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Electronic Relaxation in Large Molecules

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In this paper we consider the problem of the radiative decay of electronically excited states of a large molecule. We have considered both intramolecular vibronic coupling and the interaction with the radiation field. Compound states for a system of decaying indistinguishable levels are constructed using the Fano method. General expressions for the radiative decay rate are derived and applied for the statistical limit of intramolecular vibronic coupling. On a time scale shorter than a typical intramolecular recurrence time the radiative decay is exponential, and the reciprocal lifetime consists of independent contributions of radiative and nonradiative components. The experimental implications of these results for large and medium-size molecules are discussed.

I. INTRODUCTORY REMARKS

A quantum relaxation process in an atom, a molecule, or a solid is conventionally treated by considering the interaction between two (zero-order) parts of the physical system: a dynamic part which consists of a manifold of discrete energy levels, and a dissipative part which is characterized by a continuous spectrum. A relaxation process takes place when a compound state of the total system decays into the continuum. Familiar examples are the decay of nuclei, the radiative decay of an atom or a molecule, atomic and molecular autoionization processes, molecular predissociation processes, and unimolecular chemical dissociation reactions. At the risk of triviality, let us point out that the zero-order levels of the dynamic and of the dissipative subsystems cannot be considered as proper eigenstates of the physical system. As the zero-order levels of the two subsystems are degenerate, extensive configuration interaction is induced by the (small) interaction terms which couple the dynamic and the dissipative parts. The zero-order states of the physical system have no real physical significance, and the physical properties of the system such as the absorption coefficient, the linewidth, and the relaxation time have to be derived by a formalism which involves the compound states of the system. These compound states are customarily represented in terms of a superposition of zero-order states. The choice of the basis set is merely a matter of convenience. An important problem in this context is how an atomic or molecular excited state is prepared and under what circumstances it is meaningful to consider the time development of such states. Obviously, all time-dependent transitions between stationary molecular states are radiative in nature; however, provided that the excitation process produces the molecular system in a mixed state consisting of superposition of proper eigenstates of the system, a relaxation process is expected to occur.

The existence of radiationless intramolecular electronic relaxation processes in isolated polyatomic molecules is now well established for large molecules.[1] The nuclear kinetic-energy operator has been shown[2-7] to provide the major interaction term which is responsible for the occurrence of radiationless transitions in large molecules. Naturally, other intramolecular interaction terms may modify the mixing. Thus, for example, spin–orbit interactions have to be included in the case of mixing of quasidegenerate vibronic components which correspond to two electronic states of different multiplicity. In excited electronic states of polyatomic molecules, the Born–Oppenheimer separability conditions for electronic and nuclear motion break down in view of intramolecular (vibronic, spin–orbit, etc.) coupling between any zero-order vibronic level φ_s and a dense manifold of (zero order) vibronic levels $\{\varphi_l\}$ corresponding to a lower electronic state. The breakdown of the Born–Oppenheimer approximation prevails for all excited states of polyatomic molecules. We have recently considered a proper representation of molecular eigenstates $\{\psi_n\}$ in the absence of the radiation field which are displayed as a superposition of Born–Oppenheimer states. In the statistical limit of intramolecular vibronic coupling when the density ρ of vibronic states is sufficiently high to exceed the reciprocal of the vibronic coupling term, v, between the zero-order Born–Oppenheimer states, considerable configuration mixing takes place. In this limit, when[7]

$$v\rho \gg 1 \qquad (1)$$

inhomogenous line broadening is expected. The linewidth is given by[7]

$$\Delta = 2\pi v^2 \rho. \qquad (2)$$

The crucial role of the high density of states in the manifold $\{\varphi_l\}$ was qualitatively discussed by Robinson.[6]

The problem of intramolecular radiationless decay in an isolated molecule was recently treated[7] by considering the time evolution of a coherently excited

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[7] M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).

molecular state, which can be displayed as a time-dependent superposition of the eigenstates of the molecular Hamiltonian, each of which is a time-independent superposition of Born–Oppenheimer states. In that treatment, the radiative decay of the excited state was not taken into account. In the statistical limit the nonradiative decay of the amplitude of the zero-order state is exponential, being characterized by the lifetime

$$\tau=\hbar/2\pi v^2\rho. \tag{3}$$

This situation is encountered provided that the energetic criterion (1) is satisfied, and that the nonradiative decay occurs on a time scale t, so that

$$t\ll\hbar\rho. \tag{4}$$

This relation establishes a recurrence time t_r for the occurrence of the nonradiative intramolecular relaxation process, as for times longer than $\hbar\rho$ the amplitude of φ_s in the time-dependent wavefunction will increase again. This definition of the recurrence time introduces the notion of irreversibility for the intramolecular radiationless process. In the case of large molecules, such as naphthalene and anthracene, both the density of states is sufficiently large and the recurrence time is sufficiently long, so that intramolecular relaxation is expected to take place in the isolated molecule.

This treatment of radiationless transitions which considered a closed channel decaying into a single open channel (of the dense vibronic manifold) is not complete, as the radiative decay process has to be also considered. The radiationless transition is not an isolated decay process but should emerge from a unified description of the radiative decay of the large molecule. The radiative decay of a polyatomic molecule should properly account for the decay of a large number of closely spaced levels.[8] This radiative decay in the statistical limit was recently considered by Jortner and Berry[8] by extending Kelly's[9] treatment to account for interference effects in the radiative decay of a large number of closely spaced coherently excited molecular eigenstates. Some approximations introduced because of mathematical convenience in that treatment such as a step-function approximation for the line shape of the inhomogenously broadened line were later refined by Chock.[10] The crucial assumption introduced in that work is that the decay of the amplitude of each molecular eigenstate, say, ψ_n, can be described by an independent radiative lifetime $\hbar\Gamma_n^{-1}$ [see Eq. (27), Ref. 5]. From studies[11] of interference effects in the decay of coherently excited states, it is apparent that the damping matrix is diagonal only for a system of distinguishable levels (i.e., states characterized by a different symmetry, e.g., Zeeman components), while for the case of indistinguishable levels (i.e., levels characterized by the same symmetry and by the same polarization) the application of a diagonal form for the damping matrix leads to the violation of basic conservation laws, and a more general treatment has to be applied. Obviously, the radiative decay of the molecular eigenstates, all characterized by the same polarization, corresponds to the case of indistinguishable levels. It is not surprising that the previous treatment by Jortner and Berry[8] led to the following difficulties:

(a) The experimental radiative decay time τ_{exptl} determined by photon counting methods was obtained in the form

$$\tau_{\text{exptl}}^{-1}=(\Gamma/\hbar)n^{-1}+\tau^{-1}, \tag{5}$$

where $n=\Delta\rho$ is the number of levels in the half-width of the inhomogenously broadened line and Γ is the radiative width (or reciprocal lifetime) of the zero-order state φ_s which can be determined from the integrated absorption coefficient. The resulting "dilution" of the radiative lifetime $h\Gamma^{-1}$ is inconsistent with the conventional intuitive notion that

$$\tau_{\text{exptl}}^{-1}=(\Gamma/\hbar)+\tau^{-1}. \tag{5'}$$

(b) The quantum yield Y was obtained as the ratio of the radiative and nonradiative widths:

$$Y=(\Gamma/\hbar)\tau=\Gamma/\Delta=\Gamma\rho/n. \tag{6}$$

This result is plausible for the limit $\Delta\gg\Gamma$ (e.g., $Y\ll1$). However, when $\Gamma>\Delta$, which is a plausible case on physical ground, one gets $Y>1$. This difficulty is similar to the violation of conservation laws encountered in our previous work,[11b] when difficulties were encountered in the study of the decay of a set of indistinguishable levels using a diagonal form for the damping matrix.

In the present work, we shall apply the general methods previously obtained by us for the radiative decay of indistinguishable levels.[11b] The Fano method[12] can be applied for the treatment of the radiative decay of a manifold of closely spaced levels.[11b] This radiative decay problem can be handled by constructing compound states of the system which are displayed as a superposition of the zero-order molecular eigenstates $\{\psi_n\}$ and the radiative continuum. It should be pointed out that in the presence of the radiation field the molecular eigenstates $\{\psi_n\}$ are no longer proper eigenstates of the total Hamiltonian of the system, which now includes a radiative interaction term. The time evolution of the nonstationary excited states of the system can be described either in terms of a super-

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[8] J. Jortner and R. S. Berry, J. Chem. Phys. **48**, 2757 (1968).

[9] R. L. Kelly, Phys. Rev. **147**, 376 (1966).

[10] D. Chock, Ph.D. thesis, University of Chicago, 1968.

[11] (a) A solution of the two-level problem encountered in level anticrossing was presented by K. E. Lassila, Phys. Rev. **135**, A1218 (1964). (b) The general form of the damping matrix for a large number of closely spaced decaying levels was given by M. Bixon, Y. Dotham, and J. Jortner, "Interference Effects in the Radiative Decay of Coherently Excited States," Mol. Phys. (to be published).

[12] U. Fano, Phys. Rev. **124**, 1866 (1961).

position of the Born–Oppenheimer states or alternatively by the molecular eigenstates basis. The choice of the basis set is just a matter of convenience. When the Born–Oppenheimer basis is employed, the radiative decay of the polyatomic molecule is represented in terms of a closed channel (the zero-order state φ_s) interacting with the vibronic manifold $\{\varphi_i\}$ and with an open channel which consists of the radiation field continuum. Only in the statistical limit can the manifold $\{\varphi_i\}$ be considered as a second open channel. On the other hand, when the molecular eigenstates basis set is employed interference effects are introduced in the formalism of the radiative decay process. In the present treatment we shall adopt the molecular eigenstates basis. By this choice we are able to derive a general model for the radiative decay of a polyatomic molecule characterized by an arbitrary level density ρ. Our general results are applicable both for the statistical limit and in the case of a sparse distribution of levels as encountered in triatomic molecules.[13,14] Compound states of the system will be constructed, and the relevant decay processes will be considered. The present treatment is based on the implicit assumption that radiative level shifts can be neglected. Within this approximate framework we are able to provide a self-consistent solution to the problem of radiationless transitions in large molecules.

II. THE RADIATIVE DECAY OF ELECTRONIC EXCITED STATES OF POLYATOMIC MOLECULES

In the treatment of the general problem of the radiative decay of an excited molecular level, one has to consider both intramolecular vibronic coupling effects and the interaction with the radiation field. The complete Hamiltonian of the system, H, can be conveniently decomposed into the following contributions:

$$H = H_{\rm el} + H_{\rm rad} + H_{\rm int} \tag{7}$$

and

$$H_{\rm el} = H_{\rm BO} + H_{\rm v}. \tag{8}$$

The molecular Hamiltonian $H_{\rm el}$ consists of the Born–Oppenheimer Hamiltonian $H_{\rm BO}$ and the intramolecular coupling term $H_{\rm v}$ arising from the nuclear kinetic-energy operator, spin–orbit interactions, etc. $H_{\rm rad}$ is the Hamiltonian corresponding to the free radiation field, and $H_{\rm int}$ involves the radiation–matter interaction term.

The zero-order states of the system are taken to correspond to the eigenstates of the Hamiltonian

$$H_0 = H_{\rm BO} + H_{\rm rad}, \tag{9}$$

which correspond to molecular zero-order vibronic states plus photons. Consider first the eigenstates $\{\varphi_l\}$ of $H_{\rm BO}$ derived from conventional calculations carried out in the Born–Oppenheimer approximation. We can consider the set $\{\varphi_l\}$ to include the vibronic state φ_s, the vibronic manifold $\{\varphi_i\}$, and the ground state φ_0. It is assumed that the set of the Born–Oppenheimer sets is complete, so that

$$\sum_{\text{all } l} |\varphi_l\rangle\langle\varphi_l| = 1. \tag{10}$$

Now let E_l be the energy corresponding to the Born–Oppenheimer state φ_l; then we can write

$$H_{\rm BO} = \sum_{\text{all } l} |\varphi_l\rangle E_l \langle\varphi_l|, \tag{11}$$

and

$$H_{\rm v} = H_{\rm el} - H_{\rm BO}. \tag{12}$$

The zero-photon and one-photon eigenstates of $H_{\rm rad}$ will be denoted by $|\,\text{vac}\rangle$ and by $|\,\mathbf{k},\mathbf{e}\rangle$, respectively, which satisfy the eigenvalue equations $H_{\rm rad}\,|\,\text{vac}\rangle = 0$ and $(H_{\rm rad} - \hbar k)\,|\,\mathbf{k},\mathbf{e}\rangle = 0$. $\mathbf{k}$ is the photon wavenumber and $\mathbf{e}$ its polarization vector. The excited zero-order states of the system will correspond to zero-photon states. Without causing too much confusion we can suppress the zero-photon states and write $\varphi_s \equiv |\,\varphi_s;\text{vac}\rangle$ or $\varphi_i \equiv |\,\varphi_i;\text{vac}\rangle$. The electronic ground state of the system corresponds to the one-photon states $|\,\varphi_0;\mathbf{k},\mathbf{e}\rangle$. Provided that all the radiative decay channels are characterized by the same polarization they can be unambiguously specified by their energy $E = \hbar k$, so that the zero-order states $|\,\varphi_0;\mathbf{k},\mathbf{e}\rangle$ can be then denoted by φ_E, where it is understood that these continuum states are normalized per unit energy.

