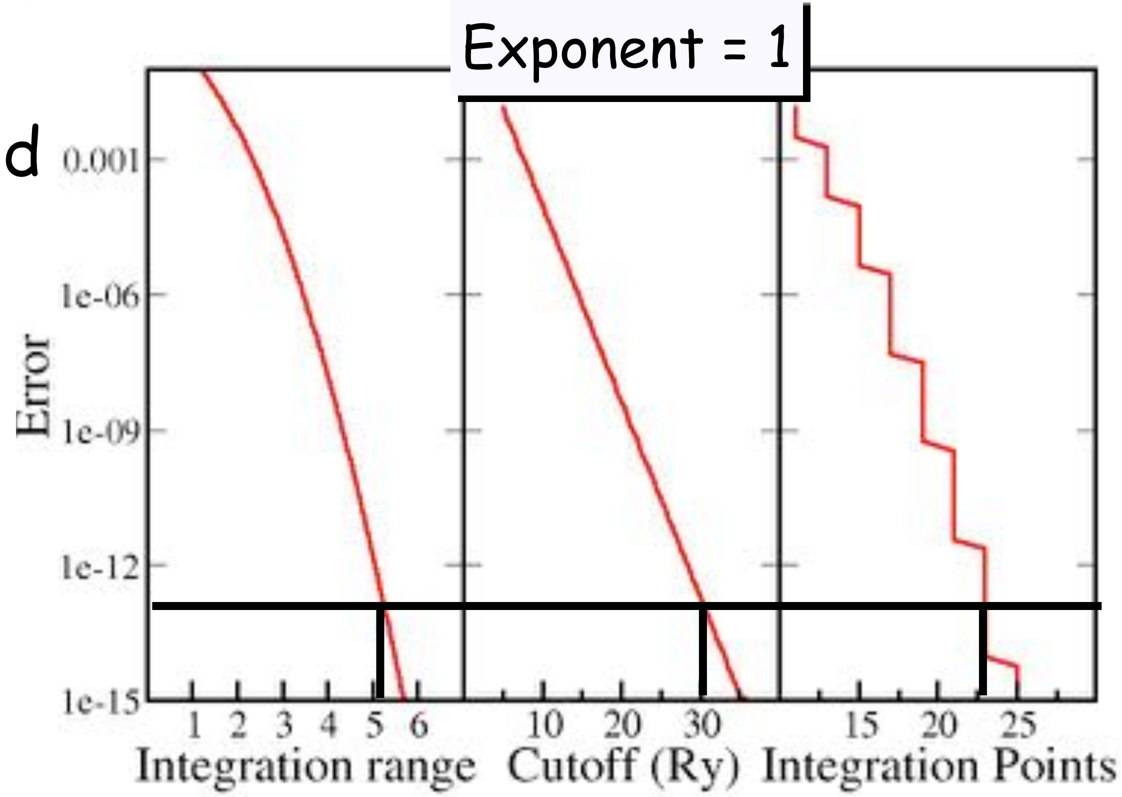
Multiple Grids

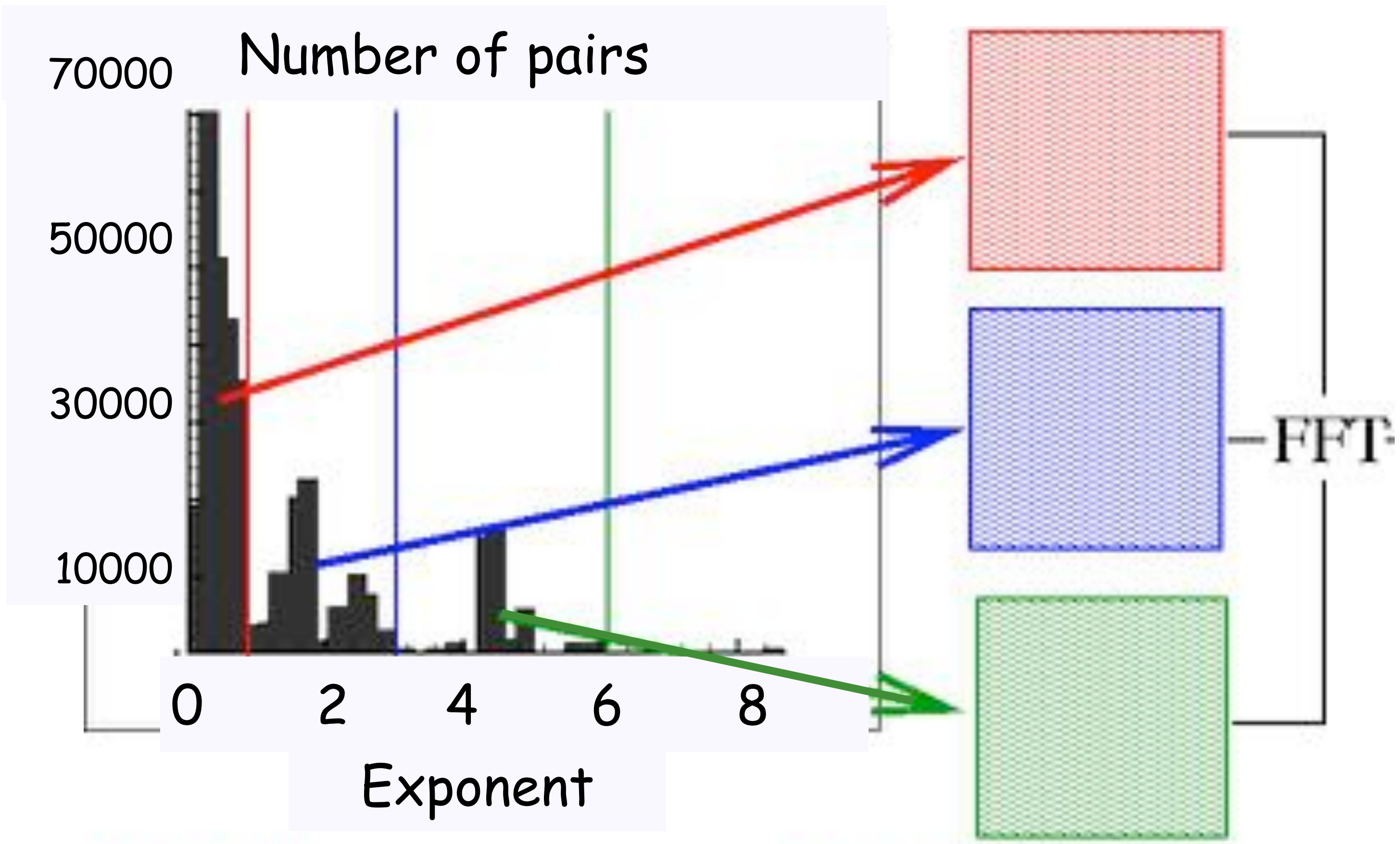
$$E^i_{\mathrm{cut}} = \frac{E^1_{\mathrm{cut}}}{\alpha^{(i-1)}}, \qquad i = 1..N$$

