and some coefficient.[31] After evaluating all of the reduced matrix elements and writing out all of the coefficients we have

$$\langle\phi_{j+1,\nu}(\mathbf{r}_2,\mathbf{r}_3)|\mathcal{H}_{ss}(\text{eff})|\phi_{j\nu}(\mathbf{r}_2,\mathbf{r}_3)\rangle$$

$$=-\alpha^2\sigma\bar{Q}_n[(j+1)^2-\nu^2]^{1/2}\frac{3(j+1)^2-l(l+1)-6}{4(j+1)(2l-1)(2l+3)}$$

$$\times\left[\frac{(j+l+3)(l+j)(j-l+2)(l-j+1)}{(2j+1)(2j+3)}\right]^{1/2}. \quad \text{(A7)}$$

To compute the second-order energy correction, the needed off-diagonal matrix elements have the following simple expressions:

$$\langle\phi_{2,\nu}(^3P_2)|\mathcal{H}(\text{eff})+\mathcal{H}_{ss}(\text{eff})|\phi_{1,\nu}(^3P_1)\rangle$$

$$=\tfrac{1}{2}\alpha^2\sigma\left(\frac{4-\nu^2}{3}\right)^{1/2}(Q_n-\tfrac{2}{5}\bar{Q}_n) \quad \text{(A8)}$$

and

$$\langle\phi_{3,\nu}(^3D_3)|\mathcal{H}(\text{eff})+\mathcal{H}_{ss}(\text{eff})|\phi_{2,\nu}(^3D_2)\rangle$$

$$=\tfrac{1}{3}\alpha^2\sigma[\tfrac{2}{5}(9-\nu^2)]^{1/2}\left(Q_n-\frac{5}{14}\bar{Q}_n\right). \quad \text{(A9)}$$

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Nonorthogonal Formulation of Hartree-Fock Perturbation Theory*

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Perturbation theory, up to first order in the wave function and second order in the energy, is formulated for a many-electron system without requiring the perturbed one-electron states to be orthogonal. The most general self-consistent coupled equations, referred to as Method 1, form the counterpart of Langhoff, Karplus, and Hurst's (LKH) Method *a* for orthogonal orbitals. The uncoupling of the perturbations $\delta\psi_i$, $\delta\psi_j$ to the zero order wave functions ψ_i^0 and ψ_j^0 produces equations referred to as Method 2. Further approximation in the Method-2 equations yields a set of equations called Method 3. Methods 2 and 3 are counterparts of LKH's Method *b*, but have computational advantages over Method *b* in that normalization and orthogonalization are accomplished in a particularly simple fashion. In comparing the uncoupled Method-3 equations with Dalgarno's equations, an additional difference is found involving the overlap integral between perturbed states, besides the difficulty pointed out by LKH. Application of the Method-2 and -3 equations is made to the spin-polarization problem of the Fe^{+3} ion, leading to a hyperfine constant in reasonable agreement with earlier unrestricted Hartree–Fock (UHF) calculations. A comparison between results obtained by Methods 2 and 3 and Dalgarno's equations permits a relative evaluation of these methods. We have also studied the effect of indirect spin polarization of the *s* electrons through the action of the *p* electrons which are in turn polarized by the unpaired *d* electrons. This contribution is found to be about 10% of the direct effect.

I. INTRODUCTION

In a recent paper, Langhoff, Karplus, and Hurst[1] (LKH) have examined some methods of applying perturbation theory to Hartree-Fock systems. In particular they showed that some important terms were omitted in the perturbation equations derived by Dalgarno[2] which led to inconsistencies. Thus, in the Hartree-Fock equation for the zero-order wave function, the Coulomb and exchange terms can be written in either of two equivalent forms:

$$h_i^{\text{Ce}}(1)u_i^0(1)=\sum_{j=1,j\neq i}^{N}[\langle u_j^0(2)|r_{12}^{-1}|u_j^0(2)\rangle u_i^0(1)$$

$$-\langle u_j^0(2)|r_{12}^{-1}|u_i^0(2)\rangle u_j^0(1)] \quad (1)$$

$$=\sum_{j=1}^{N}[\langle u_j^0(2)|r_{12}^{-1}|u_j^0(2)\rangle u_i^0(1)$$

$$-\langle u_j^0(2)|r_{12}^{-1}|u_i^0(2)\rangle u_j^0(1)]=h(1)^{\text{Ce}}u_i^0(1). \quad (2)$$

However, this is only true if the one-electron Hamiltonian acts on the zero-order wave function u_i^0, since in this case the self-Coulomb and self-exchange terms cancel. When the Hamiltonian acts on a first-order correction to the wave function, there is no such can-

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[1] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[2] A. Dalgarno, Proc. Roy. Soc. (London) A251, 282 (1959).

cellation. This lack of equivalence of the alternate forms (1) and (2) was responsible for the difficulty that crept into Dalgarno's formulation of Hartree-Fock perturbation equations. LKH have demonstrated that such an omission has more significance than being merely a further approximation. Thus, in an N-electron perturbation problem Dalgarno's equation determines the perturbation to a given electron in the presence of N other electrons instead of $N-1$, and so corresponds to a physically incorrect model.

