
COMPUTATION THE HARTREE-FOCK ENERGY OF GROUND STATE FOR BORON ATOM AND ISO ELECTRONIC SERIES

Abstract: Partition method have been used to calculate the Hartree-Fock energy of ground state for Boron atom and like ions such as C+1 and N+2 in addition to study some important atomic properties using Hartree – Fock approximation in position space. Finally all the studied properties are calculated using atomic units.

Key words: Hartree- Fock approximation, position space, Atomic properties, Electronic series.

Language: English


Introduction

Hartree-fock atomic wave function are independent-particle-model approximations to the nonrelativistic Schrodinger’s equation for stationary states . the use of Slater determinants accounts for the Pauli principle ,and for an N-electron system the HF equations yield N Hartree – Fock spin orbitals. In conventional Hartree-Fock calculation, the spin orbitals are expressed as products of a radial function times spherical harmonic times a spin function, the radial functions are taken to depend only on the quantum numbers $n$ and $\ell$, and the total wave function is required to be an Eigen function of the total orbital and spin angular momentum ; the form of the spin orbitals guarantees that $L_z$, $S_z$, and parity are good quantum numbers. Conventional HF is also known as restricted HF [1].

Schrödinger equation was formulated by the Austrian physicist Erwin Schrödinger it describes how the quantum states of a physical systems changes in time. It is also called wave function an state vector [2]. The wave function $\Psi$, sometimes known as the state function of a system is a function of each particles coordinates (position and spin) and time, it provides a complete description of quantum system [3]. It is well known that the computation of atomic and molecular multielectron properties requires solutions of the Schrödinger equation more accurate than the results obtained from the hartree-fock (HF) equation. The variation method for improving the HF solution in which the interelectronic coordinates are explicitly included in the wave function was first introduced by Hylleraas [4]. The Hartree-Fock (HF) method gives roughly 99% of the total electronic energy where ignores the correlation between electronic [5].

Theory

The two-particle radial density distribution function $D(r_1,r_2)$, is the measure of probability of finding two-electrons simultaneously and their radial coordinates are in the range $r_1$ to $r_1+dr_1$, and $r_2$ to $r_2+dr_2$, or is the probability density of finding an electron at a radius $r_1$ and another electron at $r_2$ simultaneously. This function is related by other function is called the two-particle radial density distribution function, that could tell us about how the different movements of the two electron as a result of mutual influence between them, as well as in the stabilization of one electron and noticing the change in the conduct of the another. And can be used in the calculation of the one–electron radial distribution function $D(r_i)$. The two-particle radial density distribution function $D(r_1,r_2)$ is defined as [6].

\[
D(r_1,r_2) = \left( \frac{N!}{2} \right) r_1^2r_2^2 \int |\psi(x_1,...,x_N)|^2 \, dx_3,...,dx_N d\Omega_3 d\Omega_2
\]
Where \((r_1, O_1)\) is the polar coordinate of the vector \(r\), it can be written \(D(r_1, r_2)\) as [7]

\[
D(r_1, r_2) = \int \Gamma(r_1, r_2) r_1^2 r_2^2 dO_1 dO_2
\]  

(2)

Where \(\Gamma(r_1, r_2)\) is define two-particle density, by integrate \(D(r_1, r_2)\) over the second electron we get of the one–electron radial density distribution function \(D(r_1)\) represents the probability density function of finding an electron at a distance \(r\) from the coordinate origin, i.e., the nucleus.

