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Interference effects in sequential decay

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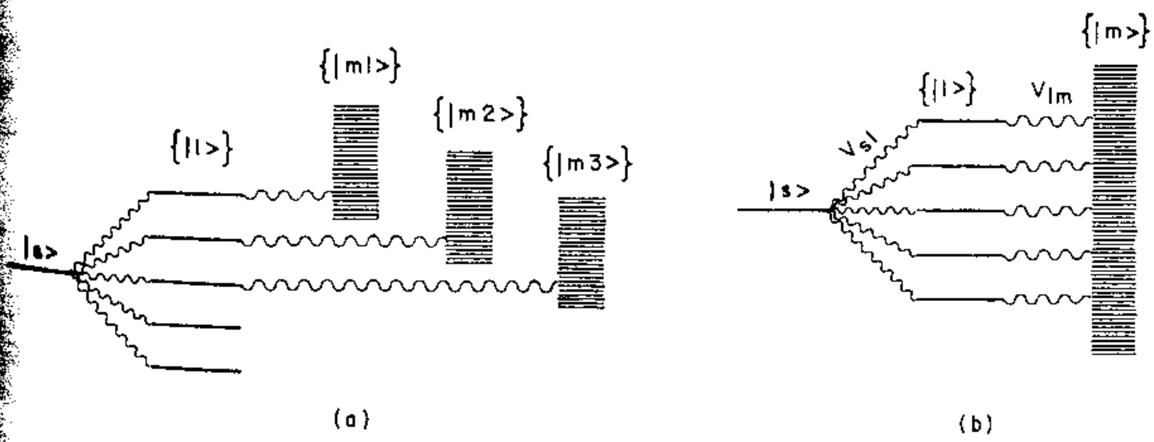
In this paper we utilize the Green's function method to study sequential decay processes which involve interference effects. The model system involves a zero-order discrete state coupled to a set of continua, which are themselves coupled together, while the coupling matrix elements are energy independent. Interference effects in parallel and consecutive decay involving two continua result in the retardation of the decay rate of the initial state and in the reversal of the branching ratio for the population of the two continua. Finally, a general solution was provided for the problem of sequential decay involving multiple continua.

1. INTRODUCTION

In this note we consider some features of the decay of excited molecular tes. Most previous theoretical work in this field focused attention on the ay features of a single molecular resonance [1]. It is often found that astable states decay by a sequential decay process. A sequential decay cess is one in which initially excited zero-order state, which carries all the llator strength from the ground state, is coupled to either one intermediate e or to a sparse or dense manifold of intermediate states which, in turn, are pled to a final dissipative (radiative or non-radiative) continuum. Two eme physical situations can be now considered : (*a*) each of the intermediate



ure 1. Coupling schemes for sequential decay. (*a*) No interference. (*b*) Interference.

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states are coupled to a different final continuum [2–5]; (*b*) all the intermediate states are coupled to the same continuum [6, 7]. These two types of sequential decay processes are portrayed in figure 1.

Sequential decay processes of type (*a*) do not exhibit interference effects, whereas those of type (*b*) do exhibit interference. Typical examples of these different decay schemes have been treated in the literature. Type (*a*) processes have a long history. Familiar examples involve sequential radioactive decay of nuclei and the decay of elementary particles. Recent treatments of internal conversion in molecules and non-radiative decay of a small molecule in a medium [3] was described in terms of type (*a*) processes. A complete treatment was provided by both the Green's functions method [5] and the Wigner–Weisskopf scheme [4]. The importance of interference effects in type (*b*) processes was elucidated by Mies and Krauss [6] in their formulation of unimolecular reactions. More recently Rice *et al.* [7] have proposed that certain photochemical dissociation reactions [8] are type (*b*) processes. Rice *et al.* [7 a] did not solve the complex equations for interfering sequential decay, and this was only very recently accomplished [7 b, 9].

