ON THE THEORY OF
RESONANT SCATTERING

with applications to radiationless transitions
in organic molecules and photoelectron spectroscopy

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STELLINGEN

I

Het bewijs van Morse en Feshbach van de algemene vorm van de Green's operator behorende bij een niet-Hermitische operator vergelijking is slechts geldig als geen degeneraties in de eigenwaarden van de niet-Hermitische operator voorkomen.

P.M. Morse, H. Feshbach, Methods of theoretical physics I
(Mac Graw Hill, 1953) p. 884

II

Ten gevolge van de voorafgaande stelling is de behandeling door Levine van interne excitatie van moleculen bij botsingen onjuist.

R.D. Levine, Quantum mechanics of Molecular Rate processes,
(Oxford, 1969) p. 187

III

De afleiding door Robinson van de waarschijnlijkheid per eenheid van tijd van een stralingsloze overgang in een geëxciteerd molecuul dat geen interactie heeft met zijn omgeving is aan bedenkingen onderhevig.

G.W. Robinson, J. Chem. Phys. 47, 1967 (1967)

IV

De conclusie van Baker, Betteridge, Kemp en Kirby uit hun vergelijkend onderzoek van de ionizatiepotentialen van furaan, isoxazool, pyrrool en pyrrazool om de invloed van een stikstof-atoom met een lone-pair op het π -electronensysteem te bepalen, is slechts dan correct, wanneer het stikstof lone-pair een grotere attractie ondervindt van een naburig zuurstof atoom dan van een koolstof atoom, waaraan een waterstof atoom verbonden is. Het verschil is van de orde 1.5 eV.

A.D. Baker, D. Betteridge, N.R. Kemp, R.E. Kirby,
Chem. Comm. 286 (1970)

V

De argumenten, waarop Joussot-Dubien en Houdard-Pereyre concluderen dat de photochemische ringopening van pyridine verloopt via een n- π^* aangeslagen toestand zijn niet in overeenstemming met de experimentele resultaten van Wilzbach.

K.E. Wilzbach, D.J. Rausch, J.A.C.S. 92, 2178 (1970)
J. Joussot-Dubien, J. Houdard Pereyre,
Bull. Soc. Chim. de France 8, 2619 (1969)

VI

De methode van Anderson voor de nitrering van azuleen met Cu-nitraat in azijnzuuranhydride heeft meer toepassingsmogelijkheden dan valt af te leiden uit de opmerkingen van Keller en Heilbronner.

W. Keller-Schierlein in E. Heilbronner en D. Ginsberg,
Non-Benzenoid compounds (1959)

VII

De opmerking van Vilesov en Akopyan dat bij de ionizatie van benzeen in de buurt van de ionizatie-drempel sprake is van emissie van een electron, dat vervolgens weer wordt ingevangen door hetzelfde ion, is op zichzelf niet zinvol. Het voorkomen hiervan impliceert echter dat interferentie optreedt tussen directe en auto-ionizatie, wat het door hen gevonden minimum in de photo-ionizatie cross-sectie kan verklaren

F.E. Vilesov, M.E. Akopyan in B.S. Neporent.
Elementary photoprocesses in molecules (consultant-bureau New York 1968)
pag. 31.

VIII

De keuze van het roterende coordinatenstelsel voor de berekening van de energie van het H_2 molecuul van Kolos en Wolniewicz en die voor de berekening van de verstrooiing van twee atomen aan elkaar van Smith verschillen slechts hierin dat de hoeken θ en ϕ van Smith gelijk zijn aan $\frac{\pi}{2} - \theta_k$ en $- \phi_k$, waar θ_k en ϕ_k de hoeken in het poolcoordinatenstelsel zijn van Kolos en Wolniewicz.

W. Kolos, L. Wolniewicz, Rev. Mod. Phys. 35, 473 (1963)
F.T. Smith, Phys. Rev. 179, 111 (1969)

IX

De berekening van Buckingham, Orr en Sichell over de hoekafhankelijkheid van electronen geemitteerd bij photo-ionizatie van moleculen is aanvechtbaar.

A.D. Buckingham, B.J.Orr, J.M. Sichell, Phil. Trans. Roy. Soc. Lond. A 268, 147 (1970)

X

Bij het gebruik van verstrekte plastic-folies om het dichroïsme van erop aangebrachte moleculen te meten kan men het best eerst de folies verstrekken en vervolgens de kleurstof op het oppervlak brengen, aangezien dan gecorrigeerd kan worden op de eigenabsorptie van het folie.
Dit in tegenstelling tot andere hiertoe gebruikte methoden.

F. Dörr, Ang. Chemie 78, 457 (1966)

XI

Geloof en natuurwetenschap sluiten elkaar niet uit, maar raken elkaar in de creativiteit, zonder welke beide niet levensvatbaar zijn.

W. Pauli, C.G. Jung, Naturerklärung and Psyche (Rascher, Zürich 1952)
B. Russell, Mysticism and Logic (Allen and Unwin 1963)

XII

De huidige maatschappelijke problemen zullen dan slechts worden opgelost wanneer wordt ingezien dat zij qualitatief verschillen van die problemen welke er waren voor de opkomst van de moderne natuurwetenschap. Dit geldt speciaal voor het probleem van oorlog en vrede.

A. Szent-Györgyi, De krankzinnige aap (Bruna, Utrecht 1970)

XIII

Het is een merkwaardige coincidentie dat de nummers van de eerste pagina's van twee artikelen door dezelfde auteur in hetzelfde tijdschrift over hetzelfde onderwerp, dezelfde zijn, als het getal van het jaar dat zij gepubliceerd zijn.

G.W. Robinson, R.P. Frosch, J.Chem. Phys. 37, 1962 (1962)
G.W. Robinson, J. Chem. Phys. 47, 1967 (1967)

R.A. van Santen Leiden, 21 april 1971

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
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CONTENTS

CHAPTER I

GENERAL INDRODUCTION

Examples of resonant scattering.

Let us consider an experiment in which a beam of low-energy electrons (0-20 eV) penetrates into a collision chamber with gaseous molecules of very low pressure. Most of the electrons will pass the collision chamber undisturbed but a part will suffer collisions which may lead to a deviation from its original direction without loosing energy or collisions which lead to energy-transfer to the molecule.

As a quantity to characterize these collisions one introduces the concept of cross-section, with dimensions of an area. Studying the cross-section as a function of the kinetic energy of incoming electrons maxima may appear at particular energies, which indicate the formation of transient negative ions (1). One way of thinking about these transient negative ions is to consider them as the result of the capture of an electron in one of the empty orbitals of the molecule. The resulting negative ion states will be unstable and decay into a molecule and an electron.

The negative ion state will only be formed if the energy of the electron before collision matches the energy of the, nearly discrete, negative ion state. This makes the strong energy-dependence of the cross-section understandable and one sees that in addition to the cross-section the decay-time is a second characteristic.

If energy-conditions are favourable the negative ion-state can be considered as the capture of the electron by an excited molecule. After the decay of the negative ion the molecule may remain in its groundstate or in one of its excited states. Not only electronic states but also vibrational and rotational states may be excited (2).

All these processes are examples of resonant scattering. One speaks of an isolated resonance if only one single state of the compound particle formed by target and scattered particle is involved. If several states of the compound particle cooperate in the scattering process one speaks of overlapping resonances. This may occur when several excited states of the negative ion differ little in energy. They can occur, for instance, when vibrational states are excited. Extensive experimental work on the scattering of low-energy electrons by molecules naturally made feel the need of a deeper understanding the phenomena of resonant scattering. This was the primary aim of this thesis.

Aspects of resonant scattering.

In the case of an isolated resonance the cross-section behaves Lorentzian as a function of energy and the corresponding decay of compound state is purely exponential. In the case of overlapping resonances, however, peculiar effects may occur. The decay can not only be modulated by oscillations but also by terms linear in powers of the time variable.

In chapter II a theory is presented which treats the corresponding behaviour of cross-section in detail and also of the third quantity which characterizes the resonant process the time delay. The time delay is the time between the instant a particle hits a target and the moment it leaves it. It appeared that no theory of resonant scattering existed which unified the time-dependent properties (decay and time delay) and the time-independent one (cross-section). The treatment, given in chapter II, leads to such an unifying theory and the existing time-independent and time-dependent theories follow directly from it.

Radiationless transitions.

A nice illustration of the effects of overlapping resonances is provided by the process of radiationless transitions in organic molecules, which are treated in chapter III. Here a photon is captured by a molecule and the excited molecular-state decays. When the possibility of radiationless transitions is present the resulting excited state of the molecule must be considered as a superposition of many vibrational states. The effect is a much smaller decay-time than when

there is no interaction with the vibrations. This can be interpreted as the dissipation of excitation-energy into vibrational states of the molecule.
The deviations of purely exponential decay which can occur when radiationless transitions are present and when excitation of more than one state is possible show the many kinds of time-dependence which can occur in the case of overlapping resonances.

Photoionization.

Absorption of a photon may also lead to the ionization of the molecule.
When the molecule is first excited into a discrete state and an electron is then emitted the process is called auto-ionization. This is also an example of resonant scattering and is treated in chapter II.
When electrons are emitted by photoionization from atoms the angular distribution behaves as $A+B\cos^2\chi$. Here χ is the angle between the direction of polarized incident light and the direction the electron is measured and A and B are constants. Only dipole transitions are assumed to occur. The reason for this simple distribution is the spherical symmetry of the atoms. Therefore, when molecules which have no spherical symmetry are photoionized, deviations of this distribution may in general be expected. It appears, however, that in a number of cases the electrons emitted from molecules will have the same kind of distribution as those emitted from atoms (3). This is when the molecules can be considered as non-rotating but with an isotropic distribution of their orientations. Then, in fact, the spherical symmetry is present. In chapter IV the conditions under which this model will hold are derived. If in the photoionization process rotational excitation is not neglected the selection rules appear to differ from those which apply to rotational excitation associated with electronic excitation to discrete states.
The analysis of the photoionization process also yields a clear physical illustration of the concept of time delay.

References:

1. H.H. Brongersma, thesis Leiden (1968).
2. J.N. Bardsley, F. Mandl, Rep. Progr. Phys. 1968, 471.
3. J.C. Tully, R.S. Berry, B.J. Dalton, Phys. Rev. 176, 95 (1968).

CHAPTER II

ON THE THEORY OF RESONANT SCATTERING

An unified description of the evolution of quantum mechanical systems in time is still an intriguing goal in the theory of time-dependent phenomena. An attempt has been made to develop such a theory to provide an explanation of a variety of physical and chemical processes.

Some examples of such processes are:

an atom emitting light (1), auto-ionization of atoms (2),

the collision of an electron with a molecule and the formation of an intermediate state (3,4), the dissipation of electronic energy by radiationless transitions in molecules (5), predissociation (6), unimolecular reactions (7) and last but not least the scattering of molecules by molecules via an intermediate complex (8,9), an elementary event in a chemical reaction (10).

Part of these processes can be considered as examples of resonant scattering; i.e., they proceed via the formation and subsequent breakdown of one or more transient states. The other processes can be considered as examples of systems which are prepared in an unstable state which will then decay.

Typical quantities whose behaviour can be used to characterize resonant scattering are (12):

time delay, which gives the timelapse between asymptotic states (18) and

cross-section, which gives information on the spread in energy of scattered or emitted particles.

The unstable state is characterized by its

decay-time, which in the case of exponential decay has a simple meaning

and equals the inverse of the decay rate.
In this study the time delay is simply the lifetime of a virtual state formed by the colliding systems and is directly related to the rate of decay of this state (18). It is therefore possible to describe the two processes within the same formalism*) as will be shown.
The study of the above mentioned quantities has received a new stimulus by the development of ingenious novel experimental techniques during the last twenty years.

The complicated situation of multi-resonance is often seen in molecular systems. The reason is that it is necessary to consider transitions between many states rather than just between two. For example, a transition between two electronic states is practically always modified by simultaneous transitions between a large number of vibrational and rotational states. Therefore, emphasis has been placed on the problem of many overlapping resonances.

The development of the theory has largely profitted from the work of theoretical physicists, who have demonstrated the power of the concept of resonant scattering in nuclear physics (13). In studying the extensive literature it appeared that existing time-independent theories can be traced to three different resonance theories. One was proposed by Feshbach (14), an other by Fano (2), and the third by Kapur and Peierls (15). They concentrated on calculating the cross-section of resonant scattering processes. The two first authors use boundary-conditions of the wave function on an infinite distance from the target. The third theory uses boundary conditions on a sphere with finite radius around the target. It will be shown that the two first theories can be formulated as special cases of a more general theory. This is not possible for Kapur and Peierls' theory, since there boundary conditions are used on a sphere of finite radius around the target. This type of boundary conditions is incompatible with the theory to be presented**). It has been observed that the starting point and formal results of Feshbach's and Fano's theories are equivalent (9, 17), but a further analysis reveals important differences.

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*) Recently W. Kerkes (11) developed a theory on the time-dependence of particles, emphasizing the scattering character of these processes. This is in concordance with the theory to be presented here.

**) Applications of the theory of Kapur and Peierls can be found in ref. (16)

In the development of this theory significant differences in both theories will occasionally be pointed out. This will provide a key to the understanding of complications which occur in the case of multi-resonance. It will appear that the effect of overlapping resonances can be made explicit using Feshbach's method, whereas in Fano's method these effects are implicitly dealt with. To study the time-development one can use the eigenfunctions given by the above theories to solve the time-dependent Schrödinger equation.

The derivation is started directly with the time-dependent Schrödinger equation so as to derive the expression which gives the time-dependence of the resonant process in a completely general way. The method used is closely related to the existing time-dependent theories of Heitler (1), Messiah (12) and Goldberger and Watson (18), designed to study the decay of an excited state.
The stationary properties of the process are then derived by using the procedures known from scattering theory to convert the time-dependent theory to a time-independent one (10).
It is only at this stage of the derivation that the eigenfunctions of the total Hamiltonian appear.
The conceptual advantage of this method is that it shows the essential part which the initial condition plays. In addition, the correspondence between stationary and non-stationary properties becomes very clear and the equations from which the time-dependence of the processes is to be derived are more easy to solve than those occurring in the first method. Application of this very general formalism to the problem of multi-resonance leads to an important new condition which, when not satisfied, can result in not only a non-exponential but also to a non-oscillatory time decay. This behaviour appears to be connected with a time delay which is predicted to be pulsed.

An expression for the auto-ionization in the case of multi-resonance, which is a generalization of the famous result of Fano (2) for one resonance, is also presented. A number of known results are shown to follow as a specialization from the theory giving connections not previously recognized.

II.1 Ground work

A derivation is proposed which converts the time-dependent non-relativistic Schrödinger equation:

$$i \frac{\partial}{\partial t} \psi(t) = H\psi(t) \qquad (\hbar=1,\ H=H^{\dagger}) \tag{1)}$$

by a Laplace-transform (19) to the time-independent Laplace-transformed equation 2) incorporating the initial condition at t':

$$(z-H)\,\bar{\psi}(z) = i\,e^{izt'}\,\psi(t') \tag{2)}$$

Here $\bar{\psi}(z)$ is the Laplace-transform of $\psi(t)$:

$$\bar{\psi}(z) = \int_{t'}^{\infty} e^{izt}\,\psi(t)\,dt \tag{3)}$$

The solution of 2) is given by:

$$\bar{\psi}(z) = \frac{i}{z-H}\,e^{izt'}\,\psi(t') = iG(z)\,e^{izt'}\,\psi(t') \tag{4)}$$

where $G(z) = \dfrac{1}{z-H}$

$\psi(t)$ is recovered by taking the inverse Laplace-transform:

$$\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\,G(z)\,\psi(t')\,dz \qquad t>t' \tag{(5)}$$

$$= 0 \qquad t<t'$$

Here $i\eta$ has to be taken above the singularities of $G(z)\,\psi(t')$.
If it is desired to calculate the state with reversed causality conditions we find:

$$\psi(t) = -\frac{1}{2\pi i}\int_{-\infty-i\eta}^{+\infty-i\eta} dz\ e^{-iz(t-t')}\,G(z)\,\psi(t')\,dz \qquad t<t' \tag{6)}$$

$$= 0 \qquad t>t'$$

The following Laplace-transform is now applied:

$$\overline{\psi}(z) = \int_{-\infty}^{t'} e^{izt}\,\psi(t)\,dt \qquad 7)$$

In the case of formula 5) the problem is to determine the resolvent G(z). The extended Hilbert-space is divided into two parts with the projection-operators P and Q, which are not specified at the moment except for their properties 9). It must be remembered that hereafter, P will project on the continuous states and Q on the discrete states of a certain operator. The reason that this division is useful is that the initial condition of 1) can be formulated as:

$$P\psi(t') = \psi(t') \text{ and } Q\psi(t') = 0 \qquad 8)$$

The division is not new, for Messiah used the same method. He, however, projects on only one (unstable) discrete state and therefore loses the interference effects which may occur in the case of many discrete states. The projection-operators P and Q satisfy the relationships:

$$P + Q = 1;\; P = P^{\dagger};\; Q = Q^{\dagger};\; Q^2 = Q;\; P^2 = P;\; PQ = QP \quad 9)$$

It is only necessary to give the relationships:

$$P + Q = 1;\; P = P^{\dagger};\; P^2 = P \qquad 10)$$

Using $G^P(z)$ and $G^Q(z)$ which are given by the definitions:

11a) $G^P(z) = P\,\frac{1}{z - H}\,P$ c) $G^{PQ}(z) = P\,\frac{1}{z - H}\,Q$

b) $G^Q(z) = Q\,\frac{1}{z - H}\,Q$ d) $G^{QP}(z) = Q\,\frac{1}{z - H}\,P$

the behaviour of $P\psi(t)$ and $Q\psi(t)$ in time can be derived. Using initial conditions 8) it is seen that:

$$P\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\; e^{-iz(t-t')}\; G^P(z)\;\psi(t') \qquad 12a)$$

$$Q\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\ G^{QP}(z)\,\psi(t') \qquad \text{12b)}$$

If instead of taking 8) as initial conditions the initial conditions $P\psi(t') = 0;\ Q\psi(t') = \psi(t')$ are taken, it is observed that:

$$P\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\ G^{PQ}(z)\ \psi(t') \qquad \text{12c)}$$

$$Q\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\ G^{Q}(z)\ \psi(t') \qquad \text{12d)}$$

The interpretation of equation 12a) is as follows: when one starts with a $\psi(t')$ given in the P projected part of the extended Hilbert space, to calculate the P projected part of the time-development of $\psi(t)$ one has to work on it with the evolution-operator:

$$U_{PP}(t-t') = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\ G^{P}\ (z) \qquad \text{13a)}$$

To calculate the time-development of the projected part of $\psi(t)$ in the extended Hilbert space orthogonal to the initial condition, one has to work on $\psi(t')$ with the evolution-operator:

$$U_{QP}(t-t') = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')}\ G^{QP}(z) \qquad \text{13b)}$$

The procedure to follow is to now calculate $G^{P}(z)$, $G^{Q}(z)$, $G^{QP}(z)$ and $G^{PQ}(z)$ using the method of Messiah (12) and Harris (6). The poles are determined after having specified P and Q and then the Cauchy-integral method is used to calculate 12). The result is then applied to a calculation of the characteristic properties of the resonant system.

II.2 Derivation of the general formulae

H is divided into two parts:

14) $H = H_d + H^n$, where

15a) $H_d = PHP + QHQ$ the diagonal part

b) $H^n = PHQ + QHP$ the non-diagonal part

The following operator-relations are used:

16a) $\frac{1}{z-H} = \frac{1}{z-H_d} + \frac{1}{z-H_d} H^n \frac{1}{z-H}$

b) $\frac{1}{z-H} = \frac{1}{z-H_d} + \frac{1}{z-H} H^n \frac{1}{z-H_d}$

c) $G^{QP}(z) = G^Q(z) H^n P \frac{1}{z-H_d} P$

d) $G^{QP}(z) = Q \frac{1}{z-H_d} QH^n G^P(z)$

e) $G^{PQ}(z) = G^P(z) H^n Q \frac{1}{z-H_d} Q$

f) $G^{PQ}(z) = P \frac{1}{z-H_d} PH^n G^Q(z)$

Using also 9) and 10) the following formulae are derived:

17a) $G^P(z) = P(z - PHP - PH^nQ \frac{1}{z-H_d} QH^nP)^{-1}P$

b) $\quad = P \frac{1}{z-H_d} P \; (1 + PH^n G^Q(z) H^n P \frac{1}{z-H_d} P)$

c) $\quad = P \frac{1}{z-H_d} P \; (1 + PH^n Q \frac{1}{z-H_d} QH^n G^P(z))$

d) $G^Q(z) = Q(z - QH_dQ - QH^nP \frac{1}{z-H_d} PH^nQ)^{-1}Q$

e) $\quad = Q \frac{1}{z-H_d} Q \; (1 + QH^n G^P(z) H^n Q \frac{1}{z-H_d} Q)$

f) $\quad = Q \frac{1}{z-H_d} Q \; (1 + QH^nP \frac{1}{z-H_d} PH^n G^Q(z))$

Formulae d, e, f can be derived from a, b, c by interchanging P and Q. The spectral representation of H_d is in general:

18a) $$H_d = \sum_{\gamma} \int_{E\gamma} dE\ \psi_\gamma(E) > E < \psi_\gamma(E) + \sum_{i,\gamma} \psi_{i,\gamma} > E_i < \psi_{i,\gamma}$$

b) $$<\psi_\gamma(E) \mid \psi_{\gamma'}(E') > = \delta_{\gamma\gamma'}\, \delta(E-E') ; \quad c) < \psi_{i,\gamma}\, \psi_{i',\gamma'} > = \delta_{ii'}\, \delta_{\gamma\gamma'}$$

d) $$<\psi_\gamma(E) \mid \psi_{i,\gamma'} > = 0$$

It is proposed to describe the phenomenon of a resonance as a discrete state made unstable by coupling with the continuous states. For discrete states $\psi_{i,\gamma} >$ is chosen and for continuous states $\psi_\gamma(E) >$.

The discrete states are made unstable by coupling with the continuous states by the operator H^n. Note that $\psi_\gamma(E) >$ and $\psi_{i,\gamma} >$ are not eigenstates of H!

The following choice is made for P and Q ***):

19a) $$P = \sum_{\gamma} \int_{E_\gamma} dE\ \psi_\gamma(E) > < \psi_\gamma(E)$$

b) $$Q = \sum_{i,\gamma} \psi_{i,\gamma} > < \psi_{i,\gamma}$$

This choice selects in 17) the forms to be chosen for $G^P(z)$ and $G^Q(z)$ in 12). For the initial conditions: $P\psi(t') = \psi(t')$; $Q\psi(t') = 0$ one chooses:

20a) $$P\psi(t) = -\frac{1}{2\pi i} \int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')} P \frac{1}{z-H_d} P(1+PH^n G^Q(z) H^n P \frac{1}{z-H_d})\, \psi(t')$$

b) $$Q\psi(t) = -\frac{1}{2\pi i} \int_{-\infty+i\eta}^{+\infty+i\eta} dz\ e^{-iz(t-t')} G^Q(z) H^n P \frac{1}{z-H_d} P\psi(t')$$

***) In practice first the projection-operators are defined, and then H^d, see ref. (3).

For the other conditions: $P\psi(t') = 0$; $Q\psi(t') = \psi(t')$ one chooses:

$$\text{c)}\quad P\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\; e^{-iz(t-t')}\,P\frac{1}{z-H_d}PH^nG^Q(z)\,\psi(t')$$

$$\text{d)}\quad Q\psi(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\; e^{-iz(t-t')}\,G^Q(z)\,\psi(t')$$

In the above formulae $G^Q(z) = Q(z-QH_dQ-QH^nP\frac{1}{z-H_d}PH^nQ)^{-1}Q$. This is formula 17d).

$O(z)^{-1}$ is defined as:

$$O^{-1}(z) = (z-QH_dQ - QH^nP\frac{1}{z-H_d}PH^nQ)^{-1} \qquad 21)$$

Formulae 20) are in a suitable form for the calculation of the desired physical quantities. Formula 17b) in 20a); formula 16c) in 20b); formula 16f) in 20c) and formula 17d) in 20d) have been chosen. The reason for those choices is that it was desired to use formula 17d) in all calculations for $G^Q(z)$ in order to avoid the use of formula 17a) for $G^P(z)$. This is because the choice of 19) can give for $QH^nP\frac{1}{z-H_d}PH^nQ$ a very slow z dependence, which we wish to use to calculate the inverse $O(z)^{-1}$, defined in 21) (20).

In the case where Q projects on one discrete state, 21) is precisely the formula that Messiah (12) used to calculate the decay-time of an excited state. O(z) itself can be found in the same form in the work of Feshbach (14) and Levine (10). In their work, O(z)=0 is the modified time-independent Schrödinger equation giving an effective Hamiltonian with a so-called optical potential. The choice of P here is however slightly different.

Formulae 17b) and c) and also 17e) en f) are new. Formulae c) and f) will not be used but b) is very suitable for the calculation of the cross-sections and time delay in the scattering problem. Formulae 16d) and 17d) can be found in the work of Mower (21) as well as in that of Goldberger and Watson (18). One is interested in O(x), for in evaluating 20) it is possible to take lim $\eta \to 0$, because $\frac{1}{z-H}$ has only poles along the real axis. Equation A8) of the appendix A gives for the matrix $O^{-1}(x)$ in the basis Q:

$$O^{-1}(x) = [x\ I - (E + \Delta(x)) + i\pi\Gamma(x)]^{-1} \qquad 22)$$

where the matrices $E, \Delta(x)$ and $\Gamma(x)$ are defined by A7) and I is unit matrix and $\Delta(x)$ and $\Gamma(x)$ are slowly x dependent.

To determine the matrix-elements of this inverse it is possible to apply Cramer's rule directly as in ref. (21) or to use a similarity transformation to bring first $O(x)$ to its most simple form. The last method has the advantage of giving the poles explicity, and it has been used for that reason.

The matrix E is diagonal and Δ and Γ are Hermitian. Attention is drawn to the relationship:

condition I: $$[E + \Delta(x), \Gamma(x)] = 0 \qquad 23)$$

When condition I is satisfied, $E + \Delta(x)$ and $\Gamma(x)$ can be diagonalized by the same unitary transformation.

