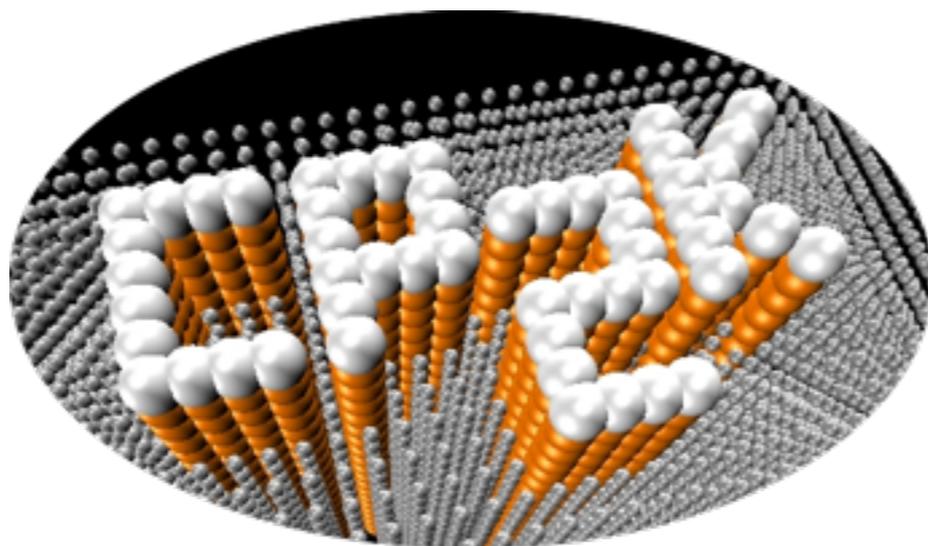


CP2K UK WORKSHOP 2014  
27-28 August 2014, London UK

# GPW (GAPW) electronic structure calculations

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<http://www.cp2k.org>

# CP2K overview

- ☀ Fortran95, 1'000'000 lines of code, rapid development
- ☀ Freely available, open source, GNU General Public License
- ☀ Community Developers Platform (UZH, IBM Research, ETHZ, PNL, LLNL, PSI, U Bochum, EPCC UK, .....
- ☀ User community through Google groups
- ☀ MPI and OpenMP parallelisation, CUDA C extensions : porting on >100'000 cores and to GPUs
- ☀ Quality control: automatic regression and memory leak (>2000)
- ☀ Force Methods: KS/OF DFT (vdw), Hybrid, MP2, RPA, Classical Force Fields, QM/MM, DFTB, semi-empirical, mixed
- ☀ Sampling Methods: GeoOpt, CellOpt, Molecular Dynamics, Ehrenfest MD, FES and PES tools (Metadynamics), Monte Carlo, PIMD
- ☀ Properties and spectroscopy (vibrational, IR, TDDFT, NMR, EPR, NEXAFS, Raman...)
- ☀ External Library: Lapack/BLAS, ScaLapack/BLACS, MPI, OpenMP, FFTW, libint, libxc, ELPA
- ☀ Internal library for handling sparse matrices (DBC SR)

# 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)
- ☀ Orbital Transformations (OT)
- ☀ Diagonalisation and Mixing
  - ☀ Metals

# DFT

## Why DFT?

- ☀ Explicit inclusion of electronic structure
- ☀ Predictable accuracy (unlike empirical approaches)
- ☀ Knowledge of electronic structure gives access to evaluation of many observables
- ☀ Better scaling compared to many quantum chemistry approaches

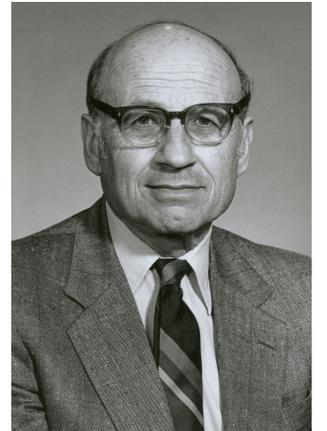
# Hohenberg-Kohn theorems

## Theorem I

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

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

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



Walter Kohn

☀ The density is the probability distribution of the wave functions

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

the potential and hence also the total energy are  
unique functional of the electronic density  $n(\mathbf{r})$

# HK Total energy

Theorem II: The total energy is variational

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

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

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

# Kohn-Sham: non-interacting electrons

Electronic density

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

no repulsion

Kinetic energy

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

External energy

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

Exact solution

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

# Kohn-Sham: non-interacting electrons

## Classical e-e repulsion

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

## Kohn-Sham functional

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

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

non-classical part

# KS Equations

## Orthonormality constraint

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

## Variational search in the space of orbitals

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

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

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

# KS Equations

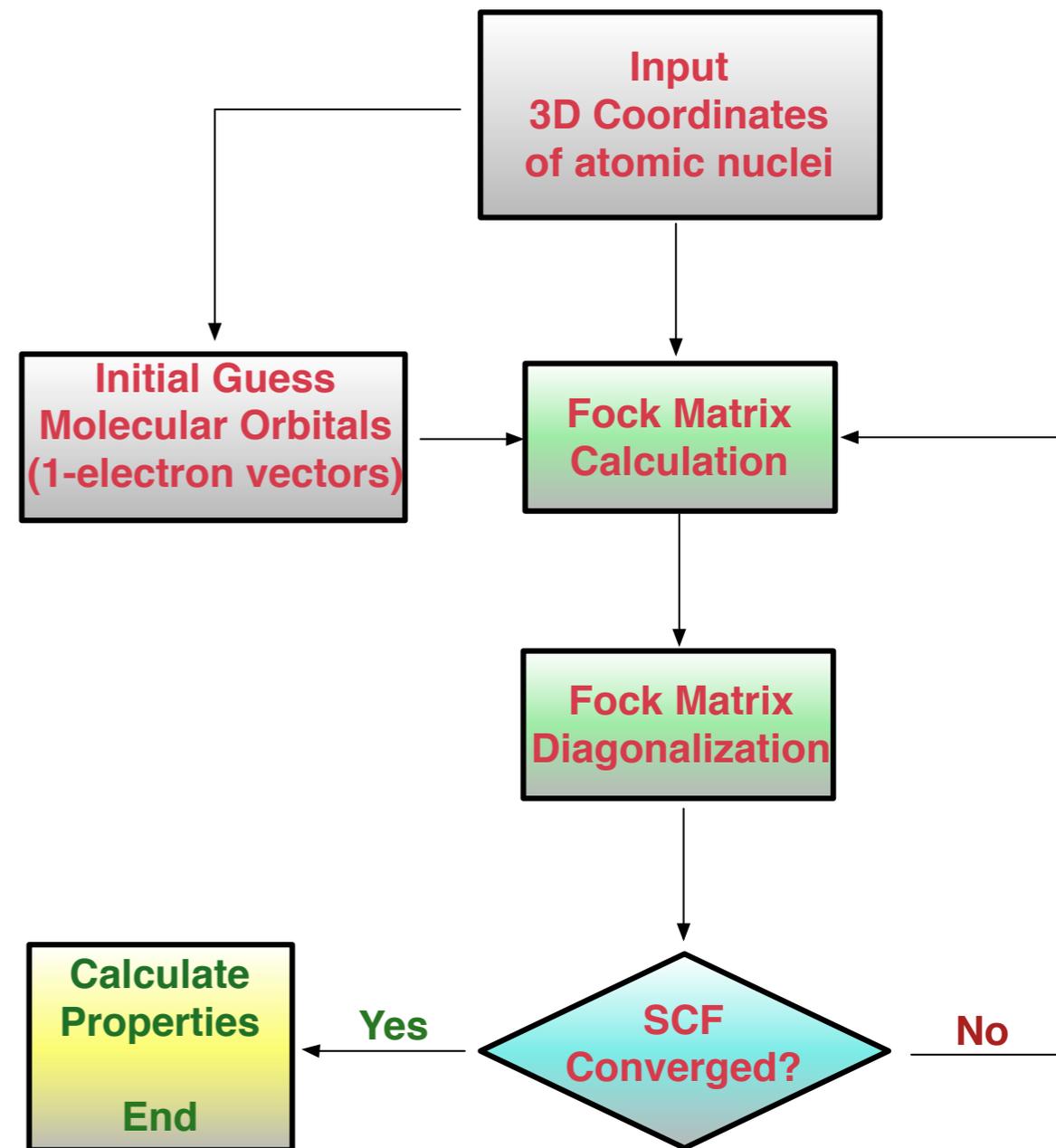
$\epsilon_{ij}$  diagonal

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

- ☀ KS equations looking like Schrödinger equations
- ☀ coupled and highly non linear
- ☀ **Self consistent solution** required
- ☀  $\epsilon$  and  $\psi$  are help variables
- ☀ **KS scheme in principle exact** ( $E_{\text{xc}}?$ )

# Self-consistency

- 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

# Local Density Approximation

Uniform electron gas

$$E_{\text{xc}}^{\text{LDA}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(n) d\mathbf{r}$$

$$V_{\text{xc}}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}^{\text{LDA}}[n]}{\delta n(\mathbf{r})} = \varepsilon_{\text{xc}}(n(\mathbf{r})) + n(\mathbf{r}) \frac{\partial \varepsilon_{\text{xc}}(n)}{\partial n}$$

Two contributions

$$\varepsilon_{\text{xc}}(n) = \varepsilon_{\text{x}}(n) + \varepsilon_{\text{c}}(n)$$

Dirac ex-functional

QMC interpolation (Ceperly-Alder)

Applicable with slow-varying densities

# Generalised Gradient Approximation

## Gradient expansion

$$E_{\text{xc}}^{\text{GGA}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(n) F_{\text{xc}} [n, \nabla n, \nabla^2 n, \dots] d\mathbf{r}$$

## GGA derivation

- ☀ Explicit form not known
- ☀ Theoretical approach: by fulfilling formal conditions as sum rules, long range decay, scaling rules, high/low density limits, etc.
- ☀ Fit parameters to experimental results (mol. database)

# Basis Set Representation

KS matrix formulation when the wavefunction is expanded into a basis

System size  $\{N_{el}, M\}$ ,  $\mathbf{P}$   $[M \times M]$ ,  $\mathbf{C}$   $[M \times N]$

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

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

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

Variational  
principle  
Constrained  
minimisation  
problem

KS total energy

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

Matrix formulation of the KS equations

$$\mathbf{K}(C)\mathbf{C} = \mathbf{T}(C) + \mathbf{V}_{\text{ext}}(C) + \mathbf{E}^{\text{H}}(C) + \mathbf{E}^{\text{xc}}(C) = \mathbf{S}\mathbf{C}\epsilon$$

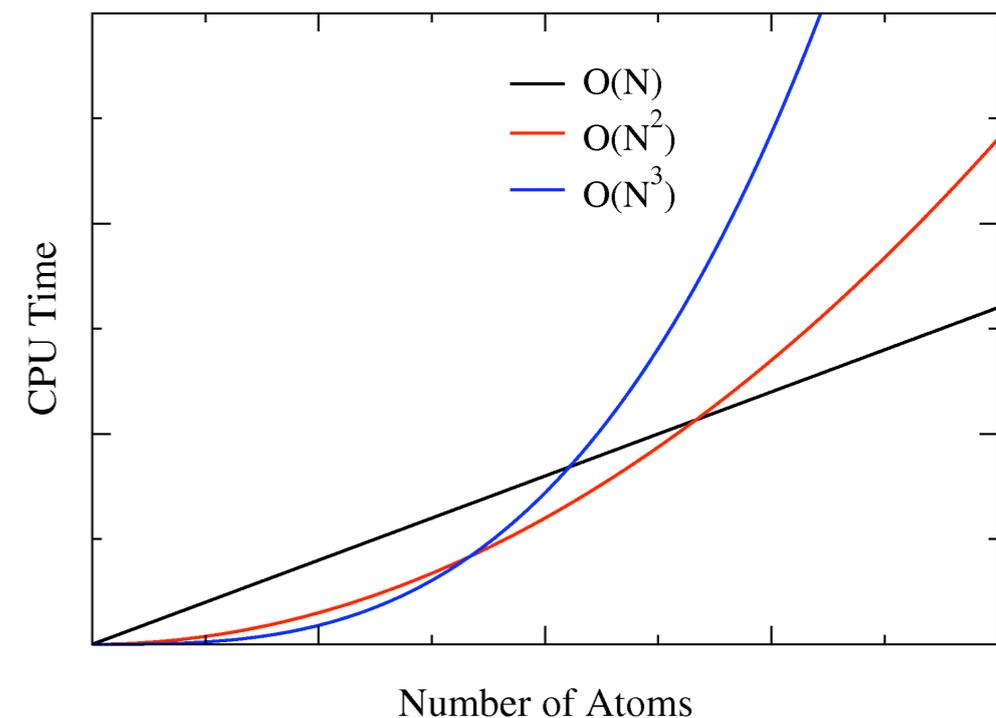
# Critical Tasks

- ☀ 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**
- ☀ Mixed to take best of two worlds, **GPW**: over-completeness
- ☀ Augmented basis set, **GAPW**: domains