In their formulation of the perturbation theory, LKH have made the restriction that the perturbed orbitals be orthogonal. We believe that some advantages in numerical computation accrue from relaxing this condition, and it is the purpose of this paper to give the relevant theory. We believe such an approach is important for the following reasons:

(1) There is a purely academic desire to have a complete, correct theory available in terms of nonorthogonal orbitals.

(2) The LKH equations (a) require for their validity subsidiary orthogonality conditions

$$\langle u_i^0 | u_j' \rangle + \langle u_i' | u_j^0 \rangle = 0 . \qquad (3)$$

Equations (b) and (d) are valid under conditions (3) as well as the more stringent conditions

$$\langle u_i' | u_j^0 \rangle = 0 , \qquad (4)$$

which have the advantage of avoiding coupling between u_i' and u_j'. The incorporation of Eqs. (3) or (4) into a numerical solution of the LKH equations introduces difficulties. It could be argued that the (in general) nonorthogonal solutions of the LKH equations could be orthogonalized by some procedure and reiterated. However, such orthogonalized functions are then no longer solutions of the original equations, and there appears to be no guarantee that such an iterative procedure will converge to orthogonal solutions. By relaxing the orthogonality condition we are able to develop below suitable perturbation equations whose solutions can be subsequently orthogonalized in a particularly simple fashion if desired.

(3) The LKH equations may be solved by a variational procedure utilizing the minimization of the appropriate functionals. In such a case the incorporation of the orthogonality conditions (3) or (4) presents no particular difficulty except that it leads to a loss of flexibility by reducing the number of independent variation parameters. Since the accuracy of the variation procedure can sometimes depend critically on the choice of variation parameters,[3] minimization of the functional appropriate to the nonorthogonal theory has advantages in avoiding loss of flexibility.

(4) The uncoupled LKH Eqs. (b) and Dalgarno's equations (LKH Method *c*) both reduce to the set of equations LKH Method *d* if a local approximation is used. We will show below that if the local approximation is made in the nonorthogonal orbital equivalents of Methods *b* and *c*, the two sets of equations do not become identical. Since some previous authors[4] have used the nonorthogonal Dalgarno equations, it is of interest to see if the corrected equations predict significantly different results.

(5) If a local approximation is used for the exchange integrals, a noniterative procedure is available for solving the resulting uncoupled equations. This proves to be numerically very convenient and has been used for the results presented in Sec. IV.

In Sec. II we develop the relevant equations for the nonorthogonal theory. In Sec. III we discuss the significance of the various stages of approximation by comparison with LKH's equations, and indicate the procedure used for their solution. An application to the calculation of the hyperfine field in the ion Fe^{+3} is made in Sec. IV both as a test of the methods suggested here and because of its current interest.[5] Section V is a summarizing discussion.

II. DERIVATION OF PERTURBATION EQUATIONS

To derive the equations for the nonorthogonal orbitals we repeat the derivation of the Hartree-Fock equation with the orthogonality condition relaxed. The starting point is the expression for the expectation value of a symmetric operator taken between determinantal wave functions:

$$\langle F \rangle = \sum_p \epsilon_p \int \prod_{i=1}^{N} u_i^*(i) F u_{pi}(i) d\tau_i \Bigg/ \sum_p \epsilon_p \int \prod_{i=1}^{N} u_i^*(i) u_{pi}(i) d\tau_i , \qquad (5)$$

where p is a permutation and ϵ_p is $+1$ (-1) for an even (odd) permutation. The integration symbol is meant to include the summation over spin coordinates.

We expand this expression, retaining terms only up to second order in nonorthogonality. The denominator is expanded using the familiar binomial theorem. We may assume without loss of generality that the perturbed orbitals are normalized. Putting

$$F = \sum_i \left(f_i + \tfrac{1}{2} \sum_{j \neq i} g_{ij} \right) , \qquad (6)$$

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[3] As an example, see N. Bessis, H. Lefebvre-Brion, and C. M. Moser [Phys. Rev. 124, 1124 (1961)], where a change in the number of basis states from six to seven changes the nitrogen atom hyperfine constant by about 20 to 60% for two alternate procedures.

