Adaptive solver of Kohn-Sham equation for an atom‡

Zbigniew Romanowski

E-mail: romz@wp.pl
Interdisciplinary Centre for Materials Modelling, ul. Pawinskiego 5a, 02-106 Warsaw, Poland

Abstract. Adaptive numerical algorithm solving Kohn-Sham equation for confined in spherical cavity atom is presented. The Kohn-Sham equation is solved by high order finite element method with Lobatto polynomials as basis set. Based on this method the adaptive algorithm is proposed, what leads to simple and efficient algorithm. The details of the adaptive algorithm are discussed. Numerical results for N, Al, Ga and In atoms are provided. Using this procedure very high accuracy were obtained with very few number of mesh nodes.

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1. Introduction

High order finite element method (FEM) is very promising tool for solving real scientific and engineering problems. Many books and articles were published concerned with the finite element theory and its application [1, 2, 3, 4]. The strength of the FEM is its generality – it can be applied to broad class of partial differential equations defined over one, two or three dimensional domain. The second source of the strength of FEM is the availability of the adaptive algorithms [5, 6, 7]. For FEM the adaptive algorithm can be particularly efficient, because of the locality of the polynomial basis set used to span the linear piecewise polynomial space, where the solution of the partial differential equation is searched.

The goal of an adaptive algorithm is to provide highly accurate solution with relatively modest requirements of computer resources comparing to algorithms based on the uniform grids. The adaptive algorithms are particularly desired in atomic and molecular physics, where the behavior of electron density or wavefunction strongly depends on the spatial position relative to positions of atoms.

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In this paper the application of h-adaptive algorithm for solving Kohn-Sham equation [8, 9] for an atom within the framework of Density Functional Theory [10, 11, 12] is discussed. Recently, we have published the paper [13], where the details of the algorithm solving this problem based on FEM with B-splines were presented. The algorithm published in Ref. [13] was designed to work properly on any mesh, however, no adaptability was proposed.

In the present paper we propose simple yet efficient h-adaptive algorithm. The adaptive algorithm is based on the high order finite element method [3, 2] with Lobatto polynomials as basis set. The application of this method to problems in one dimension leads to sparse matrices. Moreover, the elements of matrices can be easily obtained analytically or numerically applying Gauss quadratures [14].

The structure of the paper is as follows. In Section 2 the definition and the properties of Lobatto polynomials are listed. The algorithm of constructing the basis functions for FEM is also discussed. In Section 3 the DFT equations, specific for an atom, are listed in concise form. In Section 4 the adaptive algorithm is described. The adaptive algorithm is simple and is discussed for Poisson equation and Kohn-Sham eigenproblem. The presented adaptive algorithm was implemented in `RAtom` program. In the last section numerical results for N, Al, Ga, In atoms obtained by `RAtom` program are presented.

2. Basics of high order finite element method

2.1. Lobatto polynomials

The key ingredient of high order finite element method are Lobatto polynomials [3, 2]. Their numerical properties (after discretization of differential equation) lead to set of algebraic equations with well conditioned matrices. Lobatto polynomials are defined on the interval $[-1, 1]$ as follows

$$\psi_0(s) = (1 - s)/2 \tag{1a}$$

$$\psi_1(s) = (1 + s)/2 \tag{1b}$$

$$\psi_k(s) = \int_{-1}^{s} \tilde{P}_{k-1}(t)\mathrm{d}t \qquad \text{for } k \geq 2 \tag{1c}$$

In the above equation $\tilde{P}_k(t)$ is normalized Legendre polynomial

$$\tilde{P}_k(t) = \frac{P_k(t)}{||P_k(t)||}, \tag{2}$$

where $P_k(t)$ denotes Legendre polynomial [15] and $||P_k||$ denotes its norm

$$||P_k||^2 = \int_{-1}^{1} P_k^2(t)\mathrm{d}t. \tag{3}$$

Since Legendre polynomials are explicitly given, then the explicit formulas for Lobatto polynomials may be obtained. For convenience a few first Lobatto polynomials are

