

# Electronic structure calculation with exact pseudopotential and interpolating wave basis set

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## Abstract

Electronic structure calculations are mostly carried out with Coulomb potential adapted basis sets like STO or contracted GTO. With other basis or for heavy elements the pseudopotentials may appear as a practical alternative. Here, we introduce the exact pseudopotential (EPP) to remove the Coulomb singularity and test it for orbitals of small atoms with the interpolating wave basis set. We apply EPP to a Galerkin method with a basis set consisting of Deslauriers–Dubuc scaling functions on the half-infinite real interval. We demonstrate the EPP Galerkin method by computing the hydrogen atom 1s, 2s, and 2p orbitals and helium atom configurations He 1s<sup>2</sup>, He 1s2s <sup>1</sup>S, and He 1s2s <sup>3</sup>S. We compare the performance of our approach to that of finite–difference approach, which is another practical method for spherical atoms. We find the accuracy of the EPP Galerkin method very good.

## 1 Introduction

The Coulomb singularity in hamiltonian may appear as a challenge in electronic structure calculations. Singularity adapted Slater type atomic orbitals (STO) basis is the usual solution to this, and also, gaussian type contracted basis functions (GTO) have turned out to be useful with sufficient accuracy. The latter one is more popular due to other practical advantages.

Pseudopotentials removing the singularity are another type of solution to this problem. In case the core electrons do not play an essential role in the problem at hand or valence electrons are expanded in plane waves, like it is with heavy elements or periodic crystalline systems. In those cases the pseudopotentials typically replace the nuclei and a number of core electrons with their charge distribution, and possibly, some other core properties.

One-dimensional interpolating wavelets have been used for atomic computations for example in [1]. There we used ordinary Deslauriers-Dubuc interpolating wavelets [2, 3, 4, 5, 6] defined on the whole real axis so that we had to include the negative real axis into the computations, too. We handled the singularity at the origin by excluding the scaling function at the origin from the basis. That is

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why we did not need pseudopotentials. We used the nonstandard operator form to compute the various operators needed in the computations. We computed the Schrödinger equation of hydrogenlike atoms (ions) and Hartree-Fock equations of some light many-electron atoms (helium, lithium, beryllium, neon, sodium, magnesium, and argon). In this article we make similar computations for hydrogen and helium atoms but we use a different method to handle the singularity of the potential. We handle the singularity by computing the Schrödinger and Hartree-Fock equations for a range of variables  $r \in [a, \infty[$  which does not contain the origin.

Interpolating wavelets are a biorthogonal wavelet family. Since the dual scaling functions and dual wavelets of these functions are finite sums of Dirac delta functions the matrix elements involving interpolating wavelets usually require evaluating some function in a finite set of points. An interpolating wavelet family is defined by a mother scaling function  $\varphi$ , mother wavelet  $\psi$ , and four finite filters  $h_j$ ,  $g_j$ ,  $\tilde{h}_j$ , and  $\tilde{g}_j$  where  $j = -m, \dots, m$ . The functions  $\varphi$ ,  $\psi$ ,  $\tilde{\varphi}$ , and  $\tilde{\psi}$  satisfy equations

$$\varphi(x) = \sum_{j=-m}^m h_j \varphi(2x - j), \quad (1)$$

$$\psi(x) = \sum_{j=-m}^m g_j \varphi(2x - j), \quad (2)$$

$$\tilde{\varphi}(x) = \sum_{j=-m}^m \tilde{h}_j \tilde{\varphi}(2x - j), \quad (3)$$

and

$$\tilde{\psi}(x) = \sum_{j=-m}^m \tilde{g}_j \tilde{\varphi}(2x - j). \quad (4)$$

The two-index basis functions and dual basis functions are

$$\varphi_{j,k}(x) = \varphi(2^j x - k), \quad (5)$$

$$\psi_{j,k}(x) = \psi(2^j x - k), \quad (6)$$

$$\tilde{\varphi}_{j,k}(x) = 2^j \tilde{\varphi}(2^j x - k), \quad (7)$$

and

$$\tilde{\psi}_{j,k}(x) = 2^j \tilde{\psi}(2^j x - k). \quad (8)$$

A wavelet basis consists of scaling functions  $\varphi_{j_0,k}$ ,  $k \in \mathbb{Z}$ , and wavelets  $\psi_{j,k}$ ,  $j \geq j_0$ ,  $k \in \mathbb{Z}$ , where  $j_0 \in \mathbb{Z}$  is the minimum resolution level. The expansion of an arbitrary (regular enough) function  $f : \mathbb{R} \rightarrow \mathbb{R}$  in the wavelet basis is

$$f(x) = \sum_{k \in \mathbb{Z}} s_k \varphi_{j_0,k}(x) + \sum_{j \geq j_0} \sum_{k \in \mathbb{Z}} d_{j,k} \psi_{j,k}(x). \quad (9)$$

Arias [7] and Engeness and Arias [8] developed 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. On the other hand, we use the interpolating dual scaling functions and wavelets for the computation of matrix elements.