When condition I is not satisfied, the matrix $O(x)$ is a general complex matrix so that the simplest form to which it can be brought by a similarity transformation is the Jordan-canonical form (22). Thus, when condition I is satisfied, the matrix-element O^{-1}_{ij} can be written:

$$O^{-1}_{ij}(x) = \sum_k U_{ik}(x) \frac{1}{x - F_k + i\pi\Lambda_k} U^{-1}_{kj}(x) \qquad 24)$$

where $U^{-1}_{ki}(x) = U^{*}_{ik}(x)$. When condition I is not satisfied, the matrix-element $O^{-1}_{il}(x)$ must be written as:

$$O^{-1}_{il}(x) = \sum_j \sum_{k=j}^{j+\nu_j} S_{ij} \frac{(-1)^{\nu^j_{k-1}}}{(x - a_j)^{\nu^j_k}} S^{-1}_{kl}\ ; \quad (k \geq j) \qquad 25)$$

For details of the derivation see appendix A. The matrix-elements S_{ij}

do not form an unitary matrix now, and $\nu^j_k = 1$ in case there are no degeneracies. a_j will consist of a real and an imaginary part whose general properties are given by A17).

The mathematical formalism is now developed well enough to discuss the physical aspects of the problem. In the next paragraph 3 the decay in time of an excited state will be studied and the modifications due to 25) of the behaviour usually found.

It is of interest to mention the recent papers of J. Jersak (23) and M. Simonius (24). The first author studying a system of n-interacting particles also used the Jordan-canonical form of a matrix, which inverse played a similar part as $O^{-1}_{ij}(x)$ in his calculation of time decay. The second author also derives the general form of this matrix by stressing the inaccuracy of the velocity of an unstable particle.

In § 4 the scattering problem is studied and the form of the wave function appropriate for the derivation of the transition-matrix is derived. Using a theorem proposed by Feshbach (15), two expressions for the Transition-matrix are derived. One expression is in terms of $E + \Delta$ and Γ and the other in terms of the so-called Resonance-Reactance operator. This result is very important because it provides a link between the results using 24) and 25) and the usual results in terms of the Resonance-Reactance operator. This not only clarifies the properties of the Transition-matrix but also gives a new kind of behaviour for the time delay, which was until now not predicted. After those derivations, it is possible to discuss the interference effects of many resonant states, where formula 25) plays an important role. Finally the connection between the proposed theory and the existing resonance theories of Fano and Feshbach is discussed.

II. 3. Decay-time

Equations 20c) and 20d) deal with the possibility of starting at t=t' with a discrete state. The decay of an arbitrary state ψ_i at t'=0 is now studied. In case condition I 23) is satisfied, it is possible to use 24) in 20) to give:

$$< \psi_i \mid Q\psi(t) > = \sum_k U_{ik} e^{-iF_k t - \pi\Lambda_k t} U^{-1}_{ki} \qquad 26)$$

It is assumed that the matrix-elements of U_{ik}, F_k and Λ_k are independent of x and finite; for details see (12, 18, 20, 21). In these references it is shown that this assumption permits one to neglect terms which behave like $t^{-3/2}$ or to higher negative order. This implies that this formula and 29) should not be used for very short times.****)

The functions $\psi_{\gamma,i}(E)$ must not describe resonant scattering. Furthermore only terms for which $\Lambda_k > 0$ contribute to 26) and 30). Then the solution $Q\psi(t)$ will have only a physical significance and the contour of the integration can take care of it. In the case where $E+\Delta$ and Γ are diagonal in the basis ψ, it is seen that:

$$<\psi_i|Q\psi(t)> = e^{-iF_i t-\pi\Lambda_i t} \qquad 27)$$

Equation 27) is a well known result yielding a purely exponential decay of ψ_i:

$$|<\psi_i|Q\,\psi(t)>|^2 = e^{-2\pi\Lambda_i t} \qquad 28)$$

In the case where ψ_i is not an eigenfunction of $E + \Delta$ and Γ deviations of the purely exponential decay occur. For example when there are only two eigenvalues whose Λ's are the same and when the matrix-elements U_{ik} are real one finds:

$$|<\psi_i|Q\psi(t)>|^2 = e^{-2\pi\Lambda t}\{a + b\cos(F_1-F_2)t\} \qquad 29)$$

where: $a = (U_{i1}U_{1i}^{-1})^2 + (U_{i2}U_{2i}^{-1})^2$

$b = U_{i1}U_{1i}^{-1}U_{i2}U_{2i}^{-1}$

An exponential decay is seen which is modulated by a cosine with a frequency given by the energy-difference.

In case of different Λ's and U_{ik} complex, a sum of exponential decaying

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****) Problems of renormalization and divergencies in the self-energy are evaded by those assumptions. They are treated in more detail in ref. (18, 20).

terms is found modulated by sine as well as cosine terms. An example of the so-called quantum-beats phenomenon (25) occurs here. In case condition I is not satisfied one must use 25) and one finds:

$$<\psi_i|Q\psi(t)>= \sum_j \sum_{k=j}^{j+\nu_j} S_{ij} \frac{(-it)^{\nu_k^j-1}}{(\nu_k^j-1)!} e^{-ia_j t} S^{-1}_{ki} \; ; \; (k\geq j) \; ; \; a_j = F_j - i\pi\Lambda j \qquad 30)$$

When there is only one discrete state 30) reduces to 27). In case there are two discrete states and $a_1 \neq a_2$, the behaviour will be as in 29). However, if $a_1 = a_2$ one sees:

$$|<\psi_i|Q\psi(t)>|^2 = e^{-2\pi\Lambda t}\{|S_{i1}|^2|S_{1i}^{-1}|^2 + |S_{i2}|^2|S_{2i}^{-1}|^2 + \qquad 31)$$

$$+ i(S^*_{i1}S_{2i}^{-1} - S_{i1}S^{*\,-1}_{2i})t + |S_{i1}|^2|S_{2i}^{-1}|^2 t^2\}$$

The coefficients of the powers of t are real, as expected.

In 31) a third kind of time-dependence is observed. In the two-state problem considered there an exponential decay modified by a power series in t up to t^2 is seen.

In ref. (21, 26) the time-dependence of a resonant two-state problem is also investigated and the possibility of the same kind of time-dependence is derived. In ref. (21) Cramer's rule is used to determine the inverse 22) and in ref. (26) use is made of Fano's theory. We have seen how here their results appear as a specialization of the proposed general formula 30).

To summarize, the new results of this section indicate that a non-exponential decay is possible, where this deviation from exponential decay is a finite power series in t, if condition I is not satisfied and the values a_j are degenerate. The highest possible power of the series in t is given by $2(m-1)$, where m is the degeneracy of a_j.

II.4. The scattering problem

$\psi_\gamma(E')$ has to satisfy boundary conditions at an infinite distance of target and scattered particle, such that when $t' \longrightarrow -\infty$ a wave packet formed from $\psi_\gamma(E')$ states will represent the particle without interaction with the target before scattering.
S. Sunakawa (27) has made a careful study to show that in scattering theory a wave packet may be used of an infinitely small width when $t' \longrightarrow -\infty$. He derives the correct boundary conditions for the Green's functions in the scattering equations by studying the transition from a finite to an infinite small width.
Therefore it is possible to take as initial condition:

$$\psi(t') = \psi_{\gamma'}(E')e^{-iE't'} \qquad 31)$$

One substitutes 31) into 20^{a}) and 20^{b}) and uses 19); giving:

$$P\psi_{\gamma'}(t) = -\frac{1}{2\pi i}\,\psi_{\gamma'}(E')> \int_{-\infty+i\eta}^{+\infty+i\eta} dz\,\frac{e^{-iz(t-t')}}{z-E'}\;e^{-iE't'} + \int_{-\infty+i\eta}^{+\infty+i\eta} dz\;e^{-iz(t-t')}$$

$$\sum_{\gamma''}\int_{E_{\gamma''}} dE\,\frac{\psi_{\gamma''}(E)><\psi_{\gamma''}(E)}{z-E}\,H^n\,[O(z)]^{-1}H^n\psi_{\gamma'}(E')>\frac{e^{-iE't'}}{z-E'} \qquad 32a)$$

and

$$Q\psi_{\gamma'}(t) = -\frac{1}{2\pi i}\int_{-\infty+i\eta}^{+\infty+i\eta} dz\;e^{-iz(t-t')}\,Q\,[O(z)]^{-1}H^n\,\psi_{\gamma'}(E')>\frac{e^{-iE't'}}{z-E'} \qquad 32b)$$

A new function, $\Phi_\gamma(E')$ is defined by the relations:

$$Q\,\Phi_\gamma(E') = \lim_{t-t' \to \infty} e^{iE't}Q\,\psi_\gamma(t) \qquad 33a)$$

$$P\,\Phi_{\gamma}(E') = \lim_{t-t'\to\infty} e^{iE't}P\,\psi_{\gamma}(t) \qquad 33b)$$

$e^{iE't}Q\psi_{\gamma}(t)$ will be first considered. In this expression, $Q\psi_{\gamma}(t)$ describes the behaviour of the discrete states in time. According to 32b) the integral over z has contributions from the singularities of $[O(z)]^{-1}$ which gives a time-dependence like 26) and 30) and a contribution from the singularity of $(z-E')^{-1}$. When one now multiplies by $e^{iE't}$ and examines the result for times large as compared with the decay-times, only the contribution from the last singularity remains, therefore:

$$Q\Phi_{\gamma'} = Q[O(E')]^{-1}H^{n}\psi_{\gamma'}(E')> \qquad 34)$$

In 32a) the first term is integrated giving an unaltered wave. The second term has contributions of two kinds of singularities which are similar to those encountered in 32b)

The contribution of $\sum_{\gamma''}\int_{E_{\gamma''}} dE\,\frac{|\psi_{\gamma''}(E)><\psi_{\gamma''}(E)|}{z-E}$ to 33b) will vanish[†].

After multiplying $P\psi_{\gamma}(t)$ with $e^{iE't}$ the result is calculated again for times large as compared with the decay-times and given by:

$$P\Phi_{\gamma'}> = \psi_{\gamma'}(E')> + \lim_{\epsilon\to 0}\sum_{\gamma''}\int_{E_{\gamma''}} dE\,\frac{\psi_{\gamma''}(E)><\psi_{\gamma''}(E)}{E'-E+i\epsilon}\,H^{n}[O(E')]^{-1}H^{n}\psi_{\gamma'}(E')> \qquad 35)$$

In 34) and 35) the stationary states of scattering theory have been derived. This corresponds with experiments where one scatters with a beam of particles of well defined energy.

When t → ∞ the wavepacket formed from $\psi_{\gamma}(E)$ will contain, in general, a contribution from scattered waves. To calculate the cross-section, therefore, one must consider more than only the interaction of the continuous states with discrete states, which gives the contribution of resonant scattering. In general there is also the contribution of the direct scattering which is due to the difference between $PH_{d}P$ and H_{0}, where H_{0} describes

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[†] Direct calculation shows that it contributes due to branch-points with terms of order t^{-1}.

particle and target without interaction, and:

$$H_o|\xi_\gamma(E)\rangle = E|\xi_\gamma(E)\rangle \qquad 36)$$

The interaction causing the direct scattering is given by:

$$\underline{H'} = PH_dP - H_o \qquad 37)$$

It can be easily shown that:

$$\psi_{\gamma'}(E')\rangle = \xi_{\gamma'}(E')\rangle + \lim_{\epsilon \to 0} \sum_{\gamma''} \int_{E_{\gamma''}} dE \frac{\psi_{\gamma''}(E)\rangle\langle\psi_{\gamma''}(E)|}{E'-E+i\epsilon} \underline{H'}\, \xi_{\gamma'}(E')\rangle \qquad 38a)$$

$$= \xi_{\gamma'}(E')\rangle + \lim_{\epsilon \to 0} \sum_{\gamma''} \int_{E_{\gamma''}} dE \frac{\xi_{\gamma''}(E)\rangle\langle\xi_{\gamma''}(E)|}{E'+E+i\epsilon} \underline{H'}\, \psi_{\gamma'}(E')\rangle \qquad 38b)$$

These equations describe the direct scattering explicitly.
When use is made of the identity:

$$\sum_{\gamma'} \int_{E_{\gamma'}} dE \frac{|\psi_{\gamma'}(E)\rangle\langle\psi_{\gamma''}(E)|}{E_1-E+i\epsilon} = \sum_{\gamma'} \int_{E_{\gamma'}} dE \frac{|\xi_{\gamma'}(E)\rangle\langle\xi_{\gamma'}(E)|}{E_1-E+i\epsilon} +$$

$$+ \sum_{\gamma''\gamma'} \int_{E_{\gamma'}} dE' \int_{E_{\gamma''}} dE'' \frac{|\xi_{\gamma'}(E')\rangle\langle\xi_{\gamma'}(E')|}{E_1-E'+i\epsilon} \underline{H'} \frac{|\psi_{\gamma''}(E'')\rangle\langle\psi_{\gamma''}(E'')|}{E_1-E''+i\epsilon} \qquad 39)$$

and 38b) and 34) are substituted into 35) one observes:

$$P\Phi_\gamma\rangle = \xi_\gamma(E)\rangle + \lim_{\epsilon \to 0} \sum_{\gamma'} \int_{E_{\gamma'}} dE' \frac{\xi_{\gamma'}(E')\rangle\langle\xi_{\gamma'}(E')|}{E-E'+i\epsilon} \underline{H'}\, P\Phi_\gamma\rangle +$$

$$+ \lim_{\epsilon \to 0} \sum_{\gamma'} \int_{E_{\gamma'}} dE' \frac{\xi_{\gamma'}(E')\rangle\langle\xi_{\gamma'}(E')|}{E-E'+i\epsilon} H^n\, Q\Phi_\gamma\rangle \qquad 40)$$

This expression has a form which enables one to use conventional scattering theory (28) to find the transition matrix and time delay.

II.4a. The Transition-matrix

The differential cross-section is given by:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\gamma' \leftarrow \gamma} = \frac{k_{\gamma'}}{k_{\gamma}} \, |T_{\gamma' \leftarrow \gamma}(E)|^{2} \qquad 41)$$

In 41) k_{γ} is the relative momentum before scattering and $k_{\gamma'}$ the relative momentum afterwards and $T_{\gamma' \leftarrow \gamma}(E)$ is called the Transition-matrix.
From 40), one finds for this Transition-matrix:

$$42)\text{ a} \quad T_{\gamma' \leftarrow \gamma}(E) = <\xi_{\gamma'}(E)| \, \underline{H'} \, |P\Phi_{\gamma}(E)> + <\xi_{\gamma'}(E) \, | \, H^{n} \, | \, Q\Phi_{\gamma}(E)>$$

$$42)\text{ b} \quad = <\xi_{\gamma'}(E)| \, \underline{H'} \, |\psi^{+}_{\gamma}(E)> + <\psi^{-}_{\gamma'}(E) \, |H^{n} \, | \, Q\Phi_{\gamma}(E)>$$

Here $\psi^{+}_{\gamma}(E)$ is the function given by 38) and $\psi^{-}_{\gamma}(E)$ is given by

$$\psi^{-}_{\gamma}(E)> = \xi_{\gamma}(E)> + \lim_{\epsilon \to 0} \sum_{\gamma'} \int_{E_{\gamma'}} dE' \, \frac{\psi^{-}_{\gamma}(E')><\psi_{\gamma'}^{-}(E')|}{E-E'-i\epsilon} \, \underline{H'} \, \xi_{\gamma'}(E)> \qquad 43a)$$

$$= \xi_{\gamma}(E)> + \lim_{\epsilon \to 0} \sum_{\gamma'} \int_{E_{\gamma'}} dE' \, \frac{\xi_{\gamma'}(E)><\xi_{\gamma'}(E)|}{E-E'-i\epsilon} \, \underline{H'} \xi_{\gamma}^{-}(E)> \qquad 43b)$$

To derive 42b) from 42a) equation 34) has been substituted for $Q\Phi_{\gamma}$ into 35) giving:

$$P\Phi_{\gamma}(E')> = \psi_{\gamma}^{+}(E')> + \lim_{\epsilon \to 0} \sum_{\gamma''} \int_{E_{\gamma''}} dE \, \frac{\psi_{\gamma''}^{+}(E)><\psi_{\gamma''}^{+}(E)}{E'-E+i\epsilon} \, \Big| H^{n} \, Q\Phi_{\gamma}> \qquad 44)$$

This expression for $P\Phi_{\gamma}(E)$ is then substituted into 42a) and use is made of 43a). The essential result that the total Transition-matrix is a sum of the Transition-matrix of direct scattering and the one of resonant scattering*****) is found in 42b). The Transition-matrix of direct scattering is given by:

$$T^{d}_{\gamma' \leftarrow \gamma} = <\xi_{\gamma'}|\underline{H'}|\psi^{+}_{\gamma}> \qquad 45)$$

The Transition-matrix of resonant scattering is:

$$T^{R}_{\gamma' \leftarrow \gamma} = <\psi^{-}_{\gamma'}|H^{n}|\, Q\Phi_{\gamma}(E)> \qquad 46)$$

Using $Q\Phi_{\gamma}(E)$ is 34) and $O^{-1}(E)$ given in 22) it is possible to derive:

$$T^{R}_{\gamma' \leftarrow \gamma} = <\psi^{-}_{\gamma'}|H^{n}|Q\,[O(E)]^{-1}\,Q\,H^{n}\psi^{+}_{\gamma}(E)> \qquad 47)$$

$$= <\psi^{-}_{\gamma'}|H^{n}|Q\,\frac{1}{EI-(E+\Delta)+i\pi\Gamma}\,Q\,H^{n}{}^{+}_{\gamma}(E)> \qquad b)$$

Equation 47) expresses $T^{R}_{\gamma' \leftarrow \gamma}$ in $E + \Delta$ and Γ and reduces to the well-known result when $E + \Delta$ and Γ are numbers instead of matrices. The consequences of this generalized formula for the behaviour of the cross-section will be discussed in II. 5.

Using S-matrix formalism, the result 47) is connected with the results of formal scattering theory. The Resonance-Reactance operator is defined as:

$$K_{R} = K^{\dagger}_{R} = -\pi P\delta(E-H_{d})\,PH^{n}Q\,\frac{1}{EI-(E+\Delta)}\,QH^{n}P\delta(E-H_{d})P \qquad 48)$$

It is shown in appendix B that $T^{R}_{\gamma' \leftarrow \gamma}$ can be expressed in K_{R}:

$$T^{R}_{\gamma' \leftarrow \gamma} = -\frac{1}{\pi}<\psi^{-}_{\gamma'}\left|\frac{K_{R}}{1-iK_{R}}\right|\psi^{+}_{\gamma}> \qquad 49)$$

*****) A fact already used by H. Feshbach in his article (14). For a further discussion refer to II. 7.

One can now use 38), 42) and 49) to find for the total Transition-matrix:

$$T_{\gamma'\leftarrow\gamma} = <\xi_{\gamma'}|\underline{H}'|\frac{1}{1-iK_R}|\psi_{\gamma}^{+}> - \frac{1}{\pi}<\chi_{\gamma'}|\frac{K_R}{1-iK_R}|\psi_{\gamma}^{+}> \qquad 50)$$

In the above formulation, use has been made of:

$$\chi_{\gamma'}(E)> = \xi_{\gamma'}(E)> + P\frac{1}{[P\delta(E-H_d)PH^nQ]}QH^nP\frac{Pr.P.}{E-H_d}P\underline{H}'\xi_{\gamma'}(E)>^{******)}$$

A second operator needed is the Resonance-Phase operator which is defined by the operator relation:

$$\sigma_R = \sigma_R^{\dagger} = \tan^{-1} K_R \qquad 51)$$

One can express 50) in σ_R and finds:

$$T_{\gamma'\leftarrow\gamma} = <\xi_{\gamma'}|\underline{H}'|\, e^{i\sigma_R}\cos\sigma_R|\psi_{\gamma}^{+}> - \frac{1}{\pi}<\chi_{\gamma'}|e^{i\sigma_R}\sin\sigma_R|\psi_{\gamma}^{+}> \qquad 52)$$

Equation 57) shows the important result that, also in the case of more than one discrete state, the direct scattering and resonant scattering have an opposite phase behaviour as function of σ_R. This fact was mentioned by Fano (2) who derived 52) with the operator σ_R (with real eigenvalues) replaced by a real variable (see II.6). 47) and 48) can now be used to derive the behaviour of the time delay.

******) Pr.P indicatex the use of the principal value of the integral

$$\int dE'\psi(E')>\frac{1}{E-E'}<\psi(E')$$

II.4b. The time delay.

When $|\alpha>$ is a solution of equation:

$$\sigma_R |\alpha> = \sigma_\alpha |\alpha> \qquad 53)$$

the resonant part of 50) can be written as:

$$T^R_{\gamma' \to \gamma} = -\frac{1}{\pi} \sum_\alpha < \psi^-_{\gamma'} |\alpha> e^{i\sigma_\alpha} \sin \sigma_\alpha <\alpha| \psi^+_\gamma > \qquad 54)$$

Formula 25) is used to find the form analogous to 54) using the expression 47) for T^R and yields:

$$T^R_{\gamma' \leftarrow \gamma} = - \sum_{i,l} \sum_j \sum_{k=j}^{j+\nu_j} <\psi^-_{\gamma'} |H^n| \psi_i > S_{ij} \left(\frac{e^{i\sigma_j} \sin \sigma_j}{\pi \Lambda_j} \right)^{\nu^j_k} S^{-1}_{kl} < \psi_l |H^n| \psi^+_\gamma > \qquad 55)$$

Here σ_j is defined by:

$$\tan \sigma_j = - \frac{\Lambda_j}{E-F_j} \qquad 56)$$

The time delay (29) due to channel defined by 53) is given by:

$$\Delta t_\alpha = \frac{2 d\sigma_\alpha}{dE} = \frac{2}{1 + K^2_\alpha} \frac{d}{dE} K_\alpha \geq 0 \qquad 57)$$

Here $K_R |\alpha> = K_\alpha |\alpha>$ because:

$$[K_R , \sigma_R] = 0 \qquad 58)$$

57) can be found by applying the wave-packet method (30) to 54) and assuming that the energy-dependence of $< \psi^-_\gamma |\alpha>$ and $< \alpha | \psi^+_\gamma >$ can be neglected.
The time delay due to discrete state j is found by using 55) and applying again the wave-packet method.
It is then given by:

$$\Delta t_{jk} = 2n_{jk} \frac{d}{dE} \sigma_j \geq 0 \qquad 59)$$

Here again it is assumed that only σ_j is energy dependent. In 56) n_{jk} ranges from ν_k^j, $\nu_k^j - 1, \ldots \ldots 1$. The fact that 57) and 59) are greater than or equal zero is a characteristic of resonant scattering processes (28).

The point has now been reached for the derivation of the mathematical expressions of the physical quantities which characterize the scattering process. One can now start a discussion of the physical phenomena caused by the occurrence of many resonant levels.

II.5. DISCUSSION OF THE INTERFERENCE EFFECTS OF MANY RESONANCES

The situation where $T^d_{\gamma' \leftarrow \gamma} = 0$ will be treated here. The situation where $T^d_{\gamma' \leftarrow \gamma} \neq 0$ will be discussed in II.6.

It is possible to express $T^R_{\gamma' \leftarrow \gamma}$ into two kinds of variables.
Formula 47b) relates $T^R_{\gamma' \leftarrow \gamma}$ to $E + \Delta$ and Γ, whereas formula 50) relates $T^R_{\gamma' \leftarrow \gamma}$ to the Resonance-Reactance operator or Resonance-Phase operator as is shown in 52).

In II.5a a novel feature of the time delay derived with formula 59) will be discussed. In addition the relationship with the corresponding behaviour of the cross-section and decay-time will be given. This will be illustrated in II.5b with a detailed discussion of the case of 2 discrete states, which are eigenvalues of $E + \Delta$ and the matrix Γ with equal matrix elements. These paragraphs clarify and extend the behaviour of the cross-section found with formula 49) of $T^R_{\gamma' \leftarrow \gamma}$ as is discussed in II.5c.

II.5a.

In 30) it has been seen that degeneracies in the eigenvalues of O(E) can lead to non-exponential decay of an excited state when condition I is not satisfied.

The corresponding behaviour of the time delay can be found using equation 59). The physical definition of time delay is the difference in time a particle needs to cover a certain distance in the case where there is no collision and when the particles do collide. The fact that a positive time delay is found here indicates that the time a particle needs in the last case is larger than in the first case. (This is not always necessarily the case). Inspecting formula 59) the following phenomenon is observed. When $n_{jk} = 1$ 59) is similar in form to 57), but when $n_{jk} \neq 1$, the time delay appears to be pulsed with intervals $2 \frac{d}{dE} \sigma_j$ and the ratio of intensities can be found using 55). This is a novel phenomenon which only appears when there are degeneracies and condition I is not satisfied.

Formulae 24) and 25) are now used in 47). When condition I is satisfied and one has the formal possibilities of only degeneracies the differential cross-section given by 41) is

$$\frac{d\sigma}{d\Omega}_{\gamma' \leftarrow \gamma} = \frac{k_{\gamma'}}{k_\gamma} \frac{1}{(E - F_j)^2 + \pi^2 \Lambda_j^2} \left| \sum_{j,\gamma''} < \psi_\gamma^-(E) \left| H^n \right| \psi_{j\gamma''} >< \psi_{j\gamma''} \left| H^n \right| \psi_\gamma^+ > \right|^2 \tag{60a}$$

When condition I is not satisfied one finds the relationship:

$$\frac{d\sigma}{d\Omega}_{\gamma' \leftarrow \gamma} = \frac{k_{\gamma'}}{k_\gamma} \left| \sum_{i,l} \sum_{j} \sum_{k=j}^{j+\nu_j} < \psi_{\gamma'}^- \left| H^n \right| \psi_i > S_{ij} \frac{(-1)^{\nu_k^j - 1}}{(E - F_j + i\pi\Lambda_j)^{\nu_k^j}} S_{kl}^{-1} \, x \right.$$

$$\left. x < \psi_l \left| H^n \right| \psi_\gamma^+ > \right|^2$$

From 60a) a simple relation between the decay-time τ_j and width Δw_j is derived:

$$\Delta w_j = \frac{1}{\tau_j} \; . \tag{61}$$

This is the well-known result when there is one state resonance. When ν_k^j is 1, the same result is found in 60b). When $\nu_k^j \neq 1$ the energy-dependence of $\frac{d\sigma}{d\Omega}$ remains symmetric around F_j, but we cannot find a simple relation as in 61) between time-decay and linewidth. This is firstly, because of the deviation of simple exponential decay in the timedependence and secondly, because the powers of $\frac{1}{(E - F_j) + i\pi\Lambda_j}$ strongly diminish the linewidth originating from those terms in which they occur. The linewidth due to the term $\left\{ \frac{1}{(E - F_j)^2 + \pi^2 \Lambda_j^2} \right\}^n$ is, for example, given by:

$$\Delta w_j = 2\left(\sqrt{\sqrt[n]{2} - 1}\right)\pi\Lambda_j \leq 2\pi\Lambda_j \qquad 62)$$

The more general case where there are also different values of F_j and Λ_j yields a sum of terms like 60) and 60b). There will also appear cross-terms which have an energy-dependence as for example:

$$\frac{1}{(E-F_j + i\pi\Lambda_j)^{\nu_k^j}} \; \frac{1}{(E-F_1 + i\pi\Lambda_1)^{\nu_m^1}} \qquad 63)$$

The real part of 63) contributes to $\frac{d\sigma}{d\Omega}$. The contribution of 63) will be small when $| F_j - F_1 | \gg \Delta w_j$ and $| F_j - F_1 | \gg \Delta w_1$.

