states differing in the wave functions of two electrons at most. If the initial wave functions of these two electrons are symbolized by A, B and the final ones by C, D, then it can be shown that the matrix component will be just as for a two-electron problem involving only these two electrons:

$$\tfrac{1}{2}\int \begin{vmatrix} A^*(1) & B^*(1) \\ A^*(2) & B^*(2) \end{vmatrix} (2/r_{12}) \begin{vmatrix} C(1) & D(1) \\ C(2) & D(2) \end{vmatrix} dv_1 dv_2.$$

If now A, B, C, D represent modulated functions, it is easy to show that unless the sum of the $\mathbf{k}$'s for A and B equals the sum for C and D, the integral over the crystal will vanish. If this condition is satisfied, however, the integration of dv_1 only over the cell surrounding one atom will lead to just $1/N$th of the whole integral, if N is the number of atoms. Furthermore, if dv_1 is integrated over one cell, the major contribution to the integral will come when dv_2 is integrated over the same cell. Now within a given cell, the wave functions of all the states of a single band are similar. Thus if A and B refer to states of the same band, the first determinant will be small, and if C and D states of the same band the second determinant will be small, verifying our statement that the matrix component is large only when A and B refer to different bands, and C and D refer to different bands.

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Approximation to Discrete Quantum States by Iteration

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A method is described by which successive approximations to the wave functions and energies of stationary states can sometimes be obtained in a form allowing definite limits of error to be stated. Two examples in which the solution is otherwise known are worked out and the rate of approximation is found to be rapid.

THE ITERATION PROCESS

CONSIDER the homogeneous linear equation

$$N\psi=\lambda D\psi, \tag{1}$$

where N and D are two Hermitian operators operating on a range of functions ψ of certain variables x. Suppose a function φ_0 in the range can be expanded in the series

$$\varphi_0=c_1\psi_1+c_2\psi_2+\cdots, \tag{2}$$

where ψ_r are proper functions of (1) corresponding to proper values λ_r (some of which may be distributed continuously). Then, if we operate on φ_0 repeatedly with $N^{-1}D$ giving the sequence of functions φ_1, φ_2, $\cdots$ such that

$$N\varphi_{n+1}=D\varphi_n, \tag{3}$$

we shall have $\varphi_n=\lambda_1^{-n}c_1\psi_1+\lambda_2^{-n}c_2\psi_2+\cdots$. (4)

Thus, if Eq. (1) has a discrete proper value of lowest absolute value, λ_s, and if the coefficient of the corresponding proper function ψ_s in φ_0, *viz.* c_s, does not vanish,

$$\varphi_n\sim\lambda_s^{-n}c_s\psi_s \quad (n\to\infty), \tag{5}$$

converging geometrically: and we have a process for approximating to ψ_s.

When a function φ approximating ψ_s has been found, if Eq. (1) has a discrete proper value next lowest in absolute value to λ_s, we can approximate in like manner to its corresponding proper function by replacing φ_n at each stage by

$$\varphi_n-\{(\psi^*\varphi_n)/(\psi^*\psi)\}\psi, \tag{6}$$

where ψ^* is the (Hermitian) conjugate to ψ and $(\psi^*\psi)$ means their summed product.

LIMITS OF ERROR

We can usually find from an approximate proper function ψ, by modifying it if necessary so that the zeros of $N\psi'$ and $D\psi'$ coincide, a function ψ' such that bounds μ and ν exist for which

$$\mu\leq(N\psi'/D\psi')\leq\nu \quad (\text{all } x). \tag{7}$$

There is then a corresponding proper value λ of (1) satisfying

$$\mu\leq\lambda\leq\nu. \tag{8}$$

If in particular D is positive definite, and if Eq. (1) has a discrete lowest proper value, λ_1,

so that the corresponding proper function ψ_1 is nodeless and minimizes $(\psi^*N\psi)/(\psi^*D\psi)$ in the range; then, for any nodeless function φ in the range, a lower bound μ exists such that

$$\mu \leq N\varphi/D\varphi \quad (\text{all } x), \tag{9}$$

and then $$\mu \leq \lambda_1 \leq (\varphi^*N\varphi)/(\varphi^*D\varphi). \tag{10}$$

(If an upper bound ν also exists, the Ritz expression $(\varphi^*N\varphi)/(\varphi^*D\varphi)$ is less than ν and is a better approximation to λ_1.)

