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A New Interpretation of Hund's First Rule

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The diagonal elements of the first and second order spinless density matrices have been calculated for the lowest excited ^1P and ^3P terms of Be, B^+ and C^{++} using wavefunctions at different levels of approximations published in the literature. The analysis of these functions has resulted in a new interpretation of Hund's first rule in terms of an anisotropic screening effect.

Key words: Hund's rule – Screening effect, anisotropic ~ – Be

1. Introduction

The explanation of Hund's first rule, that the higher spin multiplet of an atomic system has the lower energy, was for many years based on the knowledge of the Fermi hole: since two electrons with the same spin cannot occupy the same point in space, the electrons in the higher multiplet term were assumed further apart on the average, thus lowering the interelectronic repulsion energy of this term.

During the last few years this explanation has proved invalid for the first members of an isoelectronic sequence [1–7, 10].

Based on a detailed analysis of wavefunctions for the ^1P and ^3P terms of the configuration $(1s)^2(2s)^1(2p)^1$ for Be, B^+ and C^{++}, we have been able to explain Hund's first rule as an anisotropic screening effect essentially arising because of the antisymmetry principle. This explanation is also valid for the first few members of the isoelectronic sequence.

2. Earlier Investigations Concerning the Interpretation of Hund's First Rule

From Refs. [1–7, 10] it is evident that the well-known explanation of Hund's first rule is invalid for a number of neutral atoms, and the lower energy of the higher

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multiplet term in actual fact is due to a lower electron-nucleus attraction energy. In Ref. [1] Kohl has analysed the ^1S and ^3S terms arising from the $(1s)^1(2s)^1$ configuration of the He-atom on the basis of correlated wavefunctions. His results showed that the mean interelectronic distance is greater in the ^1S than in the ^3S term, and the interelectronic repulsion energy is smaller in the ^1S term in obvious contradiction to the usual conception of the two terms.

Messmer and Birss [2] have shown the interelectronic repulsion energy to be larger in 2 ^3P He than in 2 ^1P He. Katriel [3, 4], Colpa and Islip [5] and Killingbeck [6] reached the same conclusion studying the isoelectronic sequence with two electrons.

Katriel [7] also analysed the ^3P, ^1D and ^1S terms arising from the $(1s)^2(2s)^2(2p)^2$ configuration of the isoelectronic sequence containing six electrons. He found that the electron repulsion energy is largest in the ^3P term and smallest in the ^1S term of the neutral atom.

Tatewaki and Tanaka [9] have used the CI wavefunctions published by Tatewaki *et al.* [8] to calculate the mean interelectronic distance in the $^1P^o$ and $^3P^o$ terms arising from the $(1s)^2(2s)^1(2p)^1$ configuration of Be, B^+ and C^{++}. The calculated mean distances turned out to be smaller in the ^3P than in the ^1P term for Be and B^+, whereas the opposite result was reached for C^{++}.

Colpa *et al.* [10] have studied a number of isoelectronic sequences and in all cases found that the lower energy of the highest multiplet term of the neutral systems was caused by a lower electron-nucleus attraction energy.

3. The Wavefunctions Forming the Basis of the Present Analysis

The wavefunctions chosen are those published by Tatewaki *et al.* [8]. They used the wavefunctions in a study of the correlation hole in the ^1S, $^1P^o$ and $^3P^o$ terms of Be, B^+ and C^{++} [9].

Tatewaki *et al.* [8] have published five different types of wavefunctions for the isoelectronic sequence with four electrons for all integer nuclear charges between four and ten. Four of these wavefunctions were based on the independent particle model, while the fifth was a limited configuration interaction function (CI).

The four different types of wavefunctions within the independent particle model may be written as

$$\psi(^1P, {}^3P)=\sqrt{\tfrac{1}{2}}\{|\phi_{1s}^+\phi_{1s}^-\phi_{2s}^+\phi_{2p}^-|\pm|\phi_{1s}^+\phi_{1s}^-\phi_{2s}^-\phi_{2p}^+|\}$$

where − goes with the ^1P and + with the ^3P term. In all cases the orbitals consisted of Slater type functions. For the two least complicated wavefunctions each orbital was approximated by a single Slater type function with exponent either determined by Slater's screening rules (SO) or by minimizing the total energy (STO). The orbitals in the remaining two wavefunctions were expressed in terms of two (DZ) respectively four (HF) Slater type functions with all exponents determined by energy minimization.

