

## WHAT IS THE NATURE OF INTRAMOLECULAR COUPLING RESPONSIBLE FOR INTERNAL CONVERSION IN LARGE MOLECULES?

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We discuss the criteria for the specification of a proper basis set for describing electronic relaxation processes in large molecules.

It is now well established that the decaying electronically excited states of large molecules should be described in terms of resonance (compound) states [1–3]. To assert whether the physical phenomenon of the decay of an excited electronic state of a “statistical” large molecule can be described as two independent processes of excitation followed by decay, or as a single quantum-mechanical process, one has to specify the duration of the excitation time relative to the reciprocal width of the resonance. When the temporal duration of the exciting photon field is short relative to the reciprocal width of the metastable state it is possible to separate the excitation and decay processes and to consider radiative and non-radiative decay times. On the other hand, when the exciting photon field is characterized by high energy resolution (being switched on for long periods) resonance scattering involves a single quantum-mechanical process and one can then consider the determination of optical line shapes, cross sections for resonance fluorescence and emission quantum yields. The lifetime is then obtained from the reciprocal resonance width. The physical information derived from “short time” and “long time” excitation processes is equivalent.

The basic physical model for a single molecular resonance in the statistical limit [1–3] rests on the following assumptions:

- (a) A single zero order state  $|s\rangle$  carries oscillator strength from the ground state  $|0\rangle$ .
- (b)  $|s\rangle$  is intramolecularly coupled to a zero order quasicontinuum  $\{|D\rangle\}$ .
- (c) The quasicontinuum is optically inactive.
- (d) Other optically active zero order states  $|b\rangle$  (which correspond to different vibronic components of the same electronic state as  $|s\rangle$  or to other electronic states) are well separated from  $|s\rangle$  relative to their total widths.

Conditions (a) and (c) pertain to the excitation process of the resonance both in “short time” and “long time” experiments. Condition (b) implies the existence of a finite width of the resonance in “long time” experiments and intramolecular decay for a “short time” experiment. Conditions (a)–(d) were taken to imply that the line shape is lorentzian (and the decay is exponential); thus if (c) does not hold, a Fano-type line shape [4] will result, while if (d) is violated, interference effects in the line shape and in the decay will be exhibited. Several authors have implied that when conditions (a)–(d) are satisfied the resonance width is given by the Fermi Golden Rule  $\Gamma = 2\pi|s|V|D|^2\rho_l$  (where the total molecular hamiltonian is separated into  $H = H_0 + V$ , and where  $\rho_l$  is the density of states  $\{|D\rangle\}$ ). When radiative decay is also considered, the radiation field provides an additional independent decay width  $\Gamma_R$  the total width being  $\Gamma_t = \Gamma + \Gamma_R$ . If molecular systems would adhere to conditions (a)–(d) life would be simple. However, in real systems the role of off-resonance coupling with other states  $|b\rangle$  (see fig. 1) is crucial, and the simple Golden Rule expression should be modified. This point, which was not realized in several recent works [7,8] leads to considerable confusion concerning the choice of the basis set for describing electronic relaxation processes.

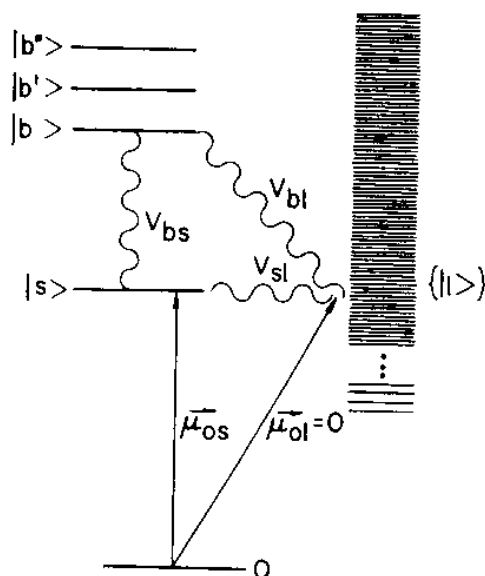


Fig. 1. A schematic representation of the relevant molecular states and couplings. Arrows indicate dipole coupling via the interaction with the radiation field. Wavy lines represent intramolecular coupling.