Table 1. Explicit expressions for Lobatto polynomials, $\psi_k(s)$, for $k \leq 10$.

k	$\psi_k(s)$
0	$(1-s)/2$
1	$(1+s)/2$
2	$\frac{1}{2}\sqrt{\frac{3}{2}}(s^2-1)$
3	$\frac{1}{2}\sqrt{\frac{5}{2}}(s^2-1)s$
4	$\frac{1}{8}\sqrt{\frac{7}{2}}(s^2-1)(5s^2-1)$
5	$\frac{1}{8}\sqrt{\frac{9}{2}}(s^2-1)(7s^2-3)s$
6	$\frac{1}{16}\sqrt{\frac{11}{2}}(s^2-1)(21s^4-14s^2+1)$
7	$\frac{1}{16}\sqrt{\frac{13}{2}}(s^2-1)(33s^4-30s^2+5)s$
8	$\frac{1}{128}\sqrt{\frac{15}{2}}(s^2-1)(429s^6-495s^4+135s^2-5)$
9	$\frac{1}{128}\sqrt{\frac{17}{2}}(s^2-1)(715s^6-1001s^4+385s^2-35)s$
10	$\frac{1}{256}\sqrt{\frac{19}{2}}(s^2-1)(2431s^8-4004s^6+2002s^4-308s^2+7)$

listed in Table 1. Based on the definition $(1a)$-$(1c)$ it can be shown [3, 2] that Lobatto polynomials fulfill the conditions

$$\psi_k(-1) = \begin{cases} 1 & \text{for } k=0 \\ 0 & \text{for } k=1 \\ 0 & \text{for } k \geq 2 \end{cases} \qquad \psi_k(1) = \begin{cases} 0 & \text{for } k=0 \\ 1 & \text{for } k=1 \\ 0 & \text{for } k \geq 2 \end{cases} \tag{4}$$

The above properties are important when Lobatto polynomials are applied in finite element method, since continuity of the approximated function can be easily achieved.

2.2. Basis functions for high order finite element method

Each FEM requires the basis set over the domain of differential equation. The construction of basis sets starts from dividing the domain into the non-intersecting parts. For each part the basis set is constructed. For one dimensional case the parts are intervals and each part has two or one neighboring part. In FEM the solution of differential equation is searched in the piecewise polynomial space spanned on the basis functions for each part. The part plus its basis functions is called the element.

In high order FEM the basis functions on element are polynomials of high order. Because of properties given in Eq. (4) for Lobatto polynomials it is easy to construct a basis set of any order, which leads to continuous piecewise polynomial space. To obtain the basis for element $[a,b]$ the mapping $X : [-1,1] \mapsto [a,b]$ is introduced

$$X(s) = As + B, \tag{5}$$

where

$$A = \frac{b-a}{2} \qquad \text{and} \qquad B = \frac{b+a}{2}. \tag{6}$$

Since $b > a$, then $A > 0$ and $A \leq B$. Moreover, since X is a linear function, then the mapping $X^{-1} : [a, b] \mapsto [-1, 1]$

$$X^{-1}(x) = \frac{x - B}{A} \tag{7}$$

inverse to X (*i.e.* having the properties $X^{-1}(X(s)) = s$ for $s \in [-1, 1]$) always exists. Based on the mapping X^{-1} the basis functions on the interval $[a, b]$ are constructed as a superposition

$$\phi_i(x) = \psi_i(X^{-1}(x)). \tag{8}$$

Since X^{-1} is well defined for $x \in [a, b]$, then $\phi_i(x)$ is also well defined for any $x \in [a, b]$.

2.3. Discretization procedure

The basis functions ϕ_i from Eq. (8) are defined for each element. Since the set $\{\phi_i\}$ is linearly independent [2, 3], the linear functional space can be spanned on them. Then, the searched solution is represented as a linear combination of the basis functions $\{\phi_i\}$. The expansion coefficients are evaluated based on the Galerkin formulation [16] of FEM, *i.e.* the residual must be orthogonal to each basis function. Discretization based on the Galerkin method transforms: (i) the ordinary differential equation to set of algebraic equations, (ii) the differential eigenvalue problem to algebraic generalized eigenvalue problem. When basis functions are constructed using Lobatto polynomials, then the matrices are sparse and their elements can be easily evaluated analytically or numerically.

