

and expanding the exponential function in a Taylor series. Noting that¹²

$$\int_0^\infty t^\mu K_0(t) dt = 2^{\mu-1} \left[\Gamma\left(\frac{\mu+1}{2}\right) \right]^2,$$

we obtain

$$H(x) = \pi^{-1} \sum_{n=0}^{\infty} \sin\left(\frac{3}{4}n\pi\right) [\Gamma(1 + \frac{1}{4}n)]^2 (2x)^n / n!. \quad (\text{A4})$$

The series converges for all x .

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Hartree-Fock Wave Functions without Symmetry and Equivalence Restrictions and the Calculation of Hyperfine-Structure Expectation Values for the Lowest 2P States of Boron and Lithium*

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The spin-polarized (SPHF) and unrestricted (UHF) Hartree-Fock equations are solved for the lowest 2P states of Li and B. The orbitals are not symmetry adapted with respect to $\bar{1}^2$ in the UHF approximation for these states. The most important admixture, and the only one that has been taken into account here, is d_0 admixture into the s orbitals. The UHF determinant is not an eigenfunction of \bar{L}^2 and \bar{S}^2 . Various aspects of this fact are pointed out and discussed. The admixture of d character into the orbitals will depend heavily on exchange. It will lead to substantial corrections to hyperfine-structure expectation values. The results agree well with Sternheimer's for the quadrupole terms for B and Li. For the spin dipolar term, the results agree with the first-order perturbation-theory results of Lyons *et al.* for Li and with the "polarization function" results of Schaefer *et al.* for B. Configuration interaction and second-order perturbation-theory results are also discussed in this connection.

I. INTRODUCTION

The unrestricted Hartree-Fock method (UHF) and the spin-polarized Hartree-Fock method (SPHF) are of great interest for the explanation of atomic hyperfine structure.¹ The two methods are equivalent for spherically symmetric states. For other states, SPHF is only an approximation to UHF. In this paper we shall study the UHF method for the lowest 2P states of Li and B.

In the derivation of the SPHF equations the orbitals are assumed to be symmetry adapted, i. e., to be of the form

$$\varphi_{nlm_l m_s}(\vec{r}) = R_{nlm_s}(r) Y_{lm_l}(\theta, \phi) \xi_{m_s}(\xi), \quad (1)$$

where Y_{lm_l} is a spherical harmonic and ξ_{m_s} is a spin function. The radial functions R can be different in orbitals with different spins (different m_s).² For open-shell states the resulting SPHF orbitals will also be found to be different. This depends on the exchange interaction between the core orbitals and the outer orbitals with the same spin. As one result we will get magnetic effects,³ for instance, hyperfine-structure effects. The Fermi contact term in hyperfine structure is defined by

$$f = 4\pi \left\langle \sum_{i=1}^N \delta(\vec{r}) \sigma_{z_i} \right\rangle, \quad \sigma_{z_i} \xi_{1/2}(i) = \xi_{1/2}(i), \quad (2)$$

$$\sigma_{z_i} \xi_{-1/2}(i) = -\xi_{-1/2}(i).$$

In a one-determinantal approximation we get

$$f = 4\pi \sum_{i=1}^N 2m_{s_i} R_i^2(0) , \quad (3)$$

where N is the number of orbitals.

If the core functions are not restricted to be the same [as in the restricted Hartree-Fock method (RHF)], we get a contribution to f from the core orbitals. In favorable cases when contributions from different shells do not cancel each other to any large extent, the SPHF method usually gives quite good agreement with experiment. This is true, for instance, for 2S states of the alkali atoms and the 3P state of Be.⁴ For larger atoms and ions one has in some cases obtained good agreement^{5,6} and in other cases bad agreement with experiments.^{6,7} SPHF has also been used in the form of spin-polarized energy bands in crystals⁸ and has here contributed much to the understanding of magnetic phenomena.

A natural extension of SPHF is to allow the radial wave functions for electrons in the same shell with different m_l values to be different.⁹ With this orbital-polarized Hartree-Fock method (OPHF), one has obtained magnetic hyperfine-structure constants in good agreement with experiments for the lowest 2P states of Al, Na, K, Sc²⁺, and Cl.¹⁰

In this paper we will go one step further and investigate the full UHF method. To be able to write the orbitals in symmetry-adapted form (1), one has to assume that the electron is moving in a spherically symmetric field. This is not the case for the s electrons in states with $L \neq 0$. For the 2P states, the s orbitals will, for instance, get d_0 admixture.¹¹ The orbitals will be eigenfunctions of \mathcal{L}_z and the inversion operator but not of \mathcal{L}^2 .

Admixtures of this kind will be important for the hyperfine-structure expectation values, which in addition to the contact term [Eq. (2)] are the following¹:

$$l = \left\langle \sum_{i=1}^N (\mathcal{L}_{z_i} / r_i^3) \right\rangle , \quad (4)$$

$$d = 2(\pi/5)^{1/2} \left\langle \sum_{i=1}^N [Y_{20}(i) / r_i^3] \sigma_{z_i} \right\rangle , \quad (5)$$

$$q = 4(\pi/5)^{1/2} \left\langle \sum_{i=1}^N [Y_{20}(i) / r_i^3] \right\rangle . \quad (6)$$

$Y_{20}(i) = Y_{20}(\theta_i, \phi_i)$ are spherical harmonics. l and d are magnetic dipole interactions, like the contact term, between the nucleus and the electrons. l is the orbital and d is the spin dipolar term, q represents the electric quadrupole interaction between the nucleus and the electrons.

In order to get symmetry-adapted orbitals according to Eq. (1), one usually makes a spherical averaging of the potential before solving for the orbitals.¹² Equivalently, one may simply truncate

the linear space in which the orbitals are allowed to vary, to consist of only one symmetry species. This is, of course, a restriction. It was called a symmetry restriction by Nesbet¹³ to separate it from the equivalence restrictions. The relaxation of the latter leads to SPHF and OPHF.

