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Calculation of the Magnetic Hyperfine Constant of the Nitrogen Atom

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The magnetic hyperfine constant for the $^4S_{3/2}$ state of the N^{14} atom has been calculated from a configuration interaction (CI) function built from the usual Hartree-Fock (HF) representation (where the orbitals are linear combinations of analytic functions) plus all singly-excited and some doubly-excited $s\rightarrow s$ configurations. We have found that the polarization of the s orbitals can be reasonably well represented by a basis set consisting of two series of Laguerre polynomials each of which is multiplied by an exponential function. If the energy is minimized with respect to the exponents of all s functions, then the calculated hyperfine constant appears to be in good agreement with experiment. For six s functions, the magnetic constant is found to be 13 Mc/sec (experimental 10.45 Mc/sec). Using seven s basis functions, the constant is 11 Mc/sec. We show in this paper that a configuration interaction function built from the usual HF representation plus all singly-excited $s\rightarrow s$ configurations is equivalent, *to first order*, to what Löwdin has called the extended Hartree-Fock representation. In addition, we show that the magnetic constant calculated from the spin-polarized (or unrestricted Hartree-Fock) function should be relatively close to that calculated from the CI function of HF plus singly excited configurations.

I. INTRODUCTION

The isotropic magnetic hyperfine constant a of an atom is given by[1]

$$a=\frac{8\pi}{3}\frac{\beta_n\beta_e}{IJ}\langle\Psi|\sum_i\delta(r_i)s_{zi}|\Psi\rangle, \tag{1}$$

where Ψ is the wave function for the electrons, β_n and β_e the nuclear and electronic magnetic moments, I the spin of the nucleus, J the total momentum of the electrons, and r_i the distance from electron i to the nucleus. This expectation value for certain paramagnetic atoms and ions, such as the nitrogen atom in its ^4S ground state, using the usual Hartree-Fock (HF) single-determinant representation, is zero in contradiction to experiment.[2] There are several different kinds of functions which can adequately take into account the polarization of the paired orbitals.

(A) A configuration interaction (CI) function built from the usual HF function plus excited $s\rightarrow s$ configurations could be used.[3–5] The most important contribution to the contact operator comes from singly-excited configurations. This kind of function has the decided advantage of being an eigenfunction of S^2, but in the present state of our computer programs it also has the decided disadvantage of being rather tedious to obtain.

(B) A single determinant representation can be used where different space orbitals are employed for the paired spin orbitals. This kind of function is called the unrestricted Hartree-Fock or spin-polarized[6] (SP) function. This representation has the great advantage of being practicable even for large systems but appears to have the disadvantage of not being an eigenfunction of S^2.

(C) The projection of this spin-polarized function can be carried out to obtain the desired spectroscopic state. This has been done for Li,[7] and it has been found that though the spin-polarized function is almost all in the doublet state, the value of the magnetic constant calculated from the projected function is considerably less than that obtained from the unprojected function. This large change is due to the fact that now the orbitals no longer minimize the energy of the function.

(D) It would be better to use orbitals which minimize the energy of the multideterminantal function. Löwdin[8] has called this kind of function the extended Hartree-Fock (EHF) representation. Unfortunately the difficulties that would be encountered in its calculation are very considerable and, as far as we know, such a wave function has never actually been determined.

In a forthcoming paper by Freeman and Watson[9] the interest will be concentrated on the results on the magnetic hyperfine constant of nitrogen that have been obtained from spin-polarized functions of types (B) and (C). In this paper we shall be interested in the calculation of this constant for the nitrogen atom using a CI function of type (A) where the SCF orbitals are linear combinations of analytic functions, following the method applied by Nesbet[5] to Li. As it is well known that the calculated magnetic constant varies very rapidly as a function of the exponents of the orbitals, we have been most interested in the magnetic constant given by the function where all exponents are varied to give the minimum energy.

