

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

I. FORMULATION OF THE METHOD FOR AN EIGENVALUE PROBLEM WITHOUT SYMMETRY CONDITIONS

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[Manuscript received June 26, 1959]

Summary

The aim of this paper and those following is to formulate and explore a new method, suitable for use with an electronic digital computer, for the solution of eigenvalue-eigenfunction problems in many variables, with the aim of applying the method to the Schrödinger wave equation.

In this method, an expression for an eigenfunction F , depending on the variables x, y, \dots, z , is sought in the form

$$F = F(x, y, \dots, z) = \sum_i f_i(x) g_i(y) \dots h_i(z), \dots \quad (\mathbf{A})$$

which is a sum of products of functions of one variable; the functions of one variable are represented numerically, and are determined with the aid of the variation principle, so as to give a "best" representation of F of this form. This may be contrasted with the Rayleigh-Ritz method, in which each term of the series (\mathbf{A}) is, apart from a multiplying coefficient, an analytic function determined in advance, only the coefficients being determined by the variation principle. In view of this contrast, it would be expected that the present method would give a more accurate expression for F with a given number of terms, and may therefore be regarded as an attempt to solve the problem of the slow convergence of the Rayleigh-Ritz procedure for complex problems.

The method is worked out in detail only for the fundamental solution. The stationary condition by which the functions of one variable are determined is shown, subject to certain reservations, to be a minimum condition (theorem 3), and the convergence of the procedure is discussed.

A way is suggested for obtaining an initial estimate of the eigenfunction, for the iterative improvement which the method prescribes.

I. INTRODUCTION

The outstanding property of the Schrödinger wave equation from the computer's point of view is that its solution is an inseparable function of many variables. One must represent any function either by a table of numbers or by a rule by which such a table could be generated (the rule being commonly embodied in an analytic expression) or by a partial table together with a rule for generating the rest of the table. For a function of many variables, full and direct tabulation is impossible, as the following rough calculation shows. If a function of one variable requires 100 tabular entries for close enough description,

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then, roughly speaking, for a function of 30 variables, such as the wave function of the sodium cation, $100^{30}=10^{60}$ tabular entries would be needed. At 1 cm^2 per entry, the wave function would cover the Earth about 10^{40} times. From the impossibility of making such a table D. R. Hartree concluded that the wave equation cannot be solved accurately (Hartree 1957).

This problem is overcome in Rayleigh's method by using an almost entirely analytic representation of the wave function. Rayleigh's method consists in setting up, as a representation of the solution, an analytic expression containing some variable parameters, and then determining the "best" values of these parameters by using the minimum property of eigenvalues. The form of analytic expression must be more-or-less guessed. Rayleigh's method has been used in most attempts to obtain accurate *ab initio* solutions of the many-electron wave equation. The form of Rayleigh's method most used is the "Rayleigh-Ritz" method in which the analytic expression is a linear combination of given functions and the variable parameters are the coefficients of the linear combination. If the given functions form a complete set, then, in principle, by allowing enough of them to enter the linear combination, a solution of arbitrarily small inaccuracy could be obtained. However, it is not possible to tell which members of the complete set are the best ones to use except by trying them out.

The method proposed represents the eigenfunction by a partial tabulation, without restricting it. It seeks an expression for an eigenfunction depending on the variables x, y, \dots, z in the form

$$\sum_i f_i(x)g_i(y) \dots h_i(z) \dots \dots \dots (*)$$

that is, a series in which each term is a product of one-dimensional functions. The one-dimensional functions are represented by tables of numbers, and are determined by the nature of the problem, through the minimum property of eigenvalues, so that each term added is a "best" term of this form; in contrast, in the Rayleigh-Ritz method, each term is determined, apart from its multiplying coefficient, in advance. In any practical application of the Rayleigh-Ritz method, moreover, each term is a product of functions of one variable (in order that the numerical integrations should be feasible). This comparison, in view of the degree of accuracy which has been attained in some applications of the Rayleigh-Ritz method (see, for example, Boys and Price 1954), suggests that the proposed method would provide an accurate representation of wave functions sufficiently compact to be capable of being handled by a high speed electronic digital computer with a large store. The imposition of the form (*) does not restrict the solution for a reason which may be expressed loosely as follows: if

$$\chi_i(x), \quad i=1, 2, \dots,$$

is a complete set of functions in a range $-R \leq x \leq R$, then the set of products

$$\chi_i(x)\chi_j(y) \dots \chi_k(z), \quad i=1, 2, \dots; \quad j=1, 2, \dots; \dots; \quad k=1, 2, \dots;$$

is a complete set in

$$-R \leq x \leq R, \quad -R \leq y \leq R, \quad \dots, \quad -R \leq z \leq R$$