One-dimensional interpolating multiresolution analysis in space  $C_u(\mathbb{R})$  consisting of uniformly continuous bounded functions in  $\mathbb{R}$  has been constructed in [4]. One-dimensional interpolating multiresolution analysis in space  $C_0(\mathbb{R})$  consisting of continuous functions in  $\mathbb{R}$  vanishing at infinity has been constructed in [5]. Both of these constructions are based on Deslauriers-Dubuc functions [2, 3]. Donoho [5] constructs wavelets on a finite real interval, too. We compute the energies of hydrogen atom 1s, 2s, and 2p orbitals and helium atom configurations He 1s<sup>2</sup>, He 1s2s <sup>1</sup>S, and He 1s2s <sup>3</sup>S with the EPP method. We use both Galerkin method with interpolating wavelets and finite difference method. We denote the pointwise product of functions  $f$  and  $g$  by  $f \star g$ . We use atomic units throughout this article ( $e = m_e = \hbar = 4\pi\epsilon_0 = 1$ ).

Suppose that we have a system consisting of a positively charged nucleus at the origin and  $N$  electrons. In EPP method we choose some small radius  $r_0$  so that inside the sphere with radius  $r_0$  the wavefunctions of the system are approximated by hydrogenic wavefunctions and the actual computations are done only for values  $r \geq r_0$ . Actually we define a basis set for half-infinite interval  $[0, \infty[$  and make a change of variables  $s = r - r_0$ . For Hartree-Fock calculations the Slater integrals are computed by

$$\begin{aligned} \tilde{y}_{ab}^0(s) &= \frac{Q_{ab}}{s + r_0} + \frac{1}{s + r_0} \int_0^s \bar{P}_a(s') \bar{P}_b(s') ds' \\ &+ \int_s^\infty \frac{1}{s' + r_0} \bar{P}_a(s') \bar{P}_b(s') ds' \end{aligned} \quad (10)$$

where  $s \geq 0$  and  $Q_{ab}$  is a system-dependent quantity that approximates the contribution of the EPP core region to the Slater integral.

## 2 Interpolating Wavelets on Half-Infinite Interval

This derivation is based on section 3 in [5]. We construct a basis set on half-infinite interval  $\mathbb{R}_0 = \{r \geq 0 | r \in \mathbb{R}\}$ . We define  $\varphi$  to be a Deslauriers-Dubuc scaling function of some order  $D$  and  $\varphi_{j,k}(x) := \varphi(2^j x - k)$  for  $j, k \in \mathbb{Z}$ . We define a wavelet expansion of a function  $f$  on  $\mathbb{R}_0$  by

$$\tilde{f} := \sum_{k=0}^D \beta_{j,k} \varphi_{j,k}^\# + \sum_{k=D+1}^\infty \beta_{j,k} \varphi_{j,k}. \quad (11)$$

When we use a finite basis of size  $W$  we have

$$\tilde{f} := \sum_{k=0}^D \beta_{j,k} \varphi_{j,k}^\# + \sum_{k=D+1}^{W-1} \beta_{j,k} \varphi_{j,k} \quad (12)$$

We must have  $W > 2D$  so that functions  $\varphi_{j,k}^\#(x)$ ,  $0 \leq k \leq D$ , vanish for  $x \geq 2^{-j}W$ . This kind of truncation of the basis requires that the function  $f$  approximately vanishes for  $x > 2^{-j}W$ .

Suppose that we are given samples  $\beta_{j,k} = f(2^{-j}k)$  for  $k \in \mathbb{N}$  and  $f$  is some function from  $[0, \infty[$  into  $\mathbb{R}$ . We define  $\pi_j^\#$  to be the polynomial of degree  $D$  for

which  $\pi_j^\#(2^{-j}k) = f(2^{-j}k)$  for all  $k = 0, \dots, D$ . We define

$$\tilde{\beta}_{j,k} := \pi_j^\#(2^{-j}k) \quad (13)$$

for  $k < 0$  and

$$\tilde{\beta}_{j,k} := \beta_{j,k} \quad (14)$$

for  $k \geq 0$ . Now  $f$  can be extrapolated onto the whole real line by

$$\tilde{f} = \sum_{k=-\infty}^{\infty} \tilde{\beta}_{j,k} \varphi_{j,k}. \quad (15)$$

