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Criteria of Goodness for Approximate Wave Functions

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The relations between the root-mean-square error of an approximate ground state wave function, the energy error, and the root-mean-square local energy deviation are exhibited and discussed. Computations of these quantities for helium wave functions containing errors of different character and magnitude are presented, and are shown to indicate that the errors in wave functions of the Hylleraas type are of increasingly short range character as these functions are made more flexible. The form of variational process which will give a wave function most satisfactory for a given purpose is discussed with illustrative computations relating to the diamagnetic susceptibility of He. It is found that the energy error associated with a wave function may be a comparatively unsatisfactory criterion of goodness.

IN this note we wish to discuss the three simplest criteria for the goodness of an approximate ground state wave function, and their relation to the most desirable type of variational procedure for obtaining such a function.

Let ψ_1 be the correct wave function for the ground state of a system, and let $\psi_2, \psi_3 \cdots$ be the correct wave functions for the other states of the system with the same fundamental symmetry characteristics (e.g., in the case of He, the other singlet S states, if spin energy is neglected). The corresponding energies we will denote by $E_1 < E_2 < E_3 < \cdots$.

Let ψ be the approximate normalized wave function for the ground state, associated with the energy $E = \int \psi^* H \psi d\tau$. The variational principle assures us that $E \geqslant E_1$. We now define ψ_x, a normalized function characterizing the nature of the error in ψ, by

$$\psi_x = (1 - a_1^2)^{-\frac{1}{2}} (\psi - a_1 \psi_1) \tag{1}$$

where $$a_1 = \int \psi_1^* \psi d\tau.$$

This integral will exist provided only that ψ_1 and ψ are quadratically integrable, as we have assumed, and the resulting ψ_x will be a well-behaved function orthogonal to ψ_1. Then

$$\psi = a_1 \psi_1 + a_x \psi_x, \tag{2}$$

$a_x = (1 - a_1^2)^{\frac{1}{2}}$ measuring the amount of the deviation function ψ_x appearing in ψ.

As practical measures of the inaccuracy of ψ we take: q, the root-mean-square error in ψ,

$$q = \left[\int (\psi - \psi_1)^2 d\tau\right]^{\frac{1}{2}} \tag{3}$$

ϵ, the energy error $\epsilon = E - E_1$ (4)

δ, the root-mean-square local energy deviation

$$\delta = \left[\int \{(H - E)\psi\}^2 d\tau\right]^{\frac{1}{2}}. \tag{5}$$

All these quantities exist for trial functions of the sort most commonly used and, of course, must vanish as $\psi \rightarrow \psi_1$, $E \rightarrow E_1$.

We can also characterize ψ_x by means of similar quantities:

$$E_x = \int \psi_x^* H \psi_x d\tau, \quad \epsilon_x = E_x - E_1, \\ \delta_x^2 = \int [(H - E)\psi_x]^2 d\tau. \tag{6}$$

The significance of these quantities may be illustrated by supposing ψ to be expanded in terms of the correct eigenfunctions:

$$\psi = a_1 \psi_1 + a_2 \psi_2 + \cdots \tag{7}$$

and $\psi_x = \left(\sum_{n=2}^{\infty} a_n^2\right)^{-\frac{1}{2}} (a_2 \psi_2 + \cdots + a_n \psi_n + \cdots$.

Then $$\epsilon_x = \sum_{n=2}^{\infty} a_n^2 (E_n - E_1) \Big/ \sum_{n=2}^{\infty} a_n^2 \tag{8}$$

is an average value of $E_n - E_1$ weighted with the squares of the coefficients of the higher states in the expansion of ψ, while

$$\delta_x^2 = \sum_{n=2}^{\infty} a_n^2 (E_n - E)^2 \Big/ \sum_{n=2}^{\infty} a_n^2 \tag{9}$$

is a similarly weighted average of $(E_n - E)^2$.

Since ψ_x is orthogonal to ψ_1, the variation principle assures us that

$$\epsilon_x \geqslant E_2 - E_1. \tag{10}$$

From $\int[(H-E)\psi_x-(E_x-E)\psi_x]^2d\tau \geqq 0$, we find also that

$$\delta_x \geqq E_x-E=\epsilon_x-\epsilon. \tag{11}$$

It is obvious from Eqs. (8) and (9) that $\kappa=\delta_x/(\epsilon_x-\epsilon)\geqq 1$ will be larger the broader the range of energies for which there are important terms in the expansion (7).