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
```

# GPW Ingredients

linear scaling KS matrix computation for GTO

☀ Gaussian basis sets (many terms analytic)

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

☀ Pseudo potentials

☀ Plane waves auxiliary basis for Coulomb integrals

☀ Regular grids and FFT for the density

☀ Sparse matrices (KS and P)

☀ Efficient screening

# Gaussian Basis Set

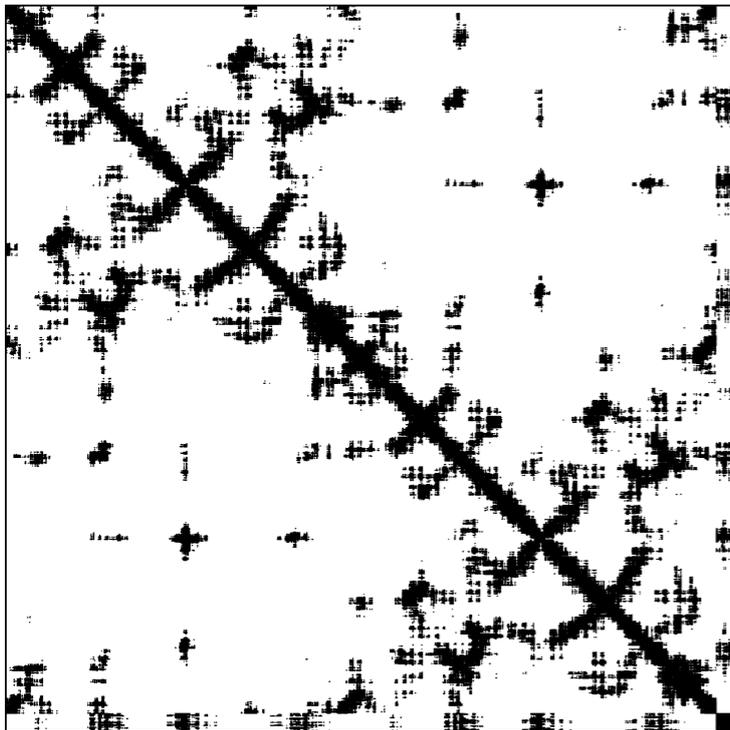
- Localised, atom-position dependent GTO basis

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

- Expansion of the density using the density matrix

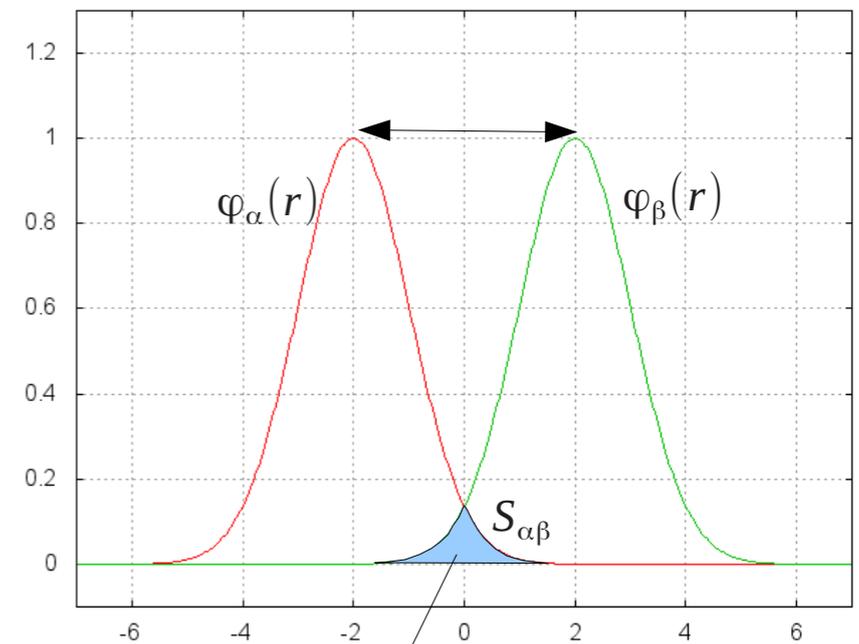
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_{\mu}(\mathbf{r}) \varphi_{\nu}^*(\mathbf{r})$$

Operator matrices are sparse



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

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



# Analytic Integrals

## Cartesian Gaussian

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

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

## Obara-Saika recursion relations

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

Obara and Saika JCP 84 (1986), 3963

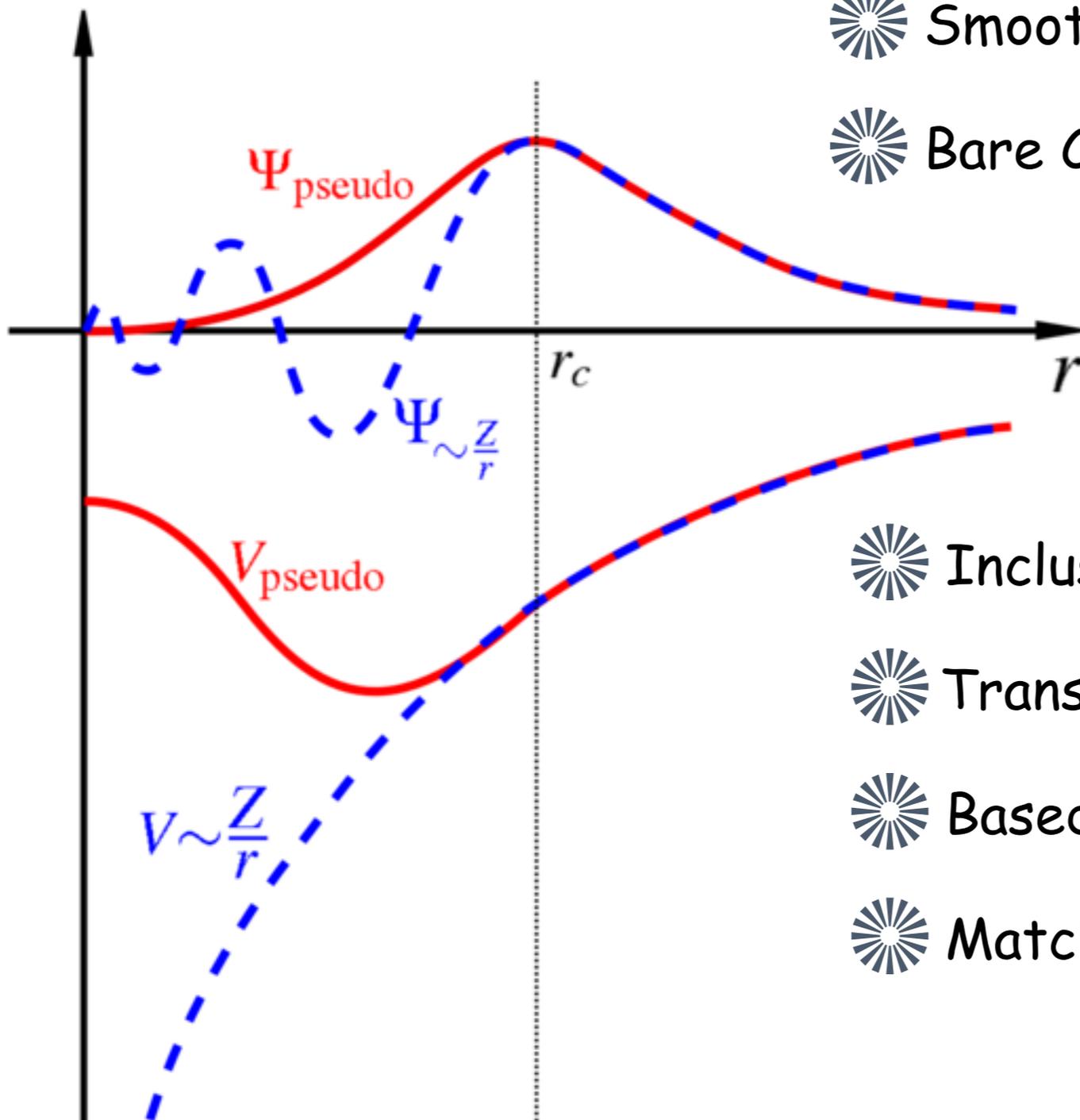
# Basis Set Library

## GTH\_BASIS\_SETS ; BASIS\_MOLOPT ; EMSL\_BASIS\_SETS

