Effects of a Supplementary Quadrature in the Collocation Method for Solving the Hartree Fock Equations in *Ab-initio* calculations

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Abstract: - The collocation method for solving the Hartree-Fock equations of the self-consistent field in large atomic and molecular systems is analyzed and a method for improving its performances by supplementary analytical and numerical quadrature is proposed. We used monomial and Chbyshev type trial functions and the collocation points were equidistant or Chebyshev polynomial roots. The singularities have been avoided by a function change and analytical expressions have been obtained for the most part of the integrated terms in the matrix elements, except the Hartree-Fock potential which is treated separately in a similar way. This a-priori analytical treatment ensures a greater speed and a lower condition number of the matrix necessary for the expansion's coefficient calculus, with an important effect on the overall precision and speed. Some numerical results are presented and compared with well-known types of orbitals, demonstrating the performance increasing in terms of precision and computing effort.

Key-Words: - *Ab–initio* methods, self consistent field, Hartree-Fock equations, Collocation, Evanescence

1 Introduction

Numerically solving the Hartree-Fockk (HF) equations for many atoms systems is a very computing-demanding task, as a large number of differential equations (up to several thousands) have to be iteratively dealt until the self consistency is achieved. These types of calculations are very important in quantum chemistry, science of materials, molecular biology, etc. That is why a great interest is shown for developing high performance methods for integrating the differential equations of the self consistent field, and any improvement of the performances by using new techniques are very important in applying the ab-initio methods for larger atomic systems, taking into account the limited power of the available computers.

It is known that for each electron of each atom, the wave function satisfy the Schrödinger equation with a special potential that have a coulombian part due to the nucleus $V_N = -\dfrac{Z}{r}$ and an electron interaction part given by the Hartree-Fock potential V_{HF} (which generally neglects the correlations effects).

$$\left[-\frac{1}{2}\nabla^2 + V_N \right]\Psi_i(\mathbf{r}) + V_{HF}\Psi_i(\mathbf{r}) = \varepsilon_i \Psi_i(\mathbf{r}) \quad (1)$$

Taking into account that each electron interacts repulsively with all the others the Hartree term may be written as:

$$V_H = \sum_j \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \sum_j \int \frac{|\Psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad (2)$$

where we replaced as usual the electric charge density $\rho(\mathbf{r})$ with the square of the modulus of the wavefunction.

Also, considering the total wave function as a Slater determinant and introducing the antisymmetrisation of the wave function, an exchange term is necessary due to the Pauli principle applied to the fermions

$$V_E = -\sum_j \delta_{s_i s_j} \int d\mathbf{r}' \frac{\Psi_j^*(\mathbf{r}')\Psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (3)$$

We notice that only the interactions between electrons with different spins s_i, s_j have to be added to the total exchange potential, and its sign is inverse to the Hartree term.

Thus, the classical Hartree-Fock equations (HF) for a one-electron wave function $\Psi_i(\mathbf{r})$ may be written as [1]:

$$\left[-\frac{1}{2}\nabla^2 + \frac{Z}{r} \right]\Psi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{\left|\Psi_j(\mathbf{r}')\right|^2}{\left|\mathbf{r}-\mathbf{r}'\right|}\Psi_i(\mathbf{r})$$

$$-\sum_j \delta_{s_i s_j} \int d\mathbf{r}' \frac{\Psi_j^*(\mathbf{r}')\Psi_i(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|}\Psi_i(\mathbf{r}) = \varepsilon_i \Psi_i(\mathbf{r}) \qquad (4)$$

Another important term is due to the correlation effect of the electrons kinematics and it may be included in various ways in the framework of the Density Functional Theory (DFT) [2]. These approaches reveal some rather sophisticated potentials and exchange-correlation terms. Thus, the exchange term may have several forms, as: exact HF exchange, Slater local exchange functional Becke[3], Perdew-Wang[4,5,6], Vosko-Wilk-Nusair (VWN)[7], Zunger[8], Lee-Yang-Parr[9].

Concerning the numerical methods, the algorithms and the mathematics used in these calculations, there are many popular techniques that may be considered, each of them with their advantages and disadvantages [10]. Here the possibilities are also diversified, as the form of the self consistent equations may be purely differential or integro-differential, due to the exchange and correlation terms. Some methods, as the Multi-configurational self-consistent field, are even more computer expensive as they use linear combinations of Slater determinants to approximate the wavefunction [12] or the two electrons integrals calculations using Lebedev and Gauss-Legendre Angular Quadrature Schemes combined with Linear Scaling Methods [13].