As each coefficient  $\tilde{\beta}_{j,k}$  is a linear functional of coefficients  $\beta_{j,k'}$  we may define extrapolation weights  $e_{k,k'}^\#$  so that

$$\tilde{\beta}_{j,k} = \sum_{k'=0}^D e_{k,k'}^\# \beta_{j,k'} \quad (16)$$

for  $k < 0$ . When  $f := \varphi_{j,l}$  we have

$$\tilde{\beta}_{j,k} = e_{k,l}^\# \quad (17)$$

where  $l \in \{0, \dots, D\}$ . Consequently the quantities  $e_{k,l}^\#$  can be computed by polynomial interpolation of functions  $\varphi_{j,l}$ . As

$$\text{supp } \varphi_{j,k} \subset 2^{-j}[k - D, k + D] \quad (18)$$

we need only values  $k \in \{-D, \dots, -1\}$ . We define

$$\varphi_{j,k}^\# := \varphi_{j,k} + \sum_{l < 0} e_{l,k}^\# \varphi_{j,l} \quad (19)$$

for  $k = 0, \dots, D$ . Note that

$$\langle \tilde{\varphi}_{j,k}, \varphi_{j,l}^\# \rangle = \delta_{k,l} \quad (20)$$

for  $k \geq 0$  and  $0 \leq l \leq D$ . Let  $A$  be a linear operator from  $C_0(\mathbb{R})$  to  $C_0(\mathbb{R})$ . The matrix elements  $A_{k,l}$ ,  $l = 0, \dots, D$  are given by

$$\langle \tilde{\varphi}_{j,k}, A\varphi_{j,l}^\# \rangle = \langle \tilde{\varphi}_{j,k}, A\varphi_{j,l} \rangle + \sum_{\alpha < 0} e_{\alpha,l}^\# \langle \tilde{\varphi}_{j,k}, A\varphi_{j,\alpha} \rangle. \quad (21)$$

Let  $v(f)$  denote the coefficient vector  $(\beta_{j,k})_{k=0}^{W-1}$  defined by equation (12) and define

$$M(f) := (f(2^{-j}k)\delta_{k,k'})_{k,k'=0}^{W-1, W-1} \quad (22)$$

for some function  $f : \mathbb{R} \rightarrow \mathbb{R}$ .

### 3 Schrödinger Equations of Hydrogen-like Atoms and Helium Atom in Our Basis

#### 3.1 Hydrogen-like Atoms

See [9, 10, 11, 12] for the Schrödinger equation of the hydrogen atom and Hartree-Fock equations of atoms. See also [1] for the representation of the Hartree-Fock equations in an interpolating wavelet basis. By doing a change of variables  $s := r - r_0$  the Schrödinger equation of a hydrogen-like atom in interval  $r \geq r_0$  takes the form

$$\left( -\frac{1}{2} \frac{d^2}{ds^2} - \frac{Z}{s+r_0} + \frac{l(l+1)}{2(s+r_0)^2} \right) \bar{P}(s) = E\bar{P}(s), \quad s \geq 0 \quad (23)$$

where  $Z$  is the charge of the nucleus,  $l$  is the angular momentum quantum number, and  $\bar{P}(s) = P(r_0 + s)$  for  $s \geq 0$ .

We define the second derivative filter by

$$a_k := \langle \tilde{\varphi}, D^2 \varphi(\cdot - k) \rangle \quad (24)$$

Matrix elements of the Laplacian operator  $L$  are computed by

$$L_{k,l} := \langle \tilde{\varphi}_{j,k}, L \varphi_{j,l}^\# \rangle = 2^{2j} \left( a_{l-k} + \sum_{\alpha=-D}^{-1} e_{\alpha,l}^\# a_{\alpha-k} \right) \quad (25)$$

for  $0 \leq l \leq D$  and

$$L_{k,l} := \langle \tilde{\varphi}_{j,k}, L \varphi_{j,l} \rangle = 2^{2j} a_{l-k} \quad (26)$$

for  $D < l < W$ . Note that matrix  $L$  is generally not hermitian. The potential energy operator is computed as a diagonal matrix

$$\hat{V}_{k,k} = V(2^{-j}k) \quad (27)$$

where

$$V(y) = -\frac{Z}{y+a} \quad (28)$$

for  $y \geq 0$ . The centrifugal potential is computed in the same way.

#### 3.2 Hartree-Fock Equations for the Helium Atom

Define the Slater integrals

$$y_{ab}^0(r) = \int_{r'=0}^{\infty} P_a(r') \gamma(r, r') P_b(r') dr' \quad (29)$$

where  $a$  and  $b$  denote some atomic orbitals and

$$\gamma(r, r') = \frac{1}{\max\{r, r'\}}. \quad (30)$$

We use symbol  $y$  instead of  $Y$  to avoid confusion with spherical harmonics. By doing a similar change of variables  $s := r - r_0$  the Hartree-Fock equation of the ground state of the helium atom in interval  $r \geq r_0$  takes the form

$$\left( -\frac{1}{2} \frac{d^2}{ds^2} - \frac{2}{s+r_0} + y_{1s1s}^0(s+r_0) \right) \bar{P}_{1s}(s) = \varepsilon_{1s} \bar{P}_{1s}(s), \quad s \geq 0. \quad (31)$$

