

# **Gaussian and Plane Waves Method (GPW)**

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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

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

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

$$E(\{\Phi_i\}) = - \sum_i \frac{f_i}{2} \int \Phi_i \nabla_i \Phi_i dr + \int V_{\text{ext}}(r)\rho(r)dr \\ + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{\text{xc}}[\rho]$$

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

## Kohn–Sham DFT (III)

- Kinetic energy

$$E_{\text{kin}} = -\frac{1}{2} \sum_i f_i (\Phi_i | \nabla^2 | \Phi_i)$$

- External energy (electron-nuclei interaction)

$$E_{\text{ext}} = \int V_{\text{ext}}(r) \rho(r) dr$$

- Hartree (classical Coulomb) energy

$$E_{\text{H}} = \int \int \frac{\rho(r)\rho(r')}{|r-r'|} dr' dr$$

- Exchange-correlation (non-classical Coulomb) (XC) energy

$$E_{\text{xc}} = \int F[\rho] dr$$

- 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

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

Orthogonality

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

Density matrix

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

Density

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

Energy

$$E = \text{Min}_{\mathbf{c}} [E_{\text{kin}}(\mathbf{c}) + E_{\text{ext}}(\rho) + E_{\text{H}}(\rho) + E_{\text{xc}}(\rho)]$$

# 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
- XC energy and integrals: numerical integration
- Overlap integrals: analytic

# Hartree Energy

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

## Electrostatic Energy

$$E_{\text{Coulomb}} = \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' \quad \text{electron-electron interaction}$$
$$- \sum_A Z_A \int \frac{\rho(r)}{|r-R_A|} dr \quad \text{electron-core interaction}$$
$$+ \sum_{A<B} \frac{Z_A Z_B}{|R_A - R_B|} \quad \text{ion-ion interaction}$$

## Hartree Energy

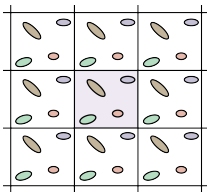
Define a total charge density: electronic charge + Gaussian atomic charges:

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

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

$$\begin{aligned} E_{\text{Coulomb}} = & \frac{1}{2} \iint \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r - r'|} dr dr' && \text{long range interaction} \\ & - \sum_A Z_A \int \frac{\text{erfc}(\alpha(r - R_A))}{|r - R_A|} \rho_e(r) dr && \text{short range interaction} \\ & + \sum_{A < B} E_{\text{pair}}(R_A - R_B) && \text{short range pair interaction} \\ & - \sum_A E_{\text{self}} && \text{self interaction correction} \end{aligned}$$

## Periodic Boundary Condition (PBC)



- Optimal for condensed phase systems (avoids interface effects)
- Bloch states, Brillouin zone sample, see k-points
- Energy per simulation cell
- $\Gamma$  point simulation (Integration with single point at  $(0,0,0)$ )
- $(\alpha|\mathcal{O}|\beta) \rightarrow \sum_L (\alpha(0)|\mathcal{O}|\beta(L))$

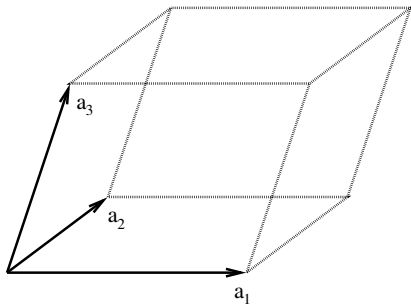
# Plane Waves (PW)

## 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 conveniently connected by Fourier transform.

The expansion of the periodic part of the functions defined in real space includes only the  $\mathbf{G}$  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**

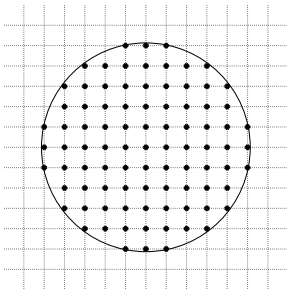
$$\langle \varphi_{\mathbf{G}'} | \varphi_{\mathbf{G}} \rangle = \delta_{\mathbf{G}', \mathbf{G}}$$

- 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

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



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

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.