II. 5b.

The case of interaction with two discrete states will now be discussed. For simplicity, the matrix Γ is chosen to have equal matrix elements, Γ and the eigenvalues of $E + \Delta$ are given by E_1 and E_2. There is also only one scattering channel labelled γ.

Now $[E + \Delta \, . \, \Gamma] \neq 0$.

The transition matrix $T_{\gamma \leftarrow \gamma}$ is now found to be

$$T = 2\,\Gamma \frac{E - \frac{1}{2}(E_1 + E_2)}{(E - E_1)\,(E - E_2) + 2\pi i\Gamma\{E - \frac{1}{2}(E_1 + E_2)\}} \qquad 64)$$

The roots of the denominator are:

$$E^{\pm} = \tfrac{1}{2}(E_1 + E_2) + i\pi\Gamma \pm \tfrac{1}{2}\sqrt{(E_1 - E_2)^2 - 4\pi^2\Gamma^2} \qquad 65)$$

It is, therefore, possible to distinguish three cases:

$$(E_1 - E_2)^2 \gg 4\pi^2\Gamma^2 \qquad 66a)$$

$$(E_1 - E_2)^2 = 4\pi^2\Gamma^2 \qquad b)$$

$$(E_1 - E_2)^2 \ll 4\pi^2\Gamma^2 \qquad c)$$

When 66a) is satisfied one can approximate 64) to find:

$$T = 2\Gamma \frac{E - \frac{1}{2}(E_1 + E_2)}{(E - E_1 + i\pi\Gamma)(E - E_2 + i\pi\Gamma)} \approx 2\Gamma \left\{ \frac{1}{(E - E_1 + i\pi\Gamma} + \frac{1}{E - E_2 + i\pi\Gamma} \right\} \qquad 67)$$

The cross-section given by 41) is equal to $|T|^2$ and goes through zero when $E = \frac{1}{2}(E_1 + E_2)$. It behaves approximately Lorentzian when $E \approx E_1$ or $E \approx E_2$.

The time-development is given by:

$$|<\varphi|\psi(t)>|^2 = \tfrac{1}{2} e^{-2\pi\Gamma t} [1 + \cos(E_1 - E_2)t] \qquad 68)$$

Two values for the time delay are found, with the same intensities:

$$\text{a)} \quad \Delta t_1 = \frac{2\pi\Gamma}{(E - E_1)^2 + \pi^2\Gamma^2} \qquad \text{b)} \quad \Delta t_2 = \frac{2\pi\Gamma}{(E - E_2)^2 + \pi^2\Gamma^2} \qquad 69)$$

When 66b) is satisfied the Transition-matrix is given by:

$$T = 2\Gamma \frac{E - \frac{1}{2}(E_1 + E_2)}{\{E - \frac{1}{2}(E_1 + E_2) + i\pi\Gamma\}^2} \qquad 70)$$

The cross-section now shows a dip. The maxima of 67) are nearly collapsed. The T-matrix shows a double pole.[††]

The time-development is given by:

$$|<\varphi|\psi(t)>|^2 = e^{-2\pi\Gamma t}(1 - 2\pi\Gamma t + \pi^2\Gamma^2 t^2) \qquad 71)$$

The time delay is equal to:

[††] Goldberger and Watson (18) were the first to discuss the possibility of a double pole in the T-matrix. Newton (28) discussed also the corresponding decay.

$$a)\ \Delta t_1 = \frac{2\pi\Gamma}{\left\{E - \frac{1}{2}(E_1 + E_2)\right\}^2 + \pi^2\Gamma^2} \qquad b)\ \Delta t_2 = \frac{4\pi\Gamma}{\left\{E - \frac{1}{2}(E_1 + E_2)\right\}^2 + \pi^2\Gamma^2} \qquad 72)$$

The intensity of Δt_2 is $\frac{\pi^2\Gamma^2}{1+4\pi^2\Gamma^2}$ times that of Δt_1.

This behaviour is expected, as was mentioned in II. 5a, when there are degeneracies in the Jordan-Canonical form of the matrix **O**.
In appendix C a derivation of 70) showing that this is indeed the case will be given.

When 66c) is satisfied it is observed when E_1 equals E_2:

$$T = \frac{2\Gamma}{E - E_1 + i2\pi\Gamma} \qquad 73)$$

The cross-section now behaves purely Lorentzian. For the decay-time it is of course found that:

$$\tau = \frac{1}{4\pi\Gamma} \qquad 74)$$

And the time delay is given by:

$$\Delta\tau = \frac{4\pi\Gamma}{(E - E_1)^2 + 4\pi^2\Gamma^2} \qquad 75)$$

The behaviour of the cross-section is highly reminiscent of the behaviour of the absorption spectrum in N. M. R. and E. S. R.-experiments when exchange is possible (38).
However, novel information about the behaviour of corresponding time delay and time-development of the signals has been given.

In the expression 50) which relates $T^{R}_{\gamma' \leftarrow \gamma}$ with K_R, the discrete states can be chosen to be eigenfunctions of $E + \Delta$. One's task seems to be easier in this case because it is not necessary to consider the complications due to non-Hermiticity as in II. 5a, b. Pursuing the analysis somewhat further it will appear, however, that other difficulties arise. The relationship with the previous discussions in II. 5a and II. 5b will become clear when comparing the present results with those obtained by Mies (17) who studied the multi-resonance case with a formula like 50) which he derived using the Fano-method. For this purpose, we will emphasize a so-called overlap matrix, introduced by Mies, which in our notation is given by:

$$V_{ij} = \frac{\sum\limits_{\gamma''} < \Phi_i | H^n | \psi_{\gamma''}(E) > < \psi_{\gamma''}(E) | H^n | \Phi_j >}{\left[\sum\limits_{\gamma} | < \Phi_i | H^n | \psi_{\gamma}(E) > |^2\right]^{\frac{1}{2}} \left[\sum\limits_{\gamma'} | < \Phi_j | H^n | \psi_{\gamma'} > |^2\right]^{\frac{1}{2}}} \tag{76a}$$

$$= \frac{\Gamma'_{ij}}{(\Gamma'_{ii} \cdot \Gamma'_{jj})^{\frac{1}{2}}} \tag{76b}$$

The last expression showing the close relationship between V_{ij} and Γ'_{ij} is found by comparing the matrix-elements occurring in 76) with the matrix-elements of Γ', which reads: $\Gamma'_{ij} = \sum\limits_{\gamma''} < \Phi_i | H^n | \psi_{\gamma''}(E) > < \psi_{\gamma''}(E) | H^n | \Phi_j >$

c.f. appendix A. The accent in 76) means that instead of the functions ψ_i which are eigenfunctions of E the function Φ_i which are eigenfunctions of $E + \Delta$ are used.

Because of Schwarz's inequality:

$$0 \leq |V_{ij}| \leq 1 \tag{77}$$

It is evident that condition I : $[E + \Delta, \Gamma] = 0$ is equivalent to:

$$V_{ij} = \delta_{ij} \tag{78}$$

The matrix-elements $K^{R}_{\gamma' \leftarrow \gamma}$ (E) of the matrix associated with the operator K_R is given by:

$$K^{R}_{\gamma' \leftarrow \gamma} = \sum_{i} < \psi_{\gamma'} \left| H^{n} \right| \Phi_{i} > \frac{1}{E - E_{i}} < \Phi_{i} \left| H^{n} \right| \psi_{\gamma} > \qquad 79)$$

Therefore when condition I is satisfied, because of 78) using 50) and 79) one finds:

$$T^{R}_{\gamma' \leftarrow \gamma} = \sum_{\gamma''} \sum_{i} < \psi^{-}_{\gamma'} \left| \psi_{\gamma''} \right> < \psi_{\gamma''} \left| H^{n} \right| \Phi_{i} > \frac{\delta_{i,\gamma''}}{E - E_{i} + i\pi \left| < \psi_{\gamma''} \left| H^{n} \right| \Phi_{i} > \right|^{2}}$$

$$< \Phi_{i} \left| H^{n} \right| \psi_{\gamma''} > < \psi_{\gamma''} \left| \psi^{+}_{\gamma} \right> \qquad 80)$$

The Kronecher-delta $\delta_{i\gamma''}$ assures that each discrete state Φ_j is coupled with a different continuous state (channel) so as to fullfill 78).
Equation 80) can also be found from 47b) using condition I, so in this case equations 47) and 50) are similar.
The other extreme is $V_{ij} = 1$ for all i and j. Now condition I is not satisfied and $V_{ij} = 1$ implies that there is no preferential coupling of a discrete state with a continuous one. One therefore writes as in ref. (17):

$$< \Phi_{i} \left| H^{n} \right| \psi_{\gamma} > = f_{\gamma} v_{i} \qquad 81)$$

The matrix-element $K^{R}_{\gamma' \leftarrow \gamma}$ is then found to be:

$$K^{R}_{\gamma' \leftarrow \gamma} = f^{*}_{\gamma'} f_{\gamma} \left(\sum_{i} \frac{\left| v_{i} \right|^{2}}{E - E_{i}} \right) \qquad 82)$$

The problem now is to diagonalize a Hermitian matrix with matrix-elements $f^{*}_{\gamma'} f_{\gamma}$. It is possible to find an unitary matrix L, such that

$$f_{\gamma'} f_{\gamma} = \sum_{\gamma''} L^{-1}_{\gamma'\gamma''} m_{\gamma''} L_{\gamma''\gamma} \qquad 83)$$

with $m_{\gamma''}$ real.

When $V_{ij} = 1$, $T^{R}_{\gamma' \leftarrow \gamma}$ is defined as:

$$T^{R}_{\gamma' \leftarrow \gamma} = \sum_{\gamma''} \sum_{\gamma'''} \sum_{\gamma''''} < \psi^{-}_{\gamma'} | \psi_{\gamma''} > L^{-1}_{\gamma'', \gamma'''} L_{\gamma''', \gamma''''} < \psi_{\gamma''''} | \psi^{+}_{\gamma} > x$$

$$x \frac{1}{\left\{ m_{\gamma'''} \left(\sum_{i} \frac{|v_i|^2}{E - E_i} \right) \right\}^{-1} + i\pi} \qquad 84)$$

In 80) and 84) all the matrix-elements must be calculated with energy equal to E. The energy-dependence of 84) is found by studying:

$$\frac{1}{\left\{ m_{\gamma''} \left(\sum_{i} \frac{|v_i|^2}{E - E_i} \right) \right\}^{-1} + i\pi} \qquad 85)$$

The poles and order of the poles determine the behaviour of $T^{R}_{\gamma' \leftarrow \gamma}$. Expression 84) has to be compared with 48) when 25) is substituted therein. Here the behaviour of $T^{R}_{\gamma' \leftarrow \gamma}$ is known and because condition I is not satisfied it is possible that $\nu^{j}_{k} \neq 1$. As is discussed in II.5a, this can result in a collapse of lines. The peculiar narrowing effect noted by Mies (17) when $V_{ij} \neq 1$ can now be related to very well-known phenomena in different fields (38) as, for instance, cross-relaxation in N.M.R. (37). Those phenomena are described in terms of a matrix like O and occur when condition I is not satisfied.

It may be of interest to note that in two papers (17) and (7) systems behave as if condition I is satisfied in spite of $V_{ij} = 1$.

This behaviour becomes understandable if it is realized that it occurs when the non-diagonal elements of Γ are large compared with the energy-differences.

When using a basis which diagonalizes Γ, $E + \Delta$ becomes non-diagonal, but the non-diagonal elements are small compared to the diagonal elements. Therefore, $[(E + \Delta), \Gamma] \sim 0$.

II.6. INTERFERENCE BETWEEN DIRECT AND RESONANT SCATTERING; THE GENERALIZED FANO EQUATION.

U. Fano (2) in his treatment of auto-ionization phenomena has shown that a peculiar asymmetry in the energy-dependence of the cross-section finds its origin in the interference between direct ionization and ionization by way of an intermediate discrete state. The formalism developed in this chapter enables one to find a new generalized expression for the Transition-matrix in this case:

$$T_{\gamma' \leftarrow o} = < \psi^-_{\gamma'} \,|\, e^{i\sigma_R} \cos \sigma_R PT \,|\, \psi_o > +$$

$$- \frac{1}{\pi} < \psi^-_{\gamma'} \,|\, e^{i\sigma_R} \sin \sigma_R \,|\, [P\delta(E - H_d)\, PH^n Q]^{*-1}\, Q'T\, \psi_o > \qquad 86)$$

The derivation is given in Appendix D.

Here $< \psi^-_\gamma | T | \psi_o >$ is the matrix-element of the interaction of electromagnetic field with the continuum state $\psi^-_\gamma(E)$ and ground state ψ_o of the atom or molecule; $< \Phi_i | T | \psi_o >$ is the matrix-element of the interaction of electromagnetic field with the discrete excited state Φ_i and ground state ψ_o. One can treat the electromagnetic field as time-independent by second-quantizing it.

Q' is defined by:

$$Q' = Q + QH^n P \frac{\text{Pr. P.}}{E - H_d} P \qquad 87)$$

H^n represents the interaction of discrete and continuous states of the molecule without the electro-magnetic field present.

Remember that in 86) σ_R is an operator.

That formula is worked out for the cases $V_{ij} = \delta_{ij}$ and $V_{ij} = 1$.

In the first case one finds analogous to 80):

$$T_{\gamma' \leftarrow o} = \sum_\mu < \psi_{\gamma'} | \mu > \frac{(\epsilon_\mu + q_\mu)}{(\epsilon_\mu + i)} < \mu | T | \psi_o > \qquad 88)$$

In the following formulae:

$$\epsilon_\mu = \frac{E - E_\mu}{\pi |V_\mu|^2} \; ; \quad q_\mu = \frac{< \Phi'^d_\mu |T| \psi_o >}{\pi V^*_\mu < \mu|T|\psi_o >} \tag{89)}$$

Φ'^d_μ is a solution of 87) and $V_\mu = < \mu |H^n| \Phi'^d_\mu >$. $|\mu >$ is a continuous state and Φ'^d_μ is a discrete state. One sees that in cases where there are only one discrete state and one continuous state 88) reduces to the famous result of Fano in Ref. (2).

When $V_{ij} = 1$ one finds by using 87):

$$T_{\gamma \leftarrow o} = \sum_{\gamma', \gamma'', \gamma'''} < \psi^-_\gamma | \psi_{\gamma'} > L^{-1}_{\gamma'\gamma''} \frac{\epsilon_{\gamma''} + q_{\gamma'''}}{\epsilon_{\gamma''} + i} L_{\gamma''\gamma'''} < \psi_{\gamma'''} |T| \psi_o > \tag{90)}$$

But now:

$$\epsilon_\gamma = \left\{ \pi\, m_\gamma \left(\sum_i \frac{|v_i|^2}{E - E_i} \right) \right\}^{-1} \; ; \quad q_\gamma = \frac{1}{\pi < \psi_\gamma |T| \psi_o >} \, x$$

$$x < \psi_\gamma | \frac{1}{\{P \delta (E - H_d)\, PH^n Q\}^*} Q'T | \psi_o > \tag{91)}$$

When one compares 90) with 88) it is evident that the essential difference is in the definition of ϵ_γ in both cases. So the discussion is analogous to that of equation 86).

Expressions 90) and 88) have been derived by using the operator relations:

$$e^{i\sigma_R} \cos \sigma_R = \frac{1}{1 - iK_R} \; ; \quad e^{i\sigma_R} \sin \sigma_R = \frac{K_R}{1 - iK_R} \; ; \tag{92)}$$

and the definition of K_R in 49). The E_i and E_μ of 89) and 91) are eigenvalues of $E + \Delta$.

In present literature an example of the first case giving 88) can be found in a treatment of Bardsley (4) on molecular resonant states. The second case giving 90) can be found in the paper of Mies 17).

Comparing equations 52) and 86) one sees that also in the case of resonant scattering of particles the same behaviour appears as in auto-ionization. Experimental verification can, for example, be found in the work of Ehrhardt (31) and McGowan (32).

II. 7. CONNECTION WITH EXISTING RESONANCE THEORIES OF FANO AND FESHBACH.

In appendix B it is shown that the theory presented here leads to a formula for the S-matrix:

$$S_{\gamma' \leftarrow \gamma}(E) = < \psi^{-}_{\gamma'}(E) \,\Big|\, \frac{1 + i\,K_R}{1 - i\,K_R} \,\Big|\, \psi^{+}_{\gamma}(E) > \qquad 93)$$

This is equivalent to the one derived by Mies (17) using Fano's method. Because the S-matrix contains all information about the scattering problem this equivalence proves that all of the time-independent results presented here are essentially the same as those derived with Fano's method.

However, in dealing with some problems the theory presented here has definite advantages. For example, application of it to the problem of multi-resonance clarifies many features as seen in the discussion of II. 5. There it was shown that pecularities found by Mies by explicit calculation with the aid of electronic computers followed analytically from the study of the effect of $E + \Delta$ and Γ matrices.

Expression 93) also has a form which is very similar to the one Feshbach (14c) derived. This similarity, however, is only formal, because the choice of our projection-operators (19) is different from that of Feshbach. In the work of Feshbach, P projects only on the open channels, whereas in this work P projects on all continuous channels.

A consequence of Feshbach's definition is that the trace of Δ will always be negative. The formalism presented here not only includes the Feshbach resonances but also resonances which give a positive shift with respect to a discrete state and the discrete states are not restricted to a region below an inelastic channel (34, 35).

Equation 86) shows, for the general case, how the asymmetry in the cross-section appears as a function of the operator σ_R.

O'Malley and Geltman (33) showed that in the case of resonant scattering by one discrete state their result, derived with Feshbach's formalism is equivalent to that derived with Fano's method.

52) and 86) show explicitly that also in the general case of many resonances the equivalence can be established.

It may also be illuminating to use an other way to compare the present approach with those of Fano and Feshbach.

The trial function $\Phi(E)$ used in Fano's method to diagonalize the total Hamiltonian is chosen as a linear combination of discrete and continuous states. It is, therefore, given by:

$$\Phi(E) = \sum_{i,\gamma} a_{i,\gamma}(E)\,\psi_{i,\gamma} + \sum_{\gamma} \int_{E_\gamma} dE'\, b\,(E,E')\,\psi_\gamma(E') \qquad 94)$$

With the choice of projection operators 19) it is clear that the eigenfunctions used to diagonalize the total Hamiltonian have the same form.

The following relationship between $P\Phi_\gamma(E)$ and $Q\Phi_\gamma(E)$ can be derived and is found by 44):

$$P\,(E-H)\,P\Phi_\gamma = PHQ\Phi_\gamma \qquad 95a)$$

$$Q\,(E-H)\,Q\Phi_\gamma = QHP\Phi_\gamma \qquad 95b)$$

The function:

$$\Phi_\gamma = P\Phi_\gamma + Q\Phi_\gamma \qquad 96)$$

is therefore an eigenfunction of the total Hamiltonian H and has the same form as 94).

It is of interest to note that equations 95) are in a form identical to the one Feshbach uses to start his derivation (14). Remember, however, the differences in projection-operators.

Equation 20) which enables one to calculate the time-development of $\psi(t)$

will now be compared with similar formulae derived on the basis of Fano's method.

Mies and Kraus (7) and Bixon, Jortner and Dothan (26) have used Fano's method to calculate the coefficients $a_{i,\gamma}(E)$ and $b_{\gamma}(E,E')$ of 94). As soon as these are known they calculate the time-development of $\psi(t)$. With initial condition $P\psi(t) = \psi(t') = 0$; $Q\psi(t') = 0$ the equation to evaluate is then:

$$\psi(t) = \int dE \left\{ \sum_{j,\gamma'} a_{\gamma,\gamma'}(E)\, b^{*}_{\gamma}(E,E')\, \psi_{j,\gamma'} + \sum_{\gamma'} \int_{E_{\gamma'}} dE''\, b_{\gamma'}(E,E'')\, b^{*}_{\gamma}(E,E')\psi_{\gamma''}(E'') \right\} x$$

$$x\; e^{-iE(t-t')}\; e^{-iE't'} \qquad 97)$$

When $P\psi(t') = 0$: $Q\psi(t') = \psi_{j,\gamma}(t')$, one finds for $\psi(t)$:

$$\psi(t) = \int dE \left\{ \sum_{i,\gamma'} a_{i,\gamma'}(E)\, a^{*}_{j,\gamma}(E)\psi_{i,\gamma'} + \sum_{\gamma'} \int_{E_{\gamma'}} dE' a^{*}_{j,\gamma}\, b_{\gamma'}(E,E')\, \psi_{\gamma'}(E') \right\} x$$

$$x\; e^{-iE(t-t')}\; e^{-iE_j t'} \qquad 98)$$

Comparison of equations 97) and 98) with equation 20) shows the much more transparant structure of the latter.

This section will be closed with some remarks on the evaluation of $T^{R}_{\gamma' \leftarrow \gamma}$. When the eigenvalueproblem $K_R |\alpha\rangle = K_\alpha |\alpha\rangle$ can be solved formula 50) of $T^{R}_{\gamma' \leftarrow \gamma}$ can be used.

When this is not possible it may appear to be advantageous to try to invert $EI - (E + \Delta - i\pi\Gamma)$ and to use formula 47b) for $T^{R}_{\gamma' \leftarrow \gamma}$.

The work of Mies (17) is an example of the first method; the work of Mower (21) of the second.

Appendix A

One defines:

$$A1) \quad O(z) = Q\,(z - H_d - QH^{n}P \frac{1}{z - H_d} PH^{n}Q)\,Q$$

and its inverse must be found. According to 5) equations 12) are to be evaluated with $z = x + iy$ in which x and y real and $y > 0$. The operator H is Hermitian, so has only real eigenvalues.

One can therefore take $\lim y \to 0$. One then finds for $\lim_{y \to +0} O(z) \equiv O(x)$:

$$O(x) = Q\left(x - H_d - QH^nP \frac{\text{Pr.P.}}{x - H_d} PH^nQ + i\pi QH^nP\,\delta(x - H_d)\, PH^nQ\right)Q \qquad \text{A2)}$$

Using 18) and 19) one finds for O(x):

$$O(x) = \sum_{i,\gamma} \sum_{i',\gamma'} \psi_{i,\gamma} > \{\delta_{ii'}\, \delta_{\gamma\gamma'} (x - E_i) - \Delta^{i,\gamma}_{i',\gamma'} + i\pi\Gamma^{i,\gamma}_{i',\gamma'}\} < \psi_{i',\gamma'} \qquad \text{A3)}$$

Defining in A4):

$$\Delta^{i,\gamma}_{i',\gamma'} = \sum_{\gamma''} \int_{E_{\gamma''}} dE < \psi_{i,\gamma} \left|H^n\right| \psi_{\gamma''}(E) > \frac{1}{x-E} < \psi_{\gamma''}(E) \left|H^n\right| \psi_{i',\gamma'} > \qquad \text{A4)}$$

$$\Gamma^{i,\gamma}_{i',\gamma'} = \sum_{\gamma''} \int_{E_{\gamma''}} dE < \psi_{i,\gamma} \left|H^n\right| \psi_{\gamma''}(E) > \delta(x-E) < \psi_{\gamma''}(E) \left|H^n\right| \psi_{i',\gamma'} > \qquad \text{A5)}$$

One defines the matrix **E** with the elements: $E_{i,\gamma}\, \delta_{ii'}\, \delta_{\gamma\gamma'}$

" " " " Δ " " " : $\Delta^{i,\gamma}_{i',\gamma'} = \Delta^{i',\gamma'*}_{i,\gamma}$ A6)

" " " " Γ " " " : $\Gamma^{i,\gamma}_{i',\gamma'} = \Gamma^{i',\gamma'*}_{i,\gamma}$

The problem has been reduced to finding the inverse of the matrix O(x):

$$O(x) \equiv x\,\mathbf{I} - (\mathbf{E} + \Delta(x)) + i\pi\Gamma(x) \qquad \text{A7)}$$

where **I** the unit-matrix.

It is assumed in this chapter that the x-dependence of Δ, Γ can be neglected (12, 18, 20).

From A5) it immediately follows that

$$\text{trace } \Gamma \geq 0 \qquad \text{A8)}$$

Two possibilities must be discussed:

$$[E + \Delta,\ \Gamma] = 0 \qquad \text{9a)}$$

$$[E + \Delta,\ \Gamma] \neq 0 \qquad \text{9b)}$$

Case a (condition I) is simple to deal with. It is possible to diagonalize $E + \Delta$ and Γ by the same unitary transformation:

$$U^{\dagger}\ O\ U = xI - F + i\pi\Lambda \qquad \text{A10)}$$

Here U is unitary and F and Λ are real and diagonal.
A8) applies also to Λ. One now finds for the inverse of:

$$O^{-1} = U(xI - F + i\pi\Lambda)^{-1}\ U^{\dagger} \qquad \text{A11)}$$

Case b (condition I is not satisfied) is less simple to deal with.
Two theorems of ref. (22) are used:

1) Any complex matrix may be transformed into Jordan-canonical form by means of a similarity transformation.
2) Let (μ) be an arbitrary matrix with $e'_1, e'_2 \ldots e'_n$ as its right eigenvectors and right generalized eigenvectors. Let (τ) be the matrix whose columns are the vectors $e'_1, e'_i \ldots e_n$. Then $(\tau)^{-1}(\mu)(\tau)$ is a matrix in the Jordan-canonical form and the rows of $(\tau)^{-1}$ are left eigenvectors or left generalized eigenvectors of (μ).

