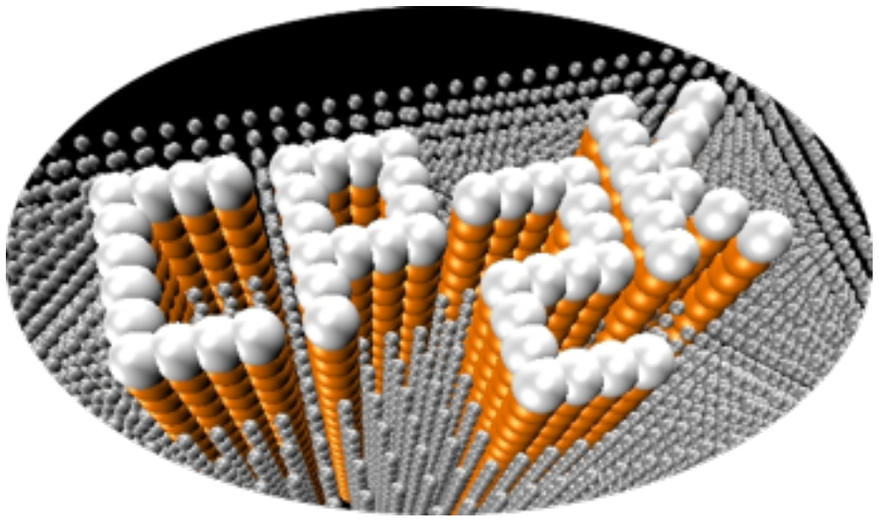
Parallel Materials Modelling Packages @ EPCC

23-25 April 2014, London UK

GPW (GAPW) electronic structure calculations

Marcella Iannuzzi

Department of Chemistry, University of Zurich



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 parallelization, 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)

Outline

Ground state KS-DFT and ab initio MD

- Gaussian and Plane Wave method (GPW)
  - Basis sets and pseudo potentials
- Gaussian Augmented Plane Wave method (GAPW)
- Orbital Transformations (OT)
- Diagonalisation and Mixing
  - Metals
- Born-Oppenheimer Molecular Dynamics
  - Stability and efficiency

DFT

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

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

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

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

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

KS total energy

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

Variational principle
Constrained minimization problem

Matrix formulation of the Schrödinger equations

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

Critical Tasks

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

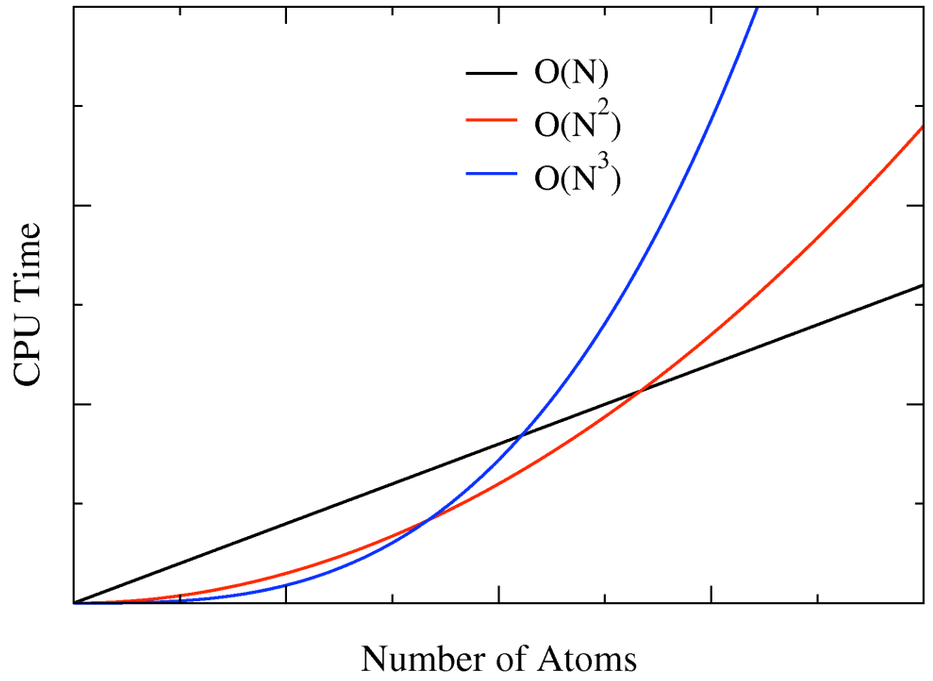
O(N) scaling in basis set size

Big systems: biomolecules, interfaces, material science

1000+ atoms

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

several ps a day



GPW Ingredients

linear scaling KS matrix computation for GGA

- Gaussian basis sets (many terms analytic)

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

- Pseudo potentials
- Plane waves auxiliary basis for Coulomb integrals
- Regular grids and FFT for the density
- Sparse matrices (KS and P)
- Efficient screening

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

Gaussian Basis Set

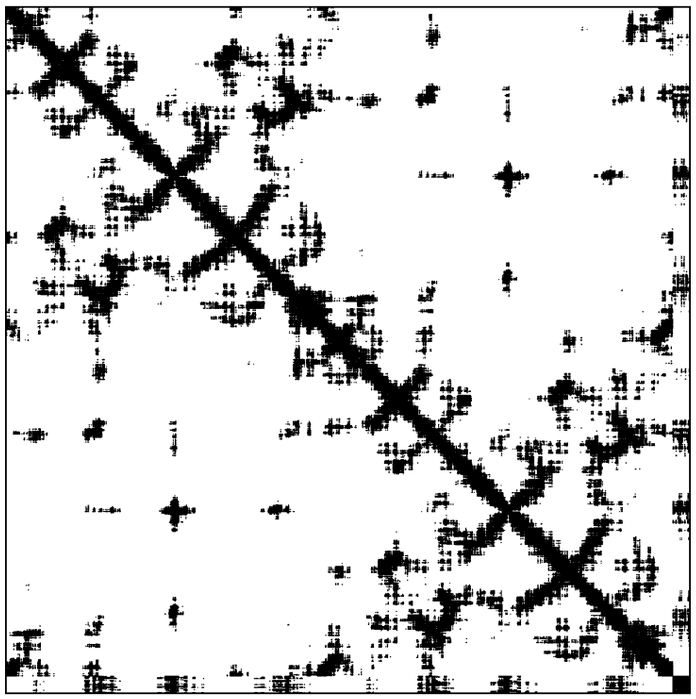
- Localised, atom-position dependent GTO basis

$$\varphi_\mu(\mathbf{r}) = \sum_m d_{m\mu} g_m(\mathbf{r}) \qquad g_m(\mathbf{r}) = x^{m_x} y^{m_y} z^{m_z} e^{-\alpha_m r^2}$$

- Expansion of the density using the density matrix

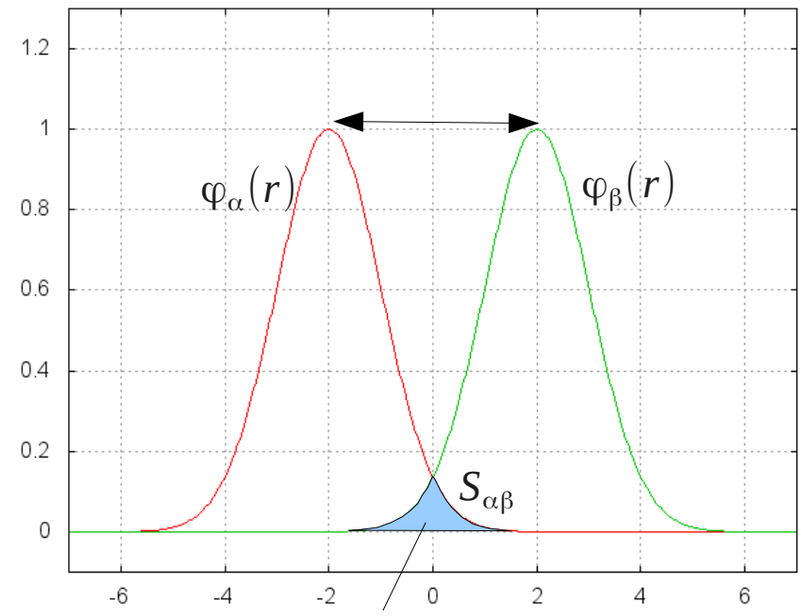
$$n(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu} \varphi_\mu(\mathbf{r}) \varphi_\nu^*(\mathbf{r})$$

Operator matrices are sparse



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

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



Basis Set library

GTH_BASIS_SETS ; BASIS_MOLOPT ; EMSL_BASIS_SETS

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

```
O  6-31Gx 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  6-311++G3df3pd    6-311++G(3df,3pd)
9
1 0 0 6 1
   8588.50000000        0.00189515
   1297.23000000        0.01438590
    299.29600000        0.07073200
     87.37710000        0.24000100
     25.67890000        0.59479700
      3.74004000        0.28080200
1 0 1 3 1 1
     42.11750000        0.11388900        0.03651140
      9.62837000        0.92081100        0.23715300
      2.85332000       -0.00327447        0.81970200
1 0 1 1 1 1
      0.90566100        1.00000000        1.00000000
1 0 1 1 1 1
      0.25561100        1.00000000        1.00000000
1 2 2 1 1
      5.16000000        1.00000000
1 2 2 1 1
      1.29200000        1.00000000
1 2 2 1 1
      0.32250000        1.00000000
1 3 3 1 1
      1.40000000        1.00000000
1 0 1 1 1 1
      0.08450000        1.00000000        1.00000000
```

