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Z-Dependent Comparison of the Unrestricted and Conventional Hartree-Fock Approximation

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An expression is derived for the difference of the second-order term in the Z expansion of the unrestricted and conventional Hartree-Fock energy. The unrestricted Hartree-Fock energy includes some of the interactions with configurations with the same azimuthal quantum numbers, but differing in one principal quantum number and having a different coupling scheme. A similar expression is derived for a quantity related to the hyperfine splitting.

I. INTRODUCTION

PROPOSALS have been made from time to time to relax the equivalence restriction in the standard Hartree-Fock (HF) procedure, and allow electrons with different spins to have different radial functions.[1] This approach is referred to as the unrestricted Hartree-Fock (UHF) method and represents a means of improving the Hartree-Fock approximation. The results for some specific cases[2–4] indicate that the UHF method gives better values of the total energy and the hyperfine splitting, though the improvement in the energy is small. In this paper the unrestricted and conventional Hartree-Fock approximations are compared using the Z-expansion approach suggested by Layzer[5] in which the wave functions are expanded in terms of hydrogenic functions. This, at the same time makes possible a comparison of each approximation with the perturbation expansion of the exact, nonrelativistic problem.

The types of configurations that will be considered are those consisting of complete groups plus one incomplete group, not more than half-filled, whose electrons all have the same spin. In such cases the dependence of the radial wave function on the spin can be attributed to exchange polarization. The UHF method may also be applied to configurations such as $1s^2\,{}^1S$, but in this case the usual Z expansion no longer applies and a series expansion in terms of $Z^{-1/2}$ is required.[6]

The nonrelativistic Hamiltonian of an N-electron system with nuclear charge Z is given in atomic units by

$$H=-\sum_i\left(\tfrac{1}{2}\Delta_i+\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}}.$$

On the introduction of a new variable, $\rho=Zr$, this becomes

$$H=Z^2(H_0+Z^{-1}V),$$

where

$$H_0=-\sum_i\left(\tfrac{1}{2}\Delta_i+\frac{1}{\rho_i}\right),\quad V=\sum_{i<j}\frac{1}{\rho_{ij}}.$$

In this form it is evident that Z^{-1} may be treated as a perturbation parameter and that, by means of perturbation theory, the properties of many-electron systems can be expanded in inverse powers of the nuclear charge Z. Furthermore the eigenkets of H_0 can be constructed from hydrogenic functions.

Let $|(n)\gamma SL\rangle$ and $|(n)\gamma SL\rangle_0$ denote antisymmetric eigenkets of H and H_0, respectively, where (n) represents the set of principle quantum numbers $(n_1,n_2,\cdots,n_N)$ and γ represents any additional quantum numbers required to distinguish states with the same S and L. Then the perturbation expansion

$$|(n)\gamma SL\rangle=|(n)\gamma SL\rangle_0+Z^{-1}|(n)\gamma SL\rangle_1+O(Z^{-2})$$

results in an expression for the energy in the form

$$E=Z^2E_0+ZE_1+E_2+O(Z^{-1}) \tag{1}$$

with

$$E_0=-\sum_{i=1}\frac{1}{2n_i^2}.$$

The latter is independent of γ so that, according to first-order perturbation theory for degenerate states, the zero-order eigenkets must be such that the matrix ${}_0\langle(n)\gamma SL|V|(n)\gamma' SL\rangle_0$ is diagonal. This condition defines a zero-order mixing of configurations with the same principal quantum numbers but with different azimuthal quantum numbers.[7] Let $|0\rangle$ denote such an eigenket and let $|k\rangle$ represent an arbitrary eigenket of H_0. Then

$$E_1=\langle 0|V|0\rangle$$

and

$$E_2=\mathop{\mathbf{S}'}_{k}\frac{\langle 0|V|k\rangle^2}{E_0(0)-E_0(k)},$$

where the sum $\mathbf{S}'$ includes an integration over the continuum and the prime indicates that states k, for

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[7] D. Layzer, Ann. Phys. (N.Y.) **8**, 271 (1959).

