DMol^3

A Standard Tool for Density-Functional Calculations

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Introduction

What is DMol³?

· **all-electron DFT-code**

· **basis functions are localized atomic orbitals (LCAO)**

· **can be applied to:**

 · **free atoms, molecules and clusters**

 · **solids and surfaces (slabs)**

Topic of this talk

Characteristics of the DMol³ approach to DFT (*selected* aspects)

History

"DMol" = **_d_**ensity functional calculations on **_mol_**ecules

Main author:

Bernard Delley

Further contributions by:

J. Andzelm	R.D. King-Smith
J. Baker	D. Ellis
G. Fitzgerald	many more...

- **first fragments**   **early 1980's**
  (full potential electrostatics, numerical atomic orbitals)
- **total energy functional**   **1983**
- **electrostatics by partitioning**   **1986**
- **first release of DMol by Biosym**   **1988**
- **forces**   **1991**
- **parallel version**   **1992**
- **DSolid**   **1994**
- **geometry optimization**   **1996**
- **unification of DMol and DSolid**
  ⊳ DMol³   **1998**
- **molecular dynamics**   **2002**

Localized Basis Sets

Why?

- **high accuracy (cusp, asymptotic behaviour)**
- **high efficiency (few basis functions ⊳ small matrix size)**

What?

- **Gaussian type orbitals   (GTO's)**
- **Slater type orbitals   (STO's)**
- **numerical atomic orbitals (AO's)**

Idea:

Most DFT codes use numerical integration (i.e. for XC-part)
⊳ in DMol^3: numerical techniques used wherever possible
⊳ AO's can be used

DMol³ Basis Functions

- exact DFT-spherical-atomic orbitals of
  - neutral atoms
  - ions
  - hydrogenic atoms
- radial functions are calculated in the setup (free atom)
- implemented as numerically tabulated functions

Properties:
- maximum of accuracy for a given basis set size
- infinitely separated atoms limit treated *exactly*
- small number of additional functions needed for polarization
- square integrability, cusp singularities at the nuclei

Basis Set Example: Al

Atomic energy

minimal: **Al 1s, 2s, 2p, 3s, 3p**   ▷ **E = -242.234806 Ha**
9 AOs

dn: **Al^{2+} 3s, 3p**   ▷ **E = -242.234845 Ha**
13 AOs

dnd: **$z = 5$ 3d**   ▷ **E = -242.235603 Ha**
18 AOs

dnp: **$z = 4$ 3p, $z = 7.5$ 4f**   ▷ **E = -242.235649 Ha**
28 AOs

Quality test:
lowering of total energy by adding basis functions
(*variational principle*)

Basis Set Example: Al

Radial Basis Functions
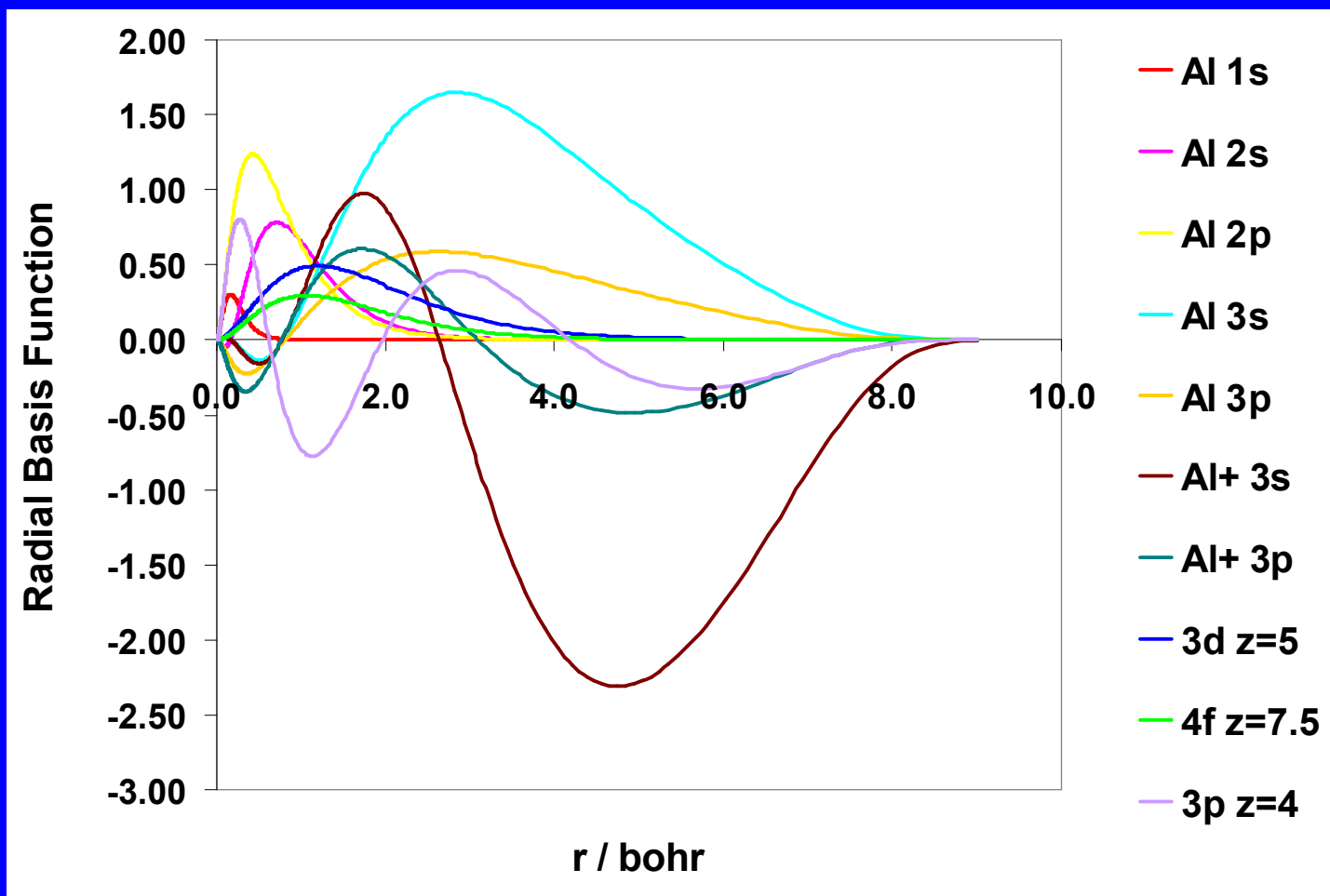
Basis Set Convergence