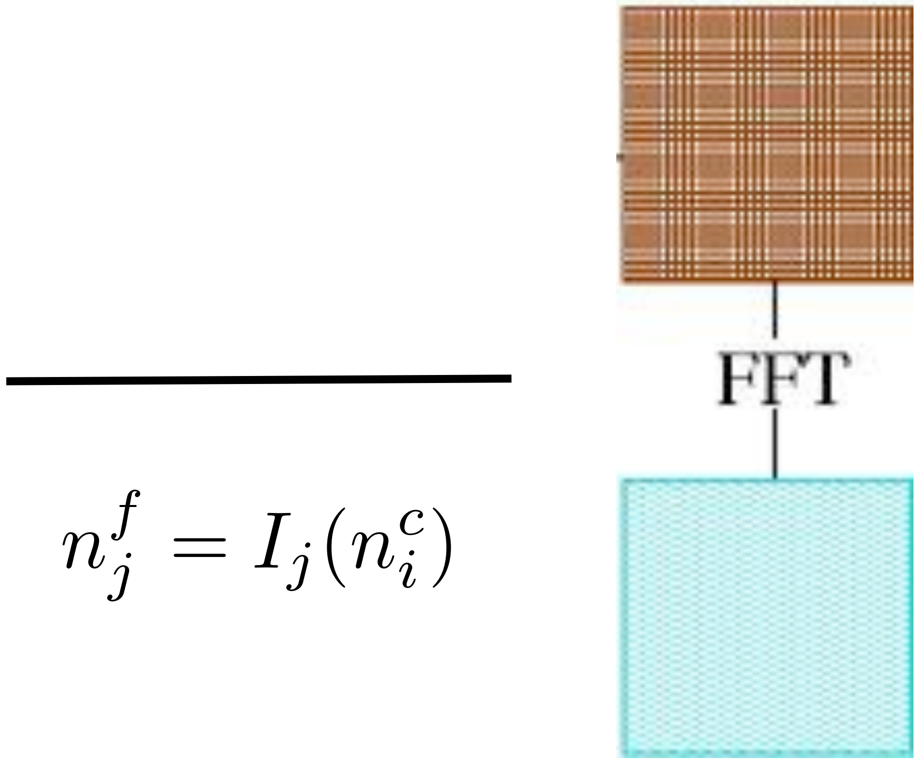
the exponent of Gaussian product selects the grid
number of grid points is exponent-independent

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

Accuracy
=> Relative Cutoff
~30 Ry







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

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

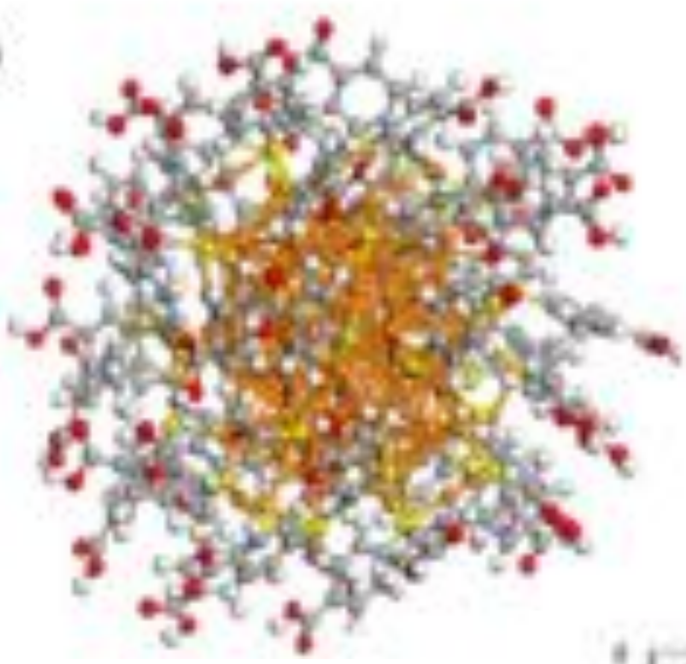
CP2K DFT input

```
&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
```

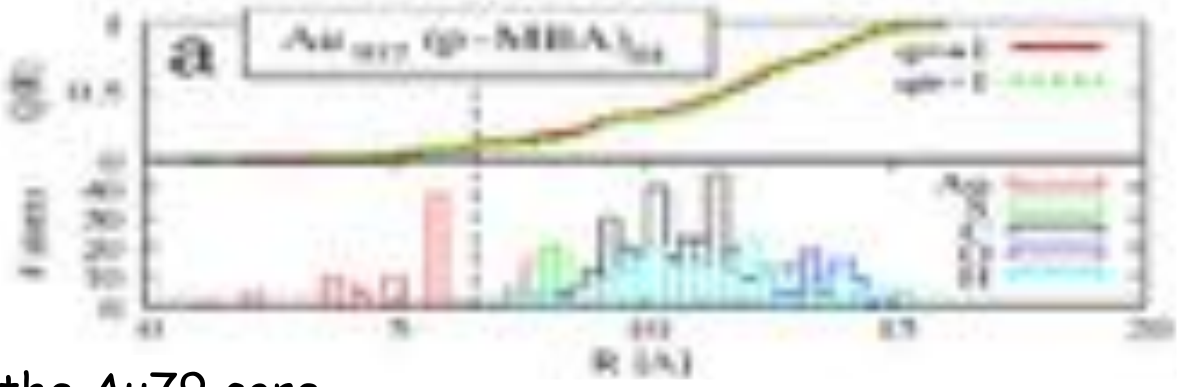
DFT for very large systems



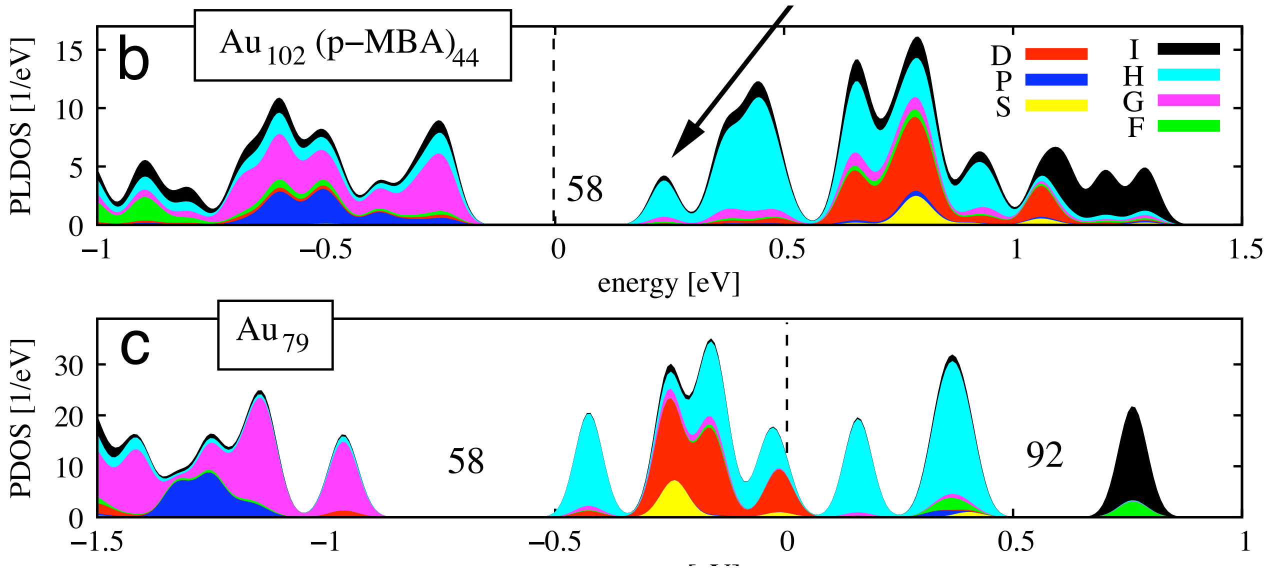
Ligand-protected Au cluster
762 atoms, ~3400 el.
as superatom complex

Rubredoxin in water solution
~2800 atoms, ~ 55000 N_{ao}
117s/scf 1024 CPUs (XT3),
80% parallel efficiency

