

# Electronic structure calculations with interpolating tensor product wavelet basis

Tommi Höynälänmaa \* and Tapio T. Rantala  
Physics, Tampere University,  
P. O. Box 692, FI-33101 Tampere, Finland

April 12, 2022

## Abstract

We introduce a basis set consisting of three-dimensional Deslauriers–Dubuc wavelets and numerically solve the Schrödinger equations of hydrogen atom, helium atom, hydrogen molecule ion, hydrogen molecule, and lithium hydride molecule with Hartree–Fock and DFT methods. We also compute the 2s and 2p excited states of hydrogen. The Coulomb singularity at the nucleus is handled by using a pseudopotential. Results are compared with those of CCCBDB and BigDFT. The eigenvalue problem is solved with Arnoldi and Lanczos methods, and the Poisson equation with GMRES and CGNR methods. The various matrix elements are computed using the biorthogonality relations of the interpolating wavelets.

## 1 Introduction

In principle, properties of a quantum physical system are computed by solving its Schrödinger equation. However, the Schrödinger equation usually has to be approximated for real world computations with several particles. The approximate solution is often computed with Hartree–Fock (HF) or Density Functional Theory (DFT) method. Using the HF method and a finite basis set leads to the Roothaan–Hall equations that are a generalized matrix eigenvalue problem. Wavelets can be used as a basis set for the HF and DFT methods.

Wavelets and scaling functions are functions generated by translations and dilatations of the so called mother wavelet and mother scaling function. Interpolating wavelets use a mother scaling function satisfying the cardinal interpolating property  $\varphi(k) = \delta_{k,0}$  where  $k$  is an integer. Orthonormal wavelets form an orthonormal basis in function space  $L^2(\mathbb{R})$ . Both of these wavelet types can be generalized to multivariate functions.

One-dimensional interpolating wavelets in function space  $C_u(\mathbb{R})$  consisting of bounded and uniformly continuous functions on  $\mathbb{R}$  are defined in Ref. [1]. One-dimensional interpolating wavelets in function space  $C_0(\mathbb{R})$  consisting of functions on  $\mathbb{R}$  vanishing at infinity are defined in Ref. [2]. Deslauriers–Dubuc wavelets have also been discussed in Refs. [3] and [4]. Compactly supported

---

\*corresponding author

interpolating wavelets have been generalized to multiple dimensions in Refs. [5] and [6]. Fukuda, Kinoshita, and Suzuki [7] have studied unconditional convergence of wavelet expansions. They have shown that uniformly convergent wavelet expansions even for continuous functions do not always converge unconditionally in  $L^\infty(\mathbb{R})$ .

Arias [8] and Engeness and Arias [9] develop formalism for electronic structure calculations with interpolating wavelets so that matrix elements of the operators are computed as usual and overlap matrices are used in the matrix form of the Schrödinger equation. Lippert *et al.* [10] introduce a Lagrangian based formalism for the multiresolution analysis of electronic structure. Arias [8] uses carbon atom and  $N_2$  molecule as examples. Engeness and Arias [9] use calcium and aluminum atoms and  $O_2$  and  $H_2O$  molecules as examples.

Fischer and Defranceschi use Daubechies wavelets [11] for computation of hydrogenlike atoms [12]. They develop an iterative method based on nonstandard operator form of the Schrödinger operator. Their work shows that this method is well suited for computations of hydrogenlike atoms. Fischer and Defranceschi have represented Hartree–Fock equations in an orthonormal wavelet basis [13]. They have also analyzed the Hartree–Fock method with continuous wavelet transform [14]. They apply continuous wavelet transform to the hydrogenic Schrödinger equation and develop an iterative scheme to solve it. Wei and Chou [15] have used orthonormal wavelets in self-consistent electronic structure calculations within the local-density approximation. They analyze  $H_2$  and  $O_2$  molecules. Tymczak and Wang [16] use orthonormal Daubechies wavelets for quantum molecular dynamic computations and develop a wavelet selection scheme for the computations. They use e.g. hydrogen atom and  $H_2$  molecule as examples. Their method show systematic convergence with increased grid size. Yamaguchi and Mukoyama [17] have done electronic structure calculations with the Hartree–Fock method and Meyer wavelets. Iyengar and Frisch [18] have studied relationship between Gaussian basis sets and wavelets. Höynälänmaa *et al.* [19] have used interpolating wavelets to solve the Hartree–Fock equations of some atoms using the Central Field Approximation. The authors were able to compute all the relevant operators (matrices) analytically.

Han, Cho, and Ihm [20] develop an all-electron density-functional program using the Mexican hat wavelet. They analyze  $H_2$ ,  $CO$ , and  $H_2O$  molecules and  $1s$  core-ionized  $C^*O$  and  $CO^*$  molecules. Their method shows very good performance over the plane-wave based methods. Genovese *et al.* [21] and Mohr *et al.* [22] have implemented a software package BigDFT that implements the DFT method for quantum physical systems using three-dimensional Daubechies wavelets as a basis function set.

Because the number of basis functions is so large 3-dimensional quantum physical problems cannot usually be solved by explicitly constructing the matrix of the Hamiltonian operator. We have to use proper iterative algorithms to solve the Roothaan–Hall equation. Execution time of the solution tends to be slow when there are plenty of basis functions. We use 3-dimensional tensor product Deslauriers–Dubuc wavelets to solve the wave equations of the hydrogen and helium atoms, hydrogen molecule ion, hydrogen molecule, and lithium hydride molecule. Self-consistent iteration and Hartree–Fock or DFT methods are used for many electron systems.

We use atomic units throughout this article ( $e = m_e = \hbar = 4\pi\epsilon_0 = 1$ ). The notation for wavelet basis functions and filters is similar to Ref. [5]. The

computation of matrix elements is similar to Ref. [6]. The atomic unit names “Hartree” and “Bohr” are abbreviated as Ha and B. Pseudopotentials are used for two purposes: to handle the singularities of the potential at nuclei and to approximate the core electrons so that they need not be calculated in the computation. We define

$$Z(n) := \{k \in \mathbb{Z} : |k| \leq n\}. \quad (1)$$

The new issue in this article is that we compute electronic structure with three-dimensional interpolating tensor product wavelets and use the dual MRA in the computation of the matrix elements of the various operators needed in electronic structure computations.

## 2 Solving the Schrödinger Equations

### 2.1 General

Suppose that we have a system with  $n$  electrons and  $m$  nuclei each of which has  $Z_i$  protons. Suppose also that each nucleus is located at position  $\mathbf{R}_i$ . In Born–Oppenheimer approximation we assume that the electrons and the nuclei move independently from each other. Consequently the wavefunction separates to a function of electronic coordinates and a function of nuclear coordinates. We do not consider the vibrational and rotational states. In this article we are interested in the electronic orbitals only. For electrons the Coulomb potential of the nuclei is

$$V_{\text{N}}(\mathbf{r}) = - \sum_{i=1}^m \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} \quad (2)$$

and the internuclear repulsion energy

$$E_{\text{R}} = \sum_{i=1}^{m-1} \sum_{j>i}^m \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}. \quad (3)$$

For an atom we have  $E_{\text{R}} = 0$ . We denote the wavefunction of a system by  $\gamma$ , because symbol  $\psi$  is used for wavelets. If the grid spacing (see section 3.1) is not a (usually negative) power of two we have to make a change of variables  $\mathbf{r} = a\mathbf{r}'$  in the Schrödinger equation. Here one unit in the computation grid corresponds to  $a$  Bohrs.

### 2.2 Single-electron System

The Schrödinger equation of a single electron system is

$$\left( -\frac{1}{2}\nabla^2 + V_{\text{N}} \right) \gamma = E\gamma \quad (4)$$

and the total energy

$$E_{\text{total}} = E + E_{\text{R}}. \quad (5)$$

The wave equation of a single-electron system is solved by the Implicitly Restarted Arnoldi Method [23, 24]. The Arnoldi method is able to compute other than the lowest eigenvalue, too.

