



COMPUTATION OF ELECTRONIC STRUCTURE OF AN ATOM IN THE HARTREE-FOCK APPROXIMATION



O.S. Ayanninuola^{1*}, I.I. Ewa¹, I. Umar¹, M.S. Liman²

¹Department of Physics, Nasarawa State University, PMB 1022, Keffi, Nigeria

²Department of Physics, Federal University Lafia, Nasarawa State, Nigeria

*Corresponding author: ayanninuola@gmail.com

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Abstract: In this work, FORTTRAN program has been applied to evaluate the energy level of generally small atomic systems. The program was specifically directed to compute the Hartree-Fock equations. The ground state structures of small atomic systems are obtained using Hartree-Fock approximation. The total energies calculated for each of the state (1s, 2s, 2p) approximately agreed with those of experimental results as compared. Due to non-linearities introduced by Hartree-Fock approximation, the equations are solved using non-linear method such as iteration. The physical implication of this important finding has helped to identified clearly the parameter space accessible to the Hartree-Fock method.

Keywords: Atom, energy density, electronic structure, hartree-fock, orbital, wave function

Introduction

In computational Physics and computational chemistry the Hartree-Fock (HF) method is an approximation method for determination of the ground-state wave function and ground state energy of a quantum many-body system (Nesbet, 2003). The Hartree-Fock method assumes that the exact N-body wave function of the system can be approximated by a single Slater determinant where the particles are fermions or by a single permanent if the particles are bosons of N spin-orbitals. Invoking the variational principle one can derive a set of N coupled equations for the N spin-orbitals. Solution of these equations yield the Hartree-Fock wave function and energy of the system, which are approximations of the exact ones (Adhikari, 1998). The Hartree-Fock method finds its typical application in the solution of the electronic Schrodinger equation of atoms, molecules and solids but it has also found widespread uses in nuclear Physics (Gray, 1996). This thesis will focus on applications in electronic structure theory.

Analytically, it is difficult to solve many-quantum system. In this work we shall develop a FORTRAN program that will enhance the determination of electronic structure and energies of light atomic system. The aim of this work is to solve the Hartree-Fock equations using the following objectives: Determine the ground state structure of small atomic system, develop a computer program (FORTRAN) to compute the total energies of the states (1s, 2s, 2p), compare the result with those of experiments. In the sense that, one could reproduce fairly well the observed transitions level observed in the X-ray region. The existence of a non-zero quantum defect was attributed to electron-electron repulsion which clearly does not exist in the isolated hydrogen atom. This repulsion resulted in partial screening of the bare nuclear charge. These early researchers later introduced other potentials containing additional empirical parameters with the hope of better reproducing the experimental data. Hartree sought to do away with empirical parameters and solve the many-body time independent Schrödinger equation from fundamental physical principals (Veillard, 2006).

The Hartree-Fock (HF) method is a variational method that provides the wave function of a many-body system assumed to be in the form of a Slater determinant for fermions and a product wave function for bosons. It treats correctly the statistics of the many-body system, antisymmetry for fermions and symmetry for bosons under the exchange of particles. The variational parameters of

the method are the single-particle wave function composing the many-body wave function (Froese, 1997). Ring (2000), found out that the total energy E^{HF} is not equal to the sum of the single-particle energies; these energies include a term generated by the two-body interaction of a given particle with all the others. When the single-particle energies are added, the interactions are counted twice. The two-body interaction depends for some systems on the local density of particles. This is often the case in nuclear Physics, where this density dependence can be justified by elimination of the very repulsive core of most bare nucleon-nucleon interaction.

Doves (1987), calculated the electronic structure of α -quartz using the periodic Hartree-Fock method and found out that the cluster type calculations on molecules such as $\text{H}_6\text{Si}_2\text{O}_7$ accurately reproduce the charge density in the neighborhood of the bridging oxygen. Geometry optimizations yield realistic values of the SiO bond length and of the SiOSi angle. Gray *et al.* (2003) observed characteristic maximum and minimum in the one-electron radial density demonstrating the shell structure of atoms. It becomes necessary for the quest of knowledge to study the electronic structure of many-quantum systems using Hartree-Fock approximation method. Meanwhile other approximation methods can as well be employed in executing this same task in any further research.

