

# Developments in the Resonance Theory of the Color of Dyes: Correlation Function Approach

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It is assumed that the low-lying electronic states of dye-like molecules can be adequately represented using a finite number of wave functions related to resonance structures. With this assumption a theory of the dipole susceptibility for dyes is constructed, using the fluctuation – dissipation or correlation function approach. Consideration of the waxing and waning of the correlation functions as involved in the result for the susceptibility gives a certain legitimacy to describing a dye molecule interacting with radiation as going from one resonance structure to another. This is elucidated through the coupled pendulum analogy.

Es wird angenommen, daß die niedrigliegenden Elektronenzustände farbstoffartiger Moleküle durch eine begrenzte Anzahl von Wellenfunktionen, die mit Resonanzstrukturen verwandt sind, dargestellt werden können. Mit dieser Annahme wird eine Theorie der Dipol-Suszeptibilität für Farbstoffe aufgebaut, wobei man die Form der Fluktuations-, Dissipations- oder Korrelations-Funktionen benutzt. Überlegungen bezüglich Zu- und Abnahme der Korrelationsfunktionen im Zusammenhang mit der Suszeptibilität berechtigen dazu, ein Farbstoff-Molekül, das mit Strahlung in Wechselwirkung tritt, als von einer Resonanzstruktur in die andere übergehend zu betrachten. Dies wird durchsichtig, wenn man die Analogie zum gekoppelten Pendel diskutiert.

On suppose que les plus bas états électroniques de molécules du type colorants peuvent être convenablement représentés en utilisant un nombre fini de fonctions d'ondes liées aux structures de résonance. Dans ce cadre une théorie de la susceptibilité dipolaire des colorants est construite en utilisant l'approche des fonctions de corrélation ou de fluctuation-dissipation. Si l'on considère la croissance et la décroissance des fonctions de corrélation impliquée dans le résultat obtenu pour la susceptibilité il est légitime de décrire une molécule de colorant en interaction avec le rayonnement comme oscillant entre les différentes structures de résonance. Ceci est élucidé à l'aide de l'analogie du pendule couplé.

## Introduction

Before the discovery of quantum mechanics, the standard approach to the theory of spectra was through the classical mechanics of driven multiply-periodic systems. Thus, in the simplest case,

$$f = -kx + eEe^{i\omega t} = m\ddot{x}$$

leads, through the substitution  $x = Ae^{i\omega t}$ , to the result ( $\omega_0^2 = k/m$ )

$$\frac{A}{E} = \frac{e/m}{\omega_0^2 - \omega^2}.$$

The quantity  $A/E$ , the amplitude per unit driving field, is an example of a susceptibility. The resonance at  $\omega_0$  appears in the context: the  $A/E$  ratio expressed as a function of  $\omega$ .

Now a recent development, the fluctuation-dissipation theorem, is serving to refocus interest on the direct calculation of susceptibilities. According to this theorem the Fourier transform of the decay of a fluctuation — in our case the decay of a correlation function — will be a susceptibility. The theorem is often expressed and used as a mixture of mechanics and statistical mechanics, but only the zero-temperature version, which involves a pure ground state expectation value, will be needed here. The theorem has found particular use in application to infinite systems because through its use one is able to introduce damping in a systematic way, and because one can deal with large numbers, yet low concentrations of excitations and/or particles realistically through the notion of linear response. In fact, the idea of using the theorem for finite undamped systems is perhaps not an immediately attractive one. Nevertheless a direct calculation of susceptibility has the same appeal as in the case of the simple calculation above, in that emphasis on the role of the stationary states gives way to the broader result: the susceptibility as a function of  $\omega$ .

In this paper we shall be treating the electronic spectra of dye-like molecules. The states of such molecules can be described using wave functions corresponding to resonance structures, typically, structures carrying charges. The electric moments and the time evolution (as Fourier analysed) of the several resonance structures are found to carry the information needed for building up a theory of the susceptibility. As a consequence one is encouraged to pay attention to temporal sequences of resonance structures and the corresponding paths traced out by their charges<sup>1</sup>.

### Partial Susceptibility Expansion

We shall at first proceed rather formally. As a convenient point of departure, we may adopt the known expression for the dipole susceptibility [1] (see Appendix)

$$\chi = i\theta \langle N0 | [\boldsymbol{\mu}(t), \boldsymbol{\mu}(0)] | N0 \rangle |_{\omega} \quad (1)$$

where  $\theta$  is the Heaviside function,  $|N0\rangle$  is the ground state ket in the Schrödinger representation at  $t=0$ , and the  $\boldsymbol{\mu}$ 's are Heisenberg operators for the electric moment vector at times  $t$  and 0. The  $\omega$  notation means the Fourier transform. (The presence of this last feature results from the fact that (1) comes from a treatment of a system interacting with a sinusoidal external driving field — the light.)