The matrix elements of the Hamiltonian between the zero-order states are taken to be in the form

$$\begin{aligned}
&\langle\varphi_s\,|\,H\,|\,\varphi_i\rangle = v_i, &&\langle\varphi_s\,|\,H\,|\,\varphi_s\rangle = E_s,\\
&\langle\varphi_i\,|\,H\,|\,\varphi_j\rangle = E_i\delta_{ij}, &&\langle\varphi_E\,|\,H\,|\,\varphi_{E'}\rangle = E\delta(E-E'),\\
&\langle\varphi_s\,|\,H\,|\,\varphi_E\rangle = W_E, &&\langle\varphi_i\,|\,H\,|\,\varphi_E\rangle = 0.
\end{aligned} \tag{13}$$

The following simplifying assumptions are introduced at this stage:

(a) Only the zero-order state φ_s carries oscillator strength; furthermore, it is assumed that the coupling φ_s and φ_E is constant per unit energy range of the radiation field continuum, so that $W_E = W$.

(b) The manifold $\{\varphi_i\}$ is characterized by uniformly spaced levels, with the separation $\epsilon = \rho^{-1}$, where ρ is the (constant) density of vibronic states. The zero-order energies are

$$E_i = E_s + \alpha + i\epsilon, \qquad i = 0, \pm 1, \pm 2, \cdots \tag{14}$$

where $\alpha = E_s - E_0$.

(c) The vibronic coupling matrix elements are constant, so that $v_i = v$ for all i.

We shall diagonalize the Hamiltonian in two stages. First, we consider the construction of the proper molecular eigenstates. Following our previous procedure the eigenstates of $H_{\rm el}$ can be displayed as a superposi-

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[13] A. E. Douglas and K. P. Huber, Can. J. Phys. 43, 74 (1965).

[14] A. E. Douglas, J. Chem. Phys. 45, 1007 (1966).

tion of the quasidegenerate Born–Oppenheimer states. Thus the excited molecular states $\{\psi_n\}$ are given in the form

$$\psi_n=\alpha_s^n\varphi_s+\sum_i\beta_i^n\varphi_i, \qquad (15)$$

with energies E_n.

The mixing coefficients are given in the form

$$|\,\alpha_s^n\,|^2=v^2[(E_n-E_s)^2+v^2+(\pi v^2/\epsilon)^2]^{-1}. \qquad (16)$$

The ground state of the molecular Hamiltonian can be adequately represented by the Born–Oppenheimer function φ_0. Hence the two sets of functions $\{\psi_n\}$ and $\{\varphi_E\}$ are eigenfunctions of $H_{\mathrm{el}}+H_{\mathrm{rad}}$. The Hamiltonian matrix elements in the new representation are

$$\langle\psi_n\,|\,H\,|\,\psi_m\rangle=E_n\delta_{nm}, \qquad (17)$$

$$\langle\psi_n\,|\,H\,|\,\varphi_E\rangle=W_n. \qquad (18)$$

The applications of Eqs. (10) and (13) result in

$$W_n=\langle\psi_n\,|\,\varphi_s\rangle\langle\varphi_s\,|\,H\,|\,\varphi_E\rangle=\alpha_s^nW. \qquad (18')$$

The eigenstates of the system can be displayed as a superposition of the first-order states

$$\psi_E=\sum_n a_n(E)\psi_n+\int dE'C_{E'}(E)\varphi_{E'}. \qquad (19)$$

The mixing coefficients are obtained from the set of equations

$$E_na_n(E)+\int dE'W_nC_{E'}(E)=Ea_n(E), \qquad (20)$$

$$\sum_n W_n^*a_n(E)+E'C_{E'}(E)=EC_{E'}(E). \qquad (21)$$

Fano's method[12] is now directly applicable; Eq. (21) is formally solved,

$$C_{E'}(E)=[(E-E')^{-1}+Z(E)\delta(E-E')]\sum_n W_n^*a_n(E). \qquad (22)$$

The function $Z(E)$ will be determined later. The substitution of Eq. (22) into Eq. (20) leads to the result

$$E_na_n(E)+\sum_m F_{nm}a_m(E)+Z(E)W_n\sum_m W_m^*a_m(E)=Ea_n(E), \qquad (23)$$

where

$$F_{nm}=P\int dE'\,\frac{W_nW_m^*}{E-E'}, \qquad (24)$$

which corresponds to the radiative level shift terms. The matrix elements W_n and W_m are assumed to be independent of the energy so that $F_{nm}=0$. Then we get

$$Z(E)W_n\sum_m W_m^*a_m(E)=(E-E_n)a_n(E). \qquad (25)$$

The multiplication of Eq. (25) by $W_n^*/(E-E_n)$ followed by summation over n leads to

$$Z(E)\sum_n[W_n^*W_n/(E-E_n)]\sum_m W_m^*a_m(E)=\sum_n W_n^*a_n(E), \qquad (26)$$

and hence the following expression for $Z(E)$ is obtained:

$$Z(E)=\{\sum_n[\,|\,W_n\,|^2/(E-E_n)]\}^{-1}. \qquad (27)$$

Now, using Eq. (25), we can express $a_n(E)$ with the aid of the sum $\sum_m W_m^*a_m(E)$ so that

$$a_n(E)=Z(E)[W_n/(E-E_n)]\sum_m W_m^*a_m(E). \qquad (28)$$

This sum can be evaluated by applying the orthonormalization conditions for the set $\{\psi_E\}$:

$$\langle\psi_{\bar{E}}\,|\,\psi_E\rangle=\sum_n a_n^*(\bar{E})a_n(E)+\int dE'C_{E'}^*(\bar{E})C_{E'}(E)=\delta(\bar{E}-E). \qquad (29)$$

Substituting Eqs. (22) and (28) into Eq. (29), one gets, after some manipulations,

$$|\sum_n W_n^*a_n(E)\,|^2[\pi^2+Z^2(E)]+\sum_n\sum_m a_n^*(\bar{E})\{1+[W_nW_m^*/(\bar{E}-E)]\times[Z(E)-Z(\bar{E})]\}a_m(E)=\delta(E-\bar{E}). \qquad (30)$$