Inserting into (3), (4), (5) expression (2) for ψ, and assuming that $\int\psi^*H\psi_1d\tau=\{\int\psi_1^*H\psi d\tau\}^*$, (for a discussion of this assumption, which is clearly less severe than the usual expansion in series, see our preceding paper on the Hylleraas method) we find:

$$q^2=2-2a_1=2-2(1-a_x^2)^{\frac{1}{2}}, \tag{12}$$

$$\epsilon=a_x^2\epsilon_x, \tag{13}$$

$$\delta^2=\epsilon^2+a_x^2(\delta_x^2-\epsilon^2). \tag{14}$$

Eliminating a_x between (12) and (13) we get

$$q^2-\tfrac{1}{4}q^4=a_x^2=\epsilon/\epsilon_x \tag{15}$$

or, if ψ is a fairly good approximation to ψ_1,[1]

$$q^2 \cong \epsilon/\epsilon_x. \tag{16}$$

Eliminating a_x between (13) and (14) we obtain

$$\delta^2=\epsilon[\epsilon+(\delta_x^2-\epsilon^2)/\epsilon_x] \tag{17}$$

whence $\quad \delta^2/\delta_x^2 \cong \epsilon/\epsilon_x \quad$ or $\quad \delta^2 \cong \epsilon\epsilon_x\kappa^2. \qquad (18)$

From (15) and (17) we obtain finally,

$$q^2 \cong (\epsilon^2/\delta^2)\kappa^2. \tag{19}$$

In a concrete problem we know ψ, E_1 and E_2, and can compute E, ϵ and δ. For the other quantities we can fix limits by use of the above equations.

$$\begin{gathered} E_2-E_1<\epsilon_x<(\delta^2+\epsilon^2)/\epsilon, \\ 1<\kappa^2<\delta^2/\epsilon(E_2-E_1-2\epsilon), \\ \epsilon^2/(\delta^2+\epsilon^2)<q^2-\tfrac{1}{4}q^4<\epsilon/(E_2-E_1). \end{gathered} \tag{20}$$

As an illustration of the usefulness of this analysis, we now present results of calculations on three approximations to the ground state function for the helium atom (Table I). With r_1, r_2 and r_{12} representing the distances of electron 1 and 2 from the nucleus, and their mutual separation, respectively, the functions are

$$\psi_A=Ce^{-2(r_1+r_2)},$$

$$\psi_B=Ce^{-2(r_1+r_2)}[1+c(r_1-r_2)^2],$$

$$\psi_C=e^{-2(r_1+r_2)}[c_0+c_1r_{12}+c_2(r_1-r_2)^2 +c_3(r_1+r_2)+c_4(r_1+r_2)^2+c_5r_{12}^2].$$

In making the computations E_1 was taken as the apparent limit of convergence of the non-relativistic treatment as obtained by subtracting the relativity correction[2] from the observed term value. The first excited singlet level of the system is observed to be 20.51 ev higher.

The most striking characteristic of these results is the slow decrease of δ as the function is improved, compared with that of ϵ. Eq. (19) shows that this must occur in general if the "improvement" of the function involves a reduction of the root-mean-square error.[3] Associated with this is the increase in $\kappa^2\epsilon_x$ which is easily understood as follows: The error in the wave functions may be roughly divided into two parts; long range errors arising from the use of poor effective shielding constants in the construction of the function (as in the case of ψ_A) or of comparatively inflexible functions of any sort, and short range errors associated with the singularities in the energy when the particles are close together. In the neighborhood of these singularities the curvature of the correct wave function will be large and change rapidly. Unless the approximate functions are especially designed to be good in these regions, an increase in flexibility by the introduction of parameters such as appear in ψ_c will only slowly reduce the error here. Thus as the function is improved ψ_x will become more

TABLE I. *Approximations to the ground state function for the helium atom.*

Function	ϵ, ev	δ, ev	$\kappa^2\epsilon_x$, ev	κ	δ_x, ev	q
A	4.2	28.4[1]	190.	<3.1	61. $<$	$0.15<q<0.47$
B	0.72	14.2[1]	280.	<3.7	76. $<$	$0.051<q<0.19$
C	0.019	3.5[2]	660.	<5.7	116. $<$	$0.0054<q<0.031$

[1] From data of D. H. Weinstein, Phys. Rev. **41**, 839 (1932).
[2] J. H. Bartlett, Jr., J. J. Gibbons, Jr., and C. G. Dunn. Phys. Rev. **47**, 679 (1935).