In this paper we will mean by UHF the method where both equivalence and symmetry restrictions are relaxed. The virtue of the UHF method is expressed by the Møller-Plesset theorem¹⁴; in a perturbation-theory treatment with UHF as the "unperturbed" state, we get no singly excited determinants to first order. There will then be no first-order contributions to the one-particle density or density matrix.^{14,15} All important first-order corrections that are necessary in approximate Hartree-Fock treatments like RHF, SPHF, or OPHF are included in the UHF function itself.

One example of this is the Sternheimer shielding.¹⁶ Sternheimer calculated the perturbation of the electronic core by the nuclear quadrupole, and included the interaction between these induced moments and the p orbital in the quadrupole interaction between the nucleus and the electrons. One can get essentially the same result by studying the moments induced in the core by the p electron.¹⁷ If we do a self-consistent treatment, we get the UHF approximation. In the UHF method, we will also get an important correction to d , due only to exchange.

The limitations of the UHF approximation lies in the fact that it is a one-determinantal approximation with no statistical correlation between electrons with different spins. It is customary to define correlation effects as improvements beyond the UHF approximation.^{18,19} Correlation effects are known to be important for the Fermi contact term in some cases such as those of the nitrogen and phosphorus atoms.^{20,7} In the course of the completion of this work, an examination of corrections to f , l , d , and q for the boron atom was done by Brown, Smith, and the present author.²¹ The correlation corrections were found to be very important for this atom, particularly for the contact term and the quadrupole term. Still it is of great importance, however, to examine the UHF corrections even for systems where they are only a part of the total corrections. It was also found in the mentioned work²¹ that if what corresponds to the UHF corrections are calculated by configuration interaction methods one may get very erratic results. This can be avoided in the UHF method.

The symmetry properties of the UHF orbitals are investigated in Sec. II. In the UHF method, one must pay special attention to the fact that the UHF determinant is not a pure 2P -state wave function. It has also been suggested that the "conven-

tional" minimum that is obtained here is not the lowest minimum.²²⁻²⁵ The orbitals corresponding to this absolute minimum would have a lower degree of symmetry than those discussed here. Even in closed-shell cases, there would then exist minima where the orbitals are not symmetry adapted. This is also discussed in Sec. II.

Details of the calculation will be given in Sec. III. The numerical accuracy will be discussed. In Sec. IV, the result is interpreted and, in Sec. V, compared with other calculations and experiments.

II. RELAXATION OF SYMMETRY RESTRICTIONS

We assume that we are dealing with an N -particle state which can be reasonably well described by a single Slater determinant. We do not assume anything about the form of the orbitals, and we know that the Hartree-Fock equations can be written in the form

$$\mathcal{H}_0 \varphi_i = \epsilon_i \varphi_i, \quad i = 1, \dots, N. \quad (7)$$

If we solve the equation by an analytic expansion method²⁶ we get, for each choice of basis functions, self-consistency for a certain minimum in energy. In order to get the exact UHF solution, we must use a complete basis. If we use an expansion in terms of spherical harmonics and a complete radial set, all the spherical harmonics should in principle be present. This is, of course, impossible in practice and we have to examine how the problem can be simplified.

In the SPHF method we solve our one-electron equations in each diagonal symmetry block separately. To get UHF we must examine which off-diagonal matrix elements, coupling different symmetry blocks, are different from zero for each particular atomic state.¹³ Let us assume that we start from a single normalized Slater determinant ϕ_0 of the same symmetry as the true wave function and symmetry-adapted orbitals. We give the determinant a variation $\delta \varphi_k$ through one of its orbitals

$$\begin{aligned} \delta \varphi_k &= \epsilon \varphi_a, \\ \langle \varphi_a | \varphi_k \rangle &= 0 \text{ for all occupied } \varphi_k. \end{aligned} \quad (8)$$

We compute the change δE in the energy expectation value $E = \langle \phi_0 | H | \phi_0 \rangle$ to first order in ϵ and find the well-known result,²⁷ $\delta E = 0$ equivalent to

$$\langle \phi_k^a | H | \phi_0 \rangle = 0. \quad (9)$$

ϕ_k^a is the Slater determinant where φ_a is substituted for φ_k .

We thus get an energy improvement if $\langle \phi_k^a | H | \phi_0 \rangle$ is different from zero. This can happen only when there is a common symmetry component for ϕ_k^a and ϕ_0 . As an example we may take the case when ϕ_0

is an S-state RHF determinant. It is no loss of generality to assume that φ_a (and then ϕ_k^a) is symmetry adapted. To obtain an energy improvement ϕ_k^a must be an S state and then φ_a must have the same symmetry properties as φ_k . This means that the orbitals will remain symmetry adapted in the iteration procedure. It is no constraint to assume symmetry-adapted orbitals, and the Møller-Plesset theorem¹⁴ applies to the SPHF function. Similarly RHF does not represent a constrained extremum for closed shells. If one orbital would change if the equivalence restrictions were "relaxed" the equivalent orbital would change correspondingly and thus the two orbitals would still have the same spatial part.