It is not possible to find a unitary matrix as in A11) and in the case of degeneracies of the eigenvalues of O, the inverse O^{-1} will not have only first order poles.
Let the matrix S be the matrix of the right eigenvectors and right generalized eigenvectors of O. One then finds for its inverse O^{-1}:

$$O^{-1} = S\ C\ S^{-1} \qquad \text{A12)}$$

with

$$C = [S^{-1} \; O \; S]^{-1} \qquad \text{A12b)}$$

It is then possible to write for a matrix-element of O^{-1}:

$$[O^{-1}]_{il} = \sum_j \sum_{k=j}^{j+\nu_j} S_{ij} \frac{(-1)^{\nu^j_k - 1}}{(x - a_j)^{\nu^j_k}} S^{-1}_{kl} \quad (k \geq j) \qquad \text{A13)}$$

ν^j_k ranges from $\nu^j_j = 1$ to ν'_j. ν'_j is the index of the eigenvalue a_j.
C can be rearranged so that it is possible to start with specific a_j and $\nu_j = \nu_j'$ which is the index of a_j. If one then goes from j to j+1, ν_{j+1} is ν'_j minus 1. This is repeated untill $\nu_{j+1} = 1$.
The following possibilities now exist:

a) $a_{j+l+1} = a_j$

or

b) $a_{j+l+1} \neq a_j$

In the case of a) one can find a new ν'_{j+l+1}, smaller than ν'_j and the procedure repeates. The sum of the maximum values ν'_j, $\nu'_{j+l+i} \dots$ is equal to the multiplicity of a_j.
Case b) is a repetition of above with a different eigenvalue.
Because of A8):

$$\text{Im} \sum_j a_j \leq 0 \qquad \text{A14)}$$

defining:

$$-\pi \Lambda_j = \text{Im}\, a_j \qquad \text{A15)}$$
$$F_j = \text{Re}\, a_j$$

Methods to find the Jordan-canonical form and S can be found, for example, in ref. (22).

Appendix B. Proof of equation $T^R_{\gamma' \leftarrow \gamma} = \frac{1}{\pi} < \psi^-_{\gamma'} | \frac{K_R}{1-i\,K_R} | \psi^+_\gamma >$ and derivation of S-matrix.

According to 33) and 38) $Q\Phi^+_\gamma(E)$ is a solution of:

$$Q\,(E\,I - E - \Delta + i\pi\Gamma)\,Q\Phi^+_\gamma(E) = QH^n\psi^+_\gamma\,(E)$$

B1)

Using the definitions of Δ and Γ and dividing B1) by $Q(EI - E - \Delta)Q$ one observes:

$$1 + i\pi[Q(E\,I - E - \Delta)Q]^{-1}QH^nP\,\delta(E - H_d)\,PH^nQ\Phi^+_\gamma\,(E) =$$

$$[Q(E\,I - E - \Delta)Q]^{-1}QH^nP\,\delta(E - H_d)\,P\psi^+_\gamma\,(E)$$

The inverse of $E + \Delta$ is well defined because of its Hermitian property. Define:

$$A = Q\,(E\,I - E - \Delta)\,Q^{-1}\,QH^nP\ \ (E - H_d)P$$

B3)

$$B = P\,\delta(E - H_d)\,PH^nQ$$

The use of equations B3) gives:

B4)

$$(1 + i\pi\,AB)\,Q\Phi^+_\gamma = AP\psi^+_\gamma$$

Now it is possible to use the equality $A(1+i\pi BA)^{-1} = (1+i\pi AB)^{-1}A$ (14c). $Q\Phi^+_\gamma$ is now given by:

$$Q\Phi^+_\gamma = A(1+i\pi BA)^{-1}P\psi^+_\gamma$$

B5)

$$= Q(EI - E - \Delta)Q^{-1}QH^nP\,\delta(E - H_d)\,P\frac{1}{1 - iK_R}P\psi^+_\gamma$$

where K_R is defined as in 44).

According to 42)

$$T^{R}_{\gamma' \leftarrow \gamma} = \langle \psi^{-}_{\gamma'}(E) \,|\, H^{n} \,|\, Q\Phi^{+}_{\gamma}(E) \rangle$$

Substitute B5) into this expression and re-apply the definition of K_R:

$$T^{R}_{\gamma' \leftarrow \gamma} = -\frac{1}{\pi} \langle \psi^{-}_{\gamma'} \,|\, \frac{K_R}{1 - i K_R} \,|\, \psi^{+}_{\gamma} \rangle \qquad \text{B6)}$$

Using the relationship:

$$\langle \psi^{-}_{\gamma'}(E) \,|\, \psi^{+}_{\gamma}(E) \rangle = \langle \xi_{\gamma'}(E) \,|\, \xi_{\gamma}(E) \rangle - 2\pi i \langle \xi_{\gamma'}(E) \,|\, \underline{H'} \,|\, \psi^{+}_{\gamma}(E) \rangle \qquad \text{B7)}$$

which together with 40) yields:

$$T_{\gamma' \leftarrow \gamma}(E) = \frac{1}{2\pi i} \langle \xi_{\gamma'}(E) \,|\, \xi_{\gamma}(E) \rangle - \langle \psi^{-}_{\gamma'} \,|\, \frac{1 + iK_R}{1 - iK_R} \,|\, \psi^{+}_{\gamma} \rangle \qquad \text{B8)}$$

One therefore finds for the S-matrix of the system:

$$S_{\gamma' \leftarrow \gamma}(E) = \langle \psi^{-}_{\gamma'}(E) \,|\, \frac{1 + iK_R}{1 - iK_R} \,|\, \psi^{+}_{\gamma}(E) \rangle \qquad \text{B9)}$$

The unitary Resonance S-operator of the system can therefore be defined as:

$$S_R = \frac{1 + iK_R}{1 - iK_R} \qquad \text{B10)}$$

The Hermitian Resonance-Phase operator is defined by:

$$\sigma_R = \tan^{-1} K_R = \sigma_R^{\dagger} \qquad \text{B11)}$$

which leads to the expression

$$S_R = e^{2i\sigma_R} \qquad \text{B12)}$$

Appendix C. Derivation of expression 70) for the Transition-matrix using the Jordan-canonical form of the matrix **O**.

The matrix **O**(E) is given by A7)

$$\mathbf{O}(E) = E\,I - E - \Delta + i\pi\Gamma$$

In case 66b) when $E_1 - E_2 = 2\pi\Gamma$, **O**(E) can be written as:

$$\text{C1)} \qquad \mathbf{O}(E) = \left\{ E + i\pi\Gamma - (E_2 + \pi\Gamma) \right\} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \pi\Gamma \begin{pmatrix} 3 & i \\ i & 1 \end{pmatrix}$$

One wishes to find the matrix **C** , which is in its Jordan-canonical form,

$$\mathbf{O}^{-1} = \mathbf{S}\ \mathbf{C}\ \mathbf{S}^{-1}$$

The matrix **S** and its inverse $\mathbf{S}^{-1}$ are used to find the Jordan-canonical form of **O**(E), which is the matrix $\mathbf{C}^{-1}$ given by A13b):

$$\mathbf{C}^{-1} = \mathbf{S}^{-1}\ \mathbf{O}\ \mathbf{S}$$

Using for **S** and $\mathbf{S}^{-1}$ the matrices:

$$\text{C2)} \qquad \mathbf{S} = \begin{pmatrix} -i & 0 \\ 1 & -1 \end{pmatrix} ; \qquad \mathbf{S}^{-1} = \begin{pmatrix} i & 0 \\ i & -1 \end{pmatrix}$$

one finds:

$$\text{C3)} \qquad \mathbf{C}^{-1} = \left\{ E - i\pi\Gamma - (E_2 + \pi\Gamma) \right\} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \pi\Gamma \begin{pmatrix} 2 & 1 \\ 0 & 2 \end{pmatrix}$$

Therefore, the matrix $\mathbf{C}^{-1}$ is a linear combination of the unity-matrix and a matrix in its Jordan-canonical form of index 2.

For C one finds:

C4)
$$C = \begin{bmatrix} \frac{1}{E - (E_2+\pi\Gamma) + i\pi\Gamma} & - \frac{\pi\Gamma}{\{E - (E_2-\pi\Gamma) + i\pi\Gamma\}^2} \\ 0 & \frac{1}{(E - (E_2+\pi\Gamma) + i\pi\Gamma} \end{bmatrix}$$

which gives for O^{-1} :

C5)
$$O^{-1} = \begin{bmatrix} \frac{1}{E - (E_2+\pi\Gamma) + i\pi\Gamma} - \frac{\pi\Gamma}{\{E - (E_2+\pi\Gamma) + i\pi\Gamma\}^2} & \frac{-i\pi\Gamma}{\{E - (E_2+\pi\Gamma + i\pi\Gamma\}^2} \\ \frac{-i\pi\Gamma}{\{E - (E_2+\pi\Gamma) + i\pi\Gamma\}^2} & \frac{1}{E - (E_2+\pi\Gamma) + i\pi\Gamma} - \frac{\pi\Gamma}{\{E - (E_2+\pi\Gamma) + i\pi\Gamma\}^2} \end{bmatrix}$$

Using result C5) and expression 47a) for T one finds:

C6)
$$T = 2\Gamma \frac{E - (E_2+\pi\Gamma)}{\{E - (E_2+\pi\Gamma) + i\pi\Gamma\}^2}$$

With $E_1 - E_2 = 2\pi\Gamma$ this gives expression 70)

Appendix D. Derivation of the generalized Fano-equation 86).

The Transition-matrix of photoionization which is first order in the electromagnetic field is given by:

D1)
$$T_{\gamma \leftarrow 0} = < \phi_\gamma^- \, |T| \, \psi_0 >$$

Here ψ_o is the ground-state of the molecule or atom and Φ_γ^- is the continuous eigenstate with such boundary conditions that a wave packet constructed with it represents at $t \to +\infty$ an incoming particle at an infinite distance from the target. Using 32) and 33) $P\Phi_\gamma^-$ and $Q\Phi_\gamma^-$ can be found:

$$\text{D2}):\quad \text{a)}\quad P\Phi_\gamma^- = \psi_\gamma^- + \lim_{\epsilon \to 0} \frac{1}{E - PHP - i\epsilon} PH^nQ \frac{1}{E\,I - (E + \Delta) - i\pi\Gamma} QH^nP\psi_\gamma^-$$

$$\text{b)}\quad Q\Phi_\gamma^- = Q \frac{1}{E\,I - (E + \Delta) - i\pi\Gamma} QH^nP\psi_\gamma^-$$

Substituting K_R, which is defined by 49):

$$K_R = -\pi\, P\,\delta(E-H_d)\, PH^nQ \frac{1}{E - (E + \Delta)} QH^nP\,\delta(E-H_d)P$$

one then finds:

$$\text{a)}\quad < P\,\Phi_\gamma^-|T|\psi_o > = < \psi_\gamma^-|T|\psi_o > + i < \psi_\gamma^- | \frac{K_R}{1-i\,K_R} T|\psi_o >$$

$$- \frac{1}{\pi} < \psi_\gamma^- | \frac{K_R}{1-i\,K_R} \left[P\,\delta(E-H_d) PH^nQ \right]^{*-1} QH^nP \frac{\text{Pr. P.}}{E - H_d} PT|\psi_o > \qquad \text{D3)}$$

$$\text{b)}\quad < Q\Phi_\gamma^-|T|\psi_o > = -\frac{1}{\pi} < \psi_\gamma^- | \frac{K_R}{1-i\,K_R} \left[P\,\delta(E-H_d) PH^nQ \right]^{*-1} QT|\psi_o >$$

We use the definition of Q' 87):

$$Q' = Q + QH^nP \frac{\text{Pr. P.}}{E - H_d}$$

After adding D3a) to D3b), which is equal to D1), one uses the identity:

D4) $$< \psi_\gamma^- |T| \psi_o > = < \psi_\gamma^- | \frac{1 - iK_R}{1 - iK_R} T|\psi_o >$$

and the definition of σ_R,

$$K_R = \tan \sigma_R$$

so as to find:

$$T_{\gamma \leftarrow o} = < \psi_\gamma | e^{i\sigma_R} \cos \sigma_R \; PT|\psi_o > - \frac{1}{\pi} < \psi_\gamma^- | e^{i\sigma_R} \sin \sigma_R$$

$$[P\,\delta(E-H_d) PH^n Q]^{*-1} \; Q'T|\psi_o >$$

REFERENCES:

1. W.Heitler, Quantum Theory of radiation, 3e edition, Oxford (1954).

2. U.Fano, Phys.Rev. 124, 1866 (1961).

3. J.C.Y.Chen, J.Chem.Phys. 40, 3507 (1964).

4. J.Jortner, S.A. Rice, R.M. Hochstrasser, Adv. in Photochem. 7, 149 (1969).

6. R.A. Harris, J.Chem.Phys. 39, 978 (1963).

7. F.H. Mies, M.Krauss, J.Chem. Phys. 45, 4455 (1966).

8. F.T. Smith , J.Chem.Phys. 36, 248 (1962).

9. F.H. Mies, J.Chem.Phys. 51, 787 (1969).

10. R.D. Levine, Quantum mechanics of Molecular Rate Processes, Oxford (1969).

11. W. Kerler, Zeitschrift für Physik, 234, 330 (1970).

12. A. Messiah, Quantum mechanics I, II, North Holland (1963).

13. J.M. Blatt, V.F. Weisskopf, Theoretical Nuclear Physics, Wiley (1952).

14a. H. Feshbach, Ann. of Phys. 5, 357 (1958).

b. " " " " " 19, 287 (1962).

c. " " " " " 43, 410 (1967).

15. P.L. Kapur, R. Peierls, Proc.Roy.Soc. A166, 277 (1938).

16. A. Herzenberg, K.L. Kwok, F. Mandl, Proc.Phys.Soc. 84, 472 (1964).

17. F.H. Mies, Phys.Rev. 175, 164 (1968).

18. M.L. Goldberger, K.M. Watson, Collision theory, Wiley (1965).

19. K. Ingolfson, Helv.Phys.Acta. 40, 240 (1967).

20. M. Friedrich, Comm.Math. Phys 2, 327 (1966).

21. L. Mower, Phys.Rev. 142, 790 (1966).

22. a. G. Birkhoff, S. Mac Lane, A survey of modern Algebra, Mac Millan (1954).

b. F.R. Gantmacher, The theory of matrices, Chelsea (1960).

c. B. Friedman, Principles and techniques of applied mathematics, Wiley (1966).

23. J. Jersák, Helv.Phys. Acta 43, 93 (1970).

24. M. Simonius, Helv.Phys.Acta 43, 223 (1970).

25. J. Jortner, R.S. Berry, J.Chem.Phys. 48, 2757 (1968).

26. M. Bixon, J. Jortner, Y.Dothan, Mol.Phys. 17, 109 (1969).

27. S. Sunakawa, Progr. Theor.Phys. 14, 175 (1955).

28. R.G. Newton, Scattering Theory of waves and particles, Mc.Graw Hill (1966).

29. F.T. Smith, Phys.Rev. 118, 349 (1960).

" " " " " 119, 2098 (1960).

30. Ta-You Wu, Takashi Ohmura, Quantum theory of scattering, Prentice Hall (1962).

31. H. Ehrhardt in "A survey of phenomena of ionized gasses", Vienna (1969).

32. J.W. McGowan, Phys. Rev. Letters 17, 1207 (1966).

33. T.F. O'Malley, S. Geltman, Phys. Rev. 137, A1344 (1965).

34. See H.S. Taylor e.a. J. Chem. Phys. 45, 2872 (1966).

35. J.N. Bardsley, F. Mandl, Rep. Progr. Phys. 1, 471 (1969).

36. M. Bixon, J. Jortner, J. Chem. Phys. 50, 4061 (1969).

37. A. Ben Reuven, Adv. in Atomic and Molecular Physics, 5, 219 (1969).

38. A. Abragam, The Principles of Nuclear Magnetism, Oxford (1961) p. 447.

CHAPTER III

ANALYSIS OF THE JORTNER-STEPANOV THEORY OF RADIATIONLESS TRANSITIONS IN ORGANIC MOLECULES.

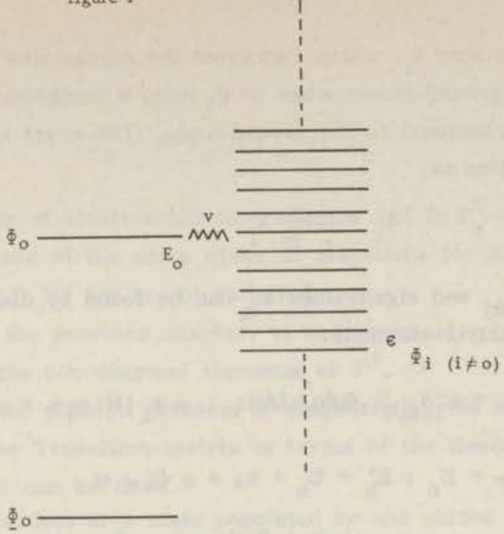
When molecules absorb electromagnetic radiation, excitation of an electron can take place. Deexcitation of an excited molecular state can occur in two ways. Firstly by stimulated or spontaneous emission of radiation and secondly by radiationless dissipation of energy into other states of the molecule itself or by energy transfer by collisions with other molecules. In this chapter the intramolecular energy dissipation mechanism will be discussed.

In large molecules it appears that the high density of vibrational states can give rise to small decay-times at low pressures. The Jortner-Stepanov model (1,2) is an attempt to explain this. In this model absorption of a photon from the electromagnetic field is accompanied by excitation of an electron from the ground-state to an higher electronic state according to the Franck-Condon principle. The vibronic levels of this electronic state are coupled with the vibronic levels of lower electronic states, which carry no oscillator strength.

In the simplest form of the model only one vibronic level of the excited-electronic state is excited and this level is assumed to be coupled with an infinite number of other vibronic-states from the lower electronic levels by a coupling v. Their energy-difference is assumed to be equal and given by ϵ (see figure 1).

In the real system this coupling is thought to arise from Herzberg-Teller coupling (5), the breakdown of the Born-Oppenheimer approximation (1)

figure 1



Jortner-Stepanov's model of radiationless transitions
(see text for explanation of symbols)

or spin-orbit coupling (18).

For the development of the theory, however, the coupling v needs not to be specified.

The same model will be used in this chapter and the methods developed in chapter II will be applied to unravel the things implicit to it.

First the conditions are derived that the infinite manifold of discrete vibrational states can be treated as a quasi-continuum. The results are essentially the same as found by other authors, but direct application of the theory of overlapping resonances enables us to avoid pitfalls which one encounters in some of the earlier papers on the subject.

Then the model is extended with a second electronic state, which can be excited and the interference phenomena due to the coupling between these states are discussed.

The different kinds of behaviour of those systems, which are predicted in chapter II, are again found. But now they can be shown to correspond to clear physical situations.

The use of the methods developed in chapter II are here again nicely demonstrated. The profit of the presented treatment is that it unifies many different phenomena into one theory.

III.1. THE JORTNER-STEPANOV MODEL OF RADIATIONLESS TRANSITIONS.

Suppose the states Φ_i, which represent the eigenstates of the molecule orthogonal to the ground-states when v= 0, form a complete and orthonormal set in the space orthogonal to the ground-state. The exact excited states ψ_k can then be written as:

$$1) \qquad \psi_k = \sum_j a_{kj} \Phi_j$$

The coefficients a_{kj} and eigenvalues E_k' can be found by diagonalizing a matrix with the matrix-elements:

$$2) \qquad < \Phi_k|H|\Phi_l > = E_l' \delta_{k,l} \quad (k\neq o,\ l\neq o); \qquad < \Phi_k|H|\Phi_l > = v\,\delta_{k,o}\ (l\neq o);$$

$$< \Phi_o|H|\Phi_o > = E_o \ : \ E_k' = E_o + k\epsilon + \alpha \ (k < o)$$

$$= E + (k-1)\,\epsilon + \alpha \ (k > o)$$

The function Φ_o represents the excited state which carries oscillator-strength. The label k in 2) can range from $-\infty$ to $+\infty$.

Let the ground-state be represented by a wavefunction $\underline{\Phi}_o$ and the interaction with the electromagnetic field by a coupling H'. When second-quantization is used, H' is time-independent.

The states ψ_i defined by equation 1) are the discrete states that have interaction H' with the continuous states, where a photon is present and the molecule is in ground-state $\underline{\Phi}_o$. In the resonant process excitation occurs from $\underline{\Phi}_o$ to ψ_i by absorption of a photon. The formalism developed in chapter II can now be used. The transition amplitude can be expressed in the inverse of the matrix **O** (II, 47b). The matrix **O** is in the case treated here:

$$3) \qquad \mathbf{O} = E\,I - E^{\psi} + i\pi\Gamma^{\psi}$$

The matrix E^{ψ} is the matrix of the eigenvalues of ψ. The matrix Δ^{ψ} has been neglected because the matrix-elements of Δ^{ψ} are small compared to the matrix-elements of E^{ψ} and Γ^{ψ}, for they are of the order of the radiative line-shift.

Because the electromagnetic field forms the continuum, the matrix-elements of Γ^{ψ} (II, A6) can now easily be calculated:

4) $$\Gamma_{ij}^{\psi} = a_{io}^{*} a_{jo} \Gamma_o^r$$

where

5) $$\Gamma_o^r = |< \Phi_o | H' | \underline{\Phi}_o >|^2 \rho_e$$

ρ_e is the density of electromagnetic-radiation and $2\pi \Gamma_o^r$ the radiative width. Because $a_{io}^* a_{jo}$ are of the same order of magnitude for all values of i and j, condition I II, 23) is not satisfied.

As is shown in the previous chapter, it is in general not permissable to simply neglect the non-diagonal elements of Γ^{ψ}. *)

To circumvent the difficult problem of diagonalizing the matrix 4), the expression of the Transition-matrix in terms of the Resonance-Reactance operator II, 49) can be tried.

Let $\Phi_{\vec{\epsilon}}$ be the product of a state populated by one photon with polarization-direction $\vec{\epsilon}$ and $\underline{\Phi}_o$. The matrix-elements of the Resonance-Reactance operator K_R are:

6) $$< \Phi_{\vec{\epsilon}} | K_R | \Phi_{\vec{\epsilon}} > = - \pi \Gamma_o^r \sum_j |a_{jo}|^2 \frac{1}{E - E_j^{\psi}}$$

The Transition-matrix, found by using 6), can be elaborated and one can find the resulting expressions in ref. (7, 21).

In chapter II it was already mentioned that this expression must be equivalent to the result of the Fano-method. This is the method used in ref. (7, 21) to derive the Transition-matrix and the resulting expression of the Transition-matrix is very complicated.

There exists, however, a much simpler method by using the states Φ_i as a base instead of the states ψ_i. By using partitioning techniques (9, 10) and formula II, 47b) of the Transition-matrix, one finds:

7) $$T = \frac{|< \Phi_{\vec{\epsilon}} | H' | \Phi_o >|^2}{E - E_o - v^2 \sum_{i \neq o} \frac{1}{E - E_i'} + i\pi \Gamma_o^r}$$

E is the energy of photon and molecule before absorption or after emission.

---

*) In ref(6) the solution of the problem is given with the assumption that Γ^{ψ} is diagonal.

Using the definitions 2) one finds:

8)
$$\sum_{i=-\infty}^{+\infty} \frac{1}{E - E'_i} = \frac{\pi}{\varepsilon} \cot \left(\pi \frac{E - E_o - \alpha}{\varepsilon} \right) \qquad (i \neq 0)$$

The zero's of $E - E_o - \frac{\pi v^2}{\varepsilon} \cot \left(\pi \frac{E - E_o - \alpha}{\varepsilon} \right) + i\pi \Gamma_o^r$ have to be studied. When substitution 9) is performed:

9)
$$E - E_o - \alpha = \frac{\varepsilon}{\pi} (x + iy)$$

where x and y are real, x and y have to satisfy:

10a)
$$\frac{\varepsilon^2}{\pi^2 v^2} \left(\frac{\pi}{\varepsilon} \alpha + x \right) = \text{Re} \cot \, (x + iy)$$

10b)
$$\frac{\varepsilon^2}{\pi^2 v^2} \left(y + \frac{\pi^2 \Gamma_o^r}{\varepsilon} \right) = \text{Im} \cot \, (x + iy)$$

Equations 10a) and 10b) are graphically represented in figures 2) and 3). One uses expressions:

11a)
$$\text{Re} \cot \, (x + iy) = \frac{\sin 2x}{- \cos 2x + \cosh 2y}$$

11b)
$$\text{Im} \cot \, (x + iy) = - \frac{\sinh 2y}{- \cos 2x + \cosh 2y}$$

In figure 2) the full lines represent -Re cot (x + iy) and the dotted line $- \frac{\varepsilon^2}{\pi^2 v^2} \left(\frac{\pi}{\varepsilon} \alpha + x \right)$. In figure 3) the full lines represent -Im cot (x + iy) and the dotted line $- \frac{\varepsilon^2}{\pi^2 v^2} \left(y + \frac{\pi^2 \Gamma_o^r}{\varepsilon} \right)$.

If $|y|$ is unequal to zero, it is seen in figure 2) that instead of periodic infinite values, finite maxima and minima in -Re cot (x + iy) appear, which are a periodic function of x. If $|y|$ grows larger the maxima and minima grow smaller.