From this result one gets [using Eq. (25)]

$$|\sum_n W_n^*a_n(E)\,|^2=[\pi^2+Z^2(E)]^{-1}. \qquad (31)$$

Using a representation in which the coefficients $a_n(E)$ are real, Eqs. (28) and (31) lead to the result

$$a_n(E)=[W_n/(E-E_n)]\{Z^2(E)/[\pi^2+Z^2(E)]\}^{1/2}. \qquad (32)$$

At this stage we have finally obtained all the necessary information concerning the compound states of the system, which can be displayed in the form

$$\psi_E=\sum_n a_n(E)[\alpha_s^n\varphi_s+\sum_i\beta_i^n\varphi_i]+\int dE'C_{E'}(E)\varphi_{E'}. \qquad (33)$$

Only the coefficients of φ_s are of real interest, as only this zero-order state does carry oscillator strength. These coefficients are given by Eqs. (16) and (32). The representation (33) displays a resonance corresponding to a superposition of the zero-order state φ_s interacting with the discrete or quasicontinuous manifold $\{\varphi_i\}$ and with the radiative continuum $\{\varphi_E\}$. The manifold $\{\varphi_i\}$ does not interact with the $\{\varphi_E\}$ continuum. The case of a discrete state interacting with two noninteracting continua was treated by Fano.[12] One should notice that Eqs. (15) and (33) correspond to two complementary descriptions of the proper eigenstates of the system, which can be displayed either in terms of the Born–Oppenheimer basis set or by the molecular eigenstates basis.

Consider now the "preparation" of the excited state. We start with the system in the ground state, φ_0. At a time $t=0$ an excitation process is applied. Without loss of generality we can assume that the duration of the perturbation is short on the time scale of the decay of the excited state, so that the time-dependent perturbation $T^x(t)$ can be represented as a delta function $T^x(t)=T^x\delta(t)$, where T^x is a time-independent coupling operator.

The resulting excited state can be then represented as a superposition of the eigenstates ψ_E:

$$\Psi(t=0)=\int dE\langle\varphi_0\mid T^x\mid\psi_E\rangle\psi_E. \tag{34}$$

The properties of this excited state can be further elucidated by considering the completeness properties of the basis set $\{\psi_E\}$ and of the Born–Oppenheimer basis set, so that

$$\int dE\mid\psi_E\rangle\langle\psi_E\mid=\mid\varphi_s\rangle\langle\varphi_s\mid+\sum_i\mid\varphi_i\rangle\langle\varphi_i\mid=1.$$

Application of these relations leads to the simple result $\Psi(t=0)=\langle\varphi_0\mid T^x\mid\varphi_s\rangle\varphi_s$. Thus the delta-function excitation process "prepares" the system in a metastable state which just corresponds to the zero-order Born–Oppenheimer state φ_s which carries oscillator strength from the ground state. This result is not surprising since the delta-function excitation process is equivalent to the use of a white excitation spectrum. We have thus established the connection between the present treatment[7] and the Robinson–Frosch–Siebrand–Lin approach.[3–6] In order to obtain a general expression for the radiative decay of a polyatomic molecule we shall proceed using the representation (34) for the initial excited state.

The transition element appearing in Eq. (34) is proportional to the amplitude of the state ϕ_s in the eigenstate Ψ_E. This amplitude, which we will call $a_s(E)$, is obtained from Eq. (33) in the form

$$a_s(E)=\langle\varphi_s\mid\psi_E\rangle=\sum_n a_n(E)\langle\varphi_s\mid\psi_n\rangle=\sum_n a_n(E)\alpha_s^n. \tag{35}$$

The resulting excited state which we normalize to unity is therefore displayed in the form

$$\Psi(t=0)=\int dE\sum_n\alpha_s^n a_n(E)\psi_E. \tag{36}$$

The time development of this excited state is simply obtained by incorporating the phase development of the eigenstates into Eq. (36), and one gets

$$\Psi(t)=\sum_n\alpha_s^n\int a_n(E)\psi_E\exp\left(-\frac{i}{\hbar}Et\right)dE. \tag{37}$$

We are now able to consider some properties of the system which are amenable to experimental determination. The fluorescence rate is given by

$$\dot{P}(t)=(2\pi/\hbar)\mid\langle\varphi_0\mid T\mid\Psi(t)\rangle\mid^2\rho_k, \tag{38}$$

where ρ_k is the density of final states in the radiation field and T corresponds to the transition operator. Let $\Gamma/\hbar$ be the theoretical radiative decay probability of the zero-order state φ_s, where the corresponding radiative width is

$$\Gamma=2\pi\mid\langle\varphi_0\mid T\mid\varphi_s\rangle\mid^2\rho_k=2\pi W^2. \tag{39}$$

We shall also define the amplitude $A_s(t)$ of the zero-order φ_s in the excited state $\Psi(t)$ at time t, so that

$$\begin{aligned}A_s(t)=\langle\varphi_s\mid\Psi(t)\rangle&=\sum_n\alpha_s^n\int a_n(E)\langle\varphi_s\mid\psi_E\rangle\exp\left(-\frac{i}{\hbar}Et\right)dE\\&=\sum_n\sum_m\alpha_s^n\alpha_s^m\int a_n(E)a_m(E)\exp\left(-\frac{i}{\hbar}Et\right)dE.\end{aligned} \tag{40}$$

With the aid of Eqs. (39) and (40) we set

$$\dot{P}(t)=(\Gamma/\hbar)\mid A_s(t)\mid^2. \tag{41}$$

Now, making use of Eqs. (18a) and (32), we write

$$A_s(t)=W^2\int\frac{Z^2(E)}{\pi^2+Z^2(E)}\sum_n\frac{(\alpha_s^n)^2}{E-E_n}\sum_m\frac{(\alpha_s^m)^2}{E-E_m}\exp\left(-\frac{i}{\hbar}Et\right)dE. \tag{42}$$

$Z(E)$ is given by Eq. (27). The sum $\sum_n(\alpha_s^n)^2/(E-E_n)$ appearing in Eq. (42) can be evaluated using Eq. (16). As we are interested in the limiting case defined by Eq. (1), we can write the relevant sum in the form

$$\begin{aligned}\sum_n[(\alpha_s^n)^2/(E-E_n)]&=\sum_n\{[(E_n-E_s)/v]^2+(\pi v^2/\epsilon)^2\}^{-1}(E-E_n)^{-1}\\&=\sum_{n=-\infty}^{\infty}[n^2(\epsilon/v)^2+(\pi v^2/\epsilon)^2]^{-1}(E-E_s-n\epsilon)^{-1}.\end{aligned} \tag{43}$$