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[1] Equations involving the sign $\sim$ have an approximate validity when ϵ is small as compared with E_2-E_1.

[2] H. Bethe, *Handbuch der Physik*, Vol. 24, p. 384.

[3] Possible decreases in κ which might lead to a contrary behavior are limited by the inequality $\kappa<1$, and are in any case unlikely to occur, as is indicated by the argument to follow immediately.

and more concentrated in the small regions where the particles are close together. By analogy with the Fourier expansion in one dimension of a function which vanishes except in a small region, we can see how the expansion as in Eq. (7) of ψ_x will be modified as this process goes on. Thus we will expect that the most important terms will tend to be those of higher and higher energy, so that ϵ_x will rise, while at the same time the range in energy of the important high energy terms will increase, giving larger κ and δ_x. Long range errors are clearly important in ψ_A and ψ_B, and should be fairly well eliminated from ψ_c.

According to Eq. (20) we have $q^2 \gtrsim \epsilon/(E_2-E_1)$, a relation given by Eckart.[4] Thus we can place on q an upper limit which decreases with $\sqrt{\epsilon}$; that q is actually considerably smaller than this limit and decreases more rapidly with decreasing ϵ is indicated by the considerations of the preceding paragraph concerning the behavior of E_x, which we have replaced by E_2 in deriving this equation. A check on optimism in this respect is provided, however, by our lower limit for q.

Through δ may be interpreted as the root-mean-square value of a "local energy error," its value must not be confused with the error in the computed energy, which is necessarily a much smaller quantity if ψ is at all a good function (cf. Eqs. (18), (19)).

From the foregoing analysis we can draw some conclusions concerning the form of variational process which will give a wave function most satisfactory for a given purpose. In the computation of such properties of an atom as radial charge density or diamagnetic susceptibility what we have termed long range errors will be very important, while short range errors will tend to cancel out. On the other hand, in the computation of hyperfine structure constants long range errors will be of little importance if only the wave function is correct when the electrons are near the nucleus. Thus it may be advantageous to adjust the parameters in a function of given form in different ways, depending on the use to which this wave function is to be put. Now ϵ, δ^2, $\epsilon^{1+|K|}/\delta^2$, etc., are all positive quantities which approach zero as ψ approaches ψ_1; thus minimization of each one will give a variational procedure yielding a function useful for a given purpose.[5] Eq. (18) shows that minimization of δ^2 tends to give a function with small values of ϵ_x and κ, in preference to a value of ϵ which is as small as possible. This process then picks out a function which has a comparatively large root-mean-square error, (Eq. (16)), but one in which the short range errors are reduced at the expense of an increase in long range errors. Such a function should thus be particularly suitable for computations of hyperfine structures. On the other hand, minimization of $\epsilon^{1+|K|}/\delta^2$ is a process tending to give particularly large values of ϵ_x and thus small long range errors.

TABLE II. *Results obtained for the helium atom by minimizing* δ^2, ϵ, ϵ/δ^2.

	Minimize δ^2	Minimize ϵ	Minimize ϵ/δ^2
α	1.804	1.6875	1.647
ϵ, ev	1.88	1.52	1.56
δ, ev	24.7	25.6	26.3
$\kappa^2\epsilon_x$, ev	320.	430.	450.
q	$0.076 < q < 0.30$	$0.060 < q < 0.28$	$0.059 < q < 0.28$
$(r_1^2)_{\text{Av}}+(r_2^2)_{\text{Av}}$	1.84	2.11	2.21

As an illustration of the varying results given by these processes we consider again the helium atom. The assumed wave function is of the simple type constructed from hydrogenic orbitals with adjustable effective shielding, the space part being, for the ground state,

$$\psi = (\alpha^3/\pi)e^{-\alpha(r_1+r_2)}.$$

Elementary computations give

$$E = (2\alpha^2 - 6\tfrac{3}{4}\alpha)Rh,$$
$$\delta^2 = (8\alpha^4 - 30\alpha^3 + (29+5/48)\alpha^2)(Rh)^2.$$

The results obtained by minimizing δ^2, ϵ, ϵ/δ^2 are summarized in Table II. (Minimization of ϵ/δ^2 cannot be shown in general to lead one toward the ground state function, but with the particular type of variation available here it is a method of getting a larger value of δ with little increase in ϵ, as is clear from Table II.) Included in the table are computed values of $(r_1^2)_{\text{Av}}+(r_2^2)_{\text{Av}}$, which enters the computation of the diamagnetic

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[4] C. Eckart, Phys. Rev. **36**, 878 (1930).

