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Ground –State Total Energy of Small Atomic Systems Using the Hartree-Fock Method

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Abstract

We present the ground-state total energies of the first ten elements of the periodic table using the Fortran code developed by Koonin and Meredith in 1989 based on the Hartree-Fock method. Our results are in good agreement with previous results obtained using other theoretical and experimental methods.

Keywords: Hartree-Fock, atomic systems, many-body problem, many-electron problem.

1.0 Introduction

In computational physics and chemistry, the Hartree-Fock method [1, 2, 3] is a method of approximation for the determination of the ground state wave function and ground state energy of a quantum many-body system. The method assumes that the exact, N-body function of the system can be approximated by a single Slater determinant [4, 5]. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. Solution of these equations yields the Hartree-Fock wave function and energy of the system, which are approximations of the exact ones.

The Hartree-Fock method finds its typical application in the solution of the electronic Schrödinger equation of atoms, molecules and solids but it has also found widespread use in nuclear physics. For molecules, Hartree-Fock is the central starting point for most *ab initio* quantum chemistry methods. The discussion here is only for the restricted Hartree-Fock method, where the atom or molecule is a closed shell system with all orbitals (atomic and molecular) doubly occupied. The method, despite its physically more accurate picture, was little used until the advent of electronic computers in the 1950s due to the much greater computational demands over the earlier Hartree method and empirical models [6]. Initially, both the Hartree method and Hartree-Fock method were applied exclusively to atoms, where the spherical symmetry of the system allowed one to greatly simplify the problem. These approximate methods were (and are) often used together with the central field approximation, to impose that electrons in the same shell have the same radial part, and to restrict the variational solution to be a spin eigen function. Even so, solutions by hand, of the Hartree-Fock equations for a medium sized atom were laborious; small molecules required computational resources far beyond what was available before 1950 [6].

2.0 Materials and Methods

We used the FORTRAN code developed by Koonin & Meredith (1989) [6]. The self consistent field approximation (Hartree-Fock) is known to be an accurate description of many of the properties of multi-electron atoms and ions. In this approximation, each electron is described by a separate single particle wave function (as distinct from the many electron wave function) that solves a Schrödinger-like equation. The potential appearing in this equation is that generated by the average motion of all of the other electrons, and so depends on their single particle wave functions. The result is a set of non-linear eigenvalue equations.

For a large atom with many electrons, the accurate solution of the Hartree-Fock equation is a considerable task. However, if we consider the ground state of systems with at most 10 electrons (requiring three shells: 1s, 2s and 2p), then the numerical work can be managed in a reasonable amount of time. A lattice of several hundred points with a redial step size of $\leq$0.01Å extending out to $\approx$ 3Å should be sufficient for most cases (Koonin & Meredith, 1989) [6].

The Hamiltonian for N electrons moving about a heavy nucleus of charge Z located at the origin can be written as:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} - \sum_{i=1}^{N} \frac{Z_e^2}{r_i} + \frac{1}{2} \sum_{i \neq j=1}^{N} \frac{e^2}{r_{ij}} \qquad (1)$$

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Here, the (r_i) are the locations of the electrons, m and –e are the electron mass and charge, and $r_{ij} = r_i - r_j$ is the separation between electron i and j. The three sums in (1) embody the electron kinetic energy and the electron repulsion. As is appropriate to the level of accuracy of the self consistent field approximation, we have neglected much smaller terms, such as those associated with the spin-orbit attraction, hyperfine interaction, recoil motion of the nucleus, and relativity.

A proper quantum mechanical description requires that we specify the spin state of each electron in addition to its location. This can be done by giving its spin projection on some fixed quantization axis, $ð_i = \pm ½$ for convenience, we will use the notation $x_i \equiv (r_i, ð_i)$ to denote all of the coordinates (space and spin) of electron i, the self consistent field methods are based on the Rayleigh – Ritz variational Principle, which states that the ground state eigen function of the Hamiltonian, ψ (x_1, x_2 -----x_N), is that wave function that minimizes the expectation value of H,

$$E = \langle \psi / H / \psi \rangle \tag{2}$$

Subject to the constraints that ψ obey the Pauli principles (i.e. that it be anti-symmetric under the interchange of any two of the x's) and that it be normalized to unity:

$$\int /\psi/^2 d_x^N = 1 \tag{3}$$

(The notation d_x^N means integration over all of the spatial coordinates and summation over all the spin coordinates of the N electrons). Furthermore, this minimum value of E is the ground states energy. A calculation of (2) for any normalized and multi symmetric trial function ψ therefore furnishes an upper bound to the ground state energy.