Materials and Methods

The Hartree-Fock method is typically used to solve the time-independent Schrödinger equation for a multi-electron atom or molecule as described in the Born-Oppenheimer approximation. Since there are no known solution for many-electron systems (hydrogenic atoms and the diatomic hydrogen cat ion being notable one-electron exceptions), the problem is solved numerically. Due to the nonlinearities introduced by the Hartree-Fock approximation, the equations are solved using a nonlinear method such as iteration, which gives rise to the name "self-consistent field method" (Tinkham, 2003).

$$E = \sum_{\alpha=1}^N \left\langle \alpha \left| \frac{p^2}{2m} \right| \alpha \right\rangle + \int \left[-\frac{ze^2}{r} + \frac{1}{2} \phi(r) \right] \rho(r) d^3r - \frac{1}{2} \sum_{\alpha\alpha'=1}^N \delta_{\sigma\alpha\alpha'} \left\langle \alpha\alpha' \left| \frac{e^2}{r_{ij}} \right| \alpha\alpha' \right\rangle \dots (1)$$

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

$$\left\langle \alpha \left| \frac{p^2}{2m} \right| \alpha \right\rangle = -\frac{\hbar^2}{2m} \int X_{\alpha}^*(r) \nabla^2 X_{\alpha}(r) d^3r, \dots (2)$$

The electron density is the sum of single-particle densities,

$$\rho(r) = \sum_{\alpha=1}^N |X_{\alpha}(r)|^2 \quad \dots (3)$$

The electrostatic potential generation by the electrons is

$$\phi(r) = e^2 \int \frac{1}{r-r'} \rho(r') d^3r' \quad \dots (4)$$

So that,

$$\nabla^2 \phi = -4\pi e^2 \rho(r), \quad \dots (5)$$

And the exchange matrix elements of the inter-electron repulsion are

$$\langle \alpha\alpha' | \frac{e^2}{r_{ij}} | \alpha\alpha' \rangle = e^2 \int X_{\alpha}(r) X_{\alpha'}(r) X_{\alpha}(r') X_{\alpha'}(r') d^3r d^3r' \dots (6)$$

The interpretation of the various terms in Equation (1) is straightforward. The kinetic energy is the sum of the kinetic energies of the single particle orbitals, while the electron-nucleus attraction and direct inter-electron repulsion are just what would be expected from a total charge of $-N$ distributed in space with density $\rho(r)$. The final term in equation (1) is the exchange energy, which arises from the anti-symmetry of the trial wave. It is a sum over all pairs of orbital with the same spin projection; pairs of orbitals with different spin projections are "distinguishable" and therefore do not contribute to this term.

The two-electron problem

For two electrons that don't interact with each other, the ground state of their motion around a nucleus in the $1s^2$ configuration; that is, both electrons are in the same real, spherically symmetric spatial state, but have opposite spin projections. It is therefore natural to take a trial wave function for the interacting system that realizes this same configuration; the corresponding two single-particle wave functions are

$$\Psi(X) = \frac{1}{(4\pi)^{2r}} R(r) \left| \pm \frac{1}{2} \right\rangle \quad \dots (7)$$

So that many-body wave functions Equation (3.9)

$$\Psi = \frac{1}{\sqrt{2}} \frac{1}{4\pi r_1 r_2} R(r_1) R(r_2) \left[\left| +\frac{1}{2} \right\rangle \left| -\frac{1}{2} \right\rangle - \left| -\frac{1}{2} \right\rangle \left| +\frac{1}{2} \right\rangle \right] \quad \dots (8)$$

This trial wave function is anti-symmetric under the interchange of the electron spins but is symmetric under the interchange of their space coordinates. It respects the Pauli principle, since it is anti symmetric under the interchange of all variables describing the two electrons. The normalization condition Equation (4) becomes.

$$\int_0^{\infty} R^2(r) dr = 1 \quad \dots (9)$$

While the energy Equation (1.1) becomes

$$E = \frac{\hbar^2}{2m} \int_0^{\infty} \left(\frac{dR}{dr} \right)^2 dr + \int_0^{\infty} \left[-\frac{2e^2}{r} + \phi(r) \right] \rho(r) 4\pi r^2 dr \quad \dots (10)$$

With equation (1.1) reduces to

$$\rho(r) = 2x \frac{1}{4\pi r'} R^2(r) 4\pi r' dr = 2 \quad \dots (11)$$

And equation (1.5b) becomes

$$\frac{1}{r'} \frac{d}{dr} \left[r' \frac{d\phi}{dr} \right] = -4\pi e^2 \rho \quad \dots (12)$$

$$R(r) = 2 \left[\frac{z^*}{\alpha} \right]^{\frac{1}{2}} \frac{z^* r}{\alpha} e^{-\frac{z^* r}{\alpha}} \quad \dots (13)$$

Where: α is the Bohr radius. The energy Equation (12) is then minimized as a function of Z^* to find an approximate to the wave function and energy.

$$z^* = z \frac{5}{16}; \quad E = \frac{e^2}{\alpha} \left[z^2 \frac{5}{8} z + \frac{25}{256} \right] \quad \dots (14)$$

In carrying out this minimization, it is amusing to note that the kinetic energy scales as Z^{*2} , which all of the potential energies scale as Z^* , so that, at the optimal Z^* , the kinetic energy is $-1/2$ of the potential. This is a specific case of a more general virial theorem pertaining to the Hartree-Fock approximation (Ismail, 1992). See Step 1 below.

