G(A)PW Electronic Structure Theory

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Dynamics of Condensed Matter

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Die Universität der Informationsgesellschaft

CP2K: The Swiss Army Knife of Molecular Simulations

- Static Calculations
  - Energy & Structure Optimization
  - Properties: NMR, EPR & XAS
- Sampling Techniques
  - MC & MD
  - Ehrenfest Dynamics
  - Accelerated FES: Metadynamics
- Energy & Force Methods
  - *Quickstep*: PP-DFT (GPW)
  - Semiempirical QC & TB Methods
  - Classical Molecular Mechanics
  - Embedding Methods (QM/MM)

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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

Density Functional Theory

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

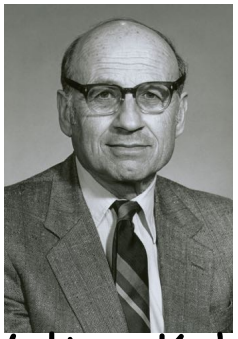
Hohenberg-Kohn Theorems

Theorem I

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

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

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



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(r)

Hohenberg-Kohn 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 Energy Functional

Electronic density

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

no repulsion

Kinetic energy of non interacting electrons

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

Electronic interaction with the external potential

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

Exact solution

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

Kohn-Sham 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

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

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

Kohn-Sham Equations

Orthonormality constraint

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

Variational search in the space of orbitals

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

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

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

Kohn-Sham Equations

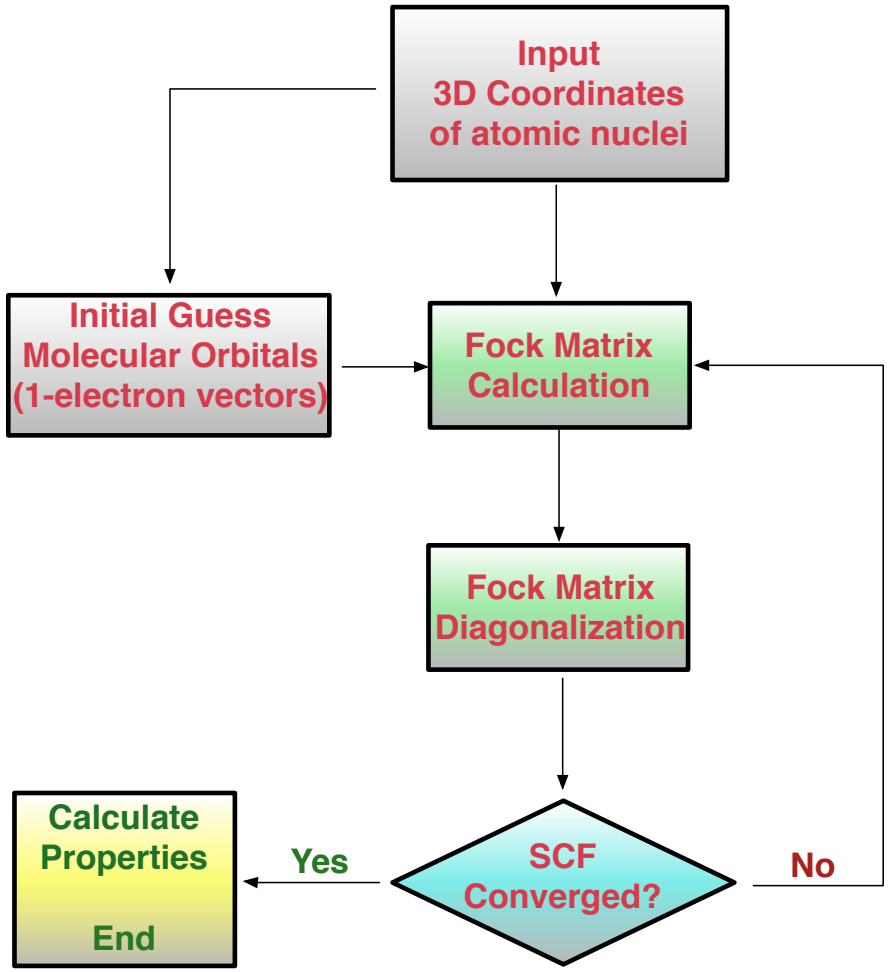
ϵ_{ij} **diagonal**

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

- 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
- .....



until self-consistency to required precision

Local Density Approximation

Uniform electron gas

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

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

Two contributions

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

Dirac ex-functional

QMC interpolation (Ceperly-Alder)

Applicable with slow-varying densities

Generalized Gradient Approx.

Gradient expansion

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n)F_{\mathrm{xc}}\left[n, \nabla n, \nabla^2 n, ...\right] d\mathbf{r}$$

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)

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 (DBCSR)

Basis Set Representation

Kohn-Sham formalism: matrix formulation when the wavefunction is expanded into a basis

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

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

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

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

Density functional

Variational principle
Constrained minimization problem

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

Matrix equation

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

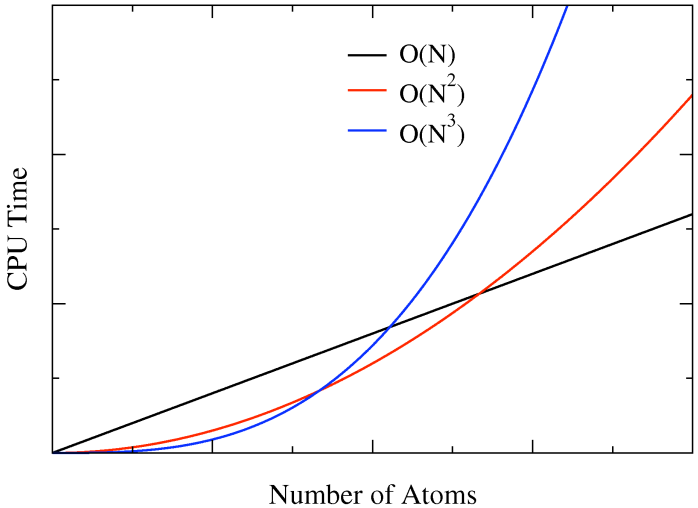
Critical Tasks

- *Construction of the Kohn-Sham matrix*
  - *Coulomb potential*
  - *XC potential*
  - *HF/exact exchange*
- *Fast and robust minimization 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



Quickstep

- Gaussian basis sets
- Plane waves auxiliary basis for Coulomb integrals
- Regular grids and FFT
- Sparse matrices, efficient screening, linear scaling KS matrix computation
- All-electron calculations with GAPW
- Fast/robust direct wavefunction optimizer (OT)

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

Gaussian Basis Sets

- good results already for small basis sets
- correspondence to the intuitive chemical picture
- all-electron description
- can be tuned for each application (and even each atom)
- no implicit periodicity
- non-orthogonal
- depend on the atomic positions (Pulay forces)
- basis set superposition error (BSSE)
- systematic improvement is less straightforward
- over-completeness causes linear dependencies

Plane Waves Basis Sets

- orthogonal
- independent of the atomic positions (no Pulay forces)
- no basis set superposition error (BSSE)
- systematic improvement simply by increasing the cutoff
- implicit periodicity
- no selective tuning possible
- large number of basis functions is needed
- pseudo potentials are needed
- chemical information not directly accessible

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

Gaussian Basis Set

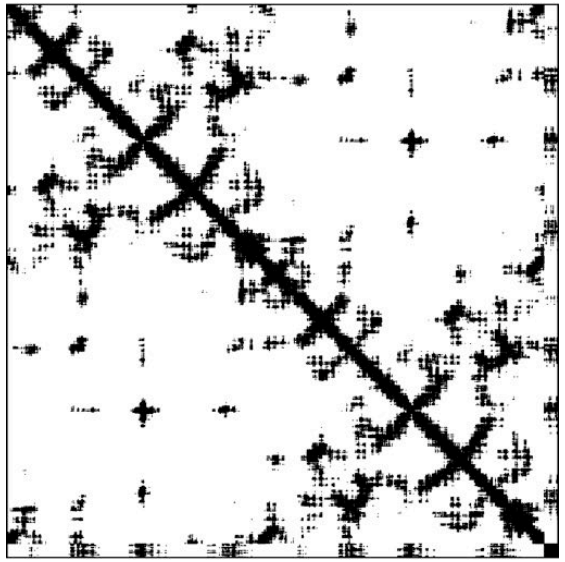
- Localised, atom-position dependent GTO basis

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

- Expansion of the density using the density matrix

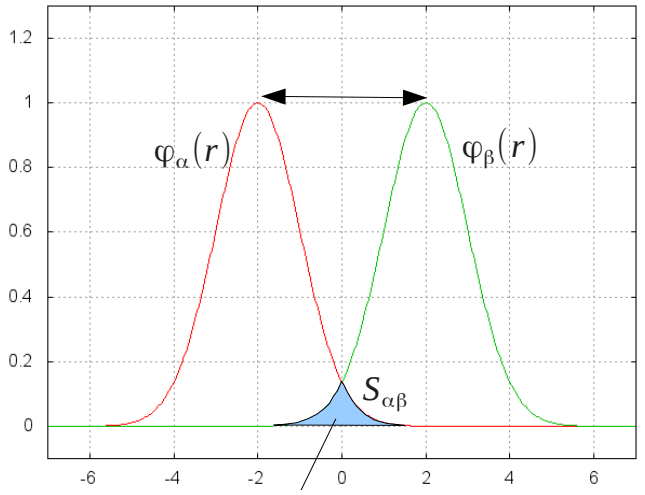
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu^*(\mathbf{r})$$

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

O-S 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

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

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

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

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
```

GTO Basis Sets in CP2K

The repository contains several GTO libraries

cp2k/data/

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

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

Basis Set Library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

```
 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  5  3  3
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       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
```

Basis Set Library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

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 2 0 1 7 1 1
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     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
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     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
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     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
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     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
```

Basis Set Library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

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 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  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
```

```
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      1297.23000000        0.01438590
       299.29600000        0.07073200
        87.37710000        0.24000100
        25.67890000        0.59479700
         3.74004000        0.28080200
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        42.11750000        0.11388900        0.03651140
         9.62837000        0.92081100        0.23715300
         2.85332000       -0.00327447        0.81970200
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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
```
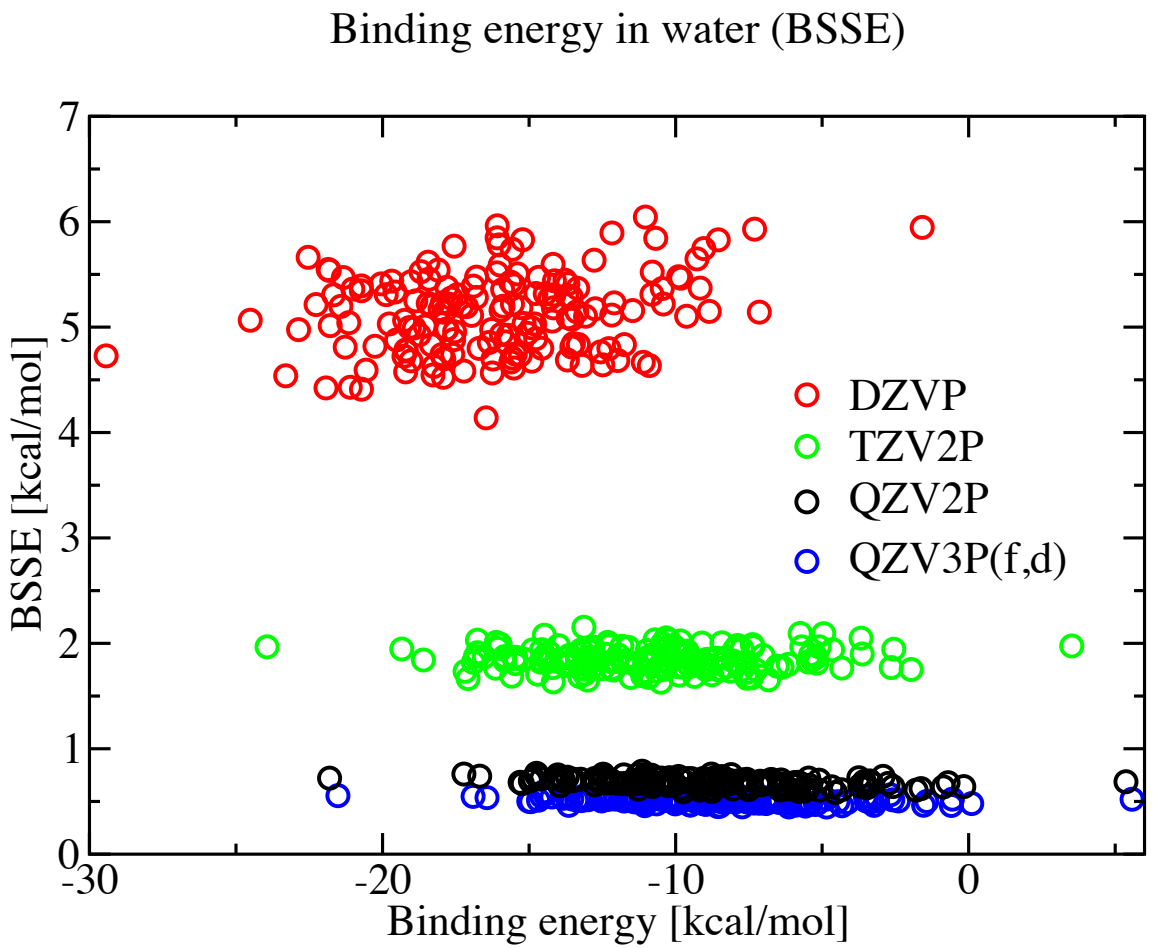
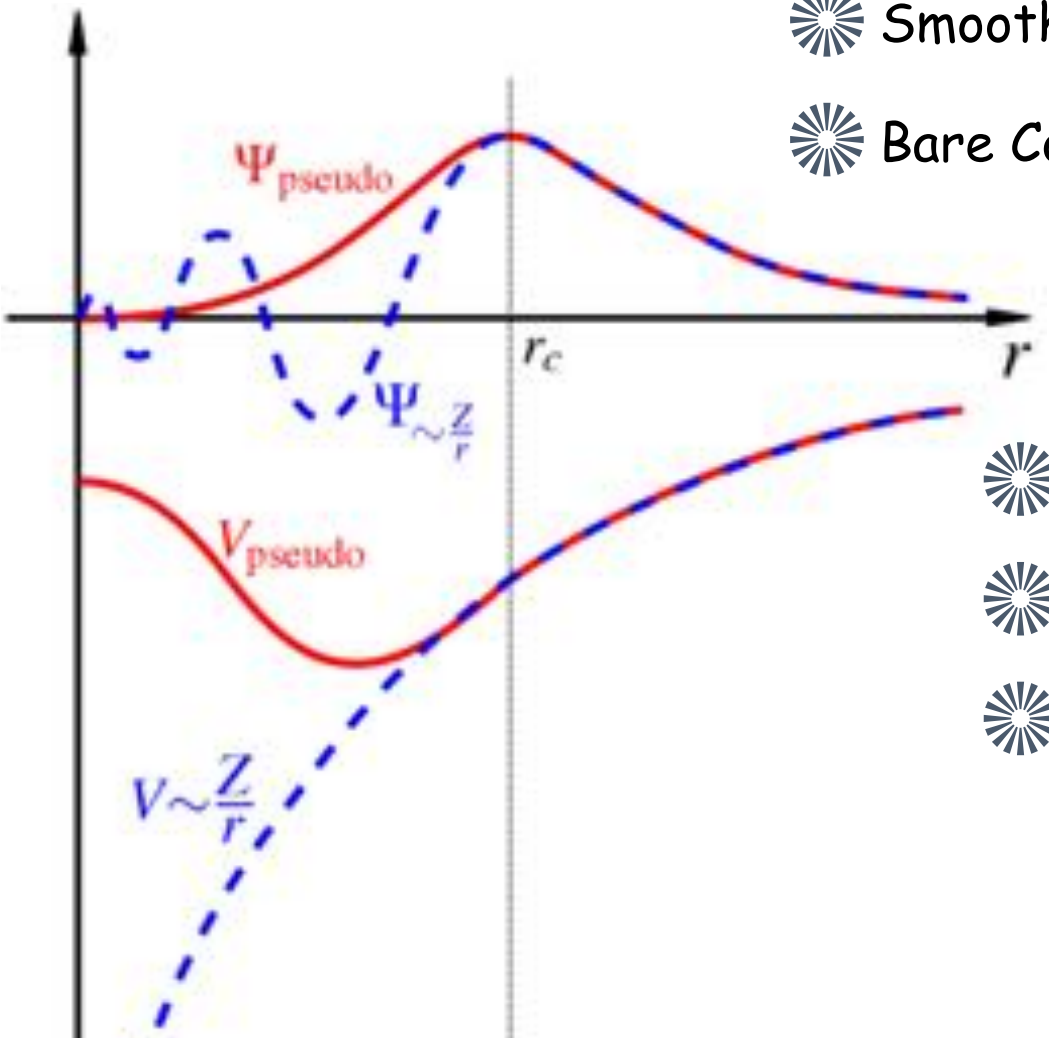

Basis Set Superposition Error

BSSE in liquid water



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 Pseudopotentials

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

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

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

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

analytically — part of ES

- Non-Local PP with Gaussian type projectors

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

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

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 Generation for O

