

Solution of atomic orbitals in an interpolating wavelet basis

Tommi Höynälänmaa* and Tapio T. Rantala†

Institute of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland

Keijo Ruotsalainen‡

Mathematics Division, Department of Electrical Engineering, University of Oulu, P.O. Box 4500, FI-90014 Finland

(Received 7 July 2004; published 2 December 2004)

The Schrödinger equation of hydrogenic atoms and the Hartree-Fock equations of some many-electron atoms are solved using interpolating wavelets as basis functions. The nonstandard operator form is used to compute operators in basis sets including multiple resolution levels. We introduce an algorithm for converting matrices from nonstandard operator form to standard operator form. We also consider the different components of the Hamiltonian and Fock operators separately and derive analytic formulas for their evaluation. Extension to many-electron atoms is done within the Hartree-Fock formalism. Convergence of atomic parameters such as orbital eigenvalues with respect to the number of resolution levels is inspected numerically for hydrogenlike atoms (ions) and some light many-electron atoms (helium, lithium, beryllium, neon, sodium, magnesium, and argon).

DOI: 10.1103/PhysRevE.70.066701

PACS number(s): 02.60.-x, 31.15.Ne, 71.15.Ap

I. INTRODUCTION

Use of wavelets for solving differential equations and partial differential equations in physics has recently been investigated in the literature [1–8]. One particular application is solving the Schrödinger equation of a quantum mechanical system using wavelets as basis functions. Fischer and Defranceschi have used Daubechies wavelets [9,10] to solve the Schrödinger equation of hydrogenlike atoms [2] and they have also analyzed the Hartree-Fock method with continuous wavelet transform [6]. Electronic structure calculations with the Hartree-Fock (HF) method and wavelets have also been done by Yamaguchi and Mukoyama [11].

Most authors have used compactly supported orthonormal wavelets for electronic structure calculations. Daubechies wavelets have been used by Fischer and Defranceschi [2] and Wei and Chu [3], Meyer wavelets by Yamaguchi and Mukoyama [4], and Mexican hat wavelets by Cho *et al.* [5]. Orthonormal wavelet families provide several useful properties—they possess recursive refinement relations [10], and they lead to fast discrete wavelet transform for multi-resolution analysis.

Interpolating wavelets are a biorthogonal wavelet family. They are not an orthonormal basis of $L^2(\mathbb{R})$. Interpolating wavelets enable simple computation of matrix elements and expansion of functions in a basis function set because of the special form of the dual scaling functions and dual wavelets [8,12]. Since the dual scaling functions and dual wavelets are sums of δ functions the integrals involving these functions usually require evaluating some function in a finite set of points. Goedecker and Ivanov [7] have used interpolating

wavelets to solve the Coulomb problem. Wavelet methods are closely connected to point-grid based methods that also generalize to higher than one dimension [13,14]. Lippert *et al.* [12] have used interpolating wavelets in point-grid based methods. Mann has done Hartree-Fock calculations using point sets with logarithmic scaling [15]. The basis function sets that we have used, where the accuracy is increased by adding basis functions of finer resolution levels near the nucleus, resemble this kind of point grid. In our treatment of the HF method matrices of all the necessary operators are computed and calculations are implemented as matrix and vector operations. We are able to derive analytic formulas for the matrix elements. We handle the various singularities in a similar way as Johnson *et al.* [16].

Representation of operators in orthonormal wavelet bases has been studied, for example, by Beylkin *et al.* [17–19]. We introduce an algorithm to compute the standard operator form (SOF) of an arbitrary operator from its nonstandard operator form (NSOF). The nonstandard operator form decouples different resolution levels, which is an important aspect for numerical approaches. We chose to use standard operator form because it enables the direct use of standard matrix and vector algorithms (e.g., solution of the matrix eigenproblem). However, for large basis sets and several resolution levels the SOF computations become slow and taking advantage of the special structure of NSOF matrices might make the computations significantly faster.

In the next section we first present the relevant concepts of hydrogenlike atoms. Then the Hartree-Fock formalism for many-electron atoms is briefly summarized. We present details of the basis set in Sec. III and the formulation of HF equations using interpolating wavelets in Sec. IV. The structure of matrices in standard and nonstandard operator form is presented in Sec. V [8,17,19]. Section VI discusses details of the computation of various operators and some other computational aspects. We give some numerical results in Sec. VII and conclusions are presented in the last section.

*Corresponding author.

Electronic address: tommy.hoynalanmaa@iki.fi

†Electronic address: tapio.rantala@tut.fi

‡Electronic address: keijo.ruotsalainen@oulu.fi

We use atomic units [20,21] throughout this article ($e = m = \hbar = 4\pi\epsilon_0 = 1$). We use the symbol A to denote a matrix of an arbitrary linear operator \hat{A} in the given basis. The vector space spanned by the basis function set S is denoted by $L(S)$.

II. SCHRÖDINGER EQUATIONS OF ATOMS

A. Schrödinger equation of a hydrogenlike atom

Due to the spherical symmetry of atoms the three-dimensional one-electron Schrödinger equation $\hat{H}\psi = \varepsilon\psi$ of hydrogenlike atoms is separated into a one-dimensional radial part and a two-dimensional angular part. The exact solutions to the latter are spherical harmonics $Y_{\ell m_\ell}$ where ℓ and m_ℓ are the orbital quantum number (angular momentum quantum number) and orbital magnetic quantum numbers, respectively. Writing $R_{n\ell}$ for the radial wave function, the hydrogenlike orbitals are $\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta, \phi)$, where n is the principal quantum number. The radial Schrödinger equation for a hydrogenlike atom is

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} \right] P_{n\ell}(r) = \varepsilon_{n\ell} P_{n\ell}(r), \quad (1)$$

where Z is the atomic number, $\varepsilon_{n\ell}$ are the orbital energies, and $P_{n\ell}(r) = rR_{n\ell}(r)$ are the radial wave functions multiplied by r . The functions $P_{n\ell}(r)$ are called wave functions too. In general, the radial wave function $P_{n\ell}$ has $n - \ell - 1$ nodes [22].

The Hamiltonian \hat{H} consists of three parts as

$$\hat{H} = \hat{T} + \hat{V} + \hat{C}_\ell, \quad (2)$$

where

$$\hat{T} = -\frac{1}{2} \frac{d^2}{dr^2}, \quad (3)$$

$$\hat{V} = -\frac{Z}{r}, \quad (4)$$

$$\hat{C}_\ell = \frac{\ell(\ell+1)}{2r^2}. \quad (5)$$

With a finite basis function set $\{\zeta_p(r)\}_{p=1}^N$ the approximate solutions P_i of Eq. (1) can be expanded as

$$P_i = \sum_{p=1}^N c_i^{(p)} \zeta_p. \quad (6)$$

In case a finite biorthogonal wavelet basis set is used Eq. (1) is represented as a matrix eigenproblem

$$Hc = \varepsilon c, \quad (7)$$

where H is given by

$$H = (H_{pq})_{p,q=1}^N = \int_{\mathbb{R}} \tilde{\zeta}_p(r) \hat{H} \zeta_q(r) dr \quad (8)$$

and

$$c_i = (c_i^{(p)})_{p=1}^N. \quad (9)$$

The functions $\tilde{\zeta}_p(r)$ are so called dual basis functions (see Sec. III). Equations (7) and (8) are consequences of the biorthogonality relations (26)–(29). Diagonalization of the eigenproblem (7) for each orbital i yields N eigenvectors

$$c_j = (c_j^{(p)})_{p=1}^N \quad (10)$$

and the corresponding eigenvalues ε_j as a solution. We choose the eigenvalue ε_i of eigenvector c_i so that the wave function corresponding to the eigenvector has $n_i - \ell_i - 1$ nodes and satisfies the boundary conditions at zero and infinity. Note that all functions $P_{n\ell}(r)$ vanish at both limits. If we change the unit system so that the new unit of length is u atomic units of length and the energy is not changed, the Schrödinger equation (1) of the hydrogen atom becomes

$$\left(-\frac{1}{2} \frac{1}{u^2} \frac{d^2}{dr^2} - \frac{1}{u} \frac{Z}{r} + \frac{1}{u^2} \frac{\ell(\ell+1)}{2r^2} \right) P_{n\ell}(r) = \varepsilon_{n\ell} P_{n\ell}(r) \quad (11)$$

and the Hamiltonian \hat{H} and its components are changed according to Eq. (11).