$$\delta(E - 2\varepsilon \int_0^{\infty} R^2 dr) = 0 \quad \dots (15)$$

Where ε is a Lagrange multiplier to be determined after variation so that the solution is properly normalized. The standard techniques of variational calculus then lead to

$$\int_0^{\infty} dR(r) \left[-4 \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - 4 \frac{ze^2}{r} + 2\phi(r) - 4\varepsilon \right] R(r) dr = 0, \dots (16)$$

Which is satisfied if resolves the Schrödinger-like equation

$$\left[\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{ze^2}{r} + 1/2 \phi(r) - \varepsilon \right] R(r) = 0 \quad \dots (17)$$

Choosing ε (the "single-particle energy") to be an eigenvalue of the single-particle Hamiltonian appearing in Equation (17) ensures that R is normalizable. Equations (12, 17) are the two coupled non-linear differential equation in one dimension that forms the Hartree-Fock approximation to the original six-dimensional Schrodinger equation. Note that only one-half of ϕ appears in equation (17) since each electron interacts only with other and not "with itself" (Ismail, 1992).

Many electron systems

In many-electron systems, spherical symmetry of the density and potential are by no means guaranteed. In principle, non-spherical solutions should be considered, and such "deformed" wavefunctions are in fact the optimal ones for describing the structure of certain nuclei (Dill, 2006).

To understand what the problem is, let us assume that the potential ϕ is spherically symmetric. The solutions to the single particle Schrödinger equation in such a potential are organized into "shells", each characterized by an orbital angular momentum, l , and a radial quantum number, n . Within each shell, all $2(2l + 1)$ orbital associated with the various values of m and the projection of the orbital angular momentum, m , are degenerate. The orbital have the form;

$$x_{\alpha}(r) = \frac{1}{r} R_{nl}(r) Y_{lm}(\hat{r}); \int_0^{\infty} R_{nl}^2(r) dr = 1 \quad \dots (18)$$

Thus, we introduce the number of electrons in each shell, N_{nl} , which can take on integer value between 0 and $2(2l + 1)$, and using the wave functions Equation (18), write the density Equation (1) as;

$$\rho(r) = \frac{1}{4\pi r^2} \sum_{nl} N_{nl} R_{nl}^2(r); \int_0^{\infty} \rho(r) 4\pi r^2 dr = \sum_{nl} N_{nl} = N \quad \dots (19)$$

In writing this expression, we have used the identity

$$\sum_{m=-l}^l |Y_{lm}(\hat{r})|^2 = \frac{2l + 1}{4\pi}$$

In the same spirit, the energy functional Equation can be generalized to open-shell situation as;

$$E = \sum_{nl} N_{nl} \frac{\hbar^2}{2m} \int_0^{\infty} \left[\left(\frac{dR_{nl}}{dr} \right)^2 + \frac{l(l+1)}{r^2} R_{nl}^2 \right] dr +$$

$$\int_0^{\infty} \left[-\frac{ze^2}{r} + \frac{1}{2} \phi(r) \right] \rho(r) 4\pi r^2 dr + E_{ex} \quad \dots (20a)$$

With the exchange energy being

$$E_{xc} = -\frac{1}{4} \sum_{nlml'} N_{nl} N_{nl'} \sum_{\lambda=|l-l'|}^{l+l'} \begin{bmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{bmatrix}^2 I_{nl, nl'}^{\lambda} \quad \dots (20b)$$

In this expression, I is the integral

$$I_{nl, nl'}^{\lambda} = e^2 \int_0^{\infty} dr \int_0^{\infty} dr' R_{nl}(r) R_{nl'}(r) \frac{r^{\lambda}}{r^{\lambda+1}} R_{nl'}(r') R_{nl}(r') \quad \dots (21)$$

Where $r <$ and $r >$ are the smaller and larger of r and r' and the 3-j symbol vanishes when $l + l' + \lambda$ is odd.

Lagrange multipliers ε_{nl} are introduced to keep each of the radial wave function normalized and, after some algebra, we have

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{ze^2}{r} + \phi(r) - \varepsilon_{nl} \right] R_{nl}(r) = -F_{nl}(r), \dots (22a)$$

With;

$$F_{nl}(r) = -\frac{e^2}{2} \sum_{n'l'} N_{n'l'} R_{n'l'}(r) \sum_{\lambda=|l-l'|}^{l+l'} \begin{bmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{bmatrix}^2 J_{nl, n'l'}^{\lambda} \dots (1.22b)$$

$$J_{nl, n'l'}^{\lambda} = \frac{1}{r^{\lambda+1}} \int_0^r R_{n'l'}(r') R_{nl}(r) r^{\lambda} dr' + r^{\lambda} \int_r^{\infty} \frac{R_{n'l'}(r') R_{nl}(r')}{r^{\lambda+1}} dr' \dots (22c)$$

