second-order Stark effect but no time modulation is introduced. The similarity of the equations of c(t) and e(t) in Eq. (A9) with those of a(t) and b(t)in Eqs. (A6) shows that we have similar results as Eqs. (A7) except that the expression of  $\gamma$  is different as shown above and

$$\boldsymbol{\epsilon} = \frac{1}{2} (2\omega - \omega_0 - \delta_c + \delta_e).$$

The expressions of  $\gamma$  in Eqs. (A7) and (A11) are used in the text.

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#### PHYSICAL REVIEW A

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# Correlation Effects on Hyperfine-Structure Expectation Values for the Boron <sup>2</sup>P Ground State\*

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Pure correlation effects on the hyperfine structure of atomic boron were investigated and found to be important. A natural spin-orbital expansion of the well-correlated 187-term wave function of Schaefer and Harris was used. Pure correlation effects are those contributions to an expectation value obtained when the wave function is improved beyond the best possible Slater determinant (the best overlap determinant). Our results indicate that the unrestricted Hartree-Fock method yields valuable information about the orbital and spin magnetic dipolar and electric quadrupolar terms, but gives unreliable results for the Fermi contact term. Utilizing both experimental and theoretical results, the Fermi contact term f was estimated as  $0.096a_0^{-3}$ , and the quadrupolar nuclear-shielding factor  $\gamma$  as 0.093.

#### **INTRODUCTION**

Correlation effects have proven to be important in some cases for the explanation of experimental atomic hyperfine-structure parameters. Calculations of hyperfine structure for the boron atom have been made by Schaefer, Klemm, and Harris. Their two wave functions, the polarization wave function<sup>1</sup> and the first-order wave function, <sup>2</sup> include some correlation effects, and yield 17 and 45%, respectively, of the correlation energy. For the present investigation, a wave function which includes as much correlation as possible is required. An earlier 187-term wave function by Schaefer and Harris<sup>3</sup> (which yields about 89% of the correlation energy) is the best available. A natural spin-orbital (NSO) expansion of this wave function has been given by Brown and Smith. <sup>4</sup>

The expectation values that contribute to the hyperfine structure are as follows<sup>5</sup>:

 $f = 4\pi \langle \sum_{i} \delta(\vec{\mathbf{r}}_{i}) \sigma_{zi} \rangle , \qquad (1)$ 

$$l = \langle \sum_{i} (\hat{\mathbf{1}}_{zi} / r_{i}^{3}) \rangle , \qquad (2)$$

$$d = 2(\frac{1}{5}\pi)^{1/2} \langle \sum_{i} [Y_{20}(i)/r_{i}^{3}]\sigma_{zi} \rangle , \qquad (3)$$

$$q = 4(\frac{1}{5}\pi)^{1/2} \left\langle \sum_{i} [Y_{20}(i)/r_{i}^{3}] \right\rangle , \qquad (4)$$

where  $\sigma_{zi}$  is the usual Pauli spin operator such that  $\sigma_{zi} \alpha(i) = \alpha(i)$ ;  $\sigma_{zi} \beta(i) = -\beta(i)$ .  $Y_{20}(i) = Y_{20}(\theta_i, \varphi_i)$  is one of the ordinary spherical harmonics. f, l, and d arise from magnetic dipole interaction between the nucleus and the electrons; f is the Fermi contact term, l is the orbital term, and d is the spin dipolar term. q represents the electric quadrupole interaction between the nucleus and the electrons. The expectation values are evaluated for the  $(J = L + S, M_J = J)$  state (LS-coupling assumed). The magnetic hyperfine constants  $A_J$  will then be particular linear combinations of these f, l, and d for each J value; for the <sup>2</sup>P state of  $B''^{1,2}(q = 2.0023)$ :

$$A_{3/2} = 114.0039 \left[ l + \frac{1}{2} q \left( d + \frac{1}{3} f \right) \right], \tag{5a}$$

$$A_{1/2} = 114.0039 \left[ 2l - \frac{1}{2}q(10d + \frac{1}{3}f) \right] .$$
 (5b)