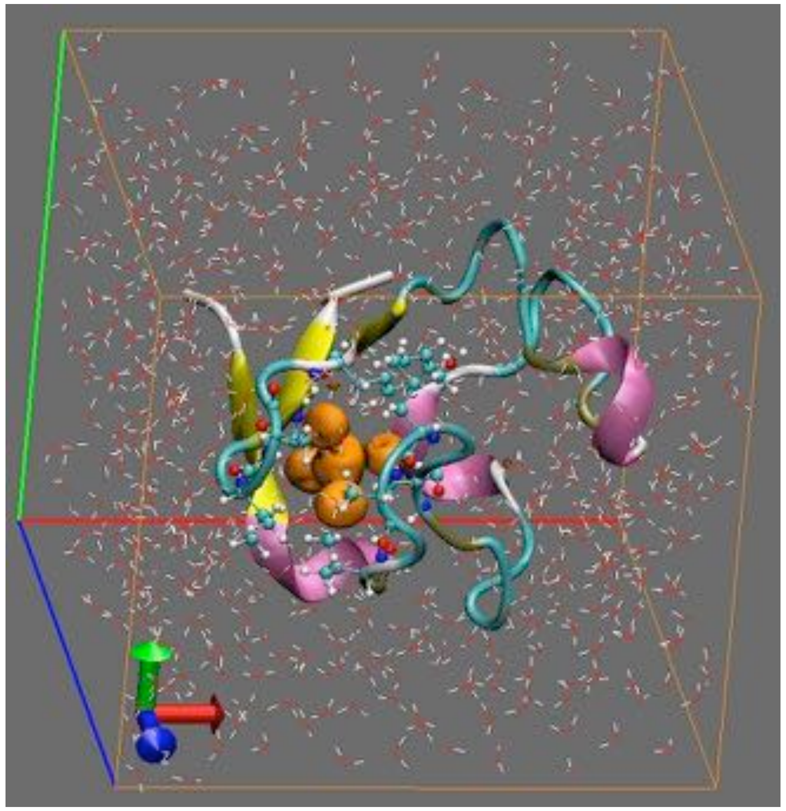
$$Q(R) = 4\pi \int_0^R \Delta n(r) r^2 dr \qquad \Delta n(r) = n^0(r) - n^q(r)$$



