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VARIATION-PERTURBATION METHOD FOR EXCITED STATES

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Variation-Perturbation Method for Excited States*

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ABSTRACT

The first order wave function, X_1 , in the perturbation method can be obtained by a variational principle instead of summing the usual infinite series with a large continuum contribution. For a ground state or the lowest state of a given symmetry suitable trial functions $\tilde{X}_1$, are chosen to attain E_2 as a minimum. This method is extended here to any excited state, m . To obtain X_1^m , the expression

$$\tilde{E}_2^m = \left\{ 2 \langle \phi_0^m, (H_1 - E_1^m) \tilde{X}_1^m \rangle + \langle \tilde{X}_1^m, (H_0 - E_0^m) \tilde{X}_1^m \rangle \right\} \geq E_2^m$$

is to be minimized with $\tilde{X}_1^m$ in the form $\tilde{X}_1^m = \bar{X}_1^m + \sum_{k=0}^{m-1} \frac{\phi_0^k \langle \phi_0^k, H_1 \phi_0^m \rangle}{E_0^m - E_0}$

and $\tilde{X}_1^m$ orthogonal to the known unperturbed functions of the states lower than m . The X_1 gives also the third order energy.

In the perturbation solution of the eigen value problem, $H\psi = E\psi$, the first order wave function, χ_1 , determines the energy to third order and the resulting energy will be an upper limit¹ to the exact E . The usual perturbation method

¹See the footnote (6) of: O. Sinanoglu, Phys. Rev. (To be published).

gives χ_1 , E_2 , etc. in terms of the spectral representation of unperturbed Hamiltonian, H_0 . The resulting infinite sums are very difficult to evaluate because the largest contributions to them come from the continuum part² of the set of eigenfunctions

²See e.g. P. O. Löwdin, "Advances in Chemical Physics", Vol. II, Interscience Publishers, New York, 1959.

of H_0 . Instead χ_1 can be obtained by choosing suitable trial functions to make a certain expression, given below, stationary. For the ground state or the lowest state belonging to a given irreducible representation of the group of H , the exact χ_1 makes this expression a minimum. Then one simply tries to attain this minimum to get the best χ_1 . Hylleraas³ has used this method

³H. A. Hylleraas, Z. Physik., 65, 209 (1930).

to obtain a very good approximation to the χ_1 and the second order energy, E_2 , of the helium atom.

For excited states which are not automatically orthogonal to the lower states by symmetry, the stationary expression will not be a minimum, and the variation-perturbation method described above must be modified. The purpose of this article is to develop such a modified variational principle by which trial functions, $\tilde{\Psi}_1$, for an excited state, can be varied to attain a certain minimum subject to some restrictions. This is similar to what happens in the ordinary variation method, $\delta \left\{ \frac{\langle \Psi, H\Psi \rangle}{\langle \Psi | \Psi \rangle} \right\} = 0$, where the energy of an excited state will be obtained as a minimum only if the trial functions are restricted so as to be orthogonal to the exact eigenfunctions of all lower states. However, these exact functions are in general not known. In contrast, we shall show that the minimum principle to be developed here for the χ_1 of excited states involves only the known unperturbed eigenfunctions of the lower states.

Consider an unperturbed Hamiltonian, H_0 , and a perturbation λH_1 with $H = H_0 + \lambda H_1$, $H\Psi = E\Psi$ and $H_0\phi_0^k = E_0^k\phi_0^k$ where ϕ_0^k is the kth unperturbed eigenfunction. The usual perturbation expansion for the mth exact eigenstate of H is (for $\lambda = 1$)

$$\Psi^m = \phi_0^m + \chi_1^m + \dots \quad (1)$$

$$E^m = E_0^m + E_1^m + E_2^m + E_3^m + \dots$$

The first order wave function, χ_1^m , satisfies the non-homogeneous equation

$$(H_0 - E_0)\chi_1 = (E_1 - H_1)\phi_0 \quad (2)$$

where $E_1 = \langle \phi_0, H_1 \phi_0 \rangle$. This equation will have a solution only if $(E_1 - H_1)\phi_0$ is orthogonal to the solutions of the homogeneous equation, $(H_0 - E_0)\phi = 0$. Thus, either ϕ_0 must be non-degenerate or else it must be chosen such that the above orthogonalization condition is satisfied (removal of degeneracy in first order). Equation (2) determines χ_1 to within an arbitrary multiple of ϕ_0 . If this multiple is fixed so that $\langle \phi_0, \chi_1 \rangle = 0$, E_2 and E_3 will be given by