If we now have a P state like $(1s^2 2p)$ or $(1s^2 2s^2 2p)$ and we have already arrived at SPHF we have the possibility to improve the energy further by letting φ_k be one of the s orbitals and φ_a be a d orbital.¹¹ The determinant $\phi_{2s^2 \beta}^{3d \beta} = (1s \alpha, 1s' \beta, 2s \alpha, 3d_0 \beta, 2p_x \alpha)$, for instance, has a 2P component of odd parity which means that

$$\langle \phi_{2s^2 \beta}^{3d \beta} | H | \phi_0 \rangle \neq 0. \quad (10)$$

φ_a must have the same m_l and m_s as φ_k , otherwise $\langle \phi_k^a | H | \phi_0 \rangle = 0$. It is easy to see that d admixture in the s orbitals is the only possibility in the first iteration. In the next iterations we may get additional admixtures since the determinant resulting from the first iteration is no longer a pure P state. The final determinant will still be an eigenfunction of total L_z , S_z , and the inversion operator. The final orbitals will be of the form¹¹

$$s \xi_{m_s} - (R_0 Y_{00} + R_2 Y_{20} + R_4 Y_{40} + \dots) \xi_{m_s}, \quad (11)$$

$$p_{m_l} \xi_{m_s} - (R_1 Y_{1m_l} + R_3 Y_{3m_l} + \dots) \xi_{m_s},$$

where Y_{lm} are spherical harmonics, R_i are radial functions, and ξ_{m_s} are the spin function. The orbitals will thus still be symmetry adapted with respect to L_z , S_z , and space inversion.

In this paper only the d_0 admixture will be included. The other admixtures are of second order compared to the d_0 admixture, which itself will be found to be quite small. The UHF determinant will only approximately be an eigenfunction of L^2 and S^2 . This means that we must check that the determinant has no component of the same symmetry as that of the underlying states. Another important thing is that the UHF determinants with different M_L values are not connected any longer by step-up and step-down operators as for a pure L state. In our case, the degeneracy between the UHF determinants D_{M_L} will split, so that D_0 has lower energy than $D_{\pm 1}$. We will only be interested in D_1 here. This is an almost pure ${}^2P_{3/2}$ state, and is easier to deal with

for the calculation of hyperfine structure, whereas D_0 has both ${}^2P_{3/2}$ and ${}^2P_{1/2}$ as major components. The UHF functions that we will consider are thus not the lowest UHF solutions neither for Li nor B. However, they are probably the lowest with $M_L = 1$.

The admixture of wrong symmetry components in the UHF determinant has in many papers been advanced as an argument against using the UHF approximation. If we let the UHF determinant be the first term in an expansion of the true wave function, the components with wrong symmetry will be cancelled by the remaining terms in the expansion, since the true wave function has pure symmetry. It was thought that if the correct symmetry component is projected out from the UHF (or SPHF) determinant one would get a more reliable wave function with more reliable expectation values. Conversely, if worse values are obtained, as for the contact term for the Li ground state, the UHF value was considered fortuitous and without physical meaning.

This is not a valid argument, however, as was pointed out by Pratt²⁸ and Marshall.²⁹ Take the Li 2S ground state as an example. The UHF function has the form

$$\Psi = \alpha_3 (u_1 u_2 u_3 \alpha \beta \alpha) . \quad (12)$$

Also the determinants

$$\begin{aligned} \Psi' &= \alpha_3 (u_1 u_2 u_3 \alpha \alpha \beta), \\ \Psi'' &= \alpha_3 (u_1 u_2 u_3 \beta \alpha \alpha) \end{aligned} \quad (13)$$

"show up" in the expansion of the true wave function. If we project Ψ onto a pure 2S function we get

$$\begin{aligned} \Psi_1 &= \frac{1}{3} \alpha_3 [u_1 u_2 u_3 (2 \alpha \beta \alpha - \beta \alpha \alpha - \alpha \alpha \beta)] \\ &= \frac{2}{3} \Psi - \frac{1}{3} \Psi'' - \frac{1}{3} \Psi' . \end{aligned} \quad (14)$$

But the coefficients for the three determinants involved have more freedom to vary than is expressed by Eq. (14), because of the spin degeneracy. Instead, we must consider

$$\begin{aligned} \Psi_{12} &= \alpha_3 \{ u_1 u_2 u_3 [C_1 (2 \alpha \beta \alpha - \beta \alpha \alpha - \alpha \alpha \beta) \\ &\quad + C_2 (\alpha \beta \alpha - \beta \alpha \alpha)] \} . \end{aligned} \quad (15)$$

To get something comparable to or better than UHF we must determine C_1 and C_2 variationally and optimize the orbitals. This can be done for very small atoms like Li.³⁰ The calculated constant term is close to or slightly better than the UHF value.³⁰ But the essential thing is that the argument against using UHF is false.^{28,29} The discussion above holds also when we have admixtures of incorrect spatial-symmetry components.

When we derived the form of the orbitals we assumed that we started the iteration cycle with the SPHF function. Thus the possibility is not excluded

that we arrive at a different energy minimum, perhaps a lower one, if we start from a different function and allow for all possible variations^{22,23,25} (for instance, general spin orbitals).

This could happen also for S states like the Be ground state, where the orbitals, for instance, could get p admixture.²⁴ Such atomic orbitals have never been published to the author's knowledge, but that could be explained by the fact that in probably all Hartree-Fock calculations so far one has only allowed for symmetry-adapted orbitals. There does not seem to be any mathematical proof that this can not happen.

Such a situation, where there are two different Hartree-Fock solutions which both correspond to true extreme points ($\delta E = 0$ for arbitrary infinitesimal variations) and both are good approximations to the same state, appears to be very unlikely, however. Goddard has hinted²⁴ that for Be, with the ordinary ground-state configuration ($1s^2 2s^2$), there is a lower minimum with p admixtures in the orbitals. According to our discussion, it would not be possible to arrive at this hypothetical minimum by starting from the ordinary $RHF = SPHF = UHF$ orbitals.