We shall be needing to expand the ground state ket in terms of orthonormal basis functions,  $|st\rangle$ , not themselves stationary state functions:

$$|N0\rangle = \sum_s c_s |s0\rangle \quad (2a)$$

(The  $c$ 's are time independent.) Thus the full Schrödinger ket is

$$|N0\rangle e^{i\omega_N t}.$$

Here  $\omega_N$  means  $W_N/\hbar$  and can be thought of as the energy of the ground state in a system of units such that  $\hbar = 1$ . Since each  $|st\rangle$  is supposed to be a solution of

<sup>1</sup> One is not encouraged to think this way about stationary states in the absence of an external perturbation.

the Schrödinger equation then also

$$\sum_r c_r |rt\rangle$$

is a solution. Considering the equality of the respective solutions at  $t=0$

$$|N0\rangle e^{i\omega Nt} = \sum_r c_r |rt\rangle.$$

Now suppressing  $t$  in  $|rt\rangle$ , taking the conjugate and rearranging, this becomes

$$\langle N0| = e^{i\omega Nt} \sum_r c_r^* \langle r|. \quad (2b)$$

We can write a selected component, say  $z$ , of the electric moment operator in the Schrödinger representation as the dyadic

$$\mu_z(0) = \sum_{ij} z_{ij} |i0\rangle \langle j0| \quad (3a)$$

where

$$z_{ij} = \langle i0| \sum_v e_v z_v(0) |j0\rangle$$

and the sum is over the charges and  $z$  coordinates of the particles. Correspondingly, the time-dependent operators in the Heisenberg representation can be expressed<sup>2</sup>

$$\mu_z(t) = \sum_{ij} z_{ij} |i\rangle \langle j|. \quad (3b)$$

With the  $z$  component of  $\mu$  the only non-vanishing one through which the system is driven and for which the response is sought we have ((1) and (3))

$$\chi = \chi_+ + \chi_- \quad (4)$$

where

$$\chi_+ = i\theta \sum_{ijkl} \langle N0| z_{ij} |i\rangle \langle j| z_{kl} |k0\rangle \langle l0| N0\rangle |_{\omega}$$

and

$$\chi_- = -i\theta \sum_{ijkl} \langle N0| z_{ij} |i0\rangle \langle j0| z_{kl} |k\rangle \langle l| N0\rangle |_{\omega}.$$

Looking just at  $\chi_+$  and bringing in (2) we have, further,

$$\begin{aligned} \chi_+ &= i\theta e^{i\omega Nt} \sum_r c_r^* \langle r| \sum_{ijkl} z_{ij} |i\rangle \langle j| z_{kl} |k0\rangle \langle l0| \sum_s c_s |s0\rangle |_{\omega} \\ &= i\theta e^{i\omega Nt} \sum_{rsjk} c_r^* c_s z_r z_{ks} \langle j| k0\rangle |_{\omega}. \end{aligned}$$

Now defining

$$\omega_+ = \omega_N + \omega \quad (5a)$$

and

$$g_{jk}^+ = i\theta \langle j| k0\rangle |_{\omega_+} \quad (5b)$$

<sup>2</sup> This can be understood by writing the dyadic with greater explicitness namely as

$$\sum_i |it\rangle \langle it| \mu_z(t) \sum_j |jt\rangle \langle jt|$$

and observing that

$$\langle it| \mu_z(t) |jt\rangle = \langle i0| \sum_v e_v z_v(0) |j0\rangle.$$

we find

$$\chi_+ = \sum_{rsjk} c_r^* c_s z_{rj} z_{ks} g_{jk}^+ . \quad (5c)$$

The expression  $i\theta \langle j|k0\rangle$ ,  $g_{jk}$  before the transform is taken, is a correlation function. The evaluation of  $\chi_-$  is similar and leads to

$$\chi_- = \sum_{rsjk} c_r c_s^* z_{jr} z_{sk} (g_{jk}^-)^* \quad (6c)$$

where

$$g_{jk}^- = i\theta \langle j|k0\rangle|_{\omega_-} \quad (6b)$$

and

$$\omega_- = \omega_N - \omega . \quad (6a)$$

The system of Eqs. (4), (5), and (6) is equivalent to a component of the tensor Eq. (1) but now with the feature that correlation functions related to selected basis functions have been brought in.