Lefebvre and Beswick [9] have treated a specific example of a type (*b*) process by the method of Fano and Pratts [10], which was developed primarily to treat physical problems involving true continua. Fano and Pratts' formalism [10] is rather complicated when extended beyond the treatment of a single resonance. It would not be easy to apply that formalism to problems involving more than one discrete state and two continua.

It is our purpose in this note to present a treatment of type (*b*) sequential decay processes by the Green's function method. In our opinion this method is easier and more transparent than the method used in previous work [9–11]. The present technique can easily be extended to handle more complicated problems involving interference effects in sequential decay via several continua. Our results should be applicable to optically induced fragmentation processes in large molecules.

2. Interference effects in parallel and sequential decay involving two continua

Consider the simplest case of parallel and sequential consecutive decay displayed in figure 2 (*a*), where the initial zero order state $|s\rangle$ is coupled to two zero order continua $\{|l\rangle\}$ and $\{|m\rangle\}$, which are themselves coupled together.

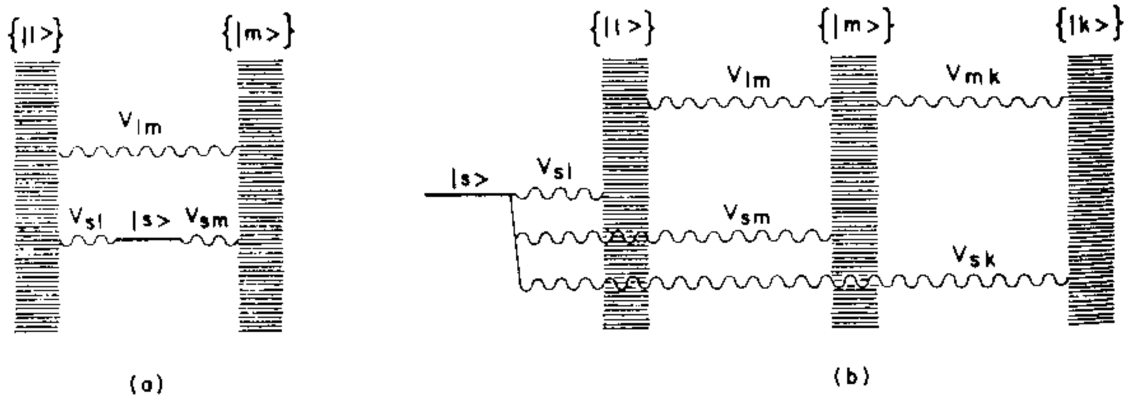

Figure 2. Models for sequential decay with interference. (*a*) Parallel and consecutive decay involving two continua. (*b*) Sequential decay involving multiple continua.

The total hamiltonian of the system is $H=H_0+V$, where $|s\rangle$, $\{|l\rangle\}$ and $\{|m\rangle\}$ are eigenfunctions of H_0 while V induces the coupling between the zero-order states. The Green's operator is

$$G(E)=\frac{1}{E-H+i\eta}=\frac{1}{E-H_0-V+i\eta}; \quad \eta\to 0^+ \tag{1}$$

and its pertinent matrix elements are

$$G_{ij}(E)=\langle i|G(E)|j\rangle; \quad i, j\equiv|s\rangle; \quad \{|l\rangle\}; \quad \{|m\rangle\}. \tag{2}$$

The time evolution of the system can be represented as a superposition

$$\Psi(t)=C_s(t)|s\rangle+\sum_{\{|l\rangle\}} C_l(t)|l\rangle+\sum_{\{|m\rangle\}} C_m(t)|m\rangle. \tag{3}$$

where the sums over the continuum states [3] should be replaced by the integrations over the densities of states ρ_l and ρ_m in the two continua, i.e.

$$\sum_{\{|l\rangle\}} \to \int dE_l\rho_l; \quad \sum_{\{|m\rangle\}} \to \int dE_m\rho_m. \tag{4}$$