B. Hartree-Fock equations

The Schrödinger equation $\hat{H}\Psi = E\Psi$ of a many-electron atom leads to Hartree-Fock equations in the central field approximation and with Slater determinant wave functions [20–22]. The Slater integrals between the two radial wave functions P_i and P_j are defined as

$$Y_{ij}^\kappa(r) = \int_0^\infty P_i(r') \gamma^\kappa(r, r') P_j(r') dr', \quad (12)$$

where

$$\gamma^\kappa(r, r') = \frac{r^\kappa}{r_{>}^{\kappa+1}}, \quad (13)$$

$$r_{<} = \min\{r, r'\}, \quad (14)$$

$$r_{>} = \max\{r, r'\}. \quad (15)$$

The HF equation for the orbital P_i with the principal quantum number n_i and orbital quantum number ℓ_i is

$$\begin{aligned} & \left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell_i(\ell_i+1)}{2r^2} + D_i(r) \right) P_i(r) \\ & = \varepsilon_i P_i(r) + \sum_{j(\neq i)=1}^Q w_j \delta_{\ell_i \ell_j} \varepsilon_{ij} P_j(r) + E_i(r), \end{aligned} \quad (16)$$

where

$$D_i(r) = \sum_{j=1}^Q (w_j - \delta_{ij}) Y_{jj}^0(r) - (w_i - 1) A_i(r), \quad (17)$$

$$E_i(r) = \sum_{j(\neq i)=1}^Q w_j B_{ij}(r) P_j(r), \quad (18)$$

and

$$A_i(r) = \frac{2\ell_i + 1}{4\ell_i + 1} \sum_{\kappa > 0} \begin{pmatrix} \ell_i & \kappa & \ell_i \\ 0 & 0 & 0 \end{pmatrix}^2 Y_{ii}^\kappa(r), \quad (19)$$

$$B_{ij}(r) = \frac{1}{2} \sum_{\kappa} \begin{pmatrix} \ell_i & \kappa & \ell_j \\ 0 & 0 & 0 \end{pmatrix}^2 Y_{ji}^\kappa(r), \quad (20)$$

$$Z \text{ is the atomic number,} \quad (21)$$

$$Q \text{ is the number of orbitals,} \quad (22)$$

$$w_i \text{ is the number of electrons in orbital } i, \quad (23)$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \text{ is the Wigner 3-}j \text{ symbol.} \quad (24)$$

The wave functions $P_i(r)$ are normalized with the condition

$$\int_0^\infty [P_i(r)]^2 dr = 1. \quad (25)$$

The nondiagonal Lagrange multipliers ε_{ij} , $i \neq j$, that ensure orthogonality of the orbitals may be neglected for closed-shell atoms. We neglect the nondiagonal Lagrange multipliers for open-shell atoms, too, and the exact orthogonality of atomic orbitals is not preserved for them.

III. INTERPOLATING WAVELETS AS BASIS SET

A. Biorthogonal wavelet families

For a more detailed description of the biorthogonal wavelet families and interpolating wavelets, see Ref. [8]. A biorthogonal wavelet family of degree m is characterized by four filters h_j , g_j , \tilde{h}_j , and \tilde{g}_j . The degree m is chosen to be even and large enough so that all the nonzero elements of the filters are included by the indices $j = -m, \dots, m$. The two-index basis functions are

$$\varphi_i^k(x) = \varphi(2^k x - i), \quad (26)$$

$$\psi_i^k(x) = \psi(2^k x - i), \quad (27)$$

$$\tilde{\varphi}_i^k(x) = 2^k \tilde{\varphi}(2^k x - i), \quad (28)$$

$$\tilde{\psi}_i^k(x) = 2^k \tilde{\psi}(2^k x - i). \quad (29)$$

The index k is called the scaling index and the index i the translation index.

The functions φ , ψ , $\tilde{\varphi}$, and $\tilde{\psi}$ satisfy the following refinement relations:

$$\varphi(x) = \sum_{j=-m}^m h_j \varphi(2x - j), \quad (30)$$

$$\psi(x) = \sum_{j=-m}^m g_j \varphi(2x - j), \quad (31)$$

$$\tilde{\varphi}(x) = \sum_{j=-m}^m \tilde{h}_j \tilde{\varphi}(2x - j), \quad (32)$$

$$\tilde{\psi}(x) = \sum_{j=-m}^m \tilde{g}_j \tilde{\varphi}(2x - j). \quad (33)$$

The basis functions defined by Eqs. (26)–(29) satisfy the biorthogonality relations

$$\int_{-\infty}^{\infty} \tilde{\varphi}_i^k(x) \varphi_j^k(x) dx = \delta_{ij}, \quad (34)$$

$$\int_{-\infty}^{\infty} \tilde{\psi}_i^k(x) \varphi_j^q(x) dx = 0, \quad k \geq q, \quad (35)$$

$$\int_{-\infty}^{\infty} \psi_i^k(x) \tilde{\varphi}_j^q(x) dx = 0, \quad k \geq q, \quad (36)$$

$$\int_{-\infty}^{\infty} \psi_i^k(x) \tilde{\psi}_j^q(x) dx = \delta_{kq} \delta_{ij}. \quad (37)$$

B. Construction of the basis function set

To preserve the orthogonality relations of the basis functions the scaling functions and wavelets in the basis cannot be chosen arbitrarily. The basis set $B = \{\zeta_1, \dots, \zeta_N\}$ consists of scaling functions φ_i^k of resolution level $k = k_{\min}$ and wavelets ψ_i^k of resolution levels $k = k_{\min}, \dots, k_{\max}$. The dual basis functions are defined by

$$\tilde{\zeta}_j = \begin{cases} \tilde{\varphi}_i^k & \text{if } \zeta_j = \varphi_i^k, \\ \tilde{\psi}_i^k & \text{if } \zeta_j = \psi_i^k. \end{cases} \quad (38)$$

Different resolution levels of the basis are denoted as $S_{k_{\min}}, D_{k_{\min}}, \dots, S_{k_{\max}}, D_{k_{\max}}$, where S means a set consisting of scaling functions and D a set consisting of wavelets. This kind of basis is used directly for the standard operator form. For the nonstandard operator form, S_k parts with indices $k = k_{\min} + 1, \dots, k_{\max}$ are inserted in the basis. We define N_k to be the number of basis functions in S_k and M_k to be the number of basis functions in D_k . For $S_k = \{\varphi_{i_1}^k, \dots, \varphi_{i_{N_k}}^k\}$ we define $\mu_{k,\alpha} = i_\alpha$ and for $D_k = \{\psi_{i_1}^k, \dots, \psi_{i_{M_k}}^k\}$ we define $\nu_{k,\alpha} = i_\alpha$. The NSOF basis function set $B_{\text{NSOF}} = \{\zeta_1, \dots, \zeta_{N_{\text{NSOF}}}\}$ consists of parts $S_{k_{\min}}, D_{k_{\min}}, \dots, S_{k_{\max}}, D_{k_{\max}}$. The basis functions in the parts $S_{k_{\min}}, D_{k_{\min}}, \dots, D_{k_{\max}}$ are the same as in the corresponding parts of the basis set B . The basis functions in the parts $S_{k_{\min}+1}, \dots, S_{k_{\max}}$ are chosen so that $L(S_k, D_k) \subset L(S_{k+1})$. The radial wave function we want to expand should be zero at the nucleus. We exclude the function $\varphi_0^{k_{\min}}$ from the basis in order to force the wave functions $P_{n\ell}$ to be zero at $r=0$. This

also makes the matrix of operator \hat{R} , defined by

$$(\hat{R}f)(r) = |r|f(r), \quad (39)$$

nonsingular (an empirical observation). See also Ref. [16] for the handling of singularities. The projection of an arbitrary function f in $L^2(\mathbb{R})$ to the space spanned by a finite number of basis functions is

$$f(x) = \sum_i v_i^{(k_{\min})} \varphi_i^{k_{\min}}(x) + \sum_{k=k_{\min}}^{k_{\max}} \sum_i w_i^{(k_{\max})} \psi_i^k(x). \quad (40)$$

In this article, a vector consisting of coefficients of S_k basis functions is denoted by $v^{(k)}$ and a vector consisting of coefficients of D_k basis functions by $w^{(k)}$.

