NON RADIATIVE TRANSITIONS

Neil Robertson

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Non-Radiative Transitions

A thesis presented by
Neil Robertson
to the
University of St. Andrews
in application for the Degree of
Doctor of Philosophy.

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Abstract, on the thesis

"Non-Radiative Transitions", by Neil Albert Robertson

This thesis describes theoretical research into multiphonon non-radiative transitions in solids. These processes occur when an impurity centre electron which has been raised to an excited state returns to its ground state by emitting phonons into the lattice rather than by emitting light.

The original contribution of this thesis is concerned with certain theoretical aspects of non-radiative transitions. For the first time the Molecular Crystal Model originally developed by Holstein to study small-polaron motion is used to investigate this problem. In particular, the effect that weak dispersion of the vibrational modes has on the transition rates is studied. The inclusion of weak dispersion is essential for a rigorous treatment of non-radiative transitions, and without this feature the transition rates are not well defined. We also use the well known single configuration coordinate model to derive recombination rates, giving particular attention to the unequal frequency case. Finally an adaptation of the Molecular Crystal Model is considered which more closely resembles real physical systems in that the electron is coupled to both crystalline modes and a local mode.

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Part I: The Single Configurational Coordinate Model

Part II: The Molecular Crystal Model

Part III: The Molecular Crystal Model taking weak but finite dispersion into account.

Part IV: The incorporation of a local mode in the Molecular Crystal Model.

CHAPTER 1

Introduction

This thesis describes theoretical research into multiphonon non-radiative transitions in solids. Such processes take place in molecules and impurity centres in crystals. From an experimental point of view non-radiative processes are most important when they quench competing radiative transitions. This situation may arise as follows: After absorbing light an electron on a crystalline impurity centre originally in its ground state is raised to an excited state. Luminescence may then follow as the electron returns to the ground state and emits a photon. Alternatively, this luminescence may be quenched if the electronic relaxation is accompanied by the emission of phonons into the lattice in a multiphonon non-radiative transition. Ideally the experimentalist would like a theory with the ability to predict the occurrence of luminescence at a given impurity centre. However, estimates of the actual magnitude of non-radiative processes have proved almost impossible to obtain; instead researchers have concentrated mostly on the variation with temperature which such processes exhibit.

The original contribution of this thesis is concerned with certain theoretical aspects of non-radiative transitions. For the first time the Molecular Crystal Model, originally developed by Holstein[1] to study small-polaron motion is used to study non-radiative transitions. In particular the effect that weak dispersion has on the transition rates in the Molecular Crystal Model is studied. The recombination rates which result are somewhat more complicated than those derived by previous investigators (e.g. Englman and Jortner[2]). We also use the well known single configuration coordinate model to derive recombination rates, giving particular attention to the unequal frequency case. Finally we consider an adaptation of the Molecular Crystal Model which more closely resembles real physical systems in that the electron is coupled to both crystalline modes and a local mode. We have published some of these results previously (Robertson and Friedman, I and II).[3,4]

This introductory chapter contains a brief non-mathematical account of the theory of non-radiative transitions. The physical processes which give rise to the principal transition rates are then discussed and finally there is a description of the basic contents of each chapter in the thesis.

We calculate recombination rates using two models, the Single Configurational Coordinate Model henceforth denoted by S.C.C.M. and the Molecular Crystal Model henceforth denoted by M.C.M. Both these models are considerably simplified versions of the real systems studied in the laboratory. However, they are believed to contain most of the essential features required in the recombination problem. One of the prerequisites for the occurrence of non-radiative transitions is the existence of some form of electron-lattice coupling. In the S.C.C.M. the electron is coupled to only one local mode, while in the M.C.M. the electron is coupled to all the crystalline modes.

The S.C.C.M. is the simpler of the two models. The lattice is described by only one generalised coordinate, x, which could be the breathing mode of an impurity in a crystal. The Born-Oppenheimer method which has been discussed quite extensively in the literature is used to treat the electron-lattice interaction. The physical basis of this method lies in the electronic motion being much more rapid than the nuclear motion so that the electronic wavefunctions are assumed to be capable of adjusting instantaneously to changes of nuclear position. Thus the electronic wavefunctions $\varphi_i(r,x)$ and their energy eigenvalues $E_i(x)$ depend parametrically on the lattice configuration, x. The lattice is assumed to move in a potential which includes not only the simple harmonic oscillator potential $\frac{1}{2}M\omega_0^2x^2$ but also the electronic energy eigenvalue $E_i(x)$. We assume that $E_i(x)$ contains a linear interaction term, $-A_ix$, with the electron-lattice coupling constant A_i depending on which electronic state is occupied. Thus, because the nuclei move in a potential $-A_ix+\frac{1}{2}M\omega_0^2x^2$ the lattice wavefunctions are displaced simple harmonic oscillator states $\mathcal{F}_m[\alpha(x-\Delta x^{i})]$ where $\alpha=\left(\frac{M\omega_0}{\hbar}\right)^{\frac{1}{2}}$ and where the displacement $\Delta x^{i}=A_i/M\omega_0^2$. Since the lattice equilibrium displacement depends on which electronic state is occupied, the potential energy curves are displaced with respect to one another as shown in fig 1.1* with the relative displacement being $\Delta x=\Delta x^{(1)}-\Delta x^{(0)}$. It is the coupling strength $E_M=\frac{\alpha^2\Delta x^2}{2}$ which proves to be a very important parameter throughout the theory. (See fig 1.1).

However, the states $\varphi_i(r,x)\mathcal{F}_m[\alpha(x-\Delta x^{(i)})]$ are not stationary in the Born-Oppenheimer approximation as a perturbation arises from the nuclear kinetic energy acting upon the configuration dependent electronic wavefunctions $\varphi_i(r,x)$. These so called 'non-adiabatic' terms provide the coupling between the electronic states and are the origin of the recombination processes. There are two non-adiabatic terms which have different electronic and vibrational factors. The first type consists of the terms of the form $\int d\underline{r}\,\varphi_0^*(r,x)\frac{\partial^2}{\partial x^2}\varphi_1(r,x)\,.\,I_{mn}$ where $I_{mn}=\int dx\,\mathcal{F}_m[\alpha(x-\Delta x^{(0)})]\,\mathcal{F}_n[\alpha(x-\Delta x^{(1)})]$ is the vibrational overlap integral of displaced simple harmonic oscillators. This term yields the simplest transition probabilities and we shall call this henceforth the standard term. The other type of non-adiabatic process involves terms of the form $\int d\underline{r}\,\varphi_0^*(r,x)\frac{\partial}{\partial x}\varphi_1(r,x)\,.\,I'_{mn}$ where the vibrational factor $I'_{mn}=\int dx\,\mathcal{F}_m[\alpha(x-\Delta x^{(0)})]\frac{\partial}{\partial x}\mathcal{F}_n[\alpha(x-\Delta x^{(1)})]$. We shall henceforth call these terms the 'derivative' non-adiabatic terms. The recombination rates which arise from both kinds of

*Figures are at end of chapter.

non-adiabatic process will be considered in this thesis.

We will assume throughout this thesis that the non-adiabatic terms are small enough to be treated by time-dependent perturbation theory. There is no real theoretical or experimental justification for this assumption. However, even if the non-adiabatic terms are small there is still a fundamental problem whith the use of time-dependent perturbation theory in the S.C.C.M. For the application of time-dependent perturbation theory to be valid, the system must relax into final states which form a continuum over the energy range. If this condition is not satisfied then no well defined transition probabilities exist. However, in the S.C.C.M. the final states are quite discrete, being separated from one another by a single phonon energy, $\hbar\omega_0$. Throughout Part I we will essentially replace the Dirac delta function which expresses energy conservation by a Kronecker delta function to obtain sensible transition rates. This is a fundamental difficulty with the S.C.C.M., for unless the electron is coupled to lattice modes as well, or unless the S.C.C.M. energy levels are broadened, the results derived using this model are not entirely rigorous.

To overcome these difficulties we have adapted the M.C.M. to study non-radiative processes. This model was originally developed by Holstein to investigate small polaron motion. The lattice in the M.C.M. consists of a set of N diatomic molecules with harmonic intra-atomic potentials. These simple harmonic oscillators are coupled to one another by suitable intermolecular coupling terms. There is an extra electron in the molecular chain which is localised on one of the molecules. This electron is considered to have only two states, a ground state (0) and an excited state (1). As in the S.C.C.M., the Born-Oppenheimer approximation is assumed valid in that the energy eigenvalue of the extra electron on the p'th molecule contains a linear term, $-A_i x_p$. This linear electron-lattice interaction forms part of the potential in which the lattice moves. Thus, the lattice wavefunction is a poduct of displaced simple harmonic oscillator wavefunctions, $\prod_k \mathcal{F}_{n_k}[\alpha_k(q_k-\Delta q_k^{(i)})]$ where q_k is the k'th normal coordinate.

The 'standard' and 'derivative' non-adiabatic terms in the Hamiltonian are assumed to be small perturbations which give rise to non-radiative transitions. However, unlike the S.C.C.M. the existence of finite dispersion of the crystalline modes in the M.C.M. provides a continuum of final states, so that the application of perturbation theory is on a firm foundation. In part II we investigate the M.C.M. in the limit of zero dispersion for which we find the same non-radiative transition rates resulting from the 'standard' non-adiabatic terms as occur in the S.C.C.M. In part III we will consider the effects of dispersion in the M.C.M. explicitly finding considerably modified results. Finally, in Part IV we discuss a development of the M.C.M. in which the electron is coupled to both a local mode and to all the crystalline modes. This more realistic model yields more complicated transition rates than those obtained from the previous treatments.

We now discuss the recombination rates obtained in Parts I and II using the 'standard' non-adiabatic terms. For all these results we assume that the electronic energy difference is an integral number of phonons, $\Delta E = p\hbar\omega_o$. We do not discuss the more general case, $\Delta E \neq p\hbar\omega_o$, until explicit account is taken of dispersion in Part III. The various principal results are also referenced by their text equation numbers here.

The transition probability at the absolute zero of temperature is

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_o}\exp\left(-\frac{E_M}{\hbar\omega_o}\right)\left(\frac{E_M}{\hbar\omega_o}\right)^p\frac{1}{p!}, \qquad (1.1) \quad (3.19)$$

where K is the electronic factor, $K = \int d\underline{r}\, \varphi_0^*(r,x) \frac{\partial^2}{\partial x^2} \varphi_1(r,x)$,

while E_M is the coupling strength, (see fig 1.1)

$$E_M = \frac{\alpha^2 \Delta x^2}{2}.$$

This result is often written in the form it assumes in the statistical limit $p = \frac{\Delta E}{\hbar\omega_0} \gg 1$, namely,

$$W_{T=0} = \frac{|K|^2}{\hbar}\left[\frac{2\pi}{\hbar\omega_0 \Delta E}\right]^{\frac{1}{2}} \exp\left\{-\frac{\Delta E}{\hbar\omega_0}\left[\log\left(\frac{\Delta E}{E_M}\right) - 1\right]\right\} \exp\left(-\frac{E_M}{\hbar\omega_0}\right). \quad (1.2)\ (3.2$$

Thus, if the electronic energy difference, ΔE, is large the recombination rate decreases exponentially with increasing ΔE.

The transition rate in the finite temperature, weak coupling

? limit $\frac{E_M}{\hbar\omega_0} \gg 1$ is

$$W_T = [1 + N(\omega_0)]^p\, W_{T=0} \text{ where } N(\omega_0) = [\exp(\beta\hbar\omega_0) - 1]^{-1}. \quad (1.3)\ (3.21).$$

In the high temperature $\beta\hbar\omega_0 \ll 1$, strong coupling $\frac{E_M}{\hbar\omega_0} \gg 1$ limit the recombination rate is

$$W_T = \frac{|K|^2}{\hbar}\left[\frac{\pi}{kTE_M}\right]^{\frac{1}{2}} \exp(-\beta E_b) \quad (1.4)\ (3.22)$$

where E_b is the 'activation' energy shown in fig 1.1. This is the well known activation energy, 'over the barrier' type of transition.

The various cases for which the above results are relevant will be discussed in the following chapters.

We now discuss briefly the physical processes which give rise to these recombination rates. These processes depend on whether we are using the S.C.C.M. or the M.C.M.; in the S.C.C.M., p phonons are emitted into one local mode while in the M.C.M. each of the N crystalline modes may either remain unaltered or else emit or absorb one phonon *. From the point of view of the M.C.M., the absolute zero and finite temperature processes occur by the emission of one phonon into each of p modes with the remaining modes having their phonon occupation numbers unchanged. However, in the high temperature $\beta\hbar\omega_0 \ll 1$ strong coupling $\frac{E_M}{\hbar\omega_0} \gg 1$ case more general types of multiphonon process take place provided $\neq$? that they conserve energy. In fact, for $\Delta E = p\hbar\omega_0$ the multiphonon processes which take place are those in which $p+q$ modes each emit one phonon while q modes each absorb a phonon, where q is summed over all possible values consistent with energy conservation.

From the point of view of the S.C.C.M. non-radiative transitions take place when p phonons are emitted into the local mode. In the weak coupling case (see fig 1.2), the crossover point x_c lies well above the minimum of the excited state curve. Hence at finite temperatures only those initial states well below the crossover point have a significant probability of occupation. Thus, the recombination proceeds by quantum mechanical processes which tunnel under the potential energy barrier. Since the probability of emission of one phonon into a mode is $1 + N(\omega_0)$[where $N(\omega_0) = [\exp(\beta\hbar\omega_0) - 1]^{-1}$, the thermal probability of occupation of a mode, frequency, ω_0] the probability of emission of p phonons is $[1 + N(\omega_0)]^p$. This is the origin of the transition rate (1.2), $W_T = [1 + N(\omega_0)]^p W_{T=0}$. This case is to be contrasted with

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*At this point it is useful to clarify our use of the terms 'emission' and 'absorption' of phonons. We always mean that a phonon is emitted into a mode, so that the occupation number increases by one. Similarly, a phonon is absorbed from a mode so that the phonon occupation number decreases by one.

the high temperature $\beta\hbar\omega_0 \ll 1$, strong coupling $\frac{E_M}{\hbar\omega_0} \gg 1$ case. Here the probability of occupation of the initial vibrational states in the vicinity of the crossover is significant, (see fig 1.3). Hence the transition may occur classically by a process which moves over the potential energy barrier. From a classical point of view, the recombination rate is proportional to the probability that the system reaches the crossover point x_c and then moves over into the ground electronic state. The probability that the system does reach the crossover point x_c is proportional to $\exp(-\beta E_b)$.

We conclude this introductory chapter with a brief description of the contents of each chapter in the thesis. Chapter 2 is a review of previous experimental and theoretical work done on the recombination problem. We then give in the main body of the text a fairly complete account of the various theoretical approaches to non-radiative transitions. In part I we adopt the S.C.C.M. which is the simplest model used to treat non-radiative transitions. This model is employed in Chapter 3 to derive the well-known recombination rates which we have just discussed using both the 'standard' and the 'derivative' non-adiabatic terms. These calculations were first performed by Kiel[5] for the standard terms, while Struck and Fonger[6] have employed a different method to derive the transition probabilities using the 'derivative' terms. The part of this chapter which derives transition rates with the 'standard' non-adiabatic terms has been published, (Robertson and Friedman, I)[3]. We extend these results in Chapter 4, calculating the vibrational overlap integral for potential energy wells which have different curvatures. (i.e. different frequencies of vibration associated with the ground and first excited states.) The results thus obtained are very complicated so that we discuss only the transition rate at the absolute zero of temperature. We discuss the possibility of an 'energy gap' law if certain conditions are satisfied. These calculations were performed without realising that the general result had already been derived by Hutchisson.[7] The 'energy-gap' law case is a new application of existing theory which is to be published, (Robertson and Friedman, II).[4]

In Part II of this thesis we use Holstein's[1] molecular crystal model (M.C.M.) to study the recombination problem for the first time, assuming no dispersion of the optical modes. In Chapter 5 we employ the 'standard' non-adiabatic terms to derive the well known transition probabilities which we have already obtained using the S.C.C.M. in Chapter 3. This work has already been published, (Robertson and Friedman, I).[3] In Chapter 7 we calculate the more complex contributions to the recombination rate which result from the 'derivative' non-adiabatic terms. We obtain the same results as Huang and Rhys[8] found originally with a model similar to the M.C.M. in which the electron is coupled to all the crystalline modes. However, our method of calculation is quite different and more general. Finally in Chapter 6 we rederive the results of Chapter 5 using combinatorial arguments. This alternative method of calculation is less formal than our previous techniques but gives more physical insight into the problem. This calculation is very similar to the method Huang and Rhys adopted in their paper.

We present in Part III original calculations of recombination rates in the M.C.M. which take weak but finite dispersion into account, We find in Chapter 8 that the resulting transition rates are considerably modified from those derived in Parts I and II. We distinguish between 'on resonance' transition rates when $\Delta E = p\hbar\omega_0$ and 'off resonance' transition rates when $\Delta E \neq p\hbar\omega_0$. When the resonance condition is satisfied, the transition rate is an additive series of terms, with the first term being the recombination rate we have already derived. When the resonance condition is not satisfied, not all terms in the series have the same sign, so that the recombination rate is reduced compared with the resonance case. In particular in the series for the exactly off-resonance case $\Delta E = (p+\frac{1}{2})\hbar\omega_0$ successive terms have alternating signs suggesting a local minimum in the recombination rate as a function of ΔE . Some of this material is to be published, (Robertson and Friedman, II).[4] In Chapter 9 we use a different method of calculation to derive similar results.

We have assumed in all our calculations that the electron is either coupled to one local mode or to all the perfect crystalline modes. However experimental evidence on optical absorption, (Dean and Henry)[9] points strongly to electrons on impurity centres being coupled to both local and crystalline modes of vibration. In the final chapter of this thesis, Chapter 10, we incorporate a local mode into the M.C.M. Unfortunately, in this more complex model for the recombination problem some of the parameters which were previously well defined become phenomenological. However, although some of the discussion is more qualitative than before, this model seems useful as recombination may take place by the emission of phonons into both local and lattice modes.

Most of the results for recombination rates have been derived using the M.C.M. which is a specific model. However, the Hamiltonian in the M.C.M. has a very general form so that the recombination rates derived using it have a wide applicability. This point is discussed more fully in the summary of Chapter 5 on page 79.

Fig 1.1: The S.C.C.M. diagram.

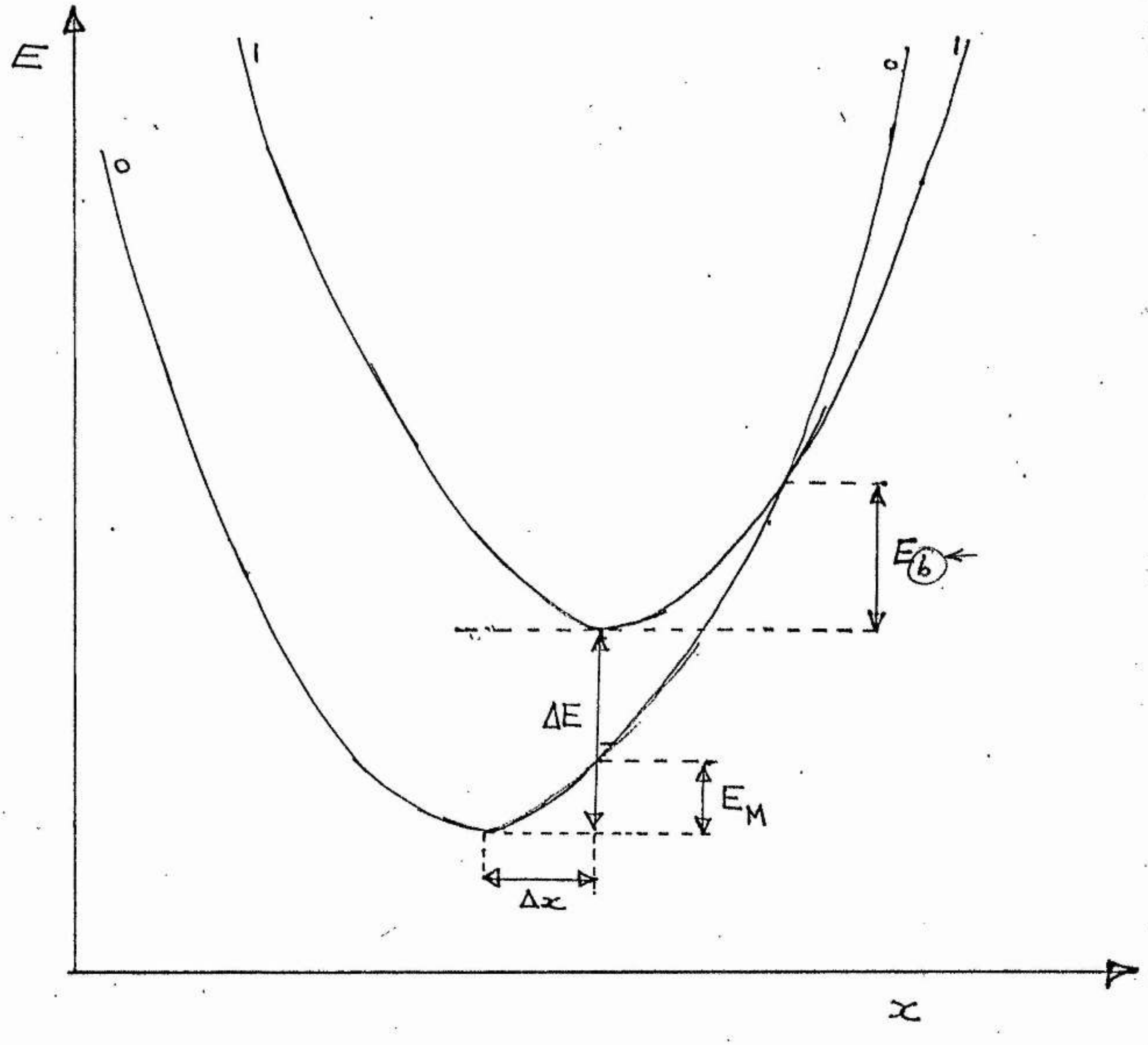


Fig 1.2: The S.C.C.M. diagram; weak coupling $\left(\frac{E_M}{\hbar\omega_0} \ll 1\right)$ case.

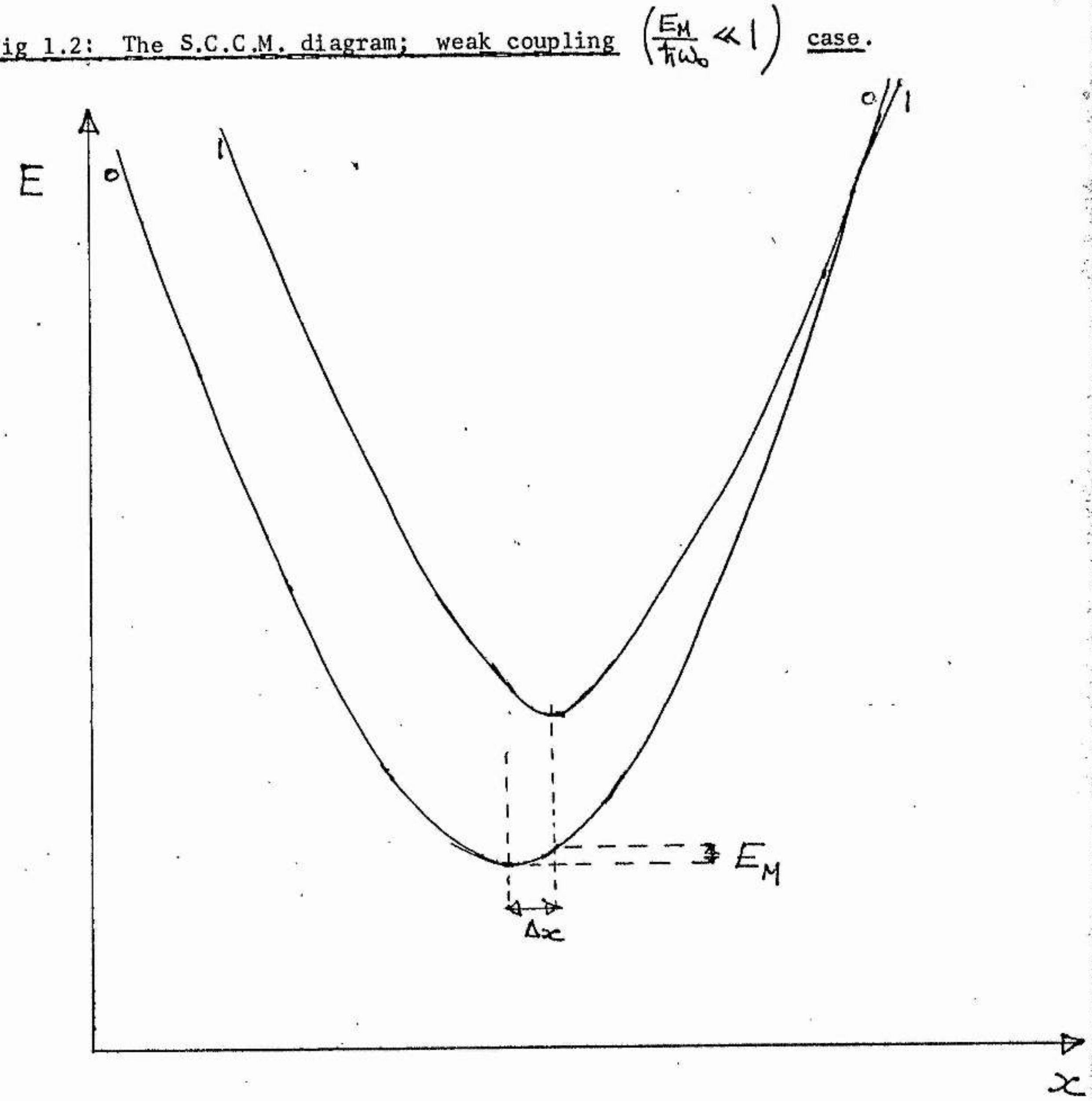
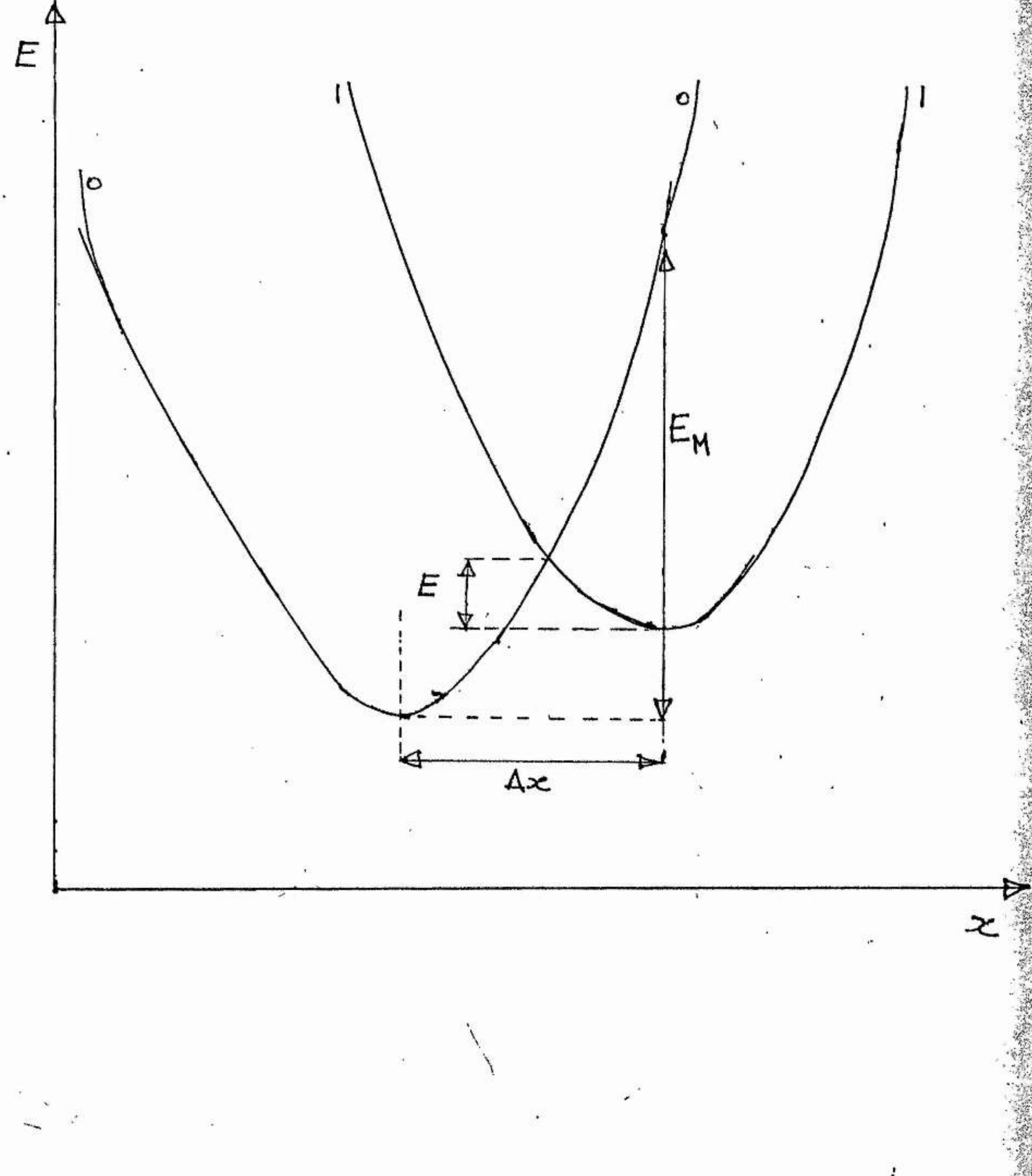


Fig 1.3: The S.C.C.M. diagram; strong coupling $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$ case.



CHAPTER 2

Review

There have been many papers written on the related subjects of non-radiative transitions and the absorption of light at impurity centres in crystals. These papers fall into two categories, firstly those involving the S.C.C.M. in which the electron interacts with only a single local mode, and secondly those in which the electron interacts with all the crystalline modes. In addition to papers dealing with the solid state, there have been many papers dealing with both radiative and non-radiative processes in molecules. A good review of this work in molecular physics is that written by Frank-Kamenetskii and Lukaskin.[10]

Frenkel[11] wrote one of the first papers to deal with non-radiative processes in 1930. He did not consider recombination between localised electronic states on impurity sites in crystals. Instead he considered n-electron states for which the ground state consists of each electron being in its ground state while there are n first excited states in each of which one electron has been raised to its first excited state. Due to interatomic interactions each of the n excited states has a slightly different energy so that a continuum of excited states results. These electron states are what were later to become known as Frenkel excitons. Frenkel was the first to apply the ideas of molecular physics to the solid state. According to previously accepted theory non-radiative decay occurred from the excited electronic states due to the perturbation caused by anharmonic terms in the lattice potential. However, since the electronic energy difference is of the order of one hundred phonons the perturbing terms which could produce the emission of such a large number of phonons would have to be of a very high order indeed. The resulting non-radiative transition rates would be very small. Frenkel developed the idea from molecular physics that the vibrational states of the lattice are dependent on which electronic state is occupied. He calculated the changes in equilibrium position and frequency of the lattice modes which occur. He then computed the vibrational overlap integrals, commenting that only changes in equilibrium position and not changes in frequency are important for crystalline modes. Despite this great advance the true Born-Oppenheimer theory of the electron-lattice interaction was not developed and, in particular, Frenkel still used anharmonic terms as the perturbation rather than the non-adiabatic terms. The calculational methods he employed to calculate the transition rates are basically combinatorial.

Contemporary with Frenkel's paper is Hutchisson's[7] (1930) work on the absorption band spectra of symmetrical diatomic molecules such as Na_2, K_2, I_2 and H_2. This was the first paper to introduce the S.C.C.M. into the field of molecular physics. The perturbation which acts to produce the absorption of light is the electric dipole moment acting between the initial and final electron-lattice states. The Condon approximation is used so that Hutchisson was the first to calculate the vibrational overlap integrals using the generating function method. Hutchisson's calculations take into account both a relative displacement of the oscillators and different frequencies. Our results derived in Chapter 4 agree with his calculations. Hutchisson goes on to use experimental values of the relative displacements and frequencies for the aforementioned diatomic molecules to calculate the absorption line strengths. When Hutchisson compared his results with experiment he found that the agreement was reasonably good and for Na_2 particularly good. Hutchisson discovered that the values of the vibrational overlap integrals are quite sensitive to the size of the relative displacement of the potential energy curves.

More than twenty years after Frenkel's paper was published the controversy over the origin of non-radiative transitions still continued.

Kubo's[12] (1952) paper on the thermal ionization of trapped electrons on impurity centres in crystals used the Born-Oppenheimer theory to describe the electron-lattice interaction with non-adiabatic terms acting as the perturbation. Kubo contrasted his treatment with that of Goodman, Lawson and Schiff[13] (1947) who used the variation of potential which the electron experiences as the lattice vibrates as the perturbation which produces non-radiative transitions. Kubo contended that the resultant non-radiative transition rates are much too small.

In Kubo's treatment the trapped electron is coupled to all the crystalline modes of the lattice which have no dispersion. An interesting feature of Kubo's treatment is the alteration of frequency but not equilibrium position of each lattice mode when the electron changes from the hydrogen-like 1-s state of the impurity to the plane wave state in the conduction band. Kubo used the Slater sum for a harmonic oscillator to calculate the transition rates. The non-radiative transitions occur between the states illustrated in figure 2.1. It was found that the ionization rate was given by $W_T(p) \simeq 4\nu_1 \left(\frac{\rho}{2}\right)^{p-1} \exp\left[-\frac{\epsilon_0}{kT}\right]$ at low temperatures and $W_T(p) = \frac{4\nu_1}{\beta} \exp\left[-\frac{\epsilon^*}{kT}\right]$ at high temperatures.

In these expressions $\varepsilon_0 = \Delta E = p\hbar\omega_0$, $\nu_1 = 64\left(\frac{m_e}{M}\right)(\omega_0\omega_1)^{1/2}$; $\epsilon^* = \Delta E + E_b$ and ρ is the fractional change of frequency when the electron changes state.

Thus, this early paper revealed the classical 'activation energy law' for high temperatures. At low temperatures the low-lying vibrational levels belonging to the ground electronic state must be activated classically to the same energy as the ground vibrational level of the excited electronic state resulting in the factor, $\exp\left[-\frac{\varepsilon_0}{kT}\right]$. The system then tunnels under the potential energy barrier to the excited electronic state.

One of the best known early papers which dealt with non-radiative transitions in depth was that written by Huang and Rhys[8] in 1951. The first topic which this paper is concerned with is the absorption of light by F-centres in ionic crystals. The absorption lines are broadened due to the emission and absorption of lattice phonons concurrently with the absorption of light. The excited F-centre state lies below the conduction band but even so photoconductivity results. Years earlier Mott[14] had suggested that this photoconductivity arises from a radiationless transition in which the electron in the excited F-centre state absorbs phonons from the lattice to raise itself into the conduction band. This photoconductivity is observed to vary with temperature as $\exp(-W/kT)$.

In the Huang-Rhys model the Born-Oppenheimer method is followed. A continuum model is used for the lattice and the electron interacts with this through the static charge distribution due to its own wavefunction. This allows specific values to be calculated for the linear electron-lattice coupling constants. This contrasts with most other treatments including the present one in which the electron-lattice coupling constant is assumed to be a phenomenological constant. However a weakness of this model is the lack of any dispersion in the crystalline modes.

The electric dipole term acting between the initial and final electron-lattice states is the perturbation which allows the optical absorption. The non-radiative transition arises from the 'derivative' non-adiabatic terms which result in the recombination rates which we derive in Chapter 7. The actual method of calculation employed is the combinational type which we use in Chapter 6. A disadvantage with this type of calculation is that it would be very difficult to extend to the general case where there is finite dispersion of the lattice modes. Huang and Rhys eventually derive the temperature activation type law $\exp\left[-\frac{W}{kT}\right]$ which is required to explain the observed photoconductivity.

In 1955 Kubo and Toyozawa[15] published a paper in which they dealt with more general forms of coupling of the electron to the lattice. The Huang-Rhys treatment was restricted to the interaction of an impurity electron in an ionic crystal with longitudinal optical modes which have no dispersion. Kubo and Toyozawa not only introduced dispersion into the optical modes but considered the interaction of an impurity electron in a non-polar crystal with longitudinal acoustic modes. However, although formal expressions are presented for the transition rates in these cases, the only explicit results obtained refer to interaction of the impurity electron with dispersionless optical modes. In particular the 'derivative' non-adiabatic terms are used to derive the same recombination rates that Huang and Rhys had previously calculated.

Kubo and Toyozawa employ the generating function method which is a completely different technique of calculation to that used by Huang-Rhys. This method involves taking a Laplace transform of the optical absorption rates and when the inverse transform is taken the moments of the optical absorption band may be calculated.

Kubo and Toyozawa question the common assumption that all the lattice vibrational modes extend throughout the crystal. In particular quadratic terms in the impurity electron-lattice interaction which cause modes to change their frequencies may well produce some vibrational modes which are localised around the impurity site. These modes interact more strongly with the impurity electron than the crystalline vibrational modes. However no calculations using these ideas are actually performed.

The Huang-Rhys model predicted that non-radiative transitions at an F-centre in KCl are negligible at low temperatures. Hence, there was surprise when it was discovered by Klick (1954) that this centre does not luminesce. In 1955 Dexter, Klick and Russell[16] put forward a novel idea to account for these experimental results. These authors believe the non-radiative transition process occurs before the thermalisation which ensures a canonical distribution over the vibrational levels takes place. Thus, as thermalisation proceeds there will be a time, before there is a canonical distribution over the vibrational states, at which those levels in the vicinity of the crossover C in figure 2.2 may have a large probability of being occupied. The non-radiative transition rate from these states is large and thus recombination takes place. Thus the criterion for luminescence to be very weak at low temperatures is that the system falls through the crossover point during the thermalisation process. Hence, luminescence does not occur if in fig 2.2, C lies below B. In all our work we do assume that there is a canonical distribution over the initial vibrational levels. In 1967 Siebrand[17] considered radiationless transitions in polyatomic molecules such as aromatic hydrocarbons which interact with a solvent at low temperatures. The role of the solvent is to absorb the vibrational energy which the molecule gains after deexcitation of the electron. In Siebrand's model the electron interacts with all the normal modes of vibration of the molecule. The treatment of the non-adiabatic factors,

$$\int \chi_f \left[\int \varphi_0(\underline{r}, \{q_{\gamma_i}\}) \sum_k \frac{\partial^2}{\partial q_{\gamma_k}^2} \varphi_1(\underline{r}, \{q_{\gamma_i}\}) d\underline{r} \right] \chi_i \, dq_{\gamma_1} \cdots dq_{\gamma_N}$$

where r is the electronic coordinate and $\{q_{\gamma_k}\}$ are the molecular normal coordinates, is different from our method. Siebrand does not use the Condon approximation in which the electronic factor

$$\int \varphi_0(\underline{r}, \{q_{\gamma_i}\}) \sum_k \frac{\partial^2}{\partial q_{\gamma_k}^2} \varphi_1(\underline{r}, \{q_{\gamma_i}\}) d\underline{r}$$

is a constant. Instead he expands this electronic factor about the equilibrium molecular positions, $\{q_{\gamma_k}^{0}\}$,

$$\int \varphi_0(\underline{r}, \{q_{\gamma_i}\}) \sum_k \frac{\partial^2}{\partial q_{\gamma_k}^2} \varphi_1(\underline{r}, \{q_{\gamma_i}\}) d\underline{r} = \sum_{n=1}^{\infty} \frac{\partial K}{\partial q_{\gamma_n}} (q_{\gamma_n} - q_{\gamma_n}^{(0)}) + \text{higher terms.}$$

The transition rates which result from the use of the linear term only are very similar to those derived using the simple vibrational overlap integrals.

Siebrand used the general vibrational overlap factors previously derived by Hutchisson for the $T = 0$ case. We discuss the form of these transitional probabilities in Chapter 4. Siebrand showed that if the electronic energy difference is large $\left(\frac{\Delta E}{\hbar\omega_0} \gg 1\right)$ then frequency shifts (distortions) dominate the radiationless transition rate rather than shifts in equilibrium distance (displacements). Indeed the relative importance of these two effects for non-radiative transitions is reversed compared with radiative transitions. Siebrand finally concluded that the recombination rate decreases exponentially with increasing electronic energy gap, ΔE .

Another relevant paper was that written by Kiel[5] in 1965. This paper is concerned with radiative rather than non-radiative transitions with the impurity absorption bands in solids being calculated.

Kiel's description of the Born-Oppenheimer electron-lattice states is quite enlightenning. The potential in which the nuclei move when the electron is in its ground state is $\sum_k \frac{1}{2} M\omega_{k,0}^2 q_k^2$ where $\{q_k\}$ are the normal coordinates. However, in general, when the electron is in its excited state the nuclei move in the potential $\sum_k \frac{1}{2} M\omega_{k,1}^2 (q_k')^2$ where the new normal coordinates $\{q_k'\}$ are different from $\{q_k\}$. This alteration of the normal coordinates makes the calculation of transition rates very complicated. Alternatively the potential in which the lattice moves when the electron is in its excited state may be written in terms of the old normal coordinates as,

$$\sum_k A_k q_k + \frac{1}{2}\sum_k M\omega_{k,1}^2 q_k^2 + \sum_{j\neq k} V_{jk} q_j q_k .$$

If the last term were not present the vibrational wavefunction for the excited state would be a product of harmonic oscillator functions of q_k, with displaced equilibrium positions due to the linear terms $A_1 q_k$ and with frequencies $\omega_{k,1}$ instead of $\omega_{k,0}$. However, the cross terms in

q_j, q_k couple together all the modes q_i rendering this description invalid. Kiel uses the variational principle to find the vibrational wavefunctions which take account of the coupling terms $V_{kj}q_jq_k$. Using this method it is found that the wavefunctions $\mathcal{F}_n^1$ are solutions of,

$$\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_k^2}+\frac{1}{2}M\omega_{k,1}^2 q_k^2+q_k\left[A_k+\sum_{j\neq k}V_{kj}\int\mathcal{F}_n^{1*}(q_j)\,q_j\,\mathcal{F}_n^1(q_j)\,dq_j\right]\right\}\mathcal{F}_n^1(q_j)$$
$$=E_{n,1}\,\mathcal{F}_n^1(q_k).$$

From the form of this equation it is seen that the normal coordinates $\{q_k\}$ appropriate to the electron in its ground state are retained. The solution for the vibrational wavefunction $\mathcal{F}_n^1$ is a displaced harmonic oscillator wavefunction with frequency $\omega_{k,1}$. However, the linear interaction constant which gives rise to the displacement of the oscillator is no longer A_k but it now becomes $A_k+\sum_{j\neq k}V_{kj}\int\mathcal{F}_n^{1*}(q_j)\,q_j\,\mathcal{F}_n^1(q_j)\,dq_j$ Thus, the general features of the radiationless decay problem are not changed even when the normal coordinates of the lattice are altered when the electron deexcites. The only change arises with the relative displacement of the two potential energy curves being no longer related to simply the linear electron lattice interaction constant A_k. Kiel proceded to discuss the transition rates due to displaced simple harmonic oscillators with the same frequency, obtaining the same expression for the vibrational overlap integral as we do in Chapter 3.

A more recent paper on radiationless transitions in large molecules was published by Englman and Jortner[2] in 1970. The electron is coupled to all the normal modes of the molecule. The 'standard' non-adiabatic terms are used to calculate the transition probability using a generating function method similar to Kubo and Toyozawa.[15] The harmonic oscillators are assumed to be displaced but with the same frequency. This is in disagreement with Siebrand's[17] assumption of the primary importance of frequency shifts in the large aromatic hydrocarbons such as benzene considered here. Englman and Jortner consider both the strong and the weak coupling cases. In the strong coupling, high temperature regime they derived the temperature activated transition probability which we find in Chapters 3 and 5. However, they state that such high temperatures as are required here $(\beta\hbar\omega_c \ll 1)$are not actually achieved in practice. They also derive a strong coupling, $\frac{E_M}{\hbar\omega_c} \gg 1$, low temperature $(\beta\hbar\omega_0 \gg 1$ result, $W_T = \sqrt{\frac{4\pi}{E_M\hbar\langle\omega\rangle}}\,|K|^2 \exp\left(-\frac{2E_b}{\hbar\langle\omega\rangle}\right)$ where $\langle\omega\rangle$ is the average phonon frequency. However, Englman and Jortner are not aware of any large molecules which actually satisfy the large coupling criterion, $\frac{E_M}{\hbar\omega_0} \gg 1$. Next, the weak coupling limit, $\frac{E_M}{\hbar\omega_0} \ll 1$ at absolute aero, $T = 0$ is considered; a saddle point method being used to derive the energy gap law. We do not believe that the conditions for the applicability of this method are satisfied and we derive the energy gap law using our own methods in Chapter 5. The energy gap law is valid for many non-radiative transitions in aromatic hydrocarbons C_xH_y such as benzene. As we have previously commented Siebrand has calculated a similar exponential decrease in transition rate with increasing electronic energy difference ΔE assuming that frequency shifts rather than relative displacements are important.

Another interesting recent paper was written by Warren-Moos[18] (1970). Relaxation processes between Stark groups in the $(4f)^n$ energy levels in rare earth salts are discussed. Typical, 'host' cyrstals are $LaCl_3$, $LaBr_3$ and LaF_3 while the rare earth ions involved are Dy and Nd. The 4f orbits of the rare-earth ions are so deeply buried within the electronic shell that the energy levels of the $(4f)^n$ configuration are only slightly perturbed. As a result of this relatively weak interaction with the lattice, Warren-Moos uses the picture of an isolated ion slightly perturbed by the surrounding crystal. The Born-Oppenheimer picture is not used; the electronic states are those ones appropriate for the nuclei in their equilibrium positions. The interaction of the rare earth ion with the lattice which produces the non-radiative transition is assumed to be due to the modulation of the crystalline field by the motion of the ions.

The resulting transition rates are so complex that a phenomenological approach is used. This results in an 'energy gap' law at T = 0, and the temperature dependence, $W_T=[1+N(\omega_0)]^p W_{T=0}$ at finite temperatures. Thus the same type of non-radiative transition rates result even although a different model from the standard Born-Oppenheimer type is used. Both these results are well founded experimentally for the rare earth ions in crystals studied by Warren-Moos. At absolute zero the non-radiative transition rates decrease rapidly with increasing electronic energy difference, ΔE as in figure 2.3. For large electronic energy difference ΔE, relaxation of an excited state takes place radiatively but for small ΔE the radiative process is quenched. The temperature dependence $W_T=[1+N(\omega_0)]^p W_{T=0}$ is illustrated in figure 2.4. Thus, although when p is large, $W_{T=0}$ is very small, W_T does increase more rapidly with increasing temperatures in this case than when p is small. Warren-Moos also finds that hydrated crystals such as $Eu(NO_3)_3.6H_2O$ are poor fluorescers. In this case the electronic state is coupled to local modes of the H_2O molecule which have high frequencies. The energy gap law is $W_{T=0}=B\exp\{-p[\log(\frac{\Delta E}{E_M})-1]\}$, so that if the vibrational frequency is large, the number of phonons emitted $p=\frac{\Delta E}{\hbar\omega_0}$ is small and thus the relaxation rate is large. Hence, non-radiative processes are important and quench the competing radiative process in hydrated crystals.

In the recent paper Struck and Fonger[20] (1975) have investigated the absorption and emission of light at impurities in crystals together with the temperature quenching of this emission by non-radiative processes.

This paper contains detailed comparison between numerical values of the theoretical expressions for the non-radiative rates and experimental values.

The S.C.C.M. is used to treat both radiative and non-radiative processes. In regard to energy considerations for the non-radiative transitions, Struck and Fonger comment that at least one phonon from the continuum of lattice modes is required to conserve energy. However, no attempt is made to discover the alterations to the transition rates resulting from this kind of process. The vibrational overlap integrals are not calculated using the generating function method but by the application of the Manneback[19] recursion formulas.

Struck and Fonger study non-radiative transition rates for various numerical values of the coupling strength E_M and the electronic energy difference ΔE. For each case they calculate numerical values for the vibrational overlap integrals $I^2_{p+m,m}$ and the thermally weighted Frank-Condon factors $(1-r_0)\, r_0^m\, I^2_{p+m,m}$ where $r_0 = \exp[-\beta\hbar\omega_0]$. Finally numerical values for $W_T = N_{10} \sum_{m=0}^{\infty} (1-r_0)\, r_0^m\, I^2_{p+m,m}$ are calculated assuming a numerical value for the electronic factor N_{10}. The transition rate W_T is studied as a function of temperature and the quenching of the corresponding radiative transitions is given.[11] The first case dealt with is the finite temperature, weak coupling case illustrated in figure 2.5. [The 'Small-offset multiphonon emission' case in the terminology of Struck and Fonger.] The non-radiative processes are found to be insignificant at low temperatures but to increase with temperature to quench competing radiative processes. An example of this type of transition is the $4f \rightarrow 4f$ rare earth process investigated by Warren-Moos.[18]

Another characteristic type of non-radiative transition identified is the 'fast bottom crossover' illustrated in figure 2.6. In this case the vibrational overlap integrals $I_{p+m,m}$ are all large and do not increase a great deal with increasing quantum number, m. The resulting non-radiative transition rates are large and quench competing radiative processes for all temperatures. Struck and Fonger give as examples of the 'fast bottom' crossover the fast Eu^{3+}CTS $\rightarrow {}^5D$ feeding in oxysulphides and fast $Cr^{3+}\ {}^4T_2 \rightarrow {}^2E$ feeding in Al_2O_3.

The 'low-temperature tunnelling crossover' illustrated in figure 2.7 is similar to the 'fast bottom crossover'. However, for small vibrational quantum number m, $I^2_{p+m,m}$ is very small because these terms represent quantum mechanical tunnelling processes. However, once m is large enough for the crossover point to be reached there is a vast increase in the vibrational overlap integrals, $I^2_{p+m,m}$. The resulting non-radiative transition rates are very small at low temperatures but increase very rapidly over a small temperature range. The competing radiative transitions are thus present below a certain temperature but are rapidly quenched once this temperature has been reached. An example of the low temperature tunnelling crossover is the quenching of the $Tm^{3+}\ {}^3P_0 \rightarrow {}^3F_4$ narrow line emission in La_2O_2S.

The final case dealt with by Struck and Fonger is the 'outside crossover' illustrated in figure 2.8. For this type of non-radiative transition the vibrational overlap integrals $I^2_{p+m,m}$ are small for small m but increase with increasing m. Thus the non-radiative transition rates increase as the temperature rises. This rate of increase of the recombination rates is greater than in the 'weak coupling' case but less than in the 'low temperature tunnelling crossover' case. An example of the 'outside crossover' type of non-radiative transition is the $Cr^{3+}\ {}^4T_2 \rightarrow {}^4A_2$ in Al_2O_3 It is interesting that in none of the various types of non-radiative transitions is a temperature dependence of the 'activation type', $W_T \propto \exp[-E_b/kT]$ observed.

In a later paper, Struck and Fonger[6] (1976) extend their previous work to cover transition rates in the S.C.C.M. using the 'derivative' non-adiabatic terms. Denoting this transition rate by $W_{p,\frac{\partial}{\partial x}}$ compared with the transition rate due to the 'standard' non-adiabatic terms W_p [where $\Delta E = p\hbar\omega_0$] Struck and Fonger find

$$W_{p,\frac{\partial}{\partial x}} = 2\left\{\frac{E_A - E_p(T)}{\hbar\omega_0}\right\} W_p .$$

In this expression for $W_{p,\frac{\partial}{\partial x}}$, E_A is the activation energy, while $E_p(T)$ is the activation energy obtained by fitting the transition rate to an activation energy law as shown below,

$$A_p \exp\left[-\frac{E_p(T)}{kT}\right] = 2\pi\frac{|K|^2}{\hbar^2}\sum_{m=0}^{\infty}(1-r_0)\,r_0^m\, I^2_{p+m,m} \quad \text{where} \quad r_0 = \exp[-\beta\hbar\omega_0]$$

Struck and Fonger find that $E_p(T)$ is given by

$$E_p(T) = (\langle m\rangle_p - \langle m\rangle)\hbar\omega_0$$

where $\langle m\rangle$ is the thermal probability of occupation of the local mode, $\langle m\rangle = [\exp(\beta\hbar\omega_0) - 1]^{-1}$ while $\langle m\rangle_p$ is the average value of m at which the non radiative transition takes place,

$$\langle m\rangle_p = \frac{\sum_{m=0}^{\infty} m(1-r_0)\,r_0^m\, I^2_{p+m,m}}{\sum_{m=0}^{\infty}(1-r_0)\,r_0^m\, I^2_{p+m,m}}$$

Now, at the absolute zero of temperature $T=0$, $E_p(0)=0$ so that $W_{p,\frac{\partial}{\partial x}} = \frac{2E_A}{\hbar\omega_0}W_p$. We will prove this result in Chapter 3, although we are unable to show the more general result

$$W_{p,\frac{\partial}{\partial x}} = 2\left\{\frac{E_A - E_p(T)}{\hbar\omega_0}\right\} W_p$$

using our methods. As the temperature increases so does $E_p(T)$ so that $W_{p,\frac{\partial}{\partial x}}$ becomes smaller compared to W_p.

Struck and Fonger conclude that the magnitude and temperature

?

dependence of the 'standard', W_p and the 'derivative', $W_{p,\frac{\partial}{\partial x}}$ transition rates are similar and would be very difficult to distinguish experimentally.

Figure 2.1: The configuration coordinate diagram considered by Kubo.