If l, d, and f are in  $a_0^{-3}$ , the  $A_J$ 's will be in MHz. The hyperfine constants have been determined experimentally for both the boron  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$ states, <sup>6</sup> which thus provide us with two relationships among the three unknowns f, l, and d. Thus, we cannot yet determine f, l, and d individually. An assumption that has been often used is that land d (and q) can be expressed in terms of a single parameter corresponding to the  $\langle r^{-3} \rangle$  expectation value of the p orbitals. This assumption is valid in the restricted Hartree-Fock (RHF) method and also in the spin-polarized Hartree-Fock (SPHF) method if the open-shell orbitals have the same spin ( $\langle r^{-3} \rangle = l = -5d$  for boron). Already in the unrestricted Hartree-Fock approximation (UHF) it fails, <sup>7</sup> however, and we get additional contributions to d caused by axial distortions of the s orbitals. This distortion is unequal for electrons with spin up and down because of exchange interactions with the p electron. An examination of the correlation contributions to the hyperfine structure with the help of the NSO has previously been made by Larsson and Smith<sup>8</sup> for the <sup>2</sup>S ground state of lithium. The NSO's are the eigenfunctions of the one-particle density matrix  $\rho(X_1, X_1)^9$ :

$$\int \rho(X_1, X_1') \chi_i(X_1') dX_1' = \nu_i \chi_i(X_1) ,$$
  

$$\rho(X_1, X_1) = N \int \psi(X_1, \cdots X_N) \times \psi^*(X_1', X_2, \cdots X_N) dX_2, \cdots dX_N .$$

The  $X_i$  denotes both the electronic space and spin coordinates, and  $\chi_i$  and  $\nu_i$  are the *i*th NSO and its respective occupation number or eigenvalue. For Li, the difference between the UHF and experimental values for the Fermi contact term was 2.8%. Those correlation corrections which change the UHF spin orbitals into best-overlap<sup>10</sup> (Brueckner or exact self-consistent field<sup>11</sup>) spin orbitals leave only a 0.5% error. The NSO's are not exactly Brueckner orbitals, but the difference was found to be completely negligible<sup>8</sup> for Li, and this will also be assumed here to be the case for B. The remaining corrections arise when we go bevond the one-determinant model and consider the true wave function. These pure correlation effects thus only contributed 0.5% for the lithium <sup>2</sup>S ground state. It is quite obvious that they will be much more important for boron where there is near degeneracy between several Slater determinants.

In this paper, we will study only pure correlation effects. They are obtained by subtracting the one-particle density matrix of the first NSO determinant from that of the true wave function. The pure correlation effect  $\omega$  on the expectation value of an operator  $\Omega$  is thus given by

$$\omega = \sum_{i=1}^{N} (\nu_{i} - 1) \langle \chi_{i} | \Omega | \chi_{i} \rangle + \sum_{i=N+1}^{\infty} \nu_{i} \langle \chi_{i} | \Omega | \chi_{i} \rangle .$$
 (6)

Any errors in the NSO's and the occupation numbers result purely from the deficiencies of the boron wave function in approximating the true one.<sup>4</sup> For a configuration interaction (CI) wave function including much correlation, like the one analyzed here, the errors in the NSO's with large occupation numbers will contribute most to the total error in the expectation value of a one-particle operator. For boron, the five largest occupation numbers are well above 0.9, and the total error can be expected to arise mainly from these NSO's. However, the error in  $\omega$  is quite small since the  $(\nu_i - 1)$  terms in Eq. (6) nearly cancel. We are therefore able to calculate the pure correlation effect to good accuracy, whereas the corrections obtained from the first NSO determinant are not as reliable.