The differential form is often treated by the Numerov's fifth order method, which is robust and accurate but is not self starting and require some initial iterations, as many other point by point methods of high order. A notable exception should be the forth order Runge-Kutta method but it is not well suited for boundary conditions equations as the HF ones. Some shooting method must accompany the point by point methods and, although this provides the eigenvalue of the equation (which sometimes is the main goal), it implies an iterating process that leads to a huge amount of computing effort. Furthermore, it must be used both for the wave function equation and for Poisson equation for finding the Hartree-Fock potential generated by the charge density.

An important step for improving the numerical methods' efficiency was made by Roothaan [9] who transferred the calculations to linear algebra in the form of a generalized eigenvalue problem, using non orthogonal basis set. Thus, other methods became eligible as Galerkin,

Fourier Transform Coulomb Method [13], collocation [14], finite difference [15],[16], finite element [17] etc.

2 Using the collocation method for solving the HF equations

The main goal of the numerical methods for such problems is to achieve a satisfactory precision with a minimum computing effort, as their solving is time critical in most situations. In this paper we study the performances of some spectral methods and suggest some new ways to improve them.

The radial part of each wave function in a many-body system is the solution of a second order linear differential equation

$$\mathbf{L}y(x) = s(x), \; x \subset U \in \mathbb{R} \qquad (5)$$

with boundary conditions (usually two point).

$$\mathbf{B}u(y) = 0, \; y \in \partial U \qquad (6)$$

The weighted residuals methods use a test function $v(x)$ for the minimization of the residual

$$R := \mathbf{L}u(x) - s(x) \qquad (7)$$

produced by a trial function

$$u(x) = \sum_{i=0}^{n} c_i \varphi_i(x) \approx y(x) \qquad (8)$$

where the basis set $\{\varphi_i(x)\}$ is usually chosen as Chebyshev polynomials, Legendre polynomials, trigonometric functions, etc.

Among these methods, a popular one for such two point boundary problem is the collocation method, which uses test functions of the form $v_j(x) = \delta(x - x_j)$, where x_j are the m collocation points chosen equidistantly or as the roots of Legendre or Chebyshev polynomials. Thus, performing the inner product with the test function, the equation (5) becomes

$$\sum_{i=0}^{n} \mathbf{L}\varphi_i(x_j)c_i = s(x_j), 0 \le j \le n-1 \qquad (9)$$

leading to a m linear equations system for the unknowns c_i:

$$\sum_{i=0}^{n} b_{ki}c_i = s_k, 0 \le k \le m-1 \qquad (10)$$

It may be written in a matrix form by separating the free terms as:

$$\Phi \cdot \mathbf{C} = \mathbf{F} \qquad (11)$$

The advantage is that, as usually met within the spectral methods, the evanescence property occurs, which exponentially decreases the truncation errors as the number of terms in the expansion (8) of the

trial function. On the other hand, the main disadvantage of the method is the Φ matrix condition number which increases rapidly with n and may produce important round-off errors.

Some proper choices and some additional techniques have to be considered for a good compromise between these aspects.

3 Additional ways for improving the performances of collocation method

The equidistant collocation point is not always a good choice, as it could emphasize the Runge phenomenon: increased truncation errors towards the boundaries and even loss of convergence.

A better choose is sometimes in the roots of the Chebyshev polynomials which avoid the Runge phenomenon, and may be simply calculated:

$$x_j = -\frac{B-A}{2}\cos\frac{(2j+1)\pi}{2n} + \frac{B+A}{2}, \ j=0...n \ (12)$$

where A and B are the limits of the domain of the independent variable x.

For choosing the basis set we notice that the goal is the minimization of computing time, and our suggestion is to analytically perform as much calculations as possible. The equation (9) assumes the availability of the first and the second derivative of the basis set functions. Of course, they may be obtained numerically, but this increases both the computing time and the overall errors.

That is why it should be proper to choose basis set functions with analytically known derivatives, and to expand equation (9) analytically before performing the numerical calculations.

We also propose, where it is possible, a quadrature of both terms, as it is known that numerical quadrature is a very fast and precise method (Gauss-Legendre for example). By integrating the terms of the series expansion of the trial functions, the resulting coefficients are lower if the following condition is satisfied:

$$B < n \tag{13}$$

Consequently, the linear system's matrix condition number tends to decrease, so that the round-off errors decrease also. Our results presented in the next section show an obvious increase in precision and speed.

In the following we present the results obtained with monomial functions and Chebyshev functions, because they have simple formulae both for differentiation and integration.