```
&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
```

Pseudopotential Library

GTH_POTENTIALS

$N_{\rm el}(s)$ $N_{\rm el}(p)$ $N_{\rm el}(d)$ ...

$r_{\rm loc}^{\rm PP}$ N_C $C_1^{\rm PP}$ ... $C_{N_C}^{\rm PP}$

N_p

r_1 $n_{\rm nl}^1$ $\{h_{ij}^1\}_{ij=1...n^1}$

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

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
```

GPW Functional

Gaussian and plane waves (GPW) method:

$$
\begin{aligned}
E^{\text{elec}}[n] &= E^{\text{T}}[n] + E^{\text{V}}[n] + E^{\text{H}}[n] + E^{\text{XC}}[n] \\
&= \sum_{\mu\nu} P^{\mu\nu} \langle \varphi_\mu(\boldsymbol{r}) \mid -\frac{1}{2}\nabla^2 \mid \varphi_\nu(\boldsymbol{r}) \rangle + \\
&\quad \sum_{\mu\nu} P^{\mu\nu} \langle \varphi_\mu(\boldsymbol{r}) \mid V^{\text{PP}}_{\text{loc}}(r) \mid \varphi_\nu(\boldsymbol{r}) \rangle + \\
&\quad \sum_{\mu\nu} P^{\mu\nu} \langle \varphi_\mu(\boldsymbol{r}) \mid V^{\text{PP}}_{\text{nl}}(\boldsymbol{r}, \boldsymbol{r}') \mid \varphi_\nu(\boldsymbol{r}') \rangle + \\
&\quad 4\pi\,\Omega \sum_{|\boldsymbol{G}|<G_{\text{C}}} \frac{\tilde{n}^*(\boldsymbol{G})\,\tilde{n}(\boldsymbol{G})}{\boldsymbol{G}^2} + \\
&\quad \int \tilde{n}(\boldsymbol{r})\,\varepsilon_{\text{XC}}[\tilde{n}]\,d\boldsymbol{r}
\end{aligned}
$$

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&\quad \sum_{\mu\nu} P^{\mu\nu} \langle \varphi_\mu(\boldsymbol{r}) \mid V_{\text{loc}}^{\text{PP}}(r) \mid \varphi_\nu(\boldsymbol{r}) \rangle + \\
&\quad \sum_{\mu\nu} P^{\mu\nu} \langle \varphi_\mu(\boldsymbol{r}) \mid V_{\text{nl}}^{\text{PP}}(\boldsymbol{r}, \boldsymbol{r}') \mid \varphi_\nu(\boldsymbol{r}') \rangle + \\
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&\quad \int \tilde{n}(\boldsymbol{r})\,\varepsilon_{\text{XC}}[\tilde{n}]\,d\boldsymbol{r}
\end{aligned}
$$

GPW Functional

Goedecker-Teter-Hutter (GTH) pseudo potentials:

Local part:

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

$$\text{with } \alpha^{\text{PP}} = \frac{1}{\sqrt{2} r_{\text{loc}}^{\text{PP}}}$$

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$$

GPW Functional

Non-local part:

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

with the Gaussian-type projectors

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

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&\quad \int \tilde{n}(\boldsymbol{r})\,\varepsilon_{\text{XC}}[\tilde{n}]\,d\boldsymbol{r}
\end{aligned}
$$

Periodic Hartree Potential via FFT

$$\boldsymbol{P} \rightarrow \rho(\mathbf{R}) \underbrace{\xrightarrow{\text{FFT}} \rho(\mathbf{G}) \rightarrow V_{\text{H}}(\mathbf{G}) = \frac{\rho(\mathbf{G})}{G^2} \xrightarrow{\text{FFT}}}_{\mathcal{O}(n \log n)} V_{\text{H}}(\mathbf{R}) \rightarrow \boldsymbol{V}$$

$$\rho(\mathbf{R}) = \sum_{\mu\nu} \boldsymbol{P}_{\mu\nu} \chi_\mu(\mathbf{R}) \chi_\nu(\mathbf{R}) = \sum_{\mu\nu} \boldsymbol{P}_{\mu\nu} \bar{\chi}_{\mu\nu}(\mathbf{R})$$

$$\boldsymbol{V}_{\mu\nu} = \sum_{\mathbf{R}} \boldsymbol{V}(\mathbf{R}) \chi_\mu(\mathbf{R}) \chi_\nu(\mathbf{R}) = \sum_{\mathbf{R}} \boldsymbol{V}(\mathbf{R}) \bar{\chi}_{\mu\nu}(\mathbf{R})$$

Efficient screening of sums using $\bar{\chi}_{\mu\nu}(\mathbf{R})$.

Screening

- Always work with primitive Gaussians
- Analytic integrals $\rightarrow$ distance screening with $R = A - B$

  Overlap $S_{\alpha\beta}$ $\varphi_\alpha(r - A) \leftrightarrow \varphi_\beta(r - B)$

  $\downarrow$ sparsity pattern

  $T_{\alpha\beta}$

- Density on the real space grid

  $$\sum_{\alpha\beta} P_{\alpha\beta}\varphi_\alpha(R)\varphi_\beta(R) \overset{\text{FFT}}{\rightarrow} \tilde{\rho}(G)$$

  $\downarrow$ overlap screening

  $P_{\alpha\beta}$ is only needed with $S_{\alpha\beta}$ sparsity pattern

- $\varphi_{\alpha\beta}(R) \neq 0$ distance (radial) screening

Screening

- All individual screening thresholds can be controlled by `EPS_DEFAULT`

  `CP2K_INPUT / FORCE_EVAL / DFT / QS`

- Problems associated with thresholds
  - Failure in Cholesky decomposition of overlap matrix
  - Combination of basis set condition number and too big `EPS_DEFAULT`
  - Inaccurate charge on real space grid
  - Too low PW cutoff and/or too big `EPS_DEFAULT` (extend of $\varphi_{\alpha\beta}$)

GPW Functional

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

Linear scaling KS matrix construction

External Potential

- Long range part (All electron and pseudopotentials)
  $V_l(\mathbf{r}) = -Z/r \qquad r \longrightarrow \infty$

- Short range part (only pseudopotentials)
  $(\alpha|V_{nl}(\mathbf{r},\mathbf{r}')|\beta) = (\alpha|p)V_p(p|\beta)$

Auxilliary core potential:

$$V_{\text{core}}(\mathbf{r}) = -\frac{Z}{r}\text{erf}[-r/R_c]$$

$$V_{\text{core}}(\mathbf{r}) = \int \frac{\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

$$\rho_c(\mathbf{r}) = -\frac{Z}{R_c^3}\pi^{-3/2}\exp[-(r/R_c)^2]$$

External Potential

$$V_l(\mathbf{r}) = V_l(\mathbf{r}) - V_{\text{core}}(\mathbf{r}) + V_{\text{core}}(\mathbf{r})$$

$$V_l(\mathbf{r}) = V_s(\mathbf{r}) + V_{\text{core}}(\mathbf{r})$$

Special case of pseudopotentials used in Quickstep

$$V_l(\mathbf{r}) = -\frac{Z}{r}\text{erf}[-r/R_c] + (C_1 + C_2 r^2 + C_3 r^4)\exp[-(r/r_{cl})^2]$$

$$V_l(\mathbf{r}) = (C_1 + C_2 r^2 + C_3 r^4)\exp[-(r/r_{cl})^2] + V_{\text{core}}(\mathbf{r})$$

Hartree Potential

Electrostatic energy:

$$
\begin{aligned}
E_{es} &= \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + \int V_{\mathsf{core}}(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|} \\
&= \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + \int\int \frac{\rho_c(\mathbf{r})\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|} \\
&= \frac{1}{2}\int\int \frac{\rho_{tot}(\mathbf{r})\rho_{tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' - \frac{1}{2}\int\int \frac{\rho_c(\mathbf{r})\rho_c(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\mathbf{R}_A-\mathbf{R}_B|} \\
&= \frac{1}{2}\int\int \frac{\rho_{tot}(\mathbf{r})\rho_{tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + E_{\mathsf{overlap}} - E_{\mathsf{self}}
\end{aligned}
$$

$$\rho_{tot}(\mathbf{r}) = \rho(\mathbf{r}) + \rho_c(\mathbf{r})$$

Hartree Potential

$$E_{es} = \frac{1}{2}\int\int \frac{\rho_{tot}(\mathbf{r})\rho_{tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}d\mathbf{r}' + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{R_{AB}}\text{erfc}\left[\frac{R_{AB}}{R_c}\right] - \sum_A \frac{1}{\sqrt{2\pi}}\frac{Z_A^2}{R_c}$$

- Long range term ($\rho_{tot}(\mathbf{r})$)
- Short range pair potential term (erfc)
- Self energy term

Auxiliary Basis Set

- Long range term : Non-local Coulomb

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

- 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 Poisson equation

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

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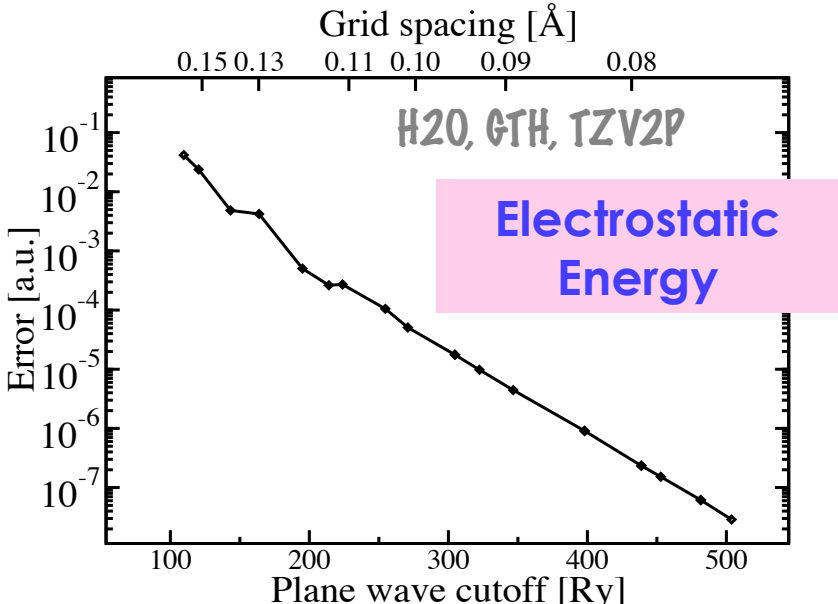

Real-Space Integration

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

Real-Space Integration

Finite cutoff and simulation box define a real space grid

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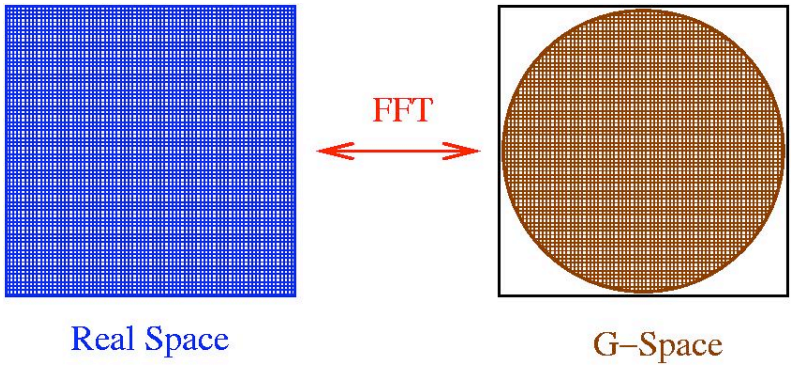
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r}) \rightarrow \sum_{\mu\nu} P_{\mu\nu}\bar{\varphi}_{\mu\nu}(\mathbf{R}) = n(\mathbf{R})$$