In our calculations on 2P states the potential seen by the s electrons deviates from being spherically symmetric by the influence of a full p orbital. This leads to only small admixtures in the s orbitals. Suppose now we have another self-consistent minimum with a determinantal wave function which is an as-good-or-better approximation to the exact wave function for the level in question as the ordinary Hartree-Fock determinant. Since we have obtained self-consistency for both determinants, we would have a case where a difference in input orbitals causes an equally large difference in the output orbitals. This is thus not in agreement with our experience in the present calculations, where a large distortion in the spherically symmetric potential caused only a small distortion in the spherical symmetric orbitals. The possibility to obtain two Hartree-Fock minima for the same atomic state in a case when the Hartree-Fock determinant is a good approximation does not, therefore, seem to be compatible with the self-consistency requirement.³¹

III. CALCULATION OF SPHF AND UHF FUNCTIONS

With orbitals of the form Eq. (11), our eigenvalue problem Eq. (7) splits into two, one for orbitals of even parity and one for orbitals of odd parity. The one with even parity splits into one block with spin up and one with spin down. We make the approximation that the even-parity orbitals are of the form

$$(s, d)_0 = R_0(r) Y_{00}(\theta, \phi) + R_2(r) Y_{20}(\theta, \phi) , \quad (16)$$

(disregarding spin) and that the p orbital remains symmetry adapted as in SPHF;

$$p_+ = R_1(r) Y_{11}(\theta, \phi). \quad (17)$$

The analytic expansion method was used²⁶ and the basis functions (Slater-type orbitals) are listed in Table I.

Rather than making an extensive variation of the exponent parameters of a small basis set (as is customary), quite large basis sets were used (Table I). We then get a safe convergence of the contact term and the other expectation values we are studying. The latter converged even slower than the contact term. Many d -type basis functions were therefore included. The basis functions were chosen to have their peaks well distributed over the region where the Hartree-Fock orbitals have a not-too-small amplitude. The Hartree-Fock orbitals have a long-range behavior like $\exp[-(-2\epsilon_i)^{1/2}r]$, except orbitals which have exchange interaction with the p orbital and decrease more slowly.³² One should not use basis orbitals which decrease slower than what corresponds to the correct long-range behavior. As can be seen from Table I, such orbitals have been used (except for the B, $2p$ orbital). One may then get a weak oscillatory behavior at long range, but this is negligible. An accu-

rate SPHF function was first determined. From there only a few more iterations were needed to get UHF self-consistency.

IV. RESULTS

The axial distortions for boron have been plotted in Figs. 1 and 2. The $2p_+\alpha$ orbital is located in a horizontal ring [$p_+ = R(r) \sin\theta e^{i\phi}$]. We see that the exchange effect is such that the $2s\alpha$ orbital is attracted to the $2p_+\alpha$ orbital. The $ns\beta$ orbitals are repelled towards the poles by the direct Coulomb repulsion. The exchange effect is about twice as large as the direct Coulomb effect in the L -shell region. In the K -shell region, however, the direct repulsion was stronger giving a total net repulsion for the α orbitals. This is the case also for the Li K shell.

The exclusion principle thus, through the exchange term in the Hartree-Fock equations, gives rise to a considerable "attraction" between orbitals with the same spin. In addition to the angular attraction demonstrated by Figs. 1 and 2, there is a radial attraction, which is present also in the SPHF approximation. The $1s\alpha$ orbital expands slightly in comparison to the $1s\beta$ orbital, whereas the $2s\alpha - 2p\alpha$ exchange leads to such a substantial gain in energy that both the orbitals get contracted. One manifestation of the $1s\alpha$ expansion is the discovery by Handy *et al.*³² that the $1s\alpha$ long-range behavior is determined essentially by the orbital energy $\epsilon_{2p\alpha}$ and not by $\epsilon_{1s\alpha}$. The $1s\beta$ orbital on the other hand has a long-range behavior determined by $\epsilon_{1s\beta}$, namely, $\exp[(-2\epsilon_{1s\beta})^{1/2}r]$.

This dramatic exchange effect between an s and a p orbital can be understood by looking at a Slater determinant D with an $ns\alpha$ and a $2p_+\alpha$ orbital (or at the two-particle reduced density matrix for the total wave function),

$$D = [R_{ns}(r_1) R_{2p}(r_2) Y_{11}(\theta_2, \phi_2) - R_{ns}(r_2) R_{2p}(r_1) Y_{11}(\theta_1, \phi_1)] \alpha(\xi_1) \alpha(\xi_2). \quad (18)$$

If we put one electron at $r_2 = a$, $\theta_2 = 90^\circ$, $\phi_2 = 0^\circ$, and look at the amplitude of D when No. 1 is in the (x, y) plane ($\theta_1 = 90^\circ$) and at the same distance from the nucleus ($r_1 = a$) we get

$$D(\phi_1) = R_{ns}(a) R_{2p}(a) (1 - e^{i\phi_1}),$$

i. e., electron 1 is almost completely on the other side of the nucleus. The repulsion from the other electron is smaller on an average if No. 2 is in the (x, y) plane than if it is on the z axis at the same distance from the nucleus ($r_2 = a$, $\theta_2 = 0$). The exchange effect is in other words dominating over the direct Coulomb repulsion and the $2s$ orbital will get an increased density in the (x, y) plane.

In a similar way, we may look at the radial at-

TABLE I. List of basis functions. $(i, \alpha) = r^i e^{-\alpha r}$;
 $(i, \alpha) - (i, \beta) = r^i (e^{-\alpha r} - e^{-\beta r})$.

