Study of atomic properties for subshells of the systems have $Z=12-16$ by using Hartree-Fock approximation

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Abstract
The atomic properties are important to describe of the dynamics in atoms for the two-electron atomic systems studied in this work include the atom Mg, and like ions Al$^{+1}$, Si$^{+2}$, P$^{+3}$ and S$^{+4}$. Hartree-Fock approximation are used to determine the atomic properties like one electron radial density function $D(r_1)$ and its expectation value $\langle r_1^n \rangle$, inter electron distribution function $f(r_{12})$ and its expectation value $\langle r_{12}^n \rangle$, standard deviation for one and two electrons $\Delta r_1$, $\Delta r_{12}$, expectation values for all energies $\langle V_{en} \rangle$, $\langle V_{ee} \rangle$, $\langle V \rangle$, $\langle T \rangle$, $\langle E \rangle$.

Key words: Hartree-Fock Method, two electrons radial density function, inter electron distribution function and its expectation values.

1-Introduction
Classical physics is dominated by two fundamental concepts. The first is the concept of a particle, a discrete entity with definite position and momentum which moves in accordance with Newton's laws of motion. The second is the concept of an electromagnetic wave, an extended physical entity with a presence at every point in space that is provided by electric and magnetic fields which change in accordance with Maxwell's laws of electromagnetism. The classical world picture is neat and tidy: the laws of particle motion account for the material world around us and the laws of electromagnetic fields account for the light waves which illuminate this world. [1]

Schrödinger's equation to multiple electron atoms The electron is not dissolved Analytical approximation the methods should be applied in order for wave functions or Other physical attributes than Quantum mechanics Calculation [2]

Hartree-Fock (HF) equations It was first suggested by Fock in 1930 Since then, HartreeFock has taken a centralized method A role in atomic studies and Molecular electronic structure Hartree-Fock (HF) method is Known for his success in Calculate the electron properties
Systems, in particular, Ground state properties of the atoms. Based on the principle of difference Numerical and algebraic [3].

Numerical computational methods for atomic Hartree-Fock equations have been developed by Froese Fischer. The one-particle Green's function approach and related many-body methods have been extensively used to calculate ionization and electron attachment spectra of atoms and molecules. Detailed accounts of the diverse techniques developed in this field and an overview of applications can be found in recent review articles [4,5].

2-theory

The Hartree-Fock (HF) approximation ignores the correlation between electrons but gives roughly 99% of the total electronic energy. We start from the standard N-electron Hamiltonian (in Hartree atomic units \( e = \hbar = m_e = 1 \) used throughout)

\[
\hat{H} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} \tag{1}
\]

Where: \( \hat{T}_e \) the electron kinetic energy

\( \hat{V}_{en} \) attractive electron-nucleus potential operator

\( \hat{V}_{ee} \) is the two-electron Coulomb repulsion operator

\[
\hat{T}_e = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 \tag{2}
\]

Where is \( \nabla_i^2 \) the Laplacian operator

\[
\hat{V}_{en} = \frac{Ze^2}{r_i} \tag{3}
\]

\[
\hat{V}_{ee} = \langle \sum_{i\neq j}^{N} \frac{e^2}{r_{ij}} \rangle \tag{4}
\]

\( r_i \) are the electron-nucleus distances for the electron(1) and electron(2) \( r_{ij} \) is the interelectronic distances

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \frac{Z}{r_i} + \hat{V}_{HF} \tag{5}
\]

The introduction of this effective potential means that each electron is subjected to a field that models the effect of the other electrons in the system. In The Hartree-Fock approximation, the many body wave function \( \psi(x_1, x_2, ..., x_N) \) approximated by a single slater determinant. We can write wave function as

\[
\Psi_{HF} = \det((\phi_1(x_1)\phi_2(x_2) ... \phi_N(x_N)))
\]
\[ \Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \ldots & \phi_N(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \ldots & \phi_N(x_N) \\ \phi_3(x_1) & \phi_3(x_2) & \ldots & \phi_N(x_N) \end{vmatrix} \quad (6) \]

The factor \( \frac{1}{\sqrt{N!}} \) ensures the normalization condition on the wavefunction. Here the variables \( x_i \) include the coordinates of spin and space. \( \phi_i(x_{ij}) \) terms are called spin orbitals and these spin orbitals are orthonormal functions, which are spatial orbitals times a spin function. The wave function \( \Psi_{HF} \) in equation (6) is clearly antisymmetric because interchanging any pair of particles is equivalent to interchanging two columns and hence changes the sign of the determinant. Moreover, if any pair of particles are in the same single-particle state, then two rows of the Slater determinant are identical and the determinant vanishes, in agreement with the Pauli exclusion principle.