Screening Truncation

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



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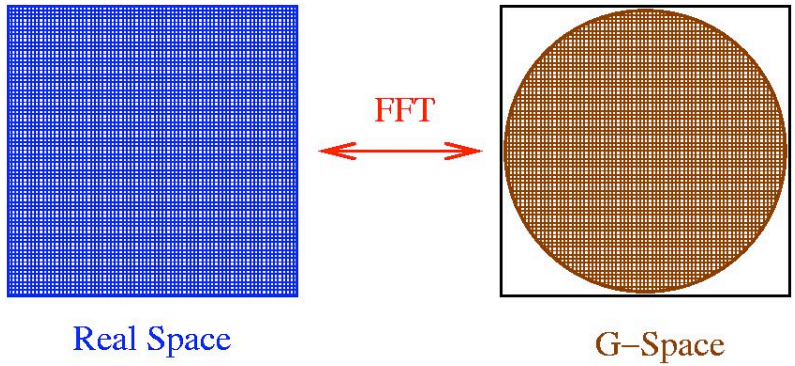


- Numerical approximation of the gradient

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

- XC evaluated on the grid

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

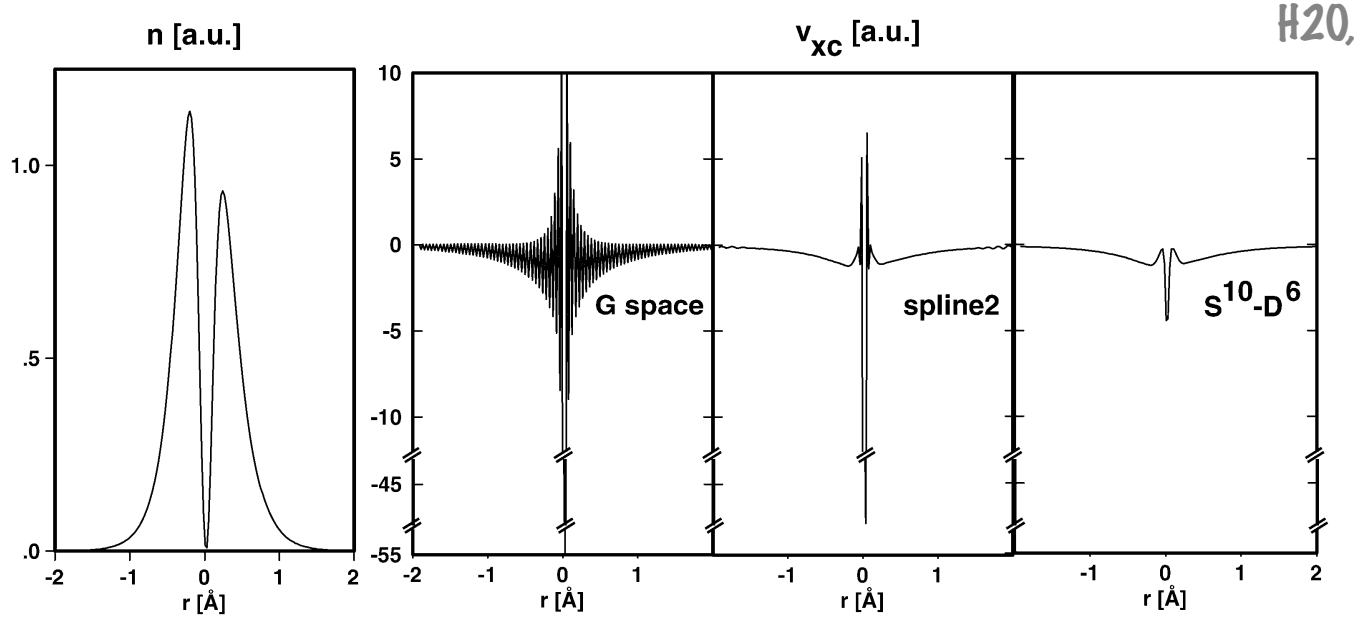
- Real space integration

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

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

Energy Ripples

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



close to O along HOH bisector

Small variations of the total energy as atoms move relative to the grid

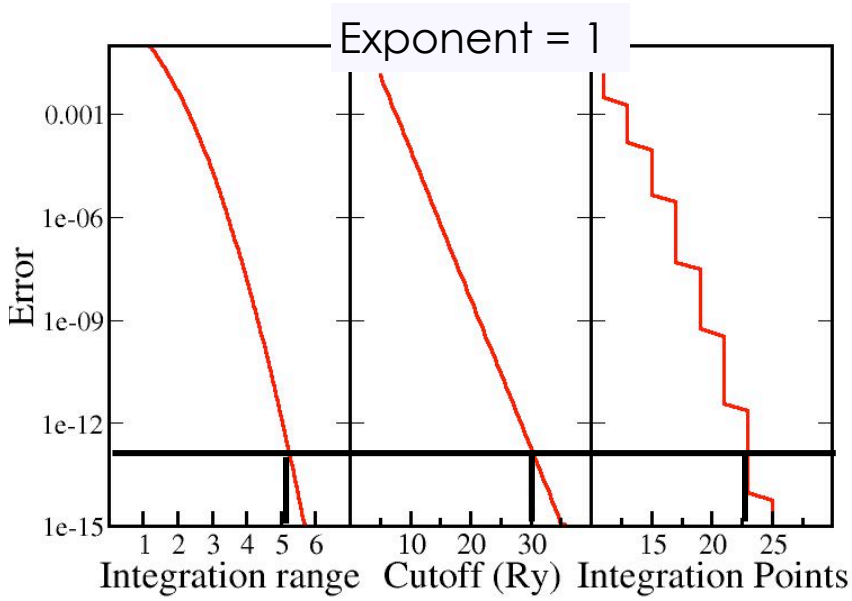
Multigrids

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

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



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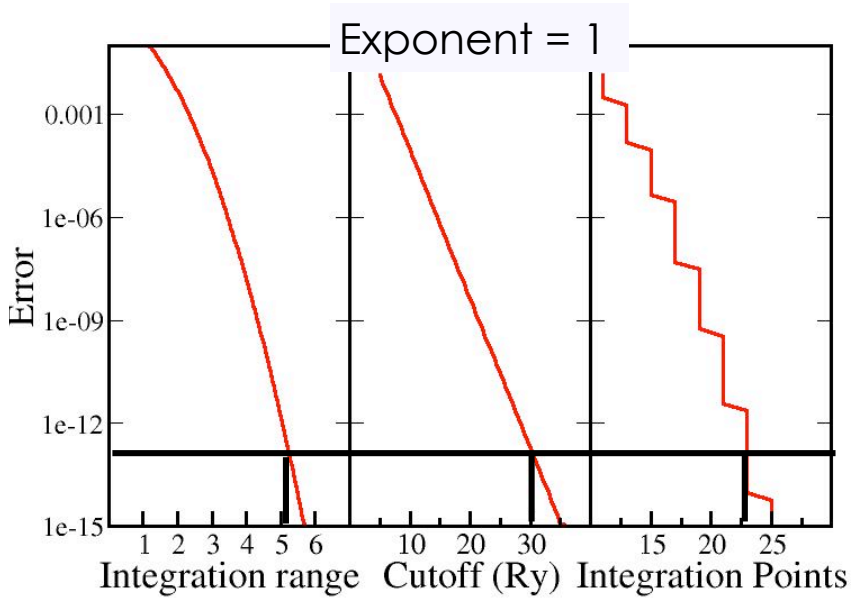
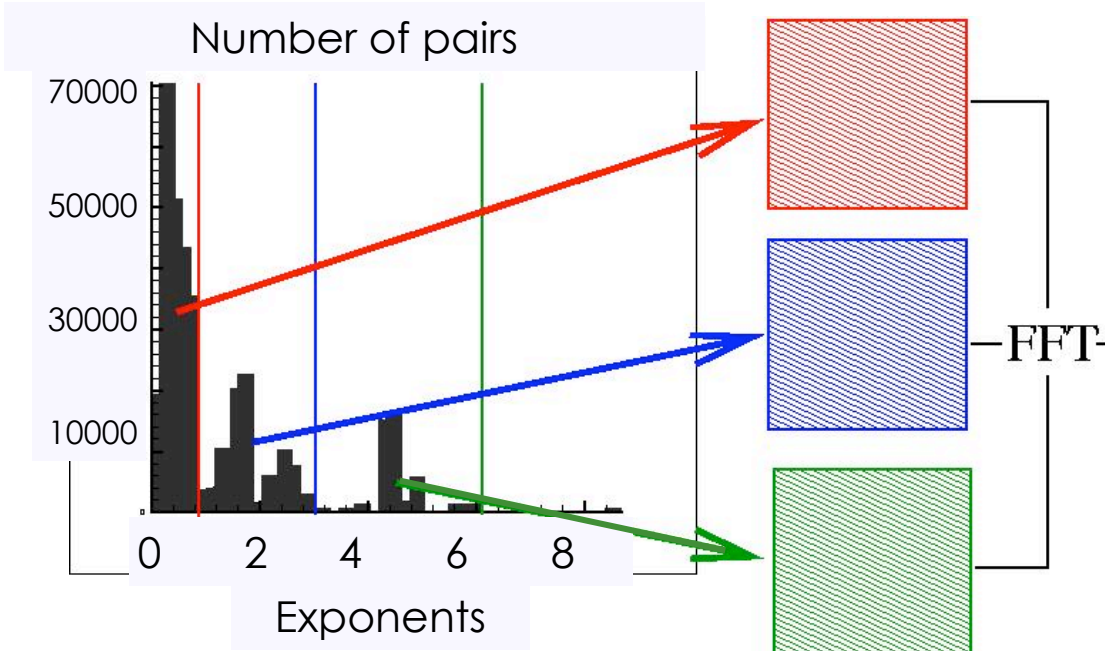
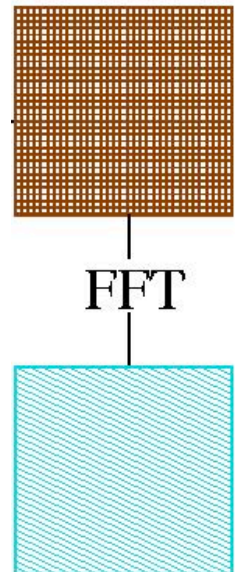




$$n_j^f = I_j(n_i^c)$$



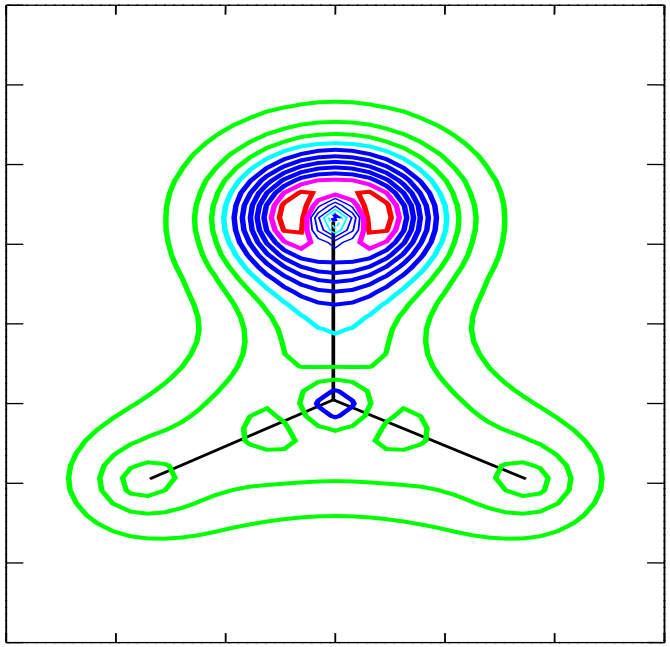
CP2K DFT Input

```
&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
```

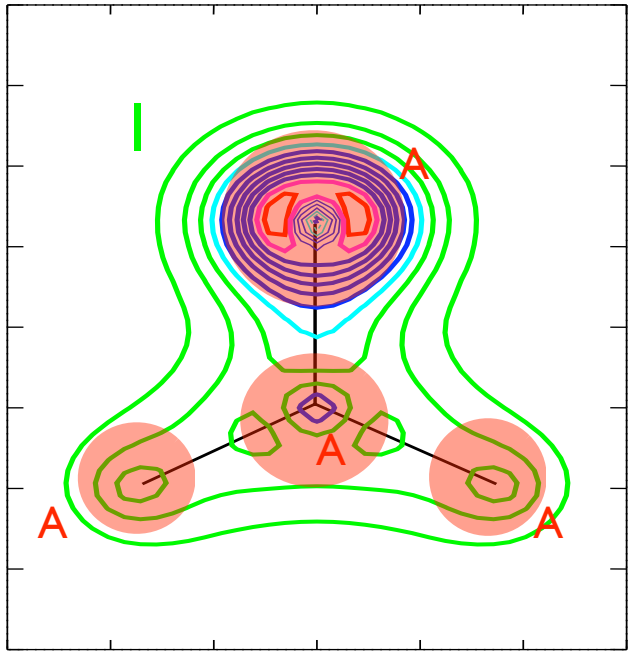
Hard & Soft Densities



Formaldehyde

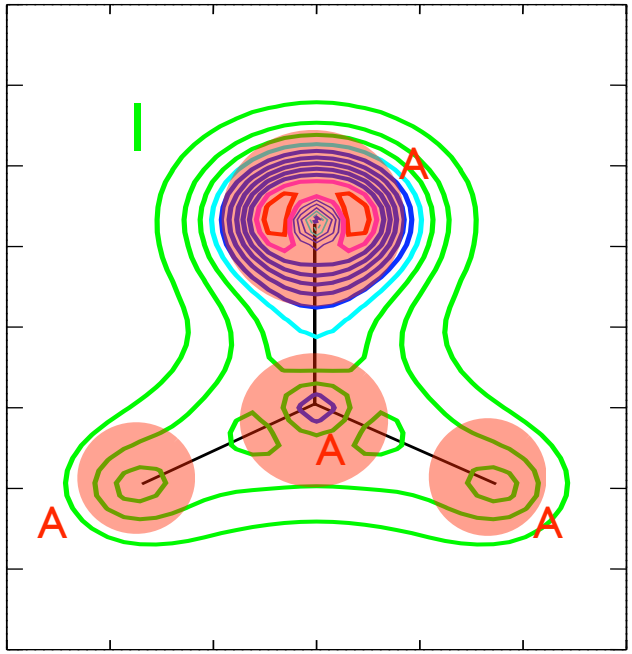
- Pseudopotential ⇨ frozen core
- Augmented PW ⇨ separate regions (matching at edges)
  LAPW, LMTO (OK Andersen, PRB **12**, 3060 (1975)
- Dual representation ⇨ localized orbitals and PW
  PAW (PE Bloechl, PRB, **50**, 17953 (1994))