The last mentioned wavefunction (HF) is close to the Hartree-Fock limit. Its orbitals, extended by a 3*s*-, a 3*p*- and a 3*d*-orbital, were used to determine a CI function including the (2*p*2*s*), (3*p*2*s*), (3*s*2*p*), (3*d*2*p*), (3*p*3*s*) and (3*d*3*p*) configurations.

4. The Missing Connection between Mean Values and Most Probable Spatial Configurations of the Particles

4.1. One-Electron Densities

Using the wavefunctions from [8] in the STO, HF and CI approximations the electron densities $r^2P(r)$ were calculated by means of the expression

$$P(r)=\sum_i \sum_{s_i} |c_i|^2 \phi^*_{s_i}(r)\phi_{s_i}(r)$$

where s_i runs over the occupied orbitals in the i'th determinant, and c_i is the coefficient of this determinant in the wavefunction. (The electron density is normalized to the total number of electrons in the system.)

The electron densities based on the HF wavefunctions are shown in Figs. 1a, b for the ^1P and ^3P terms of Be and B^+. It is noticed that the electron density for the neutral atom as well as for the positive ion is more diffuse in the ^1P term than in the ^3P term. The effect is most pronounced for the neutral atom, and has here been well known since Hartree and Hartree's work [11].

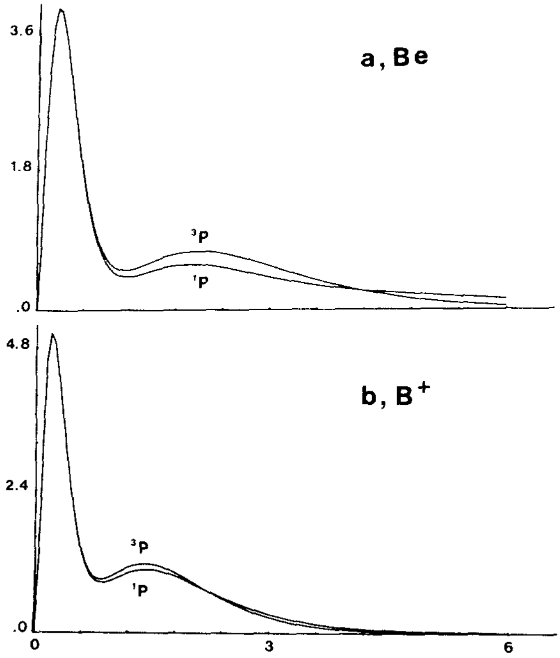

Fig. 1. Electron densities of the ^1P and ^3P terms of Be and B^+ as calculated from wavefunctions in the HF approximation. (Densities are normalized to 4 electrons, and distances are in a.u.)

Figs. 2a–d show the differences between the electron densities arising from the STO and CI functions with respect to the ones arising from the HF functions for the ^1P and ^3P terms of Be and B^+.

The flexibility introduced with the HF functions as compared to the STO functions is purely a radial in–out effect. This causes a spreading of charge for the systems considered except for ^1P Be, in which case a contraction occurs in the L shell.

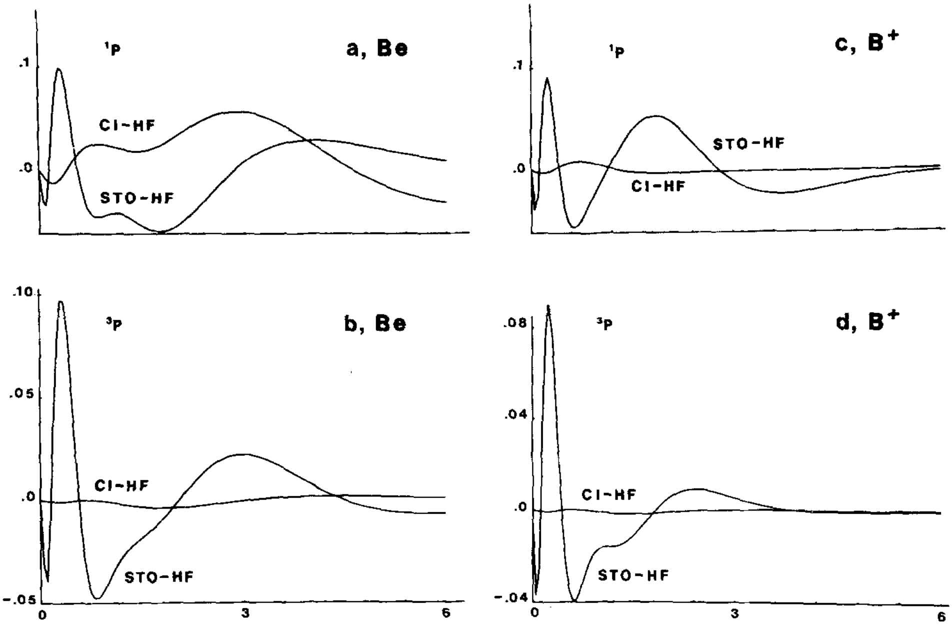

Fig. 2. Differences between the electron densities arising from the STO and the CI wavefunctions relative to those arising from the HF functions for the ^1P and ^3P terms of Be and B^+. (Distances in a.u.)

