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On a Variational Method for Determining Excited State Wave Functions

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A variational method is proposed which results in an approximate wave function for an excited state which has the maximum overlap with the true excited state eigenfunction. The method involves the calculation of the quantities $E = \langle \Phi | H | \Phi \rangle$ and $\Delta = \langle \Phi | (H - E)^2 | \Phi \rangle$, but is free of the constraint that the trial function Φ must remain orthogonal to all states of the same symmetry which lie beneath it. One must know, however, an approximation to the true eigenvalue. A discussion is given on how one might gain the latter information, lacking knowledge of the spectrum, from the repeated application of the method.

Es wird eine Variationsmethode vorgeschlagen, die auf eine genäherte Wellenfunktion für einen angeregten Zustand führt, welche sich maximal mit der wahren Eigenfunktion des angeregten Zustandes überlappt. Die Methode ermöglicht die Berechnung der Größen: $E = \langle \Phi | H | \Phi \rangle$ und $\Delta = \langle \Phi | (H - E)^2 | \Phi \rangle$, ist aber frei von der Nebenbedingung, daß die Versuchsfunktion Φ orthogonal zu allen benachbarten Zuständen mit derselben Symmetrie bleiben muß. – Man will jedoch eine Näherung des wahren Eigenwertes wissen. – Eine Diskussion darüber, wie man durch wiederholte Anwendung der Methode letztere Information gewinnen kann, ohne Kenntnisse über das Spektrum zu besitzen, wird durchgeführt.

Méthode variationnelle pour la détermination d'une fonction d'onde d'un état excité présentant le recouvrement maximum avec la fonction d'onde exacte. La méthode implique le calcul de $E = \langle \Phi | H | \Phi \rangle$ et $\Delta = \langle \Phi | (H - E)^2 | \Phi \rangle$ mais ne comporte pas la contrainte d'orthogonalité de la fonction d'essai Φ à tous les états inférieurs de même symétrie. On doit cependant connaître une valeur approchée de la valeur propre exacte. Discussion sur la manière dont on peut obtenir cette valeur approchée sans connaître le spectre, par application répétée de la méthode.

1. Introduction

For the exact wave function Ψ of an eigenstate the following equations hold,

$$E = \langle \Psi | H | \Psi \rangle = W, \tag{1}$$

$$\Delta = \langle \Psi | H^2 - E^2 | \Psi \rangle = 0 \tag{2}$$

and if Ψ is an eigenstate with $E = W \neq W'$, where W' is the energy of another state of the same symmetry with the corresponding eigenfunction Ψ', then

$$\langle \Psi | \Psi' \rangle = 0 . \tag{3}$$

For a trial function Φ, one has $E = \langle \Phi | H | \Phi \rangle > W_0$, where W_0 is the true ground state energy. Indeed if Φ were capable of attaining the exact form of Ψ_0, the exact ground state eigenfunction, one would have $E = W_0 = \langle \Psi_0 | H | \Psi_0 \rangle$.

Likewise for a calculation of an excited state, if the trial function Φ is capable of attaining the form of Ψ_k under a variation, then a stationary state is obtained with $E = W_k = \langle \Psi_k | H | \Psi_k \rangle$. In both cases the true eigenvalues are obtained by finding the stationary value from $\delta E = 0$ for the case of a trial function which can become the eigenfunction under variation.

For an excited state Ψ_k of the same symmetry as the ground state Ψ_0, $\delta E = \delta \langle \Phi | H | \Phi \rangle = 0$ is a necessary condition for finding a stationary value E which approximates W_k; but it is not sufficient. One must also take account of Eq. (3). Thus with Eqs. (1) and (3), using Φ in place of Ψ, one has necessary and sufficient conditions so that $\Phi \to \Psi_k$: $\delta \langle \Phi | H | \Phi \rangle = 0$ and $\langle \Phi | \Phi_0 \rangle = 0$. But the condition $\langle \Phi | \Phi_0 \rangle = 0$ is rather restrictive, especially if Φ_0 is not a very good approximation to Ψ_0. Hence it is desirable to find another approach for excited states.