```
O 6-31Gx 6-31G*
O SZV-MOLOPT-GTH SZV-MOLOPT-GTH-q6
4
1 0 6 1
2 0 127 0 1 1 7 0 0 0 1 0.00183110
5484.67170000 0.00183110 O 6-311++G3df3pd 6-311++G(3df,3pd)
12.015954705512 0.060190841200 0.036543638800 9
825.23495000 0.01395010 0.0995679273
5.108150287385 -0.129597923300 0.120927648700
188.04695000 0.06844510 0.95364 -0.3011422449
2.048398039874 0.118175889400 0.251093670300
52.90456000 0.73434 -0.6971724029 0.4750857083
0.832381575582 0.462964485000 0.352639910300
16.80727000 0.450353782600 0.294708645200
0.352316246455 0.450353782600 0.294708645200
# 0.142977330880 0.092715833600 0.173039869300
0.00726110600 0.009726110600
15.33961600 -0.11077750 0.07087430
# 3.59993360 -0.14802630 0.33975280
O DZVP-MOLOPT-GTH DZVP-MOLOPT-GTH-q6 1 0 1 3 1 1
4 4.01376180 1.13076700 0.72715860
1 0 1 1813043855492 0.1510165999 0.0000000000 -0.0995679273 0.0000000000
2 0 27 2 2 1 580 484191 0.00000000 195364 0.0000000000000000 -0.3011422449 0.0000000000
12.015954705512 0.060190841200 0.065738617900 0.036543638800 -0.034210557400 0.014807054400
2 2 1017597373434 -0.6971724029 0.000000000000 -0.4750857083 0.000000000000 0.85332000
5.108150287385 -0.129597923300 0.110885902200 0.120927648700 -0.120619770900 0.068186159300
0.80000000 0.388632 0.00000000 1.33622 -1.000000000000 0.3798777957 1.000000000000
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
O 6-31Gx 6-31G* 0.00726110600 0.003825849600 0.009726110600 0.032498979400 -0.005771736600
4 5484.67170000 0.00183110
# 825.23495000 0.01395010
O TZVP-MOLOPT-GTH TZVP-MOLOPT-GTH-q6 1 2 2 1 1
4 188.04695000 0.06844510 1.29200000 1.00000000
1 52.90456000 419938232 0.1989598460 0.0000000000 0.0000000000 -0.0595856940 0.0000000000 0.0000000000
2 0 27 3 3 1 780 495696 47019300 78339 0.0000000000 0.0000000000 -0.1875649045 2.05000000000000000000
12.015954705512 -0.060190841200 0.065738617900 0.041006765400 0.036543638800 -0.034210557400 -0.000592640200 0.014807054400
5.79963300 3.7704 3.38 3.88 2.55 700 0.000000000000 0.000000000000 0.000000000000 0.000000000000
1 0.108150287385 -0.129597923300 0.110885902200 0.080644802300 0.120927648700 -0.120619770900 0.009852349400 0.068186159300
2 0.48398039874 0.118175889400 -0.053732406400 -0.067639801700 0.251093670300 -0.213719464600 0.001286509800 0.290576499200
15.33961600 0.11077750 0.07087430
0.832381575582 0.462964485000 -0.572670666200 0.352639910300 -0.473674858400 1.063344189500
# 3.59993360 -0.14802630 0.33975280
0.352316246455 0.450353782600 0.186760006700 0.722792798300 0.294708645200 0.484848376400 0.530504764700 0.307656114200
1.01376180 1.13076700 0.72715860
1 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
0.27000580 1.00000000 1.00000000
1 2 2 1 1
0.80000000 1.00000000
```

# Pseudopotentials

- ☼ 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
- ☼ Based on atomic calculations
- ☼ Matching of orbital energies and shapes (AE)

# Generate PP

## Reference

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

## PP

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

## Normconserving

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

## Separable: local, nonlocal

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

# GTH Pseudopotentials

☀ Norm-conserving, separable, dual-space

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

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

analytically part of ES

☀ Non-Local PP with Gaussian type projectors

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

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

Accurate and  
Transferable

Scalar  
relativistic

Few parameters

Goedecker, Teter, Hutter, PRB **54** (1996), 1703;

Hartwigsen, Goedecker, Hutter, PRB **58** (1998) 3641

# 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

$N_{\text{el}}(s)$	$N_{\text{el}}(p)$	$N_{\text{el}}(d)$	...
$r_{\text{loc}}^{\text{PP}}$	$N_C$	$C_1^{\text{PP}}$	... $C_{N_C}^{\text{PP}}$
$N_p$			
$r_1$	$n_{\text{nl}}^1$	$\{h_{ij}^1\}_{ij=1\dots n^1}$	