Metallicity of the Au79 core



M. Walter et al., PNAS, 105, 9157 (2008)

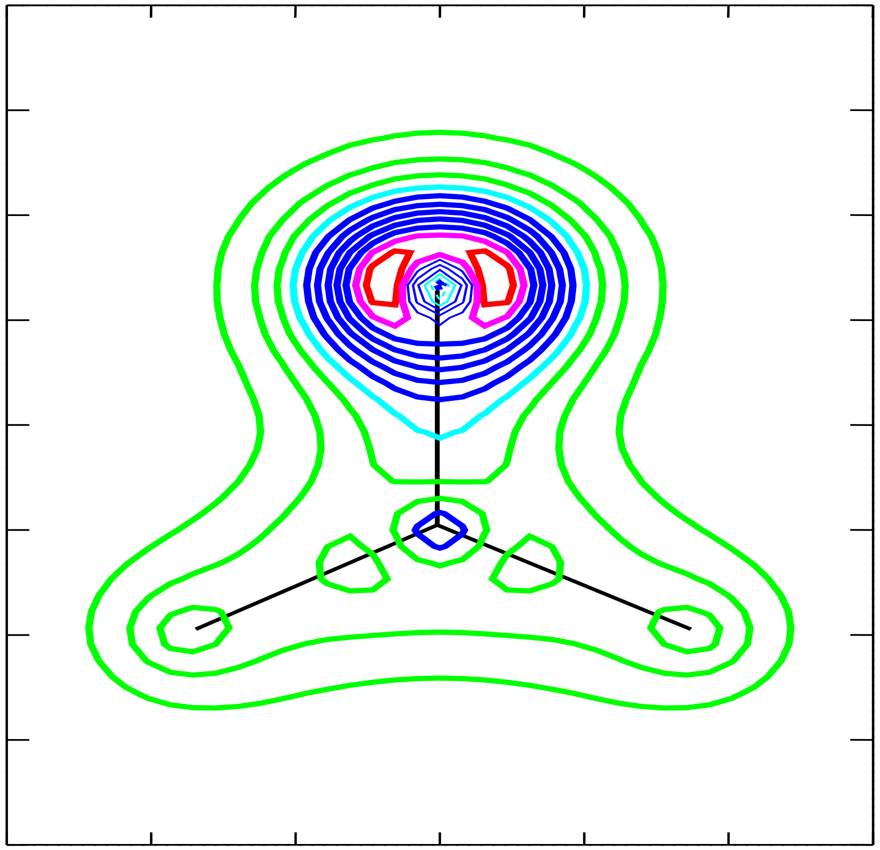


Solvated metallo-protein

Sulpizi et al, JPCB ,**111**, 3969, 2007

http://www.cp2k.org/science

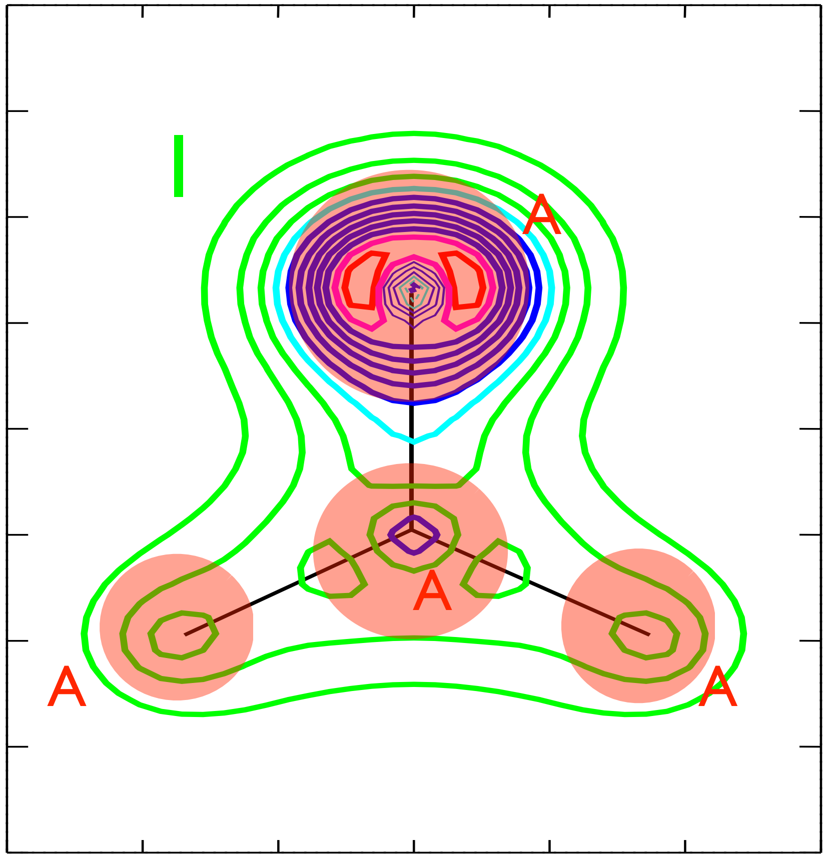
Hard and Soft Densities



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



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

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

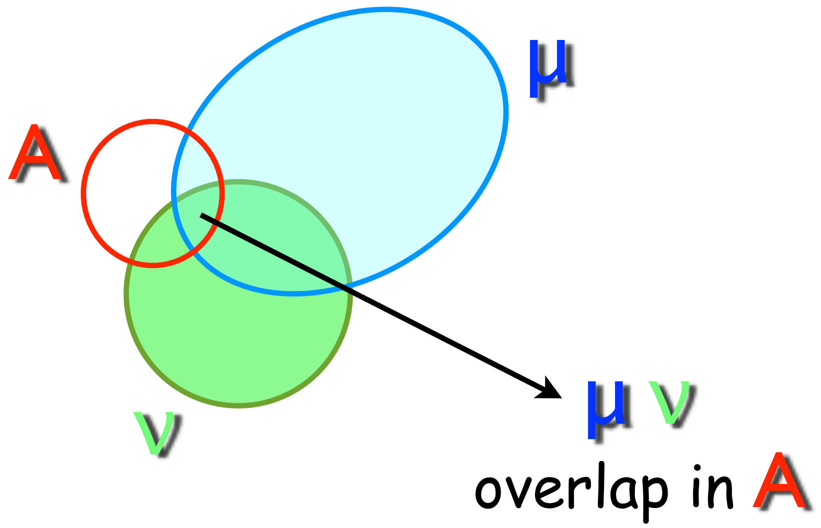
$$\left.\begin{aligned} n(\mathbf{r}) &- n_A(\mathbf{r}) = 0 \\ \tilde{n}(\mathbf{r}) &- \tilde{n}_A(\mathbf{r}) = 0 \end{aligned}\right\} \mathbf{r} \in A$$

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

Gaussian Augmented Plane Waves

Local Densities

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



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

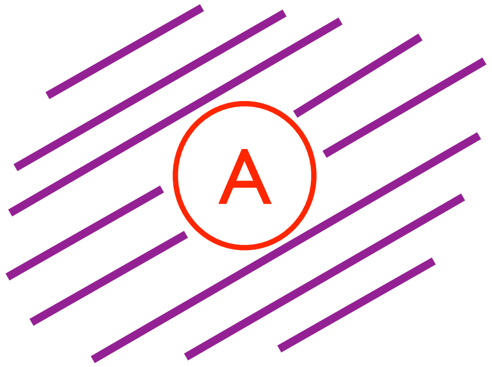
$$E[n] = \int V_{loc}(\mathbf{r}) n(\mathbf{r}) = \int \left\{ \tilde{V}_{loc}(\mathbf{r}) + \sum_A V^A_{loc}(\mathbf{r}) + \sum_A \tilde{V}^A_{loc}(\mathbf{r}) \right\}$$

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

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

Density Dependent Terms: ES

Non local Coulomb operator



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

Compensation charge

Same multipole expansion as the local densities

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

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

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

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

GAPW Input

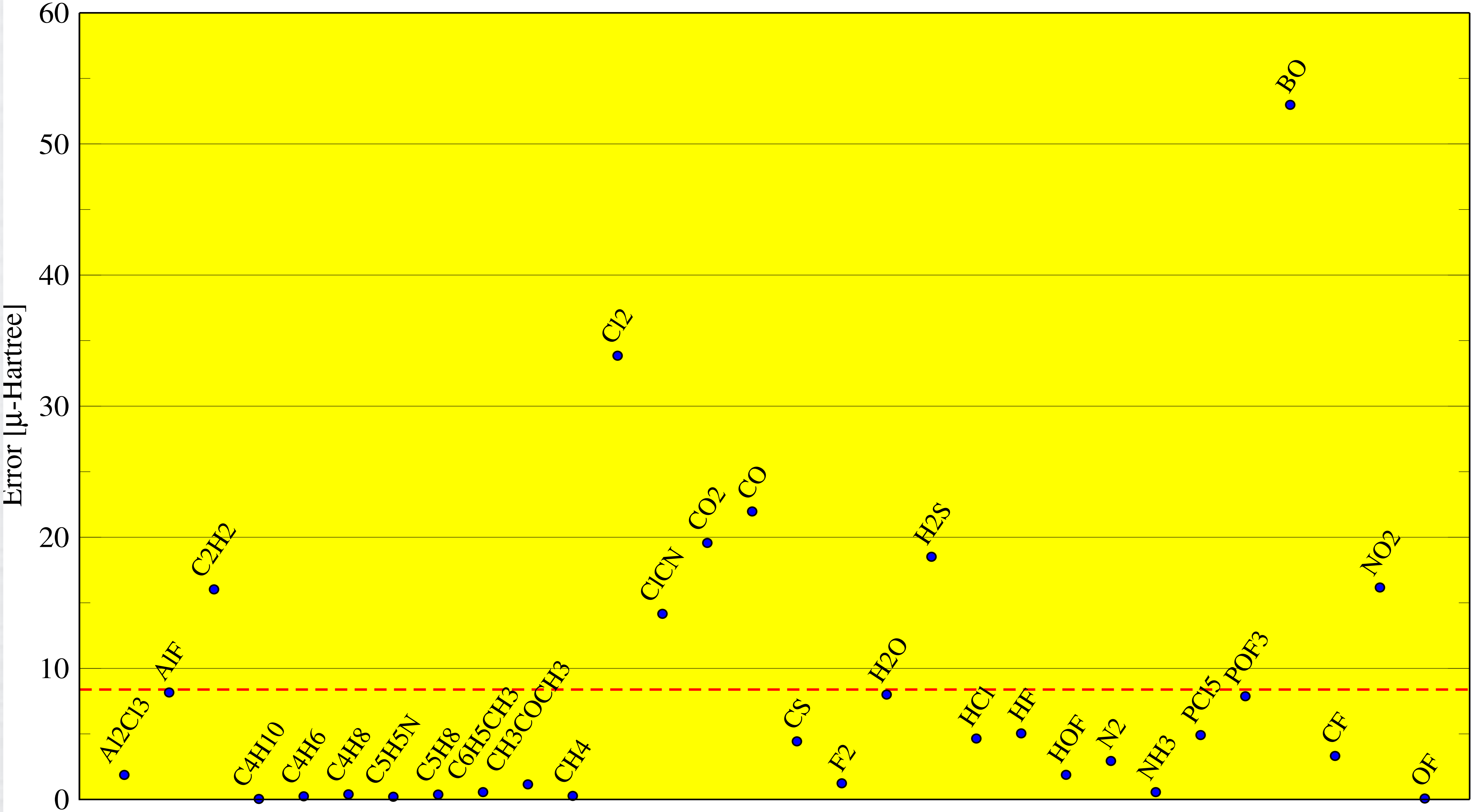
```
&DFT
  …
      &QS
        EXTRAPOLATION ASPC
        EXTRAPOLATION_ORDER 4
        EPS_DEFAULT 1.0E-12
        METHOD GAPW
        EPS_DEFAULT 1.0E-12
        QUADRATURE    GC_LOG
        EPSFIT        1.E-4
        EPSISO        1.0E-12
        EPSRHO0       1.E-8
        LMAXN0        4
        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
```