3.1 Use of monomial functions with quadrature

The trial function may be expanded in monomial functions as:

$$u(x) = \sum_{i=0}^{n} c_i x^i \tag{14}$$

Separating the first two coefficients and imposing the two point boundary conditions:

$$y(A) = y_i, \ y(B) = y_f \tag{15}$$

we may write:

$$u(x) = c_0 + xc_1 + \sum_{i=2}^{n} c_i x^i \tag{16}$$

$$c_0 = y_f - \sum_{i=1}^{n} c_i B^i \tag{17}$$

$$c_1 = \frac{y_f - y_i}{B-A} - \sum_{i=2}^{n} c_i \frac{B^i - A^i}{B-A} \tag{18}$$

There is the possibility of forming directly the system (11), but our numerical results prove that better results are obtained if an integration (analytical if possible) of the two members of the equations is made at this point.

For a constant coefficients linear second order equation

$$a_1 y''(x) + a_2 y'(x) + a_3 y(x) = f(x) \tag{19}$$

the matrix in equation (11) will have the elements:

$$\Phi_{ji} = a_1 i(x_j^{i-1} - A^{i-1}) + a_2(x_j^i - A^i) + a_3 \frac{x_j^{i+1} - A^{i+1}}{i+1}$$

$$\Phi_{j0} = a_3(x_j - A)$$

$$\Phi_{j1} = a_2(x_j - A) + \frac{a_3(x_j^2 - A^2)}{2} \tag{20}$$

$$i = 2,3,...,n; \ j = 0,1,...n-1$$

$$F_j = \int_A^{x_j} f(x)dx - \Phi_{j0} - \Phi_{j1} \tag{21}$$

By solving the system (11) for $c_i, i = 2,3,...,n$, calculating c_1 from eq. (18) and c_0 from eq. (17), the solution is given by eq. (16).

If the coefficients are not constant, the analytical treatment of the matrix elements, if possible, provides a greater speed to the overall process, as our results show in the next section.

Thus, if the coefficients are functions of the independent variable:

$$a_1(x)y''(x) + a_2(x)y'(x) + a_3(x)y(x) = f(x) \tag{22}$$

one should try to express the matrix elements in the following form:

$$\Phi_{ji} = b_1(x_j)i(i+1)x_j^{i-2} + b_2(x_j)\left(ix_j^{i-1} - \frac{A^i - B^i}{A-B}\right)$$

$$+ b_3(x)\left(x_j^i - B^i - x_j\frac{A^i - B^i}{A-B}\right)$$

$$\Phi_{j0} = b_3(x_j)y_f - b_2(x_j)\frac{y_f - y_i}{B-A} \tag{23}$$

$$\Phi_{j1} = b_3(x_j)x_j\frac{y_f - y_i}{B-A}$$

$$i = 2,3,...,n; \; j = 0,1,...n-1$$

$$F_j = \int_A^{x_j} f(x)dx - \Phi_{j0} - \Phi_{j1} \tag{24}$$

where the coefficients $b_1(x_j), b_2(x_j)$ and $b_3(x_j)$ should be obtained by integrating by parts the corresponding terms in the expansion of the equation (22).

For the self consistent field equations, that use a model requiring variable coefficients, the analytical integration is not possible when the Hartree-Fock potential is not known analytically. However, we will present a way to adapt the method to this specific kind of equations in the next section.

3.2 Use of Chebyshev polynomials with quadrature

The trial function may be expanded in Chebyshev polynomials of the first kind $T_i(x)$ as:

$$u(x) = \sum_{i=0}^n c_i T_i(x) \tag{25}$$

$$u(x) = c_0 + xc_1 + \sum_{i=2}^n c_i T_i(x) \tag{26}$$

$$c_0 = y_f - \sum_{i=1}^n c_i T_i(B) \tag{27}$$

$$c_1 = \frac{y_f - y_i}{B-A} - \sum_{i=2}^n c_i\frac{T_i(B) - T_i(A)}{B-A} \tag{28}$$

For linear differential equation with constant coefficients as (19), one may integrate (analytically or numerically) $f(x)$ and the matrix elements are:

$$\Phi_{ji} = a_i i\left[U_{i-1}(x_j) - U_{i-1}(A)\right] + a_2\left[T_i(x_j) - T_i(A)\right]$$

$$+ a_3\frac{T_{i-1}(x_j) - T_{i-1}(A)}{2(i-1)}$$

$$\Phi_{j0} = a_3(x_j - A) \tag{29}$$

$$\Phi_{j1} = a_2(x_j - A) + \left[a_2 + \frac{a_3(x+A)}{2}\right]$$

$$i = 2,3,...,n; \; j = 0,1,...n-1$$

$$F_j = \int_A^{x_j} f(x)dx - \Phi_{j0} - \Phi_{j1} \tag{30}$$

where $U_i(x)$ are the Chebyshev polynomials of the second kind.

If the coefficients are not constant, one could either perform a supplementary analytical quadrature for every term and use adapted formulae or use a numerical method for the quadrature.