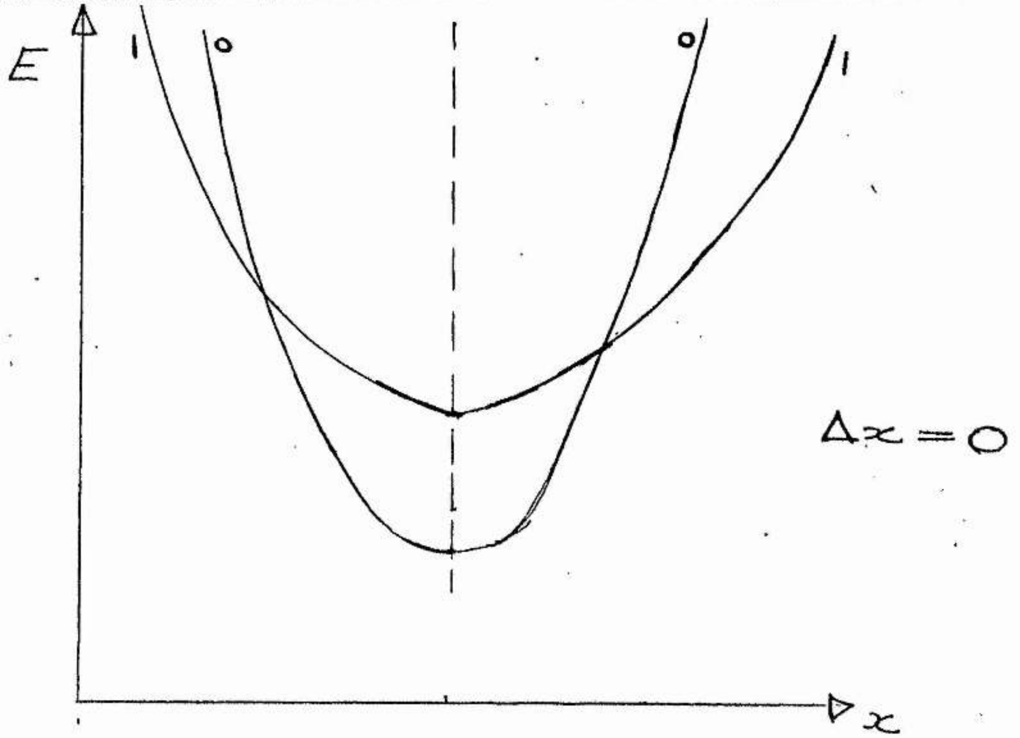


Figure 2.2: The criterion for luminescence.

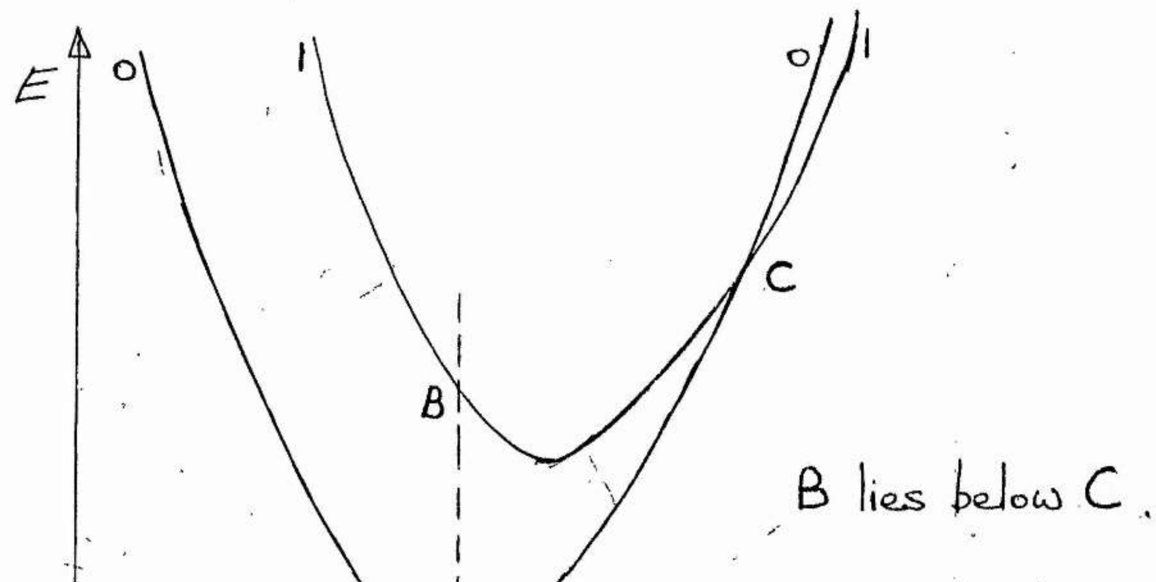


Figure 2.3: The Recombination Rate as a function of electronic energy gap ΔE as found by Warren-Moos.

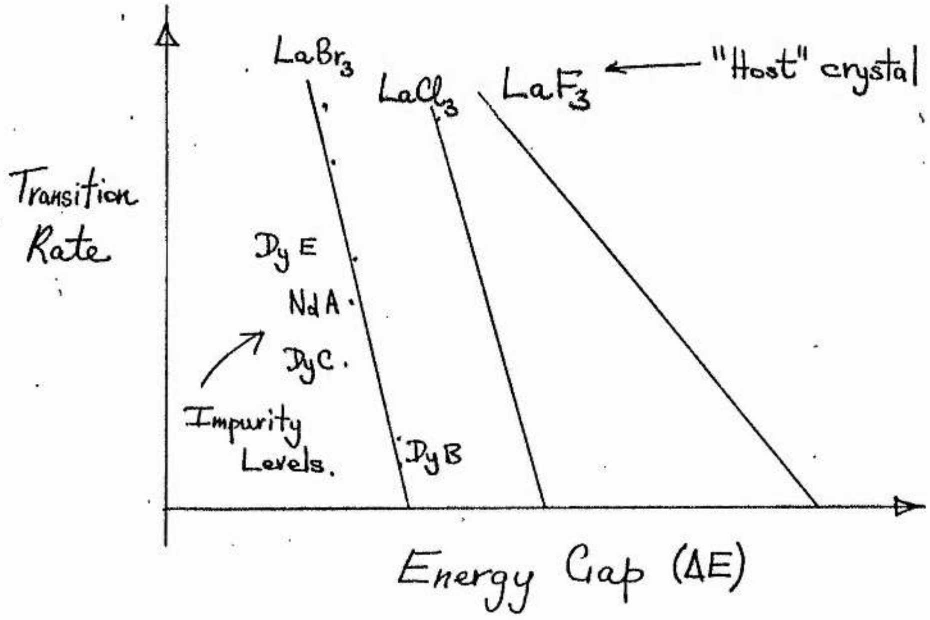


Figure 2.4: The Temperature Dependence of the Recombination Rates as found by Warren-Moos.

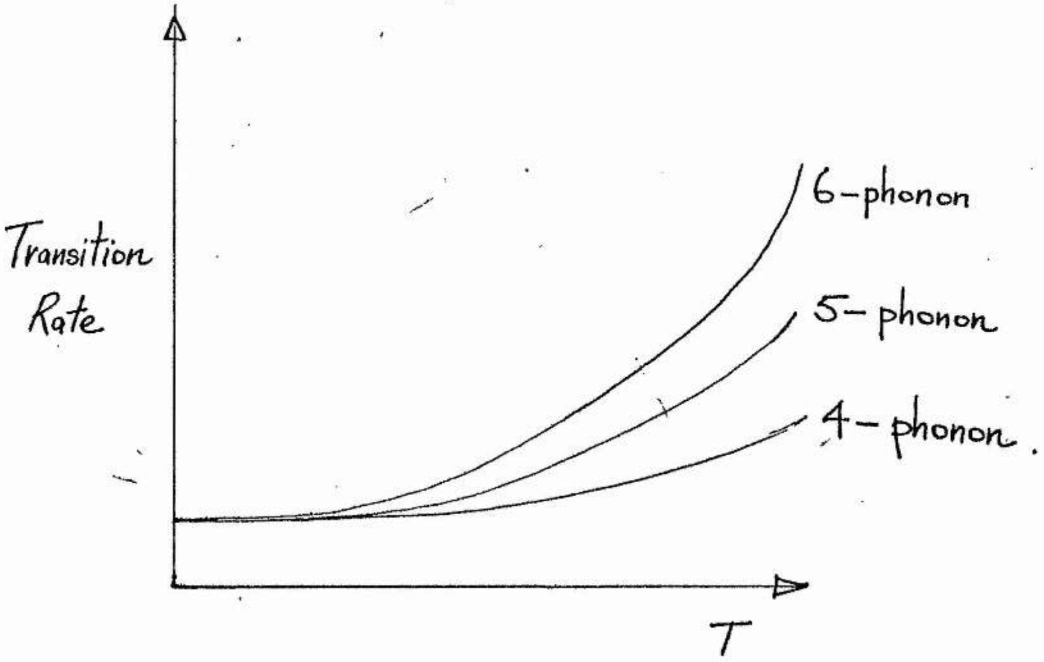


Figure 2.5: The S.C.C.M., Weak Coupling Case.

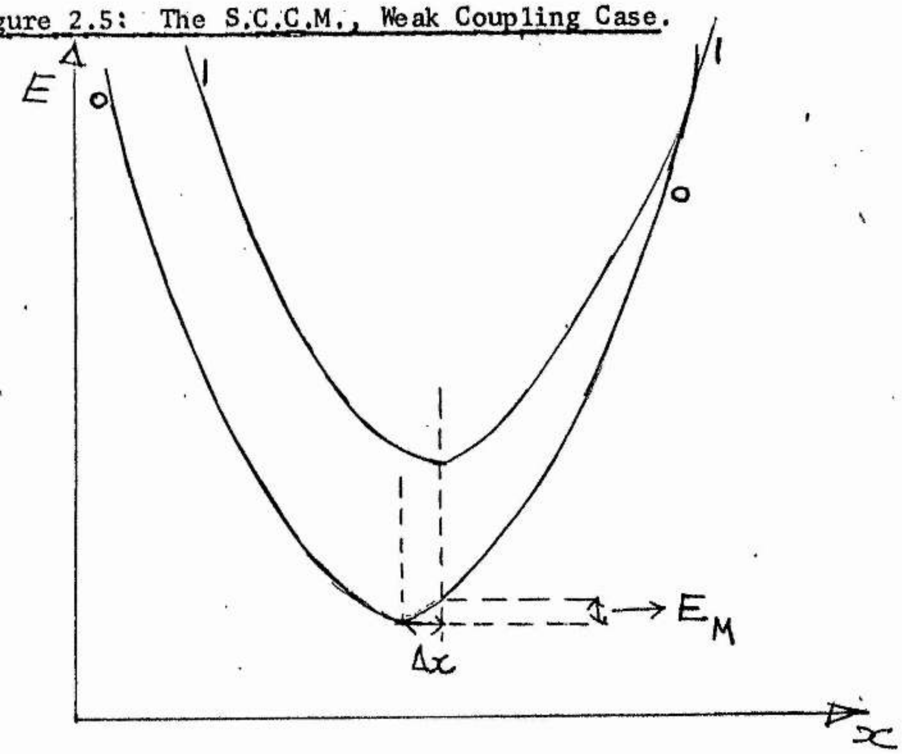


Figure 2.6: The S.C.C.M., Fast Bottom Crossover.

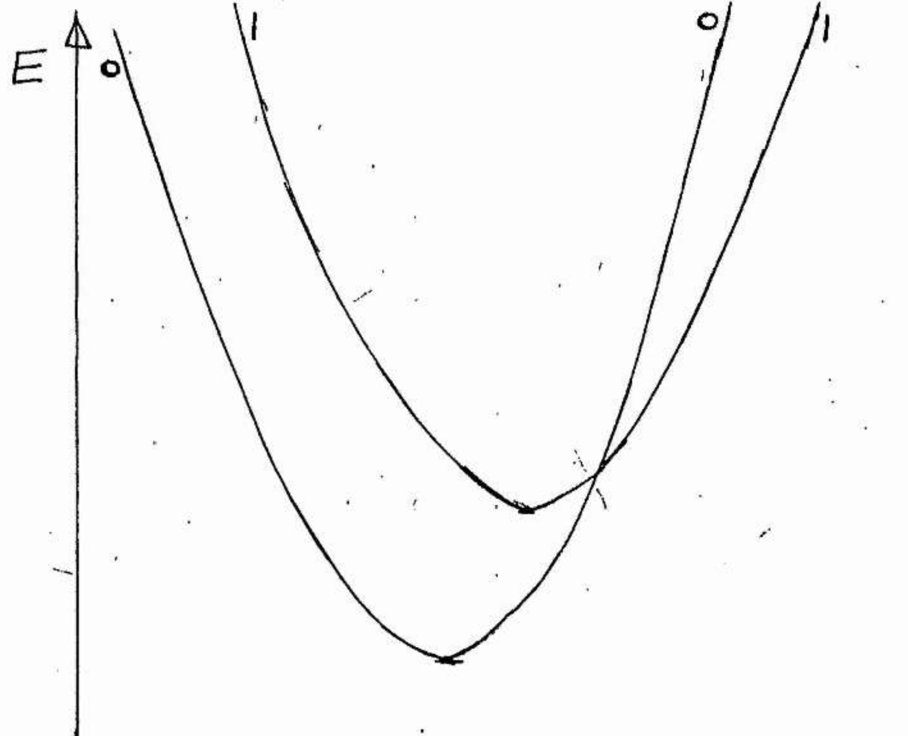


Figure 2.7: The S.C.C.M., Low temperature tunnelling crossover.

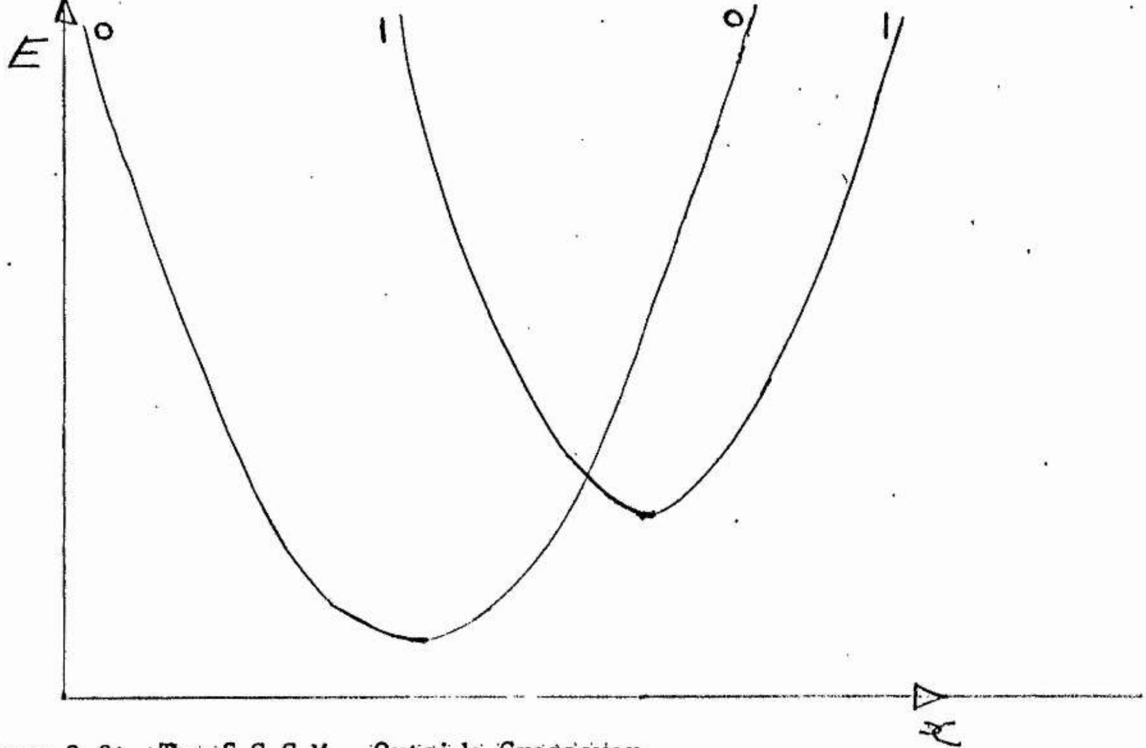
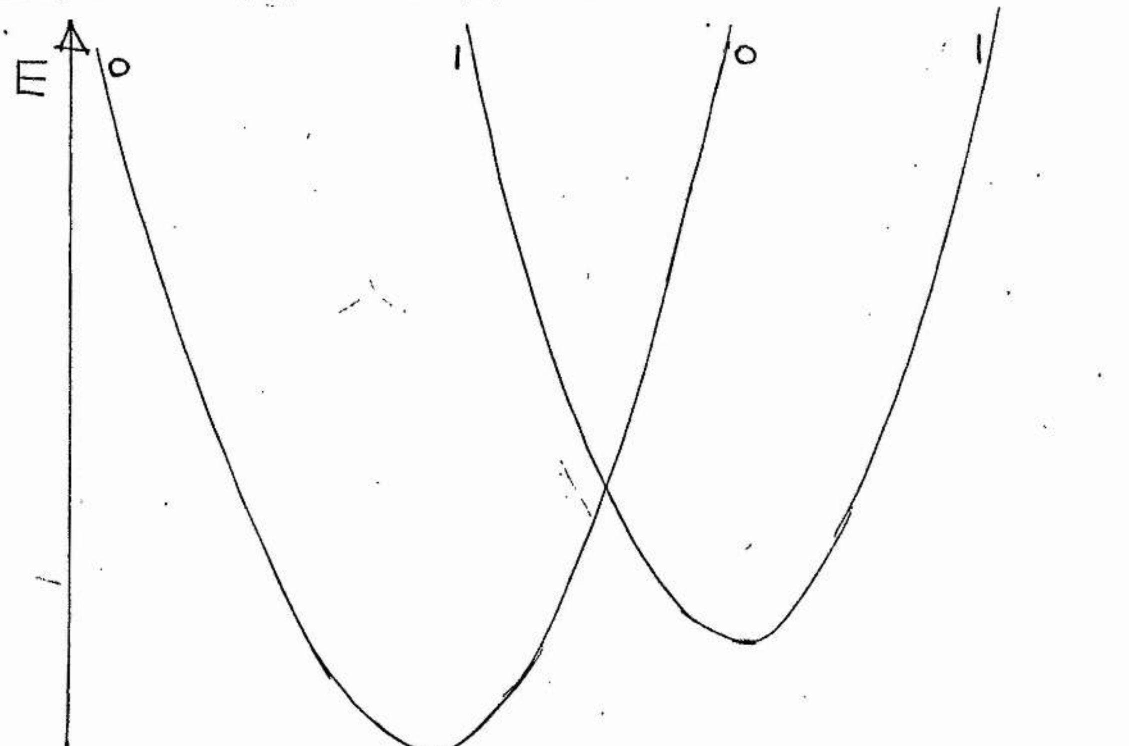


Figure 2.8: The S.C.C.M., Outside Crossover.



Part 1

The Single Configurational Coordinate Model.

CHAPTER 3

The Single Configurational Coordinate Model

The simpler of the two models we use to study non-radiative transitions is the single configurational coordinate model, (S.C.C.M.) in which the electron is coupled to only one local vibrational mode. This contrasts with the molecular crystal model, (M.C.M.) introduced in Chapter 5 which includes coupling of the electron to all the crystalline modes of vibration. Despite this simplicity, the S.C.C.M. may represent some aspects of the recombination problem more realistically than the M.C.M. as the impurity centres in crystals where recombination often occurs may be strongly coupled to a few local modes. However, the S.C.C.M. does suffer from difficulties regarding energy conservation. These difficulties are discussed briefly in this chapter and more fully in chapters 8 and 10. Finally, not least of the advantages which the S.C.C.M. gives us is the use of the rather famous little S.C.C.M. diagram to think about the physical processes involved in the recombination problem.

We shall now calculate the recombination rates using time-dependent perturbation theory. These calculations are not original but they have been independently rederived. We consider the Schrödinger equation,

$$i\hbar \frac{d\Psi}{dt} = H_T \Psi \qquad (3.1)$$

where the S.C.C.M. Hamiltonian H_T is

$$H_T = -\frac{\hbar^2}{2m_e}\nabla_r^2 + U(r,x) - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + \frac{1}{2}M\omega_0^2 x^2. \qquad (3.2)$$

Here, x is the single configurational coordinate, $-\frac{\hbar^2}{2m_e}\nabla_r^2$, $-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}$ are the electronic and lattice kinetic energies respectively, $U(r,x)$ ← ? is the molecular potential in which the electron moves, while $\frac{1}{2}M\omega_0^2 x^2$ is the quadratic lattice potential energy.

As a general solution of (3.1) we write

$$\Psi = a_0(t)\varphi_0\chi^0_m \exp\left[-iE_{0,m}\frac{t}{\hbar}\right] + a_1(t)\varphi_1\chi^1_n \exp\left[-iE_{1,n}\frac{t}{\hbar}\right], \quad (3.3)$$

where in the Born-Oppenheimer approximation the electronic wavefunctions $\varphi_i(r,x)$ and their energy eigenvalues $E_i(x)$ depend on the lattice configuration. The electronic wavefunctions $\varphi_i(r,x)$ are solutions of

$$\left[-\frac{\hbar^2}{2m_e}\nabla_r^2 + U(r,x)\right]\varphi_i(r,x) = E_i(x)\varphi_i(r,x). \quad (3.4)$$

The simplest assumption about the energy eigenvalue $E_i(x)$ we can make is that it contains a linear electron-lattice interaction term,

$$E_i(x) = E_i - A_i x. \quad (3.5)$$

the significance of which will be discussed shortly. In the Born-Oppenheimer approximation the potential in which the nuclei move includes the electron lattice interaction terms so that the vibrational states χ^i_n are solutions of

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + \frac{1}{2}M\omega_0^2x^2 - A_i x\right]\chi^i_n = \mathcal{E}^i_n\chi^i_n,$$

which may be written as

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2} + \frac{1}{2}M\omega_0^2\left(x - \frac{A_i}{M\omega_0^2}\right)^2 - \frac{A_i^2}{2M\omega_0^2}\right]\chi^i_n = \mathcal{E}^i_n\chi^i_n. \quad (3.6)$$

Thus the vibrational wavefunctions χ^i_n are displaced simple harmonic oscillator functions

$$\chi^i_n = N_n H_n\left[\alpha(x-\Delta x^{(i)})\right]\exp\left[-\frac{1}{2}\alpha^2(x-\Delta x^{(i)})^2\right], \quad (3.7)$$

where $N_n = \left(\frac{\alpha}{\pi^{1/2}2^n n!}\right)^{\frac{1}{2}}$, $\alpha = \left(\frac{M\omega_0}{\hbar}\right)^{\frac{1}{2}}$, and the lattice energy eigenvalues $\mathcal{E}^i_n$ are,

$$\mathcal{E}^i_n = \hbar\omega_0\left(n+\frac{1}{2}\right) - \frac{A_i^2}{2M\omega_0^2}, \quad (3,8)$$

The lattice displacement, Δx^i depends on which electronic state is occupied since it is proportional to the linear interaction constant A_i;

$$\Delta x_i = \left(\frac{\hbar}{M\omega_0}\right)^{\frac{1}{2}} \frac{A_i}{M\omega_0^2} . \qquad (3,9)$$

The really important parameter throughout the theory is the relative displacement of the minima of the potential energy curves,

$$\Delta x = \Delta x^1 - \Delta x^0 = \frac{(A_1 - A_0)}{M\omega_0^2} \left(\frac{\hbar}{M\omega_0}\right)^{\frac{1}{2}} . \qquad (3.10)$$

This reveals the significance of the linear electron-lattice interaction term in the electronic energy, (3.5).

The S.C.C.M. diagram, figure 3.1, (p.F3.1) represents the two potential energy curves

$$\frac{1}{2}M\omega_0^2\left(x - \frac{A_0}{M\omega_0^2}\right)^2 - \frac{A_0^2}{2M\omega_0^2} + E_0 \quad \text{and} \quad \frac{1}{2}M\omega_0^2\left(x - \frac{A_1}{M\omega_0^2}\right)^2 - \frac{A_1^2}{2M\omega_0^2} + E_1 ,$$

by $\frac{1}{2}M\omega_0^2x^2$ and $\frac{1}{2}M\omega_0^2(x - \Delta x)^2 + \Delta E$ respectively. The binding energy terms $\frac{A_i^2}{2M\omega_0^2}$ have been included in the electronic energy difference, ΔE.

Initially at time t=0 the system is assumed to be in the excited electronic state as a result of the absorption of incident radiation. Thus, the initial condition for equation (3.1) is $a_1(0) = 1$ and $a_0(0) = 0$. We find in Appendix A3.1 that the perturbation which gives rise to non-radiative transitions is the nuclear kinetic energy, $-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}$ acting on the configuration-dependent electronic wavefunction $\varphi_1(\underline{r}, x)$. The quantity $|a_0(t)|^2$ is the probability for the ground state to be occupied at time t and is thus the transition probability which we wish to calculate.

We find in Appendix (A3.1), equation (A3.1.7), that $a_0(t)$ is a solution of

$$i\hbar\frac{d}{dt}a_0(t) = K^{m,n}_{0,1} \exp\left[\frac{it}{\hbar}(E_{0,m} - E_{1,n})\right] , \qquad (3.11)$$

where

$$K^{m,n}_{0,1} = -\frac{\hbar^2}{2M}\int \varphi_0^* \frac{\partial^2}{\partial x^2}\varphi_1 d\underline{r} \int \chi_m^0 \chi_n^1 dx - \frac{\hbar^2}{M}\int \varphi_0^* \frac{\partial}{\partial x}\varphi_1 d\underline{r}\int \chi_m^0 \frac{\partial}{\partial x}\chi_n^1 dx .$$

In the above expressions the validity of the Condon (3.12) approximation has been assumed in which,

$$\iint \varphi_0^*(r,x)\frac{\partial^2}{\partial x^2}\varphi_1(r,x)\,\chi_m^0\left[\underline{\alpha}(x-\Delta x^{(0)})\right]\chi_n^1\left[\underline{\alpha}(x-\Delta x^{(1)})\right]d\underline{r}\,dx$$

$$= \int \varphi_0^*(r,x)\frac{\partial^2}{\partial x^2}\varphi_1(r,x)d\underline{r}\int \chi_m^0\left[\underline{\alpha}(x-\Delta x^{(0)})\right]\chi_n^1\left[\underline{\alpha}(x-\Delta x^{(1)})\right]dx$$

We find in appendix (A5.1) that the solution of equation (3.11) is

$$|a_0(t)|^2 = \frac{4|K^{m,n}_{0,1}|^2}{(E_{0,m}-E_{1,n})^2}\sin^2\frac{1}{2}\frac{t}{\hbar}(E_{0,m}-E_{1,n}) \qquad (3.13a)$$

which gives

$$\frac{d}{dt}|a_0(t)|^2 = \frac{2\pi}{\hbar}|K^{m,n}_{0,1}|^2\delta(E_{0,m}-E_{1,n}) \qquad (3.13b)$$

where

$$|K^{m,n}_{0,1}|^2 = |K|^2 I^2_{mn} + |C|^2(I'_{mn})^2 + |KC| I_{mn} I'_{mn} . \qquad (3.14)$$

In the expression for $|K^{m,n}_{0,1}|^2$,

$$K = -\frac{\hbar^2}{2M}\int \varphi_0^*\frac{\partial^2}{\partial x^2}\varphi_1 d\underline{r} \;;\; I_{mn} = \int \chi_m^0\left[\underline{\alpha}(x-\Delta x^{(0)})\right]\chi_n^1\left[\underline{\alpha}(x-\Delta x^{(1)})\right]dx$$

$$C = -\alpha\frac{\hbar^2}{M}\int \varphi_0^*\frac{\partial}{\partial x}\varphi_1 d\underline{r} \text{ and } I'_{mn} = \int \chi_m^0\left[\underline{\alpha}(x-\Delta x^{(0)})\right]\frac{\partial}{\partial(\alpha x)}\chi_n^1\left[\underline{\alpha}(x-\Delta x^{(1)})\right]dx$$

In this chapter we consider the non-radiative transition rates which arise from both the 'standard', $|K|^2 I^2_{mn}$ and the 'derivative' $|C|^2 I'^2_{mn}$ non-adiabatic terms although the greater emphasis is placed on the former. The cross terms $|KC| I_{mn} I'_{mn}$ which are not dealt with here will give rise to similar transition rates.

The transition rates which result from the 'standard' non-adiabatic terms are considered first,

$$W_T^{(1)} = \frac{2\pi}{\hbar}|K|^2 I_{mn}^2 \, \delta(E_{0,m}-E_{1,n}). \tag{3.15a}$$

Energy conservation requires that a transition can only occur if all the vibrational states are aligned as in figure 3.1. This is certainly an artificial restriction imposed by the S.C.C.M. which will be discussed in greater detail in Chapters 8 and 10. In this chapter the vibrational states are assumed to be aligned.

We now calculate the transition rate using the alternative form

$$W_T = \frac{1}{t}|a_0(t)|^2. \tag{3.15b}$$

The expression (3.15b) considers only transitions between one initial vibrational state and one final vibrational state. However, the recombination processes take place between all the initial vibrational states and all the final vibrational states. To consider the latter process we sum over all the final vibrational states, so that

$$W_T^{(1)} = \frac{1}{t}\sum_m \frac{4|K|^2 I_{m,n}^2}{(E_{0,m}-E_{1,n})^2}\sin^2\frac{1}{2}\frac{t}{\hbar}(E_{0,m}-E_{1,n}), \tag{3.15c}$$

We now assume that anharmonic coupling of the local mode to the crystalline modes broadens the simple harmonic oscillator states so that the final vibrational states form a continuum. The density of final states $N(E)$ defined such that $N(E)dE$ equals the number of states between E and $E + dE$ is assumed to be given by the average density of states $N(E) = \frac{1}{hw_0}$.

Thus, the summation in equation (3.15c) may be replaced by an integration,

$$W_T^{(1)} = \frac{1}{t}\int_{-\infty}^{\infty}\frac{4|K|^2 I_{m,n}^2 N(E)}{(E_{0,m}-E_{1,n})^2}\sin^2\left[\frac{1}{2}\frac{t}{\hbar}(E_{0,m}-E_{1,n})\right]d(E_{0,m}-E_{1,n}), \tag{3.15d}$$

The quantity $\dfrac{\sin^2 \frac{1}{2}\frac{t}{\hbar}(E_{o,m}-E_{1,n})}{(E_{o,m}-E_{1,n})^2}$. is a sharply peaked function about $E_{o,m} = E_{1,n}$ which fact expresses energy conservation. Since $\Delta E = p\hbar\omega_c$ this results in m = n+p.

Thus, the dominant contribution to (3.15d) comes from the region near $E_{o,m} = E_{1,n}$. Assuming that $I_{m,n}$ is a slowly varying function of energy near $E_{o,m} = E_{1,n}$, equation (3.15d) may be replaced by

$$W_T = \frac{4}{t}|K|^2 I^2_{n+p,n} N(E) \int_{-\infty}^{\infty} \frac{\sin^2 \frac{1}{2}\frac{t}{\hbar}(E_{o,m}-E_{1,n})}{(E_{o,m}-E_{1,n})^2}\, d(E_{o,m}-E_{1,n}), \tag{3.15e}$$

and the "golden rule" is obtained

$$W = \frac{2\pi}{\hbar}|K|^2 I^2_{n+p,n} N(E). \tag{3.16}$$

The expression (3.16) for the recombination rate assumes that only one initial vibrational level is occupied. However, in reality after the impurity electron has been excited, anharmonicities in the Hamiltonian which couple the local mode to the crystalline modes ensure that a thermal distribution is soon achieved over the vibrational states. Thus, the probability that the initial state n is occupied is the canonical distribution $\exp[-\beta\hbar\omega_o(n+\frac{1}{2})]\left\{\sum_{n=0}^{\infty}\exp[-\beta\hbar\omega_o(n+\frac{1}{2})]\right\}^{-1}$.

Thus, the transition probability W_T is found to be

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_o}\sum_{n=0}^{\infty}\frac{I^2_{n+p,n}}{Z}\exp[-\beta\hbar\omega_o(n+\tfrac{1}{2})]. \tag{3.17}$$

In this expression, Z is the partition function

$$Z = \sum_{n=0}^{\infty}\exp[-\beta\hbar\omega_o(n+\tfrac{1}{2})].$$

To calculate the transition probability given by equation (3.1.7) we evaluate the vibrational overlap integral

$$I_{mn} = \int_{-\infty}^{\infty} \chi_m\left[\alpha(x-\Delta x)\right]\chi_n(\alpha x)dx .$$

The generating function method is used as in Schiff^{21} (1949) where the Hermite polynomials appear as coefficients in the expansion

$$\exp\left[-s^2+2s\alpha q\right] = \sum_{n=0}^{\infty} \frac{H_n(\alpha x)}{n!}s^n.$$

The detailed calculations are found in appendix (A3,2). The result found is

$$I_{mn} = \frac{\sqrt{\pi}}{\alpha} n!m!N_nN_m(\alpha\Delta x)^{m+n}\exp\left[-\frac{1}{4}\alpha^2\Delta x^2\right]\sum_{a=0}^{n}\frac{(-1)^{m-a}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{-2a}}{a!(n-a)!(m-a)!} . \quad (3.18)$$

The simplest recombination rate occurs at the absolute zero of temperature, T=0. In Appendix A3.2 we find

$$W^{(1)}_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\left(\frac{E_M}{\hbar\omega_0}\right)^p\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\frac{1}{p!} \quad (3.19)$$

where

$$E_M = \frac{\alpha^2\Delta x^2}{2}\hbar\omega_0 .$$

After recombination the p'th excited vibrational level belonging to the ground electronic state is occupied. We are implicitly assuming that there is some mechanism to dissipate this energy; the local mode is coupled to lattice modes thus resulting in a rapid transfer of the p phonons into these modes.

In order to understand how $W_{T=0}$ varies with some of the parameters in (3,19), we study the case when ΔE is large. Now, in this case, $\frac{\Delta E}{\hbar\omega_0} = p \gg 1$, the Stirling approximation for $1/p!$ can be used as in appendix (A3,2) to obtain,

$$W_{T=0} = \frac{|K|^2}{\hbar}\left[\frac{2\pi}{\hbar\omega_0\Delta E}\right]^{\frac{1}{2}}\exp\left\{-\frac{\Delta E}{\hbar\omega_0}\left[\log\left(\frac{\Delta E}{E_M}\right)-1\right]\right\}\exp\left(-\frac{E_M}{\hbar\omega_0}\right). \quad (3.20)$$

This is the so called 'energy-gap' law which shows that for a given coupling strength E_M, the probability of a radiationless transition will decrease rapidly with increasing, ΔE. This result agrees with Englman and Jortner[2] (1970), (their equation (5.4) p 155).

We also find the transition probability for finite temperatures and weak coupling $\left(\frac{E_M}{\hbar\omega_o} \ll 1\right)$,

$$W_T = [1 + N(\omega_o)]^p W_{T=0} \qquad (3.21)$$

where $N(\omega_o) = [\exp(\beta\hbar\omega_o) - 1]^{-1}$ is the expectation value for the number of phonons in the mode at temperature T. The calculational details of the result (3.21) are in Appendix A3.2. The origin of this temperature dependence may be explained quite simply as follows. In figure 3.2 which illustrates the weak coupling case it is seen that the cross-over point of the two curves is well above the equilibrium position of the excited state curve. Thus, even at finite temperatures the probability for the initial vibrational states to be occupied in the vicinity of the crossover is negligible. Only those states far below the crossover are occupied. Thus the final states can only be reached by quantum mechanical processes which tunnel through the potential energy barrier. Since the probability of emission of one phonon is $1 + N(\omega_o)$ the temperature dependence of the transition rate in which p phonons are emitted is $[1 + N(\omega_o)]^p$.

The high temperature $\beta\hbar\omega_o \ll 1$, strong coupling $\frac{E_M}{\hbar\omega_o} \gg 1$ transition probabilities calculated in Appendix A3.3 represent a quite different physical situation.

This result is

$$W_T = \frac{|K|^2}{\hbar}\left[\frac{\pi}{kTE_M}\right]^{\frac{1}{2}} \exp(-\beta E_b) \qquad (3.22)$$

where

$$E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M} .$$

The 'activation' energy E_b is the energy of the crossover point above the excited state minimum and is shown in figure 3.3 which illustrates the strong coupling case.

At high temperatures the initial vibrational states at the crossover point now have a significant probability of occupation. Thus, recombination may occur without the requirement that purely quantum mechanical tunnelling processes took place. Hence the transition probability may be expected to have characteristics typical of classical processes.. The 'activation energy' law is indeed of this type; it may even be derived using a purely classical occurence probability approach as by Holstein. In this type of analysis recombination occurs when the classical oscillator reaches the crossover point x_c and then relaxes into the ground state curve. The temperature activation factor $\exp(-\beta E_b)$ is proportional to the probability that the crossover point x_c is actually reached.

We have also derived the transition rate using the 'derivative' non-adiabatic terms finding in Appendix A3.6 that

$$W^{(2)}_{T=0} = 2|C|^2\left(\frac{E_b}{\hbar\omega_0}\right)\left(\frac{E_M}{\hbar\omega_0}\right)^p \exp\left[-\frac{E_M}{\hbar\omega_0}\right]\frac{1}{p!}, \qquad (3.23)$$

where $$C = -\frac{\hbar^2}{M}\int \varphi_0^*(r,x)\frac{\partial}{\partial x}\varphi_1(r,x)\,d\underline{r}.$$

This is very similar to the transition rate obtained using the 'standard' non-adiabatic terms. In fact,

$$\frac{W^{(2)}_{T=0}}{W^{(1)}_{T=0}} = \frac{|C|^2}{|K|^2}\left(\frac{E_b}{\hbar\omega_0}\right). \qquad (3.24)$$

The magnitude of the ratio

$$\frac{|C|^2}{|K|^2} = \frac{\left|\int d\underline{r}\,\varphi_0(r,x)\frac{\partial}{\partial x}\varphi_1(r,x)\right|^2}{\left|\int d\underline{r}\,\varphi_0(r,x)\frac{\partial^2}{\partial x^2}\varphi_1(r,x)\right|^2} \quad \text{is} \quad \frac{1}{\beta^2}.$$

Here $\beta = \left(\frac{m_e}{M}\right)^{1/4}$ where m_e is the electronic mass while M

is the Molecular mass. This result was first obtained by Chester and Houghton.[22] Thus the transition rates arising from the 'derivative' non-adiabatic terms are at least one order of magnitude larger than those obtained using the 'standard' terms.[11] A similar conclusion has been reached by Struck and Fonger.[6] This result is perhaps rather surprising as most of the results derived in this thesis and by other authors use the 'standard' non-adiabatic terms. However we believe that the general features of the transition rates derived using the derivative terms are similar to the standard well-known transition rates calculated in this chapter. In particular, in Appendix A3.7 it is shown that in the finite temperature, weak coupling $\frac{E_M}{\hbar\omega_0} \ll 1$ limit,

$$W_T^{(2)} = [1 + N(\omega_0)]^p W_{T=0}^{(2)}.$$

Thus, this form of temperature dependence of the non-radiative transitions is valid for both the 'standard' and the 'derivative' non-adiabatic terms.

Conclusions

In this chapter we have used the S.C.C.M. to calculate recombination rates. The S.C.C.M. involves a very simple model of the electron-lattice interaction in which the electron is coupled to only one local vibrational mode. The Born-Oppenheimer approximation is used so that the electronic wavefunctions $\varphi_i(r,x)$ and their energy eigenvalues $E_i(x)$ depend on the lattice configuration. The energy eigenvalues $E_i(x)$ are assumed to contain a linear electron-lattice interaction term; $E_i(x) = E_i - A_i x$. This results in displaced simple harmonic oscillator vibrational states, $\xi_n^i[\alpha(x - \Delta x^i)]$ in which the displacement depends on the electronic state occupied,

$$\Delta x^i = \left(\frac{\hbar}{M\omega_0}\right)^{\frac{1}{2}} \frac{A_i}{M\omega_0^2}.$$

We have demonstrated that the Born-Oppenheimer zero'th order states $\varphi_i(r,x)\mathcal{F}_n^i$ are not quite stationary. The configuration dependence of the electronic wavefunction results in the non-adiabatic terms,

$$-\frac{\hbar^2}{2M}\int\varphi_0(r,x)\frac{d^2}{dx^2}\varphi_1(r,x)d\underline{r}\int\mathcal{F}_m^0[\alpha(x-\Delta x^{(0)})]\mathcal{F}_n^1[\alpha(x-\Delta x^{(1)})]dx$$

and

$$-\frac{\hbar^2}{M}\int\varphi_0(r,x)\frac{\partial}{\partial x}\varphi_1(r,x)d\underline{r}\int\mathcal{F}_m^0[\alpha(x-\Delta x^{(0)})]\frac{\partial}{\partial x}\mathcal{F}_n^1[\alpha(x-\Delta x^{(1)})]dx,$$

acting as a small perturbation which allows recombination to take place. The time dependent perturbation theory results for the transition rates (3.13) are then derived using these non-adiabatic terms. The vibrational energy levels are assumed to be aligned, $\Delta E = p\hbar\omega_0$, so that energy conservation requirements are satisfied.

We then derive results (3.19) and (3.23) for the transition rates at the absolute zero of temperature using the 'standard' and the 'derivative' non-adiabatic terms respectively. Using the result (3.19) in the limit $\frac{\Delta E}{\hbar\omega_0} \gg 1$ we have derived the 'energy-gap' law, (3.20). In the weak coupling $\frac{E_M}{\hbar\omega_0} \ll 1$, finite temperature regime the result (3.21) has been derived using both the 'standard' and the 'derivative' non-adiabatic terms. This type of temperature dependence is believed to result from quantum mechanical tunnelling processes. Finally, in the high temperature $\beta\hbar\omega_0 \ll 1$, strong coupling, $\frac{E_M}{\hbar\omega_0} \gg 1$ limit we have derived the temperature activated transition rate (3.22) using the 'standard' non-adiabatic term. This form of the transition rate results from a classical 'over the barrier' type of process.

Figure 3.1: The S.C.C.M. diagram,

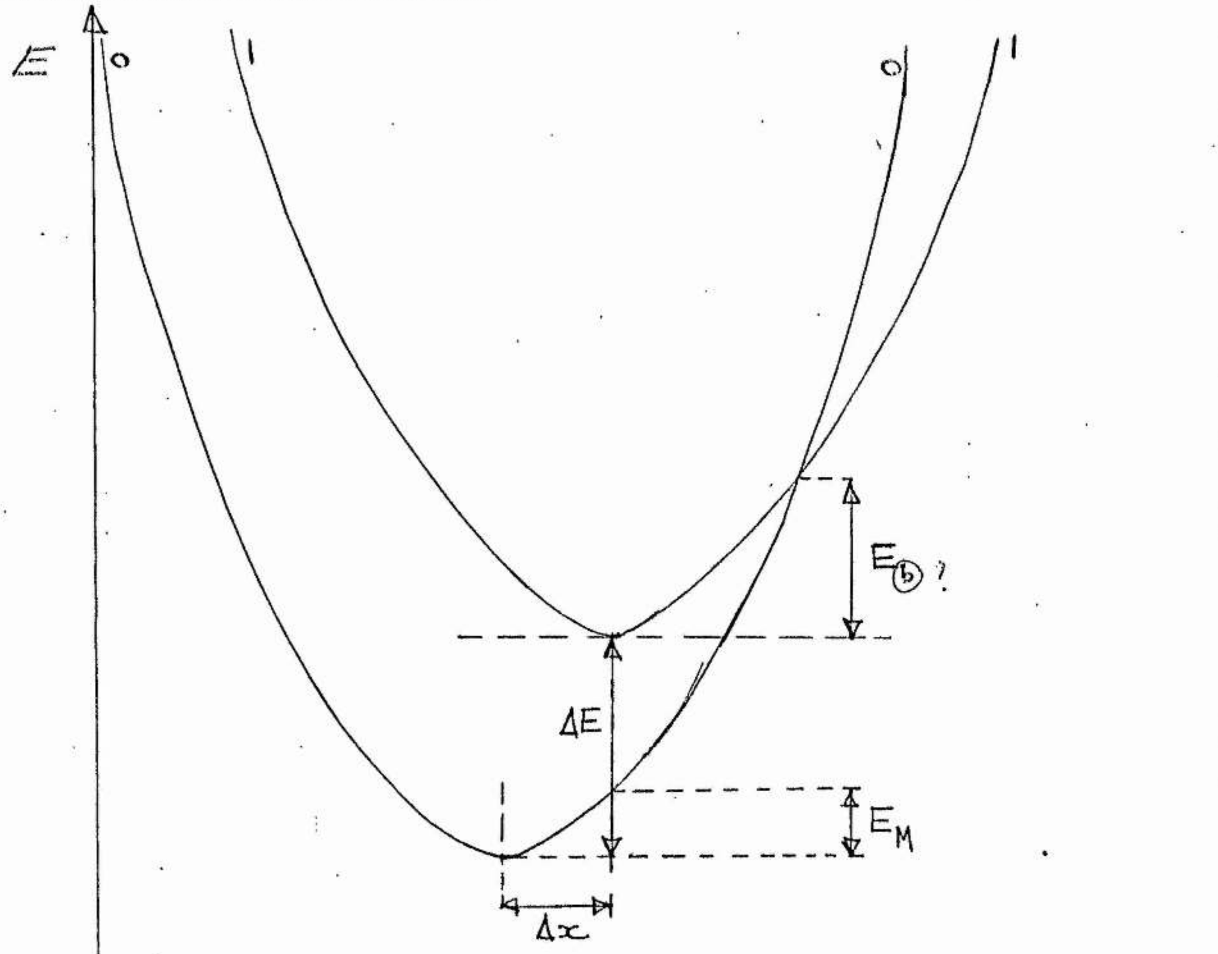


Figure 3.2: The S.C.C.M. diagram, Weak Coupling Case, $\frac{E_M}{\hbar\omega_0} \ll 1$.

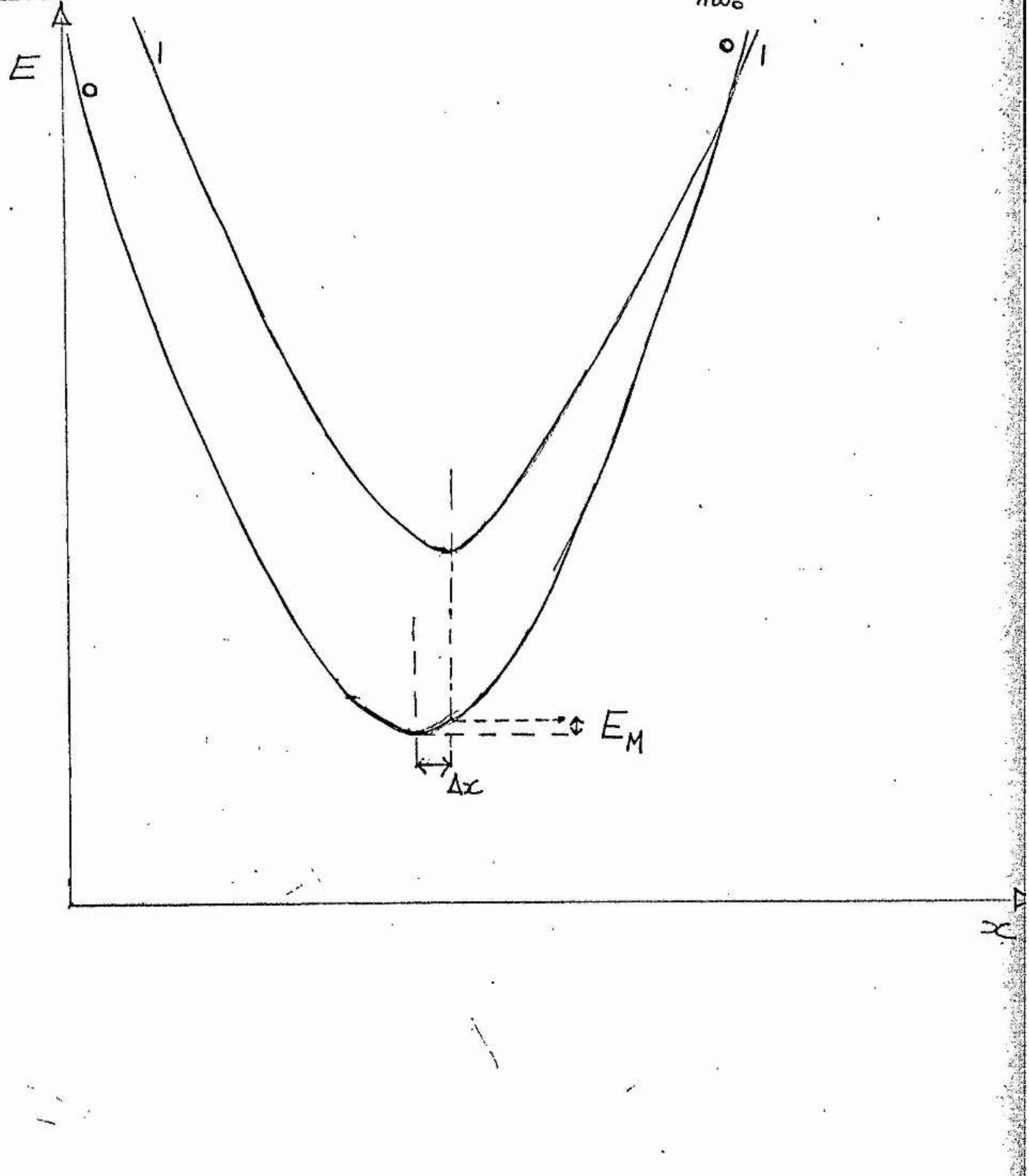
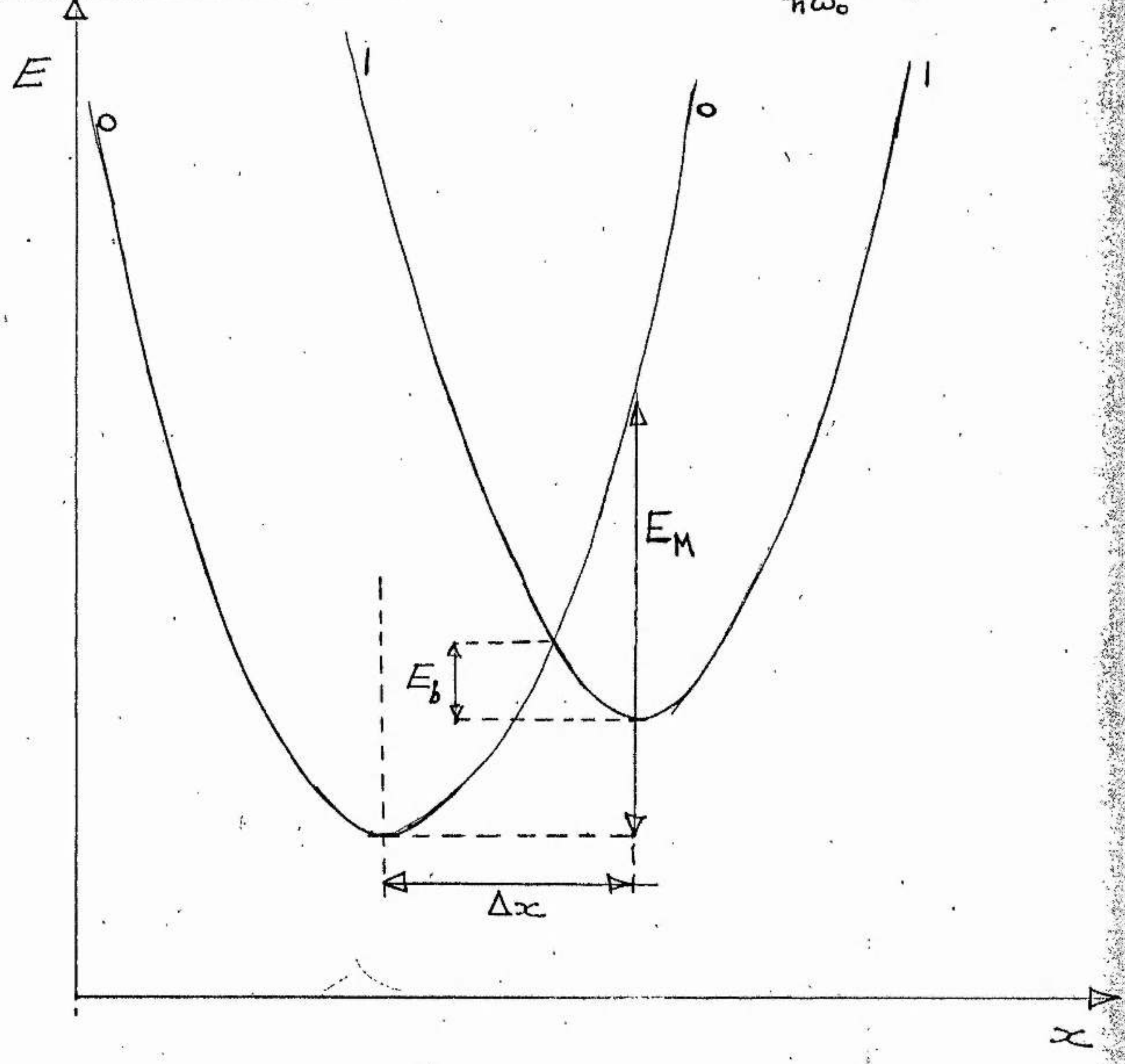


Figure 3.3| The S.C.C.M. diagram, Strong Coupling Case, $\frac{E_M}{\hbar\omega_0} \gg 1$.



APPENDIX A3.1

Derivation of the general expression for the transition probabilities in the S.C.C.M.

We wish to solve the Schrödinger equation

$$i\hbar\frac{d\Psi}{dt}=H_T\,\Psi \qquad (A3.1.1)$$

where

$$H_T=-\frac{\hbar^2}{2m}\nabla_r^2+U(r,x)-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}+\frac{1}{2}M\omega_0^2x^2, \qquad (A3.1.2)$$

In the Born-Oppenheimer approximation the zero'th order states are

$$\varphi_0(r,x)\mathcal{F}_m^0\left[\alpha(x-\Delta x^{(0)})\right] \qquad \varphi_1(r,x)\mathcal{F}_n^1\left[\alpha(x-\Delta x^{(1)})\right] \qquad (A3.1.3)$$

which have energy eigenvalues $E_{0,m}$ and $E_{1,n}$ respectively.

