Evaluation the Atomic Properties in Momentum Space for Three-electron Systems (Z=10-14) using Hartree-Fock Method

Qassim Shamkhi. AL – Khafaji
Department of physics, Kufa University, Iraq
qasimsh-alkhafaji@uokufa.edu.iq

Abstract
In this paper we study the atomic properties for three-electron systems Ne+7, Na+8, Mg+9, Al+10 and Si+11 in momentum space like one-electron radial density function $D(p_1)$, inter-electron distribution function $f(p_{12})$, Fermi hole $\Delta f_{12}(p_{12})$, one-particle expectation value $(p^n_1)$, inter-particle expectation value $(p^n_{12})$, for $n=-2$ to 2. All properties calculated using atomic units.

Keywords: Hartree-Fock, momentum space, atomic properties.

Introduction
Quantum mechanics play a fundamental role in the description and understanding of physical and chemical phenomena [Schweizer, 2002]. It is the set of laws governing the behavior of very small particles including electrons and atomic nuclei. At this small scale the usual laws of classical mechanics fail to provide an accurate description of the behavior of matter [Hill, 2010]. In 1926 Erwin Schrodinger developed an equation, called a wave equation, to describe the behavior of matter wave. By using Schrodinger's equations scientists can find the wave function which solves a particular problem in quantum mechanics. Unfortunately, it is usually impossible to find an exact solution to the equation, so certain assumptions are used in order to obtain an approximate answer for the particular problem [Iqbal, 2012]. The Hartree–Fock method (HF) is widely employed for calculations of various properties of multi-electron systems because of its internal logical rigidity and relative simplicity. It is noteworthy that the HF method enables calculation not only of the ground state but also excited states of atoms and ions, the symmetry of which differs from that of the ground state. Thus, many excited configurations giving excited states can be examined for any system [Malykhanov et al., 2008].

Theory
The Hartree-Fock approach is a method for obtaining approximate total wave functions for many-electron systems. It has been applied successfully to many areas of quantum mechanics including atomic, molecular, and solid-state systems nuclear, elementary particle fields. The method is based on both the central field approximation and the variation principle. In the central field approximation electrons are assumed to move independently of each other in an average field due to the nucleus; the other electrons are with additional assumption that the average potential is spherically symmetric [Al-Hayani 2006]. The wave function $\Psi(r_1, \ldots, r_N)$ representing the whole
electron gas is expressed as a product of \( N \) wave functions representing each electron [Sée et al., 2002].

\[
\Psi(r_1, \ldots, r_N) = \psi_1(r_1) \times \cdots \times \psi_N(r_N)
\] ..........................(1)

The basis function as a standard normalized Slater–type orbital (STO's), which is given without spin in momentum space by [E.M.Al-Robayi 2006].

\[
\chi_{nlm}(\vec{p}) = R_{nl}(\vec{p}) Y_{lm}(\theta)
\] ..............................(2)

Where \( \chi_{nlm}(\vec{p}) \) is the basis function and \( R_{nl}(\vec{p}) \) is the radial factor which describes how the wave function \( \Psi \) of the electron varies with distance from the nucleus, and the angular factor \( Y_{lm}(\theta) \).

Where \( N_{nlm} \) is a normalized constant given by [E.M.Al-Robayi 2006].

\[
N_{nlm} = \left( \frac{2\xi_{nl}}{n!} \right)^{n+0.5} \frac{1}{[(2n)!]^0.5}
\] ................................(3)

The normalized factor \( N_{nlm} \) and the radial part of the various STO's used in this work [E.M.Al-Robayi 2006].

a- for 1s orbital the normalized factor \( N_{nlm} = \sqrt{4\xi^2} \) and radial part of the various STO's:

\[
A^{-2}
\]

b- for 2s orbital the normalized factor

\[
N_{nlm} = \sqrt{4\xi^2 / 3} A^{-2}
\]

where \( A = \xi^2 + p^2 \)

where \( \xi \) is orbital exponent.