Weinstein [9] has proposed that for an excited state for which one has a trial function Φ, which cannot attain the form of an exact wave function, one can obtain an approximation to some Ψ_k by minimizing Δ, where Δ is given by $\Delta = \langle \Phi | (H - E)^2 | \Phi \rangle$.

If there exists a Φ such that $H\Phi = W_k \Phi$ (hence $\Phi = \Psi_k$), then $\Delta = 0$. As a corollary it may be stated that as $\Phi \to \Psi_k$, $\Delta \to 0$. Hence $\Phi \to \Psi_k$ implies that $\Delta \to 0$. It is on this basis that Weinstein suggested that as $\Delta \to \min$, $\Phi \to \Psi_k$. It will be shown below that, if one measures the approach of Φ to Ψ_k by the increase of the value of the integral $a_k = \langle \Phi | \Psi_k \rangle$, the minimization of Δ does not at all give the best approximation to a Ψ_k that can be obtained from a given trial function.

There are criteria for judging the goodness of Φ as an approximation to Ψ_k other than that of the maximum a_k, but a_k provides for the best overall convergence of Φ to Ψ_k. Obtaining the maximum a_k is equivalent to obtaining the smallest root-mean-square deviation of Φ from Ψ_k. As will be seen below, the other criteria are useful for obtaining good approximations to Ψ_k in certain regions of configuration space, but since a_k provides a criterion for judging the goodness of Φ as an approximation to Ψ_k over the entire configuration space, it seems that this criterion should be the one used to judge the goodness of Φ. Taking this criterion as the basic premise it will be shown below that, if one is considering the k^{th} eigenstate, *the approximate function, Φ, which has the maximum overlap with the true eigenfunction Ψ_k is determined by that Φ which gives ε^2/Δ its stationary value.* Δ is as given above and $\varepsilon^2 = (E - W_k)^2$.

In Section 2, various criteria of goodness for approximate wave functions are considered. This leads to a proposal in Section 3 of the ε^2/Δ minimization method for the determination of the best approximation to Ψ_k. In Section 4 the method is discussed in terms of the orbital approximation and a connection is made with some recent work on upper and lower bounds to eigenvalues [4]. In the last section the method, formulated in the orbital approximation, is applied to some excited states of He. The wave functions are used to calculate the expectation values of a few operators in order to judge their validity.

2. Criteria of Goodness for Approximate Wave Functions

In this section, a generalization is presented of an analysis first given by H. M. James and A. S. Coolidge [3] for the ground state of an electronic system. Here the method will be extended to apply to excited states as well.

Let Φ be an approximate normalized wave function and $E = \langle\Phi|H|\Phi\rangle$ its associated energy. Also let

$$\Phi = \sum_i a_i \Psi_i = \sum_{i \neq k} a_i \Psi_i + a_k \Psi_k ; \tag{4}$$

now

$$(\Phi - a_k \Psi_k) = \sum_{i \neq k} a_i \Psi_i \tag{5}$$

will give the deviation of Φ from the exact function Ψ_k. A deviation function can then be defined,

$$\Phi_x = (1 - a_k^2)^{-\frac{1}{2}} (\Phi - a_k \Psi_k) \tag{6}$$

where $a_k = \langle\Psi_k|\Phi\rangle$. Hence one may write

$$\Phi = a_k \Psi_k + a_x \Phi_x \tag{7}$$

where $a_x = (1 - a_k^2)^{\frac{1}{2}}$ measures the amount of the deviation function Φ_x which appears in Φ. As criteria of the inaccuracy of Φ there are: Q, the root-mean-square error in Φ

$$Q = \langle\Phi - \Psi_k|\Phi - \Psi_k\rangle^{\frac{1}{2}} \tag{8}$$

ε, the energy error

$$\varepsilon = E - W_k \tag{9}$$

and $\Delta^{\frac{1}{2}}$, the root-mean-square local energy deviation

$$\Delta^{\frac{1}{2}} = \langle\Phi|(H - E)^2|\Phi\rangle^{\frac{1}{2}} . \tag{10}$$

One may also define the quantities

$$\begin{aligned} E_x &= \langle\Phi_x|H|\Phi_x\rangle , \qquad \varepsilon_x = E_x - W_k \\ \text{and} \qquad \Delta_x &= \langle\Phi_x|(H - E)^2|\Phi_x\rangle . \end{aligned} \tag{11}$$