### 2.3 Hartree–Fock Method

For a two electron system the HF equation can be written as

$$\left(-\frac{1}{2}\nabla^2 + V_N + \frac{1}{2}V_H\right)\gamma_1 = \varepsilon_1\gamma_1 \quad (6)$$

where the Hartree potential is given by

$$V_H(\mathbf{r}) = \int_{\mathbb{R}^3} \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (7)$$

and the charge density by

$$\rho(\mathbf{r}) = 2|\gamma_i(\mathbf{r})|^2. \quad (8)$$

The Hartree potential is actually computed by solving the Poisson equation

$$\nabla^2 V_H = -4\pi\rho. \quad (9)$$

When there are more than one resolution level in an interpolating wavelet basis the matrix  $L$  of the Laplacian operator is not generally Hermitian so we cannot solve (9) directly with the conjugate gradient method. In this case we use one of the following two methods:

- conjugate gradient on the normal equations (CGNR): solve

$$L^T L V_H = -4\pi L^T \rho \quad (10)$$

with the conjugate gradient method.

- the GMRES method [25].

When the basis set consists of a single resolution level we may use ordinary conjugate gradient method to solve (9). The total energy of a two electron system is

$$E_{\text{total}} = 2\varepsilon_1 - \frac{1}{4} \int_{\mathbb{R}^3} \rho(\mathbf{r}) V_H(\mathbf{r}) d^3\mathbf{r} + E_R. \quad (11)$$

We consider restricted HF throughout this article.

### 2.4 Density Functional Theory

Suppose that we have a system with  $M$  electronic orbitals whose total wavefunction is  $\Psi$ . The Kohn-Sham equation [26, 27, 28] for the electronic structure is

$$\left(-\frac{1}{2}\nabla^2 + V_N + V_H + V_{xc}[\rho]\right)\gamma_i = E_i\gamma_i \quad (12)$$

where the charge density is

$$\rho(\mathbf{x}_1) = \sum_{s_1=\pm 1} M \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_M)|^2 d\mathbf{x}_2 \dots d\mathbf{x}_M \quad (13)$$

and the Hartree potential

$$V_H(\mathbf{r}) = \int_{\mathbb{R}^3} \rho(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (14)$$

and  $V_{\text{xc}}[\rho]$  is the *exchange-correlation potential*. We have

$$V_{\text{xc}}[\rho] = V_{\text{x}}[\rho] + V_{\text{c}}[\rho] \quad (15)$$

where  $V_{\text{x}}[\rho]$  is the *exchange potential* and  $V_{\text{c}}[\rho]$  is the *correlation potential*. In this article we have  $V_{\text{c}}[\rho] = 0$ . The exchange-correlation energy is defined by

$$E_{\text{xc}}[\rho] = E_{\text{x}}[\rho] + E_{\text{c}}[\rho] \quad (16)$$

where  $E_{\text{x}}[\rho]$  is the *exchange energy* and  $E_{\text{c}}[\rho]$  is the *correlation energy*. In this article we have  $E_{\text{c}}[\rho] = 0$ . Within the Local Density Approximation (LDA) we define

$$E_{\text{x}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{x}}[\rho](\mathbf{r}) d^3 \mathbf{r} \quad (17)$$

where  $\varepsilon_{\text{x}}[\rho](\mathbf{r})$  is the exchange energy per particle of a uniform electron gas at a density of  $\rho$ . It follows from the Kohn-Sham theorem that the exchange potential is

$$V_{\text{x}}[\rho] = \frac{\delta E_{\text{x}}[\rho]}{\delta \rho}. \quad (18)$$

We have

$$E_{\text{x}}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int (\rho(\mathbf{r}))^{4/3} d^3 \mathbf{r} \quad (19)$$

and

$$V_{\text{x}}[\rho](\mathbf{r}) = - \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{1/3}. \quad (20)$$

The total energy of the system is

$$E_{\text{KS}} = \sum_{i=1}^n E_i - \frac{1}{2} \int \rho(\mathbf{r}) V_{\text{H}}(\mathbf{r}) d^3 \mathbf{r} + E_{\text{xc}}[\rho] - \int \rho(\mathbf{r}) V_{\text{xc}}[\rho](\mathbf{r}) d^3 \mathbf{r}. \quad (21)$$

The Kohn-Sham equations are solved by a similar self-consistent iteration as the HF equations.

## 3 Three-dimensional Wavelet Basis Set

### 3.1 The Basis Set

Let  $j_{\text{min}}$  and  $j_{\text{max}}$  be the minimum and maximum resolution levels of the point grid. Let

$$Z_j = \left\{ \frac{k}{2^j} \mid k \in \mathbb{Z} \right\} \quad (22)$$

and

$$V_j = Z_j^3 \quad (23)$$

where  $j \in \mathbb{Z}$ . Define sets  $Q_j$  by

$$Q_{j_{\text{min}}} = V_{j_{\text{min}}} \quad (24)$$

$$Q_j = V_j \setminus V_{j-1} \text{ for } j > j_{\text{min}} \quad (25)$$

The point grid  $G$  shall be some finite subset of  $V_{j_{\max}}$ . We define  $G_j := G \cap Q_j$  for  $j \geq j_{\min}$ . The functions  $\varphi_{j,k}$  and  $\psi_{j,k}$  are scaling functions and wavelets belonging to an interpolating wavelet family. Functions  $\tilde{\varphi}_{j,k}$  and  $\tilde{\psi}_{j,k}$  are dual basis functions of interpolating wavelets.

Define

$$\psi_{s,j,k} := \begin{cases} \varphi_{j,k}; & \text{if } s = 0 \\ \psi_{j,k}; & \text{if } s = 1 \end{cases} \quad (26)$$

$$\tilde{\psi}_{s,j,k} := \begin{cases} \tilde{\varphi}_{j,k}; & \text{if } s = 0 \\ \tilde{\psi}_{j,k}; & \text{if } s = 1 \end{cases} \quad (27)$$

and

$$\eta_{j,k} := \begin{cases} \varphi_{j_{\min},k}; & \text{if } j = j_{\min} \\ \varphi_{j-1,k/2}; & \text{if } j > j_{\min} \text{ and } k \text{ even} \\ \psi_{j-1,(k-1)/2}; & \text{if } j > j_{\min} \text{ and } k \text{ odd} \end{cases} \quad (28)$$

$$\tilde{\eta}_{j,k} := \begin{cases} \tilde{\varphi}_{j_{\min},k}; & \text{if } j = j_{\min} \\ \tilde{\varphi}_{j-1,k/2}; & \text{if } j > j_{\min} \text{ and } k \text{ even} \\ \tilde{\psi}_{j-1,(k-1)/2}; & \text{if } j > j_{\min} \text{ and } k \text{ odd} \end{cases} \quad (29)$$

When  $\alpha \in Q_j$  and  $j \geq j_{\min}$  define

$$\zeta_{\alpha} := \eta_{j,\mathbf{k}[1]} \otimes \eta_{j,\mathbf{k}[2]} \otimes \eta_{j,\mathbf{k}[3]} \quad (30)$$

and

$$\tilde{\zeta}_{\alpha} := \tilde{\eta}_{j,\mathbf{k}[1]} \otimes \tilde{\eta}_{j,\mathbf{k}[2]} \otimes \tilde{\eta}_{j,\mathbf{k}[3]} \quad (31)$$

where  $\mathbf{k} = 2^j \alpha$ . We also define

$$\varphi_{j,\mathbf{k}} := \varphi_{j,\mathbf{k}[1]} \otimes \varphi_{j,\mathbf{k}[2]} \otimes \varphi_{j,\mathbf{k}[3]} \quad (32)$$

where  $j \in \mathbb{Z}$  and  $\mathbf{k} \in \mathbb{Z}^3$ .