4 Adapting the Hartree Fock equations for using the collocation method with quadrature

It is known that for spherically-symmetric potentials like those generated by the central forces of the Coulomb field in the atoms the wave function may be written as a product of a radial function and a spherical harmonic one

$$\Psi(r,\theta,\varphi) = R_{n\ell}(r)Y_\ell^m(\theta,\varphi) \tag{31}$$

where n is the principal quantum number and ℓ is the orbital quantum number.

We are interested in the eigenvalues of the energy, depending only on the radial part of the wave function through the principal quantum number.

As a result of this factorisation, the 3D Schrodinger equation may be reduced to a one-dimensional differential equation (the radial equation)

$$\left[-\frac{\hbar^2}{2m}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]R_{n\ell}(r)$$
$$= E_n R_{n\ell}(r) \tag{32}$$

where E_n is the eigenvalue for the energy (the orbital energy).

By a change of function as

$$u(r) \equiv rR_{n\ell}(r) \tag{33}$$

the equation (32) takes a convenient form

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right]u(r)$$
$$= E_n u(r) \tag{34}$$

By denoting $x \equiv r$ and using the natural atomic units ($\hbar = m = e = 4\pi\varepsilon = 1$) the radial part of the Hamiltonian for the electron in the central field in hydrogenoid atom is

$$H = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{Z}{x} + \frac{\ell(\ell+1)}{2x^2} \tag{35}$$

where Z is the atomic number.

Here, the second term is due to the attraction of the nucleus, while the third is due to the centrifugal force.

Thus, taking into account the supplementary interaction potentials in a real atomic system, the HF equations may be written as

$$-\frac{1}{2}\frac{d^2}{dx^2}u(x) - \frac{Z}{x}u(x) + \frac{\ell(\ell+1)}{2x^2}u(x)$$
$$+V_{HF}u(x) = E_n u(x)$$
(36)

where $u(x)$ is the radial part of the wave function modified according to eq. (33) and V_{HF} is the HF potential describing the electron interaction with the other electrons.

The Hartree potential seen by an electron i is given by (2)

$$V_{Hi}(\mathbf{r}) = \int \frac{\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$
(37)

and is the solution of the Poisson equation

$$\nabla^2 V_{Hi}(\mathbf{r}) = -\rho_j(\mathbf{r})$$
(38)

By expressing the Laplacean in spherical coordinates, taking its radial part and integrating the left member of eq. (38) over the solid angle we obtain

$$\frac{1}{x^2}\left[\frac{d}{dx}x^2\frac{d}{dx}V_{Hi}(x)\right] = -4\pi\rho_j(x)$$
(39)

Again, introducing a new function

$$U_{Hi}(x) = xV_{Hi}(x)$$
(40)

we obtain the radial part of the Poisson equation in a more convenient form

$$\frac{d^2}{dx^2}U_{Hi}(x) = -4\pi x|\Psi_j(x)|^2$$
(41)

In a similar way we may treat the Fock part of the electron-electron interaction and thus we obtain the exchange potential of an electron i due to another opposite spin electron j as

$$\frac{d^2}{dx^2}U_{Fi}(x) = -4\pi x\Psi_i^*(x)\Psi_j(x), \; j \neq i$$
(42)

We may now construct the complete HF potential using the solutions of the eqs. (41) and (42), according to eq. (4)

$$V_{HFi}(x) = \sum_{j\neq i} xU_{Hi}(x) - \sum_{j\neq i} \delta_{s_i s_j} xU_{Fi}(x)$$
(43)

Hence, the calculations will be made using eqs. (36), (41),(42) and (43). There are three types of second order differential equations with boundary conditions that we try

to calculate using the collocation method. However, one may see that it is not possible to directly integrate eq. (36), since it contains a singular point (the origin). The radial part of the wave function must be zero in origin (the electron should not be localized exactly in the nucleus), but if we try to limit its domain to a very small but non-zero value, ε, the result will strongly depend on this value.

To avoid the singularity in origin we have to make a new change of function that will transform adequately the second and the third term of the eq. (36). Consequently, we propose the following form

$$u(x) = x^2 f(x)$$
(44)

Introducing the new function in eq. (36) we finally obtain

$$-\frac{1}{2}x^2\frac{d^2}{dx^2}f(x) - 2xf'(x) - f(x) - Zxf(x)$$
$$+\frac{\ell(\ell+1)}{2}f(x) + V_{HF}(x)x^2 f(x) = E_n x^2 f(x)$$
(45)

4.1. The matrix elements for the collocation with quadrature of HF equations

As one may see, all the terms in eq. (45) may be analytically integrated if the unknown function $f(x)$ is written as a polynomial function according to eq. (8).