We use a similar basis set, denoted by B , for Hartree-Fock calculations. The scaling function $\varphi_0^{k_{\min}}$ is excluded from B due to the boundary conditions of wave functions at zero and singularities of the potential, the centrifugal potential, and the functions $1/r^{\kappa+1}$ (occurring in Slater integrals) at $r=0$. However, since the Slater integrals do not generally vanish at $r=0$ we include $\varphi_0^{k_{\min}}$ in the basis set $B_0 = B \cup \{\varphi_0^{k_{\min}}\} = \{\xi_1^{(0)}, \dots, \xi_{N'}^{(0)}\}$. The basis change matrix from B to B_0 is denoted by $L_{1 \rightarrow 0}$ and the basis change matrix from B_0 to B by $L_{0 \rightarrow 1}$. We do not need to compute the matrix of operator \hat{R}_{-1} (corresponding to division by r) in basis B_0 . We also use the basis set

$$B_s = \{\varphi_i^{k_{\max}+1} | i \in I_s\} \quad (41)$$

consisting of scaling functions of resolution level $k_{\max}+1$ where k_{\max} is the maximum resolution level in basis B and $I_s \subset \mathbb{Z}$ is finite. The basis set B_s is constructed so that $L(B) \subset L(B_s)$ and $L(B_0) \subset L(B_s)$. Expansion of an arbitrary function f in the scaling function basis B_s is given by

$$f(r) = \sum_{i \in I_s} a_i \varphi_i^{k_{\max}+1}(r). \quad (42)$$

C. Forward and backward wavelet transforms

The forward wavelet transform is defined by the equations [8]

$$s_i^{k-1} = \sum_{j=-m}^m \tilde{h}_j s_{j+2i}^k, \quad (43)$$

$$d_i^{k-1} = \sum_{j=-m}^m \tilde{g}_j s_{j+2i}^k, \quad (44)$$

where s_i^k is the coefficient for the basis function φ_i^k and d_i^k is the coefficient for the basis function ψ_i^k . The backward wavelet transform is defined by the equations [8]

$$s_{2i}^{k+1} = \sum_{j=-m/2}^{m/2} (h_{2j} s_{i-j}^k + g_{2j} d_{i-j}^k), \quad (45)$$

$$s_{2i+1}^{k+1} = \sum_{j=-m/2}^{m/2} (h_{2j+1} s_{i-j}^k + g_{2j+1} d_{i-j}^k). \quad (46)$$

The forward wavelet transform defined by Eqs. (43) and (44) can be written in matrix form as

$$v^{(k-1)} = \tilde{Z}_{S_k^{k-1}} v^{(k)}, \quad (47)$$

$$w^{(k-1)} = \tilde{Z}_{S_k^D} w^{(k)}, \quad (48)$$

where

$$\tilde{Z}_{S_k^{k-1}} = (\tilde{h}_{\mu_{k,\beta} - 2\nu_{k-1,\alpha}})_{\alpha=1, \beta=1}^{N_{k-1}, N_k}, \quad (49)$$

$$\tilde{Z}_{S_k^D} = (\tilde{g}_{\mu_{k,\beta} - 2\nu_{k-1,\alpha}})_{\alpha=1, \beta=1}^{M_{k-1}, N_k}. \quad (50)$$

The backward wavelet transform defined by Eqs. (45) and (46) can be similarly written in matrix form as

$$v^{(k+1)} = B_{S_k^{k+1}} v^{(k)} + B_{D_k^S} w^{(k)}, \quad (51)$$

where [8]

$$B_{S_k^{k+1}} = (Z_{S_{k+1}}^S)^T, \quad (52)$$

$$B_{D_k^S} = (Z_{S_{k+1}}^D)^T, \quad (53)$$

and

$$Z_{S_{k+1}}^S = (h_{\mu_{k+1,\beta} - 2\nu_{k,\alpha}})_{\alpha=1, \beta=1}^{N_k, N_{k+1}}, \quad (54)$$

$$Z_{S_{k+1}}^D = (g_{\mu_{k+1,\beta} - 2\nu_{k,\alpha}})_{\alpha=1, \beta=1}^{M_k, N_{k+1}}. \quad (55)$$

We use the symbols \tilde{Z} and Z for the forward wavelet transform instead of \tilde{F} and F (as in Ref. [8]) to avoid confusion with the Fock operator F .

D. Interpolating wavelets

Interpolating wavelets are one biorthogonal wavelet family [8,12]. For an interpolating wavelet family of degree m , the mother scaling function φ is constructed by recursively applying polynomial interpolation of degree $m-1$ to data $s_i = \delta_{i,0}$ and the mother dual scaling function is

$$\tilde{\varphi}(x) = \delta(x), \quad (56)$$

where δ is the Dirac delta function. For interpolating wavelets the coefficients h_j satisfy

$$h_j = \varphi(j/2), \quad j = -m, \dots, m. \quad (57)$$

The following symmetry equations hold for interpolating scaling functions and wavelets:

$$\varphi_i^k(x) = \varphi_{-i}^k(-x), \quad (58)$$

$$\psi_i^k(x) = \psi_{-i-1}^k(-x). \quad (59)$$

IV. SOLVING HARTREE-FOCK EQUATIONS

For an arbitrary operator \hat{A} , we denote the matrix of \hat{A} in basis B by A and the matrix in basis B_0 by $A^{(0)}$. We define some operators to be used:

$$(\hat{R}f)(r) = |r|f(r), \quad (60)$$

$$(\hat{R}_{-1}f)(r) = f(r)/|r|, \quad (61)$$

$$(\hat{U}_0f)(r) = \int_0^{|r|} f(r')dr', \quad (62)$$

$$(\hat{U}_\infty f)(r) = \int_{|r|}^\infty f(r')dr', \quad (63)$$

$$\hat{S}_\kappa = \hat{R}_{-1}^{\kappa+1} \hat{U}_0 \hat{R}^\kappa + \hat{R}^\kappa \hat{U}_\infty \hat{R}_{-1}^{\kappa+1}, \quad (64)$$

where $\kappa \in \mathbb{Z}$, $\kappa \geq 0$, and $\hat{A}^n f = \hat{A} \cdots \hat{A} f$ where \hat{A} is applied n times. Let $f \in L^2(\mathbb{R})$. We define the multiplication operator $\hat{M}(f) = \hat{A}$ by setting

$$(\hat{A}g)(r) = f(r)g(r) \quad (65)$$

for an arbitrary function $g \in L^2(\mathbb{R})$. If f is a vector (function) in a wavelet basis B' we define the matrix $M(f)$ to be the matrix of operator $\hat{M}(f)$ in the basis B' (f is kept constant). Let f and g be arbitrary vectors (functions) in the wavelet basis B' . We define $f \star g$ to be the projection of the function $h(r) = f(r)g(r)$ to $L(B')$.

We omit the nondiagonal Lagrange multipliers and Eqs. (16) can be written as matrix eigenvalue equations [23]

$$F_i c_i = \varepsilon_i c_i, \quad (66)$$

where the Fock operator F_i for orbital i is defined by

$$F_i = H_i^0 + J_i - K_i. \quad (67)$$

The wave functions P_i are given by

$$P_i = \sum_{p=1}^N c_i^{(p)} \zeta_p. \quad (68)$$

The single-electron Hamiltonian operator is defined as

$$H_i^0 = T + V + C_{\ell_i}, \quad (69)$$

where the components are defined as in the case of hydrogenlike atoms, Eqs. (3)–(5).

The Slater direct integral operator is defined by

$$\hat{J}_i = \sum_{j=1}^q (w_j - \delta_{ij}) \hat{J}_j^0 - (w_i - 1) \frac{2\ell_i + 1}{4\ell_i + 1} \sum_{\kappa > 0} \begin{pmatrix} \ell_i & \kappa & \ell_i \\ 0 & 0 & 0 \end{pmatrix}^2 \hat{J}_j^\kappa, \quad (70)$$

where

$$(\hat{J}_i^\kappa P_j)(r) = Y_{ii}^\kappa(r) P_j(r) \quad (71)$$

and the Slater exchange integral operator by

$$\hat{K}_i = \frac{1}{2} \sum_{j(\neq i)=1}^q w_j \sum_{\kappa} \begin{pmatrix} \ell_i & \kappa & \ell_j \\ 0 & 0 & 0 \end{pmatrix}^2 \hat{K}_j^\kappa, \quad (72)$$

where

$$(\hat{K}_j^\kappa P_i)(r) = Y_{ij}^\kappa(r) P_j(r). \quad (73)$$

Note that in the definition of operator \hat{K}_j^κ the argument of the operator occurs only in the Slater integral $Y_{ij}^\kappa(r)$. This operator is linear, though. For matrices of direct Slater integral operators we have

$$J_i^\kappa = L_{0 \rightarrow 1} M^{(0)} (S_\kappa^{(0)} (P_i \star P_i)) L_{1 \rightarrow 0} \quad (74)$$

and for matrices of exchange integral operators

$$K_j^\kappa = L_{0 \rightarrow 1} M^{(0)} (P_j) S_\kappa^{(0)} M^{(0)} (P_j) L_{1 \rightarrow 0}, \quad (75)$$

where

$$S_0^{(0)} = L_{1 \rightarrow 0} R^{-1} U_0 L_{0 \rightarrow 1} + U_\infty^{(0)} L_{1 \rightarrow 0} R^{-1} L_{0 \rightarrow 1} \quad (76)$$

and

$$S_\kappa^{(0)} = L_{1 \rightarrow 0} (R^{-1})^{\kappa+1} U_0 R^\kappa L_{0 \rightarrow 1} + (R^{(0)})^\kappa U_\infty^{(0)} L_{1 \rightarrow 0} (R^{-1})^{\kappa+1} L_{0 \rightarrow 1} \quad (77)$$

for $\kappa > 0$.

