

## Saddle-point technique for inner-shell-vacancy problems in quantum mechanics

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(Received 27 February 1979)

In this paper a theorem is proved which shows that a physical system with an inner-shell vacancy corresponds to the saddle-point energy solution in the Rayleigh-Ritz variation method if the vacancy is built explicitly into the wave function. This enables us to calculate the inner-shell-vacancy states of a many-body system from first principles. This method is very easy to use and should be applicable to many areas of physics.

### I. INTRODUCTION

The energy states of a complex system are usually calculated with the Rayleigh-Ritz variation method.<sup>1</sup> In some cases a secular equation is constructed and solved.<sup>2</sup> In others, mathematical equations are generated through the variation process, e.g., the Hartree-Fock equations.<sup>3</sup> This method is suitable for studying the ground-state energy as well as singly excited states in general. The fact that each of the eigenvalues of the secular equation is an upper bound and approaches the corresponding true eigenvalue monotonically as the number of parameters in the trial function increases makes the method particularly effective and convenient.<sup>4</sup> Its application has yielded highly accurate theoretical results for atomic systems in the past.<sup>5</sup> However, for inner-shell-vacancy problems in many-electron systems the energy level usually lies in the continuum with infinite numbers of lower states present. Therefore identification of the roots of the secular equation to a particular vacancy state becomes very difficult.

Ideally, if one can construct a wave function which is orthogonal to the lower continuum and the lower bound states, the vacancy state will appear and the problem is solved. This is the basic ideal behind the Feshbach projection operator,<sup>6</sup> which has been very successful in studying a two-electron system.<sup>7</sup> However, for systems with three or more electrons the method becomes impractical and encounters fundamental difficulties. Attempts have been made to circumvent this problem and a quasiprojection operator technique has been developed and applied to a three-electron system.<sup>8</sup> However, this method is difficult to apply in multiply excited energy regions where there are an infinite number of open channels, i.e., a system that can autoionize with the emission of two or more electrons.

Recently, a technique has been developed from a more physical point of view.<sup>9</sup> Instead of making the trial function orthogonal to the open channels,

a vacancy is built directly into it. Therefore, by assuming a one-particle orbital wave function  $\phi_0$ ,

$$\Psi' = A[1 - P_0(\vec{r}_j)]\Psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_M), \quad (1)$$

where

$$P_0(\vec{r}) = |\phi_0(\vec{r})\langle\phi_0(\vec{r})| \quad (1a)$$

will be a trial function with the  $\phi_0$  vacancy.  $A$  is the antisymmetrization operator. We also assume that electron  $j$  has the same symmetry as that of  $\phi_0$ ; hence  $\vec{r}_j$  is where the vacancy occurs and it is the only particle that may fill the vacancy. For this trial function the Rayleigh-Ritz variation method takes the form

$$\delta E = \delta \frac{\langle\Psi'|H|\Psi'\rangle}{\langle\Psi'|\Psi'\rangle} = 0. \quad (2)$$

If  $\psi$  is constructed with linear parameters  $C$  and nonlinear parameters  $\alpha$ , and  $\phi_0$  is constructed with parameters  $q$ , the variation of  $E$  with respect to  $C$  will lead to a secular equation whose eigenvalue is a function of  $\alpha$  and  $q$ . Reference 9 presents a theorem which shows that the true energy of the vacancy state appears as a saddle point with respect to the variation of  $\alpha$  and  $q$ . Examples with realistic systems have been carried out and highly accurate results were obtained.

In this work a detailed proof of this theorem is given. In Sec. II the theorem is restated and proven for a one-particle Hamiltonian. A useful corollary that further extends the theorem is given in Sec. III. Generalization from a one-particle to an  $M$ -particle Hamiltonian is given in Sec. IV. In Sec. V the problem with more than one vacancy is discussed. Section VI is a discussion of the connection of the present theorem with the variation principle and justifies the saddle-point technique from a more fundamental point of view.

### II. THEOREM

Since the exact orbital wave function representing the vacancy is unknown, any choice of  $\phi_0$  must

be approximate. In this case let us first establish the following theorem for a one-particle system.