$r_2$	$n^2$	$\{h_{ij}^2\}_{ij=1\dots n^2}$	

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

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

total charge distribution including  $n(\mathbf{r})$  and  $Z$

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

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

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

$$r_A^c = \sqrt{2} r_{\text{locA}}^{\text{PP}}$$

cancels the long range term of local PP

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

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

$E^{\text{ov}}$  short range, pair

$E^{\text{self}}$

# Auxiliary Basis Set



Long range term : Non-local Hartree potential

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



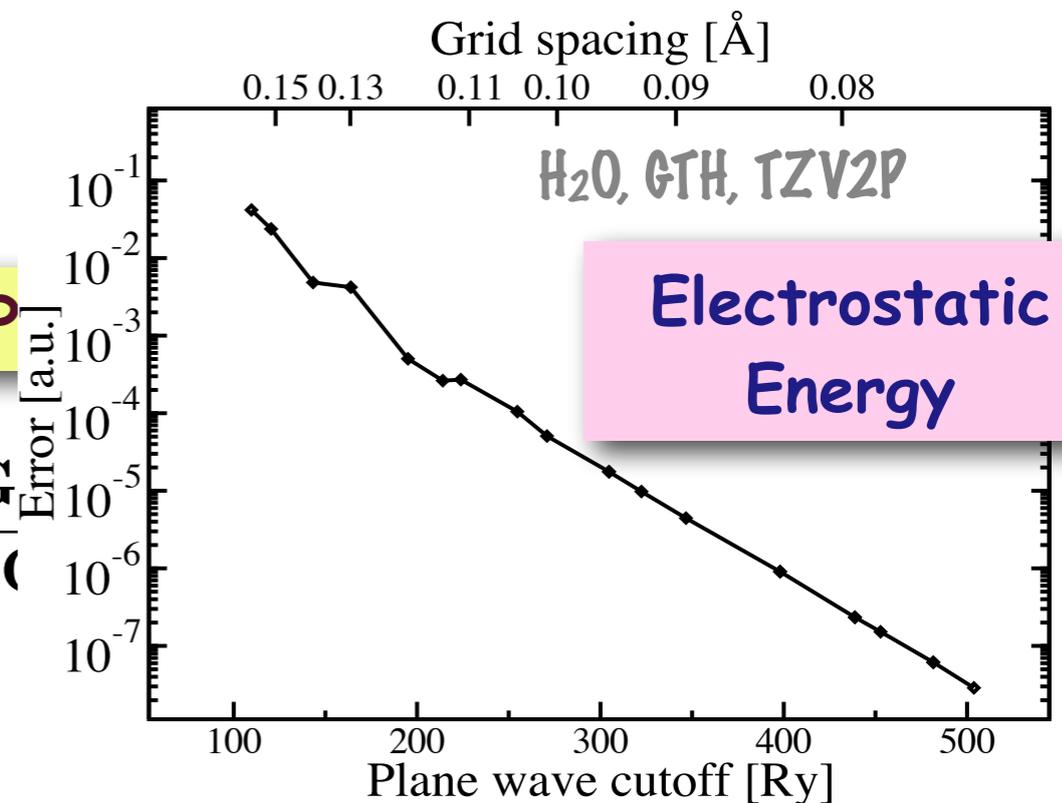
Orthogonal, unbiased, naturally periodic PW basis

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

Efficient Mapping  
FFT

Linear scaling solution of the Poisson equation

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



Electrostatic  
Energy

# Real Space Integration

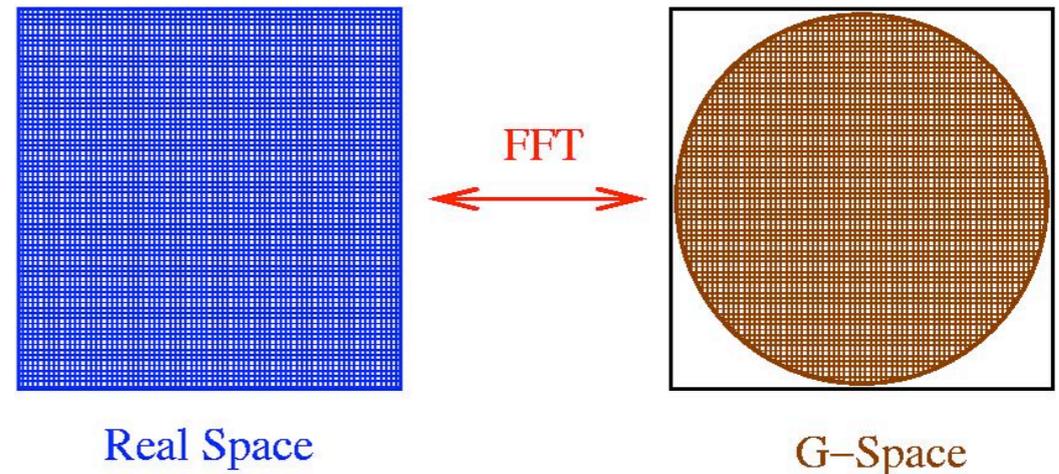
Finite cutoff and simulation box define a real space grid

## ☀ 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

$$n(\mathbf{R}) \rightarrow \nabla n(\mathbf{R})$$

## ☀ $\epsilon_{xc}$ 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

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

G. Lippert et al, Molecular Physics, 92, 477, 1997

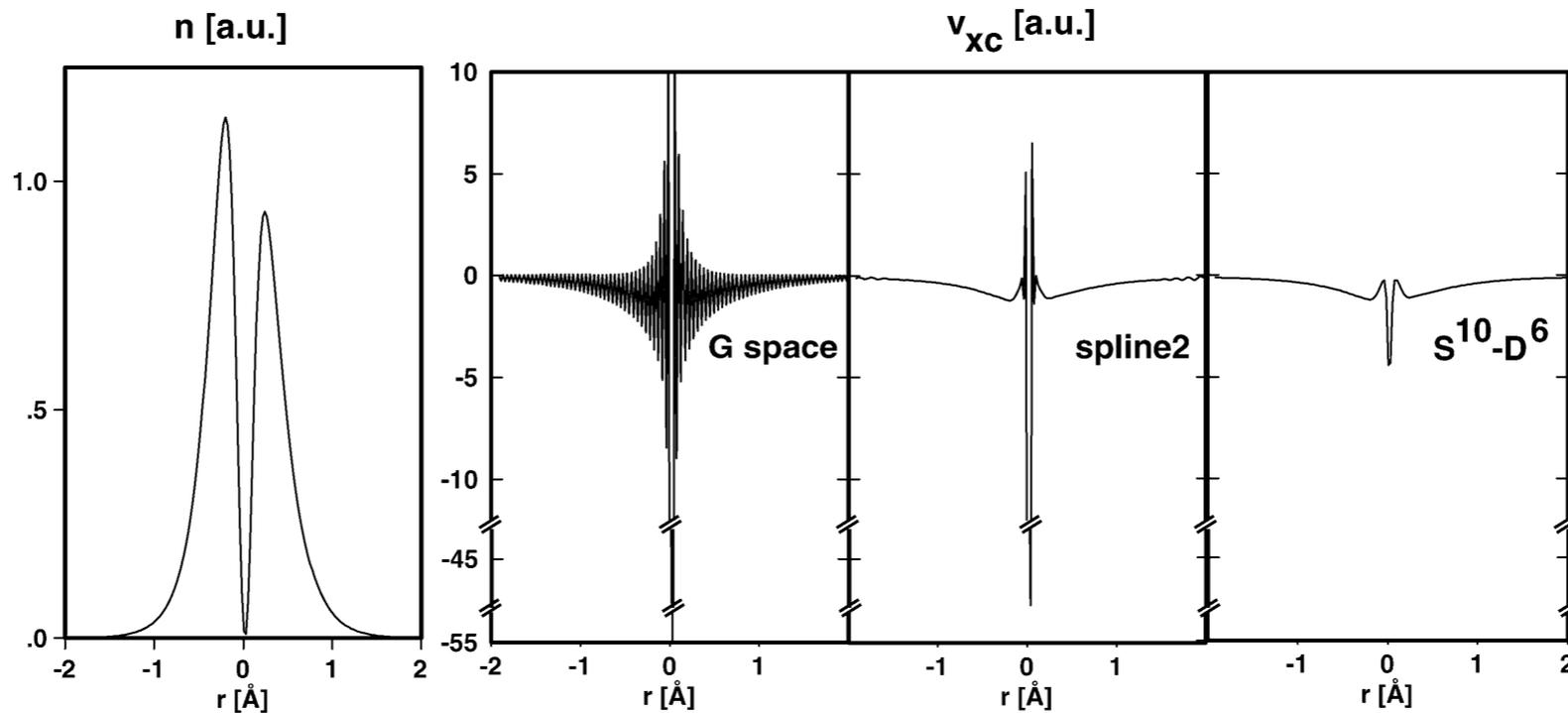
J. VandeVondele et al, Comp. Phys. Comm., 167 (2), 103, 2005

# Energy Ripples

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

H<sub>2</sub>O, BLYP  
close to 0 along  
HOH bisector

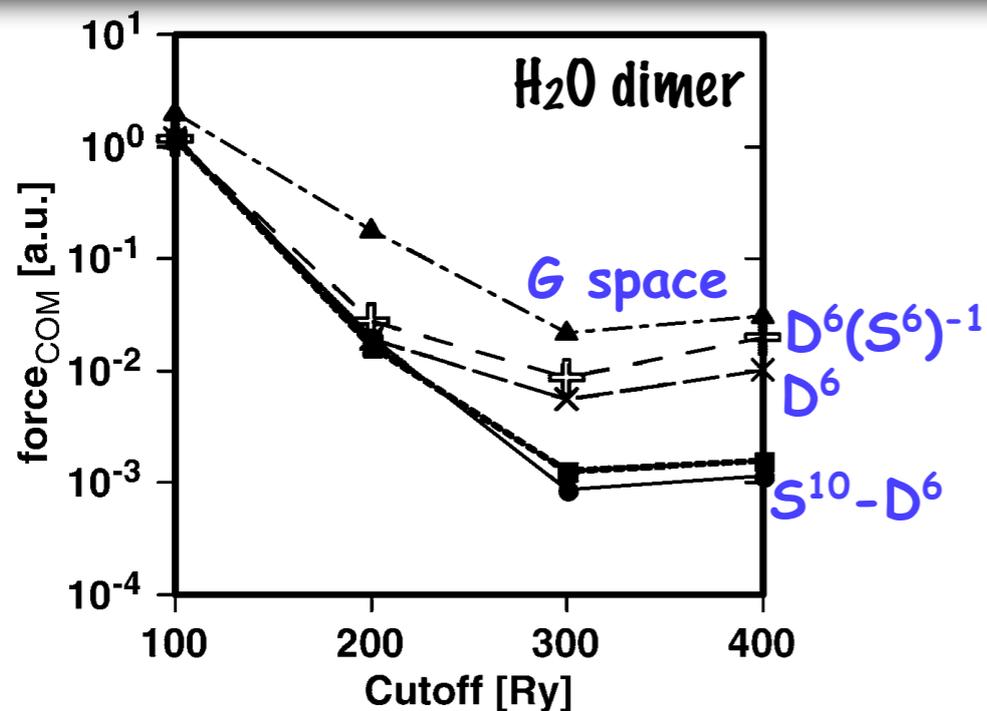
with PP  
low density  
at core



locally averaged  
n (neigh. q  
points S<sup>q</sup>)

smoothed finite  
differences (D<sup>q</sup>)

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



alternatively:  
Non-linear core corrected PP  
GAPW

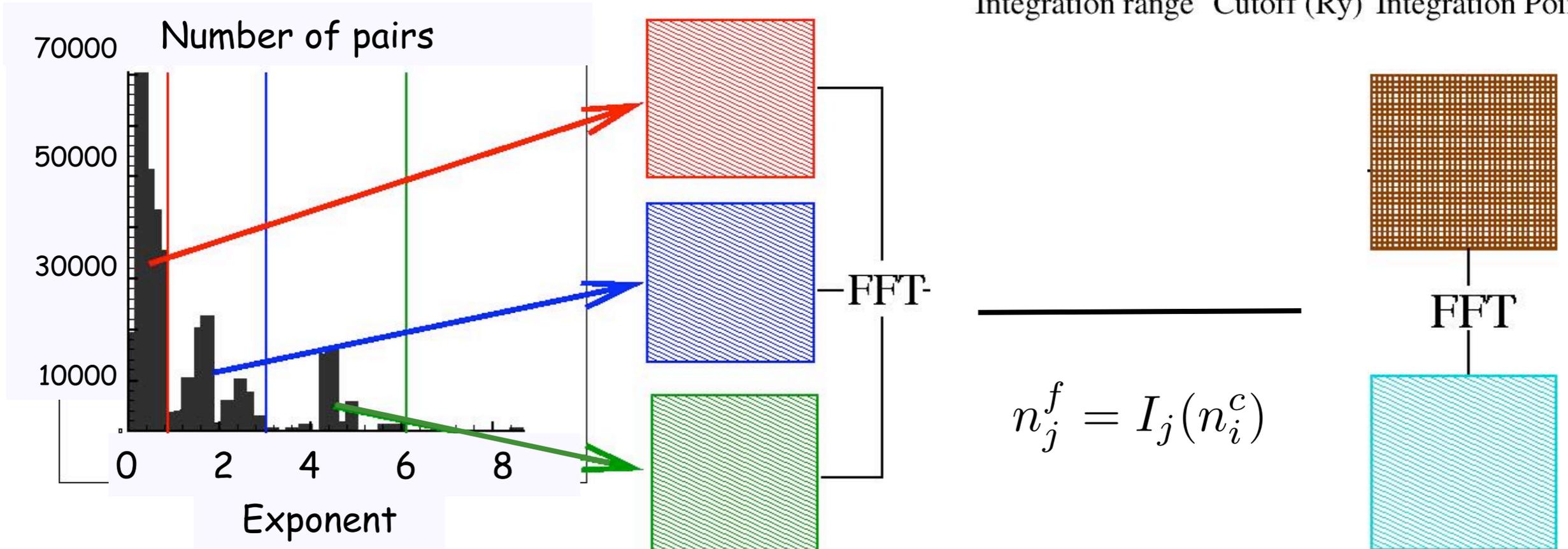
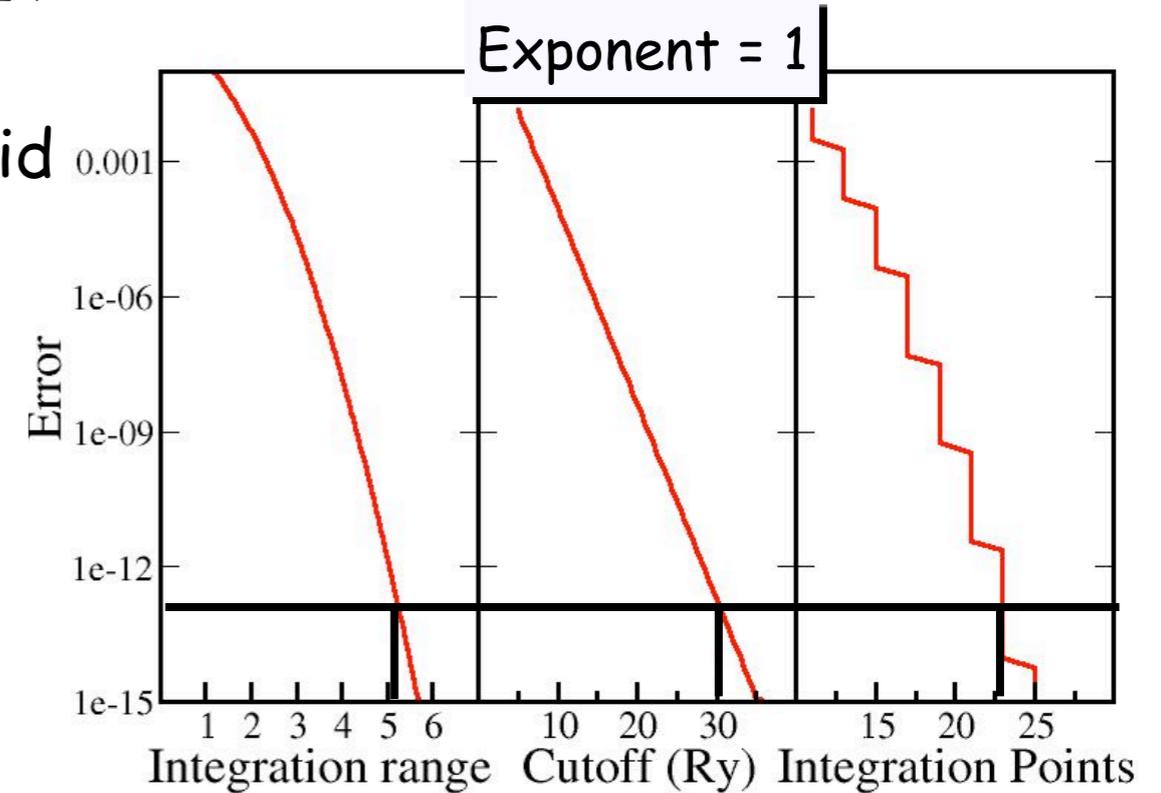
# Multiple Grids

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

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**



# GPW Functional

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

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-PADE-q1**

&END KIND

### &KIND O

BASIS\_SET **DZVP-GTH-PBE**

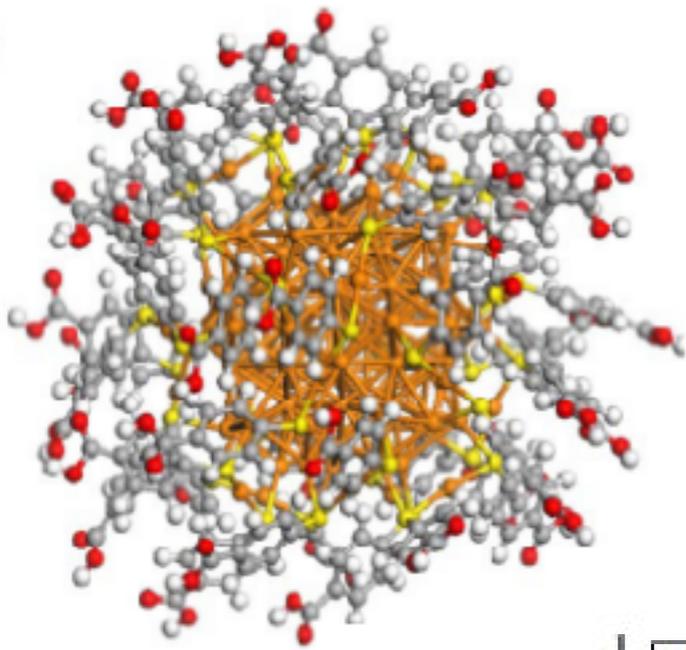
POTENTIAL **GTH-PADE-q6**

&END KIND

&END SUBSYS

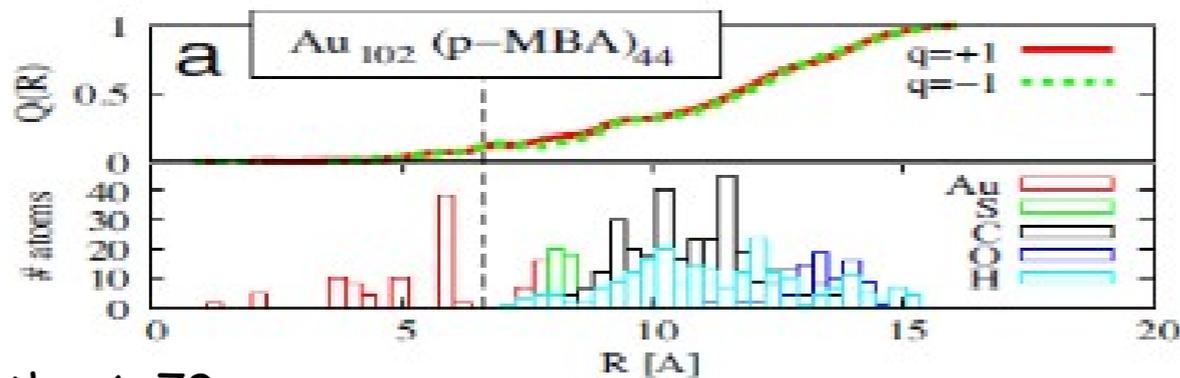
&END **FORCE\_EVAL**

# DFT for very large systems

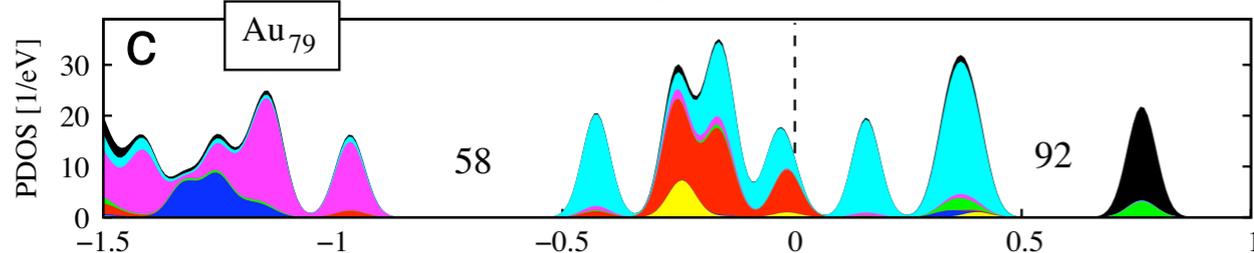
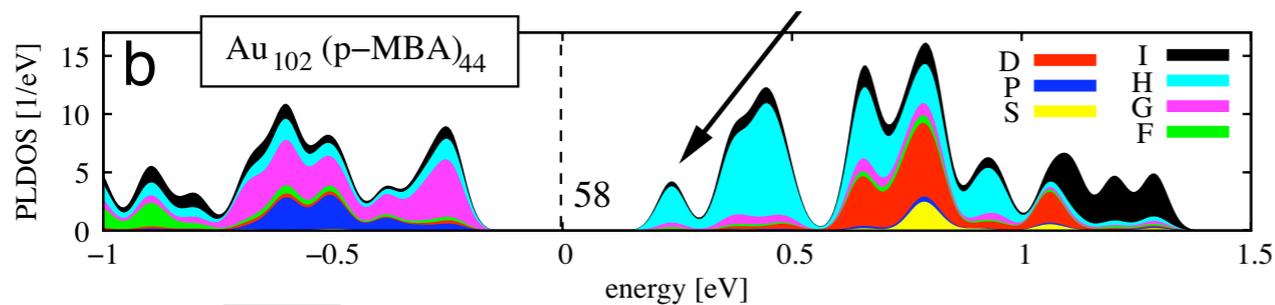


Ligand-protected Au cluster  
762 atoms, ~3400 el.  
as superatom complex

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

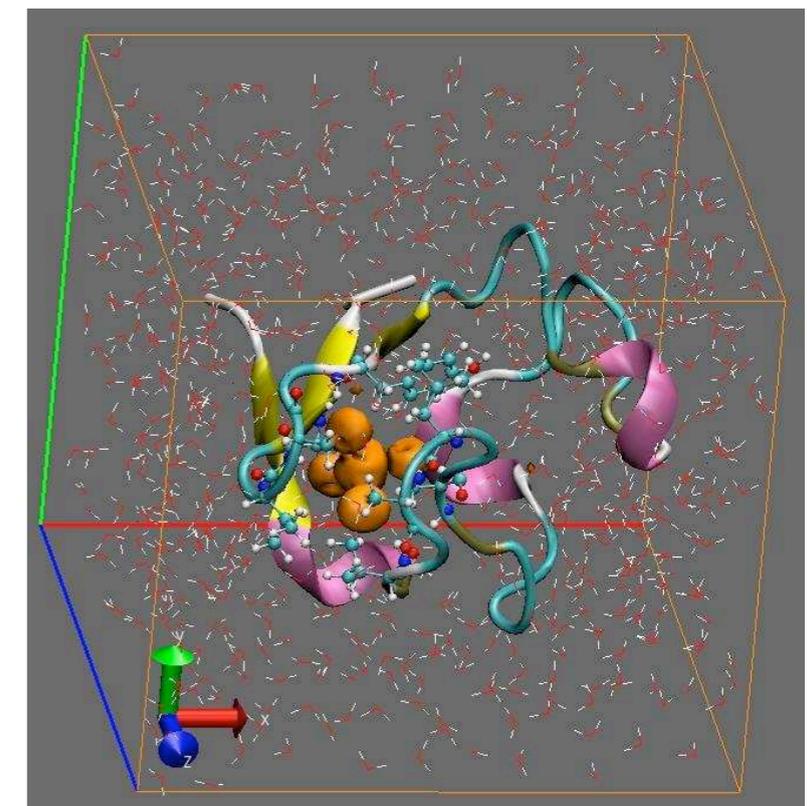


Metallicity of the Au<sub>79</sub> core



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

Rubredoxin in water solution  
~2800 atoms, ~ 55000 N<sub>ao</sub>  
117s/scf 1024 CPUs (XT3),  
80% parallel efficiency

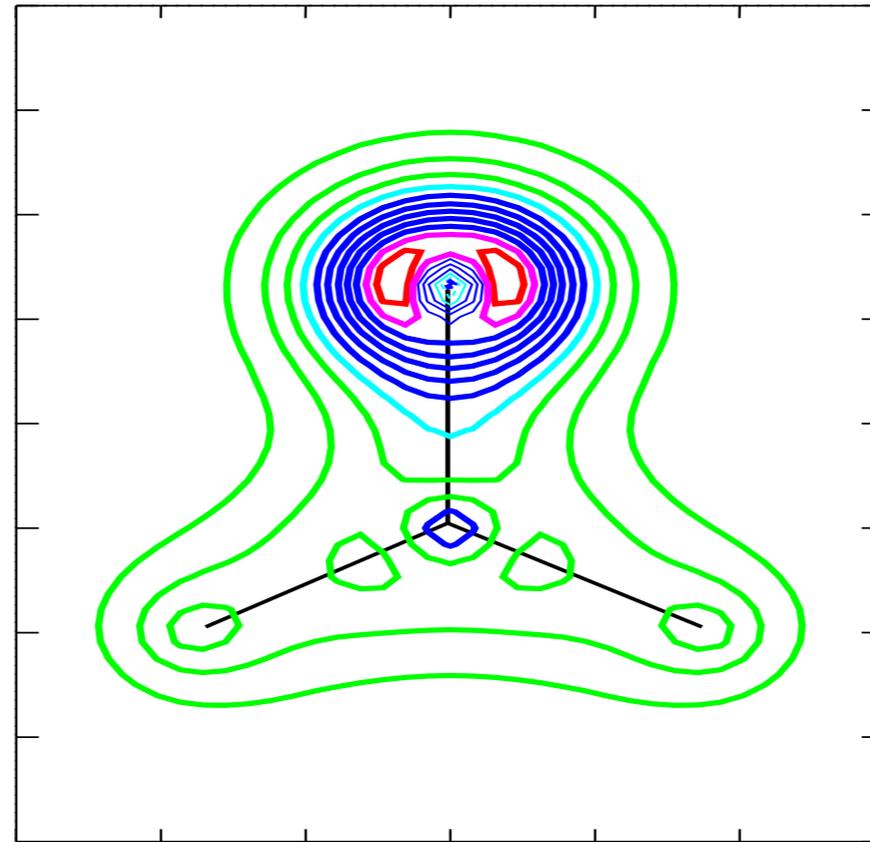


Solvated metallo-protein

Sulpizi et al, JPCB, 111, 3969, 2007

<http://www.cp2k.org/science>

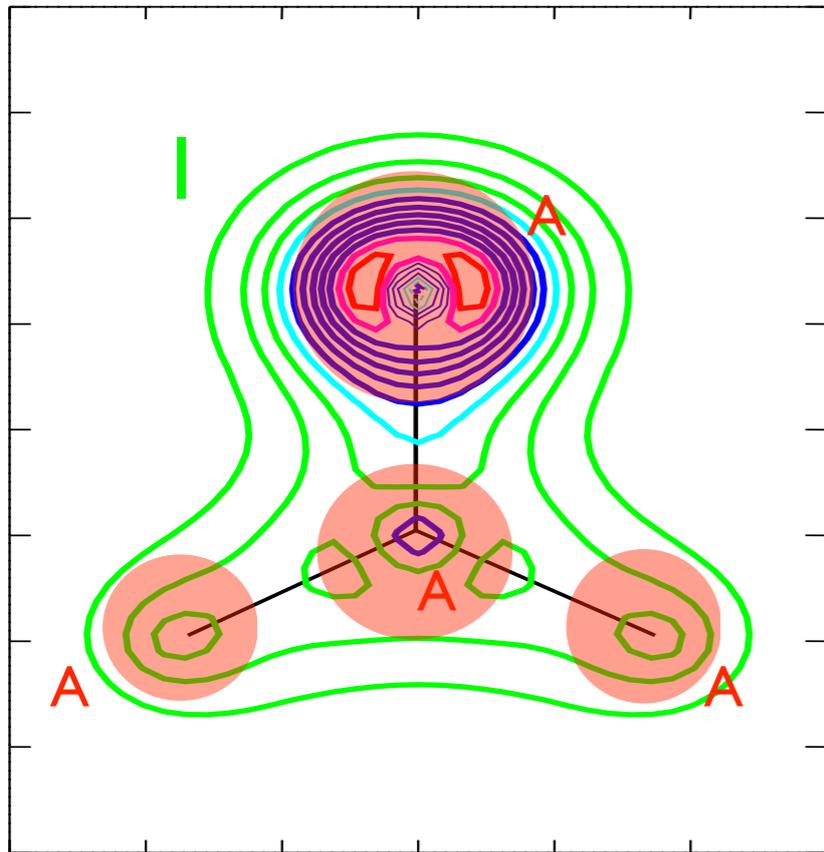
# Hard and Soft Densities



Formaldehyde

- ☀ 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 Blochl, PRB, 50, 17953 (1994))

# Partitioning of the Density



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

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

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

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

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

Gaussian Augmented Plane Waves

# Local Densities

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

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

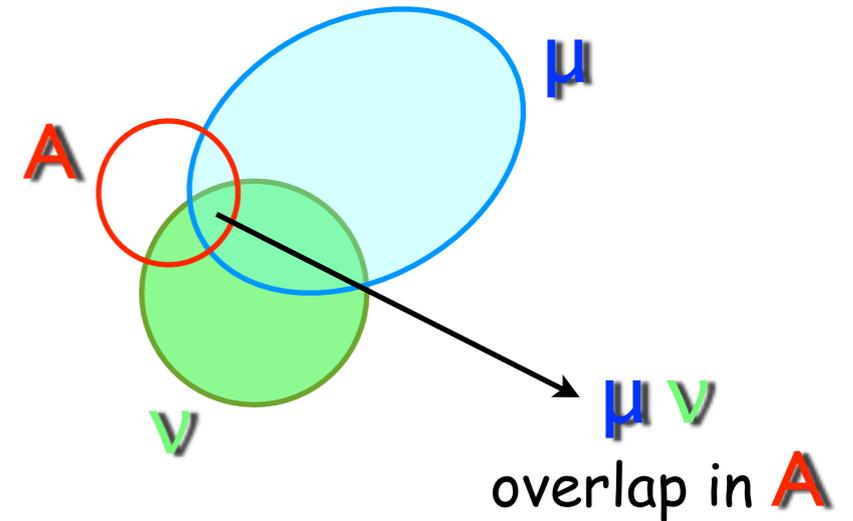
$$\chi_\mu = \sum_{\alpha} d'_{\mu\alpha} g_{\alpha}(\mathbf{r})$$