**Atomic properties**

*a- One-particle radial density distribution function \( D(p_1) \):*

The one–particle radial density function is very important for study the electrons in an atom, which means the probability of finding electrons in each shell [Al-Hayhani 2002]. The one–particle radial density function for each shell is [Al-Robayi 2006]:

\[
D(p_k)_{K(1S)} = R_{1S}^2(p_1) p_1^2
\] ........................................(4)

\[
D(p_k)_{KL(1S)} = \frac{1}{2} p_1^2 [R_{1S}^2(p_1) + R_{2S}^2(p_2)]
\] ..............................(5)
b- Inter -electron distribution function $f(p_{12})$ and Fermi hole $\Delta f_{KL}(p_{12})$:

Inter –electron distribution function can be defined as the measure of the probability distance between two electrons $i$ and $j$ respectively[ H.S.abdul baqi 2010 ]. Inter–electron distribution function $f(p_{12})$ is given by[ F. W. King et al 1991]:

$$f(p_{12}) = 0.5 \cdot p_{12} \left[ \int_{0}^{p_{12}} p_{1} dp_{1} \int_{|p_{1}+p_{2}|}^{|p_{1}-p_{1}|} \Gamma(p_{1}, p_{2}) p_{2} dp_{2} + \int_{p_{12}}^{\infty} \int_{|p_{2}|}^{|p_{12}+p_{2}|} \Gamma(p_{1}, p_{2}) p_{2} dp_{2} \right]$$ ................................(6)

Where $\Gamma(p_{1}, p_{2})$ is The electron pair density function that deserves much study because the concept of electron pairs is fundamental to chemistry[Ajit.J.Thakkar 2003 ]. A Fermi hole refers to the probability of finding two electrons together with the same spin, can be studied as a difference between the triplet state $KL(3S)$ and singlet state $KL(1S)$ for the inter-particle distribution function [Al-Robayi 2007; Al-Bayati et al., 2005 ].

$$\Delta f_{KL}(p_{12}) = f_{KL}(3S) (p_{12}) - f_{KL}(1S) (p_{12})$$ ..................................(7)

c- One – particle expectation value $\langle p_{1}^{n} \rangle$ and Inter – particle expectation value $\langle p_{12}^{n} \rangle$ :

The one-particle expectation value is defined by [Esquivelt et al., 1992 ]:

$$\langle p_{1}^{n} \rangle = \int_{0}^{\infty} D(p_{1}) p_{1}^{n} dp_{1}$$ ...........................................(8)

The inter – particle expectation value $\langle p_{12}^{n} \rangle$ is given by [King, 1991 ]:

$$\langle p_{12}^{n} \rangle = \int_{0}^{\infty} f(p_{12}) p_{12}^{n} dp_{12}$$ .........................................................(9)

Results and discussion

Table (1) shows the values of maximum one – particle density function $D_{max}(p_{1})$ in momentum space corresponding of momentum values for individual shells $(K, KaLa, KβLa)$, from these results we noted as atomic no. increases the values of $D_{max}(p_{1})$ decreases for each shell, while the values of momentum increase because that increase the attraction force which leads to decreases in the distance between the nucleus and the electrons, in order to overcome to it’s the momentum will be increased.

Fig. (1) and Fig. (2) represented the values of $p_{1}$ scaled plots of the $D(p_{1})$ for K-shell and $(KaLa≡KβLa )$ respectively. It is to be noted these as Z. increases note only dose $D(p_{1})$ becomes more diffuse but also decrease in magnitude.

Table (2), shows the values of maximum of inter –particle density function $f(p_{12})$ corresponding of the inter particle momentum values $p_{12}$, fig.(3), fig.(4) and fig.(5)
represented the $p_{12}$ scaled plots of $f(p_{12})$ for $K$- shell , $KaLa$-shell and $K\beta La$ –shell , respectively . The behavior of function $f(p_{12})$ is the same of $D(p_1)$ but noted at small $p_{12}$, the $KaLa$-shell curves give a flat region due to the presence of the Fermi effect .

Table (3), indicates the radius of Fermi hole $\Delta f_{KL}(p_{12})$ for studied systems, fig.(6) shows the relation between $\Delta f_{KL}(p_{12})$ and $p_{12}$, by investigated these results we noted that the values of radius of Fermi hole increase as $Z$ increases .