(Courant and Hilbert 1953).

Thus any function defined in the region can be expressed as a sum of products of functions of one variable.

Two suggestions have been made recently for the solution of the convergence problem presented by the Rayleigh-Ritz process. It has been suggested (Slater 1953) that a good set of one-electron functions to use in a Rayleigh-Ritz expansion would be the (complete) set of solutions of a certain self-consistent field problem. However, it is not claimed that a practical method could be based on this idea. A second suggestion (Löwdin 1955; Shull and Löwdin 1959) consists in the demonstration that a certain set of one-electron functions, the "natural spin-orbitals" must give rapid convergence. However, there does not seem to be any way of determining these without first obtaining the wave function. The present series of papers may be thought of as making another suggestion for the solution of this convergence problem.

It is assumed throughout this paper that the fundamental solution of the eigenvalue-eigenfunction or eigenvalue-eigenvector problem considered is that corresponding to the algebraically least eigenvalue; this is no restriction. This paper is concerned mainly with the determination of the least eigenvalue and its eigenfunction or eigenvector; the method is worked out in detail only for this case. It is also assumed that this eigenfunction is non-degenerate.

II. FORMULATION OF THE METHOD FOR AN EIGENVALUE PROBLEM WITHOUT SYMMETRY CONDITIONS

In order to show clearly the basic properties of the method, it is first formulated (in Part I) not for the wave equation (from whose solutions it is necessary to select those with certain symmetry properties) but for an eigenvalue problem without symmetry conditions, which will be written

$$\mathcal{H}\psi = \lambda\psi, \quad \dots\dots\dots (1)$$

where ψ is a real function of n variables (x, y, \dots, z) and \mathcal{H} is a real differential operator. ψ is the fundamental eigenfunction of \mathcal{H} and λ is the corresponding eigenvalue. The function ψ is taken to be defined in a region $-R \leq x \leq R$, $-R \leq y \leq R$, \dots , $-R \leq z \leq R$ and to be subject to the condition that it vanish on the boundary $x = \pm R$, $y = \pm R$, \dots , $z = \pm R$ of this region. \mathcal{H} is taken to be symmetric; that is, we take it that if ϕ and ψ are arbitrary functions (apart from satisfying conditions of differentiability and the boundary conditions)

$$\int_{-R}^R \dots \int_{-R}^R \phi \mathcal{H} \psi dx dy \dots dz = \int_{-R}^R \dots \int_{-R}^R \psi \mathcal{H} \phi dx \dots dz.$$

Let us write

$$Q = Q(v) = \int_{-R}^R \dots \int_{-R}^R v(x, y, \dots, z) \mathcal{H} v(x, y, \dots, z) dx dy \dots dz$$

and

$$N = N(v) = \int_{-R}^R \dots \int_{-R}^R v^2(x, y, \dots, z) dx dy \dots dz.$$

The lowest eigenvalue of (1) is the least value which Q/N assumes for any $v=v(x, y, \dots, z)$ satisfying the boundary conditions, and the eigenfunction belonging to this eigenvalue is that v which gives to Q/N its least value. Let $u(x, y, \dots, z)$ be a first guess at this lowest eigenfunction. We seek a set of n functions $f(x), g(y), \dots, h(z)$ vanishing at $\pm R$ (so that $u+fg \dots h$ satisfies the boundary condition for a solution of (1)) such that $u+fg \dots h$ is the best expression of this form for the lowest eigenfunction. Let $g(y)=g_0(y) \dots h(z)=h_0(z)$ be fixed, and let $\delta f=\delta f(x)$ be a variation of $f(x)$ which vanishes at $\pm R$. If $f(x)$ gives to Q/N its least value, Q/N being formed for $(u+f(x)g_0(y) \dots h_0(z))$, then $\delta(Q/N)=0$. Now

