Gaussian and Plane Waves Method (GPW)

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- Goedecker, S; Teter, M; Hutter, J.
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Kohn–Sham (KS) Density Functional Theory (DFT)

- Hohenberg–Kohn Theorem I
  The total energy can be calculated from a universal functional of the density.
  Existence theorem

- Hohenberg–Kohn Theorem II
  The correct density minimizes the energy functional.
  Variational principle.

- Kohn–Sham Theorem
  For each density exists a system of non-interacting particles in a local external potential with the same density.
  Orbital picture.

Kohn–Sham DFT (II)

Minimization with constraints

$$\text{Min } E(\{\Phi_i\})$$

$$\int \Phi_i(r)\Phi_j(r)dr = \delta_{ij} \qquad \int \rho(r)dr = N$$

Energy functional

$$E(\{\Phi_i\}) = -\sum_i \frac{f_i}{2} \int \Phi_i \nabla_i \Phi_i dr + \int V_{\text{ext}}(r)\rho(r)dr$$

$$+ \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr\, dr' + E_{\text{xc}}[\rho]$$

$$\rho(r) = \sum_i f_i |\Phi_i(r)|^2$$

Kohn–Sham DFT (III)

- Kinetic energy
  $$E_{\mathrm{kin}} = -\tfrac{1}{2} \sum_i f_i (\Phi_i | \nabla^2 | \Phi_i)$$
- External energy (electron-nuclei interaction)
  $$E_{\mathrm{ext}} = \int V_{\mathrm{ext}}(r) \rho(r) \, dr$$
- Hartree (classical Coulomb) energy
  $$E_{\mathrm{H}} = \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr' \, dr$$
- Exchange-correlation (non-classical Coulomb) (XC) energy
  $$E_{\mathrm{xc}} = \int F[\rho] \, dr$$
- Orbital orthogonality constraint
  $$(\Phi_i | \Phi_j) = \delta_{ij}$$
- Electron number constraint
  $$\sum_i f_i (\Phi_i | \Phi_i) = N$$

Linear Combination of Atomic Orbitals (LCAO)

Basis set

$$\Phi_i(\mathbf{r}) = \sum_\alpha c_{\alpha i}\, \varphi_\alpha(\mathbf{r})$$

Overlap

$$\mathbf{S}_{\alpha\beta} = \int d\mathbf{r}\, \varphi_\alpha^\star(\mathbf{r})\varphi_\beta(\mathbf{r})$$

Orthogonality

$$\int d\mathbf{r}\, \Phi_i^\star(\mathbf{r})\Phi_j(\mathbf{r}) = \sum_{\alpha\beta} c_{\alpha i}^\star\, \mathbf{S}_{\alpha\beta}\, c_{\beta j} = \delta_{ij}$$

Density matrix

$$\mathbf{P}_{\alpha\beta} = \sum_i f_i\, c_{\alpha i} c_{\beta i}^\star$$

Density

$$\rho(\mathbf{r}) = \sum_{\alpha\beta} \mathbf{P}_{\alpha\beta}\, \varphi_\alpha(\mathbf{r})\varphi_\beta^\star(\mathbf{r})$$

Energy

$$E = \mathrm{Min}_c[E_{\mathrm{kin}}(c) + E_{\mathrm{ext}}(\rho) + E_{\mathrm{H}}(\rho) + E_{\mathrm{xc}}(\rho)]$$

Gaussian Type Orbitals (GTO): General

- Primitive function

$$\varphi(r) = r^l Y_{lm}(\hat{r}) \exp[-\alpha(r - A)^2]$$

- Contracted GTO

$$\chi(r) = \sum_k d_k \varphi_k(r)$$

Contraction coefficients d_k and exponents are fixed.
Contraction over functions with same angular momentum.

Gaussian Type Orbitals: Advantages

- GTO's are "atomic orbital-like"

- Compact basis set (approx. 15-25 functions per atom)

- Analytic integration possible for many operators.

- Optimal for regular grids. Fourier transform is again a Gaussian.

- Compact support (finite extend)

Gaussian Type Orbitals: Disadvantages

- Non-orthogonal basis

- Linear dependencies for larger basis sets

- Complicated to generate and no easy way to improve

- Basis set superposition error (BSSE)

- Molecules (wavefunction tails) and solids have different requirements

KS-DFT with GTO Basis

- Kinetic energy integrals: analytic

- External potential integrals: analytic

- Coulomb: 4 center electron repulsion integrals (ERI)
  Mulliken notation :$(\alpha\beta|\gamma\delta)$: analytic
  CPU and memory bottleneck

- XC energy and integrals: numerical integration

- Overlap integrals: analytic

Hartree Energy

- Goal: Avoid calculation of ERI
- Combine all electrostatic energy terms

Electrostatic Energy

$$E_{\text{Coulomb}} = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} \, dr \, dr' \qquad \text{electron-electron interaction}$$

$$- \sum_A Z_A \int \frac{\rho(r)}{|r - R_A|} \, dr \qquad \text{electron-core interaction}$$

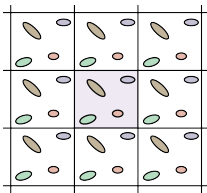$$+ \sum_{A<B} \frac{Z_A Z_B}{|R_A - R_B|} \qquad \text{ion-ion interaction}$$

Hartree Energy

Total charge density: electronic charge + Gaussian atomic charges:

$$\rho_{tot}(r) = \rho_e(r) + \sum_A \rho_A(r)$$

$$\rho_A(r) = Z_A \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha(r-A)^2)$$

$$E_{\text{Coulomb}} = \frac{1}{2} \int \int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r-r'|} \, dr \, dr' \qquad \text{long range interaction}$$

$$- \sum_A Z_A \int \frac{\text{erfc}(\alpha(r-R_A))}{|r-R_A|} \, \rho_e(r) \, dr \qquad \text{short range interaction}$$

$$+ \sum_{A<B} E_{\text{pair}}(R_A - R_B) \qquad \text{short range pair interaction}$$

$$- \sum_A E_{\text{self}} \qquad \text{self interaction correction}$$

Periodic Boundary Condition (PBC)

- Optimal for condensed phase systems (avoids interface effects)

