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Energy Dissipation in Molecular Systems



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With 85 Figures and 16 Tables

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Preface

The scope of this book is the analysis of experimental data on the energy relaxation in molecular systems using as a basis the standard theory of radiationless transitions. The main principles of this theory were established in the 1960s and early 1970s, when only a small amount of data obtained by traditional spectroscopic methods was available. Since this time, a rapid development of techniques (short-pulse and narrow-band lasers, supersonic nozzles and molecular beams, multiple-resonance techniques, the single-molecule spectroscopy) allowed the experimental studies of a large variety of molecular systems with practically unlimited time and energy resolution. In the same time, the progress of the theory opened new fields for calculations and simulation of molecular processes.

The major part of important chemical and biological processes takes place in condensed phases, where essentially intramolecular processes cannot be separated from the intermolecular interactions involving the energy exchange between the molecular system and its heat bath.

In order to separate the effects due to intrinsic properties of the molecule and those induced by the external perturbation, the studies of molecules “isolated” (i.e., collision-free during a sufficiently long time) in the gas phase and in the supersonic expansions have been widely developed. On the other hand, a better understanding of intermolecular interactions was attained in the studies of simple model systems such as two-body collisions in the gas phase, 1:1 molecular complexes, molecules trapped in rare-gas clusters and crystals. These studies allowed us to see how different intramolecular processes are modified by the environment effects.

We have at our disposal an enormous amount of data concerning the vibrational energy redistribution and relaxation, electronic energy relaxation, electron and proton transfer in a wide variety of molecular systems involving molecules isolated or dissolved in fluid or rigid solvents.

It seems to us that it is a good moment for a general discussion of key problems of the molecular dynamics based on the analysis of these data. We try to prepare this discussion by description, in the same language, of different photophysical processes.

We do not discuss the recent developments of the theory; our approach may be considered as complementary with respect to review papers and books (cf. Sect. 1.1)

focused on the theoretical aspects of photophysics and photochemistry. In any way, the basic concepts of the theory remain unchanged and only oversimplified schemes of level-coupling mechanisms used in its childhood must be replaced by a more detailed description of the coupling pattern accounting for a hierarchy of coupling chains corresponding to different time scales of sequential decay processes.

The outlines of the theory of nonradiative transitions are presented in the simplest form in Chap. 1. In Chap. 2, we review briefly principal experimental techniques with emphasis on the time- and energy-resolution that may be attained in experiments involving the pumping and probing populations of molecular excited states.

In the next chapters, we discuss the processes of the intramolecular redistribution of the vibrational energy in isolated molecules (Chap. 3), vibrational and rotational relaxation induced by the environment (Chap. 4) and electronic relaxation of isolated and medium-perturbed molecular systems (Chap. 5). At last, we briefly treat, in Chap. 6, specific processes of relaxation involving intra- and intermolecular electron or proton (hydrogen atom) transfer as examples of the simplest monomolecular photochemical processes. The review of experimental data is limited to a small number of small- and intermediate-size molecules that may be considered as representative of a larger class of molecular systems. The supermolecular ensembles (crystals and polymers) as well as biological systems are not treated here.

This book is not a manual introducing systematically the fundamental notions of a domain. It does not pretend either to be a monograph giving an extensive review of data and its complete bibliography. It may be rather considered as a tourist guide of the country of photophysics, focusing attention on several of the most famous monuments. The choice of these masterpieces is, to some extent, subjective.

We focus our attention on the physical meaning rather than on a rigorous development of the quantum-mechanical formalism. We tried to get this book accessible to everybody having a knowledge of basic notions of the quantum mechanics and molecular spectroscopy as somebody starting graduate studies of molecular physics or physical chemistry. We hope that it may be useful for some people actively working in this field.

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The Basic Notions

1.1 Introductory Remarks

The problem of nonradiative relaxation of electronically excited molecules is as old as the experimental studies in the field, called still 60 years ago luminescence, and separated from the gas-phase spectroscopy of atoms and small molecules (cf. [1]). These studies—limited in practice to condensed phases—showed that the major part of chemical compounds are nonluminescent and that the important fraction of radiation energy absorbed by the luminescent ones is dissipated in the medium without emission of light. Such a deactivation process seemed not to occur for isolated gas-phase atoms and diatomics in the absence of collisional quenching. It was, therefore, not evident whether the nonradiative relaxation is the intrinsic property of large molecules or is induced by the environment effects.