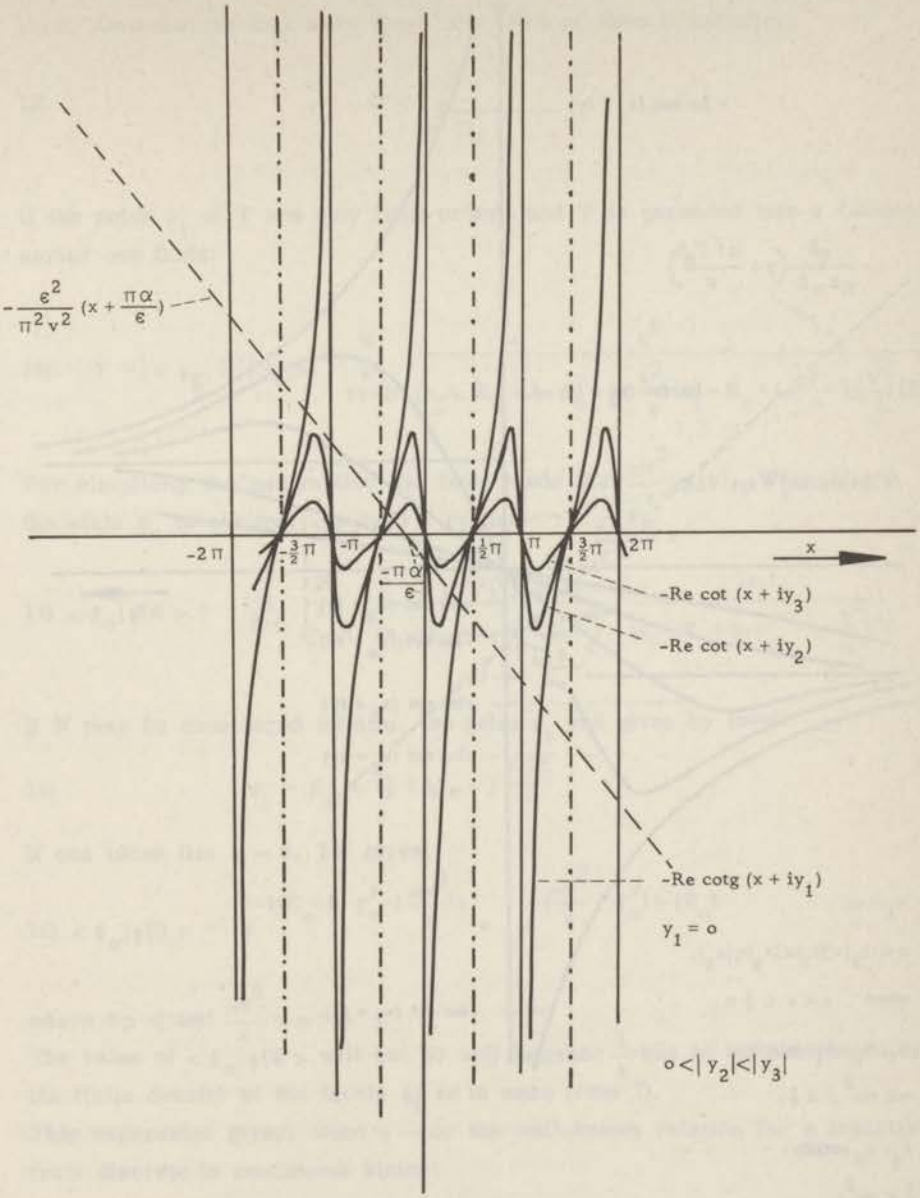
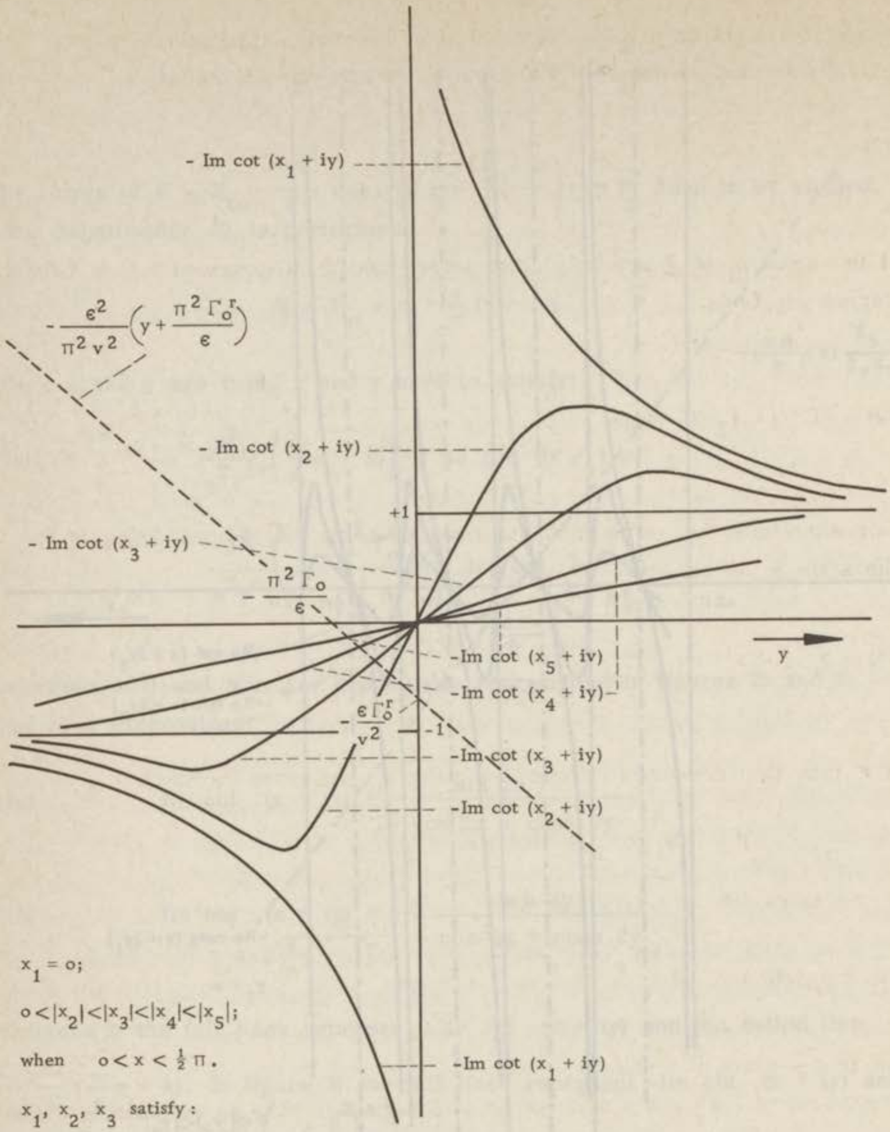

$-\frac{\epsilon^2}{\pi^2 v^2}(x+\frac{\pi\alpha}{\epsilon})$
-2π
$-\frac{3}{2}\pi$
$-\pi$
$-\frac{\pi\alpha}{\epsilon}$
$\frac{1}{2}\pi$
π
$\frac{3}{2}\pi$
2π
x
-Re cot $(x+iy_3)$
-Re cot $(x+iy_2)$
-Re cotg $(x+iy_1)$
$y_1 = o$
$o<|y_2|<|y_3|$

figure 2



$x_1 = o$;

$o < |x_2| < |x_3| < |x_4| < |x_5|$;

when $o < x < \frac{1}{2}\pi$.

x_1, x_2, x_3 satisfy:

$o \leq \sin^2 x \leq \frac{1}{2}$;

x_4, x_5 satisfy:

$\frac{1}{2} \leq \sin^2 x$.

figure 3

One reads from figure 3) that $-\frac{\pi^2\Gamma_o^r}{\varepsilon} < y < o$. If $\frac{\varepsilon\,\Gamma_o^r}{v^2} \ll 1$, y approaches 0, when $x \neq o$. It is seen from figure 2) that then many intersection points exist. One derives that when there are 4N+1 of them N satisfies:

12) $$N < \frac{v^4}{\varepsilon^2\,\Gamma_o^r}$$

If the poles z_i of T are only first order and T is expanded into a Laurent series one finds:

13) $$T = \left|\langle \Phi_{\vec{\varepsilon}} |\, H' \,|\, \Phi_o \rangle\right|^2 \sum_{i=-N}^{N} \frac{v^2}{(z_i - E_o + i\pi\,\Gamma_o^r - i\pi\,\frac{v^2}{\varepsilon})(z_i - E_o + i\pi\Gamma_o^r + i\pi\frac{v^2}{\varepsilon})(E - z_i)}$$

For simplicity the assumption has been made that $\frac{\pi v^2}{\varepsilon} \gg |v|$. When at t=0 the state Φ_o is excited, $\langle \Phi_o | \psi(t) \rangle$ reads:

14) $$\langle \Phi_o | \psi(t) \rangle = -\frac{\varepsilon}{2\pi i} \sum_{i=-N}^{+N} \left\{ \frac{e^{-iz_i t}}{(z_i - E_o + i\pi\Gamma_o^r + i\pi\frac{v^2}{\varepsilon})} - \frac{e^{-iz_i t}}{(z_i - E_o + i\pi\Gamma_o^r - i\pi\frac{v^2}{\varepsilon})} \right\}$$

If N may be considered infinite, the poles z_i are given by (α=o):

15) $$z_i = E_o + (\tfrac{1}{2} + k)\varepsilon - i\,\frac{\varepsilon\,\Gamma_o^r}{v^2}$$

If one takes lim $\varepsilon \to 0$, 14) gives:

16) $$\langle \Phi_o | \psi(t) \rangle = e^{-i(E_o - i\pi\,\Gamma_o^r - i\,\frac{\pi v^2}{\varepsilon})t} = e^{-(\frac{\pi v^2}{\varepsilon} + \Gamma_o^r)t - iE_o t}$$

where $t > o$ and $\frac{\pi v^2}{\varepsilon} > \pi\,\Gamma_o^r$.
The value of $\langle \Phi_o | \psi(t) \rangle$ will not be null because $\frac{1}{\varepsilon}$ has to be considered as the finite density of the levels Φ_i as is seen from 7).
This expression gives, when $\varepsilon \to o$, the well-known relation for a transition from discrete to continuous states:

17) $$T = \frac{\left|\langle \Phi_{\vec{\varepsilon}} | H' | \Phi_o \rangle\right|^2}{E - E_o + i\pi v^2 \rho + i\pi\,\Gamma_o^r}$$

One sees that $\rho = \frac{1}{\epsilon}$ must be read as the density of states in the continuum. The probability distribution of absorbed or emitted quanta is then (3, 17):

18) $$P_F = \frac{|<\Phi_{\vec{\epsilon}}|H'|\Phi_o>|^4}{(E - E_o)^2 + \pi^2 (\frac{v^2}{\epsilon} + \Gamma_o^r)^2}$$

The shape is seen to be purely Lorentzian. The decay-time τ is:

19) $$\tau = \frac{1}{2\pi(v^2\rho + \Gamma_o^r)}$$

τ is the decay-time expected due to two continua. The decay-rate equals:

20) $$k = 2\pi v^2 \rho + 2\pi \Gamma_o^r$$

If $\frac{\pi^2 v^2}{\epsilon^2} \gg 1$, 15) can be substituted into 14) and one finds:

21) $$<\Phi_o|\psi(t)> = \frac{\epsilon}{\pi} e^{-\frac{\epsilon\Gamma_o^r}{v^2} t - iE_o t} \left\{ \sum_{k=o}^{N} \frac{(\frac{1}{2} + k)\epsilon \sin(k + \frac{1}{2})\epsilon t + \lambda \cos(k + \frac{1}{2})\epsilon t}{(\frac{1}{2} + k)^2 \epsilon^2 + \lambda^2} + \right.$$

$$\left. - \frac{(\frac{1}{2} + k)\epsilon \sin(K + \frac{1}{2})\epsilon t + \lambda' \cos(K + \frac{1}{2})\epsilon t}{(\frac{1}{2} + k)^2 \epsilon^2 + \lambda'^2} \right\}$$

where: $$\lambda = -\frac{\epsilon\Gamma_o^r}{v^2} + \Gamma_o^r + \frac{\pi v^2}{\epsilon}$$

$$\lambda' = -\frac{\epsilon\Gamma_o^r}{v^2} + \Gamma_o^r - \frac{\pi v^2}{\epsilon}$$

The function within the braces is periodic with period $\frac{4\pi}{\epsilon}$. Its absolute value has a maximum at $t = \frac{2\pi k}{\epsilon}$ and a minimum at $t = \frac{\pi}{\epsilon} + \frac{2\pi k}{\epsilon}$.

If $e^{\frac{\pi^2 v^2}{\epsilon^2} + \frac{\pi^2 \Gamma_o^r}{\epsilon}} \gg 1$ and N can be considered infinite use can be made of:

22) $$e^{-\lambda t} \simeq \frac{\epsilon}{\pi} \sum_{k=o}^{\infty} \frac{(\frac{1}{2} + k)\epsilon \sin(k + \frac{1}{2})\epsilon t + \lambda \cos(k + \frac{1}{2})\epsilon t}{(\frac{1}{2} + k)^2 \epsilon^2 + \lambda^2}$$

with $\lambda > o$ and $o < t \ll t'$, where $t' = \frac{\pi}{\epsilon}$.
At t' the absolute value of the function has reached its minimum value, then increases as $e^{-\lambda' t}$ until its maximum value at $t' = \frac{2\pi}{\epsilon}$ is reached.
If ϵ remains finite one finds therefore an exponential decay with decay-time $\tau = \frac{1}{2\pi \frac{v^2}{\epsilon} + 2\pi \Gamma_o^r}$. This behaviour repetes with period $\frac{2\pi}{\epsilon}$ and its overall decay-time is given by:

23) $$\tau' = \frac{v^2}{2\epsilon \Gamma_o^r}$$

This is the precise formulation of the so-called statistical limit (1). Only when lim $\epsilon \to o$ no repetition occurs, but then one deals with a real continuum.

The cross-section and therefore the emission and absorption shows sharp maxima at $E = E_o + (\frac{1}{2} + k)\,\epsilon$ with width:

24) $$\frac{2\epsilon \Gamma_o^r}{v^2}$$

The maxima itself are given by the curve:

25) $$\frac{|<\Phi_o|H'|\Phi_{\vec{\epsilon}}>|^4 \; v^4}{\{(E - E_o)^2 + (\frac{\pi v^2}{\epsilon} + \pi \Gamma_o^r)^2\} \, \epsilon^2 \, \Gamma_o^{r2}}$$

The derived formulae show that a Lorentzian curve is found but build up from very small lines. If the set Φ_i is not an infinite set but a finite one essentially the same result will be got if $\frac{\pi^2 v^2}{\epsilon^2} \gg \frac{v^4}{\epsilon^2 \Gamma_o^r}$.

When $\frac{\epsilon^2}{\pi^2 v^2}$ increases the possibility exists that $\frac{\epsilon}{\pi}$, πv^2 and Γ_0^r are of the same order . In the next paragraphs the problems which then arise are discussed for two excited level systems.
On the very difficult problem of multi-level systems which one has to solve in the theory of radiationless transitions in this intermediate case, will be lightly touched, using the results found from the two level systems. It will be seen that the extension from two level to multi-level systems is non-trivial. The possible kinds of behaviour will be the same as in two level system as follows from the general theory presented in chapter II.

III.2. INTERFERENCE IN TWO LEVEL SYSTEMS.

The simplest case is that of two non-coupled levels Φ_1 and Φ_2, when there is no interaction with the electromagnetic field, which can be excited from the ground state by a photon of different direction of polarization. In the same way as is discussed in III.2, the matrix **O** can be found in this basis:

$$26)\qquad \mathbf{O} = \begin{pmatrix} E - E_1 + i\pi\Gamma_1 & 0 \\ 0 & E - E_2 + i\pi\Gamma_2 \end{pmatrix}$$

$2\pi\Gamma_1$ is the radiative width of state Φ_1. $2\pi\Gamma_2$ that of state Φ_2. E_1 and E_2 are the energies of states Φ_1 and Φ_2.

The time-development of the states Φ_1 and Φ_2 can now be found using II,26):

$$27)\qquad \psi(t) = e^{(-iE_1 - \pi\Gamma_1)(t-t')}\, c_1(t')\, \Phi_1 + e^{(-iE_2 - \pi\Gamma_2)(t-t')}\, c_2(t')\, \Phi_2$$

The time-development of $|<\Phi_1|\psi(t)>|^2$ and of $|<\Phi_2|\psi(t)>|^2$ are:

28) a) $|<\Phi_1|\psi(t)>|^2 = e^{-2\pi\Gamma_1(t-t')}\,|c_1(t')|^2$

b) $|<\Phi_2|\psi(t)>|^2 = e^{-2\pi\Gamma_2(t-t')}\,|c_2(t')|^2$

But the time-development of the state $\frac{1}{\sqrt{2}}(\Phi_1+\Phi_2)$ or $\frac{1}{\sqrt{2}}(\Phi_1-\Phi_2)$ is given by:

$$29)\quad |<\frac{1}{\sqrt{2}}(\Phi_1 \pm \Phi_2)\,|\,\psi(t)>|^2 = \frac{1}{2}e^{-2\pi\Gamma_1(t-t')}\,|c_1(t')|^2 + \frac{1}{2}e^{-2\pi\Gamma_2(t-t')}\,|c_2(t')|^2 \pm e^{-\pi(\Gamma_1+\Gamma_2)(t-t')}\{\mathrm{Re}\, c_1^*(t')\,c_2(t')\cos(E_1-E_2)(t-t') + \mathrm{Im}\, c_1^*(t')\,c_2(t')\sin(E_1-E_2)(t-t')\}$$

$c_1(t')$ and $c_2(t')$ are the coefficients of states Φ_1 and Φ_2 at t=t'.
When the states Φ_1 and Φ_2 are both excited at t=t' and one studies the time-development of the individual atoms or molecules, the last term contributes, when there is no external interaction which disturbes the phase-relation between $c_1(t')$ and $c_2(t')$. In the case this phase-relation is lost much faster than the radiative decay and oscillation frequency, there is no phase-relation between $c_1(t')$ and $c_2(t')$, so averaging deletes the contributions of the oscillating terms.
An example is broadband pulse excitation of two levels by linearly polarized light, whereas Φ_1 is assumed to be only excited by right-circular polarized light and Φ_2 is assumed to be only excited by left-circular polarized light. When the emission of linearly polarized light is studied and when $\frac{1}{E_1-E_2} << \frac{1}{\pi|\Gamma_1+\Gamma_2|}$ oscillations can be expected. They can only be measured however, when excitation takes place by a coherent light-source, because otherwise they cancel against the contributions of the other atoms or molecules.
When a Boltzmann equilibrium can be very rapidly established the phase relationship is broken and the oscillations disappear. The development in time is again exponential, but with a different decay-time given by the Fermi-Golden rule (4). In III.3 the influence of relaxation on absorption

and emission is discussed in more detail.

One sees from 28) that when no external interactions are present and excitation takes place to one of both states, no contributions to the emission will be found due to the other state.

Consider now the case that there is a time-independent external field present which couples the states Φ_1 and Φ_2. The matrix E is then not diagonal in the basis Φ_1 and Φ_2. Let the matrix-element, which originates from the coupling by the external field be a.

The matrix O is now:

$$\text{30)} \qquad O = \begin{bmatrix} E - E_1 + i\pi\Gamma_1 & a \\ a^* & E - E_2 + i\pi\Gamma_2 \end{bmatrix}$$

The solutions of det $|O| = 0$ are:

$$\text{31)} \qquad E^{\pm} = \tfrac{1}{2}\{(E_1 + E_2) - i\pi(\Gamma_1 + \Gamma_2)\} \pm \tfrac{1}{2}\sqrt{\{E_1 - E_2 - i\pi(\Gamma_1 - \Gamma_2)\}^2 + 4|a|^2}$$

The three cases which give all the different kinds of behaviour of $\psi(t)$ are:

case a: $\Gamma_1 = \Gamma_2 : \dfrac{4|a|^2}{|E_1 - E_2|^2} \ll 1$

with solutions:

$$\text{32)} \qquad E^+ = E_1 + \frac{|a|^2}{E_1 - E_2} - i\pi\,\Gamma_1$$

$$E^- = E_2 - \frac{|a|^2}{E_1 - E_2} - i\pi\,\Gamma_1$$

case b: $E_1 = E_2 : \pi^2(\Gamma_1 - \Gamma_2)^2 = 4|a|^2$

with solutions:

33) $$E^{+}_{-} = \tfrac{1}{2}\{E_1 + E_2 - i\pi(\Gamma_1 + \Gamma_2)\}$$

case c: $\Gamma_1 = \Gamma_2 : \dfrac{|E_1 - E_2|^2}{4|a|^2} \ll 1$

with solutions:

34) $$E^{+}_{-} = \tfrac{1}{2}(E_1 + E_2) \pm |a| - i\pi\Gamma$$

The time-development of $|<\Phi_1|\psi(t)>|^2$, $|<\Phi_2|\psi(t)>|^2$ and $|<\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2|\psi(t)>|^2$ is now:

In case a:

$$|<\Phi_1|\psi(t)>|^2 \sim e^{-2\pi\,\Gamma_1(t-t')}\{1 - \frac{2|a|^2}{(E_1 - E_2)^2}\cos(E_1 - E_2)(t-t')\}\,|c_1(t')|^2 \qquad \text{a)}$$

with $c_2(t') = 0$

$$|<\Phi_2|\psi(t)>|^2 \sim e^{-2\pi\,\Gamma_1(t-t')}\{1 - \frac{2|a|^2}{(E_1 - E_2)^2}\cos(E_1 - E_2)(t-t')\}\,|c_2(t')|^2 \qquad \text{b)}$$

with $c_1(t') = 0$ 35)

$$|<\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)|\psi(t)>|^2 \sim \tfrac{1}{2}|<\Phi_1|\psi(t)>|^2 + \tfrac{1}{2}<\Phi_2|\psi(t)>|^2$$

$$+\, e^{-2\pi\,\Gamma_1(t-t')}[\mathrm{Re}\{c_1(t')\,c_2^*(t')\,\cos(E_1 - E_2)(t-t') +$$

$$\mathrm{Im}\{c_1(t')\,c_2^*(t')\,\sin(E_1 - E_2)(t-t')] \qquad \text{c)}$$

To find 35) use has been made that when the roots of the det $|EI - E + i\pi\,\Gamma|$ are given by

36) $$E^{+} = E_1' - i\pi\,\Gamma_{11}'$$

$$E^{-} = E_2' - i\pi\,\Gamma_{22}'$$

the time-development of the population of Φ_1 when this state is excited at t=0 is given by:

$$|<\Phi_1|\psi(t)>|^2 = \frac{(E_1' - E_2)^2 + \pi^2 (\Gamma_{11}' - \Gamma_{22})^2}{(E_1' - E_2')^2 + \pi^2 (\Gamma_{11}' - \Gamma_{22}')^2} e^{-2\pi \Gamma_{11}' t} +$$

$$+ \frac{(E_2' - E_2)^2 + \pi^2 (\Gamma_{22} - \Gamma_{22}')^2}{(E_1' - E_2')^2 + \pi^2 (\Gamma_{11}' - \Gamma_{22}')^2} e^{-2\pi \Gamma_{22}' t} - 2 \frac{e^{-\pi \Gamma_{11}' t - \pi \Gamma_{22}' t}}{(E_1' - E_2')^2 + \pi^2 (\Gamma_{11}' - \Gamma_{22}')^2} \times \quad 37)$$

$$\times [\{(E_1' - E_2)(E_2' - E_2) + \pi^2 (\Gamma_{11}' - \Gamma_{22})(\Gamma_{22}' - \Gamma_{22})\} \cos (E_1' - E_2')t +$$

$$+ \pi \ \{(\Gamma_{22}' - \Gamma_{22})(E_1' - E_2) - (\Gamma_{11}' - \Gamma_{22}')(E_2' - E_2)\} \sin (E_1' - E_2')t]$$

The oscillating terms in 35) contribute, if $\frac{1}{|E_1 - E_2|} \ll \frac{1}{2\pi \Gamma_1}$.

When we study the time-dependent behaviour of the individual states the modulation in amplitude is of order $\frac{2|a|^2}{(E_1 - E_2)^2}$. This is in case a) very small. When there is no other mechanism that induces transitions between the states Φ_1 and Φ_2 or disturbes their phase-relationship and the states Φ_1 and Φ_2 are both excited at the same moment, in the emission of the state $\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)$ the magnitude of the modulation is of order 1. It is this situation of course which is suitable to see the quantum-beats phenomenon (11). In the experimental situation it is only seen when the different molecules are coherently excited.

When one does not excite with a coherent light-source, the effects of the coupling of state Φ_1 to Φ_2 can be seen when one studies the energy-dependence of emitted and absorbed light. When one excites with light of polarization-direction $\vec{\epsilon}_1$, there is now a small probability that light will be emitted of polarization direction $\vec{\epsilon}_2$. $T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_1}$ is in this case:

$$38) \qquad T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_1} = - \frac{<\Phi_{\vec{\epsilon}_2}|H'|\Phi_2> a <\Phi_1|H'|\Phi_{\vec{\epsilon}_1}>}{(E - E_1 + i\pi \Gamma_1)(E - E_2 + i\pi \Gamma_2)}$$

The probability of emission equals $|T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_1}|^2$.

The time-development in case b) and c) is given by equations 39) and 40):

$$\text{case b:}\quad |< \Phi_1|\Psi(t) >|^2 = e^{-\pi(\Gamma_1 + \Gamma_2)(t-t')} \{1 - \pi(\Gamma_1 + \Gamma_2)\, E_1(t-t') + + \tfrac{1}{4}\,\{\pi^2(\Gamma_1 + \Gamma_2)^2 + a^2\, E_1^2\, (t-t')^2]\,|c_1(t')|^2 \qquad 39)$$

with $c_2(t') = 0$.

$$\text{case c:}\quad |< \Phi_1|\Psi(t) >|^2 = \tfrac{1}{2}\, e^{-2\pi\,\Gamma_1(t-t')} \{1 + \cos 2|a|(t-t')\}\, |c_1(t')|^2 \qquad 40)$$

with $c_2(t') = 0$.

The probability that when one excites with light of polarization direction $\vec{\varepsilon}_1$, there is a probability that light will be emitted of direction of polarization $\vec{\varepsilon}_2$ increases going from case a) to b), and from case b) to case c), where the probability of finding light of both directions of polarization is equal. In case b) and c) is seen that the time-dependence now grows more non-exponential. The typical behaviour in case b) is caused by the double pole in the matrix-elements of $\mathbf{O}^{-1}$ (see II,5b) and ref. (14). Case 3) is also suitable to see the quantum-beat phenomenon.

