

PARTIAL DISTRIBUTION FUNCTION AND RADIAL STATISTICAL COEFFICIENTS FOR Be-ATOM

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ABSTRACT

Approximation calculations using Hartree-Fock wave function are carried out on the 2^2S ground state for the Beryllium atom in position space .For each shell in this atom the partial distribution function, radial statistical coefficients, density distributions and expectation values are studied .This properties are achieved from the partitioned form of the density distribution. The effects of the electron–spin in both inter-and intra-shell on the above properties is taken into account.

الخلاصة

اجريت في هذا البحث حسابات تجريبية استخدمت فيها الدالة الموجية لهارترى – فوك لدراسة المستوى الارضي لذرة البريليوم في فضاء الموقع. ولكل قشرة من قشر هذا النظام تم دراسة دالة توزيع الكثافة الجزئية والمعاملات الستاتيكية الشعاعية ودالة توزيع الكثافة والقيم المتوقعة . تم انجاز الخصائص المدروسة اعلاه باستخدام صيغة التجزئة لتوزيع الكثافة ،وقد تم في هذه الدراسة الاخذ بعين الاعتبار تأثير برم الالكترن لجميع القشر والقشر الداخلية مع مقارنة النتائج مع النتائج العالمية المتاحة.

INTRODUCTION

One of the first and most simple approximations aimed to solve the problem arise from repulsive of electrons in many electron system is due to Hartree in 1927 ⁽¹⁾. In this approximation ,the total wave function is constrained to be a product of N one-electron orbitals where the spin of electrons and the anti- symmetry are not take into account . The most property which is neglected by Hartree it is the indistinguishability of the electrons, and this noticed independently by Fock ⁽²⁾ and Slater ⁽³⁾ in 1930, and it was corrected again to takes the form of a so-called Slater determinant (see equation 1).

The mathematical consequence of the indistinguishability among a set of N -quantum object of the same type (such electrons,...etc) is the requirement that the total N -particle wave function after exchange any pair of a particles coordinates must either remain unchanged (symmetric), in this case, the particles are bosons and must have integer spin, or change sign (anti-symmetric) and a particles her called fermions and have semi-integer spin. Since the electrons are fermions, therefore, the total wave function must be anti-symmetric under the exchange of any pair of electrons ⁽⁴⁾. Thus, this property cannot satisfy by the Hartree product, but it is satisfy by linear combination form, which proposed by Slater determinant.

Many studies deal with the distribution function $g(r_{12}, r_1)$, Banyard and Mobbs ⁽⁵⁾ used the HF and CI systems in their studying for this function and determined the partial coulomb hole $\Delta g(r_{12}, r_1)$ for Be atom, Banyard and Reed ⁽⁶⁾ studied this distribution function by using of (FNC) and HF wave functions for HeH^+ , Al-Bayati and Banyard ⁽⁷⁾ used the CI and HF wave functions through their studying of Li-like ions in first excited state. Statistical correlations between electrons can be studies in many ways, Cooper and Pounder ⁽⁸⁾, Sharma and Thakkar ⁽⁹⁾ studied this correlation by analyzing electron correlation holes, Sanders and Banyard ⁽¹⁰⁾, Wang et al ⁽¹¹⁾ and Koga ⁽¹²⁾ examining the pair correlation density itself.

In the present paper we apply the $g(r_{12}, r_1)$ and the idea of Kutzelnigg et al ⁽¹³⁾ for statistical correlation to the ground state of Be-atom by using of HF wave function. To study these properties in depth we used portioning technique and represent the distribution function as a surface and contour diagrams.