The Hartree-Fock equations for the helium 1s2s <sup>1</sup>S configuration are

$$\left(-\frac{1}{2}\frac{d^2}{ds^2} - \frac{2}{s+r_0} + y_{2s2s}^0(s+r_0)\right)\bar{P}_{1s}(s) = \varepsilon_{1s}\bar{P}_{1s}(s) \quad (32)$$

$$\left(-\frac{1}{2}\frac{d^2}{ds^2} - \frac{2}{s+r_0} + y_{1s1s}^0(s+r_0)\right)\bar{P}_{2s}(s) = \varepsilon_{2s}\bar{P}_{2s}(s) \quad (33)$$

and for helium 1s2s <sup>3</sup>S configuration

$$\left(-\frac{1}{2}\frac{d^2}{ds^2} - \frac{2}{s+r_0} + y_{2s2s}^0(s+r_0)\right)\bar{P}_{1s}(s) = \varepsilon_{1s}\bar{P}_{1s}(s) + y_{1s2s}^0(s+r_0)\bar{P}_{2s}(s) \quad (34)$$

$$\left(-\frac{1}{2}\frac{d^2}{ds^2} - \frac{2}{s+r_0} + y_{1s1s}^0(s+r_0)\right)\bar{P}_{2s}(s) = \varepsilon_{2s}\bar{P}_{2s}(s) + y_{2s1s}^0(s+r_0)\bar{P}_{1s}(s) \quad (35)$$

### 3.3 EPP Method for the Helium Atom

We define  $P_a(r)$  to be the exact Hartree-Fock wavefunction of the orbital  $a$  of the atom. We define the operators  $\hat{U}_0$  and  $\hat{U}_\infty$  [1] by

$$(\hat{U}_0 f)(s) = \int_0^s f(s') ds' \quad (36)$$

and

$$(\hat{U}_\infty f)(s) = \int_s^\infty f(s') ds' \quad (37)$$

Define  $P_{1s,\text{hydr}}(r')$  and  $P_{2s,\text{hydr}}(r')$  to be the hydrogenic orbitals of the helium atom. We have

$$\langle \tilde{\varphi}_{j,k} \hat{U}_0 \varphi_{j,l} \rangle = 2^{-j}(\Phi(|k|-l) - \Phi-l) \quad (38)$$

and

$$\langle \tilde{\varphi}_{j,k} \hat{U}_\infty \varphi_{j,l} \rangle = 2^{-j}(1 - \Phi(|k|-l)) \quad (39)$$

where

$$\Phi(x) = \int_{-\infty}^x \varphi(y) dy. \quad (40)$$

The Slater integrals in the shifted variables are obtained from equation (10) where we set

$$Q_{ab} := \frac{\bar{P}_a(0)}{P_{a,\text{hydr}}(r_0)} \frac{\bar{P}_b(0)}{P_{b,\text{hydr}}(r_0)} \int_0^{r_0} P_{a,\text{hydr}}(r') P_{b,\text{hydr}}(r') dr'. \quad (41)$$

for the helium ground state, and

$$Q_{ab} := \int_0^{r_0} P_{a,\text{hydr}}(r') P_{b,\text{hydr}}(r') dr'. \quad (42)$$

for the excited states of helium. Define

$$q(s) := \frac{1}{s+r_0} \quad (43)$$

and

$$S_0 := M(q)U_0 + U_\infty M(q). \quad (44)$$

Now

$$v(\bar{y}_{ab}^0) = Q_{ab}v(q) + S_0(v(\bar{P}_a \star \bar{P}_b)) \quad (45)$$

where  $U_0$  and  $U_\infty$  are the matrices of operators  $\hat{U}_0$  and  $\hat{U}_\infty$  in the basis set constructed in section 2. We define  $\mathbf{v}_a = v(\bar{P}_a)$  and  $\mathbf{v}_b = v(\bar{P}_b)$ . The matrix of the exchange integral operator

$$(\hat{K}_a \bar{P}_a)(s) := \bar{y}_{ab}^0(s) \bar{P}_b(s) \quad (46)$$

is computed by

$$K_a := W_a + M(\mathbf{v}_b)S_0M(\mathbf{v}_b) \quad (47)$$

The term  $W_a \mathbf{v}_a$  approximates the first term in equation (10) as a linear function of  $\mathbf{v}_a$ . In order to do this we approximate the wavefunction  $P_a(r)$  in region  $r \in [0, r_0]$  by a linear function that is zero at the origin and  $\bar{P}_a(0)$  at  $r_0$ . We have

$$\frac{Q_{ab}}{s+r_0} \bar{P}_b(s) \approx \frac{1}{s+r_0} \bar{P}_a(0) \left( \int_{s'=-r_0}^0 \left(1 + \frac{s'}{r_0}\right) P_{b,\text{hydr}}(s'+r_0) ds' \right) \bar{P}_b(s) \quad (48)$$

