Improving the performances of the collocation method for numerically solving linear differential equations of the wavefunctions in large atomic systems

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Abstract: - The influence of analytical treatment of terms in collocation method applied to the boundary condition equations of Hartree-Fock type is presented. The explicit form of matrix elements for monomial and Chebyshev trial functions is given and some methods for increasing the speed in these time critical problems are proposed. The numerical tests indicate the possibility of decreasing the amount of computing effort up to 10 times with the proposed technique while maintaining the precision.

Key-Words: - Self consistent field, differential equation, Collocation, Trial functions, Evanescence

1 Introduction
Solving the Hartree-Fock (HF) equations for many atoms systems is very computing-demanding, as a large number of differential equations (typically several hundred) have to be dealt in an iterative way 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 new techniques are necessary for various atoms configurations 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 and an electron interaction part. The classical Hartree-Fock equations (HF) may be written as [1]:

\[
\begin{align*}
\frac{-1}{2} \nabla^2 + \frac{Z}{r} - &\sum_j \int d\mathbf{r}_j \frac{\Psi_j(r')}{|\mathbf{r} - \mathbf{r}'|} \Psi_j(r) \\
+ &\sum_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}_j \frac{\Psi_j(r')}{|\mathbf{r} - \mathbf{r}'|} \Psi_j(r) = \varepsilon_i \Psi_i(r)
\end{align*}
\] (1)

where \(\Psi_i(r)\) is the one electron wave function and the three terms stand for the nuclear interaction, electron repulsion interaction and, due to spin, the exchange interaction.

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 pros and cons[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].

The two electrons integrals are usually calculated by several methods: 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 the Galerkin, Fourier Transform Coulomb Method [13], collocation [14], finite difference [15],[16], finite element [17] etc.

2 Collocation method

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

\[ L \psi(x) = s(x), \quad x \in U, \quad s(x) \in \mathbb{R} \]  

with boundary conditions (usually two point).

\[ B \psi(y) = 0, \quad y \in \partial U \]  

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

\[ R := L \psi(x) - s(x) \]  

produced by a trial function

\[ u(x) = \sum_{i=0}^{n} c_i \phi_i(x) \approx y(x) \]  

where the basis set \( \{\phi_i(x)\} \) 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 \( \psi_j(x) = \delta(x - x_j) \), 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 (2) becomes

\[ \sum_{i=0}^{n} L \phi_i(x_j)c_i = s(x_j), \quad 0 \leq j \leq n-1 \]  

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

\[ \sum_{i=0}^{n} b_{ik} c_i = s_k, \quad 0 \leq k \leq m-1 \]  

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

\[ \Phi \cdot C = F \]  

The advantage is that, as usually met in the spectral methods, the evanescence property occurs, which rapidly decreases the truncation errors. On the other hand, the main problem of the method is the \( \Phi \) 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 a good choice, as it emphasizes the Runge phenomenon: increased truncation errors towards the boundaries and even loss of convergence. That is why we choose the roots of the Chebyshev polynomials which avoid the Runge phenomenon, and may be simply calculated:

\[ x_j = -\frac{B + A}{2} \cos \left(\frac{(2j+1)\pi}{2n}\right) + \frac{B + A}{2}, \quad j = 0...n \]  

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 (6) 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 (6) 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). 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.


2.1 Use of monomial functions with quadrature

The trial function may be expanded in monomial functions as:

\[ u(x) = \sum_{i=0}^{n} c_i x^i \]  

(10)

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

\[ y(A) = y_j, \quad y(B) = y_f \]  

(11)

we may write:

\[ u(x) = c_0 + x c_1 + \sum_{i=2}^{n} c_i x^i \]  

(12)

\[ c_0 = y_f - \sum_{i=1}^{n} c_i B^i \]  

(13)

\[ c_1 = \frac{y_f - y_j}{B - A} - \sum_{i=2}^{n} c_i \frac{B^i - A^i}{B - A} \]  

(14)

There is the possibility of forming directly the system \( X(8)X \), 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

\[ a_1 y''(x) + a_2 y'(x) + a_3 y(x) = f(x) \]  

(15)

the matrix elements are:

\[ \Phi_{ji} = a_i (x_j) (i+1) + a_j (x_j) \left( \frac{i}{x_{i+1} - A} - \frac{A^i}{A - B} \right) \]  

+ \[ a_i \left( \frac{x_j - B}{x_j - A} \right) \left( \frac{A^i}{A - B} \right) \]  

\[ \Phi_{j0} = a_i (x_j) \left( \frac{y_f - y_j}{B - A} \right) \]  

(19)

\[ \Phi_{ji} = a_i (x_j) \left( \frac{y_j - y_i}{B - A} \right) \]  

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

\[ F_j = f(x_j) - \Phi_{j0} - \Phi_{j1} \]  

(20)

2.2 Use of Chebyshev polynomials with quadrature

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

\[ u(x) = \sum_{i=0}^{n} c_i T_i(x) \]  

(21)

\[ u(x) = c_0 + x c_1 + \sum_{i=2}^{n} c_i T_i(x) \]  

(22)

\[ c_0 = y_f - \sum_{i=1}^{n} c_i (x_i - A) \]  

(23)

\[ c_i = \frac{y_f - y_i}{B - A} - \sum_{i=2}^{n} c_i \frac{T_i(B) - T_i(A)}{B - A} \]  

(24)

For linear differential equation with constant coefficients as (15), one may integrate (analytically or numerically) \( f(x) \) and the matrix elements are:

\[ \Phi_{ji} = a_i \left( \frac{x_j - A}{x_j - A} \right) + a_j \left( \frac{x_j^2 - A}{2} \right) \]  

(25)

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

\[ F_j = \int_{A}^{x_j} f(x) dx - \Phi_{j0} - \Phi_{j1} \]  

(26)

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 Numerical results and conclusion

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 up till 6 for the K shell and 10 Bohr radiuses for the L shell.

In figure 1 we present the errors dependence on the number of independent functions in the expansion (5). 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 \( n \).

An even better situation is visible in figure 2, 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. As the computational effort decreases as \( (n_z/n_l)^2 \), 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. 1. 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)

Fig. 2. 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)

The price paid is the supplementary numerical quadrature 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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