

Wavelets for electronic structure calculations and electrostatic problems

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BIGDFT

European project:

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- Group of R. Schneider (Uni Kiel)

http://www-drfmc.cea.fr/sp2m/L_Sim/BigDFT/index.en.html

Basis sets for electronic structure?

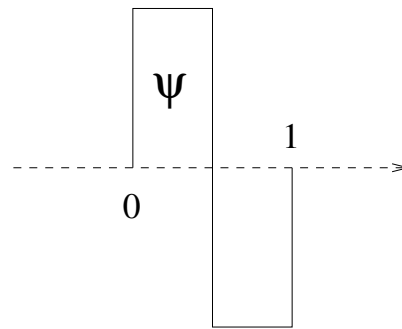
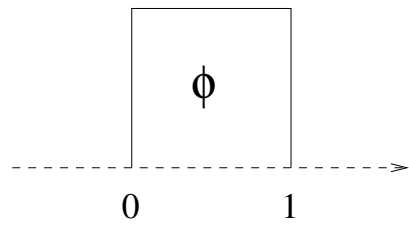
Plane waves:

- Operator approach: no need to set up Hamiltonian matrix
- FFT allows for quasi linear $M \log(M)$ scaling where M is number of plane waves
- Localization in Fourier space allows for efficient preconditioning techniques. Hence number of iterations independent of M
- Systematic convergence properties
- No localization in real space. Empty regions have to be filled with plane waves
- $O(N)$ scaling hard to achieve
- Resolution cannot adaptively be refined around the nucleus. All electron calculations impossible, hard pseudopotentials difficult.

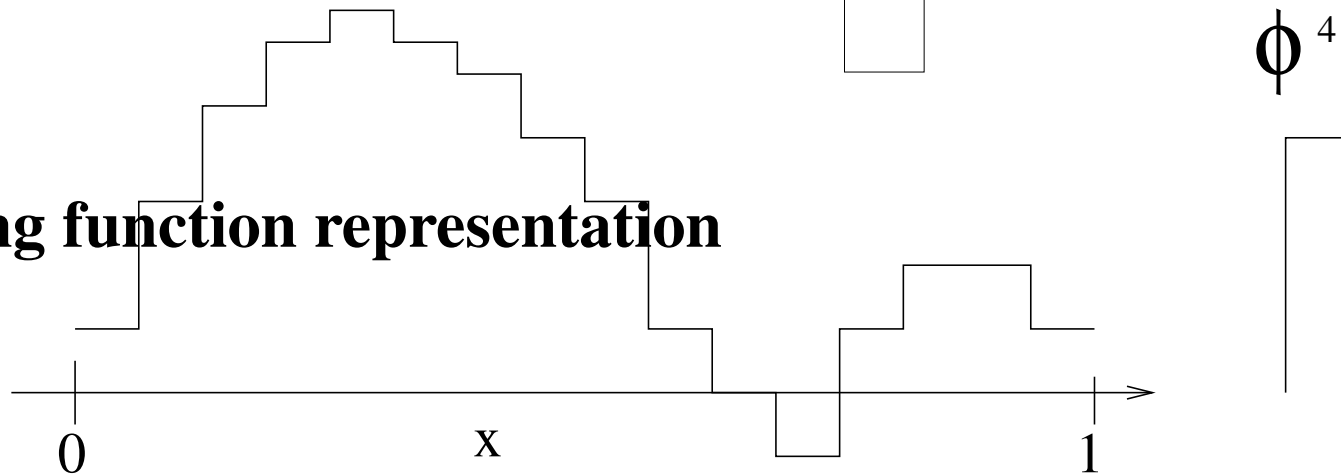
Gaussians:

- Small number of basis functions necessary for moderate accuracy
- Real space localization makes them well suited for molecules and other open structures.
- Kinetic and overlap matrix elements can be calculated analytically.
- Good description of core electrons.
- No systematic convergence. Over-completeness before convergence. This leads also to problems with $O(N)$.
- Many different recipes for generating basis sets.
- Problematic for nanostructure.

Haar wavelet ψ and scaling function ϕ



Scaling function representation



$$f(x) = \sum_j s_j^{Kmax} \phi_j^{Kmax}(x)$$

Refinement relations:

$$\phi(x) = \sum_{j=-m}^m h_j \phi(2x - j)$$

Wavelet basis sets in three dimensions

1 scaling function

7 wavelets

all are products of 1-dim scaling functions and wavelets

$$\phi_{i,j,k}(x,y,z) = \phi(x-i)\phi(y-j)\phi(z-k)$$

$$\psi_{i,j,k}^1(x,y,z) = \phi(x-i)\phi(y-j)\psi(z-k)$$

$$\psi_{i,j,k}^2(x,y,z) = \phi(x-i)\psi(y-j)\phi(z-k)$$

$$\psi_{i,j,k}^3(x,y,z) = \phi(x-i)\psi(y-j)\psi(z-k)$$

$$\psi_{i,j,k}^4(x,y,z) = \psi(x-i)\phi(y-j)\phi(z-k)$$

$$\psi_{i,j,k}^5(x,y,z) = \psi(x-i)\phi(y-j)\psi(z-k)$$

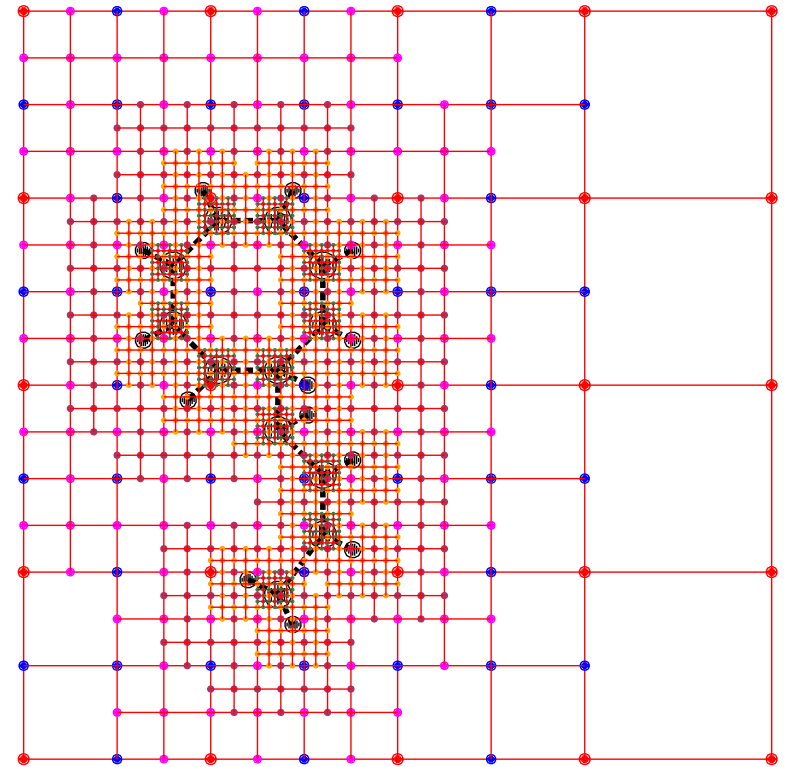
$$\psi_{i,j,k}^6(x,y,z) = \psi(x-i)\psi(y-j)\phi(z-k)$$

$$\psi_{i,j,k}^7(x,y,z) = \psi(x-i)\psi(y-j)\psi(z-k)$$

Wavelet basis sets

Properties of wavelet basis sets:

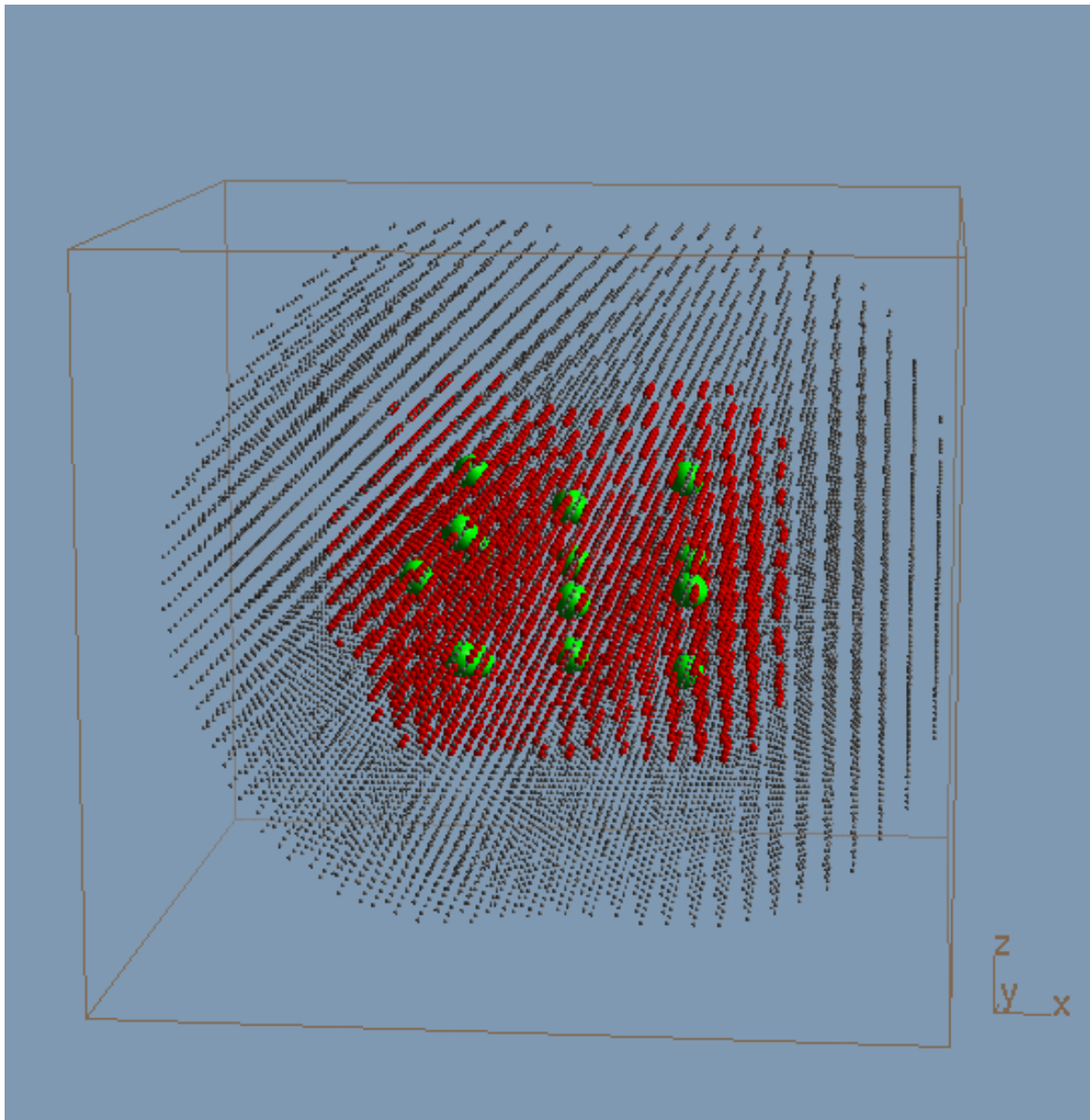
- localized both in real and in Fourier space
- allow for adaptivity



- are a systematic basis set
- A lot of obstacles had to be overcome

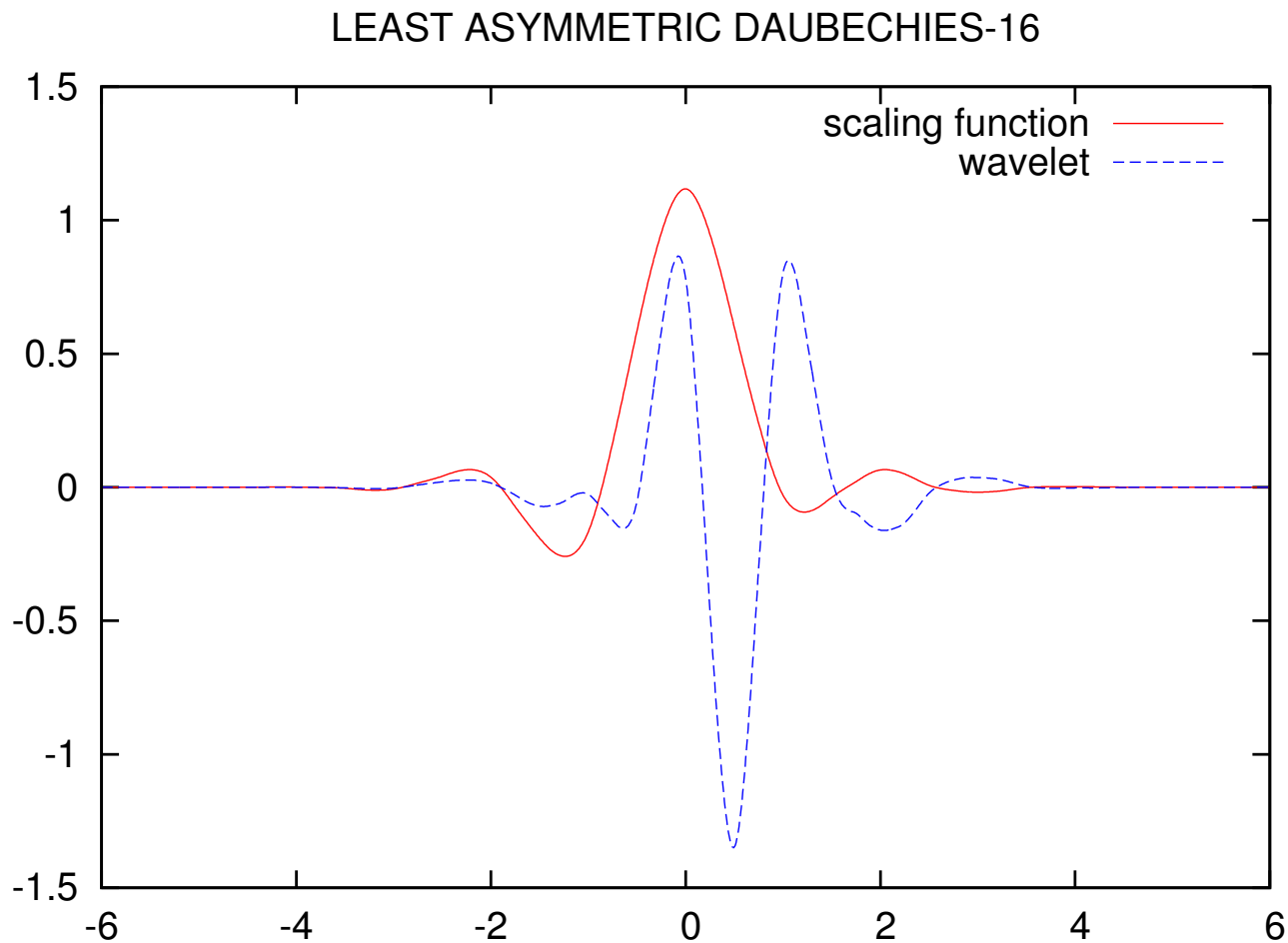
Basic choices in the BIGDFT code

- Only 2 resolution levels are used: simple adaptivity



High order Daubechies wavelets are used to represent wavefunctions

- orthogonality is very helpful (orthogonalization, nonlocal pseudopotential)
- high convergence rate



- Pseudopotentials are used
 - Pseudopotentials eliminate the chemically inactive core electrons and reduce thus the number of electron orbitals
 - Pseudopotentials are the simplest way to introduce relativistic effects into a non-relativistic calculation
 - The pseudopotential approximation is less severe than the approximate nature of the exchange correlation functional

Gaussian type separable Pseudopotentials Local part:

$$V_{loc}(r) = \frac{-Z_{ion}}{r} \operatorname{erf}\left(\frac{r}{\sqrt{2}r_{loc}}\right) + \exp\left(-\frac{1}{2}\left(\frac{r}{r_{loc}}\right)^2\right) \left(C_1 + C_2 \left(\frac{r}{r_{loc}}\right)^2 + C_3 \left(\frac{r}{r_{loc}}\right)^4 + C_4 \left(\frac{r}{r_{loc}}\right)^6 \right)$$