The one-electron orbitals used to construct the \( \phi_i \) each consist of a radial function \( R_{n\ell}(r) \) a spherical harmonic \( Y_{\ell m}(\theta, \phi) \) and a spin function \( \sigma_{ms}(s) \)

\[ \phi = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)\sigma_{ms}(s) \]

The spatial part of one-electron spin orbital may be expressed as linear combination of Slater type orbital called basis functions

\[ \Phi_{n\ell m}(r, \theta, \phi) = \sum_i C_i X_i \quad (7) \]

Where \( C_i \) the expansion coefficient determined by minimizing the energy using one of several procedures and this process is continued until \( H_{HF} \) and \( \Psi_{HF} \) converge, at which point a self-consistent field (SCF) has been achieved. This usually yields the lowest-energy single determinant within the basis. \( X_i \) is a Slater type orbital.

\[ X_{n\ell m}(\xi, r) = R_{n\ell}(\xi, r)Y_{\ell m}(\theta, \phi) \quad (8) \]

The radial part is:

\[ R_{n\ell}(\xi, r) = (2\xi)^{n+\frac{1}{2}}[(2n)!]^{-\frac{1}{2}}r^{-n-1}\exp(-\xi r) \quad (9) \]

Here, \( \xi_i > 0 \) is the orbital exponent. The quantity \( n \) occurring in eq. (9) is a positive principal quantum number of (STO). The determination of nonlinear parameters \( n \) and \( \xi \) is very important for describing the atomic orbitals.

**(2-1) Two-Particle Density \( \Gamma(x_1, x_2) \)**

The reduced quantities that we seek as basic variables for this theory are the Reduced Density Matrices (RDMs), specifically the one-electron RDM [5,6]
\[ \Gamma(x_1) = N \int |\psi(x_1, \ldots, x_N)|^2\,dx_2 \ldots dx_N \quad (10) \]

And the two – particle (2-RDM):
\[ \Gamma(x_1, x_2) = \left( \begin{array}{c} N \\ 2 \end{array} \right) \int |\psi(x_1, x_2, \ldots, x_N)|^2\,dx_3 \ldots dx_N \quad (11) \]

The two – particle density can be written as [11]
\[ \Gamma(x_1, x_2) = \frac{1}{2} \sum_{i<j}^{N} A_{ij}^* A_{ij} \quad (12) \]

Where the pair function \( A_{ij} \) can be defined as:
\[ A_{ij} = \phi_i(m)\phi_j(n) - \phi_j(m)\phi_i(n) \quad (13) \]

By substituting equation (12) into equation (13) we can find:
\[ \Gamma(x_1, x_2) = \frac{1}{2} \sum_{i<j}^{N} [\phi_i(m)\phi_j(n) - \phi_j(m)\phi_i(n)]^2 \quad (14) \]

(2-2) **Two-electron radial density distribution \( D(r_1, r_2) \)**

The two-particle radial density distribution \( D(r_1, r_2) \) in each individual electronic shell is defined by: [7]
\[ D(r_1, r_2) = r_1^2 r_2^2 \int_0^{2\pi} \int_0^{2\pi} \Gamma(r_1, r_2)\,d\Omega_1\,d\Omega_2 \quad (15) \]
\[ d\Omega_i = \sin \theta_i d\theta_i d\varphi_i \quad (16) \]

Such that:
\[ r_1^2 r_2^2 \int_0^\infty \int_0^\infty \Gamma(r_1, r_2)\,dr_1\,dr_2 = 1 \quad (17) \]

This density function is a measure of the probability of finding the two-electrons such that, simultaneously, their radial coordinates are \( r_1 \) and \( r_2 \) respectively.