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

## Fast Fourier Transform (FFT)

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

Information contained in  $\psi(\mathbf{G})$  and  $\psi(\mathbf{R})$  are equivalent.  
Transform from  $\psi(\mathbf{G})$  to  $\psi(\mathbf{R})$  and back is done using Fourier methods. If the number of grid points can be decomposed into small prime numbers fast Fourier transform techniques can be used.

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

## Integrals

$$\begin{aligned} I &= \int_{\Omega} A^*(\mathbf{r})B(\mathbf{r})d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^*(\mathbf{G})B(\mathbf{G}') \int \exp[-i\mathbf{G} \cdot \mathbf{r}] \exp[i\mathbf{G}' \cdot \mathbf{r}]d\mathbf{r} \\ &= \sum_{\mathbf{G}\mathbf{G}'} A^*(\mathbf{G})B(\mathbf{G}') \Omega \delta_{\mathbf{G}\mathbf{G}'} \\ &= \Omega \sum_{\mathbf{G}} A^*(\mathbf{G})B(\mathbf{G}) \end{aligned}$$

Parseval's theorem

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

Integrals in real space and in reciprocal space are equivalent

## Long Range Term in Coulomb Energy

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

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

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

Plane wave expansion of total charge density

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

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

## Exchange-Correlation (XC) Functionals

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

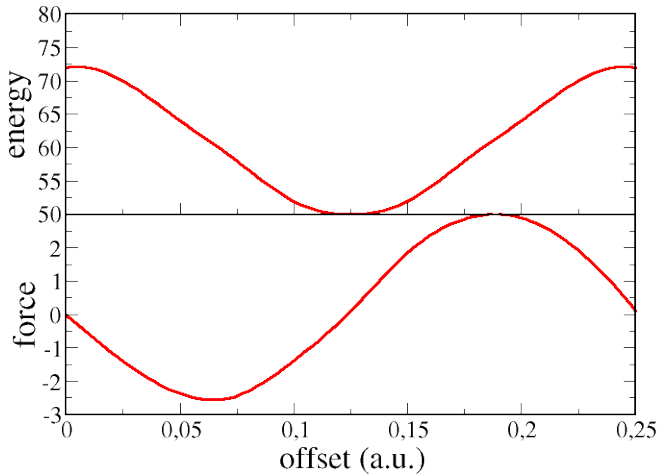
$\varepsilon_{xc}(\mathbf{G})$  is not local in  $\mathbf{G}$  space. Calculation in real space requires very accurate integration scheme.

New definition of  $E_{xc}$

$$E_{xc} = \frac{\Omega}{N_x N_y N_z} \sum_{\mathbf{R}} \varepsilon_{xc}(\mathbf{R}) \rho(\mathbf{R}) = \Omega \sum_{\mathbf{G}} \tilde{\varepsilon}_{xc}(\mathbf{G}) n(\mathbf{G})$$

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

## Energy and Force of He Atom





# KS-DFT GPW Energy

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

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:

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

$$\tilde{\rho}_{\text{tot}}(\mathbf{G}) = \tilde{\rho}(\mathbf{G}) + \sum_A \rho_A(\mathbf{G})$$

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

- $E_{\text{KS}}^{\text{GPW}}$  is variational in the GTO coefficients  $c_{\alpha i}$  alone.
- $\tilde{\rho}(\mathbf{G})$  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  $R = A - B$

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

$\downarrow$  sparsity pattern

$$T_{\alpha\beta}$$

- Density on the real space grid

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

$\downarrow$  overlap screening

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

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

# Screening

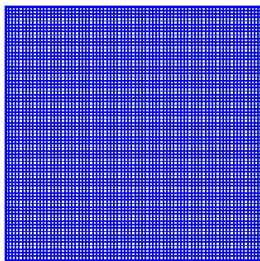
- All individual screening thresholds can be controlled by `EPS_DEFAULT`

`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  $\varphi_{\alpha\beta}$ )