Nonlocal (separable) part $H(\vec{r}, \vec{r}')$

$$H^{sep}(\vec{r}, \vec{r}') = \sum_{i=1}^2 \sum_m Y_{s,m}(\hat{r}) p_i^s(r) h_i^s p_i^s(r') Y_{s,m}^*(\hat{r}') + \sum_m Y_{p,m}(\hat{r}) p_1^p(r) h_1^p p_1^p(r') Y_{p,m}^*(\hat{r}')$$

$$p_1^l(r) = \sqrt{2} \frac{r^l e^{-\frac{1}{2}\left(\frac{r}{r_l}\right)^2}}{r_l^{l+\frac{3}{2}} \sqrt{\Gamma(l+\frac{3}{2})}}$$

$$p_2^l(r) = \sqrt{2} \frac{r^{l+2} e^{-\frac{1}{2}\left(\frac{r}{r_l}\right)^2}}{r_l^{l+\frac{7}{2}} \sqrt{\Gamma(l+\frac{7}{2})}}$$

Basic types of operations

- Application of the Hamiltonian on the wavefunctions
 - Kinetic energy
 - Separable pseudopotential energy
 - Potential energy
- Orthogonalization and orthogonality constraints
- Calculation of Hartree potential

Kinetic energy matrix elements between scaling functions

$$a_i = \int \phi(x) \frac{\partial^2}{\partial x^2} \phi(x-i) dx$$

Can be calculated exactly (Beylkin):

$$\begin{aligned} a_i &= \int \phi(x) \frac{\partial^2}{\partial x^2} \phi(x-i) dx \\ &= \sum_{\nu, \mu} 2h_\nu h_\mu \int \phi(2x - \nu) \frac{\partial^2}{\partial x^2} \phi(2x - 2i - \mu) dx \\ &= \sum_{\nu, \mu} 2h_\nu h_\mu 2^{2-1} \int \phi(y - \nu) \frac{\partial^2}{\partial y^2} \phi(y - 2i - \mu) dy \\ &= \sum_{\nu, \mu} h_\nu h_\mu 2^2 \int \phi(y) \frac{\partial^2}{\partial y^2} \phi(y - 2i - \mu + \nu) dy \\ &= \sum_{\nu, \mu} h_\nu h_\mu 2^2 a_{2i - \nu + \mu} \end{aligned}$$

We thus have to find the eigenvector \mathbf{a} associated with the eigenvalue of 2^{-2} ,

$$\sum_j A_{i,j} a_j = \left(\frac{1}{2}\right)^2 a_i$$

where the matrix $A_{i,j}$ is given by

$$A_{i,j} = \sum_{\nu,\mu} h_{\nu} h_{\mu} \delta_{j,2i-\nu+\mu}$$

Operator approach: Applying the kinetic energy operator results in a convolution with the filter a

$$(K\Psi)_i = \sum_j \Psi_j a_{i-j}$$

In the 3-dim case applying the kinetic energy operator requires a 3-dim convolution with a filter that is a product of 3 1-dim filters. The operation count is $3 N_1 N_2 N_3 L$ where L is the length of the filter.

The nonlocal part of the pseudopotential

$$H^{sep}\Psi = |P\rangle\langle P|\Psi\rangle$$

where P is essentially a Gaussian in our case.

If the expansion coefficients c_J of P in a Daubechies wavelet/scaling function basis are known then

$$\begin{aligned}\langle P|\Psi\rangle &= \int \left(\sum_I c_I \phi(\mathbf{x} - I) \right) \left(\sum_J \Psi_J \phi(\mathbf{x} - J) \right) d\mathbf{x} \\ &= \sum_J c_J \Psi_J\end{aligned}$$

Because a Gaussian is separable and a 3-dim scaling function/wavelet basis is also a product of 1-dim scaling functions/wavelets the expansion coefficients $c_{i,j,k}$ can easily be calculated with machine precision.

$$\begin{aligned}c_{i,j,k} &= \int \int \int \phi_i^k(x) \phi_j^k(y) \phi_k^k(z) \exp(-(1/2)(x^2 + y^2 + z^2)) dx dy dz \\ &= \int \phi_i^k(x) \exp(-(x^2/2)) dx \int \phi_j^k(y) \exp(-(y^2/2)) dy \int \phi_k^k(z) \exp(-(z^2/2)) dz\end{aligned}$$

The potential energy

Problem: Daubechies are not smooth enough for conventional integration schemes.

The calculation of the potential energy matrix elements U_{ij}

$$U_{ij} = \int dx \phi(x-i)V(x)\phi(x-j)$$

can in principle be done by the following methods

- Triple product method (Beylkin)
- The collocation method
- The "magic filter" method

The triple product method (variational)

We assume that the grid spacing $h=1$. If

$$V(x) = \sum_i V_i \phi^{IP}(x-i)$$

where for interpolating scaling functions

$$V_i = V(i)$$

and

$$\Psi(x) = \sum_i \Psi_i \phi(x-i)$$

with Daubechies scaling functions ϕ then

$$E_{pot} = \int \Psi(x)V(x)\Psi(x)dx = \sum_{i,j,k} \Psi_i V_j \Psi_k I_{i-j,k-j}$$

where $I_{i,k}$ is a short array

$$I_{i,k} = \int \phi(x-i)\phi^{IP}(x)\phi(x-k)dx$$

Problem: the amount of computation per grid point scales like L^4 in 3 dimensions.

(L is the dimension of the matrix I_{ij}). In particular, for $2m = 8$, $L = 20$ and $L^4 = 1.6 * 10^5$. On the other hand, the triple product method is very precise: the only source of error is the approximation of the potential.

The collocation method (non-variational)

$$U = \int \Psi(x)V(x)\Psi(x) \approx \sum_i \Psi(i)V_i\Psi(i)$$

where

$$\Psi(i) = \sum_j \Psi_j \phi(i-j)$$

The amount of computation per grid point in three dimensions is $\propto 6m$. For $2m = 8$, this gives **only 24**.

Unfortunately, the scaling functions are **not very smooth**, so the collocation method is not sufficiently precise

The "magic filter" method

A. Neelov and S. Goedecker, J. of. Comp. Phys. 217, 312-339 (2006)

We do not calculate the values of Ψ on grid points, but we calculate the values $\bar{\Psi}_i$ that represent best Ψ in a neighborhood around the grid point