projector basis (same size)

$$\{p_{\alpha}\} \quad \lambda_{\alpha} = k^{\alpha} \lambda_{min}$$

$$\langle p_{\alpha} | \varphi_{\mu} \rangle = \sum_{\beta} d'_{\mu\beta} \langle p_{\alpha} | g_{\beta} \rangle$$

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

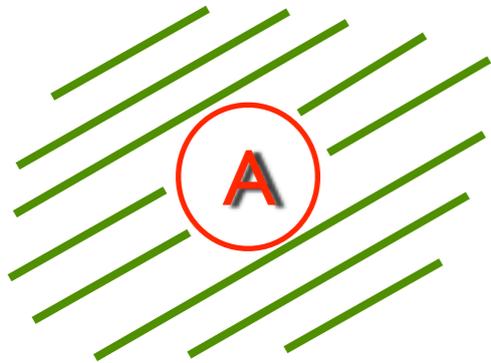


# Density Dependent Terms: XC

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

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

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

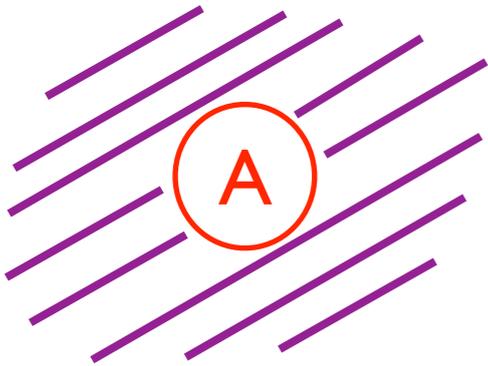


$$= \int \left\{ \tilde{V}_{loc}(\mathbf{r})\tilde{n}(\mathbf{r}) + \sum_A V_{loc}^A(\mathbf{r})n_A(\mathbf{r}) - \sum_A \tilde{V}_{loc}^A(\mathbf{r})\tilde{n}_A(\mathbf{r}) \right\}$$

# Density Dependent Terms: ES

Non local Coulomb operator

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



Same multipole expansion as the local densities

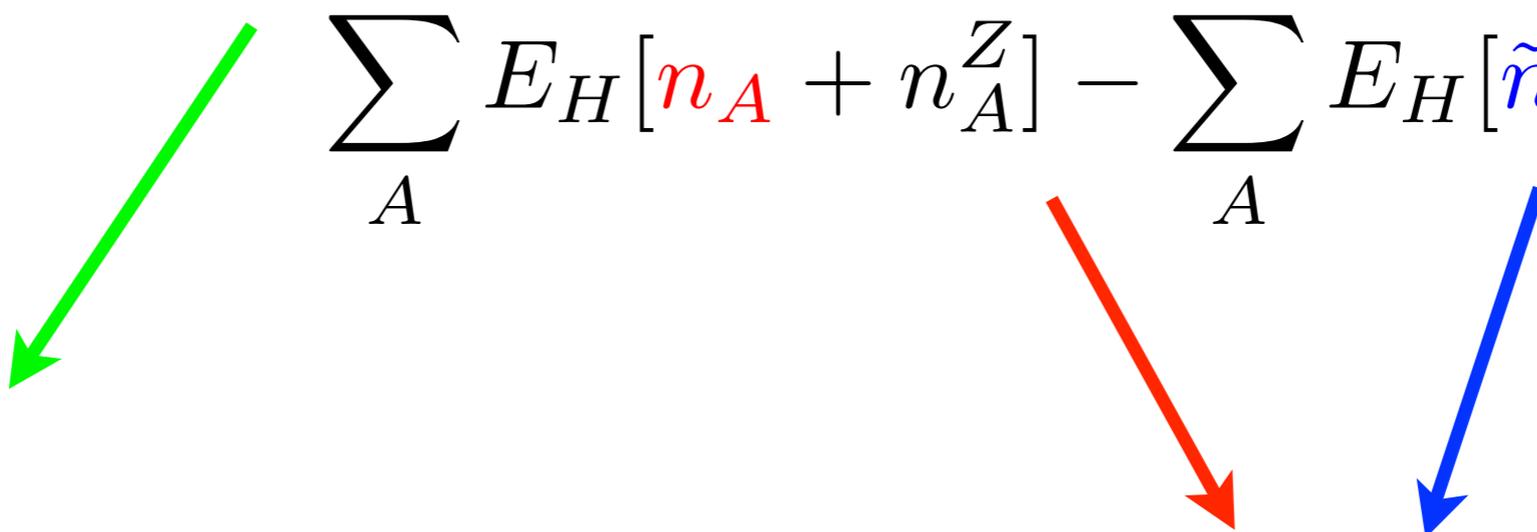
$$Q_A^L = \int \{ n_A(\mathbf{r}) - \tilde{n}_A(\mathbf{r}) + n_A^Z(\mathbf{r}) \} r^l \mathcal{Y}_{lm}(\theta\phi) r^2 dr \sin(\theta) d\theta d\phi$$

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

Interstitial region  
Atomic region

# GAPW Functionals

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

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


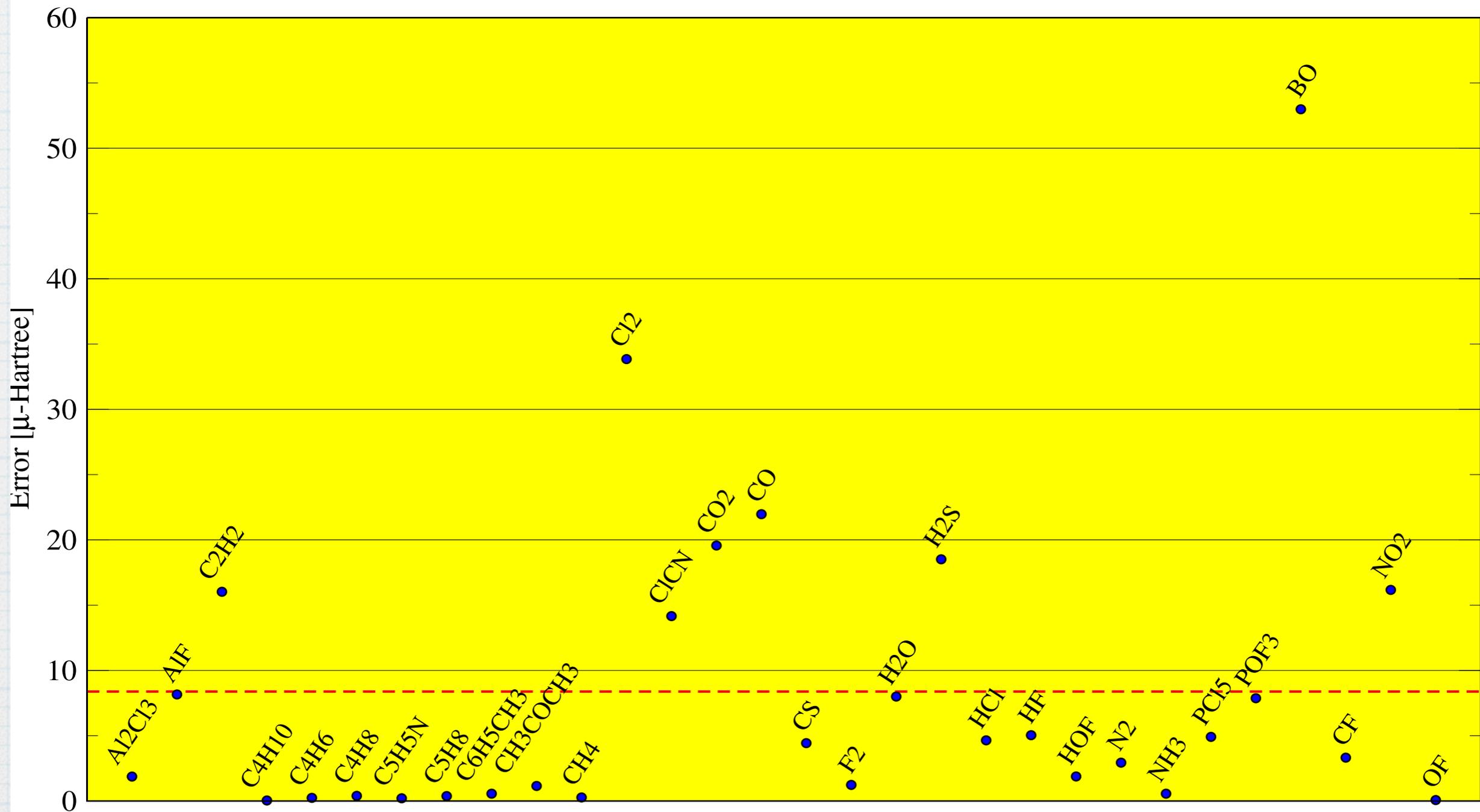
on global grids  
via collocation + FFT

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

# All-electron Calculations: CP2K vs G03



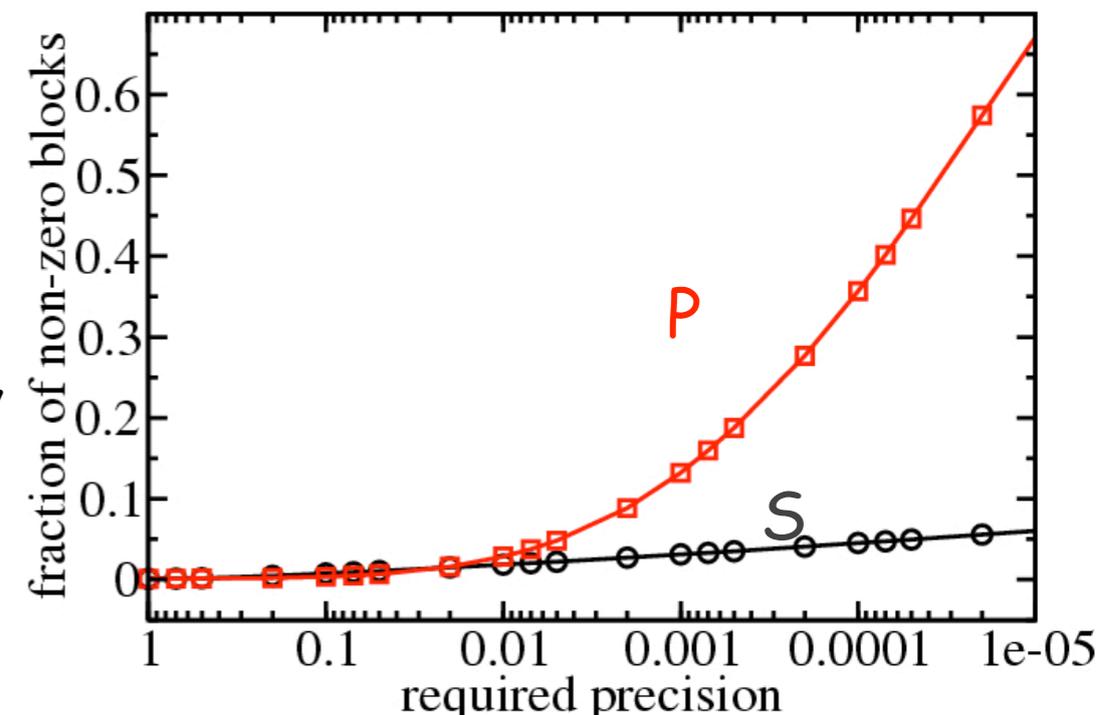
# Energy Functional Minimisation

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

- 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))

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

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



# Traditional Diagonalisation

Eigensolver from standard parallel program library: SCALAPACK

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

Transformation into a standard eigenvalues problem

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

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

Diagonalisation of  $\mathbf{K}'$  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  $\mathbf{X}$ , linearly constrained variables to parametrise the occupied subspace

not linear orthonormality constraint

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

Linear constraint

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

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

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

matrix functionals by Taylor  
expansions in  $\mathbf{X}^T \mathbf{S} \mathbf{X}$

minimisation in the auxiliary tangent space  
idempotency verified

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

CG(LS) or DIIS

Preconditioned gradients

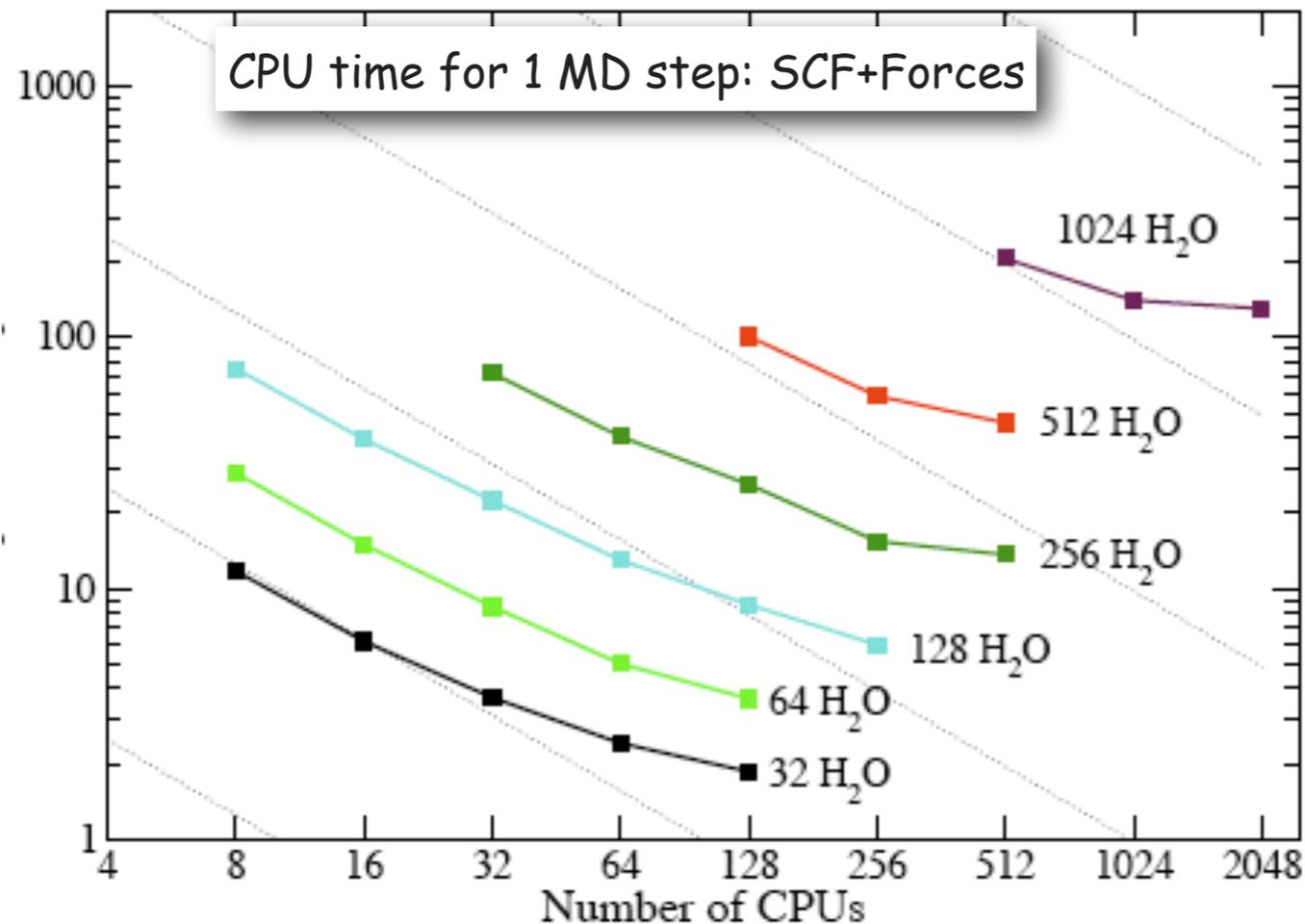
$$\mathbf{P}(\mathbf{H} - \mathbf{S}\epsilon)\mathbf{X} - \mathbf{X} \approx 0$$

- ☀️ Guaranteed convergence
- ☀️ Various choices of preconditioners
- ☀️ Limited number of SCF iterations
- ☀️ KS diagonalisation avoided
- ☀️ Sparsity of  $\mathbf{S}$  and  $\mathbf{H}$  can be exploited
- ☀️ Scaling  $O(N^2M)$  in cpu and  $O(NM)$  in memory
- ☀️ Optimal for large system, high quality basis set

# OT performance

64 H<sub>2</sub>O  
32 CPUs IBM SP4

1 SCF iter	DZVP	TZVP	TZV2P	QZV2P	QZV3P
OT	0.50	0.60	0.77	0.87	1.06
Diagonalisation	6.02	8.40	13.80	17.34	24.59



TZV2P (40 functions per H<sub>2</sub>O),  
280 Ry PW cutoff  
eps(scf) = 10<sup>-6</sup>, CRAY XT5

System	M	N
32 H <sub>2</sub> O	1280	128
64 H <sub>2</sub> O	2560	256
128 H <sub>2</sub> O	5120	512
256 H <sub>2</sub> O	10240	1024
512 H <sub>2</sub> O	20480	2048
1024 H <sub>2</sub> O	40960	4096

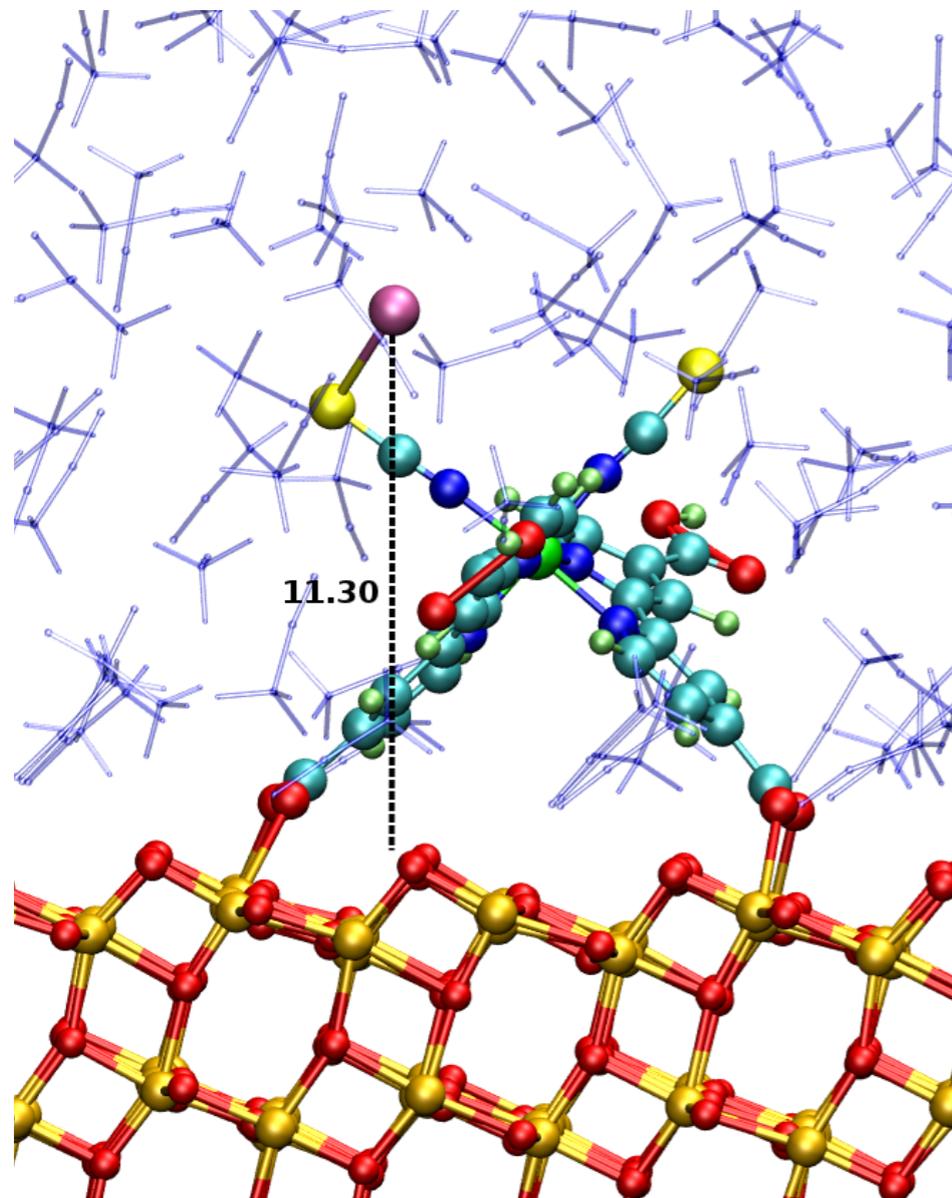
Structure optimisation 50÷100 iterations = ~1 hour for 512 H<sub>2</sub>O  
MD simulation (10 ps) 10000 iterations = ~1ps per day for 512 H<sub>2</sub>O

# 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
```