As a general solution of (A3.1.1) we write

$$\Psi=a_0(t)\varphi_0\,\mathcal{F}_m^0\exp\left[-\frac{iE_{0,m}t}{\hbar}\right]+a_1(t)\varphi_1\,\mathcal{F}_n^1\exp\left[-\frac{iE_{1,n}t}{\hbar}\right]. \qquad (A3.1.4)$$

Substituting this into (A3.1.1) we obtain

$$\begin{aligned}
&i\hbar\frac{da_0}{dt}\varphi_0\mathcal{F}_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]+i\hbar\left(-\frac{iE_{0,m}}{\hbar}\right)a_0\varphi_0\mathcal{F}_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]\\
&+i\hbar\frac{da_1}{dt}\varphi_1\mathcal{F}_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]+i\hbar\left(-\frac{iE_{1,n}}{\hbar}\right)a_1\varphi_1\mathcal{F}_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]\\
&=E_{0,m}a_0\varphi_0\mathcal{F}_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}\varphi_0(r,x)a_0\mathcal{F}_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]\\
&-\frac{\hbar^2}{M}\frac{\partial}{\partial x}\varphi_0(r,x)a_0\frac{\partial}{\partial x}\mathcal{F}_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]+E_{1,n}a_1\varphi_1\mathcal{F}_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]\\
&-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}\varphi_1(r,x)a_1\mathcal{F}_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]\\
&-\frac{\hbar^2}{M}\frac{\partial}{\partial x}\varphi_1(r,x)a_1\frac{\partial}{\partial x}\mathcal{F}_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right].
\end{aligned}$$

This gives us,

$$i\hbar\frac{da_0}{dt}\varphi_0\chi_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]+i\hbar\frac{da_1}{dt}\varphi_1\chi_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]$$

$$=-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\varphi_0(r,x)a_0\chi_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}\varphi_1(r,x)a_1\chi_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right]$$

$$-\frac{\hbar^2}{M}\frac{d}{dx}\varphi_0(r,x)a_0\frac{d}{dx}\chi_m^0\exp\left[-iE_{0,m}\frac{t}{\hbar}\right]-\frac{\hbar^2}{M}\frac{d}{dx}\varphi_1(r,x)a_1\frac{d}{dx}\chi_n^1\exp\left[-iE_{1,n}\frac{t}{\hbar}\right].$$

(A3.1.5)

We multiply both sides on the left by $\varphi_0^*(r,x)\chi_m^0[\alpha(x-\Delta x^{(0)})]\exp\left[iE_{0,m}\frac{t}{\hbar}\right]$ and integrate over electronic and lattice coordinates $\int d\underline{r}\int dx$. We will also make use of the initial conditions at t=0, $a_0(0)=0$ and $a_1(0)=1$ to assume that for all t, $a_0(t)\ll 1$ and $a_1(t)\sim 1$. We obtain, using the Condon approximation,

$$i\hbar\frac{da_0}{dt}\int\varphi_0^*\varphi_0\,d\underline{r}\int\chi_m^0\chi_m^0\,dx+i\hbar\frac{da_1}{dt}\int\varphi_0^*\varphi_1\,d\underline{r}\int\chi_m^0\chi_n^1\,dx\,\exp\left[\frac{it}{\hbar}(E_{0,m}-E_{1,n})\right]$$

$$=\left[-\frac{\hbar^2}{2M}\int\varphi_0^*\frac{d^2}{dx^2}\varphi_1\int\chi_m^0\chi_n^1\,dx-\frac{\hbar^2}{M}\int\varphi_0^*\frac{d}{dx}\varphi_1\,d\underline{r}\int\chi_m^0\frac{d}{dx}\chi_n^1\,dx\right]\exp\left[\frac{it}{\hbar}(E_{0,m}-E_{1,n})\right].$$

Using the orthonormality of the electronic wavefunctions

$$\int\varphi_i^*(r,x)\varphi_j(r,x)\,d\underline{r}=\delta_{i,j},$$

and writing, $K=-\frac{\hbar^2}{2M}\int\varphi_0^*(r,x)\frac{d^2}{dx^2}\varphi_1(r,x)\,d\underline{r}$, $C=-\frac{\hbar^2}{M}\int\varphi_0^*(r,x)\frac{d}{dx}\varphi_1(r,x)\,d\underline{r}$,

$$I_{m,n}=\int\chi_m^0[\alpha(x-\Delta x^{(0)})]\chi_n^1[\alpha(x-\Delta x^{(1)})]\,dx,\quad I'_{m,n}=\int\chi_m^0[\alpha(x-\Delta x^{(0)})]\frac{d}{dx}\chi_n^1[\alpha(x-\Delta x^{(1)})]\,d$$

(A3.1.6)

We write,

$$K_{0,1}^{m,n}=KI_{m,n}+CI'_{m,n}$$

(A3.1.7)

to obtain,

$$i\hbar\frac{d}{dt}a_0(t)=K^{m,n}_{0,1}\exp\left[\frac{it}{\hbar}(E_{0,m}-E_{1,n})\right]. \tag{A3.1.8}$$

This gives us

$$a_0(t)=\frac{-K^{m,n}_{0,1}}{(E_{0,m}-E_{1,n})}\left\{\exp\left[\frac{it}{\hbar}(E_{0,m}-E_{1,n})\right]-1\right\}. \tag{A3.1.9}$$

The probability that the electron is in the ground state at time t is thus

$$|a_0(t)|^2=\frac{|K^{m,n}_{0,1}|^2}{(E_{0,m}-E_{1,n})^2}\left|\left(\cos\left[\frac{t}{\hbar}(E_{0,m}-E_{1,n})\right]-1+i\sin\left[\frac{t}{\hbar}(E_{0,m}-E_{1,n})\right]\right)\right|^2. \tag{A3.1.10}$$

This gives us

$$|a_0(t)|^2=\frac{|K^{m,n}_{0,1}|^2}{(E_{0,m}-E_{1,n})^2}\left\{2\left(1-\cos\left[\frac{t}{\hbar}(E_{0,m}-E_{1,n})\right]\right)\right\}. \tag{A3.1.11}$$

Using,

$$1-\cos x=2\sin^2\frac{x}{2},$$

$$|a_0(t)|^2=\frac{4|K^{m,n}_{0,1}|^2}{(E_{0,m}-E_{1,n})^2}\sin^2\frac{1}{2}\frac{t}{\hbar}(E_{0,m}-E_{1,n}), \tag{A3.1.12}$$

In the limit that t → ∞ we obtain the standard perturbation theory form,

$$\frac{d}{dt}\left\{|a_0(t)|^2\right\}=\frac{2\pi}{\hbar}|K^{m,n}_{0,1}|^2N(E)\delta(E_{0,m}-E_{1,n}), \tag{A3.1.13}$$

Using (A3.1.6) and (A3.1.7) this may be written as

$$\frac{d}{dt}|a_0(t)|^2=\frac{2\pi}{\hbar}\left\{|K|^2I^2_{m,n}+|C|^2I^{1\,2}_{m,n}+|KC|I_{m,n}I^1_{m,n}\right\}N(E)\,\delta(E_{0,m}-E_{1,n}), \tag{A3.1.14}$$

APPENDIX A.3.2

Calculation of the Vibrational Overlap Integrals by the Generating Function Method

To evaluate the vibrational overlap integral,

$$I_{mn} = \int_{-\infty}^{\infty} \mathcal{F}_m[\alpha(q-\Delta q)]\,\mathcal{F}_n(\alpha q)\,dq \qquad \text{(A3,2,1)}$$

where

$$\mathcal{F}_n(\alpha x) = N_n H_n(\alpha x) \exp\left(-\tfrac{1}{2}\alpha^2 \Delta x^2\right) \qquad \alpha = \left(\frac{M\omega}{\hbar}\right)^{\frac{1}{2}}$$

we use the generating function method

$$\exp\left[-s^2 + 2s\alpha x\right] = \sum_{n=0}^{\infty} \frac{H_n(\alpha x)}{n!} s^n \qquad \text{(A3,2,2)}$$

Now,

$I_{mn} = (n!\,m!)($coefficient of $s^n t^m$ in the following integral I),

where

$$I = N_n N_m \exp\left[-s^2 - t^2 - 2t\alpha\Delta x - \frac{\alpha^2 \Delta x^2}{2}\right] \int_{-\infty}^{\infty} \exp\left[-\alpha^2 x^2 + \alpha x(2t + 2s + \alpha\Delta x)\right] dx \qquad \text{(A3,2,3)}$$

We evaluate I by completing the square of the argument of the exponential function inside the integrand.

Then we use the result

$$\int_{-\infty}^{\infty} e^{-\alpha^2 x^2}\,dx = \frac{\sqrt{\pi}}{\alpha} \qquad \text{(A3,2,4)}$$

We obtain,

$$I = \frac{\sqrt{\pi}}{\alpha} N_n N_m \exp\left[-\frac{\alpha^2 \Delta x^2}{4}\right] \exp\left[2st + \alpha\Delta x(s-t)\right] \qquad \text{(A3,2,5)}$$

To calculate I_{mn} we perform the following operation

$$\left.\frac{d^m}{dt^m}\frac{d^n}{ds^n} I\right]_{s,t=0} \quad (m > n) \qquad \text{(A3,2,6)}$$

evaluating the resultant at s = t = 0.

We find that

$$\frac{d^n}{ds^n} I = \frac{\sqrt{\pi}}{\alpha} N_n N_m \exp\left[-\frac{\alpha^2 \Delta x^2}{4}\right] \exp\left[2st + \alpha \Delta x (s - t)\right] (\alpha \Delta x + 2t)^n$$

(A3,2,7)

To find $\frac{d^m}{dt^m} \frac{d^n}{ds^n} I$ we use the Leibnitz rule,

$$\frac{d^m}{dt^m}\left[X(t) Y(t)\right] = \sum_{a=0}^{m} \frac{m!}{(m-a)!\,a!} \frac{d^a}{dt^a} X(t) \frac{d^{(m-a)}}{dt^{(m-a)}} Y(t) \qquad \text{(A3,2,8)}$$

We obtain,

$$\frac{d^m}{dt^m} \frac{d^n}{ds^n} I =$$

$$\frac{\sqrt{\pi}}{\alpha} N_n N_m \exp\left(-\tfrac{1}{4}\alpha^2 \Delta x^2\right) \exp\left[\alpha \Delta x s\right] \sum_{a=0}^{m} \frac{n!\,m!\,(\alpha \Delta x + 2t)^{n-a} (2s - \alpha \Delta q)^{m-a}}{(n-a)!\,a!\,(m-a)!} \exp\left[(2s - \alpha \Delta x) t\right]$$

(A3,2,9)

Evaluating at s=t=o and remembering that m > n we obtain,

$$I_{mn} = \frac{\sqrt{\pi}}{\alpha} N_n N_m n!\,m! \sum_{a=0}^{n} \frac{(-1)^{m-a} (\alpha \Delta x)^{m+n} \left(\frac{\alpha \Delta x}{\sqrt{2}}\right)^{-2a}}{a!\,(n-a)!\,(m-a)!}$$

(A3,2,10)

APPENDIX A3.3

I; Calculation of the transition probability at absolute zero, $W_{T=0}$.

We know that if $\Delta E = p\hbar\omega_0$

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0} I_{p,0}^2 \tag{A3.3.1}$$

Now, from (A3.2.10),

$$I_{mn} = \frac{\sqrt{\pi}}{\alpha} N_n N_m n!\, m! \sum_{a=0}^{n} \frac{(-1)^{m-a}(\alpha\Delta q)^{m+n}\left(\frac{\alpha\Delta q}{\sqrt{2}}\right)^{-2a}}{a!\,(n-a)!\,(m-a)!}.$$

Using

$$N_n = \left(\frac{\alpha}{\pi^{1/2} 2^n n!}\right)^{1/2}$$

$$I_{p0} = \frac{(-\alpha\Delta q)^p}{2^{p/2}(p!)^{1/2}} \exp\left(-\tfrac{1}{4}\alpha^2\Delta q^2\right). \tag{A3.3.2}$$

Thus,

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\left(\frac{\alpha^2\Delta q^2}{2}\right)^p \exp\left(-\frac{1}{2}\alpha^2\Delta q^2\right)\frac{1}{p!}. \tag{A3.3.3}$$

II: Calculation of the Transition Probability in the Weak Coupling, Finite Temperature Case.

Now $\Delta E = p\hbar\omega_0$, so that energy conservation requirements mean that we only consider the vibrational overlap integrals $I_{n+p,n}$.

Using (A3.2.10) we find that

$$I_{n+p,n} = \sqrt{n!(n+p)!}\left(\frac{1}{2}\alpha^2\Delta q^2\right)^{p/2}\exp\left[-\frac{1}{4}\alpha^2\Delta q^2\right]\sum_{a=0}^{n}\frac{(-1)^{n+p-a}\left(\frac{1}{2}\alpha^2\Delta q^2\right)^{n-a}}{a!(n-a)!(n+p-a)!} \tag{A3.3.4}$$

We are investigating the weak coupling limit where $\frac{1}{2}\alpha^2\Delta q^2 \ll 1$. Hence, we want the smallest power of $(\frac{1}{2}\alpha^2\Delta q^2)^{n-a}$ in the sum, which is the term for which $a = n$. Doing this, we find that,

$$I_{1+p,1}^2 = \exp\left[-\frac{1}{2}\alpha^2\Delta q^2\right]\left(\frac{1}{2}\alpha^2\Delta q^2\right)^p \frac{1}{p!}\left[\frac{p+1}{1!}\right] \tag{A3,3,5}$$

In general,

$$I_{n+p,n}^2 = \exp\left[-\frac{1}{2}\alpha^2\Delta q^2\right]\left(\frac{1}{2}\alpha^2\Delta q^2\right)^p \frac{1}{p!}\left[\frac{(p+n)!}{n!\,p!}\right] \tag{A3.3.6}$$

or $$I^2_{n+p,n} = \left[\frac{(p+n)!}{n!\,p!}\right] I^2_{p,0}$$

W_T, the transition probability at temperature T is,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \sum_{n=0}^{\infty} \frac{1}{Z} I^2_{n+p,n} \exp\left[-\beta\hbar\omega\left(n+\tfrac{1}{2}\right)\right] \qquad \text{(A3.3.7)}$$

where, for the harmonic oscillator,

$$Z = \sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega_0\left(n+\tfrac{1}{2}\right)\right] = \left[1-\exp(-\beta\hbar\omega)\right]^{-1} \exp\left[-\tfrac{1}{2}\beta\hbar\omega\right] \qquad \text{(A3,3.8)}$$

We obtain,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \left[1-\exp(-\beta\hbar\omega_0)\right] \exp\left[-\tfrac{1}{2}\alpha^2\Delta q_\nu^2\right] \left(\tfrac{1}{2}\alpha^2\Delta q_\nu^2\right)^p \frac{1}{p!} \sum_{n=0}^{\infty} \frac{(p+n)!}{n!\,p!} \exp(-\beta n\hbar\omega_0) \qquad \text{(A3,3,9)}$$

Now, the expectation value for the number of phonous of frequency ω at temperature T is

$$\langle N\rangle_T = \left[\exp(\beta\hbar\omega)-1\right]^{-1}, \qquad 1+\langle N\rangle_T = \left[1-\exp(-\beta\hbar\omega)\right]^{-1}.$$

Hence,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \exp\left(-\tfrac{1}{2}\alpha^2\Delta q_\nu^2\right) \left(\tfrac{1}{2}\alpha^2\Delta q_\nu^2\right)^p \frac{1}{p!} \left(1+\langle N\rangle_T\right)^p \qquad \text{(A3,3,10)}$$

in the weak coupling limit $\alpha^2\Delta q_\nu^2 \ll 1$.

Hence, in the weak coupling limit

$$W_T = \left(1+\langle N\rangle_T\right)^p W_{T=0}. \qquad \text{(A3,3,11)}$$

III: The Transition Probability at absolute zero in the limit that $p = \frac{\Delta E}{\hbar\omega_0}$ is large; the 'Energy Gap' Law.

We have derived

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \left(\frac{\alpha^2\Delta q_\nu^2}{2}\right)^p \exp\left(-\tfrac{1}{2}\alpha^2\Delta q_\nu^2\right) \frac{1}{p!} \qquad \text{(A3,3,3)}$$

When p is large we use Stirling's formula,

$$\frac{1}{p!} \longrightarrow \frac{1}{\sqrt{2\pi p}}\, p^{-p} \exp(-p) \qquad \text{(A3,3,12)}$$

We put

$$E_M = \tfrac{1}{2}\alpha^2\Delta q_\nu^2$$

Writing, $\left(\frac{E_M}{\hbar\omega_0}\right)^{p} = \exp\left[\frac{\Delta E}{\hbar\omega_0}\log\frac{\Delta E}{\hbar\omega_0}\right]$

and $p^{-p} = \left(\frac{\Delta E}{\hbar\omega_0}\right)^{-\frac{\Delta E}{\hbar\omega_0}} = \exp\left[-\frac{\Delta E}{\hbar\omega_0}\log\frac{\Delta E}{\hbar\omega_0}\right]$

We find that

$$W_{T=0} = \frac{|K|^2}{\hbar}\left[\frac{2\pi}{\hbar\omega_0\Delta E}\right]^{1/2}\exp\left\{-\frac{\Delta E}{\hbar\omega_0}\left[\log\left(\frac{\Delta E}{E_M}\right)-1\right]\right\}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)$$

in the limit that $p = \frac{\Delta E}{\hbar\omega_0}$ is large. (A3,3,13)

This is the so-called 'Energy Gap' Law.

APPENDIX A3.4

The Transition Probability in the High Temperature, Strong Coupling Limit

By high temperature, strong coupling we mean the regimes in which $\beta\hbar\omega_0 \ll 1$ and $\alpha^2\Delta x^2 \gg 1$ respectively.

W_T, the transition probability at temperature T has already been given

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{n=0}^{\infty}\exp\left[\tfrac{1}{2}\beta\hbar\omega_0\right]\left(1-\exp(-\beta\hbar\omega)\right)I^2_{n+p,n}\exp\left[-\beta\hbar\omega_0\left(n+\tfrac{1}{2}\right)\right] \tag{A3.4.1}$$

We have already derived the general expression for $I_{n+p,n}$ (A3.3.4)

$$I_{n+p,n} = \sqrt{n!(n+p)!}\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p/2}\exp\left[-\tfrac{1}{4}\alpha^2\Delta x^2\right]\sum_{a=0}^{n}\frac{(-1)^{n+p-a}\left(\frac{1}{2}\alpha^2\Delta x^2\right)^{n-a}}{a!\,(n-a)!\,(n+p-a)!} \tag{A3.4.2}$$

We express $I_{n+p,n}$ in terms of the associated Laguerre function,

$$L_t^{(\alpha)}(u) = (t+\alpha)!\sum_{a'=0}^{t}\frac{(-u)^{a'}}{(t-a')!\,a'!\,(a'+\alpha)!} \tag{A3.4.3}$$

Writing $a = t-a'$, $L_t^{(\alpha)}(u)$ becomes

$$L_t^{(\alpha)}(u) = (t+\alpha)!\sum_{a=0}^{t}\frac{(-u)^{t-a}}{a!\,(t-a)!\,(t-a+\alpha)!} \tag{A3.4.4}$$

In particular,

$$L_n^{p}\left(\tfrac{1}{2}\alpha^2\Delta x^2\right) = (n+p)!\sum_{a=0}^{n}\frac{\left(-\frac{1}{2}\alpha^2\Delta x^2\right)^{n-a}}{a!\,(n-a)!\,(n+p-a)!} \tag{A3.4.5}$$

so that we obtain

$$I_{n+p,n} = \left[\frac{n!}{(n+p)!}\right]^{\frac{1}{2}}\left(\tfrac{1}{2}\alpha^2\Delta x^2\right)^{p/2}\exp\left[-\tfrac{1}{4}\alpha^2\Delta x^2\right](-1)^p L_n^{p}\left(\tfrac{1}{2}\alpha^2\Delta x^2\right) \tag{A3.4.6}$$

Substituting (A3,4,6) into the general expression for W_T (A3,4,1)

we obtain,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\left(\tfrac{1}{2}\alpha^2\Delta x^2\right)^{p}\exp\left[-\tfrac{1}{2}\alpha^2\Delta x^2\right]\left[1-\exp(-\beta\hbar\omega)\right]\sum_{n=0}^{\infty}\frac{n!}{(n+p)!}\left[L_n^{p}\left(\tfrac{1}{2}\alpha^2\Delta x^2\right)\right]^2\exp^{n}(-\beta\hbar\omega_0) \tag{A3,4,1}$$

Following Copson,

$$\sum_{n=0}^{\infty}L_n^{(\alpha)}(x)L_n^{(\alpha)}(y)\frac{t^n n!}{(n+\alpha)!} = \frac{(xyt)^{-\frac{1}{2}\alpha}}{(1-t)}\exp\left[-\frac{(x+y)t}{1-t}\right]I_\alpha\left\{\frac{2\sqrt{xyt}}{1-t}\right\} \tag{A3.4.8}$$

we obtain,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\left(\frac{\alpha^2\Delta x^2}{2}\right)^p \exp\left(-\frac{1}{2}\alpha^2\Delta x^2\right)\left[1-\exp(-\beta\hbar\omega)\right]\frac{\left[\left(\frac{1}{2}\alpha^2\Delta x^2\right)^2\exp(-\beta\hbar\omega_0)\right]^{-\frac{p}{2}}}{\left[1-\exp(-\beta\hbar\omega_0)\right]}$$

$$\times \exp\left[-\frac{\alpha^2\Delta x^2\exp(-\beta\hbar\omega_0)}{1-\exp(-\beta\hbar\omega_0)}\right] I_p\left[\frac{\alpha^2\Delta x^2\exp(-\beta\hbar\omega/2)}{1-\exp(-\beta\hbar\omega_0)}\right]$$

This becomes,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{1}{2}\alpha^2\Delta x^2\right)\exp\left[\frac{\beta\hbar\omega_0 p}{2}\right]\exp\left[-\frac{\alpha^2\Delta x^2\exp(-\beta\hbar\omega_0)}{1-\exp(-\beta\hbar\omega_0)}\right]$$

$$\times I_p\left[\frac{\alpha^2\Delta x^2\exp\left(-\frac{\beta\hbar\omega_0}{2}\right)}{1-\exp(-\beta\hbar\omega_0)}\right] \qquad \text{(A3.4.9)}$$

In (A3.4.9) the argument of the modified Bessel function

$\frac{\alpha^2\Delta x^2\exp\left(-\frac{\beta\hbar\omega_0}{2}\right)}{1-\exp(-\beta\hbar\omega_0)} \gg 1$ in the strong coupling $\alpha^2\Delta x^2 \gg 1$ high temperature $\beta\hbar\omega_0 \ll 1$ regime.

Now, we make use of the large argument approximation of the modified Bessel functions.

$$I_p(z) \xrightarrow{z \text{ large}} \frac{1}{\sqrt{2\pi z}}\exp(z)\left(1-\frac{p^2}{2z}\right)$$

$$I_p(z) \sim \frac{1}{\sqrt{2\pi z}}\exp\left(z-\frac{p^2}{2z}\right) \qquad \text{(A3.4.10)}$$

Using this approximation (A3.4.9) becomes

$$W_T \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{1}{2}\alpha^2\Delta q^2\right)\exp\left(\beta\hbar\omega_0\frac{p}{2}\right)\exp\left[-\frac{\alpha^2\Delta x^2\exp(-\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)}\right]$$

$$\times\frac{1}{\sqrt{\frac{2\pi\alpha^2\Delta x^2\exp(-\beta\hbar\omega_0/2)}{1-\exp(-\beta\hbar\omega_0)}}}\exp\left[\frac{\alpha^2\Delta x^2\exp(-\beta\hbar\omega_0/2)}{1-\exp(-\beta\hbar\omega_0)}\right]\exp\left[\frac{-p^2(1-\exp(-\beta\hbar\omega_0))}{2\alpha^2\Delta x^2\exp(-\beta\hbar\omega_0/2)}\right]$$

$$\text{(A3.4.11)}$$

We examine the various factors in (A3.4.11) separately. First of all, we investigate the pre-exponential factors in the high temperature limit, $\beta\hbar\omega_0 \ll 1$.

$$\frac{2\pi|K|^2}{\hbar^2\omega_0}\left(\frac{2\pi\alpha^2\Delta x^2\exp\left(-\frac{\beta\hbar\omega_0}{2}\right)}{1-\exp(-\beta\hbar\omega_0)}\right)^{-\frac{1}{2}} = \left(\frac{2\pi}{\hbar\omega_0}\right)\frac{|K|^2}{\hbar}\frac{1}{\left(\frac{2\pi\alpha^2\Delta x^2}{\beta\hbar\omega_0}\right)^{\frac{1}{2}}} \qquad \text{(A3.4.12)}$$

This factor becomes, $\dfrac{|K|^2}{\hbar}\left[\dfrac{2\pi\beta}{\alpha^2\Delta x^2\hbar\omega_0}\right]^{\frac{1}{2}}$.

Writing $E_M = \dfrac{\alpha^2\Delta x^2}{2}\hbar\omega_0$ (A3.4.12) becomes $\dfrac{|K|^2}{\hbar}\left[\dfrac{\pi}{E_M\hbar\omega_0 kT}\right]^{\frac{1}{2}}$ (A3.4.13)

The exponential factors in (A3.4.11) may be arranged as follows.

$$\exp\left[\beta\hbar\omega_0\frac{p}{2}\right]\exp\left[-\alpha^2\Delta x^2\left(\frac{1}{2}+\frac{e^{-\beta\hbar\omega_0}}{1-e^{-\beta\hbar\omega_0}}-\frac{e^{-\frac{\beta\hbar\omega_0}{2}}}{1-e^{-\beta\hbar\omega_0}}\right)\right]\exp\left[-\frac{p^2(1-e^{-\beta\hbar\omega_0})}{2\alpha^2\Delta x^2 e^{-\frac{\beta\hbar\omega_0}{2}}}\right]$$

(A3.4.14)

The last factor here

$$\exp\left[-\frac{p^2(1-e^{-\beta\hbar\omega_0})}{2\alpha^2\Delta x^2 e^{-\beta\hbar\omega_0/2}}\right] \sim \exp\left[-\frac{p^2\beta\hbar\omega_0}{2\alpha^2\Delta x^2}\right]$$

Writing

$$E_M = \frac{\alpha^2\Delta x^2}{2}\hbar\omega_0 \quad \text{and} \quad \Delta E = p\hbar\omega_0$$

this factor is

$$\exp\left[-\frac{\beta\Delta E^2}{4E_M}\right] \qquad \text{(A3.4.15)}$$

The middle factor in (A3.4.14) is more difficult,

$$\exp\left[-\alpha^2\Delta x^2\left(\frac{1}{2}+\frac{e^{-\beta\hbar\omega_0}}{1-e^{-\beta\hbar\omega_0}}-\frac{e^{-\frac{\beta\hbar\omega_0}{2}}}{1-e^{-\beta\hbar\omega_0}}\right)\right]$$

$$= \exp\left[-\alpha^2\Delta x^2\left\{\frac{1+e^{-\beta\hbar\omega_0}-2e^{-\beta\hbar\omega_0/2}}{2(1-e^{-\beta\hbar\omega_0})}\right\}\right] \qquad \text{(A3.4.16)}$$

In the high temperature limit $(\beta\hbar\omega_0 \ll 1)$ this becomes,

$$\exp\left[-\alpha^2\Delta x^2\left\{\frac{1+1-\beta\hbar\omega_0+\frac{1}{2}(\beta\hbar\omega_0)^2-2\left[1-\frac{\beta\hbar\omega_0}{2}+\frac{1}{2}\left(\frac{\beta\hbar\omega_0}{2}\right)^2\right]}{2(1-\{1-\beta\hbar\omega_0\})}\right\}\right]$$

$$= \exp\left[-\alpha^2\Delta x^2\left\{\frac{(\beta\hbar\omega_0)^2}{4}\frac{1}{2\beta\hbar\omega_0}\right\}\right]$$

$$= \exp\left[-\frac{\beta E_M}{4}\right] \qquad \text{(A3.4.17)}$$

Combining (A3.4.11), (A3.4.13)→ (A3.4.17) we finally obtain

$$W_T = \frac{|K|^2}{\hbar}\left[\frac{\pi}{kTE_M}\right]\exp\left[-\beta\left(\frac{E_M}{4}-\frac{\Delta E}{2}+\frac{\Delta E^2}{4E_M}\right)\right] \qquad \text{(A5.3.18)}$$

in the high temperature, $\beta\hbar\omega_0 \ll 1$, strong coupling $\kappa^2\Delta x^2 \gg 1$ limit.

Here, the activation energy is,

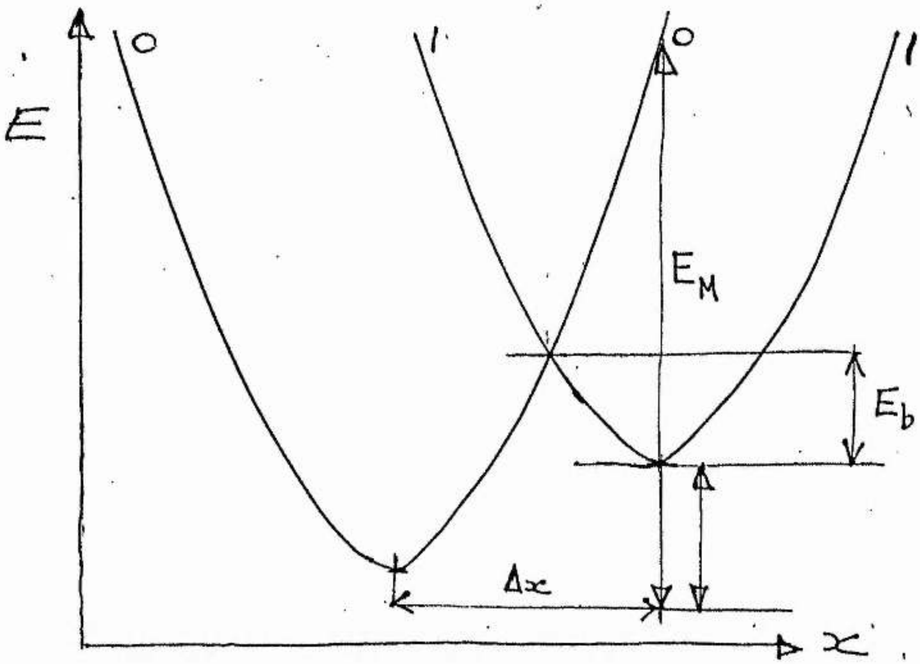
$$E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M}$$

Thus,

$$W_T = \frac{|K|^2}{\hbar}\left[\frac{\pi}{kTE_M}\right]\exp(-\beta E_b) \qquad \text{(A3.4.19)}$$

APPENDIX A3.5

Calculation of the Activation Energy E_b.



The single configuration coordinate diagram, fig A3.5 is reproduced above. Here we wish to calculate the activation energy E_b in terms of the energies ΔE and E_M.

Now, $E_M = \frac{1}{2} M\omega_0^2 \Delta x^2$ (A3.5.1).

The value of x at the crossover, x_c, is given by

$$\frac{1}{2} M\omega_0^2 x_c^2 = \frac{1}{2} M\omega_0^2 (x_c - \Delta x)^2 + \Delta E \qquad \text{(A3.5.2)}$$

This gives us,

$$x_c = \frac{E_M + \Delta E}{M\omega_0^2 \Delta x} \qquad \text{(A3.5.3)}$$

Substituting (A3.5.3) into the expression for E_b,

$$E_b = \frac{1}{2} M\omega_0^2 x_c^2 - \Delta E \qquad \text{(A3.5.4)}$$

gives us

$$E_b = \frac{(E_M - \Delta E)^2}{4E_M} \qquad \text{(A3.5.5)}$$

APPENDIX A3.6

Calculation of the transition rate $W_T^{(2)}$ due to the 'derivative' non adiabatic terms.

The 'derivative' transition rate

$$W_T^{(2)} = |C|^2 \sum_m (1-r_0) r_0^m I'^{\,2}_{m+p,m} \qquad \text{(A3.6.1)}$$

where the 'derivative' vibrational overlap integral is

$$I'_{m+p,m} = \int \Phi_{m+p}(\alpha x) \frac{d}{d(\alpha x)} \Phi_m[\alpha(x-\Delta x)]\, d(\alpha x). \qquad \text{(A3.6.2)}$$

We wish to express $I'_{m+p,m}$ in terms of the ordinary vibrational overlap integrals $I_{n,m}$.

Now,

$$\Phi_m[\alpha(x-\Delta x)] = N_m H_m[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2}$$

so that,

$$\frac{d}{\partial(\alpha x)} \Phi_m[\alpha(x-\Delta x)] = N_m \frac{d}{d(\alpha x)} H_m[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2} + N_m H_m[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2}\{-[\alpha(x-\Delta x)]\}. \qquad \text{(A3.6.3)}$$

Now,

$$\frac{d}{d(\alpha x)} H_m[\alpha(x-\Delta x)] = 2m H_{m-1}[\alpha(x-\Delta x)] \qquad \text{(A3.6.4)}$$

so that

$$\frac{d}{d(\alpha x)} \Phi_m[\alpha(x-\Delta x)] = 2m N_m H_{m-1}[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2} - N_m\, \alpha(x-\Delta x) H_m[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2} \qquad \text{(A3.6.5)}$$

Also,

$$\alpha(x-\Delta x) H_m[\alpha(x-\Delta x)] = \tfrac{1}{2} H_{m+1}[\alpha(x-\Delta x)] + m H_{m-1}[\alpha(x-\Delta x)]. \qquad \text{(A3.6.6)}$$

Thus, (A3.6.5) becomes

$$\frac{d}{d(\alpha x)} \Phi_m[\alpha(x-\Delta x)] = m N_m H_{m-1}[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2} - \tfrac{1}{2} N_m H_{m+1}[\alpha(x-\Delta x)]\, e^{-\frac{1}{2}\alpha^2(x-\Delta x)^2} \qquad \text{(A3.6.7)}$$

Using, $N_m = \left(\frac{\alpha}{\pi^{\frac{1}{2}} 2^m m!}\right)^{\frac{1}{2}}$ we can easily show that

$$\frac{d}{d(\alpha x)}\Phi_m\left[\alpha(x-\Delta x)\right] = \left(\frac{m}{2}\right)^{\frac{1}{2}}\Phi_{m-1}\left[\alpha(x-\Delta x)\right] - \left(\frac{m+1}{2}\right)^{\frac{1}{2}}\Phi_{m+1}\left[\alpha(x-\Delta x)\right]. \qquad \text{(A3.6.8)}$$

Thus, the derivative matrix element, $I'_{m+p,m}$ (A3.6.2) becomes

$$I'_{m+p,m} = \left(\frac{m}{2}\right)^{\frac{1}{2}} I_{m+p,m-1} - \left(\frac{m+1}{2}\right)^{\frac{1}{2}} I_{m+p,m+1}. \qquad \text{(A3.6.9)}$$

Hence, the transition rate $W_T^{(2)}$ (A3.6.1) is

$$W_T^{(2)} = |c|^2 \sum_{m=0}^{\infty} (1-r_0) r_0^m \left\{\left(\frac{m}{2}\right) I^2_{m+p,m-1} - 2\left(\frac{m}{2}\right)^{\frac{1}{2}}\left(\frac{m+1}{2}\right)^{\frac{1}{2}} I_{m+p,m-1} I_{m+p,m+1} + \left(\frac{m+1}{2}\right) I^2_{m+p,m+1}\right\}. \qquad \text{(A3.6.10)}$$

CASE 1

The transition rate at $T=0$, $W^{(2)}_{T=0}$

At $T=0$, only the lowest initial vibrational state ($m=0$) is occupied. Thus, at $T=0$, the general expression for $W_T^{(2)}$ (A3.6.10) becomes

$$W^{(2)}_{T=0} = \frac{|c|^2}{2} I^2_{p,1}. \qquad \text{(A3,6.11)}$$

We have already derived, the general expression for the vibrational overlap integral, I_{mn} (A3. 3, 4), which is

$$I_{mn} = (n!\,m!)^{\frac{1}{2}}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{m+n} \exp\left[-\frac{1}{4}\alpha^2\Delta x^2\right] \sum_{a=0}^{n} \frac{(-1)^{m-a}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{-2a}}{a!\,(n-a)!\,(m-a)!}. \qquad \text{(A3.6.12)}$$

Thus,

$$I_{p,1} = (p!)^{\frac{1}{2}}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{p+1} \exp\left[-\frac{1}{4}\alpha^2\Delta x^2\right]\left\{\frac{(-1)^p}{p!} + \frac{(-1)^{p-1}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{-2}}{(p-1)!}\right\}. \qquad \text{(A3.6.13)}$$

Thus,

$$I^2_{p,1} = p!\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p+1} \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right]\left\{\frac{(-1)^{2p}}{(p!)^2} + \frac{2(-1)^{2p-1}\left(\frac{\alpha\Delta x}{\sqrt{2}}\right)^{-2}}{(p-1)!\,p!} + \frac{(-1)^{2(p-1)}\left(\frac{\alpha^2\Delta x^2}{2}\right)^{-2}}{[(p-1)!]^2}\right\}. \qquad \text{(A3,6.14)}$$

We find that we can write,

$$I^2_{p,1} = \left\{\left(\frac{\alpha^2\Delta x^2}{2}\right) - 2p + p^2\left(\frac{\alpha^2\Delta x^2}{2}\right)^{-1}\right\} I^2_{p,0} \tag{A3.6.15}$$

where $I^2_{p,0} = \left(\frac{\alpha^2\Delta x^2}{2}\right)^p \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right]\frac{1}{p!}$.

However,

$$I^2_{p,1} = \frac{4E_b}{\hbar\omega_0} I^2_{p,0} \tag{A3.6.16}$$

where, E_b is the activation energy defined in Chapter 3,

$$E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M}$$

where, $E_M = \frac{\alpha^2\Delta x^2}{2}\hbar\omega_0$ and $\Delta E = p\hbar\omega_0$

Thus, using (A3;6,16) in (A3.6.11) we obtain

$$W^{(2)}_{T=0} = 2|C|^2\frac{E_b}{\hbar\omega_0}\left(\frac{E_M}{\hbar\omega_0}\right)^p\frac{1}{p!}\exp\left[-\frac{E_M}{\hbar\omega_0}\right]. \tag{A3.6.17}$$

CASE 2

The transition rate in the weak coupling limit, $\frac{\alpha^2\Delta x^2}{2} \ll 1$

For the 'standard' transition rates we have already shown using the general expression for the vibrational overlap integral I_{mn} (A3.6.12) that when $\frac{\alpha^2\Delta x^2}{2} \ll 1$ then (see A3,3,6)

$$I^2_{m+p,m} = \frac{(p+m)!}{p!\,m!} I^2_{p,0}. \tag{A3.6.18}$$

Using (A3.6.18) it is easily shown that

$$W_T = [1 + N(\omega_0)]^p W_{T=0}.$$

We now wish to show that the relation (A3.6.18) holds for the 'derivative' matrix elements $I'_{m+p,m}$ as well.

We have shown that,

$$W_{T=0} = \left\{ \left(\frac{\alpha^2\Delta x^2}{2}\right) - 2p + p^2\left(\frac{\alpha^2\Delta x^2}{2}\right)^{-1} \right\} \left(\frac{\alpha^2\Delta x^2}{2}\right)^{p} \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right] \frac{1}{p!} .$$

In the weak coupling limit,

$$W_{T=0} \cong p\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1} \exp\left(-\frac{1}{2}\alpha^2\Delta x^2\right) \frac{1}{(p-1)!} . \qquad \text{(A3.6.19)}$$

We have shown that,

$$I'^{2}_{m+p,m} = \left(\frac{m}{2}\right) I^{2}_{m+p,m-1} - 2\left(\frac{m}{2}\right)^{\frac{1}{2}}\left(\frac{m+1}{2}\right)^{\frac{1}{2}} I_{m+p,m-1} I_{m+p,m-1}$$
$$+ \left(\frac{m+1}{2}\right) I^{2}_{m+p,m+1} .$$

Using the general expression for the vibrational overlap integral I_{mn} , (A3.6.12) we find that to the lowest powers of $\frac{\alpha^2\Delta x^2}{2}$ the various overlap integrals are

$$I^{2}_{m+p,m+1} \cong (m+p)!(m+1)! \left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1} \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right] \left\{ \frac{1}{[(m+1)!\,(p-1)!]^2} \right.$$
$$\left. - \frac{2\left(\frac{\alpha^2\Delta x^2}{2}\right)}{(m+1)!\,m!\,p!\,(p-1)!} + \frac{\left(\frac{\alpha^2\Delta x^2}{2}\right)^2}{(m!\,p!)^2} \right\} \qquad \text{(A3.6.20)}$$

$$I^{2}_{m+p,m-1} \cong \frac{(m+p)!}{(m-1)!} \frac{1}{[(p+1)!]^2} \left(\frac{\alpha^2\Delta x^2}{2}\right)^{p+1} \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right] . \qquad \text{(A3.6.21)}$$

and

$$I_{m+p,m-1} I_{m+p,m+1} \cong \left\{ \frac{(m+p)!}{[(m+1)!\,(m-1)!]^{1/2}} \right\} \frac{\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p}}{(p+1)!\,(p-1)!} \exp\left(-\frac{1}{2}\alpha^2\Delta x^2\right) . \qquad \text{(A3.6.22)}$$

Now, from (A3.6.19), in the weak coupling limit $\frac{\alpha^2\Delta x^2}{2} \ll 1$, $W_{T=0}$ is of order $\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1}$

We see that the only term in $I'^{2}_{m+p,m}$ which is of order $\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1}$ is the first part of (A3.6.20).

Thus,

$$I'^{2}_{m+p,m} = \frac{(m+1)}{2} \left\{ \frac{(m+p)!}{(m+1)!\,[(p-1)!]^2} \right\} \left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1} \exp\left[-\frac{1}{2}\alpha^2\Delta x^2\right] . \qquad \text{(A3.6.22)}$$

We find that

$$I_{m+p,m} = \frac{(m+p)!}{m!\,p!}\left\{\frac{p}{2}\left(\frac{\alpha^2\Delta x^2}{2}\right)^{p-1}\exp\left(-\frac{1}{2}\alpha^2\Delta x^2\right)\frac{1}{(p-1)!}\right\}. \qquad \text{(A5.1.24)}$$

Comparing this with (A3.6.18) we see that

$$I^{12}_{m+p,m} = \frac{(m+p)!}{m!\,p!}\,I^{12}_{p,0}. \qquad \text{(A3.6.25)}$$

Thus, $$W^{(2)}_{T} = [1 + N(\omega_0)]^{P}\,W^{(2)}_{T=0}. \qquad \text{(A3.6.26)}$$

CHAPTER 4

The generalisation of the S.C.C.M. to include different vibrational frequencies for the ground and excited electronic states

We will extend the results of Chapter 3 in this chapter to include the effect on the transition rates of different vibrational frequencies ω_0 and ω_1 for the lattice states belonging to the ground and excited electronic states respectively. The two curves in the S.C.C.M. diagram, figure 4.1 have different curvatures in this situation, The general vibrational overlap integral I_{mn} will be calculated for this case with the same generating function method we have already used in Chapter 3, The overlap integrals which result are very complex and we only consider in any detail $I_{p,0}$, which is appropriate to the recombination rate at T=0. There is a discussion at the conclusion of this chapter about whether an energy gap law is valid at the absolute zero of temperature. The results of this chapter will appear in Robertson and Friedman II.[4]

We now give a brief discussion of the modifications to our previous treatment of the S.C.C.M. required so that the lattice states belonging to the ground and excited electronic states have different frequencies.

We recall that in Chapter 3 the configuration dependent electronic wavefunctions $\varphi_i(r,x)$ are solutions of

$$\left[-\frac{\hbar^2}{2m_e}\nabla_r^2 + U(r,x)\right]\varphi_i(r,x) = E_i(x)\varphi_i(r,x) \tag{4.1}$$

while their energy eigenvalues $E_i(x)$ were

$$E_i(x) = E_i - A_i x . \tag{4.2}$$

In this chapter a quadratic electron-lattice interaction term will be included in $E_i(x)$ in addition to the linear term already incorporated in (4.2),

$$E_i(x) = E_i - A_i x + B_i x^2. \qquad (4.3)$$

We have already shown in Chapter 3 how the linear term results in a displacement of the vibrational states. It will be demonstrated in this chapter how the quadratic term gives rise to a change in the local frequency which depends on the electronic state. Thus, the vibrational wavefunctions $\mathcal{F}_n^i$ are solutions of

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega_0^2 x^2 - A_i x + B_i x^2\right]\mathcal{F}_n^i = E_{i,n}\,\mathcal{F}_n^i \qquad (4.4)$$

where the eigenfunctions $\mathcal{F}_n^i$ and eigenvalues $E_{i,n}$ are given by

$$\begin{aligned} \mathcal{F}_n^i &= N_n H_n(\alpha_i x)\exp\left[-\tfrac{1}{2}\alpha_i^2(x-\Delta x_i)^2\right] \\ E_{i,n} &= \hbar\omega_i(n+\tfrac{1}{2}). \end{aligned} \qquad (4.5)$$

Consideration of equations (4.4) and (4.5) show the oscillator frequency ω_i to be given by

$$\tfrac{1}{2}M\omega_0^2 + B_i = \tfrac{1}{2}M\omega_i^2$$

so that,

$$\omega_i^2 = \omega_0^2 + \frac{2B_i}{M}. \qquad (4.6)$$

Throughout this chapter we will simply assume that the vibrational states belonging to the ground and excited electronic states have frequencies ω_0 and ω_1 respectively. The vibrational overlap integral I_{mn} is calculated,

$$I_{mn} = \int_{-\infty}^{\infty} \mathcal{F}_m[\alpha_0(x-\Delta x)]\,\mathcal{F}_n(\alpha_1 x)\,dx \qquad (4.7)$$

where

$$\mathcal{F}_n(\alpha_i x) = N_n H_n(\alpha_i x)\exp\left[-\tfrac{1}{2}\alpha_i^2 x^2\right],$$

while

$$N_n = \left(\frac{\alpha_i}{2^n n!}\right)^{\frac{1}{2}} \qquad \alpha_i = \left(\frac{M\omega_i}{\hbar}\right)^{\frac{1}{2}}.$$

Following Chapter 3 we evaluate the overlap integrals using the generating function method in which the Hermite polynomials appear as coefficients in the expansion,

$$\exp\left[-s^2 + 2s\alpha_i x\right] = \sum_{n=0}^{\infty} \frac{H_n(\alpha_i x)}{n!} s^n .$$

The detailed calculations for the evaluation of the overlap integral I_{mn} are found in appendix (A4.1).

The result we find is

$$I_{mn} = \frac{(\alpha_1\alpha_0)^{\frac{1}{2}}}{\alpha_2}(n!m!)^{\frac{1}{2}} \exp\left[-\frac{\alpha_0^2\Delta x^2}{4}(1-\delta)\right]\left[\frac{\alpha_1\Delta x(1+\delta)}{\sqrt{2}}\right]^n\left[\frac{\alpha_0\Delta x(\delta-1)}{\sqrt{2}}\right]^m$$
$$\times\sum_{a=0}^{n/2}\sum_{b=0}^{m}\sum_{c=0}^{(m-b)/2}\frac{(-1)^a\delta^{c+a}\left(\frac{\alpha_0\Delta q_c}{2}\right)^{-b}\left[\alpha_1\Delta x(1+\delta)\right]^{-2a}\left[\alpha_0\Delta x(\delta-1)\right]^{-b-2c}}{a!\,c!\,b!\,(m-b-2c)!\,(n-2a-b)!} . \qquad (4.8)$$

which agrees with Hutchisson's[7] findings. At the time we did this calculation we were not aware of Hutchisson's original work. This result for I_{mn} (4.8) is very complicated. Throughout the remainder of this chapter attention will be directed to the simplest case $I_{p,0}$ which is appropriate for the transition probability at absolute zero, T=0.

In addition, the unequal frequency case poses more difficult energy conservation problems than were met with in Chapter 3. For, even although the m'th and n'th vibrational levels have the same energy as in figure 4.1 the m+1'th and n+1'th energy levels are not then aligned since $\hbar\omega_0 \neq \hbar\omega_1$. Thus a transition does not take place into every final state but only into those levels which are aligned with some initial vibrational state. However, in dealing with the transition rate at absolute zero, T=0, we simply assume that the 0'th and p'th vibrational states belonging to the excited and ground electronic states have the same energy as shown in figure 4.2. In the real situation, it is expected that vibrational dispersion or level broadening will ensure energy conservation.

The transition rate at absolute zero (T=0) is then,

$$W_{T=0} = \frac{2\pi |K|^2}{\hbar^2 \omega_0} I_{p,o}^{2} \tag{4.9}$$

Using the general expression for the vibrational overlap integral $I_{m,n}$ (4.8) we find

$$I_{p,o} = C D^{p} \exp(-E) (p!)^{\frac{1}{2}} \sum_{c=0}^{\frac{p}{2}, \frac{(p-1)}{2}} \frac{1}{c!(p-2c)!} \frac{1}{(2u^2)^c} \tag{4.10}$$

where

$$\alpha_2^2 = \tfrac{1}{2}(\alpha_0^2 + \alpha_1^2), \quad \delta = (\omega_0 - \omega_0)/(\omega_0 + \omega_1)$$

$$u^2 = \alpha_0^2 \Delta x^2 (1-\delta^2)/2\delta, \quad C = (\alpha_0 \alpha_1)^{1/2}/\alpha_2$$

$$D = \alpha_0 \Delta x (\delta - 1)/\sqrt{2}, \quad E = \alpha_0^2 \Delta x^2 (1-\delta)/4$$

An interesting special case of this overlap integral, $I_{p,o}$ which has been discussed previously by Siebrand occurs when the curves are undisplaced, ($\Delta x = 0$). We find that

$$\left.\begin{aligned} I_{p,o} &= \frac{C\left[(p!)^{1/2}(\delta/2)^{p/2}\right]}{(p/2)!} \quad &\text{(p even)} \\ I_{p,o} &= 0 \quad &\text{(p odd)} \end{aligned}\right\} \tag{4.11}$$

Thus, even though the curves are undisplaced ($\Delta x = 0$), their differing curvatures result in an overlap integral $I_{p,o}$ which is not necessarily zero. Now, for undisplaced curves the o'th vibrational wavefunction is even about its equilibrium position while the pth vibrational wavefunction is even or odd about the same equilibrium position according to whether p is even or odd. Thus the parity of the vibrational wavefunctions results in the vibrational overlap integral $I_{p,o}$ being zero if p is odd.

A similar case, which is believed to occur for impurities in GaP arises when the coupling is weak ($\alpha\Delta x \ll 1$) and the curvatures are different. This situation is illustrated in figure (4.2). Mott[23] has speculated that at absolute zero the transition probability is of the 'energy-gap' type.

To approximate this situation in equation (4.10) only the $c = \frac{p}{2}$ and $c = \frac{p}{2} - 1$ terms are retained if p is even while only the $c = \frac{p-1}{2}$ term is retained if p is odd. Doing this, we find that

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0} I^2_{p,0}$$

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0} C^2 p! \exp(-2E) \frac{(\delta/2)^p}{[(p/2)!]^2} \qquad \text{(p even)}$$

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0} C^2 p! \exp(-2E) (\delta/2)^{p-1} \frac{\mathcal{D}^2}{[(\frac{p-1}{2})!]^2} \qquad \text{(p odd)} \qquad (4.12)$$

We note here that, as expected from equation (4.11), the value of $W_{T=0}$ is much smaller when p is odd than when p is even. This arises as the p odd value of $W_{T=0}$ contains an additional factor D^2 where $\mathcal{D}=\alpha_0\Delta x(\delta-1)/\surd$ which is very small in the weak coupling limit

The quantity $\delta = (\omega_0 - \omega_1)/(\omega_0 + \omega_1)$ may either be positive or negative; however the factors involving δ in the expressions (4.12) for $W_{T=0}$ are always positive, since $\delta^p > 0$ for p even while $\delta^{p-1} > 0$ for p odd.

To evaluate the (p even) value of $I^2_{p,0}$ in the statistical limit $(p \gg 1)$ we use the Stirling approximation,

$$\frac{1}{p!} \sim (2\pi p)^{-\frac{1}{2}} p^{-p} \exp(p),$$

obtaining the following result,

$$I_{p,0}^{\;2} \simeq C^2 \exp[-2E](2\pi p)^{-\frac{1}{2}}\delta^{P}. \qquad (4.13)$$

Provided $\delta > 0\ (\omega_0 > \omega_1)$, δ^P may be written in the form $\exp[\log \delta^P]$ so that the expression for the transition rate (4.12) becomes

$$W_{T=0} \simeq \frac{2\pi|K|^2}{\hbar^2\omega_0} C^2 \exp(-2E)(2\pi p)^{-\frac{1}{2}} \exp\left[-\frac{\Delta E}{\hbar\omega_0}\{-\log\delta\}\right], \qquad (4.14)$$

which is the 'energy gap law' form. However this is a modified form of the energy gap law as the transition probability now depends on the difference of vibrational frequencies as well as the electronic energy difference Δ E. In fact since $-\log\delta$ is large when $\delta \ll 1$ the relaxation rate will be sensitive to frequency changes as well as alterations in Δ E. The case illustrated in figure 4.2, the oxygen impurity in GaP does indeed have $\omega_0 > \omega_1$.

Now, when $\omega_0 > \omega_1$ then $0 < \delta < 1$ so that $\log\delta < 0$ and thus $-\log\delta > 0$.

Hence the 'energy gap' law factor, $\exp\left[-\frac{\Delta E}{\hbar\omega_0}\{-\log\delta\}\right]$ in equation (4.14) indicates that at absolute zero (T=0) as Δ E increases the non-radiative transition probability decreases rapidly.

Conclusions

In this chapter we have extended our previous results to include the situation in which the vibrational states belonging to the ground and excited electronic states have different frequencies ω_0 and ω_1 respectively.

We have again used the generating function method to evaluate the vibrational overlap integral,

$$I_{mn} = \int \mathcal{F}_m[\alpha_0(x-\Delta x)]\,\mathcal{F}_n(\alpha_1 x)\,dx.$$

The resulting expression for $\mathcal{I}_{mn}$ is very complicated and our investigation is restricted to the vibrational overlap integral which is appropriate for recombination at absolute zero, T=0. The general expression for $\mathcal{I}_{\beta o}$ is given by equation (4.10). The resulting transition rates are investigated for two special cases, the first of which involved undisplaced curves, $\Delta x = 0$, for which we find equation (4.11). We have also considered the situation in which there is weak coupling $(\alpha \Delta x \ll 1)$ and different frequencies, [equation (4.12)] as this case may occur for certain impurities in GaP. The Stirling approximation for large $p = \frac{\Delta E}{\hbar \omega_o}$ is applied to this result to obtain the 'energy gap' law form given by equation (4.14).

Figure 4.1: The S.C.C.M. diagram, situation in which the potential energy wells have different curvatures.