The case $\Gamma_2 = 0$ is of interest to the discussion of III.2.
There $\Gamma_1 = \Gamma_o^r$ and $2\pi\,\Gamma_o^r$ is the radiative width of the state Φ_o. In the representation Φ_i the matrix is non-diagonal. The set Φ_i is restricted now to one other state Φ_1 and ε is the difference between the diagonal elements of **E** . α is assumed to be zero. The non-diagonal elements of **E** are v.
The time-dependent behaviour can now easily be found. The matrix **O** is equal to 30) except that $\Gamma_1 = \Gamma_o^r$, $E_1 - E_2 = \varepsilon$ and $|a| = |v|$.
The three cases which can be distinguished now are:

$$\text{case a):}\quad \frac{|\varepsilon^2 - \pi^2\,\Gamma_o^{r2}|}{v^2} \ll 1\ ;\quad \frac{\varepsilon\,\pi\,\Gamma_o^r}{v^2} \ll 1$$

$$\text{case b):}\quad \frac{\varepsilon}{v^2} \ll 1;\quad \pi^2\,\Gamma_o^{r2} = v^2;\quad \frac{\varepsilon\,\pi\,\Gamma_o^r}{v^2} \ll 1$$

case c: $\dfrac{v^2}{\epsilon^2 - \pi^2 \Gamma_o^{r^2}} \ll 1; \quad \dfrac{\epsilon \pi \Gamma_o^r}{\epsilon^2 - \pi^2 \Gamma_o^{r^2}} \ll 1$

The time-dependence of Φ_o is in the three cases:

$$\text{case a)}: |<\Phi_o|\psi(t)>|^2 = \tfrac{1}{2}\, e^{-\pi \Gamma_o^r (t-t')} \{1 + \cos 2|v|(t-t')\} |c_1(t')|^2 \qquad \text{41a)}$$

$$\text{case b)}: |<\Phi_o|\psi(t)>|^2 = e^{-\pi \Gamma_o^r (t-t')} [1 - \pi \Gamma_o^r (t-t') + \{(E_1 + \tfrac{1}{2}\epsilon)^2 - \tfrac{1}{4}\pi^2 \Gamma_o^{r^2}\} \times$$

$$\times (t-t')^2] |c_1(t')|^2 \qquad \text{41b)}$$

$$\text{case c)}: |<\Phi_o|\psi(t)>|^2 = e^{-2\pi \Gamma_o^r (t-t')} \left[1 - \frac{2|v|^2}{\epsilon^2} \cos \epsilon t\right] \qquad \text{41c)}$$

The situation now is completely altered compared to the case that Φ_o is coupled to an infinite set of states. The proportion of ϵ, $\pi \Gamma_o^r$ and $|v|^2$ are in case a) those of the statistical limit considered in III.2.
The decay-time in case a) is, however, two times longer than when $v=0$. Because the inequality $|v| \gg \pi \Gamma_o^r$ is satisfied, the modulation in the time-dependence contributes to 41a), its amplitude is of order 1. The behaviour of 41a) is that of a damped oscillator. The probability-distribution of emitted photons will show two maxima at distance $|v|$ from one another. The shape around each maximum will be approximately Lorentzian, the width $\pi \Gamma_o^r$, that is half of the original radiative linewidth.
When $|v|$ decreases and satisfies b), the width of the level Φ_o is as large as its interaction with Φ_1 and the non-oscillatory but non-exponential behaviour 41b) appears. The two maxima of emitted photons have collapsed, but the shape of the probability curve is non-Lorentzian. If $|v|$ is so small that it satisfies c), the exponential behaviour of the time-development of Φ_o is modulated by very small oscillations, because $2\pi \Gamma_o^r < \epsilon$. The exponential decay-time is here the original radiative one and two times smaller than in 41a).

One can now sketch what happens when more states are coupled with Φ_o.

When $|v|^2$ remains a constant, the relations of case a) will less well be satisfied, because the distance between the other levels and Φ_0 increases. This means that maxima will appear between the two already present at a distance $|v|$. The width of the individual lines will be very small. The time-dependent behaviour will be a superposition of terms like 41a). The interference of these terms results in the exponential decay discussed in III.2. In the case $|\Gamma_0^r| = 0$, this has been shown by Rhodes (15). It is seen that the full oscillations have to be taken into account.

It is also seen from 41a) that there is in fact a competition between the lengthening of the time of radiative decay-time because of the coupling with other states and a shortening due to the interference of the oscillating terms. A discussion of these intermediate cases can be found in ref. (21). The phenomena described here are only directly applicable to an experimental situation when the relaxation times due to external interactions are very large and there are also no other reasons of broadening. The discussion applies only to one single atom or molecule. One has to be careful to apply it directly to a sample of molecules. The relaxation-mechanism that can be treated within the formalism of chapter II is that of radiationless transitions according to the Jortner-Stepanov model. In the next paragraph the time-development of the excited states and energy dependence in absorption and emission will be derived of two excited states where these relaxation-mechanisms are important.

III.3. INTERFERENCE EFFECTS WHEN TWO EXCITED STATES ARE COUPLED AND RADIATIONLESS TRANSITIONS ARE IMPORTANT.

Two examples of large molecules, in which radiationless transitions are possible, are treated.

In case a) two excited states are coupled by the radiation-field to the ground-state and each has a different direction of polarization. These states are coupled with one another by radiationless transitions, so they can be considered to have an interaction with an extra continuum, which couples them.

The matrix Γ therefore is non-diagonal and has the matrix-elements:

42) $$\Gamma_{11} = \Gamma^{r}_{11} + v_1^2 \rho_1; \quad \Gamma_{22} = \Gamma^{r}_{22} + v_2^2 \rho_2; \quad \Gamma_{12} = \Gamma_{21} = v_1 v_2 \rho_3$$

Γ^{r}_{11} and Γ^{r}_{22} are the contributions to Γ due to the coupling with the electromagnetic field; v_1 and v_2 are parameters which give the coupling of states 1 and 2 to the quasi-continuum of vibrational-states in the molecule and ρ is the density of this quasi-continuum. The matrix **E** is diagonal and has the diagonal-elements E_1 and E_2. This case is also considered in ref. (8), but the method used is different.

In case b) one discrete state carries oscillator-strength, but is coupled by a direct mechanism (not via a continuum) with a second discrete state which, in its turn, is coupled with a quasi-continuum which induces radiationless-transitions. (The direct mechanism can be, for instance, spin-orbit coupling). The matrix Γ has in this case the matrix-elements:

43) $$\Gamma_{11} = \Gamma^{r}_{11}; \quad \Gamma_{12} = \Gamma_{21} = 0; \quad \Gamma_{22} = v^2 \rho$$

$2\pi\,\Gamma^{r}_{11}$ is the radiative width of level Φ_1.

The matrix **E** , however, is now non-diagonal and has the matrix-elements:

44) $$E_{11} = E_1; \quad E_{22} = E_2; \quad E_{12} = E^{*}_{21} = v_{12}$$

Here v_{12} represents the coupling between two discrete states.

III.3a. Two discrete states coupled by a quasi-continuum.

Using equation II,47b) for the T-matrix, the expressions are:

a. $$T_{\vec{\epsilon}_1 \leftarrow \vec{\epsilon}_1} = \langle \Phi_{\vec{\epsilon}_1} | H' | \Phi_1 \rangle \frac{E - E_2 + i\pi\Gamma_{22}}{\det |E\,I - E + i\pi\Gamma|} \langle \Phi_1 | H' | \Phi_{\vec{\epsilon}_1} \rangle$$

b. $$T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_2} = \langle \Phi_{\vec{\epsilon}_2} | H' | \Phi_2 \rangle \frac{E - E_1 + i\pi\Gamma_{11}}{\det |E\,I - E + i\pi\Gamma|} \langle \Phi_2 | H' | \Phi_{\vec{\epsilon}_2} \rangle$$

c. $$T_{\vec{\epsilon}_1 \leftarrow \vec{\epsilon}_2} = \langle \Phi_{\vec{\epsilon}_1} | H' | \Phi_1 \rangle \frac{-i\pi\Gamma_{12}}{\det |E\,I - E + i\pi\Gamma|} \langle \Phi_2 | H' | \Phi_{\vec{\epsilon}_2} \rangle$$

d. $$T_{\vec{\varepsilon}_2 \leftarrow \vec{\varepsilon}_1} = < \Phi_{\vec{\varepsilon}_2} | H' | \Phi_1 > \frac{-i\pi\, \Gamma_{21}}{\det | E\, I - E + i\pi\, \Gamma |} < \Phi_1 | H' | \Phi_{\vec{\varepsilon}_1} > \qquad 45)$$

$\vec{\varepsilon}_1$ and $\vec{\varepsilon}_2$ denote the polarization-direction of the absorbed or emitted photon. Φ_1 and Φ_2 denote the two states which carry oscillator-strength. The behaviour that will be found will be similar to that discussed in (II, 5b), when one puts $\Gamma_{11} = \Gamma_{22} = \Gamma_{12}$. This approximation is very well when v_1 equals v_2 and ρ_1 equals ρ_2 and equals ρ_3, because Γ^r_{11} and Γ^r_{22} are much smaller than the non-radiative decay-rates. In this approximation one can distinguish the three cases:

case I: $|E_1 - E_2|^2 \gg |\Gamma|^2\, 4\pi^2$

case II: $|E_1 - E_2|^2 = |\Gamma|^2\, 4\pi^2$

case III: $|E_1 - E_2|^2 \ll |\Gamma|^2\, 4\pi^2$

In case I

46a) $$T_{\vec{\varepsilon}_1 \leftarrow \vec{\varepsilon}_1} = \Gamma^r_{11} \frac{1}{E - E_1 + i\pi\, \Gamma_{11}}$$

b) $$T_{\vec{\varepsilon}_1 \leftarrow \vec{\varepsilon}_2} = T_{\vec{\varepsilon}_2 \leftarrow \vec{\varepsilon}_1} \sim 0$$

c) $$T_{\vec{\varepsilon}_2 \leftarrow \vec{\varepsilon}_2} = \Gamma^r_{22} \frac{1}{E - E_2 + i\pi\, \Gamma_{22}}$$

Expressions 46) show that the system behaves as two isolated resonances and the corresponding time-dependent behaviour can be found in II. 5). The decay-rate is determined by the non-radiative decay.

When $|E_1 - E_2|^2$ grows smaller but does not yet satisfy relationship II, the complete expressions 45) have to be used. When the roots of the det $| E\, I - E + i\pi\, \Gamma |$ are given by:

47) $$E_a = E_1' - i\pi\, \Gamma_{11}'$$

$$E_b = E_2' - i\pi\, \Gamma_{22}'$$

It is seen from 37) that the exponential decay, corresponding to 46), now will be modulated with a frequency $|E_1' - E_2'|$. Therefore when the coupling Γ_{12} cannot be neglected a modulation with frequency $|E_1' - E_2'|$ of the decay will be expected. The amplitude of these oscillations will however be small.

When $|E_1 - E_2| = 2\pi\,\Gamma$ one finds:

$$48a)\quad T_{\vec{\epsilon}_1 \leftarrow \vec{\epsilon}_2} = \Gamma_{11}^r \left[\frac{1}{E - \frac{1}{2}(E_1 + E_2) + i\pi\,\Gamma_{11}} - \frac{\frac{1}{2}(E_1 - E_2)}{\{E - \frac{1}{2}(E_1 + E_2) + i\pi\,\Gamma_{11}\}^2}\right]$$

$$b)\quad T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_1} = < \Phi_{\vec{\epsilon}_2} |H'| \Phi_2 > < \Phi_1 |H'| \Phi_{\vec{\epsilon}_1} > \frac{-i\pi\,\Gamma_{21}}{\{E - \frac{1}{2}(E_1 + E_2) + i\pi\,\Gamma_{11}\}^2}$$

This behaviour can only be found in the exact case when $\Gamma_{11} = \Gamma_{22}$. When $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ are interchanged in 48), the expressions are the same except that the labels 1 and 2 have also to be interchanged. The linewidths in case II will not be Lorentzian and will be approximately half of the linewidths of case I).
This is an example of the situation where the T-matrix has a double pole. When Φ_1 is excited at t= 0, its time-development is given by:

$$49)\qquad |< \Phi_1 | \psi(t) >|^2 = e^{-2\pi\,\Gamma_{11} t}\,\{1 + (\pi\, v^2 \rho)^2\, t^2\}$$

In case III one finds:

$$50a)\quad T_{\vec{\epsilon}_1 \leftarrow \vec{\epsilon}_1} = \Gamma_{11}^r \frac{E - E_2 + i\pi(\Gamma_{22}^r + v^2\rho)}{\{E - \frac{1}{2}(E_1 + E_2) + i\pi\,\Gamma^r\}\,\{E - \frac{1}{2}(E_1 + E_2) + i\pi\,(\Gamma^r + 2v^2\rho)\}}$$

$$b)\quad T_{\vec{\epsilon}_2 \leftarrow \vec{\epsilon}_1} = \frac{< \Phi_{\vec{\epsilon}_2} |H'| \Phi_2 > (-i\pi\, v^2\rho) < \Phi_1 |H'| \Phi_{\vec{\epsilon}_1} >}{\{E - \frac{1}{2}(E_1 + E_2) + i\pi\,\Gamma^r\}\,\{E - \frac{1}{2}(E_1 + E_2) + i\pi(\Gamma^r + 2v^2\rho)}$$

The radiative decay is now taken into account again, for otherwise the population of the levels remains a constant for large times as can be seen in 52).

Γ^r is defined as:

51) $$\Gamma^r = \tfrac{1}{2}(\Gamma^r_{11} + \Gamma^r_{22})$$

When Φ_1 is excited at t= 0, the time-development is given by:

52) $$|<\Phi_1|\Psi(t)>|^2 = \frac{1}{4}\, e^{-2\pi\Gamma^r t}\left[1 + 2\,e^{-2\pi v^2 \rho t} + e^{-4\pi v^2 \rho t}\right]$$

The time-development will appear only as a superposition of exponentially decaying terms and the decay-rate will be $2\pi\Gamma^r$ if $t \gg \frac{1}{2\pi v^2 \rho}$.

If $\Gamma^r_{22} = 0$, one sees from 51) and 52) that the decay-rate is half of the radiative decay-rate found when no radiationless transitions occur and the decay-time is of course two times larger, if again $t \gg \frac{1}{2\pi v^2 \rho}$.

This is the same phenomenon which occurs when a rapid Boltzmann equilibrium is established between both levels. The radiative decay-time for the same case and high temperatures is then also two times larger than when no Boltzmann equilibrium is established.

The probabilities of absorption and emission are proportional to $|T|^2$. In case I) two Lorentzian curves are found as function of energy and the distance of the maxima is given by $E_1 - E_2$.
The width of the Lorentzian curve around E_1 is given by $2\pi\Gamma_{11}$, the width around E_2 by $2\pi\Gamma_{22}$ and they are therefore very large.
If one goes from case I) to case II), the shape of the two curves grows non-Lorentzian and the maxima get a smaller difference until case b) is reached. Here the two maxima cannot be separated any more, but the curves remain anti-symmetric. Going from case II to case III the curve diminishes until a very sharp Lorentzian curve is obtained.
This kind of behaviour is reminiscent to a well-known phenomenon in N.M.R. spectroscopy when two inequivalent protons can interchange positions and the absorption as function of temperature is measured (20).
One notes that when one excites with polarization direction $\vec{\varepsilon}_1$ a finite probability exists of finding a polarization direction $\vec{\varepsilon}_2$ of the emitted light.
The probability of finding direction $\vec{\varepsilon}_1$ or $\vec{\varepsilon}_2$ is in case III equal if
$< \Phi_{\vec{\varepsilon}_2} | H' | \Phi_2 > = < \Phi_{\vec{\varepsilon}_1} | H' | \Phi_1 >$

III.3b. Two discrete states coupled by a direct interaction. One of them can decay by radiationless transitions.

According to 43) and 44) the matrix **E** is non-diagonal, but Γ is diagonal. This case is formally similar to the one dealt with in III.3a because a matrix **O'** can be introduced, such that:

53) $$O' = S\,(EI - E + i\pi\Gamma)\,S^{-1} = EI - E' + i\pi\Gamma'$$

The matrices **S** can be chosen so that **E'** is a diagonal matrix. Using **S** and **O'** the equation for the Transition-matrix is now II, 47b):

54) $$T = |<\Phi_{\vec{\varepsilon}}|H'|\Phi_1>|^2 \sum_{k,l} S_{ik}[O']^{-1}_{kl}\, S^{-1}_{l1}$$

The phenomena which will appear are, therefore, analogous to those found in III.3a. This behaviour will be illustrated for some limiting cases which are of chemical interest (12, 13).

When $(E_1 - E_2)^2 \gg 4|v|^2$, there will be no coupling between the two states. Therefore:

55) $$T_{\vec{\varepsilon} \leftarrow \vec{\varepsilon}} = |<\Phi_{\vec{\varepsilon}}|H'|\Phi_1>|^2 \frac{1}{E - E_1 + i\pi\Gamma^r_{11}}$$

$(E_1 - E_2)^2 < |v|^2$ the $\det|EI - E|$ can be approximated by:

56) $$\det|EI - E| \sim \{E - \tfrac{1}{2}(E_1 + E_2) + |v_{12}|\}\,\{E - \tfrac{1}{2}(E_1 + E_2) - |v_{12}|\}$$

The eigenfunction belonging to the eigenvalue $\frac{1}{2}(E_1 + E_2) + |v_{12}|$ is given by $\psi_1 = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)$ and the other is $\psi_2 = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2)$.

In the new representation ψ, one finds a matrix Γ^{ψ} with matrix-elements:

57) $$\Gamma^{\psi}_{11} = \tfrac{1}{2}\Gamma^r_{11} + \tfrac{1}{2}v^2\rho = \Gamma^{\psi}_{22};\quad \Gamma^{\psi}_{12} = \Gamma^{\psi}_{21} = \tfrac{1}{2}\Gamma^r_{11} - \tfrac{1}{2}v^2\rho$$

$T_{\vec{\varepsilon} \leftarrow \vec{\varepsilon}}$ is:

58) $$T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}} = \frac{1}{2}\,\frac{\Gamma_{11}}{(E - E_1^{\psi} + i\pi\,\Gamma_{11}^{\psi})(E - E_2^{\psi} + i\pi\,\Gamma_{22}^{\psi}) + \pi^2\,|\Gamma_{12}^{\psi}|^2}\,[2E - (E_1^{\psi} + E_2^{\psi}) + 2i\pi v^2 \rho]$$

The three cases one has to distinguish now are:

a) $2\,|v_{12}| \gg 2\pi\,\Gamma_{12}^{\psi}$
b) $2\,|v_{12}| = 2\pi\,\Gamma_{12}^{\psi}$
c) $2\,|v_{12}| \ll 2\pi\,\Gamma_{12}^{\psi}$

Remember that $(E_1^{\psi} - E_2^{\psi})^2 = 4\,|v_{12}|^2$ and $\pi v^2 \rho \gg \Gamma_{11}$
In case a) for $T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}}$ is found:

59) $$T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}} = \frac{\Gamma_{11}}{(E - E_1^{\psi} + i\pi\,\Gamma_{11}^{\psi})(E - E_2^{\psi} + i\pi\,\Gamma_{22}^{\psi})}\,[E - \tfrac{1}{2}(E_1^{\psi} + E_2^{\psi}) + i\pi v^2 \rho\,]$$

The time-development is now:

60) $$|\langle \Phi_1 | \psi(t) \rangle|^2 = \tfrac{1}{2}\, e^{-\pi(\Gamma_{11}^{r} + v^2\rho)\,t}\,(1 + \cos 2\, v_{12}\, t)$$

Oscillations superposed on the on the exponential decay will appear, for $\frac{1}{2\,|v_{12}|} \ll \frac{1}{\pi\,\Gamma_{11}^{r} + v^2 \rho}$. The decay-rate is determined by the non-radiative decay.

Case b) gives us for $T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}}$:

61) $$T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}} = \Gamma_{11}\left\{\frac{1}{E - \tfrac{1}{2}(E_1^{\psi} + E_2^{\psi}) + i\pi\,\Gamma_{11}^{\psi}} + \frac{\tfrac{1}{2}\, i(\pi\,\Gamma_{11}^{r} + 3\,\pi\, v^2 \rho)}{[E - \tfrac{1}{2}(E_1^{\psi} + E_2^{\psi}) + i\pi\,\Gamma_{11}^{\psi}]^2}\right\}$$

This is only valid in the exact case when $E_1 = E_2$.
The time-development is given by:

62) $$|\langle \Phi_1 | \psi(t) \rangle|^2 = e^{-2\pi\,\Gamma_{11}^{\psi}\, t}\,\{1 + \frac{1}{4}(\Gamma_{11}^{r} + 3\pi\, v^2 \rho)\, t^2\}$$

In case c) one finds:

63) $$T_{\vec{\varepsilon}\leftarrow\vec{\varepsilon}} = \frac{\Gamma_{11}^{r}}{E - \tfrac{1}{2}(E_1^{\psi} + E_2^{\psi}) + i\pi\,(\Gamma_{11}^{r} + \frac{|v_{12}|^2}{\pi v^2 \rho})}$$

The time-development is now:

$$64)\qquad |< \Phi_1 | \psi(t) >|^2 = e^{-2\pi(\Gamma^r_{11} + \frac{|v_{12}|^2}{\pi v^2 \rho})\, t}$$

This result is the same of that of ref. (12), where 62) is derived for this specific case. $|v_{12}|$ is then the spin-orbit coupling, Φ_1 a singulet state, which carries oscillator-strength and Φ_2 a triplet-state. **)
The energy-dependence of absorption and emission, which follows from $|T|^2$ is analogous to that discussed in III. 3a.

The case that $\pi v^2 \rho >> 4 |v_{12}|^2$ is of interest for the Robinson and Frosch theory of energy relaxation in solids (19).
There the electronic level Φ_1, with radiative width $2\pi \Gamma^r_{11}$ is coupled by $|v_{12}|$ with a vibrational state Φ_2, which in its turn is coupled with a heatbath due to the environment. Its width is large and equals $2\pi v^2 \rho$. The resulting rate found from 64) is precisely the same result as theirs.

**) Recent measurements of E. Drent of the quantum yield of triacetyl as function of gas-pressure verify the decay-rates resulting from 58), 60) and 62), if one assumes $v^2 \rho$ to be proportional with the pressure (personal communication).

REFERENCES:

1. M. Bixon, J. Jortner, J.Chem.Phys. 48, 715 (1968).
2. B.I. Stepanov, V.P. Grobkovskii, Theory of luminescence, Iliffe (1968).
3. W. Heitler, Quantum theory of radiation, 3^e edition, Oxford.
4. K.F. Freed, J. Jortner, J.Chem.Phys. 52, 6272 (1970).
5. D.H. Burland, G.W. Robinson, J.Chem.Phys. 51, 4548 (1969).
6. R.F. Freed, J. Jortner, J.Chem.Phys. 50, 2916 (1969).
7. M. Bixon, J. Jortner, J.Chem.Phys. 50, 4061, (1969).
8. D.P. Chock, J. Jortner, S.A. Rice, J.Chem.Phys. 49, 610 (1968).
9. P.O. Löwdin, Studies in Perturbation theory, Prel. Research Report no. 200, Uppsala 1967.
10. M. Berrondo, K. Weiss, J.Chem.Phys. 52, 807 (1970).
11. J. Jortner, R.S. Berry, J.Chem.Phys. 48, 2757 (1968).
12. W.M. Gelbart, S.A. Rice, J.Chem.Phys. 50, 4775 (1969).
13. S.A. Rice, J.Mc Laughlin, J. Jortner, J.Chem.Phys. 49, 2756 (1968).
14. M. Bixon, J. Jortner, Y. Dothan, Mol.Phys. 17, 109 (1969).
15. W. Rhodes, J.Chem.Phys, 50, 2885 (1969).
17. N.M. Kroll, in Optique et Electronique quantiques (Les Houches, 1964).
18. A.B. Zahlan, The triplet state, Beirut, 1967.
19. G.W. Robinson, R.P. Frosch, J.Chem.Phys. 37, 1962 (1962).
20. A.Abragam, The principles of nuclear magnetism (Oxford, 1961) pag. 501.
21. M. Bixon, J. Jortner, J.Chem.Phys. 50, 3284 (1969).

CHAPTER IV

THE ENERGY AND ANGULAR DISTRIBUTION OF ELECTRONS EMITTED IN PHOTOELECTRON SPECTROSCOPY.

In molecular photoelectron spectroscopy (1), photons of a constant energy (He-resonance line e.g. 21,21 eV) are scattered by molecules in the gas-phase and the energy-spectrum of the emitted electrons is measured. When X-rays are used the method is named E.S.C.A. (Electron Spectroscopy for Chemical Analysis) (2). Changing the energy-spectrum by altering the energy of the incoming photonbeam can provide insight into the details of the ionization process (3, 4, 6). The angular distribution of emitted photons can also be measured (5).

Here it will be shown that the energy of emitted electrons is defined by the difference between photon-energy and ionization-energy in agreement with the intuitively expected result. Photoelectron spectroscopy, therefore, provides a method of easily finding the many ionization potentials of a molecule or atom.
In addition the intensity problem will be discussed in view of the angular distribution.

The general formula for the angular distribution of electrons emitted from atoms by linearly polarized light in dipole approximation is well-known (7, 8, 9) and given by distribution I:

$$1) \qquad \frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \beta\, P_2\,(\cos X)\right]$$

The angle between the direction of emitted electron and direction of the polarized light is indicated by χ; σ is the total cross-section and β is an angle-independent parameter. The same angular distribution is found in the photo-ionization of molecules, when the molecules may be considered as fixed in space and their orientational distribution is isotropic (10). The restrictions which have to be satisfied to obtain distribution I are derived for those cases where rotational motion is included. There is also a short discussion of what happens when these restrictions are not satisfied.

The results are that distribution I is found when:

a) The difference in rotational energies is small compared with the energy transferred to the electron.

b) The time delay, which is a measure of the rate of the ionization process, is small compared to the rotation-time of the molecule.

Deviations of distribution I can be expected when rotational excitation is resolved.

The derivation is related to the one used in ref. (11) in a study of resonant scattering of electrons by molecules. The method used gives directly distribution I in the case of atom-ionization. The argument is then similar to Yang's (12).

IV.1. THE ENERGY OF EMITTED ELECTRONS.

The Hamiltonian H of a molecule can be written as:

$$1)\quad H = \sum_i T^{el}(r_i) + \sum_k T^n(R_k) + \sum_{i<j} \frac{e^2}{|r_{ij}|} + \sum_{k<l} \frac{Z_k Z_l}{|R_{kl}|} - \sum_{i,k} \frac{Z_k e^2}{|r_i - R_k|}$$

Its form is invariant for transformation to the Center of mass coordinate system when the motion of the Center of mass is separated out. In the following this is assumed to be done and 1) is then the Hamiltonian of the molecule in Center of mass-system.

The following notation is used:

$r_1, \ldots, r_n$ denote space-coordinates of the electrons

$R_1, \dots, R_n$ denote space-coordinates of the nuclei
$T^{el}(r_i)$ denotes the kinetic energy of electron i, $T^n(R_i)$ denotes the kinetic energy of nucleus i.