(2-3) **One – Particle Radial Density Function \( D(r_j) \)**

The radial density distribution function \( D(r_1) \) is a measure of the probability of finding an electron in each shell and it is defined as [8]:
\[ \]
\[ D(r_1) = \int_0^\infty D(r_1, r_2) dr_2 \] (18)

\((2-4)\) One-particle expectation value \( \langle r_1^n \rangle \)

The one-particle expectation value \( \langle r_1^n \rangle \) can be calculated from [9]:

\[ \langle r_1^n \rangle = \int D_{ij}(r_1) r_1^n dr_1 \] (19)

In the case \((n=0)\) one can calculate the normalization condition as a result of \( \langle r_1^n \rangle \)

\((2-5)\) Standard Deviation

The standard deviation of the distance of the test electron \( r_1 \) from the nucleus, is defined as [10]:

\[ \Delta r_1 = \sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \] (20)

\((2-6)\) inter-particle distribution function \( f(r_{12}) \)

The radial electron-electron distribution function, which describes the probability of locating two electrons separated by distance \( r_{12} \) from each other

\[ f(r_{12}) = \int \Gamma_{ij}(r_1, r_2) dr_1 dr_2 / dr_{12} \] (21)

\( f(r_{12}) \) representing a function of the distribution of the distance between electron 1 and electron 2

\((2-7)\) The inter-particle expectation values \( \langle r_{12}^n \rangle \)

The inter-particle expectation values \( \langle r_{12}^n \rangle \) can be calculated from [11]

\[ \langle r_{12}^n \rangle = \int f_{ij}(r_{12}) r_{12}^n dr_{12} \] (22)

\((2-8)\) Standard Deviation \( \Delta r_{12} \)

The standard deviation of the inter electronic distance of the two electrons, is defined as [11]

\[ \Delta r_{12} = \sqrt{\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2} \] (23)

3-Results and Discussion

Table (1): The locations and maximum values of the \( D(r_1, r_2) \) for studied systems
Atom or ion | 1S | 2S | 3S | 2P
|---|---|---|---|---|
| | r 1 | Dm(r1) | r 1 | Dm(r1) | r 1 | Dm(r1) | r 1 | Dm(r1) |
| Mg | 0.085 | 6.2129 | Peak1 | 0.067 | 0.31548 | Peak1 | 0.066 | 0.011566 |
| | | | Peak2 | 0.547 | 1.5538 | Peak2 | 0.468 | 0.046016 |
| | | | Peak3 | 2.593 | 0.34492 |
| Al$^{+1}$ | 0.079 | 6.7482 | Peak1 | 0.062 | 0.36235 | Peak1 | 0.061 | 0.022094 |
| | | | Peak2 | 0.497 | 1.7419 | Peak2 | 0.42 | 0.08438 |
| | | | Peak3 | 2.039 | 0.49021 |
| Si$^{+2}$ | 0.073 | 7.2842 | Peak1 | 0.057 | 0.41031 | Peak1 | 0.055 | 0.033583 |
| | | | Peak2 | 0.455 | 1.9316 | Peak2 | 0.381 | 0.12399 |
| | | | Peak3 | 0.706 | 0.61864 |
| P$^{+3}$ | 0.068 | 7.8202 | peak | 0.053 | 0.45879 | Peak1 | 0.052 | 0.045737 |
| | | | Peak2 | 0.349 | 0.16393 | Peak2 | 0.381 | 0.12399 |
| | | | Peak3 | 1.484 | 0.73945 |
| S$^{+4}$ | 0.064 | 8.357 | peak1 | 0.059 | 0.4866 | Peak1 | 0.049 | 0.058366 |
| | | | peak2 | 0.388 | 2.3115 | Peak2 | 0.322 | 0.20391 |
| | | | Peak3 | 1.315 | 0.85546 |