Pseudopotentials

- Norm-conserving, separable, dual-space GTH

- 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

PP 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
```

Electrostatic Energy

Periodic system

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

total charge distribution including n(r) and Z

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

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

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

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

cancels the long range term of local PP

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

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

E^{ov} short range, pair

E^{self}

Auxiliary Basis Set

- Long range term : Non-local Hartree potential

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

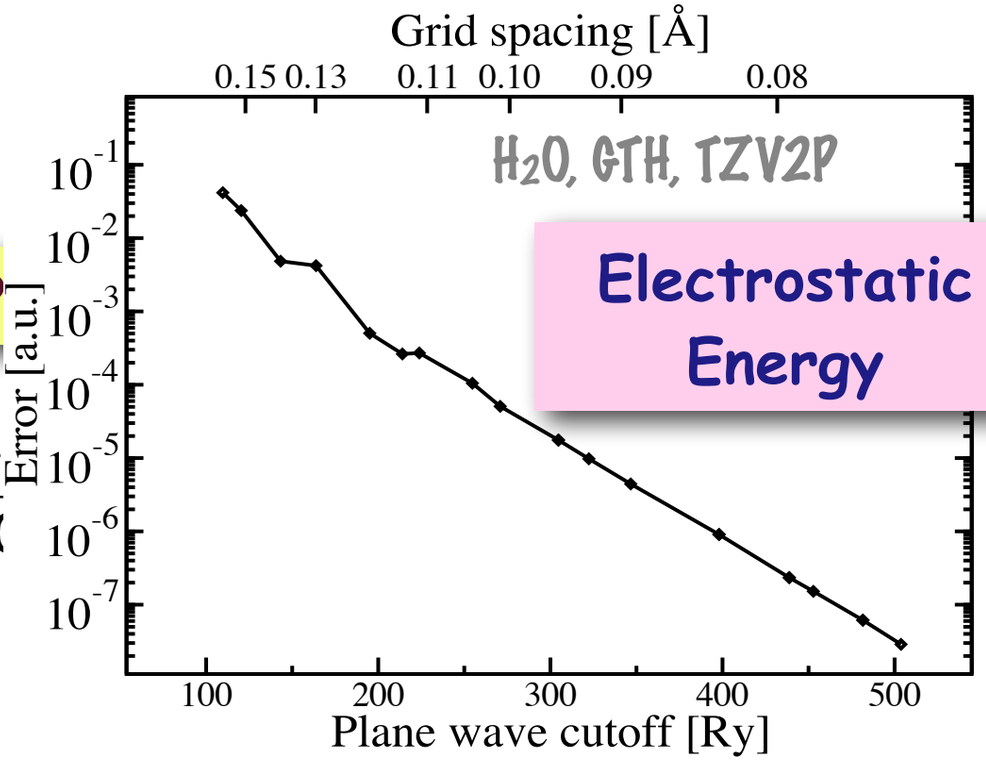
- Orthogonal, unbiased, naturally periodic PW basis

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

Efficient Mapping FFT

Linear scaling solution of the P

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



Electrostatic Energy

Real Space Integration

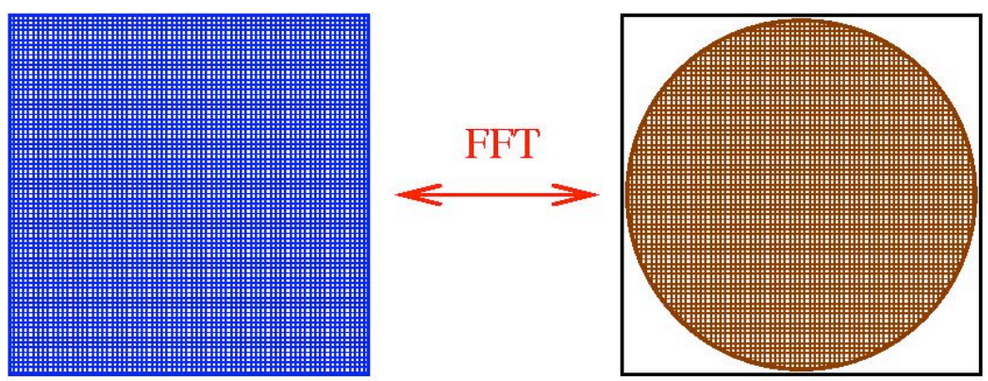
Finite cutoff and simulation box define a real space grid

- Density collocation

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

Screening Truncation

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



- Numerical approximation of the gradient

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

- ϵ_{XC} and derivatives evaluated on the grid

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

- Real space integration

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

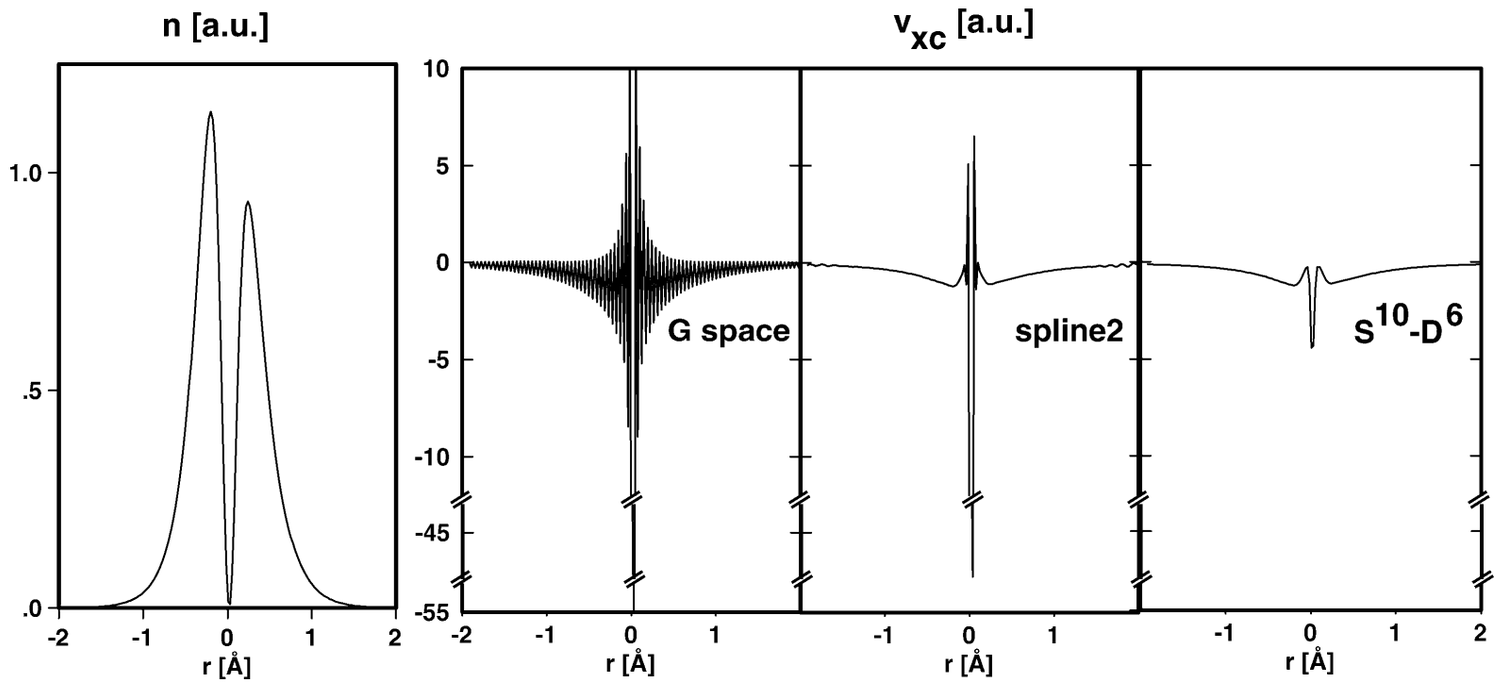
G. Lippert et al, Molecular Physics, 92, 477, 1997
J. VandeVondele et al, Comp. Phys. Comm.,167 (2), 103, 2005

Energy Ripples

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

H_2O, BLYP close to O along HOH bisector

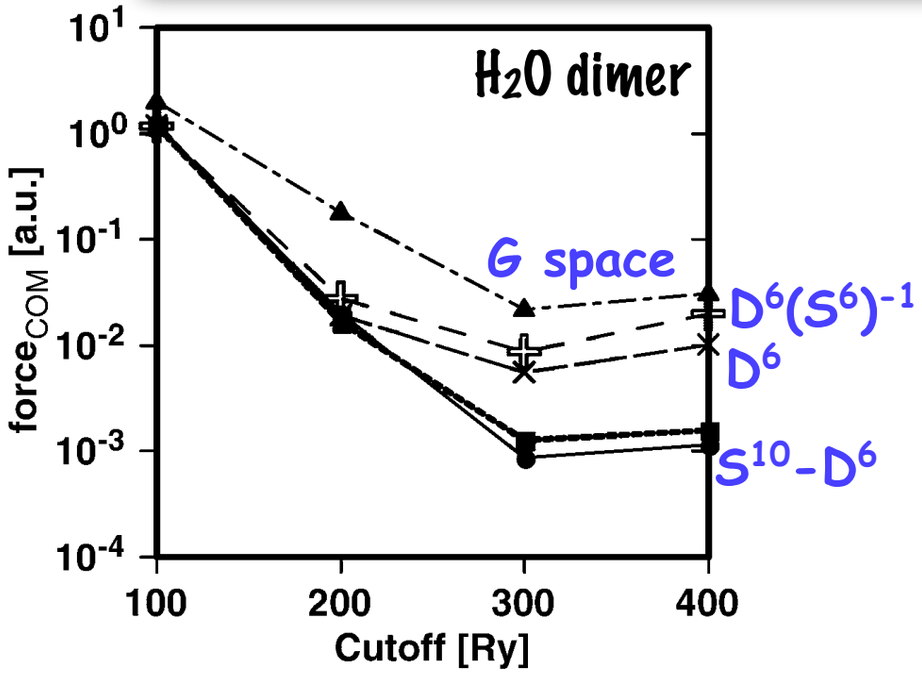
with PP low density at core



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

smoothed finite differences (D^q)

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



alternatively:
Non-linear core corrected PP
GAPW

Multiple Grids

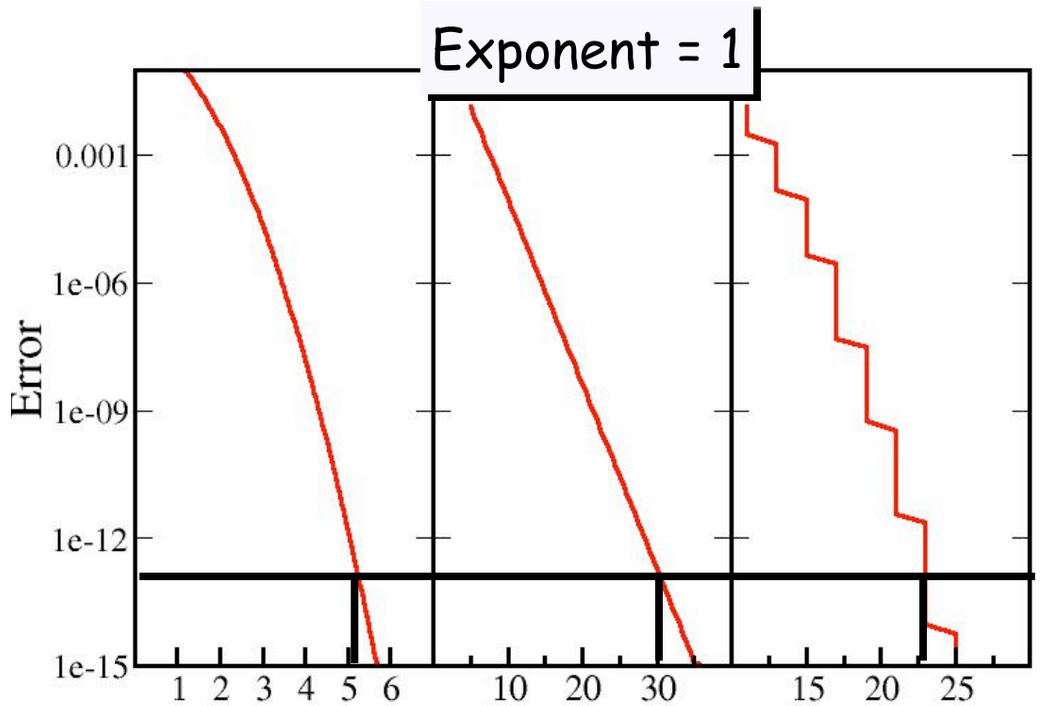
$$E^i_{\rm cut} = \frac{E^1_{\rm cut}}{\alpha^{(i-1)}}, \qquad i = 1..N$$

the exponent of Gaussian product selects the grid

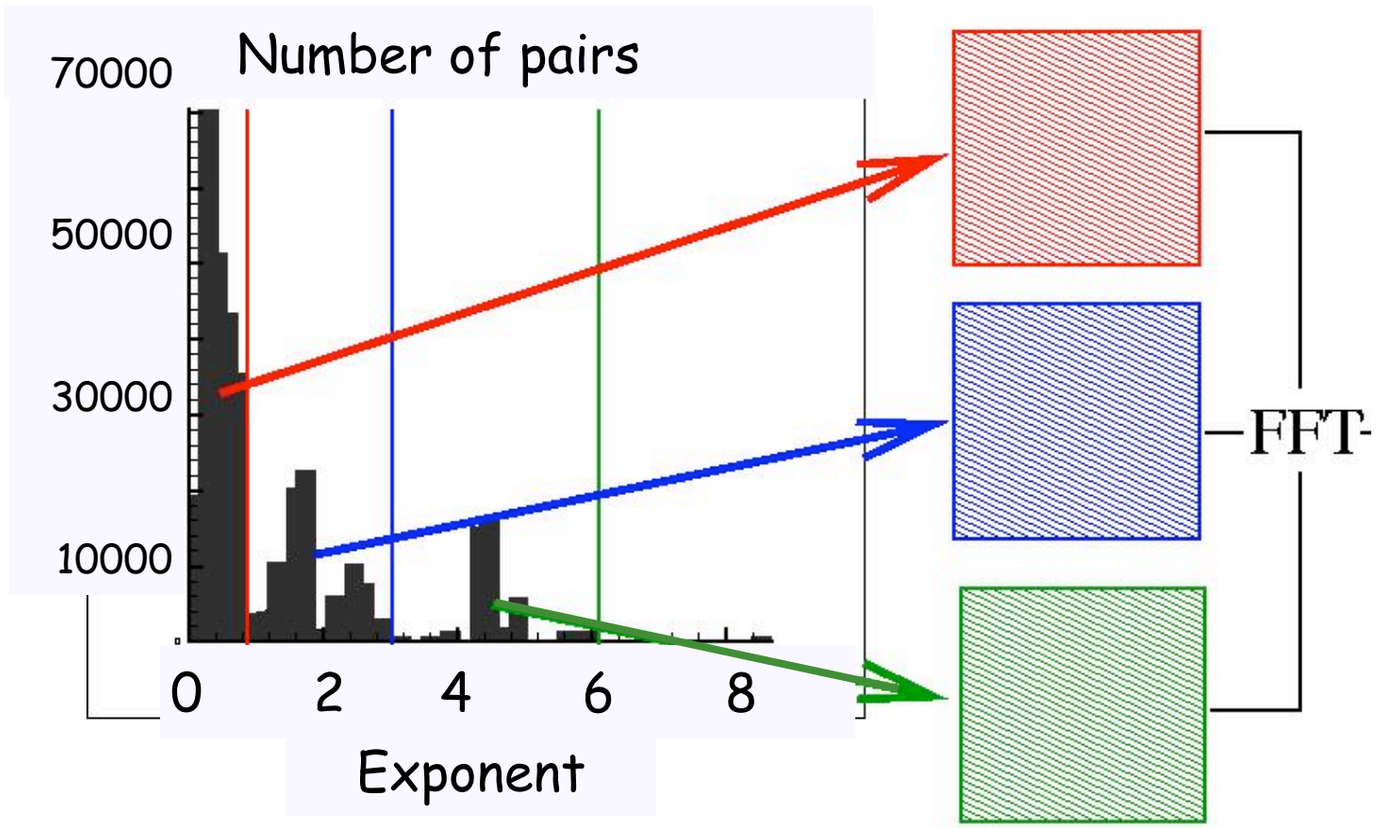
number of grid points is exponent-independent

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

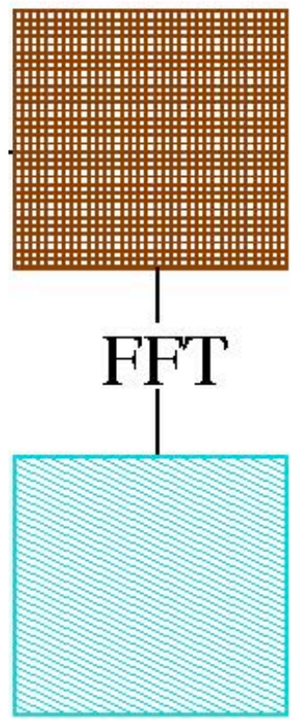
Accuracy
=> Relative Cutoff
~30 Ry



Integration range	Cutoff (Ry)	Integration Points



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

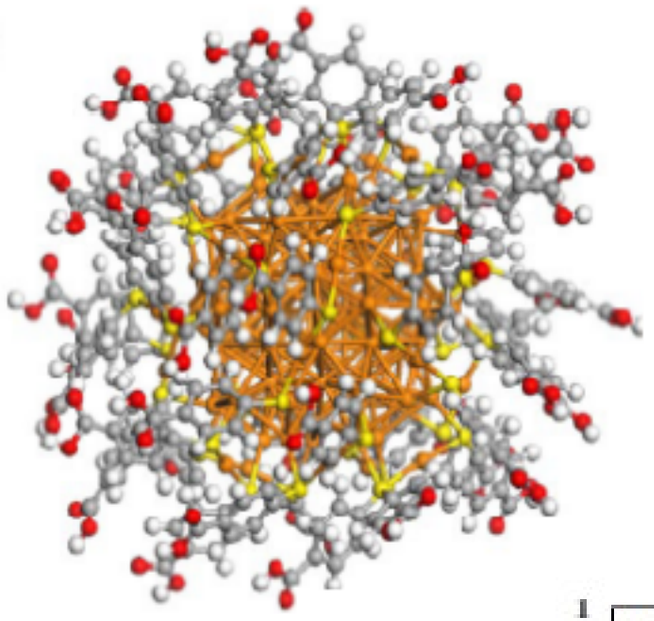


GPW Functional

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

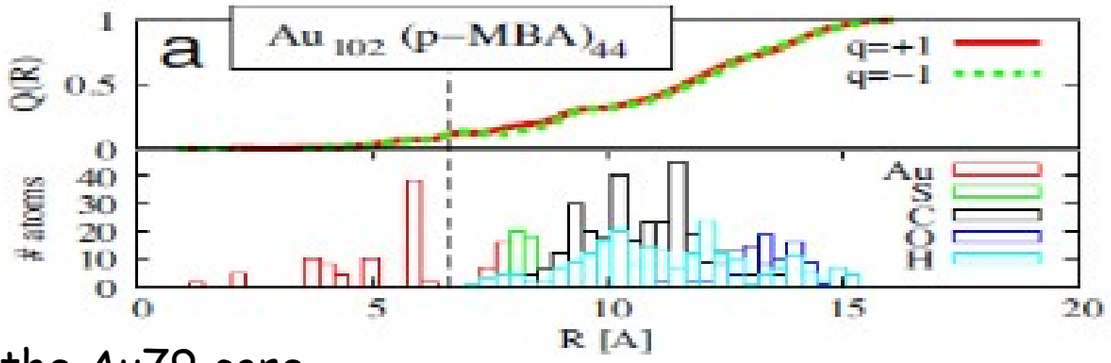
Linear scaling KS matrix construction

DFT for very large systems

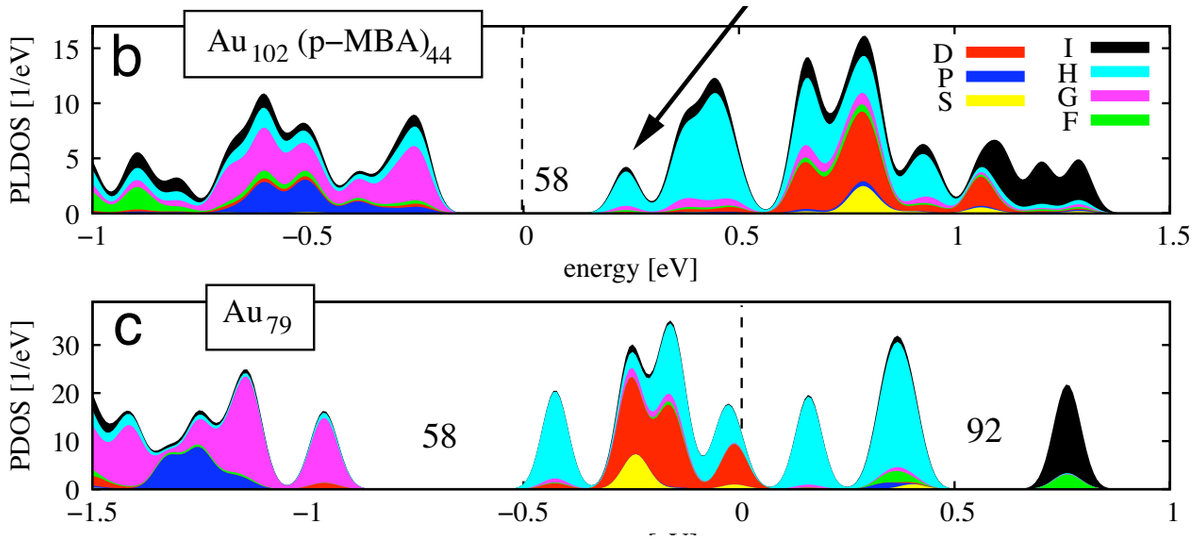


Ligand-protected Au cluster
762 atoms, ~3400 el.
as superatom complex

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

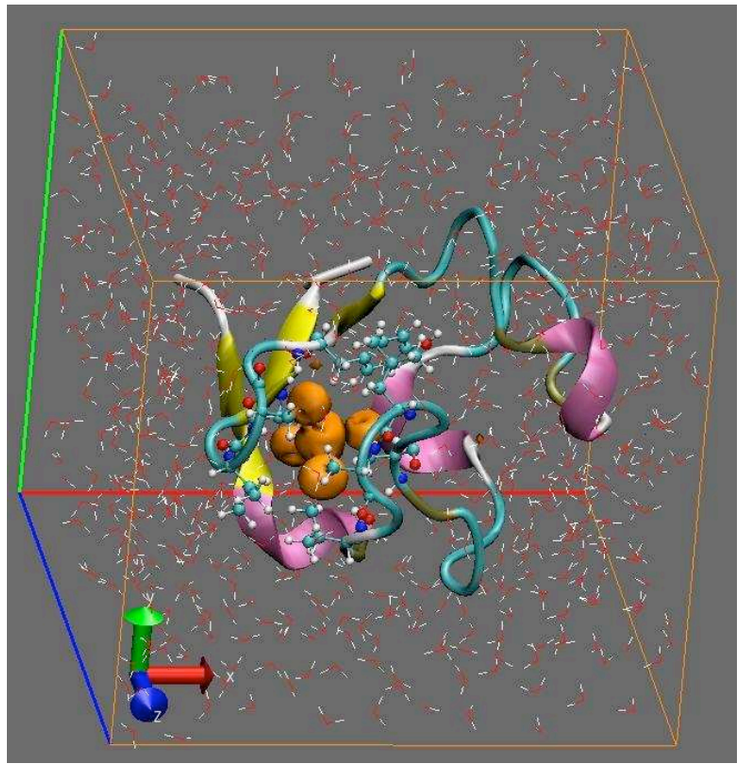


Metallicity of the Au79 core



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

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



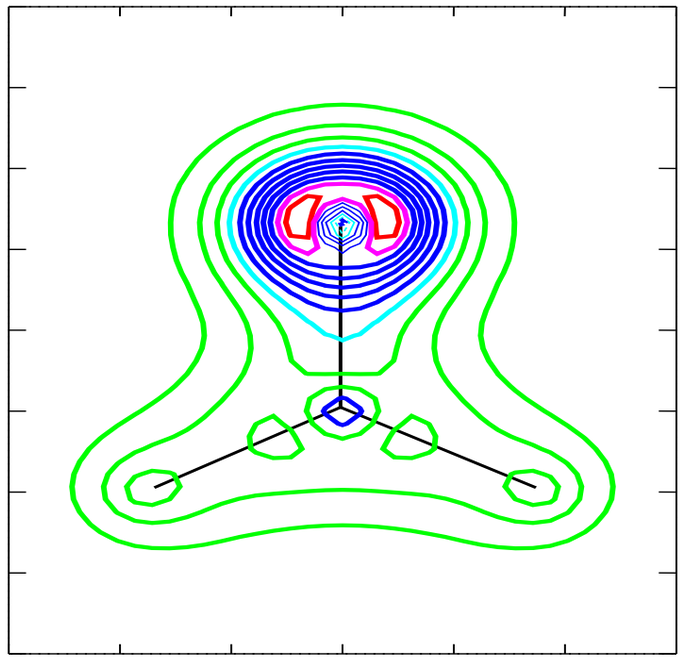
Solvated metallo-protein

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

http://www.cp2k.org/science

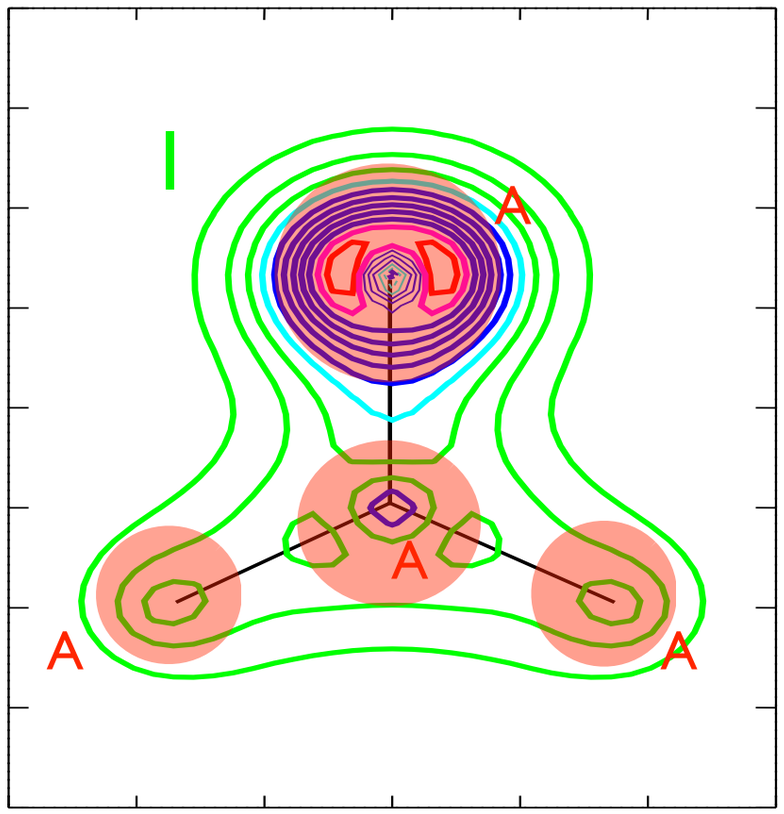
Hard and Soft Densities

Formaldehyde



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