The Hartree-Fock approximation is based on restricting the trial value function to be a Slater determinant.

$$\psi(x_{1,}\, x_2 \ldots \ldots, x_N) = (N!)^{-\frac{1}{2}} \det \psi_\alpha\,(x_j) \tag{4}$$

Here, the $\psi_\alpha\,(x_j)$ are a set of N orthonormal single particle wave functions; they are functions of the coordinates of only a single electron. The determinant is that of the N x N matrix formed as α and x_i each take on their N possible values, while factors $(N!)^{-\frac{1}{2}}$ ensure that ψ is normalized according to (3). The physical interpretation of this wave function is that each of the electrons moves independently in an orbital ψ_α under the average influence of all the other electrons. This turns out to be a good approximation to the true wave function of an atom because the smooth coulomb interaction between the electrons average out many of the details of their motions. Using the properties of determinants it is easy to see that ψ has the required anti symmetry under interchange of any two electrons (a determinant change sign whenever any two of its columns are interchanged) and that ψ is properly normalized according to equation (3) if the single particle wave functions are orthonormal:

$$\int \psi_a^*(x)\ \psi_\alpha{}'(x)\, dx = \delta\alpha\alpha' \tag{5}$$

Since the Hamiltonian (1) does not involve the electron spin variable, the spins decoupled from the space degrees of freedom, so that it is useful to write each single particle wave function as a product of space and spin functions:

$$\psi_\alpha(x) = \chi\alpha(r)/\delta\alpha) \tag{6}$$

Where $\delta\alpha = \pm ½$ is the spin projection of the orbital α. The orthonormality constraint (5) then takes the form

$$\delta\sigma_\alpha\sigma_{\alpha'} \int \chi_\alpha^*(r)\chi_{\alpha'}(r) d_r^3 = \delta\alpha\alpha' \tag{7}$$

so that orbitals can be orthogonal by either their spin or space dependence.

The computation of the energy (2) using the wave function defined by (4-6) is straight forward but tedious. After some algebra, we have:

$$E = \sum_{\alpha=1}^N \langle \alpha \left|\frac{p^2}{2_m}\right| \alpha\rangle + \int \left[-\frac{Ze^2}{r} + \frac{1}{2}\,\emptyset\,(r)\right]\rho(r) d_r^3 - \frac{1}{2}\sum_{\alpha,\alpha'=1}^N \delta\sigma_a\sigma_{a'}\,\langle \alpha\alpha' \left|\frac{e^2}{r_{ij}}\right| \alpha'\alpha\rangle \tag{8}$$

In this expression, the one body matrix elements of the kinetic energy are:

$$\langle \alpha \left|\frac{P^2}{2m}\right| \alpha\rangle = \frac{-\hbar^2}{2m}\int X_\alpha^*(r)\,\nabla^2 X_\alpha(r) d_r^3 \tag{9}$$

The electron density is the sum of single-particle densities

$$\rho(r) = \sum_{\alpha=1}^N |\chi_\alpha(r)|^2 \tag{10}$$

The electrostatic potential generated by the electron is:

$$\phi(r) = e^2 \int \frac{1}{|r-r'|}\,\rho(r') d_{r'}^3 \tag{11}$$

so that

$$\nabla^2 \emptyset = -4\pi e^2\,\rho(r) \tag{12}$$

And he exchange matrix elements of the inter electron repulsion are:

$$\langle \alpha\alpha' \left|\frac{e^2}{r_{ij}}\right| \alpha'\alpha\rangle = e^2 \int \chi_\alpha^*(r)\chi_{\alpha'}^*(r') \frac{1}{|r-r'|}\chi_{\alpha'}(r)\chi_\alpha(r') d_r^3 d_{r'}^3 \tag{13}$$