This is apparent when we compare the expectation values for NSO and UHF determinants in Ta-

		A			
Orbitals		f	l	d	q
$(s, d)_0 \alpha 1$	NSO	436.2923	0	-0.0001	-0.0001
	UHF	433.6177	0	0.0002	0.0004
$(s, d)_0 \beta 1$	NSO	- 437.2455	0	0.0022	-0.0044
	UHF	- 434.7674	0	-0.0074	0.0147
$(s, d)_0 \alpha 2$	NSO	16.3637	0	-0.0019	-0.0038
	UHF	18.3395	0	-0.0032	-0.0063
$(s, d)_0 \beta 2$	NSO	- 15.5545	0	-0.0022	0.0045
	UHF	- 16.9657	0	-0.0035	0.0071
<i>p</i> <b></b>	NSO	0	0.7786	-0.1557	-0.3114
	UHF	0	0.7828	-0.1566	-0.3131
Sum	NSO	-0.1440	0.7786	-0.1577	-0.3152

0.2241

TABLE I. Expectation values for NSO and UHF determinants (units:  $a.u.^{-3}$ ).

ble I. The contribution to d and q from the  $(s, d)_0$ orbitals is a polarization correction caused by the occupied  $p_{\perp}\alpha$  orbital. The major part is caused by first-order corrections to the RHF s orbitals and shows up also in the UHF method. The correction to q from UHF is essentially equivalent<sup>5,7</sup> to the Sternheimer correction.<sup>12</sup> In Table I we find, however, great discrepancies between the UHF and NSO results. The contribution to q from  $(s, d)_0 \beta$ is for instance - 0.0001 compared to 0.0218 from UHF. From  $(s, d)_0 \alpha$  it is - 0.0039 compared to - 0.0059 from UHF. These discrepancies are mainly due to deficiencies in the CI wave function. The d-orbital basis is, to mention one thing, very small and inadequate in describing these polarization contributions.<sup>7</sup>

UHF

We also note that the l value for the NSO p orbital is lower than the l value for the UHF p orbital. The RHF value of l is 0.7755. The UHF p orbital will be localized nearer to the nucleus owing to the improved treatment of exchange, giving an l value of 0.7828. We expect the NSO *p* orbital to be still closer to the nucleus. Comparing with other atoms, there is for instance a 7% increase in l for the  $\text{Li}^2 P$  state owing to correlation corrections.<sup>13</sup> Our result, l = 0.7786, is therefore hard to explain in view of the fact that the 187-term wave function yields as much as 89% of the correlation energy and also contains many singly substituted determinants. We contend that the l value for the NSO porbital should be higher, which also, of course, means a numerically larger contribution to d and q from the p orbital. This correlation correction to the p orbital is also absent from the polarization<sup>1</sup> and first-order functions<sup>2</sup> since these wave functions do not include very much correlation.

#### Electric Quadrupole Term q

Contributions from orbital Nos. 6-9 in Table II

give rise to a large positive correction (+0.0184). This correction is larger than the Sternheimer correction<sup>12</sup> which for *B* is approximately the sum of the two values given earlier<sup>7</sup> (see Table I), 0.0218 + (-0.0059) = 0.0159. The correction mentioned first is caused by the double excitations

-0.1704

$$2s^2 - 2p_0\alpha + 2p_0\beta, \tag{7}$$

$$2s^2 + 2p_{-}\alpha + 2p_{+}\beta$$
. (8)

The  $2p_{\star} \alpha$  orbital is occupied, which makes the following excitation impossible:

$$2s^2 \rightarrow 2p_+ \alpha + 2p_-\beta . \tag{9}$$

Since we have

0.7828

$$\int Y_{20} Y_{10}^* Y_{10} = 2/(5)^{1/2},$$
  
$$\int Y_{20} Y_{11}^* Y_{11} = -1/(5)^{1/2},$$

there will be a positive correction to q as a result.

We see from Table II that the high occupation numbers from orbitals 6-9 correspond well to the decrease from unity of the occupation numbers of the 2s orbitals (Nos. 4 and 5), and thus we can conclude that the excitations in Eqs. (7) and (8) are involved. This conclusion is also supported by other calculations on the "2s-2p degeneracy effect".<sup>14</sup> The occupation numbers from these papers agree well with ours for the  $2p_0\alpha$ ,  $2p_0\beta$ ,  $2p_{-}\alpha$ , and  $2p_{-}\beta$  orbitals.