- Bloch states, Brillouin zone sample, see k-points

- Energy per simulation cell

- Γ point simulation (Integration with single point at (0,0,0))

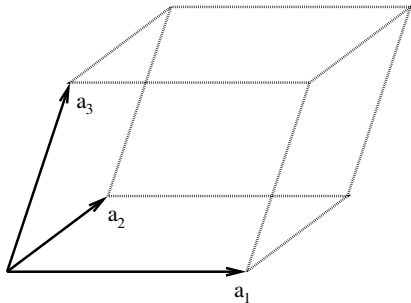- $(\alpha|\mathcal{O}|\beta) \rightarrow \sum_L (\alpha(0)|\mathcal{O}|\beta(L))$

Plane Waves (PW)

Definition

$$\varphi(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

+ orthogonal

+ independent of atomic positions

$\pm$ naturally periodic

– many functions needed

Computational Box

- Box matrix : $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$

- Box volume : $\Omega = \det \mathbf{h}$

Lattice Vectors

- Direct lattice $\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]$
- Direct lattice vectors : $\mathbf{L} = i \cdot \mathbf{a}_1 + j \cdot \mathbf{a}_2 + k \cdot \mathbf{a}_3$
- Reciprocal lattice $2\pi(\mathbf{h}^t)^{-1} = [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3]$

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$$

- Reciprocal lattice vectors : $\mathbf{G} = i \cdot \mathbf{b}_1 + j \cdot \mathbf{b}_2 + k \cdot \mathbf{b}_3$

Direct and reciprocal space are connected by Fourier transforms.
The expansion of the periodic part of the functions defined in real space includes only the **G** that satisfy the PBC: Fourier decomposition.

Properties of Plane Waves

$$\varphi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}]$$

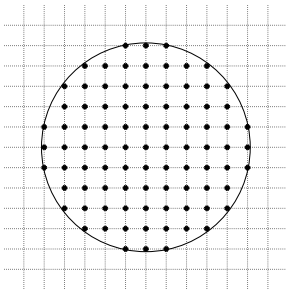- Plane waves are periodic wrt. box $\mathbf{h}$
- Plane waves are orthonormal

$$\langle \varphi_{\mathbf{G'}} | \varphi_{\mathbf{G}} \rangle = \delta_{\mathbf{G'},\mathbf{G}}$$

- Plane waves are complete

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}]$$

Cutoff: Finite Basis Set

$$\frac{1}{2} G^2 \le E_{\text{cut}}$$

$$N_{\text{PW}} \approx \frac{1}{2\pi^2} \Omega \, E_{\text{cut}}^{3/2} [a.u.]$$

Basis set size depends on volume of box and cutoff only

Real Space Grid

Sampling Theorem: Interval $\Delta = \frac{L}{N}$; Nyquist critical frequency $f_c = \frac{1}{2\Delta}$
For a given plane wave cutoff (frequency) there is a minimum number of equidistant real space grid points needed for the same accuracy.

$$\text{Real space grid:} \qquad \mathbf{R}_i = (i-1)\Delta$$

Fast Fourier Transform (FFT)

$$\psi(\mathbf{G}) \longleftrightarrow \psi(\mathbf{R})$$

Information contained in $\psi(\mathbf{G})$ and $\psi(\mathbf{R})$ are equivalent.

Fourier transform	N^2 operations
fast Fourier transform	$N \log[N]$ operations

Integrals

$$I = \int_\Omega A^\star(\mathbf{r})B(\mathbf{r})d\mathbf{r}$$

$$= \sum_{\mathbf{G}\mathbf{G}'} A^\star(\mathbf{G})B(\mathbf{G}') \int \exp[-i\mathbf{G}\cdot\mathbf{r}]\exp[i\mathbf{G}'\cdot\mathbf{r}]d\mathbf{r}$$

$$= \sum_{\mathbf{G}\mathbf{G}'} A^\star(\mathbf{G})B(\mathbf{G}')\,\Omega\,\delta_{\mathbf{G}\mathbf{G}'} = \Omega\sum_{\mathbf{G}} A^\star(\mathbf{G})B(\mathbf{G})$$

Parseval's theorem

$$\Omega\sum_{\mathbf{G}} A^\star(\mathbf{G})B(\mathbf{G}) = \frac{\Omega}{N}\sum_i A^\star(\mathbf{R}_i)B(\mathbf{R}_i)$$

Integrals in real space and in reciprocal space are equivalent

Long Range Term in Coulomb Energy

$$E_{\mathrm{LRT}} = \frac{1}{2} \int \int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r - r'|} dr\, dr' = \int V_H(r)\rho_{tot}(r)\, dr$$

where $V_H(r)$ is the solution of Poisson equation

$$\nabla^2 V_H(r) = -4\pi \rho_{tot}(r)$$

Plane wave expansion of total charge density

$$\rho_{tot}(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{tot}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \qquad V_H(G) = 4\pi \frac{\rho_{tot}(G)}{G^2}$$

$$E_{\mathrm{LRT}} = \frac{2\pi}{\Omega} \sum_{\mathbf{G}} \frac{\rho_{tot}^*(\mathbf{G})\rho_{tot}(\mathbf{G})}{\mathbf{G}^2}$$

Exchange-Correlation (XC) Functionals

$$E_{\mathrm{xc}} = \int d\mathbf{r}\, \varepsilon_{\mathrm{xc}}(\mathbf{r})\, \rho(\mathbf{r}) = \Omega \sum_{\mathbf{G}} \varepsilon_{\mathrm{xc}}(\mathbf{G}) \rho^{\star}(\mathbf{G})$$