THEORY AND WAVEFUNCTION

In the Hartree-Fock system, the total anti-symmetric wave functions written as Slater determinant⁽¹⁴⁾:-

$$\Psi(x_1, \dots, x_N) = |\psi_1(x_1), \psi_2(x_2), \dots, \psi_N(x_N)\rangle, \tag{1}$$

In this equation the Dirac notations represent the Slater determinant and the normalization constant (N) , the one-electron orbital, in addition to, normalized property, it is also mutually orthogonal⁽¹⁵⁾

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad i, j = 1, 2, \dots, N \tag{2}$$

Also, we used one-electron wave function ψ_i dependent also on the spin σ , thus, our wave function is spin-orbitals. A general spin-orbital may be written as⁽⁴⁾:-

$$\psi(x) = \alpha(r)\alpha(\sigma) + \beta(r)\beta(\sigma) \tag{3}$$

Where the functions α and β corresponding to the spin-up and spin-down.

Every one-electron orbital function $\varphi(r)$ consists of normalized Slater type orbitals⁽¹⁶⁾:-

$$\varphi_{nml\zeta}(r) = R_n^l(r) Y_l^m(\theta, \phi) \tag{4}$$

Where $R_n^l(r) = N r^{n-1} \exp(-\zeta r)$, $N = (2\zeta)^{-0.5} / \sqrt{(2n)!}$, n, l and m are quantum numbers and ζ is called exponent parameter.

In many electron systems, the Hamiltonian is given by⁽¹⁷⁾:-

$$\hat{H} = \hat{T} + \hat{V}_{eN} + \hat{V}_{ee} = -\sum_{i=1}^N 1/2 \nabla_i^2 - \sum_{i=1}^N Z/r_i + 1/2 \sum_{i \neq j}^N 1/r_{ij} \tag{5}$$

or

$$\hat{H} = \sum_{i=1}^N h_i + 1/2 \sum_{i=1}^N 1/r_{ij} \tag{6}$$

Where r_i in equation (5) is the distance of one electron to the nucleus.

Then:

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_i \langle \Psi | h_i | \Psi \rangle + 1/2 \sum_{i \neq j} \langle \Psi | 1/r_{ij} | \Psi \rangle \tag{7}$$

This leads to:-

$$\langle \hat{H} \rangle = \langle \hat{h}_i \rangle + 1/2 \langle 1/r_{ij} \rangle \tag{8}$$

Now, we will use from the $\langle \hat{h}_i \rangle$ to calculate the expectation value for r_i and then calculates the partial distribution function $g(r_{12}, r_1)$ and radial statistical coefficients.

To satisfy our goal we will use the partitioning technique to studying each two-electron in one shell, and use the wave function in terms of the radial two-particle density distribution $\Gamma_{ij}(r, r_{21})$ which obtained from⁽⁵⁾ :-

$$\Gamma_{ij}(r_1, r_2) = 1/2 [\psi_i(x_1)\psi_j(x_2) - \psi_j(x_1)\psi_i(x_2)]^2 \tag{9}$$

By substituting the equations (3 and 4) in equation (9) and integrating over spin and angular function we can get:-

For intra-shell $K_\alpha K_\beta$ (K^1S) $i = 1, j = 2$:-

$$\Gamma_{12}(r_1, r_2) = R_{1s}^2(r_1) R_{1s}^2(r_2) \tag{10}$$

For inter-shell KL(³S) $i = 1, j = 3$:-

$$\Gamma_{13} = \Gamma_{24} = 1/2 \times \left[R_{1s}(r_1)^2 R_{2s}(r_2)^2 - 2R_{1s}(r_1)R_{2s}(r_1)R_{2s}(r_2)R_{1s}(r_2) + R_{2s}(r_1)^2 R_{1s}(r_2)^2 \right] \quad (11)$$

For inter-shell KL(¹S) $i = 1, j = 4$:-

$$\Gamma_{14} = \Gamma_{23} = 1/2 \times \left[R_{1s}(r_1)^2 R_{2s}(r_2)^2 + R_{2s}(r_1)^2 R_{1s}(r_2)^2 \right] \quad (12)$$

For the intra-shell L(¹S) $i = 3, j = 4$:-

$$\Gamma_{34}(r_1, r_2) = R_{2s}^2(r_1)R_{2s}^2(r_2) \quad (13)$$

Now the partial distribution function is given by :-

$$g(r_{12}, r_1) = 1/2 \left[\int_{|r_{12}-r_1|}^{|r_{12}+r_1|} \Gamma_{ij}(r_1, r_2) r_2 dr_2 \right] r_{12} \quad (14)$$

Where r_{12} is the distance between the two electrons.