Let us compare this result with the polarization function and first-order function results. It is evident from the construction of these wave functions that the first one exhibits only the Sternheimer effect whereas the latter includes also the 2s-2p near-degeneracy effect. The absolute value of q for both functions is probably too small, however, because of lack of correlation effects on the p orbital as mentioned in the Introduction.

The orbital Nos. 10-14 contribute -0.0053 to q.

-0.2973

i	Туре	$\nu_i$	$\nu_i f_i$	$\nu_i l_i$	$\nu_i d_i$	$\nu_i q_i$
1	$(s, d)_0 \alpha$	0.9990067	435.8590	•••	-0.0001	-0.0001
2	$(s, d)_0\beta$	0.9990015	- 436.8089		0.0022	-0.0044
3	$p_*\alpha$	0.9780017		0.7615	-0.1523	-0.3046
4	$(s,d)_0 \alpha$	0.9482820	15.5174		-0.0018	-0.0036
5	$(s,d)_0\beta$	0.931 926 6	-14.4956		-0.0021	0.0042
6	$p_{-}\alpha$	0.026 976 5	• • •	-0.0243	-0.0049	-0.0097
7	$p_0\beta$	0.0267095	• • •	•••	-0.0095	0.0191
8	$p_0 \alpha$	0.0249516			0.0090	0.0180
9	$p_{+}\beta$	0.0247312		0.0224	0.0045	-0.0090
10	$d_{*} \alpha$	0.0092580		0.0041	-0.0006	-0.0012
11	$p_{-\beta}$	0.0084837		-0.0078	0.0016	-0.0031
12	$d_* \alpha$	0.0046848		0.0010	0.0001	0.0003
13	$p_*\alpha$	0.0034625	° ° °	0.0023	-0.0005	-0.0009
14	$d_{++}\beta$	0.002 900 7	0 • 0	0.0013	0.0002	-0.0004
15	$(s,d)_0 \alpha$	0.0024800	0.1181	•••	0.0000	0.0000
16	$(s,d)_0\beta$	0.0024577	-0.1990		-0.0000	0.0000
17	$d_{*}\beta$	0.0015176		0.0003	-0.0000	0.0001
18	$(s,d)_0 \alpha$	0.0010828	0.1023	•••	-0.0000	-0.0000
19	$d_{}\beta$	0.0003964		-0.0003	0.0000	-0.0001
20	$(s,d)_0\beta$	0.000 338 8	-0.5220		-0.0000	0.0000
21	$(s,d)_0 \alpha$	0.0003287	0.4891		-0.0001	-0.0002
22	$d_{-}\beta$	0.0002678	• • •	-0.0001	-0.0000	0.0000
23	$p_{\star}\alpha$	0.0002153		0.0123	-0.0025	-0.0049
24	$p_{\star}\beta$	0.000 203 9		0.0076	0.0015	-0.0031
25	$d_{}\alpha$	0.000 201 0		-0.0001	-0.0000	-0.0000
26	$p_0\beta$	0.0001849		•••	-0.0052	0.0104
27	$p_{-}\alpha$	0.0001830	• • •	-0.0131	-0.0026	-0.0052
28	$p_0 \alpha$	0.0001808	• • •		0.0052	0.0105
29	$p_{-}\beta$	0.0001800		-0.0121	0.0024	-0.0048
30	$(s, d)_0\beta$	0.0001773	-0.0040		-0.0000	0.0000
31	$d\_\alpha$	0.000 158 8	•• •	-0.0001	0.0000	0.0000
32	$p_{+}\beta$	0.0001568	• • •	0.0055	0.0011	-0.0022
33	$p\_\beta$	0.0001390	• • •	-0.0011	0.0002	-0.0004
34	$d_{**}\alpha$	0.0001043		0.0001	-0.0000	-0.0000
35 - 82		0.0006681	0.0008	0.0023	-0.0003	-0.0006
Tota1		5.000 000 0	0.0572	0.7617	-0.1545	-0.2960
w		• • •	0.2012	-0.0169	0.0032	0.0192

TABLE II. Expectation values in the density matrix expansion (units:  $a_0^{-3}$ ) and the pure correlation effects  $\omega$  according to Eq. (6) as calculated from the 187-term wave function.