$$\begin{aligned}\delta Q &= \delta \left(\int \dots \int u \mathcal{H} u dx \dots dz + 2 \int \dots \int fg \dots h \mathcal{H} u dx \dots dz \right. \\ &\quad \left. + \int \dots \int fg \dots h \mathcal{H} fg \dots h dx \dots dz \right) \\ &= 2 \delta f \left(\int \dots \int g \dots h \mathcal{H} u dy \dots dz \right) dx \\ &\quad + 2 \delta f \left(\int \dots \int g \dots h \mathcal{H} g \dots h dy \dots dz \right) f dx,\end{aligned}$$

where the integrations are from $-R$ to R in each variable. Similarly,

$$\delta N = 2 \delta f \left(\int \dots \int g \dots h u dy \dots dz \right) dx + 2 \delta f \left(\int \dots \int g^2 \dots h^2 dy \dots dz \right) f dx.$$

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

$$\begin{aligned}\delta f \{ &\int \dots \int g \dots h \mathcal{H} u dy \dots dz + \left(\int \dots \int g \dots h \mathcal{H} g \dots h dy \dots dz \right) f \\ &- (Q/N) \int \dots \int g \dots h u dy \dots dz - (Q/N) \left(\int \dots \int g^2 \dots h^2 dy \dots dz \right) f \} dx = 0.\end{aligned}$$

If this holds for any variation δf , then f satisfies the equation

$$\begin{aligned}&\left(\int \dots \int g \dots h \mathcal{H} g \dots h dy \dots dz \right) f - (Q/N) \left(\int \dots \int g^2 \dots h^2 dy \dots dz \right) f \\ &+ \int \dots \int g \dots h \mathcal{H} u dy \dots dz - (Q/N) \int \dots \int g \dots h u dy \dots dz = 0.\end{aligned}\tag{2}$$

Equation (2) is formed for $g(y)=g_0(y) \dots h(z)=h_0(z)$.

If $f(x)g_0(y) \dots h_0(z)$ is small enough, that is, if $u(x, y, \dots, z)$ is near enough to the lowest eigenfunction of (1), then Q/N in (2) can be formed for $f=0$ and taken as constant, so that (2) becomes simply a differential equation for f . Anyway, it is to be expected that iterative solution of (2) would lead to a solution $f(x)=f_1(x)$ which is "self-consistent" (i.e. which is yielded by (2) with Q/N formed for $u+f_1(x)g_0(y) \dots h_0(z)$) and moreover is that f which gives to $Q(u+fg_0 \dots h_0)/N(u+fg_0 \dots h_0)$ its least value. Keeping $f=f_1$ fixed, the "best" $g=g_1$ is then determined, by solving the equation corresponding to (2) for g , in which the functions other than f and g are kept fixed at the same values as before. It may again be unnecessary to get a strictly self-consistent solution for g , that is, it may be sufficient to form Q/N for $(u+f_1g_0 \dots h_0)$ and treat it as a constant. The process is then repeated for each of the n functions up to $h(z)$, and the cycle then repeated as many times as is necessary to obtain reasonable convergence. The functions finally obtained, $f_\omega, g_\omega, \dots, h_\omega$, (say), determine new approximations $v_1=u+f_\omega g_\omega \dots h_\omega$ and $Q(v_1)/N(v_1)$ to the lowest eigenfunction and eigenvalue of (1). Denoting the k th improved approximation by

$v_k(x, y, \dots, z)$, v_k would be expected to converge to the lowest eigenfunction as $k \rightarrow \infty$, since this can be expressed exactly by means of a series

$$u(x, y, \dots, z) + \sum_{k=1}^{\infty} f_k(x)g_k(y) \dots h_k(z),$$

as noted in the introduction.