Going to the CI approximation hardly any changes occur in the one-electron densities of ^1P, ^3P B^+ and ^3P Be. This is expected, since the HF approximation should offer a fair description of one-electron properties. Nevertheless, the CI function for ^1P Be to a great extent cancels the changes occurring in the one-electron density going from the STO to the HF approximation.

Table 1 shows the mean values of the individual terms of the Hamiltonian for the ^1P and ^3P terms of Be, B^+ and C^{++}.

The mean values $\langle r \rangle$ of the distance between the nucleus and an electron for the ^1P terms nicely reflect the differences in the one-electron densities arising from wavefunctions at different levels of approximation. However, no correlation exists between the mean values of the electron–nucleus attraction energy $(-\langle z/r \rangle)$ and the different one-electron densities. Conversely, for the ^3P terms the $\langle r \rangle$ values

Table 1. Mean values of the total energy E, the electron-nucleus attraction energy $-\langle z/r \rangle$, the interelectronic repulsion energy $\langle 1/r_{12} \rangle$ and the distance between the nucleus and an electron $\langle r \rangle$. (All numbers in a.u.)

		Be		B^+		C^{++}	
Wavefunction		^1P	^3P	^1P	^3P	^1P	^3P
	STO	14.3724	14.4933	23.8828	24.0956	35.9263	36.2023
$-E$[a]	HF	14.3947	14.5115	23.9128	24.1201	35.9612	36.2357
	CI	14.4198	14.5182	23.9554	24.1270	36.0060	36.2428
	STO	32.838	33.390	53.941	54.274	79.771	80.142
$-\langle z/r \rangle$	HF	32.912	33.412	53.958	54.315	79.818	80.206
	CI	33.046	33.410	53.971	54.314	79.824	80.208
	STO	4.093	4.403	6.175	6.083	7.918	7.737
$\langle 1/r_{12} \rangle$	HF	4.123	4.389	6.132	6.075	7.896	7.735
	CI[b]	4.206	4.374	6.060	6.060	7.812	7.722
	STO	2.071	1.550	1.086	1.051	0.818	0.802
$\langle r \rangle$	HF	2.042	1.562	1.110	1.049	0.823	0.798
	CI	2.052	1.565	1.115	1.050	0.825	0.798

[a] From Ref. [8]. [b] For $^1P^o$ and $^3P^o$ according to Ref. [9].

correlate nicely with $-\langle z/r \rangle$, but these values do not correlate with the one-electron densities.

4.2. Two-Electron Densities

The wavefunctions in the STO, HF and CI approximations were also used in calculating explicit expressions for the diagonal elements of the spinless second order density matrix averaged over the components of a multiplet. The resulting function Ω_2 depends solely on the lengths r_1 and r_2 of the radius vectors to the two electrons and the angle θ between the radius vectors.

Physically the function Ω_2 is describing the number of electron pairs in distinct spatial arrangements (Ω_2 is normalized to 6, the total number of pairs).

Figs. 3a–c show how the Ω_2's derived from the CI function vary with θ for distinct, chosen values of r_1 and r_2 for the ^1P and ^3P terms of Be, B^+ and C^{++}.

Figs. 5 and 6 in the appendix show in more detail Ω_2 as a function of r_1 and r_2 for discrete values of θ for the ^1P, ^3P terms of Be.

If Ω_2 was worked out using the SO functions the following relationship would hold:

$$\Omega_2^{SO}(r_1, r_2, \theta; {}^1P) = \Omega_2^{SO}(r_1, r_2, 180° - \theta; {}^3P).$$

This feature is recognizable in the HF approximation, and even the Ω_2's derived from the CI functions show some reminiscences of it, especially for the positive ions.