which $E_0(0)=E_0(k)$, are to be omitted. The structure of E_2 has been considered in detail by Layzer, Horak, Lewis, and Thompson.[8]

For simplicity let us assume that $|0\rangle$ is associated with a single configuration specified by the quantum numbers $(n_1l_1,n_2l_2,\cdots,n_Nl_N,\gamma SL)$, where γ now indicates the coupling scheme to be used in constructing $|0\rangle$ from hydrogenic kets. Since V is a two-electron operator, the quantum numbers for the state k may differ for at most two electrons and, in order that $E_0(k)\neq E_0(0)$, the principal quantum number must differ for at least one electron. These requirements allow a convenient classification of the intermediate states k:

(i) States differing in one principal quantum number but with the same azimuthal quantum numbers and the same coupling scheme;

(ii) same as in (i) but with a different coupling scheme;

(iii) states differing in one principal quantum number and at least one azimuthal quantum number;

(iv) states differing in two principal quantum numbers.

Layzer has shown that the constant term of the energy in the Hartree-Fock approximation, E_2^{HF}, consists precisely of the summation over states of type (i). In a more recent paper, Layzer *et al.*[8] point out that the contributions from intermediate states of type (i)–(iii) denoted by E_2' involve a comparatively small number of single sums and can therefore readily be evaluated, whereas the remainder E_2'' involves a larger number of triple sums.

In this paper an expression is derived for the difference, $E_2^{\mathrm{UHF}}-E_2^{\mathrm{HF}}$, when the configurations consist of complete groups and q equivalent electrons all with parallel spins. In these cases, the difference increases as q^2 when no off-diagonal energy parameters are involved in either scheme and consists of some fraction of the summation over the intermediate states of type (ii). A comparison with results derived by Layzer *et al.* shows that for the $1s^22s\ {}^2S$ term, the unrestricted Hartree-Fock method includes exactly one-third of this contribution. The improvement in the energy is shown to be small compared to the correlation energy, $E_2-E_2^{\mathrm{HF}}$.

The unrestricted Hartree-Fock method has been more successful in improving the agreement with experiment in the case of hyperfine splitting than in the case of the total energy, particularly when the interaction of the nucleus with s electrons plays a major role. The factor directly related to the radial distribution of s electrons is the contact term, $\rho_+-\rho_-$, where ρ_+ and ρ_- represent the densities at the nucleus of electrons with positive and negative spin, respectively. In this connection it is convenient to define $\langle f\rangle=4\pi(\rho_+-\rho_-)$. The Z expansions of $\langle f\rangle$ in the UHF and HF scheme differ in the terms of first order. An expression is derived for this difference which turns out to be linear in q. Tables are included for determining the first-order difference for a variety of configurations.

II. SECOND-ORDER ENERGY DIFFERENCE, $E_2^{\mathrm{UHF}}-E_2^{\mathrm{HF}}$

Consider a configuration of the type $(n_1l_1)^{q_1}(n_2l_2)^{q_2}\cdots\times(n_rl_r)^{q_r}(nl)^q$, where the first r groups are all complete and the nl group is at most half filled. If the electrons in the incomplete group all have parallel spins, the energy associated with the Slater determinant based on a set of orthogonal, one-electron functions, $\varphi_i(n,l,m_l,m_s)$, represents an approximation to the energy of the term with highest multiplicity though it is no longer an eigenfunction of S^2. However, Marshall[9] has shown that as long as certain exchange integrals are small compared to "promotion energies" the single-determinant approximation will result in better spin densities than a projected form. Furthermore, in the case of Li, Sachs[2] found the single-determinant form to yield almost a pure doublet. The single-determinant form will be assumed here.

In the Hartree-Fock scheme the radial factors of the one-electron functions depend only on the nl quantum numbers, whereas in the unrestricted scheme they depend on the spin as well. These two different assumptions result in two different expressions for the energy, E^{HF} and E^{UHF}, respectively.

Let us denote the radial function by $P(n_il_i)$ in the HF scheme and by $P(n_il_i^+)$ and $P(n_il_i^-)$ in the UHF scheme. Without any loss of generality we may assume the electrons in the nl group all to have $+$ spin so that $P(nl^-)\equiv 0$.