Following classical work in molecular and solid state physics [6] it was widely accepted [1-3,5] that the zero order states  $|s\rangle$  and  $\{|l\rangle\}$  can be taken as Born-Oppenheimer states, whereupon the nuclear kinetic energy operator provides the coupling term for internal conversion. This approach has been challenged by Burland and Robinson [7] and by Sharf and Silbey [8] who claimed that the "Herzberg-Teller coupling is more effective in causing radiationless transitions than the breakdown of the Born-Oppenheimer approximation" [7]. In view of this lively controversy we shall attempt to consider the problem of the nature of intramolecular coupling in internal conversion by discussing the general separation of the hamiltonian, the form of the resonance width in a realistic system and the general criteria for the choice of a basis set for specifying electronic relaxation processes.

Consider the dissection of the molecular hamiltonian  $H = T_R + T_r + U(r, R)$  where  $r$  and  $R$  represent electronic and nuclear coordinates,  $T$  represents kinetic energies, while  $U(r, R)$  is the potential energy. Let  $|nv\rangle$  be any complete set of molecular zero order functions where electronic and nuclear motion has been separated arbitrarily (so that the first index refers to the electronic state, while the second index labels the vibrational state). We can then define the projection operator  $P_{nv} = |nv\rangle\langle nv|$ . Utilizing the completeness assumption  $\sum_{n,v} P_{nv} = 1$ , and the trivial relation  $H = \sum_{n,v} P_{nv} H \sum_{n,v} P_{n,v}$  we can then define

$$H = H_0 + V, \quad (1)$$

where

$$H_0 = \sum_{nv} P_{n,v} H P_{n,v} \quad (1a)$$

and

$$V = \sum_{nv} \sum_{n'v'} P_{nv} H P_{n'v'} \quad (1b)$$

$nv \neq n'v'$

We shall now consider the adiabatic (A) and crude adiabatic (CA) basis sets assuming that each set is complete<sup>†</sup>.

<sup>†</sup> It can easily be demonstrated that a molecular function can be expanded in terms of either the (orthonormal) adiabatic or the crude adiabatic set. This is a necessary but not sufficient condition for completeness.

In the Born–Oppenheimer representation  $|nv\rangle = \varphi_n^A(\mathbf{r}, \mathbf{R}) \chi_{nv}^A(\mathbf{R})$  where the electronic  $\varphi_n^A$  and the nuclear  $\chi_{nv}^A$  wavefunctions satisfy the well known equations

$$[T_r + U(\mathbf{r}, \mathbf{R})] \varphi_n^A(\mathbf{r}, \mathbf{R}) = E_n(\mathbf{R}) \varphi_n^A(\mathbf{r}, \mathbf{R}), \quad [T_R + E_n(\mathbf{R}) + \langle \varphi_n^A | T_R | \varphi_n^A \rangle] \chi_{nv}^A(\mathbf{R}) = E_{nv}^A \chi_{nv}^A(\mathbf{R}), \quad (2)$$

so that

$$H_0^A = \sum_{nv} |\varphi_n^A \chi_{nv}^A\rangle E_{nv}^A \langle \varphi_n^A \chi_{nv}^A|, \quad (3)$$

while

$$V^A = \sum_{nv} \sum_{n'v'} |\varphi_n^A \chi_{nv}^A\rangle \left( \langle \varphi_n^A | \frac{\partial U / \partial \mathbf{R}}{\partial \mathbf{R}} | \varphi_{n'}^A \rangle \frac{\partial}{\partial \mathbf{R}} \langle \chi_{n'v'}^A | \right) + \frac{1}{2} \langle \chi_{nv}^A | \langle \varphi_n^A | \frac{\partial^2}{\partial R^2} | \varphi_{n'}^A \rangle | \chi_{n'v'}^A \rangle \langle \varphi_n^A \chi_{n'v'}^A |, \quad (4)$$