*Theorem:* Let  $H(\vec{r})$  be a Hermitian operator with normalized eigenfunctions  $\psi_0(\vec{r}), \psi_1(\vec{r}), \dots, \psi_i(\vec{r})$  and corresponding nondegenerate eigenvalues  $E_0, E_1, \dots, E_i$ . Define a normalized function

$$\phi_0(\vec{r}) = \sum_{j=0}^N t_j \psi_j(\vec{r}) \tag{3}$$

for any  $N \geq 1$ . Let the eigenvalues of the secular equation of  $H$  in the subspace orthogonal to  $\phi_0$  be  $\lambda_1, \lambda_2, \dots, \lambda_i$ .

Consider  $\lambda_i$  as a function of the  $\{t_j\}$ ; then  $\lambda_i$  is an extremum and  $\lambda_i = E_i$  when  $t_i = 0$ .

*Proof:* For simplicity, let us assume the eigenfunctions and  $\{t_j\}$  are all real. To solve for the eigenvalues  $\lambda$ , we first construct the trial function

$$\psi(\vec{r}) = C_0 \phi_0(\vec{r}) + \sum_{i=1}^M C_i \psi_i(\vec{r}), \quad M \geq N, \tag{4}$$

where the  $C$ 's are the linear parameters to be optimized. In the subspace of interest we have

$$\begin{aligned} \psi'(\vec{r}) &= (1 - |\phi_0\rangle\langle\phi_0|)\psi(\vec{r}) \\ &= \sum_{i=1}^N C_i [\psi_i(\vec{r}) - t_i \phi_0(\vec{r})] + \sum_{i=N+1}^M C_i \psi_i(\vec{r}). \end{aligned} \tag{5}$$

We now proceed to construct the secular equation for  $H$ . Since the second term on the right-hand side of Eq. (5) is eigenfunctions of  $H$  and orthogonal to the first term, we may omit this part without affecting the solutions of  $\lambda_i$  for  $i = 1$  to  $N$ . The matrix element of the secular equation takes the form

$$\begin{aligned} \langle (\psi_i - t_i \phi_0) | H - \lambda | (\psi_j - t_j \phi_0) \rangle \\ = (E_i - \lambda) \delta_{ij} - t_i t_j (E_i + E_j - \lambda - \langle H \rangle), \end{aligned} \tag{6}$$

where

$$\langle H \rangle = \langle \phi_0 | H | \phi_0 \rangle = \sum_{i=0}^N t_i^2 E_i \tag{6a}$$

and

$$t_0^2 = 1 - \sum_{i=1}^N t_i^2. \tag{6b}$$

Thus the secular equation is given by

$$\begin{vmatrix} (E_1 - \lambda) - t_1^2(2E_1 - \lambda - \langle H \rangle) & \cdots & -t_1 t_j (E_1 + E_j - \lambda - \langle H \rangle) & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ -t_1 t_i (E_1 + E_i - \lambda - \langle H \rangle) & \cdots & (E_i - \lambda) \delta_{ij} - t_i t_j (E_i + E_j - \lambda - \langle H \rangle) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0. \tag{7}$$

This equation is a function of  $t^2$  only. This can be seen by dividing the  $i$ th row by  $t_i$  and the  $j$ th column by  $t_j$ , and obtaining

$$\begin{vmatrix} \frac{E_1 - \lambda}{t_1^2} - (2E_1 - \lambda - \langle H \rangle) & \cdots & -(E_1 + E_j - \lambda - \langle H \rangle) & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ -(E_1 + E_i - \lambda - \langle H \rangle) & \cdots & \frac{E_i - \lambda}{t_i t_j} \delta_{ij} - (E_i + E_j - \lambda - \langle H \rangle) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0. \tag{8}$$

Hence if Eq. (7) is expanded explicitly as a function of  $\lambda$  and  $\{t_j\}$ , it can be written in the form

$$\sum_{n=0}^N \lambda^n f_n(t_1^2, t_2^2, \dots, t_N^2) = 0. \tag{9}$$

Differentiating this equation with respect to  $t_i$ , we get

$$\begin{aligned} \frac{\partial \lambda}{\partial t_i} \sum_{n=1}^N n \lambda^{n-1} f_n(t_1^2, t_2^2, \dots, t_N^2) \\ + \sum_{n=0}^N \lambda^n f'_n(t_1^2, t_2^2, \dots, t_N^2) 2t_i = 0, \end{aligned} \tag{10}$$

where  $f'_n$  is the derivative of  $f_n$  with respect to the argument  $t_i^2$ . Equation (10) is valid for any  $\{t_j\}$ ; hence at  $t_i = 0$  either  $\lambda = 0$  or  $\partial \lambda / \partial t_i = 0$ . To determine which of these two conditions is true we set  $t_i = 0$  in Eq. (7).