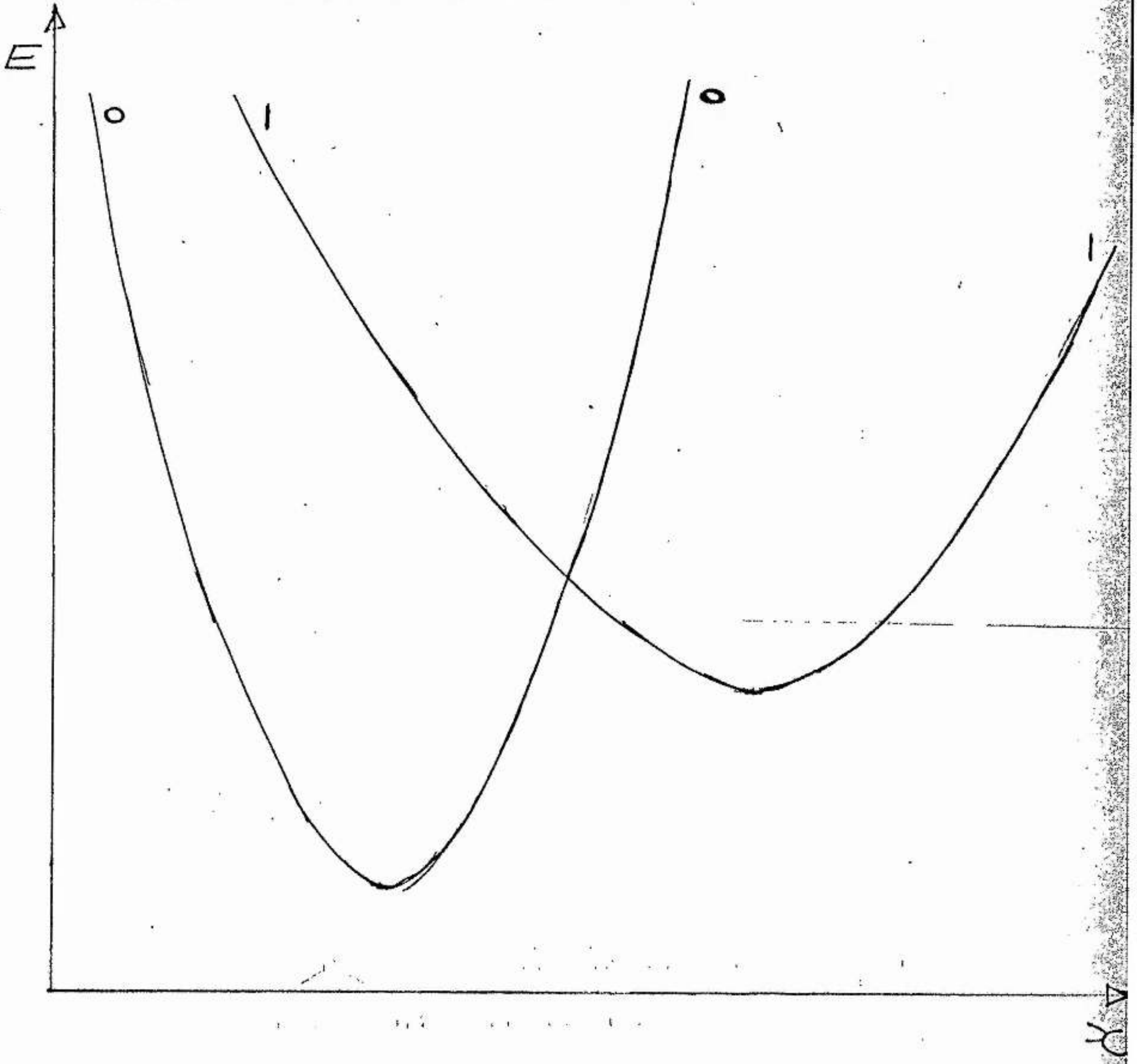
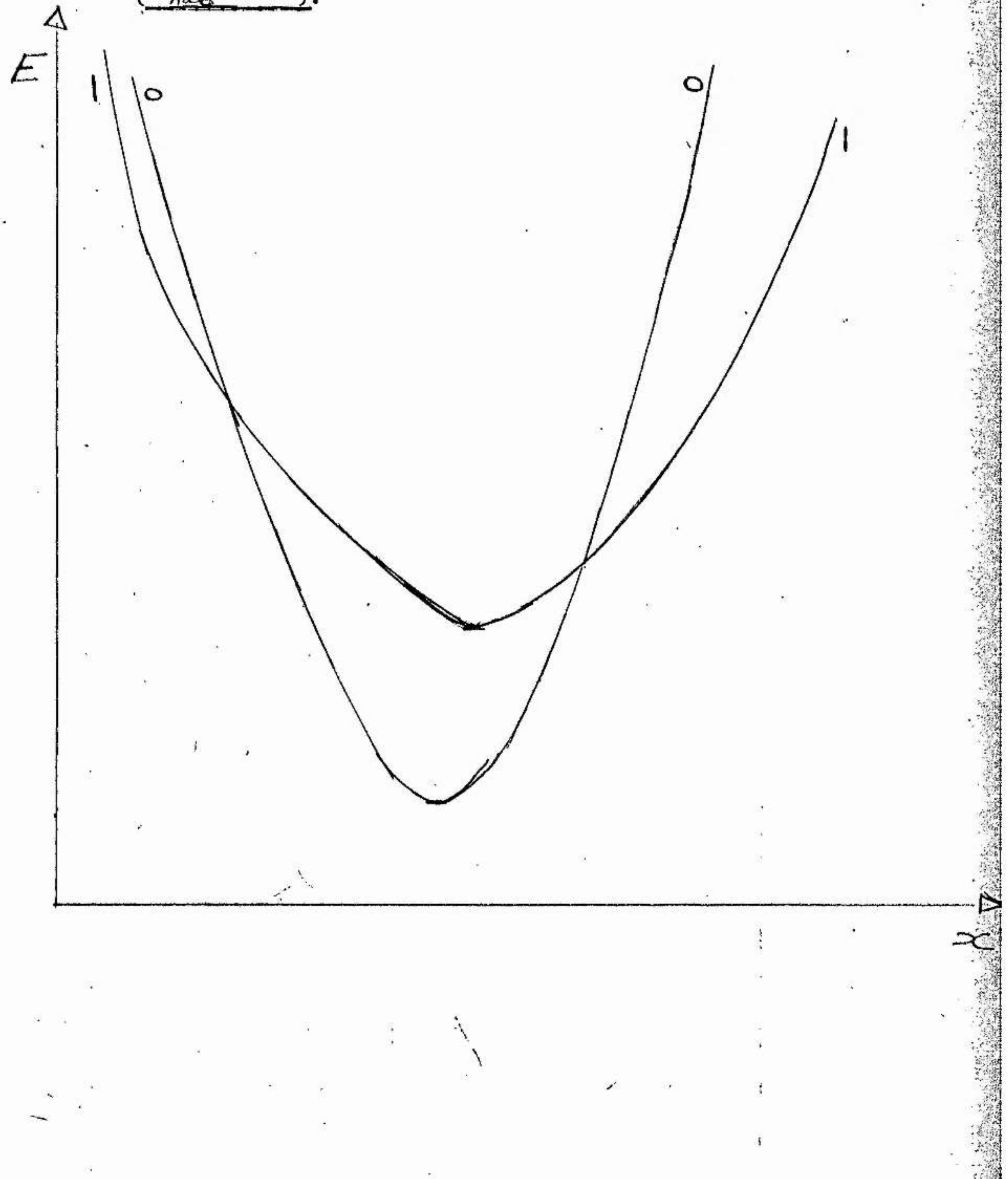


Figure 4.2: The S.C.C.M. diagram, different curvatures, weak coupling ($\frac{E_M}{\hbar\omega_0} \ll 1$).



APPENDIX A4.1

Calculation of the vibrational overlap integral in the S.C.C.M. when the ground and excited state oscillators have different frequencies.

In this appendix we consider the case when the ground and excited state oscillators have frequencies ω_0 and ω_1 respectively,

We evaluate,

$$I_{mn} = \int_{-\infty}^{\infty} \mathfrak{F}_m[\alpha_0(x-\Delta x)]\,\mathfrak{F}_n(\alpha_1 x)\,dx \qquad \text{(A4.1.1)}$$

where, $\alpha_0 = \left(\frac{M\omega_0}{\hbar}\right)^{1/2}$ and $\alpha_1 = \left(\frac{M\omega_1}{\hbar}\right)^{\frac{1}{2}}.$

Here $\mathfrak{F}_n(\alpha x) = N_n H_n(\alpha x)\, e^{-\frac{1}{2}\alpha^2 x^2}$, $N_n = \frac{\alpha}{\pi^{1/2} 2^n n!}$.

Hence,

$$I_{mn} = N_n N_m \int_{-\infty}^{\infty} H_m[\alpha_0(x-\Delta x)] \exp[-\tfrac{1}{2}\alpha_0^2(x-\Delta x)^2]\, H_n(\alpha_1 x) \exp[-\tfrac{1}{2}\alpha_1^2 x^2]\,dx. \qquad \text{(A6.1.2)}$$

Following the procedure adopted in Chapter 3, we use the generating function method

$$\exp[-s^2 + 2s\alpha x] = \sum_{n=0}^{\infty} \frac{H_n(\alpha x)}{n!} s^n. \qquad \text{(A6.1.3)}$$

Thus,

$$I_{mn} = N_n N_m \left\{ \text{ coefficient of } s^n t^m \text{ in } I \right\} \qquad \text{(A6.1.4)}$$

where

$$I = \int_{-\infty}^{\infty} e^{-s^2 + 2s\alpha_1 x - t^2 + 2t[\alpha_0(x-\Delta x)] - \frac{1}{2}\alpha_1^2 x^2 - \frac{1}{2}\alpha_0^2 (x-\Delta x)^2}\, dx. \qquad \text{(A6.1.5)}$$

Here, we evaluate I which we write in the form

$$I = \exp[-(s^2+t^2) - 2t\alpha_0\Delta x - \tfrac{1}{2}\alpha_0^2\Delta x^2] \times \int_{-\infty}^{\infty} \exp[-\tfrac{1}{2}(\alpha_0^2+\alpha_1^2)x^2 + (2s\alpha_1 + 2t\alpha_0 + \alpha_0^2\Delta x)x]\,dx. \qquad \text{(A4.1.6)}$$

Writing $\alpha_2^2 = \frac{1}{2}(\alpha_0^2 + \alpha_1^2)$ we find by completing the square in (A4.1.6) that

$$I = \frac{\sqrt{\pi}}{\alpha_2} \exp\left[-\tfrac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4 \Delta x^2}{4\alpha_2^2} + \left(\frac{\alpha_1^2}{\alpha_2^2} - 1\right)s^2 + \frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2^2} s\right] \times \exp\left[\left(\frac{\alpha_0^2}{\alpha_2^2} - 1\right)t^2 - 2t\alpha_0\Delta x + \frac{\alpha_0^3}{\alpha_2^2}\Delta x\, t + \frac{2st\alpha_0\alpha_1}{\alpha_2^2}\right]. \qquad \text{(A4.1.7)}$$

Now, we extract the coefficient of s^n from I.

To do this we perform the following operation on I

We evaluate $\left.\frac{d^n}{ds^n} I\right|_{s=0}$ (A4.1.8)

We calculate,

$$\frac{d^n}{ds^n} I = \frac{\sqrt{\pi}}{\alpha_2} \exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4\Delta x^2}{4\alpha_2^2} + \left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2 - 2t\alpha_0\Delta x + \frac{\alpha_0^3\Delta x}{\alpha_2^2}t\right]$$

$$\times \frac{d^n}{ds^n}\left\{\exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2 + \left(2\frac{\alpha_1\alpha_0}{\alpha_2^2}t + \frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right)s\right]\right\}. \quad \text{(A4.1.9)}$$

Using the Leibnitz formula,

$$\frac{d^n}{dx^n}\left[f(x)g(x)\right] = \sum_{a=0}^{n} \frac{n!}{(n-a)!\,a!}\left\{\frac{d^a}{dx^a}f(x)\right\}\left\{\frac{d^{(n-a)}}{dx^{(n-a)}}g(x)\right\} \quad \text{(A4.1.10)}$$

We obtain

$$\frac{d^n}{ds^n} I = \frac{\sqrt{\pi}}{\alpha_2} \exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4\Delta x^2}{4\alpha_2^2} + \left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2 - 2t\alpha_0\Delta x + \frac{\alpha_0^3}{\alpha_2^2}\Delta x\, t\right]$$

$$\times \sum_{a=0}^{n} \frac{n!}{a!(n-a)!} \frac{d^a}{ds^a}\left\{\exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2\right]\right\} \frac{d^{(n-a)}}{ds^{(n-a)}}\left\{\exp\left[\left(\frac{2\alpha_1\alpha_0 t}{\alpha_2^2} + \frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2^2}\right)s\right]\right\}$$

which is,

$$\frac{d^n}{ds^n} I = \frac{\sqrt{\pi}}{\alpha_2} \exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4\Delta x^2}{4\alpha_2^2} + \left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2 - 2t\alpha_0\Delta x + \frac{\alpha_0^3\Delta x}{\alpha_2^2}t\right]$$

$$\times \sum_{a=0}^{n} \frac{n!}{a!(n-a)!}\left[\frac{2\alpha_1\alpha_0 t}{\alpha_2^2}\;\frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2^4}\right]^{n-a} \exp\left[2\frac{\alpha_1\alpha_0}{\alpha_2^2}t + \frac{\alpha_1\alpha_0^2}{\alpha_2}\Delta x\right] \frac{d^a}{ds^a}\left\{\exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2\right]\right\}$$

(A4.1,11)

What we require is $\frac{d^m}{dt^m}\frac{d^s}{ds^n} I =$

$$\frac{\sqrt{\pi}}{\alpha_2} \exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4\Delta x^2}{4\alpha_2^2} + \frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2}s\right] \sum_{a=0}^{n} \frac{n!}{a!(n-a)!} \frac{d^a}{ds^a} \exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2\right]$$

$$\times \frac{d^m}{dt^m}\left\{\left[\frac{2\alpha_1\alpha_0}{\alpha_2^2}t + \frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2^2}\right]^{n-a} \exp\left\{\left[\frac{\alpha_0^2}{\alpha_2^2}-1\right]t^2 + \left[\frac{\alpha_0^3\Delta x}{\alpha_2^2} - 2\alpha_0\Delta x + \frac{2\alpha_1\alpha_0 s}{\alpha_2^2}\right]t\right\}\right. \quad \text{(A4.1.12)}$$

To calculate the expression in (A6.1.12) of the form

$$\frac{d^m}{dx^m}\left[f(x)g(x)h(x)\right]$$ we use the Leibnitz formula,

$$\frac{d^m}{dx^m}\left[f(x)g(x)h(x)\right]=\sum_{b=0}^{m}\frac{m!}{b!(m-b)!}\frac{d^b}{dx^b}\left[f(x)g(x)\right]\frac{d^{(m-b)}}{dx^{(m-b)}}h(x)$$

$$=\sum_{b=0}^{m}\frac{m!}{b!(m-b)!}\sum_{c=0}^{b}\frac{b!}{c!(b-c)!}\frac{d^c}{dx^c}f(x)\frac{d^{(b-c)}}{dx^{(b-c)}}g(x)\frac{d^{(m-b)}}{dx^{(m-b)}}h(x)$$

$$=\sum_{b=0}^{m}\sum_{c=0}^{b}\frac{m!}{(m-b)!\,c!\,(b-c)!}\frac{d^c}{dx^c}f(x)\frac{d^{(b-c)}}{dx^{(b-c)}}g(x)\frac{d^{(m-b)}}{dx^{(m-b)}}h(x). \qquad \text{(A4.1.13)}$$

Thus, $$\frac{d^m}{dt^m}\frac{d^n}{ds^n}I=\frac{\sqrt{\pi}}{\alpha_2}\exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2+\frac{\alpha_0^4\Delta x^2}{4\alpha_2^2}+\frac{\alpha_1\alpha_0^2}{\alpha_2}\Delta x s\right]$$

$$\times\sum_{a=0}^{n}\frac{n!}{a!(n-a)!}\frac{d^a}{ds^a}\left\{\exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2\right]\right\}\sum_{b=0}^{m}\sum_{c=0}^{b}\frac{m!}{(m-b)!\,c!\,(b-c)!}$$

$$\times\frac{d^{(m-b)}}{dt^{(m-b)}}\left[\frac{2\alpha_1\alpha_0}{\alpha_2^2}t+\frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right]\frac{d^c}{dt^c}\left\{\exp\left[\left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2\right]\right\}$$

$$\times\frac{d^{(b-c)}}{dt^{(b-c)}}\left\{\exp\left[\left(\frac{\alpha_0^3\Delta x}{\alpha_2^2}-2\alpha_0\Delta x+\frac{2\alpha_1\alpha_0}{\alpha_2^2}s\right)t\right]\right\}. \qquad \text{(A4.1.14)}$$

We now wish to calculate the various derivatives in (A4.1.14)

(i) $$\frac{d^{(m-b)}}{dt^{(m-b)}}\left[2\frac{\alpha_1\alpha_0}{\alpha_2^2}t+\frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right]^{n-a}$$

$$=\frac{(n-a)!}{(n-a-m+b)!}\left(\frac{2\alpha_1\alpha_0}{\alpha_2^2}\right)^{m-b}\left[2\frac{\alpha_1\alpha_0}{\alpha_2^2}t+\frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right]^{(n-a)-(m-b)} \qquad \text{(A4.1.15)}$$

and

(ii) $$\frac{d^{(b-c)}}{dt^{(b-c)}}\left\{\exp\left[\left(\frac{\alpha_0^3\Delta x}{\alpha_2^2}-2\alpha_0\Delta x+2\frac{\alpha_1\alpha_0}{\alpha_2^2}s\right)t\right]\right\}$$

$$=\left[\frac{\alpha_0^3}{\alpha_2^2}\Delta x-2\alpha_0\Delta x+\frac{2\alpha_0\alpha_1}{\alpha_2^2}s\right]^{(b-c)}\exp\left[\left(\frac{\alpha_0^3}{\alpha_2^2}\Delta x-2\alpha_0\Delta x+\frac{2\alpha_1\alpha_0}{\alpha_2^2}s\right)t\right]. \qquad \text{(A4.1.16)}$$

The most difficult derivative is

$$\text{(iii)}\quad \frac{d^c}{dt^c}\exp\left[\left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2\right].$$

This is very complicated but since we later put $s=t=0$ we need only consider the part of $\frac{d^c}{dt^c}\exp\left[\left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2\right]$ which is non zero when $t=0$.

Now,

$$\frac{d^c}{dt^c}\exp\left[\beta t^2\right] = \frac{d^{(c-1)}}{dt^{(c-1)}}\left[\frac{d}{dt}\exp(\beta t^2)\right] = \frac{d^{(c-1)}}{dt^{(c-1)}}\left[2\beta t\exp(\beta t^2)\right]$$

$$= \sum_{a=0}^{c-1}\frac{(c-1)!}{a!\,(c-1-a)!}\,\frac{d^a}{dt^a}(2\beta t)\,\frac{d^{(c-1-a)}}{dt^{(c-1-a)}}\exp(\beta t^2).$$

We obtain

$$\frac{d^c}{dt^c}\exp(\beta t^2) = 2\beta t\,\frac{d^{(c-1)}}{dt^{(c-1)}}\exp(\beta t^2) + 2\beta(c-1)\frac{d^{(c-2)}}{dt^{(c-2)}}\exp(\beta t^2)$$

We repeat the process with $\frac{d^{(c-1)}}{dt^{(c-1)}}\exp(\beta t^2)$ and $\frac{d^{(c-2)}}{dt^{(c-2)}}\exp(\beta t^2)$. (A4.1.17)

We see that the first term in (A4.1.17) will always have factors of t in it and hence is zero at $t=0$. However, the second term in (A.4.1.17) has non-zero terms of the form,

$$2\beta(c-1)\frac{d^{(c-2)}}{dt^{(c-2)}}\exp(\beta t^2) = (2\beta)^2(c-1)(c-3)\frac{d^{(c-4)}}{dt^{(c-4)}}\exp(\beta t^2).$$

Thus, we obtain

$$\left.\frac{d^c}{dt^c}\exp(\beta t^2)\right]_{t=0} = (2\beta)^{\frac{c}{2}}(c-1)(c-3)\,.\,.\,.\,.5.3.1 \qquad (c \text{ even})$$

$$= 0 \qquad (c \text{ odd}). \qquad \text{(A4.1.18)}$$

Writing,

$$\frac{d^a}{ds^a}\exp\left[\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)s^2\right] = X_a$$

and (A4.1.19)

$$\frac{d^c}{dt^c}\exp\left[\left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)t^2\right] = Y_c$$

$$X_a = \left\{2\left(\frac{\alpha_1^2}{\alpha_2^2}-1\right)\right\}^{\frac{a}{2}}(a-1)(a-3)\cdots 3.1.\ (a\ \text{even})\ ;\ X_a = 0\ (a\ \text{odd})$$

$$Y_c = \left\{2\left(\frac{\alpha_0^2}{\alpha_2^2}-1\right)\right\}^{\frac{c}{2}}(c-1)(c-3)\cdots 3.1.\ (c\ \text{even})\ ;\ Y_c = 0\ (c\ \text{odd}).$$

We obtain $\left.\frac{d^m}{dt^m}\frac{d^n}{ds^n} I\right]_{s=0,\,t=0}$

$$= \frac{\sqrt{\pi}}{\alpha_2}\exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4}{4\alpha_2^2}\Delta x^2\right]$$

$$\times\sum_{a=0}^{n}\sum_{b=0}^{m}\sum_{c=0}^{b}\frac{n!\,m!}{a!\,(n-a)!\,(m-b)!\,c!\,(b-c)!}X_a Y_c\frac{(n-a)!}{(n-a-m+b)!}\left(\frac{2\alpha_1\alpha_0}{\alpha_2^2}\right)^{m-b}$$

$$\times\left(\frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right)^{(n-a)-(m-b)}\left(\frac{\alpha_0^3\Delta x}{\alpha_2^2} - 2\alpha_0\Delta x\right)^{b-c}. \qquad \text{(A4.1.20)}$$

Thus, I_{mn} (from A4.1.4) is given by

$$I_{mn} = \frac{\sqrt{\pi}}{\alpha_2}N_n N_m\exp\left[-\frac{1}{2}\alpha_0^2\Delta x^2 + \frac{\alpha_0^4}{4\alpha_2^2}\Delta x^2\right]$$

$$\times\sum_{a=0}^{n}\sum_{b=0}^{m}\sum_{c=0}^{b}\frac{n!\,m!}{a!\,(n-a)!\,(m-b)!\,c!\,(b-c)!}X_a Y_c\frac{(n-a)!}{(n-a-m+b)!}\left(\frac{2\alpha_1\alpha_0}{\alpha_2^2}\right)^{m-b}$$

$$\times\left(\frac{\alpha_1\alpha_0^2}{\alpha_2^2}\Delta x\right)^{(n-a)-(m-b)}\left(\frac{\alpha_0^3}{\alpha_2^2}\Delta x - 2\alpha_0\Delta x\right)^{b-c}.$$

(A4.1.21)

APPENDIX A4.2

The Vibrational Overlap Integral $\mathcal{I}_{mn}$ expressed in a simpler form.

We would like to express the vibrational overlap integral $\mathcal{I}_{mn}$ in a different form from (A4.1.21)

The expression (A4.1.21) for $\mathcal{I}_{mn}$ contains the summation

$$S_{mn} = \sum_{a=0}^{n}\sum_{b=0}^{m}\sum_{c=0}^{b} \frac{X_a Y_c \left(\frac{2\alpha_1\alpha_0}{\alpha_2^2}\right)^{m-b}\left(\frac{\alpha_1\alpha_0^2\Delta x}{\alpha_2^2}\right)^{(n-a)-(m-b)}}{a!\,c!\,(m-b)!\,(b-c)!\,(n-a-m+b)!}\left[\alpha_0\Delta x\left(\frac{\alpha_0^2}{\alpha_2^2}-2\right)\right]^{b-c}. \tag{A4.2.1}$$

where

$$X_a = \left\{2\left[\frac{\alpha_1^2}{\alpha_2^2}-1\right]\right\}^{\frac{a}{2}}(a-1)(a-3)\cdots 5.3.1 \quad (a \text{ even})$$

$$= 0 \quad (a \text{ odd}) \tag{A4.2.2}$$

$$Y_c = \left\{2\left[\frac{\alpha_0^2}{\alpha_2^2}-1\right]\right\}^{\frac{c}{2}}(c-1)(c-3)\cdots 5.3.1 \quad (c \text{ even})$$

$$= 0 \quad (c \text{ odd}).$$

We define the parameter $\delta = \dfrac{\omega_0-\omega_1}{\omega_0+\omega_1}$ (A4.2.3) and express some of the earlier factors in terms of δ,

$$\frac{\alpha_0^2}{\alpha_2^2} - 1 = \delta \qquad \frac{\alpha_1^2}{\alpha_2^2} - 1 = -\delta.$$

Using (A4.2.2) and (A4.2.4) we find that

$$S_{mn} = \sum_{a=0,2}^{n}\sum_{b=0}^{m}\sum_{c=0,2}^{b} \frac{(-2\delta)^{\frac{a}{2}}(2\delta)^{\frac{c}{2}}\left(\frac{2}{\alpha_0\Delta x}\right)^{m-b}\left[\alpha_1\Delta x(1+\delta)\right]^{n-a}\left[\alpha_0\Delta x(\delta-1)\right]^{b-c}}{(m-b)!\,(b-c)!\,(n-a-m+b)!\,a(a-2)\cdots 2\,c(c-2)\cdots 2}. \tag{A4,2,5}$$

Now, we write

$$a = 2a'$$

so that

$$
\begin{aligned}
& a(a-2)\cdots 2 \\
&= 2a'(2a'-2)\cdots 2 \\
&= 2(a')2(a'-1)\cdots 2(1) \\
&= 2^{a'}a'! .
\end{aligned}
\tag{A4.2.6}
$$

Thus,

$$S_{mn} = \sum_{a'=0,1}^{n/2} \sum_{b=0}^{m} \sum_{c'=0,1}^{b/2} \frac{(-2\delta)^{a'}(2\delta)^{c'}\left(\frac{2}{\alpha_0\Delta x}\right)^{m-b}\left[\alpha_1\Delta x(1+\delta)\right]^{n-2a'}\left[\alpha_0\Delta x(\delta-1)\right]^{b-2c'}}{a'!\,c'!\,2^{(a'+c')}(m-b)!\,(b-2c')!\,(n-2a'-m+b)!} . \tag{A4.2.7}$$

This is

$$S_{mn} = \sum_{a=0}^{n/2} \sum_{b=0}^{m} \sum_{c=0}^{b/2} \frac{\delta^{a+c}(-1)^a\left(\frac{\alpha_0\Delta x}{2}\right)^{b-m}\left[\alpha_1\Delta x(1+\delta)\right]^{n-2a}\left[\alpha_0\Delta x(\delta-1)\right]^{b-2c}}{a!\,c!\,(m-b)!\,(b-2c)!\,(n-2a-m+b)!} . \tag{A4.2.8}$$

Writing $b' = m-b$, S_{mn} becomes

$$S_{mn} = \sum_{a=0}^{n/2} \sum_{b'=0}^{m} \sum_{c=0}^{(m-b')/2} \frac{\delta^{a+c}(-1)^a\left(\frac{\alpha_0\Delta x}{2}\right)^{-b'}\left[\alpha_1\Delta x(1+\delta)\right]^{n-2a}\left[\alpha_0\Delta x(\delta-1)\right]^{m-b'-2c}}{a!\,c!\,b'!\,(m-b'-2c)!\,(n-2a-b')!} . \tag{A4.2,9}$$

Using (A4.1.21) and (A4.2.9) we finally obtain,

$$
\begin{aligned}
I_{mn} = {} & \frac{(\alpha_1\alpha_0)^{1/2}}{\alpha_2}(n!\,m!)^{1/2}\exp\left[-\frac{\alpha_0^2\Delta x^2}{4}(1-\delta)\right]\left[\frac{\alpha_1\Delta x(1+\delta)}{\sqrt{2}}\right]^n\left[\frac{\alpha_0\Delta x(\delta-1)}{\sqrt{2}}\right] \\
& \times \sum_{a=0}^{n/2} \sum_{b=0}^{m} \sum_{c=0}^{(m-b)/2} \frac{\delta^{c+a}(-1)^a\left(\frac{\alpha_0\Delta x}{2}\right)^{-b}\left[\alpha_1\Delta x(1+\delta)\right]^{-2a}\left[\alpha_0\Delta x(\delta-1)\right]^{-b-2c}}{a!\,c!\,b!\,(m-b-2c)!\,(n-2a-b)!} .
\end{aligned}
\tag{A4.2,10}
$$

APPENDIX A4.3

Calculation of the energy-gap law.

We have shown (4.12) that,

$$W_{T=0} \cong \frac{2|K|^2\pi}{\hbar^2\omega_0} C^2 p! \exp(-2E) (\delta/2)^p [(p/2)!]^{-2}. \qquad (A4.3.1)$$

When $p = \frac{\Delta E}{\hbar\omega_0} \gg 1$ we approximate $p!$ by the Stirling approximation

$$\frac{1}{p!} \sim (2\pi p)^{-\frac{1}{2}} p^{-p} e^{p}. \qquad (A4.3.2)$$

Similarly,

$$\frac{1}{(p/2)!} \sim (\pi p)^{-\frac{1}{2}} \left(\frac{p}{2}\right)^{-\frac{p}{2}} e^{p/2} \text{ , so that } \frac{1}{[(p/2)!]^2} \sim (\pi p)^{-1} (p/2)^{-p} e^{p} \qquad (A4.3.3)$$

Thus, substituting (A4.3.2) and (A4.3.3) into (A4.3.1)

$$W_{T=0} \cong \frac{2|K|^2\pi}{\hbar^2\omega_0} C^2 \exp(-2E) \left(\frac{\pi p}{2}\right)^{-\frac{1}{2}} \delta^p \qquad (A4.3.4)$$

Writing, $\delta^p = \exp[\log \delta^p] = \exp[p \log \delta] = \exp\left[-\frac{\Delta E}{\hbar\omega_0}\{-\log \delta\}\right].$

We have derived the energy gap law

$$W_{T=0} \cong \frac{2|K|^2\pi}{\hbar^2\omega_0} C^2 \exp[-2E] \left(\frac{\pi p}{2}\right)^{-\frac{1}{2}} \exp\left[-\frac{\Delta E}{\hbar\omega_0}\{-\log \delta\}\right].$$

(A4.3.5)

PART II

The Molecular Crystal Model

CHAPTER 5

The Molecular Crystal Model

In this chapter we develop Holstein's[1] molecular crystal model (M.C.M.) so that it may be used to calculate recombination rates. The principal difference between this model and the S.C.C.M. is the coupling of the electron to all the crystalline modes of vibration rather than to just one local mode. A major advantage of this model is that the system relaxes into a continuum of final energy states provided by the dispersion of the crystalline modes thus allowing well defined transition rates. Although the calculation of the recombination rate (5.32) is quite general the final evaluations of this expression in the various special cases are all restricted to the limit of zero dispersion. We will find the same non-radiative transition rates resulting as have already been derived using the S.C.C.M. The recombination rates will be evaluated taking explicit account of finite dispersion in Chapter 8.

In this chapter we review the M.C.M. originally developed by Holstein[1] and extend the model to include two electronic states on one molecule and non-adiabatic perturbation terms in the Hamiltonian. The M.C.M. consists of a one-dimensional row of diatomic harmonic oscillators which are coupled to one another by bilinear intermolecular terms.

The Hamiltonian for the M.C.M. is,

$$H_T = H_e + H_L \tag{5.1}$$

where
$$H_L = \sum_{m=1}^{N} \left\{ -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2 x_m^2 + \frac{1}{2}M\omega_1^2 x_m x_{m+1} \right\} \tag{5.2}$$

and
$$H_e = -\frac{\hbar^2}{2m_e}\nabla_r^2 + \sum_{m=1}^{N} U(\underline{r} - m\underline{a}, x_m). \tag{5.3}$$

In these expressions, N is the number of molecules in the crystal, m_e and M are the electronic and molecular masses respectively, while $-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2}$ and $\frac{1}{2}M\omega_0^2 x_m^2$ are respectively the kinetic and harmonic potential energies of the m'th diatomic molecule. The bilinear terms which couple together adjacent molecules are $\frac{1}{2}M\omega_1^2 x_m x_{m+1}$. The electron's kinetic energy is $\frac{-\hbar^2}{2m_e}\nabla_r^2$, while the potential in which it moves due to the m'th molecule $U(\underline{r}-m\underline{a},x_m)$ displays a parametric dependence on the local coordinate, x_m.

We follow the view adopted in the S.C.C.M. regarding the electron-lattice interaction assuming the Born-Oppenheimer treatment to be valid.

The electronic wavefunctions which are localised on the m'th molecular sites, $\varphi_i(\underline{r}-m\underline{a},x_m)$ are solutions of

$$\left[\frac{-\hbar^2}{2m_e}\nabla_r^2+U(\underline{r}-m\underline{a},x_m)\right]\varphi_i(\underline{r}-m\underline{a},x_m)=E_i(x_m)\varphi_i(\underline{r}-m\underline{a},x_m) \tag{5.4}$$

and a linear electron-lattice interaction is assumed as in the S.C.C.M.,

$$E_i(x_m)=E_i-A_i x_m. \tag{5.5}$$

We are here considering the electronic state to be determined by only one of the potentials, $U(\underline{r}-p\underline{a},x_p)$. Thus, the resulting electronic levels are strictly localised small polaron states and not extended states. The effect of the electronic transfer integrals

$$J=\int\varphi^*(\underline{r}-(p+1)x_{p+1})\,U[\underline{r}-(p+1)\underline{a},x_{p+1}]\,\varphi(\underline{r}-p\underline{a},x_p)\,d\underline{r},$$

which Holstein[1] used to obtain electronic hopping motion is also not included here. These assumptions are made as we are here interested only in electronic recombination between localised states on one molecular site. The inclusion of the transfer integrals J would result in recombination processes in which the electron could hop to a neighbouring site. However, the inclusion of the lattice coupling terms $\frac{1}{2}M\omega_1^2 x_p x_{p+1}$ is essential if we are to allow for energy dissipation.

Following the Born-Oppenheimer treatment the electronic energy eigenvalue $E_i(x_m)$ then forms part of the lattice potential energy so that the vibrational states $\mathcal{F}$ are solutions of

$$\left\{\sum_{m=1}^{N}\left[\frac{-\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2}+\frac{1}{2}M\omega_0^2 x_m^2+\frac{1}{2}M\omega_1^2 x_m x_{m+1}\right]+E_i-A_i x_p\right\}\mathcal{F}=E\mathcal{F}. \qquad (5.6)$$

Changing to normal coordinates $\{q_k\}$ defined by

$$q_k=\left(\frac{2}{N}\right)^{\frac{1}{2}}\sum_{g=1}^{N}x_g\sin(kg+\pi/4) \qquad (5.7)$$

the vibrational states $\mathcal{F}$ are solutions of

$$\left\{\sum_{k}\frac{-\hbar^2}{2M}\frac{\partial^2}{\partial q_k^2}+\frac{1}{2}M\omega_k^2\left(q_k-\Delta q_{k,p}^{(i)}\right)^2+E_i\right\}\mathcal{F}=E\mathcal{F} \qquad (5.8)$$

where the displacement of the k'th normal mode, $\Delta q_{k,p}^{(i)}$ is

$$\Delta q_{k,p}^{(i)}=\left(\frac{2}{N}\right)^{\frac{1}{2}}\frac{A_i}{M\omega_k^2}\sin(kp+\pi/4). \qquad (5.9)$$

The dispersion relation of the normal modes is given by

$$\omega_k^2 = \omega_0^2 + \omega_1^2 \cos k, \qquad (5.10)$$

where $k = \frac{2\pi K}{N}$ and $-(N-1) \leqslant K \leqslant (N-1)$.

The solution of equation (5.8) for the lattice wavefunctions $\mathcal{F}$ is,

$$\mathcal{F} = \prod_k \Phi_{n_k^i}\left[\alpha_k\left(q_k - \Delta q_{k,p}^{(i)}\right)\right] = \Phi_{i,\{n_k^i\}}, \qquad (5.11)$$

where the Φ 's are simple harmonic oscillator functions given by

$$\Phi_n(\alpha q) = N_n H_n(\alpha q) \exp\left(-\tfrac{1}{2}\alpha^2 q^2\right). \qquad (5.12)$$

In this expression $H_n(\alpha q)$ are the standard Hermite polynomials, $\alpha = \left(\frac{M\omega}{\hbar}\right)^{\frac{1}{2}}$ and $N_n = \left(\frac{\alpha}{\pi^{\frac{1}{2}} 2^n n!}\right)^{\frac{1}{2}}$.

As has just been shown, in the Born-Oppenheimer picture the zero'th order solution to the Schrödinger equation $H_T \Psi = \varepsilon \Psi$ is a simple product of electronic and lattice wavefunctions $\varphi_i(\underline{r} - p\underline{a}, x_p)\mathcal{F}$. However, we will find that the configuration dependence of the electronic wavefunction ensures that these states $\varphi_i(\underline{r} - p\underline{a}, x_p)\mathcal{F}$ are not stationary. Thus, if initially at $t = 0$ the electron is in its excited state due to the absorption of radiation, there is a finite probability that as time developes the electron will return to its ground state.

The Schrodinger equation is,

$$i\hbar \frac{d\Psi}{dt} = H_T \Psi, \qquad (5.13)$$

and we consider the following general solution,

$$\Psi = \sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\, \varphi_i(\underline{r} - p\underline{a}, x_p) \prod_k \Phi_{n_k^i}\left[\alpha_k\left(q_k - \Delta q_{k,p}^{(i)}\right)\right] \exp\left[-i E_{i,\{n_k^i\}} \frac{t}{\hbar}\right]. \qquad (5.14)$$

Substituting (5.14) into (5.13) the solution for $a_{0,\{m_k^0\}}$ is found, assuming the ground electronic state is not occupied at $t=0$. The details of this calculation are in Appendix A5.1.. We find, (A5.1.11),

$$i\hbar\,\dot{a}_{0,\{m_k^0\}} = \sum_{\{n_k^1\}} a_{1,\{n_k^1\}}(t)\exp\left[\frac{it}{\hbar}\left(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}}\right)\right]\left[\sum_{k'} K''_{k',1}\prod_k I_{m_k^0,n_k^1}+K'_{k',1}I'_{m_{k'}^0,n_{k'}^1}\prod_{k\neq k'} I_{m_k^0,n_k^1}\right],$$

where (5.15)

$$\left.\begin{aligned}
K''_{k,1} &= \int d\underline{r}\,\varphi_0^*(\underline{r}-p\underline{a},x_p)\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_{\gamma k}^2}\varphi_1(\underline{r}-p\underline{a},x_p)\right\}\\
K''_{k,1} &= \int d\underline{r}\,\varphi_0^*(\underline{r}-p\underline{a},x_p)\left\{-\frac{\hbar^2}{M}\frac{\partial}{\partial q_{\gamma k}}\varphi_1(\underline{r}-p\underline{a},x_p)\right\}\\
I_{n_k^0,n_k^1} &= \int dq_{\gamma k}\,\Phi_{n_k^0}\left[\alpha_k(q_{\gamma k}-\Delta q^{(0)}_{\gamma k,p})\right]\Phi_{n_k^1}\left[\alpha_k(q_{\gamma k}-\Delta q^{(1)}_{\gamma k,p})\right]\\
I'_{n_k^0,n_k^1} &= \int dq_{\gamma k}\,\Phi_{n_k^0}\left[\alpha_k(q_{\gamma k}-\Delta q^{(0)}_{\gamma k,p})\right]\frac{\partial}{\partial q_{\gamma k}}\Phi_{n_k^1}\left[\alpha_k(q_{\gamma k}-\Delta q^{(1)}_{\gamma k,p})\right].
\end{aligned}\right\} \quad (5.16)$$

The transition probability W_T is calculated by summing over all the final vibrational states,

$$W_T = \sum_{\{m_k^0\}}\frac{d}{dt}\left|a_{0,\{m_k^0\}}(t)\right|^2. \quad (5.17)$$

This expression is evaluated in Appendix A5,1., in which we find,

$$\begin{aligned}
W_T = \frac{2\pi}{\hbar^2}\sum_{\{m_k^0\},\{n_k^1\}}&\left[1-\exp(-\beta\hbar\omega_0)\right]\exp\left[-\beta\hbar\omega_0\right]^{n_k^1}\Big\{\sum_{k'}|K''_{k',1}|^2\prod_k I^2_{m_k^0,n_k^1}\\
&+\sum_{k'}|K'_{k',1}|^2 I'^2_{m_{k'}^0,n_{k'}^1}\prod_{k\neq k'} I^2_{m_k^0,n_k^1}\\
&+\sum_{k'}|K''_{k',1}K'_{k',1}|\,I_{m_{k'}^0,n_{k'}^1}I'_{m_{k'}^0,n_{k'}^1}\prod_{k\neq k'} I^2_{m_k^0,n_k^1}\\
&+\sum_{k'}\sum_{k''}|K'_{k',1}K'_{k'',1}|\left(I_{n_{k'}^0,n_{k'}^1}I'_{n_{k'}^0,n_{k'}^1}\right)\left(I_{n_{k''}^0,n_{k''}^1}I'_{n_{k''}^0,n_{k''}^1}\right)\prod_{k\neq k',k''} I^2_{n_k^0,n_k^1}\Big\}\\
&\times\delta\left(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}}\right).
\end{aligned} \quad (5.18)$$

Thus, the configuration dependence of the electronic wavefunction gives rise to the nuclear kinetic energy acting as a small perturbation on the zero'th order states. These perturbations are known as the 'non-adiabatic' terms. We will follow the nomenclature adopted for the S.C.C.M. and always refer to the first two terms in expression (5.18) as the 'standard' and the 'derivative' terms respectively. The remaining two terms are the contributions to the transition rate from the interference terms. In the remaining part of this chapter we shall calculate the transition probabilities using only the standard non-adiabatic terms which give results which may be interpreted physically in a fairly straightforward fashion.

Having found the general form of the transition probability (5.18) we now evaluate the transition probability using the standard terms and following the procedure adopted by Holstein[1] in his well known paper.

The following definitions are made:

$$W_T^{(1)} = \frac{1}{Z} \sum_{\{n_k^1\}} W_{\{n_k^1\}}^{(1)} \exp\left[-\sum_k \beta\hbar\omega_k\left(n_k^1 + \tfrac{1}{2}\right)\right], \qquad (5.19)$$

where $$W_{\{n_k^1\}}^{(1)} = \sum\nolimits_{\{n_k^0\}} W\left(1, \{n_k^1\} \rightarrow 0, \{n_k^0\}\right), \qquad (5.20)$$

and $$Z = \sum_{\{n_k\}} \exp\left[-\beta\hbar\omega_k\left(n_k + \tfrac{1}{2}\right)\right].$$

Now,

$$W\left(1, \{n_k^1\} \rightarrow 0, \{n_k^0\}\right)$$

$$= \frac{2}{\hbar^2} \sum_{k'} |K_{k',1}^{11}|^2 \Pi_k I^2_{n_k^0, n_k^1} \frac{\partial}{\partial t} \Omega\left[\sum\nolimits_k \hbar\omega_k\left(n_k^0 - n_k^1\right) - \Delta E\right], \qquad (5.22)$$

where $\frac{\partial}{\partial t}\Omega(x) = \frac{1}{2}\int_{-t}^{t} \exp\left[\frac{ixt'}{\hbar}\right] dt'$ is the Dirichlet representation of the Dirac delta function.

The non-adiabatic terms may be written,

$$\sum_{k'} |K''_{k',1}|^2 = \sum_{k'} \left| \int d\underline{r}\, \varphi_0^*(\underline{r}-p\underline{a}, x_p) \left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{\gamma_{k'}}^2} \varphi_1(\underline{r}-p\underline{a}, x_p) \right\} \right|^2$$

$$= \sum_{m} \left| \int d\underline{r}\, \varphi_0^*(\underline{r}-p\underline{a}, x_p) \left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_m^2} \varphi_1(\underline{r}-p\underline{a}, x_p) \right\} \right|^2$$

$$= \left| \int d\underline{r}\, \varphi_0^*(\underline{r}-p\underline{a}, x_p) \left\{ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_p^2} \varphi_1(\underline{r}-p\underline{a}, x_p) \right\} \right|^2, \quad \text{so that}$$

$$\sum_{k'} |K''_{k',1}|^2 = |K_1|^2. \qquad (5.23)$$

To progress with (5.22) we require to evaluate the vibrational overlap integral $I_{n_k^0, n_k^1}$,

$$I_{n_k^0, n_k^1} = \int dq_{\gamma_k}\, \Phi_{n_k^1}[\alpha_k(q_{\gamma_k} - \Delta q_{\gamma_{k,p}}^{(1)})]\, \Phi_{n_k^0}[\alpha_k(q_{\gamma_k} - \Delta q_{\gamma_{k,p}}^{(0)})]. \qquad (5.24)$$

Writing the relative displacement $\Delta q_{\gamma_{k,p}}$ as

$$\Delta q_{\gamma_{k,p}} = \Delta q_{\gamma_{k,p}}^{(1)} - \Delta q_{\gamma_{k,p}}^{(0)} \qquad (5.25)$$

the vibrational overlap integral may be written as

$$I_{n_k^0, n_k^1} = \int dq_{\gamma_k}\, \Phi_{n_k^0}[\alpha_k q_{\gamma_k}]\, \Phi_{n_k^1}[\alpha_k(q_{\gamma_k} - \Delta q_{\gamma_{k,p}})]. \qquad (5.26)$$

The general expression for the vibrational overlap integral $I_{n_k^0, n_k^1}$ derived in the S.C.C.M. which was evaluated in Chapter 3 is

$$I_{n_k^0, n_k^1} = \exp\left[-\tfrac{1}{4}\alpha_k^2 \Delta q_{\gamma_k}^2\right] (n_k^0!\, n_k^1!)^{\frac{1}{2}} \left(\frac{\alpha_k^2 \Delta q_{\gamma_k}^2}{2}\right)^{\frac{n_k^0 + n_k^1}{2}} \sum_{a=0}^{n_k^1} \frac{(-1)^{n_k^0 - a} \left(\frac{\alpha_k \Delta q_{\gamma_k}}{\sqrt{2}}\right)^{-2a}}{a!\,(n_k^0 - a)!\,(n_k^1 - a)!}.$$

For the M.C.M., in which the relative displacement

$\Delta q_{\gamma_k} = \left(\frac{2}{N}\right)^{\frac{1}{2}} \frac{(A_1 - A_0)}{M\omega_0^2} \sin(kp + \pi/4)$ we retain only those terms in

$I_{n_k^0, n_k^1}^2$ up to order $\frac{1}{N}$.

Doing this the only non-zero $I_{n_k^0, n_k^1}$ are found to be

$$\left.\begin{aligned} I_{n_k^1+1, n_k^1} &= -(1+n_k^1)^{1/2}\left(\frac{\gamma_k}{2N}\right)^{1/2} \\ I_{n_k^1, n_k^1} &= 1-(n_k^1+\tfrac{1}{2})\frac{\gamma_k}{2N} \\ I_{n_k^1-1, n_k^1} &= (n_k^1)^{1/2}\left(\frac{\gamma_k}{2N}\right)^{1/2}. \end{aligned}\right\} \qquad (5.27)$$

where, the coupling constant, $\gamma_k = \dfrac{(A_1-A_0)^2}{M\omega_k^2\hbar\omega_k}$. (5.28)

Using the definitions (5.19), (5.20) and (5.21) the transition rate $W_T^{(1)}$ is found to be,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2 Z}\sum_{\{n_k^0\},\{n_k^1\}}\int_{-t}^{t}\exp\left[-\sum_k \beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\right]\prod_k I^2_{n_k^0, n_k^1}\exp\left[\frac{it'}{\hbar}\left\{\sum_k \hbar\omega_k(n_k^0-n_k^1)-\Delta E\right\}\right], \qquad (5.28)$$

This becomes, on using the expressions for the vibrational overlap integrals, (5,27),

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2 Z}\sum_{\{n_k^1\},\{n_k^0\}}\int_{-t}^{t}\exp\left[-\sum_k \beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\right]\prod_k\left\{\left[1-(n_k^1+\tfrac{1}{2})\frac{\gamma_k}{N}\right]\delta_{n_k^1, n_k^0}\right.$$
$$\left.+\left(\frac{\gamma_k}{2N}\right)\left[(1+n_k^1)\delta_{n_k^0, n_k^1+1}+n_k^1\,\delta_{n_k^0, n_k^1-1}\right]\exp\left[\frac{it'}{\hbar}\left\{\sum_k \hbar\omega_k(n_k^0-n_{k'}^1)-\Delta E\right\}\right]\right]dt'. \qquad (5,29)$$

which is, on performing the sum over the final vibrational quantum numbers $\{n_k^0\}$,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2 Z}\sum_{\{n_k^1\}}\int_{-t}^{t}dt'\exp\left[-\sum_k \beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\right]\prod_k\left\{\left[1-(n_k^1+\tfrac{1}{2})\frac{\gamma_k}{N}\right]\right.$$
$$\left.+\frac{\gamma_k}{2N}\left[(1+n_k^1)\exp(it'\omega_k)+n_k^1\exp(-it'\omega_k)\right]\exp\left[\frac{-it'}{\hbar}\Delta E\right]\right. . \qquad (5.30)$$

We take the thermal average of this expression,

$\dfrac{1}{Z}\sum_{\{n_k^1\}}[\quad]\exp[-\beta\hbar\omega_k(n_k+\tfrac{1}{2})]$ by replacing each quantum number n_k^1 by its thermal average value, $\langle n_k^1\rangle_T = [\exp(\beta\hbar\omega_k)-1]^{-1}$ following Holstein

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\int_{-t}^{t}\prod_k\left\{\left[1-(n_k+\tfrac{1}{2})\frac{\gamma_k}{N}\right]+\frac{\gamma_k}{2N}\left[(1+n_k)\exp(i\omega_k t')+n_k\exp(-i\omega_k t')\right]\right\}\exp\left[-\frac{i\Delta E t'}{\hbar}\right]. \qquad (5.31)$$

Writing the exponentials of imaginary argument in terms of sine and cosine functions, we obtain,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\int_{-t}^{t} dt' \exp\Big\{\sum_k \frac{\gamma_k}{N}\Big[-(n_k+\tfrac{1}{2}) + \tfrac{1}{2}\big\{(1+n_k)\exp(i\omega_k t') + n_k\exp(-i\omega_k t')\big\}\Big]\Big\}\exp\Big(-\frac{i\Delta E t'}{\hbar}\Big)$$

which becomes

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\int_{-t}^{t} \exp\Big\{\sum_k \frac{\gamma_k}{N}\Big[-(n_k+\tfrac{1}{2}) + (n_k+\tfrac{1}{2})\cos\omega_k t' + \tfrac{i}{2}\sin\omega_k t'\Big]\Big\}\exp\Big(-\frac{i\Delta E t'}{\hbar}\Big)dt'. \tag{5.32}$$

This expression for the transition rate, (5.32) has also been derived by O'Rourke[24] (1953) [his equation (29), p.268]. We can also show that this transition probability and that derived by Englman and Jortner[2] (1970) [their equation (3.4), p.152] are identical. An alternative form of expression (5.32) is obtained by taking the real part, with the imaginary part being, of course, zero. Doing this and writing $n_k + \frac{1}{2} = \frac{1}{2}\coth\frac{\beta\hbar\omega_0}{2}$ (5.32) becomes,

$$W_T = \frac{|K_1|^2}{\hbar^2}\exp\Big\{-\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\Big\}\int_{-t}^{t}\exp\Big[\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\sum_k\frac{\cos\omega_k t'}{N}\Big]$$

$$\times\cos\Big[\frac{\gamma_0}{2}\sum_k\frac{\sin\omega_k t'}{N} - \frac{\Delta E}{\hbar}t'\Big]dt'. \tag{5.33}$$

We introduce the change of variable $t' = \frac{i\beta\hbar}{2} + \tau$, so that expression (5,33) becomes,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\Big(\frac{\Delta E\beta}{2}\Big)\int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}}\exp\Big(-\frac{i\Delta E}{\hbar}\tau\Big)\exp\Big[-\sum_k\frac{2\gamma_k}{N}\Big(\coth\frac{\beta\hbar\omega_k}{2} - \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\Big)\Big]d\tau. \tag{5.34}$$

This expression is evaluated in the limit of high temperature $(\beta\hbar\omega_0 \ll 1)$ and strong coupling $\frac{\gamma_0}{2} = \frac{E_M}{\hbar\omega_0} \gg 1$, using a saddle point method. We find that the exact condition for the applicability of the saddle point technique is $\dfrac{-p}{\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}} \ll 1$, while the saddle points occur at

$$\tau_1 = \frac{\pi n}{\omega_0} \text{ (n, integer) and } \tau_2 = \frac{-p}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}, \tag{5.36}$$

having written τ in complex form, $\tau = \tau_1 + i\tau_2$. All the calculational details of this saddle point method are to be found in Appendix A5.2.

We assume that the only significant contribution to the transition rate arises from the central saddle point $(\tau_1 = 0)$. This assumption may be justified if there is finite dispersion, but in the zero dispersion limit considered here each saddle point actually makes an equal contribution to the transition rate. The explicit consideration of the effect of dispersion on the transition rates in the M.C.M. is left until Chapter 8.

We find that in the high temperature, $\beta\hbar\omega_0 \ll 1$, strong coupling, $\frac{E_M}{\hbar\omega_0} \gg 1$, limit the same temperature activated transition rate results as has been derived previously (3.22) using the S.C.C.M.,

$$W_T^{(1)} = \frac{|K|^2}{\hbar^2}\left[\frac{\pi}{kTE_M}\right]^{\frac{1}{2}}\exp(-\beta E_b), \tag{5.37}$$

where the activation energy E_b is given by

$$E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M}. \tag{5.38}$$

Finally, we have evaluated the transition rate at the absolute zero of temperature, $W_{T=0}$ starting from expression (5.34). The major contribution to the integral is assumed to come from an interval $\frac{2\pi}{\omega_0}$ centred at the origin, although once again this assumption is only valid if dispersion is present. The same result is derived for the transition rate $W_{T=0}$ in Appendix A5.3 as has previously been obtained using the S.C.C.M. (3.19),

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\left(\frac{E_M}{\hbar\omega_0}\right)^p\frac{1}{p!}. \tag{5.39}$$

Thus, the M.C.M. yields the same recombination rates as the S.C.C.M. which is at first sight a surprising result considering the differences between the two models. However, this feature may be clarified as follows. We consider a crystal which consists of N Einstein oscillators which are not coupled together. Then, the description of the lattice vibrations in terms of either N local oscillators or N crystalline modes of vibration which have no dispersion is equally valid. Only the coupling together of the local oscillators and the resulting finite dispersion in the crystalline modes distinguishes the two descriptions. Thus, the prediction of identical transition rates by the S.C.C.M. and the M.C.M. in which there is no dispersion may not be so surprising after all.