# Dye Sensitized Solar Cell

In situ electronic spectroscopy and dynamics



- ☼ 1751 atom computational cell, 864 (TiO<sub>2</sub>), 60 dye+electrolyte, 828 solvent
- ☼ 9346 electrons, 22951 basis functions
- ☼ MD simulation using PBE (DFT+U)
- ☼ CPU time on 1024 cores Cray-XT5
- ☼ SCF iteration: 13.7 seconds
- ☼ MD time step: 164 seconds

dye-iodide complex attached to TiO<sub>2</sub>

F. Schiffmann et al., PNAS 107 4830 (2010)

# Linear Scaling SCF

- Based on sparse matrix matrix multiplications

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

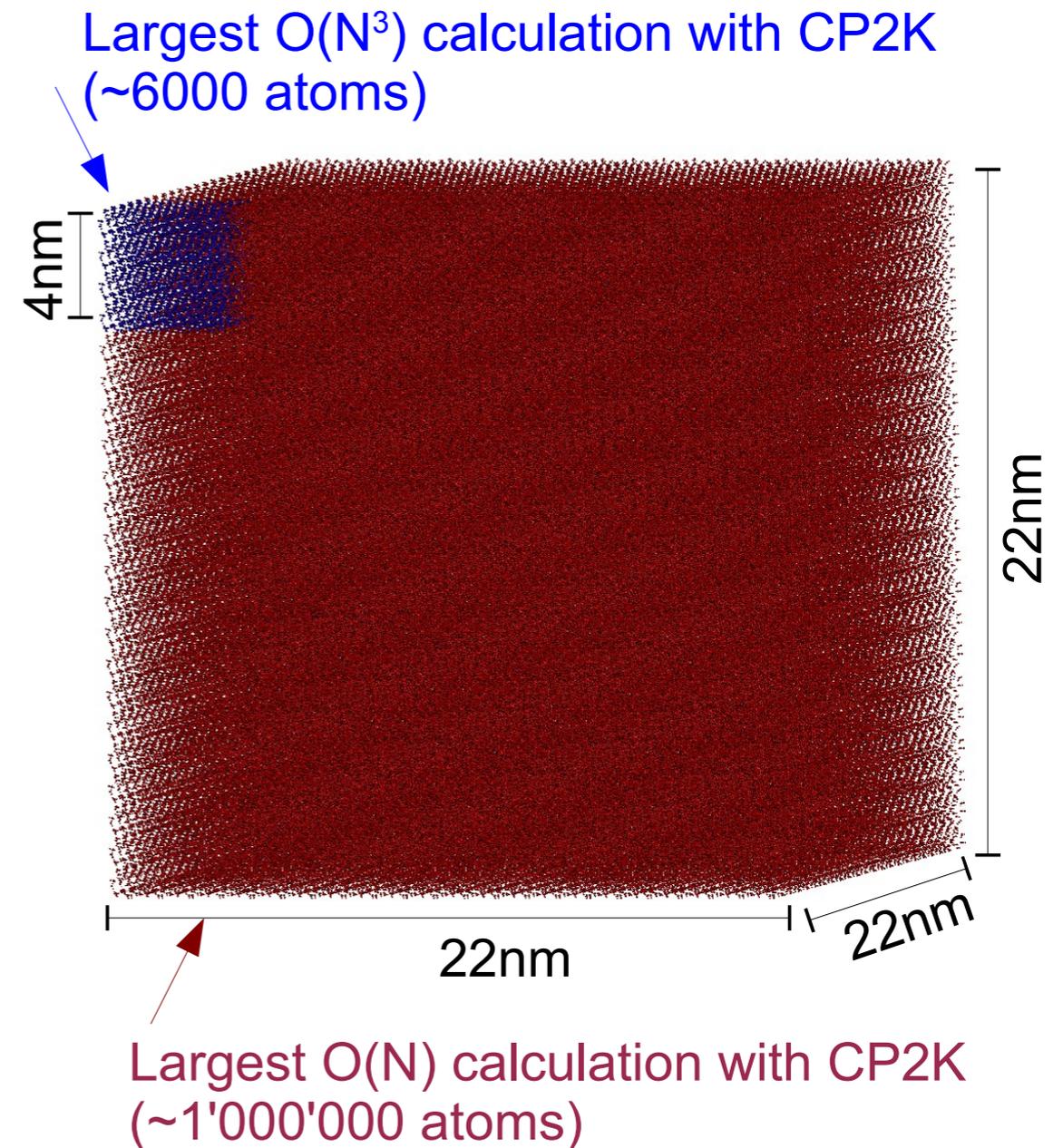
- Self consistent solution by mixing

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

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

- Chemical potential by bisecting until

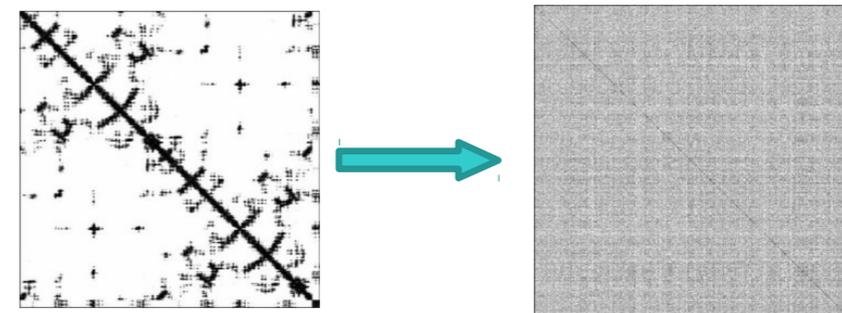
$$\mu_{n+1} : |\text{trace}(P_{n+1}S) - N_{el}| < 1/2$$



# Sparse Matrix Library

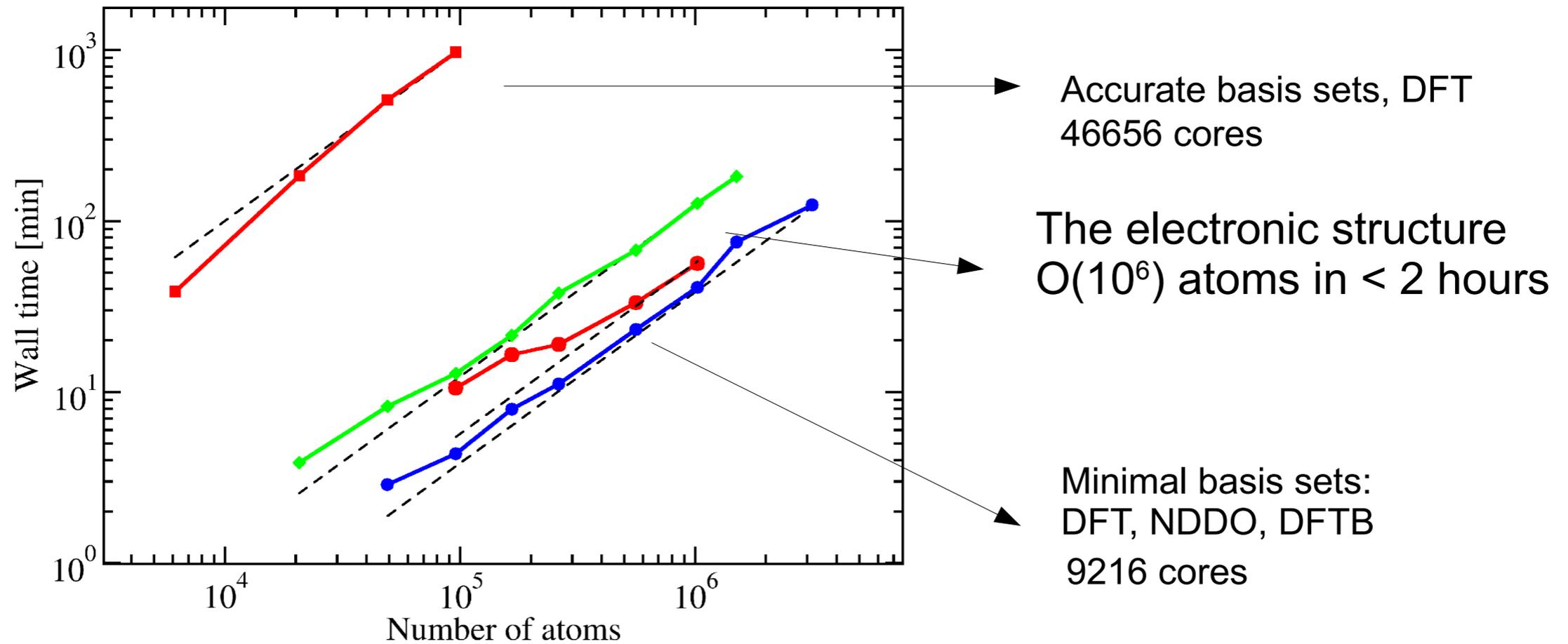
## DBCSP: Distributed Blocked Compressed Sparse Row

- ☀ 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**

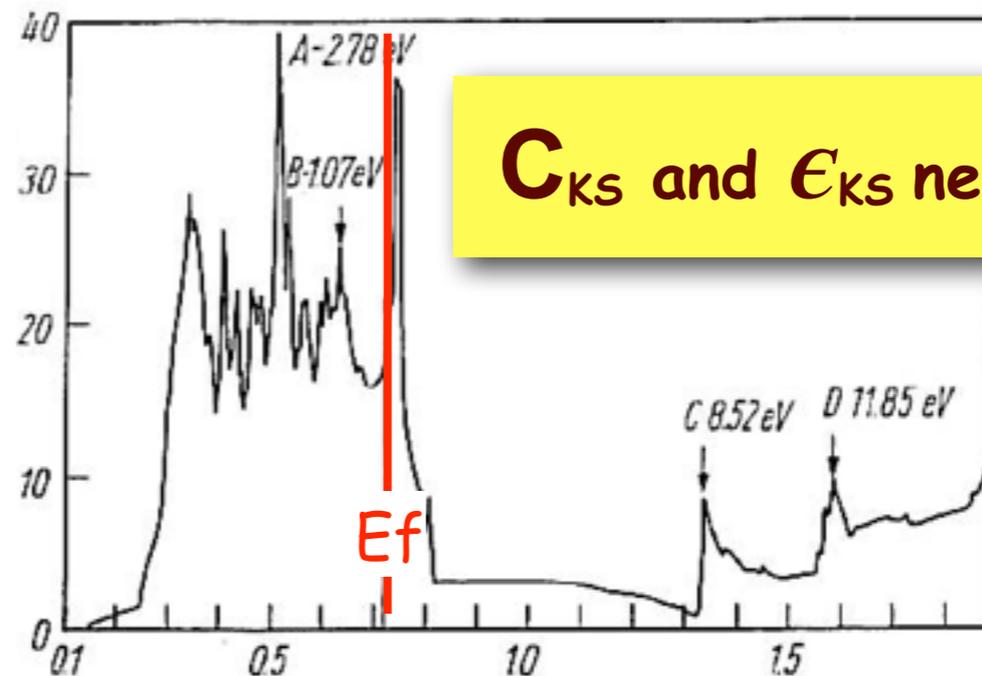
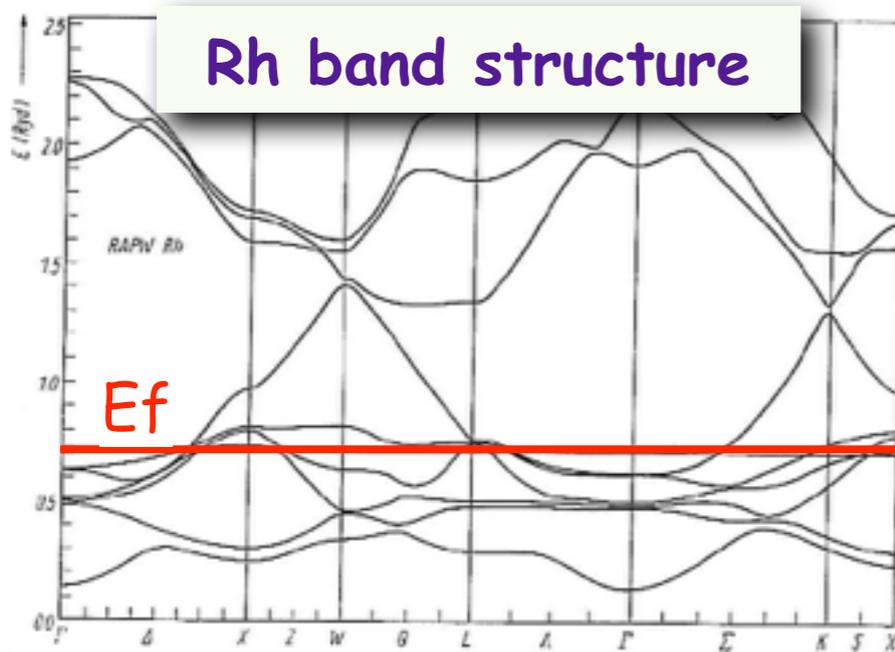
# Millions of atoms



Bulk liquid water. Dashed lines represent ideal linear scaling.