### 3.2 Backward and Forward Wavelet Transforms

Let

$$f = \sum_{\alpha \in G} c_{\alpha} \zeta_{\alpha} \quad (33)$$

where  $c_{\alpha} \in \mathbb{R}$  for all  $\alpha \in G$ . Let  $c = (c_{\alpha})_{\alpha \in G}$ . Define  $v = (v_{\alpha})_{\alpha \in G}$  by setting

$$v_{\alpha} = f(\alpha). \quad (34)$$

We define forward wavelet transform  $U$  and backward wavelet transform  $W$  by setting  $U(v) = c$  and  $W(c) = v$ . Mappings  $U$  and  $W$  are linear. We compute the forward wavelet transform  $U$  using an algorithm somewhat similar to [29]. Define matrix  $P^{(j)}$  by

$$P_{\alpha,\beta}^{(j)} = \delta_{\alpha,\beta} \quad (35)$$

where  $\alpha \in G_j$  and  $\beta \in G$  and matrix  $E^{(j)}$  by

$$E_{\alpha,\beta}^{(j)} = \delta_{\alpha,\beta} \quad (36)$$

where  $\alpha \in G$  and  $\beta \in G_j$ . Define

$$W_{\alpha,\beta}^{(j,j')} = \zeta_\beta(\alpha) \quad (37)$$

where  $\alpha \in G_j$  and  $\beta \in G_{j'}$ . We have

$$W = \sum_{j=j_{\min}}^{j_{\max}} \sum_{j'=j_{\min}}^j E^{(j)} W^{(j,j')} P^{(j')} \quad (38)$$

For forward wavelet transform we have

$$U = \sum_{j=j_{\min}}^{j_{\max}} E^{(j)} U^{(j)} \quad (39)$$

$$U^{(j)} = J^{(j)} \left( P^{(j)} - \sum_{j'=j_{\min}}^{j-1} W^{(j,j')} U^{(j')} \right), \quad (40)$$

$$\text{for } j > j_{\min} \\ U^{(j_{\min})} = P^{(j_{\min})} \quad (41)$$

$$J^{(j)} = \left( W^{(j,j)} \right)^{-1} \quad (42)$$

When

$$f = \sum_{\beta \in G_j} c_\beta \zeta_\beta \quad (43)$$

we have

$$c_\alpha = \langle \tilde{\zeta}_\alpha, f \rangle = \left\langle \tilde{\zeta}_\alpha, \sum_{\beta \in G_j} f(\beta) \varphi_{j,2^j \beta} \right\rangle = \sum_{\beta \in G_j} \langle \tilde{\zeta}_\alpha, \varphi_{j,2^j \beta} \rangle f(\beta). \quad (44)$$

Consequently

$$J_{\alpha,\beta}^{(j)} = \langle \tilde{\zeta}_\alpha, \varphi_{j,2^j \beta} \rangle \quad (45)$$

and we do not have to invert matrix  $W^{(j,j)}$ .

An operator representing pointwise multiplication of a function  $f$  by another in the given computation grid is

$$M = UDW \quad (46)$$

where  $D$  is a diagonal matrix with values of the function  $f$  at the grid points in the diagonal. The local pseudopotentials are computed this way.

### 3.3 Matrix Elements of the Laplacian Operator

Laplacian operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (47)$$

is approximated by linear operator  $L = L^{(x)} + L^{(y)} + L^{(z)}$  where

$$L_{\alpha, \alpha'}^{(x)} = \int_{\mathbb{R}^3} \tilde{\zeta}_\alpha(\mathbf{x}) \frac{\partial^2}{\partial x^2} \zeta_{\alpha'}(\mathbf{x}) d\tau \quad (48)$$

$$L_{\alpha, \alpha'}^{(y)} = \int_{\mathbb{R}^3} \tilde{\zeta}_\alpha(\mathbf{x}) \frac{\partial^2}{\partial y^2} \zeta_{\alpha'}(\mathbf{x}) d\tau \quad (49)$$

$$L_{\alpha, \alpha'}^{(z)} = \int_{\mathbb{R}^3} \tilde{\zeta}_\alpha(\mathbf{x}) \frac{\partial^2}{\partial z^2} \zeta_{\alpha'}(\mathbf{x}) d\tau \quad (50)$$

for  $\alpha, \alpha' \in G$ . Let  $\alpha = 2^{-j}(k_x, k_y, k_z) \in G \cap Q_j$  and  $\alpha' = 2^{-j'}(k'_x, k'_y, k'_z) \in G \cap Q_{j'}$ . We define

$$l = \begin{cases} j-1, & \text{if } j > j_{\min} \\ j, & \text{if } j = j_{\min} \end{cases} \quad (51)$$

$$l_x = \begin{cases} \frac{k_x}{2}, & \text{if } k_x \text{ even and } j > j_{\min} \\ \frac{k_x-1}{2}, & \text{if } k_x \text{ odd and } j > j_{\min} \\ k_x, & \text{if } j = j_{\min} \end{cases} \quad (52)$$

$$t_x = \begin{cases} 0, & \text{if } j = j_{\min} \text{ or } j > j_{\min} \text{ and } k_x \text{ even} \\ 1, & \text{if } j > j_{\min} \text{ and } k_x \text{ odd} \end{cases} \quad (53)$$

$$l_y = \begin{cases} \frac{k_y}{2}, & \text{if } k_y \text{ even and } j > j_{\min} \\ \frac{k_y-1}{2}, & \text{if } k_y \text{ odd and } j > j_{\min} \\ k_y, & \text{if } j = j_{\min} \end{cases} \quad (54)$$

$$t_y = \begin{cases} 0, & \text{if } j = j_{\min} \text{ or } j > j_{\min} \text{ and } k_y \text{ even} \\ 1, & \text{if } j > j_{\min} \text{ and } k_y \text{ odd} \end{cases} \quad (55)$$

$$l_z = \begin{cases} \frac{k_z}{2}, & \text{if } k_z \text{ even and } j > j_{\min} \\ \frac{k_z-1}{2}, & \text{if } k_z \text{ odd and } j > j_{\min} \\ k_z, & \text{if } j = j_{\min} \end{cases} \quad (56)$$

$$t_z = \begin{cases} 0, & \text{if } j = j_{\min} \text{ or } j > j_{\min} \text{ and } k_z \text{ even} \\ 1, & \text{if } j > j_{\min} \text{ and } k_z \text{ odd} \end{cases} \quad (57)$$



and similar definitions for  $l', l'_x, t'_x, l'_y, t'_y, l'_z$ , and  $t'_z$ . Elements of matrices are computed by

$$L_{\alpha, \alpha'}^{(x)} = \begin{cases} \begin{aligned} &2^{2\iota} a(t_x, t'_x, l' - \iota, l'_x - 2^{\iota - \iota} l_x) \\ &\cdot s(t_y, t'_y, l' - \iota, l'_y - 2^{\iota - \iota} l_y) \\ &\cdot s(t_z, t'_z, l' - \iota, l'_z - 2^{\iota - \iota} l_z), \end{aligned} & \text{if } \iota \leq l' \\ \begin{aligned} &2^{2l'} a(t_x, t'_x, l' - \iota, l_x - 2^{\iota - l'} l'_x) \\ &\cdot s(t_y, t'_y, l' - \iota, l_y - 2^{\iota - l'} l'_y) \\ &\cdot s(t_z, t'_z, l' - \iota, l_z - 2^{\iota - l'} l'_z), \end{aligned} & \text{if } \iota > l' \end{cases} \quad (58)$$

$$L_{\alpha, \alpha'}^{(y)} = \begin{cases} \begin{aligned} &2^{2\iota} s(t_x, t'_x, l' - \iota, l'_x - 2^{\iota - \iota} l_x) \\ &\cdot a(t_y, t'_y, l' - \iota, l'_y - 2^{\iota - \iota} l_y) \\ &\cdot s(t_z, t'_z, l' - \iota, l'_z - 2^{\iota - \iota} l_z), \end{aligned} & \text{if } \iota \leq l' \\ \begin{aligned} &2^{2l'} s(t_x, t'_x, l' - \iota, l_x - 2^{\iota - l'} l'_x) \\ &\cdot a(t_y, t'_y, l' - \iota, l_y - 2^{\iota - l'} l'_y) \\ &\cdot s(t_z, t'_z, l' - \iota, l_z - 2^{\iota - l'} l'_z), \end{aligned} & \text{if } \iota > l' \end{cases} \quad (59)$$

$$L_{\alpha, \alpha'}^{(z)} = \begin{cases} \begin{aligned} &2^{2\iota} s(t_x, t'_x, l' - \iota, l'_x - 2^{\iota - \iota} l_x) \\ &\cdot s(t_y, t'_y, l' - \iota, l'_y - 2^{\iota - \iota} l_y) \\ &\cdot a(t_z, t'_z, l' - \iota, l'_z - 2^{\iota - \iota} l_z), \end{aligned} & \text{if } \iota \leq l' \\ \begin{aligned} &2^{2l'} s(t_x, t'_x, l' - \iota, l_x - 2^{\iota - l'} l'_x) \\ &\cdot s(t_y, t'_y, l' - \iota, l_y - 2^{\iota - l'} l'_y) \\ &\cdot a(t_z, t'_z, l' - \iota, l_z - 2^{\iota - l'} l'_z), \end{aligned} & \text{if } \iota > l'. \end{cases} \quad (60)$$