$\varepsilon_{\mathrm{xc}}(\mathbf{G})$ is not local in G space. Calculation in real space requires very accurate integration scheme.
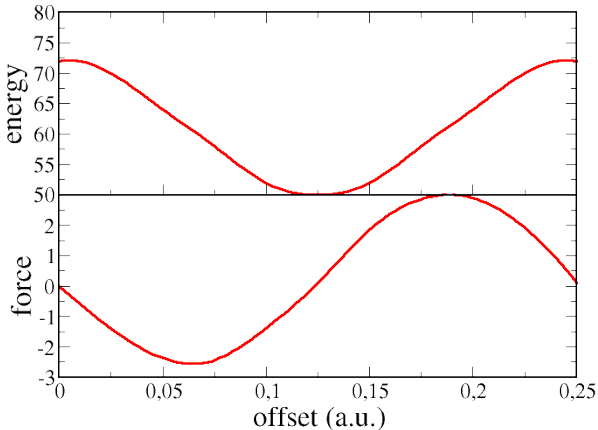
New definition of E_{xc}

$$E_{\mathrm{xc}} = \frac{\Omega}{N_{\mathrm{x}} N_{\mathrm{y}} N_{\mathrm{z}}} \sum_{\mathbf{R}} \varepsilon_{\mathrm{xc}}(\mathbf{R}) \rho(\mathbf{R}) = \Omega \sum_{\mathbf{G}} \tilde{\varepsilon}_{\mathrm{xc}}(\mathbf{G}) n(\mathbf{G})$$

where $\tilde{\varepsilon}_{\mathrm{xc}}(\mathbf{G})$ is the finite Fourier transform of $\varepsilon_{\mathrm{xc}}(\mathbf{R})$.

Energy and Force of He Atom

Only translations by a multiple of the grid spacing do not change the total energy. This introduces a small modulation of the energy hyper surface, known as "ripples".

KS-DFT GPW Energy

$$E_{\mathrm{KS}}^{\mathrm{GPW}} = E_{\mathrm{kin}}(P) + \delta E_{\mathrm{ext}}(P) + E_{\mathrm{xc}}(\tilde{\rho}) + E_{\mathrm{H}}(\tilde{\rho}) + E_{\mathrm{ovrl}} - E_{\mathrm{self}}$$

Gaussian orbital part:

$$\Phi_i(r) = \sum_{\alpha} c_{\alpha i} \varphi_{\alpha}$$

$$P_{\alpha\beta} = \sum_{i} f_i c_{\alpha i} c_{\beta i}$$

PW part:

$$\tilde{\rho}(G) = \sum_{\alpha\beta} (\varphi_{\alpha} \cdot \varphi_{\beta})(G)$$

$$\tilde{\rho}_{\mathrm{tot}}(G) = \tilde{\rho}(G) + \sum_{A} \rho_A(G)$$

$$(\varphi_{\alpha} \cdot \varphi_{\beta})(G) = \varphi_{\alpha\beta}(G)$$

- $E_{\mathrm{KS}}^{\mathrm{GPW}}$ is variational in the GTO coefficients $c_{\alpha i}$ alone.
- $\tilde{\rho}(G)$ is a function of $c_{\alpha i}$ and the auxiliary PW basis

Efficient Calculation of GPW Energy

Screening

- Always work with primitive Gaussians

- Analytic integrals $\rightarrow$ distance screening with $R = A - B$

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

  $\qquad\qquad \downarrow \qquad\quad$ sparsity pattern

  $\qquad T_{\alpha\beta}$

- Density on the real space grid

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

  $\qquad\qquad \downarrow$ overlap screening

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

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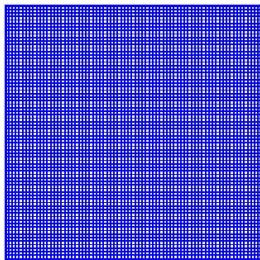
Screening

- 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`
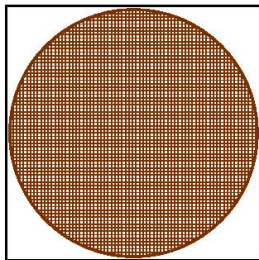   (extend of $\varphi_{\alpha\beta}$)

Real Space Grid

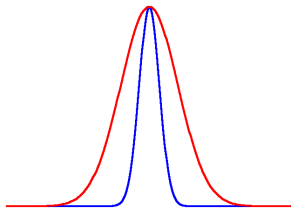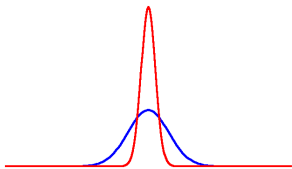Finite cutoff and computational box define a real space grid $\{\mathbf{R}\}$

FFT

Real Space

G−Space

Gaussians and Plane Waves
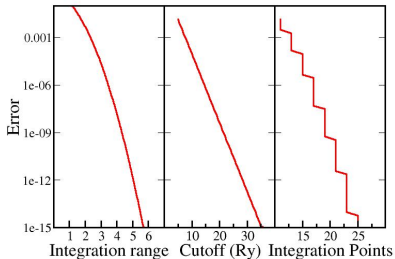
$$\sqrt{\frac{\alpha}{\pi}} \exp\left(-\alpha r^2\right) \quad \xrightarrow{\text{FFT}} \quad \exp\left(-\frac{\mathbf{G}^2}{4\alpha}\right)$$

- Efficient screening in R space
- Exponential convergence for integration
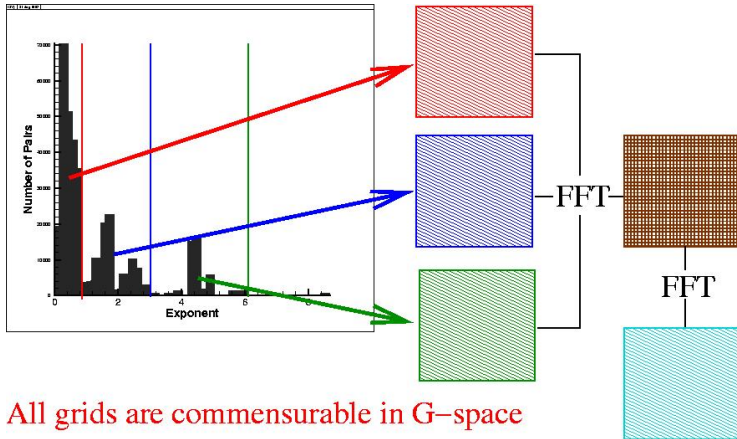
GTOs and PW

Integration

For the integartion of a Gaussian function with exponent 1 an accuracy of 10^{-10} requires an integration range of 10 bohr, a cutoff of 25 Rydberg, resulting in 22 integration points.