Thus, we first have to calculate the Hartree-Fock potential. We will express it also as a monomial expansion and use the collocation method with quadrature for solving the Poisson eqs. (41) and (42).

$$U_{Hi} = \sum_{k=0}^{m} d_k x^k$$
(46)

$$U_{Fi} = \sum_{k=0}^{m} g_k x^k$$
(47)

As in any self-consistent method, we start with an approximate wave function, for example the hydrogenoid type and solving the corresponding linear systems similar with eq. (11) we obtain the coefficients d_k and g_k, hence a first iterated HF potential.

The matrix elements for these two equations will be, according to eqs. (20) and (21) the following

$$\Phi_{ji} = i(x_j^{i-1} - A^{i-1})$$

$$\Phi_{j0} = 0$$

$$\Phi_{j1} = 0 \tag{48}$$

$$i = 2,3,...,n; \quad j = 0,1,...n-1$$

$$F_{jH} = -4\pi \int_A^{x_j} x \left| \Psi_0(x) \right|^2 dx \tag{49}$$

$$F_{jF} = -4\pi \int_A^{x_j} x \Psi_0^*(x) \Psi_0(x) dx \tag{50}$$

where eq. (49) stands for the Hartree term and eq. (50) stands for the Fock term.

Constructing the two potentials according to eqs. (46) and (47) we may obtain the complete HF potential seen by the electron i, by using the eq. (43).

$$V_{HFi}(x) = \sum_{\substack{j=0 \\ j \neq i}}^{N} \left(\sum_{k=0}^{m} d_k - \delta_{s_i s_j} \sum_{k=0}^{m} g_k \right) x_j^{k+1} \tag{51}$$

where N is the total number of electrons in the system.

Now, using the form (51) for the HF potential we may find the matrix elements for solving the HF equations (45).

$$\Phi_{ji} = \sum_{\substack{j=0 \\ j \neq i}}^{N} \left(\sum_{k=0}^{m} d_k - \delta_{s_i s_j} \sum_{k=0}^{m} g_k \right) \left(x_j^{k+i+3} - A^{k+i+3} \right)$$

$$-E_{ni}\left(x_j^{i+2} - A^{i+2} \right) - Z\left(x_j^{i+1} - A^{i+1} \right)$$

$$+ \left[\frac{\ell(\ell+1)}{2} - \frac{1}{2}i^2 - \frac{3}{2}i - 1 \right]\left(x_j^i - A^i \right)$$

$$\Phi_{j0} = \sum_{\substack{j=0 \\ j \neq i}}^{N} \left(\sum_{k=0}^{m} d_k - \delta_{s_i s_j} \sum_{k=0}^{m} g_k \right) \left(x_j^{k+3} - A^{k+3} \right)$$

$$-E_{ni}\left(x_j^2 - A^2 \right) - Z\left(x_j - A \right)$$

$$\Phi_{j1} = \sum_{\substack{j=0 \\ j \neq i}}^{N} \left(\sum_{k=0}^{m} d_k - \delta_{s_i s_j} \sum_{k=0}^{m} g_k \right) \left(x_j^{k+4} - A^{k+4} \right)$$

$$-E_{ni}\left(x_j^3 - A^3 \right) - Z\left(x_j^2 - A^2 \right)$$

$$+ \left[\frac{\ell(\ell+1)}{2} - 3 \right]\left(x_j - A \right)$$

$$i = 2,3,...,n; \quad j = 0,1,...n-1 \tag{52}$$

Equation (11) will give the coefficients c_i of the wavefunction and it will be constructed according to eq. (14).

The process have to be completed for all the N electrons in the atomic system in this iteration and then the wave functions will be used in the next iteration for finding the new HF potential. Also, using these wave functions new values of the orbital energy E_{ni} of each electron will be obtained. Afterwards the iterative process will be repeated until the self consistency is achieved (the changes of the eigenvalues become smaller than an imposed quantity).

4.2. Verifying the transformed radial equation in some known cases

If we consider the case of hydrogenoid atoms, the HF potential is zero and the wave functions are analytically known in terms of second kind confluent hypergeometric functions $U(a,b,z)$ (Kummer function) and generalized Laguerre polynomials. In this case we may verify that the equation (45) leads to the known results.

Indeed, we solved analytically this equation and obtained the general solution

$$f(x) = \frac{1}{x} e^{-\frac{x}{n} + \ell \ln x} L_{n-\ell-1}^{2\ell+1}\left(\frac{2x}{n} \right) C_1$$

$$+ \frac{1}{x} e^{-\frac{x}{n} + \ell \ln x} U\left(\ell-n+1, 2\ell+2, \frac{2x}{n} \right) C_2 \tag{53}$$

The two constants involved may be obtained from physical considerations. Thus, the wave function must be zero in origin and at infinity and its square integral over the positive real axis (the total localization probability) must be equal to 1 (the normalization condition)

$$\int_0^{\infty} \left| u(x) \right|^2 dx = 1 \tag{54}$$

However, taking into account the relationship between the confluent hypergeometric function and the generalized Laguerre polynomial

$$L_n^a(x) = \frac{(a+1)_n}{n!} {}_1F_1(-n, a+1, x) \tag{55}$$

a single constant must be calculated from the normalization condition.