The filters  $a$  and  $s$  are defined by

$$a(t_1, t_2, j, k) = \int_{\mathbb{R}^3} \tilde{\psi}_{t_1, 0, 0}(x) \frac{\partial^2}{\partial x^2} \psi_{t_2, j, k}(x) d\tau, \quad \text{for } j \geq 0 \quad (61)$$

$$a(t_1, t_2, j, k) = \int_{\mathbb{R}^3} \tilde{\psi}_{t_1, -j, k}(x) \frac{\partial^2}{\partial x^2} \psi_{t_2, 0, 0}(x) d\tau, \quad \text{for } j < 0 \quad (62)$$

$$s(t_1, t_2, j, k) = \int_{\mathbb{R}^3} \tilde{\psi}_{t_1, 0, 0}(x) \psi_{t_2, j, k}(x) d\tau, \quad \text{for } j \geq 0 \quad (63)$$

$$s(t_1, t_2, j, k) = \int_{\mathbb{R}^3} \tilde{\psi}_{t_1, -j, k}(x) \psi_{t_2, 0, 0}(x) d\tau, \quad \text{for } j < 0. \quad (64)$$

Filter  $a$  is computed with formulas

$$a(0, 0, j, k) = 2^{2j}a_0(k) \text{ for } j \geq 0 \quad (65)$$

$$a(0, 0, -1, k) = 4 \sum_{\mu=-m}^m h_\mu a(0, 0, 0, \mu - k) \text{ for } j = -1 \quad (66)$$

$$a(0, 0, j, k) = 4 \sum_{\mu=-m}^m h_\mu a(0, 0, j+1, k - 2^{-j-1}\mu) \text{ for } j < -1 \quad (67)$$

$$a(0, 1, j, k) = a(0, 0, j+1, 2k+1), \text{ for } j \geq 0 \quad (68)$$

$$a(0, 1, -1, k) = 4a_0(1-k) \quad (69)$$

$$a(0, 1, j, k) = 4a(0, 0, j+1, k - 2^{-j-1}), \text{ for } j < -1 \quad (70)$$

$$a(1, 0, 0, k) = \sum_{\nu=-m}^m \tilde{g}_\nu a(0, 0, -1, \nu - 2k) \quad (71)$$

$$a(1, 0, j, k) = 4 \sum_{\nu=-m}^m \tilde{g}_\nu a(0, 0, j-1, k - 2^{j-1}\nu), \text{ for } j > 0 \quad (72)$$

$$a(1, 0, j, k) = \sum_{\nu=-m}^m \tilde{g}_\nu a(0, 0, j-1, 2k + \nu), \text{ for } j < 0 \quad (73)$$

$$a(1, 1, j, k) = a(1, 0, j+1, 2k+1), \text{ for } j \geq 0 \quad (74)$$

$$a(1, 1, -1, k) = 4a(1, 0, 0, 1-k) \quad (75)$$

$$a(1, 1, j, k) = 4a(1, 0, j+1, k - 2^{-j-1}), \text{ for } j < -1 \quad (76)$$

where

$$a_0(k) := \int_{\mathbb{R}} \tilde{\varphi}(x) \frac{\partial^2}{\partial x^2} \varphi(x-k) dx. \quad (77)$$

Filter  $s$  is computed with formulas

$$s(0, 0, j, k) = \delta_{k,0}, \text{ for } j \geq 0 \quad (78)$$

$$s(0, 0, -1, k) = h_k \quad (79)$$

$$s(0, 0, j, k) = \sum_{\mu=-m}^m h_\mu s(0, 0, j+1, k - 2^{-j-1}\mu), \text{ for } j < -1 \quad (80)$$

$$s(0, 1, j, k) = 0, \text{ for } j \geq 0 \quad (81)$$

$$s(0, 1, -1, k) = \delta_{k,1} \quad (82)$$

$$s(0, 1, j, k) = s(0, 0, j+1, k - 2^{-j-1}), \text{ for } j < -1 \quad (83)$$

$$s(1, 0, 0, k) = 0 \quad (84)$$

$$s(1, 0, j, k) = \sum_{\nu=-m}^m \tilde{g}_\nu \delta_{k, 2^{j-1}\nu}, \text{ for } j > 0 \quad (85)$$

$$s(1, 0, j, k) = 0, \text{ for } j < 0 \quad (86)$$

$$s(1, 1, 0, k) = \delta_{k,0} \quad (87)$$

$$s(1, 1, j, k) = 0, \text{ for } j \neq 0 \quad (88)$$

## 4 Constant and Interpolated Pseudopotentials

The Coulomb potential arising from a single nucleus is

$$V(r) = -\frac{Z}{r} \quad (89)$$

where  $Z$  is the charge of the nucleus.

We avoid the singularity of (89) at the origin by using a pseudopotential. We define  $c$  to be the cutoff point of the pseudopotential and  $D$  to be the degree of the interpolating polynomial used in the pseudopotential. Actually we use  $c = 2^{-j_{\max}}$  where  $j_{\max}$  is the highest resolution level in the wavelet basis. Parameter  $D$  has to be an odd integer and we define  $n = (D + 1)/2$ . We define

$$V_1(r) := -\frac{1}{r}, \quad r \geq 0, \quad (90)$$

$$\mathbf{s} := (-nc, -(n-1)c, \dots, -2c, -c, c, 2c, \dots, (n-1)c, nc), \quad (91)$$

and

$$\mathbf{t}[i] := V_1(\mathbf{s}[i]) \quad (92)$$

where  $i = 1, \dots, 2n$ . Let  $P$  be the interpolating polynomial of degree at most  $D$  having value  $\mathbf{t}[i]$  at point  $\mathbf{s}[i]$  for  $i = 1, \dots, 2n$ . Now we define the interpolated pseudopotential with

$$V_{\text{interp}}(r) := \begin{cases} V_1(r), & r \geq c \\ P(r), & r < c \end{cases} \quad (93)$$

The actual pseudopotential of a nucleus with charge  $Z$  and location  $\mathbf{R}$  is then

$$V(\mathbf{r}) = ZV_{\text{interp}}(|\mathbf{r} - \mathbf{R}|). \quad (94)$$

Function  $V_{\text{interp}}$  with different values of  $c$  is plotted in figure 1. We may also use the cut pseudopotential defined by

$$V_{\text{cut}}(r) := \begin{cases} V_1(r), & r \geq c \\ -\frac{1}{c}, & r < c \end{cases} \quad (95)$$

where  $c = 2^{-j_{\max}-1}$ .

## 5 HGH Pseudopotential

By using pseudopotentials the number of computed orbitals can be reduced and since the pseudo wavefunctions are smoother than all-electron wavefunctions the basis function set can also be reduced. In a pseudopotential computation only the valence electrons are actually computed and the effect of the core electrons is handled by replacing the nuclear potential with a pseudopotential. We use the Hartwigsen-Goedecker-Hutter (HGH) pseudopotential [30, 21] in these computations.