The usefulness from the expense the one–electron radial density distribution function \(D(r_1)\) in the determination of the expectation value for one-electron \(\langle r_1^n \rangle\).

\[
\langle r_1^n \rangle = \int_{-\infty}^{\infty} D(r_1) r_1^n dr_1
\]  

(3)

A measure of the spread or diffuseness of the one–particle radial density distribution function \(D(r_1)\), may be obtained by evaluating \(\Delta r_1\), the root-mean-square deviation is defined as [8].

\[
\Delta r_1 = [\langle r_1^2 \rangle - \langle r_1 \rangle^2]^{1/2}
\]  

(4)

\[
f(r_{12}) = 0.5 \times r_{12} \left[ \int_{r_{12} - r_1}^{r_{12}} \int r_2 R^2_{12}(r_1) R^2_{12}(r_2) r_2 dr_2 \right] + \int_{r_{12} + r_1}^{\infty} \int r_2 R^2_{12}(r_1) R^2_{12}(r_2) r_2 dr_2
\]  

(6)

The inter-particle expectation value \(\langle r_{12}^n \rangle\) is given by the relation [11].

\[
\langle r_{12}^n \rangle = \int_{0}^{\infty} f(r_{12}) r_{12}^n dr_{12}
\]  

(7)

The spread or diffusion of the inter-particle distribution function \(f(r_{12})\) about the mean value \(\langle r_{12}^n \rangle\) is given by the standard deviation \(\Delta r_{12}\) which is defined as

\[
\Delta r_{12} = [\langle r_{12}^2 \rangle - \langle r_{12} \rangle^2]^{1/2}
\]  

(8)

\(\Delta r_{12}\) will determine the diffuse of the electron-electron distribution function \(f(r_{12})\) for each shell.

The total energy \((E)\) corresponds to the expectation value of the Hamiltonian with respect to \(\psi\) given by [13]

\[
\langle E \rangle = \left\langle \psi \left| \sum_{i=1}^{N} \left( -\frac{Z}{r_i} - \frac{1}{2} \nabla_i^2 + \frac{1}{r_{ij}} \right) \right| \psi \right\rangle
\]  

(9)

Notice that [14]:

\[
\langle T \rangle = -\frac{1}{2} \int \psi^* \left( \sum_{i=1}^{N} \nabla_i^2 \right) \psi d\tau
\]  

(10)

Another function related with \(\Gamma(r_1, r_2)\) is the radial electron-electron distribution function, which describes the probability of locating two electrons separated by distance \(r_{12}\) from each other, was first introduced by Coulson and Neilson in their study of electron correlation for He(1S) in the ground state. For atoms with more than two electrons, the radial electron-electron distribution function has a very convenient and unambiguous formulation in terms of the two-particle density matrix [9]:

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

(5)

\(f(r_{12})\) representing a function of the distribution of the distance between electron 1 and electron 2 (this quantity fully determines the expectation value of the electronic Coulomb repulsion). It can be used in the calculation of the inter-particle expectation value \(\langle r_{12}^n \rangle\) for two-particle, and used for the calculation Fermi hole and coulomb hole, \(r_{12}\) is the inter-particle distance \(r_{12} = |r_1 - r_2|\). The inter-particle distribution function \(f(r_{12})\) is defined as[10].

\[
\langle V \rangle = \int \psi^* \left[ \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i<j}^{N} \frac{1}{r_{ij}} \right] \psi d\tau
\]  

(11)

Where:

\[
< V_{ee} > = \int \psi^* \sum_{i<j}^{N} \left| \frac{1}{r_{ij}} \right| \psi d\tau
\]  

(12)

\[
< V_{en} > = \int \psi^* \sum_{i}^{N} \left| -\frac{Z}{r_i} \right| \psi d\tau
\]  

(13)

If an N-electron atomic wave function satisfies the virial theorem then the energy expectation value is related to the potential energy by

\[
\langle E \rangle = \frac{1}{2} \langle V \rangle
\]  

(14)