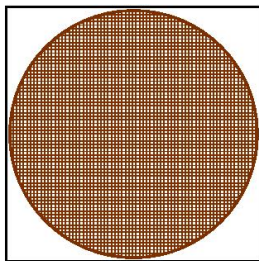
## Real Space Grid

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



Real Space

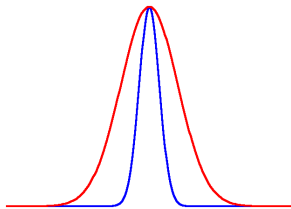
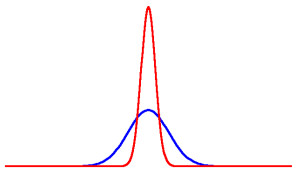
FFT  
↔



G-Space

## Gaussians and Plane Waves

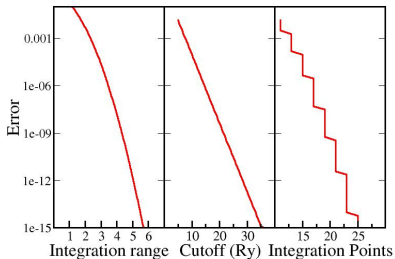
$$\sqrt{\frac{\alpha}{\pi}} \exp(-\alpha r^2) \xrightarrow{\text{FFT}} \exp\left(-\frac{\mathbf{G}^2}{4\alpha}\right)$$



- Efficient screening in R space
- Exponential convergence for integration

# GTOs and PW

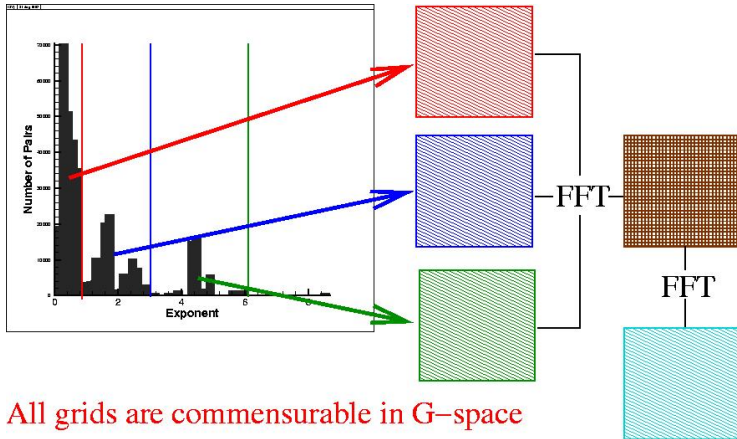
## Integration



For the integration 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.

$\approx 5000$  integration points/integral batch

# Multigrid



## PW Cutoff

- Density expansion

PW cutoff and multigrid settings determine accuracy and efficacy 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

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

LDA vs. GGA vs. Meta-functionals

$\rho$  vs.  $(\nabla\rho)^2/\rho^{4/3}$  vs.  $\tau$

DENSITY\_CUTOFF, GRADIENT\_CUTOFF, TAU\_CUTOFF

in FORCE\_EVAL / DFT / XC

See more advanced options

in FORCE\_EVAL / DFT / XC / XC\_GRID

# Coulomb Potential

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

$\underbrace{\hspace{15em}}_{\mathcal{O}(n \log n)}$

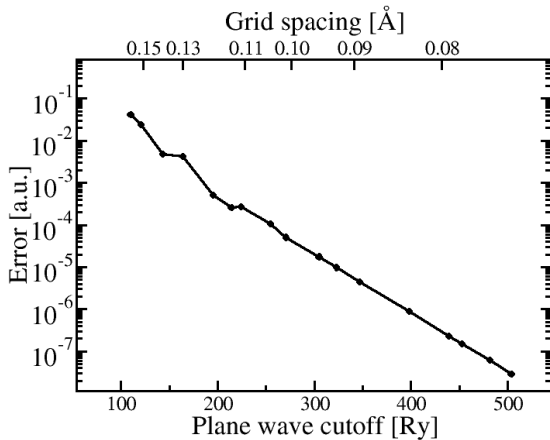
$$\rho(\mathbf{R}) = \sum_{\mu\nu} \mathbf{P}_{\mu\nu} \chi_{\mu}(\mathbf{R}) \chi_{\nu}(\mathbf{R}) = \sum_{\mu\nu} \mathbf{P}_{\mu\nu} \bar{\chi}_{\mu\nu}(\mathbf{R})$$