Li	s	(0, 2.7), (1, 2.7), (2, 2.7), (3, 2.7), (0, 0.65), (1, 0.65), (2, 0.507), (2, 1.0), (3, 1.0), (2, 5.0), (3, 5.0), (2, 9.0)	
		d	(2, 2.7), (3, 2.7), (2, 1.0), (3, 1.0), (2, 5.0), (3, 5.0), (2, 9.0)
		p	(0, 2.7) - (0, 0.65), (1, 2.7), (2, 2.7), (3, 2.7), (1, 0.65), (2, 0.507), (2, 1.0), (3, 1.0), (2, 5.0), (3, 5.0), (2, 9.0)
B	s	(0, 4.7), (1, 4.7), (2, 4.7), (3, 4.7), (1, 1.3), (0, 0.7886), (2, 1.1), (2, 1.6), (3, 1.6), (2, 2.7), (2, 9.0), (3, 9.0)	
		d	(1, 4.7) - (1, 1.3), (2, 4.7), (3, 4.7), (2, 1.1), (2, 1.6), (3, 1.6), (2, 2.7), (2, 9.0), (3, 9.0)
		p	(0, 4.7) - (0, 0.7886), (1, 4.7), (2, 4.7), (3, 4.7), (1, 1.3), (2, 1.1), (2, 1.6), (3, 1.6), (2, 2.7), (2, 9.0), (3, 9.0)

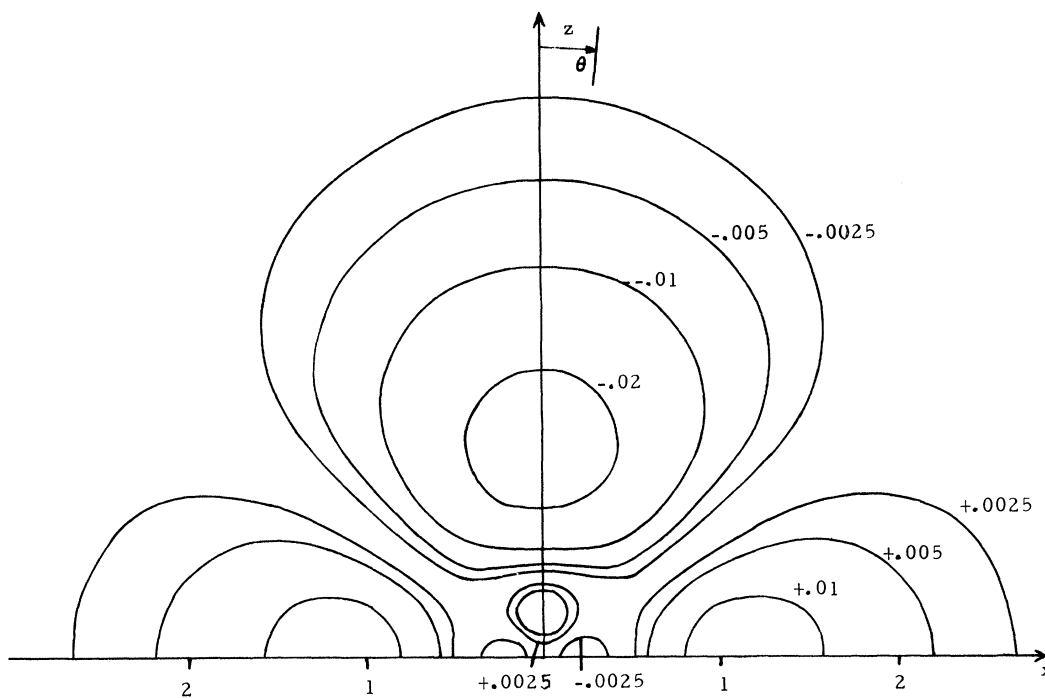


FIG. 1. Density distortions $(4\pi\{[R_0(r)Y_{00} + R_2(r)Y_{20}]^2 - [R_0(r)Y_{00}]^2\})$ for s electrons with the same spin as the $2p$ orbital ($2p_+ \sim e^{i\phi} \sin\theta$).

traction of the $1s$ orbital. An electron in the K shell will more likely have the other electron, if it is also in the K -shell region, on the other side of the nucleus, thus cancelling part of the nuclear

attraction. Whether this leads to an expansion of the s orbital as for $1s$ or a contraction as for $2s$ has to be determined by calculation.

The angular distortions shown in Figs. 1 and 2

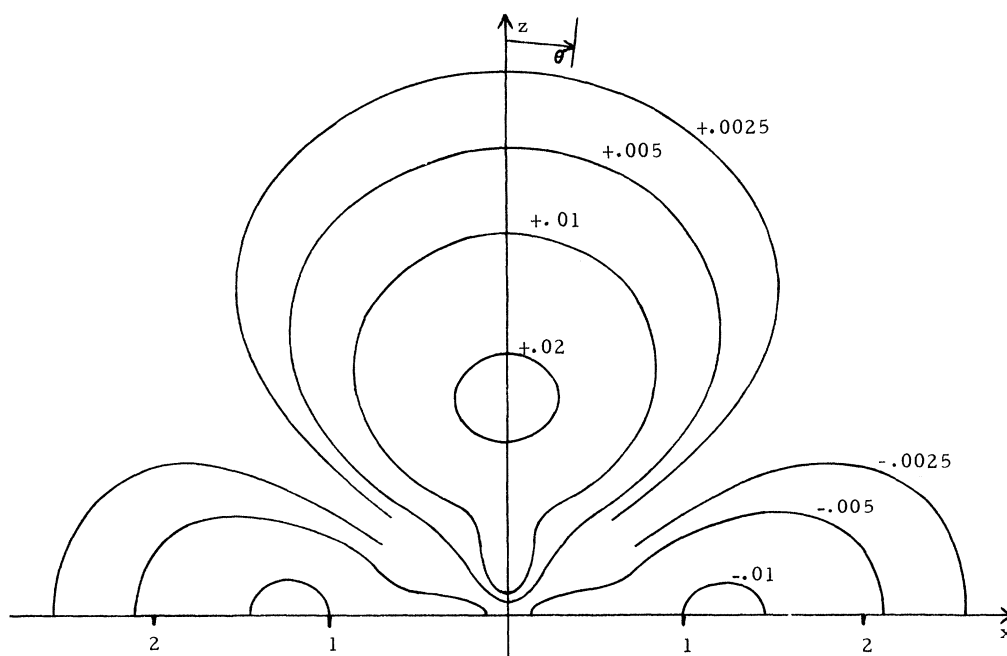


FIG. 2. Density distortions $(4\pi\{[R_0(r)Y_{00} + R_2(r)Y_{20}]^2 - [R_0(r)Y_{00}]^2\})$ for s electrons with spin opposite to that of the $2p$ orbital ($2p_+ \sim e^{i\phi} \sin\theta$).

explain the additional contributions to d and q given in Tables II and III.