All-electron Calculations:CP2K vs G03



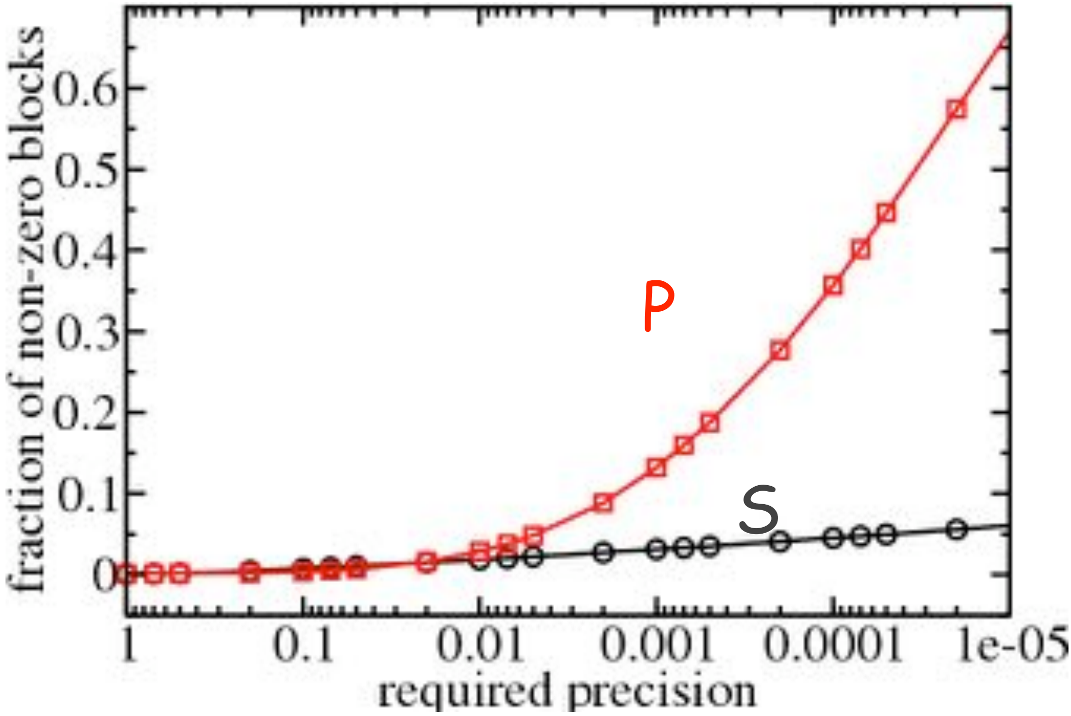
Energy Functional Minimisation

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

- 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))

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

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



Traditional Diagonalisation

Eigensolver from standard parallel program library: SCALAPACK

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

Transformation into a standard eigenvalues problem

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

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

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

DIIS for SCF convergence acceleration: few iterations

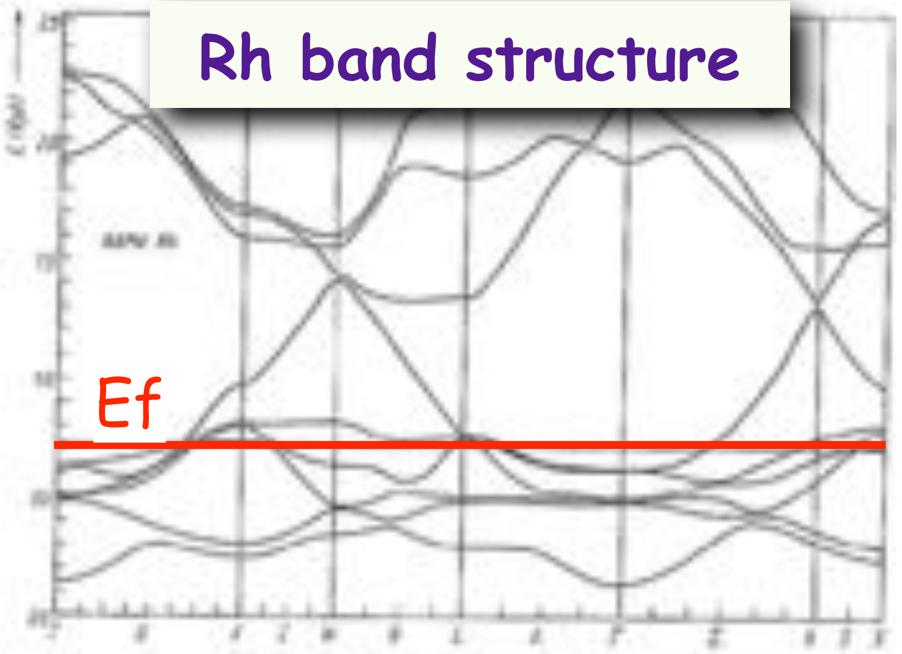
error matrix

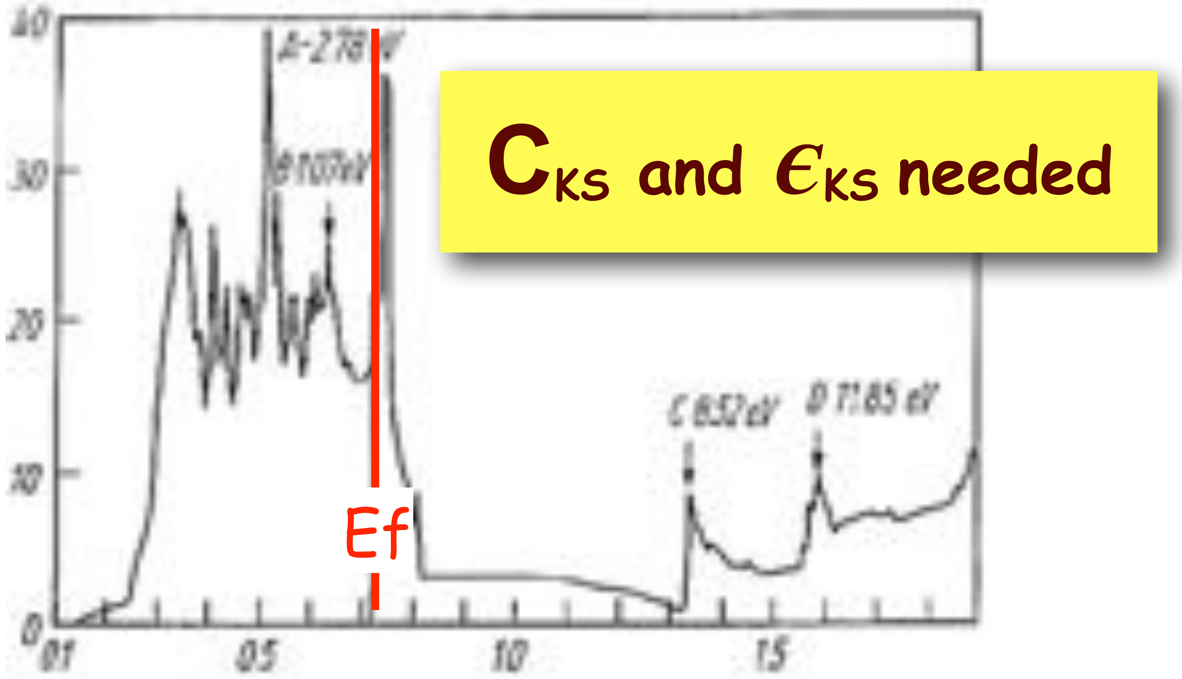
$$\mathbf{e} = \mathbf{KPS} - \mathbf{SPK}$$