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

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

# Accuracy of Plane Wave Expansion

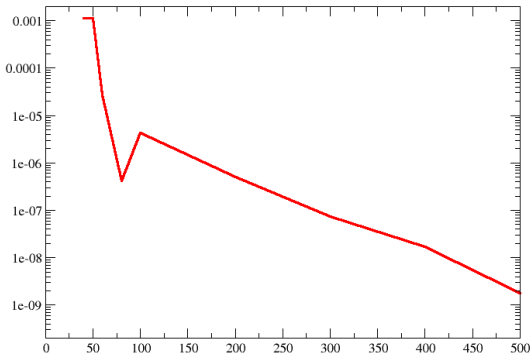
## Coulomb Energy



# Accuracy of Plane Wave Expansion

## XC Energy

PBE functional, Bulk Silicon



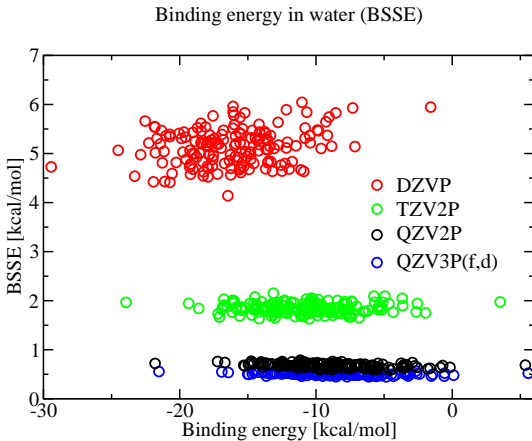
## Accuracy and Numerical Errors

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

| eps_def | cutoff   | ngrids | time | Energy       |
|---------|----------|--------|------|--------------|
| -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)

## BSSE in liquid water



## 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
- Use Wavelet solvers  
Genovese et al, JCP 2006, 125 074105
- Use 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 transferred from atomic reference calculation
- Core electrons of different atoms do not overlap

## Remaining Problems

- Valence wavefunctions have to be orthogonalized to core states  
→ nodal structures → 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

$$E_{\text{XC}}(\rho_c + \rho_v) = E_{\text{XC}}(\rho_c) + E_{\text{XC}}(\rho_v)$$

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)  
 $\Rightarrow \Phi_j^V(\mathbf{r})$  and  $\epsilon_j$ .
2. Pseudize  $\Phi_j^V \Rightarrow \Phi_j^{\text{PS}}$
3. Calculate potential from

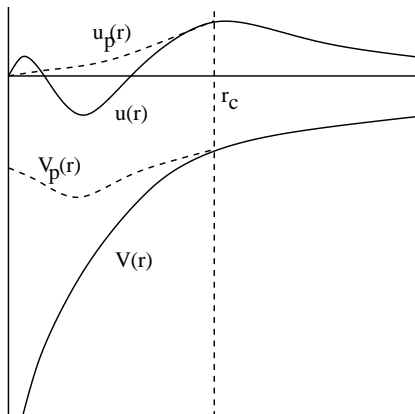
$$(T + V_i(\mathbf{r})) \Phi_j^{\text{PS}}(\mathbf{r}) = \epsilon_j \Phi_j^{\text{PS}}(\mathbf{r})$$

4. Calculate pseudopotential by unscreening of  $V_i(\mathbf{r})$

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

$V_i^{\text{PS}}$  is state dependent !

# Pseudization of Valence Wavefunctions



# Semi-local Pseudopotentials

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

## Separation of Local and Nonlocal Parts

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

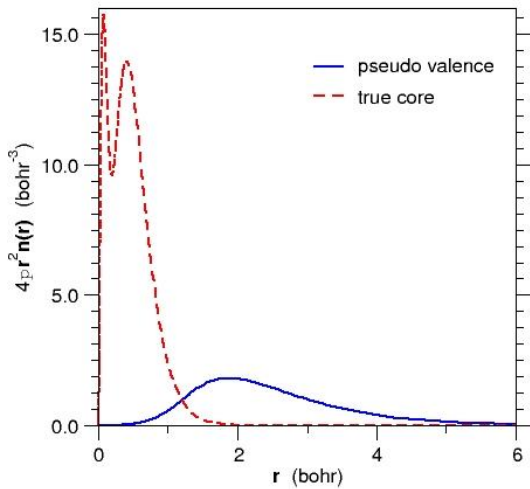
$$V^{\text{PS}}(\mathbf{r}, \mathbf{r}') = \sum_{L=0}^{L_{\text{max}}} (V_L^{\text{PS}}(r) - V_{\text{loc}}^{\text{PS}}(r)) |Y_L\rangle \langle Y_L| + V_{\text{loc}}^{\text{PS}}(r)$$