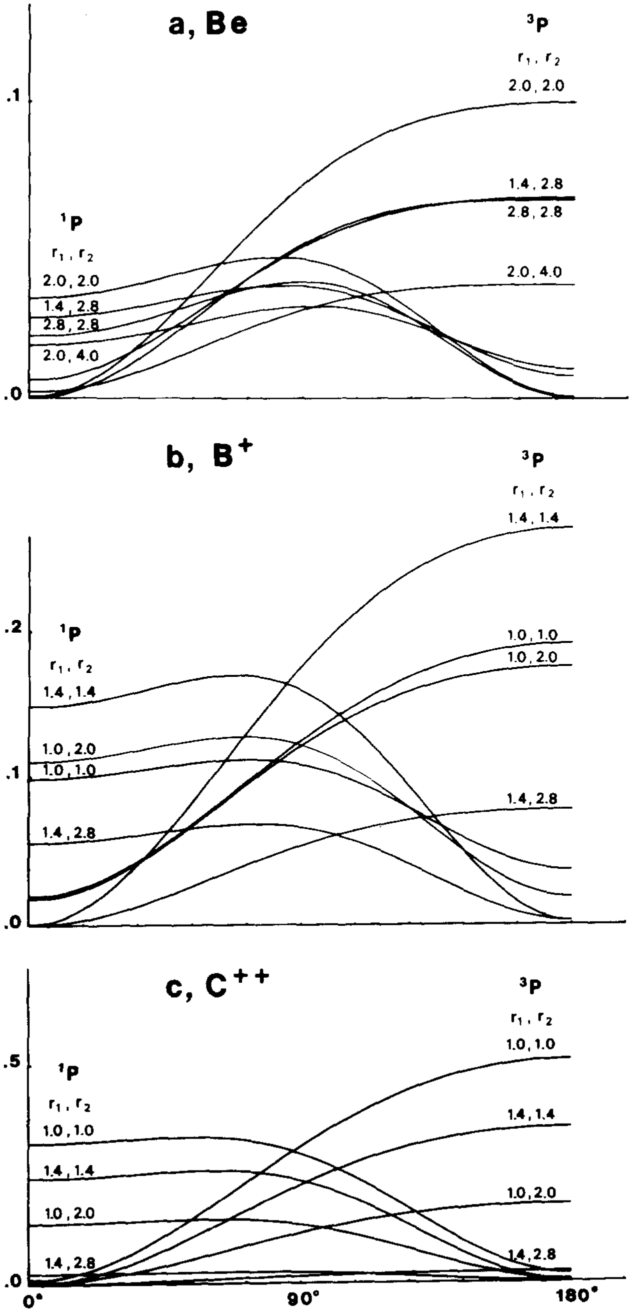

Fig. 3. The two-electron density function Ω_2 arising from the CI wavefunctions for the ^1P and ^3P terms of Be, B^+ and C^{++}. The Ω_2's are plotted for discrete values of r_1 and r_2 (in a.u.) as indicated in the figures, and as function of θ, (Ω_2 is normalized to 6 electron pairs)

Whereas the Ω_2 functions for the ^1P terms derived from the HF functions assume their largest values, when the two electrons are occupying the same point in space, a distinct angular correlation is introduced with the CI functions, as seen in Figs. 3a–c. The angular correlation is most pronounced for the neutral atom, but it is recognizable even for the doubly charged ion.

Except for the Ω_2's derived from the CI functions for the ^1P terms, the most characteristic features of the Ω_2 functions are, that they assume their maximum values for those spatial arrangements of the particles, which are consistent with the earlier interpretation of Hund's first rule.

Looking at the expectation values of $1/r_{12}$ as resulting from the different terms and approximations (Table 1), it is then obvious, that the usual interpretation of Hund's rule is not applicable to the neutral atom, and even for the monopositive ion it is questionable.

5. A New Interpretation of Hund's First Rule

As noticed from Figs. 3, 5 and 6 the most characteristic features of the wavefunctions for the ^1P and ^3P terms of the Be isoelectronic sequence are the correlation effects built into the wavefunctions at the approximation level of the independent particle model due to the antisymmetry principle.

This correlation increases the probability of finding the electrons with larger angles between the radius vectors in the ^3P term than in the ^1P term, and as a result the electrons in the higher multiplet term get closer to the nucleus.

The nucleus in the higher multiplet term is thus screened to a smaller extent than in the lower multiplet term, and as shown in Fig. 4 this is an anisotropic effect.