Table (2): Expectation values $\langle r_1^n \rangle$ for atoms $-2 \geq n \geq 2$ and standard deviation $\Delta r_1$
### Table (3): The location and maximum values of the inter-particle distribution function \( f(r_{12}) \) for studied systems

| atom or ion | 1s | 2s | 3s | 2p |
|-------------|----|----|----|----|
|             | \( r_{12} \) | \( f_m(r_{12}) \) | \( r_{12} \) | \( f_m(r_{12}) \) | \( r_{12} \) | \( f_m(r_{12}) \) |
| Mg          | 0.144 | 4.5538 | 0.855 | 0.966 | 4.086 | 0.209 | 0.786 | 0.921 |
| Al\(^{1+} \) | 0.133 | 4.9465 | 0.775 | 1.078 | 3.157 | 0.283 | 0.699 | 1.057 |
| Si\(^{2+} \) | 0.123 | 5.3396 | 0.707 | 1.191 | 2.622 | 0.347 | 0.626 | 1.1927 |
| P\(^+3 \)    | 0.114 | 5.7336 | 0.648 | 1.304 | 2.258 | 0.406 | 0.567 | 1.3277 |
| S\(^{4+} \)  | 0.107 | 6.1279 | 0.597 | 1.416 | 1.99 | 0.461 | 0.52 | 1.4608 |

### Table (4): Expectation values \( \langle r_{12}^n \rangle \) where \(-2 \geq n \geq 2\) and standard deviation \( \Delta r_{12} \) for studied system

| atom | shell | \( \langle r_{12}^1 \rangle \) | \( \langle r_{12}^{-1} \rangle \) | \( \langle r_{12}^2 \rangle \) | \( \langle r_{12}^4 \rangle \) | \( \Delta r_{12} \) |
|------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mg   | 1s    | 89.1            | 7.206           | 0.1908          | 0.0459          | 0.0975          |
|      | 2s    | 2.85            | 1.316           | 0.9788          | 1.1423          | 0.4292          |
|      | 3s    | 0.12            | 0.279           | 4.5793          | 24.812          | 1.96            |
|      | 2p    | 2.97            | 1.348           | 0.9854          | 1.1944          | 0.4726          |
| Al\(^{1+} \) | 1s | 105             | 7.824           | 0.1757          | 0.0389          | 0.0897          |
|      | 2s    | 3.53            | 1.464           | 0.8777          | 0.9162          | 0.382           |
|      | 3s    | 0.22            | 0.372           | 3.4046          | 13.586          | 1.4122          |
|      | 2p    | 3.83            | 1.534           | 0.8618          | 0.909           | 0.4078          |
| atom | shell | \(\langle V_{cm}\rangle\) | \(\langle V_{ee}\rangle\) | \(\langle V_t\rangle\) | \(\langle T\rangle\) | \(\langle E_t\rangle\) |
|------|-------|----------------|----------------|----------------|----------------|----------------|
| Mg   | 1s    | -278.346       | 7.20559        | -271.14041     | 135.570205     | -135.570205   |
|      | 2s    | -50.58624      | 1.31556        | -49.27068      | 24.63534       | -24.63534     |
|      | 3s    | -9.58488       | 0.27869        | -9.30619       | 4.653095       | -4.653095     |
|      | 2p    | -140.51952     | 20.22075       | -120.29877     | 60.149385      | -60.149385    |
|      | sum   | -479.03664     | 29.02059       | -450.01605     | 225.008025     | -225.008025   |
| Al\(^{2+}\) | 1s | -327.32596     | 7.82411        | -319.50185     | 159.750925     | -159.750925   |
|      | 2s    | -61.11664      | 1.46342        | -59.65232      | 29.82616       | -29.82616     |
|      | 3s    | -14.0374       | 0.3717         | -13.6657       | 6.83285        | -6.83285      |
|      | 2p    | -172.04304     | 23.0061        | -149.03694     | 74.51847       | -74.51847     |
|      | sum   | -574.52304     | 32.66623       | -541.85681     | 270.928405     | -270.928405   |
| Si\(^{2+}\) | 1s | -380.28956     | 8.44297        | -371.84659     | 185.923295     | -185.923295   |
|      | 2s    | -72.66532      | 1.61357        | -71.05175      | 35.525875      | -35.525875    |
|      | 3s    | -18.72864      | 0.45375        | -18.27489      | 9.137445       | -9.137445     |
|      | 2p    | -206.56608     | 25.7832        | -180.78288     | 90.39144       | -90.39144     |
|      | sum   | -678.2496      | 36.29349       | -641.95611     | 320.978055     | -320.978055   |
| P\(^{3+}\) | 1s | -437.2551      | 9.0629         | -428.1922      | 214.0961       | -214.0961     |
|      | 2s    | -85.2255       | 1.76311        | -83.46239      | 41.731195      | -41.731195    |
|      | 3s    | -23.7663       | 0.5307         | -23.2356       | 11.6178        | -11.6178      |
|      | 2p    | -244.0782      | 28.5504        | -215.5278      | 107.7639       | -107.7639     |
|      | sum   | -790.3251      | 39.90711       | -750.41799     | 375.208995     | -375.208995   |
| S\(^{4+}\) | 1s | -498.21184     | 9.68316        | -488.52868     | 244.26434      | -244.26434    |
|      | 2s    | -98.51136      | 1.91282        | -96.59854      | 48.29927       | -48.29927     |
|      | 3s    | -29.1968       | 0.60479        | -28.59201      | 14.296005      | -14.296005    |
|      | 2p    | -284.45568     | 31.28505       | -253.17063     | 126.585315     | -126.585315   |
|      | sum   | -910.37568     | 43.48582       | -866.88986     | 433.44493      | -433.44493    |
Fig (1): Relation between the one particle radial density distribution function $D(r_1)$ and the position $(r_1)$
1) From table (1) and Fig. (1) observed when the distance equal to zero from the nucleus, the probability of finding an electron equal to Zero \( \text{when } r = 0 \) \( D(r_1) = 0 \). This means that the electron is not found in the nucleus and when the distance is far from nucleus, the probability of finding an electron equal to Zero also \( \text{when } r = \infty \) \( D(r_1) = 0 \). That means the electron is not found out the atom.  