3. DFT equations for an atom

As described below in `RAtom` program DFT equations for an atom are solved. This program is dedicated to solve the non-linear Kohn-Sham eigenvalue problem for an atom located in infinitely deep spherical cavity of radius $r_c > 0$. This condition enforces the eigenfunctions to be equal zero on the sphere of radius r_c.

The main source of difficulties arises from the non-linear form of Kohn-Sham equation

$$\Big[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\ell(\ell+1)}{2r^2} + V(r) \Big] R_{n,\ell}(r) = \varepsilon_{n,\ell} R_{n,\ell}(r), \tag{9}$$

which depends on the angular quantum number ℓ. The above equation is a set of independent equations for $\ell = 0, \ldots, \ell_{\max}$, where $\ell_{\max}$ is determined by the number of electrons N in the analyzed atom. For each ℓ, N_ℓ smallest eigenvalues $\varepsilon_{n,\ell}$ and corresponding eigenfunctions $R_{n,\ell}$ must be found, where $N_{n,\ell}$ is determined, based on the number of electrons in analyzed atom. Since the atom is located in the spherical cavity of radius r_c, the functions $R_{n,\ell} : [0, r_c] \mapsto \mathbb{R}$ must fulfill Dirichlet boundary conditions

$$R_{n,\ell}(0) = R_{n,\ell}(r_c) = 0. \tag{10}$$

In Eq. (9), $V(r)$ is an effective potential, given as a sum

$$V(r) = -\frac{Z}{r} + V_{\mathrm{h}}(r) + V_{\mathrm{xc}}(r), \tag{11}$$

where Z is the number of protons, V_{h} is a hartree potential and V_{xc} is an correlation-exchange potential defined by an adequate approximation. In `RAtom` program hartree potential V_{h} is obtained as a solution of Poisson equation which, for one dimensional case, is reduced to ordinary differential equation

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[rV_{\mathrm{h}}(r)] = -4\pi\varrho(r) \tag{12}$$

with Dirichlet boundary conditions obtained from explicit [17] solution

$$V_{\mathrm{h}}(r) = 4\pi\Big[\frac{1}{r}\int_0^r t^2\varrho(t)\mathrm{d}t + \int_r^\infty t\varrho(t)\mathrm{d}t\Big], \tag{13}$$

where $\varrho : [0, r_{\mathrm{c}}] \mapsto \mathbb{R}^+$ is electron density. Since the spherical symmetry is assumed, the electron density is given by

$$\varrho(r) = \frac{1}{4\pi r^2}\sum_{n,\ell}(2\ell+1)f_{n,\ell}R_{n,\ell}^2(r), \tag{14}$$

where $f_{n,\ell}$ are an occupation factors of (n,ℓ) eigenstate which sum up to the number of electrons $N = \sum_{n,\ell} f_{n,\ell}$. Since Kohn-Sham equation (9) is non-linear differential eigenvalue problem, it is solved iteratively in self consistent field (SCF) loop. In `RAtom` program the sum of eigenvalues

$$E_{\mathrm{e}} = \sum_{n,\ell}\varepsilon_{n,\ell} \tag{15}$$

is set as termination criterion for SCF loop. If the difference of E_{e} in two consecutive iterations is smaller than 10^{-7} hartree, then SCF loop in `RAtom` is terminated.

Because of multi resolution of functions $R_{n,\ell}$, usually exponential mesh is applied [18, 19, 20] to solve radial Schrödinger equation or radial Kohn-Sham (9) equation [21, 13]. In the present paper, to solve radial Kohn-Sham equation (9) the h-adaptive algorithm is applied. Our h-adaptive algorithm starts from uniform mesh, selects appropriate elements and splits them into two halves. For each adaptive loop the Kohn-Sham eigenvalue problem (9), discretized by finite element method, is solved by the method described in Section 2. The adaptive loop is repeated until the selected expansion coefficients of eigenfunctions are smaller than required threshold. Additionally, the adaptive algorithm is applied for Poisson equation (12). The details of the adaptive procedure are given in the next Section.