Summary

In this chapter we have calculated recombination rates using the M.C.M. The general assumptions made to calculate the recombination rates are very similar to those previously used for the S.C.C.M. in Chapter 3. In particular, the additional electron considered is assumed to be coupled linearly to one local oscillator, (5.5). However, each oscillator is now coupled to its nearest neighbours so that when the situation is described in terms of normal coordinates, the electron is coupled to all of these modes (5.8). The general expression derived for the recombination rate is given by equation (5.18). In this chapter we have only considered the non-radiative transitions resulting from the 'standard' non-adiabatic terms in the limit of zero dispersion. In the high temperature $\beta\hbar\omega_0 \ll 1$, strong coupling $\frac{E_M}{\hbar\omega_0} \gg 1$ limit a saddle point method has been used to derive the activation energy transition rate, (5.38). The same result has also been derived at the absolute zero of temperature, (5.38) as occurs in the S.C.C.M. However, the method of derivation is quite different from the saddle point technique used by Englman and Jortner[2].

It is important to realise that although the result for the transition probabilities, equation (5.32) was previously derived by O'Rourke[24], this was on the basis of a different model. While the electronic state in

O'Rourke's model is quite different from that in the M.C.M. both models feature an electron-lattice interaction with a linear coupling to all the crystalline modes of vibration. This results in the lattice state being a product of displaced simple harmonic oscillator wavefunctions. Thus, both models make the same predictions for that factor in the relaxation rate which arises from the lattice states but give different non-adiabatic factors K_1^2 [in equation (5.38)] as these depend on the electronic wavefunctions. Thus, even although the M.C.M. is a specific model the results for recombination rates derived using it are much more general.

APPENDIX A5.1

Derivation of the transition rates in the Molecular Crystal Model.

The Schrödinger equation is, $i\hbar\frac{d\Psi}{dt} = H_T\Psi$ (A5.1.1)

where for the M.C.M., the Hamiltonian is $H_T = H_e + H_L$, where

$$H_e = -\frac{\hbar^2}{2m_e}\nabla_r^2 + \sum_{m=1}^{N} U(\underline{r} - m\underline{a}, x_m)$$

$$H_L = \sum_{m=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2 x_m^2 + \frac{1}{2}M\omega_1^2 x_m x_{m+1}\right). \tag{A5.1.2}$$

We write as a general solution of (A5,1,1),

$$\Psi = \sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\varphi_i(\underline{r} - p\underline{a}, x_p)\Pi_k\Phi_{n_k^i}[\alpha_k(q_{\gamma k} - \Delta x_{k,p}^{(i)})]\exp\left[-i\frac{E_{i,\{n_k^i\}}t}{\hbar}\right]. \tag{A5.1.3}$$

When we substitute (A5,1,3) into (A5,1,1) we find that,

$$i\hbar\sum_{i,\{n_k^i\}}\dot{a}_{i,\{n_k^i\}}(t)\varphi_i\Pi_k\Phi_{n_k^i}\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$+i\hbar\sum_{i,\{n_k^i\}}a_{i,\{n_k^i\}}(t)\varphi_i\Pi_k\Phi_{n_k^i}\left(-\frac{iE_{i,\{n_k^i\}}}{\hbar}\right)\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$=\sum_{i,\{n_k^i\}}a_{i,\{n_k^i\}}(t)\left\{\sum_{m=1}^{N}-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2x_m^2 + \frac{1}{2}M\omega_1^2x_mx_{m+1} - \frac{\hbar^2}{2m_e}\nabla_r^2 + \sum_{m=1}^{N}U(\underline{r} - m\underline{a}, x_m)\right\}$$

$$\times\left\{\varphi_i(\underline{r} - p\underline{a}, x_p)\Pi_k\Phi_{n_k^i}[\alpha_k(q_k - q_{\gamma k,p}^{(i)})]\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]\right\}. \tag{A5.1.4}$$

The R.H.S. of (A5.1.4) is

$$\sum_{i,\{n_k^i\}}a_{i,\{n_k^i\}}(t)\left\{\sum_{m=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2x_m^2 + \frac{1}{2}M\omega_1^2x_mx_{m+1} + E_i - A_ix_p\right) + \sum_{\substack{m=1\\m\neq p}}^{N}U(\underline{r} - m\underline{a}, x_m)\right\}$$

$$\times\varphi_i(\underline{r} - p\underline{a}, x_p)\Pi_k\Phi_{n_k^i}[\alpha_k^i(q_{\gamma k} - \Delta q_{\gamma k,p}^{(i)})]\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]. \tag{A5.1.5}$$

The terms involving $\sum_{m=1, m\neq p}^{N} U(\underline{r}-m\underline{a}, x_m)$ will not be considered here. These terms give rise to electronic hopping motion, which Holstein has studied comprehensively.

Changing to the normal coordinates $\{q_k\}$ defined by text equation (5.7) (A5.1.5) becomes

$$\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\left\{\sum_{k'} -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_{k'}^2}+\frac{1}{2}M\omega_{k'}^2(q_{k'}-\Delta q_{k',p}^{i})^2+E_i\right\}$$

$$\times\varphi_i(\underline{r}-p\underline{a},x_p)\prod_k \Phi_{n_k^i}\left[\alpha_k^i(q_k-\Delta q_{k,p}^{(i)})\right]\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]. \qquad \text{(A5.1.6)}$$

We are able to write (A5,1,6) as,

$$\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)E_{i,\{n_k^i\}}\varphi_i(\underline{r}-p\underline{a},x_p)\prod_k \Phi_{n_k^i}\left[\alpha_k(q_k-\Delta q_{k,p}^{(i)})\right]\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$+\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\sum_{k'} -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_{k'}^2}\varphi_i(\underline{r}-p\underline{a},x_p)\prod_k \Phi_{n_k^i}\left[\alpha_k(q_k-\Delta q_{k,p}^{(i)})\right]\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$+\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\sum_{k'} -\frac{\hbar^2}{M}\frac{\partial}{\partial q_{k'}}\varphi_i(\underline{r}-p\underline{a},x_p)\frac{\partial}{\partial q_{k'}}\Phi_{n_{k'}^i}\left[\alpha_{k'}(q_{k'}-\Delta q_{k',p}^{(i)})\right]\prod_{k\neq k'}\Phi_{n_k^i}\left[\alpha_k(q_k-\Delta q_{k,p}^{(i)})\right]$$

$$\text{where}\quad E_{i,\{n_k^i\}}=E_i+\sum_k(n_k^i+\tfrac{1}{2})\hbar\omega_k. \qquad \times\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right] \qquad \text{(A5.1.7)}$$

Combining (A5,1,7) with the L.H.S. of (A5.1.4) we find that

$$i\hbar\sum_{i,\{n_k^i\}} \dot{a}_{i,\{n_k^i\}}(t)\varphi_i\prod_k \Phi_{n_k^i}\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$=\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\sum_{k'} -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_{k'}^2}\varphi_i(\underline{r}-p\underline{a},x_p)\prod_k \Phi_{n_k^i}\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right]$$

$$+\sum_{i,\{n_k^i\}} a_{i,\{n_k^i\}}(t)\sum_{k'} -\frac{\hbar^2}{M}\frac{\partial}{\partial q_{k'}}\varphi_i(\underline{r}-p\underline{a},x_p)\frac{\partial}{\partial q_{k'}}\Phi_{n_{k'}^i}\left[\alpha_{k'}(q_{k'}-\Delta q_{k',p}^{(i)})\right]\prod_{k\neq k'}\Phi_{n_k^i}\exp\left[-iE_{i,\{n_k^i\}}\frac{t}{\hbar}\right], \qquad \text{(A5,1.8)}$$

We multiply both sides of (A5,1,8) on the left hand side by

$$\varphi_0^*(\underline{r}-p\underline{a},x_p)\prod_k \Phi_{m_k^0}\left[\alpha_k(q_k-\Delta q_{k,p}^{(0)})\right]\exp\left[+iE_{0,\{m_k^0\}}\frac{t}{\hbar}\right]$$

and then integrate over both the electronic and lattice coordinates

$$\int d\underline{r}\prod_k\int dq_k.$$

We assume that initially at $t=0$, that all the vibrational states belonging to the ground electronic state are unoccupied.

$$a_{0,\{n_k^0\}}(0) = 0.$$

We also assume that the Condon approximation is valid,

$$\int \underline{dr}\, \Pi_k \int dq_{\gamma k}\, \varphi(\underline{r}, \{q_k\}) \mathcal{F} = \int \underline{dr}\, \varphi(\underline{r}, \{q_k\}) \Pi_k \int dq_k\, \mathcal{F}. \qquad \text{(A5.1.9)}$$

We also make use of the orthogonality of the electronic wavefunctions,

$$\int \varphi_i(\underline{r} - p\underline{a}, x_p)\varphi_j^*(\underline{r} - p\underline{a}, x_p)\underline{dr} = \delta_{i,j}. \qquad \text{(A5.1.10)}$$

Having made all these approximations, (A5.1.8) becomes

$$i\hbar\, \dot{a}_{0,\{m_k^0\}}(t)$$
$$= \sum_{\{n_k^1\}} a_{1,\{n_k^1\}}(t) \Big[\sum_{k'} K''_{k',1} \Pi_k I_{m_k^0, n_k^1} + K'_{k',1} I'_{m_{k'}^0, n_{k'}^1} \Pi_{k \neq k'} I_{m_k^0, n_k^1}\Big] \exp\Big[\frac{it}{\hbar}(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})\Big]$$

where we have written (A5.1.11)

$$K''_{k,1} = \int \underline{dr}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\Big(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_{\gamma k}^2}\varphi_1(\underline{r} - p\underline{a}, x_p)\Big)$$

$$K'_{k,1} = \int \underline{dr}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\Big(-\frac{\hbar^2}{M}\frac{\partial}{\partial q_{\gamma k}}\varphi_1(\underline{r} - p\underline{a}, x_p)\Big)$$

$$I_{n_k^0, n_k^1} = \int dq_{\gamma k}\, \Phi_{n_k^0}\big[\alpha_k(q_{\gamma k} - \Delta q_{\gamma k,p}^{(0)})\big] \Phi_{n_k^1}\big[\alpha_k(q_k - \Delta q_{\gamma k,p}^{(1)})\big]$$

$$I'_{n_k^0, n_k^1} = \int dq_{\gamma k}\, \Phi_{n_k^0}\big[\alpha_k(q_{\gamma k} - \Delta q_{\gamma k,p}^{(0)})\big] \frac{\partial}{\partial q_{\gamma k}} \Phi_{n_k^1}\big[\alpha_k(q_{\gamma k} - \Delta q_{\gamma k,p}^{(1)})\big].$$

In (A5.1.11) we write

$$V_{\{m_k^0, n_k^1\}} = \sum_{k'} \Big(K''_{k',1} \Pi_k I_{m_k^0, n_k^1} + K'_{k',1} I'_{m_{k'}^0, n_{k'}^1} \Pi_{k \neq k'} I_{m_k^0, n_k^1}\Big) \qquad \text{(A5.1.12)}$$

so that we have

$$i\hbar\, \dot{a}_{0,\{m_k^0\}}(t) = \sum_{\{n_k^1\}} a_{1,\{n_k^1\}}(t)\, V_{\{m_k^0, n_k^1\}} \exp\Big[\frac{it}{\hbar}(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})\Big]. \qquad \text{(A5.1.13)}$$

Thus,

$$a_{0,\{m_k^0\}}(t) = -\sum_{\{n_k^1\}} a_{1,\{n_k^1\}}(t)\, V_{\{m_k^0, n_k^1\}} \frac{\Big\{\exp\Big[\frac{it}{\hbar}(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})\Big] - 1\Big\}}{(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})} \qquad \text{(A5.1.14)}$$

We are interested in

$$|a_{0,\{m_k^0\}}(t)|^2.$$

$$\doteq \sum_{\{n_k^1\}} a^2_{1,\{n_k^1\}} |V_{\{m_k^0, n_k^1\}}|^2 \left|\frac{\exp\Big[\frac{it}{\hbar}(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})\Big] - 1}{(E_{0,\{m_k^0\}} - E_{1,\{n_k^1\}})}\right|^2.$$

This is

$$|a_{0,\{m_k^0\}}(t)|^2=\sum_{\{n_k^1\}} a^2_{1,\{n_k^1\}}|V_{\{m_k^0,n_k^1\}}|^2\frac{2\left(1-\cos\left[\frac{t}{\hbar}(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}})\right]\right)}{(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}})^2}.$$

Now, the transition probability into the state $(0,\{m_k^0\})$ is

$$\frac{d}{dt}|a_{0,\{m_k^0\}}(t)|^2=\sum_{\{n_k^1\}} a^2_{1,\{n_k^1\}}|V_{\{m_k^0,n_k^1\}}|^2\frac{2\sin\left[\frac{t}{\hbar}(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}})\right]}{(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}})\hbar} \qquad \text{(A5.1.15)}$$

Using the relation $\lim_{t\to\infty}\frac{\sin\left(\frac{\Delta E t}{\hbar}\right)}{\pi\left(\frac{\Delta E}{\hbar}\right)}=\delta(\Delta E)$ (A5.1.16), we obtain

$$\frac{d}{dt}|a_{0,\{m_k^0\}}(t)|^2=\frac{2\pi}{\hbar}\sum_{\{n_k^1\}} a^2_{1,\{n_k^1\}}|V_{\{m_k^0,n_k^1\}}|^2\delta(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}}). \qquad \text{(A5.1.17)}$$

Now,

$$W_T=\sum_{\{m_k^0\}}\frac{d}{dt}|a_{0,\{m_k^0\}}(t)|^2.$$

We assume that the initial vibrational states have the thermal probability of occupation,

$$|a^2_{0,\{n_k^1\}}|=\frac{\prod_k\exp[-\beta\hbar\omega_k(n_k^1+\frac{1}{2})]}{Z}, \quad \text{where} \quad Z=\sum_{\{n_k^1\}}\prod_k\exp[-\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})].$$

We find

$$W_T=\frac{2\pi}{\hbar^2}\sum_{\{m_k^0\}}\sum_{\{n_k^1\}}\frac{\exp[-\beta(\sum_k\hbar\omega_k(n_k^1+\frac{1}{2}))]}{Z}|V_{\{m_k^0,n_k^1\}}|^2\delta(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}}). \qquad \text{(A5.1.18)}$$

Using the expression for $V_{\{m_k^0,n_k^1\}}$ (A5.1.10), we finally obtain for the transition rate,

$$\begin{aligned}W_T=\frac{2\pi}{\hbar^2}\sum_{\{m_k^0\}}\sum_{\{n_k^1\}}\frac{\exp[-\sum_k\beta\hbar\omega_k(n_k+\frac{1}{2})]}{Z}\Big\{&\sum_{k'}|K''_{k',1}|^2\prod_k I^2_{m_k^0,n_k^1}\\ &+\sum_{k'}|K'_{k',1}|^2 I'^2_{m_{k'}^0,n_{k'}^1}\prod_{k\neq k'}I^2_{m_k^0,n_k^1}\\ &+\sum_{k'}\sum_{k''}|K'_{k',1}K'_{k'',1}|(I_{m_{k'}^0,n_{k'}^1}I'_{m_{k'}^0,n_{k'}^1})(I_{m_{k''}^0,n_{k''}^1}I'_{m_{k''}^0,n_{k''}^1})\prod_{k\neq k',k''}I^2_{m_k^0,n_k^1}\Big\}\delta(E_{0,\{m_k^0\}}-E_{1,\{n_k^1\}}\end{aligned}$$

(A5.1.19)

This is the text equation (5.18).

APPENDIX A5.2

The evaluation of the transition probability in the high temperature $\beta\hbar\omega_0 \ll 1$ strong coupling $\alpha^2\Delta q_r^2 \gg 1$ limit using a saddle point method.

We evaluate here, expression (5,35)

$$W_T = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E \beta}{2} - \sum_k \frac{\gamma_k}{2N}\coth\frac{\beta\hbar\omega_k}{2}\right] \int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}} \exp\left[\sum_k \frac{\gamma_k}{2N}\operatorname{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau - \frac{i\Delta E}{\hbar}\tau\right] d\tau \tag{A5.2.1}$$

In the limit of zero dispersion, this becomes

$$W_T = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E \beta}{2} - \frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\right] \int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}} \exp\left[\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau - \frac{i\Delta E}{\hbar}\tau\right] d\tau\,. \tag{A5.2.2}$$

The saddle point method requires us to find the maxima of the integrand of (A5.2.2) which is

$$\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau - \frac{i\Delta E}{\hbar}\tau\,. \tag{A5.2,3}$$

At the maxima, the following condition is satisfied,

$$\frac{d}{d\tau}\left\{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau - \frac{i\Delta E}{\hbar}\tau\right\} = 0\,. \tag{A5.2.4}$$

We find this gives us the condition,

$$\sin\omega_0\tau = -\frac{i\Delta E}{\hbar}\,\frac{1}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}} \tag{A5.2.5}$$

Writing τ in its real and imaginary parts, $\tau = \tau_1 + i\tau_2$ we find that (A5,2,5) becomes,

$$\sin\omega_0\tau_1\cosh\omega_0\tau_2 + i\cos\omega_0\tau_1\sinh\omega_0\tau_2 = -\frac{i\Delta E}{\hbar}\,\frac{1}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\,. \tag{A5.2.6}$$

Equating real and imaginary parts, we obtain

$$\left.\begin{aligned} &\sin\omega_0\tau_1\cosh\omega_0\tau_2 = 0 \\ &\cos\omega_0\tau_1\sinh\omega_0\tau_2 = -\frac{\Delta E}{\hbar}\,\frac{1}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}} \end{aligned}\right\} \tag{A5.2.7}$$

Thus, the equations (A5,2,7) are satisfied provided that,

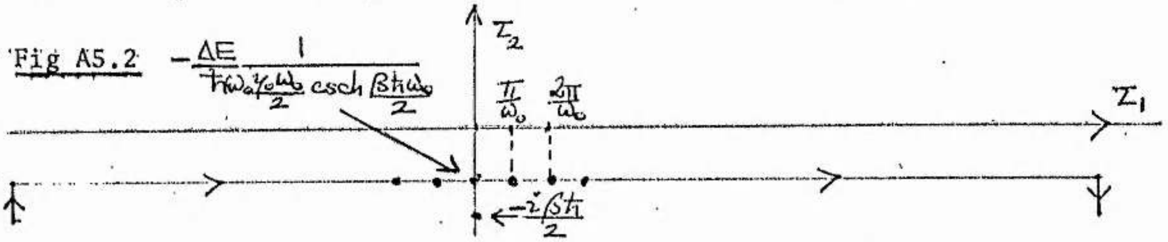
$\omega_0\tau_1 = \pi n$ (n integer) and

$$\tau_1 = \frac{\pi n}{\omega_0} \tag{A5,2,8}$$

$$\sinh\omega_0\tau_2 = -\frac{\Delta E}{\hbar}\,\frac{1}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\,. \tag{A5,2,9}$$

Hence the path of integration is as shown below in fig A5.2.

Fig A5.2



The maxima of the integrand are clearly shown on this figure. We assume here that only the maximum at $\tau_1 = 0$ contributes to the transition rate. Actually, in the zero dispersion limit each maxima makes an equal contribution. Only when dispersion becomes finite does the central maximum become dominant. We evaluate the central maximum at $\tau_1 = 0$, $\sinh\omega_0\tau_2 = -\frac{\Delta E}{\hbar\omega_0}\frac{1}{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}$. In the high temperature $\beta\hbar\omega_0 \gg 1$, strong coupling $\gamma_0 \gg 1$ limit,

$-\frac{\Delta E}{\hbar\omega_0}\frac{1}{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}} \ll 1$, so that $\sinh\omega_0\tau_2 \sim \omega_0\tau_2$.

Thus, $\tau_2 = -\frac{\Delta E}{\hbar\omega_0}\frac{1}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}$

When, $\Delta E = p\hbar\omega_0$,

$$\tau_2 = \frac{-p}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}} . \qquad \text{(A5.2.10)}$$

Substituting $\tau_1 = 0$, $\tau_2 = \frac{-p}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}$ into (A5,2,2) and expanding $\cos\omega_0\tau_1$ as $1 - \frac{\omega_0^2\tau_1^2}{2}$ we obtain

$$W_T = \frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\beta\hbar\omega p}{2} - \frac{i\Delta E}{\hbar}\left(\frac{-ip}{\frac{\gamma_0\omega_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right)\right\}$$

$$\times\exp\left\{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cosh\frac{p}{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right\}\int_{-\infty}^{\infty}\exp\left[\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\left(-\frac{\omega_0^2\tau_1^2}{2}\right)\right]d\tau_1 . \qquad \text{(A5,2,11)}$$

Using the small argument approximation for $\cosh x \sim 1 + \frac{x^2}{2}$ and the integral $\int_{-\infty}^{\infty} e^{-a^2\tau^2}d\tau = \frac{\sqrt{\pi}}{a}$ we obtain for (A5,2,11)

$$W_T = \frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{\gamma_0}{2}\left(\coth\frac{\beta\hbar\omega_0}{2} - \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right) + \frac{\beta\hbar\omega_0 p}{2} - \frac{p^2}{\frac{\gamma_0}{2}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right\}$$

$$\times\exp\left\{\frac{p^2}{\gamma_0\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right\}\sqrt{\frac{\pi}{\frac{\gamma_0}{4}\omega_0^2\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}} . \qquad \text{(A5.2.12)}$$

This is

$$W_T^{(1)} = \frac{2|K_1|^2}{\hbar^2\omega_0}\sqrt{\frac{\pi}{\gamma_0 \operatorname{csch}\frac{\beta\hbar\omega_0}{2}}}\exp\left\{-\frac{\gamma_0}{2}\left(\coth\frac{\beta\hbar\omega_0}{2} - \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right) + \beta\hbar\omega_0\frac{p}{2} - \frac{p^2}{\gamma_0 \operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right\} \quad \text{(A5.2.13)}$$

Writing $\frac{\gamma_0}{2} = \frac{E_M}{\hbar\omega_0}$ we obtain finally for the transition rate

$$W_T^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2\omega_0\sqrt{2E_M \operatorname{csch}\frac{\beta\hbar\omega_0}{2}}}\exp\left[-\frac{E_M}{\hbar\omega_0}\left(\coth\frac{\beta\hbar\omega_0}{2} - \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right) + \frac{\beta\hbar\omega_0 p}{2} - \frac{p^2}{\frac{2E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}\right].$$

(A5,2,14)

This is the same expression which we derived for the S.C.C.M. in the high temperature, strong coupling limit in Appendix 3.4, equation (A3.4.11). Thus we can make use of the arguments of chapter 3 to obtain the temperature activated form of the transition rate,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\left[\frac{\pi}{kTE_M}\right]^{\frac{1}{2}}\exp(-\beta E_b) \quad \text{(A5.2.15)}$$

where $E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M}$.

This is the text equation (5.37).

APPENDIX A5.3

Calculation of the recombination rate at absolute zero, $W_{T=0}$ in the M.C.M.

We start from equation (5,34) of the text,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right\} \int_{-t}^{t} \exp\left[\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\sum_k \frac{\cos\omega_k t'}{N}\right]$$
$$\times\cos\left[\frac{E_M}{\hbar\omega_0}\sum_k \frac{\sin\omega_k t}{N} - \frac{\Delta E}{\hbar}t'\right]dt' . \quad \text{(A5.3.1)}$$

In the limit of zero dispersion this becomes

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right\}\int_{-t}^{t}\exp\left[\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\cos\omega_0 t'\right]\cos\left[\frac{E_M}{\hbar\omega_0}\sin\omega_0 t' - \frac{\Delta E}{\hbar}t'\right]dt'.$$

(A5.3.2)

We write, $$\left.\begin{aligned} a &= \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} \\ a' &= \frac{E_M}{\hbar\omega_0}\ ;\ x = \omega_0 t \end{aligned}\right\} \quad \text{(A5.3.3)}$$

so that $W_T^{(1)}$ is now written as

$$W_T^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right\}\left\{\frac{1}{2\pi}\int_{-\pi}^{\pi}\exp[a\cos x]\cos[a'\sin x - px]\frac{dx}{\omega_0}\right\}, \quad \text{(A5.3,4)}$$

where we have assumed that the major contribution to the integrand comes from the region $-\pi$ to π . Once again this assumption can only be valid if dispersion is present.

We use the result

$$\frac{1}{2\pi}\int_{-\pi}^{\pi}dx\exp[a\cos x]\cos[a'\sin x - (p+\Delta)x]$$
$$= \frac{(a^2 - a'^2)^{p/2}}{(a-a')^p} I_p\left[\sqrt{a^2 - a'^2}\right] \quad \text{(A5,3,5)}$$

where $I_p\left[\sqrt{a^2-a'^2}\right]$ is a modified Bessel function.

Using (A5,3,5), $W_T^{(1)}$ (A5,3,4) becomes

$$W_T^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right\}\left[\frac{\left(\frac{E_M}{\hbar\omega_0}\right)^2\left(\coth^2\frac{\beta\hbar\omega_0}{2} - 1\right)}{\left(\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} - \frac{E_M}{\hbar\omega_0}\right)^2}\right]^{\frac{p}{2}} I_p\left[\frac{E_M}{\hbar\omega_0}\sqrt{\coth^2\frac{\beta\hbar\omega_0}{2} - 1}\right].$$

(A5,3.6)

As $T \to 0$, $\beta \to \infty$ and $\coth\frac{\beta\hbar\omega_0}{2} \to 1$.

Thus in (A5.3.6) we use the small argument approximation for $I_p(x)$

which is, $I_p(x) \xrightarrow{x\to 0} \left(\frac{x}{2}\right)^p \frac{1}{p!}$ (A5.3.7)

We obtain for the transition rate

$$W^{(1)}_{T=0} = \frac{2\pi |K_1|^2}{\hbar^2 \omega_0} \exp\left\{-\frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2}\right\} \frac{1}{2^p} \frac{1}{p!} \left(\frac{E_M}{\hbar\omega_0}\right)^p \left\{\frac{\left(\coth^2\frac{\beta\hbar\omega_0}{2} - 1\right)}{\left(\coth\frac{\beta\hbar\omega_0}{2} - 1\right)}\right\}^p \tag{A5.3.8}$$

As $\beta\to\infty$, we must be careful how we take the limit of $\dfrac{\coth^2\frac{\beta\hbar\omega_0}{2} - 1}{\coth\frac{\beta\hbar\omega_0}{2} - 1}$. (A5.3.9)

We write $\coth\frac{\beta\hbar\omega_0}{2} = 1+\delta$ and take the limit as $\delta \to 0$.

Thus, (A5.3.9) becomes

$$\lim_{\delta\to 0} \frac{(1+\delta)^2 - 1}{1+\delta-1} = \lim_{\delta\to 0} \frac{2\delta+\delta^2}{\delta} = 2. \tag{A5.3.10}$$

Thus, using (A5.3.10) in (A5.3.8) we obtain the standard form for the transition rate at the absolute zero of temperature.

$$W_{T=0} = \frac{2\pi |K_1|^2}{\hbar^2 \omega_0} \exp\left\{-\frac{E_M}{\hbar\omega_0}\right\} \left(\frac{E_M}{\hbar\omega_0}\right)^p \frac{1}{p!}.$$

This is the text equation (5.39).

Chapter 6

The Derivation of the Recombination Rates in the Molecular Crystal Model using combinatorial arguments.

We have already derived the recombination rates in the M.C.M. using a formal analysis in Chapter 5. This method of calculation is formal in the sense that none of the intermediate steps between the Fermi Golden Rule expression for the transition probability and the final recombination rates obtained can be interpreted in terms of physical processes.

We now present an alternative method of calculating the recombination rates based on the combinatorial approach adopted by Huang-Rhys[8] in their paper. This technique possesses the decided advantage of physical transparency in that the intermediate steps of the argument may now be interpreted in terms of multiphonon processes. We comment at this stage that the combinatorial arguments presented in this chapter only yield that factor in the transition probability which derives from the vibrational overlap integral. The transition probability itself is obtained by multiplying the combinatorial results by the electronic and time-dependent perturbation theory factors $\frac{2\pi}{\hbar}|K|^2 N(E)$. The same assumptions regarding the M.C.M. are made as in Chapter 5, in particular there is no dispersion of the crystalline modes, so that the density of states is approximated by $N(E) = \frac{1}{\hbar\omega_0}$. Also, the electronic energy difference ΔE is an integral number of phonons, $\Delta E = p\hbar\omega_0$.

First of all, we consider the transition probability at the absolute zero of temperature, T=0, at which each mode initially has only its zero-point energy. When the recombination process occurs, p of the N lattice modes increase their phonon occupation number by one. We consider first the probability that one such process should occur and then multiply this probability by the total number of such processes which are allowed.

The crystalline modes are numbered 1, 2, ... N. If modes 1, 2. . . . . p increase their phonon occupation number by one while modes p+1, ... N remain unaltered then the probability for this process to occur is,

$$A = \prod_{k=1}^{p} I_{1,0}^{2} \prod_{k=p+1}^{N} I_{0,0}^{2}, \qquad (6.1)$$

where I_{n_k+1,n_k} is the probability amplitude that the k'th mode emits one phonon.

The vibrational overlap integrals have already been derived in Chapter 5, (5.27). These are,

$$\left.\begin{aligned} I_{n_k+1,n_k} &= -(1+n_k)^{1/2}\left(\frac{\gamma_0}{2N}\right)^{\frac{1}{2}} \\ I_{n_k,n_k} &= 1-\left(n_k+\tfrac{1}{2}\right)\left(\frac{\gamma_0}{2N}\right) \\ I_{n_k-1,n_k} &= n_k^{1/2}\left(\frac{\gamma_0}{2N}\right)^{\frac{1}{2}}, \end{aligned}\right\} \qquad (6.2)$$

where the coupling constant $\gamma_0 = \frac{(A_1 - A_0)^2}{M\omega_0^2\hbar\omega_0}$ in the zero dispersion limit.

Using (6.2), (6.1) becomes,

$$A = \prod_{k=1}^{p}\left(\frac{\gamma_0}{2N}\right)\prod_{k=p+1}^{N}\left(1-\frac{\gamma_0}{2N}\right), \qquad (6.3)$$

so that,

$$A \approx \left(\frac{\gamma_0}{2N}\right)^{p} \exp\left[-\sum_{k=p+1}^{N}\frac{\gamma_0}{2N}\right],$$

$$A \approx \left(\frac{\gamma_0}{2N}\right)^{p} \exp\left[-\sum_{k}\frac{\gamma_0}{2N}\right].$$

Finally, we obtain

$$A \approx \left(\frac{\gamma_0}{2N}\right)^{p} \exp\left[-\frac{\gamma_0}{2}\right]. \qquad (6.4)$$

Thus, the probability for this type of process to occur is exceedingly small, being proportional to $\frac{1}{N^p}$. However, the number of processes in which p modes each emit one phonon must also be considered. It may easily be shown using simple combinatorial considerations that the number of ways in which p modes out of a total of N may each emit one phonon is

$$B = \frac{N(N-1) - - \cdots (N-p+1)}{p!} \qquad (6.5)$$

where a factor $\frac{1}{p!}$ has been included since phonons are indistinguishable.

Now, $N(N-1) - - \cdots (N-p+1) = N^p\left(1-\frac{1}{N}\right) \cdot \cdots \cdot \left(1-\frac{p+1}{N}\right)$

$\cong N^p$ remembering that $N \gg p$.

Multiplying A (6.4) by B (6.5) we conclude that the transition probability at absolute zero, $W_{T=0}$ is given by,

$$W_{T=0} \propto \left(\frac{\gamma_0}{2}\right)^p \exp\left(-\frac{\gamma_0}{2}\right)\frac{1}{p!}. \qquad (6.6)$$

The transition probability $W_{T=0}$ is obtained by multiplying the expression (6.6) by $\frac{2\pi|K|^2}{\hbar^2\omega_0}$ and noting that $\frac{\gamma_0}{2} = \frac{E_M}{\hbar\omega_0}$ to find

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\frac{1}{p!}\left(\frac{E_M}{\hbar\omega_0}\right)^p \exp\left(-\frac{E_M}{\hbar\omega_0}\right) \qquad (6.7)$$

This is a very important result which we have already derived in chapter 3 using the S.C.C.M. If p is large, we may then use the Stirling approximation for p! to obtain the energy gap law result, (3.28). It is interesting to note that the factor $\frac{1}{p!}$ in result (6.7) is a direct consequence of phonons being indistinguishable.

The next situation considered is the transition probability in the weak coupling $\left(\frac{E_M}{\hbar\omega_0} \ll 1\right)$, finite temperature case. As in the absolute zero (T=0) situation we consider only those processes in which p out of N modes each emit one phonon. This assumption will be justified later for the weak coupling situation when the high temperature, strong coupling case is discussed.

Suppose, as before, that the modes 1,2,........p each emit one phonon while the modes p+1,.......... N have their phonon occupation numbers unchanged. Thus, a contribution to the transition rate, W_T, of the form

$$A = \prod_{k=1}^{p} I^2_{n_k+1,n_k} \prod_{k=p+1}^{N} I^2_{n_k,n_k} , \qquad (6.8)$$

arises.

Using the expressions (6.2) for the vibrational overlap integrals,

$$A = \prod_{k=1}^{p} \frac{1}{N} \gamma_0 \left(\frac{1+n_k}{2}\right) \prod_{k=p+1}^{N} \left[1 - \frac{\gamma_k}{N}\left(n_k + \frac{1}{2}\right)\right]. \qquad (6.9)$$

As before in the absolute zero temperature case there are

$$B = \frac{N(N-1)\cdots\cdots(N-p+1)}{p!} \sim \frac{N^p}{p!}$$ terms similar to (6.9).

However, now each of these transition probabilities must be weighted with the thermal probability of occupation of the initial state which is

$$\exp\left[-\beta\hbar\omega_0 \sum_k \left(n_k + \frac{1}{2}\right)\right] Z^{-1} \quad \text{where} \quad Z = \sum_{\{n_k\}} \exp\left[-\beta\hbar\omega_0 \sum_k \left(n_k + \frac{1}{2}\right)\right].$$

Having done this all combinations $\{n_k\}$ are summed to obtain,

$$W_T \propto \frac{1}{Z} \sum_{\{n_k\}} \left(\frac{\gamma_0}{N}\right)^p \prod_k^p \left(\frac{n_k+1}{2}\right) \exp\left[-\frac{\gamma_0}{N} \sum_{k=p+1}^{N} \left(n_k + \frac{1}{2}\right)\right] \frac{N^p}{p!} \exp\left[-\beta\hbar\omega_0 \sum_k \left(n_k + \frac{1}{2}\right)\right], \qquad (6.10)$$

which becomes

$$W_T \propto \frac{1}{Z} \sum_{\{n_k\}} \frac{\gamma_0^p}{p!} \exp\left[-\gamma_0\left(n_k + \frac{1}{2}\right)\right] \prod_{k=1}^{p} \left(\frac{n_k+1}{2}\right) \exp\left[-\beta\hbar\omega_0 \sum_k \left(n_k + \frac{1}{2}\right)\right]. \qquad (6.11)$$

This transition probability W_T becomes on replacing $\frac{1}{Z}\sum_{\{n_k\}} f(n_k)$ by $f(\langle n \rangle_T)$, where $\langle n \rangle_T$ is the thermal probability of occupation,

$$\langle n\rangle_T = [\exp(\beta\hbar\omega_0) - 1]^{-1},$$

$$W_T \propto \left(\frac{\gamma_0}{2}\right)^p \frac{1}{p!} \exp[-\gamma_0(\langle n\rangle_T + \tfrac{1}{2})](1+\langle n\rangle_T)^p. \qquad (6.12)$$

To obtain the transition probability W_T, we multiply (6.12) by $\frac{2\pi|K|^2}{\hbar^2\omega_0}$ and note that $\frac{\gamma_0}{2} = \frac{E_M}{\hbar\omega_0}$ to find

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \exp\left[-\frac{E_M}{\hbar\omega_0}(1+2\langle n\rangle_T)\right]\left(\frac{E_M}{\hbar\omega_0}\right)^p \frac{1}{p!}(1+\langle n\rangle_T)^p. \qquad (6.13)$$

Comparing (6.13) with the transition probability at absolute zero, $W_{T=0}$ (6.7) we note that, apart from the different exponential factors,

$$W_T = (1+\langle n\rangle_T)^p W_{T=0}. \qquad (6.14)$$

This well known result has previously been derived in the finite temperature, weak coupling limit using both the S.C.C.M. and the M.C.M. In the weak coupling limit, it has been assumed that the only processes allowed are those in which p phonons are emitted. However, we must justify this assumption, as at finite temperatures multiphonon processes may occur in which phonons are absorbed as well as emitted. When $\Delta E = p\hbar\omega_0$ the simplest such process allowed by energy conservation requirements is one in which p+1 phonons are emitted while 1 phonon is absorbed. To see why such processes do not contribute in the weak coupling limit, we note that the probability of a transition occuring in which p phonons are emitted is proportional to γ_0^p (6.6). However, it will shortly be demonstrated that the probability for p+1 phonons to be emitted and 1 absorbed is proportional to γ_0^{p+2}, (6.16). Thus, our assumption that in the weak coupling limit only those processes in which p phonons are emitted are important is justified.

Next, we rederive the transition rate in the high temperature

$(\beta\hbar\omega_0 << 1)$, strong coupling $\frac{E_M}{\hbar\omega_0} \gg 1$ regime. Since the coupling constant $\gamma_0 = \frac{E_M}{\hbar\omega_0}$ is no longer small the procedure of the previous paragraph in which only those processes in which p phonons are emitted were considered is no longer justified. It is now necessary to consider all the kinds of multiphonon processes which are consistent with energy conservation. When $\Delta E = p\hbar\omega_0$, the multiphonon processes which are allowed are those in which p+q phonons are emitted while q are absorbed,

We will consider initially the simplest case in which p+1 phonons are emitted while one phonon is absorbed.

The vibrational modes 1,2,..........p+1 each emit one phonon while the p+2'th mode absorbs a phonon.

This results in a contribution to the transition probability W_T,

$$C = \prod_{k=1}^{p+1} I^2_{n_k+1, n_k} \, I^2_{n_{p+2}-1, n_{p+2}} \prod_{k=p+3}^{N} I^2_{n_k, n_k} . \tag{6.15}$$

This becomes on using the expressions for the vibrational overlap integrals,

$$C = \prod_{k=1}^{p+1} \left\{\frac{\gamma_0}{N}\left(\frac{n_k+1}{2}\right)\right\}\left\{\frac{\gamma_0}{N}\left(\frac{n_{p+2}}{2}\right)\right\} \exp\left[-\frac{\gamma_0}{N}\sum_{k=p+2}^{N}\left(n_k+\frac{1}{2}\right)\right],$$

which becomes,

$$C \cong \left(\frac{\gamma_0}{2N}\right)^{p+2} \prod_{k=1}^{p+1} (1+n_k)\, n_{p+2} \exp\left[-\frac{\gamma_0}{N}\sum_{k=1}^{N}\left(n_k+\frac{1}{2}\right)\right] . \tag{6.16}$$

The number of ways in which this type of process in which p+1 phonons are emitted and 1 absorbed may occur is

$$D = \frac{N(N-1)\cdots\cdots(N-p)\{N-(p+1)\}}{(p+1)!} \sim \frac{N^{p+2}}{(p+1)!} . \tag{6.17}$$

On taking the thermal average $\frac{1}{Z}\sum_{\{n_k\}}\exp\left[-\beta\hbar\omega_0\sum_k\left(n_k+\frac{1}{2}\right)\right]$ of the processes represented by expression (6,16) a contribution to the transition probability $W_T(1)$ is obtained,

$$W_T(1) = \left(\frac{\gamma_0}{2}\right)^{p+2}(1+\langle n\rangle_T)^{p+1}\langle n\rangle_T \exp\left[-\gamma_0\left(\langle n\rangle_T+\frac{1}{2}\right)\right]\frac{1}{(p+1)!} \cdot \qquad (6.18)$$

Next, we consider the most general type of multiphonon processes in which p+q phonons are emitted while q phonons are absorbed, If the vibrational modes 1,......... p+q each emit one phonon while the modes p+q+1,............ p+2q each absorb a phonon this results in a contribution to the transition probability W_T, of

$$C = \prod_{k=1}^{p+q} I^2_{n_k+1,n_k} \prod_{k=p+q+1}^{p+2q} I^2_{n_k-1,n_k} \prod_{k=p+2q+1}^{N} I^2_{n_k,n_k} . \qquad (6.19)$$

Using the expressions for the vibrational overlap integrals (6.2), this becomes

$$C = \prod_{k=1}^{p+q}\left\{\frac{\gamma_0}{N}\left(\frac{n_k+1}{2}\right)\right\}\prod_{k=p+q+1}^{p+2q}\left\{\frac{\gamma_0}{N}\left(\frac{n_k}{2}\right)\right\}\exp\left[-\frac{\gamma_0}{N}\sum_{k=p+2q+1}^{N}\left(n_k+\frac{1}{2}\right)\right],$$

which is

$$C \cong \left(\frac{\gamma_0}{2N}\right)^{p+2q}\prod_{k=1}^{p+q}(1+n_k)\prod_{k=p+q+1}^{p+2q+1} n_k \exp\left[-\frac{\gamma_0}{N}\sum_{k=p+2q+1}^{N}\left(n_k+\frac{1}{2}\right)\right] \qquad (6.20)$$

The number of ways in which this type of process may occur is

$$D = \frac{N(N-1)\cdots(N-[p+q-1])}{(p+q)!}\,\frac{\{N-(p+q)\} - - - - .\{N-2q\}}{q!} \sim \frac{N^{p+2q}}{(p+q)!\,q!} \qquad (6.21)$$

Combining B6.20) and (6.21) we obtain a contribution to the transition rate, $W_T(q)$

$$W_T(q) \cong \left(\frac{\gamma_0}{2}\right)^{p+2q}\prod_{k=1}^{p+q}(1+n_k)\prod_{k=p+q+1}^{p+2q} n_k \exp\left[-\gamma_0\sum_{k=p+2q+1}^{N}\left(n_k+\frac{1}{2}\right)\right]\frac{1}{(p+q)!\,q!}$$

On taking the thermal average, $W_T(q)$ becomes,

$$W_T(q) \cong \left(\frac{\gamma_0}{2}\right)^{p+2q}(1+\langle n\rangle_T)^{p+q}(\langle n\rangle_T)^{q}\exp\left[-\gamma_0\left(\langle n\rangle_T+\frac{1}{2}\right)\right]\frac{1}{(p+q)!\,q!} \qquad (6.22)$$

To obtain the transition rate W_T we sum the contributions from each type of multiphonon process, $W_T(q)$ and multiply by the factor $\frac{2\pi|K|^2}{\hbar^2\omega_0}$,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{q=0}^{\infty} W_T(q). \qquad (6.23)$$

Thus, W_T becomes

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\left\{\left(\frac{E_M}{\hbar\omega_0}\right)(1+\langle n\rangle_T\right\}^p \exp\left[-\frac{2E_M}{\hbar\omega_0}\left(\langle n\rangle_T+\frac{1}{2}\right)\right]$$
$$\times\sum_{q=0}^{\infty}\left\{\left(\frac{E_M}{\hbar\omega_0}\right)^2(1+\langle n\rangle_T)\langle n\rangle_T\right\}^q\frac{1}{(p+q)!\,q!}. \qquad (6.24)$$

Using the identity,

$$\sum_{s=0}^{\infty}\frac{\left(\frac{1}{4}x^2\right)^s}{s!(s+p)!} = \left(\frac{1}{2}x\right)^{-p} I_p(x)$$

where $I_p(x)$ is the modified Bessel Function, we obtain

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left[-\frac{2E_M}{\hbar\omega_0}\left(\langle n\rangle_T+\frac{1}{2}\right)\right]\left\{\frac{(1+\langle n\rangle_T)}{\langle n\rangle_T}\right\}^{p/2} I_p\left[\frac{E_M}{2\hbar\omega_0}\sqrt{(1+\langle n\rangle_T)\langle n\rangle_T}\right]$$

This expression may easily be shown to be identical to the general form of the transition rate obtained for the S.C.C.M. in Chapter 3, [equation (A3.4.9)].

We show in Appendix A3.4 that in the high temperature ($\beta\hbar\omega_0 \ll 1$), strong coupling $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$ limit the transition rate assumes the temperature activated form,

$$W_T = \frac{|K|^2}{\hbar}\sqrt{\frac{\pi}{kTE_M}}\exp(-\beta E_b), \qquad (6.25)$$

where E_b is the activation energy given by

$$E_b = \frac{E_M}{4} - \frac{\Delta E}{2} + \frac{\Delta E^2}{4E_M} . \qquad (6.26)$$

Conclusions

We have calculated the transition rates in the M.C.M. using a combinatorial analysis which gives more physical insight into the problem than the more formal analysis adopted previously.

In the general case, the multiphonon processes which are allowed by energy conservation when $\Delta E = p\hbar\omega_0$ are of the type in which p+q lattice modes each emit one phonon while q modes absorb a phonon. The remaining N-p-2q modes have their phonon occupation numbers unchanged. By considering all such multiphonon processes, we have rederived the temperature activated recombination rate, (6.25) in the high temperature $(\beta\hbar\omega_0 \ll 1)$, strong coupling $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$ limit. The transition rates at the absolute zero of temperature, (6.7) are rederived assuming only those processes in which p phonons are emitted.

Chapter 7

The Calculation of Recombination Rates in the M.C.M. using the 'derivative' non-adiabatic terms.

In this chapter, we complete the calculation of the recombination rates in the M.C.M. when there is no dispersion. The general expression for the transition rate was derived in Chapter 5, [equation (5.18)]. There, we considered only transition rates which result from the 'standard' non-adiabatic terms. This chapter deals with the transition rates arising from the 'derivative' non-adiabatic terms and the interference terms involving the 'standard' and the 'derivative' non-adiabatic factors. In particular, we wish to discover if these additional terms significantly affect the results we have obtained so far.

We recall that the 'derivative' transition rates are given by equation (5.18),

$$W_T^{(2)} = \frac{2\pi}{\hbar^2} \sum_{\{n_k^0\},\{n_k'\}} (1-r_k) r_k^{n_k'} \sum_{k'} |K'_{k',1}|^2 \prod_{k \neq k'} I^2_{n_k^0, n_k'} \, I'^2_{n_{k'}^0, n_{k'}'} \, \delta(E_{0,\{n_k^0\}} - E_{1,\{n_k'\}}), \qquad (7.1)$$

$$W_T^{(3)} = \frac{2\pi}{\hbar^2} \sum_{\{n_k^0\},\{n_k'\}} (1-r_k) r_k^{n_k'} \sum_{k'} |K''_{k',1} K'_{k',1}| I_{n_{k'}^0, n_{k'}'} I'_{n_{k'}^0, n_{k'}'} \prod_{k \neq k'} I^2_{n_k^0, n_k'} \, \delta(E_{0,\{n_k^0\}} - E_{1,\{n_k'\}}) \qquad (7.2)$$

$$W_T^{(4)} = \frac{2\pi}{\hbar^2} \sum_{\{n_k^0\},\{n_k'\}} (1-r_k) r_k^{n_k'} \sum_{k',k''} |K'_{k',1} K'_{k'',1}| (I_{n_{k'}^0, n_{k'}'} I'_{n_{k'}^0, n_{k'}'})(I_{n_{k''}^0, n_{k''}'} I'_{n_{k''}^0, n_{k''}'})$$

$$\times \prod_{k \neq k', k''} I^2_{n_k^0, n_k'} \, \delta(E_{0,\{n_k^0\}} - E_{1,\{n_k'\}}). \qquad (7.3)$$

Here, $W_T^{(2)}$ is the recombination rate arising from the derivative matrix elements while $W_T^{(3)}$ and $W_T^{(4)}$ are the recombination rates originating from the interference terms. A discussion of the physical significance of these various transition rates is left until we have actually evaluated the contributions which they make.

A prerequisite for the calculation of all these transition rates is a knowledge of the 'derivative' vibrational overlap integral $I'_{n_k^0, n_k^1}$ which differs from the ordinary vibrational overlap integral $I_{n_k^0, n_k^1}$. Now, the 'derivative' vibrational overlap integral $I'_{n_k^0, n_k^1}$ is

$$I'_{n_k^0, n_k^1} = \int d(\alpha_k q_k)\, \Phi_{n_k^0}[\alpha_k q_k] \frac{d}{d(\alpha_k q_k)} \Phi_{n_k^1}[\alpha_k(q_k - \Delta q_k)]. \tag{7.4}$$

We use the recursion relation

$$I'_{n_k^0, n_k^1} = \left(\tfrac{1}{2} n_k^1\right)^{\frac{1}{2}} I_{n_k^0, n_k^1 - 1} - \left[\tfrac{1}{2}(n_k^1 + 1)\right]^{\frac{1}{2}} I_{n_k^0, n_k^1 + 1} \tag{7.5}$$

to evaluate the derivative vibrational overlap integral $I'_{n_k^0, n_k^1}$. Using the results of Chapter 5 (equation (5.27)) for the vibrational overlap integral, $I_{n_k^0, n_k^1}$ the following results are obtained,

$$\left.\begin{aligned}
I'_{n_k^1+2, n_k^1} &= \left[\tfrac{1}{2}(1 + n_k^1)(2 + n_k^1)\right]^{\frac{1}{2}} \left(\frac{\gamma_k}{2N}\right)^{\frac{1}{2}} \\
I'_{n_k^1+1, n_k^1} &= -\left[\tfrac{1}{2}(1 + n_k^1)\right]^{\frac{1}{2}} \left\{1 - \left(n_k^1 + \tfrac{3}{2}\right)\frac{\gamma_k}{2N}\right\} \\
I'_{n_k^1, n_k^1} &= -\left(\tfrac{1}{2}\right)^{\frac{1}{2}} (1 + 2n_k^1) \left(\frac{\gamma_k}{2N}\right)^{\frac{1}{2}} \\
I'_{n_k^1-1, n_k^1} &= \left(\tfrac{1}{2} n_k^1\right)^{\frac{1}{2}} \left\{1 - \left(n_k^1 - \tfrac{1}{2}\right)\frac{\gamma_k}{2N}\right\} \\
I'_{n_k^1-2, n_k^1} &= \left[\tfrac{1}{2} n_k^1 (n_k^1 - 1)\right]^{\frac{1}{2}} \left(\frac{\gamma_{k'}}{2N}\right)^{\frac{1}{2}}.
\end{aligned}\right\} \tag{7.6}$$

Hence the occupation number of a mode on which the 'derivative' operator acts can change by zero, one or two vibrational quantum numbers. This contrasts with the case of the ordinary vibrational overlap integral in which the occupation number can only change by zero or one as shown by equation (5.27).

The transition rates which result from $W_T^{(2)}$, $W_T^{(3)}$ and $W_T^{(4)}$ are calculated in appendices A7.1, A7.2 and A7.3, respectively. We show in these appendices that $K'_{k,1} \propto \left(\frac{1}{N}\right)^{\frac{1}{2}}$ [see equation (A7.1.2)], while $K''_{k,1} \propto \frac{1}{N}$ (A7.2.5) and $I_{n_k^0,n_k^1} I'_{n_k^0,n_k^1} \propto \left(\frac{1}{N}\right)^{\frac{1}{2}}$ (A7.2.7). However, $\left(I'_{n_k^0,n_k^1}\right)^2$ contains a term which has no factor of $\frac{1}{N}$ in it, (A7.1.7).

Thus the summation over k' in $W_T^{(2)}$ in equation (7.1)

$$\sum_{k'} |K'_{k',1}|^2 \prod_{k\neq k'} I^2_{n_k^0,n_k^1} I'^2_{n_{k'}^0,n_{k'}^1} \delta(E_{0,\{n_k^0\}} - E_{1,\{n_k^1\}}),$$

contains N terms each of which is proportional to $\frac{1}{N}$. Similarly, the summation over k' and k'' in $W_T^{(4)}$ equation (7.3), contains N^2 terms each of which is proportional to $\frac{1}{N^2}$. Thus, both $W_T^{(2)}$ and $W_T^{(4)}$ make contributions to the recombination rate.

However, the summation over k' in $W_T^{(3)}$, equation (7.2)

$$\sum_{k'} |K''_{k',1} K'_{k',1}| I_{n_{k'}^0,n_{k'}^1} I'_{n_{k'}^0,n_{k'}^1} \prod_{k\neq k'} I^2_{n_k^0,n_k^1} \delta(E_{0,\{n_k^0\}} - E_{1,\{n_k^1\}})$$

contains N terms each of which is proportional to $\frac{1}{N^2}$. Thus, this interference non-adiabatic term $W_T^{(3)}$ makes no contribution to the recombination rate in the limit of large N.

We find in Appendix A7.1 that in the zero dispersion case, $\omega_k = \omega_0$, $W_T^{(2)}$ is given by (A7.1.14) which is

$$W_T^{(2)} = \frac{|C_1|^2}{\hbar^2} \exp(-2S)(1+n) \int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E_1}{\hbar} t'\right]$$
$$+ \frac{|C_1|^2}{\hbar^2} \exp(-2S)\, n \int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E_2}{\hbar} t'\right], \quad (7.7)$$

where $\Delta E_1 = \Delta E - \hbar\omega_0$ and $\Delta E_2 = \Delta E + \hbar\omega_0$.