[4] R. P. Hurst, Martin Karplus, and T. P. Das, J. Chem. Phys. 36, 2786 (1962). P. G. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. 126, 594 (1962). H. J. Kolker and M. Karplus, J. Chem. Phys. 41, 1259 (1964).

[5] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961). D. N. E. Buchanan and G. K. Wertheim, Bull. Am. Phys. Soc. 7, 227 (1962). K. Ono, Y. Ishikawa, A. Ito, and E. Hirahara, J. Phys. Soc. Japan 17, Suppl. B1, 125 (1962).

we have

$$\langle F\rangle=\sum_i \{\langle u_i|f|u_i\rangle+\sum_{j\neq i}[\tfrac{1}{2}\langle u_iu_j|\cdot|u_ju_i\rangle-\langle u_i|f|u_j\rangle\langle u_j|u_i\rangle+\langle u_j|f|u_j\rangle\langle u_i|u_j\rangle\langle u_j|u_i\rangle+\tfrac{1}{2}\langle u_iu_j|\cdot|u_ju_i\rangle$$
$$\times\langle u_j|u_i\rangle\langle u_i|u_j\rangle+\sum_{k\neq i,j}(-\tfrac{1}{2}\langle u_iu_j|\cdot|u_ju_k\rangle\langle u_k|u_i\rangle-\tfrac{1}{2}\langle u_iu_j|\cdot|u_ku_i\rangle\langle u_k|u_j\rangle+\langle u_j|f|u_k\rangle\langle u_k|u_i\rangle\langle u_i|u_j\rangle$$
$$+\tfrac{1}{2}\langle u_iu_j|\cdot|u_ju_i\rangle\langle u_k|u_i\rangle\langle u_i|u_k\rangle+\tfrac{1}{2}\langle u_ju_k|\cdot|u_ku_j\rangle\langle u_j|u_i\rangle\langle u_i|u_j\rangle+\sum_{l\neq i,j,k}\tfrac{1}{2}\{\langle u_ju_k|\cdot|u_ku_i\rangle\langle u_l|u_j\rangle$$
$$\times\langle u_i|u_l\rangle+\langle u_ju_k|\cdot|u_iu_j\rangle\langle u_l|u_k\rangle\langle u_i|u_l\rangle+\langle u_ju_k|\cdot|u_iu_l\rangle\langle u_l|u_j\rangle\langle u_i|u_k\rangle\})]\},\quad(7)$$

where for brevity we introduce the symbols

$$\langle u_i|\cdot|u_j\rangle u_k\equiv\langle u_i(2)|g_{12}|u_j(2)\rangle u_k(1)-\langle u_i(2)|g_{12}|u_k(2)\rangle u_j(1),$$
$$\langle u_iu_j|\cdot|u_ku_l\rangle\equiv\langle u_i(1)u_j(2)|g_{12}|u_k(2)u_l(1)\rangle-\langle u_i(1)u_j(2)|g_{12}|u_l(2)u_k(1)\rangle.\quad(8)$$

The latter equations represent just the Coulomb and exchange integrals.

If f_i and g_{ij} are the appropriate energy operators this expression contains all zero-, first- and second-order energy terms in addition to some higher-order terms. We could proceed to separate out the second-order energy for the subsequent variational procedure; however, an algebraically equivalent but simpler program is to use the variational principle on the expression in (7) and subsequently use the zero-order equation to eliminite zero-order terms from the result. By rejecting from the resulting equation all terms of higher order than first order we obtain an equation for the first-order perturbation to the wave function. We will assume the zero-order wave functions to satisfy the Hartree-Fock equation

$$-\tfrac{1}{2}\nabla^2u_i^0-\frac{Z}{r}u_i^0+\sum_j\langle u_j^0|\cdot|u_j^0\rangle u_i^0=\epsilon_i^0u_i^0.\quad(9)$$

The result of carrying out the variation procedure is

$$fu_i+\sum_j\{\langle u_j|\cdot|u_j\rangle u_i-\sum_{k\neq j}\langle u_k|u_j\rangle\langle u_j|\cdot|u_k\rangle u_i-\langle u_j|[f+\sum_k(\langle u_k|\cdot|u_k\rangle-\sum_{l\neq k}\langle u_k|u_l\rangle\langle u_l|\cdot|u_k\rangle)]|u_i\rangle u_j\}$$
$$+\sum_{j\neq i}\langle u_j|u_i\rangle\langle u_i|(f+\sum_k\langle u_k|\cdot|u_k\rangle)|u_i\rangle u_j=\epsilon_iu_i.\quad(10)$$

