UCRL -9316

UNIVERSITY OF CALIFORNIA

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

For Publication in Physical Review

UCRL-9316

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

VARIATION-PERTURBATION METHOD FOR EXCITED STATES

Oktay Sinanoglu

July 1960

9316

Variation-Perturbation Method for Excited States*

By Oktay Sinanoğlu†

Department of Chemistry and Lawrence Radiation Laboratory

University of California, Berkeley 4, California

July 1960

---

*Work performed under the auspices of the U. S. Atomic Energy Commission

†Present address: Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

---

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

$$\tilde{E}_2^m = \left\{ 2 \ \langle \Phi_o^m, (H_1 - E_1^m) \ \tilde{X}_1^m \rangle + \langle \tilde{X}_1^m, (H_o - E_o^m) \ \tilde{X}_1^m \rangle \right\} \geqslant E_2^m$$

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

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, 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

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

gives X_1, E_2, etc. in terms of the spectral representation of unperturbed Hamiltonian, H_o. 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

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

of H_o. 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

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

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, $\tilde{\chi}_1$, 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 <u>exact</u> 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_o, and a perturbation λH_1 with $H = H_o + \lambda H_1$, $H\Psi = E\Psi$ and $H_o\Phi_o^k = E_o^k\Phi_o^k$ where Φ_o^k is the <u>kth</u> unperturbed eigenfunction. The usual perturbation expansion for the <u>mth</u> exact eigenstate of H is (for $\lambda = 1$)

$$\begin{aligned} \Psi^m &= \Phi_o^m + \chi_1^m + \cdots \\ E^m &= E_o^m + E_1^m + E_2^m + E_3^m + \cdots \end{aligned} \tag{1}$$

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

$$(H_o - E_o)\chi_1 = (E_1 - H_1)\Phi_o \tag{2}$$

where $E_1 = \langle\Phi_o, H_1\Phi_o\rangle$. This equation will have a solution only if $(E_1 - H_1)\Phi_o$ is orthogonal to the solutions of the homogeneous equation, $(H_o - E_o)\Phi = 0$. Thus, either Φ_o 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 X_1 to within an arbitrary multiple of Φ_o. If this multiple is fixed so that $\langle\Phi_o, X_1\rangle = 0$, E_2 and E_3 will be given by

$$E_2 = \langle\Phi_o, H_1 X_1\rangle \tag{3}$$

$$E_3 = \langle X_1, (H_1 - E_1) X_1\rangle \tag{4}$$

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, X_1^m, of equation (2) for the mth state of H, makes the expression $\tilde{E}_2^m[\tilde{X}_1^m] \equiv \left\{2\langle\Phi_o^m, (H_1 - E_1^m)\tilde{X}_1^m\rangle + \langle\tilde{X}_1^m, (H_o - E_o^m)\tilde{X}_1^m\rangle\right\}$ stationary[3], i.e.

$$\delta\,\tilde{E}_2^m[\tilde{X}_1^m] = \delta\left\{2\langle\Phi_o^m, (H_1 - E_1^m)\tilde{X}_1^m\rangle + \langle\tilde{X}_1^m, (H_o - E_o^m)\tilde{X}_1^m\rangle\right\} = 0 \tag{5}$$

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, $\tilde{X}_1^m$, the trial function, can be varied until the lowest $\tilde{E}_2[\tilde{X}_1]$ is attained.

$E_2^m\,[X_1^m]$ will be a minimum[3,4] if Φ_o^m corresponds to the

---

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

---

ground state, Φ_o^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

$$\tilde{E}_2^{\,m}\,[\delta X_1^m] = E_2^m + \langle\, \delta X_1^m,\ (H_o - E_o^m)\,\delta X_1^m \,\rangle \tag{6}$$

Thus, for $\langle\, \Phi_o,\ (H_1 - E_1)\,\delta X_1^m \,\rangle$ 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 $(H_o - E_o)\,\delta X_1^m$ in the eigenfunctions of H_o we have

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

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

$$\tilde{E}_2^{\,o}\,[\delta X_1] \geqslant E_2^o \tag{8}$$

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_o^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_o^k below Φ_o^m. Then the negative terms, $(E_o^k - E_o^m)$, do not contribute to equation (7) and we still have $\tilde{E}_2^m(\delta X_1^m) \geqslant E_2^m$. 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, $\tilde{X}_1^m$.

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

$$< \Phi_o^k, \delta X_1^m > = 0 \qquad (k < m;\ E_o^k - E_o^m < 0) \tag{9}$$

to remove the negative contribution of all the Φ_o^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

$$< \Phi_o^k, \tilde{X}_1^m > = < \Phi_o^k, X_1^m > \qquad [k = 0, 1, 2, \cdots (m-1)] \tag{10}$$

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

$$X_1^m = \frac{1}{H_o - E_o^m} [E_1^m - H_1]\ \Phi_o^m \tag{11}$$

where $(H_o - E_o)^{-1}$ is the Green's function operator,[†] $E_1^m = \langle \Phi_o^m, H_1 \Phi_o^m \rangle$ and $\langle X_1^m, \Phi_o^m \rangle = 0$. Substituting equation (11) in equation (10), and noting that $(H_o - E_o)^{-1}$ is self-adjoint since H_o is, we get

$$\langle \Phi_o^k, X_1^m \rangle = \langle \frac{1}{H_o - E_o^m} \Phi_o^k, (E_1^m - H_1) \Phi_o^m \rangle$$

$$= \frac{1}{E_o^m - E_o^k} \langle \Phi_o^k, H_1 \Phi_o^m \rangle \qquad (12)$$

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

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

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

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

$$\tilde{X}_1^m > = \bar{X}_1^m) + \sum_{k=0}^{m-1} \frac{\Phi_o^k > < \Phi_o^k, H_1 \Phi_o^m >}{E_o^m - E_o^k} \tag{13a}$$

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

$$< \bar{X}_1^m, \Phi_o^k > = 0, \qquad [k = 0, 1, 2, \cdots (m-1)] \tag{13b}$$

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

$$\tilde{E}_2^m [\bar{X}_1^m] = \Big\{ 2 < \Phi_o^m, (H_1 - E_1^m) \tilde{X}_1^m > + < \tilde{X}_1^m, (H_o - E_o^m) \tilde{X}_1^m > \Big\} \geqslant E_2^m \tag{14}$$

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 <u>exact</u> 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 <u>unperturbed</u> functions, Φ_o^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]

---

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