A simplification will be introduced at this point which corresponds in a mathematical way to our eventual interest in resonance structures – namely that the chosen basis functions make the electric moment matrix diagonal

$$z_{ij} = \langle i0 | \sum_v e_v z_v(0) | j0 \rangle = \delta_{ij} z_{ij} .$$

With this simplification our system (4), (5c), (6c) becomes

$$\begin{aligned} \chi_+ &= \sum_{jk} c_j^* c_k z_{jj} z_{kk} g_{jk}^+ , \\ \chi_- &= \sum_{jk} c_j c_k^* z_{jj} z_{kk} (g_{jk}^-)^* , \\ \chi &= \chi_+ + \chi_- . \end{aligned} \quad (7)$$

As to the reason for assuming that the electric moment matrix is diagonal: it has long been known that it is fruitful to consider dyes as involving resonance structures; or, more technically, to consider the problem quantum mechanically using basis functions corresponding to the valence bond structures [2]. What is perhaps not always realized is that the several structures useful in the theory of the color of dyes have wave functions which (because one is obtained from another through electron transfer) are approximately orthogonal [3]. What is more, for essentially the same reason, these functions approximately diagonalize the electric moment matrix.

The importance of a particular  $g$  as a contributor to  $\chi$ , (7), depends on both the  $z$ 's and the  $c$ 's. We may think of a particular  $czg$  product as a *partial susceptibility* and the expansion (7) as an expansion of  $\chi$  which brings in a "positional" aspect through the partial susceptibilities. To continue the formal development we now especially focus on the  $g$ 's.

### Set of Coupled Equations

An interesting feature of the fluctuation-dissipation approach is that one can directly compute the Fourier transforms of the correlation functions i.e. without the need to obtain the functions themselves. A brief outline of the theory of this

direct computation follows. We start with the following derivative of a product of three functions

$$\begin{aligned} & \frac{d}{dt} [\theta(t) \langle jt | k0 \rangle e^{i\omega't}] \\ &= \langle j | k0 \rangle e^{i\omega't} \frac{d}{dt} \theta + \theta e^{i\omega't} \frac{d}{dt} \langle j | k0 \rangle + i\omega' \theta e^{i\omega't} \langle j | k0 \rangle \end{aligned}$$

and the general expression for a Green's function

$$g_{jk} = i\theta \langle j | k0 \rangle \Big|_{\omega'}.$$

The derivative of the Heaviside function is the Dirac delta function  $\delta(0)$ . Upon integration of the first expression from  $t = -\infty$  to  $+\infty$  we can simplify and incorporate the second

$$\theta \langle j | k0 \rangle e^{i\omega't} \Big|_{-\infty}^{+\infty} = \langle j0 | k0 \rangle + \int_{-\infty}^{+\infty} \theta e^{i\omega't} \frac{d}{dt} \langle j | k0 \rangle + \omega' g_{jk}.$$

The LHS is zero at  $t = -\infty$  because of the  $\theta$  and is taken as zero at  $t = +\infty$  because of some assumed ultimate small damping factor ( $\omega'$  can be interpreted as having an infinitesimal imaginary part:  $\omega' = \omega'' + i\eta$ ,  $\eta > 0$ , so that  $e^{i\omega't}$  has a factor  $e^{-\eta t}$  which goes with the correlation function).

The result then is

$$\omega' g_{jk} = -\langle j0 | k0 \rangle - \theta \frac{d}{dt} \langle j | k0 \rangle \Big|_{\omega'}.$$

We may find the derivative of  $\langle j |$  by using the Schrödinger equation:

$$i \frac{d}{dt} \langle j | = \langle j | H(0)$$

which gives

$$\omega' g_{jk} = -\langle j0 | k0 \rangle + i\theta \langle j | H(0) | k0 \rangle \Big|_{\omega'}. \quad (8)$$

Preliminary quantum mechanical work with valence bond structures and an ordinary Hamiltonian can be expressed concisely, once the various matrix elements have been computed (or inferred from symmetry and related considerations, as is sometimes good enough). Thus

$$H(0) = \sum_{rs} |r0\rangle \omega_{rs} \langle s0| \quad (9)$$

where

$$\omega_{rs} = \langle r0 | H(0) | s0 \rangle \quad (\hbar = 1).$$

With (9) we may rewrite (8) as involving other  $g$ 's. Thus

$$H(0) | k0 \rangle = \sum_{rs} |r0\rangle \omega_{rs} \langle s0 | k0 \rangle = \sum_r |r0\rangle \omega_{rk}$$

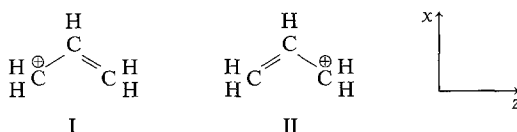
which leads to

$$\omega' g_{jk} = -\langle j0 | k0 \rangle + \sum_r g_{jr} \omega_{rk}. \quad (10)$$

Eqs. (10) for fixed  $j$  and variable  $k$  constitute a set of coupled equations<sup>3</sup>, a finite set if it develops (as we shall be assuming) that a finite set is sufficient to describe the ground state susceptibility<sup>4</sup>.