This should be compared with $W_T^{(1)}$ given by equation (5.32) of Chapter 5 which may be written as

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp(-2S) \int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right]. \qquad (7.8)$$

We will write the two terms of $W_T^{(2)}$ in equation (7.7) as $W_T^{(2)} = W_T^{(2,a)} + W_T^{(2,b)}$ where

$$W_T^{(2,a)} = \frac{|C_1|^2}{\hbar^2} \exp(-2S)(1+\mathcal{N}) \int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E_1}{\hbar} t'\right], \qquad (7.9)$$

where

$$\Delta E_1 = \Delta E - \hbar\omega_0 , \qquad C_1 = \int d\underline{r}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\left[-\frac{\hbar^2}{M}\frac{\partial}{\partial x_p} \varphi_1(\underline{r} - p\underline{a}, x_p)\right]$$

and

$$W_T^{(2,b)} = \frac{|C_1|^2}{\hbar^2} \exp(-2S)\mathcal{N} \int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E_2}{\hbar} t'\right], \qquad (7.10)$$

where

$$\Delta E_2 = \Delta E + \hbar\omega_0 .$$

Thus, apart from the different electronic factors $|C_1|^2$ and the additional factors $\mathcal{N}$ and $(1+\mathcal{N})$, $W_T^{(2,a)}$ and $W_T^{(2,b)}$ differ from $W_T^{(1)}$ only in that ΔE has been replaced by ΔE_1 and ΔE_2 respectively. Now in the expression for $W_T^{(1)}$ equation (7.8) the factor $\int_{-t}^{t} dt' \exp[F_1(t')] \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right]$ represents the emission of a net number of phonons, $p = \frac{\Delta E}{\hbar\omega_0}$ into the optical modes. We suggest the following physical interpretation of the transition probabilities $W_T^{(2,a)}$ and $W_T^{(2,b)}$. The $\frac{\partial}{\partial q}$ operator is assumed to distinguish one of the lattice modes from the others. In $W_T^{(2,a)}$ the factor $(1+\mathcal{N})$ represents the emission of one phonon into this mode. Energy conservation then requires that a net number of phonons, $p - 1 = \frac{\Delta E_1}{\hbar\omega_0}$ are emitted into the remaining N-1 modes.

This is exactly what the factor $\int_{-t}^{t} dt' \exp[F_1(t')] \cos[F_2(t') - \frac{\Delta E_1}{\hbar} t']$ in the expression for $W_T^{(2,a)}$, equation (7.9) represents. Thus we have been able to interpret the transition rate $W_T^{(2,a)}$ in terms of fundamental physical processes.

The interpretation of $W_T^{(2,b)}$ given by equation (7.10) is similar. In this case the mode which has been separated from the other modes by the $\frac{\partial}{\partial q}$ operator has a phonon absorbed from it, this process being proportional to N. Energy conservation then requires that a net number of phonons, $p+1 = \frac{\Delta E_2}{\hbar\omega_0}$ are emitted into the remaining N-1 modes. This is exactly what the other factor in $W_T^{(2,b)}$ equation (7.10), $\int_{-t}^{t} dt' \exp[F_1(t')] \cos[F_2(t') - \Delta E_2 \frac{t'}{\hbar}]$ represents.

We note that at the absolute zero of temperature $T = 0$, only $W_T^{(2,a)}$ contributes to the transition rate,

$$W_T^{(2,a)} = \frac{|C_1|^2}{\hbar^2} \exp(-2S) \int_{-t}^{t} dt' \exp[F_1(t')] \cos[F_2(t') - \frac{\Delta E_1}{\hbar} t'] , \qquad (7.11)$$

where $\Delta E_1 = \Delta E - \hbar\omega_0$.

Thus $W_{T=0}^{(2,a)}$ behaves as if the electronic energy difference ΔE has been reduced by one optical phonon $\hbar\omega_0$ to become ΔE_1. This is essentially the same result as we found for the recombination rate due to the 'derivative' non-adiabatic terms for the S.C.C.M. in Chapter 3, equation (3.23),

$$W_{T=0}^{(2)} = \frac{|C_1|^2}{2} I_{p,1}^2 = 2|C_1|^2 \left(\frac{E_b}{\hbar\omega_0}\right)\left(\frac{E_H}{\hbar\omega_0}\right)^p \frac{1}{p!} \exp\left(-\frac{E_H}{\hbar\omega_0}\right)$$

The transition rates $W_T^{(4)}$ which are evaluated in Appendix A7.3 are found to be very complicated and we further contract our notation to write,

$$X_p = \int_{-t}^{t} dt' \exp[F_1(t')] \cos[F_2(t') - \frac{\Delta E}{\hbar} t'] , \qquad (7.12)$$

so that $W_T^{(1)}$ given by equation (7.8) becomes

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp(-2S)X_p \,. \qquad (7.13)$$

The results we find for $W_T^{(4)}$ are given by equation (A7.3.22),

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2}\sum_{k',k''}\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|(\gamma_{k'}\gamma_{k''})^{1/2}\exp(-2S)$$
$$\times\left\{\left[(n+\tfrac{1}{2})^2+\tfrac{1}{2}n(n+1)\right]X_p-(n+\tfrac{1}{2})\left[nX_{p+1}+(1+n)X_{p-1}\right]+\tfrac{1}{4}\left[n^2X_{p+2}+(1+n)^2X_{p-2}\right]\right\}. \qquad (7.14)$$

These results for $W_T^{(2)}$ equation (7.7) and $W_T^{(4)}$ equation (7.14) agree essentially with the solutions obtained by Huang and Rhys,(8) [their equations (6.11) ⟶ (6.14)]. However, we have calculated these results using a different, more general method.

The interpretation of the various terms of $W_T^{(4)}$ in equation (7.14) is similar to the discussion already given for the similar terms in $W_T^{(2)}$. However, now two modes are separated from the continuum of lattice modes by $\frac{\partial}{\partial q}$ operators. We find that, in $W_T^{(4)}$ modes on which $\frac{\partial}{\partial q}$ operators act may have their phonon occupation numbers unaltered; these processes are proportional to $(n+\frac{1}{2})$. Thus, the first term in $W_T^{(4)}$ [equation (7.14)] is proportional to $(n+\frac{1}{2})^2X_p$. Energy conservation then requires a net number of phonons, $p=\frac{\Delta E}{\hbar\omega_0}$, to be emitted into the remaining N-2 lattice modes; this part of the process is represented by the factor X_p. All the other contributions to $W_T^{(4)}$ may be interpreted in a similar fashion.

A feature of $W_T^{(4)}$ revealed by the expression (7.14) which we find puzzling is the negative sign for the term, proportional to $-(n+\frac{1}{2})\left[nX_{p+1}+(1+n)X_{p-1}\right]$. Certainly, provided $W_T^{(1)}+W_T^{(2)}+W_T^{(3)}>0$ there is no difficulty; however, it is not obvious that this is the case.

At the absolute zero of temperature, $T=0$, the transition rate $W_T^{(4)}$ becomes

$$W_{T=0}^{(4)} = \frac{4}{\hbar^2 N^2} \sum_{k',k''} \left| \sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1 \right|^2 (\eta_{k'}\eta_{k''})^{1/2} \exp(-2S)$$
$$\times \left\{ \frac{1}{4}X_p - \frac{1}{2}X_{p-1} + \frac{1}{4}X_{p-2} \right\}. \qquad (7.15)$$

Thus, $W_{T=0}^{(4)}$ is considerably more complicated than $W_{T=0}^{(2,a)}$ given by equation (7.11) and does not have any counterpart in the transition rates due to the 'derivative' non-adiabatic terms in the S.C.C.M.

Summary

In this chapter we have calculated the contribution to the recombination rate in the M.C.M., without dispersion, from the 'derivative' non-adiabatic terms. Expressions for the transition rates $W_T^{(2)}$ and $W_T^{(4)}$ have been found, given by equations (7.7) and (7.14) respectively. We give a discussion of the interpretation of these transition rates in terms of simple physical processes.

APPENDIX A7.1

The calculation of the transition rate $W_T^{(2)}$.

In this appendix we will evaluate the general expression for $W_T^{(2)}$ given by the text equation (7.1)

$$W_T^{(2)} = \frac{2\pi}{\hbar} \sum_{\{n_k^0\},\{n_k^1\}} (1-r_k) r_k^{n_k^1} \sum_{k'} |K_{k',1}^{1}|^2 \prod_{k\neq k'} \mathcal{I}^{2}_{n_k^0, n_k^1} \left(\mathcal{I}^{1}_{n_{k'}^0, n_{k'}^1}\right)^2 \delta\left(E_{0,\{n_k^0\}} - E_{1,\{n_k^1\}}\right)$$

where $r_k = \bar{e}^{\beta\hbar\omega_k}$. (A7.1.1)

Now, using $\frac{d}{dq_k} = \sum_m \frac{dx_m}{dq_k}\frac{d}{dx_m}$ and the transformation (5.7),

$x_m = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_{k'} q_{k'} \sin\left(k'm + \pi/4\right)$ we may write

$K_{k',1}^{1} = \int d\underline{r}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\left(-\frac{\hbar^2}{2M}\frac{d}{dq_{k}}\varphi_1(\underline{r} - p\underline{a}, x_p)\right)$ in the form

$$K_{k',1}^{1} = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sum_m \sin\left(km + \pi/4\right) \int d\underline{r}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\left(-\frac{\hbar^2}{M}\frac{d}{dx_m}\varphi_1(\underline{r} - p\underline{a}, x_p)\right).$$

Thus,

$$K_{k',1}^{1} = \left(\frac{2}{N}\right)^{\frac{1}{2}} \sin\left(k'p + \pi/4\right) C_1 \qquad \text{(A7.1.2)}$$

where

$$C_1 = \int d\underline{r}\, \varphi_0^*(\underline{r} - p\underline{a}, x_p)\left(-\frac{\hbar^2}{M}\frac{d}{dx_p}\varphi_1(\underline{r} - p\underline{a}, x_p)\right). \qquad \text{(A7.1.3)}$$

Thus, the factor in (A7.1.1)

$$\sum_{k'} |K_{k',1}^{1}|^2 \left(\mathcal{I}^{1}_{n_{k'}^0, n_{k'}^1}\right)^2 \prod_{k\neq k'} \mathcal{I}^{2}_{n_k^0, n_k^1}$$

becomes

$$\left(\frac{2}{N}\right) \sum_{k'} \sin^2\left(kp + \pi/4\right) |C_1|^2 \left(\mathcal{I}^{1}_{n_{k'}^0, n_{k'}^1}\right)^2 \prod_{k\neq k'} \mathcal{I}^{2}_{n_k^0, n_k^1}$$

which is

$$\frac{|C_1|^2}{N} \sum_{k'} \left(\mathcal{I}^{1}_{n_{k'}^0, n_{k'}^1}\right)^2 \prod_{k\neq k'} \mathcal{I}^{2}_{n_k^0, n_k^1}$$

Next, we use the expressions given in the main body of the text for $\mathcal{I}_{n_k^0, n_k^1}$ (5.27) and $\mathcal{I}^{1}_{n_k^0, n_k^1}$ (7.6) to obtain,

$$W_T^{(2)}=\frac{2|C_1|^2}{N\hbar^2}\sum_{k'}\sum_{\{n_k^0\},\{n_k^1\}}\frac{1}{Z}\int_{-t}^{t}\exp\Big[-\sum_k\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\Big]$$

$$\times\Big\{\tfrac{1}{2}(1+n_{k'}^1)(2+n_{k'}^1)\Big(\frac{\gamma_{k'}}{2N}\Big)\delta_{n_{k'}^0,n_{k'}^1+2}+\tfrac{1}{2}n_{k'}^1(n_{k'}^1-1)\Big(\frac{\gamma_{k'}}{2N}\Big)\delta_{n_{k'}^0,n_{k'}^1-2}$$

$$+\tfrac{1}{2}(1+n_{k'}^1)\{1-(n_{k'}^1+\tfrac{3}{2})\}\delta_{n_{k'}^0,n_{k'}^1+1}+\tfrac{1}{2}n_{k'}^1\{1-(n_{k'}^1-\tfrac{1}{2})\tfrac{\gamma_{k'}}{N}\}\delta_{n_{k'}^0,n_{k'}^1-1}$$

$$+\tfrac{1}{2}\frac{\gamma_{k'}}{2N}(1+2n_{k'}^1)^2\delta_{n_{k'}^0,n_{k'}^1}\Big\}\prod_{k\neq k'}\Big\{\Big[1-(n_{k'}^1+\tfrac{1}{2})\frac{\gamma_k}{N}\Big]\delta_{n_{k'}^1,n_{k'}^0}$$

$$+\Big(\frac{\gamma_k}{2N}\Big)\Big[(1+n_k^1)\delta_{n_k^0,n_k^1+1}+n_k^1\delta_{n_k^0,n_k^1-1}\Big]\Big\}\exp\Big[\frac{it'}{\hbar}\Big\{\sum_k\hbar\omega_k(n_k^0-n_k^1)-\Delta E\Big\}\Big].$$

(A7.1.4)

Summing over the final states $\{n_k^0\}$, (A7.1.4) becomes

$$W_T^{(2)}=\frac{2|c_1|^2}{\hbar^2N}\sum_{k'}\sum_{\{n_k^1\}}\frac{1}{Z}\int_{-t}^{t}\exp\Big[-\sum_k\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\Big]\exp\Big[\frac{-it'\Delta E}{\hbar}\Big]$$

$$\times\Big\{\tfrac{1}{2}(1+n_{k'}^1)(2+n_{k'}^1)\Big(\frac{\gamma_{k'}}{2N}\Big)e^{2i\omega_{k'}t}+n_{k'}^1(n_{k'}^1-1)\frac{\gamma_{k'}}{4N}e^{-2i\omega_{k'}t'}$$

$$+\tfrac{1}{2}(1+n_{k'}^1)\{1-(n_{k'}^1+\tfrac{3}{2})\tfrac{\gamma_{k'}}{N}\}e^{i\omega_{k'}t'}+\tfrac{1}{2}n_{k'}^1\{1-(n_{k'}^1-\tfrac{1}{2})\tfrac{\gamma_{k'}}{N}\}e^{-i\omega_{k'}t'}$$

$$+\frac{\gamma_{k'}}{4N}(1+2n_{k'}^1)^2\Big\}\prod_{k\neq k'}\Big\{\Big[1-(n_k^1+\tfrac{1}{2})\frac{\gamma_k}{N}+\frac{\gamma_k}{2N}\Big[(1+n_k^1)e^{i\omega_kt'}+n_k^1e^{-i\omega_kt'}\Big]\Big\}$$

(A7,1,5)

We perform the summation over the initial states, $\frac{1}{Z}\sum_{\{n_k^1\}}$ by simply replacing n_k^1 by their thermal equilibrium values, $\langle n_k^1\rangle=(e^{\beta\hbar\omega_0}-1)^{-1}$. Thus,

$$W_T^{(2)}=\frac{2|C_1|^2}{\hbar^2N}\sum_{k'}\int_{-t}^{t}\exp\Big\{\sum_{k\neq k'}\frac{\gamma_k}{N}\Big[-(n_k+\tfrac{1}{2})+(n_k+\tfrac{1}{2})\cos\omega_kt'+\frac{i}{2}\sin\omega_kt'\Big]\Big\}$$

$$\times\Big\{\tfrac{1}{2}(1+n_k)e^{i\omega_{k'}t'}+\tfrac{1}{2}n_{k'}^1e^{-i\omega_{k'}t'}+\frac{\gamma_{k'}}{N}\Big[\tfrac{1}{4}(1+n_{k'})(2+n_{k'})e^{-i2\omega_{k'}t'}+\tfrac{1}{4}n_{k'}(n_{k'}-1)e^{-i2\omega_{k'}t'}$$

$$-\tfrac{1}{2}n_{k'}^1(n_{k'}^1-\tfrac{1}{2})e^{-i\omega_{k'}t'}+\tfrac{1}{4}(1+2n_{k'}^1)^2\Big\}\exp\Big[-\frac{i\Delta E}{\hbar}t'\Big]dt'.$$

(A7,1.6)

In (A7.1.6) we neglect all those terms which contain the factor $\frac{1}{N}$.

We can then write (A7.1.6) in the form

$$W_T^{(2)}=\frac{2|C_1|^2}{\hbar^2 N}\sum_{k'}\int_{-t}^{t}\exp\Big\{\sum_{k'\neq k}\frac{\gamma_k}{N}\Big[-(n_k+\tfrac{1}{2})+(n_k+\tfrac{1}{2})\cos\omega_k t'+\tfrac{i}{2}\sin\omega_k t'\Big]\Big\}$$

$$\times\Big\{(n_{k'}+\tfrac{1}{2})\cos\omega_{k'}t'+\tfrac{i}{2}\sin\omega_{k'}t'\Big\}\exp\Big[-\frac{i\Delta E}{\hbar}t'\Big]dt'. \qquad \text{(A7.1.7)}$$

The expression for $W_T^{(2)}$, (A7.1.7) can be written in terms of real and imaginary parts,

$$W_T^{(2)}=\frac{2|C_1|^2}{\hbar^2 N}\sum_{k'}\int_{-t}^{t}\exp\Big\{\sum_{k\neq k'}\frac{\gamma_k}{N}\Big[(n_k+\tfrac{1}{2})(\cos\omega_k t'-1)\Big]\Big\}$$

$$\times\Big[(n_{k'}+\tfrac{1}{2})\cos\omega_{k'}t'\cos\Big\{\sum_{k'\neq k}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}-\frac{1}{2}\sin\omega_{k'}t'\sin\Big\{\sum_{k'\neq k}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}$$

$$+i(n_{k'}+\tfrac{1}{2})\cos\omega_{k'}t'\sin\Big\{\sum_{k'\neq k}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}+\frac{i}{2}\sin\omega_{k'}t'\cos\Big\{\sum_{k'\neq k}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}\Big]d$$

$$\text{(A7.1.8)}$$

Both the imaginary terms here are odd about $t'=0$ and hence are zero.

Thus,

$$W_T^{(2)}=\frac{2|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\Big\{\int_{-t}^{t}\exp\Big\{\sum_{k\neq k'}\frac{\gamma_k}{N}\Big[-(n_k+\tfrac{1}{2})+(n_k+\tfrac{1}{2})\cos\omega_k t'\Big]\Big\}$$

$$\times\Big[(n_{k'}+\tfrac{1}{2})\cos\omega_{k'}t'\cos\Big\{\sum_{k\neq k'}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}-\frac{1}{2}\sin\omega_{k'}t'\sin\Big\{\sum_{k\neq k'}\frac{\gamma_k}{2N}\sin\omega_k t'-\frac{\Delta E}{\hbar}t'\Big\}\Big]dt'.$$

$$\text{(A7.1,9)}$$

We write

$$\left.\begin{aligned}
S&=\sum_{k}\frac{\gamma_k}{2N}(n_k+\tfrac{1}{2})\\
F_1(t)&=\sum_{k\neq k'}\frac{\gamma_k}{N}(n_k+\tfrac{1}{2})\cos\omega_k t=\sum_{k\neq k'}\frac{\gamma_k}{2N}\coth(\frac{\beta\hbar\omega_0}{2}\cos\omega_k t\\
F_2(t)&=\sum_{k\neq k'}\frac{\gamma_k}{2N}\sin\omega_k t=\sum_{k\neq k'}\frac{\gamma_k}{2N}\sin\omega_k t
\end{aligned}\right\}\qquad\text{(A7.1.10)}$$

Thus (A7,1,9) can be written as

$$W_T^{(2)}=2\frac{|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\exp(-2S)\int_{-t}^{t}\exp\big[F_1(t')\big]\Big\{(n_{k'}+\tfrac{1}{2}]\cos\omega_{k'}t'\cos\Big[F_2(t')-\frac{\Delta E}{\hbar}t'\Big]$$

$$-\frac{1}{2}\sin\omega_{k'}t'\sin\Big\{F_2(t')-\frac{\Delta E}{\hbar}t'\Big\}\Big\}dt'. \qquad \text{(A7.1.11)}$$

Using cos (A + B) = cosAcosB-sinAsinB, we may write (A7.1.11) as

$$W_T^{(2)} = \frac{2|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\exp(-2S)\int_{-t}^{t}\exp[F_1(t')]\frac{1}{2}\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'+\omega_{k'}t'\right]dt'$$

$$+\frac{2|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\exp(-2S)\int_{-t}^{t}\exp[F_1(t')]n_{k'}\cos\omega_{k'}t'\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right]dt'. \qquad \text{(A7.1.12)}$$

Using $\cos A\cos B = \frac{1}{2}\{\cos(A+B)+\cos(A-B)\}$ we may write (A7.1.12) as

$$W_T^{(2)} = \frac{|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\exp(-2S)(n_{k'}+1)\int_{-t}^{t}dt'\exp[F_1(t')]\cos\left[F_2(t')-\Delta E_1^{k'}\frac{t'}{\hbar}\right]$$

$$+\frac{|C_1|^2}{\hbar^2}\sum_{k'}\frac{1}{N}\exp(-2S)n_{k'}\int_{-t}^{t}dt'\exp[F_1(t')]\cos\left[F_2(t')-\Delta E_2^{k'}\frac{t'}{\hbar}\right]$$

$$\Delta E_1^{k'} = \Delta E - \hbar\omega_{k'},\ \Delta E_2^{k'} = \Delta E + \hbar\omega_{k'}. \qquad \text{(A7.1.13)}$$

In the zero dispersion limit, $\omega_k = \omega_0 \ \forall k$ (A7.1.13) may be written as

$$W_T^{(2)} = \frac{|C_1|^2}{\hbar^2}\exp(-2S)(1+n)\int_{-t}^{t}dt'\exp[F_1(t')]\cos\left[F_2(t')-\frac{\Delta E_1}{\hbar}t'\right]$$

$$+\frac{|C_1|^2}{\hbar^2}\exp(-2S)n\int_{-t}^{t}dt'\exp[F_1(t')]\cos\left[F_2(t')-\frac{\Delta E_2}{\hbar}t'\right] \qquad \text{(A7.1.14)}$$

where

$$\Delta E_1 = \Delta E - \hbar\omega_0$$

$$\Delta E_2 = \Delta E + \hbar\omega_0.$$

This is text equation (7.7).

This should be compared with $W_T^{(1)}$, (3.24), which may be written as

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp(-2S)\int_{-t}^{t}dt'\exp[F_1(t')]\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right].$$

APPENDIX A7.2

The Calculation of $W_T^{(3)}$,

In this appendix we will show that the interference part of the transition probability $W_T^{(3)}$ (7.2) is only of order $\frac{1}{N}$ and is hence negligible. The general expression for $W_T^{(3)}$ is given by text equation (7.2).

$$W_T^{(3)}$$

$$= \frac{2\pi}{\hbar}\sum_{\{n_k^0\},\{n_k^1\}}(1-r_k)r_k^{n_k^1}\sum_{k'}\left|K^{11}_{k',1}K^{1}_{k',1}\right| I_{n_{k'}^0,n_{k'}^1} I^{1}_{n_{k'}^0,n_{k'}^1}\prod_{k\neq k'} I^{2}_{n_k^0,n_k^1}\,\delta(E_{0,\{n_k^0\}}-E_{1,\{n_k^1\}}) \qquad (A7.2.1)$$

We have already shown in Appendix A7.1 [(A7.1.2) and (A7.1.3)] that

$$K^{1}_{k',1} = \left(\frac{2}{N}\right)^{\frac{1}{2}}\sin(k'p+\pi/4)\,C_1 \qquad (A7.2.2)$$

where

$$C_1 = \int d\underline{r}\,\varphi_0^*(\underline{r}-p\underline{a},x_p)\left(-\frac{\hbar^2}{M}\frac{\partial}{\partial x_p}\varphi_1(\underline{r}-p\underline{a},x_p)\right). \qquad (A7.2.3)$$

Now,

$$K^{k''}_{k,1} = \int d\underline{r}\,\varphi_0^*(\underline{r}-p\underline{a},x_p)\left(-\frac{\hbar^2}{M}\frac{\partial^2}{\partial q_k^2}\varphi_1(\underline{r}-p\underline{a},x_p)\right). \qquad (A7.2.4)$$

Now,

$$\frac{\partial^2}{\partial q_k^2} = \frac{\partial}{\partial q_k}\left(\frac{\partial}{\partial q_k}\right) = \frac{\partial}{\partial q_k}\left[\sum_m \frac{\partial x_m}{\partial q_k}\frac{\partial}{\partial x_m}\right]$$

$$= \sum_m \frac{\partial^2 x_m}{\partial q_k^2}\frac{\partial}{\partial x_m} + \sum_m \frac{\partial x_m}{\partial q_k}\frac{\partial^2}{\partial q_k\partial x_m}.$$

$$\frac{\partial^2}{\partial q_k^2} = \sum_m \frac{\partial x_m}{\partial q_k}\frac{\partial^2}{\partial q_k\partial x_m} = \sum_m \frac{\partial x_m}{\partial q_k}\frac{\partial}{\partial q_k}\left(\frac{\partial}{\partial x_m}\right)$$

$$\frac{\partial^2}{\partial q_k^2} = \sum_m \frac{\partial x_m}{\partial q_k}\sum_n \frac{\partial x_n}{\partial q_k}\frac{\partial}{\partial x_n}\left(\frac{\partial}{\partial x_m}\right) = \sum_{m,n}\frac{\partial x_m}{\partial q_k}\frac{\partial x_n}{\partial q_k}\frac{\partial^2}{\partial x_n\partial x_m}.$$

Thus,

$$\frac{\partial^2}{\partial q_k^2} = \sum_{m,n}\left(\frac{2}{N}\right)\sin(km+\pi/4)\sin(kn+\pi/4)\frac{\partial^2}{\partial x_n\partial x_m}$$

Hence,

$$K^{11}_{k,1}$$

$$= \left(\frac{2}{N}\right)\sum_{m,n}\sin(km+\pi/4)\sin(kn+\pi/4)\int\varphi_0^*(\underline{r}-p\underline{a},x_p)\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_n\partial x_m}\varphi_1(\underline{r}-p\underline{a},x_p)\,d\underline{r}.\right.$$

Thus, as the electronic wavefunction φ_1, depends only on the local coordinate x_p,

$$K''_{k,1} = \left(\frac{2}{N}\right)\sin^2(kp+\pi/4)\int\varphi_0^*(\underline{r}-p\underline{a},x_p)\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_p^2}\varphi_1(\underline{r}-p\underline{a},x_p)\right)d\underline{r}\,. \qquad \text{(A7.2.5)}$$

From (A7.2.3) and (A7.2.5) we can see that $K'_{k,1}$ and $K''_{k,1}$ are of order $\frac{1}{\sqrt{N}}$ and $\frac{1}{N}$ respectively.

The expression for $W_T^{(3)}$ (7.2) also contains the factor $I_{n^0_{k'},n^1_{k'}}I^1_{n^0_{k'},n^1_{k'}}$. Using the expressions we have derived for $I_{n^0_k,n^1_k}$ (5.27) and $I^1_{n^0_k,n^1_k}$ (7.5) we obtain that

$$\begin{aligned}I_{n^0_k,n^1_k}I^1_{n^0_k,n^1_k}\\ =\Big\{&\left(\tfrac{1}{2}\right)^{\frac{1}{2}}(1+n^1_k)\Big\{1-\left(n^1_k+\tfrac{3}{2}\right)\tfrac{\gamma_k}{2N}\Big\}\left(\tfrac{\gamma_k}{2N}\right)^{\frac{1}{2}}\delta_{n^0_k,n^1_k+1}-\left(\tfrac{1}{2}\right)^{\frac{1}{2}}(1+2n^1_k)\Big[1-\left(n^1_k+\tfrac{1}{2}\right)\tfrac{\gamma_k}{2N}\Big]\left(\tfrac{\gamma_k}{2N}\right)^{\frac{1}{2}}\delta_{n^0_k,n^1_k}\\ &+\left(\tfrac{1}{2}\right)^{\frac{1}{2}}n^1_k\Big\{1-\left(n^1_k-\tfrac{1}{2}\right)\tfrac{\gamma_k}{2N}\Big\}\left(\tfrac{\gamma_k}{2N}\right)^{\frac{1}{2}}\delta_{n^0_k,n^1_k-1}\Big\}.\end{aligned} \qquad \text{(A7.2.6)}$$

Retaining only the largest terms (which are of order $\frac{1}{\sqrt{N}}$) in this expression we obtain

$$I_{n^0_k,n^1_k}I^1_{n^0_k,n^1_k}=\left(\frac{\gamma_k}{4N}\right)^{\frac{1}{2}}\Big\{(1+n^1_k)\delta_{n^0_k,n^1_k+1}-(1+2n^1_k)\delta_{n^0_k,n^1_k}+n^1_k\,\delta_{n^0_k,n^1_k-1}\Big\} \qquad \text{(A7,2,7)}$$

Combining (A7,2,1), (A7,2,3), (A7,2,5) and (A7,2,7) we see that the interference part of the recombination rate $W_T^{(3)}$ contains N terms each of which is of order $\frac{1}{N^{3/2}}$. Hence, $W_T^{(3)}$ is negligible.

APPENDIX A7.3

Calculation of the transition probability $W_T^{(4)}$

In this last appendix of Chapter 7, we will calculate the transition probability $W_T^{(4)}$ which is given by the text equation (7.3).

$$W_T^{(4)}=\frac{2\pi}{\hbar}\sum_{\{n_k^0\},\{n_k^1\}}(1-r_k)r_k^{n_k^1}\sum_{k'}\sum_{k''}|K^1_{k',1}\,K^1_{k'',1}|I_{n^0_{k'},n^1_{k'}}\,I^1_{n^0_{k''},n^1_{k''}}$$
$$\times(I_{n^0_{k''},n^1_{k''}}I^1_{n^0_{k''},n^1_{k''}})\prod_{k\neq k',k''}I^2_{n^0_k,n^1_k}\,\delta(E_{0,\{n_k^0\}}-E_{1,\{n_k^1\}}). \qquad \text{(A7.3.1)}$$

Using (A7,2,3) and (A7,2,4) we see that (7.3) contains N^2 terms each of which is of order $\frac{1}{N^2}$. Hence W_T^4 produces a significant contribution to the recombination rate,

Writing $K^1_{k,1}=\left(\frac{2}{N}\right)^{\frac{1}{2}}\sin(kp+\pi/4)C_1$ (7,8), and using the exponential representation of the delta function, (7,3) becomes

$$W_T^{(4)}=\frac{2}{\hbar^2N}\frac{1}{Z}\sum_{k'}2\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|\sum_{\{n_k^0\},\{n_k^1\}}\int_{-t}^{t}\exp\Big[-\sum_k\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\Big]$$
$$\times(I_{n^0_{k'},n^1_{k'}}I^1_{n^0_{k'},n^1_{k'}})(I_{n^0_{k''},n^1_{k''}}I^1_{n^0_{k''},n^1_{k''}})\prod_{k\neq k',k''}I^2_{n^0_k,n^1_k}\exp\Big[\frac{it}{\hbar}\Big\{\sum_k\hbar\omega_k(n_k^0-n_k^1)-\Delta E\Big\}\Big]d$$
(A7.3.2)

where Z is the partition function

$$Z=\sum_{\{n_k^1\}}\exp\Big[-\sum_k\beta\hbar\omega_k(n_k+\tfrac{1}{2})\Big].$$

Using (8,22) this becomes

$$W_T^{(4)}=\frac{4}{\hbar^2N}\frac{1}{Z}\sum_{k',k''}\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|\sum_{\{n_k^0\},\{n_k^1\}}\int_{-t}^{t}\exp\Big[-\sum_k\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})\Big]$$
$$\times\left(\frac{\gamma_k}{4N}\right)^{\frac{1}{2}}\Big\{(1+n^1_{k'})\delta_{n^0_{k'},n^1_{k'}+1}-(1+2n^1_{k'})\delta_{n^0_{k'},n^1_{k'}}+n^1_{k'}\delta_{n^0_{k'},n^1_{k'}-1}\Big\}$$
$$\times\left(\frac{\gamma_{k''}}{4N}\right)^{\frac{1}{2}}\Big\{(1+n^1_{k''})\delta_{n^0_{k''},n^1_{k''}+1}-(1+2n^1_{k''})\delta_{n^0_{k''},n^1_{k''}}+n^1_{k'}\delta_{n^0_{k''},n^1_{k''}-1}\Big\}$$
$$\times\prod_{k\neq k',k''}\Big\{\Big[1-(n_k^1+\tfrac{1}{2})\frac{\gamma_k}{N}\Big]\delta_{n_k^1,n_k^0}+\left(\frac{\gamma_k}{2N}\right)\Big[(1+n_k^1)\delta_{n_k^0,n_k^1+1}+n_k^1\delta_{n_k^0,n_k^1-1}\Big]\Big\}$$
$$\times\exp\Big[\frac{it'}{\hbar}\Big\{\sum_k\hbar\omega_k(n_k^0-n_k^1)-\Delta E\Big\}\Big]dt'. \qquad \text{(A7.3.3)}$$

By summing over the final states we can then write $W_T^{(4)}$ as

$$W_T^{(4)}=\frac{1}{\hbar^2 NZ}\sum_{k',k''}\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|\frac{(\gamma_{k'}\gamma_{k''})^{\frac{1}{2}}}{N}$$

$$\times\sum_{\{n_k'\}}\int_{-t}^{t}dt'\exp\Big[-\sum_k\beta\hbar\omega_k(n_k'+\tfrac{1}{2})\Big]\Big\{(1+n_{k'}')e^{i\omega_{k'}t'}-(1+2n_{k'}')+n_{k'}'e^{-i\omega_{k'}t'}\Big\}$$

$$\times\Big\{(1+n_{k''}')e^{i\omega_{k''}t'}-(1+2n_{k''})+n_{k''}'e^{-i\omega_{k''}t'}\Big\}\prod_{k\neq k',k''}\Big\{\Big[1-(n_{k''}'+\tfrac{1}{2})\frac{\gamma_k}{N}+\frac{\gamma_k}{2N}\big[(1+n_k')e^{i\omega_k t'}+n_k'e^{-i\omega_k t'}\big]\Big\}$$

$$\times\exp\Big(-\frac{i\Delta E}{\hbar}t'\Big). \qquad \text{(A7.3.4)}$$

We perform the summation $\frac{1}{Z}\sum_{\{n_k'\}}$ by replacing n_k' by their thermal equilibrium values $n_k'=(e^{\beta\hbar\omega_k}-1)^{-1}$ following Holstein[1].

Then $W_T^{(4)}$ becomes

$$W_T^{(4)}=\frac{4}{\hbar^2 N}\sum_{k',k''}\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|\frac{(\gamma_{k'}\gamma_{k''})^{\frac{1}{2}}}{N}$$

$$\times\int_{-t}^{t}dt'\Big\{(n_{k'}'+\tfrac{1}{2})(\cos\omega_{k'}t'-1)+\tfrac{i}{2}\sin\omega_{k'}t'\Big\}\Big\{(n_{k''}'+\tfrac{1}{2})(\cos\omega_{k'}t'-1)+\tfrac{i}{2}\sin\omega_{k''}t'\Big\}$$

$$\times\exp\Big\{\sum_{k\neq k',k''}\frac{\gamma_k}{N}\Big[-(n_k'+\tfrac{1}{2})+(n_k'+\tfrac{1}{2})\cos\omega_k t'+\tfrac{i}{2}\sin\omega_k t'\Big]\Big\}\exp\Big[-\frac{i\Delta E}{\hbar}t'\Big]dt'. \qquad \text{(A7.3.5)}$$

We define S, $F_1(t)$ and $F_2(t)$ as in (A7.1.10) [with the exception that the summation over k is now restricted by $k\neq k', k''$, which makes no significant difference].

The expression for $W_T^{(4)}$ becomes

$$W_T^{(4)}=\frac{4}{\hbar^2 N^2}\sum_{k',k''}\left|\sin(k'p+\pi/4)\sin(k''p+\pi/4)C_1^2\right|(\gamma_{k'}\gamma_{k''})^{\frac{1}{2}} \qquad \text{(A7.3.6)}$$

$$\times\int_{-t}^{t}dt'\exp\{F_1(t')\}\exp\Big\{i\Big[F_2(t)-\frac{\Delta E}{\hbar}t'\Big]\Big\}\Big\{(n_{k'}+\tfrac{1}{2})[\cos\omega_{k'}t'-1]+\tfrac{i}{2}\sin\omega_{k'}t'\Big\}\Big\{(n_{k''}+\tfrac{1}{2})[\cos\omega_{k''}t'-1]+\tfrac{i}{2}\sin\omega_{k''}t'\Big\}$$

We write (A7.3.6) in terms of real and imaginary contributions:

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2} \sum_{k',k''} \left| \sin(k'p+\pi/4)\sin(k''p+\pi/4) C_1^2 \right| (\gamma_{k'}\gamma_{k''})^{1/2} \int_{-t}^{t} dt' \exp\{F_1(t')\}$$

$$\times \Big\{ \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big\{ (n_{k'}+\tfrac{1}{2})[\cos\omega_{k'}t' - 1](n_{k''}+\tfrac{1}{2})[\cos\omega_{k''}t' - 1] - \tfrac{1}{4}\sin\omega_{k'}t'\sin\omega_{k''}t'$$

$$+ i\sin\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big\{ (n_{k'}+\tfrac{1}{2})[\cos\omega_{k'}t' - 1]\tfrac{i}{2}\sin\omega_{k''}t' + (n_{k''}+\tfrac{1}{2})[\cos\omega_{k''}t' - 1]\tfrac{i}{2}\sin\omega_{k'}t' \Big\}$$

$$+ \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big\{ (n_{k'}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)\tfrac{i}{2}\sin\omega_{k''}t' + (n_{k''}+\tfrac{1}{2})(\cos\omega_{k''}t' - 1)\tfrac{i}{2}\sin\omega_{k'}t' \Big\}$$

$$+ i\sin\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big\{ (n_{k'}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)(n_{k''}+\tfrac{1}{2})(\cos\omega_{k''}t' - 1) - \tfrac{1}{4}\sin\omega_{k'}t'\sin\omega_{k''}t' \Big\}\Big\}.$$

(A7.3.7)

In (A7.3.7) the real terms are even about $t'=0$ whereas the imaginary terms are odd. Hence the imaginary terms of the integral are zero. Hence, the expression for $W_T^{(4)}$ becomes

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2} \sum_{k',k''} \left| \sin(k'p+\pi/4)\sin(k''p+\pi/4)\, C_1^2 \right| (\gamma_{k'}\gamma_{k''})^{\frac{1}{2}}$$

$$\times \int_{-t}^{t} dt' \exp\{F_1(t')\} \Big\{ \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big[(n_{k'}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)(n_{k''}+\tfrac{1}{2})(\cos\omega_{k''}t' - 1) - \tfrac{1}{4}\sin\omega_{k'}t'\sin\omega_{k''}t'$$

$$- \tfrac{1}{2}\sin\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \Big[(n_{k'}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)\sin\omega_{k''}t' + (n_{k''}+\tfrac{1}{2})(\cos\omega_{k''}t' - 1)\sin\omega_{k'}t' \Big].$$

(A7.3.8)

We wish to write the factor $\int_{-t}^{t} dt' \{ \quad \}$ (A7.3.8) in the form $\sum_n C_n \int_{-t}^{t} dt' \exp\{F_1(t')\}\cos\left[F_2(t') - \Delta E_n \frac{t'}{\hbar}\right]$ and, hopefully interpret each of these terms as the result of multiphonon processes. However, to do this requires lengthy algebraic manipulations, We examine the factor in (A7.3.8)

$$(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)(\cos\omega_{k''}t' - 1)\cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right]$$

$$- \tfrac{1}{4}\sin\omega_{k'}t'\sin\omega_{k''}t'\cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right]$$

$$- \tfrac{1}{2}(n_{k'}+\tfrac{1}{2})(\cos\omega_{k'}t' - 1)\sin\omega_{k''}t'\sin\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right]$$

$$- \tfrac{1}{2}(n_{k''}+\tfrac{1}{2})(\cos\omega_{k''}t' - 1)\sin\omega_{k'}t'\sin\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right].$$

We designate these terms (A7.3.9) ⟶ (A7.3.12) respectively.

(A7,3,9) is

$$(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})(\cos\omega_{k'}t'-1)(\cos\omega_{k''}t'-1)\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right]$$

$$=(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\cos\omega_{k'}t'\cos\omega_{k''}t'\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right]$$

$$-(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\left[\cos\omega_{k'}t'+\cos\omega_{k''}t'\right]\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right]$$

$$+(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\cos\left[F_2(t')-\frac{\Delta E}{\hbar}t'\right]. \qquad \text{(A7.3.13)}$$

We designate these terms by (A7,3,14) → (A7,3,16) respectively. (A7.3.16) is the form we require, Using the identity $\cos A\cos B=\frac{1}{2}[\cos(A-B)+\cos(A+B)]$ (A7,3,15) becomes

$$-\tfrac{1}{2}(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\Big\{\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k'}t\right]+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k'}t\right]$$

$$+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t\right]+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t\right]\Big\}.$$

In the zero dispersion limit $\omega_k=\omega_0$ we have

$$-\tfrac{1}{2}(n+\tfrac{1}{2})^2\Big\{2\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}-\omega_0\right)t\right]+2\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}+\omega_0\right)t\right]\Big\}$$

$$=-(n+\tfrac{1}{2})^2\Big\{\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}-\omega_0\right)t\right]+\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}+\omega_0\right)t\right]\Big\}. \qquad \text{(A7.3.17)}$$

(A7,3,14) is $(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\cos\omega_{k'}t\cos\omega_{k''}t\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t\right]$.

Using the identity $\cos A\cos B=\frac{1}{2}[\cos(A-B)+\cos(A+B)]$ this becomes

$$\tfrac{1}{2}(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\cos\omega_{k'}t\Big\{\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t\right]+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t\right]\Big\}$$

$$=\tfrac{1}{4}(n_{k'}+\tfrac{1}{2})(n_{k''}+\tfrac{1}{2})\Big\{\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t-\omega_{k'}t\right]+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t+\omega_{k'}t\right]$$

$$+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k'}t-\omega_{k''}t\right]+\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k'}t+\omega_{k''}t\right]\Big\}.$$

In the zero dispersion limit $\omega_k=\omega_0\ \forall k$ this is

$$\tfrac{1}{4}(n+\tfrac{1}{2})^2\Big\{\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}+2\omega_0\right)t\right]+\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}-2\omega_0\right)t\right]\Big\}$$

$$+\tfrac{1}{2}(n+\tfrac{1}{2})^2\cos\left[F_2(t)-\frac{\Delta E}{\hbar}t\right]. \qquad \text{(A7.3.18)}$$

(A7.3.10) is $-\frac{1}{4}\sin\omega_{k'}t\sin\omega_{k''}t\cos[F_2(t)-\frac{\Delta E}{\hbar}t]$.

Using the identity $\sin A\cos B=\frac{1}{2}[\sin(A+B)+\sin(A-B)]$ (A7.3.10) becomes

$$-\frac{1}{8}\sin\omega_{k'}t\{\sin[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t]-\sin[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t]\}.$$

Using the identity $\sin A\sin B=\frac{1}{2}[\cos(A-B)-\cos(A+B)]$ (A7.3.10)becomes

$$-\frac{1}{16}\{\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t-\omega_{k'}t]-\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t+\omega_{k'}t]$$
$$-\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t-\omega_{k'}t]+\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t+\omega_{k'}t]\}.$$

In the zero dispersion limit this becomes

$$\frac{1}{16}\{\cos[F_2(t)-(\frac{\Delta E}{\hbar}-2\omega_0)t]+\cos[F_2(t)-(\frac{\Delta E}{\hbar}+2\omega_0)t]\} ,$$
$$-\frac{1}{8}\cos[F_2(t)-\frac{\Delta E}{\hbar}t]. \qquad (A7.3.19)$$

(A7.3.11) is

$$-\frac{1}{2}(n_{k'}+\frac{1}{2})(\cos\omega_{k'}t-1)\sin\omega_{k''}t\sin[F_2(t)-\frac{\Delta E}{\hbar}t].$$
$$=-\frac{1}{2}(n_{k'}+\frac{1}{2})\cos\omega_{k'}t\sin\omega_{k''}t\sin[F_2(t)-\frac{\Delta E}{\hbar}t]$$
$$+\frac{1}{2}(n_{k'}+\frac{1}{2})\sin\omega_{k''}t\sin[F_2(t)-\frac{\Delta E}{\hbar}t].$$

Using $\sin A\sin B=\frac{1}{2}[\cos(A-B)-\cos(A+B)]$ this is

$$-\frac{1}{4}(n_{k'}+\frac{1}{2})\cos\omega_{k'}t\{\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t]-\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t]\}$$
$$+\frac{1}{4}(n_{k'}+\frac{1}{2})\{\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t]-\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t]\}.$$

Using the identity $\cos A\cos B=\frac{1}{2}[\cos(A+B)+\cos(A-B)]$, (A7.3.12)

becomes

$$-\frac{1}{8}(n_{k'}+\frac{1}{2})\{\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t+\omega_{k'}t]+\cos[F_2(t)-\frac{\Delta E}{\hbar}t-\omega_{k''}t-\omega_{k'}t]$$
$$-\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t+\omega_{k'}t]-\cos[F_2(t)-\frac{\Delta E}{\hbar}t+\omega_{k''}t-\omega_{k'}t]\}.$$

This is, in the zero dispersion limit,

$$\frac{1}{8}\left(n+\frac{1}{2}\right)\left\{\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}-2\omega_0\right)t\right]-\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}+2\omega_0\right)t\right]\right\}$$

$$+\frac{1}{4}\left(n+\frac{1}{2}\right)\left\{\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}+\omega_0\right)t\right]-\cos\left[F_2(t)-\left(\frac{\Delta E}{\hbar}-\omega_0\right)t\right]\right\}. \tag{A7.3.20}$$

Thus, in the zero dispersion limit the term (A7.3.12) is exactly the same as (A7.3.11).

To assist brevity we will now write

$$W_T^{(1)} = \frac{|K|^2}{\hbar^2}\exp(-2S)X_p \tag{A7.3.21}$$

where

$$X_p = \int_{-t}^{t} dt' \exp\{F_1(t')\}\cos\left\{F_2(t)-\frac{\Delta E}{\hbar}t'\right\}. \tag{A7.3.22}$$

We now add (A7.3.13), (A7.3.16) → (A7.3.18), multiply this by $\exp\{F_1(t')\}$ and integrate with respect to t' from $-t$ to t, to obtain for (A7.3.9)

$$-\left(n+\frac{1}{2}\right)^2\left[X_{p+1}+X_{p-1}\right]+\left(n+\frac{1}{2}\right)^2 X_p+\frac{1}{4}\left(n+\frac{1}{2}\right)^2\left[X_{p+2}+X_{p-2}\right]+\frac{1}{2}\left(n+\frac{1}{2}\right)^2 X_p.$$

which is

$$\frac{3}{2}\left(n+\frac{1}{2}\right)^2 X_p+\frac{1}{4}\left(n+\frac{1}{2}\right)^2\left[X_{p+2}+X_{p-2}\right]-\left(n+\frac{1}{2}\right)^2\left[X_{p+1}+X_{p-1}\right]$$

Hence, using (A7.3.19) → (A7.3.12), $W_T^{(4)}$ (A7.3.8) becomes

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2}\sum_{k',k''}\left|\sin\left(k'p+\pi/4\right)\sin\left(k''p+\pi/4\right)C_1^2\right|\left(\gamma_{k'}\gamma_{k''}\right)^{1/2}\exp(-2S)$$

$$\times\left\{\frac{3}{2}\left(n+\frac{1}{2}\right)^2 X_p+\frac{1}{4}\left(n+\frac{1}{2}\right)^2\left[X_{p+2}+X_{p-2}\right]-\left(n+\frac{1}{2}\right)^2\left[X_{p+1}+X_{p-1}\right]-\frac{1}{8}X_p\right.$$

$$\left.+\frac{1}{16}\left[X_{p+2}-X_{p-2}\right]+\frac{1}{4}\left(n+\frac{1}{2}\right)\left[X_{p-2}-X_{p+2}\right]+\frac{1}{2}\left(n+\frac{1}{2}\right)\left[X_{p+1}-X_{p-1}\right]\right\}.$$

This becomes,

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2}\sum_{k',k''}\left|\sin\left(k'p+\pi/4\right)\sin\left(k''p+\pi/4\right)C_1^2\right|\left(\gamma_{k'}\gamma_{k''}\right)^{\frac{1}{2}}\left\{\left[\frac{1}{4}\left(n+\frac{1}{2}\right)^2+\frac{1}{16}-\frac{1}{4}\left(n+\frac{1}{2}\right)\right]X_{p+2}\right.$$

$$+\left[\frac{1}{4}\left(n+\frac{1}{2}\right)^2+\frac{1}{16}+\frac{1}{4}\left(n+\frac{1}{2}\right)\right]X_{p-2}-\left[\left(n+\frac{1}{2}\right)^2-\frac{1}{2}\left(n+\frac{1}{2}\right)\right]X_{p+1}$$

$$\left.-\left[\left(n+\frac{1}{2}\right)^2+\frac{1}{2}\left(n+\frac{1}{2}\right)\right]X_{p-1}+\left[\frac{3}{2}\left(n+\frac{1}{2}\right)^2-\frac{1}{8}\right]X_p\right\}.$$

We finally write $W_T^{(4)}$ in the form

$$W_T^{(4)} = \frac{4}{\hbar^2 N^2} \sum_{k',k''} \left| \sin(k'p + \pi/4) \sin(k''p + \pi/4) C_1^2 \right| (\gamma_{k'} \gamma_{k''})^{\frac{1}{2}} \exp(-2S)$$

$$\times \{ [(\eta + \tfrac{1}{2})^2 + \tfrac{1}{2}\eta(\eta+1)] X_p - (\eta + \tfrac{1}{2})[\eta X_{p+1} + (1+\eta) X_{p-1}] + \tfrac{1}{4}[\eta^2 X_{p+2} + (1+\eta)^2 X_{p-2}]$$

(A7.3.22)

This is text equation (7.14).

PART III

The Molecular Crystal Model taking weak but finite dispersion into account

Chapter 8

The Effect of Dispersion in the M.C.M.

Throughout this thesis we have used time-dependent perturbation theory to calculate the recombination rates. For this to be valid, the final states into which the system relaxes must form a continuum of energy levels. In the context of the M.C.M. this requires the existence of dispersion in the crystalline modes. In this chapter we will take finite but weak dispersion in the M.C.M. into account explicitly and show the artificial nature of the transition rates if there is no dispersion. In addition it will be demonstrated how this dispersion results in modified transition rates.

We start with the general expression for the recombination rate in the M.C.M. which already includes dispersion.
This equation (5.32), is

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\int_{-t}^{t} \exp\Big\{\sum_k \frac{\gamma_k}{N}\big[-(n_k+\tfrac{1}{2})\big]\Big\}\exp\Big\{\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2})\cos\omega_k t'\Big\}$$
$$\times\exp\Big\{i\Big[\sum_k \frac{\gamma_k}{2N}\sin\omega_k t' - \frac{\Delta E}{\hbar}t'\Big]\Big\}dt'. \qquad (8.1)$$

In Appendix 8.1, it is shown that equation (8.1) may be written as

$$W_T^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2}\exp(-2S)\left(\frac{1}{2\pi}\right)\lim_{t\to\infty}\int_{-t}^{t} dt'\exp[F_1(t')]\cos\Big[F_2(t') - \frac{\Delta E}{\hbar}t'\Big], \qquad (8.2)$$

where

$$\left.\begin{aligned} S &= \frac{E_M}{2\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} \\ F_1(t) &= \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\,\frac{1}{N}\sum_k \cos\omega_k t \\ F_2(t) &= \frac{E_M}{\hbar\omega_0}\,\frac{1}{N}\sum_k \sin\omega_k t \end{aligned}\right\} \qquad (8.3)$$

In general the electronic energy difference ΔE is not equal to an integral number of optical phonons,

$$\Delta E = (p+\Delta)\hbar\omega_0 , \quad 0 \leq \Delta \leq 1 .$$

Following Emin (1971), it is shown in Appendix A8.2 that in the weak dispersion regime $\frac{\omega_b}{\omega_0} \ll 1$, we can write,

$$W_T = 2\pi \frac{|K|^2}{\hbar^2\omega_0} \exp(-2S) \frac{1}{2\pi} \lim_{\tau\to\infty} \int_{-\omega_0\tau}^{\omega_0\tau} dx \exp\left[a\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right] \cos\left[a'\left(\frac{\omega_b}{\omega_0}x\right)\sin x - (p+\Delta)x \tag{8.4}$$

where

$$\left.\begin{aligned} a\left(\frac{\omega_b}{\omega_0}x\right) &= \frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0}x\right) \\ a'\left(\frac{\omega_b}{\omega_0}x\right) &= \frac{E_M}{\hbar\omega_0} J_0\left(\frac{\omega_b}{\omega_0}x\right) \\ x &= \omega_0 t \\ \omega_b &= \frac{\omega_1^2}{2\omega_0} . \end{aligned}\right\} \tag{8.5}$$

We divide the range of integration up into intervals of 2π. In the weak dispersion limit, $a\left[(\omega_b x)/\omega_0\right]$ and $a'\left[(\omega_b x)/\omega_0\right]$ vary little over an interval 2π. Hence we may replace $a\left[(\omega_b x)/\omega_0\right]$ and $a'\left[\frac{\omega_b x}{\omega_0}\right]$ in the interval $(2n\pi - \pi)$ to $(2n\pi + \pi)$ by their respective values at $2n\pi$, which will be denoted by a_n and a'_n. The transition probability W_T is then obtained by expressing the integral over the interval $(2n\pi - \pi)$ to $(2n\pi + \pi)$ in terms of integrals over the interval $(-\pi$ to $\pi)$. The details of these calculations are in Appendix A8.3. The final result is,

$$W_T = 2\pi \frac{|K|^2}{\hbar^2\omega_0} \exp(-2S) \left\{ A_0(p+\Delta) + 2\sum_{n=1}^{\infty} A_n(p+\Delta) \cos 2\pi n\Delta \right\}, \tag{8.6}$$

where

$$A_n(p+\Delta) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx \exp\left[a_n \cos x\right] \cos\left[a'_n \sin x - (p+\Delta)x\right] . \tag{8.7}$$

In Appendix A8.4, we use a result in Erdélyi, Magnus, Oberhettinger, Tricomi[28] [Vol 2, p.83, equation (17)] to write,

$$A_n(p+\Delta) = \left[\frac{(a_n^2 - a_n'^2)}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} \Big\{ I_{p+\Delta}\left[(a_n^2 - a_n'^2)^{\frac{1}{2}}\right] + \frac{\sin\pi(p+\Delta)}{\pi} \int_{\theta_n}^{\infty} dt \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}} \cosh t\right] \Big\}$$

where $\theta_n = \cosh^{-1} \dfrac{a_n}{a_n^2 - a_n'^2}$.

First of all, the recombination rates are investigated in which there is no dispersion of the crystalline modes. Considering equation (8.6) we observe that in this case $A_n(p+\Delta) = A_0(p+\Delta)$ for all n. Thus, in the case of zero dispersion

$$W_T = 2\pi \frac{|K|^2}{\hbar^2} \exp(-2S) A_0(p+\Delta) \Big\{ 1 + 2\sum_{n=1}^{\infty} \cos 2\pi n\Delta \Big\}. \tag{8.9}$$

It is shown in Appendix A9.5 that

$$\begin{aligned} 1 + 2\sum_{n=1}^{\infty} \cos 2\pi n\Delta &= 0 \quad \text{if } \Delta \neq 0 \\ &\to \infty \quad \text{if } \Delta = 0. \end{aligned} \tag{8.10}$$

Thus, if $\Delta \neq 0$ (off resonance) the recombination rate vanishes if there is no dispersion. When $\Delta = 0$ the series for the transition rate is infinite and W_T diverges, showing that vibrational dispersion is essential to ensure that the transition rate be finite.