The eigenfunctions of the time-independent Schrödinger equation are the solutions of:

2) $$H\psi = E\psi$$

where E is the total energy before photo-ionization. As is shown in chapter II the total energy before and after scattering has to be conserved.
ψ considered as a function of space- and spin-coordinates has to satisfy:

3) $$A\psi = \psi; \quad \text{with } A = \frac{1}{N!} \sum_P \epsilon_P P$$

Here P is a permutation operator. When it induces an even permutation $\epsilon_P = +1$, when it induces an uneven one $\epsilon_P = -1$.

It is now desired to determine equations for one-electronfunctions, which satisfy the boundary conditions of an electron emitted from a bound state. Because of the interest in ionization of single electrons the eigenstates $^+\Phi_\lambda$ of the ion are assumed to be only discrete.
We expand $\psi(x_1 \dots x_n, R)$ into the set $^+\Phi_\lambda(x_1, \dots x_{n-1}, R)$:

4) $$\psi = \sum_\lambda v^\lambda(x_n)\, {}^+\Phi_\lambda(x_1, \dots, x_{n-1}, R)$$

$x_1, \dots, x_n$ denote spin- and space-coordinates.
Because ψ has to satisfy 3) the right side of 4) has to be antisymmetrized:

5) $$\psi = \frac{1}{n} \sum_{x_i=1}^{x_{n-1}} (1 - T_{x_i, x_n}) \sum_\lambda v^\lambda(x_n)\, {}^+\Phi_\lambda(x_1, \dots, x_{n-1}, R)$$

$T_{x_i x_j}$ is the transposition operator of coordinates x_i, x_j.

To derive 5) use has been made of $^+\Phi_\lambda$ already being anti-symmetrized.
5) is substituted into 2) and is multiplied at the left with $^+\Phi_\lambda^*(x_1, \dots, x_{n-1}, R)$ and the resulting expression is integrated over the coordinates $x_1, \dots, x_{n-1}, R,$

so that only a set of equations in the variable r_n remains:

$$6)\quad \Big\{T^{el}(r_n) + \frac{1}{|r_n|_{\lambda'\lambda'}} + C_{\lambda'\lambda'} - E)\, v^{\lambda'}(r_n) + E_x^{\lambda'\lambda'}(r_n) =$$

$$= -\sum_{\lambda\neq\lambda'}\left[\left(\frac{1}{|r_n|_{\lambda'\lambda}} + C_{\lambda'\lambda}\right) v^{\lambda}(r_n) + E_x^{\lambda'\lambda}(r_n)\right]$$

The following abbreviations have been used in 6):

$$7a)\quad \frac{1}{|r_n|_{\lambda'\lambda}} = \sum_{i=1}^{n-1}\sum_j < {}^+\Phi_{\lambda'}(x_1,\dots,x_{n-1},R)\Big|\, \frac{e^2}{|r_n-r_i|} - \frac{Z_je^2}{|r_n-R_j|}\,\Big|\, {}^+\Phi_\lambda(x_1,\dots,x_{n-1},R) >$$

$$b)\quad E_x^{\lambda'\lambda}(r_n) = -\sum_{i=1}^{n-1}\sum_{i'=1}^{n-1}\sum_j < {}^+\Phi_\lambda(x_1,\dots,x_{n-1},R)\,\Big|\, T^{el}(r_n) + \frac{e^2}{|r_n-r_i|} - \frac{Z_je^2}{|r_n-R_j|}$$

$$- E + H^+(r_1,\dots,r_{n-1},R)\ \Big|\ T_{x_{i'},x_n}\ v(x_n)\ {}^+\Phi_\lambda\ (x_1,\dots,x_{n-1},R) >$$

$$c)\quad C_{\lambda'\lambda} = < {}^+\Phi_{\lambda'}(x_1,\dots,x_{n-1},R)\,\Big|\, H^+(r_1,\dots,r_{n-1},R)\,\Big|\, {}^+\Phi_\lambda(x_1,\dots,x_{n-1},R) >$$

$$d)\quad H^+(r_1,\dots,r_{n-1},R) = \sum_{i=1}^{n-1} T^{el}(r_i) + \sum_j T^n(R_j) + \sum_{i<j}\frac{Z_iZ_je^2}{|R_{ij}|} +$$

$$+ \sum_{i<j}^{n-1}\frac{e^2}{|r_{ij}|} - \sum_{i=1}^{n-1}\sum_j\frac{Z_je^2}{|r_i-R_j|}$$

Because H^+ is the Hamiltonian of the ion:

$$8)\qquad C_{\lambda'\lambda} = \delta_{\lambda'\lambda}\, E^+_{\lambda'}$$

E^+_λ is an eigenvalue of H^+.

6) is now studied when $|r_n| \to \infty$. A discussion of matrix-elements 7a) and 7b) in the case of atoms can be found in ref. (13). This discussion is not altered essentially for a molecule. The matrix-element $\frac{1}{|r_n|}_{\lambda'\lambda}$ reduces to $-\frac{e^2}{|r_n|}\delta_{\lambda'\lambda}$, if $|r_n| \to \infty$. The matrix-element $E_x^{\lambda'\lambda}(r_n)$ goes to zero in this limit, because the transposition of the coordinates results in a behaviour of $E_x^{\lambda'\lambda}(r_n)$ as a bound state function, which is zero at an infinite distance from the origin. Therefore if $|r_n| \to \infty$ equations 6) become:

9) $$(T^{el}(r_n) - \frac{e^2}{|r_n|} + E^+_{\lambda'} - E)\, v_o^{\lambda'}(r_n) = 0$$

with $v_o^{\lambda'}(r_n) = \lim\limits_{|r_n| \to \infty} v^{\lambda'}(r_n)$

Thus it is seen that $v_o^{\lambda'}(r_n)$ is a Coulomb-function with energy $E_c^{\lambda'}$ equal to:

10) $$E_c^{\lambda'} = E - E^+_{\lambda'}$$

E is defined as the total energy before ionization and given by:

11) $$E = h\nu + E_o$$

E_o is the energy of the initial-state of the molecule and $h\nu$ the energy of ionizing photon.

The energy of the emitted electron is therefore given by:

12) $$E_c^{\lambda'} = h\nu - (E^+_{\lambda'} - E_o)$$

$(E^+_{\lambda} - E_o)$ is the ionization-energy of the state λ of the ion. Relationship 12) gives the result that the energy of emitted electrons is given by the difference in photon-energy and ionization-energy.

The derivation shows that the energy of emitted electrons in Center of mass-system is independent of the details of the photo-ionization process itself. The resolution, however, depends on the magnitude and distribution of the intensity and therefore on the details of the ionization process (6).

IV.2. THE TRANSITIONPROBABILITY.

The interaction with electromagnetic radiation is given by:

13) $H'_{int} = \sum_i H'_i = \sum_i \frac{e_i}{m_i c} (\vec{A}_i \cdot \vec{p}_i)$: with 14) $\operatorname{div} \vec{A} = 0$

$\vec{A}$ is the vector-potential of incident light.

The transition amplitude for photo-ionization of the bound-state ψ_o of the molecule to state ${}^{+}\Phi_\mu$ of the ion is:

15) $$T_\mu = \sum_i < \psi_\mu | < n_\lambda - 1 | H'_i | n_\lambda > | \psi_o >$$

where $\psi_\mu = \frac{1}{n} \sum_{x_i=1}^{x_{n-1}} (1 - T_{x_i, x_n}) \, v^\mu(x_n) \, {}^{+}\Phi_\mu(x_1, \ldots, x_{n-1}, R)$ and $| n_\lambda >$ gives the photon-state in occupationnumber-representation. The photo-ionization process is assumed to be first order in the electromagnetic field. Only the electrons are assumed to interact with the electromagnetic field. $\vec{A}_i$ can be written as:

16) $$\vec{A}_i = \sum_\lambda \{ q_\lambda \vec{A}_\lambda + q^*_\lambda \vec{A}^*_\lambda \}$$

with $\vec{A}_\lambda(r_i) = \vec{e}_\lambda \, e^{i(\vec{k}_\lambda \cdot \vec{r}_i)} \sqrt{4\pi c^2}$; $\vec{e}_\lambda$ is the direction of polarization of the light.

Further:

17) $$< n_\lambda | q_\lambda | n_{\lambda+1} > = \sqrt{\frac{h}{\nu_\lambda}} \sqrt{n_\lambda + 1}$$

The other matrix-elements of q_λ are zero.

With 25), 26) and 27) one finds for 24):

18) $$T_\mu = \sqrt{\frac{h}{2\nu_\lambda}} \cdot \frac{e}{mc} \sum_i < \psi_\mu | \vec{A}_\lambda(r_i) \cdot \vec{p}_i | \psi_o >$$

In dipole-approximation is found:

$$19)\quad T = \frac{e}{mc}\sqrt{\frac{h}{2\nu_\lambda}}\,|A_\lambda| \sum_i < \psi_\mu | \vec{\epsilon}_\lambda \cdot \vec{p}_i | \psi_o > = \frac{e}{mc}\sqrt{\frac{h}{2\nu_\lambda}}\,|A_\lambda|\, T^o_\mu$$

It is seen that matrix-elements of one-electron operators have to be calculated.

For simplicity ψ_o and ψ_μ are restricted to a single product of electronic and vibronic wavefunctions. The electronic wavefunction is assumed to be restricted to one single determinant:

$$20)\quad \psi_{oo} = \frac{1}{\sqrt{n!}} \sum_P \epsilon_P\, P\, \psi^o_{\lambda_1}(x_1, R)\, \psi^o_{\lambda_2}(x_2, R) \ldots\ldots \psi^o_{\lambda_n}(x_n, R)\, \chi^o_o(R)$$

$$21)\quad \psi_{\mu k} = \frac{1}{\sqrt{n!}} \sum_P \epsilon_P\, v^{\mu k}(x_n)\, {}^+\psi^\mu_{\lambda_1}(x_1, R)\, {}^+\psi^\mu_{\lambda_2}(x_2, R) \ldots\, {}^+\psi^\mu_\lambda(x_{n-1}, R)\, {}^+\chi^\mu_k(R)$$

χ^μ_k are the vibronic wavefunctions. The dependence on vibronic states will in the following be denoted by the second label of ψ.
The one-electron functions ψ^o_λ and ${}^+\psi^\mu_\lambda$ have to satisfy:

$$22)\quad < \psi^o_{\lambda_1} | \psi^o_{\lambda_2} > = \delta_{\lambda_1 \lambda_2}$$

$$< {}^+\psi^\mu_{\lambda_1} | {}^+\psi^\mu_{\lambda_2} > = \delta_{\lambda_1 \lambda_2}; \qquad < v^{\mu k} | {}^+\psi^\mu_\lambda > = 0$$

In general $T^o_{\mu k}$ will not reduce to a simple expression, even in this approximation because of three reasons:
$v^{\mu k}$ is in general non-orthogonal to ψ^o_λ (15): ${}^+\psi^\mu_\lambda$ is non-orthogonal to ψ^o_λ and ψ^o_λ and ${}^+\psi^\mu_\lambda$ are also functions of the nuclear coordinates.
If those three restrictions are satisfied, $T^o_{\mu k}$ reduces to:

$$23)\quad T^o_{\mu k} = F^{\mu o}_{ko} < v^\mu | \vec{\epsilon} . \vec{p} | \psi^\mu_\lambda >$$

Here $F^{\mu o}_{ko}$ is a Franck-Condon factor and ψ^{μ}_{λ} is the molecular-orbital from which an electron is ionized. When Koopman's theorem and the Born-Oppenheimer (14) approximation are applicable, the result therefore is simply 23).

The function $v^{\mu k}$ is a solution of 6) solved with the correct boundary conditions.

In chapter II the energy-dependence of 19) is discussed when auto-ionization is significant. In ref. (17) this phenomenon is studied for atoms and in ref. (18) for diatomic molecules. A general review is given in ref. (6).

In molecular photoelectron spectroscopy, the factorization 23) often gives a good description (16).

IV.3. THE ANGULAR DISTRIBUTION OF ELECTRONS EMITTED FROM MOLECULES.

It will appear that distribution I: $\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}[1 + \beta\, P_2(\cos \chi)]$ can be derived when the photo-ionizationprocess is independent of the change in rotational-states of the molecule. The rotational motion has, therefore, to be taken explicitly into account. This will be done in the framework of the Born-Oppenheimer approximation. The total wavefunction then is written as a product of functions which represent the electronic, vibronic and rotational motions. The electronic- and vibronic-coordinates are defined in a coordinate system which is rotating with the molecule in the Center of mass-system. The rotational functions depend on the Eulerian angles, α, β and γ, that define the rotating coordinate-system with respect to the space-fixed coordinate-system. Changes in the momenta of inertia will be neglected.

Let $\rho_I(\alpha, \beta, \gamma)$ be the rotational wavefunction, characterized by quantum-numbers I. The expression for the differential cross-section is then:

$$24)\quad \left(\frac{d\sigma}{d\Omega}\right)_{\mu k I} = \frac{e^2}{2\pi c}\,\frac{v}{\omega}\left|< v^{\mu k I\,+}\chi^{\mu}_{k}\,\rho_I \left|\vec{\varepsilon}.\vec{p}\right| \psi^{o}_{\lambda}\,\chi^{o}_{1}\,\rho_{I_o} >\right|^2$$

v is the velocity of the emitted electron. The factor v stems from the normalization of the wavefunction of emitted electron to unit amplitude at a large distance (25). $\omega = 2\pi\nu$

The direction of polarization of incident light $\vec{\varepsilon}$ will be given in the space-fixed coordinate-system, whereas the integral over electronic- and vibrational-coordinates will be calculated in the rotated coordinate-system. The relation between the components of $\vec{p}$ in the space-fixed coordinate-system and its components in the rotated coordinate-system therefore must be used and is given by:

$$25) \qquad p_x = \sum_{x'} a_{xx'}(\alpha, \beta, \gamma) p_{x'}$$

The coefficients $a_{xx'}$ can be expressed into the matrix-elements of the representation of finite rotations $D^{(j)}_{m'm}$ (α, β, γ) (20).
The relation of the spherical harmonics $Y_{lm}(\theta, \varphi)$ in the rotated coordinate-system with the spherical harmonics in the space-fixed coordinate-system defines $D^{(j)}_{m'm}$:

$$26) \qquad Y_{lm}(\theta, \varphi) = \sum_{m'} Y_{lm'}(\theta', \varphi') D^{(l)}_{m'm}(\alpha, \beta, \gamma)$$

The direction of emitted electrons in the space-fixed coordinate-system must be calculated. The boundary-conditions with which 6) has to be solved are therefore given in the space-fixed coordinate-system and v depends on the Eulerian angles.
In A7) the general form of T is given and one sees that the dependence of α, β and γ results only from the function $v_o^{\mu k l}$ which is a Coulomb-function. This function depends only on the scalar product $(\vec{k}.\vec{r})$, where $\vec{k}$ is the momentum of emitted electron.
One can therefore expand $v_o(\vec{r})$ into $P_l(\cos \psi)$:

$$27) \quad v_o(\vec{r}) = (k\ r)^{-1} \sum_{l=0}^{\infty} (2l + 1)\, i^l u_l(k, r)\, P_l(\cos \psi) =$$

$$= \frac{4\pi}{k\ r} \sum_{l=0}^{\infty} i^l u_l(k, r) \sum_m Y^*_{lm}(\theta_k, \varphi_k)\, Y_{lm}(\theta, \varphi)$$

ψ is the angle of $\vec{r}$ with $\vec{k}$; θ_k and φ_k are the angles of $\vec{k}$ in the rotating coordinate-system and θ and φ the angles of $\vec{r}$ in the rotating coordinate-system.
26) is used to find:

$$28)\quad v_o(\vec{r}) = \frac{4\pi}{kr} \sum_{l=0}^{\infty} i^l u_l(kr) \sum_{m'} Y^*_{lm'}(\theta'_k, \varphi'_k) \sum_m D^{(l)*}_{m'm}(\alpha,\beta,\gamma)\, Y_{lm}(\theta,\varphi)$$

Here θ'_k, φ'_k are the angles of $\vec{k}$ in the space-fixed coordinate-system. The general form of $T^o_{\mu kI}$ is therefore:

$$29)\quad T^o_{\mu kI} = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma \int_0^{\infty} r^2 dr \int_{-1}^{+1} d(\cos\theta) \int_0^{2\pi} d\varphi \int d^3\vec{R}$$

$$\Big\{ \sum_{l'=0}^{\infty} \sum_{m'm} f^{\mu kI}_{l'm}(r,\theta,\varphi)\, {}^{+}\chi^{\mu *}_k(\vec{R})\, \rho^*_I(\alpha,\beta,\gamma) \sum_{x'} a_{zx'}(\alpha,\beta,\gamma)\ x$$

$$p_{x'}\, D^{(l')*}_{m'm}(\alpha,\beta,\gamma)\, \psi^o_\lambda(r,\theta,\varphi,\vec{R})\, \chi^o_l(\vec{R})\, \rho_{I_o}(\alpha,\beta,\gamma)\Big\}\, Y^*_{l'm'}(\theta'_k, \varphi'_k)$$

The direction of polarization of incident light is chosen parallel to the z-axis.

The selection rule for rotational excitation (21) is seen to be dependent now upon $D^{(l)}_{m'm}$.

It is nicely illustrated by the experiment of Herzberg (22)* on the photoionization of H_2 that this causes a change in selection rule compared to excitation of a discrete state. In appendix B the particular excitations measured are shown to follow directly from 29).

The values of l in 29) are determined by the symmetry of the molecule. The angular distribution will therefore in general be unequal to distribution I. By studying the total probability of rotational excitation the conditions to find distribution I can be derived.

The total probability of rotational excitation is:

$$30)\quad \sum_I \left(\frac{d\sigma}{d\Omega}\right)_I = \frac{e^2}{2\pi c}\ \frac{v}{\omega} \sum_I \left| < v^{\mu kI}\ {}^{+}\chi^{\mu}_k\ \rho_I \left| \vec{\varepsilon}.\vec{p} \right| \psi^o_\lambda\ \chi^o_l\ \rho_{I_o} > \right|^2$$

---

*) The aim of this experiment was a very accurate redetermation of the dissociation limit of H_2.

One looks for the conditions that equality (31) is valid:

$$\sum_I \left| < v^{\mu k I\,+} \chi_k^{\mu}\, \rho_I \left| \vec{\varepsilon}.\vec{p} \right| \psi_\lambda^o\, \chi_l^o\, \rho_{I_o} > \right|^2 = \int_0^{2\pi} d\alpha' \int_0^{\pi} \sin \beta' d\beta' \int_0^{2\pi} d\gamma' \; x$$

$$x \int_0^{2\pi} d\alpha \int_0^{\pi} \sin \beta\, d\, \beta \int_0^{2\pi} d\gamma \sum_I \left| \rho_I (\alpha', \beta', \gamma') > < \rho_I (\alpha, \beta, \gamma) \right| \; x$$

$$\text{31a)} \quad x\; \overline{\left| < v^{\mu k I\,+} \chi_k^{\mu} \left| \vec{\varepsilon}.\vec{p} \right| \psi_\lambda^o\, \chi_\lambda^o\; \rho_{I_o} > \right|^2}^{\,I'} =$$

$$\text{b)} \quad = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin \beta\, d\, \beta \int_0^{2\pi} d\gamma\, \overline{\left| < v^{\mu k\,+} \chi_k^{\mu} \left| \vec{\varepsilon}.\vec{p} \right| \psi_\lambda^o\, \chi_l^o\; \rho_{I_o} > \right|^2}^{\,I'}$$

In 31a) and b) $|T^o|^2$ is calculated for an average value I' of the rotational states. To make the transition from 31a) to 31b), the completeness relation is used:

$$\text{32)} \quad \sum_I \int_0^{2\pi} d\alpha' \int_0^{\pi} \sin \beta' d\, \beta' \int_0^{2\pi} d\gamma' \left| \rho_I (\alpha', \beta', \gamma') > < \rho_I (\alpha, \beta, \gamma) \right| = 1$$

The function v depends in two ways upon the quantumnumber I; firstly because the momentum $|\vec{k}|$ depends on the transferred energy by relation 12); secondly because the phase-shift also depends upon this energy. Two conditions are found which must be satisfied so that 31b) can be used:

$$\text{33a)} \quad | E_{I_1} - E_{I_2} | \ll \frac{\overline{k^2}^{\,I'}}{2m}$$

$$\text{b)} \quad \left| \frac{d}{dE} \sigma_\alpha \right| \ll \frac{\overline{\sigma_\alpha}^{\,I'}}{| E_{I_1} - E_{I_2} |}$$

$| E_{I_1} - E_{I_2} |$ denotes the difference in rotational energy before and after photo-ionization.

σ_α is defined in appendix A and is the phase-shift due to channel α.

$2\frac{d}{dE}\sigma_\alpha$ is the time delay of this channel and is the inverse of the rate of ionization. The energy-dependence of the states $|\alpha>$ in appendix A, which are the eigenfunctions of the phase-shift operator, is assumed to be neglegible.

The physical interpretation of inequalities 33) is:

a. The difference in rotational energy must be small compared with the energy of the electron.

b. The time delay $2\frac{d}{dE}\sigma_\alpha$ must be small compared with the rotation-time of the ion.[†]

In 31b) the cross-section still depends upon $|\rho_I\ (\alpha, \beta, \gamma)|^2$ which is the probability-density to find the molecule with angles, α, β and γ with respect to the space-fixed coordinate-system.

The function ρ_I is now more closely inspected. The spherical harmonics $Y_{lm}(\beta, \alpha)$ are the rotational functions when the molecule is linear. In a gas, where the molecules have an isotropic distribution, the weight of the states of equal l but different m is equal. In 31b), therefore, one has to sum yet over the different values of m with equal l and finds:

$$34)\qquad \sum_m |Y_{lm}(\beta,\alpha)|^2 = \frac{4\pi}{2l+1}$$

Therefore 31b) is found to be independent of $|\rho_I|^2$. In a symmetric top molecule as, for example, benzene the unnormalized eigenfunctions are given by $D^{(l)}_{mm'}(\alpha, \beta, \gamma)$ (20). Here again l is the quantumnumber of angular momentum, m of the projection of it on the axis of highest symmetry and m' along an arbitrary axis in the space-fixed coordinate-system. The norm depends only on l.

In 31b) the sum is taken over the different values of m' and because:

$$35)\qquad \sum_{m'} |D^l_{mm'}|^2 = 1$$

[†] The angular velocity of benzene is 10^{12} sec^{-1} when the temperature is 30°C. The rate of the photo-ionizationprocess has to be larger than 10^{12} sec^{-1}.

31b) is again found to be independent of $\left| \rho_{I_0} \right|^2$.
The eigenfunctions of the asymmetric rotator can be expressed as linear combinations (20) of the symmetrical top eigenfunctions. When the sum is again taken over the degenerate states, relations analogous to 34) and 35) will be valid.

Those averaging procedures are applied to 31b) and one must now evaluate:

$$36a)\ \left(\frac{d\sigma}{d\Omega}\right)_{\mu k} = \frac{e^2}{2\pi c}\,\frac{v}{\omega} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma \left| < v^{\mu k +} \chi_k^{\mu} \left| \vec{\varepsilon}.\vec{p} \right| \psi_\lambda^o \chi_1^o > \right|^2$$

$$b)\ = \frac{e^2}{2\pi c}\,\frac{v}{\omega} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma \sum_{lmm'} \sum_{l_1 m_1 m_1'} Y_{lm'}(\theta_k', \varphi_k')$$

$$Y^*_{l_1 m_1'}(\theta_k', \varphi_k')\, D^{(l)}_{m'm}(\alpha, \beta, \gamma)\, D^{(l)*}_{m_1' m_1}(\alpha, \beta, \gamma) \sum_{x'x_1'} a_{zx'}(\alpha, \beta, \gamma)\, a^*_{zx_1'}(\alpha, \beta, \gamma)$$

$$C^{\mu k}_{lm; l_1 m_1}(x'; x_1')$$

The matrix-elements C are given in the appendix C.
One uses the relationship (20):

$$37)\ Y_{lm}(\theta_k, \varphi_k)\, Y^*_{l_1 m_1}(\theta_k, \varphi_k) = \sum_{L=|l-l_1|}^{|l+l_1|} \sum_{m'=-L}^{L} \left[\frac{(2l+1)(2l_1+1)}{(2L+1)4\pi}\right]^{\frac{1}{2}}$$

$$(-1)^{m_1}\,(l0l_1\,0 | l\, l_1\, L0)\,(l\, l_1\, L\, m-m_1 | l\, m\, l_1 - m_1)\, Y_{lm'}(\theta_k', \varphi_k')$$

$$D^{(L)}_{m', m-m_1}(\alpha, \beta, \gamma)$$

where $(l\, m\, l_1 m_1 | l\, l_1\, L\, m)$ are Clebsch-Gordan coefficients, and substitutes 37) into 36b) to yield:

$$38)\ \left(\frac{d\sigma}{d\Omega}\right)_{\mu k} = \frac{e^2}{2\pi c}\,\frac{v}{\omega} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma \Bigg[\sum_{lmm'} \ \sum_{l_1 m_1 m_1'} \ \sum_{L=|l-l_1|}^{|l+l_1|} \ \sum_{m'=-L}^{L}$$

$$\left\{\frac{(2l+1)(2l_1+1)}{4\pi(2L+1)}\right\}^{\frac{1}{2}} (-1)^{m_1} (l\ 0\ l_1\ 0 | l\ l_1\ L\ 0)(l\ l_1\ L\ m-m_1 | l\ m\ l_1 - m_1)$$

$$\left\{ \sum_{x'x_1'} C^{\mu k}_{lm;l_1 m_1} (x'; x_1')\ D^{(L)}_{m';m-m_1} (\alpha,\beta,\gamma)\ a_{zx'}(\alpha,\beta,\gamma)\ a^*_{zx_1'} (\alpha,\beta,\gamma) \right\}$$

$$Y_{Lm'}(\theta_k', \varphi_k')$$

In appendix D the method of evaluating the integral over α, β and γ is described. One finds that 38) gives the distribution I: $\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\{(1+\beta\, P_2(\cos\chi)\}$ with σ and $\beta\sigma$ given in appendix C.

It is seen that distribution I depends only on the integration over the products $D^{(L)}_{m';m-1}\, a_{xx'}\, a^*_{xx_1'}$ in the integrand of 38).

When the dipole-approximation is used, this form will appear for any approximation of electronic and vibronic wavefunctions and distribution I is therefore independent from those last approximations.

The values of the matrix-elements C depend, of course, strongly on the approximation for the electronic and vibronic wavefunctions.

It is seen in 29) that deviations of distribution I occur when the rotational structure is resolved and also when the time of ionization is of the same order as the rotation-time.