Partitioning of the Density



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

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

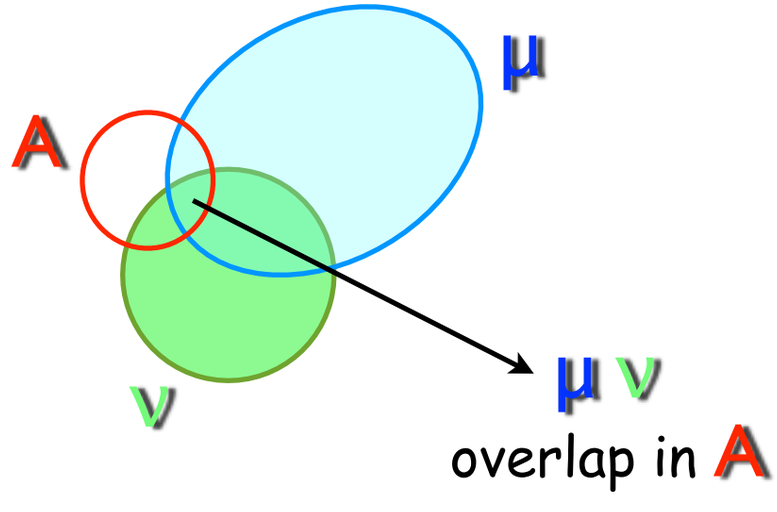
$$\left.\begin{array}{rcl} n(\mathbf{r}) & - & n_A(\mathbf{r}) = 0 \\ \tilde{n}(\mathbf{r}) & - & \tilde{n}_A(\mathbf{r}) = 0 \end{array}\right\} \mathbf{r} \in A$$

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

Gaussian Augmented Plane Waves

Local Densities

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



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

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

projector basis (same size)

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

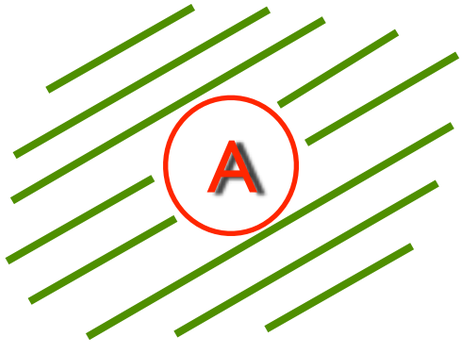
$$n_A(\mathbf{r}) = \sum_{\alpha\beta} \left[\sum_{\mu\nu} P_{\mu\nu} d'^A_{\mu\alpha} d'^A_{\nu\beta} \right] g_\alpha(\mathbf{r}) g_\beta(\mathbf{r}) = \sum_{\alpha\beta} P'^A_{\alpha\beta} \; g_\alpha(\mathbf{r}) g_\beta(\mathbf{r})$$

Density Dependent Terms: XC

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

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

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

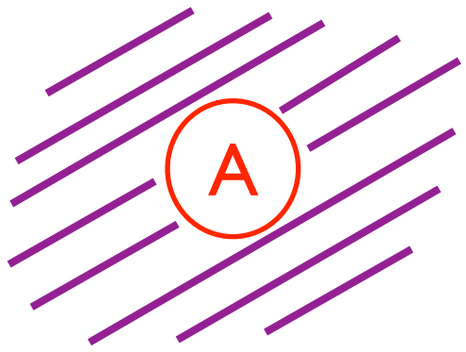


$$\times \left\{ \tilde{n}(\mathbf{r}) + \sum_A n_A(\mathbf{r}) - \sum_A \tilde{n}_A(\mathbf{r}) \right\} d\mathbf{r}$$

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

Density Dependent Terms: ES

Non local Coulomb operator



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

Compensation charge

Same multipole expansion as the local densities

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

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

Interstitial region

Atomic region

GAPW Functionals

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

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

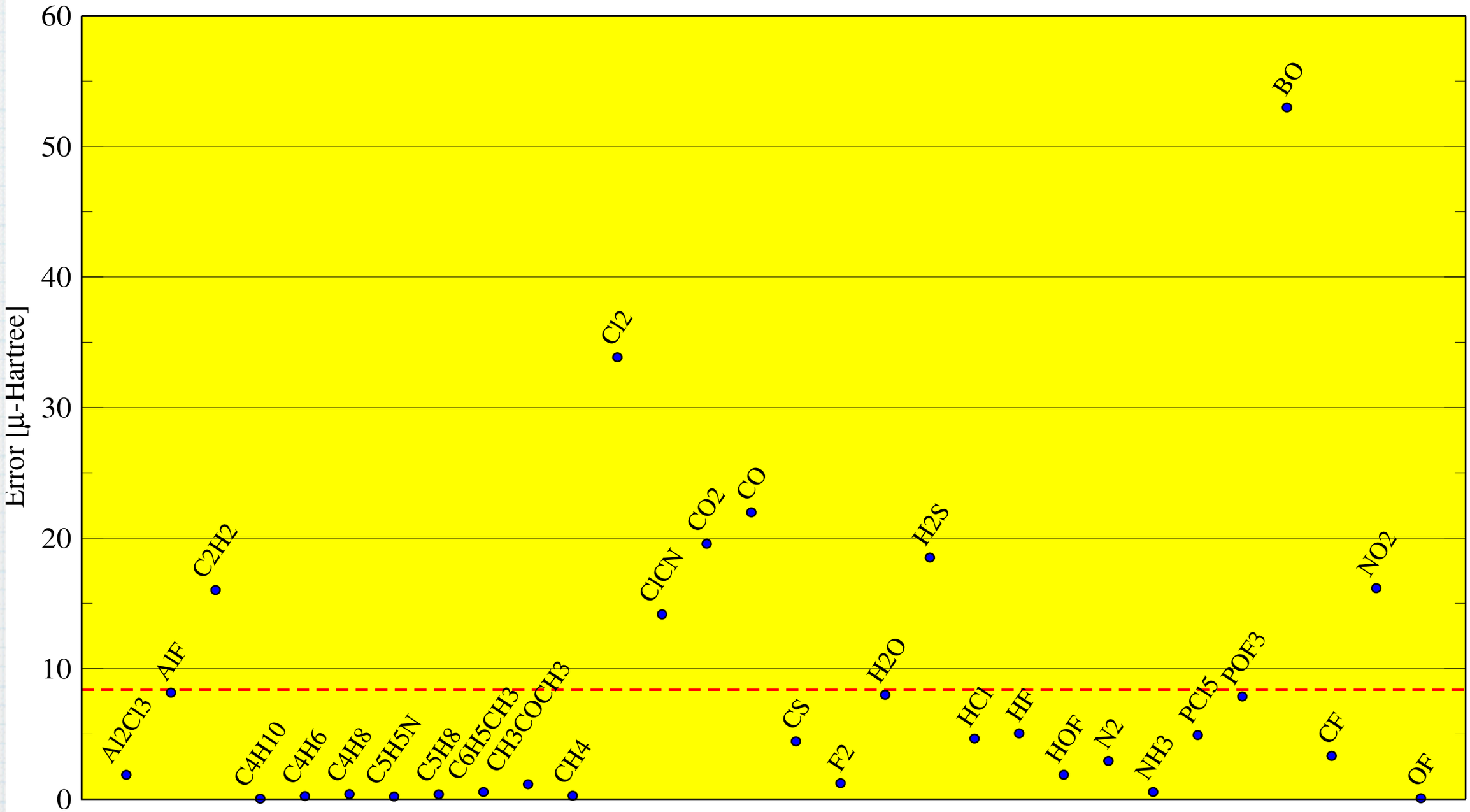
on global grids
via collocation + FFT

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

Analytic integrals
Local Spherical Grids

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

All-electron Calculations:CP2K vs GO3



Energy Functional Minimization

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

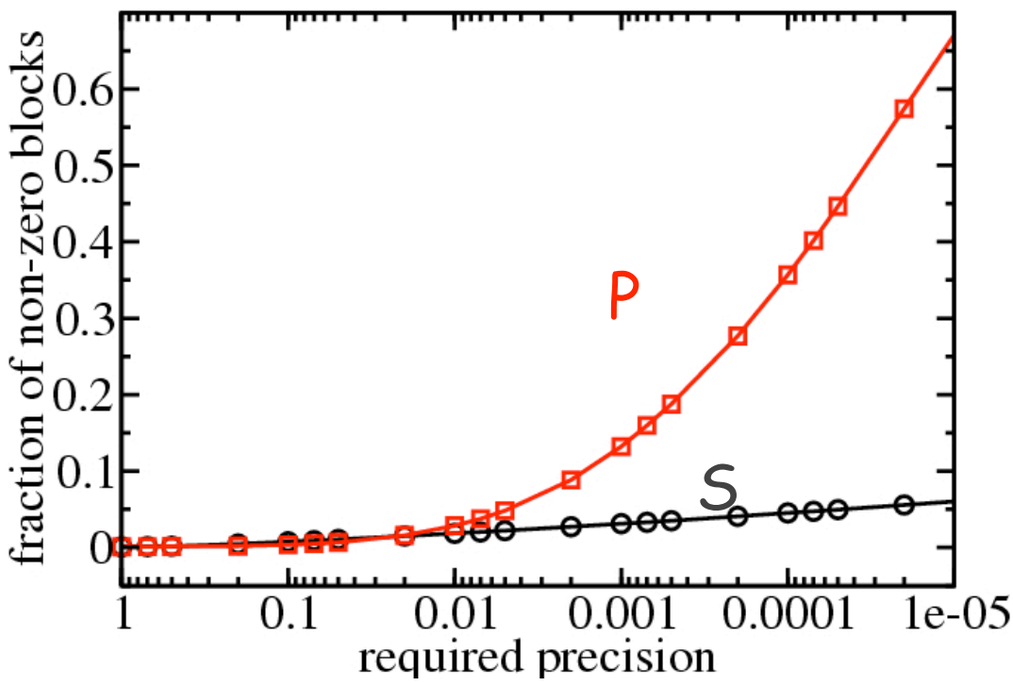
- Standard: Diagonalisation + mixing (DIIS, Pulay, J. Comput. Chem. 3, 556,(1982); iterative diag. Kresse G. et al, PRB, 54(16), 11169, (1996))

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))

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

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



Traditional Diagonalization

Eigensolver from standard parallel program library: SCALAPACK

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

Transformation into a standard eigenvalues problem

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

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

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

DIIS for SCF convergence acceleration: few iterations

error matrix

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

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

Orbital Transformation Method

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

not linear orthonormality constraint

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

Linear constraint

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

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

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

matrix functionals by Taylor expansions in X^TSX

minimisation in the auxiliary tangen

idempotency verified