So that the numerical integrations may be practicable, $u(x, y, \dots, z)$ and $\mathcal{H} = \mathcal{H}(x, y, \dots, z)$ must be expressed as sums of products of functions of (or operators on) one variable. \mathcal{H} could in general be so expressed only by an infinite series, which would have to be terminated in numerical work.

III. FORMULATION AS A METHOD OF SOLVING A NUMERICAL FORM OF EQUATION (1)

The method will now be reformulated, taking the same eigenvalue problem (1) as starting point. In this formulation the function is replaced by a vector, corresponding to a possible numerical representation of it, and the operation of differentiation of a function replaced by multiplication of the vector by a suitable matrix, which produces the appropriate finite-difference operation. There are two reasons for undertaking this second formulation. The first is to obtain a clear insight into the structure of the method, while avoiding the proverbial subtleties of the calculus of variations. While the results are obtained for one particular choice of numerical approximations, they can certainly be applied to any other sufficiently refined methods of numerical approximation which may be chosen. The second reason is that this formulation of the method could be used with advantage as it stands in the exploratory stages of the solution of a complicated problem, that is, for establishing "initial" estimates of the eigenfunction, in a way which is suggested by the example in Part II (Bassett 1959a).

In anticipation of the final aim, the solution of the wave equation, \mathcal{H} in equation (2) will be taken to be of the form

$$-\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \dots - \frac{\partial^2}{\partial z^2} + V(x, y, \dots, z).$$

Let a function $v(x, y, \dots, z)$ of N variables x, y, \dots, z defined in $-R \leq x \leq R$, $-R \leq y \leq R$, \dots , $-R \leq z \leq R$ and vanishing on the boundaries of the region be represented by a function defined at only the r^N interior points

$$(-R+lh, -R+mh, \dots, -R+ph) \quad l=1, 2, \dots, r; \quad m=1, 2, \dots, r; \\ p=1, 2, \dots, r. \quad \dots \quad (3)$$

where $h=2R/(r+1)$. The function so defined can be thought of as a vector of r^N elements. The function or vector will be written in the form $v(x, y, \dots, z)$, which may be abbreviated to v ; if it is convenient not to distinguish between the different kinds of elements of $v(x, y, \dots, z)$ then it will be written $v(X)$, where X stands for the set of variables x, y, \dots, z .

A function of one variable, of x say, defined in $-R \leq x \leq R$ and vanishing on the boundary is represented by a function defined at the r interior points

$$-R+lh \quad (l=1, 2, \dots, r),$$

that is, by a vector of r elements, which will be written in the form $f(x)$. The second derivative can then be represented by $\sum_x K(x, x')f(x')$ where $K(x, x')$ is the (x, x') th element of the symmetric $r \times r$ matrix

$$\begin{array}{ccccccc} -2/h^2 & 1/h^2 & 0 & 0 & & & \\ 1/h^2 & -2/h^2 & 1/h^2 & 0 & \dots & & \\ 0 & 1/h^2 & -2/h^2 & 1/h^2 & & & \\ & \dots & & & & & \\ & & & & \dots & 1/h^2 & -2/h^2 & 1/h^2 \\ & & & & & 0 & 1/h^2 & -2/h^2. \end{array}$$

For a function $v(x, y, \dots, z)$ a representation of the Laplacian, the sum of the second derivatives with respect to each variable in turn, at any point (3) can likewise be obtained by multiplication by a symmetric $r^N \times r^N$ matrix: thus the sum of the second derivatives of $v(x, y, \dots, z)$ is represented by

$$\sum_{x', y', \dots, z'} L(x, y, \dots, z; x', y', \dots, z') v(x', y', \dots, z'),$$

where

$$\begin{aligned} L(x, y, \dots, z; x', y', \dots, z') &= L(x', y', \dots, z'; x, y, \dots, z) \\ &= K(x, x') \delta y y' \dots \delta z z' + \delta x x' K(y, y') \dots \delta z z' + \dots + \delta x x' \delta y y' \dots K(z, z'). \end{aligned}$$

From here on H is taken to be minus the above expression, plus the expression

$$V(x, y, \dots, z) \delta x x' \delta y y' \dots \delta z z',$$

which is a diagonal matrix. Using the X notation, the function obtained by operating on $v(x)$ with H is $\sum_{X'} H(X, X') v(X')$.