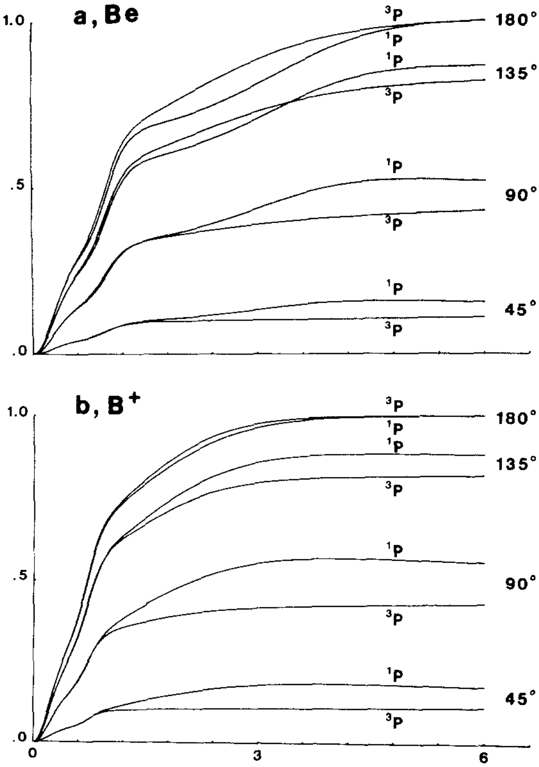

Fig. 4. The anisotropic screening effect in the ^1P and ^3P terms of Be and B^+ as calculated from the HF wavefunctions. The effect is illustrated as the conditional probability of finding electron 2 at distances in between the nucleus and electron 1 and at some distinct, chosen solid angles, which are determined by the position of the nucleus and the direction of the radius vector to electron 1. The probability is shown as a function of the distance between the nucleus and electron 1. (Distances in a.u.)

Fig. 4 shows the conditional probability of finding electron 2 at distances in between the nucleus and electron 1 and at some distinct, chosen solid angles which are determined by the position of the nucleus and the direction of the radius vector to electron 1. The probability is shown as a function of the distance between the nucleus and electron 1 for the ^1P and ^3P terms of Be and B^+.

When electron 1 is located at distances typical for the electrons in the L shell the screening effect is pronouncedly dissimilar for the two terms, when half the vertical angle of the cone defining the solid angle element is equal to or less than 90°.

This anisotropic screening effect provides an explanation of Hund's first rule, which is valid for the positive ions as well as for the neutral atom.

6. Conclusion

One- and two-electron density functions have been compared with the expectation values of the individual terms of the Hamiltonian for the lowest excited ^1P and ^3P terms of the Be isoelectronic sequence. It is realized that there is no obvious correlation between the expectation values and the most probable spatial configurations of the particles. This invalidates the usual interpretation of Hund's first rule, which is then shown to be explainable as an anisotropic screening effect essentially due to the antisymmetry principle.

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The computations were performed at NEUCC, The Regional Computing Centre at the Technical University of Denmark.

Appendix

Figs. 5 and 6 show the two-electron probability function Ω_2 for ^1P and ^3P Be for three distinct, chosen values of θ; a–c show Ω_2 as derived from the HF functions of the two terms, d–f and g–i show the differences between the Ω_2's derived from the STO and CI functions, respectively, relative to those from the HF functions.

The contour values of Ω_2 derived from the HF functions are 1.0, 0.5, 0.25, 0.125, 0.0625, 0.03125, 0.015625, 0.003125 and 0.0003125, and the same values with + and − signs have been used plotting the differences (d–f and g–i). The dotted lines show the nodes, while the full lines represent positive contours and the broken lines negative contours.

As mentioned in the text, the function Ω_2 specifies the number of electron pairs out of the 6 possible ones found in distinct spatial arrangements.