We shall show that there is a first-order equivalence between the extended Hartree-Fock function and a CI function built from the usual HF representation

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[1] E. Fermi and E. Segrè, Rend. reale accad. nazl. Lincei **4**, 18 (1933); Z. Physik **82**, 729 (1933).
[2] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **116**, 87 (1959).
[3] A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).
[4] G. F. Koster, Phys. Rev. **86**, 148 (1952).
[5] R. K. Nesbet, Phys. Rev. **118**, 681 (1960).
[6] R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960).
[7] L. M. Sachs, Phys. Rev. **117**, 1504 (1960).
[8] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[9] A. J. Freeman and R. E. Watson (to be published).

plus all the singly-excited functions which are eigenfunctions of S^2. Also we show that the SP function is equivalent to first order, to a CI function built from the usual HF representation plus all the single-excited functions, but these are not eigenfunctions of S^2. With these equivalences, the magnetic constant calculated from the SP function is approximately equal to that calculated from the EHF function if (a) first-order perturbation theory is used to calculate the wave function and (b) certain exchange integrals are neglected in calculating the energy terms. After this work was completed, we were informed of an unpublished paper by Marshall[10] along similar lines although our formulation is rather different from his.

As far as we know, the only previous work on the calculation of the magnetic constant of nitrogen has been (a) that using the formalism of the SP representation[11]; (b) the work of Das and Mukherjee[12] in which they have used a special variational procedure which is not directly comparable to the results presented here.

II. RELATION BETWEEN DIFFERENT REPRESENTATIONS

In order to simplify the demonstration, we will assume that the HF function contains doubly-occupied orbitals $\varphi_1\cdots\varphi_n$ all of the same symmetry species (say s) and singly-occupied orbitals $\psi_1\cdots\psi_m$ of another symmetry species, say p. Then the HF determinant has the form:

$$\Psi_{\mathrm{HF}}=\det|\varphi_1\bar{\varphi}_1\cdots\varphi_n\bar{\varphi}_n\psi_1\cdots\psi_m|. \tag{2}$$

The corresponding spin-polarized function is

$$\Psi_{\mathrm{SP}}=\det|\phi_1\bar{\phi}_1'\cdots\phi_n\bar{\phi}_n'\psi_1\cdots\psi_m|. \tag{3}$$

It can be shown that to first order the orbitals $\psi_1\cdots\psi_m$ are the same in both functions.[13]

The φ_i's are completed by a set of orbitals φ_{n+1}, $\varphi_{n+2}\cdots$ to give a complete set of orthonormal orbitals. We can then expand the orbitals on which the spin-polarized function is built in terms of the complete set as follows:

$$\left.\begin{aligned}\phi_i&=\varphi_i+\sum_{k\neq i}\lambda_{ik}\varphi_k,\\ \phi_i'&=\varphi_i+\sum_{k\neq i}\lambda_{ik}'\varphi_k.\end{aligned}\right. \tag{4}$$

We assume that the orbitals which minimize the usual HF representation are not much different in form from those that minimize the SP representation. Thus λ_{ik} is small, λ_{ik}^2 can be neglected and the orbitals (4) are normalized to first order. Substituting (4) in (3), then we can express Ψ_{SP} as

$$\Psi_{\mathrm{SP}}=\Psi_{\mathrm{HF}}+\sum_{ik}\left(\lambda_{ik}\Theta_{ik}+\lambda_{ik}'\Theta_{ik}'\right)+\text{terms in }\lambda^2, \tag{5}$$

where

$$\Theta_{ik}'=\det|\varphi_1\bar{\varphi}_1\cdots\varphi_i\bar{\varphi}_k\cdots\psi_1\cdots\psi_m|, \tag{6}$$

and

$$\Theta_{ik}=\det|\varphi_1\bar{\varphi}_1\cdots\varphi_k\bar{\varphi}_i\cdots\psi_1\cdots\psi_m|.$$

We shall neglect the terms in λ^2. With a change of variable, (5) can be rewritten as

$$\begin{aligned}\Psi_{\mathrm{SP}}&=\Psi_{\mathrm{HF}}+\sum_{ik}\left[\alpha_{ik}\frac{1}{\sqrt{2}}(\Theta_{ik}-\Theta_{ik}')\right.\\&\qquad\left.+\beta_{ik}\frac{1}{\sqrt{2}}(\Theta_{ik}+\Theta_{ik}')\right]\\&=\Psi_{\mathrm{HF}}+\textstyle\sum_{ik}(\alpha_{ik}A_{ik}+\beta_{ik}B_{ik}).\end{aligned} \tag{7}$$

It is easy to show that, as the orbitals φ_i are solutions of the Hartree-Fock equations, then from first-order perturbation theory $\beta_{ik}=0$.[13] In any case, considering the form of the Fermi contact operator (1) the contributions to the magnetic constant from Θ_{ik} and Θ_{ik}' will cancel one another and thus the contribution from B_{ik} will be zero.