$$\begin{vmatrix} (E_1 - \lambda) - t_1^2(2E_1 - \lambda - \langle H \rangle) & \cdots & 0 & \cdots \\ \cdots & \cdots & 0 & \cdots \\ \cdots & \cdots & 0 & \cdots \\ 0 & \cdots & E_i - \lambda & 0 \\ \cdots & \cdots & 0 & \cdots \\ \cdots & \cdots & 0 & \cdots \end{vmatrix} = 0. \tag{11}$$

That is, at least one of the solutions of  $\lambda$  will not be zero. If we call this  $\lambda, \lambda_i$ , then Eq. (11) implies

$$\lambda_i(t_1, \dots, t_{i-1}, 0, t_{i+1}, \dots, t_N) = E_i. \quad (12)$$

For this  $\lambda_i$  at  $t_i = 0$ , we have

$$\frac{\partial \lambda_i}{\partial t_i} = 0. \quad (13)$$

Therefore,  $\lambda_i$  will be an extremum with value  $E_i$ . In order to analyze and to identify the result of a calculation it is important to know the nature of this extremum. To see this we need the corollary in the next section.

### III. COROLLARY

*Corollary:* The eigenvalue  $\lambda_i$  of Eq. (7) for  $i = 1, \dots, N$  is given by

$$\lambda_i = E_i + t_i^2(E_0 - E_i) + \sum_{k=1}^N \frac{(E_0 - E_k)^2}{E_i - E_k} t_i^2 t_k^2 + O(t^6), \quad (14)$$

where  $\sum'$  implies  $k = i$  is excluded in the summation.

*Proof:* If  $\lambda_i$  is expanded in a Taylor series of  $t_i$  about  $t_i = 0$ , we have from Eqs. (12) and (13):

$$\lambda_i = E_i + \frac{1}{2} \frac{\partial^2 \lambda_i'}{\partial t_i^2} t_i^2 + \frac{1}{6} \frac{\partial^3 \lambda_i'}{\partial t_i^3} t_i^3 + \frac{1}{24} \frac{\partial^4 \lambda_i'}{\partial t_i^4} t_i^4 + \dots, \quad (15)$$

where  $\lambda_i'$  implies that the argument is evaluated at

$(t_1, \dots, t_{i-1}, 0, t_{i+1}, \dots, t_N)$  after the differentiation is taken. Now if  $t_k$  is set to be zero in Eq. (7) for all  $k \neq i$ , the secular equation becomes diagonal with the  $i$ th diagonal element given by

$$(E_i - \lambda_i) - t_i^2(2E_i - \lambda_i - \langle H \rangle) = 0; \quad (16)$$

in this case, from Eqs. (6a) and (6b),

$$\langle H \rangle = (1 - t_i^2)E_0 + t_i^2 E_i. \quad (17)$$

Equation (16) gives

$$\lambda_i = E_i + t_i^2(E_0 - E_i). \quad (18)$$

This is valid for any  $t_i$ ; compare Eqs. (18) and (15). We must have

$$\frac{\partial^n \lambda_i'(0)}{\partial t_i^n} = 0 \quad \text{for } n \geq 3 \quad (19)$$

and

$$\frac{\partial^2 \lambda_i'(0)}{\partial t_i^2} = 2(E_0 - E_i), \quad (20)$$

where  $\lambda_i'(0)$  implies that the argument of  $\lambda_i'$  is evaluated at  $t_k = 0$  for all  $k$ . Furthermore, we can expand the higher derivatives of  $\lambda_i'$  in terms of  $\{t_k\}$  about  $t_k = 0$  as

$$\frac{1}{2} \frac{\partial^2 \lambda_i'}{\partial t_i^2} = (E_0 - E_i) + \sum_k' g_{i,k}^{(2)} t_k + \sum_{j,h} g_{i,jh}^{(2)} t_j t_h + \dots, \quad (21)$$

where the superscript gives the order of derivative of  $\lambda_i'$  with respect to  $t_i$ . Equation (15) becomes

$$\lambda_i = E_i + (E_0 - E_i)t_i^2 + t_i^2 \left( \sum_k' g_{i,k}^{(2)} t_k + \sum_{j,h} g_{i,jh}^{(2)} t_j t_h + \dots \right) + t_i^3 \left( \sum_k' g_{i,k}^{(3)} t_k + \sum_{j,h} g_{i,jh}^{(3)} t_j t_h + \dots \right) + t_i^4 \left( \sum_k' g_{i,k}^{(4)} t_k \right) + O(t^6). \quad (22)$$