In both schemes the energy can be derived by the well-known determinantal method but in order to compare the two it is convenient to consider separately the following four types of interactions:

(1) interactions within complete groups,

(2) interactions between complete groups,

(3) interactions between a complete group and the incomplete group,

(4) interactions within the incomplete group.

Table I summarizes the contributions to the energy of the various interactions in the two different schemes. Then

$$E^{\mathrm{HF}}=\sum_{i=1}^{r}q_iI(n_il_i)+qI(nl)+V^{\mathrm{HF}}$$

and

$$E^{\mathrm{UHF}}=\sum_{i=1}^{r}\frac{q_i}{2}[I(n_il_i^+)+I(n_il_i^-)]+qI(nl^+)+V^{\mathrm{UHF}},$$

where V^{HF} represents the sum of contributions from the various types of interactions in the Hartree-Fock scheme, and V^{UHF} the same interactions in the un-

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[8] D. Layzer, Z. Horak, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N. Y.) *29*, 101 (1964).

[9] W. Marshall, Proc. Phys. Soc. (London) **78**, 113 (1961).

restricted scheme. Since E^{HF} is well known, E^{UHF} can be determined from Table I.

Both the Hartree-Fock and the unrestricted Hartree-Fock equations can be derived formally by differentiating the energy with respect to each wave function in turn and in each case setting the resulting integrand equal to zero. At the same time Lagrange multipliers must be introduced to satisfy normalization and orthogonality conditions. If we denote the contribution from V as $\partial V/\partial P$ the equation for $P(n_il_i)$, for example, is

$$LP(n_il_i)+\frac{1}{2q_i}\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}=\epsilon_{ij}P(n_il_i)+\sum_i{}'\ \delta(l_j,l_i)\epsilon_{ij}P(n_jl_j)\,,$$

where

$$LP(nl)=-\frac{1}{2}\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right]P(nl)\,.$$

The Z-expansion method assumes the radial functions can be represented as a series in inverse powers of Z with hydrogenic functions as zero-order functions, so that

$$P(n_il_i;r)=Z^{1/2}\{P^H(n_il_i;\rho)+Z^{-1}P_1(n_il_i;\rho)+O(Z^{-2})\}\,,\qquad \rho=Zr\,. \tag{2}$$

Then the first-order corrections are solutions of certain differential equations.[10] In order to emphasize the difference among the various functions these equations for the first-order corrections are written out in full.

$$\left(L^H+\frac{1}{2n_i^2}\right)P_1(n_il_i^+)+\frac{1}{2q_i^+}\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^+)}\right]^H$$
$$=\epsilon_{i^+i^+}{}^{(1)}P^H(n_il_i)+\sum_{j=1}^{r+1}{}'\ \delta(l_i,l_j)\epsilon_{i^+j^+}{}^{(1)}P^H(n_jl_j)\,, \tag{3.1}$$

$$\left(L^H+\frac{1}{2n_i^2}\right)P_1(n_il_i^-)+\frac{1}{2q_i^-}\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^-)}\right]^H$$
$$=\epsilon_{i^-i^-}{}^{(1)}P^H(n_il_i)+\sum_{j=1}^{r}{}'\delta(l_i,l_j)\ \epsilon_{i^-j^-}{}^{(1)}P^H(n_jl_j)\,, \tag{3.2}$$

$$\left(L^H+\frac{1}{2n_i^2}\right)P_1(n_il_i)+\frac{1}{2q_i}\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H$$
$$=\epsilon_{ii}{}^{(1)}P^H(n_il_i)+\sum_{j=1}^{r+1}{}'\ \delta(l_i,l_j)\epsilon_{ij}{}^{(1)}P^H(n_jl_j)\,. \tag{3.3}$$

In these equations $q_i^+=q_i^-=\frac{1}{2}q_i$, $i=1,\cdots,r$ and the $(r+1)$st group is identified with the nl group so that $q_{r+1}{}^+\equiv q$ and $P(n_{r+1}l_{r+1}{}^-)\equiv 0$. The superscript H indicates that hydrogenic functions (or operators) are to be used.