$$E_2 = \langle \phi_0, H_1 \chi_1 \rangle \quad (3)$$

$$E_3 = \langle \chi_1, (H_1 - E_1) \chi_1 \rangle \quad (4)$$

χ_1 does not have to be normalized, since its normalization affects the energy only to the fourth and higher orders.¹

Equation (2) can be put into an equivalent variational form. The exact solution, χ_1^m , of equation (2) for the m th state of H , makes the expression $\tilde{E}_2^m [\tilde{\chi}_1^m] = \left\{ 2\langle \phi_0^m, (H_1 - E_1^m) \tilde{\chi}_1^m \rangle + \langle \tilde{\chi}_1^m, (H_0 - E_0^m) \tilde{\chi}_1^m \rangle \right\}$ stationary³, i.e.

$$\delta \tilde{E}_2^m [\tilde{\chi}_1^m] = \delta \left\{ 2\langle \phi_0^m, (H_1 - E_1^m) \tilde{\chi}_1^m \rangle + \langle \tilde{\chi}_1^m, (H_0 - E_0^m) \tilde{\chi}_1^m \rangle \right\} = 0 \quad (5)$$

This equation provides a convenient means of approximating to χ_1^m if the extremum, $\tilde{E}_2^m [\tilde{\chi}_1^m]$, is also a minimum. Then, $\tilde{\chi}_1^m$, the trial function, can be varied until the lowest $\tilde{E}_2 [\tilde{\chi}_1]$ is attained.

$E_2^m [X_1^m]$ will be a minimum^{3,4} if ϕ_0^m corresponds to the

⁴H. A. Bethe and E. E. Salpeter, Encyclopedia of Physics, Vol. 35, Springer-Verlag, Berlin, 1957.

ground state, ϕ_0^o . To see this we write $\tilde{X}_1^m = X_1^m + \delta X_1^m$ in $\tilde{E}_2^m [\tilde{X}_1^m]$ (see equation (5)) and using equation (2) obtain

$$\tilde{E}_2^m [\delta X_1^m] = E_2^m + \langle \delta X_1^m, (H_0 - E_0^m) \delta X_1^m \rangle \quad (6)$$

Thus, for $\langle \phi_0^o, (H_1 - E_1) \delta X_1^m \rangle$ real, the first order variation of E_2^m vanishes corresponding to equation (5) and the error in E_2^m is of the second order in δX_1^m . Expanding $(H_0 - E_0^m) \delta X_1^m$ in the eigenfunctions of H_0 we have

$$\tilde{E}_2^m [\delta X_1^m] = E_2^m + \sum_{n \neq 0}^{\infty} (E_0^n - E_0^m) \langle \phi_0^n, \delta X_1^m \rangle^2. \quad (7)$$

For the ground state $E_0^n > E_0^o$ so that the last term is positive definite and therefore

$$\tilde{E}_2^o [\delta X_1] \geq E_2^o \quad (8)$$

The same minimum principle applies also to any other X_1^m if it corresponds to the lowest state of a given type of symmetry. ^{He²⁺} Since ϕ_0^m , X_1^m and δX_1^m belong to the same irreducible representation of the group of H, just by symmetry δX_1^m will be

orthogonal to all the states ϕ_0^k below ϕ_0^m . Then the negative terms, $(E_0^k - E_0^m)$, do not contribute to equation (7) and we still have $\tilde{E}_2^m(\delta X_1^m) \geq E_2^m$. Thus $(1s\ 2s)\ ^3S, ^1P$, etc. states of He can be treated just like its ground state³ by minimizing $\tilde{E}_2^m$ with suitable trial functions, $\tilde{X}_1^m$.