This summation may be performed using residue techniques, leading to the result

$$\sum_n \frac{(\alpha_s{}^n)^2}{E-E_n} = \frac{\pi v^2}{\epsilon}\left[(E-E_s)^2+\left(\frac{\pi v^2}{\epsilon}\right)^2\right]^{-1}\left[\frac{\epsilon}{\pi v^2}\operatorname{cotgh}\frac{\pi^2 v^2}{\epsilon^2}+\operatorname{cotg}\left(\frac{\pi}{\epsilon}(E-E_s)\right)\right]. \tag{44}$$

Making use of the definition $\Gamma=2\pi W^2$ [Eqs. (39) and (13)] and $\Delta=2\pi v^2\epsilon^{-1}$ [Eq. (2)], we can display the amplitude $A_s(t)$ in the final form:

$$A_s(t)=\frac{2}{\pi\Gamma}\int\frac{\exp[-(i/\hbar)Et]dE}{1+(16/\Delta^2\Gamma^2)[(E-E_s)^2+\frac{1}{4}\Delta^2]^2\{[2(E-E_s)/\Delta]\operatorname{cotgh}(\pi\Delta/2\epsilon)+\operatorname{cotg}[(\pi/\epsilon)(E-E_s)]\}^{-2}}. \tag{45}$$

With the aid of Eqs. (41) and (45) we have obtained a general equation for the radiative decay of an excited state, where vibronic coupling leads to inhomogenous line broadening. It should be borne in mind that the energetic criterion (1) is only a necessary condition for the statistical limit. The second condition is provided by the definition of the time scale for the decay process [Eq. (4)]. We now proceed to demonstrate how our equations can be simplified in the statistical limit, and what is the nature of the physical information pertaining to this case of the radiative decay of large molecules.

III. THE STATISTICAL LIMIT

We shall first make use again of Eq. (1) and set in Eq. (45) $\operatorname{cotgh}(\pi^2v^2/\epsilon^2)=1$. Then we get the amplitude equation in a somewhat simplified form:

$$A_s(t)=\frac{2}{\pi\Gamma}\int_{-\infty}^{\infty}\frac{\exp[-(i/\hbar)E_st]\exp[-(i/\hbar)Et]dE}{1+(16/\Delta^2\Gamma^2)(E^2+\frac{1}{4}\Delta^2)^2\{(2E/\Delta)+\operatorname{cotg}[(\pi/\epsilon)E]\}^{-2}}. \tag{46}$$

The analytical evaluation of this Fourier transform in the general case is not possible. However, this integral is manageable in the statistical limit when $t\ll\hbar/\epsilon$ [Eq. (4)]. It is interesting to note in passing that this restriction implies that $\hbar/\Gamma\ll\hbar/\epsilon$ (e.g., $\Gamma\gg\epsilon$) and that $\tau\ll\hbar/\epsilon$ [e.g., $n\gg1$, see Eq. (3)]. Now the integral (46) contains the function $\operatorname{cotg}(\pi/\epsilon)E$, which has a periodicity of ϵ on the energy scale. We are interested in the Fourier transform for a time scale, which is appreciably shorter than the recurrence time $\hbar/\epsilon$, whereupon the large changes in the integral which occur over an energy range of the order of ϵ are of minor importance. We may therefore average the integrand over a period of the cotangent function, and perform the Fourier transformation over the resulting averaged integrand. The proper average of the integrand is given in the form

$$\langle F(E)\rangle_{\mathrm{Av}}=\epsilon^{-1}\frac{2}{\pi\Gamma}\int_0^{\epsilon}\frac{dE'}{1+(16/\Delta^2\Gamma^2)(E^2+\frac{1}{4}\Delta^2)^2[(2E/\Delta)+\operatorname{cotg}(\pi/\epsilon)E']^{-2}}. \tag{47}$$

Note that when the energy is changed by a value of order of ϵ only the function $\operatorname{cotg}[(\pi/\epsilon)E]$ changes appreciably. By introducing the simple transformation $y=\operatorname{tg}[(\pi/\epsilon)E']$, the integral (47) is transformed into

$$\langle F(E)\rangle_{\mathrm{Av}}=\frac{2}{\epsilon\pi\Gamma}\frac{\epsilon}{\pi}\int_{-\infty}^{\infty}\frac{[(2E/\Delta)+y]^2dy}{\{[(2E/\Delta)+y]^2+(16/\Delta^2\Gamma^2)[E^2+\frac{1}{4}\Delta^2]^2\}(1+y^2)}. \tag{48}$$

Making use of the result

$$\int_{-\infty}^{\infty}\frac{(a+y)^2dy}{[(a+y)^2+C^2](1+y^2)}=\pi\frac{1+C+a^2}{1+2C+a^2+C^2}, \tag{49}$$

one gets

$$\begin{aligned}\langle F(E)\rangle_{\mathrm{Av}}&=\frac{2}{\pi\Gamma}\frac{1+(4/\Delta\Gamma)(E^2+\frac{1}{4}\Delta^2)+4(E^2/\Delta^2)}{1+(8/\Delta\Gamma)(E^2+\frac{1}{4}\Delta^2)+4(E^2/\Delta^2)+(16/\Delta^2\Gamma^2)(E^2+\frac{1}{4}\Delta^2)^2}\\&=\pi^{-1}\frac{\frac{1}{2}(\Delta+\Gamma)}{E^2+\frac{1}{4}(\Delta+\Gamma)^2}.\end{aligned} \tag{50}$$

The averaged integrand is a Lorentzian, and its Fourier transform can be readily evaluated,

$$A_s(t)=\exp\left(-\frac{i}{\hbar}E_st\right)\int_{-\infty}^{\infty}\langle F(E)\rangle_{\mathrm{Av}}\exp\left(-\frac{i}{\hbar}Et\right)dE=\exp\left(-\frac{i}{\hbar}E_st\right)\exp\left(-\frac{\Gamma+\Delta}{2\hbar}t\right). \tag{51}$$

The probability of locating the system in the state φ_s is just

$$|A_s(t)|^2 = \exp\{-[(\Gamma+\Delta)/\hbar]t\}, \tag{52}$$

while the rate of fluorescence emission [Eq. (41)] is given by

$$\dot{P}(t) = (\Gamma/\hbar)\exp\{-[(\Gamma+\Delta)/\hbar]t\}. \tag{53}$$

The fluorescence rate decays exponentially with an apparent lifetime τ_{exptl}, which is just

$$1/\tau_{\text{exptl}} = (\Gamma/\hbar) + (\Delta/\hbar), \tag{54}$$

corresponding to the sum of the inverse radiative lifetime of the state φ_s (which can be evaluated from the oscillator strength) and the inverse nonradiative lifetime $\tau = \hbar/\Delta$ [Eq. (3)].