The interpretation of the various terms in (8) is straight forward. The kinetic energy is the sum of the kinetic energies of the single particle orbital, while the electron-nucleus attraction and direct inter-electron repulsion are just what would be expected from a total charge of –Ne distributed in space with density $\rho(r)$. The final term in (8) is the exchange energy, which arises from the anti-symmetry of the trial wave function (4) depends on a set of "parameters" the values of the single particle wave function at each point in space, variation of these parameters so as to minimize the energy (8) while respecting

the constraints (7) result in a set of Euler Lagrange equations (the Hartree-Fock equations) that define the "best" determinantal wave function and give an optimal bound on the total energy [6].

3.0 Procedure

First, the code, developed by Koonin and Meredith in 1989 [6], is compiled and installed in the computer system. The programme runs interactively. You make a menu choice and change physical parameters to the system of interest. The following are then inputted: the nuclear charge for the atomic system, number of electrons in the 1s state, number of electrons in the 2s state, number of electrons in the 2p state, radial step size in Angstrom, outer radius of the lattice in Angstrom and number of iterations.

You then set the output to be displayed on the screen and also saved in a file with a filename of your choice. The code is then run which displays output on the screen and also saves the result of the run in a file.

Calculations were carried out for Hydrogen to Neon, the first ten elements of the periodic table.

The total energy for each iteration step is then recorded in a table. The results are then analyzed using the plotting software *Origin 5.0*.

4.0 Tables of Results

The computed total energies for the first ten elements of the periodic table are as follows:

Table 1: Total Energy for Hydrogen

No of iterations	Total Energy (eV)
0	-10.097
1	-8.071
2	-8.581
3	-8.484
4	-8.434
5	-8.412
6	-8.404
7	-8.401
8	-8.401
9	-8.401
10	-8.400

Table 2: Total Energy for Helium

No of iterations	Total Energy (eV)
0	-77.426
1	-77.444
2	-77.480
3	-77.547
4	-77.598
5	-77.624
6	-77.636
7	-77.638
8	-77.639
9	-77.638
10	-77.638

Table 3: Total Energy for Lithium

No of iterations	Total Energy (eV)
0	-195.763
1	-191.823
2	-189.166
3	-186.890
4	-185.451
5	-184.632
6	-184.183
7	-183.939
8	-183.812
9	-183.742
10	-183.700

Table 4: Total Energy for Beryllium

No of iteration	Total Energy (eV)
0	-386.247
1	-387.733
2	-387.764
3	-387.890
4	-388.084
5	-388.236
6	-388.321
7	-388.364
8	-388.381
9	-388.382
10	-388.382

Table 5: Total Energy for Boron

No of iterations	Total Energy (eV)
0	-635.004
1	-646.887
2	-649.469
3	-651.485
4	-652.961
5	-653.795
6	-654.139
7	-654.232
8	-654.228
9	-654.212
10	-654.183

Table 6: Total Energy for Carbon

No of iterations	Total Energy (eV)
0	-965.153
1	-989.222
2	-995.020
3	-1000.401
4	-1004.460
5	-1006.550
6	-1007.244
7	-1007.245
8	-1007.102
9	-1006.949
10	-1006.868

Table 7: TotalEenergy for Nitrogen

No of iterations	Total Energy (eV)
0	-1386.635
1	-1423.569
2	-1432.028
3	-1437.340
4	-1450.338
5	-1456.630
6	-1457.467
7	-1456.566
8	-1455.766
9	-1455.435
10	-1455.378

Table 8: Total Energy for Oxygen

No of iterations	Total Energy (eV)
0	-1909.383
1	-1958.589
2	-1968.080
3	-1983.974
4	-2005.190
5	-2013.043
6	-2012.336
7	-2009.899
8	-2008.505
9	-2008.206
10	-2008.363