## Final Form

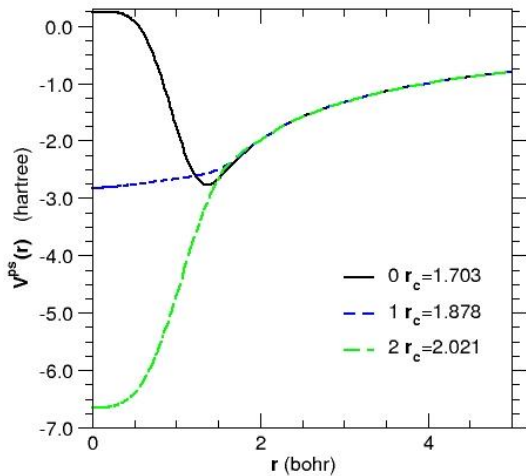
$$V^{\text{PS}}(\mathbf{r}, \mathbf{r}') = V_{\text{loc}}^{\text{PS}}(r) + \sum_{L=0}^{L_{\text{max}}} \Delta V_L^{\text{PS}}(r) |Y_L\rangle \langle Y_L|$$

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

### 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  $\varphi_L$  is the pseudo-atomic wavefunction from the reference calculation.

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

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  $\langle\Delta V_L\varphi_L | \Phi_i\rangle$ .



## 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:  $[\bar{r} = \frac{r}{r_c}]$

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

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

- Global optimization of all parameters to fit atomic orbital energies of occupied and virtual orbitals.

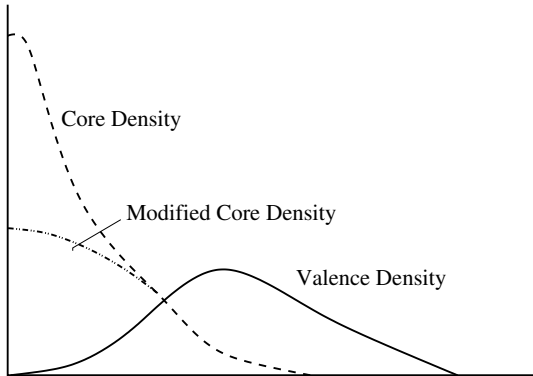
## Non-Linear Core Correction (NLCC)

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
  - 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)

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



# 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  $\rightarrow$  no lone diffuse functions, well conditioned
- diffuse primitives  $\rightarrow$  reduced BSSE
- molecularly optimized  $\rightarrow$  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      |

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

# Hartree-Fock Exchange: Hybrid Functionals

$$E_X^{\text{HF}} = \sum_{\alpha\beta} \sum_{\gamma\sigma} P_{\alpha\beta} P_{\gamma\sigma} (\alpha\gamma | \beta\sigma)$$

- Performance problems  
Density fitting methods don't work (almost).
- Periodic boundary conditions, correct limits.
- Stability for large basis sets.

Implementation in CP2K:

M. Guidon et al. J. Chem. Phys. **128** 214104 (2008)

M. Guidon et al. J. Chem. Theory Comput., **5**, 3010 (2009)



# Algorithms

- Truncated Coulomb operator or short range hybrids

$$\frac{\text{erfc}(r)}{r} \quad \begin{array}{l} \frac{1}{r_{12}}, \quad r_{12} < R_c \\ 0, \quad r_{12} > R_c \end{array}$$