An alternative method of deriving Eq. (10) is to proceed as follows: From the nonorthogonal orbitals construct a set of orthogonal orbitals, by using, for example, a symmetric orthogonalization procedure.

$$\bar{u}_i=u_i-\tfrac{1}{2}\sum_{j\neq i}\langle u_j|u_i\rangle u_j.\quad(11)$$

These orthogonal orbitals will satisfy the Hartree-Fock equation

$$f\bar{u}_i+\sum_j\langle\bar{u}_j|\cdot|\bar{u}_j\rangle\bar{u}_i=\sum_j\lambda_{ij}\bar{u}_j.\quad(12)$$

On evaluating the coefficients λ_{ij} and expanding the $\bar{u}_j$ according to Eq. (11), Eq. (10) is obtained. The justification for such a procedure lies in the fact[6] that the expectation value of any operator taken between determinantal wave functions is independent of the particular set of orbitals used in the determinants for all sets which span the same Hilbert space. That is, we may use an orthogonal or nonorthogonal set of functions to evaluate the expectation value. The variational program is then a matter of varying the appropriate number of linearly independent functions and the minimization must be independent of how we choose the functions.

We complete the derivation of the perturbation equation by expanding f and g in Eq. (10) into their component operators and separating out the first-order terms. This procedure applies equally to the cases in which the perturbing Hamiltonian has a one-electron character, such as in polarizability problems[7,8] and the cases in which the perturbation is characteristically two-electron-like such as in van der Waals-type calculations.[9] For the purpose of this paper, we will assume the perturbation potential to be one-electron-like so that we may write

$$f=-\tfrac{1}{2}\nabla^2-Z/r+h',\qquad g_{12}=\frac{1}{|r_{12}|},\quad(13)$$

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[6] This result has been demonstrated quite generally by one of the present authors (K. J. D) and is presented in an appendix in a thesis which is being submitted by S. Ray to the University of California in partial fulfillment of the requirements of Ph.D. degree, 1968 (unpublished).

[7] See, for example, R. M. Sternheimer, Phys. Rev. **127**, 1220 (1962). E. G. Wikner and T. P. Das, *ibid.* **107**, 497 (1957).

[8] P. W. Langhoff and R. P. Hurst, Phys. Rev. **139**, A1415 (1965).

[9] Joseph O. Hirschfelder, Charles F. Curtiss, and R. Byron Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

so that the perturbation equations, which we will call Method 1, reduce to

$$(h^0-\epsilon_i^0)u_i'+h'u_i^0-\sum_j \langle u_j^0|h'|u_i^0\rangle u_j^0-\sum_j \langle u_j^0|u_i'\rangle(\epsilon_j^0-\epsilon_i^0)u_j^0-\sum_j\sum_{k\neq j} (\langle u_k|u_j\rangle\langle u_j^0|\cdot|u_k^0\rangle u_i^0-\sum_l \langle u_l^0|\langle u_k|u_j\rangle$$

$$\times\langle u_j^0|\cdot|u_k^0\rangle|u_i^0\rangle u_l^0)+\sum_j [\langle u_j'|\cdot|u_j^0\rangle u_i^0+\langle u_j^0|\cdot|u_j'\rangle u_i^0-\sum_k (\langle u_k^0u_j'|\cdot|u_j^0u_i^0\rangle$$

$$+\langle u_k^0u_j^0|\cdot|u_j'u_i^0\rangle)u_k^0]=0, \quad (14)$$

where h^0 contains the Coulomb and exchange operators h^{Ce} of Eq. (2). This is a set of coupled integrodifferential equations which may be solved (possibly by iteration) for the first-order perturbations to the wave functions. They are the nonorthogonal orbital equivalents of LKH Method *a*.

We proceed to uncouple these equations by following LKH's procedure of arbitrarily deleting from the equation for u_i' all terms containing u_j' $(j\neq i)$. The result is

$$(h_i^0-\epsilon_i^0)u_i'+h'u_i^0$$
$$=\sum_j \{\langle u_j^0|u_i'\rangle(\epsilon_j^0-\epsilon_i^0)u_j^0+\langle u_j^0|h'|u_i^0\rangle u_j^0$$
$$-\langle u_j^0u_i^0|\cdot|u_i^0u_i'\rangle u_j^0+\langle u_j^0|u_i'\rangle\langle u_i^0|\cdot|u_j^0\rangle u_i^0$$
$$-\sum_k \langle u_j^0|u_i'\rangle\langle u_k^0u_i^0|\cdot|u_j^0u_i^0\rangle u_k^0\}. \quad (15)$$