Partitioning of the Density



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

Partitioning of the Density



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

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

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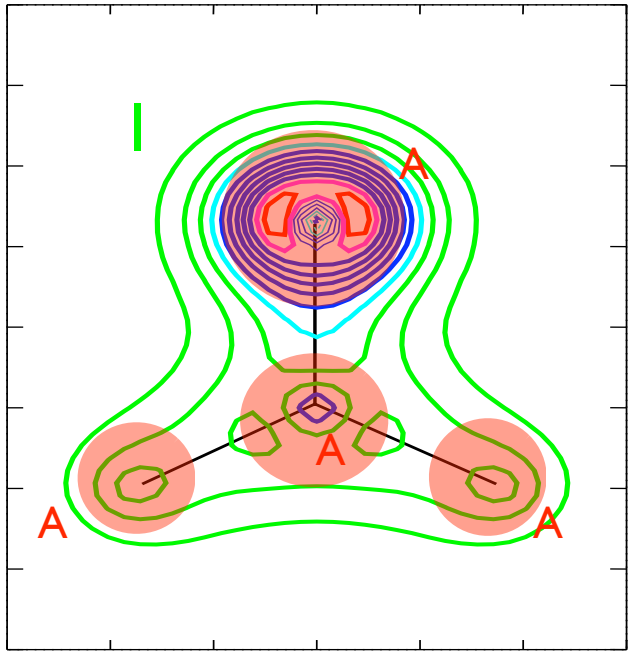

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$$n_A(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi^A_\mu \chi^A_\nu \qquad \tilde{n}(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \tilde{\varphi}_\mu \tilde{\varphi}_\nu \rightarrow \sum_{\mathbf{G}} \hat{n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{R}}$$

Gaussian Augmented Plane Waves

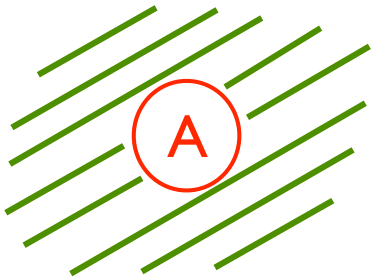
Density Dependent Terms: XC

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

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

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

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



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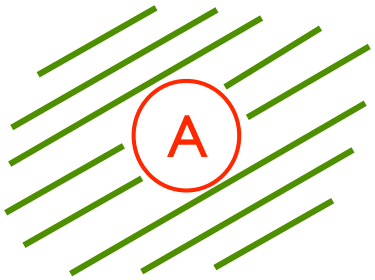
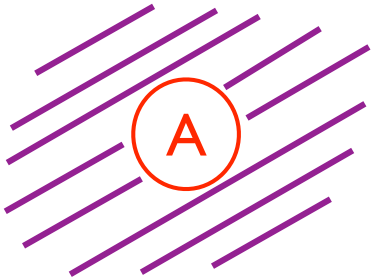


$$\times \left\{ \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \right\} d\mathbf{r}$$

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

Density Dependent Terms: ES

Non local Coulomb operator



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

Compensation charge

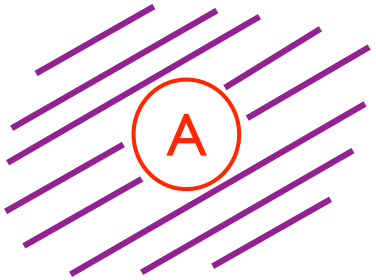
Same multipole expansion as the local densities

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

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

Density Dependent Terms: ES

Non local Coulomb operator



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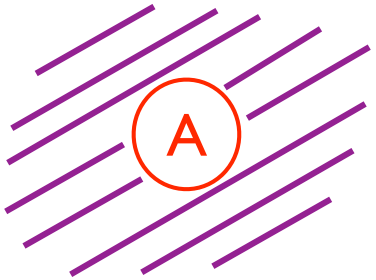
$$V[\tilde{n} + \mathbf{n}^0] + \sum_A V[n_A + n_A^Z] - \sum_A V[\tilde{n}_A + \mathbf{n}_A^0]$$

Interstitial region

Density Dependent Terms: ES

Non local Coulomb operator



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

Atomic region

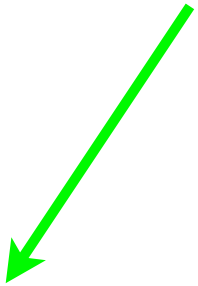
GAPW Functionals

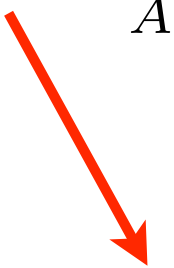
$$
\begin{aligned}
E_{xc}[n] &= E_{xc}[\tilde{n}] + \sum_A E_{xc}[n_A] - \sum_A E_{xc}[\tilde{n}_A] \\
E_H[n + n^Z] &= E_H[\tilde{n} + \mathbf{n^0}] + \\
&\quad \sum_A E_H[n_A + n_A^Z] - \sum_A E_H[\tilde{n}_A + \mathbf{n^0}]
\end{aligned}
$$

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

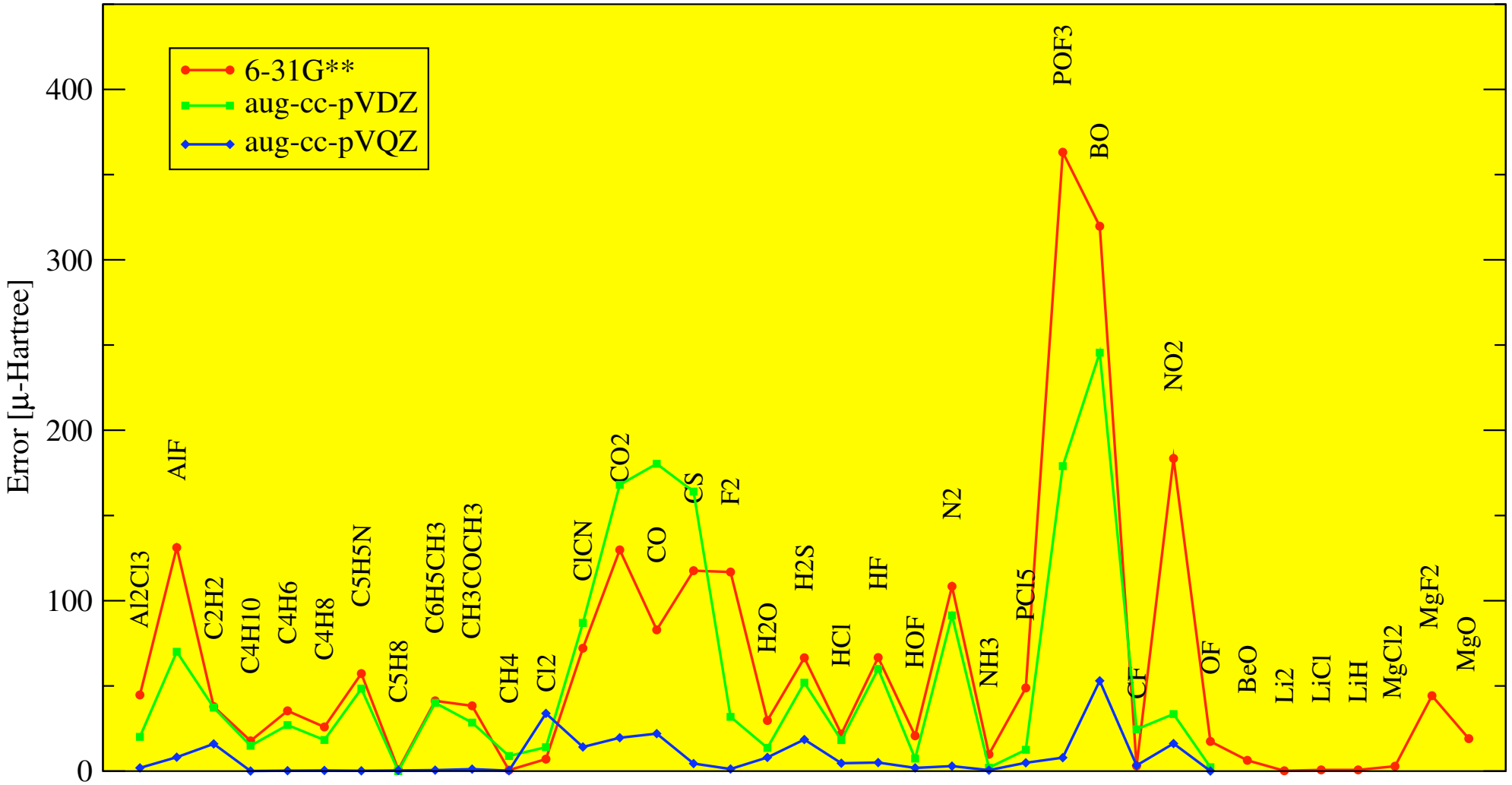
```
&DFT
  …
     &QS
       EXTRAPOLATION ASPC
       EXTRAPOLATION_ORDER 4
       EPS_DEFAULT 1.0E-12
       METHOD GAPW
       EPS_DEFAULT 1.0E-12
       QUADRATURE   GC_LOG
       EPSFIT       1.E-4
       EPSISO       1.0E-12
       EPSRHO0      1.E-8
       LMAXN0       4
       LMAXN1       6
       ALPHA0_H     10
     &END QS

&END DFT
```

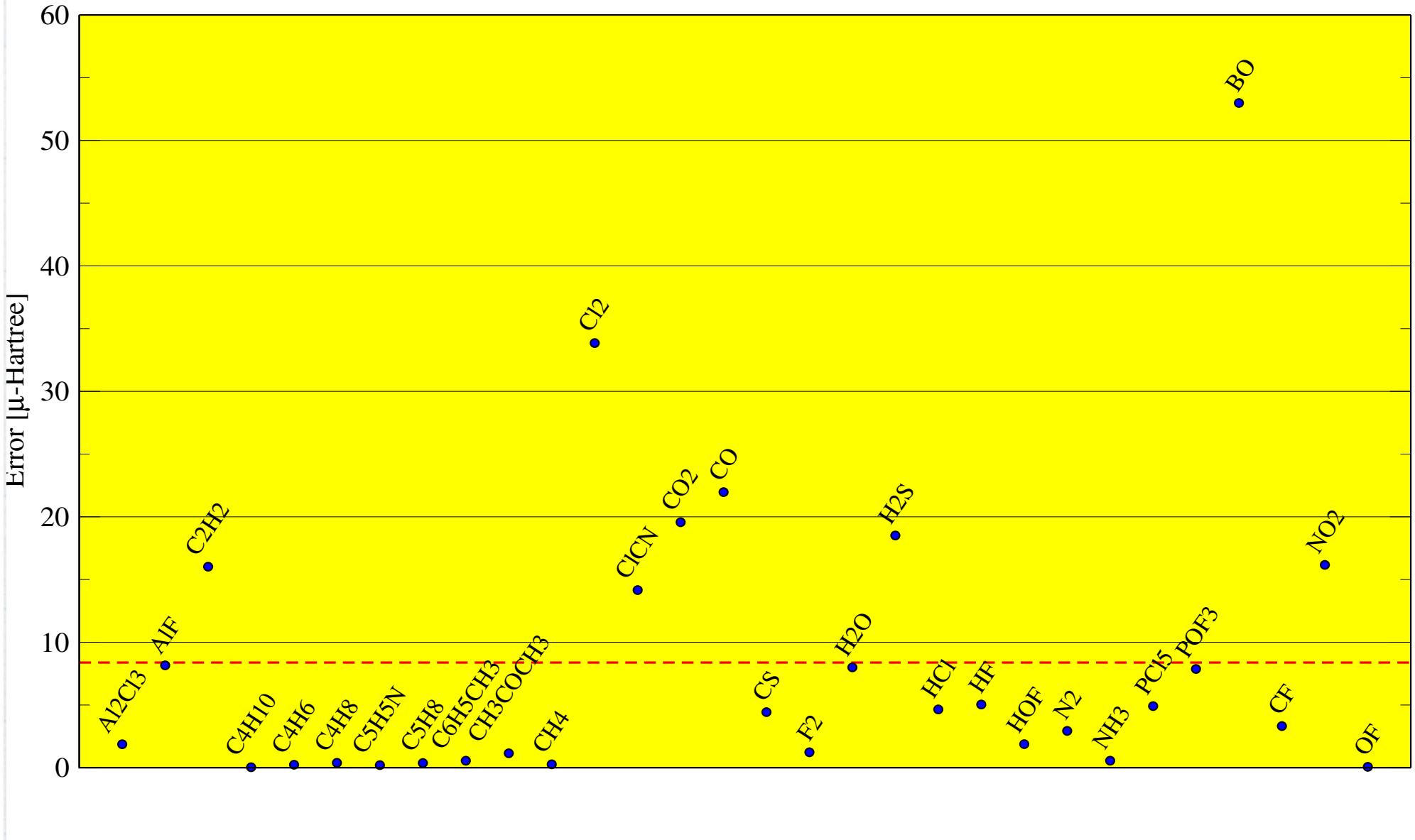
```
&SUBSYS
  …
    &KIND O
      BASIS_SET DZVP-MOLOPT-GTH-q6
      POTENTIAL GTH-BLYP-q6
      LEBEDEV_GRID 80
      RADIAL_GRID 200
    &END KIND
    &KIND O1
      ELEMENT O
#      BASIS_SET 6-311++G2d2p
      BASIS_SET 6-311G**
      POTENTIAL ALL
      LEBEDEV_GRID 80
      RADIAL_GRID 200
   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

&END SUBSYS
```

All-Electron Calculations



All-Electron Calculations



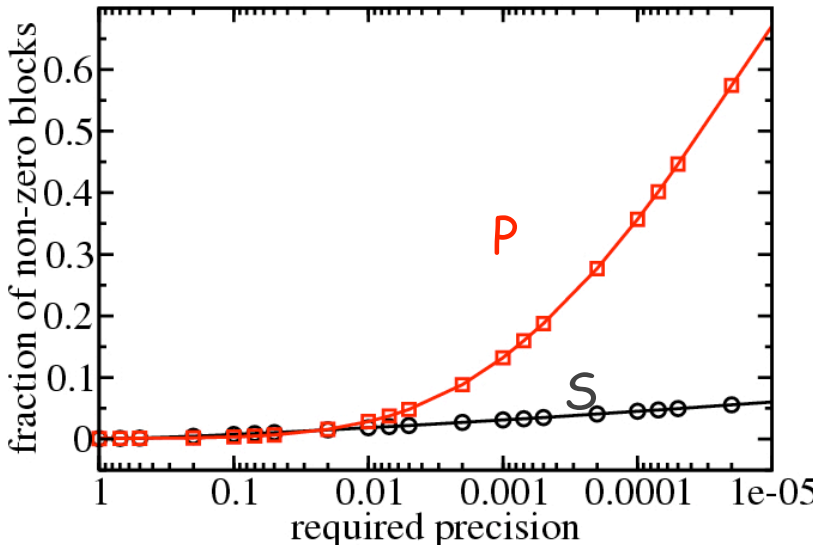
Energy Functional Minimization

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

- 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))