The evaluation of the quantum yield is straightforward. The integrated fluorescence up to time t is just

$$P(t) = \int_0^t \dot{P}(t')dt' = \frac{\Gamma}{\Gamma+\Delta}\left[1-\exp\left(-\frac{\Gamma+\Delta}{\hbar}t\right)\right]. \tag{55}$$

Under our normalization conditions the quantum yield for emission is $Y = P(\infty)$, so that

$$Y = \Gamma/(\Gamma+\Delta). \tag{56}$$

We have now recovered the well-known intuitive kinetic expressions for the decay time and for the quantum yield, which were extensively used in the past by experimentalists.

IV. LINE SHAPES FOR SEVERAL RESONANCES

The results obtained in our previous work pertaining to the observation of a Lorentzian line shape are expected to hold for the case of an isolated resonance. However, in some cases of physical interest, several zero-order Born–Oppenheimer levels, all of which carry oscillator strength, have to be considered. As an example, consider several vibronic components of a second excited singlet state, which are quasidegenerate with the vibronic manifold corresponding to the first excited singlet. If the widths of these states exceed their separation, the line shapes are expected to reveal deviation from a Lorentzian shape. In this situation of excessive inhomogenous broadening, one expects that $\Delta \approx 100$–$1000\ \text{cm}^{-1}$, which overwhelms the radiative width Γ. Hence, the radiative decay channel is of no importance. In the case of somewhat lower nonradiative widths, say $\Delta \approx 1\ \text{cm}^{-1}$ (e.g., the first excited singlet state of azulene), picosecond light pulses can be applied to study the nonradiative and the radiative decay (in this case it is expected that $Y \sim 10^{-4}$). For the limit of overlapping resonances, the best method for obtaining physical information on the system involves the study of the line shapes in optical absorption. In our treatment of this problem we can disregard the radiative decay and consider only the nature of intramolecular vibronic coupling effects.

Our model system consists now of a number of zero-order states φ_s with energies E_s $(s = 1 \cdots m)$ and which carry oscillator strength, so that the matrix elements T_{0s} $(s = 1 \cdots n)$ of the electric dipole moment are nonvanishing for optical transitions from the ground state to these states. These states are superimposed on a dense manifold of vibronic states $\{\varphi_i\}$ which do not carry oscillator strength. For simplicity, it will be assumed again that the latter states are equally spaced, and let ϵ be the spacing between these levels.

We are interested in the static molecular problem, so we consider the diagonalization of the molecular Hamiltonian. The matrix elements between the zero-order states are

$$\langle \varphi_s | H_{\text{el}} | \varphi_t \rangle = E_s \delta_{st}, \tag{57}$$

$$\langle \varphi_i | H_{\text{el}} | \varphi_j \rangle = E_i \delta_{ij}, \tag{58}$$

$$\langle \varphi_s | H_{\text{el}} | \varphi_i \rangle = v_{si} = v_s, \tag{59}$$

where we have again assumed that all the vibronic coupling matrix elements v_{si} are equal. The molecular eigenstates are expressed as a superposition of zero-order states

$$\psi_n = \sum_{s=1}^{m} \alpha_s^n \varphi_s + \sum_{i=-\infty}^{\infty} \beta_i^n \varphi_i. \tag{60}$$

The secular equations which determine the values of the expansion coefficients are

$$\alpha_s^n E_s + \sum_i \beta_i^n v_s = E_n \alpha_s^n, \tag{61}$$

$$\sum_s \alpha_s^n v_s + \beta_i^n E_i = E_n \beta_i^n. \tag{62}$$

The last equation can be solved for β_i^n, and one gets

$$\beta_i^n = (E_n - E_i)^{-1} \sum_s \alpha_s^n v_s. \tag{63}$$

Substituting this result in Eq. (61) yields

$$[v_s/(E_n - E_s)] \sum_t \alpha_t^n v_t \sum_i (E_n - E_i)^{-1} = \alpha_s^n. \tag{64}$$

Multiplication by v_s and summation over s leads to the result

$$\sum_s [v_s^2/(E_n - E_s)] \sum_t \alpha_t^n v_t \sum_i (E_n - E_i)^{-1} = \sum_s \alpha_s^n v_s \tag{65}$$

or, alternatively,

$$\sum_s [v_s^2/(E_n - E_s)] = [\sum_i (E_n - E_i)^{-1}]^{-1}. \tag{66}$$

The sum on the right-hand side of the equation is already known, so that one gets

$$\left(\sum_s \frac{v_s^2}{E_n - E_s}\right)^{-1} = \sum_i (E_n - E_i)^{-1} = -(\pi/\epsilon)\,\text{cotg}[(\pi/\epsilon)(E_n - E_0)]. \tag{67}$$

We should notice in passing that the result also provides us with the new energy levels for the system. Now we shall use the normalization condition for ψ_n to get

$$\langle\psi_n\,|\,\psi_n\rangle=1=\sum_s|\,\alpha_s^n\,|^2+\sum_i|\,\beta_i^n\,|^2=(\sum_t\alpha_t^nv_t)^2\left[\left(\sum_i\frac{1}{E_n-E_i}\right)^2\sum_s\left(\frac{v_s}{E_n-E_s}\right)^2+\sum_i\left(\frac{1}{E_n-E_i}\right)^2\right]. \tag{68}$$

The last summation on the rhs of Eq. (68) can be expressed in the form

$$\sum_i\left(\frac{1}{E_n-E_i}\right)^2=\frac{\pi^2}{\epsilon^2}\operatorname{cosec}^2\left(\frac{\pi}{\epsilon}\,(E_n-E_0)\right)=\frac{\pi^2}{\epsilon^2}\left[1+\operatorname{cotg}^2\left(\frac{\pi}{\epsilon}\,(E_n-E_0)\right)\right]. \tag{69}$$

Using the result in Eq. (67), we get

$$\sum_i\left(\frac{1}{E_n-E_i}\right)^2=\frac{\pi^2}{\epsilon^2}+\left(\sum_s\frac{v_s^2}{E_n-E_s}\right)^{-2}. \tag{70}$$

The substitution of Eq. (67) and (70) in Eq. (68) leads to

$$(\sum_t\alpha_t^nv_t)^2=\left[\sum_t\left(\frac{v_t}{E_n-E_t}\right)^2+1+\frac{\pi^2}{\epsilon^2}\left(\sum_t\frac{v_t^2}{E_n-E_t}\right)^2\right]^{-1}\left(\sum_t\frac{v_t^2}{E_n-E_t}\right)^2. \tag{71}$$