If in addition λ_1 is the proper value of least absolute value, then for the sequence given by (3) the successive ratios

$$(\varphi_0^*N\varphi_0)/(\varphi_0^*N\varphi_1)/(\varphi_0^*N\varphi_2)/\cdots \tag{11}$$

give successive approximations in excess to λ_1, (note that $(\varphi_0^*N\varphi_r)=(\varphi_s^*N\varphi_{r-s})$, so that alternate ratios are Ritz approximations using φ_0, φ_1, φ_2, $\cdots$); while the successive minimum values for varying x of the ratios

$$N\varphi_0/N\varphi_1/N\varphi_2/\cdots \tag{12}$$

(provided that the denominator is a nodeless function, which, after some point, it usually will be) give successive approximations in defect.

For problems involving absolute minima of quadratic expressions, better limits of error than that given by (10) can be obtained:[1] but the well-known comparison theorem results stated above seem to be the best available for relative minima, especially for proper values other than the lowest.

The Choice of the Operators N and D

Consider the simple case of the radial equation of S states of the hydrogen atom: in atomic units

$$-\tfrac{1}{2}\nabla^2\psi - \psi/r = E\psi, \tag{13}$$

of which the proper values are $E=-\frac{1}{2}, \cdots, -1/2n^2, \cdots$; $E>0$. Iteration with $N=-\frac{1}{2}\nabla^2 - 1/r$, $D=1$, even if it converged, would not lead to a state in which we are interested. We are not, however, limited to this form; change of scale brings the equation to

$$-\tfrac{1}{2}\nabla^2\psi - a\psi/r = b\psi \quad (a>0) \tag{14}$$

and iteration with D and N any linear combinations of ∇^2, $1/r$, and 1, would converge, if at all, to a solution of this equation (any a).

If
$$\begin{aligned} N &= -\tfrac{1}{2}\alpha\nabla^2 - \beta/r + \gamma, \\ D &= -\tfrac{1}{2}\delta\nabla^2 + \epsilon/r + \zeta, \end{aligned} \tag{15}$$

where, without loss of generality, $\alpha \geq 0$, $\delta \geq 0$: then $\epsilon \geq 0$ and $\zeta \geq 0$ are required to make D positive definite, and $\gamma > 0$ is required if $\lambda = 0$ is not to be in the continuous range of proper values, between γ/ζ and α/δ. If we take $\delta = 0$, $\zeta = 0$, there is no continuous range; and if further $\beta = 0$, the operation N^{-1} can be carried out reasonably easily.

We are thus led to take

$$\begin{aligned} N &= -\tfrac{1}{2}\nabla^2 - E \\ D &= 1/r \end{aligned} \tag{16}$$

or, in more general problems,

$$\begin{aligned} N &= T - E \\ D &= -V \end{aligned} \tag{17}$$

where T and V stand for kinetic and potential energies.

Finding the solutions of

$$T\psi - E\psi = -\lambda V\psi \tag{18}$$

corresponds to asking how large a potential energy of given form will lead to a state of energy E fixed in advance. In problems of the normal states of nuclei it is just this that we really desire to know. In problems of the normal states of atoms, a change of scale will bring the potential energy to its known value. In problems of the normal electronic states of molecules the change of scale also alters the size of the molecule; but that is in any case one of the parameters we wish to determine.

In (17) D is positive definite only if V is one-signed. This will not be true in electronic problems in general; and we shall have solutions corresponding to $-V$ also coming in; but the solution we want will usually be that for λ of lowest absolute magnitude: and once nodeless approximations to ψ are found they can be used to fix limits to E for given V from (10) with $N=T+V$ and $D=1$.

Various methods of obtaining and improving approximate wave functions have been suggested and applied by various authors:[2] the above

[1] Trefftz, Math. Ann. **100**, 503 (1928); Friedricks, Gott-Nach. Math.-Phys. Klasse, p. 13 (1929–30).

[2] E.g., Hylleraas, Zeits. f. Physik **48**, 469 (1928); Hartree, Proc. Camb. Phil. Soc. **26**, 542 (1930); Hasse, Proc. Camb. Phil. Soc. **24**, 89 (1928); Fock and Petraschen, Physik. Zeits. Sowjetunion **6**, 368 (1936).

method seems to be especially simple in theory and convenient in application to problems involving more than one variable x.