**Results and discussion**

Table 1 show that the results of one-particle expectation values for different powers \((n=-2\) to \(2)\) in addition to calculate the standard deviation for intra shells \(K_{1s}\), \(K_{1p}\), \(L_{2s}\), \(L_{2p}\), \(L_{2p}\), by comparing these results with published papers have been obtain good agreement. From this table, we noted effect the increase in atomic number with fixed the number of electrons, where observed when \(n\) takes negative values the expectation values of \(\langle r_1^n \rangle\) increase with increasing the atomic number for each shell, the values of \(\langle r_1^{-1} \rangle\) refer to attractive energy between the nucleus and the electron, while
when n takes positive values the expectation values of \( \langle r_1^2 \rangle \) are decreases because the distance between the electron and the nucleus become smallest as nuclear charge increases, also noted that the values of \( \langle r_1 \rangle \) for all systems because the attractive energy for K1s \( \beta \) is largest from another shells. The values of standard deviation are decreases as atomic number increase, also noted for each shell the maximum values of D(r1) increases when atomic number increase and location of these peaks contracted to ward of the nucleus, also observed the value of D(r1) vanishes when the distance equal zero or infinity, in the figure (1B) noted two peaks, the first represent the probability of finding the electron in small distance from the nucleus and the second represent the probability of finding the electron in 2s shell. Figure 2 represented the relation between the radial electron-electron distribution function D(r1) with the position for 1s, 2s and 2p shells respectively, where noted for each shell the behavior of D(r1) but observed in figure(2C) small peak at small distance, this results from Fermi hole.

### Table 1

**Results of one–particle expectation values and the standard deviation.**

<table>
<thead>
<tr>
<th>System</th>
<th>Shell</th>
<th>( \langle r_1^{-2} \rangle )</th>
<th>( \langle r_1^{-1} \rangle )</th>
<th>( \langle r_1 \rangle )</th>
<th>( \langle r_1^2 \rangle )</th>
<th>( \Delta r_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>K1s1b, K1b</td>
<td>44.538805</td>
<td>4.67439</td>
<td>0.32587</td>
<td>0.14336</td>
<td>0.19280</td>
</tr>
<tr>
<td>Ref.[15]</td>
<td></td>
<td>44.53802</td>
<td>4.67433</td>
<td>0.32586</td>
<td>0.14336</td>
<td>0.89462</td>
</tr>
<tr>
<td>L2s1b, L2b</td>
<td>2.02448</td>
<td>0.71288</td>
<td>1.97706</td>
<td>4.70913</td>
<td>0.89462</td>
<td></td>
</tr>
<tr>
<td>Ref.[1]</td>
<td></td>
<td>2.02447</td>
<td>0.71288</td>
<td>1.97706447</td>
<td>4.70912</td>
<td></td>
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<tr>
<td>L2p1b</td>
<td>0.52988</td>
<td>0.605007</td>
<td>2.20475</td>
<td>6.14607</td>
<td>1.13362</td>
<td></td>
</tr>
<tr>
<td>Ref.[15]</td>
<td></td>
<td>0.52988</td>
<td>0.605005</td>
<td>2.20475</td>
<td>6.14609</td>
<td></td>
</tr>
<tr>
<td>C+1</td>
<td>K1s1b, K1b</td>
<td>65.30838</td>
<td>5.66861</td>
<td>0.26811</td>
<td>0.09688</td>
<td>0.15810</td>
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<td>L2s1b, L2b</td>
<td>3.71798</td>
<td>0.96118</td>
<td>1.47558</td>
<td>2.58986</td>
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<td>L2p1b</td>
<td>1.10361</td>
<td>0.88538</td>
<td>1.47873</td>
<td>2.68530</td>
<td>0.72063</td>
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<td>N+2</td>
<td>K1s1b, K1b</td>
<td>90.66488</td>
<td>6.66398</td>
<td>0.22767</td>
<td>0.06977</td>
<td>0.13392</td>
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<td>L2s1b, L2b</td>
<td>5.93078</td>
<td>1.21136</td>
<td>1.17884</td>
<td>1.64273</td>
<td>0.50305</td>
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<td>L2p1b</td>
<td>1.84150</td>
<td>1.15110</td>
<td>1.190578</td>
<td>1.54417</td>
<td>0.53709</td>
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</table>