The HGH pseudopotential consists of a local and nonlocal part. The local part is a function of the position as the nuclear potential. The nonlocal part is

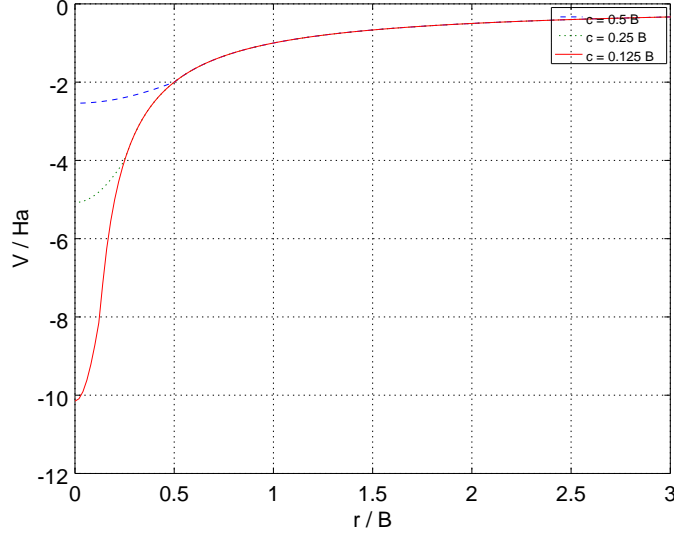


Figure 1: Pseudopotentials  $V_{\text{interp}}$  with  $D = 7$ . Parameter  $c$  is the cutoff value, see section 4.

a linear operator and it is not a function of position. The local pseudopotential is given by

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

where  $r$  is the distance from the nucleus. Note that

$$\lim_{r \rightarrow 0} \frac{-Z_{\text{ion}}}{r} \operatorname{erf}\left(\frac{r}{\sqrt{2}r_{\text{loc}}}\right) = \frac{-Z_{\text{ion}}}{r_{\text{loc}}} \sqrt{\frac{2}{\pi}} \quad (96)$$

and the local pseudopotential is defined at the origin (nucleus), too. The non-local pseudopotential is defined by

$$V_{\text{nonlocal}}[\gamma] = \mathbf{r} \in \mathbb{R}^3 \mapsto \sum_l \int V_l(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{r}') d^3 \mathbf{r}' \quad (97)$$

where

$$V_l(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^l Y_{l,m}(\hat{\mathbf{r}}) p_i^l(r) h_{i,j}^l p_j^l(r') Y_{l,m}^*(\hat{\mathbf{r}}'). \quad (98)$$

for each nucleus. The origin of the coordinate system in (98) is located at the nucleus. The functions  $p_i^l$  are defined by

$$p_i^l(r) = \frac{\sqrt{2} r^{l+2(i-1)} \exp\left(-\frac{r^2}{2r_i^2}\right)}{r_i^{l+(4i-1)/2} \sqrt{\Gamma\left(l + \frac{4i-1}{2}\right)}} \quad (99)$$

number	grid points
1	$\frac{1}{2}(Z(20))^3$
2	$\frac{1}{2}(Z(20))^3 \cup \frac{1}{4}(Z(10))^3$
3	$\frac{1}{2}(Z(20))^3 \cup \frac{1}{4}(Z(10))^3 \cup \frac{1}{8}(Z(4) \times Z(4) \times Z(10))$
4	$\frac{1}{4}(Z(60))^3$
5	$\frac{1}{2}(Z(30))^3 \cup \frac{1}{4}(Z(15))^3$
6	$(Z(38))^3 \cup \frac{1}{2}(Z(19))^3$
7	$\frac{1}{4}(Z(40))^3$
8	$(Z(10))^3 \cup \frac{1}{2}(Z(10))^3$
9	$\frac{1}{2}(Z(20))^3 \cup \frac{1}{4}(Z(20))^3$
10	$\frac{1}{4}(Z(40))^3 \cup \frac{1}{8}(Z(40))^3$
11	$(Z(10))^3 \cup \frac{1}{2}(Z(5))^3$
12	$\frac{1}{2}(Z(20))^3 \cup \frac{1}{4}(Z(10))^3 \cup \frac{1}{8}(Z(4) \times Z(4) \times Z(15))$
13	$\frac{1}{4}(Z(40))^3 \cup \frac{1}{8}(Z(20))^3$
14	$\frac{1}{4}(Z(60))^3 \cup \frac{1}{8}(Z(30))^3$

Table 1: Computation grids. Symbol  $Z$  is defined by equation (1).

where parameter  $r_l$  is given in Bohrs. The range of values  $l$  is determined by the actual pseudopotential. The spherical harmonics  $Y_{l,m}$  in equation (98) can be replaced by orthonormal linear combinations of  $Y_{l,m}$ ,  $m = -l, \dots, l$ . This allows us to avoid computation with complex valued functions.

## 6 Atomic and Molecular Orbitals

The hydrogen atom, hydrogen molecule ion, and lithium HGH computations presented here have been done with Arnoldi method. The helium, hydrogen molecule, and lithium hydride computations have been done with self-consistent iteration and Arnoldi method. When there is only one resolution level in the basis the Hamiltonian and Laplacian matrices are hermitian and the Arnoldi method reduces to a variant of the Lanczos method. When there is only one resolution level the ordinary conjugate gradient method could be used for the Poisson equation. Two methods have been used for solving the Poisson equation for the general case: CGNR and GMRES. We ran a benchmark for these methods and GMRES was 4.5 times faster when the accuracies of the results were approximately the same. All the computations use 8th order Deslauriers–Dubuc wavelets (polynomial span 7). We use interpolating polynomials of degree 7 for the pseudopotentials. In some computations the Arnoldi method did not find the desired eigenvalues. This was solved by rising the number of computed eigenvalues and the number of basis vectors in the Arnoldi method. The basis function sets (computation point grids) are presented in table 1.

The data presented in the tables in this article was obtained from our own software (denoted by TH), our own computations with BigDFT [21, 22], and CCCBDB [31]. BigDFT is a quantum mechanical computation package using Daubechies wavelets. CCCBDB is large database containing atomic and molecular data. The CCCBDB results in this article use the STO-3G basis set. Quantity  $g$  is the distance between grid points in the highest resolution level and quantity  $d$  is the distance between the nuclei in the result tables.  $E_{\text{system}}$

source	basis	$g/B$	pseudopot.	$E/\text{Ha}$
TH	7	0.25	const.	-0.487470
TH	8	0.5	const.	-0.462247
TH	9	0.25	const.	-0.487470
TH	10	0.125	const.	-0.496380
TH	7	0.25	interp.	-0.478328
TH	8	0.5	interp.	-0.439146
TH	9	0.25	interp.	-0.478328
TH	10	0.125	interp.	-0.493471
TH	7	0.25	HGH	-0.499294
TH	8	0.5	HGH	-0.589957
TH	9	0.25	HGH	-0.499295
TH	10	0.125	HGH	-0.499899
CCCBDB [31]				-0.466582
BigDFT [21, 22]			HGH	-0.499969
exact			none	-0.5

Table 2: Computation results for the hydrogen atom. Quantity  $g$  is the distance between grid points in the highest resolution level. The numbers in column “basis” refer to table 1 and “TH” means this work.

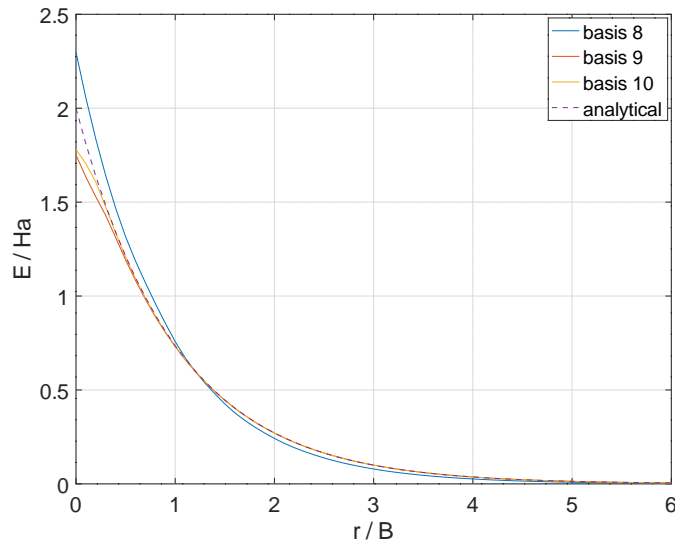


Figure 2: Radially averaged wavefunctions of the hydrogen atom for several bases. The highest curve is for basis 8, the lowest for basis 9, and the second lowest for basis 10. The dashed line is the analytical radial wavefunction. The basis numbers refer to table 1.