For our two-electron shells, the radial statistical coefficients can be introduced as⁽¹⁸⁾:-

$$\tau_r = \frac{(r_1 r_2) - (r_1)^2}{(r_1^2) - (r_1)^2}, \text{ and } \tau_{1/r} = \frac{(r_1^{-1} r_2^{-1}) - (r_1^{-1})^2}{(r_1^{-2}) - (r_1^{-1})^2} \quad (15)$$

Such that the one-electron expectation value in (a.u.) is given by⁽¹⁹⁾:-

$$\langle r_1^2 \rangle = \int_0^\infty \Gamma(r_1) r_1^2 dr_1 \quad (16)$$

$\Gamma(r_1)$ is one-particle radial density and defined as⁽¹⁸⁾ :-

$$\Gamma(r_1) = \int \Gamma(r_1, r_2) dr_2 \quad (17)$$

Finally, our parameters (c, n, ζ) are taken from atomic data and nuclear data tables for Rothaan-Hartree-Fock ground state wave function for Beryllium which cited by Ref.(20) ,and the Mathcad program used her to solve the integrations.

RESULTS AND DISSCUTION

Firstly, we can defined the distribution function $g(r_{12}, r_1)$ to represent the probability of finding an inter-electronic separation r_{12} when a test electron r_1 is located at a distance r_1 from the nucleus, where the nucleus located at the center of coordinates. Also, the integration over $g_{HF}(r_{12}, r_1)$ from $0 \rightarrow \infty$ gives the radial distribution function $D_{HF}(r_1)$ which is normalized to unity. The function $g_{HF}(r_{12}, r_1)$ is important to studying the partial coulomb holes ($\Delta g(r_{12}, r_1) = g_{exact}(r_{12}, r_1) - g_{HF}(r_{12}, r_1)$), these holes are enable us to examine the effect of electron correlation when a test electron is located at a specific distance from the nucleus.

Figure (1-a,b) represents the contour and surface diagrams behavior of $g_{HF}(r_{12}, r_1)$ against (r_{12}, r_1) for $K_\alpha K_\beta$ shell, we see the main characteristic feature located about the diagonal line where $r_{12} = r_1$ and these feature also parallel to the r_{12} axis for small r_1 . For surface diagram, we see that the maximum for $g_{HF}(r_{12}, r_1) = 3.784$ occurs at $r_1 = r_k(K_\alpha K_\beta) = 0.27$, where the r_1 represent the mode of $D_{HF}(r_1)$ for the K-shell, this mean that the higher probability of radial distribution function $D_{HF}(r_1)$ occurs at r_k (see figure 5-a). At this maximum value of $g_{HF}(r_{12}, r_1)$ we note that $r_{12} > r_1$, it is found 0.36. In contour diagram figure (1-a) we can see this behavior, but the maximum value not appears here because we select some contours to get a good picture. It is worth to mention here that the value appear in each contours represent the value of $g_{HF}(r_{12}, r_1)$ for fixed r_1 and various r_{12} .

For inter-shells KL(³S) ($K_\alpha L_\alpha = K_\beta L_\beta$) where the two electrons with same spin direction, figure (2) show us a different behaviors of $g_{HF}(r_{12}, r_1)$, where two main features appear instead of one as in K-shell. These two features are characteristic of an inter-shell distribution⁽²¹⁾. It is clear from the

contour and surface diagrams (3-a, b) that one of these features lie parallel to r_{12} axis starting from small r_{12} with value 0.386 at $r_{12}= 2.04$, $r_1= r_k= 0.26$ and the other along the diagonal axis ($r_{12}=r_1$) with value of 0.368 at $r_{12}= 2.05$ and $r_1= r_L= 2.04$. Also, the r_1 values which located the two maximum values of distribution function are the local K and L-shell modes of $D_{HF}(r_1)$ (see figure 5-b). Because of the same spin components of our two electrons the Fermi effects a raises and the consequence no value of $g_{HF}(r_{12},r_1)$ at small r_{12} for all ranges of r_1 .