$$\bar{\Psi}_i = \sum_j \Psi_j \omega_{i-j}$$

$$E_{pot} = \sum_i \bar{\Psi}_i V_i \bar{\Psi}_i$$

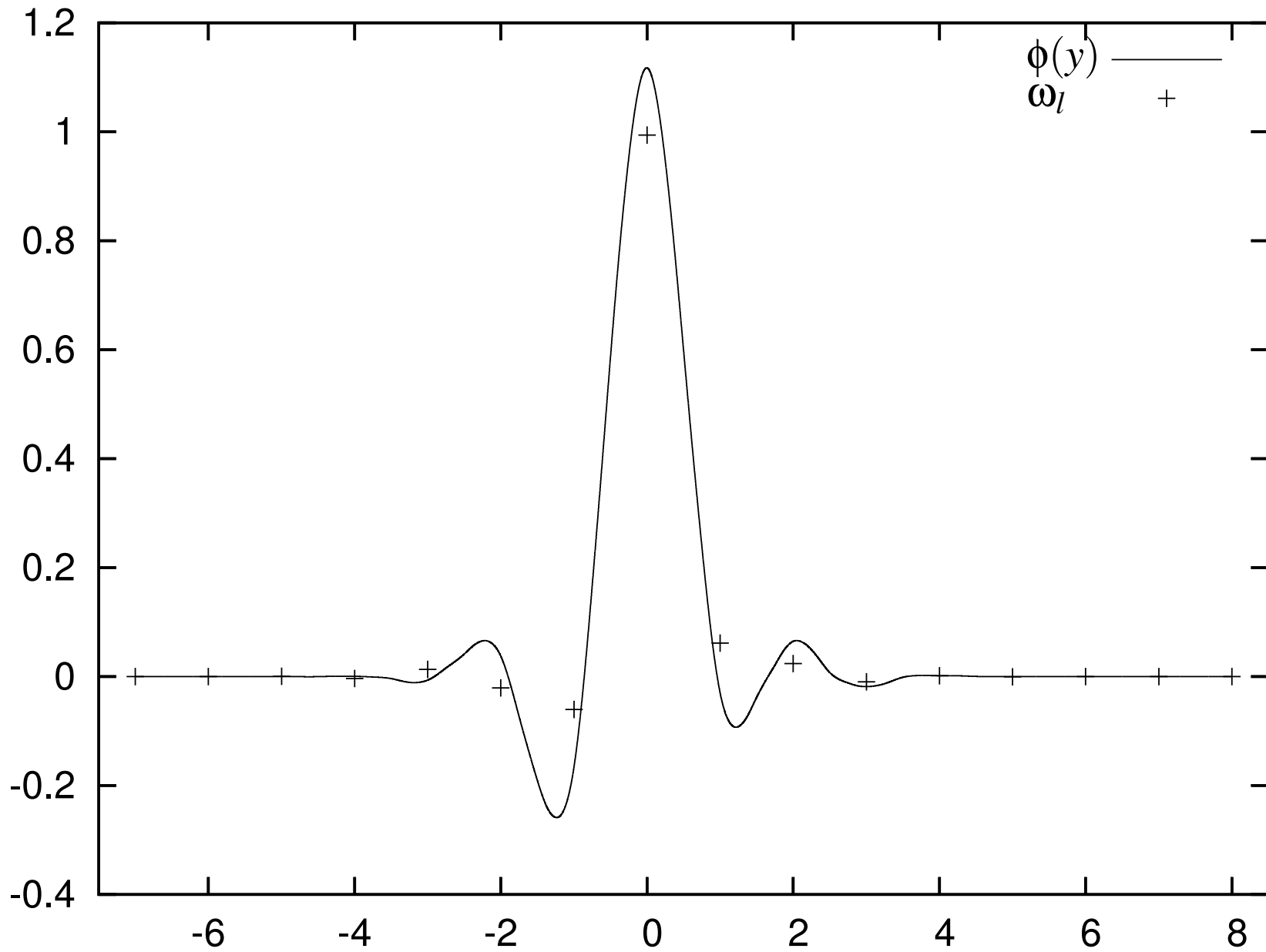


Figure 1: The magic filter values for the least asymmetric Daubechies-8 scaling function.

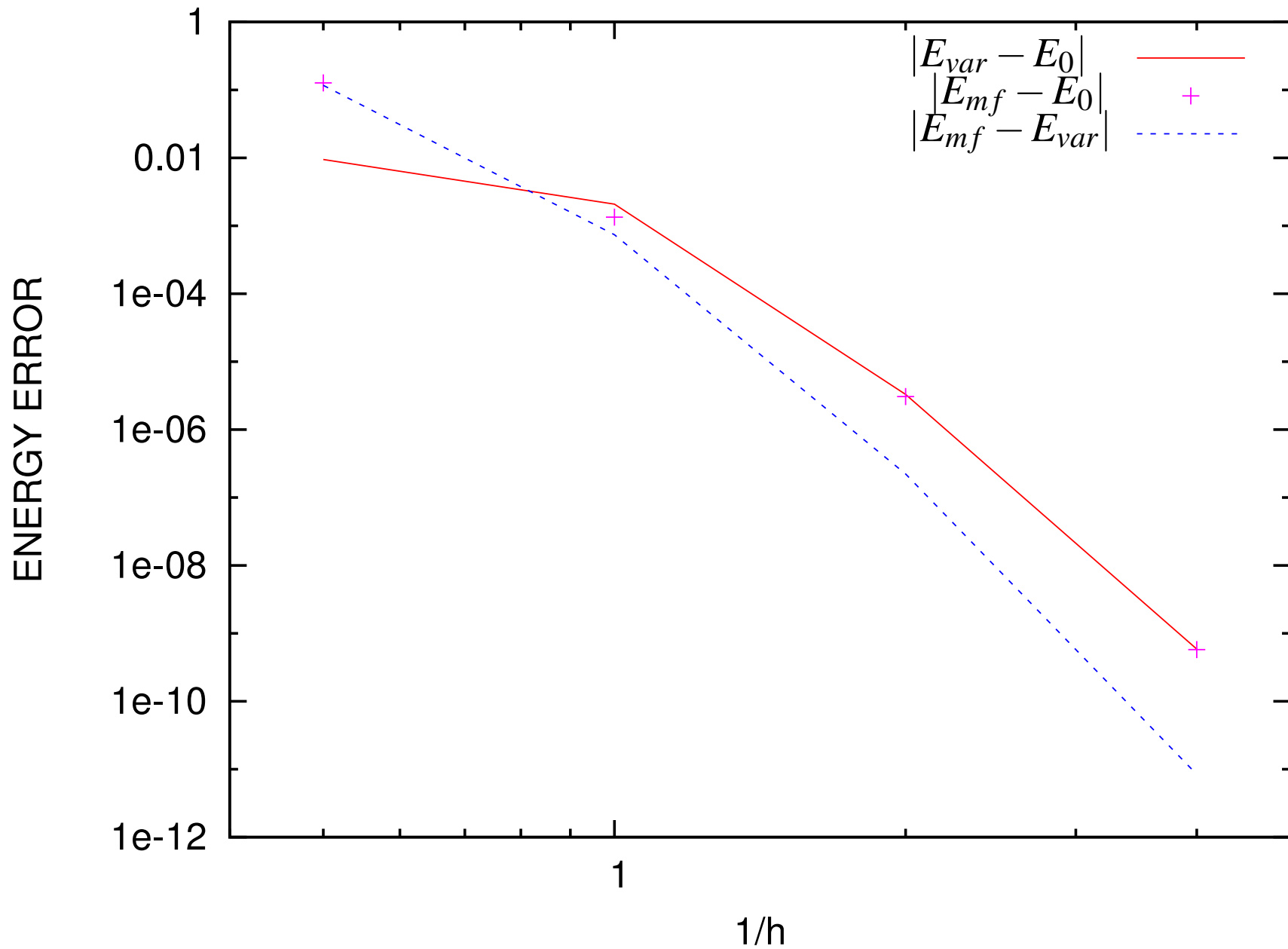


Figure 2: The result of energy minimization with the magic filter for the least asymmetric Daubechies-16 scaling functions.

Overall convergence rate in BIGDFT

- energy convergence rate: h^{14}
- convergence rate for error in wavefunctions: h^8