On the other hand, Eq. (9) can be written in the form

$$\sum_{n=0}^N \lambda^n f_n(t_1^2, t_2^2, \dots, t_N^2) \equiv \sum_{i=1}^N (\lambda_i - \lambda). \quad (23)$$

If we set  $t_m = 0$  for all  $k \neq m, i$ , we obtain

$$\sum_{n=0}^N \lambda^n f_n(0, \dots, t_m^2, \dots, 0, \dots, t_i^2, \dots, 0) \equiv c(\lambda)(\lambda_m - \lambda)(\lambda_i - \lambda), \quad (24)$$

where  $c(\lambda)$  is independent of  $t_i$  and  $t_m$ .

From Eq. (22), the third-order term on the right-hand side of Eq. (24) is

$$c(\lambda)[g_{i,m}^{(2)} t_m^2 t_i^2 (E_m - \lambda) + g_{m,i}^{(2)} t_m^2 t_i^2 (E_i - \lambda)]. \quad (25)$$

Compare this with the left-hand side of Eq. (24) and note that it is valid for all  $\lambda$ ; we now have

$$g_{i,m}^{(2)} = g_{m,i}^{(2)} = 0. \quad (26)$$

Repeat the same procedure successively, and we get

$$g_{i,k}^{(3)} = 0, \quad (27a)$$

$$g_{i,k}^{(4)} = 0, \quad (27b)$$

$$g_{i,jh}^{(2)} = 0, \quad \text{for } j \neq k, \quad (27c)$$

$$g_{i,jhl}^{(2)} = 0. \quad (27d)$$

Hence the only term to survive in the fourth order is  $g_{i, hh}^{(2)}$ . Using a similar algebraic technique, it can be shown that

$$g_{i, hh}^{(2)} = (E_i - E_0)^2 / (E_i - E_h). \quad (28)$$

Substituting Eqs. (26)–(28) into Eq. (22), Eq. (14) follows.

The nature of the extremum is clearly seen. Since it is usually the lower states that we wish to project out,  $E_0 < E_i$ ,  $\lambda_i$  will reach a maximum at  $t_i = 0$ .

In actual calculation the expansion in Eq. (3) can never be made explicitly. Instead, a functional form of  $\phi_0$  is assumed together with one or more parameters  $q$ . By varying  $q$  to a certain value,  $\lambda_i$  will reach a maximum; this is where  $t_i = 0$ .

It would be of interest to ask if it is possible to have  $t_i \neq 0$  but  $\partial t_i / \partial q = 0$ , in which case one would reach a false maximum. Although, theoretically speaking, it is not impossible, in reality it is highly unlikely unless  $t_i$  is small. In this case one can also check the solution obtained by calculating the orthogonal property against the unprojected lower states. On the other hand, this does seem to suggest that one should make a good choice of  $\phi_0$  so that the expansion in Eq. (3) may exist and that  $t_i$  is allowed to become zero when the parameter varies.

#### IV. EXTENSION TO A MANY-PARTICLE SYSTEM

Since Eq. (14) is derived for a single-particle Hamiltonian, it would be of interest to see how the theorem can be generalized to a many-body system. Let the Hamiltonian of a  $M$ -particle system be  $H(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_M)$  and let

$$\Psi_n = A\psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_M) \quad (29)$$

be an eigenfunction of  $H$  with a certain symmetry of interest. If  $\vec{r}_j$  is where the vacancy  $\phi_0$  may occur, Eq. (29) can be rewritten as

$$\Psi_n = A\psi^{(n)}(\vec{r}_1, \dots, \vec{r}_{j-1}, \vec{r}_{j+1}, \dots, \vec{r}_M)\xi_n(\vec{r}_j). \quad (30)$$

This expression need not be an approximation. To preserve the full angular correlation and to ensure that  $\Psi_n$  be the exact eigenfunction of  $H$ , one can represent  $\xi_n(\vec{r}_j)$  in the form of a column matrix and  $\psi^{(n)}$  in the form of a row matrix so that no approximation is made. In this case the projection operator will also be in matrix form.