Table (4), which represented the relation between one- particle expectation values of momentum for different values of $n$ with atomic number for each shell and the average, while the table (5) represented the relation between inter- particle expectation values of momentum for the same values of $n$ with atomic number for each shell and the average of the system.

From tables (4) and (5) we noted when $n$ negative is ( $n$=-2, -1 ), the values of $(p_{11}^n)$ and $(p_{12}^n)$ decreases for each shell and average of each system as atomic no. increases, while these increases are when they take positive values ( $n$= 1, 2 ).

The interpretation of these is results due to as $Z$ increase the distance between the nucleus and the electron also the distance between two electrons decrease which lead to increases the velocity and the momentum for overcome to the attraction energy.

Table(1): Values of momentum $p_1$ corresponding to maximum values $D(p_1)$ for studied systems.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$K$-shell</th>
<th>$KaLa$-Shell ≡$K\beta La$-Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_1$</td>
<td>$D_{max}(p_1)$</td>
<td>First peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$p_1$</td>
</tr>
<tr>
<td>Ne$^{+7}$</td>
<td>5.48</td>
<td>0.12001</td>
</tr>
<tr>
<td>Na$^{+8}$</td>
<td>5.99</td>
<td>0.11088</td>
</tr>
<tr>
<td>Mg$^{+9}$</td>
<td>6.62</td>
<td>0.10147</td>
</tr>
<tr>
<td>Al$^{+10}$</td>
<td>7.18</td>
<td>0.09464</td>
</tr>
<tr>
<td>Si$^{+11}$</td>
<td>7.76</td>
<td>0.09069</td>
</tr>
</tbody>
</table>

Table(2): Values of momentum $p_{12}$ corresponding to maximum values $f(p_{12})$ for studied systems.
### Table (3) : The radius of Fermi hole $\Delta f_{KL}(p_{12})$ using Hartree-Fock approximation for studied systems.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$p_{12}$</th>
<th>$f_{\text{max}}(p_{12})$</th>
<th>$p_{12}$</th>
<th>$f_{\text{max}}(p_{12})$</th>
<th>$p_{12}$</th>
<th>$f_{\text{max}}(p_{12})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne$^{7+}$</td>
<td>8.77</td>
<td>0.08214</td>
<td>6.73</td>
<td>0.11815</td>
<td>5.81</td>
<td>0.11619</td>
</tr>
<tr>
<td>Na$^{8+}$</td>
<td>9.67</td>
<td>0.07592</td>
<td>7.47</td>
<td>0.10809</td>
<td>6.44</td>
<td>0.10696</td>
</tr>
<tr>
<td>Mg$^{9+}$</td>
<td>10.59</td>
<td>0.06949</td>
<td>8.21</td>
<td>0.09886</td>
<td>7.06</td>
<td>0.09845</td>
</tr>
<tr>
<td>Al$^{10+}$</td>
<td>11.49</td>
<td>0.06482</td>
<td>8.95</td>
<td>0.091627</td>
<td>7.67</td>
<td>0.09168</td>
</tr>
<tr>
<td>Si$^{11+}$</td>
<td>12.39</td>
<td>0.06212</td>
<td>9.69</td>
<td>0.08632</td>
<td>8.28</td>
<td>0.08676</td>
</tr>
</tbody>
</table>