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

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



Orbital Transformation Method

Introduce auxiliary, linearly constrained variables to parametrize the occupied subspace

not linear orthonormality constraint

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

Linear constraint

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

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

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

minimization in the auxiliary tangent space, idempotency verified

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

Preconditioned gradients

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

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

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Preconditioned gradients

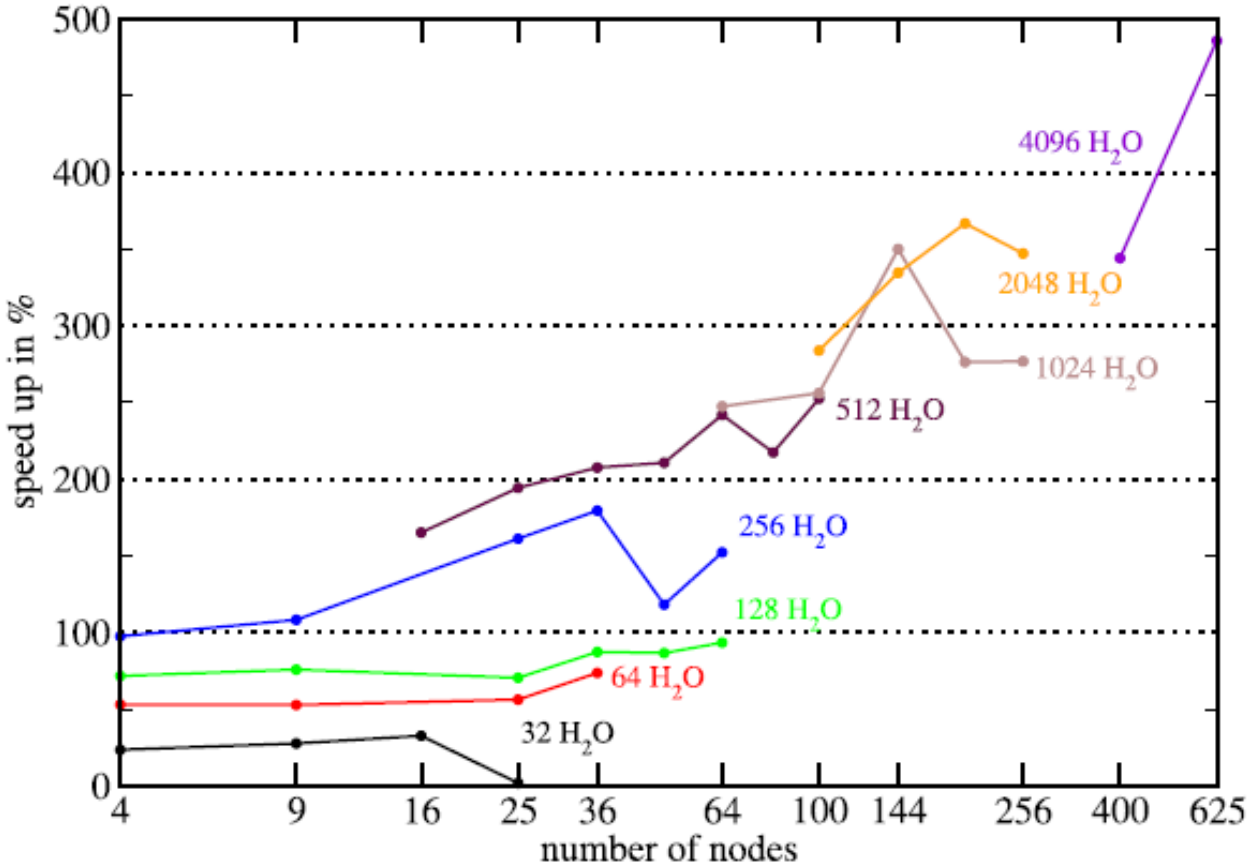
$$\mathbf{P}(\mathbf{H} - \mathbf{S}\epsilon)\mathbf{X} - \mathbf{X} \approx 0 \qquad \mathbf{X} \rightarrow \sqrt{\mathbf{P}}\mathbf{X}$$