### A Simple Example

Let us take the case of a molecule considered as requiring just two equivalent structure functions spanning the space of the stationary states of interest – the ground ( $N$ ) state and a single excited ( $V$ ) state. For the sake of concreteness we may think about the hypothetical compound allyl cation (allyl cation is in a sense a most simple prototype of a dye) with the following structures



The Schrödinger Hamiltonian in dyadic form may be taken as

$$H(0) = \beta[|10\rangle\langle 20| + |20\rangle\langle 10|].$$

Here the energy expectation value of a single structure is being taken as zero, and the two structures have the same  $\omega_{ii}$ , or energy (they are exactly “in resonance”). Using the dyadic one readily recovers the familiar interaction matrix element

$$\omega_{12} = \langle 10|H(0)|20\rangle = \beta.$$

The phases are usually picked in a natural way so as to give, in addition,  $\beta < 0$ . One also knows for this and all such two-level systems that the eigenvalues of the secular equation are  $+\beta$  and  $-\beta$ . These correspond respectively to

$$|N0\rangle = \frac{1}{\sqrt{2}}[|10\rangle + |20\rangle]$$

and

$$|V0\rangle = \frac{1}{\sqrt{2}}[|10\rangle - |20\rangle].$$

The electric moment of each structure is essentially determined by the positive charge. With the carbon on the left as origin we should have  $z_{11} = 0$  and  $z_{22} = 2D$ , say, where  $D$  is the  $z$  projection of a C–C bond length. Then

$$\mu_z(t) = z_{11}|1\rangle\langle 1| + z_{22}|2\rangle\langle 2| = 2D|2\rangle\langle 2|$$

<sup>3</sup> The equations closely resemble the ones found in the case of a linear variation calculation for the coefficients, except that the term  $\langle j0|k0\rangle$  may not be zero ( $j = k$ ), which gives, in the present instance, a set of *inhomogeneous* equations. This fact causes us to consider an approach to their solution which is a bit different from the usual approach used with secular equations.

<sup>4</sup> This would involve the magnitudes of the  $c_r$ 's, the  $z_{rs}$ 's and the  $\omega_{rs}$ 's.

and we are required to compute (7)

$$\chi = (2D)^2 c_2^2 [g_{22}^+ + (g_{22}^-)^*]$$

or, since  $c_2 = 1/\sqrt{2}$  in  $|N0\rangle$

$$= 2D^2 [g_{22}^+ + (g_{22}^-)^*].$$

Now to compute  $g_{22}^+$  and  $g_{22}^-$  we calculate the  $\omega'$  transform. This we can do either from (8) or from (10), though it is usually just as convenient to use (8). Thus

$$\begin{aligned} \omega' g_{22} &= -1 + i\theta \langle 2|H(0)|20\rangle_{|\omega'} \\ &= -1 + i\theta\beta \langle 2|10\rangle_{|\omega'} \\ &= -1 + i\beta g_{21} \end{aligned}$$

Similarly

$$\omega' g_{21} = i\beta g_{22}$$

and

$$g_{22} = \frac{-\omega'}{\omega'^2 - \beta^2}.$$

The poles of the  $\omega'$  transform are the energy levels. Then (5a) and (6a) with  $\omega_N = \beta$  give

$$g_{22}^+ = -\frac{\omega + \beta}{(\omega + \beta)^2 - \beta^2} (g_{22}^-)^* = g_{22}^- = -\frac{(-\omega + \beta)}{(-\omega + \beta)^2 - \beta^2}$$

(without damping the  $g$ 's are real) and

$$\chi = 2D^2 \frac{2\beta}{\omega^2 - 2\beta^2}.$$

The conventional transition moment is

$$\begin{aligned} &\langle N0|\mu_z(0)|V0\rangle \\ &= \frac{1}{2} [(\langle 10| + \langle 20|)(2D|20\rangle \langle 20|)(|10\rangle - |20\rangle)] = D. \end{aligned}$$

Let us call this  $\mu_{NV}$  and let us call the pole at  $-2\beta: \omega_{NV}$ . Then

$$\chi = \frac{2\mu_{NV}^2 \omega_{NV}}{\omega_{NV}^2 - \omega^2}$$

which is the usual formula for the polarizability of a two-level system.

