

Variation-Perturbation Method for Excited States*

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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, \bar{X}_1 , are chosen to attain E_2 , the second-order contribution to the energy, as a minimum. This method is extended here to any excited state, m , regardless of its symmetry. To obtain X_1^m , the expression

$$\tilde{E}_2^m = \{2\langle\Phi_0^m, (H_1 - E_1^m)\bar{X}_1^m\rangle + \langle\bar{X}_1^m, (H_0 - E_0^m)\bar{X}_1^m\rangle\} \geq E_2^m,$$

is to be minimized with \bar{X}_1^m in the form

$$\bar{X}_1^m = \bar{X}_1^m + \sum_{k=0}^{m-1} \frac{\Phi_0^k \langle\Phi_0^k, H_1 \Phi_0^m\rangle}{(E_0^m - E_0^k)},$$

with \bar{X}_1^m orthogonal to the known unperturbed functions of the states lower than m . The X_1 gives also the third-order energy. The method may be applied to such excited states as $(1s2s) {}^1S$ of He-like ions and to the similar electron pairs that arise in the writer's theory of a many-electron atom or molecule.

IN the perturbation solution of the eigenvalue problem, $H\Psi = E\Psi$, the first-order wave function, X_1 , determines the energy to third order and the resulting energy will be an upper limit¹ to the exact E . The usual perturbation method gives X_1 , E_2 , etc., in terms of the spectral representation of the 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 of H_0 . Instead, X_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 X_1 makes this expression a minimum. Then one simply tries to attain this minimum to get the best X_1 . Hylleraas³ has used this method to obtain a very good approximation to the X_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, \bar{X}_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, $\delta\{\langle\Psi, H\Psi\rangle/\langle\Psi, \Psi\rangle\} = 0$, 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 X_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 k th unperturbed eigenfunction. The usual perturbation expansion for the m th exact eigenstate of H is (for $\lambda = 1$)

$$\begin{aligned}\Psi^m &= \Phi_0^m + X_1^m + \dots, \\ E^m &= E_0^m + E_1^m + E_2^m + E_3^m + \dots.\end{aligned}\quad (1)$$

The first-order wave function, X_1^m , satisfies the non-homogeneous equation

$$(H_0 - E_0)X_1 = (E_1 - H_1)\Phi_0, \quad (2)$$

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 nondegenerate or else it must be chosen such that the above orthogonalization condition is satisfied (removal of degeneracy in first order). Equation (2) determines X_1 to within an arbitrary multiple of Φ_0 . If this multiple is fixed so that $\langle\Phi_0, X_1\rangle = 0$, E_2 and E_3 will be given by

$$E_2 = \langle\Phi_0, H_1 X_1\rangle, \quad (3)$$

$$E_3 = \langle X_1, (H_1 - E_1)X_1\rangle. \quad (4)$$

X_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, X_1^m , of Eq. (2) for the m th state of H , makes the expression $\tilde{E}_2^m[\bar{X}_1^m] = \{2\langle\Phi_0^m, (H_1 - E_1^m)\bar{X}_1^m\rangle + \langle\bar{X}_1^m, (H_0 - E_0^m)\bar{X}_1^m\rangle\}$ sta-

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¹ See the footnote 6 of O. Sinanoğlu, Phys. Rev. **122**, 493 (1961).

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

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

tionary,³ i.e.,

$$\delta \bar{E}_2^m[\bar{X}_1^m] = \delta \{ 2 \langle \Phi_0^m, (H_1 - E_1^m) \bar{X}_1^m \rangle + \langle \bar{X}_1^m, (H_0 - E_0^m) \bar{X}_1^m \rangle \} = 0. \quad (5)$$

This equation provides a convenient means of approximating to X_1^m if the extremum, $E_2^m[X_1^m]$, is also a minimum. Then, \bar{X}_1^m , the trial function, can be varied until the lowest $\bar{E}_2[\bar{X}_1]$ is attained.

