TOWARDS A METHOD FOR THE ACCURATE SOLUTION OF THE SCHRÖDINGER WAVE EQUATION IN MANY VARIABLES

III. APPLICATION OF THE GENERAL METHOD TO THE WAVE EQUATION WITHOUT SPATIAL SYMMETRY

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Summary

The method of Part I is applied to the problem of finding the lowest antisymmetric eigenfunction of the wave equation for n electrons without spatial symmetry, and the lowest antisymmetric eigenfunction of given multiplicity. Knowledge of the multiplicity of the ground state is not needed. Theorem 3 of Part I, which proves the equivalence of the central stationary condition to a minimum condition, is extended to cover the present case.

I. CHOICE OF THE SPIN FUNCTIONS

The wave equation for n electrons moving in a field of atomic nuclei regarded as fixed point charges is, in atomic units,

$$\left(-\tfrac{1}{2}\sum_j \nabla_j^2 - \sum_\alpha \sum_j \frac{N_\alpha}{r_{\alpha j}} + \sum_{i<j} \frac{1}{r_{ij}}\right)\Psi = E\Psi, \qquad \ldots\ldots\ldots\ (1)$$

where E is the energy, Ψ the wave function, and, if x_j, y_j, z_j are the Cartesian coordinates of the jth electron,

$$r_{ij}=\sqrt{\{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2\}},$$

and, if x_α, y_α, z_α are the Cartesian coordinates of the αth nucleus, which bears the charge N_α,

$$r_{\alpha j}=\sqrt{\{(x_j-x_\alpha)^2+(y_j-y_\alpha)^2+(z_j-z_\alpha)^2\}},$$

and

$$\nabla_j^2=\frac{\partial^2}{\partial x_j^2}+\frac{\partial^2}{\partial y_j^2}+\frac{\partial^2}{\partial z_j^2}.$$

We seek not merely a solution of (**1**), but a solution of (**1**) having a certain symmetry. The simplest prescription for this symmetry is that the wave function including spin is "antisymmetric", i.e. is multiplied by -1 by an odd permutation of the electron indices. Let the spin coordinates of the n electrons be denoted by s_1, s_2, . . ., s_n. An arbitrary function

$$\Phi(x_1y_1z_1s_1x_2y_2z_2s_2\ .\ .\ .\ x_ny_nz_ns_n)$$

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of space and spin coordinates can be expressed as an infinite series

$$\begin{aligned}\Phi&=\sum_k \xi_k\\ &=\sum_k f_{1k}(x_1)g_{1k}(y_1)h_{1k}(z_1)\sigma_{1k}(s_1)f_{2k}(x_2)g_{2k}(y_2)h_{2k}(z_2)\sigma_{2k}(s_2)\ldots f_{nk}(x_n)g_{nk}(y_n)h_{nk}(z_n)\sigma_{nk}(s_n),\end{aligned} \qquad \ldots\ldots\ldots\ldots (2)$$

where $\sigma_{jk}(s)=\delta_{s,\sigma_{jk}}$ and σ_{jk} may have the values $+1$ or -1. We shall write $\delta_{s,1}=\alpha(s)$ and $\delta_{s,-1}=\beta(s)$. If P is a permutation on the numbers $1, 2, \ldots, n$, let $\mathbf{O}_P$ denote the operation of permuting the electron indices in a function of space and spin. Let $\mathbf{Q}_R$ denote the operation of applying a rotation R to the spin coordinates alone. $\mathbf{O}_P$ and $\mathbf{Q}_R$ commute and we may express any function ξ of space and spin in the form