Table 9: Total Energy for Fluorine

No of iterations	Total Energy (eV)
0	-2543.378
1	-2602.578
2	-2590.604
3	-2653.928
	-2687.928
5	-2689.756
6	-2682.220
7	-2676.965
8	-2675.547
9	-2676.062
10	-2676.698

Table 10: Total Energy for Neon

No of iterations	Total Energy (eV)
0	-3298.572
1	-3363.472
2	-3358.270
3	-3445.099
4	-3488.822
5	-3488.577
6	-3476.946
7	-3469.728
8	-3468.352
9	-3469.349
10	-3470.360

Table 11: Computed Total Energies

Z	Element	Total Energy (eV)	
		Present Work	**Others**
1	Hydrogen	-8.400	-13.6 00 ref [7] -13.577 ref. [15]
2	Helium	-77.638	-79.005 ref. [8] -74.800 ref. [9] -77.500 ref. [10] -57.087 ref. [15]
3	Lithium	-183.700	-203.625 ref. [8] -203.491 ref. [11] -190.735 ref. [12] -202.729 ref. [15]
4	Beryllium	-388.382	-399.067 ref. [8] -398.746 ref. [13] -397.815 ref [14] -398.384 ref. [15]
5	Boron	-654.183	-670.950 ref. [8] -668.061 ref. [17]
6	Carbon	-1006.868	-1029.947 ref. [8] -1027.588 ref. [18]
7	Nitrogen	-1455.378	-1485.517 ref. [8]
8	Oxygen	-2008.363	-2042.851 ref. [8]
9	Fluorine	-2676.698	-2713.858 ref. [8] -2713.880 ref. [16]
10	Neon	-3470.360	-3508.176 ref. [8]