As the reader can imagine, the extension is straightforward to more complicated cases in which the number of structures is increased and in which more than one vector component of the electric moment is brought in. The algebraic computations are of the same order of difficulty as with the use of conventional procedures such as the linear variation method. Chief among the advantages of the present method is the opportunity afforded for visualization, besides which there is always the chance that unexpected benefits will be found when one has a novel way of looking at an old problem.

### Pendulum Analogy

Although we have been directly working with the Fourier transform, the information needed for the calculation of the susceptibility is contained in the correlation function – in the example,  $i\theta\langle 2|20\rangle$ . With  $\theta$  suddenly unity at  $t=0$  and with  $\langle 2|$  starting out as  $\langle 20|$  at  $t=0$  the correlation function starts out as  $i$ . As  $\langle 2|$  develops in time it gradually goes over into  $\langle 10|$ , completely so at a time we call  $\bar{t}$ , so that  $i\theta\langle 2|20\rangle=0$  at  $t=\bar{t}$ . Then  $\langle 2|$  goes back, this time to  $-\langle 20|$  and  $i\theta\langle 2|20\rangle=-i$  at  $t=2\bar{t}$  and so on. The  $\omega'$  transform has poles at  $\pm\beta$  which is equivalent to

$$i\theta\langle 2|20\rangle = \text{const. } e^{i\beta t} + \text{const.}' e^{-i\beta t}$$

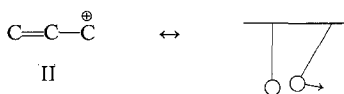
From the residues we should find also  $\text{const.} = \text{const.}'$  whence

$$i\theta\langle 2|20\rangle \sim \cos\beta t$$

and the circular frequencies for  $\langle 2|$  are  $\omega' = \pm\beta$ . However the frequency for the resonance structure,  $[2]$  ( $[2]$  is more like the probability density corresponding to  $\langle 2|$ ) is  $-2\beta$ , because already at  $2\bar{t}$   $\langle 2|$  has returned to  $\langle 20|$  in magnitude, whence  $|2\rangle\langle 2|$  has returned to  $|20\rangle\langle 20|$ .

The positive frequency pole in the susceptibility is at  $-2\beta$ , not  $-\beta$ , which suggests that the time development of the density is what governs the susceptibility. In our formal theory this is associated with the appearance of the  $\omega_+$  and  $\omega_-$  transforms which give a frequency shift in the  $\omega'$  transform (the poles of which are the energy levels) so that the ground state has zero frequency.

Now a particular merit of the fluctuation-dissipation approach is that the underlying behaviour of the correlation functions is easy to visualize, as for example through the analogy with coupled pendula. Imagine two weakly coupled pendula in resonance, and start the one on the right swinging. This is like resonance structure II

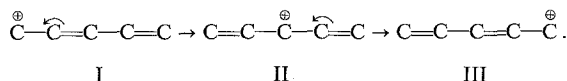


in that the locus of swinging may be taken as representing the location of the charge. In a time which may be compared with  $\bar{t}$ , only the left hand pendulum is found to be swinging, which would be linked with  $\langle 2|20\rangle \rightarrow 0$  as  $\langle 2| \rightarrow \langle 10|$  (and concomitantly  $\langle 2|10\rangle = 1$ ). The swinging motion returns to the right, and so on, and one evidently has a description of the charge moving back and forth with a certain period (and a certain frequency). The step in the calculation of  $\chi$  of taking the Fourier transform, which step represents the influence of the light as a driving force, may be considered as a device for identifying the period (or periods, if the system is multiply periodic); so that the very simple picture emerges of the susceptibility being greatest when the  $E$ -field of the light can best follow the charge.

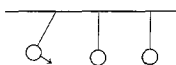


This is all unfortunately not as simple as we would hope because an analog computer of the behaviour of the correlation functions strictly applied would give us what might be called unphysical frequencies, like  $-\beta$  (and  $+\beta$ ) in the example above (i.e. the poles in the  $\omega'$  transform). Either we should need to investigate the Fourier transform of the behaviour of a correlation function times its complex conjugate (this would lead us to the physical frequency  $-2\beta$  in the example above) and find a suitable analog for this behaviour, or we should have to reconcile ourselves to the fact that the frequencies found in the pendulum analogy are really term values or energy eigenvalues in disguise, so that we would have to invoke the Bohr frequency condition before making predictions.