Consider now a general excited state which may be of the same symmetry as some of the lower states. To apply the minimum principle to the X_1^m of such a state, m , the variation δX_1^m must be restricted so as to make the error in equation (6) positive definite. Hence in equation (7) we must have

$$\langle \phi_0^k, \delta X_1^m \rangle = 0 \quad (k < m; E_0^k - E_0^m < 0) \quad (9)$$

to remove the negative contribution of all the ϕ_0^k of states lower than m . The δX_1^m above was defined as the error of the trial function, $\tilde{X}_1^m$, with respect to the exact solution X_1^m of equation (2); so the condition, equation (9) becomes

$$\langle \phi_0^k, \tilde{X}_1^m \rangle = \langle \phi_0^k, X_1^m \rangle \quad [k = 0, 1, 2, \dots, (m-1)] \quad (10)$$

The particular solution of equation (2) is formally given¹ by

$$X_1^m = \frac{1}{H_0 - E_0^m} [E_1^m - H_1] \phi_0^m \quad (11)$$

where $(H_0 - E_0)^{-1}$ is the Green's function operator,[†]

$E_1^m = \langle \phi_0^m, H_1 \phi_0^m \rangle$ and $\langle X_1^m, \phi_0^m \rangle = 0$. Substituting equation (11) in equation (10), and noting that $(H_0 - E_0)^{-1}$ is self-adjoint since H_0 is, we get

$$\begin{aligned} \langle \phi_0^k, X_1^m \rangle &= \langle \frac{1}{H_0 - E_0^m} \phi_0^k, (E_1^m - H_1) \phi_0^m \rangle \\ &= \frac{1}{E_0^m - E_0^k} \langle \phi_0^k, H_1 \phi_0^m \rangle \end{aligned} \quad (12)$$

Thus, even though we do not have X_1^m in closed form, we do know $\langle \phi_0^k, X_1^m \rangle$. This makes the choice of the trial functions, $\tilde{X}_1^m$, subject to the restriction equation (10) or (9) possible.

[†]If $(H_0 - E_0^m)^{-1}$ is written in the spectral representation of H_0 , the usual formula

$$X_1^m = \sum_{n \neq m}^{\infty} \frac{\langle \phi_0^n, H_1 \phi_0^m \rangle}{E_0^n - E_0^m} \phi_0^n$$

results. We have already mentioned the difficulty of evaluating this infinite sum.

Equations (10) and (12) show that $\tilde{X}_1^m$ must be of the form

$$\tilde{X}_1^m = \bar{X}_1^m + \sum_{k=0}^{m-1} \frac{\langle \phi_0^k | H_1 | \phi_0^m \rangle}{E_0^m - E_0^k} \phi_0^k \quad (13a)$$

and the arbitrary part, $\bar{X}_1^m$, of the trial function, $\tilde{X}_1^m$, must be kept orthogonal to the ϕ_0^k of all the states lower than m , i.e.

$$\langle \bar{X}_1^m, \phi_0^k \rangle = 0, \quad [k = 0, 1, 2, \dots, (m-1)] \quad (13b)$$

This gives the method for obtaining approximations to the X_1^m , E_2^m and E_3^m [see equation (4)] of any excited state, m . The expression

$$\tilde{E}_2^m[\bar{X}_1^m] = \left\{ 2 \langle \phi_0^m | (H_1 - E_1^m) \bar{X}_1^m \rangle + \langle \bar{X}_1^m | (H_0 - E_0^m) \bar{X}_1^m \rangle \right\} \gg E_2^m \quad (14)$$

is to be minimized subject to equations (13a, b).

In the ordinary variation method for excited states, the trial functions must be kept orthogonal to the exact eigenfunctions of all lower states. In contrast to this we note again that the variation-perturbation method given here by equations (13) and (14) require only the known unperturbed functions, ϕ_0^k , of the lower states. The method can be applied to such excited states as $(1s\ 2s)\ ^1S$ of the He-like ions to obtain the energy with explicit Z dependence^{3,4} and also to

the similar excited electron pairs that arise in the theory of a many electron atom or molecule.^{1,5}

⁵Oktay Sinanoğlu, Proc. Roy. Soc. (To be published).