The HF equations are solved by an iterative procedure. We use the standard procedure given in [22] modified for the matrix form of the HF equations presented in this section. The following input parameters are needed for the HF iteration algorithm: the weight coefficients α_i , $i = 1, \dots, Q$ [see formula (78)]; the precision parameter z_0 characterizing the desired accuracy of the solution [see formulas (79) and (80)]; and the type of matrix norm $\|\cdot\|_p$ used to test the convergence of the iteration [see formula (79)].

The algorithm for HF iteration is as follows.

(1) Compute the Fock matrices F_i for each orbital i with formula (67). We set $J_i = 0$ and $K_i = 0$ in the first step, i.e., hydrogenic wave functions are used as the first trial wave functions.

(2) Solve the matrix eigenvalue equations (66) for each orbital i . Each eigenvalue equation yields N solutions, where N is the number of basis functions. We choose the solution satisfying the following conditions: the wave function is odd with respect to inversion: $P_i(r) = -P_i(-r)$; the wave function has $n_i - \ell_i - 1$ nodes, where n_i and ℓ_i are the principal quantum number and orbital quantum number of the orbital i ; and, we choose the solution with lowest possible eigenvalue ε_i among the solutions satisfying the other two conditions.

Normalize the wavefunctions with Eq. (25). Let ε_i be the eigenvalue and P_i^{new} the normalized wavefunction for each orbital i . We need not explicitly test the boundary conditions of wave functions at zero and infinity in the method described in this article.

(3) Let P_i^{prev} be the old output wave functions from the previous iteration. Compute the new output wave functions as normalized linear combinations of the new wave functions and the old output wave functions as

$$P_i = C_i [\alpha_i P_i^{\text{new}} + (1 - \alpha_i) P_i^{\text{prev}}], \quad i = 1, \dots, Q. \quad (78)$$

The normalization coefficients C_i are determined by Eq. (25). According to Ref. [22] the values of α_i are usually about 0.5 but they may be anywhere from 0.05 to 1.1.

(4) Compute the matrices J_i^κ and K_i^κ for all the necessary combinations of i, j , and κ . Use the wave functions com-

puted in step 3. Compute the matrices J_i and K_i with Eqs. (70) and (72), substituting matrices in the place of operators.

(5) Compute the quantity

$$z = \max_{i=1, \dots, Q} \|F_i - F_i^{\text{prev}}\|_p, \quad (79)$$

where F_i^{prev} are the Fock operators from the previous iteration. If

$$z < z_0 \quad (80)$$

we have obtained self-consistent solutions for the HF equations and the iteration is stopped.

(6) Return to step 1.

Finally, we evaluate the total energy of the atom with the self-consistent solutions for the wave functions P_i and energies ε_i from the formula

$$E = \sum_{i=1}^Q w_i \varepsilon_i - \frac{1}{2} \sum_{i=1}^Q w_i \langle P_i | J_i - K_i | P_i \rangle, \quad (81)$$

where w_i are the occupation numbers.

V. STANDARD OPERATOR FORM AND NONSTANDARD OPERATOR FORM

The eigenvalue equations are solved using the standard operator form, which represents the operator in the chosen basis. The elements of matrix A of an operator \hat{A} in the SOF are defined by

$$A_{ij} = \int_{-\infty}^{\infty} \tilde{\zeta}_i(x) \hat{A} \zeta_j(x) dx, \quad (82)$$

where ζ_j , $j=1, \dots, N$, are the basis functions and $\tilde{\zeta}_i$, $i=1, \dots, N$, are the dual basis functions defined by Eq. (38).

The standard operator form of an operator can be obtained from the matrix elements in nonstandard operator form. The nonstandard operator form decouples different resolution levels in the basis set and makes derivation of explicit formulas for the matrix elements easier [8,17,19]. The nonzero blocks of nonstandard operator form A of the operator \hat{A} are defined by

$$A_{\alpha\beta}^{S_{k_{\min}} S_{k_{\min}}} = \int_{-\infty}^{\infty} \tilde{\varphi}_{\mu_{k_{\min}, \alpha}}^k(x) \hat{A} \varphi_{\mu_{k_{\min}, \beta}}^k(x) dx, \quad (83)$$

$$\alpha = 1, \dots, N_{k_{\min}}, \quad \beta = 1, \dots, N_{k_{\min}},$$

and

$$A_{\alpha\beta}^{S_k D_k} = \int_{-\infty}^{\infty} \tilde{\varphi}_{\mu_{k, \alpha}}^k(x) \hat{A} \psi_{\nu_{k, \beta}}^k(x) dx, \quad \alpha = 1, \dots, N_k, \quad (84)$$

$$\beta = 1, \dots, M_k,$$

$$A_{\alpha\beta}^{D_k S_k} = \int_{-\infty}^{\infty} \tilde{\psi}_{\nu_{k, \alpha}}^k(x) \hat{A} \varphi_{\mu_{k, \beta}}^k(x) dx, \quad \alpha = 1, \dots, M_k, \quad (85)$$

$$\beta = 1, \dots, N_k,$$

$$A_{\alpha\beta}^{D_k D_k} = \int_{-\infty}^{\infty} \tilde{\psi}_{\nu_{k, \alpha}}^k(x) \hat{A} \psi_{\nu_{k, \beta}}^k(x) dx, \quad \alpha = 1, \dots, M_k, \quad (86)$$

$$\beta = 1, \dots, M_k,$$

where $k=k_{\min}+1, \dots, k_{\max}$.

We introduce an algorithm for converting a matrix from NSOF to SOF. The NSOF blocks ($S_k S_k$, $S_k D_k$, $D_k S_k$, and $D_k D_k$) are computed on the fly. The algorithm is as follows.

Input

The NSOF basis $B=(S_{k_{\min}}, D_{k_{\min}}, \dots, S_{k_{\max}}, D_{k_{\max}})$.

The function M that calculates the NSOF matrix elements according to formulas (83)–(86).

Output. Matrix in standard operator form.

Algorithm

(1) If the basis contains only parts $S_{k_{\min}}$ and $D_{k_{\min}}$ the SOF matrix is

$$A = \begin{pmatrix} A^{S_{k_{\min}} S_{k_{\min}}} & A^{S_{k_{\min}} D_{k_{\min}}} \\ A^{D_{k_{\min}} S_{k_{\min}}} & A^{D_{k_{\min}} D_{k_{\min}}} \end{pmatrix}, \quad (87)$$

where the blocks are computed with formulas (83)–(86).

Else

(2) Compute matrix A_{prev} by calling the algorithm recursively with basis $B_{\text{prev}}=(S_{k_{\min}}, D_{k_{\min}}, \dots, S_{k_{\max}-1}, D_{k_{\max}-1})$.

(3) Compute $A^{S_{k_{\max}} D_{k_{\max}}}$ with function M according to formula (84).

(4) Compute $A^{D_{k_{\max}} S_{k_{\max}}}$ with function M according to formula (85).

(5) Compute $A^{D_{k_{\max}} D_{k_{\max}}}$ with function M according to formula (86).

(6) Calculate matrices $A^{S_{k_{\min}} D_{k_{\max}}}$ and $A^{D_{k_{\max}} S_{k_{\min}}}$ where $q=k_{\min}, \dots, k_{\max}-1$ by applying forward wavelet transforms to matrix $A^{S_{k_{\max}} D_{k_{\max}}}$ using the formulas

$$A^{S_{k_{\min}} D_{k_{\max}}} = \tilde{Z}_{S_{k_{\min}+1}}^{S_{k_{\min}}} \tilde{Z}_{S_{k_{\min}+2}}^{S_{k_{\min}+1}} \dots \tilde{Z}_{S_{k_{\max}-1}}^{S_{k_{\max}-2}} \tilde{Z}_{D_{k_{\max}}}^{S_{k_{\max}-1}} A^{S_{k_{\max}} D_{k_{\max}}}, \quad (88)$$

$$A^{D_{k_{\max}} S_{k_{\min}}} = \tilde{Z}_{S_{q+1}}^{D_{k_{\max}}} \tilde{Z}_{S_{q+2}}^{S_{q+1}} \dots \tilde{Z}_{S_{k_{\max}-1}}^{S_{k_{\max}-2}} \tilde{Z}_{D_{k_{\max}}}^{S_{k_{\max}-1}} A^{S_{k_{\max}} D_{k_{\max}}}. \quad (89)$$