We shall be developing the first of these alternatives mathematically, but before doing so let us go on to an example of the usefulness of the pendulum analogy. We are to explore the relationship between the color of allyl cation (we found  $\omega = -2\beta$  in the previous section) and the next compound in a homologous series, with three principal resonance structures



The molecule cannot go from I to III without going through II ( $\omega_{13} \approx 0$ ). Now let us take a system of three pendula in a line, the left coupled to the center, and the center to the right, as representing this molecule. We may start the first pendulum swinging to represent I.



The time required for the second to capture the swinging motion would be comparable with the half-period found in the case of just two coupled pendula. Because of the nature of the coupling, not until the center pendulum is swinging would the locus of swinging be allowed to shift to the far right. Thus the half-period for the longest period in this multiply periodic system would be substantially longer than found in the previous case. The Fourier transform would have, correspondingly, a pole at a lower frequency. This is why the color of dyes becomes "deeper" (first absorption band red-shifts) as the length of the conjugate chain is increased. It takes longer for the charge to go from one end to the other and back<sup>5</sup>.

Many such applications may be envisaged; for example, a treatment of polarization direction in which it becomes obvious that the electric vector of the light has to be lined-up on the path of the migrating charge<sup>6</sup>. Another, perhaps unex-

<sup>5</sup> The usual way of approaching this problem via stationary states would require us to think about the normal modes of the coupled pendula; the reasoning as to how the normal modes would be affected, say, going from two to three pendula is not deemed to be as transparent as the reasoning above.

<sup>6</sup> This was recognized intuitively by Lewis, G. N., Calvin, M.: *Chem. Revs.* **25**, 273 (1939).

pected, example would be that of putting so-called concerted mechanisms in organic chemistry on a more rigorous quantum mechanical footing<sup>7</sup>.

### Transform of an Evolving Density

A dyadic such as  $|j\rangle\langle j|$  represents a resonance structure developing in time as a density matrix, and an expectation value enables one to select a given aspect – as for example the  $|k0\rangle$  aspect. Thus we seek the Fourier transform of

$$\theta\langle k0|j\rangle\langle j|k0\rangle = (-i\theta\langle k0|j\rangle)(i\theta\langle j|k0\rangle).$$

Using  $G = i\theta\langle j|k0\rangle$  we denote the transform thus

$$G^*G|_{\omega}.$$

By one of the convolution theorems, namely

$$FG|_{\omega} = \frac{1}{2\pi} f * g$$

where

$$f * g = \int_{-\infty}^{+\infty} f(s)g(\omega - s) ds$$

and

$$f = F|_{\omega} \quad g = G|_{\omega}$$

we have

$$2\pi G^*G|_{\omega} = (G^*)|_{\omega} * g.$$

(The  $g$  depends on  $j$  and  $k$  but we suppress this dependence.) This together with an identity

$$(G^*)|_{\omega} = (G|_{-\omega})^*$$

gives finally

$$2\pi G^*G|_{\omega} = (g_-)^* * g_+.$$

Here  $g_+$ , the positive frequency transform, is not the same as the one defined earlier ( $g^+$  involved  $\omega_N$ ) but is directly comparable with  $g(\omega')$  used earlier.

Now let us consider the spectral decomposition of the  $g$ 's. We shall here include the infinitesimal damping factor mentioned in connection with (8) so that in effect we are dealing with  $i\theta\langle j|k0\rangle e^{-\eta t}$  and its conjugate. The decompositions are

$$g_+ = \sum_{\mu} \frac{R_{\mu}}{\omega_{\mu} - \omega - i\eta}$$

together with

$$g_-^* = \sum_{\nu} \frac{R_{\nu}}{\omega_{\nu} + \omega + i\eta}.$$

<sup>7</sup> Concerted mechanisms have been used for a long time in organic chemistry to rationalize the appearance of certain products in reactions and rearrangements. What is manifestly involved is a switching of electron pairs – at the least a convenient book-keeping scheme. What is frequently tacitly assumed is that the switching takes place sequentially! For some contemporary examples refer to *Molecular Rearrangements, Part One*, ed. by Paul de Mayo, pages 304, 310, etc. New York and London: John Wiley and Sons 1963.