In these equations, the $\epsilon^{(1)}$ matrix is completely determined by hydrogenic functions. In particular,

TABLE I. Contributions to the total energy in the Hartree-Fock and unrestricted Hartree-Fock approximation.

Type of inter-action	Contribution to E^{HF}	Contribution to E^{UHF}
1	$\frac{1}{2}q_i(q_i-1)F^0(n_il_i,n_il_i)$	$\frac{1}{4}q_i^2F^0(n_il_i^+,n_il_i^-)+\frac{1}{8}q_i(q_i-2)\times[F^0(n_il_i^+,n_il_i^+)+F^0(n_il_i^-,n_il_i^-)]$
	$A^kF^k(n_il_i,n_il_i)$	$\frac{1}{2}A^k[F^k(n_il_i^+,n_il_i^+)+F^k(n_il_i^-,n_il_i^-)]$
2	$A^0F^0(n_il_i,n_jl_j)$	$\frac{1}{4}A^0[F^0(n_il_i^+,n_jl_j^-)+F^0(n_il_i^-,n_jl_j^+)+F^0(n_il_i^+,n_jl_j^+)+F^0(n_il_i^-,n_jl_j^-)]$
	$B^kG^k(n_il_i,n_jl_j)$	$\frac{1}{2}B^k[G^k(n_il_i^+,n_jl_j^+)+G^k(n_il_i^-,n_jl_j^-)]$
3	$A^0F^0(n_il_i,nl)$	$\frac{1}{2}A^0[F^0(n_il_i^+,nl^+)+F^0(n_il_i^-,nl^+)]$
	$B^kG^k(n_il_i,nl)$	$B^kG^k(n_il_i^+,nl^+)$
4	$A^kF^k(nl,nl)$	$A^kF^k(nl^+,nl^+)$

$$\epsilon_{ii}{}^{(1)}=\int_0^\infty\frac{P^H(n_il_i)}{2q_i}\left(\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right)^H dr\,.$$

The off-diagonal energy parameters are such that the series for $P(n_il_i)$ is orthogonal to first order to that of $P(n_jl_j)$, whenever $l_i=l_j$. From the fact that

$$\epsilon_{ij}=\lambda_{ij}/2q_i\,,\quad \lambda_{ij}=\lambda_{ji}\,,$$

where λ_{ij} is a Lagrange multiplier, it follows that for $q_i\neq q_j$,

$$\epsilon_{ij}{}^{(1)}=\frac{q_j}{q_j-q_i}\int_0^\infty\left\{\frac{P^H(n_jl_j)}{2q_i}\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H-\frac{P^H(n_il_i)}{2q_j}\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_jl_j)}\right]^H\right\}dr\,.$$

When $q_i=q_j$ the two groups are complete (at least for the type of configurations considered in this paper) and the orthogonality condition is satisfied with $\epsilon_{ij}{}^{(1)}=0$. In the UHF scheme, off-diagonal parameters occur only between groups with the same spin and a complete group now consists of only $(2l+1)$ equivalent electrons. Therefore in the UHF scheme, off-diagonal parameters need not occur between s electrons.

The solution to Eq. (3.3), for example, can be expanded in terms of hydrogenic functions so that

$$P_1(n_il_i)=\mathop{\mathbf{S}'}_{m}\ \alpha_{mi}P^H(ml_i)/d_{n_im}\,,$$

where

$$d_{nm}=-(1/2n^2)+(1/2m^2)$$

and the summation includes integration over the continuum. Then

$$\alpha_{mi}=\int_0^\infty\frac{P^H(ml_i)}{2q_i}\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H dr-\delta(m,n_j)\delta(l_i,l_j)\epsilon_{ij}{}^{(1)}\quad m\neq n_i\,.$$

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[10] C. Froese, Proc. Roy. Soc. (London) A239, 311 (1957).

This result shows that the off-diagonal energy parameters merely modify certain terms in the sum. From now on we will restrict our attention to configurations in which off-diagonal parameters do not appear.