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

Metallic Electronic Structure

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


Rh band structure


C_{KS} and ϵ_{KS} 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

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

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

Fermi-Dirac

Trial density mixed with previous densities: damping oscillations

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

residual

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

minimise the residual

G preconditioning matrix damping low G

Iterative improvement of the the $n(\mathbf{r})$

Input density matrix

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

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

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

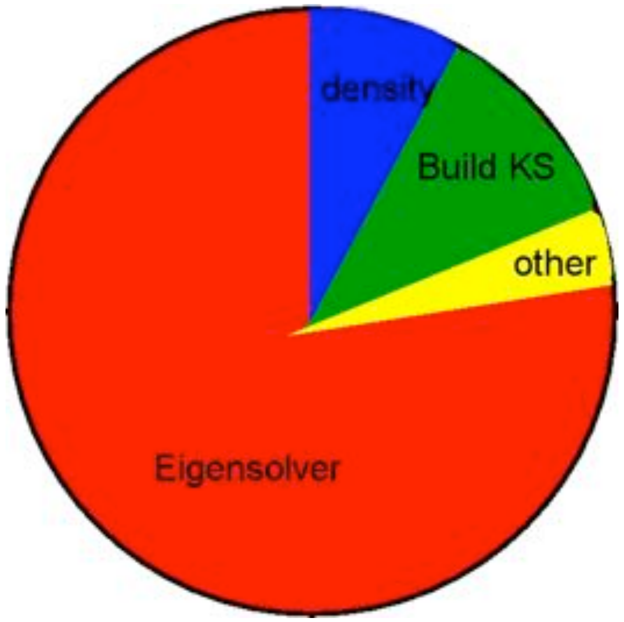
Check convergence

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

Density mixing

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

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



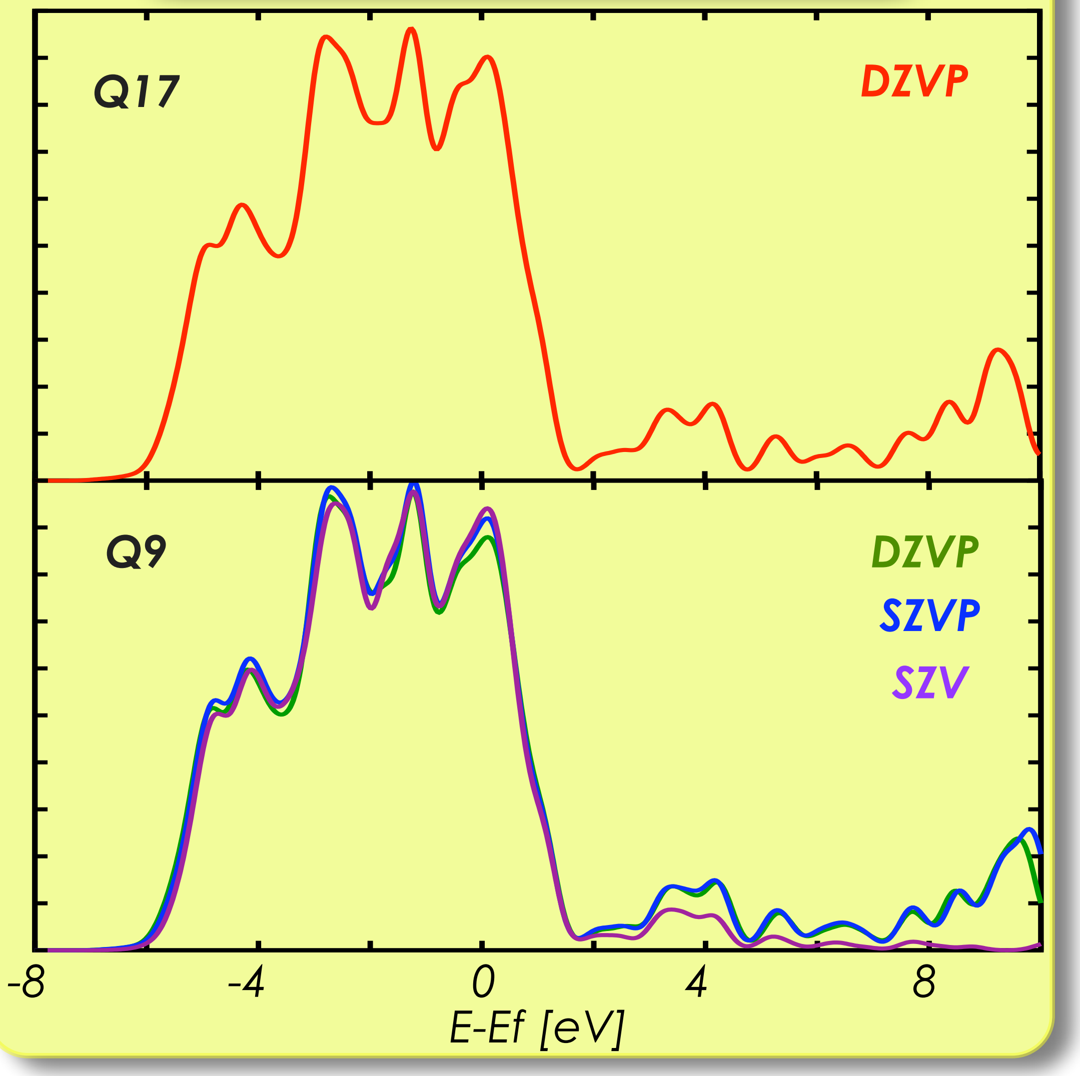
Rhodium: Bulk and Surface

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

Rh(111) d-projected LDOS

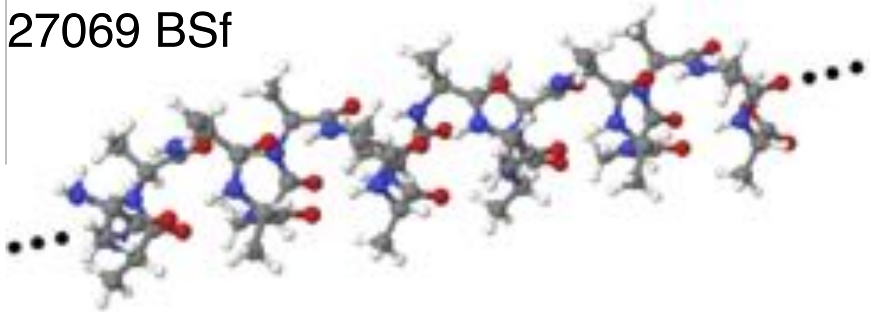


ScaLAPACK for diagonlisation

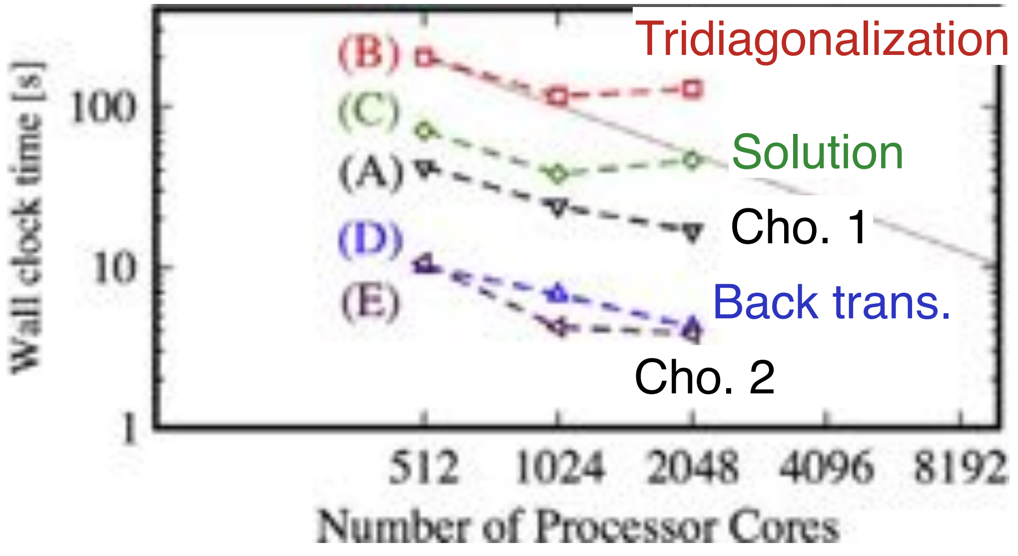
$$A \xrightarrow[\text{reduction to tridiagonal form}]{} T \xrightarrow[\text{compute eigenvalues and –vectors of T}]{} (\lambda, q_T) \xrightarrow[\text{transform eigenvectors}]{} q_A$$