4. Adaptive algorithms

In this section the adaptive algorithm is described. The present algorithm belongs to the group of h-adaptive algorithms. First, the element with the largest error is searched, and then it is split into two halves. The key aspect of the h-adaptive algorithm is the measure of error for searched solution, which must be reliable and easy to evaluate.

Our adaptive algorithm is based on the observation that the expansion coefficients of Lobatto basis functions decays rapidly when the approximate solution is close to the accurate solution. This is related to Taylor expansion, for which its finite expansion gives accurate representation of function on short interval, if the expanded function behaves well.

Actually, our algorithm is not rigorously derived. Based on many numerical experiments we observed that the elements with large expansion coefficients introduce the largest error to the searched solution. In order to decrease the error, the elements were split what improves the solution considerably. Based on this observation the algorithm was designed.

In the following section we describe the adaptive algorithm for ordinary differential equation and differential eigenvalue problem. For both problems the treatment is similar, however, slightly more complicated for eigenvalue problem where the adaptivity must by applied to any searched eigenfunction simultaneously.

4.1. Adaptive algorithm for Poisson equation

For problem studied in this paper the Poisson equation (12) is reduced to ordinary differential equation with Dirichlet boundary condition defined on the finite domain $[0, r_{\mathrm{c}}]$. The adaptive algorithm for this equation is the following.

(i) Choose initial mesh $\mathcal{T}$ and solve Poisson equation for this set using the non-adaptive FEM algorithm with Lobatto basis functions. The solution is a vector of expansion coefficients $\boldsymbol{c}$.

(ii) For each element $e \in \mathcal{T}$ find the smallest expansion coefficient. The coefficients of function ϕ_0 and ϕ_1 are not considered, since they are responsible for the continuity of the approximated solution. Let denote the smallest coefficient for element $e \in \mathcal{T}$ as c_e.

(iii) Find the element e^* corresponding to the largest coefficient c_{e} for all elements $e \in \mathcal{T}$

$$c^* = \max_{e \in \mathcal{T}} |c_e|. \tag{16}$$

Since the mesh $\mathcal{T}$ is finite, the element e^* always could be found.

(iv) If $c^* < \delta$, where δ is chosen threshold, then STOP the adaptive procedure. If not, split element e^* into two halves and GOTO point (ii).

The above presented algorithm, for each iteration, requires the solution of non-adaptive FEM problem. For one dimensional problem the matrices are small and the problem can be easily solved. For obtained solution and hence determined expansion coefficients, the element e^* corresponding to c^* is searched. This can be accomplished in linear time.

4.2. Adaptive algorithm for linearized Kohn-Sham eigenvalue problem

The Kohn-Sham equation for an atom is an eigenvalue problem with Dirichlet boundary conditions. For this equation a few eigenfunctions are searched, corresponding to the

smallest eigenvalues.

The adaptive algorithm for eigenvalue problem is analogous to the presented one in the previous Section. However, the complexity arises since the adaptivity must be applied to any searched eigenfunctions simultaneously. In order to adapt the mesh in each step, for each searched eigenfunctions simultaneously, the largest coefficients are searched for all eigenfunction. More formally the algorithm is following.

(i) Choose threshold $\delta > 0$. Choose initial mesh $\mathcal{T}$ and solve Kohn-Sham equation for this mesh using the non-adaptive FEM algorithm with Lobatto basis functions. The solution is a rectangular matrix of expansion coefficients $\boldsymbol{C}$, where each column of the matrix $\boldsymbol{C}$ is a vector of expansion coefficients for corresponding eigenfunctions.

(ii) For each element $e \in \mathcal{T}$ and for each eigenfunction i find the smallest expansion coefficient. As for Poisson equation, the coefficients of functions ϕ_0 and ϕ_1 are not considered, since they are determined from the continuity of approximated solution. Let denote the smallest coefficient for element e and eigenfunction i as $c_{e,i}$.