# Metallíc Electronic Structure

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



$C_{\text{KS}}$  and  $\epsilon_{\text{KS}}$  needed

charge sloshing and exceedingly slow convergence

- Wavefunction must be orthogonal to unoccupied bands close in energy
- Discontinuous occupancies generate instability (large variations in  $n(\mathbf{r})$ )
- Integration over k-points and iterative diagonalisation schemes

# Smearing & Mixing in G-space

Mermin functional: minimise the free energy

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

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

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

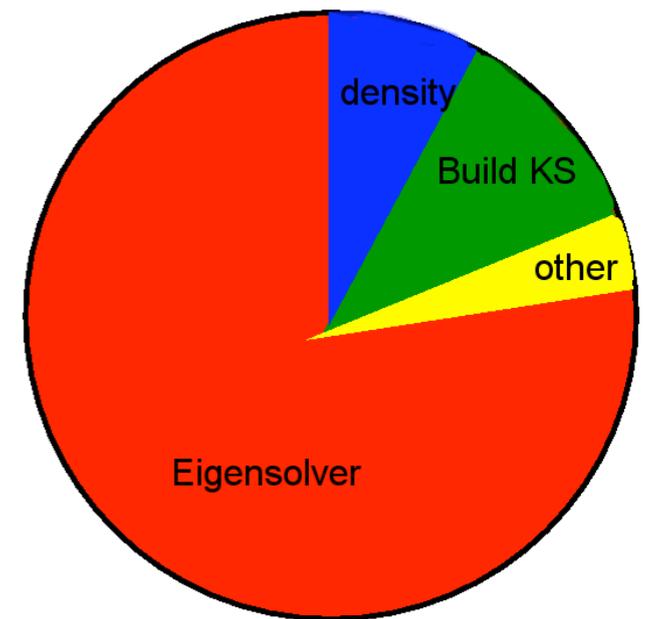
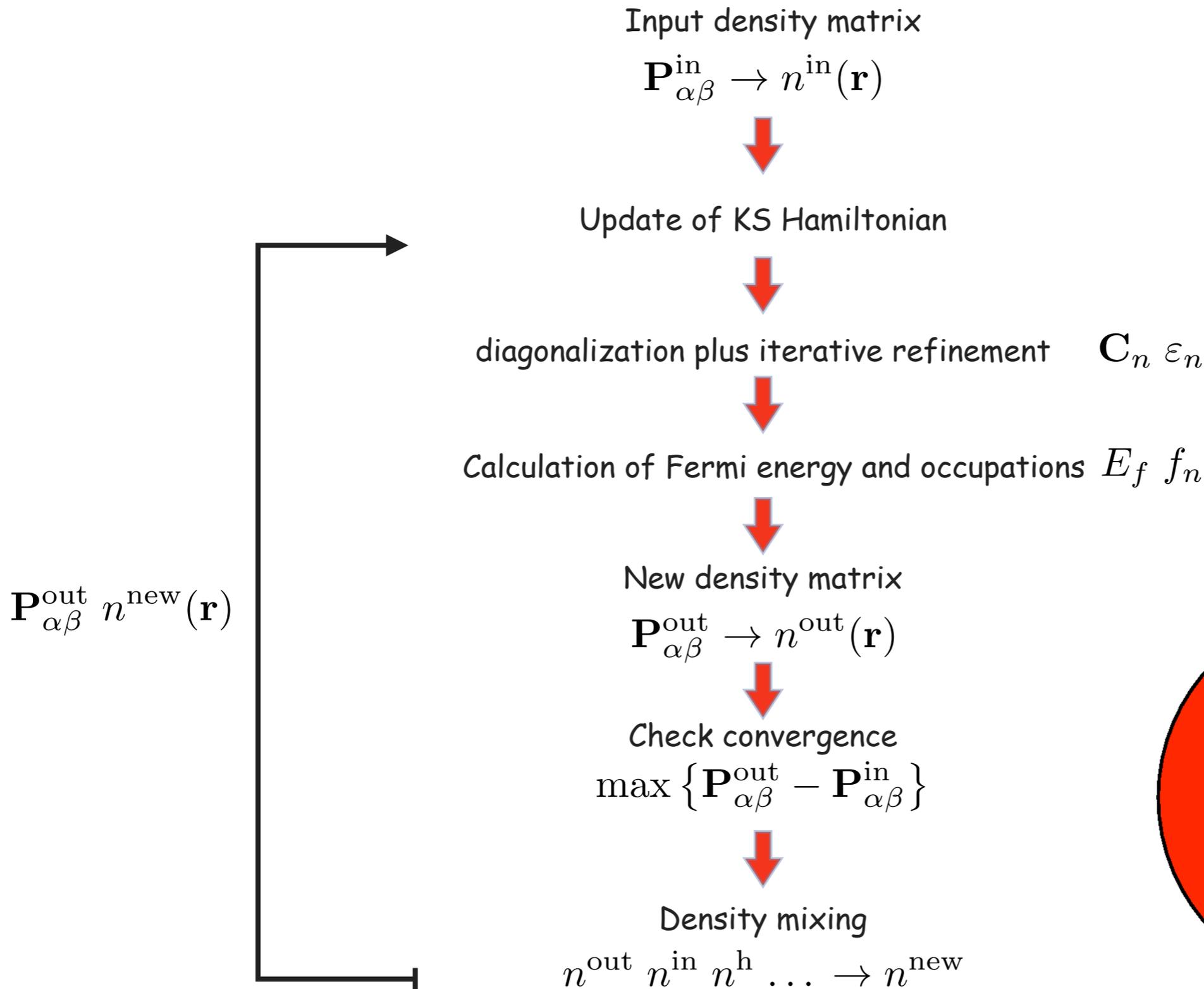
residual

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

minimise the residual

$\mathbf{G}$  preconditioning matrix damping low  $\mathbf{G}$

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



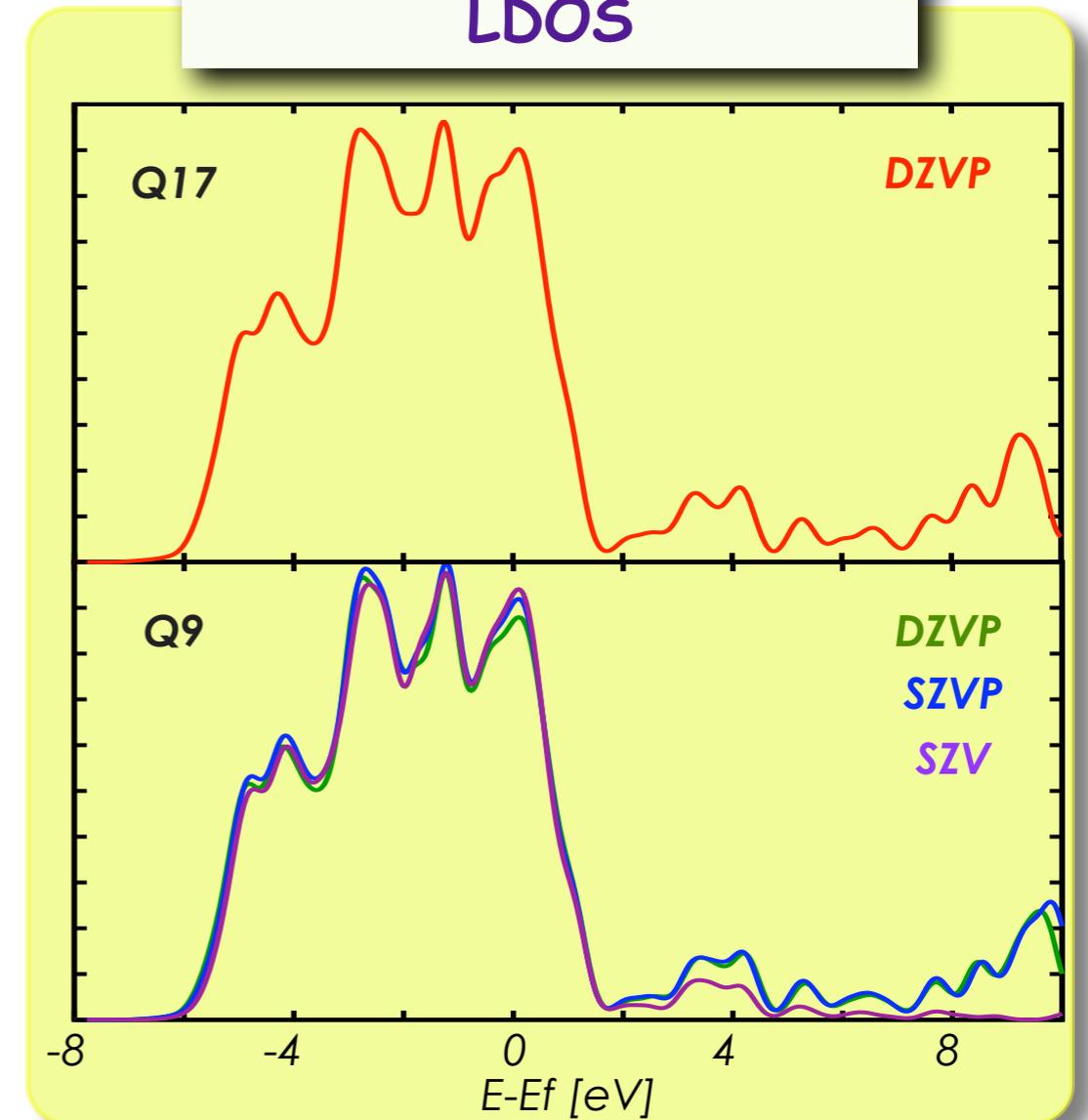
# Rhodium: Bulk and Surface

**Bulk: 4x4x4**

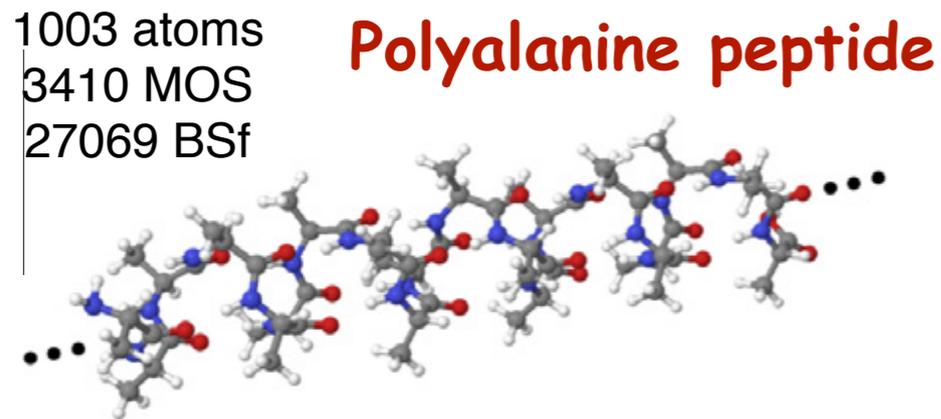
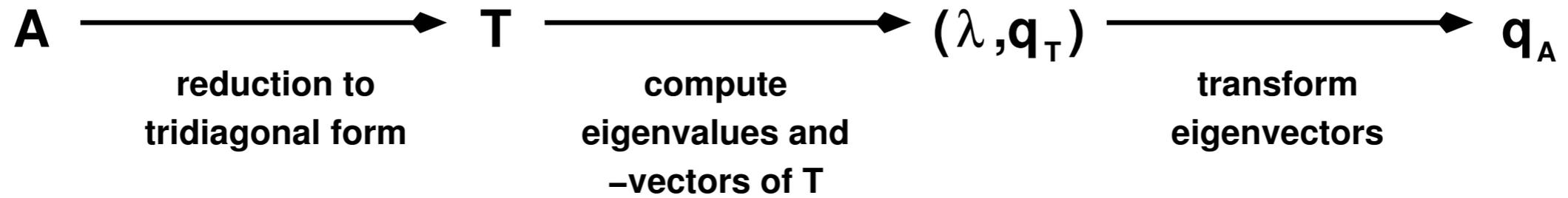
**Surface: 6x6 7 layers**

Basis	PP	$a_0$ [Å]	B[GPa]	$E_s$ [eV/Å <sup>2</sup> ]	$W_f$ [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