Following the general techniques of Goldberger and Watson [5], the amplitudes $C_i(t)$ in equation (3) are given in terms of the Fourier transforms of the matrix elements of the Green's function (equation (2)), as follows :

$$\left.\begin{aligned} C_s(t)&=\frac{1}{2\pi i}\int_{\mathscr{C}} dE\exp(-iEt)G_{ss}(E),\\ C_j(t)&=\frac{1}{2\pi i}\int_{\mathscr{C}} dE\exp(-iEt)G_{js}(E); \quad j\equiv l, m,\end{aligned}\right\} \tag{5}$$

where the contour $\mathscr{C}$ goes from infinity to minus infinity above the real axis. The probability of finding the system in the initial state $|s\rangle$ at time t is

$$P_s(t)=|C_s(t)|^2 \tag{6}$$

while the probabilities $P_l(t)$ and $P_m(t)$ to find the system in the continuum $\{|l\rangle\}$ and in the continuum $\{|m\rangle\}$, respectively, are given by

$$P_l(t)=\sum_l |C_l(t)|^2, \tag{7}$$

$$P_m(t)=\sum_m |C_m(t)|^2. \tag{8}$$

Thus the problem reduces to the evaluation of the matrix elements of the Green's function. This is most easily done by using the Dyson equation

$$G=G_0+G_0VG, \tag{9}$$

where $G_0=(E-H_0+i\eta)^{-1}$. Up to this point our treatment is completely general. In order to obtain manageable results we invoke a basic approximation, that the coupling matrix elements $V_{sl}=\langle s|V|l\rangle$, $V_{lm}=\langle l|V|m\rangle$ are energy independent.

An identical simplifying assumption was used by Lefebvre and Beswick [9]. This approximation defines an idealized model for sequential decay. In matrix form the Dyson equation becomes

$$G_{ss}=\frac{1}{E-E_s+i\eta}+\frac{V_{sl}}{E-E_s+i\eta}\sum_l G_{ls}+\frac{V_{sm}}{E-E_s+i\eta}\sum_m G_{ms}, \tag{10}$$

$$G_{ls}=\frac{V_{ls}}{E-E_l+i\eta}\,G_{ss}+\frac{V_{lm}}{E-E_l+i\eta}\sum_m G_{ms}, \tag{11}$$

$$G_{ms}=\frac{V_{ms}}{E-E_m+i\eta}\,G_{ss}+\frac{V_{ml}}{E-E_m+i\eta}\sum_l G_{ls}. \tag{12}$$

In view of the simplifying assumption concerning the energy independence of the coupling matrix elements, equations (10)–(12) can be readily solved. Summation of equations (11) and (12) over the $\{|l\rangle\}$ and $\{|m\rangle\}$ states, respectively, yields

$$\sum_l G_{ls}=V_{ls}(R_l-i\pi\rho_l)G_{ss}+V_{lm}(R_l-i\pi\rho_l)\sum_m G_{ms}, \tag{13 a}$$

$$\sum_m G_{ms}=V_{ms}(R_m-i\pi\rho_m)G_{ss}+V_{ml}(R_m-i\pi\rho_m)\sum_l G_{ls}, \tag{13 b}$$

where R_l and R_m represent the Cauchy principal part (PP) of the sums

$$R_l=PP\sum_l\frac{1}{E-E_l}=PP\int dE_l\rho_l\,\frac{1}{E-E_l}, \tag{14 a}$$

$$R_m=PP\sum_m\frac{1}{E-E_m}=PP\int dE_m\rho_m\,\frac{1}{E-E_m} \tag{14 b}$$

It should be noted that for a constant density of states $R_l=R_m=0$. For the sake of simplicity we shall neglect those terms, although they can be easily incorporated in the following treatment. Equations (13) can now be solved for the sums of the diagonal matrix elements

$$\sum_l G_{ls}=-\frac{\pi^2V_{lm}V_{ms}\rho_l\rho_m+i\pi V_{ls}\rho_l}{1+\pi^2V_{lm}{}^2\rho_l\rho_m}\,G_{ss}, \tag{15}$$

$$\sum_m G_{ms}=-\frac{\pi^2V_{ml}V_{ls}\rho_m\rho_l+i\pi V_{ms}\rho_m}{1+\pi^2V_{lm}{}^2\rho_l\rho_m}\,G_{ss}. \tag{16}$$