(7) Calculate matrices $A^{D_{k_{\max}} S_{k_{\min}}}$ and $A^{D_{k_{\max}} D_{k_{\max}}}$ where $q=k_{\min}, \dots, k_{\max}-1$ by applying backward wavelet transforms to matrix $A^{D_{k_{\max}} S_{k_{\max}}}$ using the formulas

$$A^{D_{k_{\max}} S_{k_{\min}}} = A^{D_{k_{\max}} S_{k_{\max}}} B_{S_{k_{\max}-1}}^{D_{k_{\max}}} B_{S_{k_{\max}-2}}^{S_{k_{\max}-1}} \dots B_{S_{k_{\min}+1}}^{S_{k_{\min}+2}} B_{S_{k_{\min}}}^{S_{k_{\min}+1}}, \quad (90)$$

$$A^{D_{k_{\max}} D_{k_{\max}}} = A^{D_{k_{\max}} S_{k_{\max}}} B_{S_{k_{\max}-1}}^{D_{k_{\max}}} B_{S_{k_{\max}-2}}^{S_{k_{\max}-1}} \dots B_{S_{q+1}}^{S_{q+2}} B_{D_{k_{\max}}}^{S_{q+1}}. \quad (91)$$

(8) Construct the result A from matrices calculated in steps 2, 5, 6, and 7 using the formulas

$$A_{\text{vert}} = \begin{pmatrix} A^{S_{k_{\min}} D_{k_{\max}}} \\ A^{D_{k_{\min}} D_{k_{\max}}} \\ \vdots \\ A^{D_{k_{\max}-1} D_{k_{\max}}} \end{pmatrix}, \quad (92)$$

$$A_{\text{horiz}} = \begin{pmatrix} A^{D_{k_{\max}} S_{k_{\min}}} \\ A^{D_{k_{\max}} D_{k_{\min}}} \\ \dots \\ A^{D_{k_{\max}} D_{k_{\max}-1}} \end{pmatrix}^T, \quad (93)$$

$$A = \begin{pmatrix} A_{\text{prev}} & A_{\text{vert}} \\ A_{\text{horiz}} & A^{D_{k_{\max}} D_{k_{\max}}} \end{pmatrix}. \quad (94)$$

VI. EVALUATION OF MATRIX ELEMENTS AND OTHER COMPUTATIONAL ASPECTS

A. Notation

We use the following notation for matrix elements of an operator \hat{A} in nonstandard operator form [17]:

$$\alpha_{ij}^k = \int_{-\infty}^{\infty} \tilde{\psi}_i^k(x) \hat{A} \psi_j^k(x) dx, \quad (95)$$

$$\beta_{ij}^k = \int_{-\infty}^{\infty} \tilde{\psi}_i^k(x) \hat{A} \varphi_j^k(x) dx, \quad (96)$$

$$\gamma_{ij}^k = \int_{-\infty}^{\infty} \tilde{\varphi}_i^k(x) \hat{A} \psi_j^k(x) dx, \quad (97)$$

$$s_{ij}^k = \int_{-\infty}^{\infty} \tilde{\varphi}_i^k(x) \hat{A} \varphi_j^k(x) dx. \quad (98)$$

In this section we denote the matrix of an operator \hat{A} in an arbitrary wavelet basis B (with or without the function $\varphi_0^{k_{\min}}$) by A .

B. Differentiation operator

The basic integral for a differentiation operator d^p/dx^p is defined as

$$a_i = \int_{-\infty}^{\infty} \tilde{\varphi}(x) \frac{d^p}{dx^p} \varphi(x-i) dx. \quad (99)$$

The matrix elements of operator d^p/dx^p in nonstandard operator form in an interpolating wavelet family are

$$\alpha_{ij}^k = -2^{(k+1)p} \sum_{\nu=-m}^m \tilde{g}_{\nu} a_{2j-2i+1-\nu}, \quad (100)$$

$$\beta_{ij}^k = 2^{(k+1)p} \sum_{\nu=-m}^m \sum_{\mu=-m}^m \tilde{g}_{\nu} h_{\mu} a_{2j-2i+\mu-\nu}, \quad (101)$$

$$\gamma_{ij}^k = -2^{(k+1)p} a_{2j-2i+1}, \quad (102)$$

$$s_{ij}^k = 2^{kp} a_{j-i}. \quad (103)$$

See Ref. [8].

C. Function operator

By a function operator we mean multiplication by a given function f as defined by Eq. (65). The NSOF matrix elements of a function operator in the interpolating wavelet basis are

$$\alpha_{ij}^k = f\left(\frac{2i+1}{2^{k+1}}\right) \delta_{ij}, \quad (104)$$

$$\beta_{ij}^k = h_{2i-2j+1} \left[f\left(\frac{j}{2^k}\right) - f\left(\frac{2i+1}{2^{k+1}}\right) \right], \quad (105)$$

$$\gamma_{ij}^k = 0, \quad (106)$$

$$s_{ij}^k = f\left(\frac{i}{2^k}\right) \delta_{ij}. \quad (107)$$

D. Operator \hat{R}

The operator \hat{R} is a function operator with

$$(\hat{R}g)(r) = |r|g(r). \quad (108)$$

Its NSOF matrix elements are obtained from formulas (104)–(107) where we set $f(r) = |r|$. If the basis does not contain the function $\varphi_0^{k_{\min}}$ the matrix R does not become singular and we can compute R^{-1} as an inverse matrix.

We obtain the potential energy operator as

$$V = -R^{-1} \quad (109)$$

and the centrifugal potential operator as

$$C_{\ell} = \frac{\ell(\ell+1)}{2} (R^{-1})^2. \quad (110)$$

E. Operator \hat{U}_0

The matrix elements of operator \hat{U}_0 in the nonstandard operator form are

$$\alpha_{ij}^k = -2^{-k-1} \sum_{\nu=-m}^m \tilde{g}_{\nu} [\Phi(|2i+\nu|-2j-1) - \Phi(-2j-1)], \quad (111)$$

$$\beta_{ij}^k = 2^{-k} \sum_{\nu=-m}^m \tilde{g}_{\nu} \left[\Phi\left(\left|\frac{2i+\nu}{2}\right|-j\right) - \Phi(-j) \right], \quad (112)$$

$$\gamma_{ij}^k = -2^{-k-1} [\Phi(2|i|-2j-1) - \Phi(-2j-1)], \quad (113)$$

$$s_{ij}^k = 2^{-k} [\Phi(|i|-j) - \Phi(-j)], \quad (114)$$

where $\Phi(x)$ is the integral function of the mother scaling function $\varphi(x)$. We evaluated the function Φ with numerical integration using the fourth-order Runge-Kutta method. The function Φ can also be calculated analytically using the refinement equation (30). When the distance between adjacent

TABLE I. Effects of operators on the parities of functions (“o” means odd and “e” means even).

$P_{n_i \ell_i}$	$P_{n_k \ell_k}^{\text{prev}}$	$TP_{n_i \ell_i}$	$VP_{n_i \ell_i}$	$C_\ell P_{n_i \ell_i}$	$J_{n_i \ell_i} P_{n_i \ell_i}$	$K_{n_i \ell_i} P_{n_i \ell_i}$
o	o	o	o	o	o	o
o	e	o	o	o	o	e
e	o	e	e	e	e	o
e	e	e	e	e	e	e

points in numerical integration is 2^{-8} the maximum deviation of the numerical result from the analytical one is of the order of magnitude 10^{-11} .

F. Operator \hat{U}_∞

The matrix elements of \hat{U}_∞ in the nonstandard operator form are

$$\alpha_{ij}^k = -2^{-k-1} \sum_{\nu=-m}^m \tilde{g}_\nu [\Phi(\infty) - \Phi(|2i + \nu| - 2j - 1)], \quad (115)$$

$$\beta_{ij}^k = 2^{-k} \sum_{\nu=-m}^m \tilde{g}_\nu \left[\Phi(\infty) - \Phi\left(\left|\frac{2i + \nu}{2}\right| - j\right) \right], \quad (116)$$

$$\gamma_{ij}^k = -2^{-k-1} [\Phi(\infty) - \Phi(2|i| - 2j - 1)], \quad (117)$$

$$s_{ij}^k = 2^{-k} [\Phi(\infty) - \Phi(|i| - j)]. \quad (118)$$

G. Multiplication operator

The multiplication operator $\hat{M}(f)$ is defined in Sec. IV. Let f be a vector (function) in an arbitrary wavelet basis B . We first convert the vector f in basis B to a scaling function basis B_s using formula (42). Here B_s is defined according to Eq. (41) so that $L(B) \subset L(B_s)$. Conversion is done with backward wavelet transforms. The matrix $M(f)$ is computed using the formulas for matrix elements of a function, Eqs. (104)–(107), where we set

$$f\left(\frac{i}{2^k}\right) = a_{(2^{k_{\max}+1-k})i} \quad (119)$$

and

 TABLE II. Parameters used for $1s$ orbitals of hydrogenlike atoms.