We may calculate this constant using a well known relationship for the generalized Laguerre polynomials

$$\int_0^\infty x^{a+1} e^{-x} \left[L_n^a(x) \right]^2 dx = \frac{(n+a)!}{n!}(2n+a+1) \quad (56)$$

In figures 1-4 we plotted the radial part of the wave function of a hydrogenoid atom obtained by numerically solving eq. (36) using the described collocation method with quadrature. It is obvious that the shape is correct and the numerical results will be compared in the next section with those generated by the analytical formula (53), for error analysis.
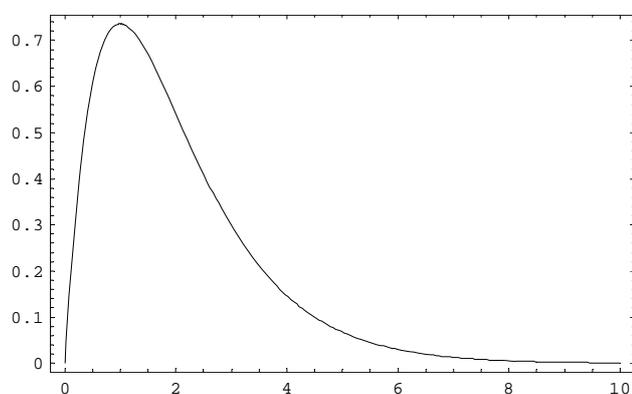
Fig. 1. The radial part of the wavefunction for $n=1, \ell=0$ and $V_{HF}=0$.
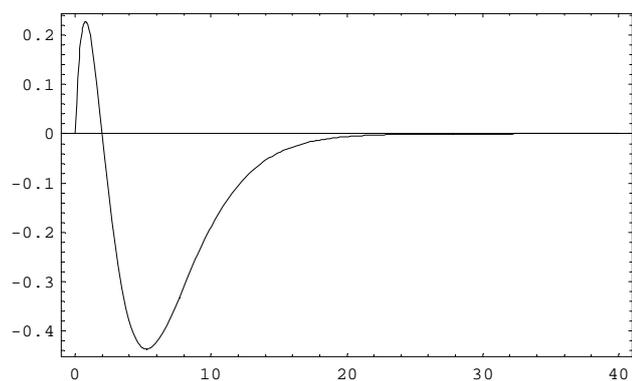
Fig. 2. The radial part of the wavefunction for $n=2, \ell=0$ and $V_{HF}=0$.
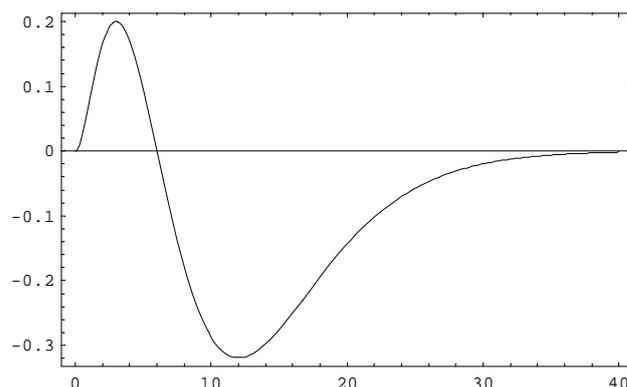
Fig. 3. The radial part of the wavefunction for $n=3, \ell=1$ and $V_{HF}=0$.
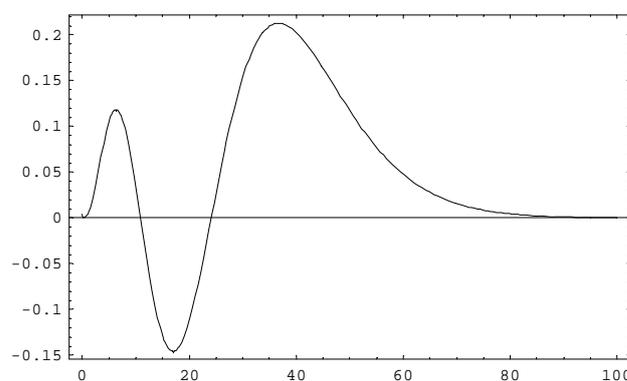
Fig. 4. The radial part of the wavefunction for $n=5, \ell=2$ and $V_{HF}=0$.