If the coefficients α_{ik} are calculated from first-order perturbation theory, then the magnetic constant which is obtained from the SP function is given by the formula:

$$a_{\mathrm{SP}}=2\sum_{ik}\frac{\langle\Psi_{\mathrm{HF}}\mathcal{H}A_{ik}\rangle}{E_{ik}-E_{\mathrm{HF}}}\langle\Psi_{\mathrm{HF}}|\sum_i\delta(r_i)s_{zi}|A_{ik}\rangle, \tag{8}$$

where $\mathcal{H}$ is the Hamiltonian consisting only of kinetic and electrostatic interaction terms

$$E_{ik}=\langle A_{ik}\mathcal{H}A_{ik}\rangle,\quad E_{\mathrm{HF}}=\langle\Psi_{\mathrm{HF}}\mathcal{H}\Psi_{\mathrm{HF}}\rangle.$$

It should be noted that the functions A_{ik} are not eigenfunctions of S^2.

The coefficients λ_{ik} in Eq. (4), obtained from the formula

$$\lambda_{ik}=-\lambda_{ik}'=\sqrt{2}\alpha_{ik}, \tag{9}$$

can be considered as giving the corrections of the first iteration to the HF orbitals φ_i which make it possible to calculate the SP orbitals ϕ_i.[13] Later on we shall give a numerical example to show that this has a rather important influence on the calculation of the magnetic constant.

A similar treatment can be made for the extended Hartree-Fock function:

$$\Psi_{\mathrm{EHF}}=\Omega\det|\phi_1^e\bar{\phi}_1^{e\prime}\cdots\phi_n^e\bar{\phi}_n^{e\prime}\psi_1\cdots\psi_m|, \tag{10}$$

where Ω is the projection operator of Löwdin[14] and where the superscript e emphasizes the fact that the minimization has been done after the projection. In a similar way, the orbitals ϕ_i^e can be expanded in the set

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[10] W. Marshall, Proc. Phys. Soc. (London) **A78**, 113 (1961).

[11] S. M. Blinder, Bull. Am. Phys. Soc. **5**, 14 (1960).

[12] T. P. Das and A. Mukherjee, J. Chem. Phys. **33**, 1808 (1960).

[13] R. Lefebvre, Cahiers phys. **381**, 1 (1959).

[14] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

$\varphi_1\cdots\varphi_n\ \varphi_{n+1}\cdots$, and after some elementary rearrangement one finds:

$$\Psi_{\mathrm{EHF}}=\Psi_{\mathrm{HF}}+\sum_{ik}\left(\alpha_{ik}{}^e\,\mathrm{Proj}A_{ik}+\beta_{ik}{}^eB_{ik}\right)+\cdots,\quad(11)$$

where $\mathrm{Proj}A_{ij}=k^{\frac{1}{2}}\Omega A_{ij}$, k being a normalization constant. Note that the projection of B_{ij} is B_{ij} and consequently $\beta_{ij}{}^e=0$. Thus, within the present approximation, the EHF function is the same as a configuration interaction function between Ψ_{HF} and all singly-excited functions. Then if, as above, the $\alpha_{ik}{}^e$'s are calculated by first-order perturbation theory the magnetic constant that would be calculated from Ψ_{EHF} is given by the expression:

$$a_{\mathrm{EHF}}=2\sum_{ik}\frac{\langle\Psi_{\mathrm{HF}}\mathcal{H}\,\mathrm{Proj}A_{ik}\rangle}{E_{\mathrm{Proj}\,ik}-E_{\mathrm{HF}}}\times\langle\Psi_{\mathrm{HF}}|\sum_i\delta(r_i)s_{zi}|\mathrm{Proj}A_{ik}\rangle,\quad(12)$$

$$E_{\mathrm{Proj}\,ik}=\langle\mathrm{Proj}A_{ik}\mathcal{H}\,\mathrm{Proj}A_{ik}\rangle.$$

If we assume that $E_{\mathrm{Proj}\,ik}\simeq E_{ik}$, i.e., certain exchange integrals are neglected, then to first order

$$a_{\mathrm{EHF}}\simeq a_{\mathrm{SP}}\quad(13)$$

(see Appendix I). Evidently, the equivalence of spin density calculated by the two types of functions is valid for all points in space. We shall give some numerical examples of this equivalence for the nitrogen atom in Sec. IV.