In the early 1960s, it was shown that radiationless processes occur in isolated polyatomic molecules in the gas phase. It was shown, for instance, that the fluorescence yield of the collision-free benzene molecule in the gas phase is nearly the same as in its solutions in aliphatic solvents [2] and that nonradiative processes occur in an isolated molecule as small as glyoxal $\text{C}_2\text{H}_2\text{O}_2$ [3].

The theory of nonradiative transitions was developed at the same time; after several pioneering works [4–7], the publication in 1968 of the Bixon and Jortner paper [8] may be considered as its birthdate. The further progress of the theory is described in a number of review papers published in the 1970s (cf. [9–13]) and in recent books [14, 15].

In this chapter we give—in a simplified form—some of the basic formulae necessary for the analysis of experimental data concerning the time evolution of excited electronic and vibrational states of molecules, isolated or interacting with their environment, the attention being focused on the former ones. The outlines of the traditional theory are presented with a few minor modifications. The semiclassical approach (the quantum theory for molecules and a classical description of radiation fields) is adopted.

The time evolution of an isolated molecule is determined by the fine details of its level patterns. The information about its dynamics may be thus deduced either from the

time-resolved monitoring of molecular systems prepared by a short-pulse excitation to a well-defined level or set of levels or from *energy-resolved* spectroscopic studies of its fine structure. We will discuss separately, after some introductory remarks (Sect. 1.2), the information from the absorption spectroscopy (Sect. 1.3) and from the time-resolved experiments (Sect. 1.4), summarized in Sect. 1.5. At last, in Sect. 1.6, we introduce some general notions concerning the dependence of transition probabilities on the energy or momentum gap between initial and final state of the system.

1.2 Excited Molecular States

1.2.1 Stationary and Quasi-Stationary States

Stationary states are normally envisaged for isolated molecules in the absence of interactions with material or radiation-field environments. The state vectors are then of the form:

$$\varphi(t) = |\varphi\rangle \exp[-iE_\varphi t/\hbar]. \quad (1.1)$$

The lowest E_φ value is usually taken as the origin of the energy axis, $E_0 = 0$, and attributed to the ground state $|0\rangle$.

When the molecule interacts with the radiation field, the ground state remains stationary but the excited states become unstable due to the spontaneous light emission: transitions to lower states $|\varphi'\rangle$. The energy difference $E_\varphi - E_{\varphi'}$ is transformed in a photon $\hbar\omega_{\varphi\varphi'}$ (Fig. 1.1). These processes are properly described in an exact quantal treatment considering the molecular and radiation-field Hamiltonians together with a light-matter interaction term. In the simpler semiclassical treatment, it is sufficient to account for the radiative decay of the excited state by introducing an imaginary part of energy,

$$E_\varphi \rightarrow \tilde{E}_\varphi = E_\varphi - i\gamma_\varphi^{\text{rad}}/2, \quad (1.2)$$

so that

$$\varphi(t) = |\varphi\rangle e^{-i\tilde{E}_\varphi t/\hbar} = |\varphi\rangle e^{-iE_\varphi t/\hbar} e^{-\gamma_\varphi^{\text{rad}} t/2\hbar}. \quad (1.3)$$

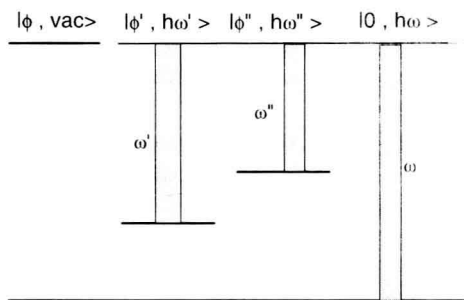


Fig. 1.1. Schematic representation of the excited level φ coupled to a set of radiative continua involving lower φ' levels

The *quasi-stationary state* thus obtained has a survival probability at time t ,

$$|\varphi(t)|^2 = e^{-\gamma_\varphi^{\text{rad}} t / \hbar}, \quad (1.4)$$

and decays by fluorescence emission with the *radiative rate*, k_φ^{rad} , related to the radiative lifetime, $\tau_\varphi^{\text{rad}}$, and to the radiative width, $\gamma_\varphi^{\text{rad}}$, by the following relation:

$$k_\varphi^{\text{rad}} = 1/\tau_\varphi^{\text{rad}} = \gamma_\varphi^{\text{rad}} / \hbar. \quad (1.5)$$

In view of the additivity of radiative transition rates, k_φ^{rad} is the sum of contributions of transition rates to all lower lying $|\varphi'\rangle$ states,

$$k_\varphi^{\text{rad}} = \sum_{\varphi'} k_{\varphi\varphi'}^{\text{rad}} = \sum_{\varphi'} A_{\varphi\rightarrow\varphi'},$$

where A are familiar Einstein coefficients for spontaneous emission,

$$A_{\varphi\rightarrow\varphi'} = \frac{32\pi}{3\hbar} \omega^3 \mu_{\varphi\varphi'}^2,$$

proportional to the square of the transition moment and to the cube of the transition frequency.