IV. 4 THE ANGULAR DISTRIBUTION OF ELECTRONS EMITTED FROM ATOMS.

Because the atom is spherical symmetric no direction of orientation of the rotational coordinate-system is preferred. This means that 38) directly applies and in any approximation of the atomic wavefunctions distribution I will be obtained with β and $\beta\sigma$ given by C2) and C3).

(μk) are, in this case, the quantumnumbers which characterize the atomic ion.

The expressions of β and $\beta\sigma$ are calculated in the case of photo-ionization from an s-or p-orbital. One assumes that the angular momentum of one electron is an appropriate quantumnumber.
In the case of photo-ionization of an electron from a s-orbital one finds:

39) $$\sigma = \frac{8\pi^2}{3} \left|A_{10}\right|^2$$

$$\beta\sigma = \frac{16\pi^2}{3} \left|A_{10}\right|^2$$

A_{10} is the matrix-element, which gives the contribution from the integral over $\vec{r}$ in C.
Because from equality:

40) $$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left\{1 + \beta \ P_2 \ (\cos \chi)\right\} = \alpha + \gamma \cos^2 \chi$$

the following relations follow:

41) $$\alpha = \frac{\sigma}{4\pi}(1 - \tfrac{1}{2}\beta); \quad \gamma = \frac{3}{2}\,\frac{\beta\sigma}{4\pi}$$

it is seen that in this case no isotropic contribution to the differential cross-section results. This is the known result (23).
In the case of photo-ionization of an electron from a p-orbital one finds:

42) $$\sigma = \frac{8\pi^2}{9}\left(\left|A_{01}\right|^2 + 2 \left|A_{21}\right|^2 \right)$$

$$\beta\sigma = \frac{16\pi^2}{9}\left\{2 \ \mathrm{Re} \ (A_{01} \ A_{21}^*) + \left|A_{21}\right|^2\right\}$$

Now an isotropic contribution is found.

Appendix A. The general form of the T-matrix in photo-ionization.

Equation 18) gives the Transition-matrix of the ionization problem. Its form is: $< \psi^- | H' | \psi_o >$. Here H' represents the interaction with electromagnetic field. The -sign of ψ^- denotes that continuous solutions of the scattering problem have to be used with boundary-conditions such that the scattered wave is an ingoing spherical wave. This is because in the ionization problem, the initial conditions must be given when $t \rightarrow \infty$..

This Transition-matrix will now be expressed in the phase-shift of emitted particle using standard collision theory (19). ψ^- is the solution of the Lippmann-Schwinger equation (26):

A1) $$\psi^- = \Phi_o + \lim_{\epsilon \rightarrow 0} \frac{1}{E - H_o - i\epsilon} O | \psi^- >$$

Φ_o is a product of emitted electron wave-function and target wave-function at an infinite distance from one another.

The functions Φ_o are eigenfunctions of H_o.

The total Hamiltonian H is

A2) $$H = H_o + O$$

Then ψ^- is also a solution of:

A3) $$\psi^- = \Phi_o + \lim_{\epsilon \rightarrow 0} \frac{1}{E-H-i\epsilon} O | \Phi_o >$$

It is assumed that H and H_o have the same spectrum.

The Transition-matrix for photo-ionization $< \psi^- | H' | \psi_o >$ is then given by:

$$< \psi^- | H' | \psi_o > = < \Phi_o | H' | \psi_o > + \lim_{\epsilon \rightarrow 0} < \Phi_o | O \frac{1}{E-H+i\epsilon} H' | \psi_o > =$$

$$= < \Phi_o | H' | \psi_o > - i\pi < \Phi_o | O + \lim_{\epsilon \rightarrow 0} O \frac{1}{E-H+i\epsilon} O \, \delta(E-H_o) \, H' | \psi_o > +$$

$$+ < \Phi_o | O + \lim_{\epsilon \rightarrow 0} O \frac{1}{E-H+i\epsilon} O \frac{\mathrm{Pr.P.}}{E-H_o} H' | \psi_o > = \qquad \text{A4a)}$$

A4b) $$= < \Phi_o | \delta (E-H_o) H' |\psi_o > - i\pi < \Phi_o |T \delta (E-H_o) H' |\psi_o > +$$

$$+ < \Phi_o |T \frac{Pr.P.}{E-H_o} H' | \psi_o >$$

where T the Transition-operator satisfies:

A5) $$T = O + \lim_{\varepsilon \to 0} O \frac{1}{E-H+i\varepsilon} O$$

Use the relation 19):

A6 $$\pi T = -K (1-iK)^{-1}$$

where K is the Hermitian Reactance operator.

Substitution of A6) into A4b) gives:

A7) $$< \psi^- |H'| \psi_o > = < \Phi_o \; |\delta(E-H_o)(1-iK)^{-1} H' | \psi_o >$$

$$\frac{1}{\pi} < \Phi_o | \frac{K}{1-iK} \frac{Pr.P.}{E-H_o} H' | \psi_o >$$

This expression must be compared with equation II,50), where A7) has been explicitly derived for the resonant case.

Let the eigenvalues of the operator K introduced in A6) be given by equation:

A8) $$K|\alpha > = K_\alpha |\alpha >$$

Because K is hermitian K_α is real.

The eigenvalues σ_α of the phase-shift operator σ can be found using the same eigenfunctions. σ is given by operator relationship:

A9) $$\sigma = \tan^{-1} K$$

A7) can be expressed into:

$$\text{A10)} \quad < \psi^- | H' | \psi_o > = \sum_\alpha < \Phi_o | \alpha > \left\{ e^{i\sigma_\alpha} \cos \sigma_\alpha < \alpha | \delta\,(E-H_o)\; H' | \psi_o > \right.$$

$$\left. - \frac{1}{\pi} e^{i\sigma_\alpha} \sin \sigma_\alpha < \alpha | \frac{\text{Pr. P.}}{E-H_o} | H' \right\} \psi_o >$$

This expression can be compared with equation II, 86).

Appendix B. The rotational excitation of H_2.

Herzberg (22) has observed the photoabsorption spectrum of H_2 from its J=0 state and found that only the J=0 and J=2 states are excited. In H_2 the quantumnumbers of angular momentum of the electron l are rather appropriate. When this approximation is used the groundstate has l = 0, so excitation can only take place to electronic states with l=1.

The selection rule for rotational excitation of the molecule follows from 29) by calculating:

$$\text{B1)} \quad \sum_{x'} \int_0^{2\pi} d\alpha \int_0^{\pi} d\beta \sin\beta \int_0^{2\pi} d\gamma \; \rho_I(\alpha,\beta,\gamma) \; a^*_{zx'}(\alpha,\beta,\gamma) \; D^{(1)}_{m'm}(\alpha,\beta,\gamma) \, \rho^*_{I_o}(\alpha,\beta,\gamma)$$

In B1) the direction of polarization of incident light is along the z-axis. The rotational eigenfunctions of a diatomic molecule are the spherical harmonics. The relationship between spherical harmonics and the matrix-elements of finite rotation are:

$$\text{B2)} \quad D^{(l)}_{mo}(\alpha,\beta,\gamma) = (-1)^m \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} Y_{l,m}(\beta,\alpha)$$

$$D^{(l)}_{om}(\alpha,\beta,\gamma) = \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} Y_{l,m}(\beta,\gamma)$$

The matrix-elements $a_{zx'}$ are only related with the matrix-elements of finite rotation $D^{(1)}_{mo}$. Because ρ_{I_o} is the spherical harmonic with J=0, it is a constant.

The possible values of the excited rotational states are therefore found by evaluating:

$$\text{B3)}\quad \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta \, d\beta \; D^{(J)}_{J_z o}(\alpha,\beta)\, D^{(1)}_{mo}(\alpha,\beta)\, D^{(1)}_{m_1' o}(\alpha,\beta)$$

The products $D^{(1)}_{mo}\, D^{(1)}_{m'o}$ yield only the $D^{(o)}_{oo}$ and $D^{(2)}_{m+m',o}$ matrix-elements as easily can be found by using (20):

$$\text{B4)}\quad D^{(j_1)}_{m_1' m_1}(\alpha,\beta,\gamma)\, D^{(j_2)}_{m_2' m_2}(\alpha,\beta,\gamma) = \sum_{j=|j_1-j_2|}^{|j_1+j_2|} (j_1 m_1' \, j_2 \, m_2' | j_1 j_2 j \, m)$$

$$D^{(j)}_{m_1'+m_2',\, m_1+m_2}\, (j_1 j_2 \, j \, m_1 + m_2 | j_1 \, m_1 \, j_2 \, m_2)$$

and that the Clebsch-Gordan coefficient $(1110|1010) = 0$.
Because of orthogonality relation:

$$\text{B4)}\quad \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\, d\beta \int_0^{2\pi} d\gamma \; D^{(j_1)}_{m_1' \, m_1}(\alpha,\beta,\gamma)\; D^{(j_2)*}_{m_2' \, m_2}(\alpha,\beta,\gamma) =$$

$$= \delta_{m_1', m_2'}\; \delta_{m_1, m_2}\; \delta_{j_1, j_2}\; \frac{1}{2j_1+1}$$

it follows that the values of J in B2) only give non zero result when J=0 or J=2.†)

Appendix C: the matrix-elements C, β and $\beta\sigma$.

$$\text{C1)}\quad C^{\mu k}_{l'm;l_1 m_1}(x';x_1') = \left\{ d^3\vec{r} \int d^3\vec{R}\; f^{\mu k}_{l'm}(\vec{r})\; p_{x'}(\vec{r})\; \psi^{o}_{\lambda}(\vec{r},\vec{R})^{+} \chi^{\mu}_{k}(\vec{R})^{*}\right.$$

$$\left. \chi^{o}_{l}(\vec{R}) \right\} \left\{ d^3\vec{r}\,' \int d^3\vec{R}'\; f^{*\mu k}_{l_1 m_1}(\vec{r}_1{}')\; p^{*}_{x_1'}(\vec{r}_1{}')\; \psi^{o*}_{\lambda}(\vec{r},\vec{R}')^{+} \chi^{\mu}_{k}(\vec{R}')\; \chi^{o*}_{l}(\vec{R}') \right\}$$

---

†) In this particular case excitation to J=1 state is also spin-forbidden.

C2)
$$\sigma = \frac{e^2}{2\pi c}\,\frac{v}{\omega}\sum_{lm}\sum_{l_1m_1}\frac{8\pi^2}{3}(2l+1)^{\frac{1}{2}}\,(2l_1+1)^{\frac{1}{2}}\,(l\ 0\ l_1\ 0|l\ l_1\ 0\ 0)$$

$$(l\ l_1\ 0\ 0|l\ m\ l_1-m_1)\ (-1)^m\left\{\underset{lm;l_1m_1}{C(x;x)} + \underset{lm;l_1m_1}{C(y;y)} + \underset{lm;l_1m_1}{C(z;z)}\right\}$$

C3)
$$\beta\sigma = \frac{e^2}{2\pi c}\,\frac{v}{\omega}\sum_{lm}\sum_{l_1m_1}\frac{8\pi^2}{5}(2l+1)^{\frac{1}{2}}\,(2l_1+1)^{\frac{1}{2}}\,(l\ 0\ l_1\ 0)\,|\,l\ l_1\ 2\ 0)$$

$$(l\ l_1\ 2\ m-m_1|l\ m\ l_1-m_1)\ (-1)^m\left\{\frac{1}{3}\delta_{-m+m_1,o}\,(2\underset{lm;l_1m_1}{C(z;z)} - \underset{lm;l_1m_1}{C(x;x)} -\right.$$

$$\left.- \underset{lm;l_1m_1}{C(y;y)}\right\}+$$

$$\frac{1}{\sqrt{6}}\delta_{-m+m_1,2}\,(\underset{lm;l_1m_1}{C(x;x)} - \underset{lm;l_1m_1}{C(y;y)} - i\underset{lm;l_1m_1}{C(y;x)} - i\underset{lm;l_1m_1}{C(x;y)})+$$

$$\frac{1}{\sqrt{6}}\delta_{-m+m_1,-2}\,(\underset{lm;l_1m_1}{C(x;x)} - \underset{lm;l_1m_1}{C(y;y)} + i\underset{lm;l_1m_1}{C(y;x)} + i\underset{lm;l_1m_1}{C(x;y)})+$$

$$\frac{1}{\sqrt{6}}\delta_{-m+m_1,-1}\,(\underset{lm;l_1m_1}{C(z;x)} + \underset{lm;l_1m_1}{C(x;z)} + i\underset{lm;l_1m_1}{C(z;y)} + i\underset{lm;l_1m_1}{C(y;z)})+$$

$$\frac{1}{\sqrt{6}}\delta_{-m+m_1,1}\,(i\underset{lm;l_1m_1}{C(z;y)} + i\underset{lm;l_1m_1}{C(y;z)} - \underset{lm;l_1m_1}{C(z;x)} - \underset{lm;l_1m_1}{C(x;z)})$$

The index (μ,k) has been suppressed in these equations.

Appendix D: Evaluation of 38).

Choose the direction of polarization of the light parallel to the z-axis. One is interested in the products of $a_{zz'}$, $a_{yz'}$ and $a_{xz'}$ with their complex conjugates.

When one expresses Cartesian coordinates into spherical coordinates and uses 26), it is found for the matrix-elements $a_{zx'}$:

D1) $$a_{zx'} = \frac{i}{\sqrt{2}} \left(D^{(1)}_{01} + D^{(1)}_{0-1}\right)$$

$$a_{zy'} = \frac{1}{\sqrt{2}} \left(D^{(1)}_{-10} - D^{(1)}_{10}\right)$$

$$a_{zz'} = -\frac{i}{\sqrt{2}} D^{(1)}_{00}$$

The products of $a_{zz'}$, $a_{yz'}$ and $a_{xz'}$ with their complex conjugates are found using B3) and (24):

D2) $$a_{zz'}a^*_{zz'} = \frac{1}{3} + \frac{2}{3} D^{(2)}_{00}$$

$$a_{yz'}a^*_{yz'} = \frac{1}{3} - \frac{1}{\sqrt{6}} \left(D^{(2)}_{02} + D^{(2)}_{0-2}\right) - \frac{1}{3} D^{(2)}_{00}$$

$$a_{xz'}a^*_{xz'} = \frac{1}{3} + \frac{1}{\sqrt{6}} \left(D^{(2)}_{02} + D^{(2)}_{0-2}\right) - \frac{1}{3} D^{(2)}_{00}$$

$$a_{zz'}a^*_{yz'} = \frac{i}{\sqrt{6}} \left(D^{(2)}_{0-1} + D^{(2)}_{01}\right)$$

$$a_{zz'}a^*_{xz'} = \frac{1}{\sqrt{6}} \left(D^{(2)}_{0-1} - D^{(2)}_{01}\right)$$

$$a_{yz'}a^*_{xz'} = \frac{i}{\sqrt{6}} \left(D^{(2)}_{0-2} - D^{(2)}_{02}\right)$$

The integral over α, β and γ which determines the contributing values of L in 38) is:

D3) $$\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta \, d\beta \int_0^{2\pi} d\gamma \; D^{(L)}_{m',m-m_1}(\alpha,\beta,\gamma)\, a_{zx'}(\alpha,\beta,\gamma)\, a^*_{zx''}(\alpha,\beta,\gamma)$$

Because the products $a_{zx'}a^*_{zx''}$, only contain matrix-elements $D^{(0)}$ and $D^{(2)}$, it is found by B4) that only L=0 and L=2 yield non-zero values of D3). The coefficients of $Y_{0,0}(\theta'_k,\varphi'_k)$ and $Y_{2,0}(\theta'_k,\varphi'_k)$ in 38) give $\frac{\beta}{4\pi}$ and $\frac{\sigma\beta}{4\pi}$. They are given explicitly in Appendix C.

REFERENCES:

1. D.W. Turner, Phil.Trans.Roy.Soc.Lond. A.268, 7 (1970).
2. K. Siegbahn, Phil.Trans.Roy.Soc.Lond. A268, 33 (1970).
3. F.I. Vilesov, Sovjet Physics Uspekhi 6, 688 (1964).
4. J.E. Collin, P. Natalis, Int. J.Mass.Spectr. and Ion Phys. 2, 231 (1969).
5. J.A.R. Samson, Phil.Trans. Roy.Soc.Lond. A 268, 141 (1970).
6. U. Fano, J.W.Cooper, Rev.Mod.Phys. 40, 441 (1970).
7. A. Sommerfeld, Atombau und Spektrallinien; II Band (Friedrich Vieweg und Sohn, Braunschweig, 1939) p. 436 a.f.
8. H.A. Bethe, Handbuch der Physik, 24, 483 (1933).
9. J. Cooper, R.N. Zane, J.Chem.Phys. 48, 942 (1968).
10. J.C. Tully, R.S. Berry, B.J. Dalton, Phys. Rev. 176, 95 (1968).
11. T.F. O'Malley, H.S. Taylor, Phys.Rev. 176, 207 (1968).
12. C.N. Yang, Phys.Rev. 74, 764 (1948)
13. M.J. Seaton, Proc.Phys. Soc. 88, 807 (1966).
14. M. Born, R. Oppenheimer, Ann. der Phys. 84, 457 (1927).
15. P.M. Johnson, S.A. Rice, J.Chem.Phys. 49, 2734 (1968).
16. D.W. Turner, D.P. May, J.Chem.Phys. 45, 471 (1966).

17a. U. Fano, Phys.Rev. 124, 1866 (1966).
   b. U. Fano, J.W. Cooper, Phys.Rev. 137, A1364 (1965).

18a. R.S. Berry, J.Chem.Phys. 45, 1228 (1966).
   b. S.E. Nielsen, R.S. Berry, Chem.Phys.Letters 2, 503 (1968).
   c. A. Russek, e.a., Phys.Rev. 167, 17 (1968).
   d. A. Russek, e.a., Phys.Rev. 180, 6 (1969).
   e. A.J. Blake, e.a., Phil.Trans.Roy.Soc.Lond. A268, 159 (1970).

19. R.G. Newton, Scattering theory of waves and particles (Mac Graw Hill, 1966).
20. A.R. Edmonds, Angular momentum in quantum mechanics (Princeton 1957).
21. G. Herzberg, Molecular spectra and structure (Van Nostrand) 1950).
22. G. Herzberg, Phys.Rev. Letters 23, 1081 (1969).
23. H.A. Bethe, E.E. Salpeter, Quantum mechanics of one and two-electron atoms (Springer, 1957), p.310.
24. Takeo Inoue, Table of the Clebsch-Gordan coefficients (Tokyo Toshe, 1966).
25. H.A. Bethe, R. Jackiw, Intermediate Quantum mechanics (second edition, Benjamin 1968).
26. B.A. Lippmann, J. Schwinger, Phys.Rev. 79, 469 (1950).

SAMENVATTING

In dit proefschrift worden enige problemen uit de chemische physica met behulp van de theorie van botsingen onderzocht.

Het eerste onderwerp is resonantie-verstrooiing. Dit proces kan worden opgevat als het invangen van een deeltje door een ander deeltje waarmee het botst, zodat deze een complex vormen, dat na verloop van tijd weer vervalt in een aantal fragmenten.

Een voorbeeld van dit proces wordt verschaft door de verstrooiing van electronen aan atomen of moleculen. Bij lage energie van de verstrooide electronen kan de botsingsdoorsnede zeer snel veranderen als functie van de energie. In het geval van resonantie-verstrooiing wordt dit verklaard door aan te nemen dat tijdelijk een negatief ion gevormd wordt. Van een stabiel ion zijn de mogelijke energie-toestanden discreet. Wanneer de levensduur van het instabiele negatieve ion voldoende groot is, wordt de situatie vergelijkbaar met die van een stabiel negatief ion met discrete toestanden. In dat geval zullen negatieve ionen als intermediair voorkomen wanneer de energie van het atoom of molecuul en electron voor verstrooiing gelijk is aan een van de energieën behorende bij een "eigentoestand" van het negatieve ion. De botsingsdoorsnede is in dit geval een zeer scherpe functie van de energie, die een zeer kleine breedte heeft gelijk aan de inverse van de levensduur vermenigvuldigd met de constante van Planck.

In een molecuul of een atoom kunnen de discrete niveaus van het bij benadering stabiel gedachte negatief ion soms zo dicht bij elkaar komen dat de breedten van de corresponderende botsingsdoorsneden van dezelfde grootte-orde worden als deze energie-verschillen. In dat geval kunnen verschillende toestanden van het negatieve ion bij dezelfde energie worden bevolkt en een eenvoudige beschouwing zoals in het bovenstaande geval kan niet meer worden gebruikt.

In het eerste geval spreekt men van geïsoleerde resonanties, in het laatste geval van overlappende resonanties.
In het geval van een geïsoleerde resonantie is het tijdsafhankelijke gedrag een exponentieel afnemende functie van de tijd en de botsingsdoorsnede is een Lorentz-functie van de energie.
In het geval van overlappende resonanties is niet alleen de botsingsdoorsnede geen Lorentz-functie meer van de energie, maar treden ook eigenaardige verschijnselen op in het tijdsafhankelijk gedrag van het als intermediair gevormde deeltje. Het tijdsafhankelijk gedrag is nu niet alleen een som van exponentieel afnemende functies in de tijd, maar kan worden gemoduleerd door oscillaties en ook door termen lineair in machten van de tijd-variabele.
In hoofdstuk II wordt dit tijdsafhankelijk gedrag, de vertraging die optreedt in de verstrooide deeltjes en de tijdsonafhankelijke grootheid, de botsingsdoorsnede, uitvoerig onderzocht.
Bij het bestuderen van de huidige literatuur bleek dat geen theorie van resonantie-verstrooiing bestaat, die de tijdsafhankelijke en tijdsonafhankelijke eigenschappen met elkaar verenigt. De verhandeling gegeven in dit proefschrift verenigt beide en leidt de bestaande tijdsonafhankelijke theorieën uit de tijdsafhankelijke theorie af.

In hoofdstuk III wordt deze theorie toegepast op stralingsloze overgangen in organische moleculen. Het proces van absorptie en het verval van de aangeslagen toestand in een andere toestand van het molecuul onder uitzending van een photon is een voorbeeld van resonantie-verstrooiing. Wanneer het aangeslagen electronische niveau een interactie heeft met een stelsel vibraties van een zeer klein energieverschil behorende bij een lagere electronische toestand, dan is het absorptie- en het daarop volgende emissie-proces een voorbeeld van een overlappend resonantie-verstrooiingsproces. In deze situatie vormen de vibraties een quasi-continuum en kan men spreken van stralingsloos verval.
De verschijnselen die optreden wanneer twee geëxciteerde toestanden een interactie hebben met hetzelfde quasi-continuum worden in detail besproken en verschaffen een physische illustratie van een aantal effecten, die in hoofdstuk II zijn voorspeld.

Absorptie van een photon kan ook tot gevolg hebben dat het molecuul ionizeert. Als het molecuul eerst wordt aangeslagen in een discrete toestand en een electron wordt vervolgens geëmitteerd dan wordt dit proces auto-ionizatie genoemd. Dit is zowel een voorbeeld van een stralingsloze overgang naar een echt continuum als een voorbeeld van resonantie-verstrooiing. Dit wordt behandeld in hoofdstuk II.

De electronen die worden geëmitteerd door photoionizatie van atomen hebben een hoekverdeling $A+B\cos^2\chi$. χ is de hoek tussen de richting van gepolariseerd licht en de richting van het geëmitteerde electron; A en B zijn energieafhankelijke grootheden. Deze hoekverdeling wordt gevonden wanneer slechts dipool-excitatie optreedt. De oorzaak dat de hoekverdeling zo'n eenvoudige functie is van de hoek is gelegen in de bol-symmetrie van de atomen.

Sinds kort is het mogelijk de hoek-verdeling van electronen die geëmitteerd worden bij de photoionizatie van moleculen te meten. Moleculen hebben in het algemeen geen bolsymmetrie en daarom zullen afwijkingen worden verwacht voor de hoekverdeling van geëmitteerde electronen.

Het blijkt echter dat in de meeste gevallen electronen geëmitteerd uit moleculen dezelfde hoekverdeling hebben als die uit atomen.

Dit kan worden verklaard doordat het photo-ionizatie proces dan zo snel gaat dat de moleculen als vastgeprikt in de ruimte kunnen worden beschouwd en de moleculen isotroop georienteerd zijn, zodat bolsymmetrie weer aanwezig is.

In hoofdstuk IV zijn de condities afgeleid dat dit geoorloofd is. Als in het photoionizatie proces de excitatie van rotaties niet wordt verwaarloosd blijken andere selectie-regels te gelden dan wanneer excitatie van rotaties gepaard aan excitatie van een electron naar een discrete toestand plaats vindt.

De hoekverdeling $A+B\cos^2\chi$ wordt slechts dan gevonden, wanneer de rotatiefijnstructuur in de emissie van electronen niet kan worden onderscheiden en de snelheid van photoionizatie groot is vergeleken met de rotatie-snelheid van het molecuul.

CURRICULUM VITAE

Na het behalen van het einddiploma gymnasium β aan het Middelburg's gymnasium begon ik in september 1963 mijn studie aan de Rijksuniversiteit te Leiden. Het candidaatsexamen in de scheikunde met bijvakken wiskunde, natuurkunde en biologie (letter G) legde ik in januari 1966 af. Mijn studie werd voortgezet op de afdeling voor theoretische organische scheikunde van Prof. Dr. L. J. Oosterhoff. Hier werkte ik onder leiding van Drs. C. A. G. O. Varma mee aan het onderzoek van lineair dichroisme van organische moleculen.
In december 1967 legde ik cum laude het doctoraal-examen af in de theoretische organische chemie met de bijvakken theoretische natuurkunde en wiskunde.

Gedurende de periode september 1965-september 1967 was ik student-assistent bij het 1^e-jaars practicum organische chemie. Vanaf september 1967-december 1967 was ik als candidaat-assistent en vanaf januari 1968 tot juni 1968 als doctoraal-assistent in dienst van de Rijksuniversiteit te Leiden. Hierna was ik als wetenschappelijk medewerker verbonden aan de afdeling Theoretische Organische scheikunde in dienst van Z. W. O. (S. O. N.).

De stimulerende gesprekken met de andere leden van de afdeling theoretische organische scheikunde heb ik zeer op prijs gesteld. Van de afdeling biofysica wil ik Drs. H. A. Otten en van het instituut voor theoretische natuurkunde Drs. J. de Goede dankzeggen voor de vele waardevolle discussies.
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