$$\xi=\xi^{(1)}+\xi^{(2)}+\ldots+\xi^{(S)}+\ldots,$$

where $\xi^{(S)}$ belongs to the irreducible representation $\mathsf{D}^{(S)}(R)$ of the rotation group with respect to $\mathbf{Q}_R$: that is, it has the symmetry with respect to $\mathbf{Q}_R$ which corresponds to the multiplicity S (Wigner 1931). Further, each $\xi^{(S)}$ can be written in the form $'\xi^{(S)}+''\xi^{(S)}$, where $'\xi^{(S)}$ is antisymmetric with respect to $\mathbf{O}_P$ and $''\xi^{(S)}$ contains no antisymmetric component, and both belong to $\mathsf{D}^{(S)}(R)$ with respect to $\mathbf{Q}_R$. Let $\mathbf{Q}_P$ denote the operation of applying a permutation to the spin coordinates alone. A function of spin which belongs to $\mathsf{D}^{(S)}(R)$ with respect to $\mathbf{Q}_R$ belongs to $A^{(S)}(P)$ with respect to $\mathbf{Q}_P$ where $A^{(S)}(P)$ is an irreducible representation of the permutation group whose character is the coefficient of $x^{\frac{1}{2}n-S}$ in

$$(1-x)(1+x^{\rho_1})(1+x^{\rho_2})\ldots(1+x^{\rho_\nu}),$$

where $\rho_1, \rho_2, \ldots, \rho_\nu$ are the cycle-lengths of P. Hence

$$\sum_P \chi^{(S)}(P)\mathbf{Q}_P\xi=\text{const.}\times\xi^{(S)},$$

where $\chi^{(S)}(P)$ is the character of P in $A^{(S)}(P)$, and

$$\sum_P \varepsilon_P\mathbf{O}_P\sum_{P'}\chi^{(S)}(P')\mathbf{Q}_{P'}\xi=\text{const.}\times{}'\xi^{(S)}, \qquad \ldots\ldots\ldots\ldots (3)$$

where $\varepsilon_P=+1$ or -1 according as P is even or odd.

This means that, given an arbitrary function ξ of space and spin, its component belonging to the irreducible representation $\varepsilon_P\mathsf{D}^{(S)}(R)$ of the direct product group of $\mathbf{O}_P$ and $\mathbf{Q}_R$ is given by the expression on the left of equation (**3**) (apart from a constant factor).

If for ξ we substitute

$$\Phi=\sum_k \xi_k$$

from (**2**), and assume that Φ is antisymmetric and has the multiplicity S, then an expression for Φ is obtained in the form

$$\sum_k \sum_P \varepsilon_P\mathbf{O}_P\sum_{P'}\chi^{(S)}(P')\mathbf{Q}_{P'}f_{1k}(x_1)g_{1k}(y_1)h_{1k}(z_1)\sigma_{1k}(s_1)\ldots f_{nk}(x_n)g_{nk}(y_n)h_{nk}(z_n)\sigma_{nk}(s_n). \qquad \ldots\ldots\ldots\ldots (4)$$

This expression is, in general, the sum of $2s+1$ orthogonal functions, one belonging to each of the $2s+1$ rows of $\varepsilon_P \mathsf{D}^{(S)}(R)$. Those terms, for which

$$\tfrac{1}{2}(\sigma_{1k}+\sigma_{2k}+\ldots+\sigma_{nk})=m,$$

belong to the mth row, the rows being numbered $-m$ to $+m$. Hence, if the spin functions are restricted to satisfy $\frac{1}{2}(\sigma_{1k}+\sigma_{2k}+\ldots+\sigma_{nk})=m$, where $|m|\leqslant S$, the expression (4) belongs to the mth row of $\varepsilon_P \mathsf{D}^{(S)}(R)$. Since the eigenvalues of (1) are independent of m, for the purpose of calculating an eigenvalue it is sufficient to choose $m=0$, if n is even, and $m=\frac{1}{2}$, if n is odd.

For example, for $n=3$, $S=1$ taking $\sigma_{1k}(s)=\alpha(s)$, $\sigma_{2k}(s)=\beta(s)$, $\sigma_{3k}(s)=\alpha(s)$ and using the abbreviation

$$\varphi_1(X_j)=f_1(x_j)g_1(y_j)h_1(z_j)$$

the series is

$$\Sigma \sum_P \varepsilon_P \mathbf{O}_P \sum_{P'} \chi^{(1)}(P')\mathbf{Q}_{P'}\varphi_1(X_1)\alpha(s_1)\varphi_2(X_2)\beta(s_2)\varphi_3(X_3)\alpha(s_3), \quad \ldots\ldots \quad (5)$$

where the subscript k has been omitted on the first summation sign and on the φ's. The elements of the group of permutations on 1, 2, 3 are (1), (12), (23), (31), (123), and (132). The characters are

$$\chi^{(1)}(1)=2,\ \chi^{(1)}(12)=\chi^{(1)}(23)=\chi^{(1)}(31)=0,\ \chi^{(1)}(123)=-1=\chi^{(1)}(132).$$