Electronic charge density also obtained by magic filter

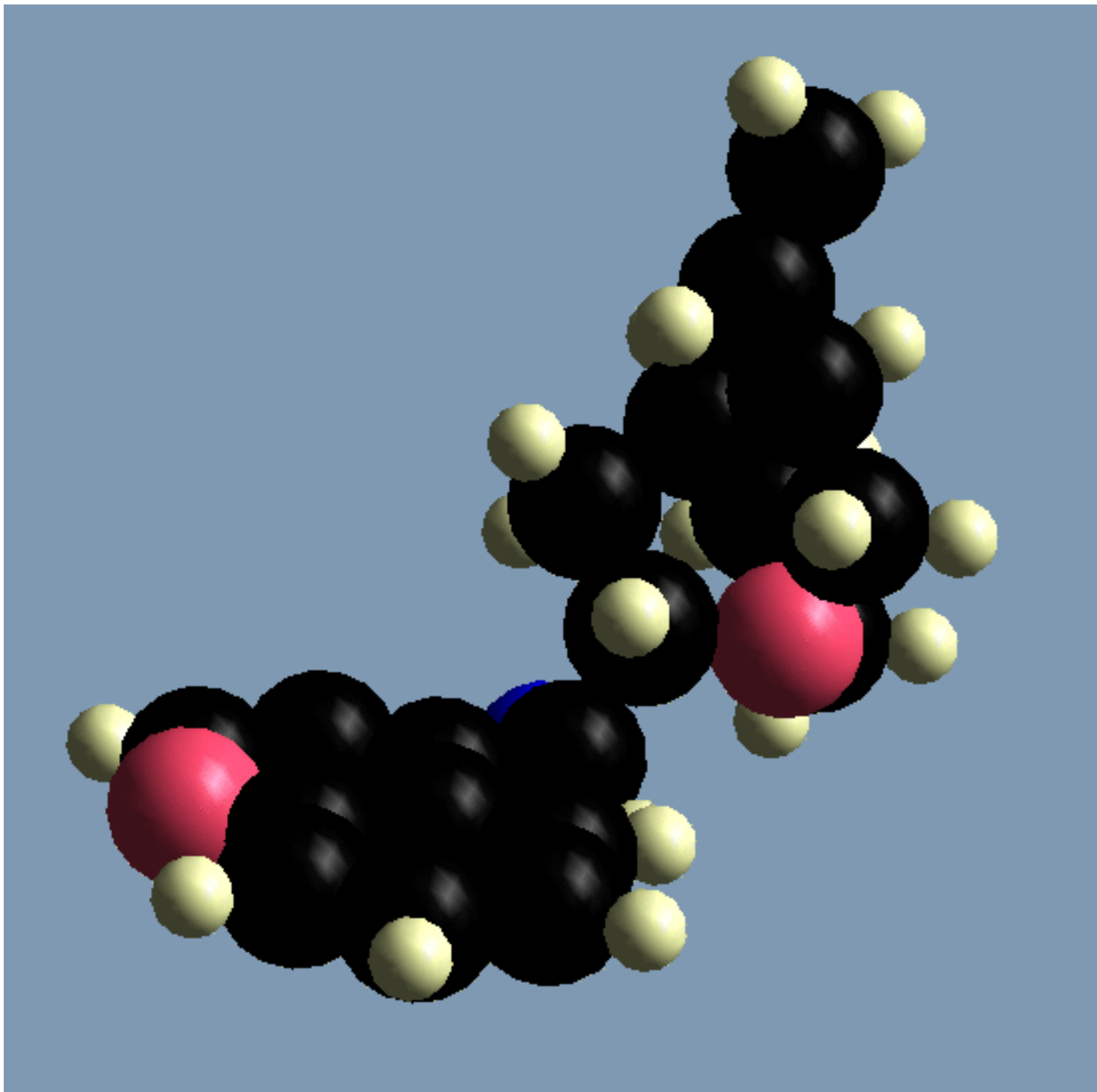
Preconditioning

The preconditioning equation

$$\frac{1}{2}(\nabla^2 + C)\vec{p} = \vec{g}$$

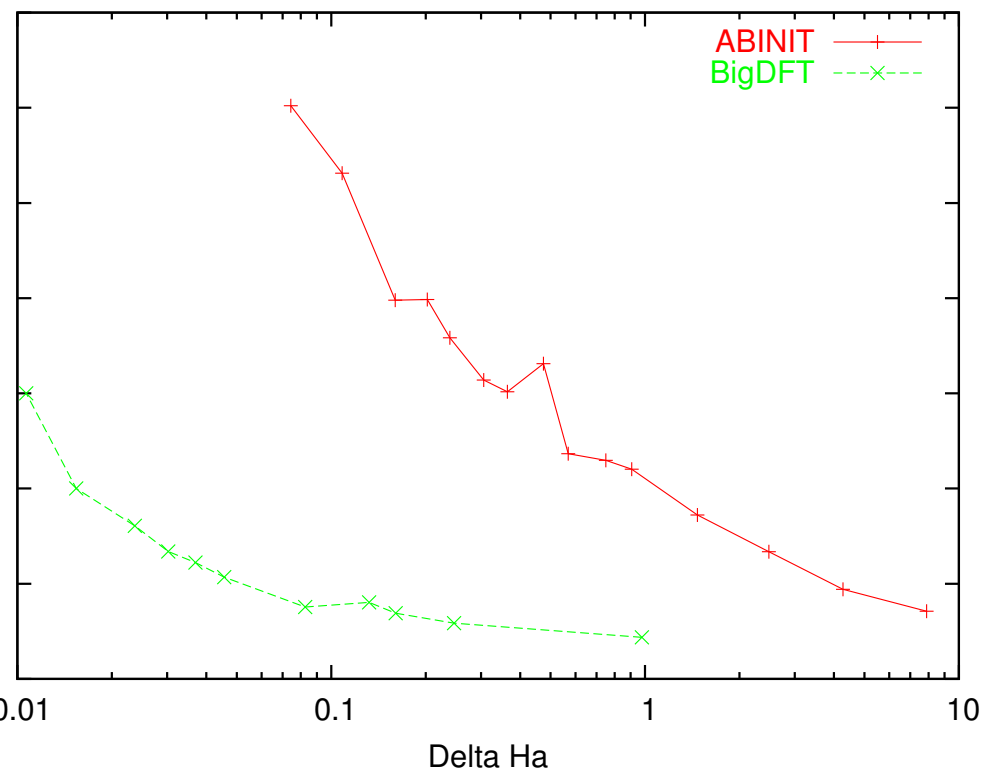
is solved iteratively by a multilevel preconditioned conjugate gradient method. 5 iterations are usually done.

Performance Tests: Cinchonidine

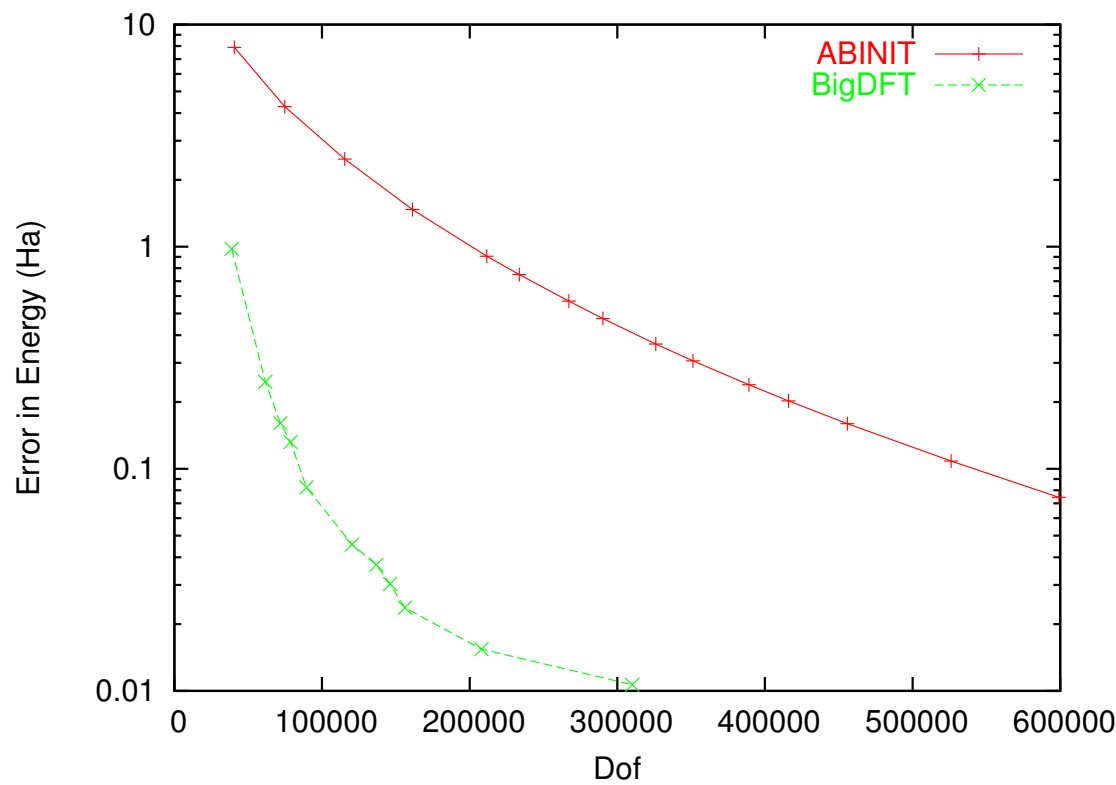


Performance Comparison with plane waves

Speed



Memory



Accuracy comparison with a Gaussian program

Quickstep program by J. Hutter's group (same pseudopotential):