The eigen value equation (22a) can be seen to be analogous to Equation (17) for the two-electron problem, except that the exchange energy has introduced a non-locality (Fock potential) embodied in F and has coupled together the eigen value equations for each of the radial

wave functions; it is easy to show that these two equations are equivalent when there is a single orbital with $l = 0$. It is useful to note that equation (22b, 22b) imply that the exchange energy can also be written as

$$E_{ex} = \frac{1}{2} \sum_{nl} N_{nl} \int_0^\infty R_{nl}(r) F_{nl}(r) dr, \dots (23a)$$

And that, by multiplying Equation (20a) by R_{nl} and integrating we can express the single Particle eigen value as (Ismail, 1992).

$$\epsilon_{nl} = \frac{\hbar^2}{2m} \int_0^\infty \left[\left(\frac{dR_{nl}}{dr} \right)^2 + \frac{l(l+1)}{r^2} R_{nl}^2 \right] dr + \int_0^\infty \left[-\frac{ze^2}{r} + \Phi(r) \right] R_{nl}^2(r) F(r) dr \dots (23b)$$

Numerical analysis

For the numerical solution of the Hartree-Fock equations, we must first adopt a system of units. For comparison with experimental value, it is convenient to measure all lengths in Angstroms and all energies in electron volts. If we use the constants,

$$\frac{\hbar^2}{m} = 7.6359 \text{ eV} \cdot \text{Å}^2; \quad e^2 = 14.409 \text{ eV} \cdot \text{Å}$$

Then the Bohr radius and Rydberg constants have their correct values,

$$\alpha = \frac{\hbar^2}{me^2} = 0.5299 \text{ Å}; \quad Ry = \frac{e^2}{2\alpha} = 13.595 \text{ eV}.$$

The attacks can be made through the following sequence of steps:

Step 1: Verify the algebra leading to the final equations presented above for the two-electron system (Equations (10, 12, and 17)) and for the multi-electron system (Equations (12, 20, 22)) have proved the viral theorem that the kinetic energy is $-\frac{1}{2}$ of the potential energy. This can be done by imagining that the single-particle wave functions of a solution to the Hartree-Fock equations are subjected to a norm-preserving scaling transformation,

$$x_\alpha(r) \rightarrow \tau^{3/2} x(\tau r) \dots (24)$$

Where τ is a dimensionless scaling parameter, show that the total kinetic energy in Equation scales as τ^2 , while all of the potential energies scale as τ . Since the energy at the Hartree-Fock solution is stationary with respect to any variation of the wave functions.

Step 2: Write a program to calculate the energy from Equation (10) if R is known at all if the lattice points. This will require writing a sub-routine that calculates ϕ by solving Equation (12) and then evaluating suitable quadrature for the various terms in Equation (19). Verify that the program is working by calculating the energies associated with the hydrogenic orbital Equation (13) and comparing it with the analytical results (remember to normalize the wave function by the appropriate discretization of Equation (18)).

Step 3: Write a subroutine that uses the shooting method to solve the radial equation for the lowest eigen value and corresponding normalized wave function R if the potential is given at the lattice point. The zero boundary condition at large distances can be taken as $R(r=L) = 0$, where L is the outer end of the lattice. (Greater accuracy, particularly for weakly bound states, can be had by imposing instead an exponential boundary condition at the outer radius). Note that the radial scale (i.e., R and the radial step size) should change with the strength of the central charge.

Verify that the subroutine works by setting ϕ and 0 and comparing, for $Z = 2$ and $Z = 4$, the calculated wave function, eigen value, and energy of the $1s$ orbital with the analytical hydrogenic values.

Step 4: Combine the subroutines developed in Steps 2 and 3 into a code that, given a value of Z , solves the two electron Hartree-Fock equations of iteration. An iteration scheme is as follows, the organization into subroutines being obvious:

- i) "Guess" an initial wave function, says the hydrogenic one Equation (13) with the appropriate value of Z^* .
- ii) Solve Equation (12) for the potential generated by the initial wave function and calculated the total energy of the system from Equation (19)
- iii) Find a new wave function and its eigen value by solving Equation (19) and normalizing according to Equation (9)
- iv) Calculate the new potential and new total energy. Then go back to (iii) and repeat (iii) and (iv) until the total energy has converged to within the required tolerance.

At each iteration, the eigen value, the total energy and the three separate contributions to the energy appearing in Equation (10) should be printed out; a plot of the wave function is also useful for monitoring the calculation. Note that the total energy should decrease as the iterations proceed and will converged relatively quickly to a minimum. The individual contributions to the energy will take longer to settle down, consistent with the fact that it is only the total energy that is stationary at the variational minimum, not the individual components; at convergence, the viral theorem discussed in Step 1 should be satisfied. Try beginning the iteration procedure with different single-particle wave functions and note that the converged solution is still the same. Vary the values of the lattice spacing and the boundary radius, L , and the certain that the results are stable under these changes.