5.0 Plots of Results

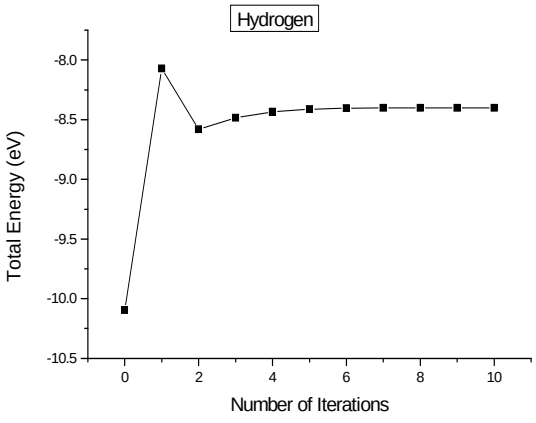

Fig. 1: Total Energy Vs Number of Iterations for Hydrogen

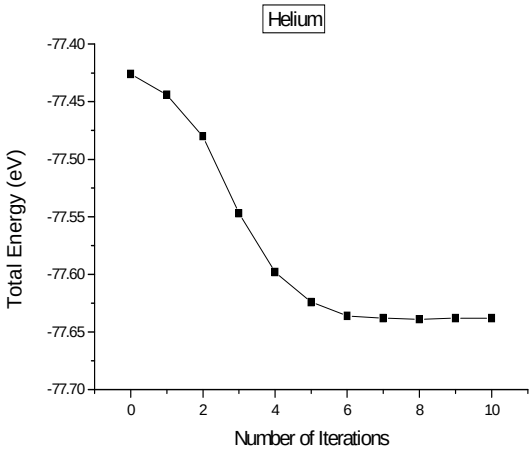

Fig. 2: Total Energy Vs Number of Iterations for Helium

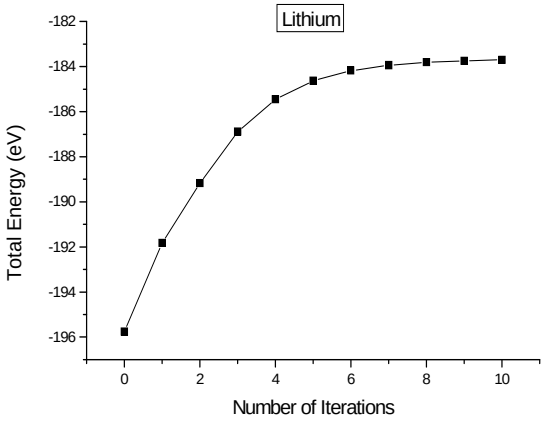

Fig. 3: Total Energy Vs Number of Iterations for Lithium

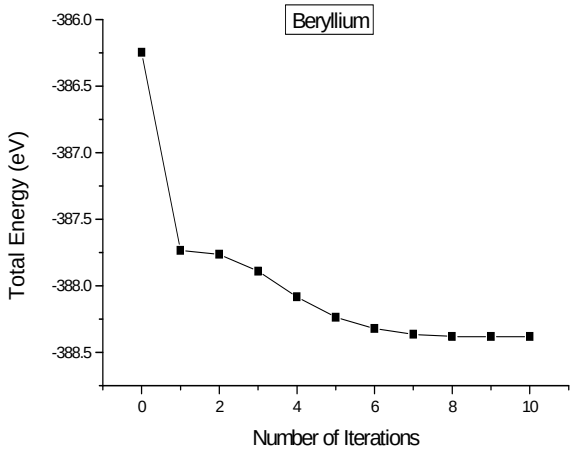

Fig. 4: Total Energy Vs Number of Iterations for Beryllium

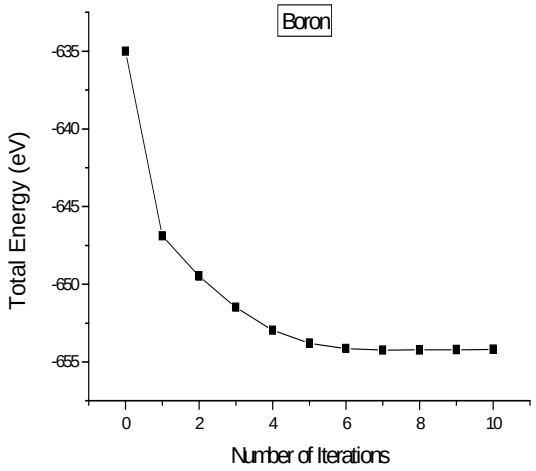

Fig. 5: Total Energy Vs Number of Iterations for Boron

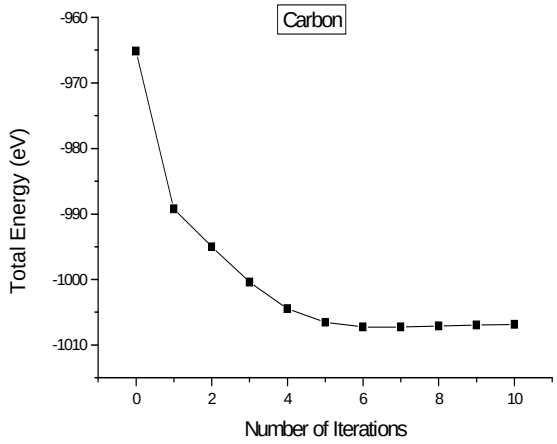

Fig. 6: Total Energy Vs number of Iterations for Carbon

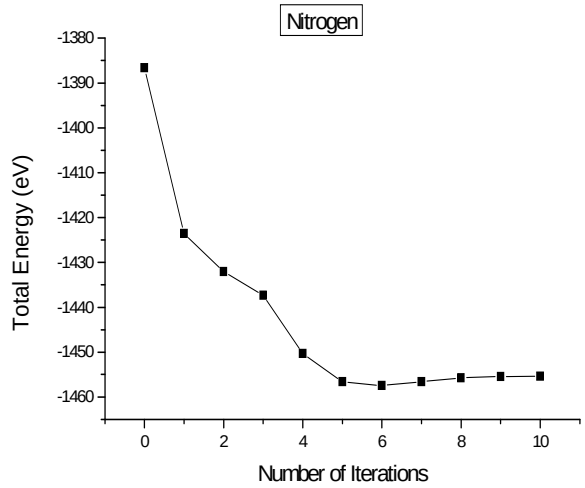