If the inequality

$$\langle\Phi_x|[(H - E) - (E_x - E)]^2|\Phi_x\rangle \geqq 0$$

is considered and the integral is expanded in terms of the above defined quantities, one finds

$$\langle\Phi_x|H^2|\Phi_x\rangle - 2E_x E + E^2 - E_x^2 + 2E_x E - E^2 \geqq 0$$

thus,

$$\langle\Phi_x|H^2|\Phi_x\rangle - 2E_x E + E^2 \geqq E_x^2 - 2E_x E + E^2 ;$$

but the left hand side is merely Δ_x, hence

$$\Delta_x \geqq (E_x - E)^2 . \tag{12}$$

From the definitions of ε_x and ε given above, it can be shown that $(E_x - E)^2 = (\varepsilon_x - \varepsilon)^2$, hence $\Delta_x \geqq (\varepsilon_x - \varepsilon)^2$. Thus one may define a quantity K^2,

$$K^2 = \frac{\Delta_x}{(\varepsilon_x - \varepsilon)^2} \geqq 1 . \tag{13}$$

Now substituting Eq. (7) into Eqs. (8)—(10) it follows that

$$Q^2 = 2[1 - a_k] = 2[1 - (1 - a_x^2)^{\frac{1}{2}}], \tag{14}$$

$$\varepsilon = a_x^2 \varepsilon_x, \tag{15}$$

$$\Delta = \varepsilon^2 + a_x^2(\Delta_x - \varepsilon^2). \tag{16}$$

From the first equality of Eq. (14) one finds the justification of the statement made in the introduction that obtaining the maximum a_k is equivalent to obtaining the smallest root-mean-square deviation.

Eliminating a_x between Eqs. (14) and (15) one finds

$$Q^2 - \frac{1}{4} Q^4 = a_x^2 = \varepsilon/\varepsilon_x \tag{17}$$

or if Φ is a fairly good approximation to Ψ_k (i.e., if ε is small when compared to $|W_k - W_{k-1}|$ and $|W_k - W_{k+1}|$), then

$$Q^2 \cong \varepsilon/\varepsilon_x. \tag{18}$$

Eliminating a_x between Eqs. (15) and (16) one obtains

$$\Delta = \varepsilon[\varepsilon + (\Delta_x - \varepsilon^2)/\varepsilon_x] \tag{19}$$

and assuming again that Φ is a fairly good approximation to Ψ_k, it follows that

$$\Delta/\Delta_x \cong \varepsilon/\varepsilon_x \quad \text{or} \quad \Delta \cong \varepsilon\varepsilon_x K^2. \tag{20}$$

Now, making use of Eqs. (18) and (20), one obtains the result

$$Q^2 \cong \left(\frac{\varepsilon^2}{\Delta}\right) K^2. \tag{21}$$

This equation interrelates the various criteria considered. Again it should be emphasized that theoretically the criterion which should be used to judge the overall quality of a wave function is the criterion of minimum Q^2 (i.e., maximum a_k).

Before proceeding to investigate Eq. (21), each of the quantities in this equation must be studied in order to understand its consequences and enable one to proceed to a method for determining the best Φ to approximate Ψ_k.

3. Determination of the Best Approximation to Ψ_k

Assume first that one has a function Φ. One may then, according to Eqs. (8) to (10), judge its accuracy. It should be noted that in applying these formulae Eq. (8) requires a knowledge of the true wave function. This is not available, of course, except for the very simplest systems; thus Eq. (8) is impractical from this point of view.

In order to use Eq. (9) one must know the true eigenvalue W_k; however for this quantity the experimentally determined energy for this state may be used, if it has been measured. Thus this method of judging accuracy usually will be available.

Finally, Eq. (10) makes no use of information other than that contained in Φ. Although this seems to be a favourable aspect of Eq. (10) it must be realized that one is only finding the local energy deviation on the basis of Φ without regard to any external standard.

The three criteria have now been considered assuming that a Φ had somehow been obtained. A more important question is whether the criteria can be used to determine a Φ.