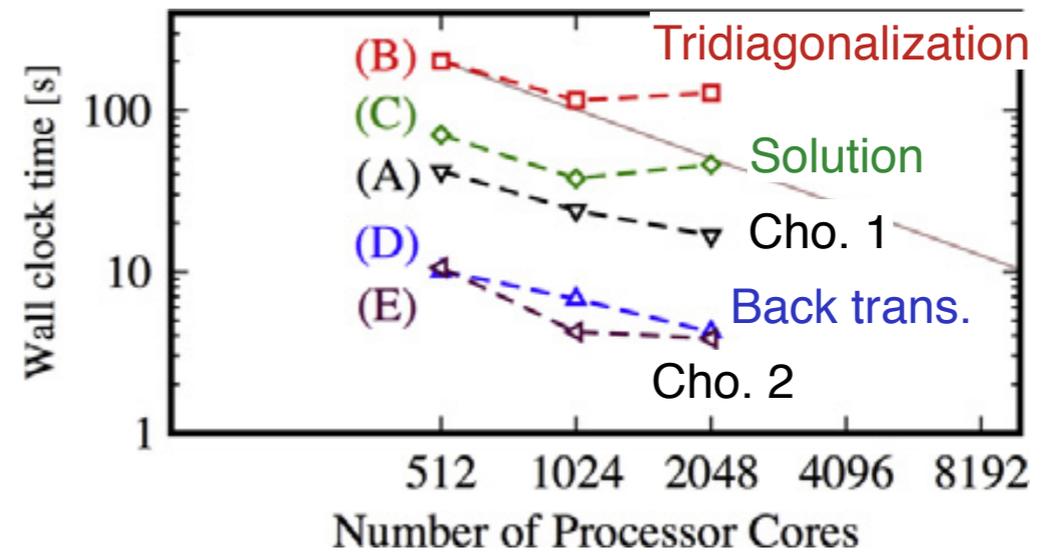
Rh(111) d-projected  
LDOS



# SCALAPACK for diagonalisation



## 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

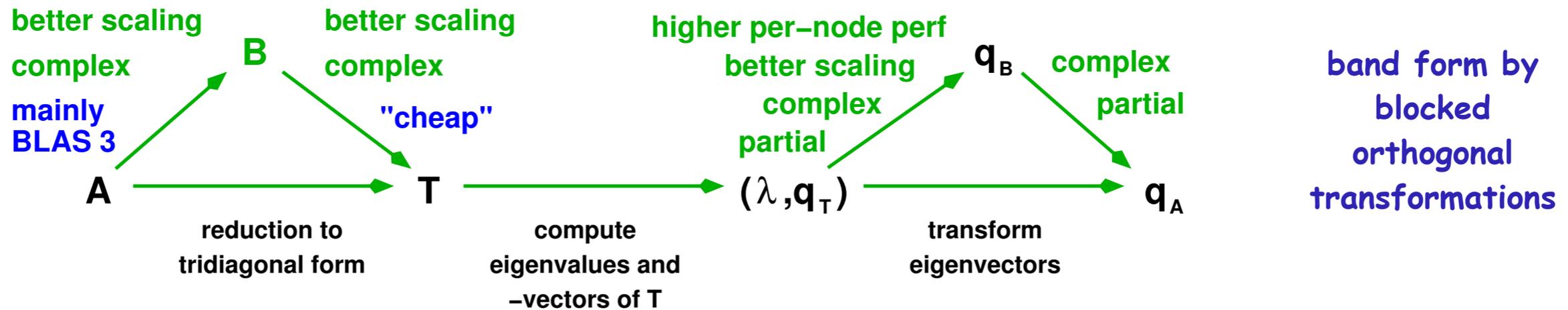
time x SCF, on CRAY XE6

>70% in eigenvalue solver

poor scaling

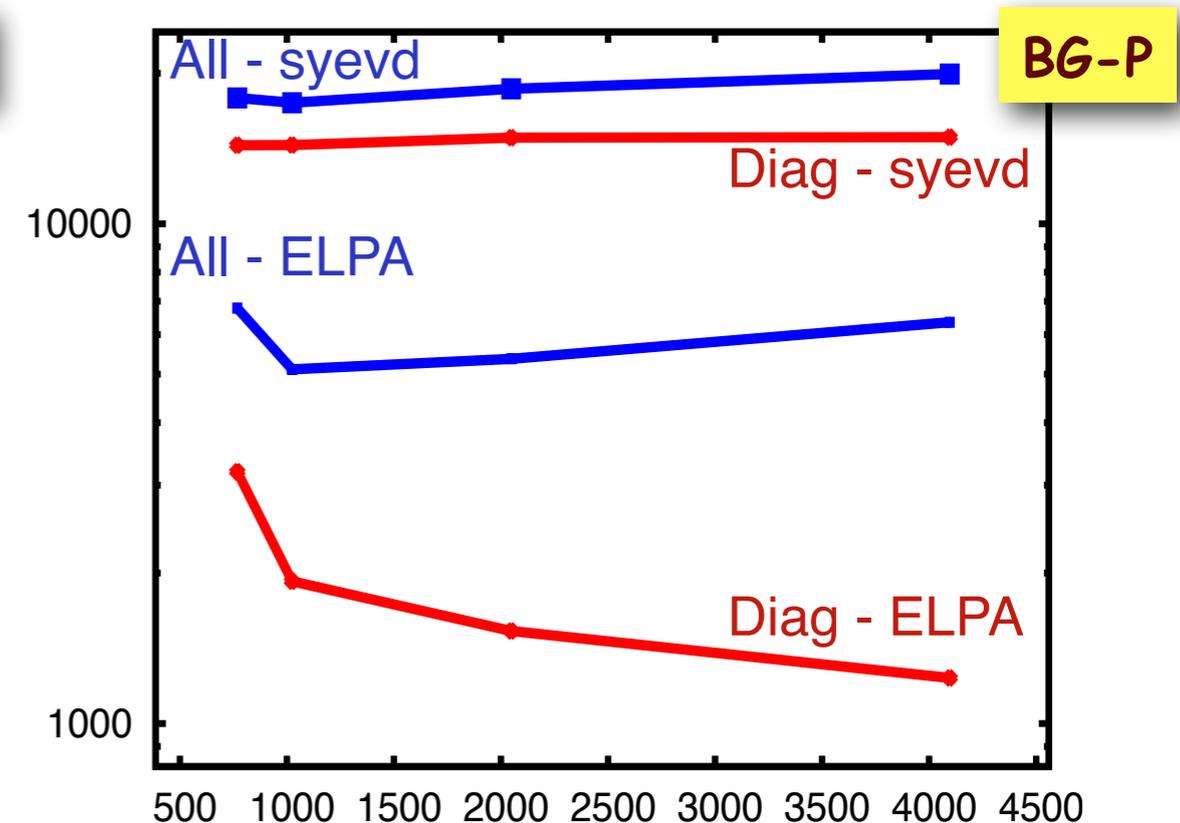
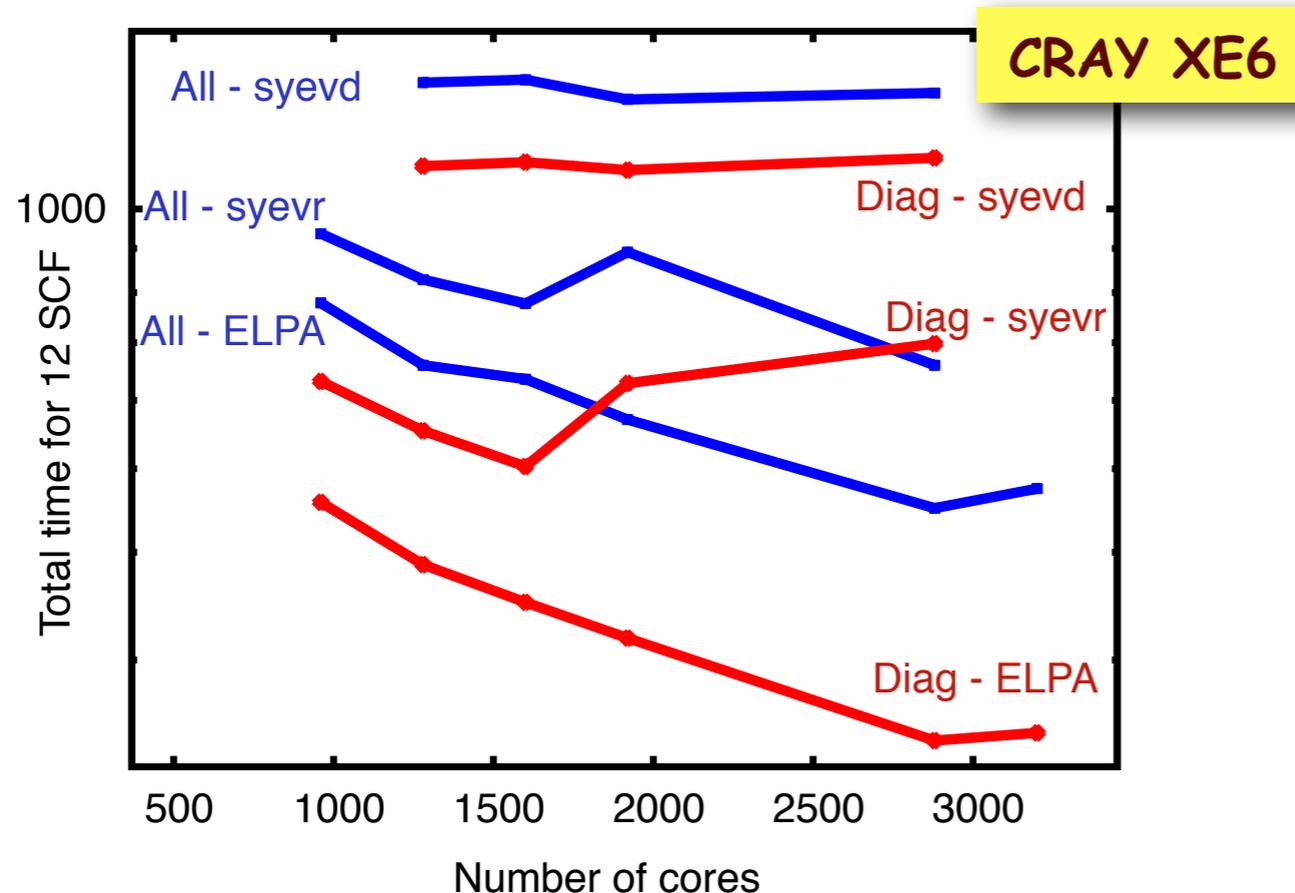
# ELPA (<http://elpa.rzg.mpg.de>)

Improved efficiency by a two-step transformation and back transformation



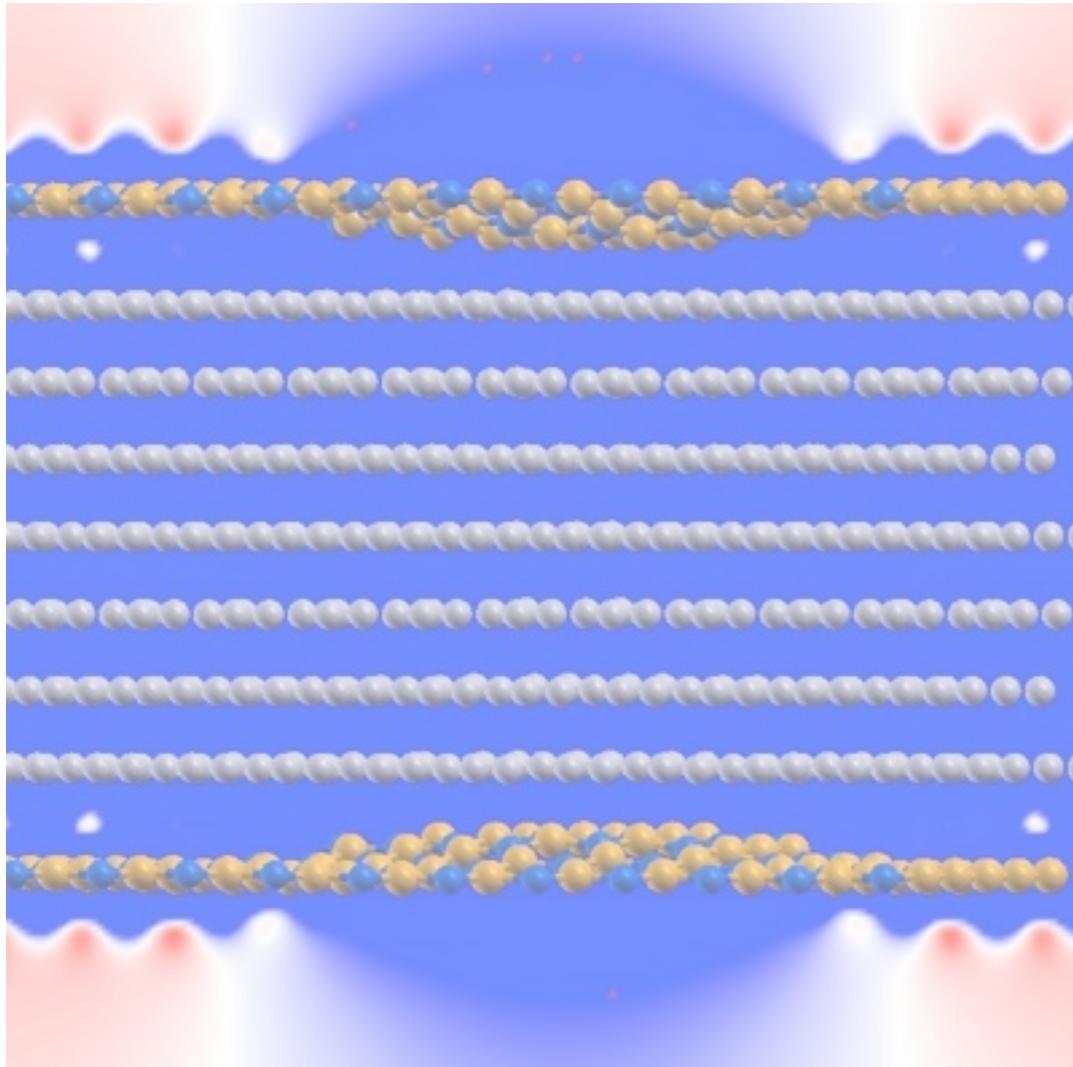
N atom= 2116; Nel = 16928;  
nmo = 10964; nao = 31740

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

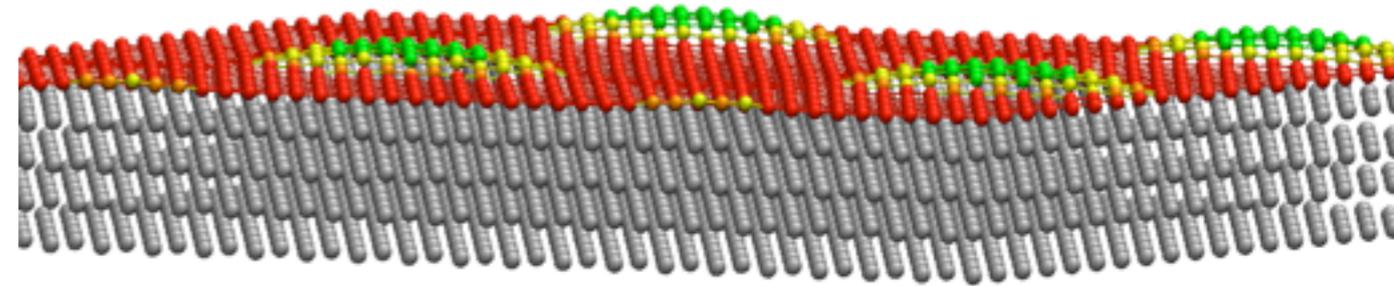


# Large metallic systems

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



**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

Slab 12x12 Rh(111) slab,  $a_0=3.801 \text{ \AA}$ , 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

# 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