The formulas for the magnetic hyperfine-structure constants have been presented in many papers before^{33,34} and we will only give the final formulas. We assume LS coupling. We then have for the ($J = L + S$) case ($g = 2.0023$),

$$A_{3/2} = K \left[l + \left(d + \frac{1}{3}f \right) \frac{1}{2}g \right], \quad (19)$$

where l , d , and f are evaluated with $M_J = J$. Using the formulas of Trees^{33,34} and the same l , d , and f as for the ${}^2P_{3/2}$ state we obtain for $A_{1/2}$:

$$A_{1/2} = k \left[2l - \left(10d + \frac{1}{3}f \right) \frac{1}{2}g \right], \quad (20)$$

where l , d , and f are expressed in atomic units $= a_0^{-3}$. We want $A_{3/2}$ and $A_{1/2}$ to be in MHz and then $k(\text{Li}^7) = 138.0807$ and $k(\text{B}^{11}) = 114.0039$.³⁵ The formulas of Trees are strictly valid only for pure states, but we do not expect the small admixture in our functions to change anything.

The contact term for lithium is -0.2318 , originating from the K shell only, whereas the boron value $+0.224$ is composed of a $1s$ contribution of -1.150 and a $2s$ contribution of 1.374 . There is thus large cancellation for B and, even if only for this reason, we should not trust very much in the UHF result.

The contact term is slightly larger for UHF than for SPHF. The value (r^{-3}) increases also, indicating that the $2p_+$ orbital is located closer to the nucleus for UHF. This depends on the improved treatment of exchange. The exchange polarization increases in general the closer the $2p_+$ orbital is to the nucleus. Thus the contact term increases slightly.

As mentioned earlier we get a lower energy if we replace the $2p_+$ or orbital by a $2p_0$ orbital. For boron the energy is then -24.5331 a.u., compared to -24.5303 when we have a $2p_+$ orbital and -24.5293 for SPHF.

V. COMPARISON WITH OTHER RESULTS AND WITH EXPERIMENTS

The results are in the SPHF case (Tables IV and V) in agreement with Goodings⁴ for Li and B and with Bagus *et al.*,⁶ for B. This applies also to

TABLE II. Contributions (in units of $10^{-3}a_0^{-3}$) to the expectation values l , d , and q [Eq. (4)–(6)] from the different orbitals for Li.

Orbital	l	$-5 \times d$	$-2.5 \times q$
$(1s+d)_0\alpha$	0	-1.0	-1.0
$(1s+d)_0\beta$	0	5.6	-5.6
$2p+\alpha$	58.6	58.6	58.6
Total	58.6	63.2	52.1

TABLE III. Contributions (in units of $10^{-2}a_0^{-3}$) to the expectation values l , d , and q [Eqs. (4)–(6)] from the different orbitals for B.

Orbital	l	$-5 \times d$	$-2.5 \times q$
$(1s+d)_0\alpha$	0	-0.1	-0.1
$(1s+d)_0\beta$	0	3.7	-3.7
$(2s+d)_0\alpha$	0	1.6	1.6
$(2s+d)_0\beta$	0	1.8	-1.8
$2p_+\alpha$	78.3	78.3	78.3
Total	78.3	85.2	74.3

orbital energies and densities at the nucleus which have not been listed here. Goodings and Bagus *et al.* used the numerical integration method. The results are better than previous analytical calculations^{36,37} by Goddard. The latter used, however, much smaller basis sets with optimized exponent parameters to get low energy. It seems that to get good convergence with analytical methods one has to use quite large basis sets in any case and it is not too important then to optimize the exponent parameters. The convergence of the spin density at the nucleus was no problem in the present calculations.

The UHF results for Li can be compared with a perturbation treatment by Lyons, Pu, and Das³⁸ and a configuration-interaction CI wave function of Weiss.³⁹ The magnetic hyperfine-structure constants were calculated from the latter wave function by Ardill and Stewart.⁴⁰ The CI wave function is missing the d admixtures in the form of $s-d_0$ singly substituted determinants. The values of l and d therefore closely satisfy $l = -5d$ and are not very reliable. The CI value of l is too small in comparison to the value of Lyons *et al.*³⁸ There is further no reason to trust in the contact term values from CI wave functions of this kind; they are known to have a very erratic behavior.

The perturbation expansion by Lyons *et al.*³⁸ is more interesting as a comparison. The (0, 0) and (0, 1) diagrams should be roughly equivalent to UHF. The results from the different orders of perturbation theory will depend on what is considered as the unperturbed state. Since this state is not UHF, some diagrams of higher order than (0, 0) and (0, 1) diagrams are needed to make a comparison with UHF meaningful. If this is kept in mind, it is not surprising to find that the contact term values do not agree very well. The small disagreement for l , d , and q can possibly also be explained in this way.

When correlation is included in the form of (1, 1) and (0, 2) diagrams we get as the probably most important effect what can be described as a correlation correction to the p orbital. The average repulsion from the core electron with different spin is

TABLE IV. Comparison of results from different methods for Li. $A_{1/2}$ and $A_{3/2}$ are calculated for Li⁷.