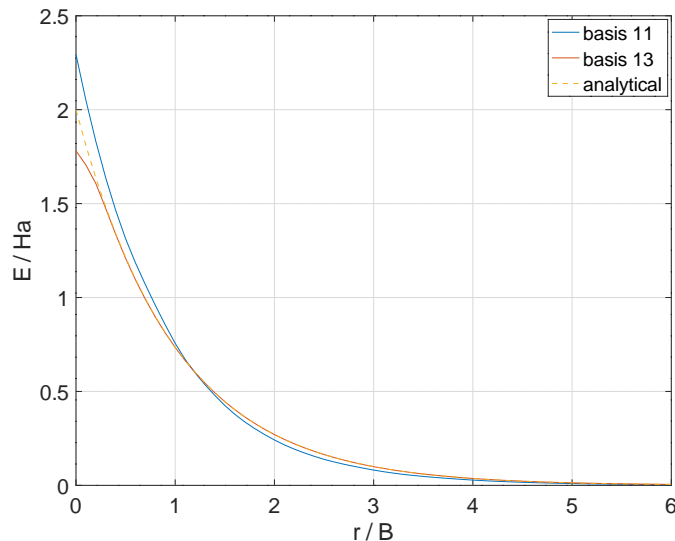


Figure 3: Radially averaged wavefunctions of the hydrogen atom for some bases. The highest curve is for basis 11 and the lowest for basis 13. The dashed line is the analytical radial wavefunction. The basis numbers refer to table 1.

Orbital	Computed energy / Ha	Exact energy / Ha
1s	-0.499295	-0.5
2s	-0.120957	-0.125
2p <sub>a</sub>	-0.123045	-0.125
2p <sub>b</sub>	-0.123045	-0.125
2p <sub>c</sub>	-0.123045	-0.125

Table 3: Energies of some orbitals of the hydrogen atom computed with the HGH pseudopotential. We labelled the resulting 2p orbitals with a, b, and c. All the orbitals presented are approximately orthogonal.

source	basis	$g/B$	exchange potential	$E/Ha$	$E_{orb}/Ha$
TH	4	0.25	HF	-2.901959	-0.971927
TH	5	0.25	HF	-2.901180	-0.970247
TH	4	0.25	LDA	-2.821511	-0.629713
TH	5	0.25	LDA	-2.819951	-0.628152
TH	14	0.125	HF	-2.916129	-0.974768
CCCBDB [31]			HF	-2.807584	
CCCBDB [31]			LSDA	-2.809599	
BigDFT [21, 22]			HF	-2.862303	
BigDFT [21, 22]			LDA	-2.833895	
HF limit [32]			HF	-2.862	-0.918

Table 4: Computation results for the helium atom. All our and BigDFT computations use HGH pseudopotential. The numbers in column “basis” refer to table 1 and “TH” means this work.

source	basis	$a/B$	$g/B$	pseudopot.	exch.	$E_{\text{system}}/\text{Ha}$	$E_{\text{binding}}/\text{Ha}$	$d/B$
TH	1	1.0	0.5	interp.	HF	-1.045883	0.167601	1.855140
TH	2	1.0	0.25	interp.	HF	-1.156554	0.199450	1.501870
TH	3	1.0	0.125	interp.	HF	-1.186176	0.210390	1.454593
TH	4	1.0	0.25	HGH	HF	-1.188779	0.190189	1.397995
TH	5	1.0	0.25	HGH	HF	-1.187995	0.189405	1.397991
TH	6	0.4	0.20	HGH	HF	-1.188547	0.189383	1.389890
TH	4	1.0	0.25	HGH	LDA	-1.157528	0.158938	1.485861
TH	5	1.0	0.25	HGH	LDA	-1.155960	0.157378	1.485851
CCCBDB <sup>a</sup>					HF	-1.117506	0.184342	1.345
CCCBDB <sup>a</sup>					LSDA	-1.157014	0.248654	1.391
BigDFT <sup>b</sup>				HGH	HF	-1.133393	0.133455	1.386175
BigDFT <sup>b</sup>				HGH	LDA	-1.136870	0.136932	1.445097
HF limit <sup>c</sup>					HF		0.132	
experimental <sup>d</sup>							0.166	1.40

Table 5: Computation results for the hydrogen molecule. The numbers in column “basis” refer to table 1 and “TH” means this work.

<sup>a</sup> Reference [31].

<sup>b</sup> Reference [21, 22].

<sup>c</sup> Reference [33].

<sup>d</sup> Reference [34, chapter 5.2].

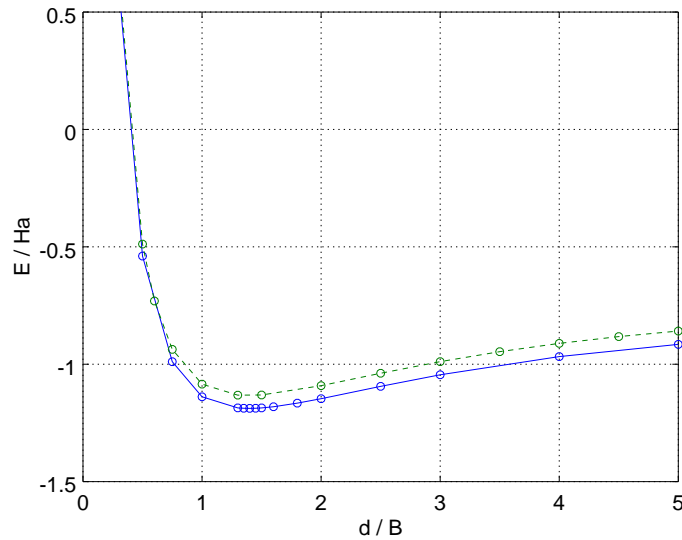


Figure 4: Energy of  $\text{H}_2$  as a function of internuclear distance calculated with Hartree–Fock method and HGH pseudopotential. The solid line is our computation with interpolating wavelets and basis set 5 and the dashed line is computed with BigDFT.



source	basis	$g/B$	pseudopot.	$E_{\text{system}}/\text{Ha}$	$E_{\text{binding}}/\text{Ha}$	$d/B$
TH	1	0.5	interp.	-0.520169	0.082028	2.371005
TH	2	0.25	interp.	-0.573665	0.095310	2.021654
TH	12	0.125	interp.	-0.589135	0.101242	2.015143
TH	11	0.5	HGH	-0.712279	0.121898	2.007951
TH	2	0.25	HGH	-0.601783	0.102460	2.006845
TH	7	0.25	HGH	-0.601636	0.102342	2.005329
TH	13	0.125	HGH	-0.602448	0.102549	1.999338
CCCBDB <sup>a</sup>				-0.582697	0.116115	2.005
BigDFT <sup>b</sup>			HGH	-0.602489	0.102520	1.995677
experimental <sup>c</sup>					0.103	2.00

Table 6: Computation results for the hydrogen molecule ion. The analytical results are equal to the experimental results. The numbers in column “basis” refer to table 1 and “TH” means this work.

<sup>a</sup> Reference [31].

<sup>b</sup> Reference [21, 22].