With DZVP basis

- errors of a few hundreds of a Hartree (.5eV, 10 kcal) in total energy
- Errors in quantities related to charge densities are presumably larger

Outlook: $O(N)$

- Very small overhead compared to cubic version
- Adaptivity in localization regions

Discrete charge distributions

$$E = \sum_{i=1,N} \sum_{j<i} \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Free boundary conditions:
 - Fast Multipole Method (FMM): $O(N)$
 - Barnes Hut: $O(N \log(N))$
- Periodic boundary conditions:
 - Ewald method: $O(N^{3/2})$
 - Fast Fourier Poisson: $O(N \log(N))$
 - Particle-Particle Particle-Mesh methods: $O(N)$ or $O(N \log(N))$
- Surface boundary conditions:
 - 2-dim Ewald Method: $O(N^2)$
 - Ordinary 3-dim Method with approximate correction terms for surface boundary conditions: $O(N \log(N))$
 - MMM2D: $O(N^{5/3})$

Continuous charge distributions

Differential equation:

$$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r})$$

Integral equation:

$$V(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Charge is given on a regular grid of N grid points. The potential has to be calculated on the same grid.

- Free boundary conditions:
 - Generalizations of FMM
 - Periodic methods with approximate corrections for free boundary conditions
- Periodic boundary conditions:
 - Fourier methods: $O(N \log(N))$
 - Multigrid methods: $O(N)$
- Surface boundary conditions:
 - Periodic methods with approximate corrections for surface boundary conditions

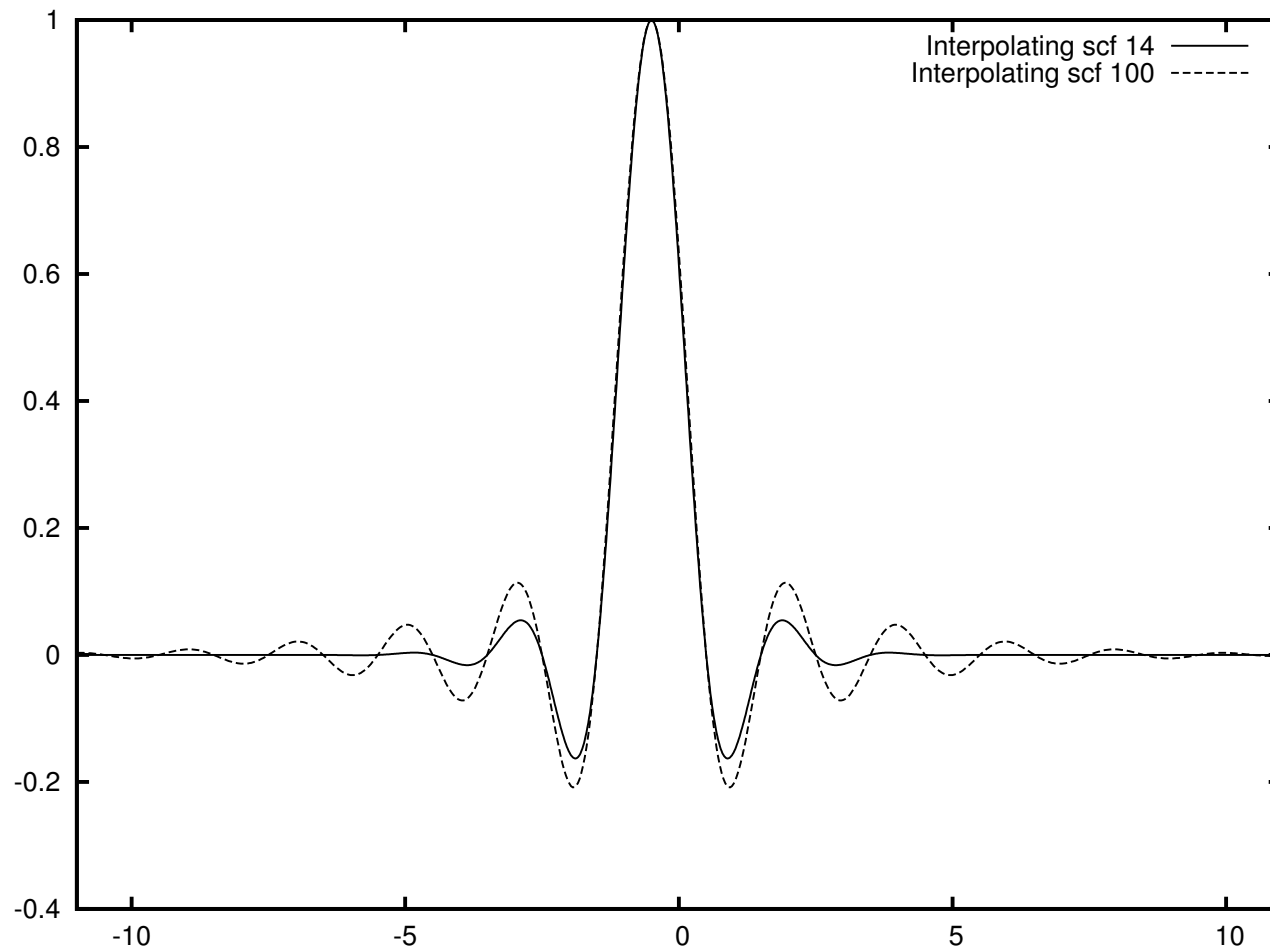
A new set of methods that have $O(N \log(N))$ scaling for

- continuous charge densities and free boundary conditions
- continuous charge densities and surface boundary conditions
- point particles (discrete charge densities) and free boundary conditions
- point particles (discrete charge densities) and surface boundary conditions

These methods can be used for

- electronic structure calculations
- classical force fields (MD simulations etc)

Interpolating scaling functions



Refinement relations:

$$\phi(x) = \sum_{j=-m}^m h_j \phi(2x - j)$$

1) Solution of Poisson's equation for free boundary conditions

L. Genovese, T. Deutsch, A. Neelov, S. Goedecker, G. Beylkin, J. Chem. Phys. 125 (2006)

Given the values of the charge density on a regular grid, $\rho_{i,j,k}$, the continuous charge distribution is represented in terms of interpolating scaling functions

$$\rho(\mathbf{r}) = \sum_{i,j,k} \rho_{i,j,k} \phi(x-i)\phi(y-j)\phi(z-k)$$

The moments of the discrete and continuous charge distributions $\rho_{i,j,k}$ and $\rho(\mathbf{r})$ are identical

$$\sum_{i,j,k} i^{l_1} j^{l_2} k^{l_3} \rho_{i,j,k} = \int d\mathbf{r} x^{l_1} y^{l_2} z^{l_3} \rho(\mathbf{r}) \quad (1)$$

if $l_1, l_2, l_3 < m$, where m is the order of the scaling functions. The potential at a grid point i_1, i_2, i_3 is given by

$$\begin{aligned} V_{i_1, i_2, i_3} &= \sum_{j_1, j_2, j_3} \rho_{j_1, j_2, j_3} \int \frac{\phi(x' - j_1)\phi(y' - j_2)\phi(z' - j_3)}{|r_{j_1, j_2, j_3} - r'|} dr' \\ &= \sum_{j_1, j_2, j_3} \rho_{j_1, j_2, j_3} K_{i_1 - j_1, i_2 - j_2, i_3 - j_3} \end{aligned}$$

The above convolution can be calculated rapidly with Fourier methods

The integral $K_{i-ip,j-jp,k-kp}$ becomes a sum of separable terms if $1/r$ is expanded in a sum of Gaussians

$$\frac{1}{r} \approx \sum_{k=1}^{89} \omega_k e^{-p_k r^2}$$

$$K_{j_1, j_2, j_3} = \sum_{k=1}^{89} \omega_k K_{j_1}(p_k) K_{j_2}(p_k) K_{j_3}(p_k)$$