## Stability in PBC

- Integral screening

$$(\mu\nu^{\mathbf{a}}|\lambda^{\mathbf{b}}\sigma^{\mathbf{b}+\mathbf{c}}) \leq |(\mu\nu^{\mathbf{a}}|\mu\nu^{\mathbf{a}})|^{\frac{1}{2}} \cdot |(\lambda\sigma^{\mathbf{c}}|\lambda\sigma^{\mathbf{c}})|^{\frac{1}{2}}$$

## Linear scaling HFX

- Integral compression

$$0.00012345566777 \longrightarrow 12345$$

## Incore storage of integrals

## Example

PBC, HSE06 functional, 6-31G(d,p) basis, Opteron 64 core

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|                   | $(\text{H}_2\text{O})_{32}$ | $(\text{H}_2\text{O})_{64}$ | $(\text{H}_2\text{O})_{128}$ | $(\text{H}_2\text{O})_{256}$ |
|-------------------|-----------------------------|-----------------------------|------------------------------|------------------------------|
| Basis functions   | 768                         | 1536                        | 3072                         | 6144                         |
| ERIs [millions]   | 761                         | 1822                        | 3439                         | 6795                         |
| Memory usage [MB] | 264                         | 536                         | 1062                         | 2130                         |
| Compression       | 7.92                        | 7.72                        | 7.64                         | 7.66                         |
| CPU-time [s]      | 25                          | 64                          | 174                          | 459                          |

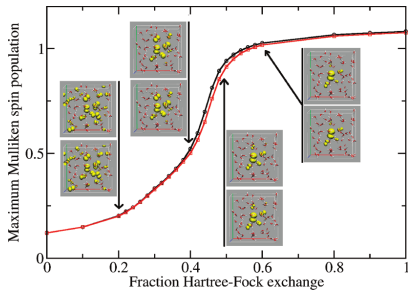
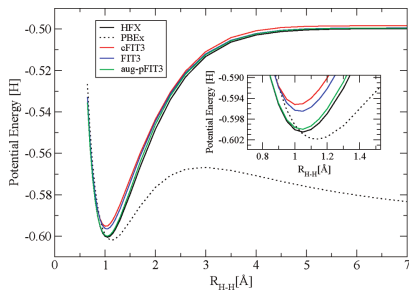
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# Auxiliary Density Matrix Method (ADMM)

$$E_x(P) \approx \tilde{E}_x(D, P) = E_x(D) + E_x^{\text{PBEX}}(P) - E_x^{\text{PBEX}}(D)$$

$$D = f(P)$$



## Benchmark: Rubredoxin

Pseudopotentials, DZVP Basis (22910 bfs), 3897 electrons

| Basis set | CPU | Functional | Timings [s]    |          |
|-----------|-----|------------|----------------|----------|
|           |     |            | Initialization | SCF Step |
| DZVP      | 256 | BLYP       | 230            | 117      |
| DZVP/FIT3 | 256 | B3LYP      | 604            | 246      |
| DZVP/FIT3 | 512 | B3LYP      | 305            | 140      |

Overhead of ADMM hybrid calculation:  $\approx 2 - 4\times$

# ADMM Methods

- M. Guidon et al, J. Chem. Theory Comput., 2010, 6, 2348-2364
  - ADMM1 : projection and full orthonormalization
  - ADMM2 : projection only
  - Block-ADMM : use selected blocks of P matrix
- P. Merlot et al, J Chem Phys. 2014, 141 094104
  - ADMMQ : projection and normalization
  - ADMMS : projection and normalization and scaling
  - ADMMP : projection and normalization and selected scaling

# ADMM Example

## Bandgap of Diamond

| method     | number of integrals | gap [eV] |
|------------|---------------------|----------|
| PBE (PBS)  |                     | 4.17     |
| PBE (ABS)  |                     | 4.37     |
| PBE0 (PBS) | 40 787 850 778 591  | 6.07     |
| PBE0 (ABS) | 23 561 509 497      | 6.25     |
| PBE0 ADMM1 | 24 816 897 009      | 6.03     |
| PBE0 ADMM2 | 24 795 460 638      | 6.02     |

# 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  $c^{\text{out}}$
4. calculate new density  $n^{\text{out}}$
5. if  $|n^{\text{in}} - n^{\text{out}}| \leq \epsilon$  stop
6. calculate new density from  $n^{\text{in}}$  and  $n^{\text{out}}$  (mixing)
7. go back to 2