In the exact quantal treatment, the radiative continuum contained in the finite volume may be described as a set of closely spaced levels with the level density ρ per cm^{-1} . The decay of the $|\varphi\rangle$ state is induced by its coupling V to this continuum and its decay rate is given by the *Fermi Golden Rule* (cf. [16, 17]),

$$k_{\varphi\rightarrow\varphi'} = \frac{2\pi}{\hbar} V^2 \rho. \quad (1.6)$$

This formula is widely applied for description of radiative and nonradiative processes involving the coupling of discrete levels to the continua.

On the other hand, γ^{rad} appears in the light-absorption measurements as the width of the spectral line of the $|0\rangle \rightarrow |\varphi\rangle$ transition. The transition induced by a monochromatic radiation field involves the linear coupling of the electric field, $\mathbf{F}(\omega, t) = \mathbf{F}_0 e^{i\omega t}$, with the dipole moment of the molecule and is proportional to the square of the interaction matrix element averaged over a time interval larger than ω^{-1} ,

$$V = \frac{1}{\Delta t} \int_0^{\Delta t} \langle \varphi(t) | \mu \mathbf{F}(t) | 0 \rangle dt. \quad (1.7)$$

The result is

$$|V(\omega)|^2 = \frac{|\mu_{0\varphi}|^2 \mathbf{F}_0^2}{(\omega_{0\varphi} - \omega)^2 + \gamma_\varphi^2 / 4\hbar^2}, \quad (1.8)$$

which represents a Lorentzian line with a homogeneous width of γ_φ [16].

1.2.2 Zero-Order and Exact Molecular States

The molecular states usually considered in molecular spectroscopy are not the eigenstates, $|\varphi\rangle$, of the exact Hamiltonian, but the eigenstates, $|n\rangle$, of the zero-order Hamiltonian neglecting the spin-orbit coupling and issued from the Born–Oppenheimer approximation. Following the adiabatic separation of the fast electronic movement from slower vibrations and rotations, the state vectors have the forms of ro-vibronic products,

$$|e, v, JKM\rangle = |\psi_e(\bar{Q})\rangle |\chi_{ev}\rangle |JKM\rangle, \quad (1.9)$$

where the electronic factor, $|\psi_e\rangle$, is defined for a fixed nuclear configuration \bar{Q} , the vibrational factor, χ_{ev} , represents the vibrations in the $|\psi_e\rangle$ electronic state and $|JKM\rangle$ characterizes a rigid rotator. In the absence of the spin-orbit coupling, the $|n\rangle$ states are pure spin states, $|\sigma\rangle$ (singlet S_i , and triplet, T_i , states in molecules with an even number of electrons).

We will refer to the basis of the vectors, $|e, v, JKM\rangle|\sigma\rangle$, as to the *zero-order* (ZO) basis. Its interest in spectroscopy is twofold:

- Their energies are determined by simple formulae with a limited number of parameters so that the positions of the whole set of ZO-states with a regular spacing may be easily calculated. The shift and splitting of the observed level with respect to its calculated position are a measure of the coupling omitted in the zero-order approximation,
- The transitions between ZO states are subject to strict selection rules.

We assume that the molecules are vibrationally and rotationally cold ($T_{\text{vib}} \rightarrow 0$ and $T_{\text{rot}} \rightarrow 0$) so that only the lowest rotational levels of the vibrationless electronic state, $|0\rangle$, are populated so that the $|n\rangle$ state may be excited uniquely by the $|0\rangle \rightarrow |n\rangle$ radiative transition. The $|n\rangle$ states are thus divided into two groups:

1. *the bright states*, $|s\rangle$, for which the $|0\rangle \leftrightarrow |s\rangle$ transitions are allowed: ($\mu_{0s} \neq 0$) and
2. *the dark states*, $|\ell\rangle$, for which they are forbidden: ($\mu_{0\ell} = 0$)