Z	u	k_{\min}	B
1	1.0	0	10
2	1.0	1	8
10	0.25	2	12
50	0.031 25	1	10
100	0.031 25	2	20

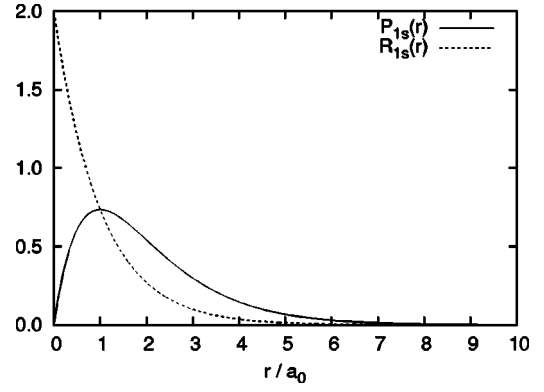


FIG. 1. Computed $1s$ radial wave functions $P_{1s}(r)$ and $R_{1s}(r)$ of the hydrogen atom with $L=8$. There is no visible deviation from the exact wave functions.

$$f\left(\frac{i}{2^{k+1}}\right) = a_{(2^{k_{\max}-k})i}. \quad (120)$$

H. Product function $f \star g$

The product function $f \star g$ is defined in Sec. IV. The vectors f and g in the arbitrary wavelet basis B are converted to the scaling function basis B_s , where $L(B) \subset L(B_s)$, so that we have

$$f(r) = \sum_i a_i \varphi_i^{k_{\max}+1}(r) \quad (121)$$

and

$$g(r) = \sum_i b_i \varphi_i^{k_{\max}+1}(r). \quad (122)$$

The expansion of the product function $h(r) = f(r)g(r)$ in the scaling function basis B_s is given by

$$h(r) = \sum_i c_i \varphi_i^{k_{\max}+1}(r), \quad (123)$$

where $c_i = a_i b_i$ for all i . To compute $f \star g$, the vector representation for the function $h(r)$ given by Eq. (123) is converted to the basis B using forward wavelet transforms.

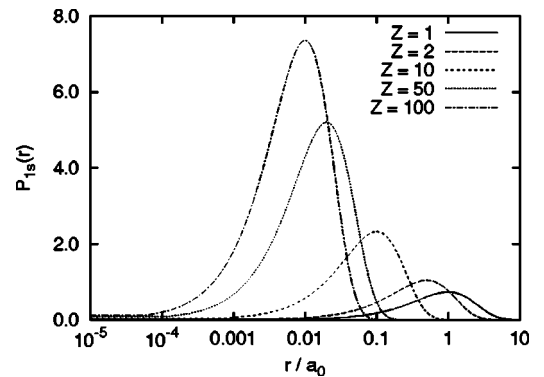


FIG. 2. Radial $1s$ wave functions $P_{1s}(r)$ of hydrogenlike atoms computed with $L=8$. Note the logarithmic scale for r .

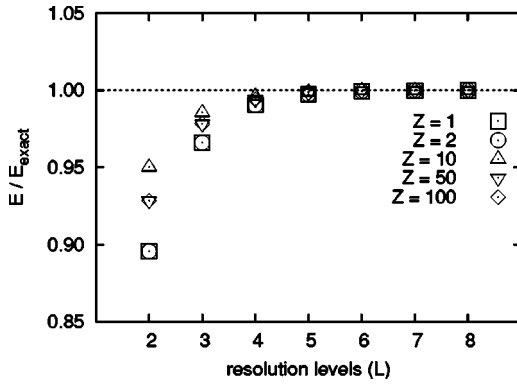


FIG. 3. The $1s$ eigenvalues of hydrogenlike atoms with $Z=1, 2, 10, 50,$ and 100 . Ratio of the computed and exact values is shown.

I. Basis change matrices $L_{1 \rightarrow 0}$ and $L_{0 \rightarrow 1}$

The matrices $L_{1 \rightarrow 0}$ and $L_{0 \rightarrow 1}$ occur only in products with other matrices. This kind of matrix products is computed by removing the row or the column corresponding to basis function φ_{\min}^k or inserting a zero row or a zero column corresponding to that basis function.

J. Evaluation of scalar products

When normalizing wave functions or evaluating the expectation values of operators we encounter integrals of the type

$$I = \int_0^\infty f(r)g(r)dr \tag{124}$$

or

$$I = \int_0^\infty f(r)(\hat{A}g)(r)dr. \tag{125}$$

We first compute the expansion (c_i) of the product function $h(r)=f(r)(\hat{A}g)(r)$ in the scaling function basis B_s (as in the case of a product function). The integral is then given by

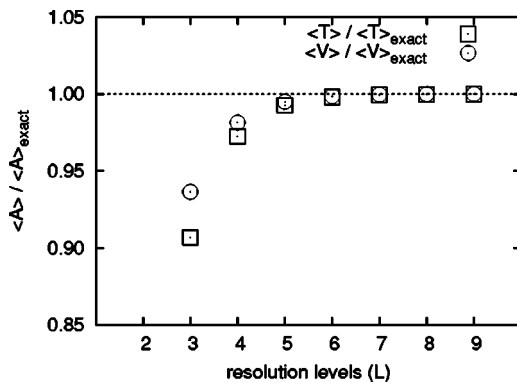


FIG. 4. Expectation values of the kinetic energy and potential energy operators for the hydrogen $1s$ orbital. Ratio of the computed and exact values is shown.

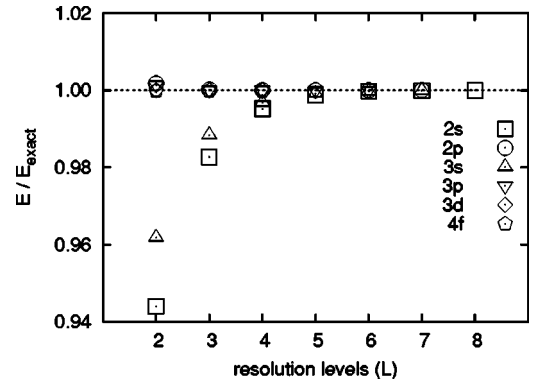


FIG. 5. Energy eigenvalues of $2s, 2p, 3s, 3p, 3d,$ and $4f$ orbitals of hydrogen with $B=15, 20, 30, 30,$ and $45,$ respectively. Ratio of the computed and exact values is shown.

$$I = \frac{1}{2^{k_{\max}+1}} \sum_{i \geq 0} c_i. \tag{126}$$

See also Refs. [24] and [25].

K. Negative values of r

A negative r coordinate has no physical meaning for radial wave functions. However, interpolating wavelets constitute a basis set for functions space $L^2(\mathbb{R})$ and their domain is the whole real axis. Interpolating wavelets and scaling functions that are located near zero (i.e., nonzero values of the functions are concentrated near zero) do not generally vanish on the negative real axis, so we are not able to exclude the negative real axis by choosing a suitable basis set. We choose the basis set so that it is symmetrical around zero, so that for each basis function $\zeta(x)$ the function $\zeta(-x)$ is also in the basis set; see Eqs. (58) and (59). We actually solve the eigenproblem in both the positive and negative real axes, i.e., if $P(r), r \in \mathbb{R}$, is a solution of the eigenproblem then both $P(r), r \geq 0$, and $P(-r), r \geq 0$, are wave functions. We may generally get either odd or even solutions to the eigenproblem, i.e., $P(r)=P(-r)$ or $P(r)=-P(-r)$. For hydrogenic computations we simply neglect the negative r part of the wave function but the situation is more complex when HF equations are solved. The operators used in HF computation yield either

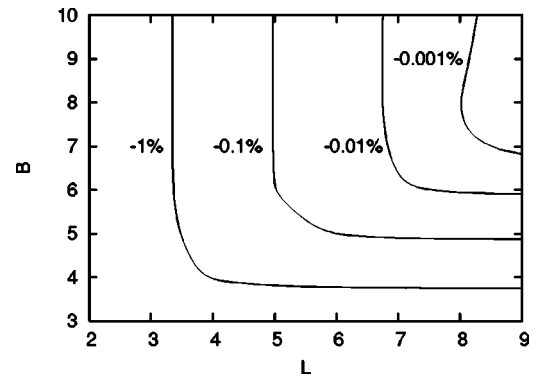


FIG. 6. Relative error of the hydrogen $1s$ orbital eigenvalue; unit of length $u=0.6$.