Two Examples Illustrating the Method

The exact solution in each of the following problems is known; and it happens that in each the iteration can be carried out analytically. In the first, radial distance; in the second radial momentum,[3] is used as independent variable.

The radial equation for a straight-sided potential hole in case of zero energy

The equation to be solved is

$$-\frac{d^2\psi}{dr^2}=\lambda V\psi, \quad \begin{matrix} V=1, & 0<r<1, & \text{with} & \psi(0)=0 \\ =0, & 1<r, & & \psi(\infty)\ \text{finite.}\end{matrix}$$

Thus

$$\varphi_{n+1}(r)=(1/r)\int_0^r\int_s^1 t\varphi_n(t)dtds, \quad r<1$$

$$=\int_0^1\int_s^1 \varphi_n(t)dtds, \quad 1<r.$$

Taking $\varphi_0=r, \quad 0<r<1$

$$=1, \quad 1<r,$$

we get $\varphi_1=r/2-r^3/6, \quad \varphi_2=5r/24-r^3/12+r^5/120,$

$$=1/3, \qquad =2/15,$$

$$\varphi_3=61r/720-5r^3/144+r^5/240-r^7/5040,$$

$$=17/315,$$

$$\cdots 0<r<1$$

$$\cdots \quad 1<r,$$

and the successive approximations in excess to λ (known to be $\pi^2/4=2.46740\cdots$) are 3, 2.5, $2.471\cdots$, $2.4678\cdots$; those in defect 0, 2, 2.4, $2.458\cdots$; (in each case the minimum is *for* $r=0$; note "$-\int \varphi_0\frac{d^2\varphi_0}{dr^2}dr"=\varphi_0(1)\left\{\frac{d\varphi_0}{dr_{1-0}}-\frac{d\varphi_0}{dr_{1+0}}\right\}=1$").

The radial equation for a simple exponential hole treated in momentum space

The equation

$$-d^2\chi/dr^2-c^2e^{-ar}\chi=-b^2\chi$$

is known to have the solution

$$\chi=J_{2b/a}((2c/a)e^{-(a/2)r}),^4$$

and $\chi(0)=0$ gives $J_{2b/a}(2c/a)=0$.

Transforming to momentum space by

$$\chi(r)=(2/\pi)^{\frac{1}{2}}\int_0^\infty \sin pr\ \psi(p)dp,$$

the equation becomes, if $\psi(-p)=-\psi(p)$,

$$(b^2+p^2)\psi(p)=\frac{c^2}{\pi}\int_{-\infty}^{\infty}\frac{a\psi(p')}{a^2+(p-p')^2}dp'.$$

Thus $\varphi_{n+1}(p)=\frac{1}{b^2+p^2}\frac{c^2}{\pi}\int_{-\infty}^{\infty}\frac{a\varphi_n(p')}{a^2+(p-p')^2}dp'$

and to a term $p/(g^2+p^2)$ in φ_n corresponds

$$\frac{c^2}{(a+g)^2-b^2}\left\{\frac{p}{b^2+p^2}-\frac{p}{(a+g)^2+p^2}\right\} \text{ in } \varphi_{n+1}.$$

Thus, taking $\varphi_0=p$, we get

$$\varphi_1=\frac{c^2p}{b^2+p^2}, \quad \varphi_2=\frac{c^4p}{(b^2+p^2)((a+b)^2+p^2)},$$

$$\varphi_3=\frac{c^6p(3a+2b)}{(b^2+p^2)((a+b)^2+p^2)((2a+b)^2+p^2)(a+2b)},$$

$$\varphi_4=\frac{c^8p\{19a^3+35a^2b+21ab^2+4b^3+ap^2\}}{(b^2+p^2)((a+b)^2+p^2)((2a+b)^2+p^2)((3a+b)^2+p^2)(a+2b)^2(a+b)},$$

$$\varphi_5=\frac{c^{10}p\{633a^5+1559a^4b+1525a^3b^2+736a^2b^3+174ab^4+16b^5+(65a^3+64a^2b+16ab^2)p^2+2ap^4\}}{(b^2+p^2)((a+b)^2+p^2)((2a+b)^2+p^2)((3a+b)^2+p^2)((4a+b)^2+p^2)(a+2b)^3(a+b)(3a+2b)},$$

and the successive approximations in excess to c^2 are ∞, ∞, ∞, $(a+2b)(2a+2b)$, $\frac{(a+2b)(3a+2b)}{2}$,

[3] The great simplification that can sometimes be obtained in this way has been pointed out by Fock, Zeits. f. Physik **98**, 145 (1936).