III. CALCULATIONS

We have used a program written by Nesbet and Watson for the IBM-704 computer to calculate SCF orbitals for atoms where the radial parts are linear combinations of analytic functions of the type $\chi_{n+1}=r^ne^{-\alpha r}$. In this program, n can be any integer and α can have any value. In choosing the values of the exponents, considerable care must be taken to avoid the maxima of different functions coming too close together; otherwise the SCF orbitals have a tendency not to be linearly independent.[15]

From these calculations a configuration interaction function was built either (a) by using first-order perturbation theory (FOP) or (b) by diagonalizing a matrix (DM). If function was of type (a), only singly excited $s\rightarrow s$ functions were used since the Fermi contact operator is a sum of one-electron operators. For functions of type (b), the important doubly-excited functions were also included. Excited configurations are of course built using the virtual SCF orbitals.[16]

The contribution to the magnetic constant of the type of excitation $\varphi_{2s}\rightarrow\varphi_{ns}$ is positive while that of $\varphi_{1s}\rightarrow\varphi_{ns}$ is negative. The resultant constant is the small difference between two large numbers. It is not surprising then that the results are somewhat sensitive to the method used to calculate the CI function.

IV. RESULTS

The simplest basis set of s functions, which can be used in the CI method to calculate the magnetic hyperfine constant of the nitrogen atom, is that which consists of one $1s$-like, one $2s$-like and one $3s$-like function (and, of course, one $2p$ function). If Slater's rules are used for the exponents, then as two of us have previously shown[17] the calculated value of a is 7.5 Mc/sec, in good agreement with the experimental value $a=10.45$ Mc/sec.[2] However these exponents do not minimize the energy of the ^4S ground state of the atom for this basis set. A triple minimization is too tedious to carry out exactly. However, among several trial functions, the one which gives the lowest energy (-54.296 atomic units) (numerical HF, -54.40_5 a.u.)[18] corresponds to a value of the magnetic constant in worse agreement with experiment (18 Mc/sec).

We have then considered more elaborate kinds of functions and, in particular, the fit that Löwdin[19] has made to the numerical HF function using analytical orbitals. For nitrogen he used five s functions (two $1s$-like, three $2s$-like) and three $2p$-like functions. Using the exponents given,[19] we have found from our (FOP) function $a=5$ Mc/sec. A fivefold minimization of the corresponding CI function would be extremely tedious indeed. Thus, even though for nitrogen the fit of Löwdin gives good results, this could perhaps be a coincidence. The fit made to the numerical function by series of analytical expressions is not, unfortunately, unequivocal. The particular choice will have a larger effect on the calculation of the magnetic constant because the virtual orbitals which determine the constant are much more sensitive to the choice of parameters than the occupied orbitals.

We have also used a representation for the s orbitals which is analogous to that used by Nesbet[5] for the magnetic constant of Li, that is, more functions of the type $1s$ (three) which do not vanish at the nucleus than functions of the type $2s$ (one). Only negative values of the magnetic constant were found and variation of the exponents did not seem to improve the results.

We then turned to the use of two series of Laguerre polynomials, each series multiplied by rather different exponential function to represent the φ_{ns} functions.

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[15] R. E. Watson, Phys. Rev. **119**, 170 (1960).

[16] For the ^4S state of nitrogen single $s\rightarrow s$ excitation gives a configuration where five electrons are associated with five different orbitals. These give rise to two independent ^4S functions one of which (B_{ik} function) has zero matrix element with the ground state but the other function ($\mathrm{Proj}A_{ik}$) has a small but nonzero matrix element with the ground state.

[17] N. Bessis and H. Lefebvre, Compt. rend. **251**, 648 (1960). In this article the sign of the contribution $\varphi_{1s}\rightarrow\varphi_{ns}$ was given incorrectly.

[18] D. Myers (private communication).