Next we freeze the configuration  $\psi^{(n)}$  and let  $\xi_{n,k}$  span the spectrum of excited energy states for all possible  $k$ .  $\xi_{n,k}$  can be generated by solving the following one-electron eigenvalue problem:

$$\int \psi^{(n)*}(\vec{r}_1, \dots, \vec{r}_{j-1}, \vec{r}_{j+1}, \dots, \vec{r}_M) \times (H - E)\Psi_n d\vec{r}_1 \cdots d\vec{r}_{j-1} d\vec{r}_{j+1} \cdots d\vec{r}_M = 0. \quad (31)$$

Therefore, the solution to Eq. (31) should be a good approximation to the Schrödinger equation

$$H\Psi_{n,k} = E_{n,k}\Psi_{n,k}, \quad (32)$$

where

$$\Psi_{n,k} = A\psi^{(n)}(\vec{r}_1, \dots, \vec{r}_{j-1}, \vec{r}_{j+1}, \dots, \vec{r}_M)\xi_{n,k}(\vec{r}_j). \quad (32a)$$

For a fixed  $n$ , the problem reduces essentially to a one-particle problem. The theorem in Secs. II and III is valid with no modification needed.

Now we let  $n$  take all possible configurations as long as  $\Psi_{m,k}$  has the proper symmetry. Note that  $\xi_{m,j}$  and  $\xi_{n,j}$  need not be identical; rather Eq. (32) should be accurate for any  $n$  and  $k$ . Because of this difference we may have a different expansion of  $\phi_0$  for each  $n$ ; hence

$$\phi_0(\vec{r}) = \sum_{k=0}^{N_n} t_{n,k} \xi_{n,k}(\vec{r}). \quad (33)$$

To construct the secular equation, a set of basis functions is chosen. Since the eigenvalue of an operator is independent of the basis set, for any suitable trial function we can make the following expansion:

$$\Psi = \sum_n \left( \sum_{k=1}^{N_n} C_{n,k} \Psi_{n,k} + C_{n,0} A\psi^{(n)}\phi_0 \right), \quad (34)$$

where  $A$  is the antisymmetrization operator and the coordinates are suppressed. The projected trial function with the vacancy  $\phi_0$  becomes

$$\Psi' = \sum_n \sum_{k=1}^{N_n} C_{n,k} A\psi^{(n)}(1 - P_0)\xi_{n,k}, \quad (35)$$

where  $P_0$  is given by Eq. (1a). Since

$$\begin{aligned} & H[A\psi^{(n)}(1 - P_0)\xi_{n,k}] \\ &= H \left( \Psi_{n,k} - \sum_{i=1}^{N_n} t_{n,i} t_{n,k} \Psi_{n,i} \right) \\ &= E_{n,k} \Psi_{n,k} - \sum_{i=1}^{N_n} t_{n,i} t_{n,k} E_{n,i} \Psi_{n,i}, \end{aligned} \quad (36)$$

if there is no degeneracy, the right-hand side is orthogonal to any  $\Psi_{m,i}$  for  $m \neq n$ . Hence the matrix element

$$\begin{aligned} & \langle A\psi^{(n)}(1 - P_0)\xi_{n,k} | H - \lambda | A\psi^{(m)}(1 - P_0)\xi_{m,i} \rangle \\ &= 0, \text{ for } m \neq n. \end{aligned} \quad (37)$$