From this point of view Eq. (8) is useless; because if Ψ_k is known, why should one want to obtain an approximation to it? Eq. (9) can be used to obtain a Φ, if one assumes that Φ is the function which minimizes ε. That is, a Φ must be found such that $\delta\varepsilon = 0$. For the ground state this is nothing more than the familiar variational principle. Eq. (9) is incapable however of giving a Φ which is an approximation to an excited state which has the same symmetry as the ground state.

Considering Eq. (10) one must find the Φ which will minimize Δ. It is the only one of the criteria which, taken alone, can yield a Φ for the ground state or any excited state. This is the basis for Weinstein's method for determining an approximate wave function, but referring again to Eq. (21), it is obvious that Weinstein's idea of minimizing Δ does not give the minimum Q^2 and thus this method *cannot* give the best overall approximation to Ψ_k. Thus looking at each of the three criteria individually and demanding that Q^2 be a minimum, an impasse seems to be reached. This impasse will be resolved by the use of Eq. (21). But first, brief consideration will be given to the types of error in the wave function which are reduced by minimization of Δ and the minimization of E; here the discussion given by James and Coolidge [3] is important.

In minimizing Δ the "local energy error" is minimized [3, 7]. That is, the errors in the wave function associated with the closeness of the electrons will be minimized. Thus the wave function which results from this type of minimization would be expected to give good values for properties which describe phenomena where the particles are close together.

In minimizing E, which can be done only for the ground state or lowest state of a given symmetry, "long range errors" are minimized [2, 3, 7]. Thus a wave function determined on this basis should be good for describing properties such as the radial density or diamagnetic susceptibility where long range errors are important. Thus by minimizing E or Δ, a wave function is obtained which has minimum error in certain regions of configuration space, rather than the minimum error over the whole of configuration space.

Now returning to Eq. (21) one may ask how one might obtain a wave function for an excited state which satisfies the criteria of minimum Q^2. From the derivation of Eq. (21) it was found that $K^2 \geqq 1$, according to Eq. (13). Thus if the right hand side of Eq. (21) is to be minimized, the smallest value K^2 can take is 1. Thus in order to obtain the minimum Q^2, the quantity ε^2/Δ should be minimized. This method allows the determination of an excited state wave function which minimizes Q^2 without a knowledge of the exact Ψ_k. This seems to be the first time that this procedure has been proposed as a method for obtaining approximations to excited state wave functions.

On the basis of the new method just proposed above, it is now known how to obtain a Φ which is the best approximation to a Ψ_k. It should be noted that the Φ_k obtained by this method for the case of a ground state need not give as good an approximation to W_0 as could be obtained by minimizing E; likewise it need not give as small a value for Δ as would be obtained by minimizing Δ; however unlike the minimization of Δ or E it does give the minimum Q^2 which is the chosen criterion for the best Φ_k.[1]

4. The Minimization of ε^2/Δ

Returning to Eq. (21) and considering the discussion given in the last section the trial function which has the maximum overlap with the true eigenfunction must be such that the variation in Q^2 should vanish. Hence one may write

$$\delta Q^2 = \delta E - \frac{\varepsilon}{2\Delta}\,\delta\Delta = 0 \tag{22}$$

or in a more condensed form,

$$\delta Q^2 = \delta E + \omega\delta\Delta = 0\,, \tag{23}$$

where ω is the constant quantity in Eq. (22). Recently a variational method for obtaining upper and lower bounds based on the use of the Temple-Kato formulae has been proposed [4] and the formulation in terms of the orbital approximation given. In that paper it is shown that the best bound, B, is given by the function which satisfies

$$\delta B = \delta E + \omega'\delta\Delta = 0\,. \tag{24}$$

Hence these two methods differ only in the value of the coefficient of $\delta\Delta$. In terms of the orbital approximation one may completely carry over the formalism of [4] to the present case with the exception that ω' of [4] must everywhere be replaced by ω as given in Eq. (22). ω enters into the formalism as a factor in the general coupling operators as given in [4]. Hence there is no need to repeat the formalism here.

In the next section the formalism of [4] will be applied, with the value of ω as given in Eq. (22), to the calculation of wave functions for the ${}^{1,3}P\,(1s, 2p)$ and ${}^{1,3}P\,(1s, 3p)$ states of the He atom.