From equations (11), (12), (15) and (16) we get

$$G_{ms}=\left(\frac{G_{ss}}{E-E_m+i\eta}\right)\left(\frac{V_{ms}-i\pi V_{ml}V_{ls}\rho_l}{1+\pi^2V_{lm}{}^2\rho_l\rho_m}\right), \tag{17}$$

$$G_{ls}=\left(\frac{G_{ss}}{E-E_l+i\eta}\right)\left(\frac{V_{ls}-i\pi V_{lm}V_{ms}\rho_m}{1+\pi^2V_{lm}{}^2\rho_l\rho_m}\right). \tag{18}$$

It will be convenient at this stage to define several auxiliary functions characterizing the decay features of the system. Let Γ_{sl} and Γ_{sm} represent the apparent zero order widths (which have no physical significance) of a state $|s\rangle$ due to its coupling to the two continua

$$\Gamma_{sl}=2\pi|V_{sl}|^2\rho_l, \tag{19}$$

$$\Gamma_{sm}=2\pi|V_{sm}|^2\rho_m. \tag{20}$$

The effective number of states in the zero order continuum $\{|m\rangle\}$ spanned by the apparent width $|V_{ml}|^2\rho_l$ will be defined by

$$N=\pi^2|V_{ml}|^2\rho_l\rho_m. \tag{21}$$

Finally we shall define two physically meaningful quantities. The width of the resonance which will determine the optical line shape and the decay of the initial state is

$$\Gamma_s=\frac{\Gamma_{sl}+\Gamma_{sm}}{1+N} \tag{22}$$

while the level shift is given by

$$D_s=2\,\frac{\pi^2\rho_l\rho_m V_{lm}V_{ms}V_{sl}}{1+N}. \tag{23}$$

Inserting equations (17) and (18) into equation (10) we obtain the following explicit expressions for the matrix elements of the Green's function :

$$G_{ss}=\frac{1}{E-E_s-D_s+\frac{i}{2}\,\Gamma_s}, \tag{24}$$

$$G_{ls}=\frac{V_{ls}-i\pi V_{lm}V_{ms}\rho_m}{(E-E_l+i\eta)\left(E-E_s-D_s+\frac{i}{2}\;\Gamma_s\right)(1+N)}, \tag{25}$$

$$G_{ms}=\frac{V_{ms}-i\pi V_{ml}V_{ls}\rho_l}{(E-E_m+i\eta)\left(E-E_s-D_s+\frac{i}{2}\,\Gamma_s\right)(1+N)}. \tag{26}$$

The time evolution of the system is now given by equations (5)–(8). It is important to note that in the case of two continua we can safely assume that the functions Γ_s, D_s, ρ_l and ρ_m are slowly varying with the energy and can be taken as constants during the integration in equations (5). The techniques of calculating the transforms of the matrix elements (25) and (26) are given by Goldberger and Watson [5]. Thus we get

$$P_s(t)=\exp\,(-\Gamma_s t), \tag{27}$$

$$P_l(t)=\frac{\Gamma_{sl}+N\Gamma_{sm}}{\Gamma_s(1+N)^2}\,[1-\exp\,(-\Gamma_s t), \tag{28}$$

$$P_m(t)=\frac{\Gamma_{sm}+N\Gamma_{sl}}{\Gamma_s(1+N)^2}[1-\exp(-\Gamma_s t). \tag{29}$$

Thus the Green's function technique provides a simple easy way for the solution of the parallel-sequential decay problem. Equation (27) was previously derived by the Fano method [9–11], while equations (28) and (29) provide an extension of the results obtained by Lefebvre and Beswick [9].

From these results we conclude that the case of parallel and consecutive decay is characterized by the following features :

(*a*) The decay of the initially prepared state is exponential, being characterized by the decay rate Γ_s.