Step 5: Use the program to solve the Hartree-Fock equations for central charges $Z = 1-9$. Compare the total energies obtained with the experimental values given in $N = 2$ column of Table 3 (These binding energies, which are the negative of the total energies, are obtained from the measured ionization potentials of atoms and ions); comparing the results also with the wave functions and associated variational energies given by Equations 13 and 14. Note that both approximations should give upper bounds to the exact energy.

It shows that for $Z = 1$, the Hartree-Fock approximation predicts that the H ion is unbound in that its energy is greater than that of the H atom and so it is energetically favorable to shed the extra electron. As can be seen from Table 3, this is not the case in the real world. In finding the $Z=1$ solution, it is discovered that convergence is quite a delicate business; it is very easy for the density to change so much from iteration to iteration that the lowest eigen value of the single-particle Hamiltonian becomes positive. One way to alleviate this problem is to prevent the density

from changing too much from one iteration to the next, for example by averaging the new density and the old following step iii) above.

Step 6: Modifies the two-electron program to treat systems in which several orbitals are involved. It is easiest first modify the calculation of the total energy for a given set of radial wave functions to include E_{ex} . This is most conveniently done by calculating and storing the F_{nl} of Equation (22b) and using Equation (23). Because of the Fock term, the Eigen value equations (22a) cannot be treated by the shooting method we have discussed. However, one scheme is to treat the F_{nl} calculated from the previous set of wave functions as an inhomogeneous term in solving for the new set of wave functions. For trial values of the e_{nl} calculated from Equation (24) using the previous set of wave functions, Equation (22) can be solved as uncoupled inhomogeneous boundary value problems using the Green's function method of Equation (12); after normalization according to Equation (18), the solutions serve as a new set of wave functions. The two-electron systems can be used to check the accuracy of the modifications; for these systems it is found that the exchange energy is $-\frac{1}{2}$ of the direct inter-electron interaction energy and that the solutions converge to the same results as those generated by the code in Step 1 (Ismail, 1992).

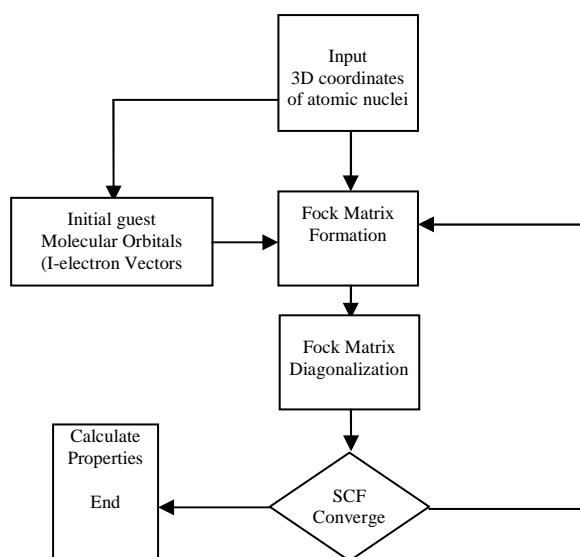


Fig. 1: A simplified algorithm flowchart illustrating the Hartree-Fock method

Input parameters for the design

- Z – Nuclear charge
- NOCC – number of electrons in each state (1s, 2s, 2p)
- DR – radial step size (Angstroms)
- NITER – number of iterations

Outputs parameters

- Ktot – total kinetic energy
- Ven – electron-nuclei
- Vee – electron-electron energies
- Vex – exchange energies
- Vtot – total potential energy
- Etot – total energies
- Vex – exchange energies
- Vtot – total potential energies
- Etot – total energies

Results and Discussion

The computed value of the total kinetic energies, total potential energies, electron-electron energies, exchange energies and the total energies of each of the state are shown in Table 1 (Iteration 0 – 19). HARTREE-FOCK solutions of small atomic systems in the filling approximation; Hartree-ock solutions for small atomic systems: Nuclear charge = 6.000, zstar = 5.067, Rmax (Angstroms) = 2.000, radial step (Angstroms) = 1.0000E-01, Occupations of the states are: 2 2 2 All energies are in eV.