With the aid of Table I, the following relationships can readily be verified:

$$\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^+)}\right]^H+\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^-)}\right]^H=\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H, \qquad i=1,\cdots,r \tag{4.1}$$

$$\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^+)}\right]^H-\frac{1}{2}\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H=\frac{1}{2}\left[\frac{\partial V_{3X}{}^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H, \qquad i=1,\cdots,r \tag{4.2}$$

$$\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(nl^+)}\right]^H=\left[\frac{\partial V^{\mathrm{HF}}}{\partial P(nl)}\right]^H, \tag{4.3}$$

where $V_{3X}{}^{\mathrm{HF}}$ is the exchange contribution to the interaction of type 3. Each of these relationships leads to a relationship among the first-order corrections. By the addition or subtraction of appropriate Eqs. (3.1)–(3.3), these can be shown to be

$$P_1(n_il_i^+)+P_1(n_il_i^-)-2P_1(n_il_i)=0, \tag{5.1}$$

$$P_1(n_il_i^+)-P_1(n_il_i)=\mathbf{S}'\,\alpha_{mi}P^H(ml_i)/d_{n_im}, \tag{5.2}$$

where

$$\alpha_{mi}=\int_0^\infty \frac{P^H(ml_i)}{2q_i}\left[\frac{\partial V_{3X}{}^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H dr,$$

$$P_1(nl^+)-P_1(nl)=0. \tag{5.3}$$

In the Z expansion of the total energy, E_0 and E_1 are entirely determined by hydrogenic functions and therefore cannot differ in our two schemes. A straightforward analysis shows that E_2 is obtained by replacing each $F^k(ij)$ by $R^k(i^1j^H;i^Hj^H)+R^k(i^Hj^1;i^Hj^H)$ and each $G^k(ij)$ by $R^k(i^1j^H;j^Hi^H)+R^k(i^Hj^1;j^Hi^H)$. If now, with the aid of Table I, we form the difference $E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HF}}$, many terms cancel because of 5.1 and 5.3, the only place where a nonzero difference appears is in the exchange interaction of type 3 so that

$$E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HF}}=\sum_{i,k}\mathop{\mathbf{S}'}_{m}\alpha_{mi}B_i{}^kR^k(ml_inl;nln_il_i)/d_{n_im}.$$

But $B_i{}^k=q_iqb_k$, where b_k's are the exchange coefficients tabulated by Slater,[11] and from (5.2), it follows that

$$\alpha_{mi}=q\sum_k b_kR^k(ml_inl;nln_il_i).$$

Therefore

$$E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HF}}=\sum_{i=1}^{r}\frac{q^2}{q_i}\mathop{\mathbf{S}'}_{m}\Big(\sum_k q_ib_kR^k(ml_inl;nln_il_i)/d_{n_im}\Big)^2.$$

TABLE II. The difference in the second order energy in the Hartree-Fock and unrestricted Hartree-Fock approximation.