Hence the expression (5) becomes

$$\begin{aligned}\Sigma[2\sum_P \varepsilon_P \mathbf{O}_P &\varphi_1(X_1)\alpha(s_1)\varphi_2(X_2)\beta(s_2)\varphi_3(X_3)\alpha(s_3)\\ -\sum_P \varepsilon_P \mathbf{O}_P &\varphi_1(X_1)\alpha(s_1)\varphi_2(X_2)\alpha(s_2)\varphi_3(X_3)\beta(s_3)\\ -\sum_P \varepsilon_P \mathbf{O}_P &\varphi_1(X_1)\beta(s_1)\varphi_2(X_2)\alpha(s_2)\varphi_3(X_3)\alpha(s_3)],\end{aligned}$$

which may be written for short

$$\Sigma[2 \text{ Det } \{\varphi_1\alpha\varphi_2\beta\varphi_3\alpha\} - \text{Det } \{\varphi_1\alpha\varphi_2\alpha\varphi_3\beta\} - \text{Det } \{\varphi_1\beta\varphi_2\alpha\varphi_3\alpha\}]. \quad \ldots \quad (6)$$

It follows that an eigenfunction belonging to any given eigenvalue, in particular the lowest eigenvalue, regardless of its multiplicity, can be expressed in the form

$$\sum_k \text{Det } \{f_{1k}(x_1)g_{1k}(y_1)h_{1k}(z_1)\alpha(s_1) \ldots f_{nk}(x_n)g_{nk}(y_n)h_{nk}(z_n)\beta(s_n)\}, \quad \ldots \quad (7)$$

where an equal number of α's and β's are to be taken if n is even, and one more α than β if n is odd.

In the next section, the stationary condition for the functions of one variable is based on the expression (7) for the wave function. If the lowest eigenvalue of multiplicity S is sought, and it is not the ground state eigenvalue, the stationary condition must be based on (4), wherein the σ's may, as above, be chosen so that $m=0$ (if n is even) and $m=\frac{1}{2}$ (if n is odd).

II. Derivation of the Stationary Condition for the Ground State

Application of the method of Part I (Bassett 1959a) to this problem, whereby the successive terms in the series expression for the eigenfunction become the determinants of (7), finds the lowest eigenfunction of the form (7), and therefore finds an eigenfunction belonging to the lowest eigenvalue which corresponds to a physical state. The determinants are built up by the type of iterative procedure described in Parts I and II (Bassett 1959*a*, 1959*b*), in which the central process is the solution of a stationary condition for a function of one variable.

Let $\mathscr{H}$ represent the differential operator in (**1**). Following the notation used in Parts I and II, let us write

$$Q=Q(\Psi)=\int\Psi\mathscr{H}\Psi\mathrm{d}\tau=(\Psi,\mathscr{H}\Psi),$$
$$N=N(\Psi)=\int\Psi^2\mathrm{d}\tau=(\Psi,\Psi),$$

where the integration is over all space and spin coordinates, and Ψ is taken to be real. Let us write $\Lambda=\Lambda(\Psi)=Q(\Psi)/N(\Psi)$. Ψ is to be expressed in the form (**7**), which we shall for the moment write

$$\Sigma\ \mathrm{Det}\ \{\varphi_1(X_1)\alpha(s_1)\ .\ .\ .\ \varphi_n(X_n)\beta(s_n)\},$$

so that

$$Q=[\Sigma\,\mathrm{Det}\ \{\varphi_1(X_1)\alpha(s_1)\ .\ .\ .\ \varphi_n(X_n)\beta(s_n)\},\ \mathscr{H}\Sigma\ \mathrm{Det}\ \{\varphi_1(X_1)\alpha(s_1)\ .\ .\ .\ \varphi_n(X_n)\beta(s_n)\}],$$

which, owing to the symmetry of $\mathscr{H}$ with respect to permutation of the electron indices, is equal to

$$n![\Sigma\varphi_1(X_1)\alpha(s_1)\ .\ .\ .\ \varphi_n(X_n)\beta(s_n),\ \mathscr{H}\Sigma\ \mathrm{Det}\ \{\varphi_1(X_1)\alpha(s_1)\ .\ .\ .\ \varphi_n(X_n)\beta(s_n)\}].$$