where  $\langle \rangle$  denotes integration in the electronic  $\mathbf{r}$  space, while  $( )$  denotes the integration in the nuclear  $\mathbf{R}$  space. In the crude adiabatic representation  $|nv\rangle = \varphi_n^{CA}(\mathbf{r}, \mathbf{R}_0) \chi_{nv}^{CA}(\mathbf{R})$  where the electronic  $\varphi_n^{CA}$  and nuclear  $\chi_{nv}^{CA}$  wavefunctions satisfy

$$[T_r + U(\mathbf{r}, \mathbf{R}_0)] \varphi_n^{CA} = E_n(\mathbf{R}_0) \varphi_n^{CA}, \quad [T_R + E_n^{CA}(\mathbf{R}_0) + \langle \varphi_n^{CA} | \Delta U(\mathbf{r}, \mathbf{R}) | \varphi_n^{CA} \rangle] \chi_{nv}^{CA}(\mathbf{R}) = E_{nv}^{CA} \chi_{nv}^{CA}(\mathbf{R}), \quad (5)$$

where  $\Delta U = U(\mathbf{r}, \mathbf{R}) - U(\mathbf{r}, \mathbf{R}_0)$  and  $\mathbf{R}_0$  is an arbitrary fixed nuclear configuration. In this representation

$$H_0^{CA} = \sum_{nv} |\varphi_n^{CA} \chi_{nv}^{CA}\rangle E_{nv}^{CA} \langle \varphi_n^{CA} \chi_{nv}^{CA}|, \quad (6)$$

$$V^{CA} = \sum_{nv} \sum_{n'v'} |\varphi_n^{CA} \chi_{nv}^{CA}\rangle \left( \langle \varphi_n^{CA} \chi_{nv}^{CA} | T_R + \Delta U(\mathbf{r}, \mathbf{R}) | \varphi_{n'}^{CA} \chi_{n'v'}^{CA} \rangle \right) \langle \varphi_{n'}^{CA} \chi_{n'v'}^{CA}|. \quad (7)$$

Eqs. (6) and (7) provide a self-consistent definition of the zero order hamiltonian and the perturbation in the CA basis. The following remarks should be made at this point:

- (1) Both A and CA (untruncated and complete) sets are adequate from the formal point of view.
- (2) The vibrational wavefunctions  $\chi^A$  and  $\chi^{CA}$  are different in the two approximations, see eqs. (2) and (5).
- (3) While the adiabatic potential surfaces  $E_n(\mathbf{R})$  are known from theoretical calculations no information is available concerning the CA potential surfaces  $\langle \varphi_n^{CA} | \Delta U(\mathbf{r}, \mathbf{R}) | \varphi_n^{CA} \rangle$ . In particular, it should be noticed that in the limiting case of  $\mathbf{R} \rightarrow \infty$  the crude adiabatic potential surfaces dissociate to the wrong energy<sup>†</sup>. Thus the high vibrational wavefunctions and zero order levels in the  $\{D\}$  manifold may differ appreciably in the A and CA representations.
- (4) Both A and CA basis sets are diagonal within the same electronic configurations, i.e.

$$\langle (nv)^{(A)} | V^A | n'v' \rangle = \langle (nv)^{(CA)} | T_R + \Delta U(\mathbf{r}, \mathbf{R}) | n'v' \rangle = 0 \quad \text{for } v \neq v'.$$

This point is well known concerning the A set but was not clearly realized concerning the CA basis.