Using Eqs. (67) and (71), one gets from Eq. (64) the following expression for the coefficient α_s^n:

$$(\alpha_s^n)^2=\left(\frac{v_s}{E_n-E_s}\right)^2\left[\sum_t\left(\frac{v_t}{E_n-E_t}\right)^2+1+\frac{\pi^2}{\epsilon^2}\left(\sum_t\frac{v_t^2}{E_n-E_t}\right)^2\right]^{-1}. \tag{72}$$

The transition amplitude from the ground state to the molecular eigenstate ψ_n is given in the form

$$\langle\varphi_0\,|\,T\,|\,\psi_n\rangle=\sum_s T_{0s}\langle\varphi_s\,|\,\psi_n\rangle=\sum_s T_{0s}\alpha_s^n. \tag{73}$$

The line shape is proportional to the square of the transition amplitude per unit energy interval:

$$L(E_n)=\epsilon^{-1}\,|\,\langle\varphi_0\,|\,T\,|\,\psi_n\rangle\,|^2=\epsilon^{-1}\,|\,\sum_s T_{0s}\alpha_s^n\,|^2=\epsilon^{-1}\left[\sum_t\left(\frac{v_t}{E_n-E_t}\right)^2+1+\frac{\pi^2}{\epsilon^2}\left(\sum_t\frac{v_t^2}{E_n-E_t}\right)^2\right]^{-1}\left|\sum_s\frac{T_{0s}v_s}{E_n-E_s}\right|^2. \tag{74}$$

Equation (74) provides a solution which is valid within the framework of our model for the line shapes of several resonances. This equation can be applied for the analysis of the higher excited singlet states of large molecules. To demonstrate a simple application of our results, consider the nonradiative decay of two identical resonances, so we set $m=2$, $v_1=v_2=v$ and $T_{01}=T_{02}=T$. From Eq. (72) we now get

$$L(E)=\frac{T^2(v^2/\epsilon)[2E-(E_1+E_2)]^2}{v^2[(E-E_1)^2+(E-E_2)^2]+(E-E_1)^2(E-E_2)^2+(\pi^2v^4/\epsilon^2)[2E-(E_1+E_2)]^2} \tag{75}$$

In the statistical limit $2\pi v^2/\epsilon=\Delta$ and $v\ll\Delta$, and we now obtain the expression for the line shape,

$$L(E)=\frac{T^2(\Delta/2\pi)[2E-(E_1+E_2)]^2}{(E-E_1)^2(E-E_2)^2+\frac{1}{4}\Delta^2[2E-(E_1+E_2)]^2}. \tag{76}$$

This result reveals a "dip" at the energy $E_n=\frac{1}{2}(E_1+E_2)$. Equation (76) is formally analgous to the line-shape equation obtained for the line shape in absorption in a system consisting of two closely spaced indistinguishable levels, derived in our previous work, except that in the latter case the radiative width (of each line) replaces the nonradiative width appearing in Eq. (76). This result clearly demonstrates the notion of nonexponential nonradiative decay when the width of two levels exceeds their spacing.

V. DISCUSSION

In the present paper we have considered the problem of the radiative decay of large molecules by the application of the Fano configuration-interaction method, by constructing compound states of the system consisting of a superposition of molecular eigenstates and radiation field states. An alternative way of approaching the problem of the radiative decay of a large number of indistinguishable levels involves the unitarity relations method previously considered by us.[11b] This method involves the solution of a differential equation for the time-dependent amplitudes of the excited states. As only the amplitudes of discrete zero photon states are considered, the operator involved is not Hermitian, but is still assumed to be linear. That treatment is based on the general consequences of probability conservation. The procedure requires the diagonalization of the general (nondiagonal) damping matrix, and the resulting complex eigenvalues and nonorthogonal eigenvectors can be then used to derive the radiative decay rate and the quantum yield. Obviously, this general method is much more complicated in real life than the Fano method, which is applicable for the case under consideration. In the appendix we present a study of the decay, demonstrating the equivalence between the unitarity relations method and the Fano scheme.

The main conclusions of the generalized theory of radiationless transitions presented herein are:

(a) The experimental radiative decay in the statistical limit is a pure exponential.

(b) The experimental radiative decay time determined on the time scale which is appreciably shorter than the recurrence time $t \ll \hbar/\epsilon$ consists of independent contributions of nonradiative and radiative components, so that $\tau_{\mathrm{exptl}}^{-1} = (\Delta/\hbar) + (\Gamma/\hbar)$. In large molecules when the recurrence time is exceedingly long, this result establishes the decay law.

(c) The nonradiative decay component $\Delta/\hbar$ in the decay time, obtained for a manifold of molecular eigenstates in an inhomogenously broadened line, corresponds to a set of indistinguishable levels. We have previously demonstrated that when the damping matrix is nondiagonal, quantum beats are expected for the spatially integrated rate of photon emission. The interference effects between a large number of closely spaced indistinguishable levels leads to intramolecular interference effects and to the shortening of the radiative lifetime in the statistical limit.

(d) The quantum yield in the statistical limit, experimentally determined on a time scale appreciably shorter than the recurrence time, is $Y = \Gamma/(\Gamma + \Delta)$. The molecule does not, of course, act as a photon trap. Rather, only a fraction Y of the absorbed photons can be remitted on the time scale $t \ll \hbar/\epsilon$. In our model, the fraction $1 - Y$ will be emitted on the time scale $t \gg \hbar/\epsilon$. In real life, the fraction $1 - Y$ may be emitted on a long time scale (but still shorter than $\hbar/\epsilon$) determined by the finite small oscillator strength of the zero-order states $\{\varphi_i\}$. Such a situation is encountered in principle for intersystem crossing. However, in this case external collisional perturbations are expected to be dominant. In the case of internal conversion the zero-order states $\{\varphi_i\}$ are not radiatively connected to φ_0; however, they are radiatively connected to the higher vibronic levels of the ground state. This situation is indeed encountered in naphthalene and anthracene when excitation to the second excited singlet results in emission from vibrationally excited levels of the first singlet to the vibrationally excited ground state.