5 Numerical results

For testing the proposed methods, we integrated numerically the radial part of the wave function equation in a Hartree-Fock model for inner atomic shells. We choose a domain from the nucleus uptill 6 for the K shell and 10 Bohr radiuses for the L shell.

In figure 5 we present the errors dependence on the number of independent functions in the expansion (8). Monomial basis set are presented, without supplementary quadrature (upper curves) and with quadrature (lower curves). By using the Chebyshev expansion similar results are obtained in most cases, but sometimes increased errors may be noticed due to the repeated recurrences used for generating the higher degree polynomials.

Both the standard procedure and the supplementary quadrature method display a clear evanescence for $n \in [10, 20]$. For larger n values, one may observe the influence of the increasing matrix condition number, so that the round-off errors exceed the decrease of the truncation errors.

The most important aspect revealed is that the errors obtained in the supplementary quadrature

are about 10 times lower than without it for the same n.
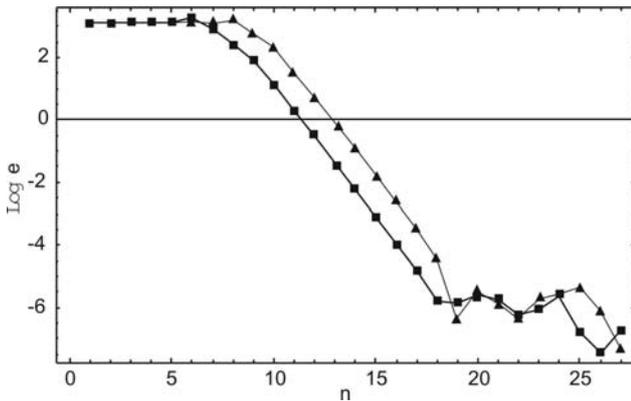
Fig. 5. The errors in evaluating the solution of the radial part of the wave function for a Hartree-Fock equation with 10 Bohr radiuses by collocation method with quadrature (boxes) and without quadrature (triangles)

An even better situation is visible in figure 6, for the K-shell electrons, where the domain may be restricted to only 6 Bohr radiuses.

We notice that for a given error of 10^{-5} the number of independent function may be decreased from 18 to 10 if the preliminary quadrature is performed. Since the computational effort decreases as $(n_2 / n_1)^2$, it will have a great impact for large calculations implying hundreds of atoms. Also, more than 5 digits are gained in precision for $n = 19$.
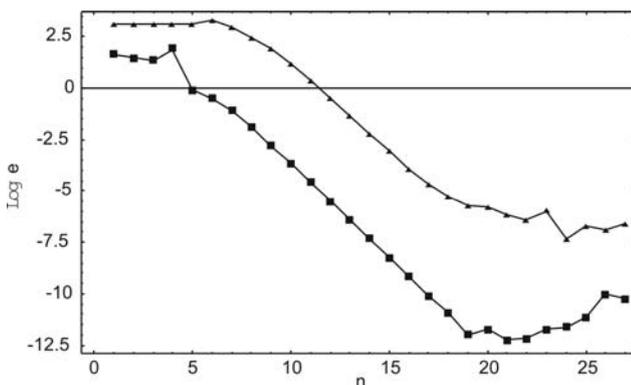
Fig. 6. The errors in evaluating the solution of the radial part of the wave function for a Hartree-Fock equation with 6 Bohr radiuses by collocation method with quadrature (boxes) and without quadrature (triangles)

We also tested the method for finding the screening of the 2s shell electrons. Using the described Hartree Fock method we calculated the effective atomic number of some elements considering the screening of the other electrons.

One may calculate the scattering amplitude $P(\Omega_1)$ for the X and gamma-ray on the 2s electrons using the analytical formulae with relativistic kinematics corrections as in [18]. Further, using the imaginary part of the forward scattering amplitude, the optical theorem gives the total cross sections for photoelectric effect

$$\sigma_{ph} = \frac{4\pi}{\alpha} \frac{m}{\omega} r_0^2 \left| \operatorname{Im} P(\Omega_1) \right|_{\theta=0} \right| \qquad (57)$$

We used the analytic formula obtained in [18] for these calculations

$$\sigma_{ph} = 2 \frac{\omega + \omega_{pp}}{2m} \frac{\lambda^5 X_1^2 \left(1 + |\tau_1|^2\right) \pi |\tau_1| |X_1|}{6m^4 \omega^4}$$

$$\times \left\{ \frac{\eta^2 X_1^2}{m^2 \omega^2} \left(1 + \frac{|\tau_1|^2}{4}\right)\left(1 - \frac{4\eta^2}{5m^2}\right) \right.$$

$$- \left(1 - \frac{\eta^2}{m^2}\right)\left[1 + 2\frac{\eta^2 X_1^2}{m^2 \omega^2} - \frac{\eta |\tau_1||X_1|}{m^2 \omega^2}\left(\eta^2 - \varepsilon m\omega\right)\right] \right\}$$

$$\times \frac{e^{-|\tau_1|\chi_1}}{e^{\pi|\tau_1|} - e^{-\pi|\tau_1|}} \qquad (58)$$

where a number of parameters depend on the effective atomic number Z_{eff} mainly through the parameter $\gamma = \left(1 - \alpha^2 Z_{eff}^2\right)^{1/2}$.