≈ 5000 integration points/integral batch

Multigrid

All grids are commensurable in G−space

PW Cutoff

- **Density expansion**

  PW cutoff and multigrid settings determine accuracy and efficiency of density expansion

  &MGRID ... &END MGRID section

  - **CUTOFF:** Maximal cutoff used in the calculation (default: 280 Ry)
  - **REL_CUTOFF:** Minimal cutoff used for Gaussian with exponent of 1 (default: 40 Ry)
  - **NGRIDS:** Total number of real space grids (cutoffs) used (default: 4)
  - **PROGRESSION_FACTOR:** factor used for cutoff reduction in multigrids (default: 3)
  - **MULTIGRID_SET:** T/F set multigrid cutoff from input (default: F)
  - **MULTIGRID_CUTOFF:** list of cutoffs for N grids

PW Cutoff

- XC functional

  Accuracy of density expansion and total PW cutoff determine XC energy accuracy

  > CP2K calculates gradient of density from plane wave expansion of density

  > Fourier interpolation may lead to negative densities in low density regions (problem is enhanced by multigrids!)

  > LDA vs. GGA vs. Meta-functionals

  > ρ vs. $(\nabla\rho)^2/\rho^{4/3}$ vs. τ

  > DENSITY_CUTOFF, GRADIENT_CUTOFF, TAU_CUTOFF

  > in `FORCE_EVAL / DFT / XC`

  > See more advanced options

  > in `FORCE_EVAL / DFT / XC / XC_GRID`

Coulomb Potential

$$\boldsymbol{P} \to \rho(\mathbf{R}) \xrightarrow{\text{FFT}} \rho(\mathbf{G}) \to V_{\text{H}}(\mathbf{G}) = \frac{\rho(\mathbf{G})}{G^2} \xrightarrow{\text{FFT}} V_{\text{H}}(\mathbf{R}) \to \boldsymbol{V}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{\mathcal{O}(n \log n)}$$
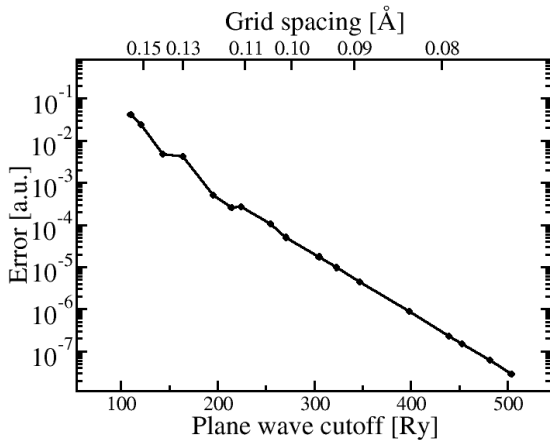
$$\rho(\mathbf{R}) = \sum_{\mu\nu} \boldsymbol{P}_{\mu\nu} \chi_\mu(\mathbf{R}) \chi_\nu(\mathbf{R}) = \sum_{\mu\nu} \boldsymbol{P}_{\mu\nu} \bar{\chi}_{\mu\nu}(\mathbf{R})$$

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

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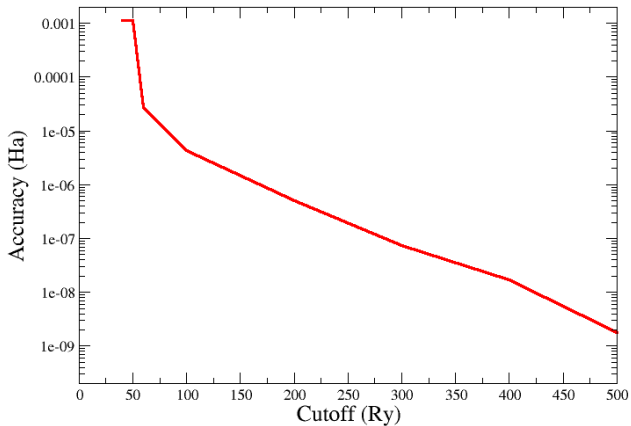
Accuracy of Plane Wave Expansion

Coulomb Energy

Accuracy of Plane Wave Expansion

XC Energy

PBE functional, Bulk Silicon

Accuracy and Numerical Errors

64 water, 2560 basis functions, LDA functional, 24 cores

| EPS_DEFAULT	cutoff(Ry)	ngrids	time(s)	Energy(Ha)
-12	280(30)	4	1.5	x.0377660911
-12	400(60)	4	2.7	x.0368292349
-12	400(60)	1	21.9	x.0368292282
-12	800(60)	6	3.0	x.0371244786
-12	800(60)	4	3.0	x.0371244689
-12	800(60)	1	76.5	x.0371244096
-8	1600(60)	6	3.7	x.0371421086
-10	1600(60)	6	4.7	x.0371296795
-12	1600(60)	6	4.7	x.0371288794
-14	1600(60)	6	4.9	x.0371287675

Basis Set Superposition Error (BSSE)

- Localized non-orthogonal AO basis sets are incomplete

- Local 'completeness' of basis depends on position of atoms

- Basis set is more complete for molecular clusters than single molecules
  $\longrightarrow$ overstabilization of bound clusters

- Overestimation of binding energies (dimers, molecules on surfaces, etc.)

- Counterpoise Correction: Estimation of BSSE

  $$E_{BSSE} \approx E_A(A+B) + E_B(A+B) - E_A(A) - E_B(B)$$

  with fragments A, B at their cluster geometry.