We need to evaluate $89 \times \max(\{n_1, n_2, n_3\})$ integrals of the type

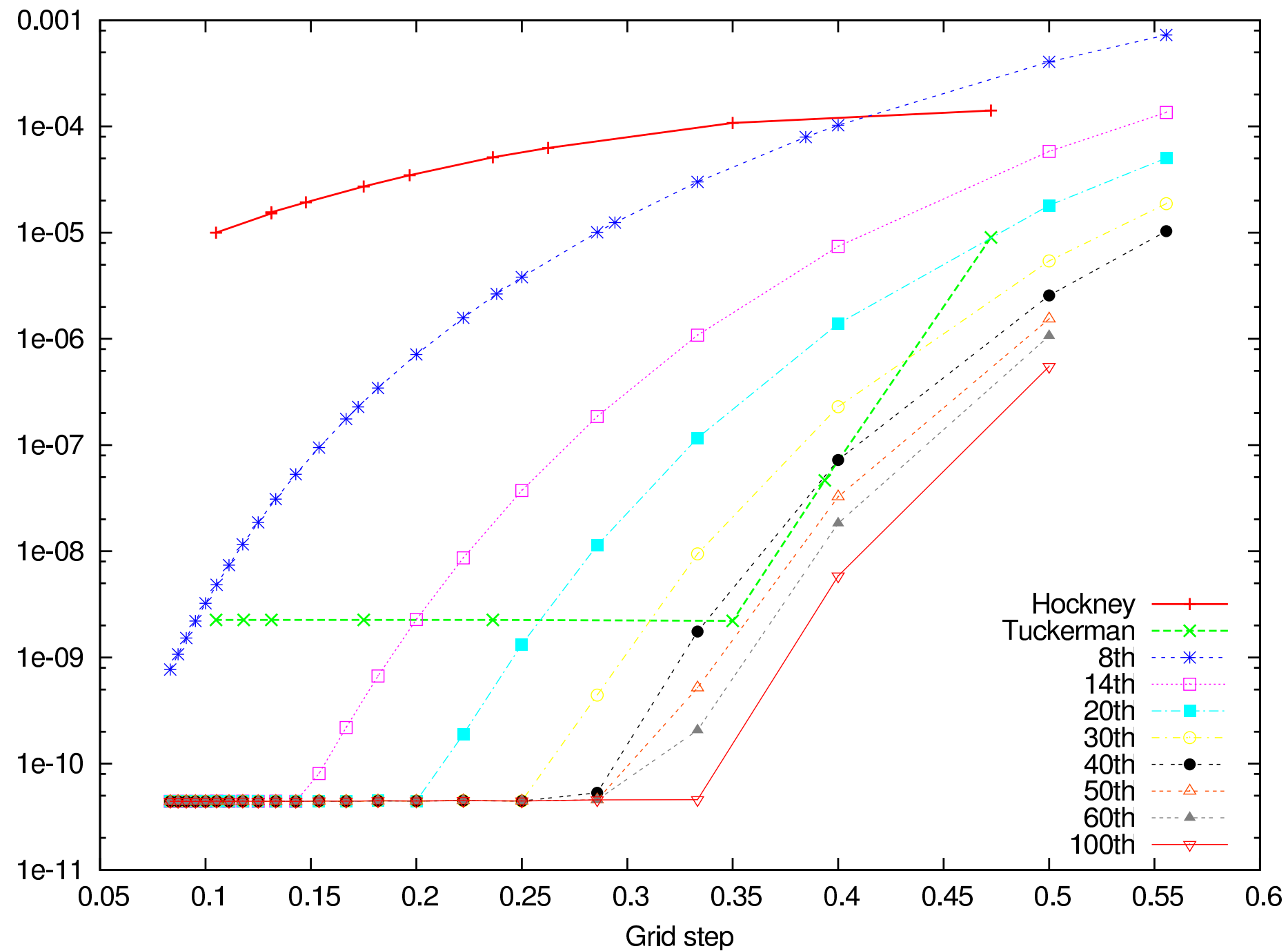
$$K_j(p) = \int \varphi_0(x) e^{-p(x-j)^2} dx$$

The efficiency in calculating the integrals can be improved using the refinement relation

$$\begin{aligned} K_i(4p) &= \int \varphi(x) e^{-4p(x-i)^2} dx \\ &= \frac{1}{2} \int \varphi(x/2) e^{-p(x-2i)^2} dx \\ &= \frac{1}{2} \sum_j h_j \int \varphi_j(x) e^{-p(x-2i)^2} dx \\ &= \frac{1}{2} \sum_j h_j K_{2i-j}(p) . \end{aligned}$$

In this way all the integrals can easily be calculated up to machine precision

Comparison of methods (as implemented in CPMD)



2) Point Particles with free boundary conditions

A. Neelov, S.A. Ghasemi, S. Goedecker, *J. Chem. Phys.* 127 (2007)

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Adding and subtracting the term corresponding to the electrostatic energy of smooth Gaussian charges $\rho_i(\mathbf{r})$

$$\rho_i(\mathbf{r}) = Q_i (G^2/\pi)^{3/2} \exp[-G^2 |\mathbf{r} - \mathbf{r}_i|^2]$$

we get:

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \left[\frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|} - \int \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \right] \\ - \frac{1}{2} \sum_{i=1}^N \int \frac{\rho_i(\mathbf{r}) \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \int \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}$$

Introducing the sum of the Gaussian charges

$$\rho(\mathbf{r}) = \sum_{i=1}^N \rho_i(\mathbf{r})$$

Then

$$U = E_{short} - E_{self} + E_{long}$$

where

$$E_{short} = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \operatorname{erfc} \left(\frac{G|\mathbf{r}_i - \mathbf{r}_j|}{\sqrt{2}} \right)$$

$$E_{self} = \frac{G}{\sqrt{2\pi}} \sum_{i=1}^N Q_i^2$$

$$E_{long} = \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

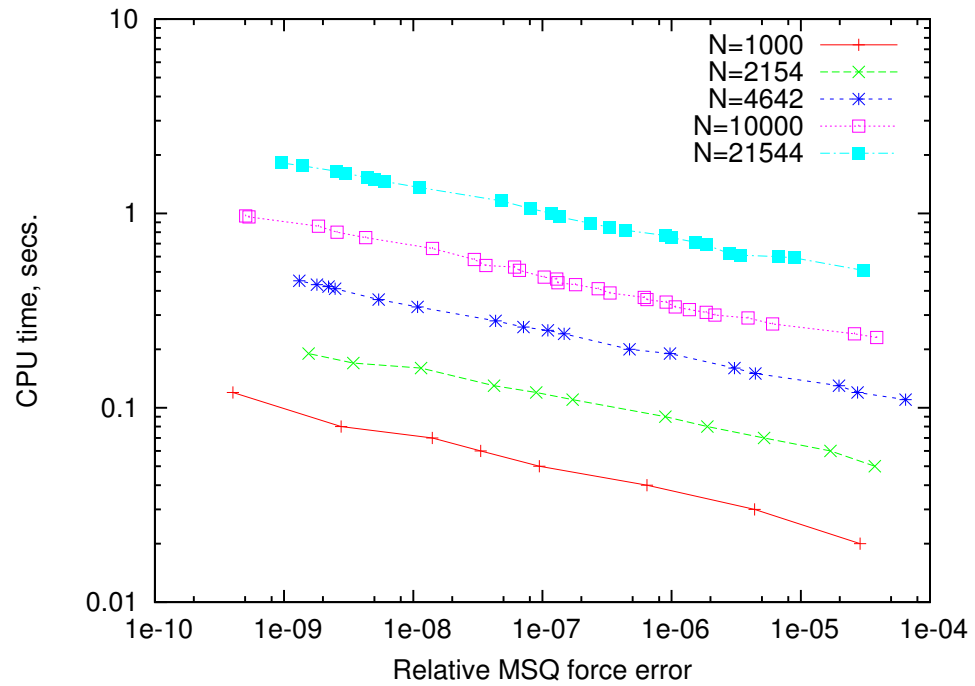
E_{long} is now approximated by

$$E_{long} \approx E_{long}^{appr} = \sum_{i_1, i_2, i_3} V_{i_1, i_2, i_3} \rho_{i_1, i_2, i_3} = \sum_{i_1, i_2, i_3} \sum_{j_1, j_2, j_3} \rho_{i_1, i_2, i_3} K_{i_1 - j_1, i_2 - j_2, i_3 - j_3} \rho_{j_1, j_2, j_3}$$