Thus, if a secular equation is constructed for  $\Psi'$ , it will be diagonal with respect to  $m$  and  $n$ . That is, the secular equation will be a product of determinants of the form

$$\begin{vmatrix} (E_{n,1} - \lambda) - t_{n,1}^2(2E_{n,1} - \lambda - \langle H \rangle_n) & \cdots & -t_{n,1}t_{n,j}(E_{n,1} + E_{n,j} - \lambda - \langle H \rangle_n) & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ -t_{n,1}t_{n,i}(E_{n,1} + E_{n,i} - \lambda - \langle H \rangle_n) & \cdots & (E_{n,i} - \lambda)\delta_{ij} - t_{n,i}t_{n,j}(E_{n,i} + E_{n,j} - \lambda - \langle H \rangle_n) & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}, \quad (38)$$

where

$$\langle H \rangle_n = \sum_{i=0}^{N_n} t_{n,i}^2 E_{n,i}. \quad (38a)$$

The solution to the secular equation now becomes

$$\begin{aligned} \lambda_{n,i} &= E_{n,i} + t_{n,i}^2(E_{n,0} - E_{n,i}) \\ &+ \sum_{k=1}^{N_n} \frac{(E_{n,0} - E_{n,i})^2}{E_{n,i} - E_{n,k}} t_{n,i}^2 t_{n,k}^2 + O(t^6) \text{ for all } n, i. \end{aligned} \quad (39)$$

Here  $E_{n,0}$  is the energy for the  $n$ th state of the  $M-1$  particle with the  $M$ th particle at the lowest configuration. Equation (39) suggests that each of the  $\lambda_{n,i}$  should appear independently as a maximum in the variation of  $q$ , with the maximum value being the eigenvalue of the Schrödinger equation.

Situations may arise where there is only one vacancy in the system but more than one particle may fill it. For example, if in Eq. (29)  $\tilde{r}_j$  and  $\tilde{r}_{j+1}$  have the same symmetry, then in order to ensure that the vacancy  $\phi_0$  be present, the trial function should take the form

$$\begin{aligned} \Psi' &= A[1 - P_0(\tilde{r}_j)][1 - P_0(\tilde{r}_{j+1})] \\ &\times \psi(\tilde{r}_1, \dots, \tilde{r}_j, \tilde{r}_{j+1}, \dots, \tilde{r}_M), \end{aligned} \quad (40)$$

with  $P_0$  defined by Eq. (1a). An example in an atomic system is the  $\text{Li}(1s2s2s)^2S$  in the multi-configuration calculation within the  $LS$ -coupling scheme.<sup>10</sup> In this case the configuration of both  $2s$  electrons should be projected to avoid having any one fill the  $1s$  vacancy.

## V. MULTIVACANCY PROBLEMS

Although Eq. (39) gives the solution for any  $n$ th state of the  $(M-1)$ -particle system and the  $i$ th state of the  $M$ th particle, in practice it is only useful for those  $(M-1)$ -particle excited states which involve single excitations; i.e., the excited state must lie below the ionization threshold of the  $(M-1)$ -electron system. For excited states with another inner shell vacancy in the  $M-1$  system, the problem can be solved as follows.

Let the second vacancy orbital be  $\phi_1$  with the same symmetry as that of particle  $k$ . The trial

function with two vacancies will be given by

$$\begin{aligned} \Psi &= A[1 - P_1(\tilde{r}_k)][1 - P_0(\tilde{r}_j)] \\ &\times \psi(\tilde{r}_1, \dots, \tilde{r}_k, \dots, \tilde{r}_j, \dots, \tilde{r}_M), \end{aligned} \quad (41a)$$

where

$$P_1(\tilde{r}) = |\phi_1(\tilde{r})\rangle\langle\phi_1(\tilde{r})|. \quad (41b)$$

Now if an expansion of Eq. (33) type is made and the expansion coefficient is expressed in terms of  $\{s_{n,i}\}$ , we may consider the  $E_{n,i}$  and  $E_{n,0}$  in Eq. (39) to be the solution of the secular equation with the vacancy  $\phi_1$  already present, i.e., with  $P_1$  projected. Define  $\epsilon_{0,0}$  as the true ground state of the system, and let  $\epsilon_{n,0}$  and  $\epsilon_{0,i}$  be the true eigenvalues of  $H$  with one inner shell vacancy, with  $\epsilon_{n,i}$  as the true energy of interest. Then

$$E_{n,0} = \epsilon_{n,0} + (\epsilon_{0,0} - \epsilon_{n,0})s_{n,0}^2 + O(s^4), \quad (42a)$$

$$E_{n,i} = \epsilon_{n,i} + (\epsilon_{0,i} - \epsilon_{n,i})s_{n,i}^2 + O(s^4). \quad (42b)$$

Substituting Eq. (42) into (39), it becomes

$$\begin{aligned} \lambda_{n,i} &= \epsilon_{n,i} + (\epsilon_{0,i} - \epsilon_{n,i})s_{n,i}^2 \\ &+ (\epsilon_{n,0} - \epsilon_{n,i})t_{n,i}^2 + O(s^2t^2), \end{aligned} \quad (43)$$

which shows again that  $\lambda_{n,i}$  is a maximum and equal to  $\epsilon_{n,i}$  at  $s_{n,i} = 0$  and  $t_{n,i} = 0$ .