Table 1: Total energies of each state (Iteration 0 – 19)

.....Iteration 0.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	252.141	-641.960	285.923	-90.984	-447.021	-194.881
2s	2	68.715	-180.857	141.035	-27.404	-67.225	1.490
2p	2	85.703	-206.831	160.586	-16.851	-63.096	22.608
Total	6	813.119	-2059.295	587.544	-135.238	-1606.989	-793.870

.....Iteration 1.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	201.535	-585.033	256.602	-78.792	-407.222	-205.688
2s	2	39.240	-138.558	110.725	-20.741	-48.574	-9.334
2p	2	60.102	-171.316	132.812	-13.231	-51.735	8.367
Total	6	601.753	-1789.813	500.140	-112.764	-1402.438	-800.685

.....Iteration 2.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	193.484	-574.589	239.612	-76.06	-411.307	-217.823
2s	2	30.196	-122.765	98.157	-18.712	-43.319	-13.124
2p	2	48.588	-152.666	116.89	-11.697	-47.472	1.116
Total	6	544.537	-1700.580	454.66	-106.469	-1352.389	-807.852

.....Iteration 3.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	194.049	-575.535	231.135	-75.969	-420.368	-226.319
2s	2	29.356	-121.359	95.243	-18.58	-44.696	-15.34
2p	2	45.162	-146.751	110.667	-11.288	-47.372	-2.209
Total	6	537.135	-1687.288	437.045	-105.836	-1356.079	-818.945

.....Iteration 4.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	195.891	-577.839	226.479	-76.188	-427.548	-231.657
2s	2	30.136	-123.06	94.772	-18.852	-47.14	-17.004
2p	2	0.886	-139.233	105.141	-10.829	-44.921	-4.032
Total	6	533.833	-1680.265	426.393	-105.87	-1359.742	-825.909

.....Iteration 5.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	197.442	-579.769	225.146	-76.662	-431.245	-233.803
2s	2	31.006	-124.956	95.333	-19.105	-48.728	-17.661
2p	2	41.931	-141.247	105.613	-10.984	-46.618	-4.687
Total	6	540.879	-1691.943	426.092	-106.711	-1372.562	331.684

.....Iteration 6.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.162	-580.663	225.132	-76.869	-432.4	-234.238
2s	2	31.79	-126.339	96.039	-19.285	-49.585	-17.796
2p	2	43.035	-143.289	106.617	-11.134	-47.806	-4.771
Total	6	545.973	-1700.583	427.788	-107.289	-1380.083	-834.11

.....Iteration 7.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.405	-580.965	225.389	-76.965	-432.541	-234.136
2s	2	32.171	-127.041	96.489	-19.376	-49.928	-17.756
2p	2	43.506	-144.144	107.155	-11.198	-48.188	-4.682
Total	6	548.163	-1704.301	429.034	-107.539	-1382.806	-834.643

.....Iteration 8.....							
State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.405	-580.965	225.389	-76.965	-432.541	-234.136
2s	2	32.171	-127.041	96.489	-19.376	-49.928	-17.756
2p	2	43.506	-144.144	107.155	-11.198	-48.188	-4.682
Total	6	548.163	-1704.301	429.034	-107.539	-1382.806	-834.643

1s	2	198.459	-581.033	225.574	-76.988	-432.447	-233.988
2s	2	32.31	-127.289	96.687	-19.408	-50.010	-17.700
2p	2	43.592	-144.297	107.32	-11.211	-48.189	-4.597
Total	6	548.722	-1705.239	429.581	-107.607	-1383.266	-834.544

.....Iteration 9.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.46	-581.035	225.656	-76.988	-432.367	-233.907
2s	2	32.336	-127.333	96.744	-19.413	-50.003	-17.667
2p	2	43.556	-144.231	107.329	-11.207	-48.109	-4.553
Total	6	548.706	-1705.199	429.729	-107.609	-1383.078	-834.373

.....Iteration 10.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.454	-581.027	225.679	-76.985	-432.333	-233.897
2s	2	32.328	-127.318	96.748	-19.411	-49.981	-17.653
2p	2	43.515	-144.155	107.305	-11.202	-48.052	-4.537
Total	6	548.595	-1705.001	429.739	-107.598	-1382.867	-834.271

.....Iteration 11.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.45	-581.023	225.68	-76.982	-432.326	-233.875
2s	2	32.318	-127.299	96.741	-19.409	-49.966	-17.648
2p	2	43.494	-144.116	107.288	-11.199	-48.027	-4.533
Total	6	548.524	-1704.875	429.708	-107.59	-1382.757	-834.232

.....Iteration 12.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.676	-76.982	-432.327	-233.878
2s	2	32.312	-127.288	96.735	-19.407	-49.96	-17.648
2p	2	43.487	-144.103	107.28	-11.198	-48.021	-4.534
Total	6	548.497	-1704.826	429.692	-107.587	-1382.721	-834.224

.....Iteration 13.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.673	-76.981	-432.329	-233.88
2s	2	32.31	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.487	-144.102	107.279	-11.198	-48.021	-4.534
Total	6	548.491	-1704.815	429.686	-107.586	-1382.712	-834.224

.....Iteration 14.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.283	96.732	-19.407	-49.957	-17.648
2p	2	43.488	-144.104	107.279	-11.198	-48.023	-4.535
Total	6	548.492	-1704.817	429.684	-107.586	-1382.719	-834.227