The partial distribution function $g_{HF}(r_{12},r_1)$ for inter-shells $KL(^1S)$ ($K_\alpha L_\beta = K_\beta L_\alpha$) represented by figure(3-a,b),this figure shows features similar to those appeared in previous inter- shells but with new feature at a distance close to nucleus. At the diagonal ($r_{12} = r_1$) and parallel axes we see that the maximum distribution is similar to the previous inter-shells in maximum and locations .Since the two electrons with opposite spin direction Fermi effect will not present, hence, additional feature "mini-shell" will appears close to the nucleus. This mini-K-shell with small value of $g_{HF}(r_{12},r_1)$ and same in shape and location the feature of K-shell, it is arise from penetrated of L-shell electron to K-shell then interacted with its electron as a consequence mini-shell seen at a small r_1 and r_{12} .

In the intra-shell (L-shell) the two electrons with the opposite spin direction, then we see that the maximum value of function $g_{HF}(r_{12},r_1)$ is less than those for previous inter-shell, it is 0.100 at $r_1=2.05$ and $r_{12} =2.11$. Figure (4-a, b) show another probability in this shell located at small value of axes, $r_1=0.21$ and $r_{12}=0.43$, the small probability of L-shell a raises from attraction interaction of our electrons because their spins.

For any intershells there is spatial interaction between the two electrons, this interaction so-called electron correlation, it is means that the motion of the electrons are statistically correlated⁽¹⁸⁾ (these effects has been partially taken into account by the Hartree-Fock model). According to standard concept for mathematical statistics and probability theory Kutzelnigg et al.⁽¹³⁾ used the statistical coefficients as a probe for the analysis of electron correlation in the atomic system, depending on some expectation values ,the expectation value $\langle r_1^n \rangle$ and $\langle r_1^n r_2^n \rangle$ for $n =-2 \rightarrow 2$ are listed in tables (1,2).

The spatial correlation can seen in the intershells that occupied by two electrons with same spin components or with opposite components. In these cases, the electrons separated by a distance between each others, therefore, spatial correlation (statistical correlation) will a raise. So, for shells (K or L) the electrons in the same shell, therefore, must be with opposite spin directions as a result, they are suffered from repulsive interaction, then no chance for spatial interaction. The last leads to all the τ for the HF wave function are zero except for the radial coefficients for intershells. Table (3) show us zero value of (K or L) shells and non zero values of intershells.

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Table (1): Some one-particle expectation values for intra-and inter shells of Be-atom.

Shell	$\langle r_1^n \rangle$ a.u.			
	n =-2	n =-1	n =1	n =2
K(¹ S)	27.7533	3.6818	0.4149	0.2329
	27.7590 ^a	3.6819 ^a	0.4149 ^a	0.2330 ^a
KL(¹ S)=KL(³ S)	14.4033	2.1020	1.5321	4.3295
	14.4080 ^a	2.1022 ^a	1.5324 ^a	4.3324 ^a
L(¹ S)	1.0555	0.5224	2.6491	8.4254
	1.0506 ^a	0.5225 ^a	2.6498 ^a	8.4318 ^a
Total ^c	14.4036	2.1020	1.5320	4.3293
	14.4078 ^b	2.1022 ^b	1.5324 ^b	4.3324 ^b

^a from reference(5).

^b calculated for ref.(5).

^c the total listed here is given by 1/6(K(¹S)+L(¹S)+KL(¹S)+3KL(³S))

Table (2): Some two-particle expectation values for intra-and inter shells of Be-atom.