Let us write Ψ in the form

$$\Psi=u(X_1s_1\ .\ .\ .\ X_ns_n)+\mathrm{Det}\ \{f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n)\},$$

and let us determine the condition that $\Lambda=Q/N$ be stationary with respect to f_1. The variation δQ of Q, consequent on a variation δf_1 of f_1, satisfies

$$\begin{aligned}\delta Q&=2[\delta\ \mathrm{Det}\ \{f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n)\},\ \mathscr{H}\Psi]\\&=2[\mathrm{Det}\ \{\delta f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n)\},\ \mathscr{H}\Psi]\\&=2n![\delta f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n),\ \mathscr{H}\Psi].\end{aligned}$$

Similarly,

$$\delta N=2n![\delta f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n),\ \Psi].$$

$\delta(Q/N)=(1/N)\{\delta Q-(Q/N)\delta N\}=0$ if and only if

$$[\delta f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n),\ \mathscr{H}\Psi-(Q/N)\Psi]=0.$$

This is true for arbitrary δf_1 if and only if

$$\begin{aligned}\int.\ .\ .\int g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n)\{\mathscr{H}\Psi-(Q/N)\Psi\}\\\times\mathrm{d}y_1\mathrm{d}z_1\ .\ .\ .\ \mathrm{d}x_n\mathrm{d}y_n\mathrm{d}z_n\mathrm{d}s_1\ .\ .\ .\ \mathrm{d}s_n=0\qquad\ldots\ldots\ldots\ (8)\end{aligned}$$

for all x_1. The functions $g_1, h_1, \ldots, h_n$ are allotted values, and an initial guess is made at f_1, which is substituted where f_1 occurs in an integral with respect to $y_1, z_1, \ldots, z_n$, and in Q/N, and (**8**) then becomes a differential equation for an improved f_1. A " self-consistent " f_1, i.e. one which, when substituted in (**8**) gives an equation whose solution is f_1, is the solution of the stationary condition. Theorems 1 and 2 below lead to theorem 3, which shows that this stationary condition is, subject to certain reservations, a unique minimum condition. Equation (**8**) can be regarded as an extended form of Hartree-Fock equation. Formulae for the individual terms on the left-hand side of (**8**) are complicated, but can be obtained in a straightforward way. Their number is reduced somewhat by the orthogonality of α and β spin functions.

In the following, a translation to " numerical form " as in Part I, Section 3, is assumed. H denotes the matrix which produces the finite-difference operation corresponding to $\mathscr{H}$, and the functions become vectors operated on by H.

Theorem 1

Let us write

$$D(f_1)=\text{Det}\,\{f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\,.\,.\,.\,f_n(x_n)g_n(y_n)h_n(z_n)\beta(s_n)\}.$$

Let ξ denote a function of x_1. Let

$$\left.\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\Lambda[u+D(f_1+t\xi)]\,\Big|_{t=0}&=0,\\ \text{and}\qquad \frac{\mathrm{d}^2}{\mathrm{d}t^2}\Lambda[u+D(f_1+t\xi)]\,\Big|_{t=0}&>0.\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots\ (\mathbf{9})$$

Let *every* ξ for which $D(\xi)$ is not identically zero satisfy equations (**9**), for $f_1={}'f$; then the same cannot be true for $f_1={}''f$, unless $D('f)$ is identically equal to $D(''f)$.