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

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

OT Method 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 Method 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
```

Iterative Refinement

$$C^* = \arg\min_C \{E[C] \mid C^T S C = 1\}$$

unconstrained functional minimization

$$Z^* = \arg\min_Z \{E[f(Z)]\} \qquad C^* = f(Z^*) \qquad f^T(Z) S f(Z) = 1 \quad \forall Z$$

approximate constraint function f_n

$$f_n(Z) \; : \; f_n^T(Z) S f_n(Z) - 1 = \mathcal{O}(\delta Z^{n+1}) \quad \forall \; Z = Z_0 + \delta Z \quad \text{if } Z_0^T S Z_0 = 1$$

$$f_1(Z) = \frac{1}{2} Z(3 - Y) \qquad f_2(Z) = \frac{1}{8} Z(15 - 10Y + 3Y^2) \qquad f_3(Z) = \frac{1}{16} Z(35 - 35Y + 21Y^2 - 5Y^3)$$

$$f_4(Z) = \frac{1}{128} Z(315 - 420Y + 378Y^2 - 180Y^3 + 35Y^4)$$

Approximate Löwdin factorization

$$Y = Z^T S Z$$

$$f_n(\ldots f_n(Z)\ldots)$$

Includes only matrix additions and multiplications
Simplifies parallelization and use sparsity

V. Weber et al, JCP, 128, 084113, 2008

Direct Minimization

Input matrices

$$h \; S \; C_0 \; p$$

Gradient

$$D_0 = -G_0 = -G[C_0]$$

loop over i

Line search to minimize

$$E[f_n(...f_n(C_i + \alpha_i D_i)...)]$$

$$C_{i+1} = f_n(...f_n(C_i + \alpha_i D_i)...)$$

$$G_{i+1} = G[C_{i+1}]$$

Apply the preconditioner

$$p \; G_{i+1}$$

CG : Polak-Ribiere

$$D_{i+1} = -G_{i+1} + \beta_i D_i$$

check convergence

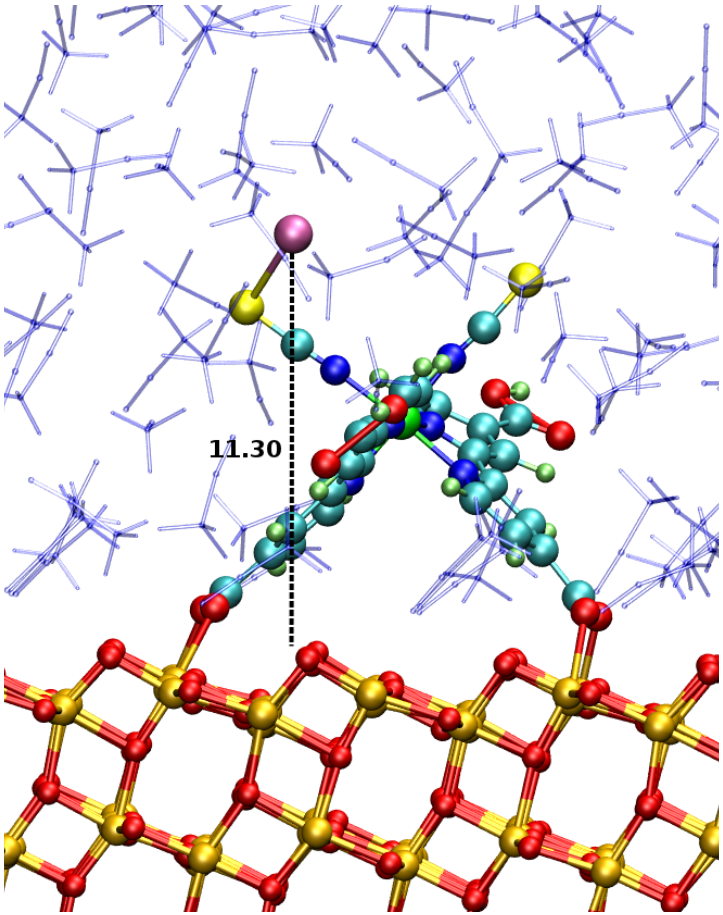
iterate refinement until

$$C_{i+1}^T S C_{i+1} - 1 < \varepsilon_{\text{refine}}$$

$$C^* \qquad E[C^*]$$

Dye-Sensitized Solar Cells

In situ electronic spectroscopy and dynamics



dye-iodide complex attached to TiO2

- 1751 atom computational cell, 864 (TiO2), 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

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

Linear-Scaling DFT

- Based on sparse matrix matrix multiplications

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

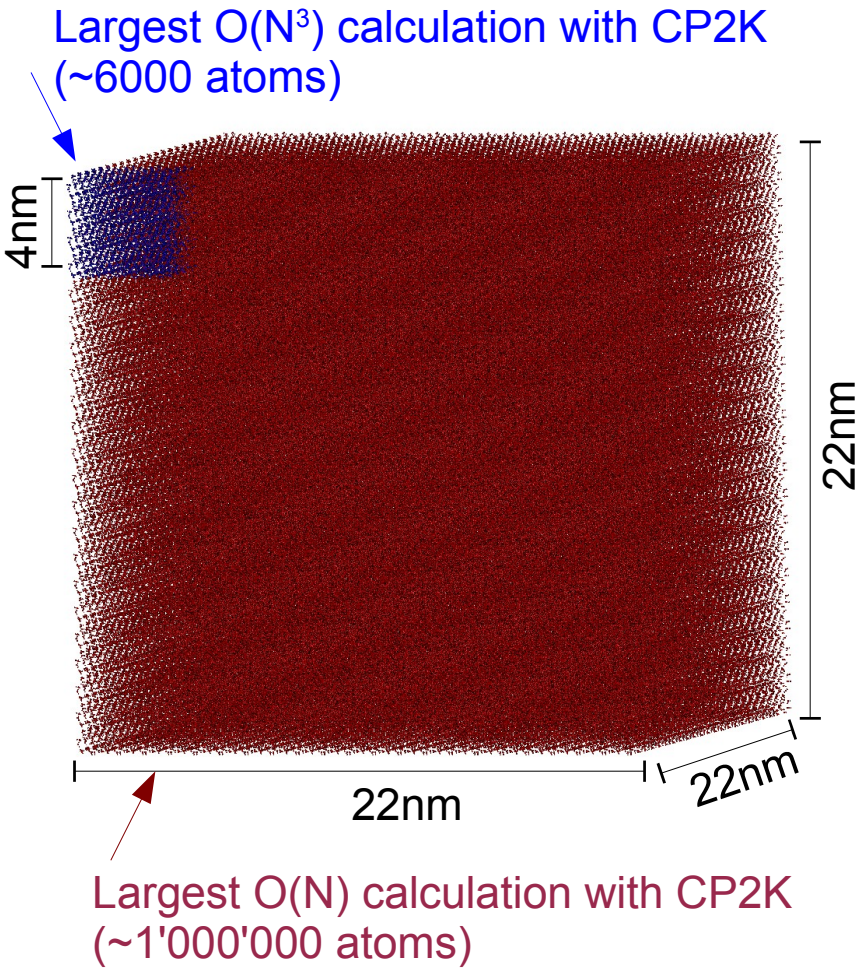
- Self consistent solution by mixing

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

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

- Chemical potential by bisecting until

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

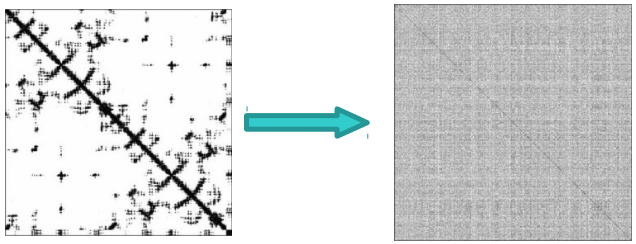


VandeVondele, Borstnik, Hutter; JCTC 10, 3566 (2012)

Sparse Matrix Library

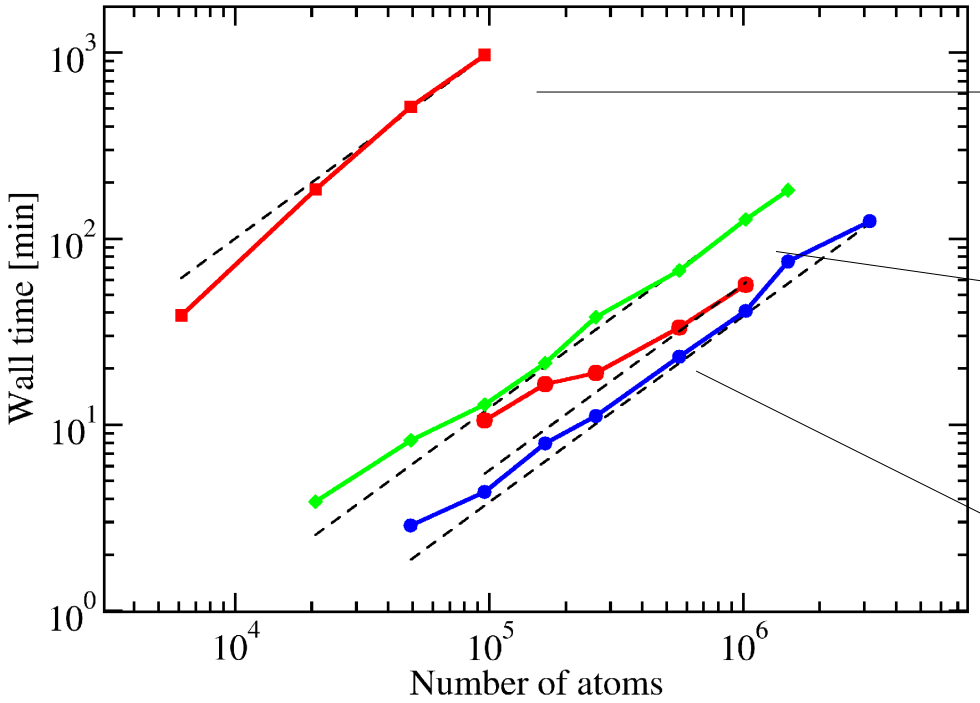
DBCSR: Distributed Blocked Compressed Sparse Row

- 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.

Traditional Diagonalization

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

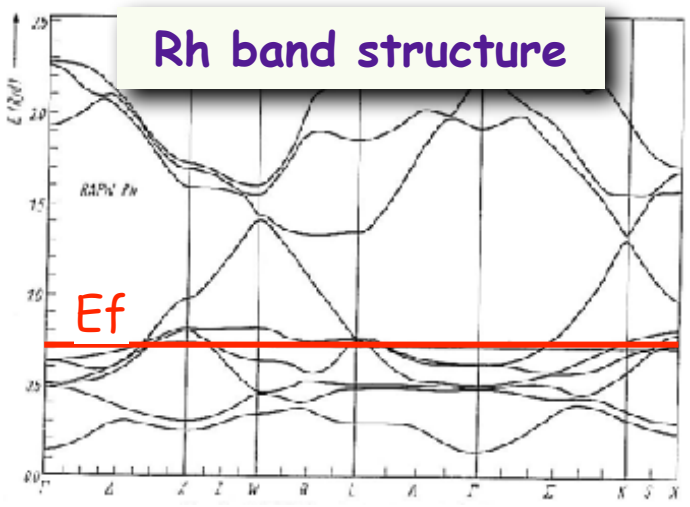
error matrix

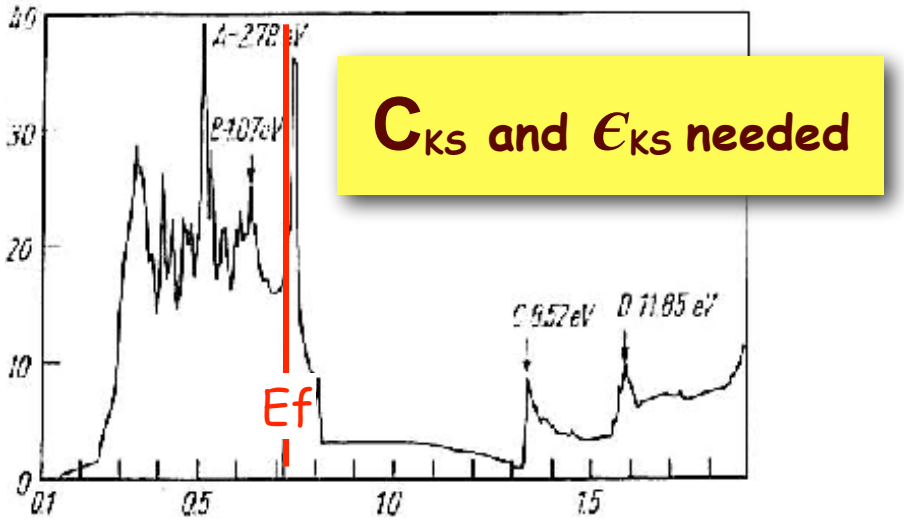
$$\mathbf{e} = \mathbf{KPS} - \mathbf{SPK}$$

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

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 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

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

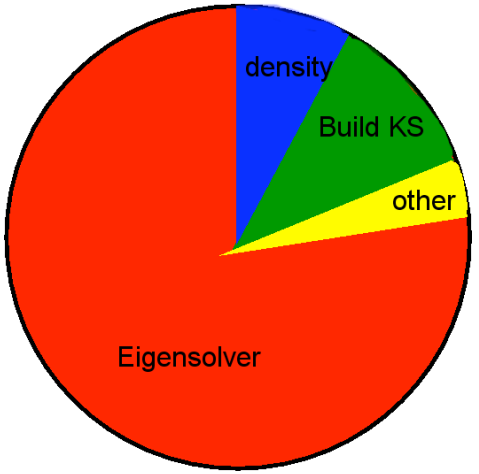
Check convergence

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

Density mixing

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

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

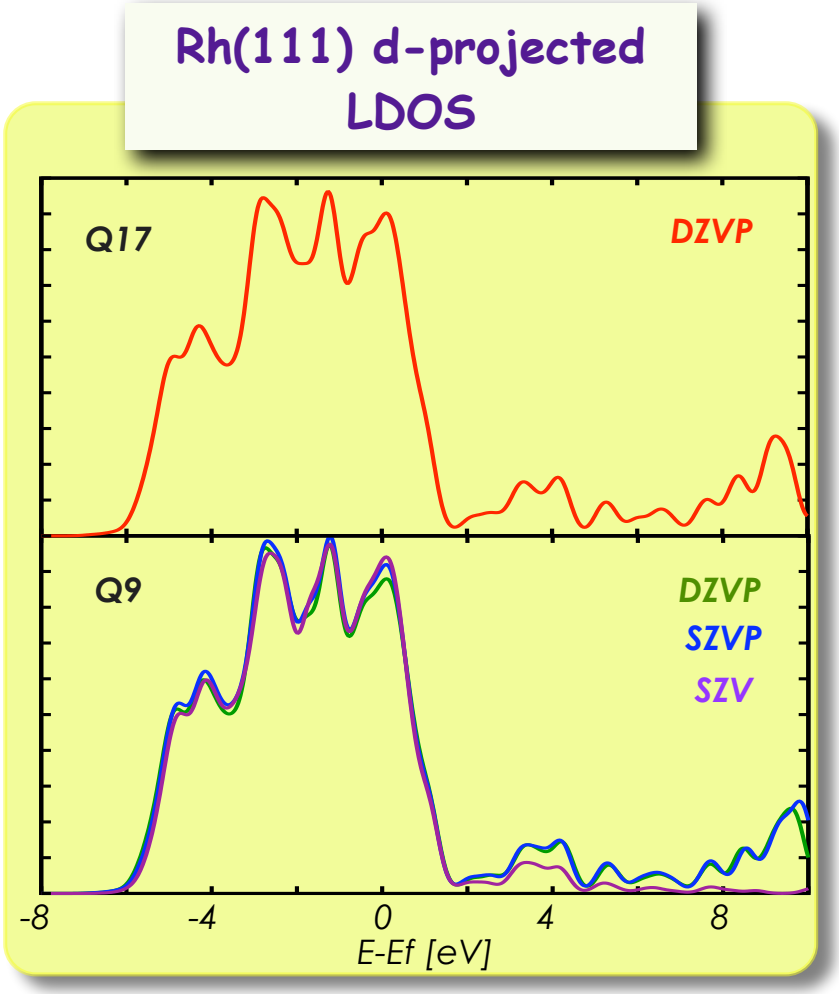


Rhodium: Bulk & Surface

Bulk: 4x4x4

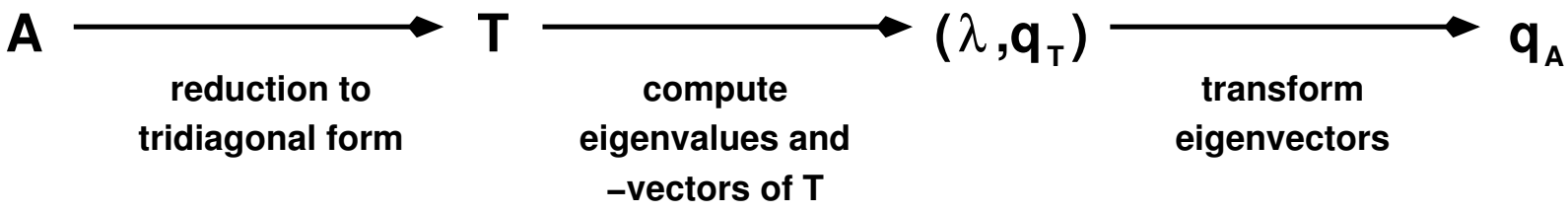
Surface: 6x6 7 layers

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



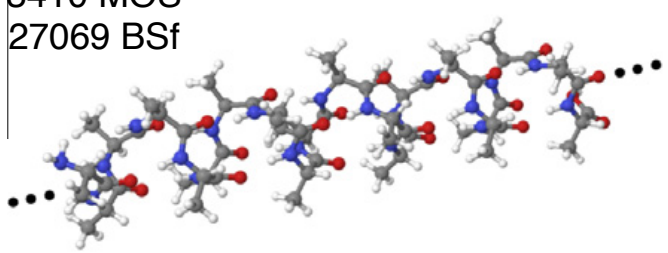
Diaz, et al. Theo Chem Acc (2013).

ScaLAPACK for diagonalization

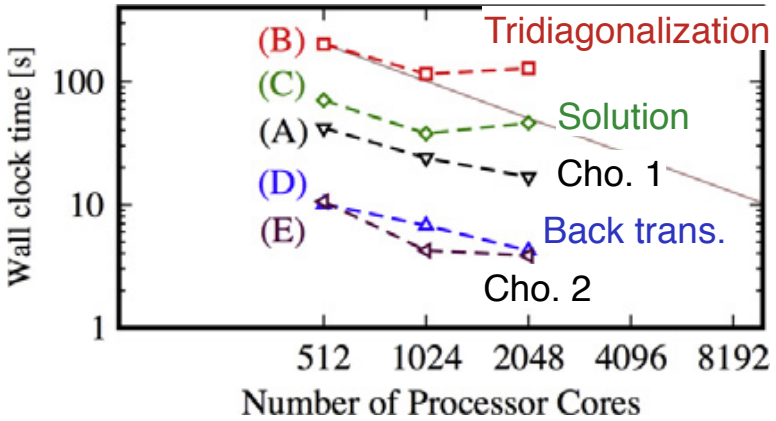


1003 atoms
3410 MOS
27069 BSf

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

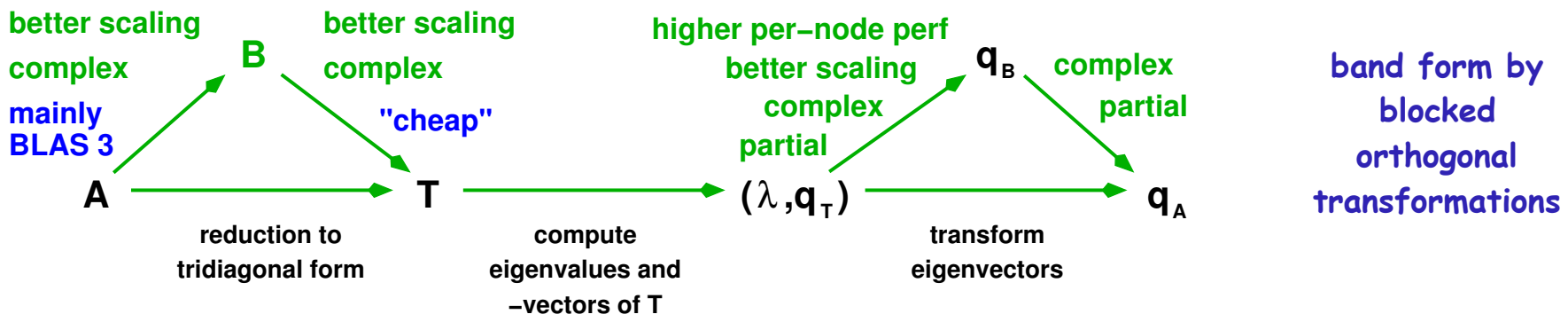
time x SCF, on CRAY XE6

>70% in eigenvalue solver

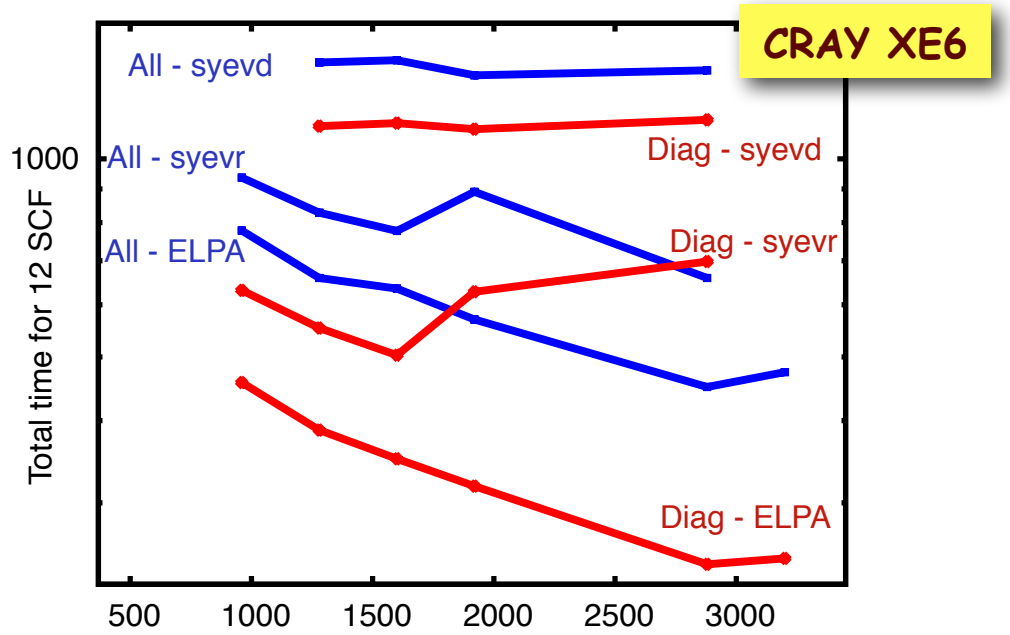
poor scaling

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

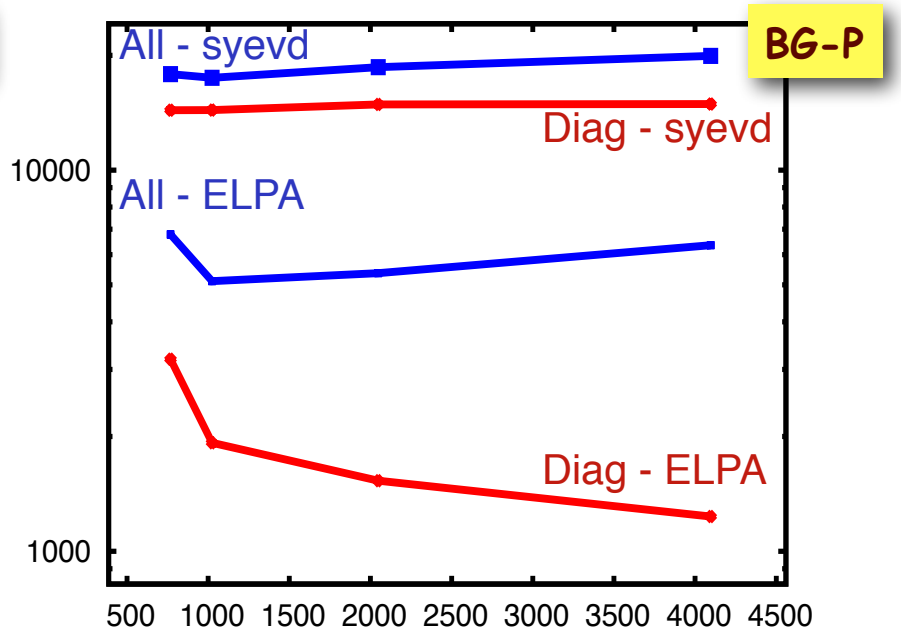
Improved efficiency by a two-step transformation and back transformation



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

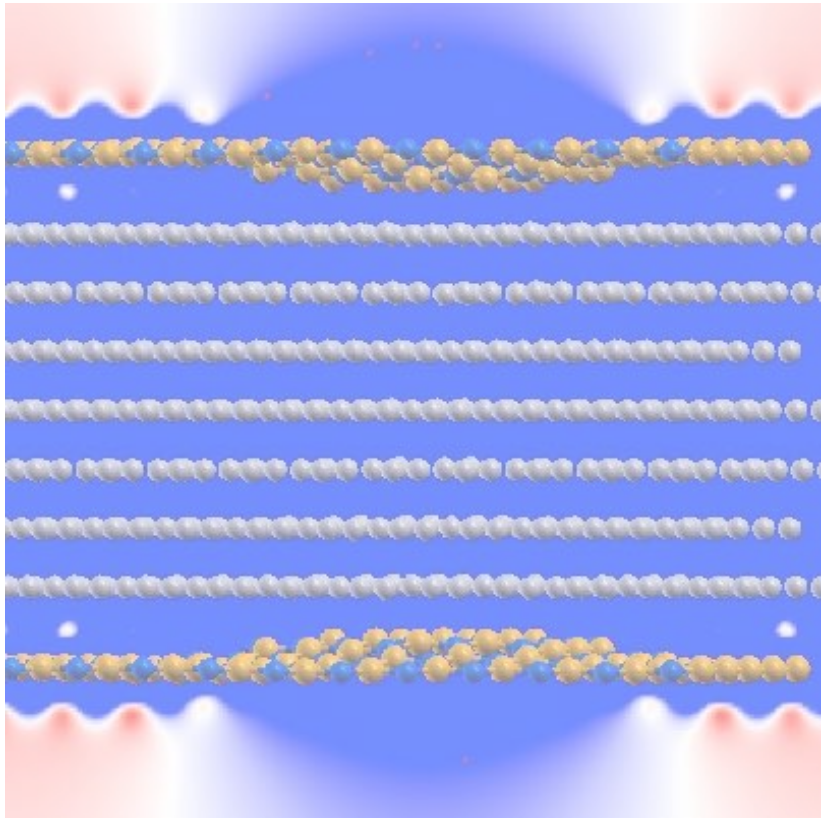


N atom= 480; Nel = 6000;
nmo = 7400; nao = 14240



Large Metallic Systems

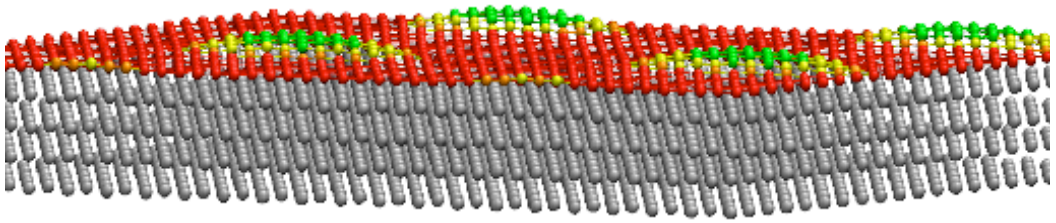
hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab



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 weeks 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 ;

~ several days per structure optimisation

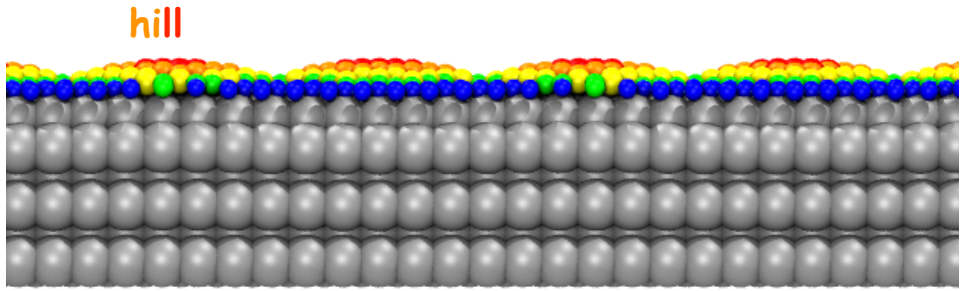
Iannuzzi et al., PRB (2013)
Cun, Iannuzzi et al, Nano Letter (2013)

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
```