(iii) For each eigenfunction i find the element e_i^* corresponding to the largest coefficient $c_{e,i}$

$$c_i^* = \max_{e \in \mathcal{T}} |c_{e,i}| \tag{17}$$

Since the mesh $\mathcal{T}$ is finite, the element e_i^* always could be found.

(iv) Choose elements e_i^* for split. If for $i \neq j$ is $e_i^* = e_j^*$, then $c_i^* = \max\{c_i^*, c_j^*\}$.

(v) If $c_i > \delta$, then split element e_i^* into two halves and GOTO point (ii). If not, STOP adaptive procedure.

The algorithm presented above is only slightly more complicated than the algorithm described for Poisson equation. This algorithm for each eigenfunction i looks for the element corresponding to the coefficient c_i^*. However, for Kohn-Sham equation for an atom, it often happens that two different eigenfunctions correspond to the same element. This 'collision' is resolved in point (iv) of the above algorithm. Actually this situation is advantageous, since one element split adapts at least two eigenfunctions. Since solution of the generalized eigenvalue problem can be time consuming 'collision' property is desired. For Kohn-Sham equation for an atom discussed in the present paper, the mesh $\mathcal{T}$ contains less than 100 elements, hence searching the element e^* is fast.

5. Numerical results

In this section the numerical results for N, Al, Ga, an In atoms are presented. The non-linear Kohn-Sham problem was solved for atoms located in the spherical cavity. The radius of the spherical cavity for N atom was $r_\mathrm{c} = 15$ bohrs and for Al, Ga, In atoms was $r_\mathrm{c} = 30$ bohrs, what corresponds to free atoms. For correlation energy the term proposed by Vosko, Wilk, Nusair (VWN) [22, 23] was used, and Slater exchange term [24] was applied to evaluate exchange energy. Lobatto polynomials of order 6 were

Table 2. Number of mesh nodes generated by adaptive procedure for N, Al, Ga and In atom for each relevant angular quantum number ℓ and for each k-th SCF iteration. Lobatto polynomials of order 6 were used.

	N		Al		Ga			In		
k	$\ell=0$	$\ell=1$	$\ell=0$	$\ell=1$	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=0$	$\ell=1$	$\ell=2$
1	15	7	16	12	22	21	4	22	26	6
2	15	10	21	17	26	26	13	31	34	20
3	15	11	23	19	26	26	14	34	34	20
$k \geq 4$	15	11	23	19	26	26	15	34	34	22

Table 3. Total energy E_t and sum of eigenvalues E_e for N, Al, Ga and In atom as a function of precision parameter δ. Lobatto polynomials of order 6 were used. Row titled NIST lists reference data [25, 21]. All values in hartree.

	N		Al		Ga		In	
δ	E_t	E_e	E_t	E_e	E_t	E_e	E_t	E_e
0.2	-53.91823	-15.09318	-237.60300	-63.86577	-1921.78703	-465.52566	-5716.34823	-1337.97929
0.1	-54.02482	-14.95394	-241.30473	-62.04903	-1921.78703	-465.52566	-5737.07131	-1337.18333
10^{-2}	-54.02501	-14.95394	-241.31551	-62.04431	-1921.84644	-465.45701	-5737.30685	-1337.04325
10^{-3}	-54.02501	-14.95394	-241.31557	-62.04431	-1921.84645	-465.45701	-5737.30905	-1337.04208
10^{-4}	-54.02501	-14.95394	-241.31557	-62.04431	-1921.84645	-465.45701	-5737.30906	-1337.04208
NIST	-54.025016	-14.953949	-241.315573	-62.044317	-1921.846456	-465.457015	-5737.309064	-1337.042079

used. SCF loop is terminated if for two consecutive iterations the difference in the sum of eigenvalues was smaller than 10^{-7} hartree.