- (5) The interstate coupling matrix elements [eq. (4)] were conventionally treated [1–3, 5, 6] by the application of the Condon approximation: (a) replacing the energy denominator in eq. (4) by the constant electronic energy gap and (b) assuming that the matrix element  $\langle \varphi_n^A | \partial U / \partial \mathbf{R} | \varphi_{n'}^A \rangle$  is independent on the nuclear configuration. The Condon approximation is invalid, both in solid state and molecular physics. We have recently [9] applied Feynman's operator technique in the weak electronic–vibrational coupling limit for the two electronic level

<sup>†</sup> We are grateful to Professor J. Musher for an illuminating discussion of this point.

system relaxing both approximations (a) and (b)<sup>†</sup>. For near resonance coupling between  $|s\rangle$  and  $|l\rangle$  we obtained

$$\langle\langle\varphi_s^A \chi_{si}^A | V^A | \varphi_l^A \chi_{lj}^A \rangle\rangle = \eta \frac{\langle\varphi_s^{CA}(r, R_0^s) | (\partial U / \partial R)_{R_0^s} | \varphi_l^{CA}(r, R_0^s) \rangle}{(\Delta E_{\kappa}^{sl} / \hbar \bar{\omega})} F_A^{si, lj}, \quad (8)$$

where  $F_A^{si, lj}$  is the Franck–Condon factor between the adiabatic functions,  $\Delta E_{\kappa}^{sl}$  is the effective electronic energy gap [3] (modified by a promoting mode) and  $\bar{\omega}$  is an average frequency. This is just the Condon approximation modified by a correction factor  $\eta$ , which exhibits [9] a linear dependence on  $\Delta E_{\kappa}^{sl} / \hbar \bar{\omega}$  and a weak dependence on the coupling strength. Thus for near resonance coupling, eq. (8) is practically independent of the energy gap, removing the paradox of Burland and Robinson [7] concerning the appreciable difference between A and CA resonance coupling, in the weak coupling limit. For off resonance coupling in the A basis (say with state  $b$ ) in the weak coupling limit we have  $\eta \approx 1$  so that

$$\langle\langle\varphi_s^A \chi_{si}^A | V^A | \varphi_b^A \chi_{bk}^A \rangle\rangle = \frac{\langle\varphi_s^{CA} | (\partial U / \partial Q)_0 | \varphi_b^{CA} \rangle}{(\Delta E_{\kappa}^{sb} / \hbar \bar{\omega})} F_A^{si, lj}. \quad (9)$$

Thus, off resonance coupling in the A basis is small.

(6) In the CA basis the coupling terms are of the same form for both near resonance and off resonance coupling

$$\langle\langle\varphi_s^{CA} \chi_{si}^{CA} | V^{CA} | \varphi_l^{CA} \chi_{lj}^{CA} \rangle\rangle = \langle\varphi_s^{CA} | \Delta U | \varphi_l^{CA} \rangle F_{CA}^{si, lj}, \quad \langle\langle\varphi_s^{CA} \chi_{si}^{CA} | V^{CA} | \varphi_b^{CA} \chi_{bk}^{CA} \rangle\rangle = \langle\varphi_s^{CA} | \Delta U | \varphi_b^{CA} \rangle F_{CA}^{si, bk}. \quad (10)$$

Thus the off resonance matrix elements in the CA basis are relatively large. The ratio of the off resonance coupling terms in the CA and A representation is  $\Delta E / \hbar \bar{\omega} \approx 10$ .