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

CG(LS) or DIIS

Preconditioned gradients

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

$$\mathbf{X}$$

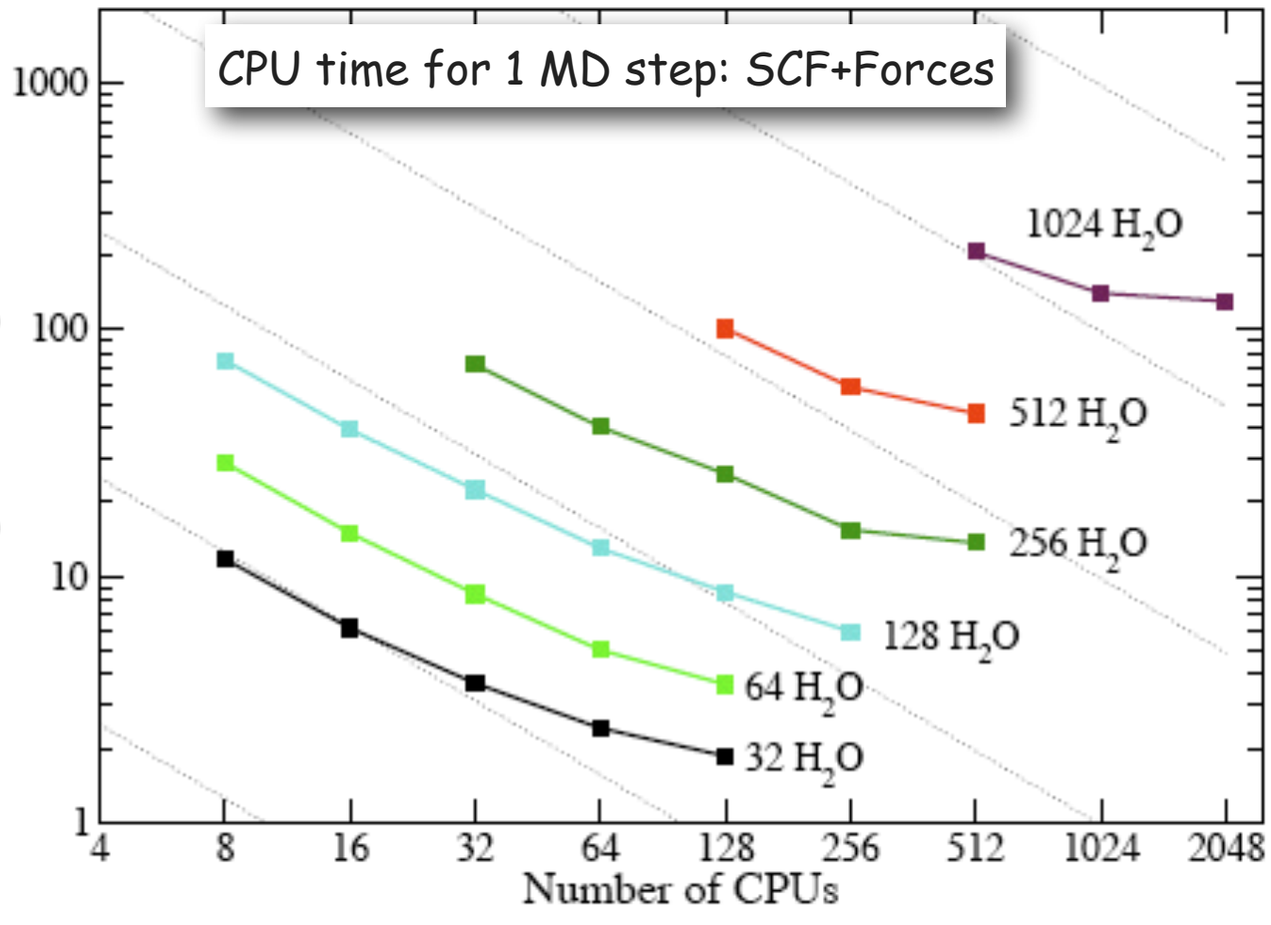
- Guaranteed convergence
- Various choices of preconditioners
- Limited number of SCF iterations
- KS diagonalisation avoided
- Sparsity of S and H can be exploited
- Scaling $O(N^2M)$ in cpu and $O(NM)$ in memory
- Optimal for large system, high quality basis set

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

OT performance

64 H_2O
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



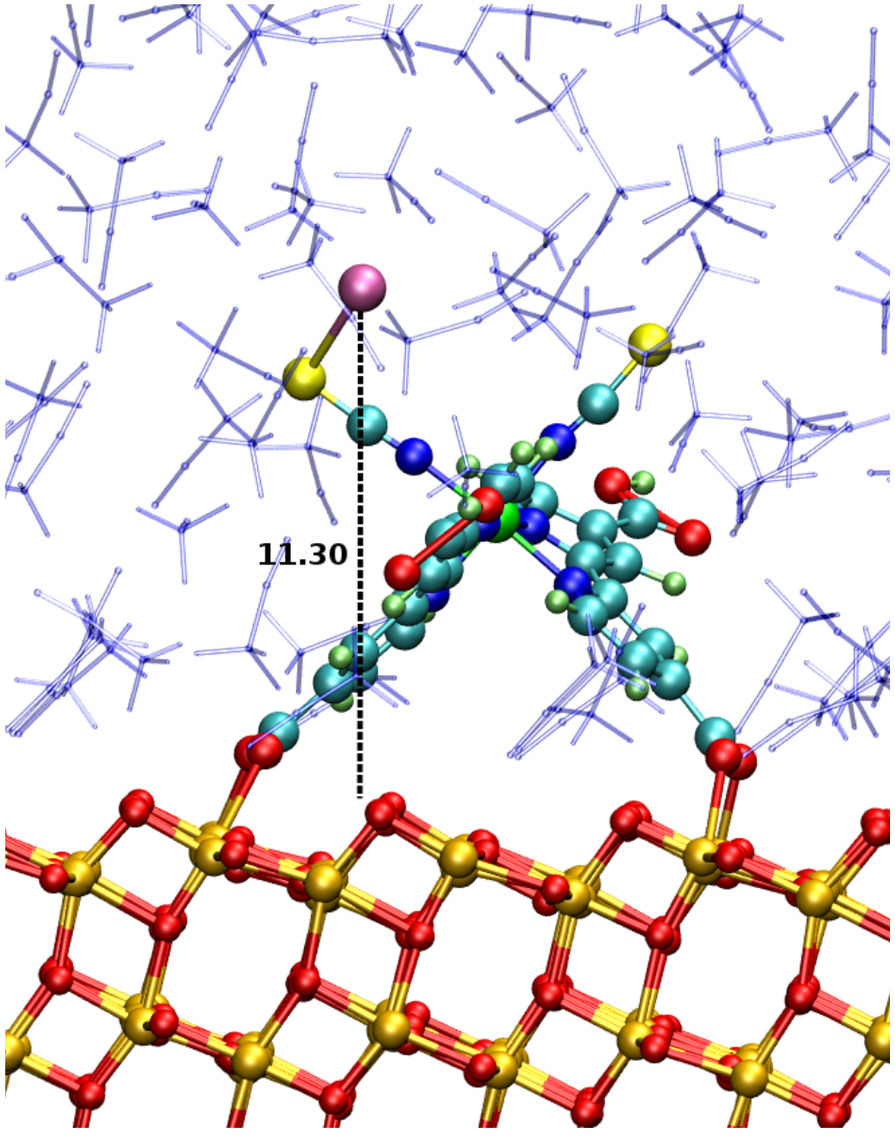
TZV2P (40 functions per H_2O),
280 Ry PW cutoff
eps(scf) = 10^{-6}, CRAY XT5

System	M	N
32 H_2O	1280	128
64 H_2O	2560	256
128 H_2O	5120	512
256 H_2O	10240	1024
512 H_2O	20480	2048
1024 H_2O	40960	4096

Structure optimisation 50÷100 iterations = ~1 hour for 512 H_2O
MD simulation (10 ps) 10000 iterations = ~1ps per day for 512 H_2O

Dye Sensitized Solar Cell

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 SCF

- Based on sparse matrix matrix multiplications

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

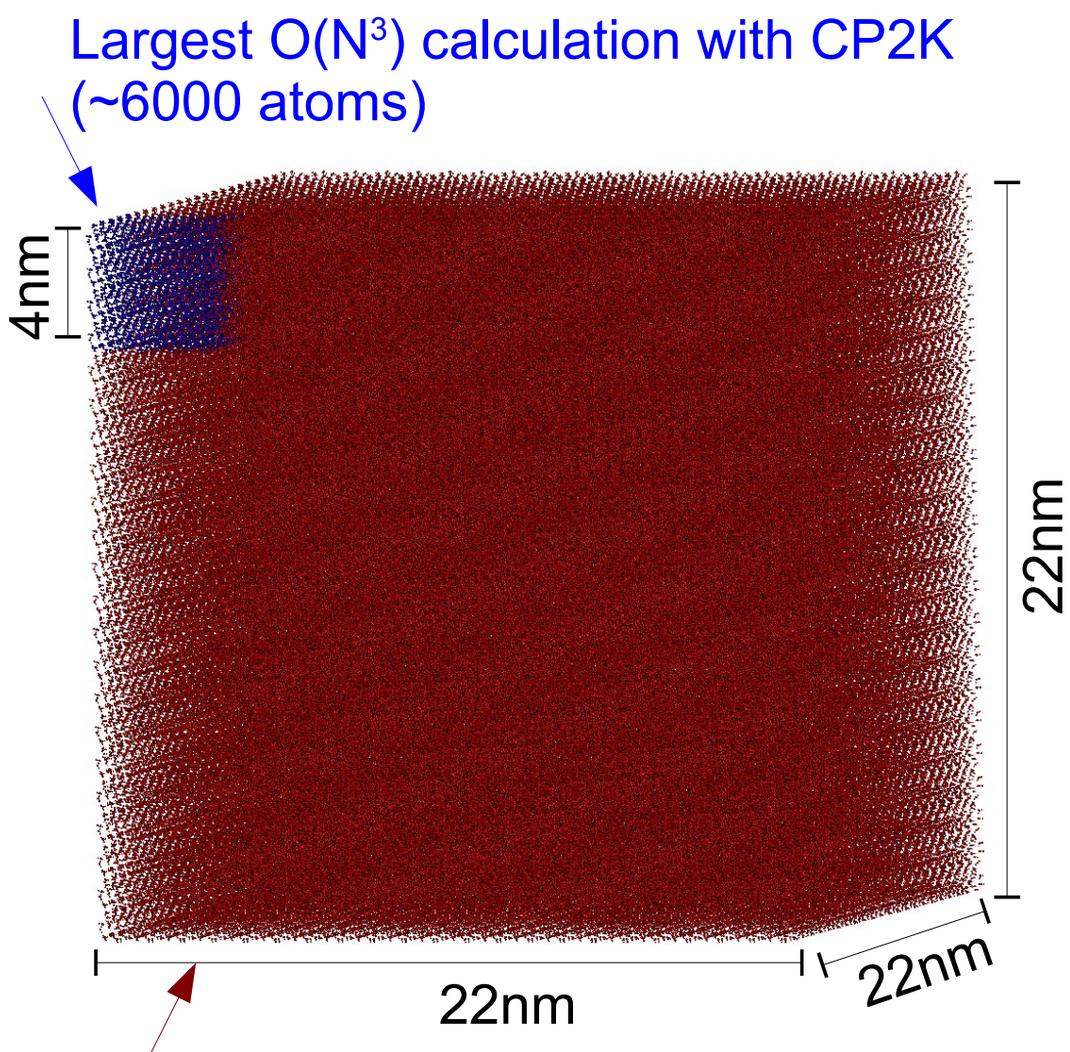
- Self consistent solution by mixing

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

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

- Chemical potential by bisecting until

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

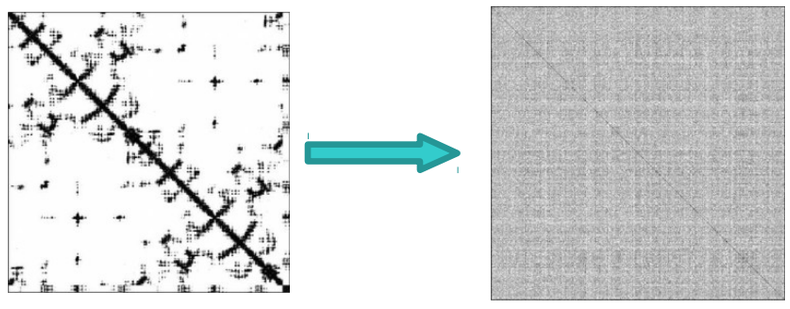


VandeVondele, Borstnik, Hutter; JCTC 10, 3566 (2012)

Sparse Matrix Library

DBCSR: Distributed Blocked Compressed Sparse Row

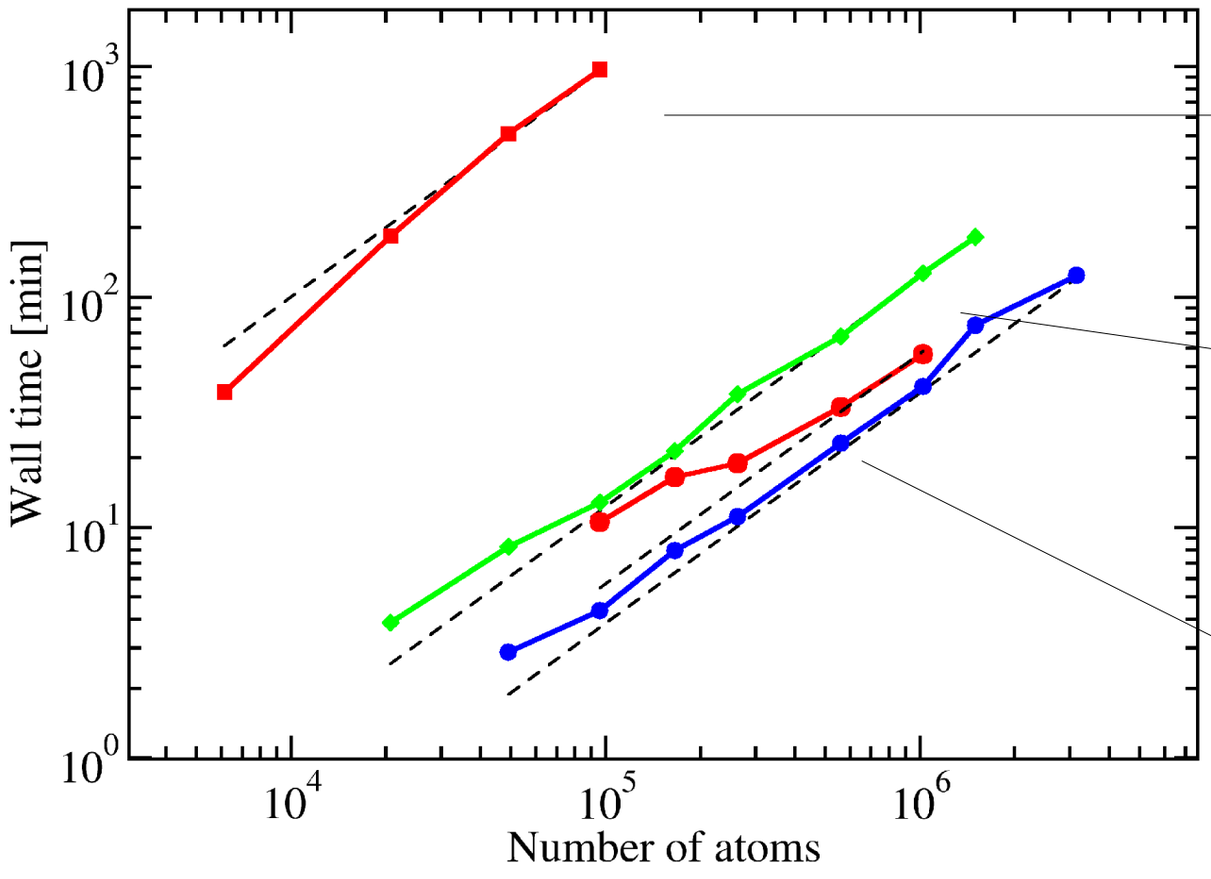
- For massively parallel architectures
- Optimised for 10000s of non-zeros per row (dense limit)
- Stored in block form : atoms or molecules
- Cannons algorithm: 2D layout (rows/columns) and 2D distribution of data
- Homogenised for load balance



given processor communicates only with nearest neighbours
transferred data decreases as number of processors increases

Borstnik, et al; submitted

Millions of atoms



Accurate basis sets, DFT
46656 cores

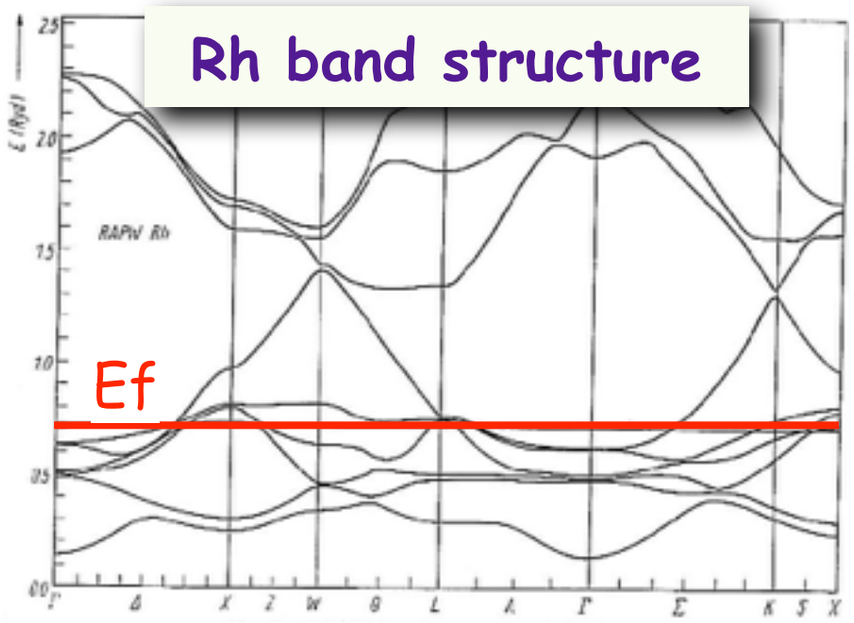
The electronic structure
O(10^6) atoms in < 2 hours

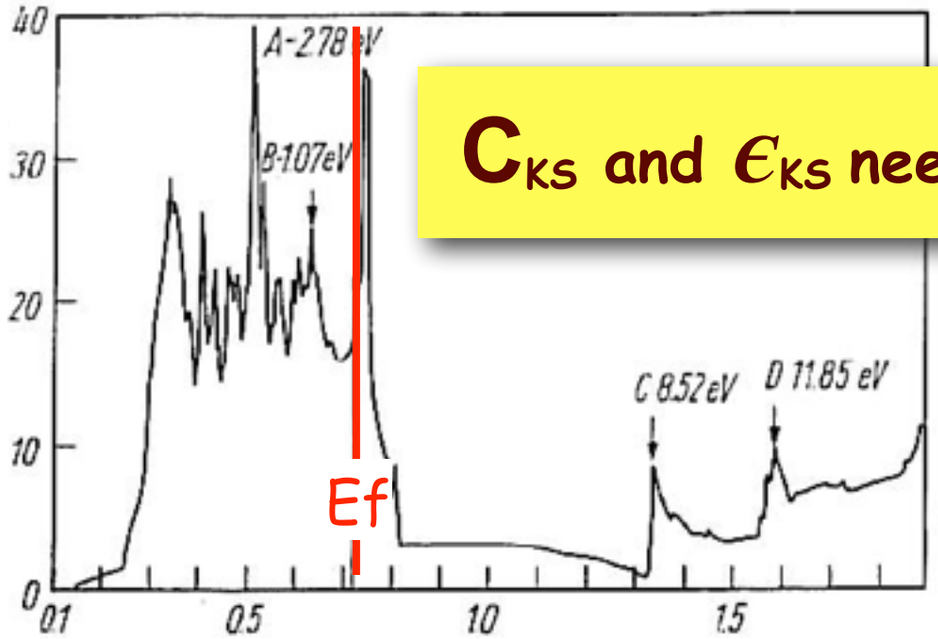
Minimal basis sets:
DFT, NDDO, DFTB
9216 cores

Bulk liquid water. Dashed lines represent ideal linear scaling.

Metallic Electronic Structure

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





charge sloshing and exceedingly slow convergence

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

Smearing & Mixing in G-space

Mermin functional: minimise the free energy

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

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

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

Fermi-Dirac

Trial density mixed with previous densities: damping oscillations

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

residual

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

minimise the residual

G preconditioning matrix damping low G

Iterative Improvement of the the n(r)

Input density matrix

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

Update of KS Hamiltonian

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

Calculation of Fermi energy and occupations $E_f \ f_n$

New density matrix

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

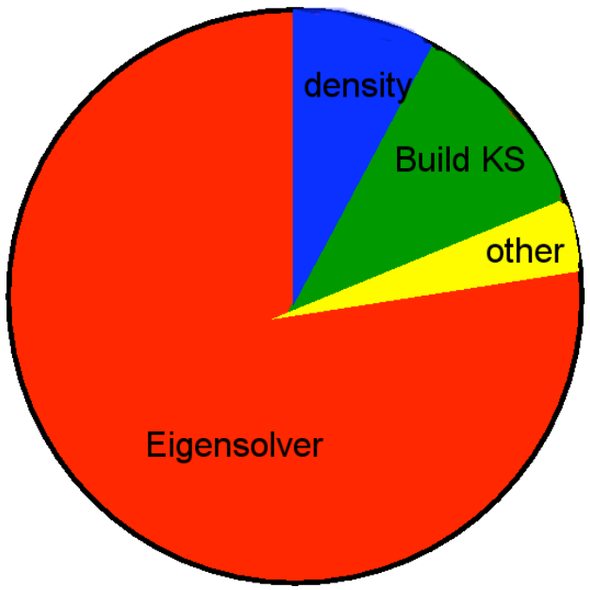
Check convergence

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

Density mixing

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

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