Then we may proceed to consider a partial contribution to the convolution involving  $N$  and a particular  $V$

$$(g_-)^* * g_+ = \frac{R_N}{\omega_N + \omega + i\eta} * \frac{R_V}{\omega_V - \omega - i\eta} \\ + \frac{R_V}{\omega_V + \omega + i\eta} * \frac{R_N}{\omega_N - \omega - i\eta} + \dots$$

The convolution integral would then be

$$R_N R_V \left[ \int_{-\infty}^{+\infty} \frac{ds}{(\omega_N + s + i\eta)(\omega_V - \omega + s - i\eta)} \right. \\ \left. + \int_{-\infty}^{+\infty} \frac{ds}{(\omega_V + s + i\eta)(\omega_N - \omega + s - i\eta)} \right].$$

The first integral has poles which may be schematically indicated thus

$$\frac{V}{N}.$$

Closing the contour in the upper half-plane gives a contribution from the  $V$  pole

$$\frac{2\pi i}{\omega_N + (-\omega_V + \omega + i\eta) + i\eta} = \frac{-2\pi i}{(\omega_V - \omega_N) - \omega - 2i\eta}.$$

The second integral has the  $N$  pole in the upper half-plane and the  $V$  pole in the lower. The  $N$  pole at  $s = -\omega_N + \omega + i\eta$  makes a contribution

$$\frac{2\pi i}{\omega_V - \omega_N + \omega + i\eta + i\eta} = \frac{2\pi i}{\omega_V - \omega_N + \omega + 2i\eta}.$$

The contribution to  $G^* G|_{\omega}$  involving  $N$  and all the  $V$  states is a sum. In the limit as  $\eta \rightarrow 0$

$$G^* G|_{\omega} = -i R_N \sum_V \left[ \frac{R_V}{(\omega_V - \omega_N) - \omega} - \frac{R_V}{(\omega_V - \omega_N) + \omega} \right] + \dots$$

The corresponding sum over  $V$  which is a factor in the expression for the ground-state susceptibility  $\chi$  as a spectral decomposition would be

$$\sum_V \left[ \frac{R_V}{(\omega_V - \omega_N) - \omega} + \frac{R_V}{(\omega_V - \omega_N) + \omega} \right].$$

The full sum which occurs in the Fourier transform of the density,  $G^* G|_{\omega}$ , differs from this in that there are terms involving  $V \rightarrow V'$  transitions, so to speak, and in the change in sign. Even so, the two expressions are much the same!

The appearance of  $V \rightarrow V'$  transitions has its counterpart in the pendulum analogy (see below). Thus an energy level pattern such as the following



would if probed by means of the pendulum analogy show a comparatively long period associated with the  $V \rightarrow V'$  transition. This could of course not be properly translated into a prediction of a low-frequency transition in the ordinary optical spectrum.

The change in sign is unimportant in the neighbourhood of a pole where the negative frequency term predominates. The reason for the change in sign probably involves the fact that the terms being considered in the Fourier transform of the density refer to absorption and stimulated emission both.

In the previous section we spoke of investigating the Fourier transform of a density, which has now been accomplished. We find, through the medium of the convolution integrals, that the frequencies are combination frequencies among the poles in the  $\omega'$  transform (i.e. among the energy levels, or term values) hence, the actual physical frequencies. To carry out the program envisaged in the previous section we should still need to develop a suitable analogy. The pendulum analogy is eminently suitable, for the following reasons. For a system of weakly-coupled identical pendula there is a high background-frequency,  $\omega_0$ , the value of which is unimportant, and in addition there are the small adjustments which arise from the coupling. Thus for two weakly coupled pendula with two normal modes we have circular frequencies:  $\omega_0 \pm \beta$ . The periods governing the locus of swinging which one finds by suitably displacing the system of coupled pendula and looking for repeats (or components of repetitive behaviour), are the reciprocals of the combinations among the frequencies of the various normal modes. For example, for two weakly coupled pendula with circular frequencies  $\omega_0 \pm \beta$  we have the combination frequency  $[(\omega_0 - \beta) - (\omega_0 + \beta)]/2\pi$  and corresponding period  $(-\chi\beta)^{-1}$ . To construct an analog in general one has to couple the pendula so that the classical adjustment frequencies match the (scaled) quantum mechanical term values. This one can accomplish by making the respective secular equations match.

A further conclusion from our examination of the Fourier transform of the density is that even the  $g(\omega')$ 's themselves may be considered as resembling Fourier transforms of the corresponding densities and vice versa — this provided that some sort of frequency shift procedure is introduced. One such procedure would be to use a Hamiltonian with the energies of the structures referred to the ground state, so that  $\omega_N = 0$ . (Another such procedure is the one already employed where the  $g(\omega')$ 's are adapted to give the partial susceptibilities through the use of (5) and (6).) If we should use a Hamiltonian which automatically takes care of the frequency shift, then the process of setting up and solving the coupled equations for  $g(\omega')$  (8) may be considered as referring not just to the correlation functions involved but in a sense also to the densities to which these correlation functions correspond. This is worth considering because of the intuitively appealing nature of the process for setting up the Eq. (8) — a process closely related to the scheme by which one proceeds from one resonance structure to another in writing down the lot of them. Pursuing the matter further we should find that when the Fourier transforms in the set of Eq. (8) are inverted, the new set looks very much like a set of coupled rate equations involving chemical species which can be converted one into another. The resemblance is not perfect owing to the presence of factors,  $\sqrt{-1}$ , which lead to oscillatory solutions.