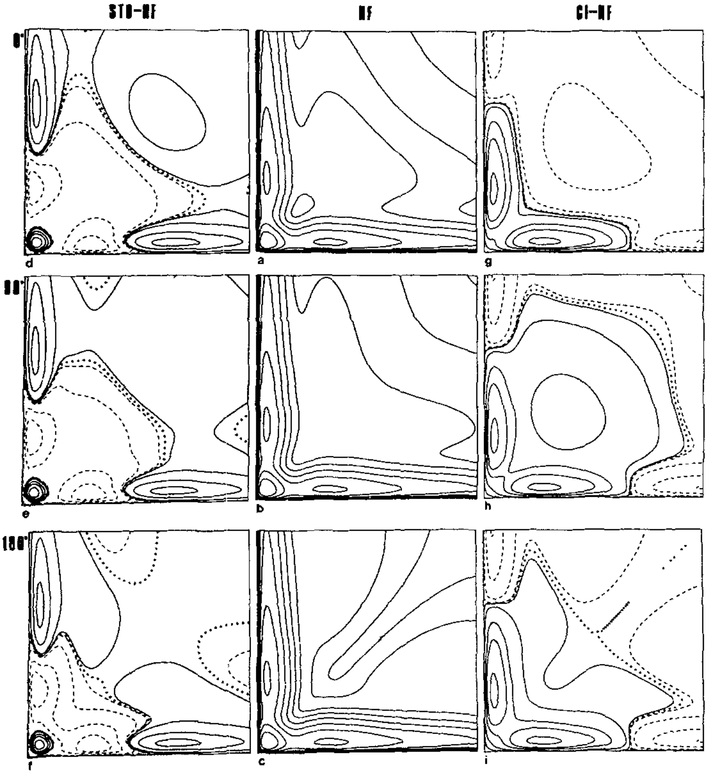

Fig. 5. The two-electron density function Ω_2 for ^1P Be. a, b and c are derived from the HF wavefunction and plotted for discrete values of θ. d, e, f, g, h and i are the differences between the Ω_2's derived from the STO and the CI functions relative to those derived from the HF functions. The abscissa and the ordinate represent the distances between the nucleus and the two electrons, which in all cases vary from 0 to 6 a.u. The values of the contours are stated in the text. (Ω_2 is normalized to 6 electron pairs)

From Figs. 5 and 6 (a, b and c) it is noticed that the diagrams show angle independent as well as angle dependent parts. The angle independent parts appear at small values of r_1 and/or r_2. Figs. 5 and 6 (a, b and c) show that the pair density is largest with both electrons in the K shell. The pair density corresponding to one electron in the K shell the other in the L shell, only reaches about half the value of the pair density corresponding to both electrons in the K shell.

While both the above-mentioned pair densities are independent of the angle between the radius vectors to the two electrons, the pair density in the L shell is strongly angle dependent. It reaches a maximum value for a specific spatial arrangement depending on the term considered.

The most striking feature of the Ω_2's derived from the HF functions are that they assume their maximum values for those spatial arrangements which are usually expected for the terms in question.

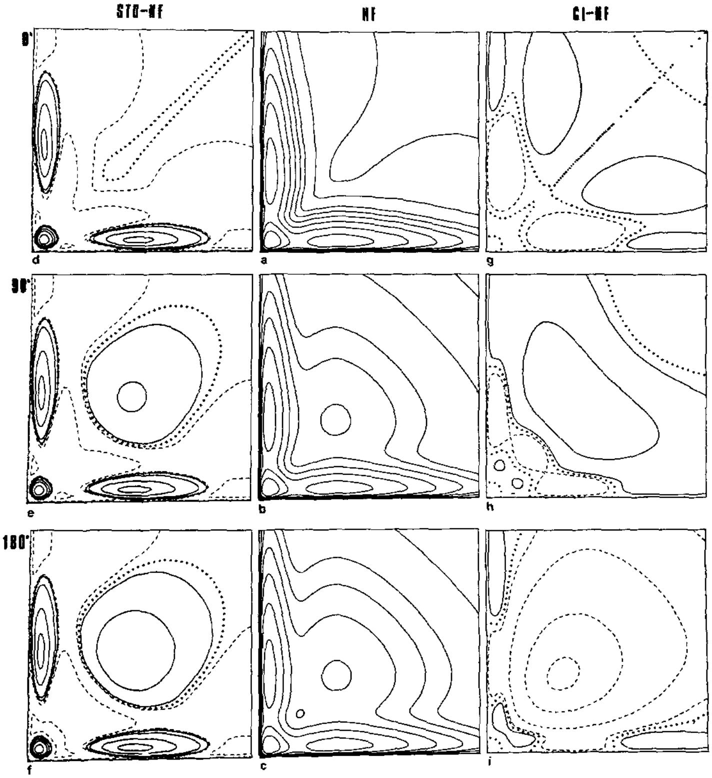

Fig. 6. The two-electron density function Ω_2 for ^3P Be. a, b and c are derived from the HF wavefunction and plotted for discrete values of θ. d, e, f, g, h and i are the differences between the Ω_2's derived from the STO and the CI functions relative to those derived from the HF functions. The abscissa and the ordinate represent the distances between the nucleus and the two electrons, which in all cases vary from 0 to 6 a.u. The values of the contours are stated in the text. (Ω_2 is normalized to 6 electron pairs)

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