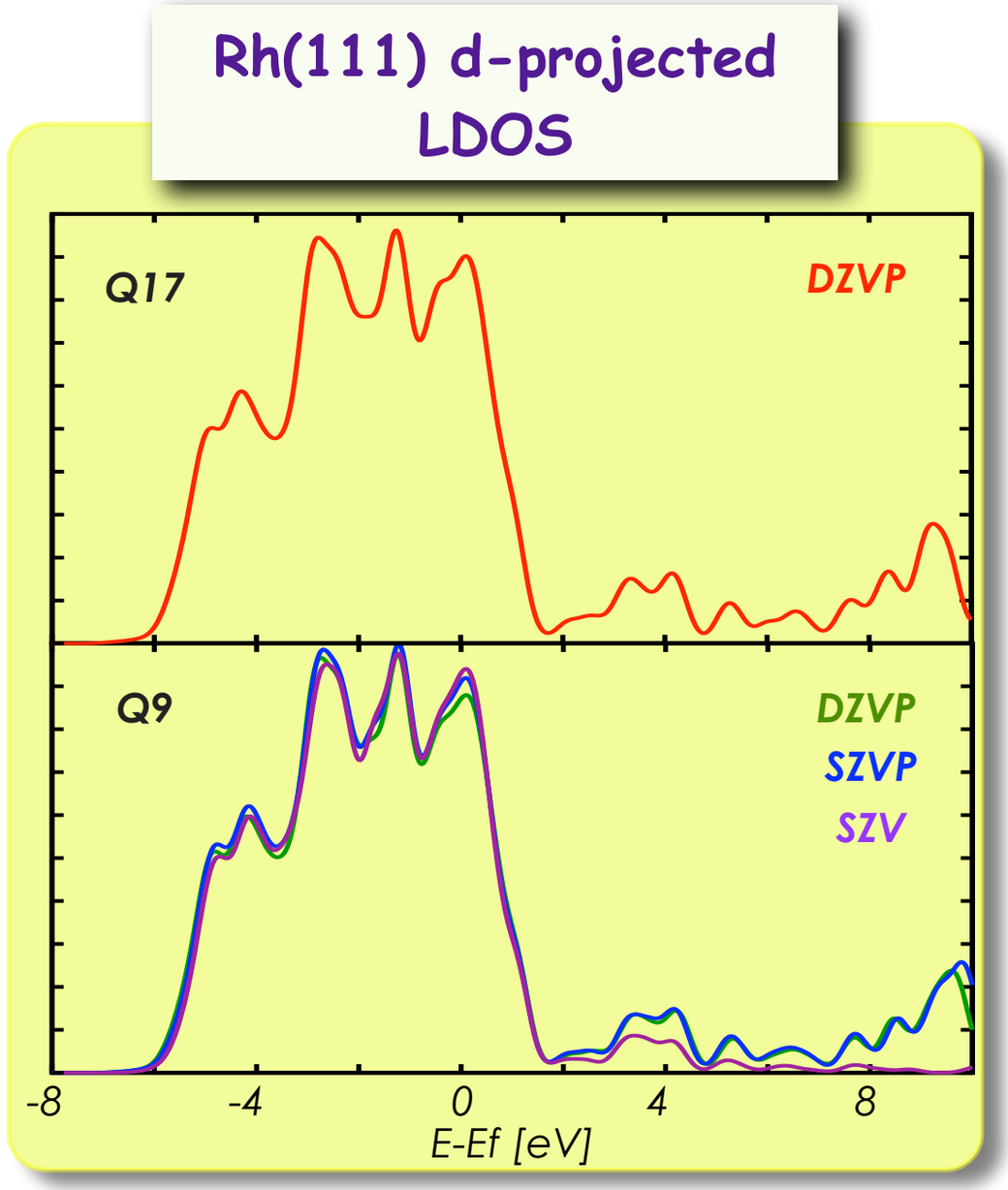


Rhodium: Bulk ans Surface

Bulk: 4x4x4

Surface: 6x6 7 layers

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

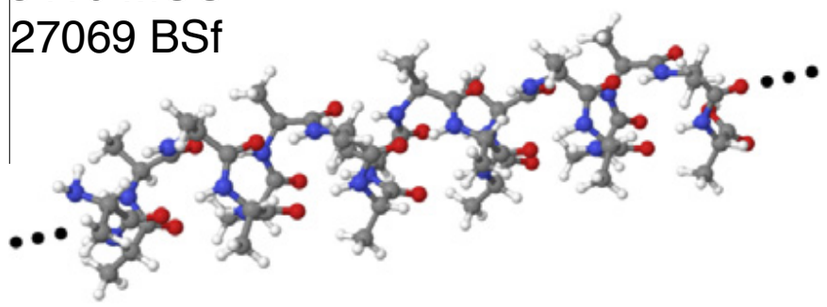


ScaLAPACK for diagonlization

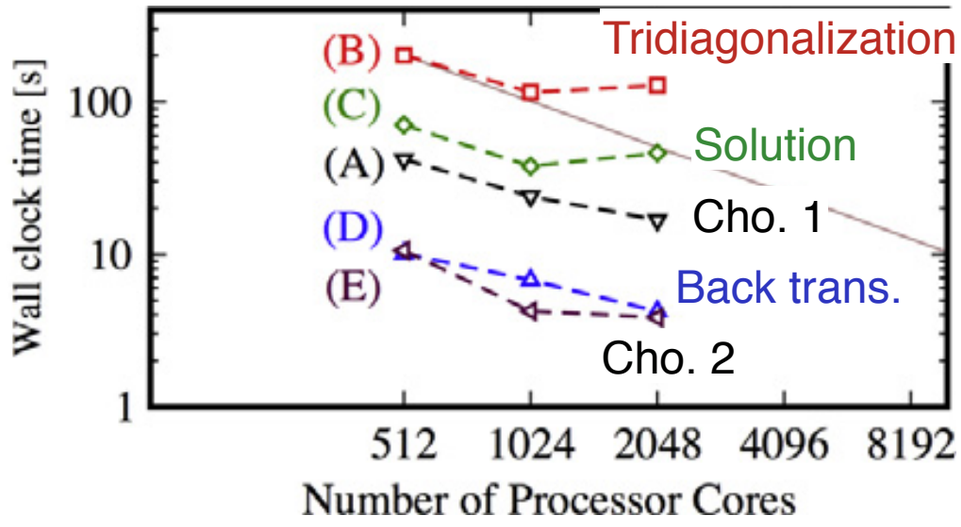
$$A \xrightarrow[\text{reduction to tridiagonal form}]{} T \xrightarrow[\text{compute eigenvalues and –vectors of T}]{} (\lambda, q_T) \xrightarrow[\text{transform eigenvectors}]{} q_A$$

1003 atoms
3410 MOS
27069 BSf

Polyalanine peptide



pdsyevd (ESSL) on IBM BGP



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

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

Syevd: D&C

Syevr: MRRR

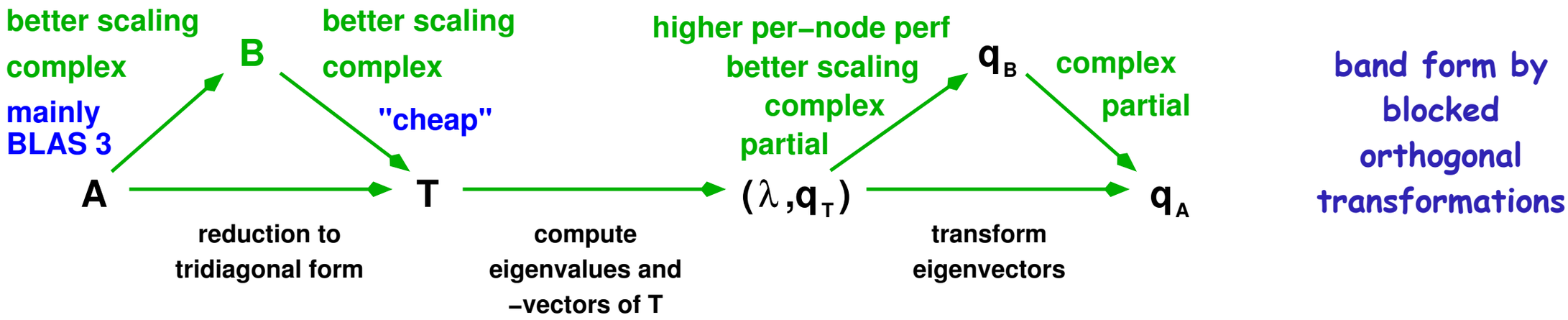
time x SCF, on CRAY XE6

>70% in eigenvalue solver

poor scaling

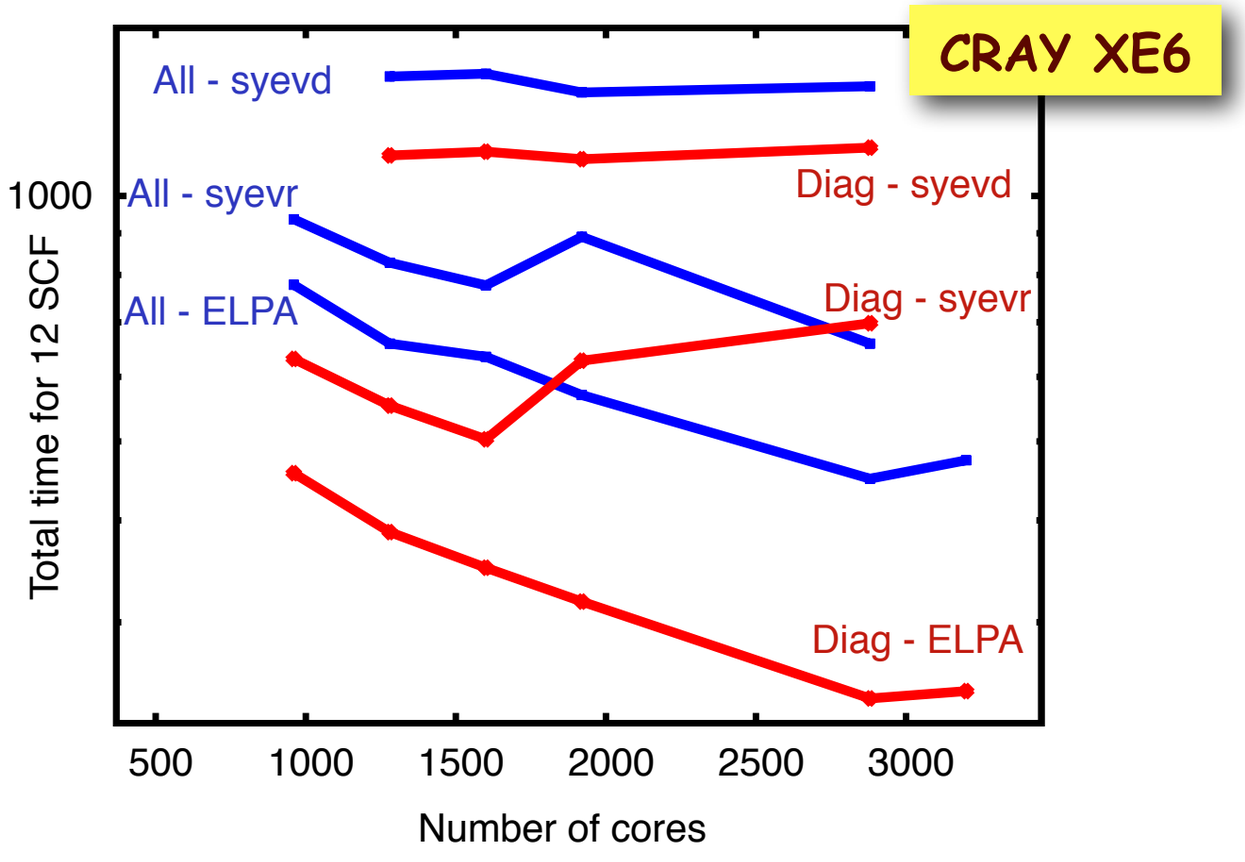
ELPA (http://elpa.rzg.mpg.de)

Improved efficiency by a two-step transformation and back transformation

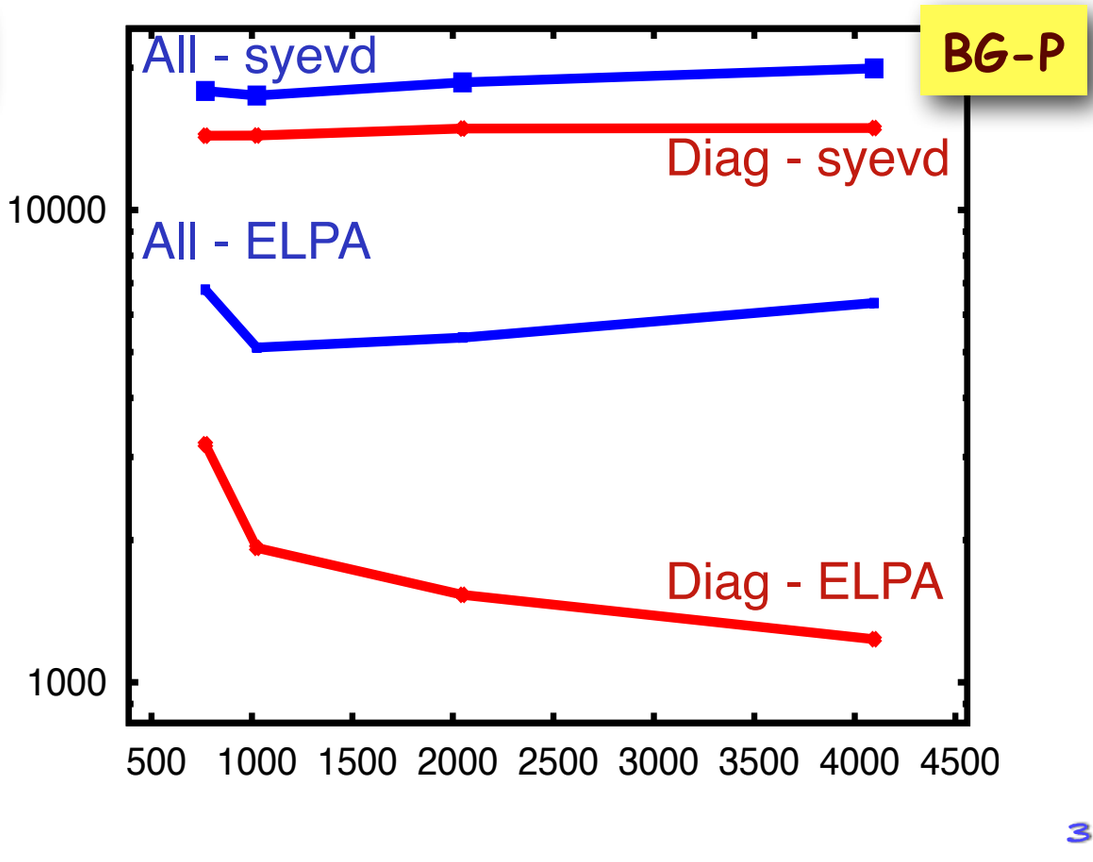


band form by blocked orthogonal transformations

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

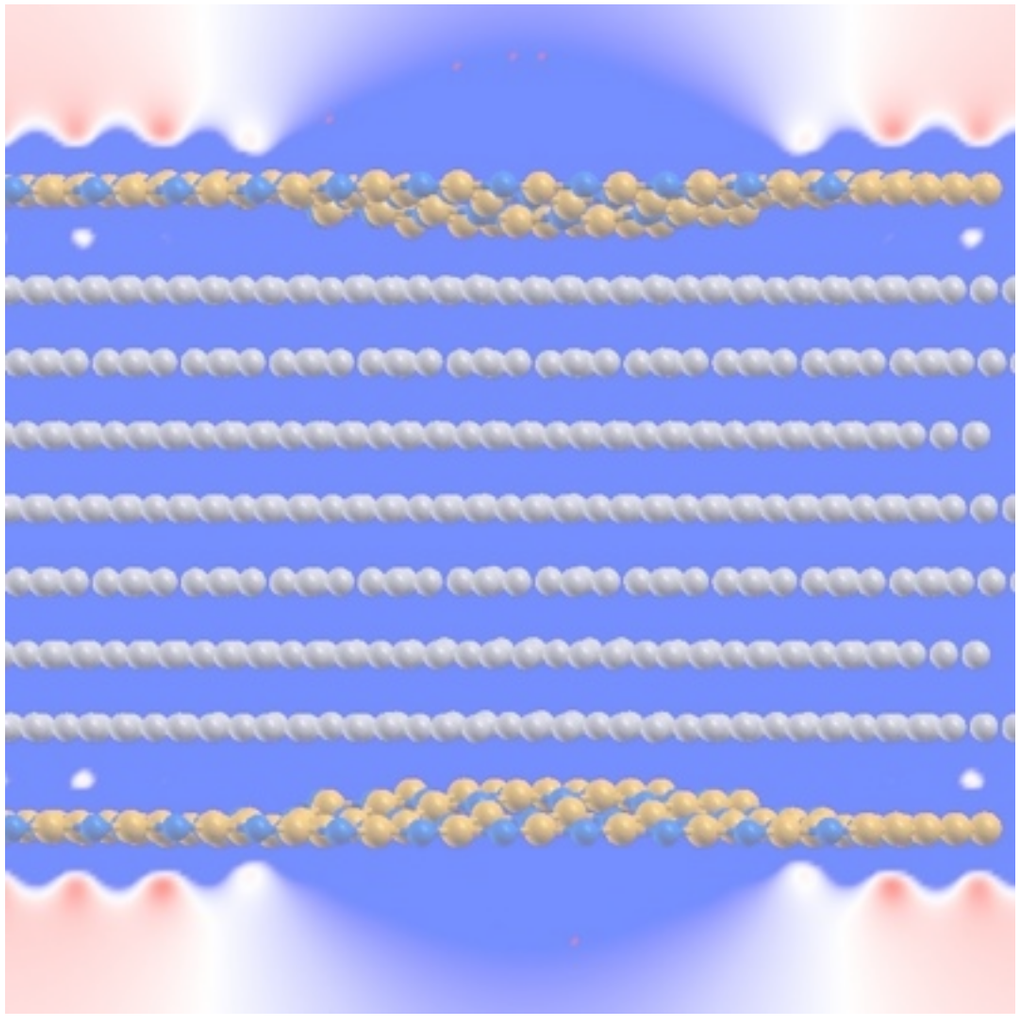


N atom= 480; Nel = 6000;
nmo = 7400; nao = 14240



Large metallic systems

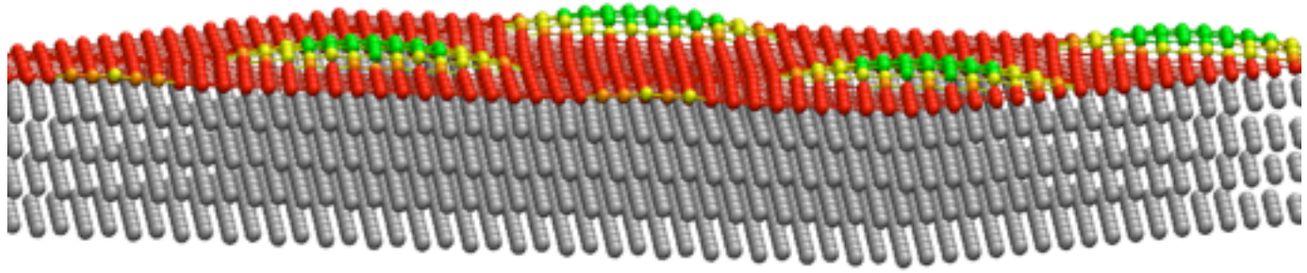
hBN/Rh(111) Nanomesh
13x13 hBN on 12x12 Rh slab



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

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

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



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

~ 25 days per structure optimisation, on 1024 cpus

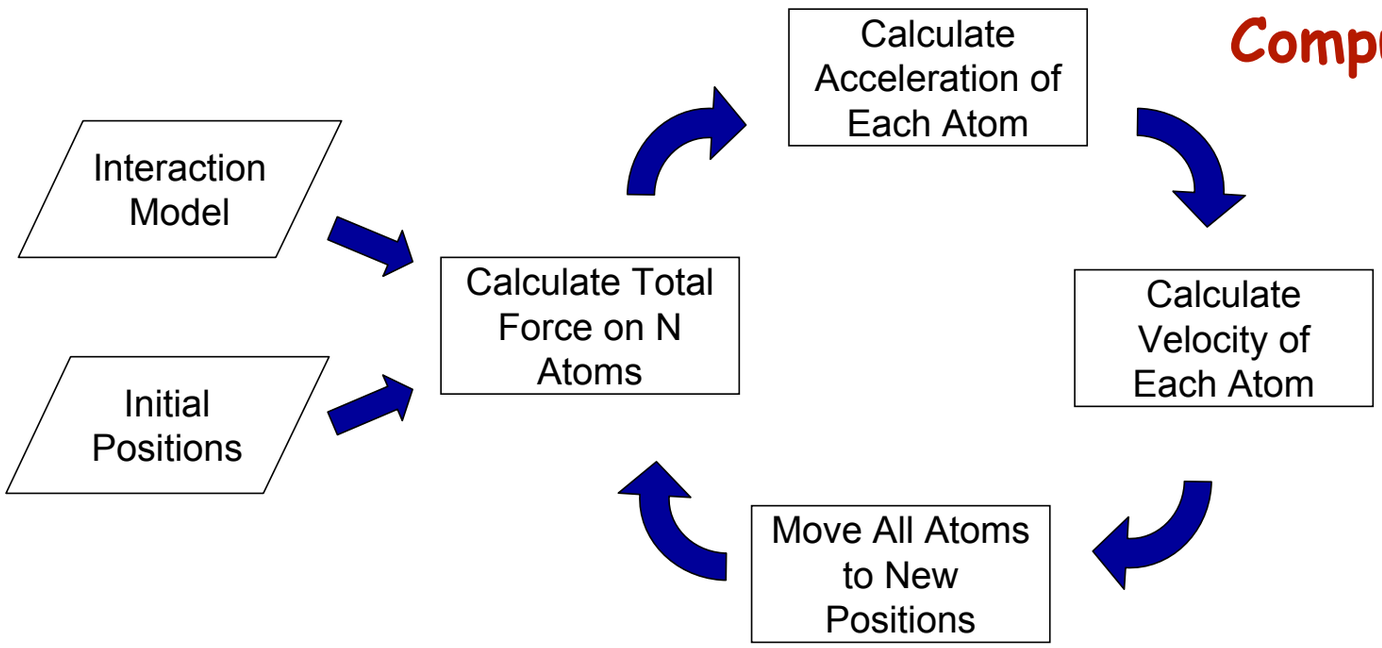
Molecular Dynamics

Given the initial conditions ({RI};{PI}), an interacting potential (H), and the thermodynamic conditions (T,V,P)

generate deterministic trajectories that sample the phase space according to statistical mechanics

M.P. Allen and D.J. Tildesley, Computer Simulations of Liquids, Claredon Press, Oxford, 1987
D. Frenkel and B. Smit, Understanding Molecular Simulations, Computer Sciences Series, Academic Press, 2002

Computational Experiment



Equations of Motion (EOM)

Set of classical particles in a potential

With a model potential depending only on the particles' coordinates
and no external sources of forces are introduced

Hamilton EOM

$$\dot{\mathbf{P}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I}$$

$$\dot{\mathbf{R}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{P}_I}$$

$$\dot{\mathbf{P}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\frac{\partial U(\{\mathbf{R}_I\})}{\partial \mathbf{R_I}} = F_I(\{\mathbf{R}_I\})$$

Conservation of energy: $\frac{dE}{dt} = \frac{d\mathcal{H}}{dt} = 0$

Lagrange EOM

$$\mathcal{L}(\{\mathbf{R}_I\}, \{\dot{\mathbf{R}}_I\}) = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - U(\{\mathbf{R}_I\})$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I}$$

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I(\{\mathbf{R}_I\})$$

Newton's second law

Numerical Integration

The system is propagated in the phase space

Discretisation of time $t_0 = 0 \ ; t_1 = \Delta t \ ; \ldots \ ; t_N = N \cdot \Delta t \ ; \ldots$

The fast time scales of the system determine the choice of time step.
A good integrator algorithm:

- Accurate for long time steps: higher order derivatives, more memory storage required
- Minimum number of force calculations
- Long time energy conservation and stability in spite of small perturbations
- Approximation of the true trajectory: Lyapunov instability
- Short time reversibility: invariant for $t \longrightarrow -t$

Velocity Verlet