BSSE in liquid water

Binding energy in water (BSSE)
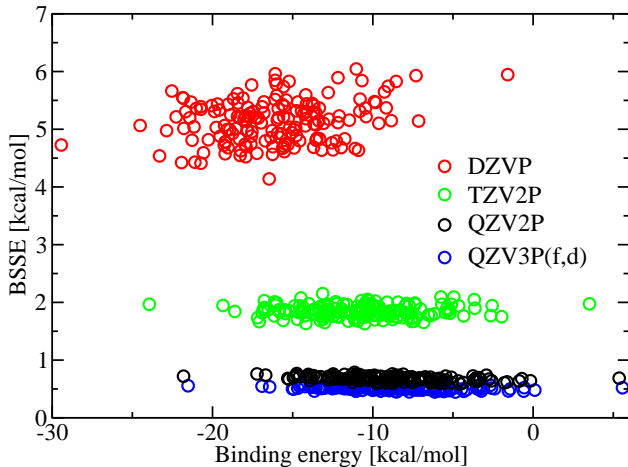
Non-Periodic Calculations using PW

Solving Poisson equation for non-periodic boundary conditions

- Analytic for spherical cutoff or cylindrical or 1-d cutoff
  Marx and Hutter, Ab initio molecular dynamics, NIC Series

- Wavelet solvers
  Genovese et al, JCP 2006, 125 074105

- Solvers by Martyna and Tuckerman
  Martyna & Tuckerman, JCP 1999, 110 2810-2821

Pseudopotentials

Why Pseudopotentials?

- **Reduction of basis set size**
  effective speedup of calculation

- **Reduction of number of electrons**
  reduces the number of degrees of freedom

- **Inclusion of relativistic effects**
  relativistic effects can be included "partially" into effective
  potentials

Frozen Core Approximation

- Replace inactive electronic degrees of freedom in the Hamiltonian by an effective potential

- The potential should be additive and transferable
  - additive   most general choice: atomic pseudopotentials
  - transferable   remove only core electrons

- Core electrons are chemically inert

- Core/Valence separation is often not clear
  in plane wave calculations: core = all filled shells

- Core wavefunctions are transfered from atomic reference calculation

- Core electrons of different atoms do not overlap

Remaining Problems

- Valence wavefunctions have to be orthogonalized to core states
  $\rightarrow$ nodal structures $\rightarrow$ high plane wave cutoff

- Pseudopotential should produce node-less functions and include Pauli repulsion

- Pseudopotential replaces Hartree and XC potential due to the core electrons

- XC functionals are not linear: approximation

$$E_{\mathrm{XC}}(\rho_{\mathrm{c}} + \rho_{\mathrm{v}}) = E_{\mathrm{XC}}(\rho_{\mathrm{c}}) + E_{\mathrm{XC}}(\rho_{\mathrm{v}})$$

This assumes that core and valence electrons do not overlap. This restriction can be overcome with the "non–linear core correction".

General Recipe

1. Atomic all–electron calculation (reference state)
   $\Rightarrow \Phi_i^{\mathrm{v}}(\mathbf{r})$ and ϵ_i.

2. Pseudize $\Phi_i^{\mathrm{v}} \Rightarrow \Phi_i^{\mathrm{PS}}$

3. Calculate potential from

$$\left(T + V_i(\mathbf{r})\right) \Phi_i^{\mathrm{PS}}(\mathbf{r}) = \epsilon_i \Phi_i^{\mathrm{PS}}(\mathbf{r})$$
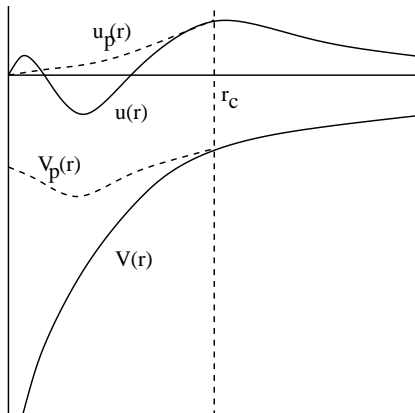
4. Calculate pseudopotential by unscreening of $V_i(\mathbf{r})$

$$V_i^{\mathrm{PS}}(\mathbf{r}) = V_i(\mathbf{r}) - V_{\mathrm{H}}(n_{\mathrm{PS}}) - V_{\mathrm{XC}}(n_{\mathrm{PS}})$$

V_i^{PS} is state dependent !

Pseudization of Valence Wavefunctions

Smooth continuation of orbitals inside a cutoff radius

Semi-local Pseudopotentials

$$V^{\mathrm{PS}}(\mathbf{r}, \mathbf{r}') = \sum_{L=0}^{\infty} V_L^{\mathrm{PS}}(r) |Y_L\rangle\langle Y_L|$$

Separation of Local and Nonlocal Parts

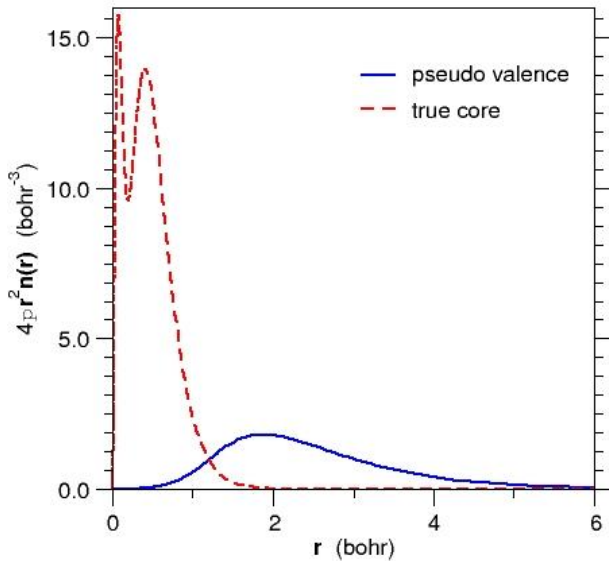Approximation: all potentials with $L > L_{\max}$ are equal to $V_{\mathrm{loc}}^{\mathrm{PS}}$

$$V^{\mathrm{PS}}(\mathbf{r}, \mathbf{r}') = \sum_{L=0}^{L_{\max}} \left(V_L^{\mathrm{PS}}(r) - V_{\mathrm{loc}}^{\mathrm{PS}}(r) \right) |Y_L\rangle\langle Y_L| + V_{\mathrm{loc}}^{\mathrm{PS}}(r)$$
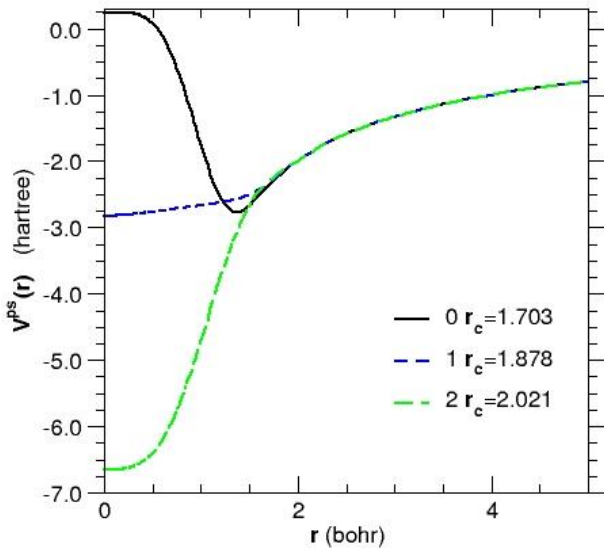
Final Form