### Appendix

We shall be treating a quantum mechanical system interacting with the radiation field considered classically – the radiation being turned on at  $t=0$ . The interaction will be taken, first, simply as

$$H_{\text{int}}(t) = \boldsymbol{\mu}(t) \cdot \mathbf{E}(t)$$

$$\mathbf{E}(t) = \theta(\bar{t} - t) f \cos \omega t$$

where  $\boldsymbol{\mu}(t)$  is a Heisenberg operator referred to the states of the system in the absence of an external field (interaction representation) and  $\theta$  is the Heaviside function. The response  $R$  is defined thus

$$R(\bar{t}) = \langle N\bar{t} | \boldsymbol{\mu}(\bar{t}) | N\bar{t} \rangle.$$

The linear response may be found using the abbreviated expansion

$$|N\bar{t}\rangle = |N0\rangle + i \int_0^{\bar{t}} H_{\text{int}}(t) |N0\rangle dt.$$

Taking  $\boldsymbol{\mu}$  parallel to  $\mathbf{E}$  for simplicity we find

$$R(\bar{t}) = if \langle N0 | \int_0^{\bar{t}} \theta[\boldsymbol{\mu}(\bar{t}), \boldsymbol{\mu}(t)] \cos \omega t | N0 \rangle dt.$$

Now we assume  $[\boldsymbol{\mu}(\bar{t}), \boldsymbol{\mu}(t)]$  depends only on the difference  $(\bar{t} - t)$  and is therefore the same as  $[\boldsymbol{\mu}(\bar{t} - t), \boldsymbol{\mu}(0)]$ . We call this difference  $\bar{t} - t = s$ . With  $s$  as the variable of integration the response becomes

$$R(\bar{t}) = if \langle N0 | \int_0^{\bar{t}} \theta[\boldsymbol{\mu}(s), \boldsymbol{\mu}(0)] \cos \omega(\bar{t} - s) | N0 \rangle ds$$

or, making use of  $\theta$  to extend the lower limit, and incorporating a trigonometric identity

$$= if \langle N0 | \int_{-\infty}^{\bar{t}} \theta[\boldsymbol{\mu}(s), \boldsymbol{\mu}(0)] (\cos \omega \bar{t} \cos \omega s + \sin \omega \bar{t} \sin \omega s) | N0 \rangle ds.$$

This has the conventional form of a following response plus a phase-shifted response

$$\chi'(\bar{t}) f \cos \omega \bar{t} + \chi''(\bar{t}) f \sin \omega \bar{t}$$

where

$$\chi'(\bar{t}) = i \langle N0 | \int_{-\infty}^{\bar{t}} \theta[\boldsymbol{\mu}(s), \boldsymbol{\mu}(0)] \cos \omega s | N0 \rangle ds,$$

$$\chi''(\bar{t}) = i \langle N0 | \int_{-\infty}^{\bar{t}} \theta[\boldsymbol{\mu}(s), \boldsymbol{\mu}(0)] \sin \omega s | N0 \rangle ds.$$

If we had used  $if \sin \omega t$  as the driving field we should have found

$$\chi' if \sin \omega \bar{t} - \chi'' if \cos \omega \bar{t}.$$

Thus for a driving field  $f e^{i\omega t}$

$$\begin{aligned} R(\bar{t}) &= \chi' f e^{i\omega t} + \chi'' (f \sin \omega \bar{t} - i f \cos \omega \bar{t}) \\ &= (\chi' - i\chi'') f e^{i\omega t}. \end{aligned}$$

With this result we may define a dipole susceptibility

$$R/E = R/f e^{i\omega t} = \chi' - i\chi'' \equiv \chi^*$$

in which case we have for the conjugate ( $\chi$  of the text)

$$\chi = \chi' + i\chi'' = i \langle N0 | \int_{-\infty}^{\bar{t}} \theta[\boldsymbol{\mu}(s), \boldsymbol{\mu}(0)] e^{i\omega s} | N0 \rangle ds.$$

If the commutator permits extension of the  $\bar{t}$  limit to  $+\infty$ , as we shall assume, and using  $t$  in place of  $s$ , we have the Fourier transform

$$\chi = i\theta \langle N0 | [\boldsymbol{\mu}(t), \boldsymbol{\mu}(0)] | N0 \rangle \Big|_{\omega}.$$

### References

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