In real systems, the $|0\rangle \leftrightarrow |\ell\rangle$ transitions may be not strictly forbidden but so weak that one can consider that $\mu_{0\ell} \approx 0$, as in the case of the $\Delta v \gg 1$ transitions between vibrational levels of the same electronic state. The bright and dark states are sometimes called radiant and nonradiant. In this book, these terms will have a different meaning: dark $|\ell\rangle$ states are *radiant* when radiative $\ell \rightarrow \ell'$ transitions to some lower lying ℓ' states (other than the $|0\rangle$ state) are allowed: $\mu_{\ell\ell'} \neq 0$ so that $\gamma_{\ell}^{\text{rad}} \neq 0$, whereas for *nonradiant* states, all $\mu_{\ell\ell'} = 0$ and $\gamma_{\ell}^{\text{rad}} = 0$ (Fig. 1.2). Most of the dark levels are radiant. For instance, the vibronic levels of higher triplet states $|T_{i>1}\rangle$ are dark because the $S_0 \leftrightarrow T_i$ transition is forbidden but are radiant when the $T_i \rightarrow T_{i-1}$ transition to a lower triplet is allowed.

The *exact molecular states* $|\varphi\rangle$ are eigenstates of the complete molecular Hamiltonian. In the zero-order representation, the molecular Hamiltonian has the form $H = H_0 + V$, where H_0 provides the ro-vibronic basis and V accounts for all the

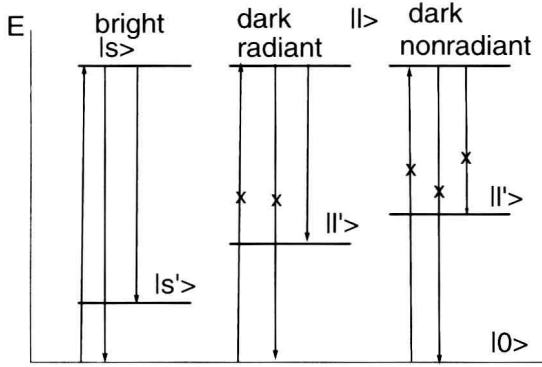


Fig. 1.2. Bright and dark (radiant and nonradiant) states (the forbidden transitions are marked by x)

residual interactions neglected in H_0 : the nonadiabaticity (non-Born–Oppenheimer terms), spin-orbit coupling, anharmonicity, Coriolis coupling, etc. which shift and mix the zero-order states. The Hamiltonian matrix is thus written as

$$\begin{array}{cccc} E_n & V_{nn'} & V_{nn''} & \dots \\ V_{n'n} & E_{n'} & V_{n'n''} & \dots \\ V_{n''n} & V_{n''n'} & E_{n''} & \dots \\ \dots & \dots & \dots & \dots \end{array}$$

In the zero-order representation, the eigenstates of the exact molecular Hamiltonian,

$$H|\varphi\rangle = E_\varphi|\varphi\rangle,$$

are given by linear superposition,

$$|\varphi\rangle = \sum_n \alpha_{\varphi n} |n\rangle = \sum_n \langle n|\varphi\rangle |n\rangle, \quad (1.10)$$

whereas

$$|n\rangle = \sum_\varphi \alpha_{\varphi n} |\varphi\rangle = \sum_\varphi \langle \varphi|n\rangle |\varphi\rangle, \quad (1.11)$$

where $\alpha_{\varphi n}$ are elements of the the inverse matrix

$$\alpha_{\varphi n} = \alpha_{n\varphi}^*.$$

The eigenstates $|\varphi\rangle$ are quasi-stationary, however, the zero-order states are not, so their temporal behaviour must be described in terms of exact states

$$|n(t)\rangle = \sum_\varphi \alpha_{\varphi n} |\varphi\rangle e^{-i\tilde{E}_\varphi t}. \quad (1.12)$$

Because the molecular eigenstates are combinations of bright and dark ZO states,

$$|\varphi\rangle = \alpha_{\varphi s} |s\rangle + \sum_{\ell} \beta_{\varphi \ell} |\ell\rangle, \quad (1.13)$$

the strict selection rules are attenuated. As long as $\alpha_{\varphi s} \neq 0$, the $0 \rightarrow \varphi$ transition moment is different from zero,

$$\mu_{0\varphi} = \alpha_{\varphi s} \mu_{0s}, \quad (1.14)$$

whereas all $\mu_{0\ell} = 0$. For instance, the weak singlet-triplet mixing induced by the spin-orbit interaction gives rise to the essentially singlet $|S'\rangle = |S\rangle + \varepsilon|T\rangle$ and essentially triplet $|T'\rangle = |T\rangle - \varepsilon|S\rangle$ states, where $\varepsilon \ll 1$. The $|S_0 \rightarrow |T'\rangle$ transition is no more strictly forbidden because $\mu_{S_0 T'} = \varepsilon \mu_{S_0 S}$.