Atomic orbitals

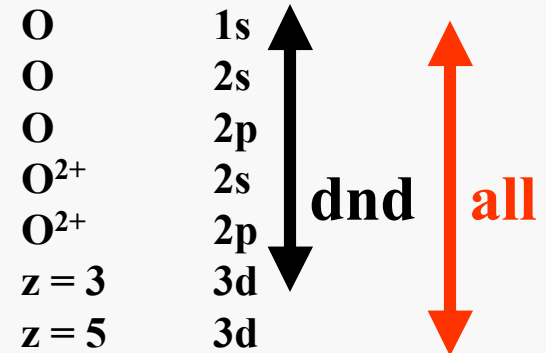quality   ▷ basis set

extension   ▷ r^{cut}

Plane waves

quality   ▷ E^{cut}

extension   ▷ infinte

Basis test for the oxygen molecule

O basis functions

O	1s
O	2s
O	2p
O^{2+}	2s
O^{2+}	2p
$z = 3$	3d
$z = 5$	3d

dnd   all
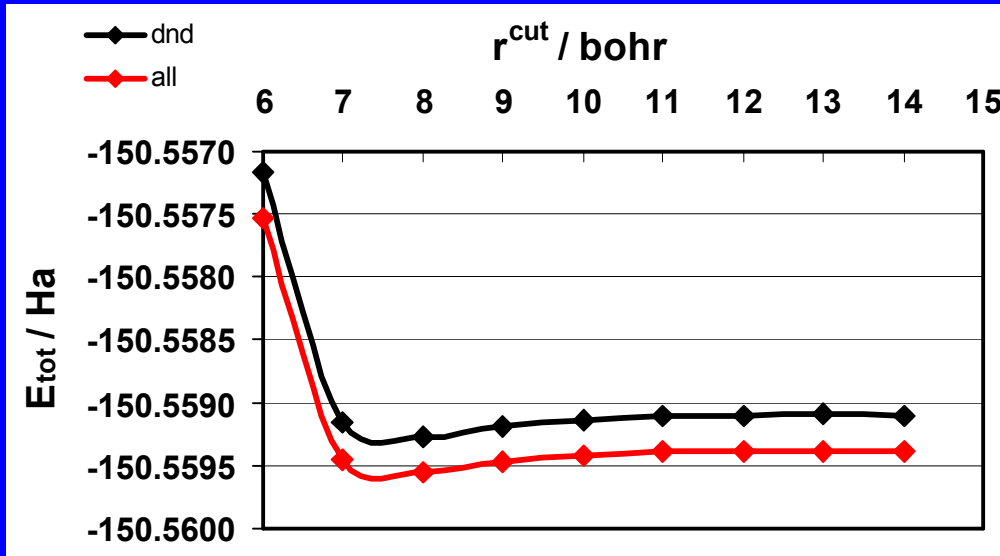
BSSE

Basis Set Superposition Error

Definition:
BSSE is a lowering of the energy when the electrons of each atom spread into the basis functions provided by the other atoms due to an incomplete basis set.