### Table 2

**Results of inter–particles expectation values and the standard deviation.**

<table>
<thead>
<tr>
<th>System</th>
<th>Shell</th>
<th>( \langle r_{12}^{-2} \rangle )</th>
<th>( \langle r_{12}^{-1} \rangle )</th>
<th>( \langle r_{12} \rangle )</th>
<th>( \langle r_{12}^2 \rangle )</th>
<th>( \Delta r_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>K1s1b, K1b</td>
<td>14.40483</td>
<td>2.89205</td>
<td>0.47651</td>
<td>0.28672</td>
<td>0.24425</td>
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<tr>
<td>K1s1b , L2s1b= K1b, L2b</td>
<td>0.47459</td>
<td>0.61005</td>
<td>2.01279</td>
<td>4.85249</td>
<td>0.89507</td>
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<tr>
<td>K1s1b, L2s1b=K1s1b, L2b</td>
<td>0.83853</td>
<td>0.64863</td>
<td>2.00848</td>
<td>4.85249</td>
<td>0.90470</td>
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<tr>
<td>K1s1b, L2p1b=K1b, L2p1b</td>
<td>0.55863</td>
<td>0.60013</td>
<td>2.23350</td>
<td>6.28944</td>
<td>1.14057</td>
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<tr>
<td>L2s1b, L2b</td>
<td>0.34455</td>
<td>0.46026</td>
<td>2.80505</td>
<td>9.41825</td>
<td>1.24496</td>
<td></td>
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<tr>
<td>L2s1b, L2p1b= L2b, L2p1b</td>
<td>0.30677</td>
<td>0.43734</td>
<td>2.99034</td>
<td>10.25520</td>
<td>1.14956</td>
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<tr>
<td>C+1</td>
<td>K1s1b, K1b</td>
<td>21.22107</td>
<td>3.51266</td>
<td>0.39190</td>
<td>0.19376</td>
<td>0.20043</td>
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<tr>
<td>K1s1b, L2s1b= K1b, L2b</td>
<td>0.81242</td>
<td>0.80316</td>
<td>1.50821</td>
<td>2.68675</td>
<td>0.64191</td>
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<tr>
<td>System</td>
<td>Shell</td>
<td>(\langle V_{ee} \rangle)</td>
<td>(\langle V_{en} \rangle)</td>
<td>(\langle V \rangle)</td>
<td>(\langle T \rangle)</td>
<td>(\langle E \rangle)</td>
</tr>
<tr>
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<td>B</td>
<td>K_{1g} K_{1g}</td>
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<td>-46.7434</td>
<td>-43.8513</td>
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<td>N^2</td>
<td>K_{1g} K_{1g}</td>
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<td>1.23876</td>
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<td>0.71473</td>
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<td>L_{2p} L_{2p} = L_{2p} L_{2p}</td>
<td>0.97410</td>
<td>0.78706</td>
<td>1.63347</td>
<td>3.18691</td>
<td>0.72019</td>
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</table>

Table 3: The expectation values of the energies for studied systems.
Figure 1 - The relation between one-electron radial density distribution function with the position
(A) $K_{1s}K_{1s}$, (B) $L_{2s}L_{2s}$ and (C) $L_{2p_0}$.
Figure 2 - The relation between the radial electron-electron distribution function with the distance between two electron

(A) $K_{1s}K_{1\beta}$, (B) $K_{1s}L_{2\alpha}=K_{1\beta}L_{2\phi}$, (C) $K_{1s}L_{2\beta}=K_{1\beta}L_{2\alpha}$,
(D) $K_{1s}L_{2\alpha}=K_{1\beta}L_{2\phi}$, (E) $L_{2s}L_{2\alpha}$, and (F) $L_{2s}L_{2\beta}=L_{2\phi}L_{2\alpha}$. 

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**Conclusions**

From these results, it can be concluded that the expectation values of \( \langle r_{1}^{n} \rangle \) and \( \langle r_{2}^{n} \rangle \) increase when \( n \) takes negative values and the inverse holds for positive values as atomic number increases while the expectation values of all energies are increase as nuclear charge increase and the results of total energy for studied systems agreement with the published papers, the maximum values of \( D(r_{1}) \) and \( f(r_{12}) \) increase and the locations of these peaks decreases as atomic number increase.

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**References:**