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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, $\tilde{\mathrm{X}}_1$, 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 $\mathrm{X}_1{}^m$, the expression

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

is to be minimized with $\tilde{\mathrm{X}}_1{}^m$ in the form

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

with $\bar{\mathrm{X}}_1{}^m$ 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 limit[1] 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 part[2] 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. Hylleraas[3] 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, $\tilde{\mathrm{X}}_1$, 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 $\Phi_0{}^k$ is the kth unperturbed eigenfunction. The usual perturbation expansion for the mth exact eigenstate of H is (for $\lambda=1$)

$$\begin{aligned}\Psi^m&=\Phi_0{}^m+\mathrm{X}_1{}^m+\cdots,\\ E^m&=E_0{}^m+E_1{}^m+E_2{}^m+E_3{}^m+\cdots.\end{aligned}\tag{1}$$

The first-order wave function, $\mathrm{X}_1{}^m$, satisfies the nonhomogeneous equation

$$(H_0-E_0)\mathrm{X}_1=(E_1-H_1)\Phi_0,\tag{2}$$

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 $\langle\Phi_0,\mathrm{X}_1\rangle=0$, E_2 and E_3 will be given by

$$E_2=\langle\Phi_0,H_1\mathrm{X}_1\rangle,\tag{3}$$

$$E_3=\langle\mathrm{X}_1,\ (H_1-E_1)\mathrm{X}_1\rangle.\tag{4}$$

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, $\mathrm{X}_1{}^m$, of Eq. (2) for the mth state of H, makes the expression $\tilde{E}_2{}^m[\tilde{\mathrm{X}}_1{}^m]\equiv\{2\langle\Phi_0{}^m,\ (H_1-E_1{}^m)\tilde{\mathrm{X}}_1{}^m\rangle+\langle\tilde{\mathrm{X}}_1{}^m,\ (H_0-E_0{}^m)\tilde{\mathrm{X}}_1{}^m\rangle\}$ 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.,

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

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

$E_2{}^m[\mathrm{X}_1{}^m]$ will be a minimum[3,4] if $\Phi_0{}^m$ corresponds to the ground state, $\Phi_0{}^0$. To see this, we write $\tilde{\mathrm{X}}_1{}^m=\mathrm{X}_1{}^m+\delta\mathrm{X}_1{}^m$ in $\tilde{E}_2{}^m[\tilde{\mathrm{X}}_1{}^m]$ [see Eq. (5)] and, using Eq. (2), obtain

$$\tilde{E}_2{}^m[\delta\mathrm{X}_1{}^m]=E_2{}^m+\langle\delta\mathrm{X}_1{}^m,\ (H_0-E_0{}^m)\delta\mathrm{X}_1{}^m\rangle. \quad (6)$$

Thus, for $\langle\Phi_0,\ (H_1-E_1)\delta\mathrm{X}_1{}^m\rangle$ 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 $\delta\mathrm{X}_1{}^m$. Expanding $(H_0-E_0)\delta\mathrm{X}_1{}^m$ in the eigenfunctions of H_0, we have

$$\tilde{E}_2{}^m[\delta\mathrm{X}_1{}^m]=E_2{}^m+\sum_{n=0}^{\infty}\ (E_0{}^n-E_0{}^m)\langle\Phi_0{}^n,\delta\mathrm{X}_1{}^m\rangle^2. \quad (7)$$

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

$$\tilde{E}_2{}^0[\delta\mathrm{X}_1]\geqslant E_2{}^0. \quad (8)$$

The same minimum principle applies also to any other $\mathrm{X}_1{}^m$ if it corresponds to the lowest state of a given type of symmetry. Then, since $\Phi_0{}^m$, $\mathrm{X}_1{}^m$ and $\delta\mathrm{X}_1{}^m$ belong to the same irreducible representation of the group of H, just by symmetry $\delta\mathrm{X}_1{}^m$ will be orthogonal to all the states $\Phi_0{}^k$ below $\Phi_0{}^m$. Then the negative terms, $(E_0{}^k-E_0{}^m)$, do not contribute to Eq. (7) and we still have $\tilde{E}_2{}^m(\delta\mathrm{X}_1{}^m)\geqslant E_2{}^m$. Thus $(1s\ 2s)\ {}^3S$, ${}^1P$, etc., states of He can be treated just like its ground state[3] by minimizing $\tilde{E}_2{}^m$ with suitable trial functions, $\tilde{\mathrm{X}}_1{}^m$.