5. Results on Some Excited States of He

The basis functions for the calculations on the excited states were taken as

$$\chi_{s,n} = \frac{(2\eta_s)^{\frac{3}{2}}}{(n+1)!\,2^{n+1}}\,(2\eta_s r)^{n-1}\exp(-\eta_s r)\,Y_{0,0}(\Theta,\phi) \tag{25}$$

$$\chi_{p,n} = \frac{(2\eta_p)^{\frac{3}{2}}}{(n+1)!\,2^{n+1}}\,(2\eta_p r)^{n}\exp(-\eta_p r)\,Y_{l,M}(\Theta,\phi) \tag{26}$$

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[1] It should be noted that care may have to be taken in this procedure. For excited states one is interested in obtaining a stationary value of ε^2/Δ which is not only consistent with $\varepsilon^2/\Delta \to 0$, but also with $\varepsilon^2 \to 0$ and $\Delta \to 0$. These are necessary conditions such that $\Phi \to \Psi_k$.

The minimum value, $\varepsilon^2/\Delta = 0$, could be obtained in two ways which are of no physical interest, namely, when either $\varepsilon^2 = 0$ and Δ remains finite, or when ε^2 is finite and Δ becomes infinite; it is obvious that the wave functions associated with these particular ε^2/Δ values are useless. It is useful therefore to check that both ε^2 and Δ remain small when a search is being made for the stationary value of ε^2/Δ; otherwise the wrong part of the hypersurface may be searched and a meaningless function obtained.

These problems were not encountered for the calculations presented here.

where the $\chi_{s,n}$ are the basis function for the s orbital and the $\chi_{p,n}$ those for the p orbital. The s and p orbitals were each represented by four basis functions in the following way

$$\phi_s = \sum_{n=1}^{4} C_{s,n} \chi_{s,n} , \tag{27}$$

$$\phi_p = \sum_{n=2}^{5} C_{p,n} \chi_{p,n} , \tag{28}$$

where the trial function may be written as

$$\Phi^{1,3} = 1/\sqrt{2}[\phi_s(1)\, \phi_p(2) \pm \phi_p(1)\, \phi_s(2)] . \tag{29}$$

Using the method described by Messmer and Birss [4], with the modification mentioned in the last section, the trial function which satisfies Eq. (23) has been determined. It has further been optimized with respect to η_s and η_p. The resulting wave functions for the ${}^1P(1s\,2p)$, ${}^3P(1s\,2p)$, ${}^1P(1s\,3p)$ and ${}^3P(1s\,3p)$ states of He are presented in Table 1.

Table 1. *Excited state wave functions – ε^2/Δ minimization method*

ϕ_s			ϕ_p		
n	η	c_n	n	η	c_n
		${}^1P$ 1s 2p			
1	2.25	0.83850	2	0.668	0.41858
2	2.25	0.16110	3	0.668	0.44990
3	2.25	0.02780	4	0.668	0.02159
4	2.25	−0.00146	5	0.668	0.17857
		${}^3P$ 1s 2p			
1	1.86	1.11008	2	0.700	0.71746
2	1.86	−0.14467	3	0.700	−0.10578
3	1.86	0.01676	4	0.700	0.46560
4	1.86	0.00726	5	0.700	−0.00067
		${}^1P$ 1s 3p			
1	1.68	1.29512	2	0.354	−1.31116
2	1.68	−0.42127	3	0.354	1.29494
3	1.68	0.10502	4	0.354	0.62949
4	1.68	−0.01848	5	0.354	−0.00507
		${}^3P$ 1s 3p			
1	2.45	0.73860	2	0.436	−1.20234
2	2.45	0.23844	3	0.436	1.48308
3	2.45	0.03785	4	0.436	−0.78487
4	2.45	0.03638	5	0.436	1.14108