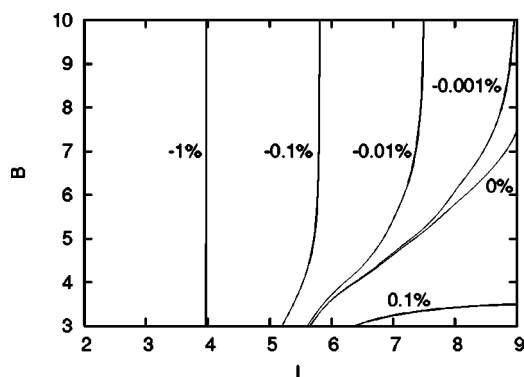


FIG. 7. Relative error of the hydrogen 1s orbital eigenvalue; unit of length $u=1.0$.

odd or even functions. The parity of the function $\hat{A}P$ depends on the parity of the function P and in the case of the direct integral and exchange integral operators also the parities of the wave functions from the previous iteration that are used to compute these operators themselves. Table I shows how the operators needed in HF computations affect the parities of the functions. The functions yielded by the exchange integral operator and the other operators would have different parities if we chose a wave function with parity different from the output wave functions of the previous iteration (second and third lines of the table). Consequently, the computation would be wrong on the negative real axis (the exchange integrals would have the wrong sign). We have to use either odd or even wave functions during the whole HF iteration. We have chosen to use odd wave functions, which have continuous first derivatives at the origin.

VII. NUMERICAL RESULTS

A. General

We use eighth-order interpolating wavelets for numerical results. The unit of length is the atomic unit unless otherwise stated. We examine the convergence of the essential physical quantities toward the known exact or accurate values when the number of resolution levels is increased. We also examine the effect of the number of basis functions in each reso-

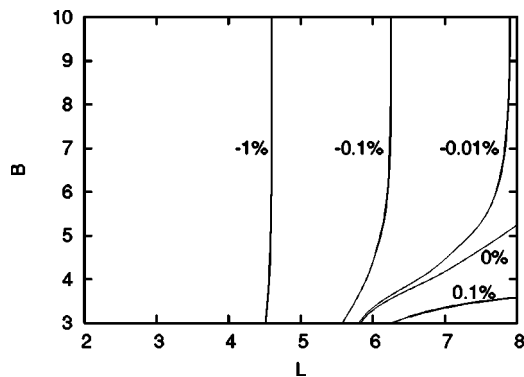


FIG. 8. Relative error of the hydrogen 1s orbital eigenvalue; unit of length $u=1.4$.

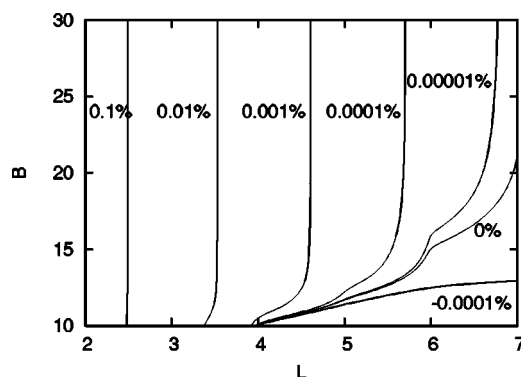


FIG. 9. Relative error of the hydrogen 2p orbital eigenvalue; unit of length $u=1.0$.

lution level. Various parameters affecting the computations are also reported.

The basis sets were formed so that there are S type basis functions $\varphi_{-2B}^{k_{\min}}, \dots, \varphi_{2B}^{k_{\min}}$ in resolution level k_{\min} and D type basis functions $\psi_{-B}^k, \dots, \psi_{B-1}^k$ for $k=k_{\min}, \dots, k_{\min}+L-2$. Here L is the number of resolution levels and B is a parameter describing the number of basis functions in each resolution level. We count $S_{k_{\min}}$ and $D_{k_{\min}}$ as two separate resolution levels. The total number of basis functions is

$$N = 4B + 2(L-1)B = 2B(L+1). \quad (127)$$

In principle, the number of resolution levels L determines the maximum possible accuracy of the computations with fixed k_{\min} and unit of length u .

B. Hydrogenlike orbitals

We solved the 1s orbitals for hydrogenlike atoms for atomic numbers $Z=1, 2, 10, 50$, and 100 using the basis sets and length units u given in Table II. The basis sets were chosen large enough to cover the relevant radial range of the wave functions. The resulting 1s radial wave functions are shown in Figs. 1 and 2. There is no visible deviation of these wave functions (computed with $L=8$) from the corresponding exact wave functions. Convergence of the eigenvalues ε_{nl} as a function of resolution level is presented in Fig. 3. The exact values are

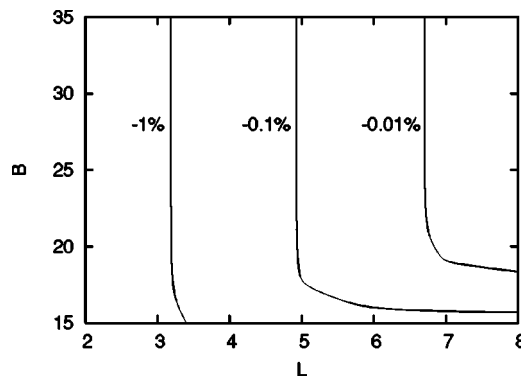


FIG. 10. Relative error of the hydrogen 3s orbital eigenvalue; unit of length $u=1.0$.

TABLE III. Parameters for HF computations.

Atom	α	k_{\min}	B	L
He	1.0	1	10	2,...,8
Li	1.0	1	20	2,...,8
Be	1.0	1	15	2,...,8
Ne	0.6	1	10	2,...,8
Na	0.7	1	20	2,...,7
Mg	0.7	1	20	2,...,7
Ar	0.7	2	25	2,...,7

$$\epsilon_{n\ell} = -\frac{Z^2}{2n^2}. \quad (128)$$

We see that accuracy within 1% is achieved already at $L=4$. Expectation values of the kinetic energy and potential energy operators \hat{T} and \hat{V} for the hydrogen $1s$ orbital ($Z=1$) are shown in Fig. 4. The most accurate ($L=9$) numerical values are $\epsilon_{1s} = -0.499\,996$, $\langle \hat{T} \rangle_{1s} = 0.499\,98$, and $\langle \hat{V} \rangle_{1s} = -0.999\,98$, the exact values for $Z=1$ being $-1/2$, $1/2$, and -1 , respectively. Other orbitals of the hydrogen atom ($2s$, $2p$, $3s$, $3p$, $3d$, and $4f$) were also calculated. We used a unit of length $u=1.0$ and minimum resolution level $k_{\min}=0$. The resulting orbital eigenvalues are shown in Fig. 5. Accuracy better than 1% is achieved at $L=4$ for all the computed orbitals. As the orbital quantum number ℓ increases the results get more accurate.

We also made a set of computations for hydrogen $1s$, $2p$, and $3s$ orbitals where both the number of resolution levels L and basis width B were varied. The hydrogen $1s$ orbital was computed with unit of length $u=0.6$, 1.0 , and 1.4 , and the other orbitals with unit of length $u=1.0$. We used $k_{\min}=0$ in these computations. The relative error of the hydrogen $1s$ eigenvalue (compared to the exact analytical result) is plotted as a contour plot in Figs. 6, 7 and 8, where the length units u are 0.6 , 1.0 , and 1.4 , respectively. Similar plots for $2p$

TABLE V. Results from Hartree-Fock calculations for lithium and sodium. Deviation from the accurate value [26] is given in parentheses so that negative deviation means that the computed value is less than the accurate value.

	Li	Na
E	-7.4321(7)	-161.3(6)
n_{iter}	17	27
ϵ_{1s}	-2.4775(3)	-40.2(3)
ϵ_{2s}	-0.196 309(14)	-2.78(2)
ϵ_{2p}		-1.521(-3)
ϵ_{3s}		-0.1817(5)
$\langle 1s 2s \rangle$	-5.7×10^{-4}	-5.9×10^{-8}
$\langle 1s 3s \rangle$		-1.4×10^{-6}
$\langle 2s 3s \rangle$		-2.8×10^{-4}

and $3s$ are presented in Figs. 9 and 10. The relative error is computed by $\Delta = (x - x_0)/x_0$ where x is the computed quantity and x_0 its exact value. For each orbital, the Schrödinger equation was solved using all combinations with $L = L_{\min}, L_{\min}+1, \dots, L_{\max}$ and $B = B_{\min}, B_{\min}+1, \dots, B_{\max}$ to cover the ranges of L and B .

Note that for fixed L the limiting value for the orbital eigenvalue as B tends to infinity is not the (physically) exact value but one with a L dependent shift. Therefore, the 0% contour appears in Figs. 7, 8, and 9.