2) when the positions of maximum values decrease when atomic number increases. these results agree with Coulomb law because increasing in attraction force leads to decreasing in the positions towards the nucleus  

3) When \( r_{12} = 0 \), \( f(r_{12}) = 0 \), and when \( r_{12} = \infty \), \( f(r_{12}) = 0 \), because the coulomb interaction neglect, when the distance between two electrons is very large.
4) In the framework, we found the one-particle expectation value $\langle r_1^n \rangle$ increases when the atomic number $Z$ increases, when $n$ take negative values -2,-1 , where the $\langle r_1^{-1} \rangle$ related to the attraction energy expectation value $\langle V_{en} \rangle = -Z \left[N\langle r_1^{-1} \rangle\right]$ , $N$ represents the number of electrons in the shell(the number of electrons in the Present work=2 for atom)

5) The attraction energy expectation values($V_{en}$) are larger than the repulsion energy expectation value $\langle V_{ee} \rangle$ because the distances between the electrons and the nucleus are smaller than the distances between the electrons

Conclusions

From these results, we Conclude

1) when the atomic number $Z$ increases , for approximations the one- particle radial density distribution function $D(r_1)$ and the inter-particle distribution function $f(r_{12})$ are increased.

2) When $Z$ increases the positions of these maximum values for approximations the one-particle radial density distribution function $D(r_1)$ ,and inter-particle distribution function $f(r_{12})$ decreases.

3) For both one-particle expectation $\langle r_1^m \rangle$ , and two particle expectation $\langle r_{12}^m \rangle$ increase when $Z$ increase and when $m = -2,-1$ and both decrease for $m = +2 ,+1$

4) The standard deviation of one– particle $\Delta r_1$ and two-particle $\Delta r_{12}$ decreases for all systems when the atomic number increases .

5) All the expectation values of the energies($V_{en}$),$\langle V_{ee} \rangle$, $\langle V \rangle$, $\langle T \rangle$ and $\langle E \rangle$ , and increase when the atomic number increases.

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