The linear Kohn-Sham eigenvalue problem and Poisson equation were solved adaptively for each SCF iteration. The adaptive loop started from 4 nodes. For each SCF iteration number of obtained mesh nodes is listed in Table 2. Since, for each angular quantum number ℓ, the dedicated eigenvalue solver was used, the number of mesh nodes for each ℓ is independent and is listed in Table 2. The values were obtained for threshold $\delta = 10^{-4}$ which leads to eigenvalue with accuracy of 10^{-5} hartree as shown be comparison to the reference values [25, 21].

From values listed in Table 2 it follows that adaptive algorithm generates small number of mesh point in order to obtain eigenvalues and total energy with accuracy of 10^{-5} hartree. For each studied atom, the largest number of mesh nodes were generated for $\ell = 0$ and the smallest for $\ell = 2$, what corresponds to steep and diffuse orbitals, respectively. Moreover, the number of mesh nodes is fixed after the first 3 or 4 SCF iterations. Hence, the additional computational cost related to adaptive algorithm has only impact on the first 3 or 4 SCF iterations and then non-adaptive procedure runs only.

In Table 3 the total energy E_t and sum of eigenvalues E_e for N, Al, Ga and In atoms, as a function of threshold parameter δ, are presented. From values listed in Table 3 it follows that for $\delta = 10^{-3}$ and $\delta = 10^{-4}$ the energies E_t and E_e are evaluated with accuracy of 10^{-5} hatree. For each studied case the number of required SCF iterations to

Table 4. Number of mesh nodes generated by adaptive procedure for N, Al, Ga and In atom for each relevant angular quantum number ℓ and for selected values of δ parameters. Lobatto polynomials of order 6 were used.

	N		Al		Ga			In		
δ	$\ell=0$	$\ell=1$	$\ell=0$	$\ell=1$	$\ell=0$	$\ell=1$	$\ell=2$	$\ell=0$	$\ell=1$	$\ell=2$
0.2	7	4	8	5	10	9	7	11	10	8
0.1	7	6	9	7	10	9	7	11	14	8
10^{-2}	8	7	9	9	12	11	9	15	18	9
10^{-3}	8	8	10	10	19	22	10	28	24	14
10^{-4}	15	11	26	26	26	26	15	34	34	22

obtain the convergence was approximately constant. Hence, the speed of convergence in SCF loop does not depend on the δ parameter if $\delta < 0.2$.

It is clear that δ parameter determines the number of mesh nodes. The number of mesh nodes obtained by adaptive procedure for various δ is listed in Table 4. It follows that number of generated mesh increases rather slowly when the δ parameter is decreased. For each studied atom the number of mesh nodes is the largest for $\ell = 0$ and the smallest for $\ell = 2$ for each considered value of δ. It should be stressed that for each relevant angular quantum number ℓ, usually more than one eigenstate is represented on the mesh. For example, for N atom and $\ell = 1$ only one state (*i.e.* 2p) must be represented on the mesh, hence only 8 nodes are required for $\delta = 10^{-3}$. However, for In atom and $\ell = 1$ four different eigenstates (*i.e.* 2p, 3p, 4p, 5p) must be represented properly on the same mesh, hence 24 nodes are required for $\delta = 10^{-3}$. Since $24/4 = 6$, then on average one p state of In atom requires less mesh points (6) than one p state of N atom (8). It follows that the proposed algorithm behaves equally well for light N atom and for heavy In atom.

6. Conclusions

The h-adaptive algorithm was proposed, which is suitable to solve both eigenvalue problem and ordinary differential equation for the one dimensional finite domain. The algorithm is based on the high order finite element method. Although it is not rigorously derived it has solid mathematical background. The algorithm has only one parameter defining the accuracy of the searched solution. The h-adaptive algorithm was applied to solve non-linear Kohn-Sham eigenvalue problem. On meshes with small number of nodes very accurate results were obtained. In order to demonstrate the usefulness of the algorithm, it was applied to obtain the Kohn-Sham eigenvalues for N, Al, Ga, In atoms with VWN and Slater approximation for correlation and exchange terms. Comparing to the reference values [25, 21] an accuracy as high as 10^{-5} hartree was obtained on meshes with less then 30 nodes.