These equations we call Method 2 which is equivalent to LKH Method *b*. A further simplification can be made by arbitrarily dropping the terms:

$$\sum_j \langle u_j^0u_i^0|\cdot|u_i^0\bar{u}_i'\rangle, \qquad \bar{u}_i'=u_i'-\sum_{k\neq i} \langle u_k^0|u_i'\rangle u_k^0. \quad (16)$$

We may expect such terms to be near zero on the same grounds[10] as those sometimes given for the neglect of nonzero off-diagonal λ matrix elements in the zero-order problem, namely, the functions in the integrand are expected to overlap only very weakly. The result is

$$(h_i^0-\epsilon_i^0)u_i'+h'u_i^0=\sum_j \{\langle u_j^0|u_i'\rangle(\epsilon_j^0-\epsilon_i^0)u_j^0$$
$$+\langle u_j^0|h'|u_i^0\rangle u_j^0+\langle u_j^0|u_i'\rangle\langle u_i^0|\cdot|u_j^0\rangle u_i^0\}. \quad (17)$$

We call this Method 3. It is instructive to compare this with Dalgarno's equation[2] for nonorthogonal orbitals

$$(h^0-\epsilon_i^0)u_i'+h'u_i^0=\sum_j \{\langle u_j^0|u_i'\rangle(\epsilon_j^0-\epsilon_i^0)u_j^0$$
$$+\langle u_j^0|h'|u_i^0\rangle u_j^0\}, \quad (18)$$

which does not have the last term on the right-hand side of (17), in addition to having h^0 instead of h_i^0 on the left as pointed out earlier by LKH.

An approximation introduced by Sternheimer[11] and used by several authors[12] is to write

$$h_i^0-\epsilon_i^0=-\tfrac{1}{2}\nabla^2+\tfrac{1}{2}\nabla^2u_i^0/u_i^0. \quad (19)$$

This is equivalent to the local approximation discussed by LKH. As has already been pointed out, Eq. (19) is an identity if the operators are acting on the zero-order wave function u_i^0, but not otherwise. It is clear that if the approximation (19) is used in Eq. (17), and the right-hand side of (19) is used for $h^0-\epsilon_i^0$ in (16), the two equations have the same left-hand sides, but different right-hand sides.

All of Eqs. (14), (15), (17), and (18) have the important property that if

$$u_i^1=u_i'$$

are solutions, so are

$$u_i^1=u_i'+\lambda_a u_a^0,$$

where λ_a is a constant and u_a^0 is an occupied zero-order orbital. This means that if solutions are obtained which are not normalized or orthogonal they may be normalized/orthogonalized by addition of a suitable admixture of the zero-order wave function and the resulting functions are still solutions of the equations, provided the original nonorthogonality is small; this last condition is the condition of validity of the equations. However, if the local approximation (19) is made in (17) and (18) we can only claim to be able to normalize the perturbed wave functions; if the local approximation is an accurate representation of the nonlocal potential actually experienced by electron *i*, then the solutions of (17) may, in addition, be orthogonalized, but if orthogonalization is attempted for the solutions of (18) the resulting functions are not solutions of the same equations. Equations (14) and (15) may be solved directly or variation-wise by minimization of the following

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[10] For a discussion, see, for example, John C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Publishing Co., New York, 1960), Vol. II, p. 24.

[11] R. M. Sternheimer, Phys. Rev. **93**, 734 (1956).

[12] M. Karplus and H. J. Kolker, J. Chem. Phys. **38**, 1263 (1963); H. J. Kolker and M. Karplus, *ibid.* **39**, 2011 (1963); T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); G. D. Gaspari, Wei-Mei Shyu, and T. P. Das, *ibid.* **134**, A852 (1964).

functionals:

$$\begin{aligned}\langle u_i'|h_i^0-\epsilon_i^0|u_i'\rangle&-\sum_j |\langle u_j^0|u_j'\rangle|^2(\epsilon_j^0-\epsilon_i^0)+\sum_j\sum_k \langle u_i'|u_j^0\rangle\langle u_k^0|u_i'\rangle\langle u_j^0u_i^0|\cdot|u_k^0u_i^0\rangle+2\,\mathrm{Re}\{\langle u_i'|h'|u_i^0\rangle\\ &-\sum_j \langle u_i'|u_j^0\rangle\langle u_j^0|h'|u_i^0\rangle+\sum_j [\langle u_j^0|u_i'\rangle\langle u_i'u_i^0|\cdot|u_j^0u_i^0\rangle+\langle u_i'u_j'|\cdot|u_j^0u_i^0\rangle]+\sum_{j\neq i}\langle u_i'u_j^0|\cdot|u_j'u_i^0\rangle\\ &-\sum_j\sum_k [\langle u_i'|u_k^0\rangle\langle u_k^0u_j'|\cdot|u_j^0u_i^0\rangle+\langle u_i'|u_k^0\rangle\langle u_k^0u_j^0|\cdot|u_j'u_i^0\rangle]-\sum_j\sum_{k\neq j}(\langle u_k'|u_j^0\rangle+\langle u_k^0|u_j'\rangle)\\ &\times\langle u_i'u_j^0|\cdot|u_k^0u_i^0\rangle+\sum_j\sum_{k\neq j}\sum_l \langle u_k'|u_j^0\rangle\langle u_i'|u_l^0\rangle\langle u_l^0u_j^0|\cdot|u_k^0u_i^0\rangle\\ &\qquad+\sum_{j\neq i}\sum_{k\neq j}\sum_l \langle u_k^0|u_j'\rangle\langle u_i'|u_l^0\rangle\langle u_l^0u_j^0|\cdot|u_k^0u_i^0\rangle\},\end{aligned}\tag{14'}$$

$$\begin{aligned}\langle u_i'|h_i^0-\epsilon_i^0|u_i'\rangle&-\sum_j |\langle u_j^0|u_j'\rangle|^2(\epsilon_j^0-\epsilon_i^0)+2\,\mathrm{Re}\{\langle u_i'|h'|u_i^0\rangle-\sum_j [\langle u_i'|u_j^0\rangle\langle u_j^0|h'|u_i^0\rangle+2\langle u_i'|u_j^0\rangle\\ &\times\langle u_j^0u_i^0|\cdot|u_i^0u_i'\rangle]+\sum_j\sum_k \langle u_j^0|u_i'\rangle\langle u_i'|u_k^0\rangle\langle u_k^0u_i^0|\cdot|u_j^0u_i^0\rangle.\end{aligned}\tag{15'}$$

III. DISCUSSION OF PROPERTIES OF THE PERTURBATION EQUATIONS: RELATION TO OTHER APPROACHES

Within the area of applicability of the Hartree-Fock method, Eqs. (15), Method 1, are expected to be the most accurate of the approaches here suggested for the perturbation problem. This method is equivalent in principle to LKH Method *a*. In fact, as we remarked in Sec. II, it is always possible to find solutions of Eqs. (15) which are orthonormal and these solutions satisfy the simplified equations

$$\begin{aligned}(h^0-\epsilon_i^0)u_i'+[h'-\langle u_i^0|h'|u_i^0\rangle+\sum_j(\langle u_i^0u_j'|\cdot|u_j^0u_i^0\rangle+\langle u_i^0u_j^0|\cdot|u_j'u_i^0\rangle)]u_i^0+\sum_j(\langle u_j'|\cdot|u_j^0\rangle+\langle u_j^0|\cdot|u_j'\rangle)u_i^0\\ =\sum_{j\neq i}[\langle u_j^0|u_i'\rangle(\epsilon_j^0-\epsilon_i^0)+\langle u_j^0|h'|u_i^0\rangle+\sum_k\langle u_j^0u_k'|\cdot|u_k^0u_i^0\rangle+\langle u_j^0u_k^0|\cdot|u_k'u_i^0\rangle]u_j^0.\end{aligned}\tag{20}$$

The left-hand side of Eq. (20) is identical to the left-hand side of the LKH Method *a* equation. The terms on the right-hand side are absent in LKH Method *a* because, for the perturbed set of orbitals, they have required the λ matrix of Eq. (12) to be diagonal. In our treatment, the diagonality requirement is not appropriate because we have not imposed orthogonality. In fact, the coefficient of u_j^0 on the right-hand side of (20) is λ_{ij}. It is clear that the solution of (20) and of LKH Method *a* can only differ by a unitary transformation of the perturbed orbitals $u_i=u_i^0+u_i'$, and such a transformation cannot alter the theoretical expectation values of any physical observables.

It frequently occurs that the full accuracy of the Hartree-Fock method is not required so that some degree of precision can be sacrified for simplicity in computation. In such a case we believe Methods 2 and 3 offer a practical approach. We can use arguments similar to those above to show the equivalence of Method 2 and Method *b*, the more stringent orthogonalization conditions (4) being necessary for this purpose instead of the condition (3) used by LKH. Method 3 is an analog of Method *b* only when expression (16) is approximately zero.