C. Hartree-Fock results for many-electron atoms

We carried out HF calculations for helium, lithium, beryllium, neon, sodium, magnesium, and argon atoms. Lithium and sodium are open-shell and the others are closed-shell atoms. The relevant computation parameters are given in Table III. The basis sets were formed the same way as for the hydrogen atom. The same value of the weight parameter α_i defined by Eq. (78) is used for all orbitals, $\alpha_i = \alpha$. The unit of length was $u=1$ in all HF calculations. A matrix one-norm

TABLE IV. Results from Hartree-Fock calculations for helium, beryllium, neon, magnesium, and argon. Deviation from the accurate value [26] is given in parentheses so that negative deviation means that the computed value is less than the accurate value.

	He	Be	Ne	Mg	Ar
E	-2.861 57(11)	-14.571(3)	-128.45(10)	-198.8(9)	-525.8(11)
n_{iter}	21	23	31	27	25
ϵ_{1s}	0.917 93(3)	-4.7318(9)	-32.73(5)	-48.7(4)	-118.2(5)
ϵ_{2s}		-0.309 25(2)	-1.928(3)	-3.75(2)	-12.29(4)
ϵ_{2p}			-0.850(-4)	-2.287(-5)	-9.577(-6)
ϵ_{3s}				-0.2525(6)	-1.274(4)
ϵ_{3p}					-0.5916(-6)
$\langle 1s 2s \rangle$		-2.6×10^{-7}	-4.2×10^{-6}	-5.6×10^{-8}	-1.8×10^{-8}
$\langle 1s 3s \rangle$				-1.6×10^{-8}	-7.8×10^{-9}
$\langle 2s 3s \rangle$				-8.9×10^{-8}	-2.5×10^{-8}
$\langle 2p 3p \rangle$					-1.4×10^{-8}

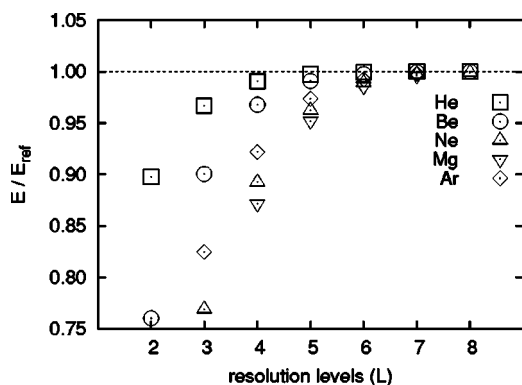


FIG. 11. Computed total energies for helium, beryllium, neon, magnesium, and argon. Ratio of computed and accurate [26] values is shown.

was used to compute the quantities z defined by Eq. (79). The value of the precision parameter z_0 was 10^{-10} in all HF computations.

The orbital eigenvalues and total energies from the most accurate computation for each atom are given in Tables IV and V. These values are compared with the values from standard HF calculations obtained from Ref. [26]. Total energies of atoms are plotted in Figs. 11 and 12. For helium, four resolution levels are needed to reach an accuracy of 1% with $k_{\min}=1$. For argon, six resolution levels are needed for this with $k_{\min}=2$. The HF calculations converged in 16 to 31 steps depending on the number of resolution levels L and weight parameter α .

The effect of neglecting nondiagonal Lagrange multipliers can be seen from the overlap integrals between orbitals. For the open-shell atoms (lithium and sodium) the largest overlap integral is of the order of magnitude 10^{-4} whereas for the closed-shell atoms all the overlap integrals are of the order of magnitude 10^{-6} or smaller.

VIII. CONCLUSIONS

We have demonstrated that interpolating wavelets can be successfully used to solve the atomic orbitals and the electronic structure of atoms. We are able to systematically increase the accuracy of the calculations by choosing the number of resolution levels and the number of basis functions in each level.

In this study we have concentrated on the basic formalism and developed it down to practical computations. Our study

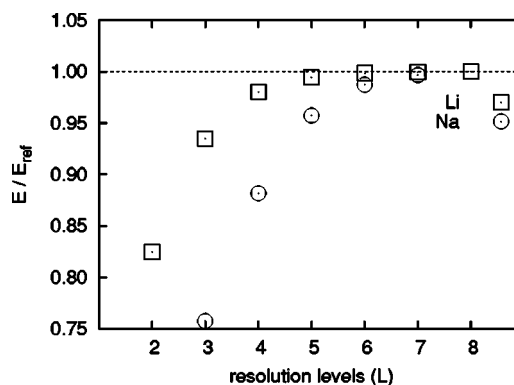


FIG. 12. Computed total energies for lithium and sodium. Ratio of computed and accurate [26] values is shown.

involves both development of algorithms, e.g., for conversion of matrices from nonstandard operator form to standard operator form, and testing with calculations. We have shown how to consider the singularity of the nuclear Coulomb potential and the centrifugal potential as well as the Slater integrals in evaluation of Hamiltonian and Fock matrix elements (see also Ref. [16]).

We have tested numerically the computation methods for the ground state of the hydrogen atom and hydrogenlike atoms, for excited states of hydrogen, and for some many-electron atoms. The numerical results converge to the accurate or reference values as the number of resolution levels increases. In principle, we should be able to make the error arising from the wavelet approximation arbitrarily small by enlarging the basis function set. Our numerical HF results support this. With a large number of resolution levels (about eight-or more) the computation time grows considerably. Depending on the properties of the algorithms we can use basis sets with fewer resolution levels (possibly only one), higher minimum resolution, and more basis functions in each level. However, the possibility of using several resolution levels is one important benefit of wavelets. It might also be possible to optimize the computation by using convolutions in the computation of backward and forward wavelet transforms and products of operators with vectors instead of simply using matrix products as done in this study.

A noticeable feature in our development for the Hartree-Fock formalism is that all relevant operators, including those representing the two-electron integrals, can be evaluated analytically.

[1] C. J. Tymczak and Xiao-Qian Wang, Phys. Rev. Lett. **78**, 3654 (1997).
 [2] P. Fischer and M. Defranceschi, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **35**, 1 (1998).
 [3] Siqing Wei and M. Y. Chou, Phys. Rev. Lett. **76**, 2650 (1996).
 [4] K. Yamaguchi and T. Mukoyama, J. Phys. B **29**, 4059 (1996).
 [5] K. Cho, T. A. Arias, J. D. Joannopoulos, and P. K. Lam, Phys. Rev. Lett. **71**, 1808 (1993).

[6] P. Fischer and M. Defranceschi, Appl. Comput. Harmon. Anal. **1**, 232 (1994).
 [7] S. Goedecker and O. V. Ivanov, Solid State Commun. **105**, 665 (1998).
 [8] S. Goedecker, *Wavelets and Their Application for the Solution of Partial Differential Equations in Physics* (Presses Polytechniques et Universitaires Romandes, Lausanne, 1998).
 [9] I. Daubechies, Commun. Pure Appl. Math. **41**, 909 (1988).

- [10] I. Daubechies, *Ten Lectures on Wavelets*, CBMS-NSF Regional Conference Series in Applied Mathematics Vol. 61 (SIAM, Philadelphia, 1992).
- [11] K. Yamaguchi and T. Mukoyama, Nucl. Instrum. Methods Phys. Res. B **124**, 361 (1997).
- [12] R. A. Lippert, T. A. Arias, and A. Edelman, J. Comput. Phys. **140**, 278 (1998).
- [13] O. V. Vasilyev, S. Paolucci, and M. Sen, J. Comput. Phys. **120**, 33 (1995).
- [14] T. A. Arias, Rev. Mod. Phys. **71**, 267 (1999).
- [15] J. B. Mann, *Atomic Structure Calculations* (Los Alamos Scientific Laboratory of the University of California, Los Alamos, NM, 1967).
- [16] B. R. Johnson, J. L. Mackey, and J. L. Kinsey, J. Comput. Phys. **168**, 356 (2001).
- [17] G. Beylkin, R. Coifman, and V. Rokhlin, Commun. Pure Appl. Math. **44**, 141 (1991).
- [18] G. Beylkin, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **6**, 1716 (1992).
- [19] G. Beylkin and J. M. Keiser, J. Comput. Phys. **132**, 233 (1997).
- [20] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics* (Oxford University Press, Oxford, 1997).
- [21] V. Schmidt, *Electron Spectrometry of Atoms using Synchrotron Radiation* (Cambridge University Press, Cambridge, 1997).
- [22] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
- [23] I. N. Levine, *Quantum Chemistry* (Allyn and Bacon, Boston, 1983).
- [24] W. Dahmen and C. A. Micchelli, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **30**, 507 (1993).
- [25] S. Bertoluzza, C. Canuto, and K. Urban, Appl. Numer. Math. **34**, 13 (2000).
- [26] Ch. Froese Fischer, *The Hartree-Fock Method for Atoms—A Numerical Approach* (Wiley, New York, 1977).