### Table (4): Expectation values of $p_{1}$ for each individual shell and the average for studied systems.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Shell</th>
<th>$\langle p_{1}^{-2} \rangle$</th>
<th>$\langle p_{1}^{-3} \rangle$</th>
<th>$\langle p_{1}^{1} \rangle$</th>
<th>$\langle p_{1}^{2} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne$^{7+}$</td>
<td>K</td>
<td>0.05929</td>
<td>0.19106</td>
<td>8.76519</td>
<td>100.10868</td>
</tr>
<tr>
<td></td>
<td>KaLa=KβLa</td>
<td>0.41226</td>
<td>0.44356</td>
<td>5.25772</td>
<td>51.11789</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.29460</td>
<td>0.35939</td>
<td>6.42670</td>
<td>67.44815</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.0496</td>
<td>0.17642</td>
<td>9.85348</td>
<td>124.02786</td>
</tr>
<tr>
<td>Na$^{8+}$</td>
<td>KαLα≡KβLα</td>
<td>0.33321</td>
<td>0.40096</td>
<td>5.86328</td>
<td>62.78656</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.23867</td>
<td>0.32612</td>
<td>7.19334</td>
<td>83.20032</td>
</tr>
<tr>
<td>Mg$^{9+}$</td>
<td>K</td>
<td>0.04147</td>
<td>0.16142</td>
<td>10.78288</td>
<td>148.34009</td>
</tr>
<tr>
<td></td>
<td>KaLa=KβLα</td>
<td>0.27486</td>
<td>0.36556</td>
<td>6.43240</td>
<td>75.14225</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.19706</td>
<td>0.29751</td>
<td>7.88256</td>
<td>99.54153</td>
</tr>
<tr>
<td>Al$^{10+}$</td>
<td>K</td>
<td>0.03560</td>
<td>0.15072</td>
<td>11.84657</td>
<td>176.78362</td>
</tr>
<tr>
<td></td>
<td>KaLa=KβLα</td>
<td>0.23076</td>
<td>0.33625</td>
<td>7.03265</td>
<td>89.06428</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.16570</td>
<td>0.27440</td>
<td>8.63729</td>
<td>118.30406</td>
</tr>
<tr>
<td>Si$^{11+}$</td>
<td>K</td>
<td>0.03161</td>
<td>0.14417</td>
<td>13.18496</td>
<td>211.95680</td>
</tr>
<tr>
<td></td>
<td>KaLa=KβLα</td>
<td>0.19662</td>
<td>0.31205</td>
<td>7.69469</td>
<td>105.08239</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.141616</td>
<td>0.25609</td>
<td>9.52478</td>
<td>140.70719</td>
</tr>
</tbody>
</table>

### Table (5) : Expectation values of $p_{12}$ for each individual shell and the average studied systems.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Shell</th>
<th>$\langle p_{12}^{-2} \rangle$</th>
<th>$\langle p_{12}^{-1} \rangle$</th>
<th>$\langle p_{12}^{1} \rangle$</th>
<th>$\langle p_{12}^{2} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.02446</td>
<td>0.12490</td>
<td>12.80160</td>
<td>200.21761</td>
<td></td>
</tr>
<tr>
<td>KaLa</td>
<td>0.02475</td>
<td>0.13868</td>
<td>9.20510</td>
<td>109.68493</td>
<td></td>
</tr>
</tbody>
</table>
**Fig. (1):** The relation between one-particle radial density function $D(p_1)$ and $p_1$ for K-shell in momentum space.
Fig.(2): The relation between one-particle radial density function $D(p_1)$ and $p_1$ for (KαLα≡KβLα-shell ) in momentum space

Fig.(3): The relation between inter-particle distribution function $f(p_{12})$ and $p_{12}$ for (K-shell) in momentum
Fig.(4): The relation between inter-particle distribution function $f(p_{12})$ and $p_{12}$ for (KαLα-shell) in momentum space.

Fig.(5): The relation between inter-particle distribution function $f(p_{12})$ and $p_{12}$ for (KβLα-shell) in momentum space.
Fig.(6):Fermi hole as a difference between the inter – particle distribution function $f(p_{12})$ of KαLα- shell and KβLα- shell in momentum space.

Conclusions

1- The maximum value of $D(p_1)$ decreases as the atomic number ($Z$) increases and the location of these maximum increases.
2- The maximum probability of pair distribution function $f(p_{12})$ decreases as atomic number increases ,while the locations of their maxima increases.
3- The radius of Fermi hole increases and the depth of them decreases as $Z$ increases.
4- For each shell as $Z$ increases the one particle radial expectation values decreases when $n$ takes negative values -1 and -2 ,and increases when $n$ take positive values 1 and 2.
5- For $n=1,2$ the inter-particle expectation values $(\langle p_{12}^n \rangle)$ increase by increasing the atomic number and decrease when $n$ takes the values -1,-2.

References