The cross sections obtained with the formula (58) and our screening model based on the described Hartree-Fock method, were compared with other calculations in the literature [19]. In Table 1 and Table 2 we present these comparisons for low and medium atomic number elements. One may notice a very good concordance, proving the correctness of our Hartre-Fock calculations for these cases. However, for greater atomic numbers and energies, the errors seem to increase. These results are rather questionable because the scattering model described in [18] is not fully relativistic and the total photoeffect cross sections formula (58) may not be very accurate. Some more complex model for gamma-ray scattering on the 2s shell electrons, including the spin effects in a full relativistic treatment, is needed for higher atomic numbers and higher energies regime, but such formulae are not yet available in the literature.

Table 1. A comparison between the total photoeffect cross sections for a 2s electron given by Scofield in [18], S_{Sc}, and the results with the effective atomic number obtained by our Hartree Fock calculations in the case of Ag.

E_I(keV)	S_{Sc}(barn)	Z_{eff}	S_{ph}(barn)	Err(%)
6.	14691.5	39.8773	15589	5.75
8.	8814.57	41.7671	8990.2	1.95
10.	5760.28	42.9468	5710.6	-0.87
15.	2461.33	44.3031	2374.4	-3.66
20.	1268.24	44.7207	226.1	-3.43
25.46	704.423	44.8551	687.93	-2.39
25.67	690.175	44.8576	674.72	-2.29
30.	466.224	44.8888	459.64	-1.43
40.	221.713	44.9047	221.87	0.07
50.	122.832	44.9062	124.02	0.95
60.	75.2459	44.9064	76.342	1.43
80.	34.3411	44.9064	34.939	1.71
100.	18.5579	44.9064	18.838	1.48
150.	6.02086	44.9064	6.0271	0.10
200.	2.71391	44.9064	2.6738	-1.5
300.	0.898171	44.9064	0.8637	-3.99
400.	0.419161	44.9064	0.3986	-5.15
500.	0.236388	44.9064	0.2247	-5.19
600.	0.150196	44.9064	0.1437	-4.47
800.	0.075702	44.9064	0.07434	-1.82
1000.	0.045777	44.9064	0.04639	1.32
1500.	0.019648	44.9064	0.02144	8.36

Table 2. A comparison between the total photoeffect cross sections for a 2s electron given by Scofield in [18], S_{Sc}, and the results with the effective atomic number obtained by our Hartree Fock calculations in the case of Ca.

E_I(keV)	S_{Sc}(barn)	Z_{eff}	S_{ph}(barn)	Err(%)
1.	73684.	14.9542	74392	0.95
1.5	33268.4	15.6313	34651	3.99
2.	18597.3	16.1473	19222	3.24
3.	7887.76	16.8401	7897.7	0.12
4.	4130.69	17.2425	4044.2	-2.13
4.01	4104.51	17.2459	4017.8	-2.15
4.04	4029.59	17.2554	3942.2	-2.21
5.	2433.89	17.4762	2358.1	-3.21
6.	1550.35	17.612	1498.1	-3.48
8.	736.227	17.7366	715.76	-2.85
10.	403.283	17.7786	396.33	-1.75
15.	129.698	17.7986	130.51	0.62
20.	56.6368	17.7999	57.806	2.02
30.	17.1783	17.8	17.74	3.16
40.	7.26553	17.8	7.5134	3.29
50.	3.70564	17.8	3.8193	2.97

6 Conclusions

Performing a preliminary analytical quadrature in the collocation method for solving the Hartre Fock differential equations has a useful effect on the speed and precision. The numerical results demonstrate a possible speed increase up to 10 times over the conventional procedure.

The price paid is sometimes the supplementary numerical quadrature (when the right side of the differential equation can not be integrated analytically) but it is not computing expensive if a Gauss-Legendre method is used.

We want to point out that the presented method has a higher speed even if the same number of collocation points is used. Indeed, one may take advantage of a number of terms in the equations that *may be reused* when implementing the algorithm, especially if analytical expressions for the results of the integrals may be obtained. Also, due to the evanescence property of the method, extrapolation of the results may significantly improve the precision, if needed.

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