(*b*) The population rate of the two continua exhibits identical time dependence of the form $[1-\exp(-\Gamma_s t)]$. The same situation prevails for parallel decay into two continua in the absence of interference.

(*c*) The branching ratio, r, for the population of the $\{|l\rangle\}$ and $\{|m\rangle\}$ continua is

$$r=\frac{P_l(t)}{P_m(t)}=\frac{\Gamma_{sl}+N\Gamma_{sm}}{\Gamma_{sm}+N\Gamma_{sl}}. \tag{30}$$

This branching ratio is time independent. The same situation prevails for parallel decay into two uncoupled continua.

(*d*) Interference effects are negligible provided that $N \ll 1$. This condition (see equation (20)) implies that

$$\pi^2|V_{ml}|^2\rho_m \ll \rho_l^{-1}, \tag{31}$$

so that interference effects can be disregarded when the coupling $|V_{ml}|$ is sufficiently weak ; whereupon the apparent width of each state in the $\{|l\rangle\}$ manifold due to coupling with the $\{|m\rangle\}$ continuum is negligible compared to the level spacing between adjacent $|l\rangle$ levels. This is, of course, the conventional condition for neglecting interference effects. Under these circumstances we regain the well-known results for parallel decay into two independent channels

$$\Gamma_s=\Gamma_{sl}+\Gamma_{sm}, \tag{32 a}$$

$$r=\Gamma_{sl}/\Gamma_{sm}, \tag{32 b}$$

where the total width is given by the sum of two independent widths while the branching ratio is the ratio of these widths.

(*e*) Interference effects in the present decay scheme set in for $N\sim 1$. The extreme limit of strong interference is of interest. This situation will be realized when $N \gg 1$ or $\pi^2|V_{ml}|^2\rho_m \gg \rho_l^{-1}$, whereupon the apparent widths of the $\{|l\rangle\}$ states due to coupling with the $\{|m\rangle\}$ continuum considerably exceed their spacing. In this event

$$\Gamma_s=\frac{\Gamma_{sl}+\Gamma_{sm}}{N} \tag{34}$$

while in terms of the coupling matrix elements and the densities of states we have

$$\Gamma_s = \frac{2}{\pi |V_{ml}|^2} \left(\frac{|V_{sl}|^2}{\rho_m} + \frac{|V_{sm}|^2}{\rho_l} \right). \tag{34 a}$$

Equation (34) demonstrates a unique feature of interference effects for parallel consecutive decay. The decay rate of the initial state is retarded, being decreased by the ' dilution ' factor N^{-1} due to interference between the continua.

The population of the two continua in the limit of strong interference is given by

$$P_l(t) = \frac{\Gamma_{sm}}{\Gamma_{sl} + \Gamma_{sm}} [1 - \exp(-\Gamma_s t)], \tag{35}$$

$$P_m(t) = \frac{\Gamma_{sl}}{\Gamma_{sl} + \Gamma_{sm}} [1 - \exp(-\Gamma_s t)].$$

Thus the population rate of the $\{|l\rangle\}$ and the $\{|m\rangle\}$ continua is governed by Γ_{sm} and by Γ_{sl} respectively. The branching ratio in this limit is given from equation (30) in the form

$$r = \Gamma_{sm}/\Gamma_{sl}. \tag{36}$$

Thus interference effects result in the reversal of the conventional branching ratio (33) obtained for simple parallel decay.

3. Sequential decay involving two continua

The problem of sequential decay involving interference between two continua (figure 1 *b*) can now be handled as a special case of the parallel-consecutive decay problem. The time evolution in the case of sequential decay will be obtained by utilizing the results of § 2 setting $V_{sm} = 0$ and consequently $\Gamma_{sm} = 0$. The resonance width (equation (22)) for this case is

$$\Gamma_s = \frac{\Gamma_{sl}}{1 + N}. \tag{37}$$

The level shift (equation (23)) in this case vanishes ($D_s = 0$) as we have neglected the R_l and R_m terms (equation (14)). If these latter are thus retained, a finite level shift would result.