<sup>c</sup> Reference [34, chapter 4.6]

source	basis	$a/B$	$g/B$	exch.	$E_{\text{system}}/\text{Ha}$	$E_{\text{binding}}/\text{Ha}$	$d/B$
TH	4	1.0	0.25	HF	-0.817817	0.117472	2.879961
TH	5	1.0	0.25	HF	-0.817030	0.116686	2.880018
TH	4	1.0	0.25	LDA	-0.811482	0.111137	3.013411
TH	5	1.0	0.25	LDA	-0.809904	0.109560	3.013474
TH	6	0.4	0.2	HF	-0.817007	0.116370	2.863496
CCCBDB <sup>a</sup>				HF		0.081274	2.855
CCCBDB <sup>a</sup>				LSDA		0.135698	2.899
BigDFT <sup>b</sup>				HF	-0.760938	0.059911	2.866004
BigDFT <sup>b</sup>				LDA	-0.776416	0.075389	2.930745

Table 7: Computation results for the lithium hydride molecule. All our and BigDFT computations were done with the HGH pseudopotential. The CCCBDB all-electron total energies are not presented in the table. The numbers in column “basis” refer to table 1 and “TH” means this work.

<sup>a</sup> Reference [31].

<sup>b</sup> Reference [21, 22].

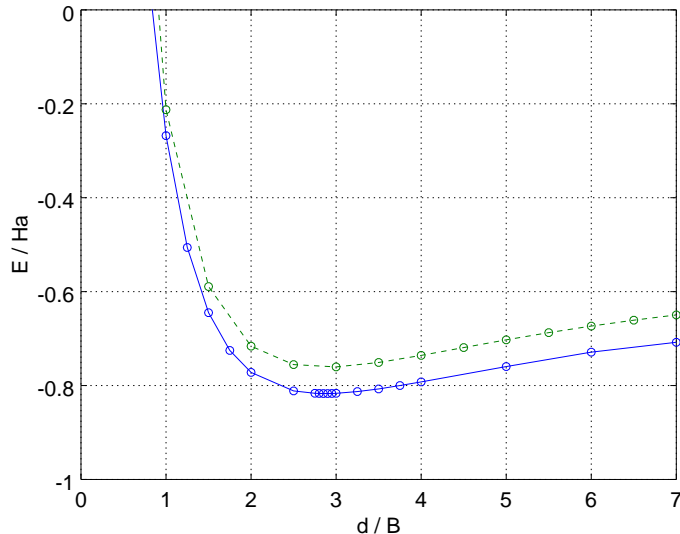


Figure 5: Total energy of the lithium hydride molecule as a function of the internuclear distance calculated with the Hartree–Fock method and HGH pseudopotential. The solid line has been computed with interpolating wavelets and basis set 5 and the dashed line with BigDFT and grid spacing  $g = 0.45$  B.

is the total energy of the system and  $E_{\text{binding}}$  is the binding energy. We used grid spacing 0.45 Ha (finer grid spacing 0.225 Ha) in all our BigDFT computations. The BigDFT parameters for determining the size of the basis set were `crmult=10.0` and `frmult=16.0`. The computations were also made with values `crmult=5.0` and `frmult=8.0` but the results did not differ significantly. Note that the total energy does not include the energies of the core electrons in the lithium hydride HGH computations. Computation using our own software use interpolating wavelets and BigDFT computations orthonormal Daubechies wavelets.

For the molecular computations the energy of the system as a function of the distance between the nuclei is computed in three points near the energy minimum and a second degree polynomial is fitted into these points. The distance between the nuclei is then the minimum point of the polynomial and the energy of the system is computed at the minimum distance. We locate the nuclei at points  $(0, 0, \pm \frac{d}{2a})$  where  $d$  is the distance between the nuclei in Bohrs. When binding energies of molecules were computed the energies of atoms were usually computed with the basis set as the molecule. When the basis was unsymmetric it was modified. For example, grid  $Z(4) \times Z(4) \times Z(10)$  becomes  $Z(4) \times Z(4) \times Z(4)$  for the atoms.

The results for hydrogen atom ground state are presented in table 2. The radially averaged ground state wavefunctions of the hydrogen atom are plotted in figures 2 and 3. A radial average of a function  $f : \mathbb{R}^3 \rightarrow \mathbb{R}$  is computed by

$$\bar{f}(r) := \frac{1}{4\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(r, \theta, \phi) \sin \theta d\phi d\theta \quad (100)$$

where  $r \in [0, \infty[$ . As the angular part of an s-type wavefunction is  $\frac{1}{2\sqrt{\pi}}$  we estimate a radial wavefunction by

$$\bar{g}(r) := \frac{1}{2\sqrt{\pi}} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} f(r, \theta, \phi) \sin \theta d\phi d\theta. \quad (101)$$

The computation of hydrogen excited states uses HGH pseudopotential and basis 9. Results are presented in table 3. The names of the excited states were obtained by computing inner products between the computed states and analytical states. The resulting orbitals are approximately orthonormal and the computed 2p states are approximately linear combinations of the analytical 2p states. The largest (in absolute value) inner product between different orbitals is  $\langle 2p_a | 2p_c \rangle = 5.428 \times 10^{-4}$ . The quality of the linear combinations can be measured by a quantity  $\sqrt{1 - \|Pf\|_2^2}$  where  $P$  is the orthogonal projection from  $L^2(\mathbb{R}^3)$  onto the space spanned by  $2p_x$ ,  $2p_y$ , and  $2p_z$ . The value of this quantity is 0.1265 for all the computed orbitals  $2p_a$ ,  $2p_b$ , and  $2p_c$ . Analytical expressions for hydrogenic orbitals can be found for example in Ref. [35].

Helium atom has been computed using the HGH pseudopotential. Results are presented in table 4. Grid spacing  $g = 0.5$  B does not give sensible results with the HGH pseudopotential. We suppose that Froese Fischer's results [32] can be regarded as the Hartree–Fock limit for helium. The computed total energies of the helium atom are quite good.

We computed the hydrogen molecule with the interpolated and HGH pseudopotentials. The computation results for the hydrogen molecule are presented in table 5. The resulting dissociation curve with the HF method, HGH pseudopotential, and basis set 5 is plotted in figure 4. When the HGH pseudopotential was used the computation worked for grid spacing  $g = 0.25$  B but did not work for spacing  $g = 0.5$  B. The results for the hydrogen molecule ion are presented in table 6.

The computed results for lithium hydride molecule are presented in table 7. Grid spacing  $g = 0.5$  B did not yield a physical dissociation curve for the HGH pseudopotential. Neither  $g = 0.5$  B nor  $g = 0.25$  B yielded a physical dissociation curve for the interpolated pseudopotential. The dissociation curve of lithium hydride computed with the Hartree–Fock method and basis set 5 is plotted in figure 5.

## 7 Conclusions

We have shown how to solve the wave equations of hydrogen and helium atoms, hydrogen molecule ion, and hydrogen and lithium hydride molecules in a three-dimensional interpolating tensor product wavelet basis. As far the authors know only Arias [8] and Engeness and Arias [9] have done this before. However, they do not use the dual interpolating MRA to evaluate matrix elements. We do that and it allows us to neglect the overlap integrals of the basis functions.

It seems to require large basis sets to obtain numerically good results for quantum physical systems. Roughly, the computations require at least ten thousand basis functions. The most accurate computed bond length of the hydrogen molecule is good and the energy satisfactory. The most accurate binding energies and internuclear distances for the hydrogen molecule ion in table 6 are very

accurate. HGH computations performed very well with grid spacing  $g = 0.25$  B but not with  $g = 0.5$  B. The same phenomenon was observed with BigDFT, too.

The BigDFT result remained approximately the same when the basis set was doubled in one dimension (i.e. the basis set was enlarged about eight times). This shows that the basis function sets in the BigDFT computations were large enough. We also found that a one level basis set can be replaced with considerably smaller two level basis set without a significant effect on the results.

It is best to use wavelet basis sets consisting of one or two resolution levels because we have then

$$\langle \psi_{s',j,k'}, \psi_{s,j,k} \rangle = \delta_{s',s} \delta_{k',k} \quad (102)$$

for all the one-dimensional dual basis functions and basis functions, which simplifies the computation of the Laplacian operator.