Physically, dispersion is essential in order that the energy released by the transition can be dissipated to the lattice. From a mathematical point of view, dispersion gives rise to a continuum of final states which is a necessary condition for the application of time dependent perturbation theory. In the absence of dispersion, a transition occurs to a discrete final state with exact conservation of energy and the transition probability is proportional to t^2. This aspect of the problem in which the recombination rate is not well defined has been discussed by de Wit[26] (1968) and Holstein[1] (1959 and recent preprint) for the case of small polaron motion.

We now consider the recombination rates when finite but weak dispersion is taken into account. The calculation of the expression for $A_n(p+\Delta)$ given by equation (8.8) is quite difficult,

$$A_n(p+\Delta)=\left[\frac{(a_n^2-a_n'^2)}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}}\left\{I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]+\frac{\sin\pi(p+\Delta)}{\pi}\int_0^\infty dt\exp\left[-(p+\Delta)t-(a_n^2-a_n'^2)^{\frac{1}{2}}\cosh t\right]$$

First of all, we evaluate $A_n(p+\Delta)$ at the absolute zero of temperature, $T=0$, the details of this calculation being in Appendix A8.6. The calculation of the first term in expression (8,8),
$C_n(p+\Delta)=\left[\frac{(a_n^2-a_n'^2)}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]$ requires some care. Since, as $T\to 0, \sqrt{a_n^2-a_n'^2}\to 0$ we use the small argument approximation for $I_p(x)$,

$$I_p(x)\cong\left(\frac{x}{2}\right)^p\frac{1}{p!}. \tag{8.11}$$

Doing this, $C_n(p+\Delta)$ is found to be

$$C_n(p+\Delta)=\frac{(a_n')^{p+\Delta}}{(p+\Delta)!}, \tag{8.12}$$

where $a_n'=\frac{E_M}{\hbar\omega_0}J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)$.

The second term in expression (8,8) is

$$B_n(p+\Delta)=\frac{\sin\pi(p+\Delta)}{\pi}\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}}\int_0^\infty dt\exp\left[-(p+\Delta)t-(a_n^2-a_n'^2)^{\frac{1}{2}}\cosh t\right].$$

This is found to be, as $T\to 0$,

$$B_n(p+\Delta)=\frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}, \tag{8.13}$$

which is a constant, independent of the index n.

The expressions for $C_n(p+\Delta)$, (8.12) and $B_n(p+\Delta)$, (8.13) are used in the general form of the transition rate, (8.6) to obtain,

$$W_{T=0} = 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{1}{(p+\Delta)!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\}$$

$$+ 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}\left\{1 + 2\sum_{n=1}^{\infty}\cos 2\pi n\Delta\right\}. \qquad (8.14)$$

The second series in expression (8.14) is zero for all values of Δ and we are left with

$$W_{T=0} = 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{1}{(p+\Delta)!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\}$$

(8.15)

The first term in this series is the expression for the recombination rate at absolute zero which we have obtained previously. Regarding the convergence of the series (8.16), the large argument approximation for $J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)$ is used.

Now,

$$J_0(x) \xrightarrow{\text{large } x} \left(\frac{2}{\pi x}\right)^{\frac{1}{2}}\cos(x-\pi/4). \qquad (8.16)$$

Thus, since

$$\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p+\Delta} \propto \left(\frac{1}{n}\right)^{p+\Delta}, \qquad (8.17)$$

the series for $W_{T=0}$ given by expression (8.15) is indeed convergent.

We note that all the terms in the expression for the transition rate, (8.16) are additive at resonance, $\Delta = 0$,

$$W_{T=0} = 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p}\frac{1}{p!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p}\right\} \qquad (8.18)$$

whereas at the exactly off resonance condition, $\Delta = \frac{1}{2}$ the terms in the series have alternating signs:

$$W_{T=0} = 2\pi \frac{|K|^2}{\hbar^2 \omega_0} \exp(-2S) \left(\frac{E_M}{\hbar\omega_0}\right)^{p+\frac{1}{2}} \frac{1}{(p+\frac{1}{2})!} \left\{ 1 + 2 \sum_{n=1}^{\infty} \left[J_0 \left(2\pi n \frac{\omega_b}{\omega_0} \right) \right]^{p+\frac{1}{2}} (-1)^n \right\}. \tag{8.19}$$

The expressions (8.18) and (8.19) appear to show that as a function of the electronic energy gap, ΔE , the transition rate has a local maximum at the resonance condition, $\Delta = 0$ and a local minimum at the exactly off-resonance condition, $\Delta = \frac{1}{2}$, though we have not been able to obtain these summations in closed form.

Next we investigate the transition probability W_T in the finite temperature, weak coupling $\left(\frac{E_M}{\hbar\omega_0} \ll 1\right)$ limit. The calculational details for this limit are in Appendix A8.7.

In the weak coupling limit,

$$(a_n^2 - a_n'^2)^{\frac{1}{2}} = \frac{E_M}{\hbar\omega_0} \left(\coth^2 \frac{\beta\hbar\omega_0}{2} - 1 \right)^{\frac{1}{2}} J_0 \left(2\pi n \frac{\omega_b}{\omega_0} \right) \ll 1,$$

so that in the evaluation of

$$C_n(p+\Delta) = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2} \right]^{\frac{p+\Delta}{2}} I_{p+\Delta} \left[(a_n^2 - a_n'^2)^{\frac{1}{2}} \right] \tag{8.20}$$

we once again use the small argument approximation for the modified Bessel function to obtain expression (A8.7.6) which is

$$C_n(p+\Delta) = \left[\left(\frac{E_M}{\hbar\omega_0}\right) J_0 \left(2\pi n \frac{\omega_b}{\omega_0} \right) (1 + N(\omega_0)) \right]^{p+\Delta} \frac{1}{(p+\Delta)!}.$$

In expression (8.20), $N(\omega_0) = [\exp(\beta\hbar\omega_0) - 1]^{-1}$ is the thermal probability of occupation of the phonon mode with frequency ω_0.

We find once again that the term

$$\mathcal{B}_n = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2} \right]^{\frac{p+\Delta}{2}} \frac{\sin \pi(p+\Delta)}{\pi} \int_0^\infty dt \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}} \cosh t \right],$$

becomes

$$\mathcal{B}_n = \frac{\sin \pi(p+\Delta)}{\pi(p+\Delta)}. \tag{8.21}$$

Hence, as in the absolute zero, $T=0$ case, the series involving the terms $B_n(p+\Delta)$ sums to zero. Thus, the transition probability in the finite temperature, weak coupling $\frac{E_M}{\hbar\omega_0} \ll 1$ case is found to be

$$W_T = 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{(1+N(\omega_0))^{p+\Delta}}{(p+\Delta)!}\left\{1+2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\}. \tag{8.22}$$

which is Appendix equation, (A8.7.9).

Comparing this result with the expression for $W_{T=0}$ equation (8.15) reveals that

$$W_T = [1+N(\omega_0)]^{p+\Delta}W_{T=0}. \tag{8.23}$$

Hence, this simple relationship which was obtained for the M.C.M. in the absence of dispersion and for the S.C.C.M. retains its validity in the finite temperature, weak coupling limit when the effect of finite dispersion is included.

The calculation of the transition probability in the high temperature $(\beta\hbar\omega_0 \ll 1)$, strong coupling $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$ limit is much more difficult.

The expression for the transition rate is

$$W_T = 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left\{C_0(p+\Delta)+B_0(p+\Delta)+2\sum_{n=1}^{\infty}\left(C_n(p+\Delta)+B_n(p+\Delta)\right)\cos 2\pi n\Delta\right\}, \tag{8.24}$$

where

$$C_n(p+\Delta) = \left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right],$$

and

$$B_n(p+\Delta) = \frac{\sin\pi(p+\Delta)}{\pi}\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]\int_0^{\infty}dt\exp\left[-(p+\Delta)t-(a_n^2-a_n'^2)^{\frac{1}{2}}\cosh t\right].$$

To simplify our later calculations, we write the transition rate in the form,

$$W_T = 2\pi \frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\left\{C_0(p+\Delta) + 2\sum_{n=1}^{\infty} C_n(p+\Delta)\cos 2\pi n\Delta\right\}$$

$$+ 2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)\,B_\infty\left\{1 + 2\sum_{n=1}^{\infty}\cos 2\pi n\Delta\right\}$$

$$+\frac{2\pi}{\hbar\omega_0}|K|^2\exp(-2S)\left\{(B_0(p+\Delta)-B_\infty) + 2\sum_{n=1}^{\infty}(B_n(p+\Delta)-B_\infty)\cos 2\pi n\Delta\right\}. \tag{8.25}$$

In this expression,

$$B_\infty = \underset{n\to\infty}{\text{Limit}}\, B_n(p+\Delta). \tag{8.26}$$

The second series in equation (8.25) is zero, as shown by equation (8.10). In the high temperature $(\beta\hbar\omega_0 \ll 1)$, strong coupling limit $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$,

$$(a_n^2 - a_n'^2)^{\frac{1}{2}} = \frac{E_M}{\hbar\omega_0}\left(\coth^2\frac{\beta\hbar\omega_0}{2} - 1\right)^{\frac{1}{2}} J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right) \gg 1, \tag{8.27}$$

provided that n is small, $\left[\text{i.e. } J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right) \sim 1\right]$. However, when n is large we use the large argument approximation,

$$J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right) \propto \left(\frac{1}{n}\right)^{\frac{1}{2}}.$$

Hence, $(a_n^2 - a_n'^2)^{\frac{1}{2}} \to 0$ for large n . (8,28)

Thus,

$$B_\infty = \underset{n\to\infty}{\text{Limit}}\, B_n(p+\Delta) = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} \frac{\sin\pi(p+\Delta)}{\pi}\int_0^\infty dt\, \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}}\cosh t\right]$$

becomes, on using equation (8,82) and the evaluation of $B_n(p+\Delta)$ in the weak coupling, finite temperature limit, equation (8.13),

$$B_\infty = \underset{n\to\infty}{\text{Limit}}\, B_n(p+\Delta) = \frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}. \tag{8.29}$$

We also note that as the argument of the exponential function becomes smaller as n increases, the terms $B_n(p+\Delta)$ actually become larger with increasing n. This is the reason behind writing W_T in the form of equation (8.25), the terms in the third series, $B_n(p+\Delta)-B_\infty < 0$ and $B_n(p+\Delta)-B_\infty \rightarrow 0$ as $n\rightarrow\infty$. We now investigate the terms in the first series for W_T in equation (8.25) which are

$$C_n(p+\Delta)=\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right].$$

For small n, $(a_n^2-a_n'^2)^{\frac{1}{2}} \gg 1$ [condition (8.27)] so that the large argument approximation is used for the modified Bessel function,

$$I_p(x)\sim\frac{1}{\sqrt{2\pi x}}\exp\left[x-\frac{p^2}{2x}\right]. \tag{8.30}$$

Using (8.30) the following result is obtained,

$$C_n(p+\Delta)=\frac{1}{\sqrt{2\pi(a_n^2-a_n'^2)^{\frac{1}{2}}}}\exp\left[+\frac{\beta\hbar\omega_0}{2}(p+\Delta)\right]\exp\left[(a_n^2-a_n'^2)^{\frac{1}{2}}-\frac{p^2}{2(a_n^2-a_n'^2)^{\frac{1}{2}}}\right]. \tag{8.31}$$

Using equations (8.29) and (8.31) we conclude that $C_n(p+\Delta)\gg B_n(p+\Delta)-B_\infty$ for small n, (8.32). Thus, we believe the only significant contribution to the transition rate W_T comes from the first series in equation (8.25),

$$W_T\cong 2\pi\frac{|K|^2}{\hbar^2}\exp(-2S)\left\{C_0(p+\Delta)+2\sum_{n=1}^{\infty}C_n(p+\Delta)\cos 2\pi n\Delta\right\},$$

$$\text{where}\quad C_n(p+\Delta)=\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]. \tag{8.33}$$

For large n, $(a_n^2-a_n'^2)^{\frac{1}{2}}\rightarrow 0$, equation (8.28) so that the small argument approximation for the modified Bessel function may be used. Following the previous discussion in the finite temperature, weak coupling regime, we deduce that the series for W_T given by equation (8.33) is convergent.

The first term in the series (8.33) is

$$2\pi\frac{|K|^2}{\hbar^2\omega_0}\exp(-2S)C_0(p+\Delta)$$

which becomes the standard temperature activated transition rate

$$\frac{|K|^2}{\hbar^2}\left(\frac{\pi}{kTE_M}\right)^{\frac{1}{2}}\exp(-\beta E_b)$$

on using the approximation given by equation (8.31).

The higher terms in the series for W_T given by equation (8.31) become smaller but are not of the temperature activated form even when the approximation (8.31) is valid. For large n, $(a_n^2 - a_n'^2)^{\frac{1}{2}} \to 0$ and the small argument approximation must be used for the modified Bessel function. Thus the calculation of the term

$$C_n(p+\Delta) = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2 - a_n'^2)^{\frac{1}{2}}\right]$$

resembles our previous discussion of the transition rate at the absolute zero of temperature. Thus for large n the contributions to the transition rate resemble the standard terms for the absolute zero temperature case rather than the temperature activated transition probability for the high temperature, strong coupling case.

In the classical high temperature limit $(kT \gg \hbar\omega_c)$ one can interpret the infinite number of contributions from the following point of view. The interaction energy of an electron occupying state i when the displacement of the occupied site is x, is given by $E^i_{int} = -A^i x$. Thus, a thermal fluctuation such that $-A^1 x_i = -A^0 x + \Delta E$, which occurs with probability proportional to $\exp(-\beta E_b)$ will permit a transition from the excited electronic state to the ground electronic state. If there is no dispersion $(\omega_k = \omega_c)$ then this configuration will occur again one period $2\pi/\omega_c$ later, and so on producing a so-called 'ringing' effect. With vibrational coupling, the modes become progressively out of phase in successive periods, reducing successive contributions to the transition rate, W_T. In particular, this is the reason why the contributions to W_T for n > 0 have not retained the temperature activated form.

Summary

In this chapter we have taken explicit account of the effect of dispersion on the non-radiative transition rates. The recombination rates are found to be given by a series,

$$W_T = 2\pi \frac{|K|^2}{\hbar^2 \omega_0} \exp(-2S) \left\{ A_0(p+\Delta) + 2\sum_{n=1}^{\infty} A_n(p+\Delta) \cos 2\pi n\Delta \right\} \quad (8.6)$$

where

$$A_n(p+\Delta) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx \exp[a_n \cos x] \cos[a_n' \sin x - (p+\Delta)x]. \quad (8.7)$$

First of all, we have shown that in the limit of zero dispersion the recombination rate is infinite when the resonance condition, $\Delta E = p\hbar\omega_0$, is satisfied and zero otherwise. These results are demonstrated by equations (8.9) and (8.10). This unrealistic result derives from the fact that the final states do not form a continuum of energy levels in the absence of dispersion and thus the condition for the application of time-dependent perturbation theory is not satisfied.

When the effect of weak but finite dispersion $\left(\frac{\omega_b}{\omega_0} \ll 1\right)$ is included we have found the transition rates at the absolute zero of temperature and in the weak coupling $\left(\frac{E_M}{\hbar\omega_0} \ll 1\right)$ finite temperature limit to be given by equations (8.15) and (8.22) respectively. The relationship,

$$W_T = [1 + N(\omega_0)]^p W_{T=0}$$

is still valid for this case. Finally we have discussed the complicated transition rates which arise in the high temperature $(\beta\hbar\omega_0 \ll 1)$, strong coupling $\left(\frac{E_M}{\hbar\omega_0} \gg 1\right)$ limit for which a simple temperature activated recombination rate is no longer valid.

APPENDIX A8.1.

Calculation of the recombination rates in the M.C.M. including dispersion.

Our starting point is the general expression in Chapter 5 for the recombination rates in the M.C.M. which includes dispersion (5.32).

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\int_{-t}^{t} \exp\left\{\sum_k \frac{\gamma_k}{N}\left[-(n_k+\tfrac{1}{2})\right]\right\}\exp\left\{\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2})\cos\omega_k t'\right\}$$
$$\times \exp\left\{i\left[\sum_k \frac{\gamma_k}{2N}\sin\omega_k t' - \frac{\Delta E}{\hbar}t'\right]\right\}dt'. \qquad (A8.1.1)$$

Writing $W_T^{(1)}$ in terms of real and imaginary parts,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\left\{\sum_k \frac{\gamma_k}{N}\left[-(n_k+\tfrac{1}{2})\right]\right\}\int_{-t}^{t} \exp\left\{\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2})\cos\omega_k t'\right\}$$
$$\times\left\{\cos\left[\sum_k \frac{\gamma_k}{2N}\sin\omega_k t' - \frac{\Delta E}{\hbar}t'\right] + i\sin\left[\sum_k \frac{\gamma_k}{2N}\sin\omega_k t' - \frac{\Delta E}{\hbar}t'\right]\right\}dt'. \qquad (A8.1.2)$$

The integrand of the imaginary component of $W_T^{(1)}$ is odd about $t'=0$.

Hence, the imaginary contribution is zero.

Now, n_k is the thermal equilibrium value.

Thus, $n_k = \dfrac{1}{e^{\beta\hbar\omega_k} - 1}$.

Hence,

$$n_k + \frac{1}{2} = \frac{1}{2}\coth\frac{\beta\hbar\omega_k}{2}. \qquad (A8,1,3)$$

Thus,

$$\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2}) = \sum_k \frac{\gamma_k}{2N}\coth\frac{\beta\hbar\omega_k}{2}.$$

In the limit of weak dispersion

$$\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2}) \sim \frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}.$$

Writing

$$E_M = \sum_k \frac{\gamma_k\hbar\omega_k}{2} \sim \frac{\gamma_0\hbar\omega_0}{2} \qquad (A8,1,4)$$

$\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2})$ becomes $\dfrac{E_M}{\hbar\omega_0}\coth\dfrac{\beta\hbar\omega_0}{2}$.

The argument of the exponential factor in (A8,1,2) is

$$\sum_k \frac{\gamma_k}{N}(n_k+\tfrac{1}{2})\cos\omega_k t = \sum_k \frac{\gamma_k}{N}\frac{1}{2}\coth\frac{\beta\hbar\omega_k}{2}\cos\omega_k t$$

which in the weak dispersion limit becomes

$$\sim \frac{\gamma_0}{2} \coth \frac{\beta\hbar\omega_0}{2} \frac{1}{N} \sum_k \cos\omega_k t \, .$$

Thus,

$$\sum_k \frac{\gamma_k}{N} \left(n_k + \frac{1}{2}\right) \cos\omega_k t = \frac{E_M}{\hbar\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \frac{1}{N} \sum_k \cos\omega_k t \, . \tag{A8.1.5}$$

Similarly, the argument of the cosine function in (A8.1.2) is

$$\sum_k \frac{\gamma_k}{2N} \sin\omega_k t \cong \frac{\gamma_0}{2} \sum_k \frac{1}{N} \sin\omega_k t = \frac{E_M}{\hbar\omega_0} \frac{1}{N} \sum_k \sin\omega_k t \, . \tag{A8.1.6}$$

Using, (A8.1,4) ⟶ (A8.1,6) in (A8,1.2)

$$W_T^{(1)} = 2\pi \frac{|K_1|^2}{\hbar^2} \exp(-2S) \left(\frac{1}{2\pi}\right) \lim_{t\to\infty} \int_{-t}^{t} dt' \exp\left[F_1(t')\right] \cos\left[F_2(t') - \frac{\Delta E}{\hbar} t'\right] \tag{A8.1.7}$$

where,

$$\left.\begin{aligned} S &= \frac{E_M}{2\hbar\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \\ F_1(t) &= \frac{E_M}{\hbar\omega_0} \coth \frac{\beta\hbar\omega_0}{2} \frac{1}{N} \sum_k \cos\omega_k t \\ F_2(t) &= \frac{E_M}{\hbar\omega_0} \frac{1}{N} \sum_k \sin\omega_k t \end{aligned}\right\} \tag{A8.1.8}$$

These are text equations (8,2) and (8,3)

These are text equations (8,2) and (8,3)

APPENDIX A8.2

Calculation of the expressions $\frac{1}{N}\sum_k \cos\omega_k t, \frac{1}{N}\sum_k \sin\omega_k t$ in the weak dispersion limit.

We may replace the summation over k by an integration,

$$A=\frac{1}{N}\sum_k \cos\omega_k t \rightarrow \frac{1}{2\pi}\int_{-\pi}^{\pi}\cos\omega_k t\,dk. \tag{A8.2.1}$$

In the M.C.M. the dispersion relation is given by

$$\left.\begin{aligned} &\omega_k^2=\omega_0^2+\omega_1^2\cos k \\ &k=\frac{2\pi K}{N}\,;\ -(N-1)\leqslant K\leqslant N-1. \end{aligned}\right\} \tag{A8.2.2}$$

Thus,

$$\omega_k=\omega_0\left[1+\left(\frac{\omega_1}{\omega_0}\right)^2\cos k\right]^{\frac{1}{2}}.$$

Thus, in the weak dispersion limit

$$\omega_k\cong\omega_0\left[1+\frac{1}{2}\left(\frac{\omega_1}{\omega_0}\right)^2\cos k\right] \tag{A8.2.3}$$

which may be written in the form

$$\left.\begin{aligned} &\omega_k=\omega_0+\omega_b\cos k \\ &\quad\text{where}\quad \omega_b=\frac{\omega_1^2}{2\omega_0}. \end{aligned}\right\} \tag{A8.2.4}$$

In the present context the 'weak dispersion' limit is when

$$\frac{\omega_b}{\omega_0}=\frac{1}{2}\left(\frac{\omega_1}{\omega_0}\right)^2\ll 1. \tag{A8.2.5}$$

Thus, (A8.2.1) becomes, in the weak dispersion limit

$$A=\frac{1}{N}\sum_k \cos\omega_k t \rightarrow \frac{1}{2\pi}\int_{-\pi}^{\pi}\cos[\omega_0 t+\omega_b t\cos k]\,dk. \tag{A8.2.6}$$

Thus, (A8.2.6) becomes

$$A=\frac{\cos\omega_0 t}{2\pi}\int_{-\pi}^{\pi}\cos[\omega_b t\cos k]\,dk-\frac{\sin\omega_0 t}{2\pi}\int_{-\pi}^{\pi}\sin[\omega_b t\cos k]\,dk.$$

Now,

$$\left.\begin{aligned} &\cos[\omega_b t\cos k]=J_0(\omega_b t)+2\sum_{n=1}^{\infty}(-1)^n J_n(\omega_b t)\cos 2nk \\ &\sin[\omega_b t\cos k]=2\sum_{n=0}^{\infty}(-1)^n J_{n+1}(\omega_b t)\cos[(2n+1)k]. \end{aligned}\right\} \tag{A8.2.7}$$

Thus,

$$A = \frac{\cos\omega_0 t}{2\pi} J_0(\omega_b t)\int_{-\pi}^{\pi} dk + \frac{\cos\omega_0 t}{2\pi} . 2\sum_{n=1}^{\infty}(-1)^n J_n(\omega_b t)\int_{-\pi}^{\pi}\cos 2nk . dk$$

$$- \frac{\sin\omega_0 t}{2\pi} . 2\sum_{n=1}^{\infty}(-1)^n J_{n+1}(\omega_b t)\int_{-\pi}^{\pi}\cos[(2n+1)k] dk$$

Now,

$$\int_{-\pi}^{\pi}\cos 2nk . dk = \frac{1}{2n}\left[\sin 2nk\right]_{-\pi}^{\pi} = 0 \qquad \text{(A8.2.7)}$$

Thus,

$$A = \frac{\cos\omega_0 t}{2\pi} . J_0(\omega_b t) . 2\pi$$

Writing,

$$x = \omega_0 t , \quad A = J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x . \qquad \text{(A8.2.8)}$$

Using this result (A8.2.8) we may also derive a result for

$$\mathcal{B} = \frac{1}{N}\sum_k \sin\omega_k t .$$

Now,

$$\mathcal{B} = \frac{1}{N}\sum_k \sin\omega_k t = -\frac{d}{dt}\left\{\frac{1}{N}\sum_k \frac{1}{\omega_k}\cos\omega_k t\right\} . \qquad \text{(A8.2.10)}$$

Thus, $\mathcal{B} \simeq \frac{1}{\omega_0}\left\{-\frac{d}{dt}\left(\frac{1}{N}\sum_k \cos\omega_k t\right)\right\}$ in the weak dispersion limit.

$$\mathcal{B} \simeq \frac{1}{\omega_0}\left\{-\frac{d}{dt}\left(J_0(\omega_b t)\cos\omega_0 t\right)\right\} \qquad \text{using (A8.2.8)}$$

$$\mathcal{B} = \frac{1}{\omega_0}\left\{-J_0'(\omega_b t)\omega_b\cos\omega_0 t - J_0(\omega_b t)(-\omega_0\sin\omega_0 t)\right\} . \qquad \text{(A8.2.11)}$$

In the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$, the first term in (A8.2.11) is negligible so that

$$\mathcal{B} = J_0(\omega_b t)\sin\omega_0 t \; ; \; \mathcal{B} = J_0\left(\frac{\omega_b}{\omega_0}x\right)\sin x . \qquad \text{(A8.2.12)}$$

Thus, we have shown in this appendix that, in the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$,

$$\left.\begin{array}{l} \frac{1}{N}\sum_k \cos\omega_k t \simeq J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x \\ \frac{1}{N}\sum_k \sin\omega_k t \simeq J_0\left(\frac{\omega_b}{\omega_0}x\right)\sin x \\ \text{where,} \\ x = \omega_0 t \end{array}\right\} \qquad \text{(A8,2,13)}$$

APPENDIX A8,3

Final calculation of the recombination rates in the M.C.M. including dispersion.

Using (A8.1.7), (A8.1.8) and (A8.2.13) we obtain

$$W_T^{(1)} = 2\pi \frac{|K_1|^2}{\hbar^2\omega_0} \exp(-2S) \frac{1}{2\pi} \lim_{t\to\infty} \int_{-\omega_0 t}^{\omega_0 t} dx \exp\left[a\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right] \cos\left[a'\left(\frac{\omega_b}{\omega_0}x\right)\sin x - (p+\Delta)x\right]$$

where

$$a\left(\frac{\omega_b}{\omega_0}x\right) = \frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0}x\right)$$

$$a'\left(\frac{\omega_b}{\omega_0}x\right) = \frac{E_M}{\hbar\omega_0} J_0\left(\frac{\omega_b}{\omega_0}x\right). \qquad \text{(A8,3.1)}$$

We divide this integral up into intervals of 2π,

$$W_T^{(1)} = 2\pi \frac{|K_1|^2}{\hbar^2\omega_0} \exp(-2S) \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \int_{(2n-1)\pi}^{(2n+1)\pi} dx \exp\left[a\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right] \cos\left[a'\left(\frac{\omega_b}{\omega_0}x\right)\sin x - (p+\Delta)x\right].$$

(A8,3.2)

Now in the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$, $a\left(\frac{\omega_b}{\omega_0}x\right)$ $a'\left(\frac{\omega_b}{\omega_0}x\right)$ are almost constant over an interval of 2π. Hence we write

$$W_T^{(1)} = 2\pi \frac{|K_1|^2}{\hbar^2\omega_0} \exp(-2S) \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \int_{(2n-1)\pi}^{(2n+1)\pi} dx \exp\left[a_n \cos x\right] \cos\left[a'_n \sin x - (p+\Delta)x\right].$$

where

$$a_n = \frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2} J_0\left(2\pi n \frac{\omega_b}{\omega_0}\right)$$

$$a'_n = \frac{E_M}{\hbar\omega_0} J_0\left(2\pi n \frac{\omega_b}{\omega_0}\right). \qquad \text{(A8.3.3)}$$

We may write (A8.3.3) in the form

$$W_T^{(1)} = 2\pi \frac{|K_1|^2}{\hbar^2 \omega_0} \exp(-2S) \Big\{ \frac{1}{2\pi} \int_{-\pi}^{\pi} dx \exp[a_0 \cos x] \cos[a_0' \sin x - (p+\Delta)x]$$

$$+ 2 \sum_{n=1}^{\infty} \frac{1}{2\pi} \int_{(2n-1)\pi}^{(2n+1)\pi} dx \exp[a_n \cos x] \cos[a_n' \sin x - (p+\Delta)x] \Big\}. \qquad \text{(A8.3.4)}$$

We examine the integral

$$I_n = \frac{1}{2\pi} \int_{(2n-1)\pi}^{(2n+1)\pi} dx' \exp[a_n \cos x'] \cos[a_n' \sin x' - (p+\Delta)x'].$$

Making the change of variable $x = x' - 2n\pi$ we obtain

$$I_n = \int_{-\pi}^{\pi} dx \exp[a_n \cos x] \cos[a_n' \sin x - (p+\Delta)x] . \cos 2n\pi(p+\Delta)$$

$$+ \int_{-\pi}^{\pi} dx \exp[a_n \cos x] \sin[a_n' \sin x - (p+\Delta)x] . \sin 2n\pi(p+\Delta). \qquad \text{(A8.3.5)}$$

The second part of I_n is zero, the integrand being odd about $x=0$.

Using (A8,3,5) in (A8,3,4) we obtain

$$W_T^{(1)} = 2\pi \left(\frac{K}{\hbar}\right)^2 \exp(-2S) \Big\{ A_0(p+\Delta) + 2 \sum_{n=1}^{\infty} A_n(p+\Delta) \cos 2\pi n \Delta \Big\}$$

where $$A_n(p+\Delta) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dx \exp[a_n \cos x] \cos[a_n' \sin x - (p+\Delta)x]. \qquad \text{(A8.3.6)}$$

These are text equations (8,6) and (8,7) respectively.

APPENDIX A8.4

Calculation of the integral $A_n(p+\Delta)$.

$$A_n(p+\Delta)=\frac{1}{2\pi}\int_{-\pi}^{\pi}dx\,\exp[a_n\cos x]\cos[a_n'\sin x-(p+\Delta)x]. \tag{A8.4.1}$$

Now, from Erdelyi et al.[28]

$$A_n(p+\Delta)=\frac{1}{\pi}\int_{0}^{\pi}dx\,\exp[a_n\cos x]\cos[a_n'\sin x-(p+\Delta)x]$$

$$=\left[\frac{a_n'+a_n}{a_n'-a_n}\right]^{\frac{1}{2}(p+\Delta)}J_{p+\Delta}\left[(a_n'^2-a_n^2)^{\frac{1}{2}}\right]+\frac{\sin[\pi(p+\Delta)]}{\pi}\int_0^{\infty}\exp[-(p+\Delta)t-a_n\cosh t-a_n'\sinh t] \tag{A8.4.2}$$

where $J_{p+\Delta}\left[(a_n'^2-a_n^2)^{\frac{1}{2}}\right]$ is a Bessel Function.

We express the first term in (A8.4.2) in terms of a Modified Bessel Function.

Now,

$$\left.\begin{aligned} a_n&=\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\,J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)\\ a_n'&=\frac{E_M}{\hbar\omega_0}\,J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right).\end{aligned}\right\} \tag{A8.4.3}$$

Thus,

$$(a_n'^2-a_n^2)^{\frac{1}{2}}=\frac{E_M}{\hbar\omega_0}J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)\left[1-\coth^2\frac{\beta\hbar\omega_0}{2}\right]^{\frac{1}{2}}.$$

Now,

$$\left[1-\coth^2\frac{\beta\hbar\omega_0}{2}\right]^{\frac{1}{2}}=\left[-\left(\coth^2\frac{\beta\hbar\omega_0}{2}-1\right)\right]^{\frac{1}{2}}=i\,\mathrm{csch}\,\frac{\beta\hbar\omega_0}{2}.$$

Hence, $(a_n'^2-a_n^2)^{\frac{1}{2}}=i\sqrt{a_n^2-a_n'^2}$

where,

$$\left.\begin{aligned}(a_n^2-a_n'^2)^{\frac{1}{2}}&=iz\\ z&=\sqrt{a_n^2-a_n'^2}\ .\end{aligned}\right\} \tag{A8.4.4}$$

Thus, the first term in (A9.4.2) is

$$C_n=\left[\frac{a_n'+a_n}{a_n'-a_n}\right]^{\frac{1}{2}(p+\Delta)}J_{p+\Delta}\left[i\sqrt{a_n^2-a_n'^2}\right]. \tag{A8.4.5}$$

Now, the series expansion of the Bessel Function is

$$J_\nu(z)=\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{1}{2}z\right)^{2m+\nu}}{m!\,\Gamma(m+\nu+1)}. \tag{A8.4.6}$$

Thus,

$$C_n=\left[\frac{a_n'+a_n}{a_n'-a_n}\right]^{\frac{1}{2}(p+\Delta)}\sum_{m=0}^{\infty}\frac{(-1)^m\left(\frac{1}{2}i\sqrt{a_n^2-a_n'^2}\right)^{2m+p+\Delta}}{m!\,\Gamma(m+p+\Delta+1)}. \tag{A8.4.7}$$

Now, $i^{2m} = (-1)^m$ thus

$$C_n = \left[\frac{a_n' + a_n}{a_n' - a_n}\right]^{\frac{1}{2}(p+\Delta)} i^{p+\Delta} \sum_{m=0}^{\infty} \frac{\left(\frac{1}{2}\sqrt{a_n^2 - a_n'^2}\right)^{2m+p+\Delta}}{m!\,\Gamma(m+p+\Delta+1)}.$$

Thus,
$$C_n = \left[\frac{a_n' + a_n}{a_n' - a_n}\right]^{\frac{1}{2}(p+\Delta)} i^{p+\Delta} I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right] \qquad \text{(A8.4.8)}$$

where $I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right]$ is a modified Bessel Function.

Now,
$$C_n = \left[\frac{(a_n' + a_n)(a_n' - a_n)}{(a_n' - a_n)^2}\right]^{\frac{1}{2}(p+\Delta)} i^{p+\Delta} I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right]$$

$$C_n = \frac{(a_n'^2 - a_n^2)^{\frac{1}{2}(p+\Delta)}}{(a_n' - a_n)^{p+\Delta}} i^{p+\Delta} I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right]$$

$$C_n = \frac{(a_n^2 - a_n'^2)^{\frac{1}{2}(p+\Delta)}(i^2)^{\frac{1}{2}(p+\Delta)}}{(a_n - a_n')^{p+\Delta}(i^2)^{p+\Delta}} i^{p+\Delta} I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right]$$

Thus,
$$C_n = \frac{(a_n^2 - a_n'^2)^{\frac{1}{2}(p+\Delta)}}{(a_n - a_n')^{p+\Delta}} I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right]. \qquad \text{(A8.4.9)}$$

The second term in (A8.4.2) is

$$B_n = \frac{\sin\pi(p+\Delta)}{\pi}\int_0^{\infty} \exp\left[-(p+\Delta)t - (a_n\cosh t + a_n'\sinh t)\right]dt. \qquad \text{(A8.4.10)}$$

Now,
$$a_n\cosh t + a_n'\sinh t = \sqrt{a_n^2 - a_n'^2}\left[\frac{a_n}{\sqrt{a_n^2 - a_n'^2}}\cosh t + \frac{a_n'}{\sqrt{a_n^2 - a_n'^2}}\sinh t\right]$$

Writing,
$$\cosh\theta = \frac{a_n}{\sqrt{a_n^2 - a_n'^2}}, \text{ then } \sinh^2\theta = \cosh^2\theta - 1,\ \sinh\theta = \frac{a_n'}{\sqrt{a_n^2 - a_n'^2}}$$

Hence,
$$a_n\cosh t + a_n'\sinh t = \sqrt{a_n^2 - a_n'^2}\left[\cosh\theta\cosh t + \sinh\theta\sinh t\right]$$

$$a_n\cosh t + a_n'\sinh t = \sqrt{a_n^2 - a_n'^2}\cosh(t+\theta) \qquad \text{(A8.4.11)}$$

Substituting (A8.4.11) into (A8.4.10) we obtain

$$B_n = \frac{\sin\pi(p+\Delta)}{\pi}\int_0^{\infty} \exp\left[-(p+\Delta)t - \sqrt{a_n^2 - a_n'^2}\cosh(t+\theta)\right]dt. \qquad \text{(A8.4.12)}$$

Making the change of variable $t' = t + \theta$, $\mathcal{B}$ becomes

$$\mathcal{B}_n = \frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty}\exp\left[-(p+\Delta)(t'-\theta) - \sqrt{a_n^2 - a_n'^2}\cosh t'\right]dt'$$

Thus,

$$\mathcal{B}_n = \frac{\sin\pi(p+\Delta)\exp[(p+\Delta)\theta]}{\pi}\int_{\theta}^{\infty}\exp\left[-(p+\Delta)t' - \sqrt{a_n^2 - a_n'^2}\cosh t'\right]dt' . \tag{A8.4.13}$$

Now,

$$\cosh\theta = \frac{1}{2}\left[\exp(\theta) + \exp(-\theta)\right] = \frac{a_n}{\sqrt{a_n^2 - a_n'^2}} \tag{A8.4.14}$$

$$\sinh\theta = \frac{1}{2}\left[\exp(\theta) - \exp(-\theta)\right] = \frac{a_n'}{\sqrt{a_n^2 - a_n'^2}} . \tag{A8.4.15}$$

Subtracting (A8.4.15) from (A8.4.14) we obtain

$$\exp[-\theta] = \frac{a_n - a_n'}{\sqrt{a_n^2 - a_n'^2}} . \quad \text{Thus,} \quad \exp[(p+\Delta)\theta] = \left[\frac{\sqrt{a_n^2 - a_n'^2}}{a_n - a_n'}\right]^{p+\Delta} . \tag{A8.4.16}$$

Thus, substituting (A8.4.16) into (A8.4.13) we obtain

$$\mathcal{B}_n = \frac{\sin\pi(p+\Delta)}{\pi}\left[\frac{\sqrt{a_n^2 - a_n'^2}}{a_n - a_n'}\right]^{p+\Delta}\int_{\theta}^{\infty}\exp\left[-(p+\Delta)t - \sqrt{a_n^2 - a_n'^2}\cosh t\right]dt \tag{A8.4.17}$$

where

$$\theta = \cosh^{-1}\frac{a_n}{\sqrt{a_n^2 - a_n'^2}} .$$

Combining (A8.4.9) and (A8.4.17) with (A8.4.2) we obtain,

$$\begin{aligned} A_n(p+\Delta) &= \frac{1}{\pi}\int_0^{\pi} dx \exp[a_n\cos x]\cos[a_n'\sin x - (p+\Delta)x] \\ &= \frac{(a_n^2 - a_n'^2)^{\frac{1}{2}(p+\Delta)}}{(a_n - a_n')^{p+\Delta}}\left\{ I_{p+\Delta}\left[\sqrt{a_n^2 - a_n'^2}\right] + \frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty}\exp\left[-(p+\Delta)t - \sqrt{a_n^2 - a_n'^2}\cosh t\right]dt\right\} . \end{aligned} \tag{A8.4.18}$$

This is the text equation (8.8).

APPENDIX A8.5

Calculation of the series, $S = 1 + 2\sum_{n=1}^{\infty}\cos 2\pi n\Delta$.

We calculate the series

$$S = 1 + 2\sum_{n=1}^{\infty}\cos 2\pi n\Delta, \qquad (A8.5.1)$$

S may be written as,

$$S = 1 + \sum_{n=1}^{\infty}\left(e^{2\pi i n\Delta} + e^{-2\pi i n\Delta}\right) \qquad (A8.5.2)$$

which becomes,

$$S = 1 + \sum_{n=1}^{\infty}\left\{(e^{2\pi i\Delta})^n + (e^{-2\pi i\Delta})^n\right\}. \qquad (A8.5.3)$$

We may include $n = 0$ in the summations

$$S = \sum_{n=0}^{\infty}(e^{2\pi i\Delta})^n + \sum_{n=0}^{\infty}(e^{-2\pi i\Delta})^n - 1. \qquad (A8.5.4)$$

This is,

$$S = \frac{1}{1 - e^{2\pi i\Delta}} + \frac{1}{1 - e^{-2\pi i\Delta}} - 1. \qquad (A8.5.5)$$

We find that

$$S = \frac{1 - e^{-2\pi i\Delta} + 1 - e^{2\pi i\Delta} - (1 - e^{2\pi i\Delta})(1 - e^{-2\pi i\Delta})}{(1 - e^{2\pi i\Delta})(1 - e^{-2\pi i\Delta})} = \frac{0}{(1 - e^{2\pi i\Delta})(1 - e^{-2\pi i\Delta})}.$$

Thus, $S = 0$, provided $\Delta \neq 0$ (A8,5,5)

When $\Delta = 0$ each term in (A8,5,1) is unity so that S diverges,

This is the text equation (8,10).

APPENDIX A8.6

Calculation of $A_n(p+\Delta)$ at $T=0$.

We have shown in Appendix A8.3 (A8.3.6) that the transition rate is,

$$W_T = 2\pi\left(\frac{K}{\hbar}\right)^2 \exp(-2S)\left\{A_0(p+\Delta) + 2\sum_{n=1}^{\infty} A_n(p+\Delta)\cos 2\pi n\Delta\right\} \qquad \text{(A8.6.1)}$$

where

$$A_n(p+\Delta) = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} \left\{ I_{p+\Delta}\left[(a_n^2 - a_n'^2)^{\frac{1}{2}}\right] + \frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty} dt \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}}\cosh t\right]\right\}. \qquad \text{(A8.6.2)}$$

Here,

$$\left.\begin{aligned} a_n &= \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\, J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right) \\ a_n' &= \frac{E_M}{\hbar\omega_0} J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\ ;\ \ \theta = \cosh^{-1}\frac{a_n}{\sqrt{a_n^2 - a_n'^2}}. \end{aligned}\right\} \qquad \text{(A8.6.3)}$$

As $T \to 0, \beta \to \infty$ and $\coth\frac{\beta\hbar\omega_0}{2} \to 1$.

Hence, $a_n \to a_n'$ and $\theta = \cosh^{-1}\frac{a_n}{\sqrt{a_n^2 - a_n'^2}} \to \infty$.

First of all, we investigate the first term

$$C_n = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} I_{p+\Delta}\left[(a_n^2 - a_n'^2)^{\frac{1}{2}}\right]. \qquad \text{(A8.6.4)}$$

Since, as $T \to 0, (a_n^2 - a_n'^2)^{\frac{1}{2}} \to 0$, the small argument approximation of the Modified Bessel Function is appropriate here.

$$I_{p+\Delta}(x) \xrightarrow{x \to 0} \left(\frac{x}{2}\right)^{p+\Delta}\frac{1}{(p+\Delta)!} \qquad \text{(A8.6.5)}$$

Using (A8.6.5) C_n becomes

$$C_n = \frac{(a_n^2 - a_n'^2)^{p+\Delta}}{2^{p+\Delta}(a_n - a_n')^{p+\Delta}}\,\frac{1}{(p+\Delta)!}. \qquad \text{(A8.6.6)}$$

Since, the numerator and denominator of (A8.6.6) are both zero at $T=0$ we must take care about their limiting behaviour. We write $a_n = a_n' + \delta$ and take the limit as $\delta \to 0$.

Thus,

$$C_n = \underset{\delta\to 0}{\text{Limit}}\left\{\left[\frac{(a_n' + \delta)^2 - a_n'^2}{2(a_n' + \delta - a_n')}\right]^{p+\Delta}\frac{1}{(p+\Delta)!}\right\}$$

i.e.,

$$C_n = \underset{\delta\to 0}{\text{Limit}}\left\{\left[\frac{a_n'^2 + 2a_n'\delta + \delta^2 - a_n'^2}{2\delta}\right]^{p+\Delta}\frac{1}{(p+\Delta)!}\right\}$$

$$C_n = \frac{(a_n')^{p+\Delta}}{(p+\Delta)!}. \qquad \text{(A8.6.7)}$$

The 2nd term is

$$\mathcal{B}_n = \left[\frac{a_n^2 - a_n'^2}{(a_n - a_n')^2}\right]^{\frac{p+\Delta}{2}} \frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty} dt \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}}\cosh t\right]. \qquad \text{(A8.6.8)}$$

Using, (A8.4.16)

$$\left[\frac{(a_n^2 - a_n'^2)^{\frac{1}{2}}}{(a_n - a_n')}\right]^{p+\Delta} = \exp\left[(p+\Delta)\theta\right]. \qquad \text{(A8.6.9)}$$

Thus as $T \to 0$,

$$\mathcal{B}_n = \underset{\theta\to\infty}{\text{Limit}}\left\{\exp\left[(p+\Delta)\theta\right]\frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty} dt \exp\left[-(p+\Delta)t - (a_n^2 - a_n'^2)^{\frac{1}{2}}\cosh t\right]\right\}. \qquad \text{(A8.6.10)}$$

As $T \to 0$, $(a_n^2 - a_n'^2)^{\frac{1}{2}} \to 0$. Hence,

$$\mathcal{B}_n = \underset{\theta\to\infty}{\text{Limit}}\left\{\exp\left[(p+\Delta)\theta\right]\frac{\sin\pi(p+\Delta)}{\pi}\int_{\theta}^{\infty}\exp\left[-(p+\Delta)t\right]dt\right.$$

$$\mathcal{B}_n = \underset{\theta\to\infty}{\text{Limit}}\left\{\exp\left[(p+\Delta)\theta\right]\frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}\exp\left[-(p+\Delta)\theta\right]\right\}$$

$$\mathcal{B}_n = \frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}. \qquad \text{(A8.6.11)}$$

Substituting (A9.6.7) and (A9.6.11) into (A9.6.1) we obtain

$$W_{T=0} = 2\pi\left(\frac{K}{\hbar}\right)^2 \exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{1}{(p+\Delta)!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_k}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\}$$
$$+ 2\pi\left(\frac{K}{\hbar}\right)^2 \exp(-2S)\frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}\left\{1 + 2\sum_{n=1}^{\infty}\cos 2\pi n\Delta\right\}. \qquad \text{(A8.6.12)}$$

The second series here is zero, for all values of Δ,

Thus,

$$W_{T=0} = 2\pi\left(\frac{K}{\hbar}\right)^2 \exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{1}{(p+\Delta)!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_k}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\}. \qquad \text{(A8.6.13)}$$

This is the text equation (8.16).

APPENDIX A8.7

Calculation of $A_n(p+\Delta)$ in the finite temperature, weak coupling limit

$$A_n(p+\Delta)=\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}}\left\{I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]+\frac{\sin\pi(p+\Delta)}{\pi}\int_{\vartheta}^{\infty}dt\,\exp\left[-(p+\Delta)t-(a_n^2-a_n'^2)^{\frac{1}{2}}\cosh t\right]\right\}, \tag{A8.7.1}$$

$$\left.\begin{aligned} a_n &= \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\,J_0\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)\\ a_n' &= \frac{E_M}{\hbar\omega_0}\,J_0\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)\\ \vartheta &= \cosh^{-1}\frac{a_n}{\sqrt{a_n^2-a_n'^2}}\,. \end{aligned}\right\} \tag{A8.7.2}$$

In the weak coupling limit, $E_M/\hbar\omega_0 \ll 1$ so that

$$(a_n^2-a_n'^2)^{\frac{1}{2}}=\frac{E_M}{\hbar\omega_0}\left(\coth^2\frac{\beta\hbar\omega_0}{2}-1\right)^{\frac{1}{2}}J_0\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)\ll 1\,.$$

Now

$$C_n=\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}}I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]. \tag{A8.7.3}$$

Since, $(a_n^2-a_n'^2)^{\frac{1}{2}}\ll 1$ we use the small argument approximation for $I_{p+\Delta}\left[(a_n^2-a_n'^2)^{\frac{1}{2}}\right]$ to obtain

$$C_n=\left[\frac{a_n^2-a_n'^2}{2(a_n-a_n')}\right]^{p+\Delta}\frac{1}{(p+\Delta)!}\,. \tag{A8.7.4}$$

Using (A8.7.2) C_n becomes

$$C_n=\left[\frac{\left(\frac{E_M}{\hbar\omega_0}\right)^2\left(\coth^2\frac{\beta\hbar\omega_0}{2}-1\right)J_0^{\,2}\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)}{2\left(\frac{E_M}{\hbar\omega_0}\right)\left(\coth\frac{\beta\hbar\omega_0}{2}-1\right)J_0\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)}\right]^{p+\Delta}\frac{1}{(p+\Delta)!}\,. \tag{A8.7.5}$$

We find that this becomes

$$C_n=\left[\left(\frac{E_M}{\hbar\omega_0}\right)J_0\!\left(2\pi n\frac{\omega_b}{\omega_0}\right)\left(1+N(\omega_0)\right)\right]^{p+\Delta}\frac{1}{(p+\Delta)!} \tag{A8.7.6}$$

where $N(\omega_0)=\dfrac{1}{e^{\beta\hbar\omega_0}-1}$ is the thermal probability of occupation of a phonon mode.

$$B_n=\left[\frac{a_n^2-a_n'^2}{(a_n-a_n')^2}\right]^{\frac{p+\Delta}{2}}\frac{\sin\pi(p+\Delta)}{\pi}\int_{\vartheta}^{\infty}dt\,\exp\left[-(p+\Delta)t-(a_n^2-a_n'^2)^{\frac{1}{2}}\cosh t\right]. \tag{A8.7.7}$$

Since, $(a_n^2-a_n'^2)^{\frac{1}{2}}\ll 1$ as in Appendix A8.6 we find

$$B_n=\frac{\sin\pi(p+\Delta)}{\pi(p+\Delta)}\,. \tag{A8.7.8}$$

Thus, as in Appendix A8.6, the series involving the $\mathcal{B}_n$'s is zero, thus using (A8.7.6) we obtain

$$W_T = 2\pi\left(\frac{K}{\hbar}\right)^2 \exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^{p+\Delta}\frac{(1+N(\omega_0))^{p+\Delta}}{(p+\Delta)!}\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_t}{\omega_0}\right)\right]^{p+\Delta}\cos 2\pi n\Delta\right\} \tag{A8.7.9}$$

in the finite temperature, weak coupling $\frac{E_M}{\hbar\omega_0} \ll 1$ limit.

This is the text equation (8,23).

Chapter 9

An alternative method of calculation of the Recombination Rates in the M.C.M.

In this chapter we calculate the recombination rates which occur in the M.C.M. using somewhat different methods than the ones employed previously. In chapter five the transition rates were calculated using a purely formal method, while in chapter six a more intuitive combinatorial method was used to obtain the same results. In this chapter, we follow Emin[27] (1974) and present a calculation in which, although the development is formal, the individual terms may be interpreted as representing simple physical processes.

Initially the calculation is restricted to the limit of zero dispersion; later, the effect of finite but weak dispersion on the transition rates is included.

The general form of the transition rate in the M.C.M. is given by equation (5.34),

$$W_T^{(1)}=\frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\right\}\int_{-t}^{t}\exp\left[\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\sum_k\frac{\cos\omega_k t'}{N}\right]\cos\left[\frac{\gamma_0}{2}\sum_k\frac{\sin\omega_k t'}{N}-\frac{\Delta E}{\hbar}t'\right]dt'$$

which becomes, on making the change of variable, $t'=\frac{i\beta\hbar}{2}+\tau$,

$$W_T^{(1)}=\frac{|K_1|^2}{\hbar^2}\exp\left\{\frac{\Delta E\beta}{2}-\frac{\gamma_0}{2}\coth\frac{\beta\hbar\omega_0}{2}\right\}\int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}}d\tau\exp\left[-\frac{i\Delta E}{\hbar}\tau\right]\exp\left[\sum_k\frac{2\gamma_k}{N}\operatorname{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\right] \tag{9.1}$$

In the zero dispersion limit we write this as

$$W_T^{(1)}=\frac{|K_1|^2}{\hbar^2}\exp\left(\frac{\Delta E\beta}{2}\right)$$

$$\times\int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}}d\tau\exp\left[-\frac{i\Delta E}{\hbar}\tau\right]\exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}+\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau\right] \tag{9.2}$$

In Appendix A9.1, the transition rate $W_T^{(1)}$ is again expressed in terms of an integrand whose path of integration lies along the real axis. The following result is found, equation (A9.1.8),

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E \beta}{2}\right] \Big\{ \int_{-t}^{t} \exp\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch}\frac{\beta\hbar\omega_0}{2} \cos\omega_0\tau\right] \cos\left[\frac{\Delta E}{\hbar}\tau\right] d\tau$$
$$+ 2\int_0^{-\frac{\beta\hbar}{2}} dt_2 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0 t \cosh\omega_0 t_2 + \frac{\Delta E}{\hbar} t_2\right]$$
$$\times \sin\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\sin\omega_0 t \sinh\omega_0 t_2 + \frac{\Delta E}{\hbar} t\right] dt_2 \Big\}. \quad (9.3)$$

We show in Appendix 9.1, equation (A9.1.13) that when explicit account is taken of weak but finite dispersion the second term in equation (9.3) is zero.

Thus, the transition rate $W_T^{(1)}$ may be written in the form,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E\beta}{2} - \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right] \int_{-\infty}^{\infty} \frac{dx}{\omega_0} \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos x\right] \cos px, \quad (9.4)$$

where $x = \omega_0\tau$ and $\Delta E = p\hbar\omega_0$.

The main difference between this method and our previous calculations is now introduced by formally expanding $\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos x\right]$ in a power series to obtain,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2\omega_0} \exp\left[\frac{\Delta E\beta}{2} - \frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}\right] \sum_{n=0}^{\infty} \frac{\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^n}{n!} \int_{-\infty}^{\infty} \cos^n x \cos px \, d \quad (9.5)$$

This integral is written as a sum of integrals over intervals of 2π, $\sum_{r=0}^{\infty} \int_{r\pi}^{(r+1)\pi} dx$ and then the origins are changed so that each integral is expressed in terms of an integral over the interval 0 to π. The details of this calculation are found in Appendix A9.2.