Shell	$\langle r_1^n r_2^n \rangle$ a.u.			
	n =-2	n =-1	n =1	n =2
K(¹ S)	770.2500	13.5562	0.1722	0.0542
	-----	13.557 ^d	0.1722 ^d	-----

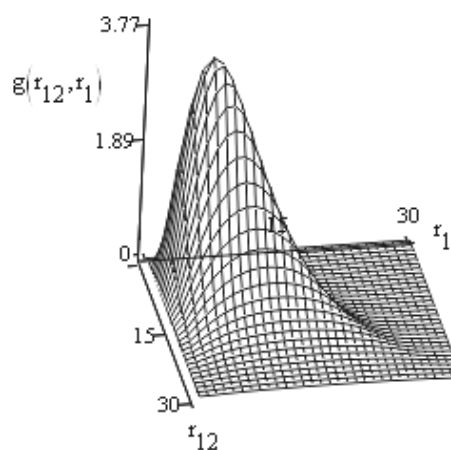
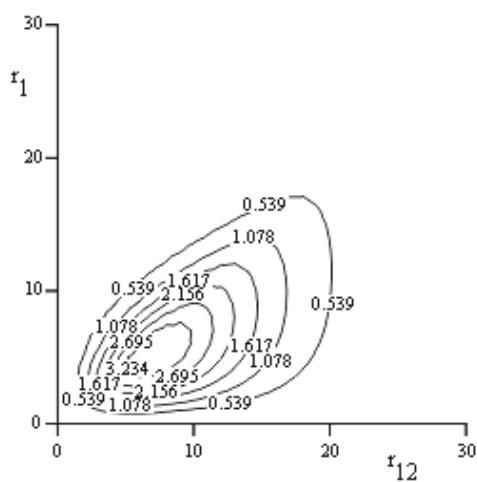
KL(³ S)	7.9839	1.7399	1.0895	1.9359
	-----	1.7400 ^d	1.0896 ^d	-----
KL(¹ S)	29.2976	1.9238	1.0994	1.9629
	-----	1.9239 ^d	1.0996 ^d	-----
L(¹ S)	1.1143	0.2730	7.0193	70.9998
	-----	0.2730 ^d	7.0199 ^d	-----
Total ^c	140.9878	3.5261	1.9282	13.1419
	-----	3.5263 ^d	1.9284 ^d	-----

^d from reference (22)

Table (3): Some radial statistical coefficients for intra-and inter shells of Be-atom.

Shell	K(¹ S)	KL(³ S)	KL(¹ S)	L(¹ S)	Total
τ_{\square}	0.0009	-0.6345	-0.6295	0.0011	-1.264 0
	0.0^e	-0.6343^e	- 0.6243 ^e	0.0^e	-1.2586^e
$\tau_{\frac{1}{r}}$	0.0	-0.2682	-0.2498	0.0	-0.5180
	0.0^e	-0.2682^e	- 0.2314 ^e	0.0^e	-0.4996^e

^e from Ref(5)



(a)
(b)

Figure (1): distribution function $g_{HF}(r_{12}, r_1)$ against (r_{12}, r_1) for K-shell (a) contour diagram (b) surface diagram (scales for figures 1→4 divided on 0.05).