Forces can be calculated exactly:

$$\begin{aligned} \frac{\partial E_{long}^{appr}}{\partial \mathbf{r}_k} &= 2 \sum_{i_1, i_2, i_3} \sum_{j_1, j_2, j_3} \rho_{i_1, i_2, i_3} K_{i_1 - j_1, i_2 - j_2, i_3 - j_3} \frac{\partial \rho_{j_1, j_2, j_3}}{\partial \mathbf{r}_k} \\ &= 2 \sum_{i_1, i_2, i_3} V_{i_1, i_2, i_3} \frac{\partial \rho_{j_1, j_2, j_3}^k}{\partial \mathbf{r}_k} \end{aligned}$$

Performance results



Lower cross-over point than FMM

3) Continuous charge distributions with surface boundary conditions

L. Genovese, T. Deutsch, S. Goedecker, accepted by J. Chem. Phys. 2007

Charge is represented as:

$$\rho(x, y, z) = \sum_{p_x = -\frac{N_x}{2}}^{\frac{N_x}{2}} \sum_{p_y = -\frac{N_y}{2}}^{\frac{N_y}{2}} \sum_{j_z = 0}^{N_z} \rho_{p_x, p_y; j_z} \exp\left(-2\pi i \left(\frac{p_x}{L_x} x + \frac{p_y}{L_y} y\right)\right) \phi\left(\frac{z}{h} - j_z\right)$$

Generalized continuous and discrete multipoles are again identical:

$$\int \int \int dx dy dz \cos\left(\frac{2\pi l_1 x}{L_x}\right) \cos\left(\frac{2\pi l_2 y}{L_y}\right) z^{l_3} \rho(x, y, z) =$$

$$L_x L_y h^{l_3+1} \sum_{j_1=0}^{N_x} \sum_{j_2=0}^{N_y} \sum_{j_3=0}^{N_z} \cos\left(\frac{2\pi l_1 j_1}{N_x}\right) \cos\left(\frac{2\pi l_2 j_2}{N_y}\right) j_3^{l_3} \rho\left(\frac{L_x}{N_x} j_1, \frac{L_y}{N_y} j_2, h j_3\right)$$

for $l_1 < N_x$, $l_2 < N_y$ and $l_3 < m$, where m is the order of the scaling function.

The expansion coefficients of the potential are related to those of the charge density by

$$V_{p_x, p_y; j_z} = -4\pi h \sum_{j'_z} K(2\pi |\vec{p}|; j_z - j'_z) \rho_{p_x, p_y; j'_z}$$

with the kernel

$$K(\mu; j) = \int_{-\infty}^{+\infty} du G(\mu; h(j - u)) \phi(u)$$

The Green function G is given by

$$\begin{aligned} G(\mu; z) &= -\frac{1}{2\mu} e^{-\mu|z|} & \mu > 0 \\ &= \frac{1}{2} |z| & \mu = 0 \end{aligned}$$

For an efficient numerical calculation of the kernel we use the refinement relations for the scaling functions and relations due to the simplicity of the Green function

As in the case of free boundary conditions, very high convergence rates for high order scaling functions

4) Point Particles with surface boundary conditions

S.A. Ghasemi, A. Neelov, S. Goedecker, submitted to J. Chem. Phys. 2007

$$E = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i,j=1}^N \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}|}$$

$$E = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i,j=1}^N \left[\frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}|} - \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}' + \mathbf{n})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right]$$

$$- \frac{1}{2} \sum_{i=1}^N \iint \frac{\rho_i(\mathbf{r}) \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \sum_{\mathbf{n}} \sum_{i,j=1}^N \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}' + \mathbf{n})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E = \frac{1}{2} \sum_{\mathbf{n}}' \sum_{i,j=1}^N \frac{Q_i Q_j \operatorname{erfc} \left[\frac{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}|}{\alpha \sqrt{2}} \right]}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}|}$$

$$- \frac{1}{\alpha \sqrt{2\pi}} \sum_{i=1}^N Q_i^2 + \frac{1}{2} \sum_{\mathbf{n}} \sum_{i,j=1}^N \iint \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}' + \mathbf{n})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_{long} = \frac{1}{2} \int_{\mathcal{V}} \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} \quad ; \quad \rho(\mathbf{r}) = \sum_{\mathbf{n}} \sum_{j=1}^N \rho_j(\mathbf{r} + \mathbf{n})$$

Along the z direction we solve now the differential equation

$$V(x, y, z) = \sum_{k, l = -\infty}^{\infty} c_{kl}(z) \exp \left[2i\pi \left(\frac{kx}{L_x} + \frac{ly}{L_y} \right) \right]$$

$$\rho(x, y, z) = \sum_{k, l = -\infty}^{\infty} \frac{\eta_{kl}(z)}{-4\pi} \exp \left[2i\pi \left(\frac{kx}{L_x} + \frac{ly}{L_y} \right) \right]$$

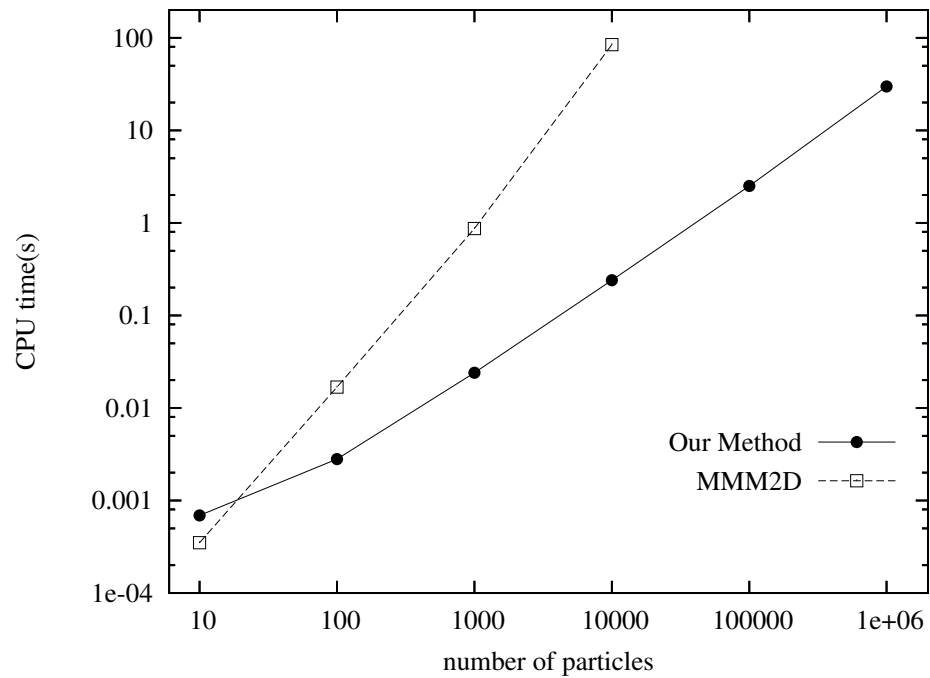
$$\left(\frac{d^2}{dz^2} - \gamma_{kl}^2 \right) c_{kl}(z) = \eta_{kl}(z)$$

$$\gamma_{kl} := 2\pi \sqrt{\frac{k^2}{L_x^2} + \frac{l^2}{L_y^2}}$$

Using a hierarchical basis based on Legendre polynomials the differential equation can be solved for the correct boundary conditions with linear scaling and with a small prefactor

Performance results

100 000 particles: 1 to several single CPU seconds (same as with free BC)



Summary

Electronic structure programs using a wavelet basis

- require less memory and are faster than plane wave programs for molecular systems.
- are more accurate than Gaussian programs
- lead in a straightforward way to $O(N)$ scaling

We have developed Poisson solvers for continuous charge densities and point particles that

- intrinsically fulfill the correct boundary conditions (free or surface)
- have a $N \log(N)$ scaling with a small prefactor
- have high convergence rates and allow for high accuracy
- where the forces are the exact derivative of the approximate energy