Plane waves: BSSE does not appear

GTO/STO Codes: BSSE can be a serious problem

DMol³: very small BSSE because of nearly perfect basis set for the separated atoms limit
=> excellent description of weak bonds (but DFT limitation)

Summary Basis Functions

Advantages

- very efficient (small) basis ⊐ fast calculations
- allows for calculations without periodic boundary conditions or less dense systems (slabs with large vacuum)
- easy physical interpretation of basis functions
- (almost) no basis set superposition error
- different basis sets for different elements possible

Disadvantages

- no systematic way to improve basis set quality
- careful tests required to construct a basis set

Numerical Integration

3 Step approach

1. **Decomposition of the total integral in 3D into a sum of independent integrals for atomic contributions**
   ⊳ partitioning

2. **Decomposition of each atomic integral into a radial and an angular part ⊳ spherical polar coordinates**

3. **Integration of the angular part on a sphere or decomposition into separate integrations for $\cup$ and $\digamma$**

Partition Functions

1. Step: Decomposition into atomic contributions

Partition functions p_a are used to rewrite integrals over all space:

$$\int f(\mathbf{r})\, d\mathbf{r} = \int \sum_a f_a(\mathbf{r}_a)\, d\mathbf{r} = \int \sum_a f(\mathbf{r}) p_a(\mathbf{r})\, d\mathbf{r}$$

▷ **Sum of atomic integrals**

$$\int f(\mathbf{r})\, d\mathbf{r} = \sum_a \int f_a(\mathbf{r}_a)\, d\mathbf{r}$$

Enables integration using *spherical polar coordinates*!

Partition Functions

Definition:

The partition function for a center a:

$$p_a(r) = \frac{g_a(r)}{\sum_b g_b(r)}$$

Normalization:

$$\sum_a p_a = 1$$

· **choose one peaked function g_a for each center** a

· **calculate the partition function for each center** a

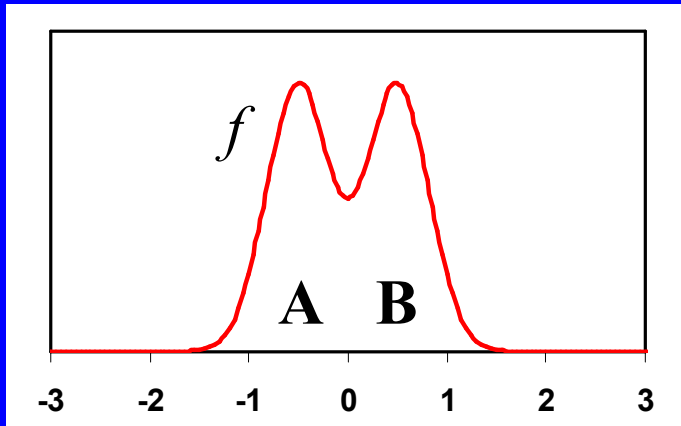**Example:** $\quad g_a = \left(\dfrac{r_a}{r_a}\right)^2$

Example:

g_a

R_a
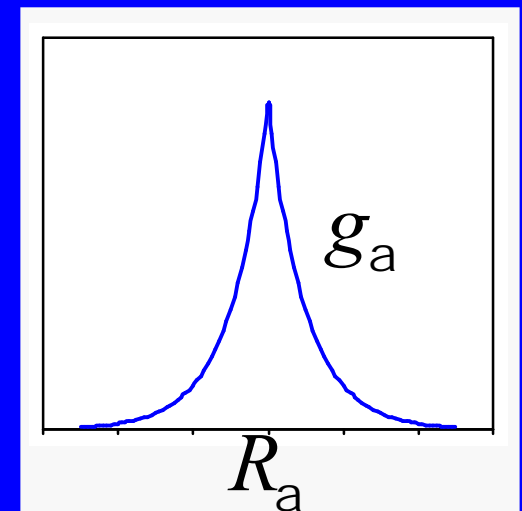
Partition Functions

Total function:

Peaked functions g_A and g_B:
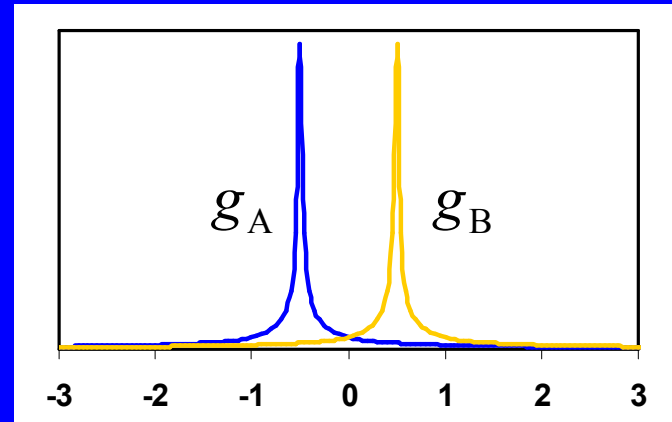
Partition functions:
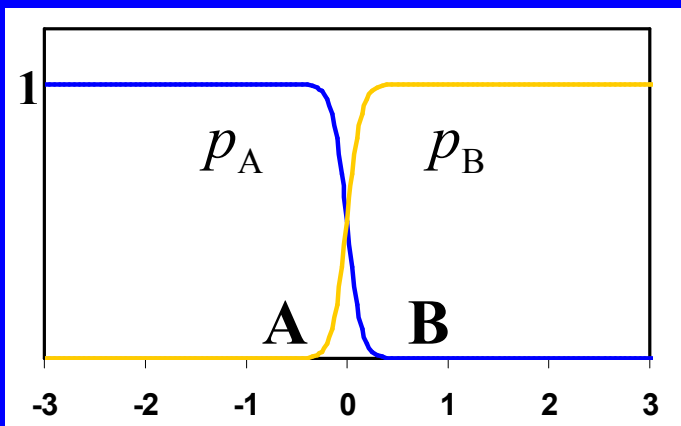
Decomposed functions:
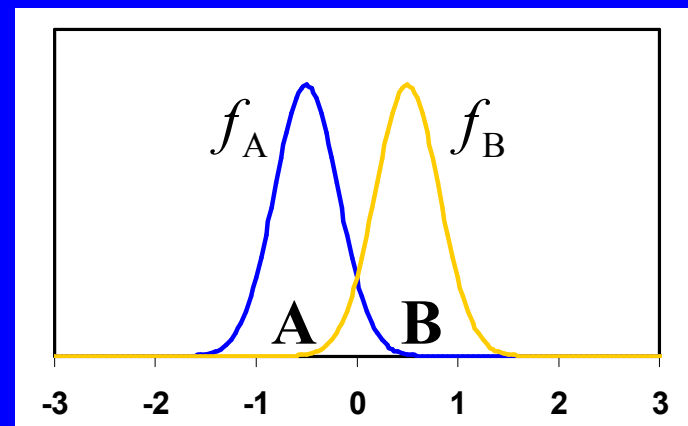
Numerical Integration
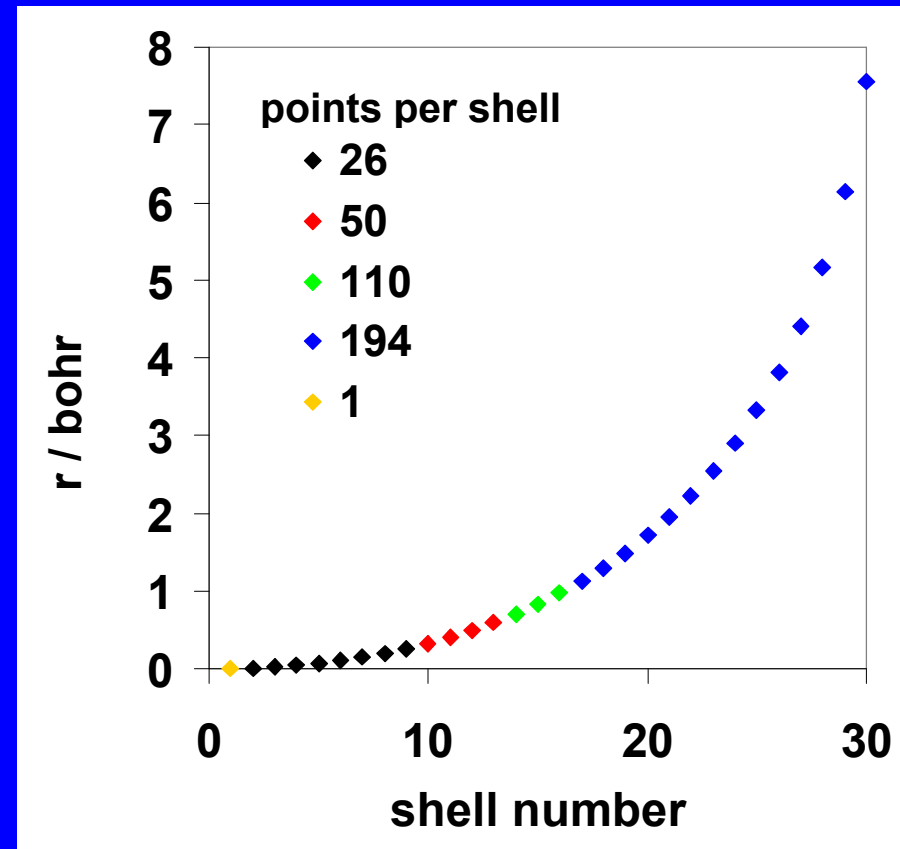
Example: O atom