Method	Paper	$-E(a.u.)$	f	l	$-5 \times d$	$-2.5 \times q$	$A_{1/2}(\text{MHz})$	$A_{3/2}(\text{MHz})$
RHF	Goddard ^a	7.365 069	0	0.058 48	0.058 48	0.058 48	32.3	6.5
RHF	Goodings ^b	...	0	0.058 56	0.058 56	0.058 56	32.4	6.5
SPHF	Goddard ^a	7.365 076	-0.2195	0.058 52	0.058 52	0.058 52	42.5	-3.6
SPHF	Goodings ^b	...	-0.231	0.058 61	0.058 61	0.058 61	43.1	-4.2
SPHF	This paper	7.365 078 0	-0.2317	0.058 61	0.058 61	0.058 61	43.1	-4.2
UHF	This paper	7.365 080 3	-0.2318	0.058 62	0.063 21	0.052 11	44.4	-4.3
Pert. theory (0, 0) + (0, 1)	Lyons <i>et al.</i> ^c	...	-0.1873	0.058 57	0.064 85	0.049 37	42.7	-2.3
Second-order pert. theory	Lyons <i>et al.</i> ^c	...	-0.2079	0.062 81	0.068 59	...	45.9	-2.8
Bethe-Goldst.	Lyons and Nesbet ^d	...	-0.2146	0.063 21	0.067 61	...	46.0	-3.0
CI	Weiss ^{e,f}	7.408 38	-0.2789	0.059 7	0.059 2	...	45.7	-6.2
Expt.		7.410 16 ^g	-0.2128 ^d	0.062 58 ^d	0.690 1 ^d	...	46.2 ± 0.4 ^b	-3.1 ± 0.1 ^d

^aReference 36.^bReference 4.^cReference 38.^dReference 41.^eReference 39.^fReference 40.^gAtomic Energy Levels, compiled by C. E. Moore, Natl. Bur. Std. Circ.

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Method	Paper	$-E(a.u.)$	f	l	$-5 \times d$	$-2.5 \times q$	$A_{1/2}(\text{MHz})$	$A_{3/2}(\text{MHz})$
RHF	Bagus and Gilbert ^a	24.529 06	0	0.7755	0.7755	0.7755	353.9	70.7
RHF	Goodings ^b	...	0	0.7756	0.7756	0.7756	353.9	70.7
SPHF	Goddard ^c	24.529 30	0.241	0.7817	0.7817	0.7817	347.5	80.4
SPHF	Goodings ^b	...	0.216	0.7819	0.7819	0.7819	348.7	79.5
SPHF	This paper	24.529 314	0.215	0.7818	0.7818	0.7818	348.5	79.5
SPHF	Bagus <i>et al.</i> ^d	24.529 32	0.215	0.7818	0.7818	0.7818	348.5	79.5
UHF	This paper	24.530 271	0.224	0.7828	0.8522	0.7432	364.5	78.3
"Pol. function"	Schaefer <i>et al.</i> ^e	24.551 294	0.092	0.7674	0.8301	0.7437	361.0	72.0
"First-order function"	Schaefer <i>et al.</i> ^f	24.587 42	0.052	0.7572	0.8167	0.6833	357.1	69.7
CI	Schaefer and Harris ^g	24.639 2	0.057	0.7617	0.7725	0.740	347.8	71.4
Expt.		24.658 ^h	366.1 ⁱ	73.3 ^j
Estimation	Brown <i>et al.</i> ^k	...	0.096	0.780	0.841	0.704	366.2	73.4

^aP. S. Bagus and T. L. Gilbert, in a paper by

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decreased resulting in a shrinking of the p orbital and an increase of l by about 7%. To get a rough idea of what happens to f and the core-polarization contribution to d and q , when the p orbital is corrected for correlation, the p orbital was simply scaled and renormalized so that an increase of l by about 7% was obtained. The UHF equations for the core orbitals were solved. f is then increased by about 8%, the distortion of the s orbitals due to exchange by about 9%, and due to the direct repulsion by about 6%. This correction does not change the total value of d and q very much but the increase in f is important. The correction ought to be represented by a (0, 3) diagram and it is surprising that Lyons *et al.* found (0, 3) diagrams negligible.

Recently, a letter appeared by Lyons and Nesbet⁴¹ where hyperfine-structure results from a so-called Bethe-Goldstone calculation by Nesbet⁴² were presented and also experimental results of f , l , and d , obtained by evaluation⁴³ of results from level-crossing experiments.⁴⁴ These results are included in Table IV. The Bethe-Goldstone results agree quite well with those of Lyons *et al.* and the experimental values. The value of f is numerically larger than that of Lyons *et al.* but not by as much as could be expected from the scaling procedure above.

The low experimental value of f compared to the UHF value can easily be explained as due to correlation effects – partly as correlation corrections to the $s\beta$ orbital, and partly as pure correlation effects depending on a lower occupation number for the $s\beta$ electron than for the $s\alpha$ electron.

Sternheimer has calculated⁴⁵ a shielding factor for Li according to

$$\gamma = -(q - q_p)/q_p, \quad (21)$$

where q_p is the p -orbital contribution to q . He used a correlation corrected p orbital.⁴⁶ To be able to compare better with his result we calculated also the shielding factors from a p orbital, that was scaled to give the same l as the one Sternheimer used. As said above the polarization contribution $q - q_p$ increases roughly proportional to the increase in q_p so the shielding factors will not be changed very much when we scale. In Table VI we see that

TABLE VI. Sternheimer shielding factors [Eq. (21)] for Li.

Method	Paper	Direct	Exchange	Total
Moment pert.	Sternheimer (Ref. 5)	0.182	-0.066	0.116
(0, 1) diag.	Lyons et al. (Ref. 38)	0.263	-0.107	0.156
UHF	This paper	0.189	-0.078	0.111
UHF + 2 <i>p</i>	This paper	0.187	-0.079	0.108
Scaling				

TABLE VII. Sternheimer shielding factors [Eq. (21)] for B.