The wavefunction  $\bar{P}_b(s)$  is taken from the previous step of the Hartree-Fock iteration. By approximating the wavefunctions by hydrogenic ones we get the hydrogenic Slater integrals

$$y_{1s1s,\text{hydr}}^0(r) = \frac{1}{r} - e^{-2Zr} \left( \frac{1}{r} + Z \right) \quad (49)$$

$$y_{2s2s,\text{hydr}}^0(r) = \frac{1}{r} + e^{-Zr} \left( -\frac{Z^3}{8} r^2 - \frac{1}{4} Z^2 r - \frac{3Z}{4} - \frac{1}{r} \right) \quad (50)$$

$$y_{1s2s,\text{hydr}}^0(r) = \frac{1}{27\sqrt{2}} (12Z^2 r + 8Z) e^{-3Zr/2} \quad (51)$$

for  $r \geq 0$ . The scalar products involving the Slater integrals are approximated as

$$\begin{aligned} \langle P_a | y_{ab}^0 | P_b \rangle &\approx \left( \frac{\bar{P}_a(0)}{P_{a,\text{hydr}}(r_0)} \right)^2 \left( \frac{\bar{P}_b(0)}{P_{b,\text{hydr}}(r_0)} \right)^2 \\ &\cdot \int_{r'=0}^{r_0} P_{a,\text{hydr}}(r') y_{ab,\text{hydr}}^0(r') P_{b,\text{hydr}}(r') dr' \\ &+ \int_{s=0}^{\infty} \bar{P}_a(s) \bar{y}_{ab}^0(s) \bar{P}_b(s) ds \end{aligned} \quad (52)$$

for the helium ground state and

$$\begin{aligned} \langle P_a | y_{ab}^0 | P_b \rangle &\approx \int_{r'=0}^{r_0} P_{a,\text{hydr}}(r') y_{ab,\text{hydr}}^0(r') P_{b,\text{hydr}}(r') dr' \\ &+ \int_{s=0}^{\infty} \bar{P}_a(s) \bar{y}_{ab}^0(s) \bar{P}_b(s) ds. \end{aligned} \quad (53)$$

for the excited states of helium.

### 3.4 Energy of the Helium Atom

The total energy of the ground state of the helium atom is

$$E(\text{He } 1s^2) = 2\varepsilon_{1s} - \langle P_{1s} | y_{1s1s}^0 | P_{1s} \rangle \quad (54)$$

The total energy of the  $1s2s \ ^1S$  configuration of the helium atom is

$$\begin{aligned} E(\text{He } 1s2s \ ^1S) &= \varepsilon_{1s} + \varepsilon_{2s} \\ &\quad - \frac{1}{2} \langle P_{1s} | y_{2s2s}^0 | P_{1s} \rangle - \frac{1}{2} \langle P_{2s} | y_{1s1s}^0 | P_{2s} \rangle \end{aligned} \quad (55)$$

and for the  $1s2s \ ^3S$  configuration

$$\begin{aligned} E(\text{He } 1s2s \ ^3S) &= \varepsilon_{1s} + \varepsilon_{2s} \\ &\quad - \frac{1}{2} \langle P_{1s} | y_{2s2s}^0 | P_{1s} \rangle - \frac{1}{2} \langle P_{2s} | y_{1s1s}^0 | P_{2s} \rangle \\ &\quad + \langle P_{1s} | y_{1s2s}^0 | P_{2s} \rangle. \end{aligned} \quad (56)$$

## 4 Combining EPP with Finite Difference Method

Finite Difference Method is a method for solving differential equations. The spatial and time domains are discretized and derivative at a point is computed with a stencil applied to the nearby points. This way the differential equation is converted to a matrix equation. The Laplacian operator is approximated by

$$u''(x) \approx \frac{u(x-h) - 2u(x) + u(x+h)}{h^2} \quad (57)$$

where  $h$  is the discretization step size.