Radial Integration Meshes

Number of radial shells

$$n = s \cdot 14 \cdot (z+2)^{\frac{1}{3}} = 30$$

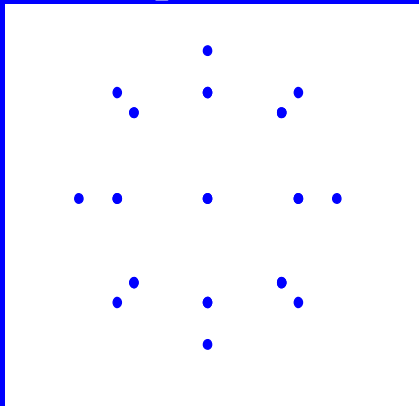z = atomic number
s = scaling factor

Numerical Integration

Example: O atom

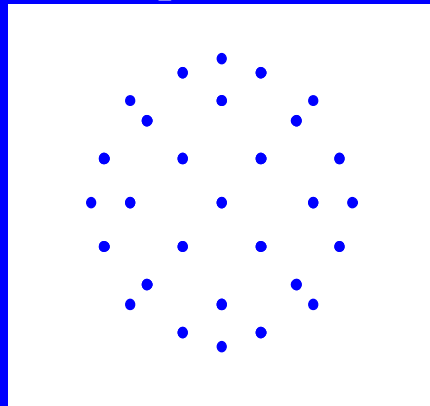## Angular Integration Meshes

- integration is done on *Lebedev Spheres*
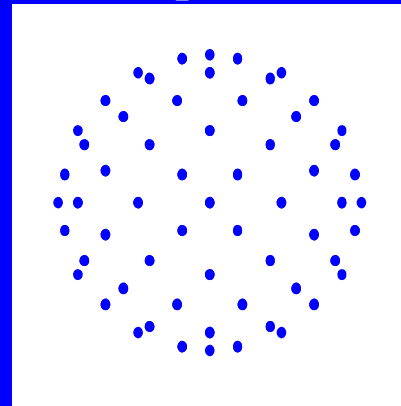- integration scheme with octahedral symmetry

Order 7	Order 11	Order 17	Order 23
26 points	50 points	110 points	194 points
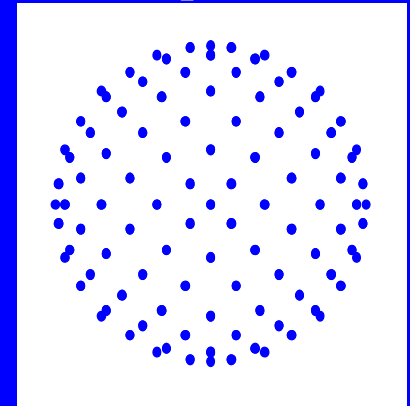
(projections of points on sphere into plane)

Numerical Integration

Example: O atom (cutoff 10 bohr)

Total Grid:
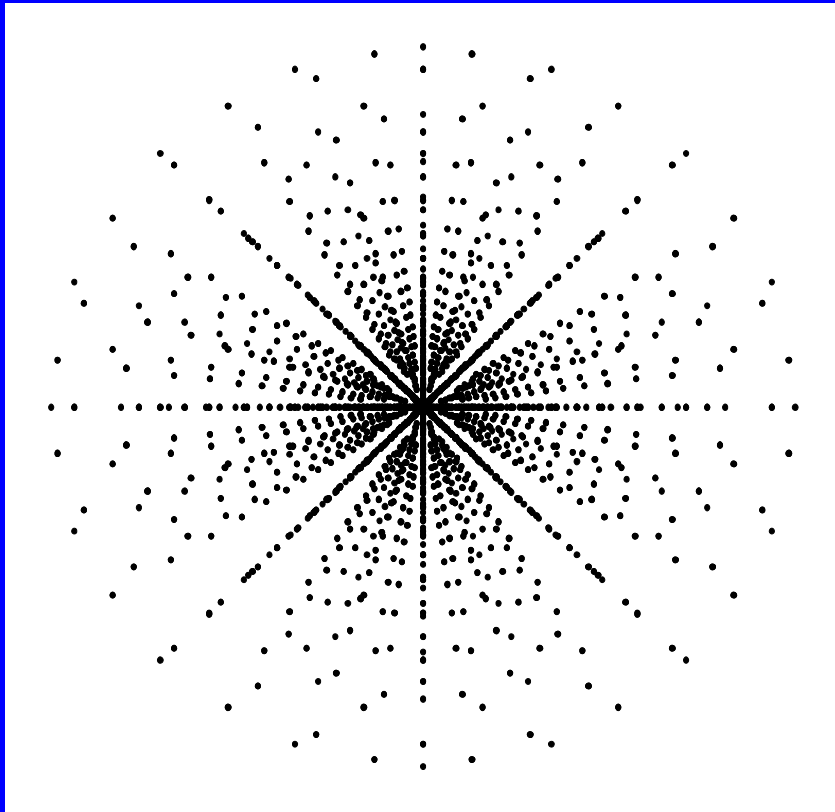
3287 points

Remarks:

- user defined grids
- higher order angular schemes are possible
- symmetry is used to reduce number of points
- a weight is assigned to each point
- in a molecule or solid a superposition of atomic meshes is used

Numerical Integration

Effect of mesh quality: total energy of the Al atom

Electrostatics

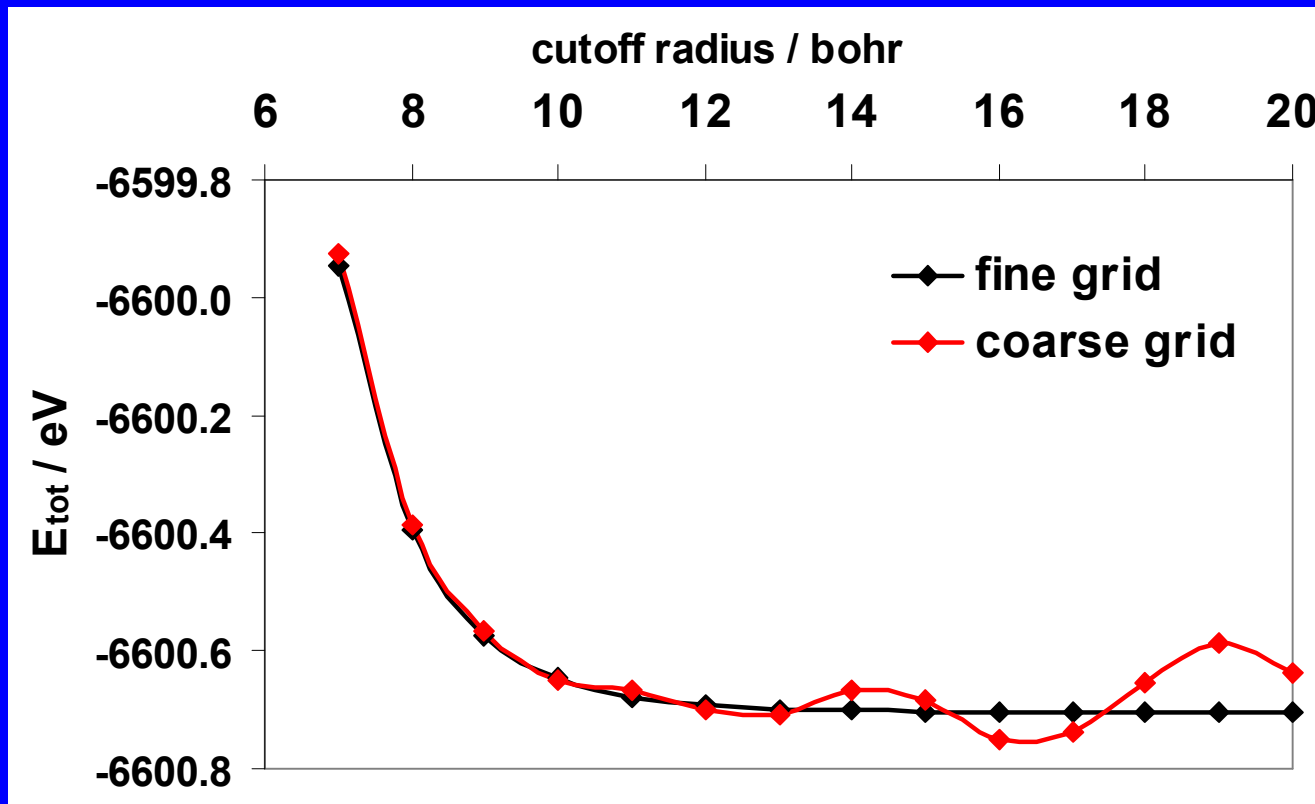**Classical electrostatic contribution in Hamiltonian**

$$J[\mathsf{r}] = \frac{1}{2} \iint \frac{\mathsf{r}(\mathbf{r}_1)\mathsf{r}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Matrix elements

Hartee-Fock

$$J_{mn} = \sum_{l=1}^{L} \sum_{s=1}^{L} P_{ls} \iint \frac{\mathsf{c}_m(\mathbf{r}_1)\mathsf{c}_n(\mathbf{r}_1)\mathsf{c}_l(\mathbf{r}_2)\mathsf{c}_s(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

DFT

$$J_{mn} = \iint \frac{\mathsf{c}_m(\mathbf{r}_1)\mathsf{c}_n(\mathbf{r}_1)\mathsf{r}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Electrostatics

Common procedure in DFT using localized basis functions:

Density-fitting using an auxiliary basis set $\{w_k\}$

auxiliary density   constraint

$$\rho(\mathbf{r}) \approx \tilde{\rho}(\mathbf{r}) = \sum_k c_k w_k(\mathbf{r}) \qquad\qquad \int \tilde{\rho}(\mathbf{r})\, d\mathbf{r} = N$$

The basis functions $\{w_k\}$ **are of the same type as for the wavefunction expansion.**

Matrix elements
O(N^3)

$$J_{mn} = \sum_k c_k \iint \frac{c_m(\mathbf{r}_1) c_n(\mathbf{r}_1) w(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Electrostatics

Approach to electrostatics in DMol^3: Overview

Step 1

> **Partitioning: decompose the electron density into atomic components**

Step 2

> **Projection onto Y_{lm} functions yields multipoles attached to the atoms**

Step 3

> **Solve Poisson's equation for each multipole (only 1-dimensional problem)**

Step 4

> **Assemble electrostatic potential from all multipoles and atoms**

DMol^3: No basis set required for density expansion!

Electrostatics

1. Step: **Partitioning** of total density ρ into atomic densities ρ_a

$\triangleright$ **like numerical integration**

2. Step: Multipole expansion of each ρ_a

$$\rho_{alm}(r) = \frac{1}{\sqrt{4\pi}}\,\frac{1}{\sqrt{2l+1}}\int Y_{alm}(\theta,\phi)\,\rho_a(r,\theta,\phi)\,d\theta\,d\phi$$

$$\rho_a(r,\theta,\phi) \approx \sqrt{4\pi}\sum_{lm}^{l_{\max}}\sqrt{2l+1}\,\rho_{alm}(r)\,Y_{alm}(\theta,\phi)$$

- **truncation of expansion at $l_{\max}$**
- **reduction to 1-dimensional radial density** $\rho_{alm}(r)$

Electrostatics

3. Step: **Calculation of the potential contributions**

Single center Poisson's equation

density decomposition

$$\nabla^2 V_a\left(r,\vartheta,\varphi\right) = -4\pi\rho_a\left(r,\vartheta,\varphi\right)$$

$$\rho_a = \sum \rho_{alm}$$

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}\frac{1}{r} - \frac{l^2}{r^2}$$

spherical Laplacian

$$V_a\left(r,\vartheta,\varphi\right) = \sum_{lm}^{l_{\max}}\frac{1}{r}V_{alm}(r)Y_{lm}(\vartheta,\varphi)$$

potential expansion

$\supset$ **set of equations for numerical evaluation of all** $V_{alm}(r)$

Electrostatics

4. Step: **Construction of the total potential from atomic contributions**

$$V_a\left(r, \cup, f\right) \vartriangleright V(\mathbf{r})$$
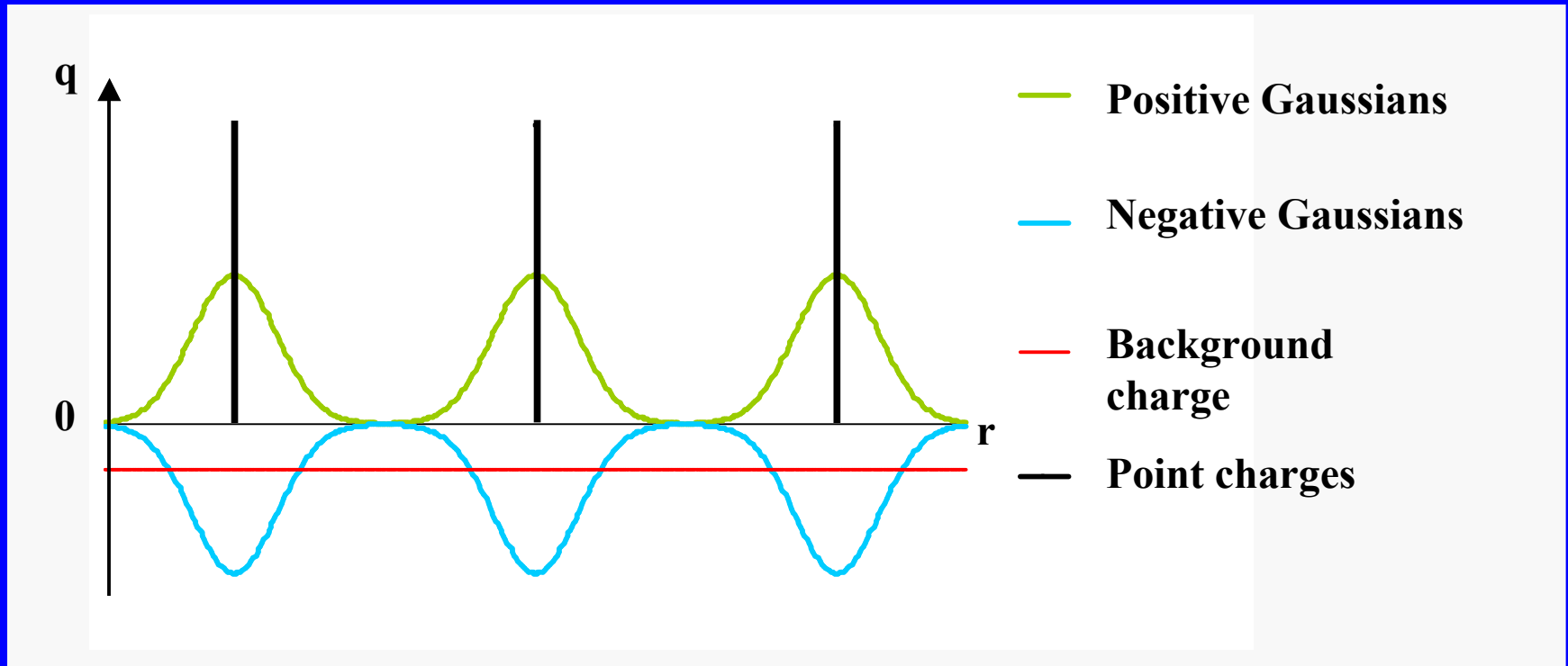
atomic mesh ⊐ **full mesh**