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

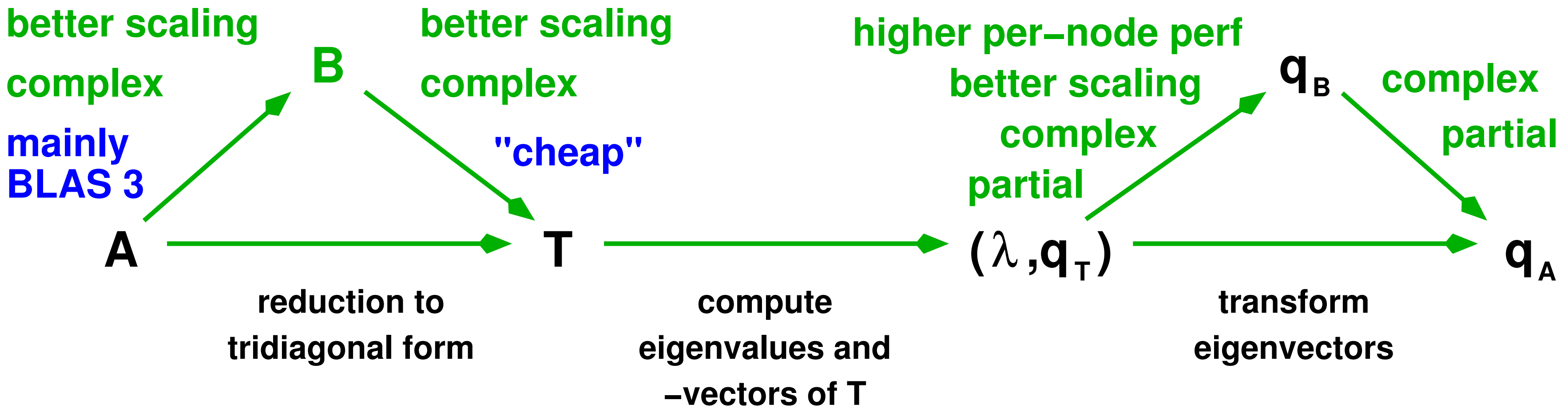
time x SCF, on CRAY XE6

>70% in eigenvalue solver

poor scaling

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

Improved efficiency by a two-step transformation and back transformation



$$\begin{tikzcd}
 & B \arrow[dr] & & & q_B \arrow[dr] & \\
A \arrow[ur] \arrow[rr] & & T \arrow[r] & (\lambda, q_T) \arrow[ur] \arrow[rr] & & q_A
\end{tikzcd}$$

A → B: better scaling, complex, mainly BLAS 3

B → T: better scaling, complex, "cheap"

A → T: reduction to tridiagonal form

T → (λ, q_T): compute eigenvalues and –vectors of T

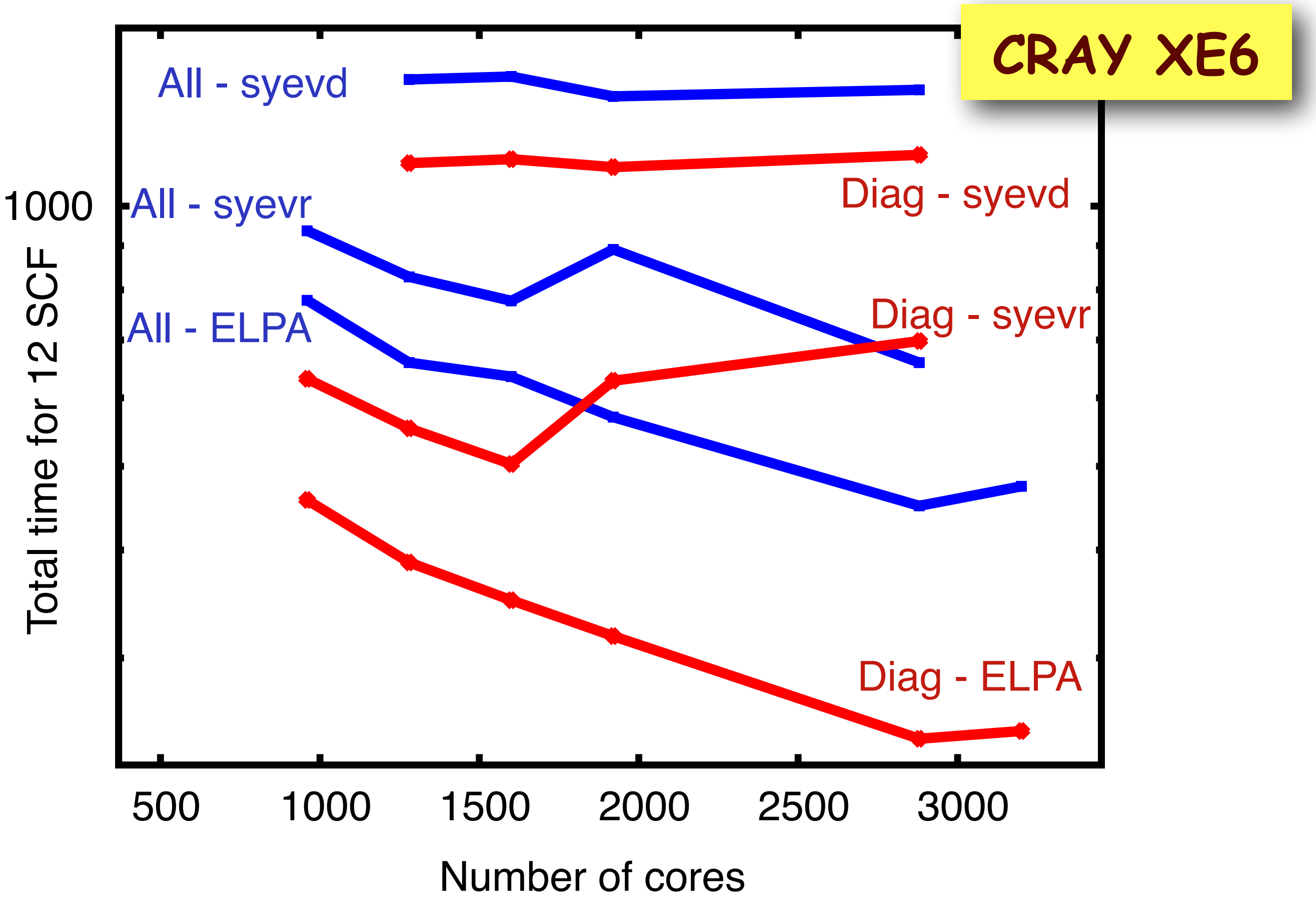
(λ, q_T) → q_B: higher per–node perf, better scaling, complex, partial