We discretize the Schrödinger equation (23) at points  $-p_j = jh$ ,  $j = 0, \dots, J+1$  where  $J$  is the number of actual computation points and  $h \in \mathbb{R}_+$  is the grid spacing. We define the discretized potential by  $v_j = \bar{V}(s_j)$ . The boundary condition at the end of the interval is set by  $p_{J+1} = 0$ . We have

$$-\frac{p_{j+1} + (-2 - 2h^2 v_j)p_j + p_{j-1}}{2h^2} = Ep_j \quad (58)$$

for  $j = 2, \dots, J$ . We handle case  $j = 1$  by extrapolating  $p_0$  linearly from  $p_1$  and  $p_2$ . We get  $p_0 = 2p_1 - p_2$  from which it follows that  $p_2 + (-2 - 2h^2 v_j)p_1 + p_0 = -2h^2 v_1 p_1$ . Hence the difference equation for  $j = 1$  is

$$v_1 p_1 = Ep_1. \quad (59)$$

In order to discretize the exchange operator  $\hat{K}_a$  we need to discretize the integral operators

$$(\hat{I}_g(f))(s) = \int_0^s g(s')f(s')ds' \quad (60)$$

and

$$(\hat{I}_g^{\text{compl}}(f))(s) = \int_s^\infty g(s')f(s')ds'. \quad (61)$$



We define

$$(I(g))_{j,k} := \begin{cases} hg_k; & k < j \\ 0; & k \geq j \end{cases} \quad (62)$$

and

$$(I^{\text{compl}}(g))_{j,k} := \begin{cases} hg_k; & k \geq j \\ 0; & k < j \end{cases} \quad (63)$$

where  $g_k = g(s_k)$ . When  $f$  is a real function define  $w(f) := (f(s_k))_{k=1}^J$ . Now the matrix of the exchange integral operator is computed by

$$K_a := W_a + K_a^0 \quad (64)$$

where  $W_a$  is computed as in the case of wavelets,

$$K_a^0 := \text{diag}(w(f_1))I(\bar{P}_b) + I^{\text{compl}}(f_1 \star \bar{P}_b), \quad (65)$$

and

$$f_1(s) := \frac{1}{s + r_0}, \quad s \geq 0. \quad (66)$$

## 5 Computations and Results

We demonstrate the EPP method by doing computations where the EPP radius  $r_0$  and the basis size  $W$  are varied. We actually select a length scale  $u = R/W$  and do a change of variables  $s = us'$  in equations (23), (31), (32), (33), (34), and (35). The length scale  $u$  specifies how many atomic units of length a length unit in our own coordinate system is. Here  $R$  is the size of the computation domain, between 10 B and 20 B. We also set  $j = 0$  for the basis set (see section 2). The relative errors of the quantities are given as

$$\varepsilon = \left| \frac{x_{\text{computed}} - x_{\text{exact}}}{x_{\text{exact}}} \right|. \quad (67)$$

The amount of discontinuity of a computed wavefunction at point  $r = r_0$  is measured by computing the relative error of the computed wavefunction value  $\bar{P}(0)$  compared to the hydrogenic wavefunction value  $P_{\text{hydr}}(r_0)$ .

The results for the ground state of the hydrogen atom are presented in figures 1 and 2, for the 2s state in figures 3 and 4, and for the 2p state in figures 5 and 6. It can be seen that the hydrogenic orbitals are approximately continuous at  $r_0$ . The results of the ground state of the helium atom are presented in figures 7 and 8. The results for He 1s2s  $^1S$  are given in figure 9 and the results for He 1s2s  $^3S$  in figure 10. As expected, the energy results are best for large values of  $W$  and small values of  $r_0$ .

The most accurate computations are in the upper left corners of the figures. The orbitals of He 1s2s are not continuous at all at  $r_0$  and no continuity plots are presented for them. The best energies (largest basis and smallest  $r_0$ ) of the computed systems are presented in table 1 for wavelets and in table 2 for the finite difference method. The accuracies of both of the methods depend on the grid spacing. The interpolating wavelet method gives better results with considerably smaller number of grid points and larger grid spacing.

The Hartree-Fock energy of the ground state of the helium atom is  $-2.8616800$  Ha [13]. Reference [14] gives Hartree-Fock energies  $-2.147$  Ha and  $-2.171$  Ha

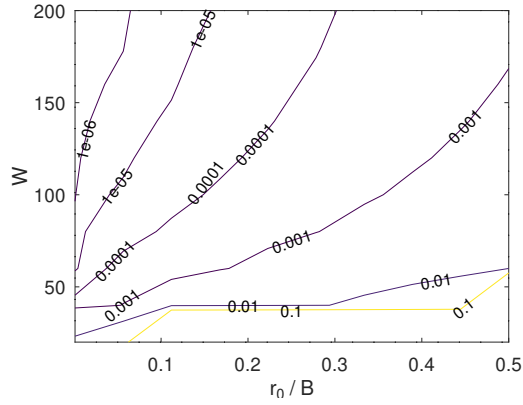


Figure 1: Hydrogen 1s orbital eigenenergy relative error. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