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 $\mathrm{X}_1{}^m$ of such a state, m, the variation $\delta\mathrm{X}_1{}^m$ must be restricted so as to make the error in Eq. (6) positive definite. Hence in Eq. (7) we must have

$$\langle\Phi_0{}^k,\delta\mathrm{X}_1{}^m\rangle=0, \quad (k<m;\ E_0{}^k-E_0{}^m<0) \quad (9)$$

to remove the negative contribution of all the $\Phi_0{}^k$ of states lower than m. The $\delta\mathrm{X}_1{}^m$ above was defined as the error of the trial function, $\tilde{\mathrm{X}}_1{}^m$, with respect to the exact solution $\mathrm{X}_1{}^m$ of Eq. (2); so the condition, Eq. (9) becomes

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

The particular solution of Eq. (2) is formally given[1] by

$$\mathrm{X}_1{}^m=\frac{1}{H_0-E_0{}^m}[E_1{}^m-H_1]\Phi_0{}^m, \quad (11)$$

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 $\langle\mathrm{X}_1{}^m,\Phi_0{}^m\rangle=0$. Substituting Eq. (11) in Eq. (10), and noting that $(H_0-E_0{}^m)^{-1}$ is self-adjoint since H_0 is, we get

$$\langle\Phi_0{}^k,\mathrm{X}_1{}^m\rangle=\left\langle\frac{1}{H_0-E_0{}^m}\Phi_0{}^k,\ (E_1{}^m-H_1)\Phi_0{}^m\right\rangle$$

$$=\frac{1}{E_0{}^m-E_0{}^k}\langle\Phi_0{}^k,H_1\Phi_0{}^m\rangle. \quad (12)$$

Thus, even though we do not have $\mathrm{X}_1{}^m$ in closed form, we do know $\langle\Phi_0{}^k,\mathrm{X}_1{}^m\rangle$. This makes the choice of the trial functions, $\tilde{\mathrm{X}}_1{}^m$, subject to the restriction Eq. (10) or (9), possible. Equations (10) and (12) show that $\tilde{\mathrm{X}}_1{}^m$ must be of the form

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

and the arbitrary part, $\bar{\mathrm{X}}_1{}^m$, of the trial function, $\tilde{\mathrm{X}}_1{}^m$, must be kept orthogonal to the $\Phi_0{}^k$ fo all the states lower than m, i.e.,

$$\langle\bar{\mathrm{X}}_1{}^m,\Phi_0{}^k\rangle=0, \quad [k=0,1,2,\cdots(m-1)]. \quad (13b)$$

This gives the method for obtaining approximations to the $\mathrm{X}_1{}^m$, $E_2{}^m$ and $E_3{}^m$ [see Eq. (4)] of any excited state, m. The expression,

$$\tilde{E}_2{}^m[\bar{\mathrm{X}}_1{}^m]=\{2\langle\Phi_0{}^m,\ (H_1-E_1{}^m)\tilde{\mathrm{X}}_1{}^m\rangle +\langle\tilde{\mathrm{X}}_1{}^m,\ (H_0-E_0{}^m)\tilde{\mathrm{X}}_1{}^m\rangle\}\geqslant E_2{}^m, \quad (14)$$

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, $\Phi_0{}^k$, 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]

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

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

$$\mathrm{X}_1{}^m\rangle=\sum_{n\neq m}^{\infty}\frac{\Phi_0{}^n\rangle\langle\Phi_0{}^n,H_1\Phi_0{}^m\rangle}{E_0{}^n-E_0{}^m},$$

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

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