The integral of a function $v(x, y, \dots, z)$ defined in $-R \leq x \leq R, \dots, -R \leq z \leq R$ and vanishing on the boundaries is taken to be represented by

$$h^N \sum_x \sum_y \dots \sum_z v(x, y, \dots, z) = h^N \sum_X v(X),$$

the summation extending over the interior points (3).

Consider now the quotient of quadratic forms

$$\frac{\sum_{x, y, \dots, z} \sum_{x', y', \dots, z'} v(x, y, \dots, z) H(x, y, \dots, z; x', y', \dots, z') v(x', y', \dots, z')}{\sum_{x, y, \dots, z} v^2(x, y, \dots, z)}$$

or

$$\frac{\sum_X \sum_{X'} v(X) H(X, X') v(X')}{\sum_X v^2(X)} \dots \dots \dots (4)$$

The expression (4) takes on its least value for a vector $v(X)$ which is a lowest eigenvector of H . That is, $v(X)$ is a solution of the equations

$$\sum_{X'} H(X, X') v(X') = \Lambda v(X) \dots \dots \dots (5)$$

with the least eigenvalue Λ .

Our task may now be stated exactly. It is to lay down a rule for getting a sequence

$$v_1(X), v_2(X), v_3(X), \dots$$

of vectors which converges to the lowest eigenvector of (5). It is assumed in this paper that there is only one such eigenvector, i.e. that the lowest eigenvalue is non-degenerate.

It is convenient to rewrite (4) using the notation

$$\sum_{x', y', \dots, z'} H(x, y, \dots, z; x', y', \dots, z') v(x', y', \dots, z') \\ = H v(x, y, \dots, z),$$

so that (4) becomes

$$\frac{\sum_{x, y, \dots, z} v(x, y, \dots, z) H v(x, y, \dots, z)}{\sum_{x, y, \dots, z} v^2(x, y, \dots, z)} \dots \dots \dots (6)$$

$\frac{h^N \sum_X v(X) H v(X)}{X}$ and $\frac{h^N \sum_X v^2(X)}{X}$ will sometimes be written $Q(v)$ and $N(v)$. The expression (6) formed for $v(x, y, \dots, z) = u(x, y, \dots, z) + f(x)g_0(y) \dots h_0(z)$ takes on its least value, for given functions u and g_0, \dots, h_0 , for a function f which satisfies

$$\delta\{Q(u + fg_0 \dots h_0)/N(u + fg_0 \dots h_0)\} = 0$$

for r independent variations δf of f

$$\frac{1}{h^N} \delta Q = \delta \sum_{x, y, \dots, z} (u + fg \dots h) H (u + fg \dots h) \\ = \sum_{x, y, \dots, z} (2\delta f g \dots h H u + 2\delta f g \dots h H f g \dots h), \\ \frac{1}{h^N} \delta N = \delta \sum_{x, y, \dots, z} (u + fg \dots h)^2 \\ = 2 \sum_{x, y, \dots, z} \delta f (u g \dots h + f g^2 \dots h^2).$$

$\delta(Q/N) = 0$ if and only if $\delta Q - (Q/N)\delta N = 0$, that is,

$$\sum_{x, y, \dots, z} \delta f \{g \dots h H u + g \dots h H g \dots h f - (Q/N) u g \dots h - (Q/N) f g^2 \dots h^2\} = 0.$$

This equation, formed for r independent functions δf , is equivalent to

$$\left(\sum_{y \dots z} g \dots h H g \dots h \right) f - (Q/N) \left(\sum_{y \dots z} g^2 \dots h^2 \right) f \\ + \sum_{y \dots z} g \dots h H u - (Q/N) \sum_{y \dots z} g \dots h u = 0. \dots (7)$$

The transformation just carried out depends on the fact that H is symmetric. Equation (7), the central equation of the method, is the "numerical" analogue of equation (2).

The lemma and theorems 1 and 2 below lead up to theorem 3, which states that the solution f of equation (7) is, subject to certain restrictions, that f which gives to Q/N its least possible value.