The local approximation of Eq. (19) is attractive for computational purposes. It includes the nuclear potential and Coulomb interactions exactly, but approximates the exchange. It should be an acceptable approximation for core electrons, where the dominance of the nuclear potential makes exchange less significant. In deriving the local potential from Eq. (19), some smoothing may be necessary at the nodes of the zero-order function. For the problem discussed in Sec. IV, no such smoothing was required with the zero-order functions[13] employed.

The use of the local approximation allows one to use a noniterative method of solution. If the accuracy of the local approximation itself is not satisfactory, it can still be used as a fast method of obtaining the trial solutions for the first iteration without the local approximation. Alternatively, an equation can be formulated for the difference between the local and nonlocal approximation solutions, which can be solved approximately and iterated if necessary. In the calculations reported here, we have used the latter method and employed only one iteration.

Finally we observe that in formulating Eq. (15), terms are dropped from Method 1 which can be given a physical interpretation and whose effect on the solutions may therefore be suspected to be significant. We can treat this by first solving (15) and then regarding

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[13] Enrico Clementi, IBM J. Res. Develop. 9, 2 (1965).

the additional terms as a further perturbation, which can again be treated by (15). Just such a situation arises in the problem reported below. We have calculated core polarization of the ion Fe^{3+} due to unpaired d^5 electrons. In addition to the direct polarization of the s states by the d spin density it is possible for the d states to polarize the p states, giving rise to a p spin density which can give an additional indirect spin polarization of the s states. The exchange terms in Eq. (14) involving the perturbation (u_j') of the p states were therefore chosen to act as further perturbation to the s states. Numerov's method was used to solve the relevant differential equations and the results are discussed in Sec. IV.

IV. APPLICATION OF NONORTHOGONAL PERTURBATION THEORY TO Fe^{+3} HYPERFINE PROBLEM

Experimental evidence of a large negative magnetic field at the nuclei of some transition elements has been ascribed to the core polarization due to unpaired conduction/valence electrons.[5,14] A method which can be used for computation of this effect in atoms and ions is the unrestricted Hartree-Fock approach.[5,14] However, it is not yet possible to carry out such calculations in solids, so perturbation techniques must be used. It is therefore of interest to gauge the usefulness of the various perturbation methods in a system which is qualitatively similar to the transition metals, but which has the advantage of simplicitly. To meet these criteria we have chosen to study the Fermi contact interaction in the ion Fe^{3+}. Because of the large number of electrons on the ion, it is impractical to attempt a solution of (14) so we have solved only the equations of methods 2 and 3, and also Dalgarno's equations using the local approximation mentioned above. We have calculated two correction terms as described in the previous section. The first corrects for use of the local approximation; the second takes into account an indirect spin polarization due to a p spin density. The results are shown in Table I.

It is seen that Methods 2 and 3 and Dalgarno are in substantial agreement. However, the difference between the results with methods 2 and 3 is an order of magnitude smaller than their individual differences from the Dalgarno equation result. Since the local approximation was employed in the first instance in solving the three equations, the only effective difference between Method 3 and the Dalgarno equation is in the last term on the right of Eq. (17) which is absent from Eq. (18). It appears then that, for this problem at least, the missing term in Dalgarno's equation is more serious in effect than the approximation (16) made in obtaining Method 3, Eq. (17), from Method 2. It must be emphasized that the differences between the numerical results for Method 3 and Dalgarno's method are dependent on the degree of nonorthogonality of the solutions initially found [if it so happens that solutions are produced satisfying (4) the solutions will be identical] and are therefore a happenstance of the numerical method. If follows that no predictions can be made for the importance of the additional terms in Method 2 other than the statement that the 5% difference in the hyperfine field found here is grounds to suspect that the effect may be significant.

As anticipated, the local approximation was found to be quite acceptable for the innermost electrons (1s and 2s), although a significant correction term was found for the 3s state. The magnitude of the indirect spin-polarization correction, amounting to 10% of the calculated hyperfine field, indicates that the original uncoupling is the most severe of the states of approximation used in our development of the perturbation equations.

The total hyperfine field at the nucleus obtained from Method 2, after including nonlocal and indirect p spin polarization effects, is -745.2 kG, in reasonable agreement with -630 kG found by Watson and Freeman using an unrestricted Hartree-Fock (UHF) procedure. This reasonable agreement indicates that the use of Method 2 for hyperfine problems in solids would be quite justifiable. The remaining discrepancy of 115.2 kG could perhaps be explained by the effect of some of the consistency terms in Method 1 which were dropped in Method 2 and also indirect spin polarization involving the effect of core s states on one another.

V. CONCLUDING REMARKS

This paper presents a generalization to nonorthogonal orbitals of equations given by LKH for the Hartree-Fock perturbation problem. They have the advantage that if solutions are found which are not normalized or orthogonalized, such conditions can be imposed on the solutions, and the resulting functions are still solutions of the equations. The predictions of expectation values of physical operators will be the same for the solution of the equations here presented and for the solutions of LKH equations.