## References

- [1] Charles K. Chui and Chun Li. “Dyadic affine decompositions and functional wavelet transforms”. In: *SIAM J. Math. Anal.* 27.3 (1996), pp. 865–890. DOI: 10.1137/0527046.
- [2] David L. Donoho. *Interpolating Wavelet Transforms*. 1992.
- [3] Gilles Deslauriers and Serge Dubuc. “Symmetric Iterative Interpolation Processes”. In: *Constr. Approx.* 5.1 (1989), pp. 49–68. DOI: 10.1007/BF01889598.
- [4] Serge Dubuc. “Interpolation through an Iterative Scheme”. In: *J. Math. Anal. Appl.* 114 (1986), pp. 185–204. DOI: 10.1016/0022-247X(86)90077-6.
- [5] Tommi Höynälänmaa. “Multiresolution Analysis for Compactly Supported Interpolating Tensor Product Wavelets”. In: *Int. J. Wavelets Multiresolut Inf. Process.* 13.2 (2015), p. 1550010. DOI: 10.1142/S0219691315500101.
- [6] S. Goedecker. *Wavelets and their application for the solution of partial differential equations in physics*. Presses Polytechniques et Universitaires Romandes, 1998.
- [7] Naohiro Fukuda, Tamotu Kinoshita, and Toshio Suzuki. “On the unconditional convergence of wavelet expansions for continuous functions”. In: *Int. J. Wavelets Multiresolut Inf. Process.* 14 (2016), p. 1650007. DOI: 10.1142/S0219691316500077.
- [8] T. A. Arias. “Multiresolution analysis of electronic structure: semicardinal and wavelet bases”. In: *Rev. Mod. Phys.* 71.1 (1999), pp. 267–311. DOI: 10.1103/RevModPhys.71.267.
- [9] Torkel D. Engeness and T. A. Arias. “Multiresolution analysis for efficient, high precision all-electron density-functional calculations”. In: *Phys. Rev. B* 65 (2002), p. 165106. DOI: 10.1103/PhysRevB.65.165106.
- [10] Ross A. Lippert, T. A. Arias, and Alan Edelman. “Multiscale Computation with Interpolating Wavelets”. In: *J. Comput. Phys.* 140 (1998), pp. 278–310. DOI: 10.1006/jcph.1998.5885.
- [11] I. Daubechies. *Ten Lectures on Wavelets*. CBMS-NSF regional conference series in applied mathematics ; 61. SIAM, 1992. DOI: 10.1137/1.9781611970104.

- [12] P. Fischer and M. Defrancheschi. “Numerical Solution of the Schrödinger Equation in a Wavelet Basis for Hydrogen-like Atoms”. In: *SIAM J. Numer. Anal.* 35.1 (1998), pp. 1–12. DOI: 10.1137/S0036142995284557.
- [13] P. Fischer and M. Defranceschi. “Representation of the atomic Hartree-Fock equations in a wavelet basis by means of the BCR algorithm”. In: *Appl. Comput. Harmon. Anal.* 1 (1994), pp. 495–506. DOI: 10.1016/B978-0-08-052084-1.50027-2.
- [14] P. Fischer and M. Defranceschi. “Iterative Process for Solving Hartree-Fock Equations by means of a Wavelet Transform”. In: *Appl. Comput. Harmon. Anal.* 1 (1994), pp. 232–241. DOI: 10.1006/acha.1994.1010.
- [15] Siqing Wei and M. Y. Chou. “Wavelets in Self-Consistent Electronic Structure Calculations”. In: *Phys. Rev. Lett.* 76.15 (1996), pp. 2650–2653. DOI: 10.1103/PhysRevLett.76.2650.
- [16] C. J. Tymczak and Xiao-Qian Wang. “Orthonormal Wavelet Bases for Quantum Molecular Dynamics”. In: *Phys. Rev. Lett.* 78.19 (1997), pp. 3654–3657. DOI: 10.1103/PhysRevLett.78.3654.
- [17] K. Yamaguchi and T. Mukoyama. “Calculations of discrete and continuum wave functions for atoms using wavelets”. In: *Nucl. Instrum. Methods Phys. Res. B* 124 (1997), p. 361. DOI: 10.1016/S0168-583X(96)00814-2.
- [18] Srinivasan S. Iyengar and Michael J. Frisch. “Effect of time-dependent basis functions and their superposition error on atom-centered density matrix propagation (ADMP): Connections to wavelet theory of multiresolution analysis”. In: *J. Chem. Phys.* 121.11 (2004), pp. 5061–5070. DOI: 10.1063/1.1780157.
- [19] Tommi Höynälänmaa, Tapio T. Rantala, and Keijo Ruotsalainen. “Solution of atomic orbitals in an interpolating wavelet basis”. In: *Phys. Rev. E* 70 (2004), p. 066701. DOI: 10.1103/PhysRevE.70.066701.
- [20] Seungwu Han, Kyeongjae Cho, and Jisoon Ihm. “Wavelets in all-electron density-functional calculations”. In: *Phys. Rev. B* 60.3 (1999). DOI: 10.1103/PhysRevB.60.1437.
- [21] L. Genovese et al. “Daubechies wavelets as a basis set for density functional pseudopotential calculations”. In: *J. Chem. Phys.* 129 (2008), p. 014149. DOI: 10.1063/1.2949547.
- [22] S. Mohr et al. “Daubechies wavelets for linear scaling density functional theory”. In: *J. Chem. Phys.* 140 (2014), p. 204110. DOI: 10.1063/1.4871876.
- [23] W. E. Arnoldi. “The principle of minimized iterations in the solution of the matrix eigenvalue problem”. In: *Quarterly of Applied Mathematics* 9 (1951), pp. 17–29. DOI: 10.1090/qam/42792.
- [24] R. B. Lehoucq and D. C. Sorensen. “Deflation Techniques for an Implicitly Restarted Arnoldi Iteration”. In: *SIAM* (1996). DOI: 10.1137/S0895479895281484.
- [25] Y. Saad and M. H. Schultz. “GMRES: A generalized minimal residual algorithm for solving nonsymmetric linear systems”. In: *SIAM J. Sci. Statist. Comput.* 7 (1986), pp. 856–869. DOI: 10.1137/0907058.
- [26] W. Kohn. “Nobel Lecture: Electronic structure of matter – wavefunctions and density functionals”. In: *Rev. Mod. Phys.* 71.5 (1999), pp. 1253–1266. DOI: 10.1103/RevModPhys.71.1253.

- [27] Yousef Saad, James R Chelikowsky, and Suzanne M Shontz. “Numerical methods for electronic structure calculations of materials”. In: *SIAM review* 52.1 (2010), pp. 3–54. DOI: 10.1137/060651653.
- [28] José M Soler et al. “The SIESTA method for ab initio order-N materials simulation”. In: *Journal of Physics: Condensed Matter* 14.11 (Mar. 2002), pp. 2745–2779. DOI: 10.1088/0953-8984/14/11/302.
- [29] O. V. Vasilyev and P. Paolucci. “A Dynamically Adaptive Multilevel Wavelet Collocation method for Solving Partial Differential Equations in a Finite Domain”. In: *J. Comput. Phys.* 125 (1996), pp. 498–512. DOI: 10.1006/jcph.1996.0111.
- [30] C. Hartwigsen, S. Goedecker, and J. Hutter. “Relativistic separable dual-space Gaussian Pseudopotentials from H to Rn”. In: *Phys. Rev. B* 58 (1998), p. 3641. DOI: 10.1103/PhysRevB.58.3641.
- [31] “Computational Chemistry Comparison and Benchmark DataBase”. URL: <http://cccbdb.nist.gov>.
- [32] Ch. Froese-Fischer. *The Hartree-Fock Method for Atoms – A Numerical Approach*. New York: John Wiley & Sons, 1977. DOI: 10.1088/0031-9112/29/4/040.
- [33] Julius Su and William A. Goddard III. *eFF User’s Guide*. May 19, 2019. URL: <http://www.wag.caltech.edu/home/jsu/UsersGuide/UsersGuide.html>.
- [34] Leon van Dommelen. *Quantum Mechanics for Engineers*. May 19, 2019. URL: <http://www.umich.edu/~ners312/CourseLibrary/Dommelen.pdf>.
- [35] Peter Atkins and Ronald Friedman. *Molecular Quantum Mechanics*. New York: Oxford University Press Inc., 2005. DOI: 10.1080/00107514.2012.678277.