The last point brings up the major difficulty associated with the use of the CA basis. Let us consider the extension of the Bixon–Jortner model (fig. 1) where the role of other excited states (which always exist in real life) is included. We shall provide a general expression for the resonance width from the optical line shape (although any other “short time” or “long time” experiment could be considered). Including the effects of radiative coupling to first order, the line shape  $\mathcal{L}(E)$  for absorption from the ground level  $|0\rangle$  is [10]

$$\mathcal{L}(E) = \text{Im} \langle 0 | \mu G \mu | 0 \rangle, \quad (11)$$

where the Green operator is

$$G(E) = (E - H + i\eta)^{-1}; \quad \eta \rightarrow 0+ \quad (12)$$

and  $\mu$  is the dipole operator. Provided that conditions (c) and (d) hold the line shape (in any basis) is

$$\mathcal{L}(E) = \text{Im} \mu_{0s} G_{ss} \mu_{s0}. \quad (13)$$

The diagonal matrix elements of the Green function are

$$G_{ss}(E) = \langle s | G(E) | s \rangle = [E - E_s - D(E) - i\Gamma(E)]^{-1}. \quad (14)$$

The level shift  $D(E)$  and width  $\Gamma(E)$  are [11]

$$D(E) = \text{Re} \langle s | \hat{R} | s \rangle; \quad \Gamma(E) = \text{Im} \langle s | \hat{R} | s \rangle \quad (15)$$

being defined in terms of the level shift operator [11]

$$\hat{R} = V + V(1 - P)\tilde{G}(E)(1 - P)V, \quad (16)$$

where

<sup>†</sup> Recently Orlandi and Siebrand [15] have calculated the correction term arising from bypassing assumption (a). Sharf and Silbey [16] have provided an approximate scheme, relaxing both assumptions (a) and (b).

$$\tilde{G} = [E - H_0 - (1-P)V(1-P)]^{-1}; \quad P = |s\rangle\langle s|. \quad (17)$$

The resonance width is just  $\Gamma(E_s)$  (in the vicinity of  $E \approx E_s$ ). It is important to notice that this total width does not correspond just to the width of the zero order state  $|s\rangle$  due to its decay into  $\{D\}$ , as the role of the  $\{b\}$  states has to be included. This is immediately apparent from the expansion (where only a single  $|b\rangle$  state has been included for simplicity)

$$\langle s|\hat{R}|s\rangle = V_{sb}\tilde{G}_{bb}V_{bs} + \sum_l V_{sl}\tilde{G}_{lb}V_{bs} + \sum_l V_{sb}\tilde{G}_{bl}V_{lb} + \sum_l \sum_{l'} V_{sl}\tilde{G}_{ll'}V_{l'b}. \quad (18)$$

Note that in the simple previous model [1-3] only the last term in (18) is retained. Now making use of the operator identity  $(E-H)^{-1} = (E-H_0)^{-1} + (E-H_0)^{-1}V(E-H)^{-1}$ , eq. (18) takes the exact form

$$\Gamma(E_s) = \Gamma_0(E_s) + \text{Im}[E - E_b - i\Gamma_b(E_s)]^{-1}(V_{sb} + \alpha + i\beta)(V_{sb} + \alpha^* + i\beta^*), \quad (19)$$

where

$$\Gamma_0(E_s) = \pi \sum_l |V_{sl}|^2 \delta(E_s - E_l) \quad (20)$$

is just the Golden Rule width. While

$$\alpha = PP \sum_l V_{bl}V_{ls}/(E - E_l), \quad (21)$$

$$\beta = \pi \sum_l V_{bl}V_{ls} \delta(E_s - E_l) \quad (22)$$

represent "mixed type" level shifts and widths connecting the states  $|b\rangle$  and  $|s\rangle$  via  $|D\rangle$ . Finally, the zero order generalized width of the state  $|b\rangle$  (neglecting a level shift term) is  $\Gamma_b(E_s) = \sum_l |V_{bl}|^2 \delta(E_s - E_l)$ . Note that  $|\beta|^2 = \Gamma_0(E_s)\Gamma_b(E_s)$ . It is amusing to note that eq. (19) is formally equivalent to the Fano line shape formula [4] (taken at a single point) and can be recast in the form

$$\Gamma(E_s) = \Gamma_0(E_s) \frac{q_s^2 + \epsilon_s^2 + 2q_s\epsilon_s \cos\theta}{1 + \epsilon_s^2}, \quad (23)$$

where  $\epsilon_s = (E_s - E_b)/\Gamma_b(E_s)$  and  $q_s \exp(i\theta) = (V_{bs} + \alpha)/\beta$ .