[19] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

The orbitals have the form:

$$\varphi_{ns}=(a_{1n}+b_{1n}r+c_{1n}r^2+\cdots)e^{-\alpha_1 r}+(a_{2n}+b_{2n}r+c_{2n}r^2+\cdots)e^{-\alpha_2 r}. \quad (14)$$

This kind of function has already been used to study polarization effects in atoms[20] and magnetic constants of atoms,[21] though a study of the results of a wide variation of parameters appears not to have been made. This type of calculation is particularly attractive since it is relatively easy to carry out a double interpolation. In addition two $2p$ functions are used. The results for both (FOP) and (DM) types of CI function are collected in Table I. The comparison with experiment seems satisfactory for both six and seven basis functions and it is better with seven than six. The seven basis functions are divided, three for the larger parameter and four for the smaller. In the (DM) calculation not only are the singly $s\rightarrow s$ configurations included, but also the double excitations of the type $(\varphi_{2s})^2\rightarrow(\varphi_{ns})^2$ (which does not have an entirely negligible effect on the magnetic constant) and $(\psi_{2p})^2\rightarrow(\psi_{3p})^2$ (which is added mainly because of its important effect in the energy). It is not possible to consider the small number of Laguerre functions used here as a complete set. Each time the number of functions is changed it is necessary to search again for a minimum.

In one case [six φ_{ns} functions Eq. (14) $\alpha_1=7$, $\alpha_2=1.5$] the value of the magnetic constant has been calculated from perturbation equations (8) and (12), (FOP) as well as from the corresponding complete CI calculation (DM). Also the values have been calculated for the same basis directly from the SP function.[22] Table II gives the results.

Using the perturbation formulas amounts, as we have said, to making the first iteration on φ_i(HF) to calculate either ϕ_i(SP) or ϕ_i^e(EHF). The difference of values given in column 2 and column 5 of Table II is due to the fact that the difference between the value at the nucleus of functions ϕ_i and ϕ_i' associated with α spin and β spin, respectively, is far greater when the iterations have converged (i.e., SP function calculated by program) than after the first iteration (i.e., perturbation equations). In addition we have indicated in Table II the value of the constants obtained from the projection of the SP function. It can be shown (cf. Appendix II) that for ${}^4S_{3/2}$ state of nitrogen $a_{\mathrm{ProjSP}}\simeq\frac{3}{5}a_{\mathrm{SP}}$. We should emphasize that in our view the use of the projected SP function seems not to be adequate because the orbitals now no longer are found from a minimization process. The value of 9 Mc/sec for the magnetic constant can be considered to be fortuitous.

TABLE I. Magnetic hfs constant of N found from CI functions.

	Six φ_{ns} functions[a]		Seven φ_{ns} functions[a]	
	FOP	DM	FOP	DM
α_1 min	6.89	6.93	7.85	8
α_2 min	1.58	1.62	2	1.9
E min (a.u.)	−54.4001	−54.4105	−54.4007	−54.4108
$\varphi_{2s}\rightarrow\varphi_{ns}$ (Mc/sec)	54	58	54	58
$\varphi_{1s}\rightarrow\varphi_{ns}$ (Mc/sec)	−46	−46	−49	−47
a (Mc/sec)[b]	8	13	5	11

[a] As given in Eq. (14).
[b] The numerical constant $(8\pi/3)(\beta_n\beta_e/IJ)=215.187a_0^3$ Mc/sec.

TABLE II. Comparison of magnetic constants calculated by different methods [six φ_{ns} functions of Eq. (14), $\alpha_1=7.0$, $\alpha_2=1.5$].

	Perturbation calculations			Complete calculations	
	a_{EHF}[a]	a_{SP}[b]	a_{ProjSP}[c]	a_{DM}	a_{SP}[d]
$2s$ contribution	54	61	37	61	108
$1s$ contribution	−46	−46	−28	−45	−75
a (Mc/sec)	8	15	9	16	33

[a] Taken from Eq. (12).
[b] Taken from Eq. (8).
[c] Taken from Eq. (21).
[d] Calculated from SP orbitals obtained from program of Nesbet and Watson.

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APPENDIX I

This is to demonstrate that from a first-order perturbation argument plus some additional restrictions there should be an approximate equality between the magnetic constants calculated from the SP and the EHF functions.