Complete group	Incomplete group	Contribution to $E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HF}}$
$(ns)^2$	$(n'l)^q$	$[q^2/2(2l+1)^2]\,\mathbf{S}'\,[R^l(ms\,ns;n'l\,n'l)]^2/d_{nm}$ if $l=0,\ m\neq n'$
$(nl)^{2(2l+1)}$	$n's$	$[1/2(2l+1)]\,\mathbf{S}'\,[R^l(ml\,nl;n's\,n's)]^2/d_{nm}$
$*(np)^6$	$(n'p)^q$	$\frac{1}{6}q^2\,\mathbf{S}'\,[R^0(mp\,np;n'p\,n'p)+\frac{2}{5}R^2(mp\,np;n'p\,n'p)]^2/d_{nm}$
$(np)^6$	$(n'd)^q$	$\frac{1}{6}q^2\,\mathbf{S}'\,[\frac{2}{5}R^1(mp\,np;n'd\,n'd)+(9/35)R^3(mp\,np;n'd\,n'd)]^2/d_{nm}$
$(np)^6$	$(n'f)^q$	$\frac{1}{6}q^2\,\mathbf{S}'\,[(9/35)R^2(mp\,np;n'f\,n'f)+(4/21)R^4(mp\,np;n'f\,n'f)]^2/d_{nm}$
$(nd)^{10}$	$(n'p)^q$	$\frac{1}{10}q^2\,\mathbf{S}'\,[\frac{2}{3}R^1(md\,nd;n'p\,n'p)+(3/7)R^3(md\,nd;n'p\,n'p)]^2/d_{nm}$
$*(nd)^{10}$	$(n'd)^q$	$\frac{1}{10}q^2\,\mathbf{S}'\,[R^0(md\,nd;n'd\,n'd)+(2/7)R^2(md\,nd;n'd\,n'd)+(2/7)R^4(md\,nd;n'd\,n'd)]^2/d_{nm}$
$(nd)^{10}$	$(n'f)^q$	$\frac{1}{10}q^2\,\mathbf{S}'\,[(3/7)R^1(md\,nd;n'f\,n'f)+(4/21)R^3(md\,nd;n'f\,n'f)+(50/231)R^5(md\,nd;n'f\,n'f)]^2/d_{nm}$

Here $d_{nm}=(-1/2n^2)+(1/2m^2)$

This result shows that the differences consist entirely of interactions with configurations with the same set of azimuthal quantum numbers differing in only one principal quantum number. In other words, it represents a summation over intermediate states k, either of type (i) or (ii). However, the Hartree-Fock approximation already includes all of the contributions from states of type (i) so this difference must represent a summation over states with a different coupling scheme. In other words the unrestricted Hartree-Fock method takes into account some of the radial correlation but neglects angular correlation which in the case of the energy, may be of considerable importance.

When off-diagonal energy parameters have to be included, additional terms are introduced. As a result the differences in Eqs. (5.1) and (5.3) are no longer zero and since these were responsible for a lot of the cancellation, a general expression is quite complex. However, in the special case of the configuration $(ns)^2(n's)$, the off-diagonal energy parameter, which occurs only in the HF scheme, simply has the effect of eliminating the term $m=n'$ from the sum in addition to the term $m=n$.

Table II lists the specific contributions to $E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HF}}$ for various complete and incomplete groups. An

TABLE III. A comparison of the difference, $E_2{}^{\mathrm{HF}}-E_2{}^{\mathrm{UHF}}$, with the correlation energy.

Configuration	$E_2{}^{\mathrm{HF}}$	$E_2{}^{\mathrm{UHF}}$	$E_2{}^{\mathrm{UHF}}-E_2{}^{\mathrm{HE}}$	$E_2{}^{\mathrm{corr}}$
$(1s)^2(2s)\ {}^2S$	−0.354549	−0.354811	0.000262	0.0544
$(1s)^2(2p)\ {}^2P$	−0.469462	−0.469779	0.000317	
$(1s)^2(2p)^3\ {}^4S$	−2.194064	−2.196922	0.002858	
$(1s)^2(2s)^2(2p)^3\ {}^4S$	−4.955063	−4.961111	0.006048	0.25
$(1s)^2(2s)^2(2p)^6(3s)\ {}^2S$	−18.169309	−18.169572	0.000263	0.404

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[11] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., 1960), Vol. II, p. 287.

TABLE IV. Values of $a_1^*(n_is^+)-a_1^*(n_is^-)$ for different outer nl electrons.

n_is \ nl	$2s$	$2p$	$3s$	$3p$	$4s$	$3d$	$4p$	$4d$	$4f$
$1s$	0.081811	−0.053897	0.022140	−0.011205	0.009064	−0.001540	−0.004191	−0.000786	−0.000018
$2s$		0.149401	0.068024	−0.013685	0.022589	−0.025076	−0.004455	−0.000135	−0.005251
$3s$				0.088925	0.059928	0.041730	−0.002018	0.001260	−0.003785
						0.006597	0.059541	0.040940	0.016909

asterisk indicates that off-diagonal parameters have been neglected.