In order to demonstrate the validity of the thesis that the wave functions obtained by the minimization of ε^2/Δ should be the best functions over the whole of configuration space, some expectation values have been calculated for these functions. If the trial function is designated as Φ, the expectation values calculated are given as

$$E = \langle \Phi | H | \Phi \rangle , \tag{30}$$

$$\langle 1/r \rangle = \frac{1}{2} \left\langle \Phi \left| \sum_{i=1}^{2} 1/r_i \right| \Phi \right\rangle , \tag{31}$$

$$\langle r \rangle = \frac{1}{2} \left\langle \Phi \left| \sum_{i=1}^{2} r_i \right| \Phi \right\rangle , \tag{32}$$

$$\langle r^2 \rangle = \frac{1}{2} \left\langle \Phi \left| \sum_{i=1}^{2} r_i^2 \right| \Phi \right\rangle , \tag{33}$$

where r_i is the distance of the i^{th} electron from the nucleus. In Table 2 a comparison is made of the expectation values calculated from the wave functions of Table 1 with those calculated from variational wave functions obtained by other methods. The other wave functions are: 1) B^L – those obtained by Messmer and Birss [5] which give the best lower bound to the eigenvalue; 2) E – those determined by the ordinary variational principle; 3) "Exact" – those determined by Schiff *et al.* [8] using 560 terms of a Pekeris type expansion. Comparing the values in the first three columns of Table 2 with those of the fourth column, it is readily seen that the ε^2/Δ wave functions give the best overall accuracy; indeed the only value predicted better by the variational principle is that of the energy and the difference there is in the fifth decimal place.

Table 2. *Comparison of expectation values calculated from various wave function*

	B^L	E	ε^2/Δ	Exact
		^1P 1s 2p		
$-E$	2.07204	2.12246	2.12243	2.12384
$\langle 1/r \rangle$	1.0457	1.1194	1.1229	1.12318
$\langle r \rangle$	6.134	2.9469	2.9223	2.91068
$\langle r^2 \rangle$	83.87	16.175	15.878	15.76565
		^3P 1s 2p		
$-E$	2.07537	2.13134	2.13132	2.13316
$\langle 1/r \rangle$	1.0490	1.1309	1.1335	1.13324
$\langle r \rangle$	6.185	2.7004	2.6813	2.67396
$\langle r^2 \rangle$	75.54	13.417	13.245	13.21174

A similar comparison is given for the ^1P 1s 3p and ^3P 1s 3p states of He in Table 3. For these states, however, the ordinary variational principle cannot be used and a method due to Davidson [1] was employed to determine wave functions which yielded the values listed under E. The other symbols have the same significance as in Table 2, with the addition that B^u lists the results obtained from the wave functions determined in some recent upper bound calculations [5]. Again the method involving the minimization of ε^2/Δ seems to give the best overall agreement with the "Exact" values of the operators considered.

In the calculations described here W_k was approximated by the experimental energy of the k^{th} state. However, in some cases experimental information may not be available; it would then be desirable to have an entirely *a priori* way of determining a Φ_k. One such possible way of determining Φ_k would be to consider the W_k as a variable; one would then minimize ε^2/Δ for each value of W_k and the desired Φ_k would be that function which gave the smallest value of the minimized ε^2/Δ's. Care would have to be exercised since the minimized ε^2/Δ values would certainly show multiple minima when considered as a function of W_k. Thus a rough estimate of W_k would be highly desirable. An investigation of this problem will be undertaken in the near future.

Table 3. *Comparison of expectation values calculated from various wave functions*

	B^L	B^U	E	ε^2/Δ	Exact
			^1P 1s 3p		
$-E$	2.03844	2.07062	2.05473	2.05472	2.05515
$\langle 1/r \rangle$	1.0448	1.0229	1.0547	1.0528	1.05497
$\langle r \rangle$	6.122	12.055	6.720	6.695	6.67954
$\langle r^2 \rangle$	86.77	296.20	92.81	92.16	91.8727
			^3P 1s 3p		
$-E$	2.03999	2.07374	2.05750	2.05745	2.05808
$\langle 1/r \rangle$	1.0474	1.0239	1.0570	1.0597	1.05802
$\langle r \rangle$	6.302	11.574	6.364	6.332	6.32113
$\langle r^2 \rangle$	88.48	268.22	82.96	82.15	82.1098

Finally, the problem of the integrals involved in calculating Δ should be mentioned. Analytical forms for all integrals, over Slater basis functions, involved in Δ for atoms are now available [6]. However, the extension of any method involving Δ to a many-electron, many-center problem presents considerable difficulties because of the number of new integrals introduced. Much work on atomic systems will have to be done in order to determine the need and desirability of tackling the integrals necessary to carry out calculations on molecules.

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