Method	Paper	Direct	Exchange	Total
Moment pert.	Sternheimer (Ref. 16)	0.142
UHF	This paper	0.139	-0.089	0.050

the agreement between Sternheimer's and our results is good. On the other hand, there is bad agreement with the (0, 1) diagrams of Lyons *et al.* and the reason for this is not known.³⁸ We have not compared with the (1, 1) and (0, 2) diagrams, since it is unclear how the shielding factor [Eq. (21)] has been calculated in this case. There is for Li only a very small correlation correction of the kind that was found for B²¹ and will be discussed below.

The boron ²*P* state has already been discussed in Ref. 21. The UHF result (Tables V and VII) should be compared to the "polarization wave-function" results. This wave function is a CI wave function including the RHF determinant and all *LS*-projected one-particle excitations with respect to the RHF determinant. Because of the projection it includes some correlation effects, which leads to a 2% decrease in the absolute values of l and d .²¹ Keeping this in mind we see in Table V that the agreement is very good (except for the contact term).

The agreement between the UHF results and the estimated results by Brown *et al.*²¹ is very good for l and d but not quite as good for q . This good agreement for l and d seems, however, to be incidental and dependent on the approximate cancellation of two correlation effects.²¹

For q there is a large correlation effect due to the $2s^2-2p^2$ excitations. These are anisotropic since the $2p_x$ orbital is occupied and there will be as a consequence an important contribution to q .

The CI values are not very good.^{47,21} The CI wave function is constructed from the RHF determinant and *LS*-projected substituted determinants. The singly substituted determinants are strongly coupled to doubly and higher substituted determinants, and the expectation values will depend heavily on small deficiencies in the wave function. The good agreement between CI and UHF for q is accidental. UHF accounts for the polarization effect, whereas CI instead accounts for the above-mentioned correlation effect. If both effects are rightly included as for the "first-order" wave function we get a much lower value.²¹

We do not expect any correlation correction on q due to the s^2-p^2 "degeneracy" for Li. First of all the p^2 excitations from the *K* shell have a much smaller probability than the p^2 excitations from the *L* shell. Second, the excited p orbitals are localized mainly in the *K*-shell region and will not over-

lap with the valence $2p$ orbital to any great extent. The excitations will then be almost isotropic.

VI. CONCLUSION

By solving the UHF equations with d_0 admixture in the s orbitals we obtained important corrections to the orbital (l), spin dipolar (d), and quadrupolar terms (q) in the hyperfine-structure spectrum. We found that the commonly used method of expressing l , d , and q in terms of a common $\langle r^{-3} \rangle$ parameter is invalid in the UHF approximation. We also got some insight into the nature of some correlation effects.

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Influence of a Strong Magnetic Field on Plasma-Broadened $2P-4Q$ ($Q=P, D, F$) He I Lines*

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The profiles of He I 4471- and 4921-Å lines and their forbidden components have been calculated for $N_e = 6 \times 10^{15}$ e cm⁻³ and $T_e = 2 \times 10^4$ °K in the presence of a 70-kG magnetic field, with the aid of an extended formulation of the impact theory. In both cases, the lines exhibit important modifications, which are not shown by isolated or completely degenerate lines in similar situations.

Recently, it has been shown¹ that the static Stark patterns of the hydrogenic lines $2P-4Q$ ($Q = P, D, F$) located at 4471 and 4921 Å in the spectrum of neutral helium are deeply modified in the presence of a static magnetic field. These lines, of great interest in plasma diagnostics, have been the object of several recent investigations^{2,3} for the case when there is no magnetic field. The purpose of this article is to present the given profiles for the case that a strong magnetic intensity confines the emitting discharge. The formalism used for that study is based on the generalized impact theory developed by Griem *et al.*⁴ conveniently extended^{1,3} in order to take into account the full structure of the static patterns in presence of combined Stark and Zeeman effects.

Then the light intensity polarized along a unit vector \hat{e} may be written

$$I(\omega, \hat{e}) = \pi^{-1} \text{Re} \int W(\vec{F}) d\vec{F} \sum_{i,j,k,l} \langle n_i | \hat{e} \cdot \vec{R} | n_j \rangle \\ \times \langle n'k | \hat{e} \cdot \vec{R} | nl \rangle \langle n_i | \langle n_j | \\ \times \{ i[\omega - \hbar^{-1}(H_n - H_{n'})] - \phi_{nn'} \}^{-1} | nl \rangle | n'k \rangle, \quad (1)$$

with \vec{R} the optical electron position vector. H_n

$[H_{n'}]$ is the atomic Hamiltonian⁵ taking into account the full static electromagnetic perturbation operating on the sublevels $|n_i\rangle$ and $|n_l\rangle$ of the upper state (n) [$|n_j\rangle$ and $|n_k\rangle$ of the lower state (n')] of the line. $\phi_{nn'}$ denotes the electron collision (or relaxation) operator.

As in most line-broadening theories, the ions are regarded as infinitely massive classical particles over the time of interest (static ion approximation). Moreover, it may be shown that the low-frequency microfield distribution⁶ $W(\vec{F})$ is rigorously unaffected⁷ in presence of a magnetic field of any strength when Doppler broadening is negligible in a thermal plasma. Therefore, it remains to evaluate the $\phi_{nn'}$ matrix elements. We restrict our attention to a sufficiently high electron density, such that the Larmor radius remains greater than the corresponding Debye length, i.e.,

$$r_G / \lambda_D = 4.544 \times 10^{-3} N_e^{1/2} / B \geq 1, \quad (2)$$

where N_e is in cm⁻³ and B in gauss.

The electron-atom interaction may then be evaluated with the usual monopole-dipole approximation and a straight-line trajectory for the perturbing electron travelling in the Debye sphere surrounding the emitter.