There are the relations[23]:

$$\mathrm{Proj}A_{ij}=k^{-\frac{1}{2}}[A_{ij}+\textstyle\sum_\nu c_\nu A_{ij}{}^\nu], \quad (15)$$

$$=k^{\frac{1}{2}}\Omega A_{ij}, \quad (16)$$

where Ω is the projection operator defined by Löwdin, k is a normalization constant, and $A_{ij}{}^\nu$ is a determinant belonging to the same configuration as A_{ij}. As A_{ij} differs from Ψ_{HF} by two spin orbitals, the matrix element of a one-electron operator between these functions will be zero. The matrix elements of the Fermi-contact operator are given by the formula [for the EHF functions (15)]:

$$\langle\Psi_{\mathrm{HF}}|\textstyle\sum_i\delta(r_i)s_{zi}|\mathrm{Proj}A_{ij}\rangle=k^{-\frac{1}{2}}\langle\Psi_{\mathrm{HF}}|\textstyle\sum_i\delta(r_i)s_{zi}|A_{ij}\rangle. \quad (17)$$

Also as Ω commutes with the Hamiltonian $\mathcal{H}$ and as $\Omega\Psi_{\mathrm{HF}}=\Psi_{\mathrm{HF}}$ we have the following relation (16):

$$\langle\Psi_{\mathrm{HF}}\mathcal{H}\,\mathrm{Proj}A_{ij}\rangle=k^{\frac{1}{2}}\langle\Psi_{\mathrm{HF}}\mathcal{H}A_{ij}\rangle. \quad (18)$$

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[20] E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957).

[21] M. H. Cohen, D. A. Goodings, and W. Heine, Proc. Phys. Soc. (London) **A73**, 811 (1959).

[22] The program of Nesbet and Watson can be used to calculate either the usual HF orbitals or SP orbitals.

[23] R. K. Nesbet, Ann. Phys. (N.Y.) **3**, 397 (1958).

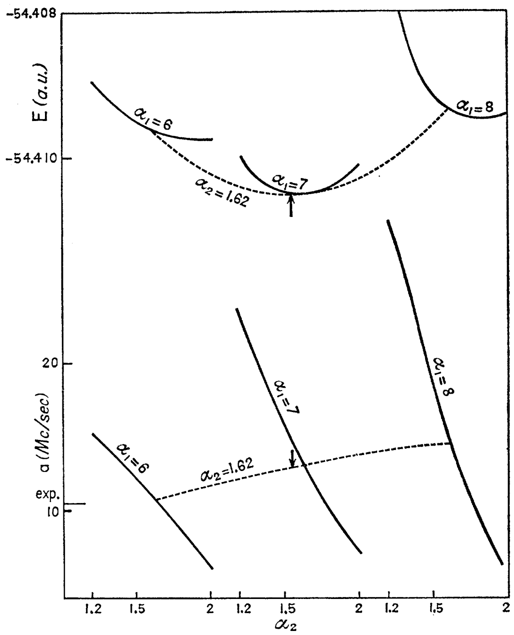

FIG. 1. Variation of energy of CI function (upper curves) and of magnetic hfs constant (lower curves) of nitrogen as function of exponents α_1 and α_2. Six basis functions are used. The arrows indicate the values of the parameters which give the minimum of energy.

The numerators in the expressions for a_{SP} of Eq. (8) and a_{EHF} of Eq. (12) are thus the same. As the denominators only differ by a few exchange integrals, one then has the relation:

$$a_{\text{SP}} \simeq a_{\text{EHF}}.$$

APPENDIX II

The projected function of the SP function can be written as

$$\begin{aligned}\Omega\Psi_{\text{SP}} &= \Omega\Big(\Psi_{\text{HF}}+\sum_{ij}\alpha_{ij}A_{ij}\Big)\\ &= \Psi_{\text{HF}}+\sum_{ij}\alpha_{ij}\Omega A_{ij},\end{aligned} \tag{19}$$

where α_{ij}; is determined from the SP function (7). This can be written (16):

$$\Omega\Psi_{\text{SP}} = \Psi_{\text{HF}}+\sum_{ij}\alpha_{ij}k^{-\frac{1}{2}}\,\text{Proj}A_{ij}. \tag{20}$$

Then the magnetic constant obtained from the projected function will be given by the formula:

$$a_{\text{ProjSP}} = 2\sum_{ij}\alpha_{ij}k^{-\frac{1}{2}}\langle\Psi_{\text{HF}}|\sum_{n}\delta(\mathbf{r}_n)s_{zn}|\text{Proj}A_{ij}\rangle. \tag{21}$$

If we substitute in this formula the value of matrix elements of the Fermi contact operator given in (17), it is easy to see that

$$a_{\text{ProjSP}} \simeq k^{-1}a_{\text{SP}}. \tag{22}$$

For nitrogen $k=5/3$; thus $a_{\text{ProjSP}} \simeq \frac{3}{5}a_{\text{SP}}$.