(e) The lowest excited states of the same multiplicity as the ground state of small molecules like SO_2, NO_2, or CS_2 are quasidegenerate, with a relatively low density of vibronic states belonging to the lower triplet and the ground state. However, because of favorable Franck–Condon vibrational overlap factors (due to changes in the molecular geometry in the excited states), the vibronic coupling terms will be quite large. In this case, $v\rho > 1$, so that inhomogenous broadening may occur. However, the recurrence time relative to $\hbar\Gamma^{-1}$ or to $\hbar\Delta^{-1}$ will be extremely short. The formal solution for the problem is obtained by Eqs. (41) and (45). Although for a time scale $t \ll \hbar/\epsilon$ the decay is given by Eq. (53), this feature cannot be experimentally observed as in this case $t \sim 10^{-12}$ sec. On the other hand, for $t \gg \hbar/\epsilon$, which is amenable to experimental observation, it is expected that the radiative decay consists of a sum of exponentials corresponding to the separate molecular eigenstates and will be roughly of the form $\exp[-(\Gamma/\hbar n)t]$, so that the apparent lifetime is lengthened.

(f) The occurence of inhomogenous broadening in moderately small molecules implies the redistribution of the intensity of the zero-order components φ_s, which induces the appearance of many new lines (corresponding to all the molecular eigenstates ψ_n) into the spectrum. This feature was indeed observed in the high-resolution spectrum of NO_2,[13] where a large number of irregularly spaced lines is observed. These general conclusions concur with the arguments presented by Douglas.[14] This problem will be the subject of another paper.[15]

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APPENDIX: THE EQUIVALENCE OF THE FANO METHOD AND THE UNITARITY RELATIONS METHOD

In this appendix we derive the formal solution for the radiative decay of a large number of coherently excited states by using an alternative method. This treatment is based on the solution of a linear differential equation or, alternatively, on the implications of general conservation relations. This problem was discussed by us in a previous work.[11b]

The time dependence of the amplitudes of the states ψ_n in the excited states are governed by the differential equation

$$(d/dt)\mathbf{a}(t) = -i\hbar\mathbf{A}\mathbf{a}(t), \tag{A1}$$

which has the solution

$$\mathbf{a}(t) = \mathbf{S}^{-1}\exp(-i\hbar\mathbf{\Lambda}t)\mathbf{S}\mathbf{a}(0), \tag{A2}$$

where $\mathbf{\Lambda}$ is a diagonal matrix whose elements are the eigenvalues of $\mathbf{A}$. $\mathbf{S}$ is the matrix of the eigenvectors

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[15] M. Bixon and J. Jortner, J. Chem. Phys. **50**, 3284 (1969).

of **A**. The elements of the matrix **A** are given in the form

$$A_{ll}=-\tfrac{1}{2}i\Gamma_l+E_l, \tag{A3}$$

$$\Psi_{ll'}=-\tfrac{1}{2}i\Gamma_{ll'}. \tag{A4}$$

In the present model $\Gamma_{ll'}=\alpha_s^l\alpha_s^{l'}\Gamma$, where Γ is the total transition probability computed for the zeroth-order state φ_s. We have therefore the following structure for the matrix **A**:

$$A_{ll}=-\tfrac{1}{2}i\Gamma(\alpha_{sl})^2+E_l, \tag{A5}$$

$$A_{ll'}=-\tfrac{1}{2}i\Gamma\alpha_s^l\alpha_s^{l'}. \tag{A6}$$

The elements of **S** and the eigenvalues of **A** can be found by solving the system of linear equations

$$\sum_{l'}A_{ll'}b_{l'}=\lambda b_l, \tag{A7}$$

which in the present case has the form

$$-\tfrac{1}{2}i\Gamma\alpha_s^l\sum_{l'}\alpha_s^{l'}b_{l'}+E_lb_l=\lambda b_l. \tag{A8}$$

The formal solution for b_l is

$$b_l=-\tfrac{1}{2}i\Gamma[\alpha_s^l/(\lambda+E_l)]\sum_{l'}\alpha_s^{l'}b_{l'}. \tag{A9}$$

Substitution of this result in Eq. (A8) yields the following equation for λ:

$$\tfrac{1}{2}i\Gamma\sum_l[(\alpha_s^l)^2/(\lambda+E_l)]=-1. \tag{A10}$$

Substituting the expression for $(\alpha_s^l)^2$, Eq. (16), into (A10) gives

$$\sum_l\left[\frac{E_l-E_s}{v^2}+\left(\frac{\pi v^2}{\epsilon}\right)^2\right]^{-1}(\lambda+E_l)^{-1}=-\frac{2i}{\Gamma}. \tag{A11}$$

The summation is carried out by residue techniques and results in the following equation:

$$\frac{2\epsilon^3}{\Gamma v^2}=-\Pi\left\{\left[\left(\frac{\lambda}{\epsilon}+i\frac{\pi v^2}{\epsilon^2}\right)\left(\frac{\lambda}{\epsilon}-i\frac{\pi v^2}{\epsilon^2}\right)\right]^{-1}\operatorname{cotg}\left(\pi\frac{\lambda}{\epsilon}\right)+\left[\left(-2i\frac{\pi v^2}{\epsilon^2}\right)\left(-i\frac{\pi v^2}{\epsilon^2}+\frac{\lambda}{\epsilon}\right)\right]^{-1}\operatorname{cotg}\left(-i\frac{\pi^2v^2}{\epsilon^2}\right)\right.$$
$$\left.+\left[\left(2i\frac{\pi v^2}{\epsilon^2}\right)\left(i\frac{\pi v^2}{\epsilon^2}+\frac{\lambda}{\epsilon}\right)\right]^{-1}\operatorname{cotg}\left(i\frac{\pi^2v^2}{\epsilon^2}\right)\right\}. \tag{A12}$$

After some rearrangements, one gets

$$-i\frac{2\epsilon^3}{\pi v^2\Gamma}\left[\left(\frac{\lambda}{\epsilon}\right)^2+\left(\frac{\pi v^2}{\epsilon^2}\right)^2\right]=\frac{\lambda\epsilon}{\pi v^2}\operatorname{cotgh}\left(\frac{\pi^2v^2}{\epsilon^2}\right)+\operatorname{cotg}\left(\pi\frac{\lambda}{\epsilon}\right) \tag{A13}$$

or, bearing in mind the definition of Δ [Eq. (2)],

$$-i\frac{4}{\Delta\Gamma}(\lambda^2+\tfrac{1}{4}\Delta^2)=\frac{2\lambda}{\Delta}\operatorname{cotgh}\left(\frac{\pi\Delta}{2\epsilon}\right)+\operatorname{cotg}\left(\pi\frac{\lambda}{\epsilon}\right). \tag{A14}$$

This equation is equivalent to the equation for the poles of the integrand in Eq. (45). This result demonstrates the equivalence of the two methods.

If the solutions to Eq. (A14) are known, one has the complete matrix **A**. The elements of **S** are the vectors **b** which can be evaluated from the knowledge of λ and with the aid of the normalization condition $\sum_l b_l^2=1$ and Eq. (A9).