For internal conversion the matrix elements are real and we get the final exact result

$$\Gamma(E_s) = \frac{\Gamma_b(E_s)(V_{sb} + \alpha)^2 + 2(E_s - E_b)\beta(V_{sb} + \alpha) + \Gamma_0(E_s)(E_s - E_b)^2}{(E_s - E_b)^2 + \{\Gamma_b(E_s)\}^2}. \quad (24)$$

For the validity limit of eq. (11) [see assumption (d)] we can assert that

$$\Gamma_b(E_s) \ll (E_s - E_b), \quad (25)$$

whereupon

$$\Gamma(E_s) \approx \Gamma_0(E_s) + \frac{2\beta(V_{sb} + \alpha)}{E_s - E_b} + \frac{\Gamma_b(V_{sb} + \alpha)^2}{(E_s - E_b)^2}. \quad (26)$$

Eqs. (24) and (26) provide us with the corrections for the Golden Rule expression. The first correction term in (26) represents the coupling of  $s - b - l - s$  while the second term [being small under condition (25)] represents double coupling between  $s - l$  and  $b - l$ . In the limit (25) we get

$$\Gamma(E_s) = \Gamma_0(E_s) + \frac{2\pi V_{sl}(E_l=E_s)V_{lb}(E_l=E_s)V_{bs}}{E_s - E_b} \rho_f(E_l=E_s). \quad (27)$$

This result brings us to a basic principle for the choice of the appropriate basis set for describing electronic relaxation processes. In real molecular systems conditions (a)–(d) are necessary but not sufficient for describing the relaxation rate in terms of the Golden Rule and we have in addition to assert that:

(e) the coupling between  $|b\rangle$  and  $|s\rangle$  and between  $|b\rangle$  and  $|D\rangle$  is negligible.

Thus the appropriate basis set has to be chosen to satisfy conditions (a)–(d) and to minimize the non-diagonal off resonance coupling terms  $V_{Ib}(E_I=E_s)$  and  $V_{bs}$ . From these general considerations we conclude that:

- (7) The adiabatic basis set is conceptually superior to the CA basis for describing electronic relaxation processes, as it involves much smaller off resonance coupling terms and thus can be described by decay in a two electronic level system.
- (8) The appreciable contamination of the zero order states  $|s\rangle$  and  $|D\rangle$  by other  $|b\rangle$  states in the CA scheme [12] implies that it is meaningless to consider the decay of an initially crude adiabatic state, as pointed out by Lefebvre [13].
- (9) The a priori reason for choosing the Born–Oppenheimer basis for describing radiationless transitions is to minimize the off resonance coupling terms. If all the off resonance states were included, the CA basis is perfectly adequate.
- (10) The choice of the basis set is arbitrary and does not reflect on the physical features of the problem. However, at the present state of our ignorance of the fine details of molecular coupling terms, only the adiabatic basis provides a sound physical description of a “two electron level system” where the role of other states is disregarded.

Finally, we would like to state one interesting shortcoming of the A basis. It can be demonstrated [14] that the adiabatic  $\{|D\rangle$  quasicontinuum does in principle carry oscillator strength from the ground state,  $\mu_{0I} \neq 0$ , so that strictly speaking the optical line shape is fanoian. The same result is obtained for the CA multilevel system [14]. However, the Fano line shape index is [14]  $q = \hbar\omega/\Gamma$ , so that in most cases of physical interest  $q \gg 1$  and the line shape is reduced to eq. (11).

The theory of electronic relaxation processes has been fraught with conceptual difficulties concerning the proper choice of the basis set. We hope that the present treatment will remove this confusion.

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