q_B → q_A: complex, partial

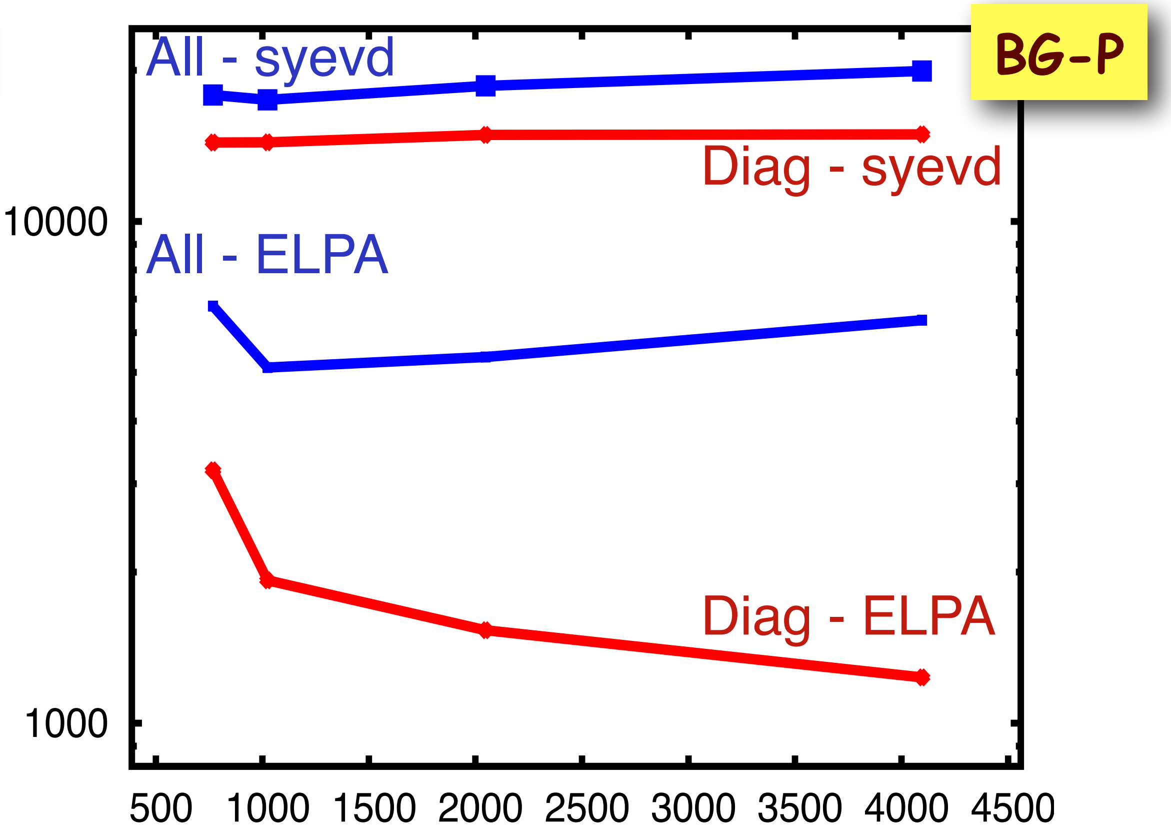
(λ, q_T) → q_A: transform eigenvectors

band form by blocked orthogonal transformations

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

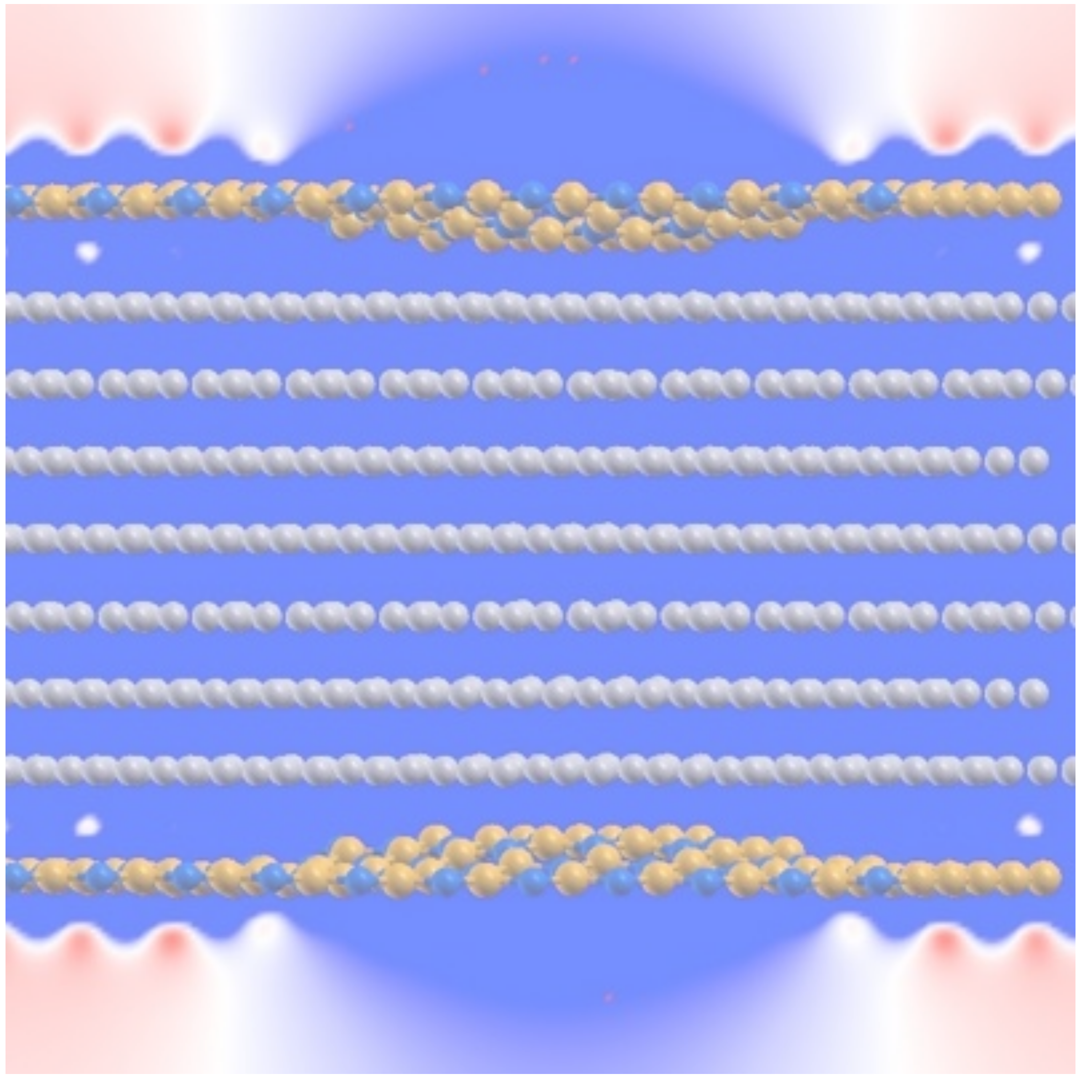


N atom= 480; Nel = 6000;
nmo = 7400; nao = 14240



Large metallic systems

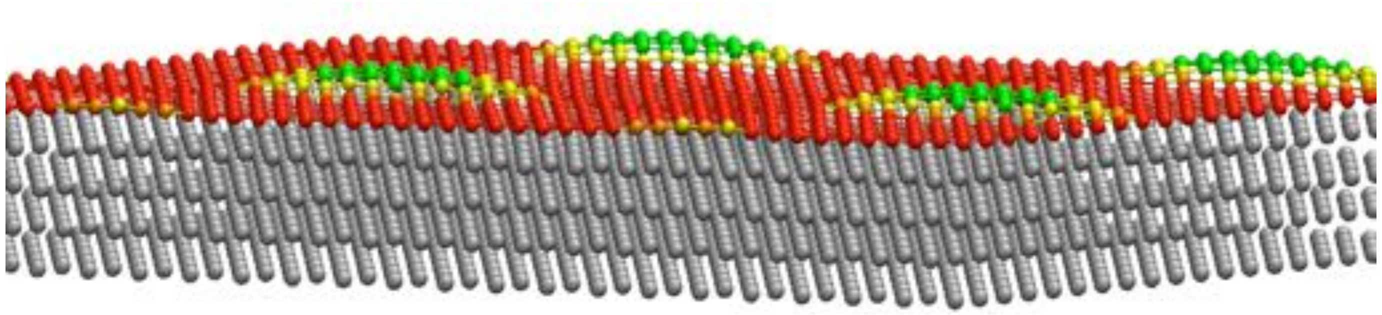
hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab



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
```