The probabilities of finding the system in the initially excited state $|s\rangle$ in the continuum $\{|l\rangle\}$ and in the second continuum $\{|m\rangle\}$ are now obtained from equations (27)–(29) in the form

$$P_s(t) = \exp(-\Gamma_s t), \tag{38}$$

$$P_l(t) = \frac{1}{1 + N} [1 - \exp(-\Gamma_s t)], \tag{39}$$

$$P_m(t) = \frac{N}{1 + N} [1 - \exp(-\Gamma_s t)]. \tag{40}$$

Equations (37)–(40) are identical with those previously derived by Lefebvre and Beswick [9], who have pointed out the basic difference between these results and the sequential decay scheme which does not involve interference effects [4].

The strength of interference effects for this sequential decay scheme is exhibited by the magnitude of the parameter N (equation (20)) relative to unity. When we would like to eliminate interference effects we have to set $N\to 0$ (or reduce the magnitude of the coupling term V_{ml}). Under these circumstances the two $\{|l\rangle\}$ and $\{|m\rangle\}$ continua tend to become decoupled and the problem reduces to that of the decay of a zero-order state into a single continuum. The case of sequential decay with interference is characterized by the following features: (*a*) The decay mode of the initially excited $|s\rangle$ state is exponential as is the case for (*a* 1) the decay into a single continuum, and (*a* 2) for sequential decay in the absence of interference. (*b*) In the absence of interference effects, i.e. $N\ll 1$, $\Gamma_s=\Gamma_{sl}$ as for cases (*a* 1) and (*a* 2). (*c*) When interference effects are prominent, i.e. $N\gg 1$, the decay rate of the initial decay rate is $\Gamma_s=\Gamma_{sl}/N$, exhibiting a retardation effect due to interference in the intermediate continuum. This retardation effect is similar to the situation encountered for the decay to an initial level via a single intermediate level to a continuum [2]. When the width of the intermediate level increases, the decay rate of the initial state is retarded. (*d*) The populations of the two continua exhibit identical time dependence. This situation drastically differs from the case of sequential decay (case (*a* 2)) in the absence of interference. (*e*) The branching ratio, r, for the population of the $\{|l\rangle\}$ and the $\{|m\rangle\}$ continua is

$$r=1/N. \tag{41}$$

When interference effects are important, i.e. $N\gg 1$ then $r\ll 1$, and the final $\{|m\rangle\}$ continuum is preferably populated. On the other hand, when $N\ll 1$ we have $r\gg 1$ and the population of the intermediate $\{|l\rangle\}$ continuum predominates. Under these circumstances the two continua become decoupled. Thus when interference effects are switched off the present sequential decay scheme does not reduce to the conventional case of consecutive decay in the absence of interference (case (*a* 2)) but rather to the simple problem of a decay into a single continuum (case (*a* 1)).

4. Interference effects in sequential decay involving multiple continua

The application of the Green's function method for the study of consecutive decay problems, which involve interference effects, can be easily extended to handle more complicated situations. The only simplifications required are (*a*) the coupling matrix elements are energy independent, (*b*) the integrals of the form R_l, R_m (equation (14)) are neglected as a matter of convenience.

To demonstrate the applicability of these techniques we consider the sequential and parallel decay problem involving two continua (figure 2 *b*). Making use of the Dyson equation (9) the matrix form of the Green's function is

$$G_{ss}=\frac{1}{E-E_s+i\eta}+\frac{V_{sl}}{E-E_s+i\eta}\sum_l G_{ls}+\frac{V_{sm}}{E-E_s+i\eta}\sum_m G_{ms}+\frac{V_{sk}}{E-E_s+i\eta}\sum_k G_{ks}, \tag{42}$$

$$G_{ls}=\frac{V_{ls}}{E-E_l+i\eta}G_{ss}+\frac{V_{lm}}{E-E_l+i\eta}\sum_m G_{ms}+\frac{V_{lk}}{E-E_l+i\eta}\sum_k G_{ks}, \tag{43}$$