$$V^{\mathrm{PS}}(\mathbf{r}, \mathbf{r}') = V_{\mathrm{loc}}^{\mathrm{PS}}(r) + \sum_{L=0}^{L_{\max}} \Delta V_L^{\mathrm{PS}}(r) |Y_L\rangle\langle Y_L|$$

- Local pseudopotential $V_{\mathrm{loc}}^{\mathrm{PS}}(r)$
- Non-local pseudopotential $\Delta V_L^{\mathrm{PS}}(r)$

Silicon: Radial densities

Silicon: Ionic pseudo potentials

Kleinman–Bylander Form

Basis set expansion with the following approximation for the identity:

$$1 = \sum_L \frac{|\varphi_L\rangle\langle \Delta V_L \varphi_L|}{\langle \varphi_L \Delta V_L \varphi_L\rangle}$$

where φ_L is the pseudo–atomic wavefunction from the reference calculation.

$$E_{\mathrm{PS}} = \sum_L \sum_i f_i \langle \Phi_i \mid \Delta V_L \varphi_L\rangle \omega_L \langle \Delta V_L \varphi_L \mid \Phi_i\rangle$$

where

$$\omega_L = \langle \varphi_L \Delta V_L \varphi_L\rangle$$

For an atom with s and p non-local potential this requires the calculation of 4 times number of states integrals $\langle \Delta V_L \varphi_L \mid \Phi_i\rangle$.

Dual-Space PP

- Goedecker et al, PRB, (1996), 54, 1703
  Hartwigsen et al, PRB, (1998), 58, 3641
  M. Krack, TCA, (2005), 114, 145

- Fully non-local: easy analytic integrals and FFTs

$$V_{pp}(r) = V_{loc}(r) + \sum_L \sum_{ij} |p_i^L\rangle h_{ij}^L \langle p_j^L|$$

- Gaussian form with few adjustable parameters: $[\bar{r} = \frac{r}{r_c}]$

$$V_{loc}(r) = -\frac{Z_{ion}}{r}\text{erf}\left[\frac{\bar{r}}{\sqrt{2}}\right] + \exp\left[-\frac{\bar{r}^2}{2}\right]\left[C_1 + C_2\bar{r}^2 + C_3\bar{r}^4 + C_4\bar{r}^6\right]$$

$$p_L^i(r) = N_{iL}(r_l)\exp\left[-\frac{r^2}{2r_l^2}\right]$$

- Global optimization of all parameters to fit atomic orbital energies of occupied and virtual orbitals.
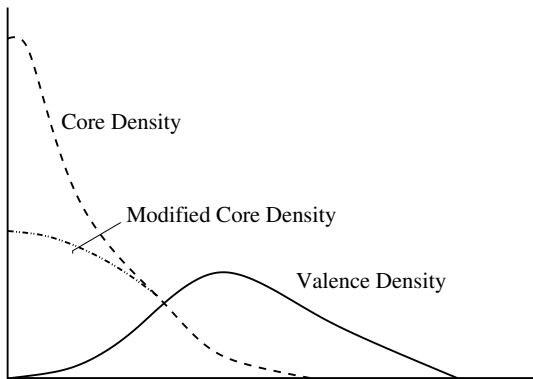
Non-Linear Core Correction (NLCC)

For many atoms (e.g. alkali atoms, transition metals) core states overlap with valence states. Linearization assumption for XC energy breaks down.

- Add additional states to valence (semi-core)

    - adds more electrons

    - needs higher cutoff

- Add core charge to valence charge in XC energy $\Rightarrow$ non–linear core correction (NLCC)
  S.G. Louie et al., Phys. Rev. B, **26** 1738 (1982)

Non-Linear Core Correction (NLCC)

$$E_{xc} = E_{xc}(n + \tilde{n}_{core}) \quad \text{where} \quad \tilde{n}_{core}(\mathbf{r}) = n_{core}(\mathbf{r}) \quad \text{if } r > r_0$$

Core Density

Modified Core Density

Valence Density

Basis Sets

Molecular Optimized Basis Sets (MOLOPT)

Goals

- Suitable for gas and condensed phase, interfaces

- Systematic increase in accuracy

- Suitable for large scale simulations
  Optimal for small number of functions
  Well conditioned

- Low BSSE for weak interactions

MOLOPT Basic idea

Use generally contracted Gaussian basis sets, including diffuse
primitives, fully optimized on molecular calculations.

- generally contracted $\longrightarrow$ no lone diffuse functions, well
  conditioned

- diffuse primitives $\longrightarrow$ reduced BSSE

- molecularly optimized $\longrightarrow$ small but accurate

MOLOPT

- generally contracted family basis, all exponents used for all angular momenta (including polarization)
- 6/7 primitive functions (pseudopotentials, valence only)
- larger sets extend smaller sets
- currently available for H-Rn

basis	1st/2nd row	Hydrogen
m-SZV	1s1p	1s
m-DZVP	2s2p1d	2s1p
m-TZVP	3s3p1d	3s1p
m-TZV2P	3s3p2d	3s2p
m-TZV2PX	3s3p2d1f	3s2p1d

Condition Numbers (Liquids)

	SZV	DZVP	TZV2P	QZV3P
water	1.00	2.97	4.46	5.64
BQ/MeOH	1.30	5.11	6.89	8.66
acetonitrile	1.34	4.15	5.69	7.46
		aug-DZVP	aug-TZV2P	aug-QZV3P
water		10.11	12.54	15.11
BQ/MeOH		11.00	13.52	13.94
acetonitrile		9.89	14.58	14.23
	m-SZV	m-DZVP	m-TZV2P	m-TZV2PX
water	0.83	3.20	4.18	4.27
BQ/MeOH	1.04	3.34	4.46	4.66
acetonitrile	1.11	3.23	4.18	4.36