The radiative character of an eigenstate $|\varphi(t)\rangle$ is represented by its projection on the bright state, $\hat{S}(t)$, called *S*-character,

$$\hat{S}(t) = |\langle s|\varphi(t)\rangle|^2 = |\langle s|\varphi\rangle|^2 e^{-\gamma_{\varphi}^{\text{rad}} t}. \quad (1.15)$$

For instance, the intensity of $|s\rangle \rightarrow |s'\rangle$ emission is given by

$$I_s(t) = k_s^{\text{rad}} \hat{S}(t), \quad (1.16)$$

where k_s^{rad} denotes the emission rate constant of the bright ZO state. The time dependence of the $\ell \rightarrow \ell'$ emission (when the ℓ state is radiant) and of the transient $\ell + h\omega = \ell''$ absorption may be expressed in terms of an analogue, $\hat{L}(t)$ projection.

1.3 Coupling Schemes and Level Patterns

In view of the large variety of molecular systems, the treatment of the coupling schemes must be adapted to different classes of molecules. Their classification is not unique. We consider as the essential criterion the existence or nonexistence of the *continua of energy* (other than the radiative continuum) coupled to discrete energy levels. Such continua may be intrinsic states of the molecule (corresponding, e.g., to dissociation or ionization) or result from the environment effects (continuum of translational energy in the gas or in the fluid solution). As will be discussed in Sect. 1.4.3, the dense sets of molecular levels may be approximated by the *quasi-continua*.

We define as a *small molecule* a system composed of discrete energy levels with widths due uniquely to the coupling to the radiative field (purely radiative widths). The excited state of this system decays radiatively with the overall ($s \rightarrow s'$ and $\ell \rightarrow \ell'$) emission quantum yield, $Q_f = 1$. On the other hand, in a *large molecule*, discrete levels are coupled to a continuum or quasi-continuum and this coupling implies the broadening (the *nonradiative width*) of discrete levels due to an irreversible transition discrete-to-continuum. In view of a competition between radiative and nonradiative decay channels, the emission yield is reduced, $Q_f \leq 1$. We will apply the term of

the *large-molecule limit* to the systems, which may be described in terms of a direct coupling of a single bright state to the continuum (quasi-continuum). We prefer this term to a somewhat misleading term of the *statistical limit*.

The main parameter of each coupling scheme is the average spacing of n -levels, $\langle \Delta E_{nn'} \rangle$, as compared with the average coupling strength $\langle V_{nn'} \rangle$. In the small-molecule limit, the perturbations involving a limited number of levels may be treated exactly in terms of $\Delta E_{s\ell}$ (of the order of $\langle \Delta E_{nn'} \rangle$) and $V_{s\ell}$ values of *individual states*. In view of the increasing number of interacting levels, the coupling in the large molecule limit is described in terms of average *effective level densities*, $\rho_{eff} = 1/\langle \Delta E_{\ell\ell'} \rangle$, and average $\langle V_{s\ell} \rangle$ values.

For a major part of molecular systems, small-molecule and large-molecule schemes do not account for the coupling between discrete $|n\rangle$ ($|s\rangle$ and $|\ell\rangle$) levels coupled in turn to the continuum (or quasi-continuum). We will use, for these systems, the term *sequential coupling case* as more precise than that of the *intermediate coupling case*.

Note that the terms small and large molecule are not necessarily related to their size. So, the predissociation of a diatomic molecule resulting from the coupling to a dissociative continuum must be treated in terms of the large-molecule limit. On the other hand, the lowest vibrational levels of the S_1 state of a molecule as large as 9,10-dichloroanthracene decay by the resonant fluorescence with $Q_f \approx 1$, the coupling to other levels of the S_1 state and to those of T_1 and S_0 states being negligible.