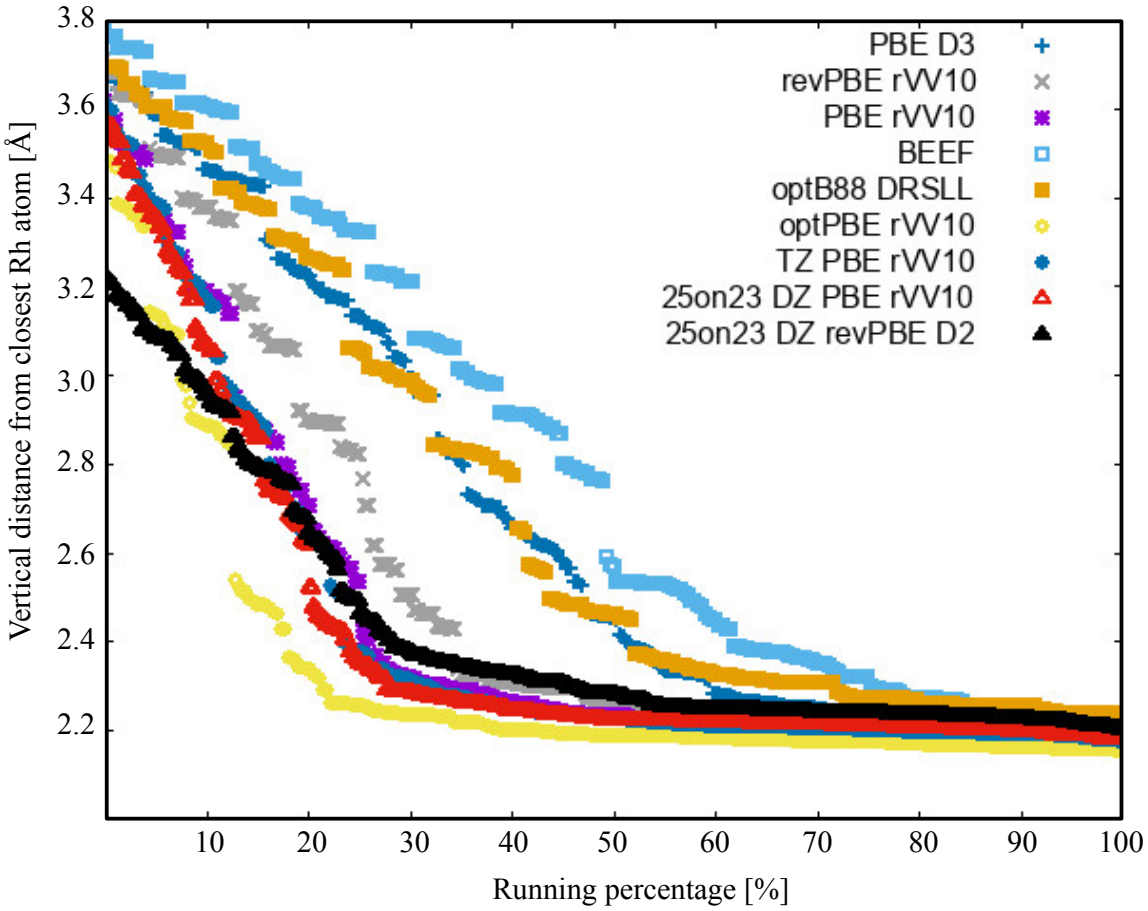
```
&XC
  &XC_FUNCTIONAL PBE
  &END
  &vdW_POTENTIAL
    DISPERSION_FUNCTIONAL PAIR_POTENTIAL
    &PAIR_POTENTIAL
        TYPE DFTD3
        PARAMETER_FILE_NAME dftd3.dat
        REFERENCE_FUNCTIONAL PBE
    &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
&END XC
```

Hills & Valleys of Graphene



Method	$h_{\min}$ (Å)	Δh (Å)
LEEM[5]	1.5 ± 0.1	-
LEED[18]	2.1 ± 0.2	1.5 ± 0.2
SXRD[21]	-	0.82 ± 0.15
HAS[19]	-	0.17 ± 0.03

Issues: binding distance
corrugation
height distribution



Electron Density: Cube File

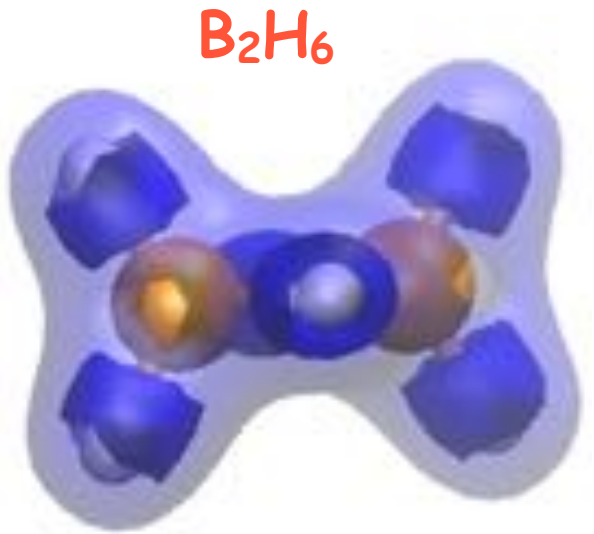
Valence density on regular grids

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

Cutoff might be too small for high resolution close to the nuclei (all electrons)

$$\psi_i(\mathbf{r}) = \sum_{\mu} C_{\mu i}\varphi_\mu(\mathbf{r}) \rightarrow \sum_{\mu} C_{\mu i}\bar{\varphi}(\mathbf{R}) = \psi_i(\mathbf{R})$$

```
-Quickstep-
 TOTAL DENSITY
   8   0.000000   0.000000   0.000000
  54   0.349949   0.000000   0.000000
  54   0.000000   0.349949   0.000000
  63   0.000000   0.000000   0.362827
   5   0.000000   9.448631   9.448631  11.338357
   5   0.000000   9.448631   9.448631  14.683172
   1   0.000000  11.322313   9.448631  13.010846
   1   0.000000   7.574948   9.448631  13.010846
   1   0.000000   9.448631  11.416848  15.778669
   1   0.000000   9.448631   7.480413  15.778669
   1   0.000000   9.448631   7.480413  10.242860
   1   0.000000   9.448631  11.416848  10.242860
 0.16324E-08 0.14425E-08 0.13016E-08 0.12075E-08 0.11584E-08 0.11533E-08
 0.11920E-08 0.12755E-08 0.14051E-08 0.15832E-08 0.18123E-08 0.20955E-08
 0.24355E-08 0.28348E-08 0.32950E-08 0.38170E-08 0.44000E-08 0.50422E-08
```



Spin Density

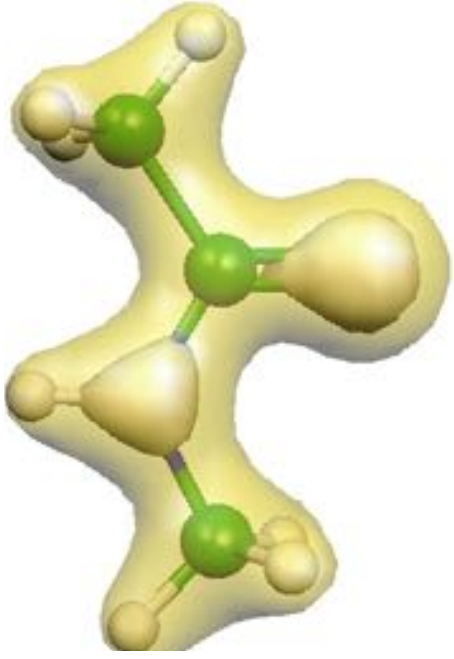
Spin polarized DFT calculations:

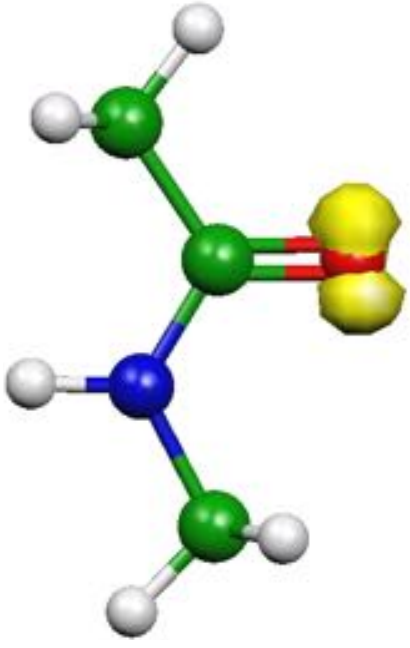
$$n^{(\alpha)}(\mathbf{r}) = \sum_{\mu\nu} P^{(\alpha)}_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) \qquad n^{(\beta)}(\mathbf{r}) = \sum_{\mu\nu} P^{(\beta)}_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r})$$

$$\Delta n_{\text{spin}}(\mathbf{r}) = n^{(\alpha)}(\mathbf{r}) - n^{(\beta)}(\mathbf{r}) \rightarrow \Delta n_{\text{spin}}(\mathbf{R})$$

H_3C-CO-NH_2-CH_3 **$(H_3C$-CO-NH_2-$CH_3)^+$**

$n(\mathbf{R})$





$\Delta n_{\text{spin}}(\mathbf{R})$

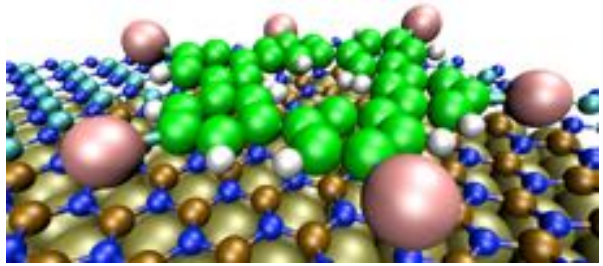
Density Difference

Changes in the electronic density due to interactions, e.g., molecule adsorbed on substrate