$$G_{ms}=\frac{V_{ms}}{E-E_m+i\eta}G_{ss}+\frac{V_{ml}}{E-E_m+i\eta}\sum_l G_{ls}+\frac{V_{mk}}{E-E_m+i\eta}\sum_k G_{ks}, \tag{44}$$

$$G_{ks}=\frac{V_{ks}}{E-E_k+i\eta}G_{ss}+\frac{V_{kl}}{E-E_k+i\eta}\sum_l G_{ls}+\frac{V_{km}}{E-E_k+i\eta}\sum_m G_{ms}. \tag{45}$$

Taking the sums over $\{|l\rangle\}$, $\{|m\rangle\}$ and $\{|k\rangle\}$ in equations (43)–(45) we get

$$\begin{pmatrix}\sum_l G_{ls}\\ \sum_m G_{ms}\\ \sum_k G_{ks}\end{pmatrix}=-i\pi\mathbf{A}^{-1}\begin{pmatrix}\rho_l V_{ls}\\ \rho_m V_{ms}\\ \rho_k V_{ks}\end{pmatrix} \tag{46}$$

where the matrix

$$\mathbf{A}=\begin{pmatrix}1 & i\pi\rho_l V_{lm} & i\pi\rho_l V_{lk}\\ i\pi\rho_m V_{ml} & 1 & i\pi\rho_m V_{mk}\\ i\pi\rho_k V_{kl} & i\pi\rho_k V_{km} & 1\end{pmatrix} \tag{47}$$

is antihermitian. The solutions of equation (46) can be subsequently inserted in equation (42) to obtain the explicit form for the Green's function.

The problem of parallel and consecutive decay involving n continuous channels is easily reduced, along the same lines, to the mathematical problem of inversion of antihermitian matrix of the nth order. The results are

$$P_s(t)=\exp(-\Gamma_s t), \tag{48}$$

$$P_i(t)=\frac{2\pi}{\Gamma_s}\rho_i|a_i|^2[1-\exp(-\Gamma_s t)], \tag{49}$$

$$a_i=\left[V_{is}-i\pi\sum_{jk}V_{sj}(\mathbf{I}-\mathbf{T})_{jk}{}^{-1}\rho_k V_{ks}\right] \tag{50}$$

where the width Γ_s and shift D_s are

$$\Gamma_s=2\pi\ \mathrm{Re}\sum_{ij}V_{si}(\mathbf{I}-\mathbf{T})_{ij}{}^{-1}\rho_j V_{js}, \tag{51}$$

$$D_s=\pi\ \mathrm{Im}\sum_{ij}V_{si}(\mathbf{I}-\mathbf{T})_{ij}{}^{-1}\rho_j V_{js}. \tag{52}$$

In these equations the indices i indicates the ith continuum, ρ_i is the density of states in the ith continuum, V_{is} is the coupling between the discrete states s and the ith continuum, and V_{ij} is the coupling between the ith and jth continua. The matrix $\mathbf{I}$ is the unit matrix and the matrix $\mathbf{T}$ has elements

$$T_{ij}=-i\pi\rho_i V_{ij}. \tag{53}$$

It is a simple matter to apply these formulae to numerical problems.

5. Discussion

We have demonstrated the wide applicability of the Green's function methods for the study of sequential decay problems involving interference between continua. The most interesting physical results emerging from the present treatment involve the retardation of the decay of the initially optically excited state due to interference effects and the effects of interference on the population of the dissipative coupled continua.

From the physical point of view these theoretical models may be of interest for the elucidation of the features of multistage photo-fragmentation processes. In this case an initially optically excited state of a large molecule decays into an intramolecular dense quasi-continuum of highly excited bound vibronic levels of a lower electronic configuration. These highly excited vibronic levels (corresponding to a low electronically excited state) may then subsequently decay into a dissociative continuum by predissociation. Under these conditions the role of interference effects may be crucial in determining the details of the photofragmentation reactions [8].

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