Proof. Let $D('f)$ be not identically equal to $D(''f)$, and let us suppose that equations (**9**), for every ξ for which $D(\xi)$ is not identically zero, are satisfied by $f={}'f$ and by $f={}''f$. Then, since $D('f)-D(''f)=D('f-{}''f)$ is not identically zero,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\alpha}\Lambda[u+D\{'f+\alpha(''f-{}'f)\}]\,\Big|_{\alpha=0}&=0,\\ \frac{\mathrm{d}^2}{\mathrm{d}\alpha^2}\Lambda[u+D\{'f+\alpha(''f-{}'f)\}]\,\Big|_{\alpha=0}&>0,\\ \frac{\mathrm{d}}{\mathrm{d}\beta}\Lambda[u+D\{''f+\beta('f-{}''f)\}]\,\Big|_{\beta=0}&=0,\\ \frac{\mathrm{d}^2}{\mathrm{d}\beta^2}\Lambda[u+D\{''f+\beta('f-{}''f)\}]\,\Big|_{\beta=0}&>0.\end{aligned}$$

Hence, writing $\alpha=t$, $\beta=1-t$, we find $\Lambda[u+D\{'f+t(''f-{}'f)\}]$ has a proper local minimum with respect to t for $t=0$ and $t=1$, which contradicts the lemma of Part I.

Theorem 2

If the functions

$$u(x_1y_1z_1s_1\,.\,.\,.\,x_ny_nz_ns_n)\ \text{and}\ g_1(y_1),\ h_1(z_1),\,.\,.\,.,\,h_n(z_n)$$

are given and

$$\Lambda(u)<\min_{\alpha_1\beta_1\gamma_1\,.\,.\,.\,\alpha_n\beta_n\gamma_n}\Lambda[\text{Det}\,\{\alpha_1(x_1)\beta_1(y_1)\gamma_1(z_1)\alpha(s_1)\,.\,.\,.\,\alpha_n(x_n)\beta_n(y_n)\gamma_n(z_n)\beta(s_n)\}],$$

there is a function f_1 for which

$$\Lambda[u+\text{Det}\,\{f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ h_n(z_n)\beta(s_n)\}]$$

assumes its least possible value. For this f_1, Λ is stationary with respect to f_1.

Proof. The proof of Theorem 2 of Part I can be easily adapted.

Theorem 3

Let the functions

$$u(x_1y_1z_1s_1\ .\ .\ .\ z_ns_n) \text{ and } g_1(y_1),\ h_1(z_1),\ .\ .\ .,\ h_n(z_n)$$

be given and let

$$\Lambda(u)\leqslant\min_{\alpha_1,\,\beta_1,\,\gamma_1,\,.\,.\,.,\,\gamma_n}\Lambda[\text{Det}\,\{\alpha_1(x_1)\beta_1(y_1)\gamma_1(z_1)\alpha(s_1)\ .\ .\ .\ \gamma_n(z_n)\beta(s_n)\}].$$

Let $\Lambda[u+\text{Det}\,\{f_1(x_1)g_1(y_1)h_1(z_1)\alpha(s_1)\ .\ .\ .\ h_n(z_n)\beta(s_n)\}]<\Lambda(u)$ and let Λ be stationary with respect to f_1. There is only one determinant $D(f_1)$ for which f_1 satisfies these conditions, and that gives to Λ its least possible value.

Proof. It is sufficient to show that, if ξ is such that $D(\xi)$ is not identically zero then

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Lambda[u+D(f_1+t\xi)]\ \Big|_{t=0}>0,$$

under the hypotheses of the theorem. Since Λ is stationary with respect to f_1,

$$\frac{\mathrm{d}}{\mathrm{d}t}\Lambda[u+D(f_1+t\xi)]\ \Big|_{t=0}=0.$$

It follows that

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Lambda\ \Big|_{t=0}=\frac{1}{N}\left(\frac{\mathrm{d}^2Q}{\mathrm{d}t^2}\ \Big|_{t=0}-\Lambda\frac{\mathrm{d}^2N}{\mathrm{d}t^2}\ \Big|_{t=0}\right),$$

that is,

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Lambda\ \Big|_{t=0}=\frac{1}{N}[Q\{D(\xi)\}-\Lambda\{u+D(f_1)\}N\{D(\xi)\}].$$

By hypothesis,

$$\frac{Q\{D(\xi)\}}{N\{D(\xi)\}}=\Lambda[D(\xi)]>\Lambda[u+D(f_1)].$$

Hence

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Lambda\ \Big|_{t=0}>0.$$

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IV. References

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