# Direct Minimization Methods

Minimum  $[E_{\text{KS}}(\mathbf{c})]$  with the constraint  $\sum_{\alpha} \mathbf{c}_{\alpha i}^* \mathbf{c}_{\alpha j} = \delta_{ij}$

## Lagrange function

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

## Gradient

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



# 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  $MN^2$

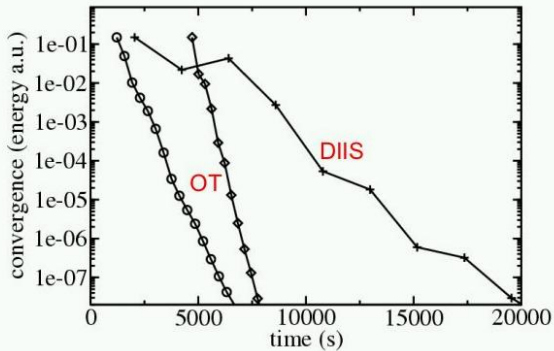
N Number of occupied orbitals

- Set of reference occupied orbitals:  $\mathbf{C}_0$
- New variables  $\mathbf{X}$

$$\mathbf{C}(\mathbf{X}) = \mathbf{C}_0 \cos \mathbf{U} + \mathbf{X} \mathbf{U}^{-1} \sin \mathbf{U}$$
$$\mathbf{U} = \left( \mathbf{X}^T \mathbf{S} \mathbf{X} \right)^{1/2}$$

- Linear constraint  $\mathbf{X}^T \mathbf{S} \mathbf{C}_0 = 0$
- Standard optimization with line search 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

$$\mathbf{x}_{M+1} = \sum_{i=1}^M c_i \mathbf{x}_i \text{ with the constraint } \sum_{i=1}^M c_i = 1.$$

# DIIS

## Ansatz

$$\text{Min} \left[ \left\langle \sum_{i=1}^M c_i \mathbf{e}_i \middle| \sum_{j=1}^M c_j \mathbf{e}_j \right\rangle \right] \quad \text{with} \quad \sum_{i=1}^M c_i = 1$$

where  $\langle . | . \rangle$  is a suitably defined scalar product. This leads to a system of linear equations with  $b_{ij} = \langle \mathbf{e}_i | \mathbf{e}_j \rangle$

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

## 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)

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

### **GDIIS (based on Newton–Raphson)**

$$\mathbf{e}_i = -\mathbf{P}\mathbf{g}(\mathbf{x}_i)$$

## Scaling of GPW Calculations

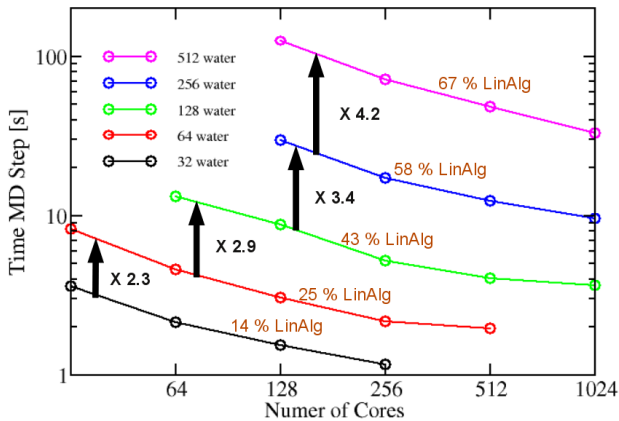
- N: Number of occupied orbitals, number of electrons
- M: Number of basis functions