1.3.1 Small Molecules

The interaction between a pair of ZO states $|n\rangle$ and $|n'\rangle$ is significant only in the case of *quasi-resonance*,

$$\frac{|V_{nn'}|}{\Delta E_{nn'}} \gg 0,$$

i.e., when the value of the coupling matrix element $V_{nn'}$ is not much smaller than the energy gap, $\Delta E_{nn'} = |E_n - E_{n'}|$. In a major part of molecular systems, the average spacing between bright $|s\rangle$ levels, $\Delta E_{ss'}$, is so large that one can consider the system as composed of single bright states interacting with one or more dark states. The radiative properties of $|\varphi\rangle$ eigenstates issued from this coupling are

$$\mu_{0\varphi} = \alpha_{\varphi s} \mu_{0s} \quad \gamma_{\varphi}^{\text{rad}} = |\alpha_{\varphi s}|^2 \gamma_s^{\text{rad}} + \sum_{\ell} |\beta_{\varphi \ell}|^2 \gamma_{\ell}^{\text{rad}} \quad (1.17)$$

because $\mu_{0\ell} = 0$ for all dark levels, but some of them are radiant ($\gamma_{\ell} \neq 0$).

The resulting level pattern depends on the relation between average value of the coupling constants $\langle V_{s\ell} \rangle$ and the average ℓ -level spacing $\langle \Delta E_{\ell\ell'} \rangle$ expressed usually in terms of the average level density, $\langle \rho_{\ell} \rangle = 1/\langle \Delta E_{\ell\ell'} \rangle$. When $\langle V_{s\ell} \rangle \langle \rho_{\ell} \rangle \ll 1$, the probability of an s - ℓ quasi-resonance is small so that only a two-level s - ℓ interaction occurs for a fraction of s -levels. This is called the *weak-coupling limit*. In contrast, the *strong-coupling case* corresponds to $\langle V_{s\ell} \rangle \langle \rho_{\ell} \rangle \geq 1$, where all (or nearly all) s -levels interact with one or more than one ℓ -level.

Weak-Coupling Limit

A good example of the weak coupling is a perturbation between two vibronic states, v_s and v_ℓ , of the s and ℓ electronic states of a diatomic molecule. In view of the conservation of the angular momentum, only the pairs of states with $J_s = J_\ell$ may interact. When the rotational constants in two states are different, $B_s \neq B_\ell$, the $J_s - J_\ell$ level spacing is J -dependent,

$$\Delta E_{s\ell}(J) = \Delta E_{s\ell}(J=0) + (B_s - B_\ell)J(J+1) + \cdots, \quad (1.18)$$

with a quasi-resonance for $J \approx \sqrt{\Delta E_{s\ell}(J=0)/(B_s - B_\ell)}$. Far from the resonance, $V_{s\ell} \ll \Delta E_{s\ell}(J)$ and the s - ℓ interaction may be neglected. The $|\varphi\rangle$ eigenstates are practically identical with zero-order $|n\rangle$ states, $|\varphi_1\rangle \approx |s\rangle$ bright state and $|\varphi_2\rangle \approx |\ell\rangle$ dark state, so that only the first one appears in the absorption spectrum. In the vicinity of the resonance, the energies E_i and wave functions φ_i ($i = 1, 2$) of eigenstates are given by current equations of a two-level system (cf. [17]) (Fig. 1.3),

$$E_1, E_2 = (E_s + E_\ell)/2 \pm \Delta E/2 \quad (1.19)$$

where

$$\Delta E_{12} = \sqrt{\Delta E_{s\ell}^2 + 4V_{s\ell}^2} \quad (1.20)$$

and

$$|\varphi_1\rangle = \cos\theta|s\rangle + \sin\theta|\ell\rangle \quad |\varphi_2\rangle = -\sin\theta|s\rangle + \cos\theta|\ell\rangle, \quad (1.21)$$

where

$$2\theta = \arctan(2V_{s\ell}/\Delta E_{s\ell}), \quad 0 \leq \theta \leq \pi/2, \quad (1.22)$$

with transition moments

$$\mu_{01} = \cos\theta\mu_{0s}, \quad \mu_{02} = -\sin\theta\mu_{0s} \quad (1.23)$$

and widths

$$\gamma_1 = \cos^2\theta\gamma_s + \sin^2\theta\gamma_\ell, \quad \gamma_2 = \sin^2\theta\gamma_s + \cos^2\theta\gamma_\ell. \quad (1.24)$$

Note that, by definition, $\theta \leq \pi/4$, so that $\cos^2\theta \geq \sin^2\theta$.

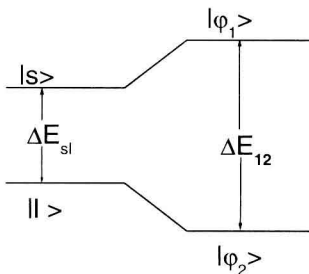


Fig. 1.3. A scheme of the two-level coupling