$\log \kappa = \log \sigma_{\mathrm{max}} / \sigma_{\mathrm{min}}$

Solving the KS Equations

Fix Point Methods

1. initial guess $n^{\text{in}}(\mathbf{r})$

2. calculate potential $V(\mathbf{r})$

3. diagonalize KS matrix, get c^{out}

4. calculate new density n^{out}

5. if $\mid n^{\text{in}} - n^{\text{out}} \mid \leq \epsilon$ stop

6. calculate new density from n^{in} and n^{out} (mixing)

7. go back to 2

Direct Minimization Methods

Minimum $[E_{KS}(c)]$ with the constraint $\sum_\alpha c_{\alpha i}^\star c_{\alpha j} = \delta_{ij}$

Lagrange function

$$\tilde{E}_{KS}[c, \Lambda] = E_{KS}(c) - \text{Tr}\left\{\Lambda(c^\dagger c - 1)\right\}$$

Gradient

$$\frac{\partial \tilde{E}_{KS}}{\partial c_{\alpha n}^\star} = \sum_\beta F_{\alpha\beta} c_{\beta n} - \sum_m c_{\alpha m} \left(\sum_{\beta\gamma} c_{\beta m}^\star F_{\beta\gamma} c_{\gamma n}\right)$$

Orbital Transformation (OT) Method

J. VandeVondele and J. Hutter, JCP **118** 4365 (2003)

- Direct optimization technique

- Similar to orbital rotation method

- Constraint is only linear

-

Memory	*MN*	M	Number of basis functions
Scaling	*MN*^{2}	N	Number of occupied orbitals

- Set of reference occupied orbitals: $\boldsymbol{C}_0$

- New variables $\boldsymbol{X}$

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

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

- Linear constraint $\quad \boldsymbol{X}^T \boldsymbol{S} \boldsymbol{C}_0 = 0$

- Standard optimization with line serach and preconditioning

OT versus Diag-DIIS
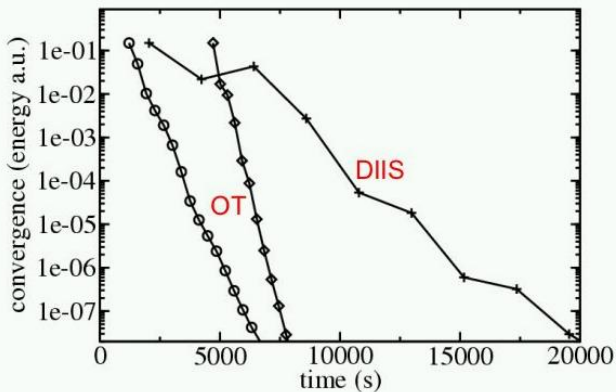
256 H2O TZV(2d,2p) 10240 BF on 4 CPUs SUN ultrasparc

Direct Inversion in Iterative Subspace (DIIS)

DIIS: Acceleration method for iterative sequences.

Basic idea : From a series of steps in an optimization procedure, try to guess a better trial vector.

In DIIS we solve exactly (by direct inversion) an optimality condition within the subspace of the parameter vectors generated by the iterations.
Assume we have generated a sequence of M parameter vectors $\{\mathbf{x_m}\}_1^M$ and that we are able to guess for each of the vectors its difference $\mathbf{e_m}$ to the stationary point.

Ansatz: Find the best linear combination of vectors $\mathbf{x}_{M+1} = \sum_{i=1}^M c_i \mathbf{x_i}$ with the constraint $\sum_{i=1}^M c_i = 1$.

DIIS

Ansatz

$$\text{Min} \left[< \sum_{i=1}^{M} c_i \mathbf{e_i} | \sum_{j=1}^{M} c_j \mathbf{e_j} > \right] \quad \text{with} \quad \sum_{i=1}^{M} c_i = 1$$

where $< .|. >$ is a suitably defined scalar product. This leads to a system of linear equations with $b_{ij} = < \mathbf{e_i} | \mathbf{e_j} >$

$$\begin{pmatrix} b_{11} & b_{12} & \ldots & b_{1m} & -1 \\ b_{21} & b_{22} & \ldots & b_{2m} & -1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ b_{m1} & b_{m2} & \ldots & b_{mm} & -1 \\ -1 & -1 & \ldots & -1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_m \\ \lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ -1 \end{pmatrix}$$

What to take for the error vectors?

Any measure for the distance from the stationary point.

AO basis sets
Hartree–Fock and Kohn–Sham Methods (Pulay)

$$\{\mathbf{e}\}_{ij} = \sum_{kl} \left(\mathbf{F}_{ik}\mathbf{P}_{kl}\mathbf{S}_{lj} - \mathbf{S}_{ik}\mathbf{P}_{kl}\mathbf{F}_{lj} \right)$$

GDIIS (based on Newton–Raphson)

$$\mathbf{e_i} = -\mathbf{P}\mathbf{g}(\mathbf{x_i}) \qquad \text{Preconditioner } \mathbf{P}$$

Preconditioner

- Preconditioner is essential for good convergence in direct minimization

- Predonditioner matrix $\mathbf{P} = \mathbf{M}^{-1}$ is applied to gradient: $\mathbf{Pg}(\mathbf{x_i})$

- Predonditioner is state dependent (FULL_ALL), single state approximations are better in memory usage and CPU time

- Predonditioner depends on Hamiltonian and should not be updated during optimizations.