References

[1] S. C. Brenner and L. R. Scott. *The Mathematical Theory of Finite Element Methods*. Springer, 1996.

[2] P. Šolín. *Partial Differential Equations and the Finite Element Method*. Wiley, 2006.

[3] P. Šolín, K. Segeth, and I. Doležel. *High-Order Finite Element Method*. CHAPMAN & HALL/CRC, London, 2004.

[4] H. Bachau, E. Cormier, P. Decleva, J. E. Hansen, and F. Martn. Applications of B-splines in atomic and molecular physics. *Rep. Prog. Phys*, 64:1601–1729, 2001.

[5] I. Babuška and T. Strouboulis. *The Finite Element Method and Its Reliability*. Oxford University Press, Oxford, 2001.

[6] L. Demkowicz. *Computing with hp-Adaptive Finite Elements, Vol. 1: One and Two Dimensional Elliptic and Maxwell Problems*. Chapman & Hall/CRC, New York, 2006.

[7] L. Demkowicz. *Computing with hp-Adaptive Finite Elements, Vol. 2: Frontiers: Three Dimensional Elliptic and Maxwell Problems with Applications*. Chapman & Hall/CRC, New York, 2007.

[8] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:1133, 1965.

[9] P. Hohenberg and W. Kohn. Ihomogeneous electron gas. *Phys. Rev.*, 136:864, 1964.

[10] H. Eschrig. *The Fundamentals of Density Functional Theory*. Teubner, Stuttgart, 1996.

[11] W. Koch and M. C. Holthausen. *A Chemist's Guide to Density Functional Theory*. Wiley, New York, 2000.

[12] R. M. Martin. *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press, Cambridge, 2004.

[13] Z. Romanowski. B-Spline finite element solution of Kohn-Sham equation for atom. *Modelling Simul. Mater. Sci. Eng.*, 16:015003, 2008.

[14] J. Stoer and R. Bulirsch. *Introduction to Numerical Analysis*. Springer, New York, 2004.

[15] M. Abramowitz and I. A. Stegun. *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*. Dover Publications, New York, 1972. `http://www.math.sfu.ca/~cbm/aands/toc.htm`.

[16] C. A. J. Fletcher. *Computational Galerkin Methods*. Springer, 1984.

[17] B. Delley. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.*, 92:508–517, 1990.

[18] C. Froese Fischer, W. Guo, and Z. Shen. Spline methods for multiconfiguration Hartree-Fock calculations. *Int. J. Quant. Chem.*, 42:849–867, 1992.

[19] C. Frose Fischer and W. Guo. Spline algorithms for the Hartree-Fock equation for the Helium ground state. *J. Comput. Phys.*, 90:486–496, 1990.

[20] C. Frose Fischer, T. Brage, and P. Jönsson. *Computational Atomic Structure*. Institute of Physics Publishing, Bristol, 1997.

[21] S. Kotochigova, Z. H. Levine, E. L. Shirley, M. D. Stiles, and C. W. Clark. Local-density-functional calculations of the energy of atoms. *Phys. Rev. A*, 55:191, 1997. (Erratum: Phys. Rev. A 56, 5191 (1997)).

[22] S. H. Vosko, L. Wilk, and M. Nusair. Accurate spin dependent electron liquid correlation energies for local spin density calculations: A critical analysis. *Can. J. Phys*, 58:1200, 1980.

[23] S. H. Vosko, L. Wilk, and M. Nusair. Influence of an improved local-spin-density correlation-energy functional on the cohesive energy of alkali metals. *Phys. Rev. B*, 22:3812, 1980.

[24] W. Koch and M. C. Holthausen. *A Chemist's Guide to Density Functional Theory*. Wiley-VCH, New York, 2000.

[25] S. Kotochigova, Z. H. Levine, E. L. Shirley, M. D. Stiles, and C. W. Clark. `http://physics.nist.gov/PhysRefData/DFTdata/contents.html`, 2007.