The quite high occupation numbers of these orbitals are due mainly to correlations between the  $p\alpha$ and  $s\beta$  orbitals. The occupation number for the  $2p_{\star}\alpha$  orbital decreases below the value 1 of the independent particle model as a result of these correlation effects, which leads to a lower absolute value of q. The total effect of the  $p\alpha$ - $s\beta$  correlations is therefore very small.

The remaining effects are small. The  $s^2$  correlations cause large individual contributions to q (from orbital Nos. 23, 24, 26–29, and 32), but this time these contributions cancel each other.

#### Spin Dipolar Term d

The 2s-2p near-degeneracy effect does not contribute, since the excited  $\alpha$  and  $\beta$  orbitals tend to give contributions of the same magnitude but different signs. In our case, we find as the only distinct effect a positive contribution of 0.0034 arising because of the decrease of the  $2p_{\star}\alpha$  orbital occupation number. This decrease is to a large extent apparently due to the excitation

$$2p_{\star} \alpha + s \beta - d_{\star \star} \alpha + p_{\star} \beta.$$
(10)

The created  $d_{**}$  orbital has a much smaller  $\langle r^{-3} \rangle$  value than the  $p_*$  and  $p_-$  orbitals and the net effect is a positive correction.

#### Orbital Magnetic Moment l

Excitations of type (10) cause a negative contribution here. The individually large contributions from orbitals No. 6, 9, 23, 24, 26, 27, 29, and 32 caused mainly by  $s^2$  correlations cancel out. When the first NSO determinant value is subtracted from the total *l* value from the density matrix, the net result is - 0.0169.

The correlation effect described by (10) was included in both the polarization function and the first-order function.<sup>1,2</sup> By looking at Eq. (2) of Ref. 3 we see that excitations of the above-mentioned kind occur in the  $1s^22s2pd_1$  configuration. The values of l from the two wave functions are 0.0154 and 0.0256 lower than the UHF value, respectively, in guite good agreement with our result. Comparing with the corresponding values for d we find that the polarization function result is 0.0044, and the first-order function value 0.0071 above this value. This should be compared with our result of 0.0032. Correlation effects of the kind (10) are probably best described by the first-order function. Our values would then be somewhat too small. in absolute value.

#### Fermi Contact Term f

This is perhaps the most interesting expectation value. The contact term is the only one that contributes to hyperfine structure in spherically symmetric systems. There has been much discussion in the literature about the validity of the SPHF and UHF methods for calculation of the contact term.<sup>5</sup> The total correlation error is mainly associated with the correlation between electrons of different spins.<sup>15</sup> One consequence of this is that the occupation numbers of the strongly occupied  $(s, d)_0$  orbitals of the true wave function are higher for those with the same spin as the unpaired electron (s). In our case it is 0.948 for  $(s, d)_0 \alpha$  and 0.932 for  $(s, d)_0 \beta$  of the L shell. The excited orbitals are only to a small extent s orbitals. The contributions from these excited s orbitals cancel each other. The correlation effect seems therefore to be caused primarily by the difference in the  $2(s, d)_0$ occupation numbers. The correction will be positive and unexpectedly large. By comparing with Table I we see that it is of the same magnitude as the UHF correction to RHF (the RHF value is zero).

#### COMPARISON WITH EXPERIMENTS

The magnetic hyperfine-structure constants calculated from different wave functions are listed in Table III. We have also listed the sum  $A_{1/2}+A_{3/2}$ which is independent of the contact term [see Eqs. (5a) and (5b)]. The UHF value is very close to the experimental value of this sum. Although the first-order function should account for the same kind of polarization as UHF plus important correlation effects, it yields a value which is too low. This can be explained by the fact that the first-order function is missing the correlation efffect on its strongly occupied p orbital, whereas the UHF function is missing both this correlation effect and the pure correlation effects, giving a cancellation of errors. The first-order function

TABLE III. Magnetic hyperfine constants (MHz) of  $B^{11}$  calculated from different wave functions.