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \mathbf{V}(t)\Delta t + \frac{\mathbf{F}(t)}{2M}\Delta t^2$$

$$\mathbf{V}(t+\Delta t) = \mathbf{V}(t) + \frac{\mathbf{F}(t+\Delta t) + \mathbf{F}(t)}{2M}\Delta t$$

- Simple: needs only forces
- Positions and velocities available at equal time
- Contains error of order Δt^4
- Time reversible
- Conserves volume in phase space: symplectic
- Long time stability
- Implemented in 3 steps: half kick/drift/half kick

Implementation of Velocity-Verlet

Half Kick -- Drift -- Half Kick

Given **R(:),V(:),F(:)** at time-step itime

Update **V(:)** by half time-step

V(:) := V(:) + dt/(2*M)*F(:)

Then update **R(:)** by the entire time-step

R(:) := R(:) + dt*V(:)

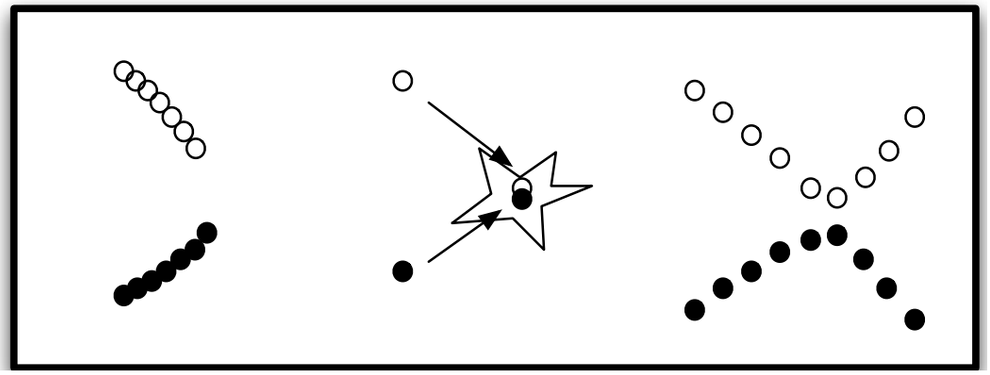
Compute the new **F(:)** by using the updated **R(:)**

Finalize the update of **V(:)** by the second half time-step

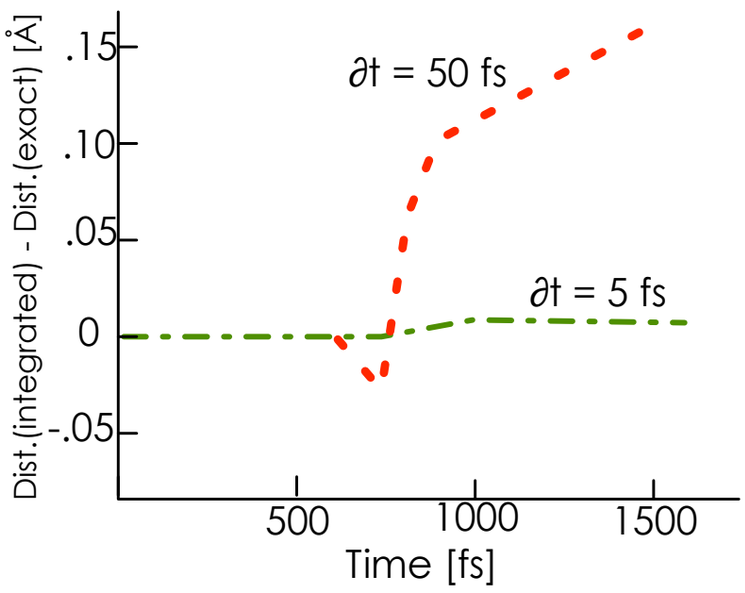
V(:) := V(:) + dt/(2*M)*F(:)

Choice of the Time Step

Compromise between **efficiency** and **reliability**



Pairwise potential
∂t = 0.5fs, 50fs, 5fs



Difference between exact and numerical trajectory

Time-step at least 10 times smaller than the fastest period of motion

Microcanonical Ensemble

$$\frac{d\mathcal{H}}{dt} = \sum_I \left[\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} \dot{\mathbf{R}}_I + \frac{\partial \mathcal{H}}{\partial \mathbf{P}_I} \dot{\mathbf{P}}_I \right] = 0$$

$$\dot{\mathbf{R}}_I = \frac{\partial \mathcal{H}}{\partial \mathbf{P}_I} \qquad \dot{\mathbf{P}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I}$$

N, V, and the internal energy E are the constants of motion

By integrating the EOM, a trajectory in the NVE ensemble is generated: micro-states probability distribution

$$Q_{NVE} = \sum_{\Gamma} \delta((\Gamma) - E)$$

Any physical quantity that can be described in terms of the available degrees of freedom is an observable

$$F_{\text{obs}} = \langle F \rangle_{\text{ens}} = \frac{1}{\tau_{\text{obs}}} \sum_t F(\Gamma(t))$$

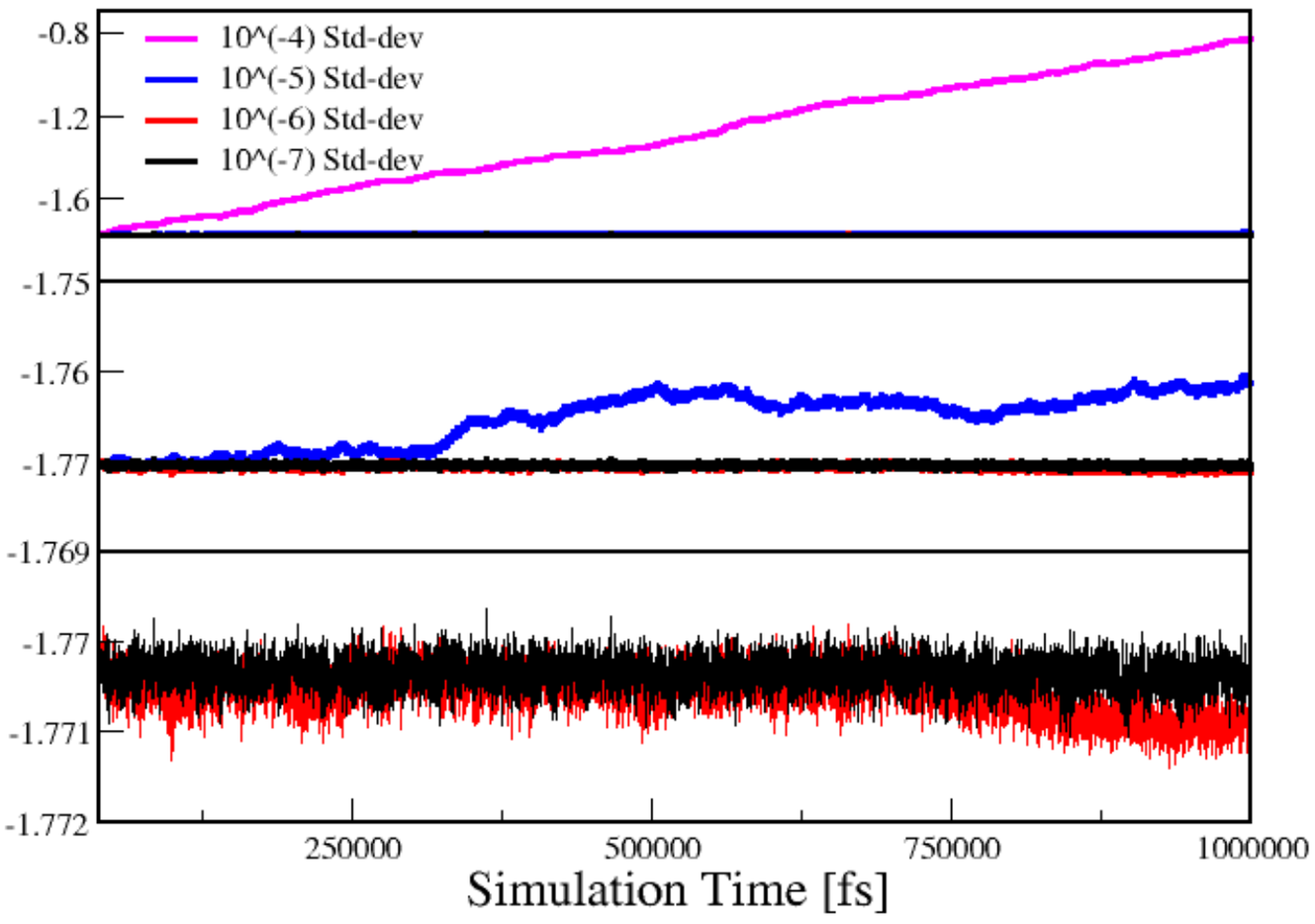
$$\mathcal{T}(\{\mathbf{P}_I\}) = \frac{1}{3Nk_B} \sum_I M_I v_I^2$$

$$T_{NVE} = \frac{1}{K} \sum_{k=1}^{K} \mathcal{T}(t_k)$$

- The instantaneous temperature fluctuates.
- Time-averages correspond to NVE ensemble averages
- Irrespective of the initial state, all accessible micro-states should be visited (ergodicity)

Test on Required Accuracy of Forces

Classical FF, 64 H2O at 330 K: TIP3P(flexible), SPME



Stability depends on accuracy of forces

Stdev. Δf Hartree/Bohr	Stdev. Energy μHartree	Drift μHartree/ns	Kelvin/ns
–	170.35	35.9	0.06
10^{-10}	179.55	-85.7	-0.14
10^{-08}	173.68	6.5	0.01
10^{-07}	177.83	-58.2	-0.10
10^{-06}	—	-385.4	-0.63
10^{-05}	—	9255.8	15.21
10^{-04}	—	972810.0	1599.31

Extended System

To extend the applicability of MD to other ensembles, the Lagrangian equations of motion need to be reformulated: the system moves in a different phase space

impose control of specific thermodynamic variables

Canonical Ensemble

Generate the correct Boltzmann distribution by coupling with a heat bath

$$\mathcal{P}_i = \frac{\exp(-E_i/k_BT)}{\sum_j \exp(-E_j/k_BT)}$$

- Andersen Thermostat: Stochastic approach
  uncorrelated stochastic collisions of randomly selected particles with the heat bath
  MC moves from one constant energy shell to another

- Nose Thermostat: Extended Lagrangian approach
  deterministic evolution derived from a properly modified Lagrangian, i.e. new EoM
  the extended system generates microcanonical ensemble in modified phase space

$$\mathcal{L}_{Nose} = \sum_I \frac{M_I}{2} s^2 \dot{\mathbf{R}}_I^2 - \mathcal{U}(\{\mathbf{R}_I\}) + \frac{Q}{2}\dot{s}^2 - g k_B T \ln s$$