Lemma. Let $H(X, X')$ be the (X, X') th element of a symmetric $m \times m$ matrix, $v=v(X)$ an m -rowed vector,

$$Q(v)=h^N \sum_{X, X'} v(X)H(X, X')v(X')=h^N \sum_X v(X)Hv(X)=(v, Hv),$$

and

$$N(v)=h^N \sum_X v^2(X)=(v, v).$$

If $u=u(X)$ is also an m -rowed vector, and γ is a variable number, $Q(u+\gamma v)/N(u+\gamma v)$ cannot have a local proper minimum with respect to γ for two different values of γ .

Proof. Suppose that two such values of γ exist. We may take one value as zero, and for the other we may assume that

$$Q(u+\gamma v)/N(u+\gamma v) \leq Q(u)/N(u). \quad \dots\dots\dots (8)$$

Now $Q(u+\gamma v)=Q(u)+2\gamma(v, Hu)+\gamma^2 Q(v)$ and $N(u+\gamma v)=N(u)+2\gamma(v, u)+\gamma^2 N(v)$. Since Q/N is stationary at $\gamma=0$,

$$(u, Hv)-Q(u)/N(u)(u, v)=0, \quad \dots\dots\dots (9)$$

and, at $\gamma=0$,

$$\frac{d^2 Q/N}{d\gamma^2} = \frac{1}{N} \left(\frac{d^2 Q}{d\gamma^2} - \frac{Q}{N} \frac{d^2 N}{d\gamma^2} \right).$$

The last equation implies that

$$Q(v) - \{Q(u)/N(u)\}N(v) \geq 0. \quad \dots\dots\dots (10)$$

The inequality (8) is equivalent to

$$Q(u)+2\gamma(v, Hu)+\gamma^2 Q(v) \leq Q(u)+2\gamma\{Q(u)/N(u)\}(u, v)+\gamma^2\{Q(u)/N(u)\}N(v),$$

that is, using (9),

$$\gamma^2 Q(v) \leq \gamma^2 \{Q(u)/N(u)\}N(v).$$

From this and equation (10) $Q(v)/N(v)=Q(u)/N(u)$ which implies that $d^2(Q/N)/d\gamma^2$ vanishes at $\gamma=0$. Now Q/N has the form $(a+b\gamma+c\gamma^2)/(a'+b'\gamma+c'\gamma^2)$ and if the first and second derivatives of this function of γ vanish at $\gamma=0$ then $a/a'=b/b'=c/c'$. Hence Q/N is independent of γ and cannot have a proper minimum with respect to γ .

Theorem 1

Let us write $\Lambda(v)=Q(v)/N(v)$ for any function v . Let $\xi=\xi(x)$ denote a function of x . Let

$$\text{and} \quad \left. \begin{aligned} \frac{d}{dt} \Lambda\{u+(f+t\xi)g \dots h\} \Big|_{t=0} &= 0, \\ \frac{d^2}{dt^2} \Lambda\{u+(f+t\xi)g \dots h\} \Big|_{t=0} &> 0. \end{aligned} \right\} \quad \dots\dots\dots (11)$$

Let every $\xi(x)$ satisfy equations (11), for $f=f'$. Then the same cannot be true for $f=f''$ unless f' and f'' are identically equal.

Proof. Let us suppose that the theorem is false, and its conditions are satisfied by $'f$ and by $''f$, where $'f$ and $''f$ are not identically equal. Then

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

Hence, writing $\alpha=t$, $\beta=1-t$, we find that

$$\Lambda\{u + ('f + t('f - ''f))g \dots h\}$$

has a proper local minimum with respect to t for $t=0$ and $t=1$, which contradicts the lemma.

Theorem 2

If the functions $u(x, y, \dots, z)$ and $g(y), \dots, h(z)$ are given and

$$\Lambda(u) < \min_{\alpha, \beta, \dots, \gamma} \Lambda\{\alpha(x)\beta(y) \dots \gamma(z)\},$$

there is a function $f=f(x)$ for which $\Lambda\{u+f(x)g(y) \dots h(z)\}$ assumes its least possible value. For this function f , Λ is stationary.