The coupled equations (Method 1) appear too complex for use in all but the simplest systems unless precision is mandatory. When some accuracy can be sacrificed for simplicity, Method 2 or Method 3 offers an attractive approach. The intermediate case in which some of the significant terms included in Method 1 but neglected in the other method need to be taken into account, can be treated satisfactorily by a repeated application of the approximate equations. It has been our experience that although the Method 2 equations are superficially more complex than the Method 3 equations, the additional complexity in numerical computation is only slight. We therefore recommend

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[14] V. Heine, Phys. Rev. **107**, 1002 (1957); J. H. Wood and G. W. Pratt, Jr., *ibid.* **107**, 995 (1957).

TABLE I. Spin density and hyperfine field in Fe^{+3} ion by various perturbation procedures.

Method	Spin density (atomic units) 1*s*	2*s*	3*s*	Total	Hyperfine field (kG)
Method 2	9.93×10^{-3}	-1.726	1.994×10^{-1}	-1.516	-795.0
Method 3	9.94×10^{-3}	-1.742	1.994×10^{-1}	-1.533	-803.7
Dalgarno	9.76×10^{-3}	-1.812	1.997×10^{-1}	-1.603	-840.2
Nonlocal Correction	1.54×10^{-5}	1.49×10^{-2}	-7.11×10^{-2}	-5.62×10^{-2}	-29.4
Indirect spin polarization correction	3.05×10^{-2}	-8.06×10^{-2}	2.012×10^{-1}	1.51×10^{-1}	79.2

Method 2 for approximate calculations, since it is less approximate with little extra effort needed.

The approach we have given is strictly a Hartree-Fock procedure, and therefore correlation effects have not been considered. This proves to be adequate for a large class of problems, but in some others, notably the core-polarization problem such as has been treated here, correlation effects are not negligible. Estimation of these effects will have to be made by some many-body methods, possibly the Bethe-Goldstone[15] and Brueckner-Goldstone[16] techniques.

The significance of the comparison of our hyperfine results with experiment, as also is the case for the UHF result, is rendered a little uncertain by the possible consequences of our total wave function not being an eigenfunction of S^2. It would be interesting to apply the nonorthogonal theory developed here to other problems such as the dipole and quadrupole polarizabilities and shielding factors. Useful comparisons could be made with the results of earlier workers[8,17] who have used the variational versions of the LKH methods *a*, *b*, and *d* for these properties.

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APPENDIX

As an example of the noniterative method used in these calculations to obtain a particular solution of the integrodifferential equation, we give here a variation of the method attributed[18] to Percival.

Consider the integrodifferential equation

$$L\psi=G+\langle\phi_1|\psi\rangle X_1+\langle\phi_2|\psi\rangle X_2\,, \tag{A1}$$

where L is a linear differential operator, and G, ϕ_1, ϕ_2, X_1, and X_2 are known functions.

We solve

$$Lu_1=G\,, \tag{A2}$$

$$Lu_2=X_1\,, \tag{A3}$$

$$Lu_3=X_2\,, \tag{A4}$$

assuming that the boundary conditions for (A1) can be applied to the solutions of (A2), (A3), and (A4). We write

$$\psi=u_1+\beta_2u_2+\beta_3u_3\,, \tag{A5}$$

where β_2 and β_3 are constants. Then

$$\begin{aligned}L\psi&=G+\beta_2X_1+\beta_3X_2\\&=G+(\langle\phi_1|u_1\rangle+\beta_2\langle\phi_1|u_2\rangle+\beta_3\langle\phi_1|u_3\rangle)X_1+(\langle\phi_2|u_1\rangle\\&\qquad+\beta_2\langle\phi_2|u_2\rangle+\beta_3\langle\phi_2|u_3\rangle)X_2\,.\end{aligned}$$

Assuming X_1 and X_2 to be linearly independent we can write the equations

$$(1-\langle\phi_1|u_2\rangle)\beta_2-\langle\phi_1|u_3\rangle\beta_3=\langle\phi_1|u_1\rangle\,, \tag{A6}$$

$$-\langle\phi_2|u_2\rangle\beta_2+(1-\langle\phi_2|u_3\rangle)\beta_3=\langle\phi_2|u_1\rangle\,. \tag{A7}$$

β_2 and β_3 can be obtained from (A6) and (A7), and the solution (A5) follows.

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[18] See R. Marriott, Proc. Phys. Soc. (London) **72**, 121 (1958).