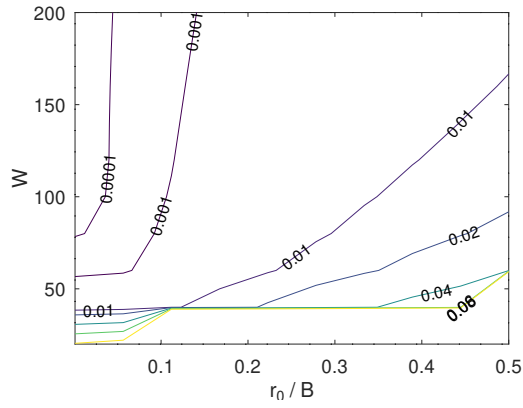


Figure 2: Relative error of the wavefunction value at the core radius for the hydrogen 1s orbital. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

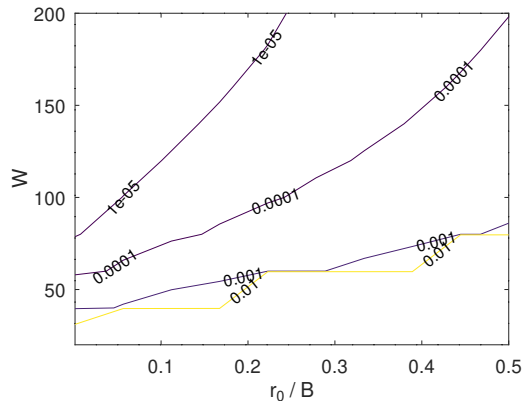


Figure 3: Hydrogen 2s orbital eigenenergy relative error. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

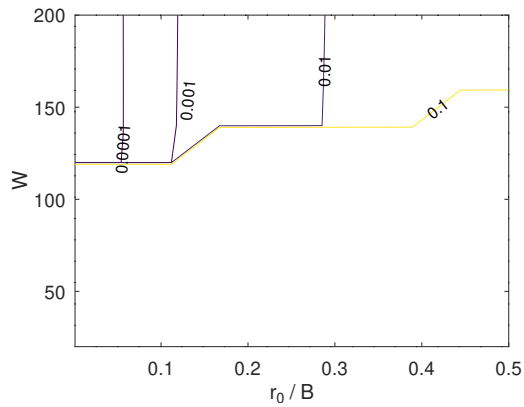


Figure 4: Relative error of the wavefunction value at the core radius for the hydrogen 2s orbital. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

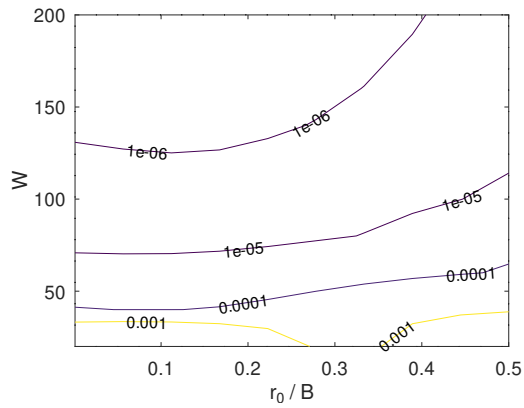


Figure 5: Hydrogen 2p orbital eigenenergy relative error. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

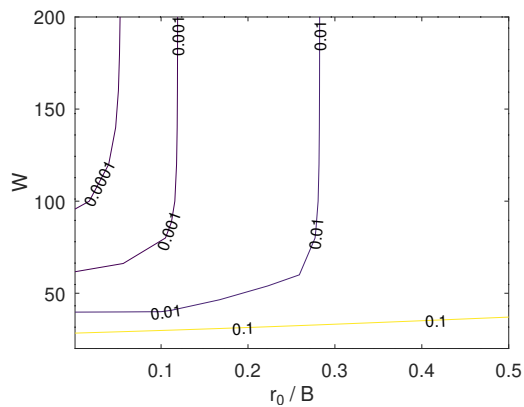


Figure 6: Relative error of the wavefunction value at the core radius for the hydrogen 2p orbital. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

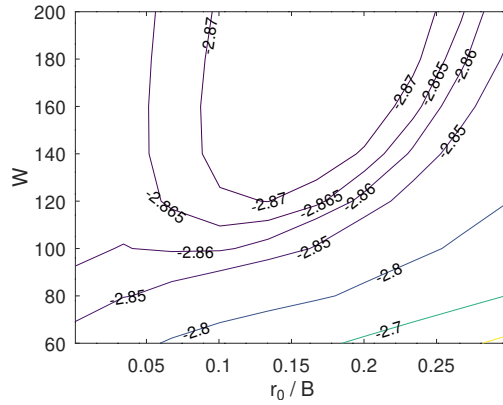


Figure 7: Energy of the ground state of the helium atom. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