Calculation of the electrostatic potential: $O(N^2)$

For periodic boundary conditions an *Ewald summation* is included.

Ewald Summation for Monopoles

Real space: point charges + negative Gaussians

Reciprocal space: background charge + positive Gaussians

Extensions to Ewald Summation

1. Generalization for lattices with **multipoles**

DMol³ contains an extension to lattices of point multipoles located at the atomic sites:

- applied to the r_{alm}
- computationally as demanding as for point charge lattices

2. Extension to monopoles and multipoles of **finite extent**

Assumption: multipoles are located inside a radius r^{cut}

Ewald terms with $r < r^{cut}$ have to be modified in the real space part, because explicit calculation of the radial details of the extended charge distribution is required.

Electrostatics

Scaling (localized basis sets)

Hartree Fock	$O(N^4)$	
DFT in general	$O(N^3)$	**Real systems:** $\circledR\ O(N^2)$
DMol^3 molecular case	$O(N^2)$	
DMol^3 solid case	$O(N^{3/2})$	

Electrostatics in DMol^3 scale almost *linearly* with system size for large systems

The Harris Functional

Kohn Sham energy functional

$$E_{KS}[\rho] = T[\rho] + E_H[\rho] + E_{XC}[\rho] + E_{ext}[\rho] + E_{nn}$$

Harris energy functional

$$E_{Harris}[\rho] = \sum_{i=1}^{N} f_i \varepsilon_i - E_H[\rho] + E_{XC}[\rho] - \int \mu_{XC}[\rho]\,\rho\,d^3r + E_{nn}$$

Original idea of the Harris functional:

- approximate DFT calculations for very large systems
- non-selfconsistent energy calculation (1 iteration only)
- approximated density = superposition of fragment densities (i.e. atomic densities)

Total Energy in DMol^3

DMol^3 uses the Harris functional (scf densities)

- the Harris functional is stationary at the same density as the Kohn-Sham functional and the two are equal in value at this point
- the curvature of E_{Harris} about the stationary point is smaller than the curvature of E_{KS}
- the density in the Harris functional does not have to be V-representable

Reduction of numerical noise

$$E_{bind} = E_{tot} - \sum E_{atom}^{ref}$$

Realization: subtraction of atomic densities from total densities in integrands

More features ...

- forces
- geometry optimization
- *ab initio* molecular dynamics and simulated annealing
- COSMO (**CO**nductor-like **S**creening **MO**del)
- transition state search
- vibrational frequencies
- Pulay (DIIS) charge density mixing
- pseudopotentials (optional)

Conclusion

- **Fast**
  - very small basis sets, matrix diagonalization O(N^3)
  - no costs for large vacuum or atom / molecules
  - efficient calculation of electrostatics
  - O(N) calculation of Hamilton and overlap matrix
- **Universal**
  - atom, molecule and cluster calculations
  - solids and slabs with periodic boundary conditions
- **Accurate results**
  - comparable to LAPW ⊳ next talk
- **Easy to use**
  - atoms are given in Cartesian coordinates

References

Introduction:

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- B. Delley in "Modern Density Functional Theory: A Tool for Chemistry", *Theoretical and Computational Chemistry Vol. 2*, Ed. by J. M. Seminario and P. Politzer, Elsevier 1995
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- B. Delley, *Comp. Mat. Sci.* <u>17</u> (2000) 122
- J. Baker, J. Andzelm, A. Scheiner, B. Delley, *J. Chem. Phys.* <u>101</u> (1994) 8894
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- B. Delley, M. Wrinn, H. P. Lüthi, *J. Chem. Phys.* <u>100</u> (1994) 5785