Dynamical Friction

Nose-Hoover EoM

The additional variable s can be interpreted as scaling factor of time.
The Lagrangian generates a dissipative dynamics, leading to a non-Hamiltonian flow. The fluctuations of the friction term generate a canonical distribution

Equations of motion

$$\ddot{\mathbf{R}}_I = \frac{\mathbf{F}_I}{M_I} - \dot{s}\dot{\mathbf{R}}_I \qquad \ddot{s} = \frac{1}{Q}\left[\sum_I M_I \dot{\mathbf{R}}_I^2 - g k_B T\right]$$

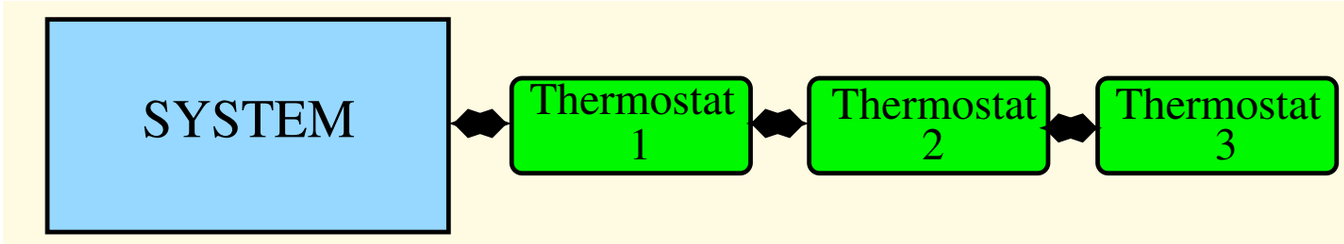
$\mathcal{T} < T$ smaller friction

$\mathcal{T} > T$ larger friction

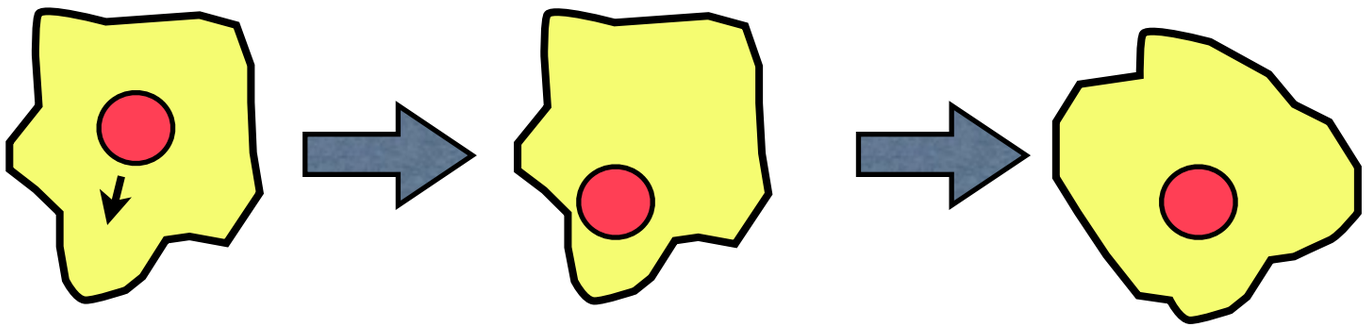
Constant of motion

$$\mathcal{H}_{\text{Nose}} = E^{NVT} = \sum_I \frac{M_I s^2 \dot{\mathbf{R}}_I^2}{2} + \mathcal{U}(\{\mathbf{R}_I\}) + \frac{Q}{2}\dot{s}^2 + g k_B T \ln s$$

Ergodicity problems can be solved by implementing a chain of thermostats



Integrators for Ab-initio MD



Born-Oppenheimer MD
Adiabatic approx.
Semiclassical approx.

$$\mathcal{L}_{\mathrm{BO}}\left(\{\mathbf{R}_I\},\{\dot{\mathbf{R}}_I\}\right)=\sum_{I=1}^{N}\frac{1}{2}M_I\dot{\mathbf{R}}_I^2-\min_{\{\phi_i\}}E_{\mathrm{KS}}\left(\{\phi_i\},\{\mathbf{R}_I\}\right)$$

No electron Dynamics

Classical equations of motion $$M_I\ddot{\mathbf{R}}_I(t)=-\nabla_I\left[\min_{\{\phi_i\}}E_{\mathrm{KS}}\left(\{\phi_i\},\{\mathbf{R}_I(t)\}\right)\right]$$

Integration step determined by the time scale
of the nuclear dynamics: ~femtoseconds

$$\mathbf{F}_I=-\left[\langle\Psi_0|\nabla_I\mathcal{H}_{\mathrm{KS}}|\Psi_0\rangle+\langle\nabla_I\Psi_0|\mathcal{H}_{\mathrm{KS}}|\Psi_0\rangle+\langle\Psi_0|\mathcal{H}_{\mathrm{KS}}|\nabla_I\Psi_0\rangle\right]$$

Forces in BO-MD

For exact eigenstates and complete basis sets, the contributions from variations of the wavefunction vanish exactly

$$\mathbf{F}_I^{HFT} = -\langle \Psi_0 | \nabla_I \mathcal{H}_{\mathrm{KS}} | \Psi_0 \rangle$$

Hellman-Feynman

$$\nabla_I \phi_i = \sum_\nu \left(\nabla_I c_{i\nu}\right)\ \varphi_\nu(\mathbf{r};\{\mathbf{R}_I\}) + \sum_\nu c_{i\nu}\ \left(\nabla_I \varphi_\nu(\mathbf{r};\{\mathbf{R}_I\})\right)$$

implicit dependence of the expansion coefficients: not exact self-consistency NSC

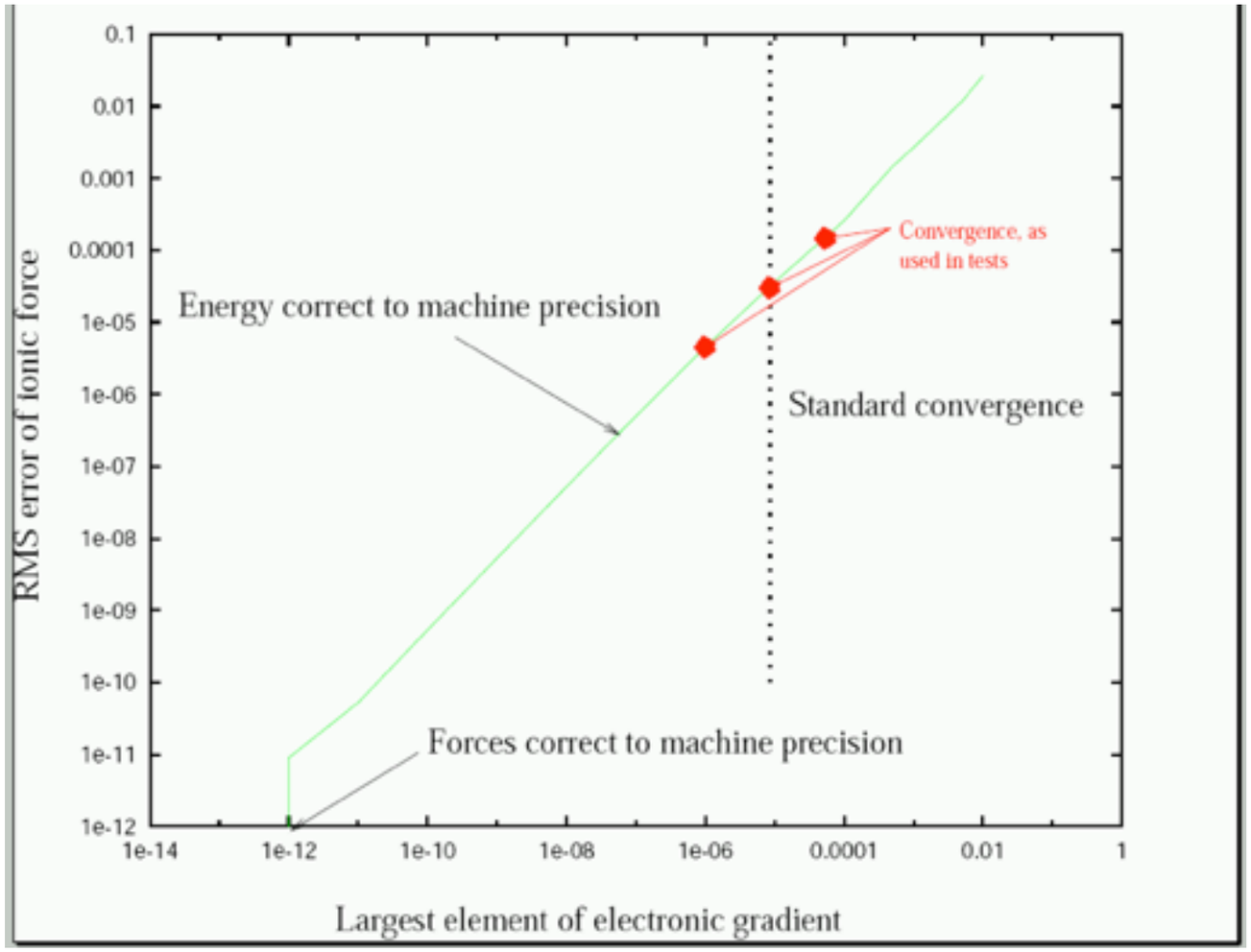
explicit dependence of the basis function IBS

$$\mathbf{F}_I^{\mathrm{NSC}} = -\int d\mathbf{r}\ (\nabla_I n)\left(V^{\mathrm{SCF}} - V^{\mathrm{NSC}}\right)$$

$$\mathbf{F}_I^{\mathrm{IBS}} = -\sum_{i\nu\mu}\left(\left\langle \nabla_I \varphi_\nu \left| H_{\mathrm{e}}^{\mathrm{NSC}} - \epsilon_i \right| \varphi_\mu \right\rangle + \left\langle \varphi_\nu \left| H_{\mathrm{e}}^{\mathrm{NSC}} - \epsilon_i \right| \nabla_I \varphi_\mu \right\rangle\right)$$

P. Bendt et al., PRL, 50, 1684 (1983)
G.P. Srivastava et al., 36, 463 (1987)

Stability in BOMD



64 H2O, 330 K, 1gr/cm^3
TZV2P, PBE, GTH, 280 Ry
0.5fs step

Reference: 1ps, SCF 10^{-10}
Unbiased initial guess

ϵ_{SCF}	MAE E_{KS} Hartree	MAE f Hartree/Bohr	Drift Kelvin/ns
10^{-08}	$1.2 \cdot 10^{-11}$	$5.1 \cdot 10^{-09}$	0.0
10^{-07}	$9.5 \cdot 10^{-10}$	$5.6 \cdot 10^{-08}$	0.1
10^{-06}	$6.9 \cdot 10^{-08}$	$4.8 \cdot 10^{-07}$	0.4
10^{-05}	$7.4 \cdot 10^{-06}$	$5.6 \cdot 10^{-06}$	2.3
10^{-04}	$3.3 \cdot 10^{-04}$	$5.9 \cdot 10^{-05}$	≈ 50

Error in Forces $\Longleftrightarrow$ MD Stability

Energy $\min_{\psi} E_{KS}[\{\psi\}]$ error 2nd order in $\delta\psi$

Forces $dE_{KS}[\{\psi\}]/d\mathbf{R}$ error 1st order in $\delta\psi$

Extrapolation Methods

Integration of electronic DOF has to be

accurate: good wavefunction guess gives improved efficiency

stable: do not destroy time-reversibility of nuclear trajectory