In order to verify the relative unimportance of this contribution to E_2, Eqs. (3) were solved numerically[12] for a variety of configurations and from the solution, E_2^{HF} and E_2^{UHF} were determined. The values for $1s^22s\,^2S$ have already been computed by Sharma[13] by analytic methods and our values agree to the six figures quoted. The results are summarized in Table III. Here $E_2^{\mathrm{corr}}=E_2-E_2^{\mathrm{HF}}$ is the constant term in the Z expansion of the correlation energy defined as the difference between the exact, nonrelativistic energy and the Hartree-Fock energy. Values of E_2^{corr} were estimated from the correlation energies published by Clementi.[14] It is obvious from Table III that the UHF scheme does little to improve the energy.

III. MAGNETIC HYPERFINE STRUCTURE

Let $a(n_il_i)=P(n_il_i;r)/r$, $r\to 0$, then

$$\langle f\rangle=\sum_i\,[a(n_is^+)^2-a(n_is^-)^2]+\delta(l,0)a(nl^+)^2$$

for the type of configurations considered here. In the conventional Hartree-Fock treatment $\langle f\rangle$ is different from zero only if an unpaired s electron is present. Obviously

$$\langle f\rangle^{\mathrm{UHF}}-\langle f\rangle^{\mathrm{HF}}=\sum_i\,[a(n_is^+)^2-a(n_is^-)^2]+\delta(l,0)[a(nl^+)^2-a(nl)^2].$$

From Eqs. (4.1) and (4.2), it follows that

$$\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^+)}\right]^H-\left[\frac{\partial V^{\mathrm{UHF}}}{\partial P(n_il_i^-)}\right]^H=\left[\frac{\partial V_{3x}{}^{\mathrm{HF}}}{\partial P(n_il_i)}\right]^H,$$

and, therefore, substitution into the difference of Eqs. (3.1) and (3.2) yields

$$a_1(n_is^+)-a_1(n_is^-)=2\,\mathbf{S}'\,\alpha_{mi}a^H(ms)/d_{n_im}$$
$$=\frac{-q}{(2l+1)}\,\mathbf{S}'\,R^l(msn_is;\,nlnl)a^H(ms)/d_{n_im}.$$

If the outer electron is an s electron, the only terms which contribute to $P_1(ns^+)-P_1(ns)$ are the off-diagonal energy parameters associated with $P_1(ns)$. These are of the form $\epsilon_{nsn_is}=-R^0(n_is\;ns;\;ns\;ns)$, so that

$$a_1(ns^+)-a_1(ns)$$
$$=-\sum_{i=0}^{r}\delta(l_i,0)R^0(n_is\;ns;\;ns\;ns)a^H(n_is)/d_{nn_i}.$$

Now, from Eq. (2) it follows that

$$a^2(ns)=Z^3[a^H(nl)+Z^{-1}a_1(nl)+O(Z^{-2})]^2$$

and therefore

$$\langle f\rangle^{\mathrm{UHF}}-\langle f\rangle^{\mathrm{HF}}=\frac{-2qZ^2}{(2l+1)}\sum_i\delta(l_i,0)$$
$$\times\mathbf{S}'\,R^l\,(ms\;n_is;\;nl\;nl)a^H(ms)a^H(n_is)/d_{n_im}$$
$$-2\delta(l,0)Z^2\sum_i\delta(l_i,0)$$
$$\times R^0(n_is\;ns;\;ns\;ns)a^H(n_is)a^H(ns)/d_{nn_i}+O(Z)\quad(6)$$

or,

$$\langle f\rangle^{\mathrm{UHF}}-\langle f\rangle^{\mathrm{HF}}=2qZ^2\sum_i\,[a_1^*(n_is^+)-a_1^*(n_is^-)$$
$$-\delta(l,0)b(n_is,ns)]a^H(n_is)+O(Z),\quad(7)$$

where $a_1^*(n_is^+)-a_1^*(n_is^-)$ is now the difference for a single outer nl electron and the constant $b(n_is,ns)$ includes the dependence on the off-diagonal parameters in the case of an outer s electron. Equation (7) shows that this difference is linear in q and affects the first-order correction.