In some cases a system may have two vacancies of the same symmetry, for example, the calculation of  $\text{Li}(2s2s2p)^2P$  state in  $LS$ -coupling scheme. In this case the physics of the problem requires that  $P_1$  and  $P_0$  be of the same functional form with the same parameters.

## VI. DISCUSSION

The variation principle can be considered as one of the most important foundations of quantum mechanics. This is because the eigenvalue equation and the variation principle of expectation value are basically equivalent. The MacDonald theorem also suggests that the calculation of excited states should be equally convenient as that of the ground state. To search for a stationary energy level by the Rayleigh-Ritz variation method is equivalent to solving the time-independent Schrödinger equation. That is,

$$\delta E = \delta \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \delta \Psi | H - E | \Psi \rangle + \langle \Psi | H - E | \delta \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (44)$$

with the trial function  $\Psi$  covering the proper Hilbert space. To require  $\delta E = 0$  to be true for arbitrary variation of any and all possible parameters in  $\Psi$ , the parameters must be at a value where

$$(H - E)\Psi = 0. \quad (45)$$

This idea is the foundation of the single-particle projection-operator technique developed in Ref. 9 and here. The physics of the problem suggests that vacancies exist in the system: hence one builds in these vacancies accordingly. The mathematics of the problem suggests that the stationary value solution corresponds to the solution to Eq. (45). Hence, within the inner-vacancy-state picture,<sup>11</sup> the method in this paper is to find the best approximate  $\Psi$  to the Schrödinger equation. It is a method of general nature and there should be no restriction on the number of particles nor the number of vacancies. For autoionization states, this solution does not represent an exact solution to the Schrödinger equation due to the absence of the continuum part in the wave function. The inclusion of this continuum may result in a slight shift of the energy position. Nevertheless, this shift must be small if the inner-shell-vacancy picture is a good description of physical reality and if the resonance state can be considered as essentially a quasibound state. In carrying out the variation calculation one assumes a trial function with a basis set and a linear parameter  $C$ . To speed convergence, a nonlinear parameter  $\alpha$  is assumed. The projection operator is constructed with a nonlinear parameter  $q$ . The usual

variation theorem requires that the energy is at a minimum with respect to the variation of  $C$  and  $\alpha$ . The theorem in Secs. II and III suggests that the true energy for inner-shell-vacancy states is at a maximum with respect to the variation of  $q$ . Combining the two theorems together, the true energy appears as a saddle point with respect to the variation of  $\alpha$  and  $q$ . The energy will be lowered monotonically<sup>4</sup> as the number of linear parameters  $C$  increases provided that the saddle-point value of  $q$  remain stable.

The saddle-point energy obtained here is somewhat different from the eigenvalue of  $QHQ$  in the Feshbach formalism. This is because the  $Q$  operator is fixed and not allowed to vary, whereas the saddle-point technique involves finding the best square-integrable wave-function approximation to the Schrödinger equation. This inner-shell-vacancy state may be degenerate with one or more continua of the same symmetry. Through the interaction of this discrete state with the degenerate continuum, a band of stationary states with a resonance profile is formed.<sup>12</sup> Hence once the inner-shell-vacancy state is formed it will autoionize with a lifetime in accordance with the half-width of the resonance profile.

One advantageous feature of the single-particle projection-operator technique is that it is very easy to carry out. Usually, it does not have more integrals to be performed other than that needed to calculate the ground state. It will, however, consume more computer time as compared with the ground-state calculation.

Inner-shell-vacancy states arise in many areas of physics and until now the theoretical methods of study have been somewhat intuitive or phenomenological. It is the hope of this author that this saddle-point technique may contribute a more satisfactory answer.

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<sup>11</sup>The author is grateful to Dr. A. Temkin and Dr. B. R. Junker for bringing this point to his attention.

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