Fig.7: Total Energy Vs Number of Iterations for Nitrogen

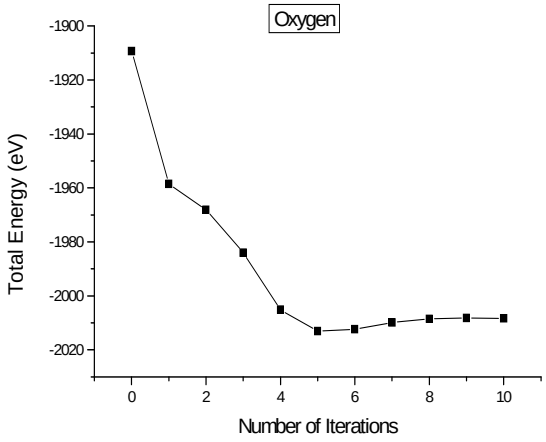

Fig. 8: Total Energy Vs Number of Iterations for Oxygen

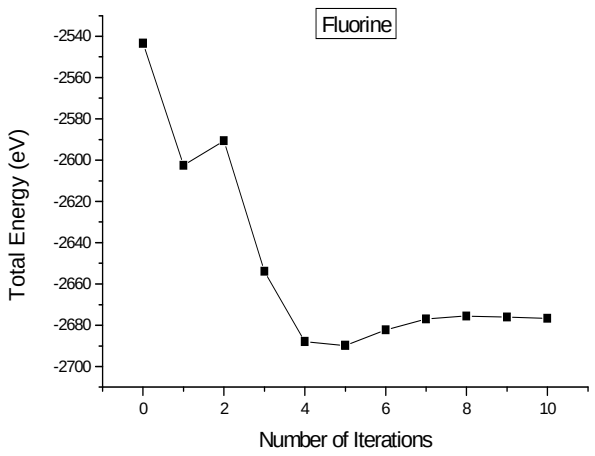

Fig. 9: Total Energy Vs Number of Iterations for Fluorine

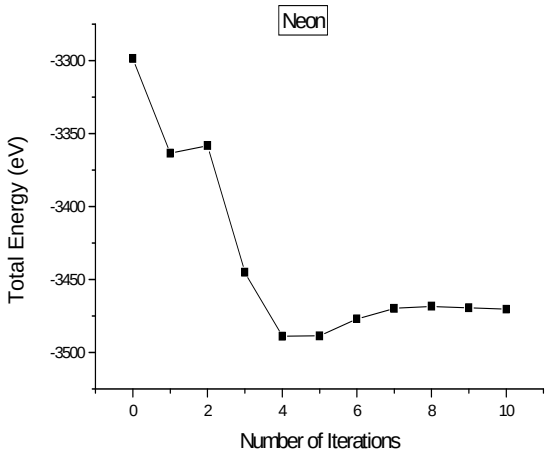

Fig. 10: Total Energy Vs Number of Iterations for Neon

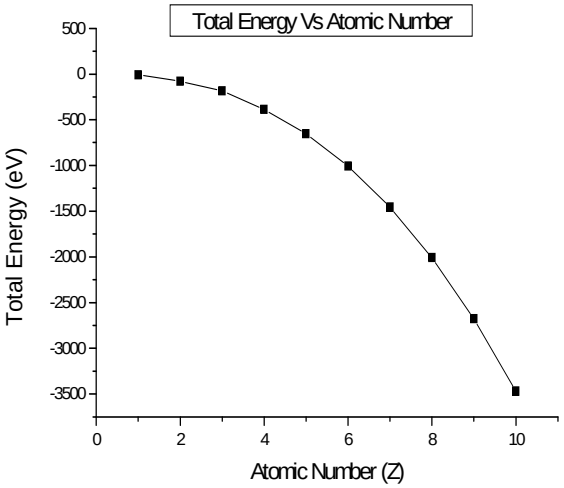

Fig. 11: Total Energy Vs Atomic Number (Z)

Discussion and Conclusion

Tables 1-10 give the computed ground state total energies of the atoms as a function of the number of iterations. Table 11 gives the summary of the computed ground state total energies for the elements studied.