Values of $a_1^*(n_is^+)-a_1^*(n_is^-)$ for a single outer electron are given in Table IV, and values of $b(n_is,ns)$ in Table V. The former essentially represents the contributions from the core. It is interesting to note that for an outer s electron the contributions are all positive, whereas, for other electrons some of the inner contributions are negative. These differences in sign agree with

TABLE V. Values of $b(n_is,ns)$.

n_is \ nl	$2s$	$3s$	$4s$
$1s$	0.016182	0.000980	0.000156
$2s$		0.025758	0.002251
$3s$			0.029543

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[12] Analytic solutions represented in terms of hydrogenic functions have the advantage of allowing a physical interpretation but for computational purposes it is simpler to solve the differential equations numerically.

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those observed by Goodings.[3] Unfortunately, the terms $O(Z)$ are still important as shown by Sharma[13]; in the case of Li and Na, the above difference tends to overcorrect the Hartree-Fock result but for larger Z, the agreement should improve.

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Theory of Sideband Production in Spectroscopic Experiments[*][†]

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In many systems which are capable of coherent scattering of radiation, satellite lines appear at regular frequency intervals about the center (carrier) line in the spectrum. Well-known examples include the Zeeman sidebands in magnetic resonance spectra and the Stark sidebands employed in microwave spectroscopy. In this paper a theory developed by Karplus to describe the latter case is generalized to cover a wider range of phenomena. The results are discussed from the point of view of nuclear magnetic resonance.

I. INTRODUCTION

SIDEBAND production in spectroscopic experiments was first studied theoretically by Karplus,[1] who described the sidebands produced about the microwave absorption lines in molecular rotational spectra by modulation of the Stark effect. Smaller,[2] and Arnold and Packard[3] independently extended these results to sidebands produced by Zeeman modulation in NMR. Burgess and Brown[4] checked some of the details of Smaller's formulas experimentally. We have become interested in this problem in connection with the possibility of detecting alignment effects upon the nuclear resonance spectra of polar liquids by modulating the electric fields used to align the molecular dipoles. The advantages of this technique have been discussed elsewhere.[5] For the analysis of this experiment, as well as several others of interest, the theory of Karplus must be extended. The following section presents a generalized form of that theory. We have followed the notation of Karplus except for the differences indicated in Table I.

II. GENERAL THEORY

Consider a system described by the following Hamiltonian:

$$\mathcal{H}(t)=\mathcal{H}_0+\mathcal{H}_1(t)+\mathcal{H}'(t)+\mathcal{H}_R(t). \qquad (1)$$

$\mathcal{H}_0$ is the large static term which establishes the steady-state energy-level differences, $\hbar\bar{\omega}_{mn}$. $\mathcal{H}_1(t)$ describes the interaction of the system with a radiation field of frequency ω, which causes transitions among the levels of $\mathcal{H}_0$. $\mathcal{H}'(t)$ is a modulation term, characterized by a frequency ω_s and an intensity $\hbar\omega'$ or by a more complicated time dependence describable by a Fourier spectrum of such sinusoids. $\mathcal{H}_R(t)$ represents the coupling (assumed weak) to a heat bath, leading to a single relaxation time τ for the properties of the system of interest. The density operator for this system may be obtained from the Hamiltonian by means of the Liouville equation

$$i\hbar(d/dt)\rho(t)=[\mathcal{H}(t),\rho(t)]. \qquad (2)$$

Equation (2) may be solved by forming matrix representations of the operators appearing in it, and solving the corresponding differential equations for the

TABLE I. Notation.

Karplus[a]	This paper
$\mathbf{H}(t)$	$\mathcal{H}(t)-\mathcal{H}_R(t)$
$\bar{\mathbf{H}}_0$	$\mathcal{H}_0$
$\mathbf{H}_0(t)-\bar{\mathbf{H}}_0$	$\mathcal{H}'(t)$
$\mathbf{V}\cos[\int_0^t\omega(t')dt']$	$\mathcal{H}_1(t)$
ν	ω_s

[a] See Ref. 1.

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