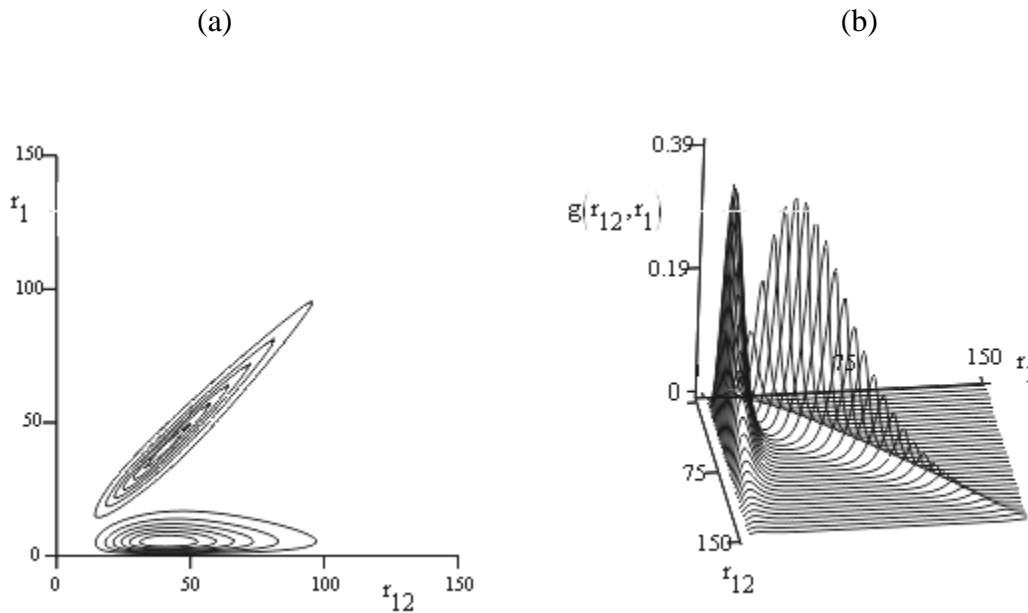


Figure (2): distribution function $g_{HF}(r_{12}, r_1)$ against (r_{12}, r_1) for KL (3S)-shell (a) contour diagram (b) surface diagram.

(a) (b)

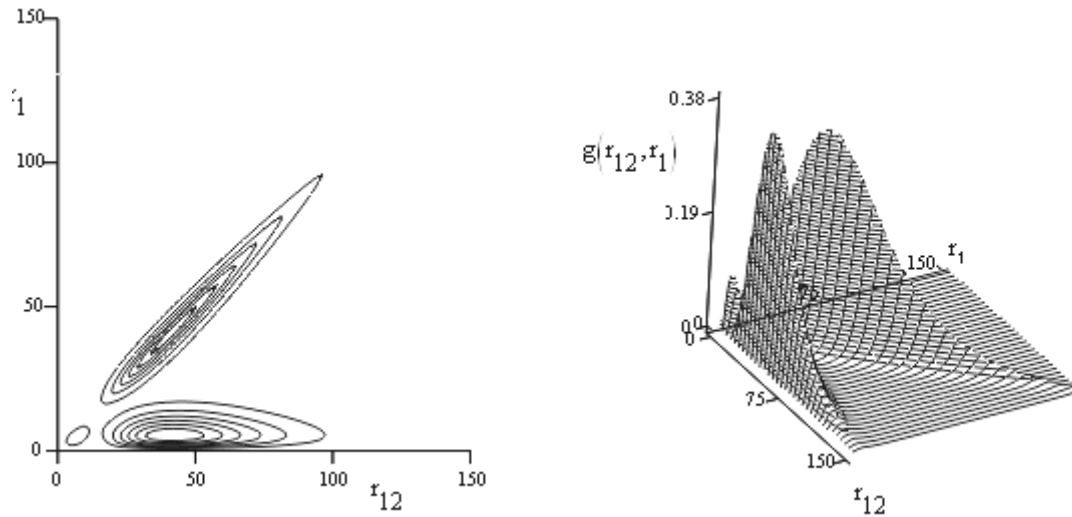
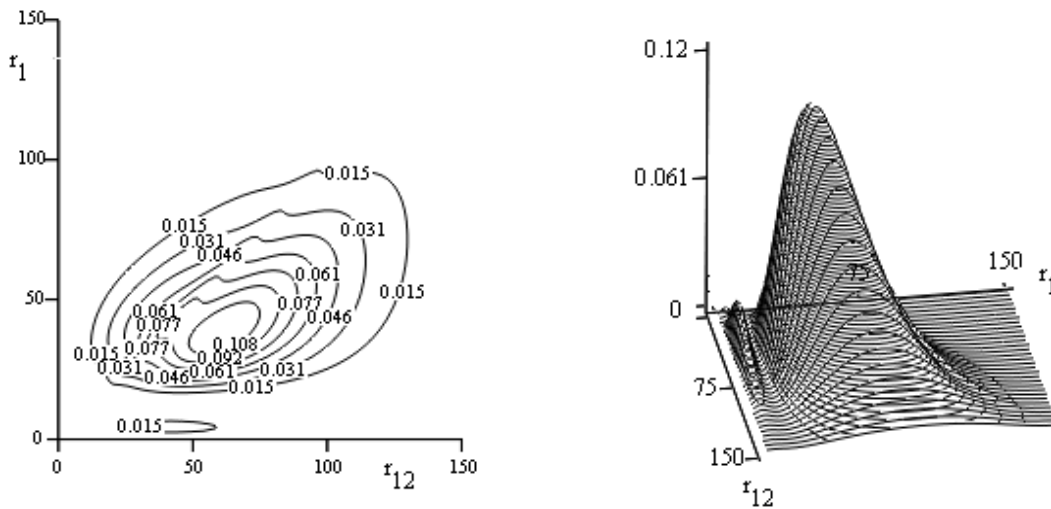