Kohn-Sham matrix  $\mathcal{O}(M \log N)$

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

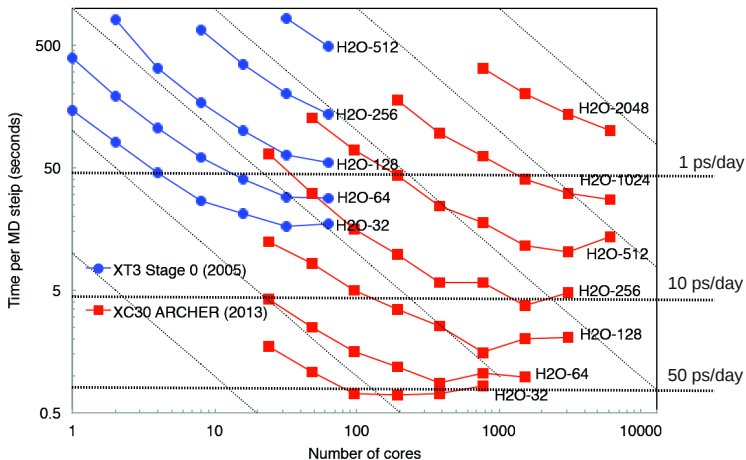
OT optimization  $\mathcal{O}(MN^2)$

# System Size Scaling





# Efficiency: GGA Functionals



## Linear Scaling KS-DFT

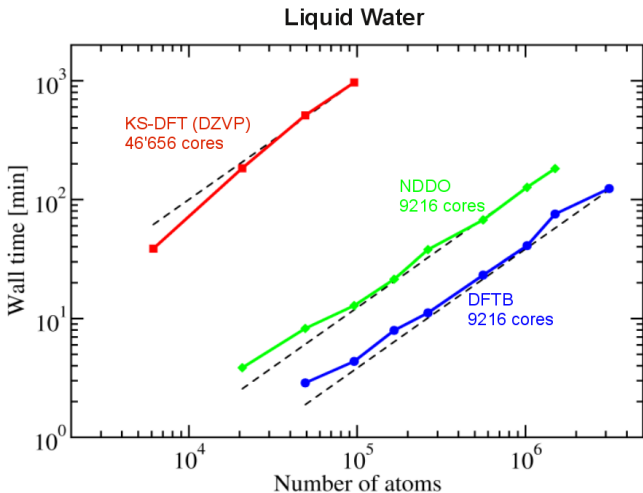
$$P = \text{sign} \left( S^{-1} H - \mu I \right) S^{-1}$$

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

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

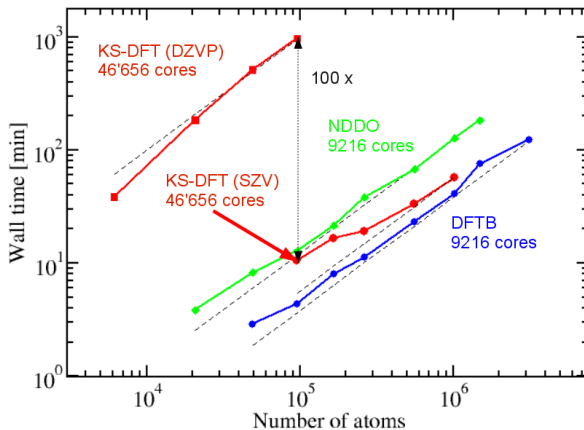
Only matrix multiplications required.

# Linear Scaling



# Linear Scaling

## Liquid Water

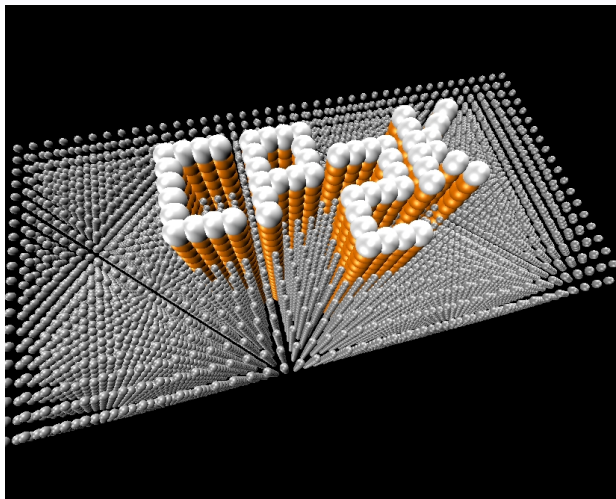


# PAO-ML

**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<sup>a</sup>**

| 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 |

<sup>a</sup>The PAO-ML method outperforms a standard DFT run with a DZVP-MOLOPT-GTH basis by a factor of at least 50X.



[www.cp2k.org](http://www.cp2k.org)