.....Iteration 15.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.283	96.732	-19.407	-49.958	-17.648
2p	2	43.48	-144.106	107.28	-11.198	-48.024	-4.535
Total	6	548.493	-1704.82	429.684	-107.586	-1382.721	-834.228

.....Iteration 16.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.489	-144.106	107.28	-11.198	-48.024	-4.535
Total	6	548.495	-1704.822	429.685	-107.586	-1382.723	-834.229

.....Iteration 17.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.489	-144.107	107.281	-11.198	-48.024	-4.535
Total	6	548.495	-1704.823	429.685	-107.586	-1382.724	-834.229

.....Iteration 18.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.489	-144.107	107.281	-11.198	-48.024	-4.535
Total	6	548.495	-1704.823	429.685	-107.586	-1382.724	-834.229

1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.489	-144.107	107.281	-11.198	-48.024	-4.535
Total	6	548.495	-1704.823	429.685	-107.586	-1382.724	-834.229

.....Iteration 19.....

State	Nocc	Ktot	Ven	Vee	Vex	Vtot	Etot
1s	2	198.449	-581.021	225.672	-76.981	-432.33	-233.881
2s	2	32.309	-127.284	96.733	-19.407	-49.958	-17.648
2p	2	43.489	-144.107	107.281	-11.198	-48.024	-4.535
Total	6	548.495	-1704.823	429.686	-107.586	-1382.723	-834.228

Table 2: The total energies of neutral atoms calculated with the relativistic Breit Pauli method by Fraga, Karkowski and Saxena and with the Hartree-Fock-Dirac formalism by Desclaux (Levente, 1991)

Atom	Z	\hat{E}_R	E_B	E_F	$\Delta\hat{E}_R\%$	$\Delta\hat{E}_B\%$
He	2	2.86137	2.86169	2.86169	-0.01	0.002
Li	3	7.43269	7.43327	7.43273	-0.0005	0.007
Be	4	14.57434	14.5752	14.57303	0.009	0.01
B	5	24.53397	24.5350	24.52906	0.02	0.02
C	6	37.70068	37.6732	37.68866	0.03	-0.04
N	7	54.42602	54.3229	54.40098	0.05	-0.14
O	8	74.85626	74.8172	74.80947	0.06	0.01

$\Delta\hat{E}_R = 100 \frac{\hat{E}_R - E_F}{\hat{E}_R}$; $\Delta\hat{E}_B = 100 \frac{\hat{E}_B - E_F}{E_B}$; \hat{E}_R = Resultant energy; E_R = the relativistic correction energy; E_F = the non-relativistic HF energy; E_B = Total energy

Table 3: Binding energies (in eV) of small atomic system by Ismail (1992)

Z	2	3	4	5	6	7	8
1	3.34						
2	78.88						
3	198.04	203.43					
4	371.51	389.71	399.03				
5	599.43	637.35	662.49	670.79			
6	881.83	946.3	994.17	1018.55	1029.81		
7	1218.76	1316.62	1394.07	1441.19	1471.09	1485.19	
8	1610.23	1743.31	1862.19	1939.58	1994.47	2029.58	2043.19
9	2054.8	2239.05	2397.05	2511.27	2598.41	2661.05	2696.03

Table 4: The density as a function of (r) for different states (1s, 2s, 2p)

Densities	The distance (r)			
0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1.00E-01	8.47E.00	3.91E-01	1.06E-01	9.18E+00
2.00E-01	7.15E.00	1.08E-01	5.31E-01	7.87E+00
3.00E-01	3.01E+00	6.24E-02	1.11E+00	4.43E+00
4.00E-01	9.83E-01	6.10E-01	1.63E+00	3.60E+00
5.00E-01	2.85E-01	1.38E+00	1.98E+00	4.00E+00
6.00E-01	7.81E-02	2.02E+00	2.15E+00	4.48E+00
7.00E-01	2.09E-02	2.40E+00	2.16E+00	4.65E+00
8.00E-01	5.60E-03	2.51E+00	2.06E+00	4.50E+00
9.00E-01	1.54E-03	2.40E+00	1.88E+00	4.09E+00
1.00E+00	4.46E-04	2.14E+00	1.65E+00	3.55E+00
1.10E+00	1.38E-04	1.80E+00	1.39E+00	2.93E+00
1.20E+00	4.59E-05	1.43E+00	1.12E+00	2.32E+00
1.30E+00	1.66E-05	1.08E+00	8.57E-01	1.74E+00
1.40E+00	6.35E-06	7.57E-01	6.16E-01	1.22E+00
1.50E+00	2.51E-06	4.87E-01	4.05E-01	7.85E-01
1.60E+00	9.64E-07	2.74E-01	2.32E-01	4.43E-01
1.70E+00	3.22E-07	1.21E-01	1.05E-01	1.97E-01
1.80E+00	6.67E-08	3.02E-02	2.64E-02	4.95E-02
1.90E+00	0.00E+00	0.00E+00	0.00E+00	2.37E-04

In connection with the total energies of atoms, calculation based on the Hartree-Fock method and calculation based

on the Briet-Pauli procedure lead to the same results in very good approximation as shown in Tables 1 and 2.