- Restart of optimization is needed if Precodnitioner is too bad (outer SCF procedure in CP2K)
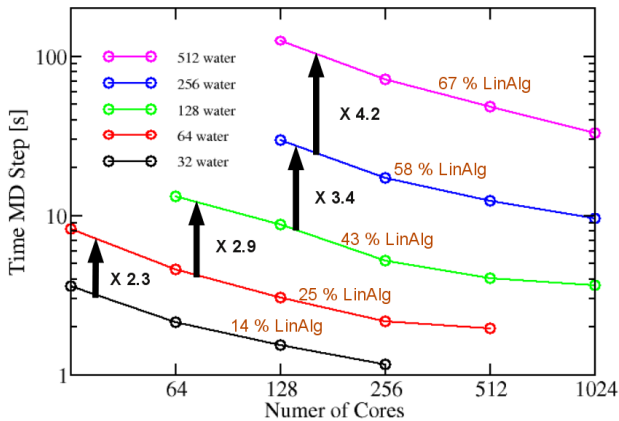
Scaling of GPW Calculations

- N: Number of occupied orbitals, number of electrons

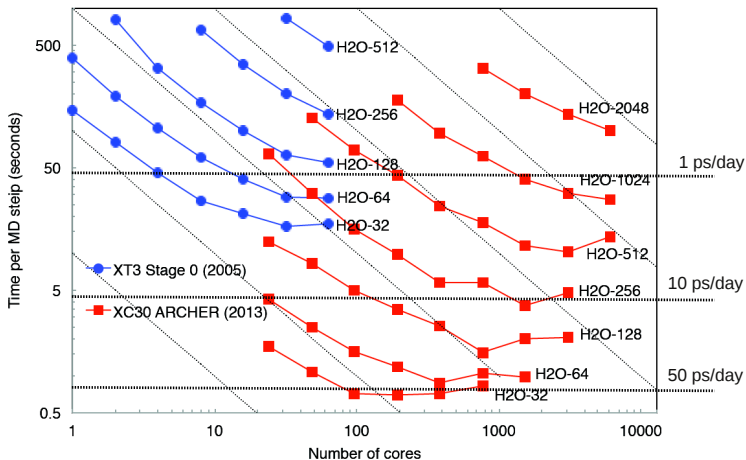- M: Number of basis functions

Kohn-Sham matrix $\mathcal{O}(MlogN)$

Density matrix (incomplete sparse) $\mathcal{O}(MN)$

OT optimization $\mathcal{O}(MN^2)$

System Size Scaling

Efficiency: GGA Functionals

Linear Scaling KS-DFT

Avoid Matrix Diagonalization
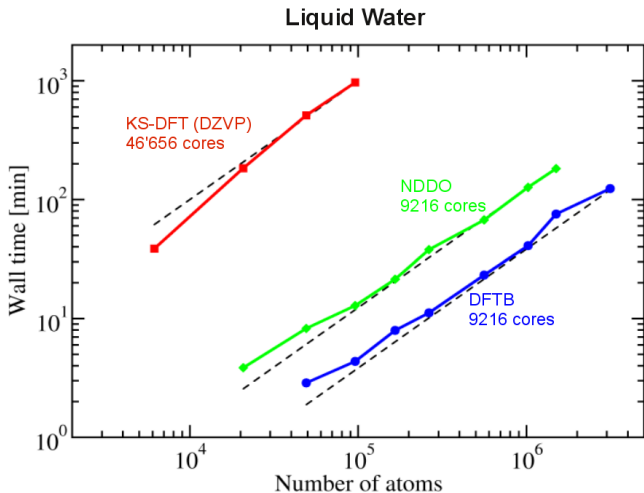
$$P = \text{sign}\left(S^{-1}H - \mu I\right) S^{-1}$$

Calculate S^{-1} and $\text{sign}(A)$ using Newton-Schultz iterations

$$A_{i+1} = \frac{1}{2}A_i\left(3I - A_i^2\right)$$
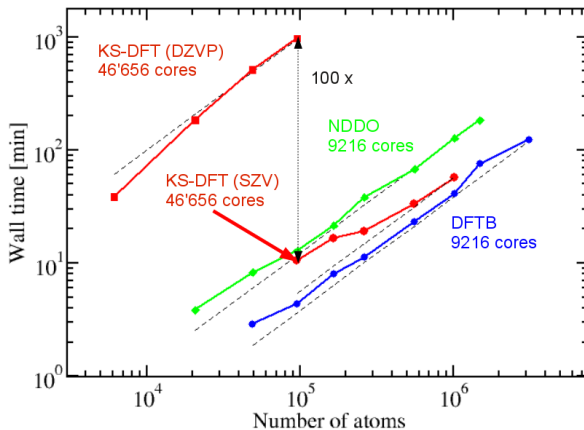
Only matrix multiplications required.

DBCSR: Sparse matrix-matrix multiplication library

Linear Scaling

Liquid Water
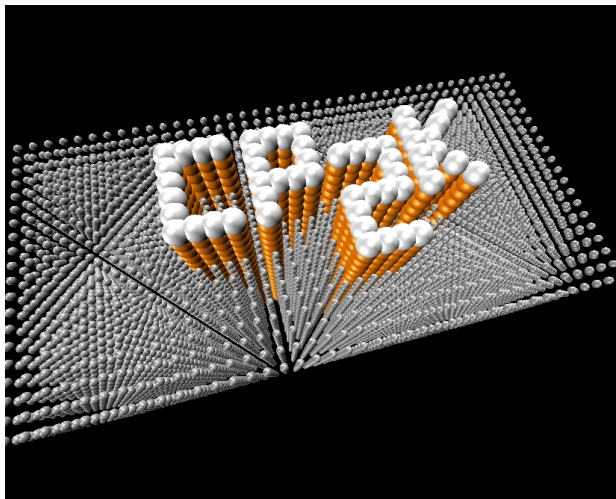
Linear Scaling

Liquid Water

PAO-ML

Table 1. Timings (seconds) for the Complete CP2K Energy Calculation (Full) and the Matrix Multiplication Part (mult) on a System Consisting of ~20000 Atoms, As Described in the Text[a]

nodes	64	100	169	256	400
		PAO-ML			
full	87	58	41	33	24
mult	23	17	13	11	8
		DZVP-MOLOPT-GTH			
full	5215	2765	1996	1840	1201
mult	5036	2655	1922	1779	1165

[a]The PAO-ML method outperforms a standard DFT run with a DZVP-MOLOPT-GTH basis by a factor of at least 50×.

O. Schütt, J. VandeVondele, J. Chem. Theory Comput. 2018, 14, 4168

www.cp2k.org