Wave function	A <sub>3/2</sub>	A <sub>1/2</sub>	$A_{3/2} + A_{1/2}$
RHF <sup>a</sup>	70.7	353.9	424.6
SPHF <sup>a</sup>	79.5	348.7	428.2
UHF <sup>b</sup>	78.3	364.5	442.8
Polarization function <sup>c</sup>	72.0	361.0	433.0
First-order function <sup>d</sup>	69.7	357.1	426.8
187-term function <sup>e</sup>	71.4	347.8	419.2
Experiment <sup>f</sup>	73.3	366.1	439.4

<sup>a</sup>D. A. Goodings, Phys. Rev. <u>123</u>, 1706 (1961).

<sup>b</sup>Reference 7.

<sup>c</sup>Reference 1.

<sup>d</sup>Reference 2. <sup>e</sup>Reference 3.

<sup>f</sup>Reference 6.

Reference 6.

value of  $A_{1/2} + A_{3/2}$  should be increased by 3.0% to agree with the experimental value. If the  $\langle r^{-3} \rangle$  value for the strongly occupied p orbital is increased by about 3.0%, the major part of l and d will also increase by 3.0% in absolute value:

$$d' = 1.030l = 0.1682$$

where the unprimed l and d are the first-order wave function values. The resulting l' and d'should be quite reliable. Then using Eqs. (5a) or (5b) and the corresponding experimental values of  $A_{1/2}$  and  $A_{3/2}$ , we may calculate the contact term:

$$A_{3/2} = 114.0039 \left\{ l' + \frac{1}{2}q(d' + \frac{1}{3}f') \right\},$$
  
$$A_{1/2} = 114.0039 \left\{ 2l' - \frac{1}{2}q(10d' + \frac{1}{3}f') \right\}$$

The results are  $f'=0.095a_0^{-3}$  from the first equation, and  $f'=0.097a_0^{-3}$  from the second. Such a close agreement supports our assumptions in the above procedure.

Presently there are no reliable calculations or measurements of the Fermi contact term for boron. If our values of about  $0.096a_0^{-3}$  for the Fermi contact term and  $0.201a_0^{-3}$  for the pure correlation effect are correct, then we would have a negative value of f for the best overlap determinant. Since the UHF function is valuable only as an approximation of this determinant, we conclude that the UHF method, which gives a positive value of 0.224, is inadequate for the calculation of the Fermi contact term for this state.

In Table IV we have listed the electric quadrupole constants as calculated from different methods. The polarization function and UHF function give similar values which can be expected, since

TABLE IV.	Expectation value	lues $q = 4(\frac{1}{5}\pi)^{1/2} \langle \sum_{i} [Y_{20}(i)/r_{1}^{3}] \rangle$	>		
from different wave functions.					

RHF <sup>a</sup>	0.3102
SPHF <sup>a</sup>	0.3128
UHF <sup>b</sup>	0.2973
Polarization function <sup>c</sup>	0.2975
First-order function <sup>d</sup>	0.2733
187-term function <sup>e</sup>	0.2960

<sup>a</sup>D. A. Goodings, Phys. Rev. <u>123</u>, 1706 (1961). <sup>b</sup>Reference 7. <sup>c</sup>Reference 1. <sup>d</sup>Reference 2.

<sup>e</sup>Reference 3.

they both take into account the polarization effect which is equivalent to Sternheimer shielding.<sup>7</sup> The first-order wave function includes also the 2s-2pdegeneracy effect, and therefore yields the most accurate result. We may also improve it further by scaling it upwards by 3.0% to arrive at q= -0.2815. This corresponds to a shielding factor  $\gamma = -(q_{\text{exact}} - q_{\text{RHF}})/q_{\text{RHF}}$  of 0.093, which is appreciably larger than the Sternheimer (UHF) shielding factor  $\gamma_{\text{UHF}} = -(q_{\text{UHF}} - q_{\text{RHF}})/q_{\text{RHF}} = 0.037$ .

## CONCLUSIONS

We found an important correction to the electric quadrupole interaction as a result of the 2s-2p degeneracy effect. For l and d we found quite

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<sup>1</sup>H. F. Schaefer, III, R. A. Klemm, and F. E. Harris, Phys. Rev. <u>176</u>, 49 (1968). The polarization wave function includes the RHF determinant and all possible configurations obtained by singly exciting the RHF determinant and then LS projecting for proper symmetry.