$E_2^m[X_1^m]$ will be a minimum^{3,4} if Φ_0^m corresponds to the ground state, Φ_0^0 . To see this, we write $\bar{X}_1^m = X_1^m + \delta X_1^m$ in $\bar{E}_2^m[\bar{X}_1^m]$ [see Eq. (5)] and, using Eq. (2), obtain

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

Thus, for $\langle \Phi_0, (H_1 - E_1) \delta X_1^m \rangle$ real, the first-order variation of E_2^m vanishes corresponding to Eq. (5) and the error in E_2^m is of the second order in δX_1^m . Expanding $(H_0 - E_0) \delta X_1^m$ in the eigenfunctions of H_0 , we have

$$\bar{E}_2^m[\delta X_1^m] = E_2^m + \sum_{n=0}^{\infty} (E_0^n - E_0^m) \langle \Phi_0^n, \delta X_1^m \rangle^2. \quad (7)$$

For the ground state $E_0^n > E_0^0$, so that the last term is positive definite and therefore

$$\bar{E}_2^0[\delta X_1] \geq E_2^0. \quad (8)$$

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. Then, 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 Eq. (7) and we still have $\bar{E}_2^m(\delta X_1^m) \geq E_2^m$. Thus $(1s\ 2s)^3S$, 1P , etc., states of He can be treated just like its ground state³ by minimizing \bar{E}_2^m with suitable trial functions, \bar{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 Eq. (6) positive definite. Hence in Eq. (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, \bar{X}_1^m , with respect to the exact solution X_1^m of Eq. (2); so the condition, Eq. (9) becomes

$$\langle \Phi_0^k, \bar{X}_1^m \rangle = \langle \Phi_0^k, X_1^m \rangle, \quad [k = 0, 1, 2, \dots, (m-1)]. \quad (10)$$

The particular solution of Eq. (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 $(H_0 - E_0^m)^{-1}$ is the Green's function operator,⁵ $E_1^m = \langle \Phi_0^m, H_1 \Phi_0^m \rangle$, and $\langle X_1^m, \Phi_0^m \rangle = 0$. Substituting Eq. (11) in Eq. (10), and noting that $(H_0 - E_0^m)^{-1}$ is self-adjoint since H_0 is, we get

$$\begin{aligned} \langle \Phi_0^k, X_1^m \rangle &= \left\langle \frac{1}{H_0 - E_0^m} \Phi_0^k, (E_1^m - H_1) \Phi_0^m \right\rangle \\ &= \frac{1}{E_0^m - E_0^k} \langle \Phi_0^k, H_1 \Phi_0^m \rangle. \end{aligned} \quad (12)$$

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, \bar{X}_1^m , subject to the restriction Eq. (10) or (9), possible. Equations (10) and (12) show that \bar{X}_1^m must be of the form

$$\bar{X}_1^m = \bar{X}_1^m + \sum_{k=0}^{m-1} \frac{\Phi_0^k \langle \Phi_0^k, H_1 \Phi_0^m \rangle}{E_0^m - E_0^k}, \quad (13a)$$

and the arbitrary part, \bar{X}_1^m , of the trial function, \bar{X}_1^m , must be kept orthogonal to the Φ_0^k for 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 Eq. (4)] of any excited state, m . The expression,

$$\begin{aligned} \bar{E}_2^m[\bar{X}_1^m] &= \{ 2 \langle \Phi_0^m, (H_1 - E_1^m) \bar{X}_1^m \rangle \\ &\quad + \langle \bar{X}_1^m, (H_0 - E_0^m) \bar{X}_1^m \rangle \} \geq E_2^m, \end{aligned} \quad (14)$$

is to be minimized subject to Eqs. (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 Eqs. (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 as done for the $(1s^2)^1S$ states^{3,4} and also to the similar excited electron pairs that arise in the theory of a many-electron atom or molecule.^{1,6}

⁵ If $(H_0 - E_0^m)^{-1}$ is written in the spectral representation of H_0 , the usual formula,

$$X_1^m = \sum_{n \neq m} \frac{\Phi_0^n \langle \Phi_0^n, H_1 \Phi_0^m \rangle}{E_0^n - E_0^m},$$

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

⁶ Oktay Sinanoğlu, Proc. Roy. Soc. (London) (to be published).

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