[5] When a quantity other than ϵ is to be minimized caution must be used. Thus δ^2 approaches zero also if $\psi \rightarrow \psi_2$; a wave function of inappropriate form might give, on minimization of δ^2 a function approximately that for some other state than the one to be treated. The corresponding value of ϵ must thus be computed as a check on which state is described by the function. Minimization of $\epsilon^{1+|K|}/\delta^2$ requires the use of a value for the correct energy, presumably obtained from experiment; it is thus a procedure interesting only in connection with the determination of wave functions.

susceptibility. The value computed for this quantity using Hylleraas' function, ψ_C,[6] is 2.46, a value which may be accepted as nearly correct. Since in computing this quantity it is desired to minimize long range errors the most reliable results should be obtained, according to our argument, by minimizing ϵ/δ^2, the least reliable by minimizing δ^2. Actually the deviations from the correct answer have the corresponding order.

It is interesting to compare these results with those for ψ_B. The low value of $\kappa^2\epsilon_x$ given by ψ_B indicates that the low value of ϵ compared to the values given in Table II, is due to reduction of short range errors. (ψ_B takes some account of the relative positions of the electrons, whereas ψ_A and the above functions do not.) Despite the smaller energy error, therefore, this is not a favorable function for the computation of $(r_1^2)_{\text{Av}}+(r_2^2)_{\text{Av}}$; actually, it gives the value 1.76, lower than any other computed.

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[6] The radial charge distribution corresponding to this function is given by Bethe, Zeits. f. Physik **55**, 431 (1929).

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Magnetic Analysis of Evaporated Bi Deposits

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The magnetic susceptibility of evaporated bismuth films ranging in thickness from 0.1μ to 4μ has been measured by a compensated Gouy method in conjunction with a Sartorius microbalance. Films above 0.5μ are found to have a susceptibility, independent of film thickness, whose value agrees well with that of a single crystal with trigonal axis parallel to the field. Below 0.5μ the susceptibility decreases as the film thickness is reduced. It is suggested that films below 0.5μ possess a microcrystalline fiber structure which merges into a phase of macrocrystalline structure above this thickness. If films less than 0.5μ were aged for long periods in vacuum an increase in the susceptibility was noted, whereas no such effect was observed when thicker films were similarly treated, the effect being ascribed to a recrystallization process. The susceptibility of thick films ($>0.5\mu$) was found to be identical when deposited, respectively, on glass, Au, Cu and Sn. The nature of the crystalline aggregate, as determined from the susceptibility, was found to be dependent on the amount of residual gas present in the apparatus when the films were deposited. As the gas pressure, during deposition, was increased from about 10^{-5} mm of Hg the susceptibility measured with the field parallel to the film normal was greater than the same quantity measured in films produced in high vacuum. The susceptibility measured when the field was perpendicular to the film normal, on the other hand, remained approximately the same in the two cases. At relatively large gas pressures (*ca.*10^{-2} mm) the resulting films possessed a susceptibility which was independent of the angle between the film normal and the magnetic field. The bearing of these results on the structure of the deposits is briefly discussed.

Introduction

THE question as to whether metallic condensates possess crystalline structure or are amorphous aggregates of atoms has, for some years, been a matter of considerable controversy. Such layers as are produced, for instance, by evaporating metal onto a cold surface in vacuum possess a number of abnormal properties as compared with bulk metal. Among these may be mentioned their very high specific resistance, and the fact that it has often been difficult or impossible to obtain from them sharply defined x-ray patterns.

In recent years such layers have been the object of renewed investigation by electron diffraction.[1] A number of such investigations have shown that evaporated films possess a crystalline structure, even down to thicknesses of a few atomic layers, the lattice spacing being identical with that of the bulk material. Kirschner found that such layers often possessed preferred orientation and that the films appeared to be composed of individual crystallites with linear dimensions, for very thin films, of the order of 10A, the particle size increasing as the thickness of the layer increased. Heating the films tended to sharpen up the diffraction lines, that is to say, the crystal

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[1] F. Kirschner, Zeits. f. Physik **76**, 576 (1932).