From Tables 1 -10, it can be seen that the calculated total energies are all negative which means that these energies bind the electrons to the nucleus. These energies decrease continuously from Hydrogen to Neon as seen in Table 11 and Figure 11.

From Figures 1-10, it can be seen that all computations converged as the plots flattened out.

From Table 11, our results, obtained using the Hartree-Fock method, are in good agreement with the results of refs. [7-18] using other methods that included the uncertainty principle, variational principle, analytical evaluation of Hylleraas integrals, perturbation method, independent particle model, quantum Monte Carlo, Hund's multiplicity rule and density functional theory.

Figure 11 shows that the computed total energy decreases with increase in atomic number which means that the total binding energy for atoms increases with atomic number.

References

[1] Heenen, P.H. and M.R. Godefroid (2012),Scholarpedia, **7** (**10**), 10545. Available online at http://www.scholarpedia.org/article/The_Hartree-Fock_Method accessed on 24/08/2013.

[2] Fischer, C.F., (1977), Hartree-Fock Method For Atoms: A Numerical Approach, John-Wiley and Sons, New York.

[3] Slater, J.C. (1951), A Simplification of The Hartree-Fock Method, Phys. Rev., vol. **81**, 385-390.

[4] Ring, P. and P. Schuck (2000), The Nuclear Many-Body Problem, Springer-Verlag, Berlin, Heidlberg.
[5] Slater, J.C. (1960), Quantum Theory of Atomic Structure, vol. **2**, Cambridge University Press, New York.
[6] Koonin, S.E. and D.C. Meredith, (1989), Computational Physics: Fortran Version, Addison-Wesley, New York.
[7] Branson, J. (2013), Quantum Physics 130, available online at http://quantummechanics.ucsd.edu/ph130/130_notes/node98.html Accessed on 24/08/2013.
[8] Gross, E.K.U. (2013), Ground State Density Functional Theory: An Overview. Available online at http://www.physik.fu-berlin.de/~ag-gross Accessed on 28/09/2013.
[9] Al-Jaber, S.M., (2010), Variational Method For Ground-State Energy of Helium Atom in N –Dimensions, **II** NUOVO CIMENTO, VOL. **125 B**, (No. **9**), pp. 1099-1108.
[10] Fitzpatric, R. (2006), Quantum Mechanics Lecture Notes, available online at http://farside.ph.utexas.edu/teaching/qmech/lectures/node128.html Accessed on 24/08/2013.
[11] Puchalski, M. and K. Pachucki (2006), Ground-state Wave Function and Energy of the Lithium Atom, Phys. Rev. A, **73**, 022503.
[12] Seung, S. and E.B. Wilson, (1967), Ground State Energy of Lithium and Three-Electron Ions by Perturbation Theory, J. Chem. Phys., **47**, 5343.
[13] Kotchoubey, A. and H. Thomas (1988), Numerical Calculation of the Energy and Wavefunction of the Ground State of Beryllium, J. Chem. Phys., **45**, 3342.
[14] Barbosa, A.G.H. and M.A.C. Nascimento (2004), Ground State of the Beryllium Atom: Reinvestigation Based on a Proper Independent Particle Model, International Journal of Quantum Chemistry, vol. **99**, issue **44**, pp. 317-324.
[15] Machin, R.B. (2004), Lectures on Quantum Mechanics, available online at http://www1.uprh.edu/rbaretti/LQMch11.html accessed on 24/08/2013.
[16] Luchow, A. and J.B. Anderson (1996), Accurate Quantum Monte Carlo Calculations for Hydrogen Fluoride and the Fluorine Atom, J. Chem. Phys., **105** (**11**), 4636-4640.
[17] Ruiz, M.B. and M. Rojas (2003), Variational Calculation of the $^2P_{1/2}$ Ground State of Boron Atom using Hydrogen-like Orbitals, Computational Methods in science and Technology, **9**, (1-2), pp. 101-112.
[18] Hongo, K., R. Maezono, Y. Kawazoe, H. Yasuhara, M.D. Tower and R.J. Needs (2004), Interpretation of Hund's Multiplicity Rule for the Carbon Atom, J. Chem. Phys., **121** (15), pp. 7144-7147.