For the radial densities the Hartree-Fock method gives a good picture of the electron distribution inside an atom by providing the one electron wave function. By providing accurate one-electron wave functions, the Hartree-fock method produces a quantity that is vitally important in many molecular and solid state calculations, besides providing the explanation of such fundamental properties as the shell structure of atoms.

The one-electron radial density in Fig. 1 shows characteristic maxima and minima, demonstrating the shell structure of atoms. The curves shows that in the area in which a maximum occurs, there is high concentration of electron density, that is, the electron density is concentrated in shell; a shell is the volume between two spheres with radii that are slightly smaller and larger than the radius at which a maximum is located. The graph itself shows the image of atom. This agrees with Gray *et al.* (2003).

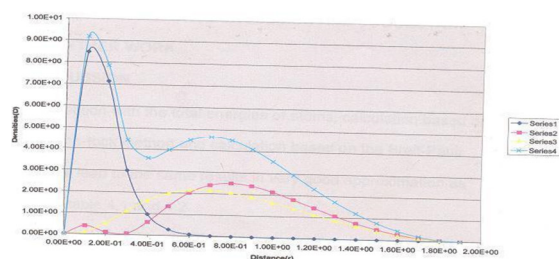


Fig. 1: The one–electronic radial densities of the 1s, 2s, and 2p electrons in the carbon atoms ($Z=6$)

The Hartree-fock method shows all atoms have the same image, that is, all atoms show the characteristic maxima and minima in their densities. The maxima signify the presence of shell in the electronic structure of atoms. Gray *et al.* (2003) also found this in his work.

Conclusion

However, these results, and similar results for other atoms, show only that the total energy can be reproduced with a high accuracy with simple expressions for the wave functions. The results do not mean that other quantities, like the total radial density, come out accurately from such calculations. These results are just the demonstration of a theorem of quantum mechanics according to which a poor

trial function can give very good results for the total energy in a variational calculation.

For the chosen atom (carbon) the total energy at 2p state in iteration of Table 1 is approximately the same as compared with that of Table 2 which Breit – Paul procedure for the carbon atom. Slightly large number of iteration is required to get the approximate value of the total energy (E_{tot}) of each of the states. Finally from Tables 1 and 2 the error in the Hartree-Fock energy of atom as compared is less or only about one percent. Levente (1991) also observed this in his work.

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c Hartree-Fock solution of small atomic systems in the
c   filling approximation
c   COMPUTATIONAL PHYSICS (FORTRAN VERSION)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      CALL INIT      !display header screen, setup parameters
5     CONTINUE      !main loop/ execute once for each set of param
      CALL PARAM     !get input from screen
      CALL ARCHON    !find the Hartree-Fock wave functions
      GOTO 5
      END
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
      SUBROUTINE ARCHON
C     find the Hartree-Fock wave function for the specified atom
Ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
C Global variables:
      INCLUDE 'IO.ALL'
      INCLUDE 'PARAM.P3'
C     Local variables:
      REAL E(MAXSTT+1, 8)           !all energies of all states
REAL FOCK (0: MAXSTP, MAXSTT)      !Fock terms
      REAL RHO (0: MAXSTP)         !density
REAL PSTOR (0: MAXSTP, MAXSTT)     !radial wave function
REAL PHI (0: MAXSTP)              !electron potential
      REAL ESP                     !single particle energy of state
      INTEGER ITER                  !iteration index
      INTEGER STATE                 !single particle state index
      REAL ZSTAR                   !optimal effective nuclear charge
      INTEGER DEVICE                !current graphing device
      INTEGER ISTOP, ISTART         !current limits on iteration
      INTEGER N_LINES               !number of lines written to screen
      INTEGER SCREEN                !send to terminal
      INTEGER PAPER                 !make a hardcopy
      INTEGER FILE                  !send to a file
C     Functions
INTEGER GETINT
      DATA SCREEN, PAPER/1, 2,3/
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
C     begin iterations with a good guess
      Mix=1.                        !no old density to mix with new
      ZSTAR=Z
      CALL HYDRGN (ZSTAR, PSTOR)     !find hydrogenic wave functions
      CALL ENERGY (E, FOCK, RHO, PSTOR) !and energy
C     optimal ZSTAR using virial theorem
      ZSTAR=Z*(E (NSTATE+1, IVTOT)/(2*E(NSTATE+1, IKTOT)))
      CALL HYDRGN (ZSTAR, PSTOR)     !find new hydrogenic wave functions

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