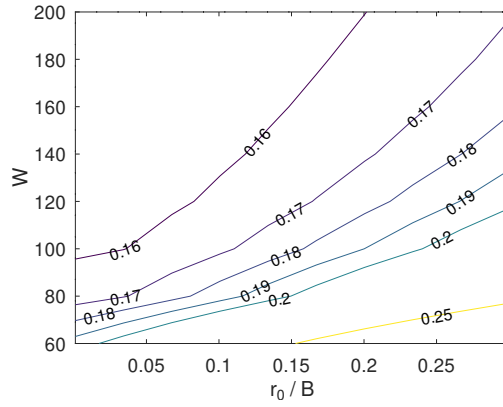


Figure 8: Relative error of the wavefunction value at the core radius for the 1s orbital of the ground state of the helium atom. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

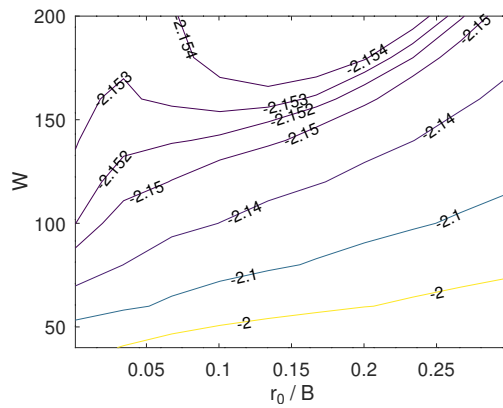


Figure 9: Helium 1s2s  $^1S$  total energy. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

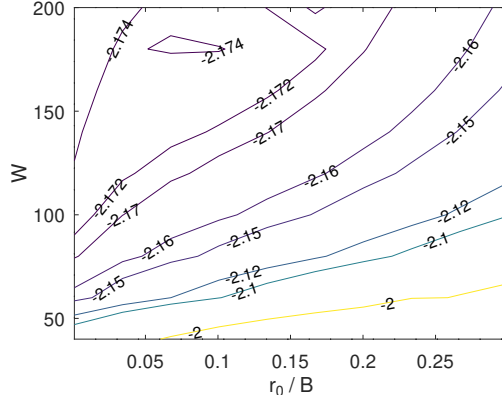


Figure 10: Helium  $1s2s\ ^3S$  total energy. Quantity  $r_0$  is the EPP radius in atomic units and quantity  $W$  is the basis size.

Table 1: The energies from the most accurate wavelet computations.

System	Energy / Ha	Number of grid points	Grid spacing / B
H 1s	-0.500000	200	0.075
H 2s	-0.125000	200	0.125
H 2p	-0.125000	200	0.125
He $1s^2$	-2.861629	200	0.075
He $1s2s\ ^1S$	-2.153148	200	0.1
He $1s2s\ ^3S$	-2.174230	200	0.1

Table 2: The energies from the most accurate finite difference computations.

System	Energy / Ha	Number of grid points	Grid spacing / B
H 1s	-0.498031	1001	0.01
H 2s	-0.124741	2001	0.01
H 2p	-0.124995	2001	0.01
He $1s^2$	-2.839010	1001	0.01
He $1s2s\ ^1S$	-2.132008	1001	0.01
He $1s2s\ ^3S$	-2.155362	1001	0.01

for the He 1s2s  $^1S$  and He 1s2s  $^3S$  configurations, respectively. Reference [15] gives quantities  $E(\text{He } 1s2s \ ^1S) - E(\text{He } 1s^2) = 0.758 \text{ Ha}$  and  $E(\text{He } 1s2s \ ^3S) - E(\text{He } 1s^2) = 0.728 \text{ Ha}$ .

The computations using the diagonalization of the Hamiltonian operator yielded some unphysical results. The physical admissibility of the wavefunctions  $P_{nl}(r)$  was characterized by condition

$$\lim_{r \rightarrow 0} P_{nl}(r) = 0. \quad (68)$$

We checked this condition by extrapolating solutions  $P_{nl}(r)$  polynomially at  $r = 0$ . Note that Fischer and Defranceschi [16] also get unphysical states in wavelet computations of hydrogen-like atoms. As expected, the orbitals of hydrogen atom are approximately continuous at  $r_0$  whereas the orbitals of helium are not.

## 6 Conclusions

There were six correct decimals in the most accurate energy of hydrogen 1s, 2s, and 2p orbitals. Helium ground state energy had four correct decimals and He 1s2s computation two correct decimals in the most accurate computations. Computation of hydrogen 1s orbital in [1] gave relative energy error about  $10^{-5}$  with 200 basis functions and EPP gives about  $10^{-6}$  with the same number of basis functions. Hydrogen 2s computations in [1] gave relative energy error about  $10^{-6}$  and EPP gives similar error with 160 basis functions. The smallest relative energy error of the helium ground state computed with EPP was about 0.00002 (200 basis functions) whereas in [1] it was about 0.00004 (180 basis functions). It turned out that the wavelet method yielded considerably better results than the finite difference method.

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