<sup>2</sup>H. F. Schaefer, III, R. A. Klemm, and F. E. Harris, Phys. Rev. <u>181</u>, 137 (1969). For boron, the first-order wave function is constructed from the RHF determinant and all configurations L-S projected from singly and doubly excited determinants with not more than one excited orbital outside of the first RHF 1s, 2s,  $2p_{+}$ ,  $2p_{0}$ ,  $2p_{-}$ set.

<sup>3</sup>H. F. Schaefer, III and F. E. Harris, Phys. Rev. <u>167</u>, 67 (1968). The "187-term" wave function includes 187 configurations giving a total of 1292 unique determinants.

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<sup>5</sup>A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, small pure correlation corrections ( $\approx -2\%$ ). Our results indicate the first-order wave-function values of l, d, and q are the most reliable ones calculated so far, but that they should probably be increased by about 3% to account for the remaining correlation effects. For the Fermi contact term we found a surprisingly large pure correlation correction.

By comparing our results with those from other methods, we found that the first-order wave function of Schaefer, Klemm, and Harris seems to have incorporated most of the polarization and pure correlation effects but is still missing correlation corrections to its strongly occupied p orbital. The UHF function includes only the polarization effect from the 2p orbital. It gives an unreliable value for the contact term.

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## Spontaneous Emission by a System of Identical Atoms\*

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The spontaneous emission of a set of N identical two-level atoms interacting with a quantized electromagnetic field is studied. The atoms are assumed to be close together compared to the mean wavelength of the emitted radiation, and their initial state is either a Dicke state or a superposition of the ground and excited state for each atom. Approximate expressions are obtained for transition probabilities, expectation values, and correlations as functions of time. The spontaneous emission for a very large separation of the atoms is also studied. In this case the directional properties of the emitted radiation, as well as the time within which the atoms decay to their ground state, depend on the position of each atom.

#### I. INTRODUCTION

In the following the evolution in time of a set of N identical atoms interacting with a quantized electromagnetic field is studied. It is assumed that the atoms lie far enough from each other so that their wave functions do not overlap. In addition it is assumed that only two levels of the energy spectrum of each atom are involved in the process of evolution, so that each individual atom is treated as a two-level system. The initial condition of the system is such that at  $t = t_0$  there are no photons present in the field and the set of atoms is in an excited state which can be prepared experimentally.

When the electromagnetic field consists of a single mode it is possible to diagonalize the Hamiltonian<sup>1</sup> and the problem can be solved exactly. It may be shown then that the energy of the excited atoms is exchanged back and forth in time between the set of atoms and the one mode of the electromagnetic field. Hence no energy dissipation of the system of atoms occurs on a long time average. In the present work it will be assumed that the electromagnetic field consists of an infinite number of modes. In this case the atoms return to their ground state after a long time interval.

When the electromagnetic field has an infinite number of modes there are various methods of

approach in solving the problem approximately. The method of approach that will be adopted here is to deal with the equations of motion of the matrix elements of the evolution operator. It turns out that there is only a finite number of such matrix elements, so that there is also a finite number of coupled equations of motion. In addition, these equations of motion are linear and hence easier to solve than, for example, the equations of motion of the operators themselves which are nonlinear. This same method of approach was used by Weisskopf and Wigner<sup>2</sup> for the first time to study the spontaneous emission of a single atom and rather recently it was also used by Ernst and Stehle<sup>3</sup> to study the spontaneous emission of Natoms. The latter investigators consider the particular case where all the atoms are excited initially, while the initial state of the set of atoms considered here is a superposition of the ground state and the excited state for each individual atom (Sec. IV).

Following a completely different approach, Dillard and Robl<sup>4</sup> have also treated the spontaneous emission of N two-level atoms which lie close together compared to the mean wavelength of the radiation. Some of the results obtained in their investigation are duplicated here in order to show explicitly that either method of approach gives identical results. In most of the present work the condition that the atoms lie close together com-