Proof. Since $\Lambda(v)$ is bounded below as v varies, $\Lambda(u+fg \dots h)$ is certainly bounded below as f varies. Let l be the greatest lower bound of Λ as f varies. Then a sequence f_n exists such that $\Lambda(u+f_n g \dots h) \rightarrow l$. If $\sum f_n^2(x) \rightarrow \infty$, then $\Lambda(f_n g \dots h) \rightarrow l$, which contradicts the hypothesis. Hence $\sum f_n^2(x)$ is bounded, and so possesses at least one limit point, $f(x)$ say, for which $\Lambda(u+fg \dots h)=l$, since Λ is a continuous function of the elements of f . The rest of the theorem may be deduced from the fact that Λ is a rational function in the elements of f .

Theorem 3

Let the functions $u(x, y, \dots, z)$ and $g(y), \dots, h(z)$ be given, and let $\Lambda(u) \leq \min_{\alpha, \beta, \dots, \gamma} \Lambda\{\alpha(x)\beta(y) \dots \gamma(z)\}$. Let $\Lambda\{u+f(x)g(y) \dots h(z)\} < \Lambda(u)$ and let Λ be stationary with respect to f . There is only one function f which satisfies these conditions, and that gives to Λ its least possible value.

Proof. It is sufficient to show that, under the hypotheses of the theorem,

$$\frac{d^2}{dt^2} \Lambda\{u + (f + t\xi)g \dots h\} \Big|_{t=0} > 0$$

for any ξ . Since Λ is stationary with respect to f ,

$$\frac{d}{dt} \Lambda\{u + (f + t\xi)g \dots h\} \Big|_{t=0} = 0.$$

It follows that

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

that is,

$$\left. \frac{d^2\Lambda}{dt^2} \right|_{t=0} = \frac{1}{N(u+fg \dots h)} \{Q(\xi g \dots h) - \Lambda(u+\xi g \dots h)N(\xi g \dots h)\}.$$

By hypothesis, $Q(\xi g \dots h)/N(\xi g \dots h) = \Lambda(\xi g \dots h) > \Lambda(u+fg \dots h)$.

Hence

$$\left. \frac{d^2\Lambda}{dt^2} \right|_{t=0} > 0.$$

IV. CONVERGENCE

There are three kinds of sequence of solutions (each member of a sequence giving an eigenvalue estimate) which the method prescribes: (i) the sequence of solutions f of equation (7) (of which it may be sufficient, for practical purposes, to take the first member) which should converge to a "self-consistent" solution; (ii) the cyclic sequence of self-consistent solutions $f, g, \dots h, f, g, \dots h, \dots$ of equation (7) and its analogues; (iii) the sequence of partial sums in the series expression for the eigenfunction.

In the example of Part II all three sequences converge, the first so rapidly that the first member of the sequence is sufficient.

(i) In the form which the stationary condition (7) assumes for a wave mechanical problem (Part III, Bassett 1959*b*), if it is looked on as a differential equation for f , the "constants" depend on f in first order. The equation is similar in this respect to the equation for the radial dependence of a one-electron function in the Hartree-Fock method with superposition of configurations (Hartree 1957) and so convergence can probably be attained in practice. In the stationary condition (7) itself, which applies to an eigenvalue problem without symmetry restrictions, the dependence of the "constants" on the solution is only second order, as only Q/N is so dependent, and no difficulty would be expected with convergence.

(ii) The convergence of the eigenvalue estimates belonging to the sequence (ii) is ensured by theorem 3, which shows that these eigenvalue estimates form a monotonic decreasing sequence, which is certainly bounded below, and if the product $fg \dots h$ does not converge, it must approach a range of equally acceptable functions.

(iii) The completeness of a suitable set of products of functions of one variable argues strongly, if loosely, for convergence of the sequence (iii), but the matter will be settled best by practical trial.

V. ACKNOWLEDGMENTS

The author would like to thank Dr. A. C. Hurley, Professor T. M. Cherry, and Mr. Bruce Craven for reading the manuscript at various stages of completeness and for making many helpful suggestions, and Dr. M. V. Wilkes for a germinal conversation.

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