- Unbiased guess

$$\mathbf{C}_{\text{init}} = \mathbf{C}_0$$

- Combinations of previous wavefunctions: unstable

- Extrapolation of the density matrix: **PS** methods, $O(MN^2)$

$$\mathbf{C}(t_n) = \sum_{m=1}^{K} (-1)^{m+1} \begin{bmatrix} K \\ j \end{bmatrix} \mathbf{C}(t_{n-m})\mathbf{C}^{\dagger}(t_{n-m})\mathbf{S}(t_{n-m})\mathbf{C}(t_{n-1})$$

- Always stable predictor corrector (ASPC) based on OT minimisation,

Kolafa J., J. Comput. Chem. 25, 335 (2004)

ASPC

Projection onto the occupied subspace

$$\mathbf{C}^p(t_n) = \sum_{m=1}^{K} (-1)^{m+1} m \frac{\binom{2K}{K-m}}{\binom{2K-2}{K-1}} \mathbf{C}(t_{m-m}) \mathbf{C}^\dagger(t_{n-m}) \mathbf{S}(t_{n-m}) \mathbf{C}(t_{n-1})$$

Reversibility $O(\Delta t^{(2K-1)})$

iterate

The corrector step minimises the error and reduces the deviation from ground state

$$\mathbf{C}(t_n) = \omega \mathrm{MIN}[\mathbf{C}^p(t_n)] + (1-\omega)\mathbf{C}^p(t_n) \qquad \omega = \frac{K}{2K-1}$$

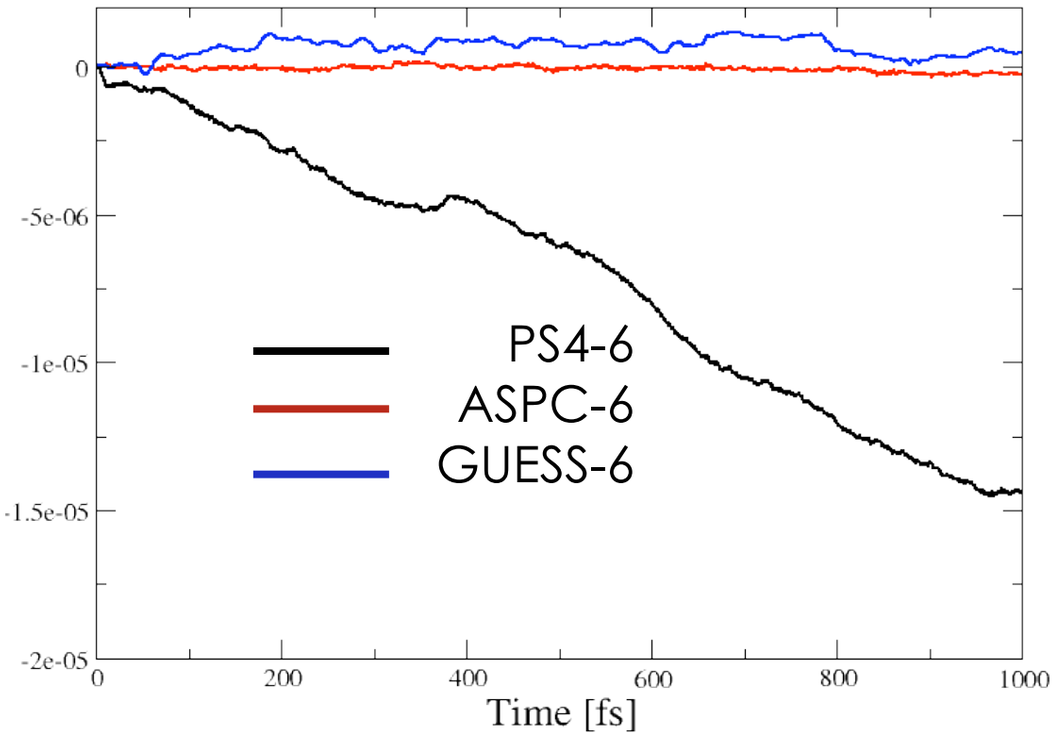
Preconditioned OT minimisation step: large move

Kolafa J., J. Comput. Chem. 25, 335 (2004),
VandeVondele et al, JCP, 118, 4365 (2003)

Efficiency and Drift

64 H2O, 330 K, 1gr/cm^3

Method	ϵ_{SCF}	Iterations	Drift (μHartree/ns)
Guess	10^{-06}	14.38	253
PS4	10^{-10}	14.95	–
PS4	10^{-08}	8.05	-195
PS4	10^{-07}	6.47	-3441
PS4	10^{-06}	5.22	-7186
PS4	10^{-05}	4.60	52771
ASPC	10^{-06}	5.01	-115
ASPC	10^{-05}	3.02	-2758
ASPC	10^{-04}	1.62	-1059843
ASPC	10^{-02}	1.03	-13219651



Gear not time reversible

Method	ϵ_{SCF}	Iterations	Drift (Kelvin/ns)
Guess	10^{-06}	14.38	0.4
ASPC(3)	10^{-06}	5.01	0.2
ASPC(3)	10^{-05}	3.02	4.5
Gear(4)	10^{-07}	6.47	5.7
Gear(4)	10^{-06}	5.22	11.8
Gear(4)	10^{-05}	4.60	86.8

Method	ϵ_{SCF}	Iterations	Drift (Kelvin/ns)
ASPC(4)	10^{-04}	1.62	1742.4
ASPC(5)	10^{-04}	1.63	1094.0
ASPC(6)	10^{-04}	1.79	397.4
ASPC(7)	10^{-04}	1.97	445.8
ASPC(8)	10^{-04}	2.06	24.1

Forces in Approximated BOMD

exact $$\mathbf{F}_{\mathrm{BO}}(\mathbf{R}) = \mathbf{F}_{\mathrm{HF}}(\mathbf{R}) + \mathbf{F}_{\mathrm{Pulay}}(\mathbf{R}) + \mathbf{F}_{\mathrm{nsc}}(\mathbf{R})$$

approximated $$\tilde{\mathbf{F}}(\mathbf{R}) = \mathbf{F}_{\mathrm{HF}}(\mathbf{R}) + \mathbf{F}_{\mathrm{Pulay}}(\mathbf{R})$$

Now assume $$\tilde{\mathbf{F}}(\mathbf{R}) + \mathbf{F}_{\mathrm{nsc}}(\mathbf{R}) = \mathbf{F}_{\mathrm{BO}}(\mathbf{R}) - \gamma_D \dot{\mathbf{R}}$$ friction

Langevin dynamics to correct the error (dissipative drift)

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I^{\mathrm{BO}} - (\gamma_D + \gamma_L)\dot{\mathbf{R}}_I + \Xi_I^D + \Xi_I^L$$

Gaussian random noise guarantees accurate Boltzmann sampling

fluctuation dissipation theorem

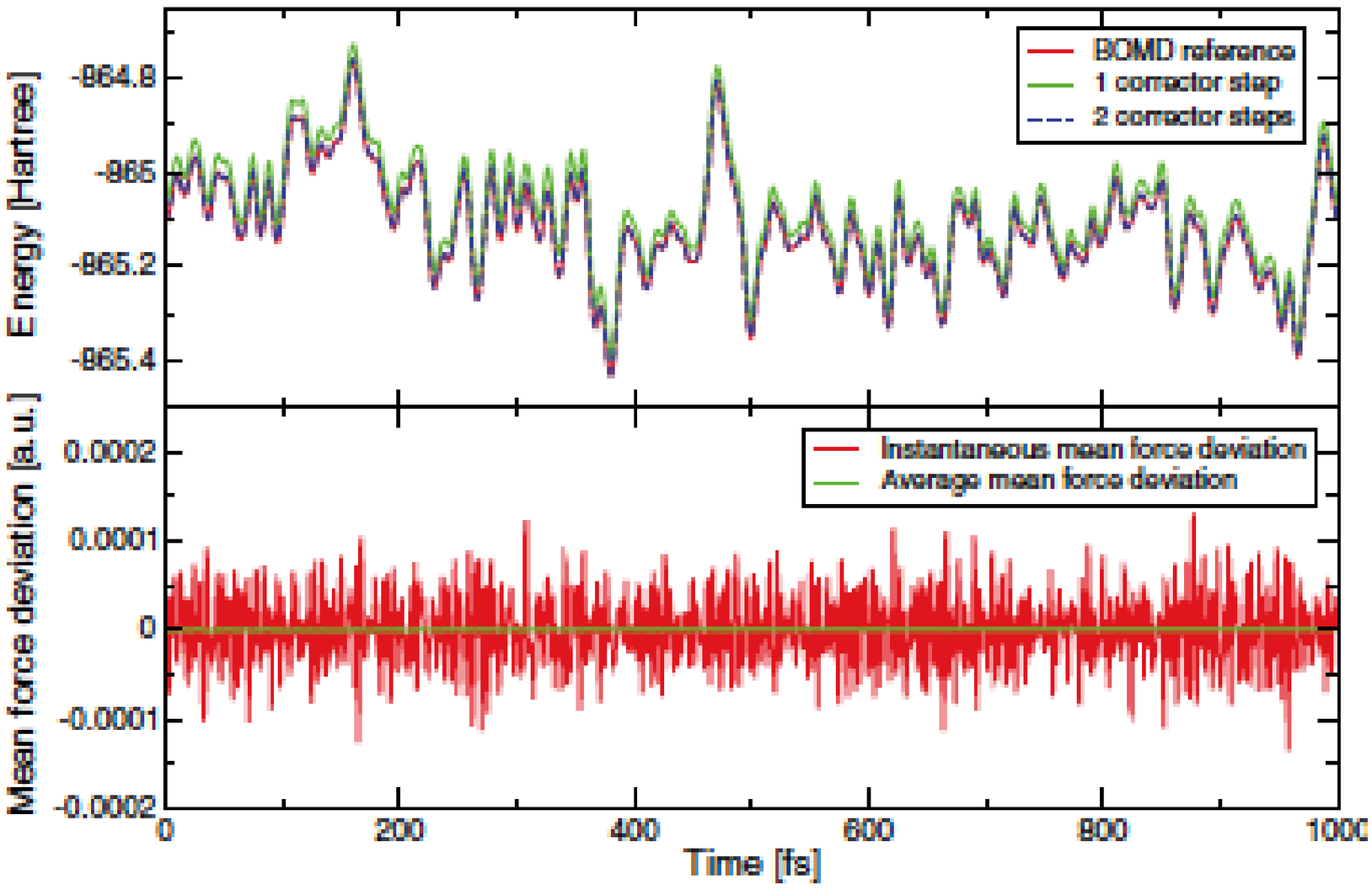
$$\langle (\Xi_I^D(0) + \Xi_I^L(0))(\Xi_I^D(t) + \Xi_I^L(t)) \rangle = 6(\gamma_D + \gamma_L) M_I k_{\mathrm{B}} T \delta t$$

given $$\left\langle \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 \right\rangle = \frac{3}{2} k_{\mathrm{B}} T$$ this determines the friction

T. Kuehne et al, PRL , 98(6), 066401 (2007)

Validation

liquid silica, 24 SiO_2 at 3500 K
Time step: Δt = 1 fs
γ_D 10^{-4} fs^{-1} , K=4

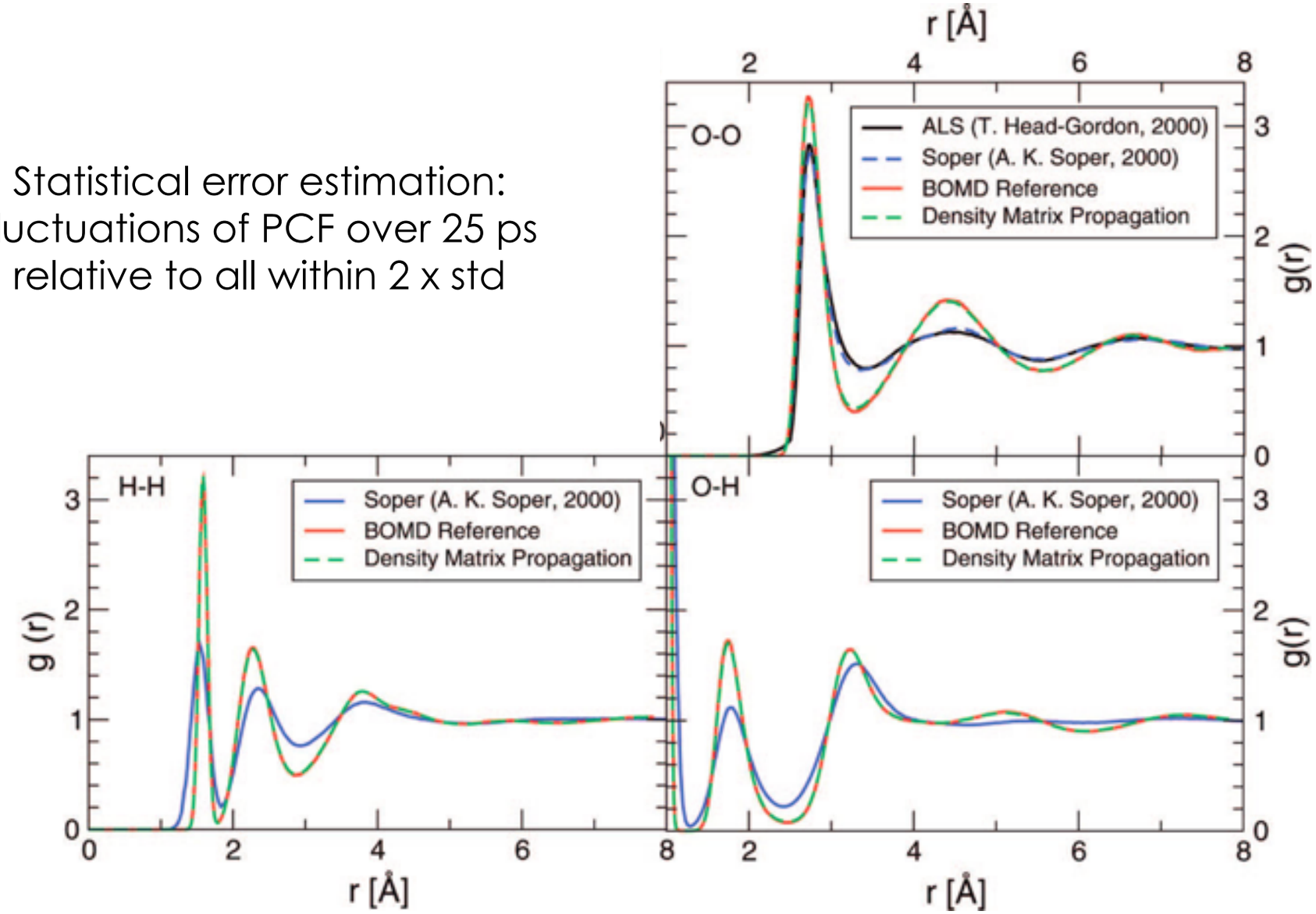


Bonds are swiftly broken and formed
Worst case scenario for P propagation, as the electronic density is rapidly varying

Liquid Water

PBE, TZV2P, 320 Ry
300 K, Δt = 0.5 fs, **25+250 ps** trajectories
γ_D 8.65 10^{-5} fs^{-1} , K=7 => 1 PC step, deviation 10^{-5} au

Statistical error estimation:
fluctuations of PCF over 25 ps
relative to all within 2 x std



T. Kuehne et al, J. Chem Theory Compt , 5(2), 235 (2008)