[4] Bethe and Bacher, Rev. Mod. Phys. **8**, 111 (1936).

$\frac{8(a+2b)(a+b)(2a+b)}{11a+10b}$, $\cdots$; and in defect (in each case the minimum is *for* $p=0$), b^2, $(a+b)^2$, $\frac{(a+2b)(2a+b)^2}{3a+2b}$, $\frac{(a+b)(a+2b)(3a+2b)(3a+b)^2}{19a^3+35a^2b+21ab^2+4b^3}$, $\frac{(a+2b)(3a+2b)(4a+b)^2(19a^3+35a^2b+21ab^2+4b^3)}{633a^5+1559a^4b+1525a^3b^2+736a^2b^3+174ab^4+16b^5}$,

Table I shows the convergence for $b=0$, $b=a$, $a=0$.

It is hoped to publish in the near future approximate solutions by this method of a number of problems for which approximations with known limits of error are not otherwise easy to obtain. The iteration for these problems has to be carried out numerically.

The author wishes to take this opportunity to thank Professor Bohr for the hospitality of his Institute last spring when he spent two months in Copenhagen. During that time the author's ideas about the above method took their present form.

TABLE I. *Convergence for $b=0$, $b=a$, $a=0$.*

$b=0$	$b=a$	$a=0$	REMARKS
$2\,a^2$ $1.5\,a^2$ $1.454\,a^2$	$12\,a^2$ $7.5\,a^2$ $6.857\,a^2$	$4\,b^2$ $2\,b^2$ $1.6\,b^2$	Approximations in excess
$1.4458\,a^2$	$6.592\,a^2$	b^2	Actual value[5]
$1.441\,a^2$ $1.421\,a^2$ $1.333\,a^2$ a^2 0	$6.380\,a^2$ $6.077\,a^2$ $5.4\,a^2$ $4\,a^2$ a^2	b^2 b^2 b^2 b^2 b^2	Approximations in defect

[5] Jahncke and Emde, *Funktiontafeln*, p. 238.

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Nuclear Spins and Magnetic Moments in the Hartree Model

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From the results of Feenberg and Wigner for the wave function and term character of the ground state of light nuclei (mass number between 6 and 16), the nuclear spins are determined. For those nuclei which contain (or lack) a single proton (or neutron) and an even number (singlet state) of particles of the other kind the considerations of Inglis suffice to determine the spin. For those nuclei which contain a half-filled p shell in one kind of particle it is necessary to calculate the fine structure splitting explicitly. From the spins thus found and with the experimental values for the magnetic moments of the proton and neutron, the nuclear magnetic moments are calculated. The effects on the nuclear moment of the Heisenberg forces and of the motion of the $1s$ shell are considered. The moment of Li^7 which is of particular interest, is calculated to be 3.07 nuclear magnetons. This is in agreement with the measured value of 3.20 n. m.

1. INTRODUCTION

IT has been pointed out by Bethe and Bacher[1] that the individual particle model (Hartree model) affords one the opportunity to construct a rational theory of nuclear spins and magnetic moments for light nuclei. On the basis of this model, by assigning quantum states and individual wave functions[2] to each nuclear particle, one can calculate, in the same manner as in atomic spectra, the energy of the various terms which arise from any given configuration of neutrons and protons. From the spin and orbital momenta of the nucleus in the ground state found in this way and from considerations as to the coupling of these momenta the magnetic moment of the nucleus may be calculated. It is to be expected that the model will break down for all but light nuclei[3] and that even for these light nuclei one can obtain only roughly correct

[1] H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 82 (1936). In §36 these authors have treated the case of the Li^6 nucleus.

[2] These are determined by a suitable auxiliary central field which may be assumed to be the same for each particle. Following the usual procedure we shall take for this field an oscillator potential.

[3] The model may be expected to give relatively reliable results for nuclei up to O^{16} where the $2p$ shell is just completed.