Figure (3): distribution function $g_{HF}(r_{12}, r_1)$ against (r_{12}, r_1) for KL ($1S$)-shell (a) contour diagram (b) surface diagram.

(a)

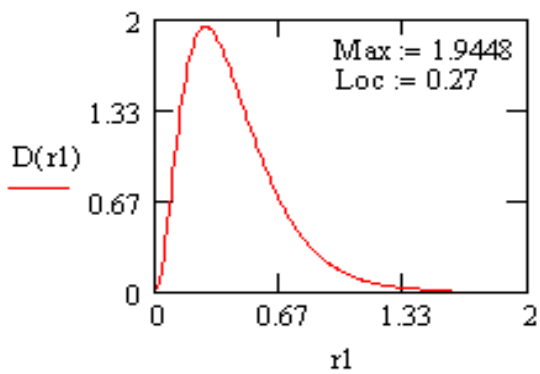
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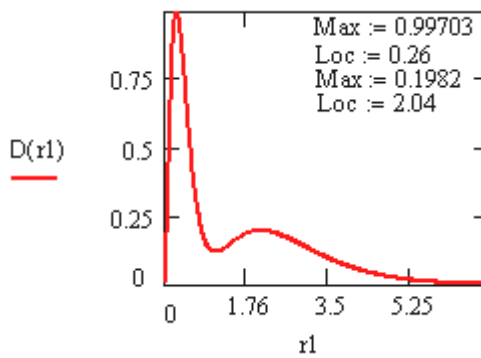
(a)

(b)

Figure (4): distribution function $g_{HF}(r_{12}, r_1)$ against (r_{12}, r_1) for L-shell (a) contour diagram (b) surface diagram.



(c)



(d)

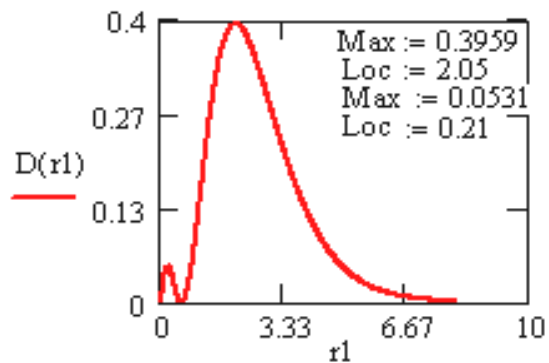
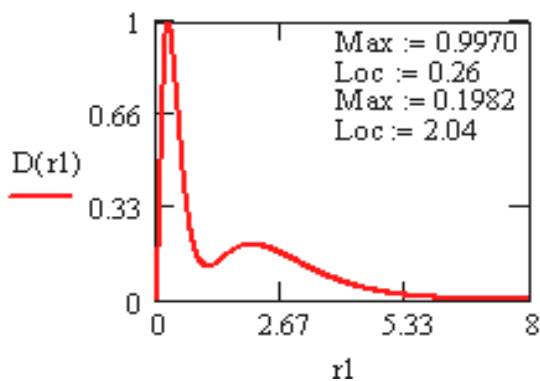


Figure (5): One particle radial density against distance for ground state of Be-atom. (a)K- shell. (b) Intershells (3S) (c) intershells (1S) (d) L-shell.