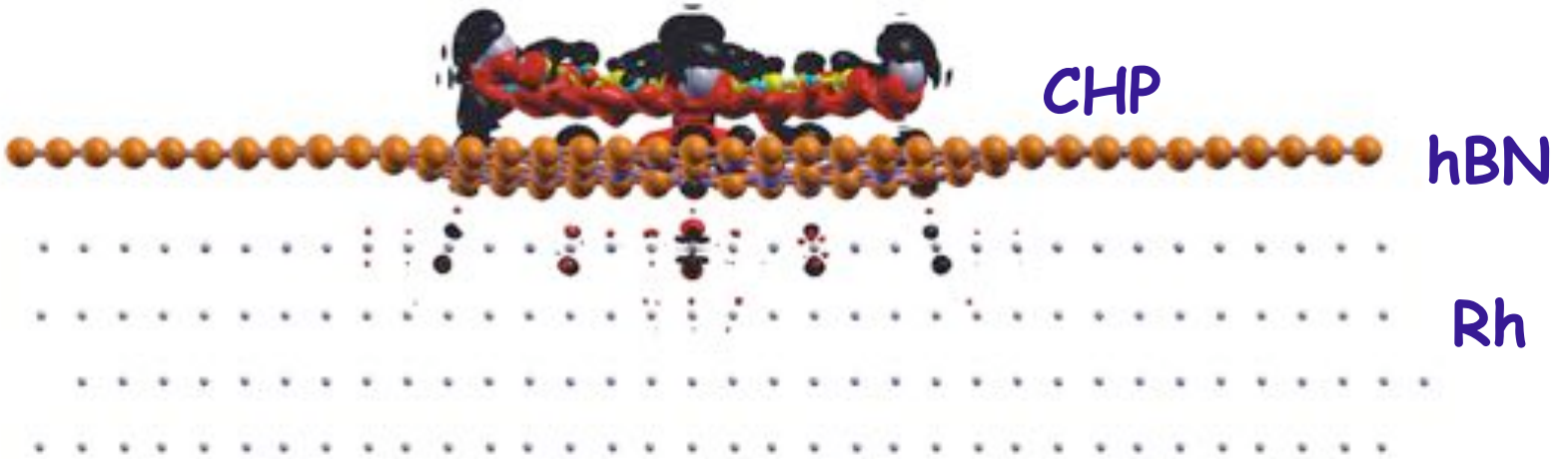
$$E_{\mathrm{ads}} = E_{\mathrm{tot}} - (E^{o}_{\mathrm{sub}} + E^{o}_{\mathrm{mol}})$$

$$E_{\mathrm{int}} = E_{\mathrm{tot}} - \left(E^{f}_{\mathrm{sub}} + E^{f}_{\mathrm{mol}}\right)$$

CHP on hBN/Rh (5 eV)



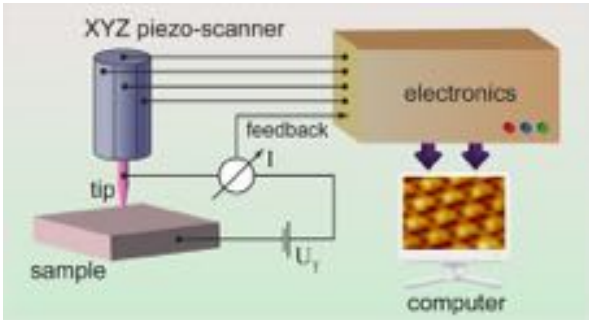
$$\Delta n_{\mathrm{int}}(\mathbf{r}) = n_{\mathrm{tot}}(\mathbf{r}) - \left(n^{f}_{\mathrm{sub}}(\mathbf{r}) + n^{f}_{\mathrm{mol}}(\mathbf{r})\right)$$



STM Images

Tersoff-Hamann approximation to mimic the iso-current topography

$$n_b(\mathbf{r}) = \sum_{i:\varepsilon_i \in [E_f - V_b : E_f]} \left[\sum_{\mu\nu} C^*_{\mu i} C_{\nu i} \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r}) \right] \rightarrow n_b(\mathbf{R})$$

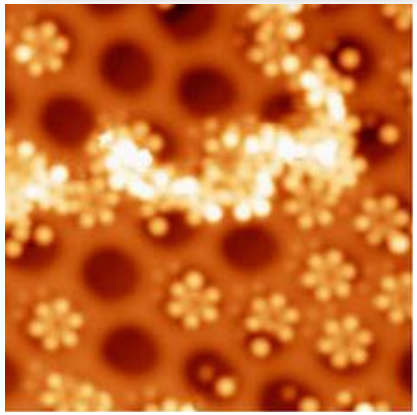


Find height at constant energy projected density

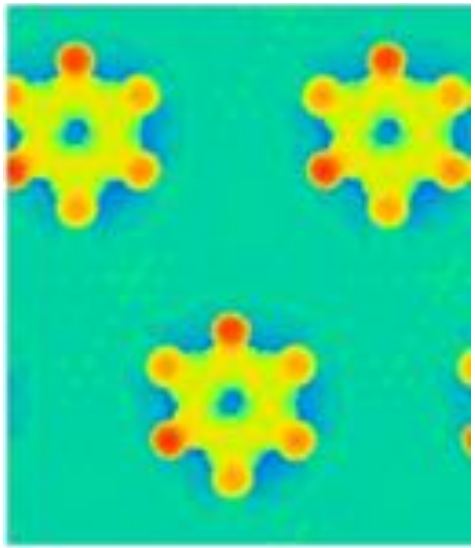
$$z : n_b(X, Y, z)\ e^{-2kR_0\sqrt{\Phi(X,Y,z)}}$$

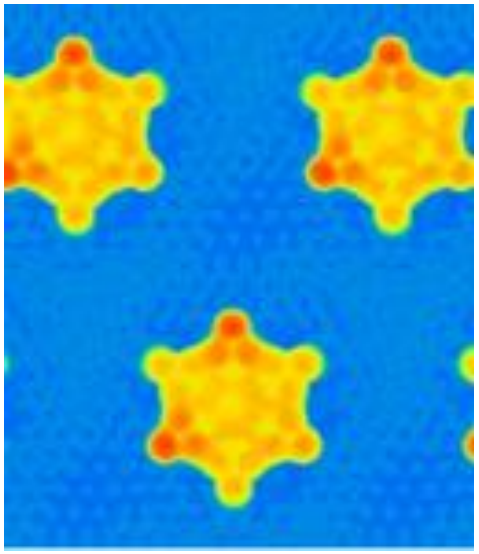
CHP on hBN/Rh (5 eV)

Vb=-1310 mV

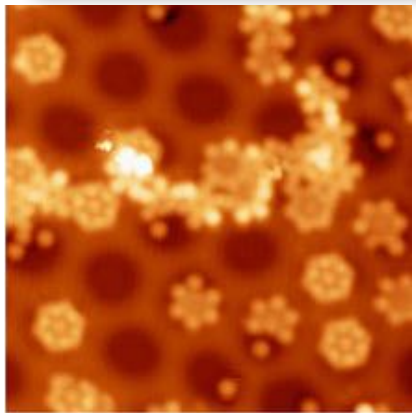


occupied states





Vb=+1480 mV



unoccupied states

Position Operator for Isolated Systems

One body operator

$$\hat{X} = \sum_{i=1}^{N} x_i$$

Expectation value

$$\langle X \rangle = \langle \Psi | \hat{X} | \Psi \rangle = \int x \; n(x) dx$$

Gauge invariance

$$\langle X \rangle_R = \langle \Psi | \hat{X} + R | \Psi \rangle = \langle X \rangle_0 + R \int \; n(x) dx = \langle X \rangle_0 + RZ$$

Position Operator with PBC

Expectation value of the position operator

$$\hat{\mathbf{R}} = \sum_i \hat{\mathbf{r}}_i \qquad \langle \mathbf{R} \rangle = \langle \Psi | \hat{\mathbf{R}} | \Psi \rangle = \int \mathbf{r} n(\mathbf{r}) d\mathbf{r} \qquad \text{(3D)}$$

Wavefunctions are periodic, result of an operator has also to be periodic

$$\Psi(\mathbf{r}) = \Psi(\mathbf{r} + \mathbf{L}) \qquad \hat{\mathbf{R}}\Psi(\mathbf{r}) \neq (\hat{\mathbf{R}} + \mathbf{L})\Psi(\mathbf{r} + \mathbf{L})$$

Many-body periodic position operator (1D)

$$\langle X \rangle = \frac{L}{2\pi} \, \mathrm{Im} \, \ln \langle \Psi \mid e^{i \frac{2\pi}{L} \hat{X}} \mid \Psi \rangle$$

Berry Phase

Electronic polarisation

$$P_{\mathrm{el}} = \lim_{L \to \infty} \frac{e}{2\pi} \, \mathrm{Im} \, \ln \langle \Psi \mid e^{i \frac{2\pi}{L} \hat{X}} \mid \Psi \rangle$$

Resta, R. (1998). Quantum-Mechanical Position Operator in Extended Systems. *Physical Review Letters*, **80**(9), 1800–1803.

Polarization

Many-body wavefunction (Bloch orbitals)

$$|\Psi\rangle = A \prod_i \prod_s \psi_{q_s,i}(\mathbf{r})$$

New set of Bloch orbitals

$$\tilde{\psi}_{q_s,m}(x) = e^{-i\frac{2\pi}{L}x}\psi_{q_s,m}(x) \qquad \frac{2\pi}{L} = G_1$$

Expectation value from overlap of determinants = determinants of overlap of orbitals

$$\langle X \rangle = -\frac{L}{2\pi} Im \ln \langle \Psi | \tilde{\Psi} \rangle = -\frac{L}{2\pi} Im \ln \det S$$

$$S_{ij}^{\alpha} = \int \psi_i(\mathbf{r}) e^{i\mathbf{G}_{\alpha\mathbf{1}}\cdot\mathbf{r}} \psi_j(\mathbf{r}) d\mathbf{r} \qquad P^{\alpha} = \frac{2e}{\mathbf{G}_{\alpha 1}} \mathrm{Im} \ln [\det \mathbf{S}^{\alpha}]$$

Localized Orbitals

- Boys spread of the orbitals through a 2-el operator $\Omega = \sum_i \langle \psi_i \psi_i | (\mathbf{r}_1 - \mathbf{r}_2)^2 | \psi_i \psi_i \rangle$
- With PBC, localize equivalent to minimize

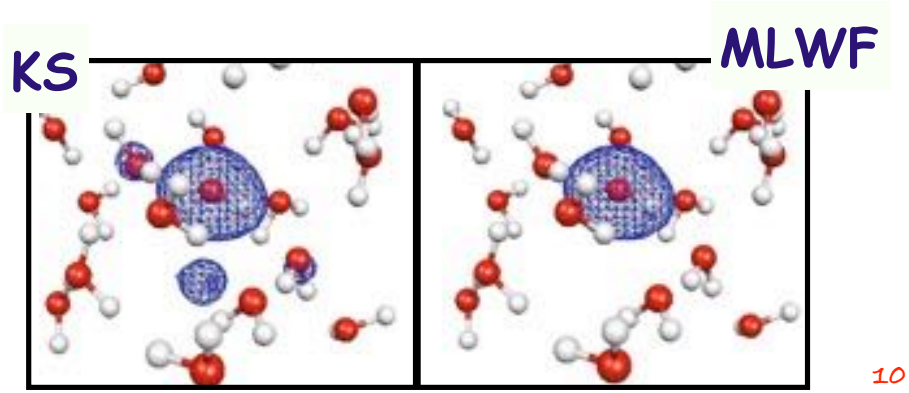
$$\Omega = \frac{1}{2\pi} \sum_s \sum_i \omega_s (1 - (|z_{si}|^2)) \qquad z_{si} = \int d\mathbf{r} \; e^{i\mathbf{k_s}\cdot\mathbf{r}} |\psi_i(\mathbf{r})|^2$$

- Find the unitary transformation

$$\tilde{\psi}_i(\mathbf{r}) = \sum_j U_{ij} \psi_i(\mathbf{r}) \qquad \frac{\partial \Omega}{\partial U_{ij}} = 0$$

- Iterative procedure (parallel Jacobi rotations)
- Centre of the charge distribution of the rotated orbital

$$\langle r_{si} \rangle = \frac{L_s}{2\pi} \mathrm{Im} \ln z_{si}$$

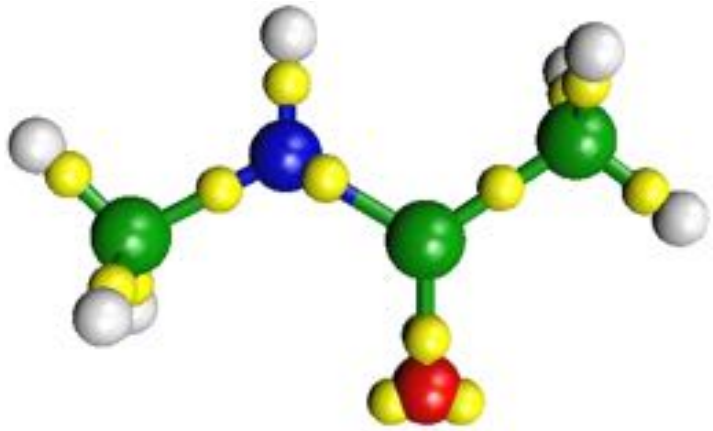


R.Resta, Phys. Rev. Lett., **82** 370 (1999);
G.Bergold et al, Phys. Rev. B, **61** 10041 (2000)

Wannier Centers

For a generalised 3D box **h**, for each maximally localised Wannier orbital

$$z_{si} = \det\mathbf{h} \int d\mathbf{r}\; e^{i\mathbf{k}_s\cdot\mathbf{r}} |\psi_i(\mathbf{r})|^2 \qquad \mathbf{r}_{si} = -\sum_t \frac{\mathbf{h}_{st}}{2\pi} \mathrm{Im}\ln z_{ti}$$



Molecular dipole moment from Wannier centres

$$\mu_s^W = e\sum_i \mathbf{r}_{si} = -e\sum_i\sum_t \frac{\mathbf{h}_{st}}{2\pi}\mathrm{Im}\ln z_{ti} = -e\sum_t \frac{\mathbf{h}_{st}}{2\pi}\mathrm{Im}\ln\prod_i z_{ti}$$

IR spectra from dipole moment autocorrelation function

$$\alpha(\omega) = \frac{4\pi\ \omega\ \tanh(\beta\hbar\omega/2)}{\hbar n(\omega) c V} \int_{-\infty}^{\infty} dt\; e^{-i\omega t} \langle P(t)\cdot P(0)\rangle$$


COFFEE BREAK