The integral is written as

$$I_{n,p} = \int_{-\infty}^{\infty} \cos^n x \cos px . dx = 2\sum_{r=0}^{\infty} (-1)^{r[p+n]} \int_0^{\pi} \cos^n x \cos px . dx. \tag{9.6}$$

Writing,

$$A_{n,p} = \int_0^{\pi} \cos^n x \cos px . dx, \tag{9.7}$$

we find that

$$\left.\begin{aligned} A_{n,p} &= \frac{\pi}{2^{p+2q}} \frac{(p+2q)!}{(p+q)!\, q!} \quad \text{if } n = p+2q \quad (q, \text{ integer}) \\ A_{n,p} &= 0 \quad n < p, \text{ or } n = p+2q+1. \end{aligned}\right\} \tag{9.8}$$

Thus, the transition rate becomes,

$$W_T^{(1)} = \frac{2\pi |K_1|^2}{\hbar^2 \omega_0} \exp\left[\frac{\Delta E \beta}{2} - \frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2}\right] \sum_{q=0}^{\infty} \frac{\left[\frac{E_M}{2\hbar\omega_0} \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^{p+2q}}{(p+q)!\, q!} \sum_{r=0}^{\infty} (-1)^{2r(p+q}. \tag{9.9}$$

Using,

$$\sum_{q=0}^{\infty} \frac{\left(\frac{1}{2}x\right)^{p+2q}}{(p+q)!\, q!} = I_p(x), \tag{9.10}$$

the transition rate becomes,

$$W_T^{(1)} = \frac{2\pi |K_1|^2}{\hbar^2 \omega_0} \exp\left[\frac{\Delta E}{2}\beta - \frac{E_M}{\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2}\right] I_p\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right] \sum_{r=0}^{\infty} 1. \tag{9.11}$$

This is the same form of the transition probability which we have previously derived for the S.C.C.M. in Chapter 3 [equation (A3.4.9)] and for the M.C.M. in Chapter 6, [equation, (6.24)]. The unphysical summation $\sum_{r=0}^{\infty} 1$ results, as in the absence of dispersion an equal contribution to the transition rate arises during each vibrational period.

The new feature of this calculation is the expansion of the exponential function in equation (9.5) which quite naturally reveals the transition rate as arising from the sum of multiphonon processes in which p+q phonons are emitted while q are absorbed. We have previously obtained the transition probability from this point of view using the more intuitive combinatorial approach in Chapter 6.

We proceed by considering the effect of dispersion on the recombination rates in the M.C.M. Once again the general expression for the transition probability equation (9.1) is the starting point,

$$W_T=\frac{|K_1|^2}{\hbar^2}\exp\left[-2S+\frac{\Delta E\beta}{2}\right]\int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}}\exp\left[-\frac{i\Delta E}{\hbar}\tau\right]\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\sum_k\frac{\cos\omega_k\tau}{N}\right]$$

where $S=\frac{E_M}{2\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}$. In this expression explicit account of dispersion is included only for those factors which depend on τ, in this case, $\sum_k\frac{\cos\omega_k\tau}{N}$. The other factors, for example, $\exp(-2S)$ are constants which are little altered by dispersion.

We use the expression derived in the previous chapter for $\frac{1}{N}\sum_k\cos\omega_k\tau$ in the weak dispersion regime $\frac{\omega_b}{\omega_0}\ll 1$,

$$\frac{1}{N}\sum_k\cos\omega_k\tau=J_0(\omega_b\tau)\cos\omega_0\tau.$$

Thus, the transition rate $W_T^{(1)}$ becomes on changing the path of integration to the real axis and writing $\Delta E=(p+\Delta)\hbar\omega_0$ and $x=\omega_0\tau$,

$$W_T^{(1)}=\frac{|K_1|^2}{\hbar^2\omega_0}\exp\left[-2S+\frac{\Delta E\beta}{2}\right]\int_{-\infty}^{\infty}dx\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right]\cos\left[(p+\Delta)x\right. \qquad (9.13)$$

A formal expansion of the exponential function in the expression for the transition rate is now performed. The details of this calculation are in Appendix A9.3.

We obtain the result given by equation (A9.3.4),

$$W_T^{(1)}=\frac{|K_1|^2}{\hbar^2\omega_0}\exp\left[-2S+\frac{\Delta E\beta}{2}\right]\sum_{n=0}^{\infty}\frac{1}{n!}\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^n\int_{-\infty}^{\infty}dx\left[J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right]^n\cos\left[(p+\Delta)x\right. \qquad (9.14)$$

We express this integral in terms of a sum of integrals over intervals of 2π, $\sum_{r=-\infty}^{\infty}\int_{(2r\pi-\pi)}^{(2r\pi+\pi)}dx$, and assume that since $J_0\left(\frac{\omega_b}{\omega_0}x\right)$ varies little over an interval $2r\pi-\pi\rightarrow 2r\pi+\pi$ in the weak dispersion limit $\frac{\omega_b}{\omega_0}\ll 1$, it may be replaced by its value at $x=2\pi r$, namely $J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)$.

Following the details in Appendix A9.3 we obtain,

$$W_T^{(1)} = \frac{2|K_1|^2}{\hbar^2\omega_0}\exp\left[-2S+\frac{\Delta E\beta}{2}\right]\sum_{n=0}^{\infty}\frac{1}{n!}\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^n A_{n,p+\Delta}$$
$$\times\left\{1+2\sum_{r=1}^{\infty}\left[J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)\right]^n\cos 2\pi r\Delta\right\}, \tag{9.15}$$

where $$A_{n,p+\Delta} = \int_0^{\pi}\cos^n x\cos\left[(p+\Delta)x\right]dx. \tag{9.16}$$

First of all, we examine the "on resonance" case, $\Delta = 0$. In this case, equation (9.8) is still valid,

$$\left.\begin{aligned} A_{n,p} &= \frac{\pi}{2^{p+2q}}\frac{(p+2q)!}{(p+q)!\,q!} \quad \text{if } n=p+2q \\ A_{n,p} &= 0 \quad \text{if } n<p, \quad \text{or } n=p+2q+1. \end{aligned}\right\} \tag{9.8}$$

Substituting equation (9,8) into expression (9.15) we obtain,

$$W_T^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp\left[-2S+\frac{\Delta E\beta}{2}\right]\sum_{q=0}^{\infty}\frac{\left[\frac{E_M}{2\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^{p+2q}}{(p+q)!\,q!}\left\{1+2\sum_{r=1}^{\infty}\left[J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)\right]^{p+2q}\right. \tag{9.17}$$

At the absolute zero of temperature, T=0, this becomes

$$W_{T=0}^{(1)} = \frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp(-2S)\left(\frac{E_M}{\hbar\omega_0}\right)^p\frac{1}{p!}\left\{1+2\sum_{r=1}^{\infty}\left[J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)\right]^p\right\}, \tag{9.18}$$

which is the same result we have previously derived in Chapter 8, equation (8,1~~6~~8).

We may write the general expression for $W_T^{(1)}$ equation (9.17) in the form

$$W_T = \frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp\left[-2S+\frac{\beta\Delta E}{2}\right]\left\{\sum_{q=0}^{\infty}\frac{\left[\frac{E_M}{2\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^{p+2q}}{(p+q)!\,q!}\right.$$
$$\left.+2\sum_{r=1}^{\infty}\left[\sum_{q=0}^{\infty}\frac{\left[\frac{E_M}{2\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)\right]^{p+2q}}{(p+q)!\,q!}\right]\right\} \tag{9,19}$$

Using the relation,

$$\left(\tfrac{1}{2}x\right)^{p}\sum_{q=0}^{\infty}\frac{\left(\frac{1}{4}x^{2}\right)^{q}}{(p+q)!\,q!}=I_{p}(x)$$

the transition rate can be expressed as,

$$W_{T}=\frac{2\pi|K_{1}|^{2}}{\hbar^{2}\omega_{0}}\exp\left[-2S+\frac{\beta\Delta E}{2}\right]\left\{I_{p}\left[\frac{E_{M}}{\hbar\omega_{0}}\operatorname{csch}\frac{\beta\hbar\omega_{0}}{2}\right]\right.$$
$$\left.+2\sum_{r=1}^{\infty}I_{p}\left[\frac{E_{M}}{\hbar\omega_{0}}\operatorname{csch}\frac{\beta\hbar\omega_{0}}{2}J_{0}\left(2\pi r\frac{\omega_{b}}{\omega_{0}}\right)\right]\right\} \tag{9.20}$$

This agrees with the result derived previously in Chapter 8, equation (8.34).

Finally, we investigate the general expression for the transition rate, equation (9.15), in the "off-resonance" case, $\Delta \neq 0$. In this case, it is found in Gradshteyn and Ryzhik[30] [p,374, 3,631,18] that if $\Delta \neq 0$ then,

$$A_{n,p+\Delta}=\frac{(-1)^{n}\sin[(p+\Delta)\pi]}{2^{n}(n+p+\Delta)}F\left[-n,-\left(\frac{p+\Delta+n}{2}\right);1-\left(\frac{p+\Delta+n}{2}\right);-1\right], \tag{9.21}$$

where $F(\alpha,\beta,y;z)$ is the hypergeometric function. Using result (9.21) in the general expression for the transition probability equation (9.15), we find

$$W_{T}^{(1)}=\frac{2|K_{1}|^{2}}{\hbar^{2}\omega_{0}}\exp\left[-2S+\frac{\beta\Delta E}{2}\right]\sum_{n=0}^{\infty}\frac{1}{n!}\left[\frac{E_{M}}{\hbar\omega_{0}}\operatorname{csch}\frac{\beta\hbar\omega_{0}}{2}\right]^{n}\frac{(-1)^{n}\sin[(p+\Delta)\pi]}{2^{n}(n+p+\Delta)}$$
$$\times F\left[-n,-\left(\frac{p+\Delta+n}{2}\right);1-\left(\frac{p+\Delta+n}{2}\right);-1\right]\left\{1+2\sum_{r=1}^{\infty}\left[J_{0}\left(2\pi r\frac{\omega_{b}}{\omega_{0}}\right)\right]^{n} \tag{9.22}$$

This is a disappointing result in that it cannot be related to the expression obtained in Chapter 8 for the transition rate in the "off-resonance" case, equation (8.25). In addition there does not appear to be any restriction on the order (n) of the multiphonon processes by which the recombination process may occur,

Summary

A different approach from that used in Chapter 8 has been employed to calculate the transition rates in the M.C.M. This method involves the formal expansion of the exponential function in equation (9.4) and it transpires that the n'th term in this expansion represents the contribution to the transition rate from the n-phonon processes. We discuss the recombination rates initially for the case of zero dispersion in which the only multiphonon processes which contribute are found to be those in which p+q phonons are emitted while q are absorbed. Therefore, the intermediate steps of this formal approach are identical to those in the more intuitive combinatorial approach discussed in Chapter 7.

We have then extended this method of calculation to the regime of weak but finite dispersion, $\left(\frac{\omega_b}{\omega_0} \ll 1\right)$ and have been able to rederive the same results as were found in Chapter 8 for the "on-resonance" case, equation (9.17). However, the result found for the "off-resonance" case, $\Delta E = p\hbar\omega_0$ equation (9.22) is obscure and cannot be related to the results of Chapter 8.

APPENDIX A9.1

Calculation of the Recombination Rate in the M.C.M. in the zero dispersion limit (I).

In the zero dispersion limit we use the form of the recombination rate given by text equation (9.2),

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right] \lim_{t\to\infty} \left\{ \int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}} d\tau \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau - ip\omega_0\tau\right. \right. \tag{A9.1.1}$$

We wish to express this transition rate (A9.1.1) in terms of an integral whose path of integration is the real axis.

Writing, $A = \frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}$ the integral under consideration is

$$I = \int_{-t-i\beta\hbar/2}^{t-i\beta\hbar/2} d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right]. \tag{A9.1.2}$$

We consider the contour integration shown below

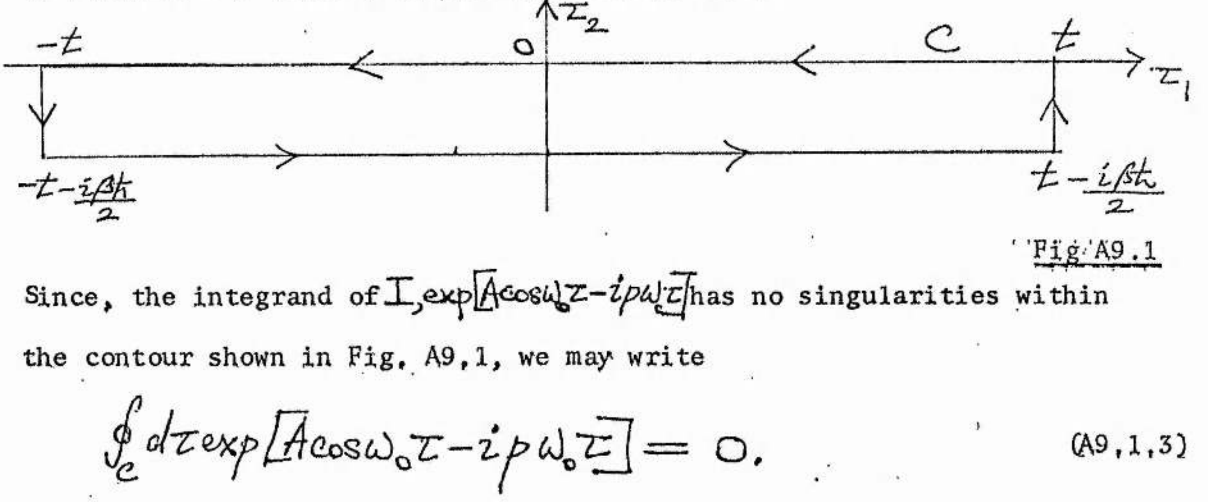


Fig. A9.1

Since, the integrand of I, $\exp[A\cos\omega_0\tau - ip\omega_0\tau]$ has no singularities within the contour shown in Fig. A9.1, we may write

$$\oint_C d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right] = 0. \tag{A9.1.3}$$

Thus, we may write

$$I = \int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}} d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right],$$

$$I = \int_{-t}^{t} d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right] + \int_{-t-\frac{i\beta\hbar}{2}}^{-t} d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right]$$
$$+ \int_{t}^{t-\frac{i\beta\hbar}{2}} d\tau \exp\left[A\cos\omega_0\tau - ip\omega_0\tau\right]. \tag{A9.1.4}$$

We express τ in terms of real and imaginary parts, $\tau = \tau_1 + i\tau_2$ to obtain,

$$I = \int_{-t}^{t} d\tau_1 \exp[A\cos\omega_0\tau_1]\exp[-ip\omega_0\tau_1]$$

$$+\int_{-\frac{\beta\hbar}{2}}^{0} i\,d\tau_2 \exp[A\cos\omega_0(-t+i\tau_2) - ip\omega_0(-t+i\tau_2)]$$

$$+\int_{0}^{-\frac{\beta\hbar}{2}} i\,d\tau_2 \exp[A\cos\omega_0(t+i\tau_2) - ip(t+i\tau_2)] . \qquad \text{(A9.1.5)}$$

This is text equation (9.3).

Thus, we may write

$$I = \int_{-t}^{t} d\tau_1 \exp[A\cos\omega_0\tau_1 - ip\omega_0\tau_1]$$

$$+\int_{-\frac{\beta\hbar}{2}}^{0} i\,d\tau_2 \exp[A\cos\omega_0 t\cosh\omega_0\tau_2 + p\omega_0\tau_2]\exp[i\{A\sin\omega_0 t\sinh\omega_0\tau_2 + p\omega_0 t\}]$$

$$+\int_{0}^{-\frac{\beta\hbar}{2}} i\,d\tau_2 \exp[A\cos\omega_0 t\cosh\omega_0\tau_2 + p\omega_0\tau_2]\exp[-i\{A\sin\omega_0 t\sinh\omega_0\tau_2 + p\omega_0 t\}] .$$

(A9.1.6)

We finally obtain

$$I = \int_{-t}^{t} d\tau_1 \exp[A\cos\omega_0\tau_1]\cos p\omega_0\tau_1$$

$$+2\int_{0}^{-\frac{\beta\hbar}{2}} d\tau_2 \exp[A\cos\omega_0 t\cosh\omega_0\tau_2 + p\omega_0\tau_2]\sin\{A\sin\omega_0 t\sinh\omega_0\tau_2' + p\omega_0 t\} .$$

(A9.1.7)

Thus, substituting (A9.1.7) into (A9.1.2) we obtain,

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right]\lim_{t\to\infty}\left\{\int_{-t}^{t} d\tau_1 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau_1\right]\cos p\omega_0\right.$$

$$+2\int_{0}^{-\frac{\beta\hbar}{2}} d\tau_2 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0 t\cosh\omega_0\tau_2 + p\omega_0\tau_2\right]\sin\left\{\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\sin\omega_0 t\sinh\omega_0\tau\right.$$

$$\left.\left. + p\omega_0 t\right\}\right\} .$$

(A9.1.8)

We now include the effects of weak but finite dispersion $\frac{\omega_b}{\omega_0} \ll 1$ when the second term in equation (A9.1.8) denoted by D is investigated.

$$\begin{aligned} D = {} & \frac{|K_1|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right] \\ & \times \lim_{t\to\infty} \left\{ 2\int_0^{-\frac{\beta\hbar}{2}} d\tau_2 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\sum_k \frac{1}{N}\cos\omega_k t\cosh\omega_0\tau_2 + p\omega_0\tau_2\right]\right. \\ & \left.\times \sin\left\{\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\sum_k \frac{1}{N}\sin\omega_k t\sinh\omega_0\tau_2 + p\omega_0 t\right\}\right\}. \end{aligned} \quad \text{(A9.1.9)}$$

We make use of the following relations found in Chapter 8 for the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$,

$$\sum_k \frac{1}{N}\cos\omega_k t = J_0(\omega_b t)\cos\omega_0 t$$

and $$\sum_k \frac{1}{N}\sin\omega_k t = J_0(\omega_b t)\sin\omega_0 t,$$

to obtain

$$\begin{aligned} D = {} & \frac{|K_1|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right] \\ & \times \lim_{t\to\infty} \left\{ 2\int_0^{-\frac{\beta\hbar}{2}} d\tau_2 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2} J_0(\omega_b t)\cos\omega_0 t\cosh\omega_0\tau_2 + p\omega_0\tau_2\right]\right. \\ & \left.\times \sin\left\{\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2} J_0(\omega_b t)\sin\omega_0 t\sinh\omega_0\tau_2 + p\omega_0 t\right\}\right\}. \end{aligned} \quad \text{(A9.1.10)}$$

The large argument approximation for $J_0(x)$ is

$$J_0(x) \sim \left(\frac{2}{\pi x}\right)^{\frac{1}{2}} \cos(x - \pi/4).$$

Thus, $\lim\limits_{t\to\infty} J_0(\omega_b t) = 0$ so that

$$\mathcal{D} \sim \frac{|K|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right]$$

$$\times \lim_{t\to\infty} \left\{2\int_0^{-\frac{\beta\hbar}{2}} d\tau_2 \exp\left[\frac{\Delta E}{\hbar}t_2\right] \sin\left[\frac{\Delta E}{\hbar}t\right]\right\}, \qquad \text{(A9.1.11)}$$

which becomes

$$\mathcal{D} \sim \frac{|K|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right] \lim_{t\to\infty} \left\{\frac{\sin\left[\frac{\Delta E}{\hbar}t\right]}{\frac{\Delta E}{\hbar}} \left[\exp\left(-\frac{\beta\Delta E}{2}\right) - 1\right]\right\}$$

(A9.1.12)

Now, the delta function is defined by

$$\delta(x) = \lim_{g\to\infty} \frac{\sin gx}{\pi x},$$

so that D given by equation (A9.1.12) becomes

$$\mathcal{D} \sim \frac{|K|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right] \exp\left[\left(-\frac{\beta\Delta E}{2}\right) - 1\right] \pi\,\delta\left(\frac{\Delta E}{\hbar}\right).$$

(A9.1.13)

We thus conclude since the electronic energy difference ΔE is non-zero, that

$$\mathcal{D} = 0.$$

Hence, the expression for the transition rate $W_T^{(1)}$, equation (A9.1.8) becomes

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right]$$

$$\times \lim_{t\to\infty} \left\{\int_{-t}^{t} d\tau_1 \exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau_1\right] \cos p\omega_0\tau_1\right\}.$$

(A9.1.14)

APPENDIX A9.2

Calculation of the Recombination Rate in the M.C.M. in the zero dispersion limit.

Our starting point here is the expression for the transition rate given by equation (A9.1.14),

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right\}\lim_{t\to\infty}\left\{\int_{-t}^{t}d\tau_1\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos\omega_0\tau_1\right.\right.$$
$$\left.\times\cos p\omega_0\tau_1\right\}. \qquad (A9.2.1)$$

Writing, $x = \omega_0\tau_1$ this becomes

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right\}\int_{-\infty}^{\infty}dx\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos x\right]\cos px. \qquad (A9.2.2)$$

We expand $\exp\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\cos x\right]$ in a power series to obtain

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2\omega_0}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2} + \frac{\Delta E\beta}{2}\right\}\sum_{n=0}^{\infty}\frac{\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^n}{n!}\int_{-\infty}^{\infty}dx\cos^n x\cos px$$

(A9.2.3)

We investigate,

$$I_{n,p} = \int_{-\infty}^{\infty}\cos^n x\cos px.dx = 2\int_0^{\infty}dx\cos^n x\cos px. \qquad (A9.2.4)$$

We may write $I_{n,p}$ as

$$I_{n,p} = 2\sum_{r=0}^{\infty}\int_{r\pi}^{(r+1)\pi}dx'\cos^n x'\cos px'. \qquad (A9.2.5)$$

Changing the limits of integration from $r\pi\to(r+1)\pi$ to $0\to\pi$ we find,

$$I_{n,p} = 2\sum_{r=0}^{\infty}\int_0^{\pi}dx\cos^n(x+r\pi)\cos[p(x+r\pi)] \qquad (A9.2.6)$$

Now, $\cos(x+r\pi)=(-1)^r\cos x$, while $\cos p(x+r\pi)=(-1)^{pr}\cos x$.

Thus, we find

$$I_{n,p}=2\sum_{r=0}^{\infty}(-1)^{r(p+n)}\int_0^{\pi}\cos^n x\cos px\,.dx. \tag{A9.2.7}$$

Now, if $n<p$ we find in Gradshteyn, Ryzhik, that

$$\begin{aligned} A_{n,p}&=\int_0^{\pi}\cos^n x\cos px\,dx \\ &=\left[1+(-1)^{n+p}\right]S\,\frac{n!}{(p-n)(p-n+2)\cdots(p+n)}. \end{aligned} \tag{A9.2.8}$$

If $n=p-2q$ (q integer) then the factor $\left[1+(-1)^{n+p}\right]=2$, otherwise $\left[1+(-1)^{n+p}\right]=0$. However, the number $S=0$ if $n=p-2q$. Thus,

$A_{n,p}=0$ if $n<p$. (A9.2.9)

If $n\geqslant p$ then

$$A_{n,p}=\left[1+(-1)^{p+n}\right]\frac{\pi}{2^{n+1}}\frac{n!}{(n-q)!\,q!} \tag{A9.2.10}$$

$$\left.\begin{aligned} &\text{Thus, if } n=p+2q,\ A_{n,p}=\frac{\pi}{2^{p+2q}}\frac{(p+2q)!}{(p+q)!\,q!} \\ &\text{and if } n=p+2q+1,\ A_{n,p}=0 \end{aligned}\right\} \tag{A9.2.11}$$

$$\text{Now, } I_{n,p}=2\sum_{r=0}^{\infty}(-1)^{r[p+n]}A_{n,p}. \tag{A9.2.7'}$$

Thus, substituting (A9.2.7') and (A9.2.11) into (A9.2.3) we obtain

$$W_T^{(1)}=\frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}+\frac{\Delta E\beta}{2}\right\}\sum_{n=0}^{\infty}\frac{\left[\frac{E_M}{\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^n}{n!} \\ \times\sum_{r=0}^{\infty}(-1)^{r[p+n]}\frac{n!}{2^n(n-q)!\,q!} \tag{A9.2.12}$$

which becomes

$$W_T^{(1)}=\frac{2\pi|K_1|^2}{\hbar^2\omega_0}\exp\left\{-\frac{E_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}+\frac{\Delta E\beta}{2}\right\}\sum_{q=0}^{\infty}\frac{\left[\frac{E_M}{2\hbar\omega_0}\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\right]^{p+2q}}{(p+q)!\,q!}\sum_{r=0}^{\infty}(-1)^{2r(p}\;. \tag{A9.2.13}$$

This is text equation (9.9).

APPENDIX A9.3

Calculation of the Recombination Rates in the M.C.M. when dispersion is included.

Following our earlier discussion, we may write in the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$, $\left(\omega_b = \frac{\omega_1^2}{2\omega_0}\right)$

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E \beta}{2} - 2S\right] \int_{-t-\frac{i\beta\hbar}{2}}^{t-\frac{i\beta\hbar}{2}} \exp\left[-\frac{i\Delta E}{\hbar}\tau\right] \exp\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \sum_k \frac{\cos\omega_k\tau}{N}\right] d\tau \tag{A9.3.1}$$

where $S = \frac{E_M}{2\hbar\omega_0} \coth\frac{\beta\hbar\omega_0}{2}$. This is text equation (9.12). We use the formula we derived in Chapter 8, (A8.2.8) for the weak dispersion regime,

$$\frac{1}{N}\sum_k \cos\omega_k\tau = J_0(\omega_b\tau)\cos\omega_0\tau \text{,}$$

We also change the limits of integration from $-t-\frac{i\beta\hbar}{2} \to t-\frac{i\beta\hbar}{2}$

We obtain

$$W_T^{(1)} = \frac{|K_1|^2}{\hbar^2} \exp\left[\frac{\Delta E \beta}{2} - 2S\right] \int_{-t}^{t} d\tau \exp\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} J_0(\omega_b\tau)\cos\omega_0\tau\right] \cos\left[\frac{\Delta E}{\hbar}\tau\right]. \tag{A9.3.2}$$

Changing the variable to $x = \omega_0\tau$ and writing $\Delta E = (p+\Delta)\hbar\omega_0$ (where $\Delta \neq$ integer), we obtain

$$W_T = \frac{|K_1|^2}{\hbar^2\omega_0} \exp\left[-2S + \frac{\Delta E\beta}{2}\right] \int_{-\infty}^{\infty} dx \exp\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right] \cos\left[(p+\Delta)x\right]. \tag{A10.3.3}$$

We write this as

$$W_T = \frac{|K_1|^2}{\hbar^2\omega_0} \exp\left[-2S + \frac{\Delta E\beta}{2}\right] \int_{-\infty}^{\infty} dx \sum_{n=0}^{\infty} \frac{\left[\frac{E_M}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0}x\right)\cos x\right]^n}{n!} \cos\left[(p+\Delta)x\right]. \tag{A9.3.4}$$

We focus attention on

$$I = \int_{-\infty}^{\infty} \left[J_0\left(\frac{\omega_b}{\omega_0}x\right)\right]^n \cos^n x \cos\left[(p+\Delta)x\right] dx. \tag{A9.3.5}$$

As before, we divide this integral into intervals over periods of 2π. In the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$, $J_0\left(\frac{\omega_b}{\omega_0}x\right)$ does not vary much over an interval 2π, and can therefore be replaced by its value at $x = 2\pi r$, $J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)$.

Doing this, we obtain

$$I = \sum_{r=-\infty}^{\infty} \int_{2r\pi-\pi}^{2r\pi+\pi} dx' \cdot \left[J_0\left(2\pi r\frac{\omega_b}{\omega_0}\right)\right]^n \cos^n x' \cos\left[(p+\Delta)x'\right].$$

Writing all these integrals over the interval $(-\pi, \pi)$ by letting

$x = x' - 2r\pi$, we obtain

$$I = \sum_{r=-\infty}^{\infty} \int_{-\pi}^{\pi} dx \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n \cos^n(x + 2r\pi) \cos\left[(p+\Delta)(x+2r\pi)\right]. \quad \text{(A9.3.5)}$$

We find

$$I = \sum_{r=-\infty}^{\infty} \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n \int_{-\pi}^{\pi} dx \cos^n x \left\{\cos[(p+\Delta)x] \cos 2\pi r(p+\Delta) - \sin[(p+\Delta)x] \sin [2\pi r(p+\Delta)\right.$$

Thus,

$$I = \sum_{r=-\infty}^{\infty} \cos 2\pi r(p+\Delta) \int_{-\pi}^{\pi} dx \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n \cos^n x \cos[(p+\Delta)x]$$

$$- \sum_{r=-\infty}^{\infty} \sin 2\pi r(p+\Delta) \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n \int_{-\pi}^{\pi} dx \cos^n x \sin[(p+\Delta)x]. \quad \text{(A9.3.6)}$$

Now, $J_0\left(-2\pi r \frac{\omega_b}{\omega_0}\right) = J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)$,

$\cos 2\pi r(p+\Delta) = \cos[-2\pi r(p+\Delta)]$,

$\sin 2\pi r(p+\Delta) = -\sin[-2\pi r(p+\Delta)]$.

Hence, when we alter the summation $\sum_{r=-\infty}^{-1}$ to $\sum_{r=1}^{\infty}$ we find that

$$I = \int_{-\pi}^{\pi} dx \cos^n x \cos[(p+\Delta)x] \left\{1 + 2\sum_{r=1}^{\infty} \cos 2\pi r(p+\Delta) \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n\right\}, \quad \text{(A9.3.7)}$$

Thus, using (A9.3.7) in (A9.3.4), we find that

$$W_T = \frac{2|K_1|^2}{\hbar^2 \omega_0} \exp\left[-2S + \frac{\Delta E \beta}{2}\right] \sum_{n=0}^{\infty} \frac{1}{n!} \left[\frac{E_H}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_b}{2}\right]^n \left\{1 + 2\sum_{r=1}^{\infty} \left[J_0\left(2\pi r \frac{\omega_b}{\omega_0}\right)\right]^n \cos 2\pi r\right.$$

$$\times A_{n,p+\Delta}. \quad \text{(A9.3.8)}$$

where $A_{n,p+\Delta} = \int_0^{\pi} \cos^n x \cos[(p+\Delta)x] dx$

This is text equation (9.14)

We find in Gradshteyn/Ryzhik that if $\Delta \neq 0$

$$A_{n,p+\Delta} = \frac{(-1)^n \sin[(p+\Delta)\pi]}{2^n (n+p+\Delta)} F\left[-n, -\left(\frac{p+\Delta+n}{2}\right); 1 - \left(\frac{p+\Delta+n}{2}\right); -1\right] \quad \text{(A9.3.9)}$$

where $F(\alpha, \beta; y, z)$ is the hypergeometric function.

Otherwise (A9.2.11) still holds, $(\Delta = 0)$

$$A_{n,p+\Delta} = [1 + (-1)^{p+n}] \frac{\pi}{2^{n+1}} \frac{n!}{(n-k)!\,k!} \qquad n = p + 2k$$

$$= 0$$

Chapter 10

The incorporation of a local mode in the Molecular Crystal Model

In Parts I, II and III of this thesis, we have calculated recombination rates using two different models, the S.C.C.M. and the M.C.M. The S.C.C.M. incorporates coupling of the impurity electron to only one local mode, while the electron in the M.C.M. interacts with all the normal crystalline modes. However, there is direct experimental evidence which suggests that both these models are inadequate for the impurity centres in crystals being studied. Dean and Henry[9] (1968) have studied radiative transitions between the shallow excited Is (E) state and the deep Is (A_1) ground state of ionized oxygen donors in gallium phosphide. This radiative transition is broadened due to the emission and absorption of phonons from the vibrational modes with which the impurity interacts. The vibronic sidebands contain phonons from the pure gallium phosphide crystalline modes in addition to the local mode phonons associated with the impurity centre. This implies that electrons in impurity centres such as Oxygen in GaP interact with both the local and the crystalline modes.

We shall attempt to include this aspect of the problem in our treatment of non-radiative transitions by incorporating one local mode into the M.C.M. It will be found that a local mode arises if a quadratic term is included in the electron-lattice interaction. Although this model leads to certain difficulties which will be discussed later, we believe it gives a more realistic description of non-radiative transitions than the models hitherto used.

The Hamiltonian for the M.C.M. is,

$$H_T = H_L + H_e, \tag{10.1}$$

where

$$\left.\begin{aligned} H_L &= \sum_{m=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2 x_m^2 + \frac{1}{2}M\omega_1^2 x_m x_{m+1}\right), \\ \text{and} \\ H_e &= -\frac{\hbar^2}{2m_e}\nabla_r^2 + \sum_{m=1}^{N} U(\underline{r}-m\underline{a}, x_m). \end{aligned}\right\} \tag{10.2}$$

In the Born-Oppenheimer approximation, the zero'th order wavefunction is a simple product of an electron and a vibrational wavefunction. We assume as in Chapter 5 that the electronic wavefunctions are solutions of

$$\left[-\frac{\hbar^2}{2m_e}\nabla_r^2 + U(\underline{r}-p\underline{a}, x_p)\right]\varphi_i(\underline{r}-p\underline{a}, x_p) = E_i(x_p)\varphi_i(\underline{r}-p\underline{a}, x_p). \tag{10.3}$$

However, a quadratic electron-lattice interaction term is now incorporated in addition to the linear term included in Chapter 5. We assume the electronic energy eigenvalue $E_i(x_p)$ to be given by

$$E_i(x_p) = E_i - A_i x_p + B_i x_p^2. \tag{10.4}$$

In this case, the lattice wavefunctions are solutions of

$$\left[\sum_{m=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2 x_m^2 + \frac{1}{2}M\omega_1^2 x_m x_{m+1}\right) - A_i x_p + B_i x_p^2\right]\chi = E\chi, \tag{10.5}$$

which may be written as

$$\left[\sum_{m=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_1^2 x_m x_{m+1}\right) + \sum_{\substack{m=1 \\ m\neq p}}^{N}\frac{1}{2}M\omega_0^2 x_m^2 + \frac{1}{2}M\omega_2^2 x_p^2 - A_i x_p\right]\chi = E\chi \tag{10.6}$$

where

$$\frac{1}{2}M\omega_2^2 = \frac{1}{2}M\omega_0^2 + B, \tag{10.7}$$

assuming

$$B_0 = B_1 = B.$$

The Hamiltonian of equation (10.6) contains quadratic and bilinear terms and so may be diagonalized in principle. Unfortunately, I have been unable to achieve diagonalization in practice. However, it may be shown that a Hamiltonian of the type given by equation (10.6) may lead to the formation of one local mode, while the remaining N-1 crystalline modes have their frequencies shifted slightly. This type of problem has been discussed by Montroll and Potts[31], (1955).

We believe that the condition for the formation of a local mode is $\frac{\omega_1^2}{\omega_2^2-\omega_0^2} \ll 1$. Actually, the local mode is never completely localised, it always has a small amplitude on the neighbouring molecules. The smaller the ratio $\frac{\omega_1^2}{\omega_2^2-\omega_0^2}$ the more localised the 'local' mode will be.

We will now express the lattice Hamiltonian in diagonal form, writing the crystalline normal coordinates as $\{q_k\}$ and the local mode coordinate as y, noting that y is not the same as x_p. It is important to realise here that the normal coordinates $\{q_k\}$ and y cannot be expressed in terms of the original lattice coordinates $\{x_m\}$. On doing this, equation (10.6) becomes,

$$\left[\sum_k -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial q_k^2} + \frac{1}{2}M\omega_k^2(q_k-\Delta q_k^{(i)})^2 - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial y^2} + \frac{1}{2}M\omega_2^2(y-\Delta y^{(i)})^2\right]\mathcal{F} = E\mathcal{F}. \tag{10.8}$$

In the S.C.C.M. when $y \equiv x_p$ the relative displacement is expressed in terms of the linear coupling constant, $\Delta x_p^{(i)} = \left(\frac{\hbar}{M\omega_0}\right)^{\frac{1}{2}}\frac{A_i}{M\omega_0^2}$ and the coupling strength E_M is given by $E_M = \frac{1}{2}M\omega_0^2\Delta x_p^2$ where $\Delta x_p = \Delta x_p^{(1)} - \Delta x_p^{(0)}$. However, now that a truly local mode no longer exists, we do not have analytical expressions for the relative displacements $\Delta y = \Delta y^{(1)} - \Delta y^{(0)}$ and $\Delta q_k = \Delta q_k^{(1)} - \Delta q_k^{(0)}$ or the coupling strengths $E_M' = \frac{1}{2}M\omega_0^2\Delta y^2$ and $E_M'' = \frac{1}{2}M\omega_0^2\sum_k \Delta q_k^2$. Thus, in this model which incorporates a local mode into the M.C.M., the most important parameters in the whole theory, the coupling strengths

$E_M{}^{1}$ and $E_M{}^{11}$, are phenomenological constants.

We will now calculate the transition rates following Holstein's[1] procedure. The zero'th order states of H_T given by equation (10.1) are,

$$\varphi_i(\underline{r}-p\underline{a},x_p)\left\{\prod_k \Phi_{N_k^i}\left[\alpha_k(q_k-\Delta q_{k,p}^{(i)})\right]\right\}\Phi_{N^i}\left[\alpha(y-\Delta y^{(i)})\right], \quad (10.9)$$

where $\Phi_{N_k^i}\left[\alpha_k(q_k-\Delta q_{k,p}^{(i)})\right]$ are displaced simple harmonic oscillator states for the crystalline modes, while $\Phi_{N^i}\left[\alpha(y-\Delta y^{(i)})\right]$ is the displaced simple harmonic oscillator state for the local mode.

The expression for the non-radiative transition probability is,

$$W_T=\frac{1}{Z}\sum_{\{N_k^i\},N^i} W_{\{N_k^i\},N^1}(1\rightarrow 0)\exp\left[-\sum_k \beta\hbar\omega_k(N_k^1+\tfrac{1}{2})-\beta\hbar\omega_2 N^1\right], \quad (10.10)$$

where

$$Z=\sum_{\{N_k^1\},N^1}\exp\left[-\sum_k \beta\hbar\omega_k(N_k^1+\tfrac{1}{2})-\beta\hbar\omega_2 N^1\right];$$

The initial quantum indices are

$i = 1$: excited electron state.

$N_k^i = N_k^1$: crystalline mode quantum numbers when the electron is in its excited state.

$N^i = N^1$: local mode quantum number when the electron is in its excited state.

Similarly, the final quantum indices are $i = 0$, $N_k^i = N_k^0$ and $N^i = N^0$ respectively.

In equation (10.10),

$$W_{\{N_k^i\},N^1}(1\rightarrow 0)=\sum_{\{N_k^0\},N^0} W(1,\{N_k^1\},N^1\rightarrow 0,\{N_k^0\},N^0), \quad (10.11)$$

where

$$W(1,\{N_k^1\},N^1\longrightarrow 0,\{N_k^0\},N^0)$$

$$=\frac{2}{\hbar^2}\left|(0,\{N_k^0\},N^0|V|1,\{N_k^1\},N^1)\right|^2\frac{\partial}{\partial t}\Omega\left[\sum_k\hbar\omega_k(N_k^0-N_k^1)+\hbar\omega_2(N^0-N^1)-\Delta E\right]$$

where $\frac{\partial}{\partial t}\Omega(x)=\frac{1}{2}\int_{-t}^{t}\exp\left(\frac{ixt'}{\hbar}\right)dt'.$ (10.12)

In equation (10.12),

$$(0,\{n_k^0\},n^0|V|1,\{n_k^1\},n^1)$$

$$=K\,\Pi_k\int dq_{\gamma k}\,\Phi_{n_k^0}\left[\alpha_k(q_{\gamma k}-\Delta q_{\gamma k}^{(0)})\right]\Phi_{n_k^1}\left[\alpha_k(q_{\gamma k}-\Delta q_{\gamma k}^{(1)})\right]$$

$$\times\int dy\,\Phi_{n^0}\left[\alpha(y-\Delta y^{(0)})\right]\Phi_{n^1}\left[\alpha(y-\Delta y^{(1)})\right]. \qquad (10.13)$$

Now, using the expressions for the vibrational overlap integral in the M.C.M. given by equation (5.27) we obtain,

$$(0,\{n_k^0\},n^0|V|,1,\{n_k^1\},n^1)$$

$$=K\,\Pi_k\Big\{\left[1-\frac{1}{N}(n_k^1+\tfrac{1}{2})\gamma_k\sin^2(kp+\tfrac{1}{2})\right]\delta_{n_k^1,n_k^0}$$

$$+\left(\frac{2}{N}\right)^{\frac{1}{2}}\gamma_k^{1/2}\sin(kp+\pi/4)\left[\left(\frac{n_k^1}{2}\right)^{\frac{1}{2}}\delta_{n_k^0,n_k^1-1}-\left(\frac{n_k^1+1}{2}\right)^{\frac{1}{2}}\delta_{n_k^0,n_k^1+1}\right]\Big\}I_{n^0n^1} \qquad (10.14)$$

where $I_{n^0n^1}$ is the vibrational overlap integral for the local mode.

Thus, expression (10.12) becomes,

$$W(1,\{n_k^1\},n^1\rightarrow 0,\{n_k^0\},n^0)$$

$$=\frac{2|K|^2}{\hbar^2}I^2_{n^0n^1}\int_{-t}^{t}\Pi_k\Big\{\left[1-\frac{1}{N}(n_k^1+\tfrac{1}{2})\gamma_k\right]\delta_{n_k^1,n_k^0}+\frac{\gamma_k}{N}\Big[\left(\frac{n_k^1}{2}\right)\delta_{n_k^0,n_k^1-1}$$

$$+\left(\frac{n_k^1+1}{2}\right)\delta_{n_k^0,n_k^1+1}\Big]$$

$$\times\exp\left[\frac{it'}{\hbar}\Big\{\sum_k\hbar\omega_k(n_k^0-n_k^1)+\hbar\omega_2(n^0-n^1)-\Delta E\Big\}\right]. \qquad (10.15)$$

Thus, $W_{\{n_k^1\},n^1}(1\rightarrow 0)$ given by equation (10.11) becomes on summing over the final state quantum numbers

$$W_{\{n_k^1\},n^1}(1\to 0)$$
$$=\frac{2|K|^2}{\hbar^2}\sum_{n^0} I^2_{n^0n^1}\int_{-t}^{t}\Pi_k\Big\{\Big[1-\frac{\gamma_k}{N}(n_k^1+\tfrac{1}{2})\Big]+\frac{\gamma_k}{N}\Big[\Big(\frac{n_k^1}{2}\Big)\exp(-i\omega_k t^1)+\Big(\frac{n_k^1+1}{2}\Big)\exp(i\omega_k t^1)\Big]$$
$$\times\exp\Big[\frac{it^1}{\hbar}\{\hbar\omega_2(n^0-n^1)-\Delta E\}\Big]dt^1. \qquad (10.16)$$

We may write equation (10.15) in the form

$$W_{\{n_k^1\},n^1}(1\to 0)$$
$$\doteq\frac{2|K|^2}{\hbar^2}\sum_{n^0} I^2_{n^0n^1}\int_{-t}^{t}dt^1\exp\Big\{\sum_k\frac{\gamma_k}{N}\Big[-(n_k^1+\tfrac{1}{2})+(n_k^1+\tfrac{1}{2})\cos\omega_k t^1+\frac{i}{2}\sin\omega_k t^1\Big]$$
$$\times\exp\Big[\frac{it^1}{\hbar}\{\hbar\omega_2(n^0-n^1)-\Delta E\}\Big]. \qquad (10.17)$$

Thus, the expression for the transition rate given by equation (10.10) becomes

$$W_T=\frac{2|K|^2}{\hbar^2 Z}\sum_{\{n_k^1\},n^1}\sum_{n^0} I^2_{n^0n^1}\int_{-t}^{t}dt^1\exp\Big\{\sum_k\frac{\gamma_k}{N}\Big[-(n_k^1+\tfrac{1}{2})+(n_k^1+\tfrac{1}{2})\cos\omega_k t^1$$
$$+\frac{i}{2}\sin\omega_k t^1$$
$$\times\exp\Big[\frac{it^1}{\hbar}\{\hbar\omega_2(n^0-n^1)-\Delta E\}\Big]\exp\Big[-\sum_k\beta\hbar\omega_k(n_k^1+\tfrac{1}{2})-\beta\hbar\omega_2 n^1\Big]. \qquad (10.18)$$

On replacing N_k^1 by its thermal average value $\langle n_k^1\rangle=[\exp(\beta\hbar\omega_0)-1]^{-1}$, we obtain

$$W_T=\frac{2|K|^2}{\hbar^2}\sum_{\{n_k^1\},n^1}\frac{I^2_{n^0n^1}\exp[-\beta\hbar\omega_2 n^1]}{\sum_{n^1}\exp[-\beta\hbar\omega_2 n^1]}$$

$$\times\int_{-t}^{t}\exp\Big\{\sum_k\frac{\gamma_k}{N}\Big[-(n_k^1+\tfrac{1}{2})+(n_k^1+\tfrac{1}{2})\cos\omega_k t^1+\frac{i}{2}\sin\omega_k t^1\Big]\Big\}\exp\Big[\frac{it^1}{\hbar}\{\hbar\omega_2(n^0-n^1)-\Delta E\}\Big]$$

(10,19)

We write $$Z_\ell = \sum_n \exp[-\beta\hbar\omega_2 n] = [\exp(\beta\hbar\omega_2) - 1]^{-1},$$

to obtain the transition rate W_T in the form,

$$W_T = \frac{2|K|^2}{\hbar^2 Z_\ell}\sum_{n^0, n'} I^2_{n^0 n'} \int_{-t}^{t} dt' \exp\Big\{\sum_k \frac{\gamma_k}{N}\Big[-(n'_k+\tfrac{1}{2}) + (n'_k+\tfrac{1}{2})\cos\omega_k t' + \tfrac{i}{2}\sin\omega$$
$$\times \exp\Big[-\frac{it'}{\hbar}\Delta E^{1}_{n^0 n'}\Big], \qquad (10.20)$$

where $$\Delta E^{1}_{n^0 n'} = \Delta E - \hbar\omega_2 (n^0 - n').$$

We finally obtain by putting $N^0 = N^1 + a$,

$$W_T = \frac{2|K|^2}{\hbar^2 Z_\ell}\sum_a \sum_{n'} I^2_{n'+a, n'} \exp[-\beta\hbar\omega_2 n']$$
$$\times \int_{-t}^{t} dt' \exp\Big\{\sum_k \frac{\gamma_k}{N}\Big[-(n'_k+\tfrac{1}{2}) + (n'_k+\tfrac{1}{2})\cos\omega_k t' + \tfrac{i}{2}\sin\omega_k t'\Big]\Big\} \exp\Big[-\frac{it'}{\hbar}\Delta E_{n^0 n'}\Big]. \qquad (10.21)$$

We may interpret the physical processes giving rise to each of the terms in expression (10,21) as follows: Each term denoted by 'a' represents a process in which 'a' phonons with total energy $a\hbar\omega_2$ are emitted into the local mode, while the remaining energy $\Delta E_{n'+a, n'} = \Delta E - a\hbar\omega_2$ is emitted into the crystalline modes. If $\Delta E = p\hbar\omega_2$ then all the energy may be emitted into the local mode (a=p) and the situation is as described by the S.C.C.M. If $\Delta E = p\hbar\omega_0$ then all the energy may be emitted into the lattice modes and the situation is as described by the M.C.M. For all other situations recombination takes place by the emission of phonons into both local and lattice modes. We now follow our treatment, given in Chapter 8, of the recombination rates using the M.C.M. in the weak dispersion limit $\frac{\omega_b}{\omega_0} \ll 1$ to obtain the transition rate in the form,

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0 Z_\ell}\sum_a\sum_r I^2_{r+a,r}\exp[-\beta\hbar\omega_2 r]$$
$$\times\exp(-2S)\{A_0(p_a+\Delta_a)+2\sum_{n=1}^{\infty}A_n(p_a+\Delta_a)\cos 2\pi n\Delta_a\}.$$

(10.22)

In this expression,

$$A_n(p_a+\Delta_a)=\frac{1}{2\pi}\int_{-\pi}^{\pi}dx\exp[a_n\cos x]\cos[a'_n\sin x-(p_a+\Delta_a)x],$$

where,

$$a'_n=\frac{E'_M}{\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)$$

$$a'_n=\frac{E'_M}{\hbar\omega_0}J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)$$

$$S=\frac{E'_M}{2\hbar\omega_0}\coth\frac{\beta\hbar\omega_0}{2}.$$

The coupling constant of the electron to the crystalline modes is

$E'_M=\sum_k\frac{\gamma_k}{2N}$ and $p_a+\Delta_a=\frac{\Delta E-a\hbar\omega_2}{\hbar\omega_0}$.

We will now investigate the type of transition rates which expression (10.22) leads to, for some special cases. The transition rate becomes at the absolute zero of temperature T=0,

$$W_{T=0}=\frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_a I^2_{a,0}\exp(-2S)\{A_0(p_a+\Delta_a)+2\sum_{n=1}^{\infty}A_n(p_a+\Delta_a)\cos 2\pi n$$

(10.23)

The especially simple case in which $\omega_2=\omega_0$ and $\Delta E=p\hbar\omega_0$ is now considered,

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a} I_{a,0}^{2} \exp(-2S)\left\{A_0(p_a) + 2\sum_{n=1}^{\infty} A_n(p_a)\right\}. \qquad (10.24)$$

It is shown in appendix A10.1 that the final result [equation (A10.1.9)] is,

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\left(\frac{E_M}{\hbar\omega_0}\right)^{p}\frac{1}{p!}, \qquad (10.25)$$

where E_M is the coupling of the electron to both the local and the lattice modes, $E_M = E_M^{1} + E_M^{11}$.
However, expression (10.25) is exactly the same form expected for an electron which is coupled to vibrational modes which all have the same frequency ω_0.

We must admit that choosing $\omega_2 = \omega_0$ is artificial in that a local mode will not appear in this case. However, being able to rederive the standard result equation (10.25) is at least satisfying.

The next case we consider, choosing $\Delta E = p\hbar\omega_2$ and $\omega_2 = 2\omega_0$ is more difficult. However, this situation is more realistic as Dean and Henry[9] give the local mode phonon energies of oxygen impurities in gallium phosphide as 24.7 and 28.4 meV while the pure crystalline transverse and longitudinal optical mode phonon energies are 44.8 and 49.8 meV respectively.

Once more expression (10.24) is used for the transition rate $W_{T=0}$ but in this case,

$$p_a = \frac{\Delta E - a\hbar\omega_2}{\hbar\omega_0} = (p-a)\frac{\omega_2}{\omega_0} = 2(p-a), \qquad (10.27)$$

so that

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p} I_{a,0}^{2} \exp(-2S)\left\{A_0[2(p-a)] + 2\sum_{n=1}^{\infty} A_n[2(p-a)]\right\}. \qquad (10.28)$$

We find in Appendix A10.2, equation (A10.2.7) that the final result is,

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0} \exp\left[-\left(\frac{E''_M}{\hbar\omega_2}+\frac{E'_M}{\hbar\omega_0}\right)\right]\left(\frac{E'_M}{\hbar\omega_0}\right)^{2p} \frac{1}{\left[\frac{i\,E'_M}{(E''_M\hbar\omega_0)^{1/2}}\right]^{2p}} \frac{1}{(2p)!}$$

$$\times H_{2p}\left[\frac{i\,E'_M}{(E''_M\hbar\omega_0)^{1/2}}\right], \qquad (10.29)$$

where H_{2p} is a Hermite polynomial.

Thus, even for this rather simple case the transition rate becomes quite complex,

The next situation we wish to consider is the temperature dependence of the transition rate in the weak coupling limit, $\frac{E'_M}{\hbar\omega_0} \ll 1$ and $\frac{E''_M}{\hbar\omega_0} \ll 1$. The general expression for this transition rate is found in Appendix A10.3, equation (A103.) to be

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0} \exp\left[-\left(\frac{E''_M}{\hbar\omega_2}+\frac{E'_M}{\hbar\omega_0}\right)\right] \sum_{a=0}^{p} \left[\frac{E''_M}{\hbar\omega_2}(1+N(\omega_2))\right]^{a} \left[\left(\frac{E'_M}{\hbar\omega_0}\right)(1+N(\omega_0))\right]^{2(p-a}$$

$$\times \frac{1}{a!\,[2(p-a)]!} \left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{2(p-a)}\right\}. \qquad (10.30)$$

We list below the various terms in the series (10,30), the physical processes they represent and their temperature dependences.

Table 10.1

Term	Temperature Dependence	
a=0	$[1+N(\omega_0)]^{2p}$	2p phonons of energy $\hbar\omega_0$ emitted into the lattice modes,
a=r (r<p)	$[1+N(\omega_0)]^{2(p-r)}(1+N(\omega_2))^{r}$	2(p-r) phonons of energy $\hbar\omega_0$ emitted into the lattice modes and r phonons into the local mode,
a=p	$(1+N(\omega_2))^{p}$	p phonons of energy $\hbar\omega_2$ emitted into the local mode,

Summary

In this last chapter we have incorporated a local mode into the M.C.M. The inclusion of this local mode is felt to be necessary as most impurities in crystals will, in fact, have local modes of vibration associated with them. Even if the recombination proceeds mainly by emission of phonons into the local mode, the direct coupling of the electron to the lattice modes provides a continuum of final energy levels, so that the application of perturbation theory is secure. The principal weakness of the model is that the most important parameters in the theory, namely the coupling constants of the electron to the local and lattice modes E_M^{11} and E_M^{1} respectively, can no longer be expressed in terms of the linear electron-lattice interaction constants A_0 and A_1. However, the coupling constants are no more phenomenological than in the M.C.M. and S.C.C.M. as the electron-lattice interaction constants have always been regarded as phenomenological themselves rather than being expressed in terms of the more microscopic parameters of the system.

In this chapter we started from the general form of the transition probability given by equation (10.11) and arrived at the final form (10.22). The recombination rate was investigated at the absolute zero of temperature and it was found that even for quite simple cases of $\Delta E, \omega_2, \omega_0$, complicated transition rates result, (equation (10.29)).

Finally we investigated the temperature dependences of the terms in the transition rate in the weak coupling limit, $\frac{E_M^{1}}{\hbar\omega_0} \ll 1$ and $\frac{E_M^{11}}{\hbar\omega_2} \gg 1$. In table 10.1 we list the various terms, the physical processes which they represent and their temperature dependence. A typical term is one which represents the emission of $2(p-r)(r<p)$ phonons of energy $\hbar\omega_0$ into the lattice modes and the emission of r phonons

each of energy $\hbar\omega_2$ $(\omega_2 = 2\omega_D)$ into the local mode. The temperature dependence of this term is $[1 + N(\omega_0)]^{2(p-r)}(1 + N(\omega_2))^r$.

APPENDIX A10.1

Calculation of transition rate $W_{T=0}$ when $\omega_2=\omega_0$ and $\Delta E=p\hbar\omega_0$.

The expression for $W_{T=0}$ when $\omega_2=\omega_0$ and $\Delta E=p\hbar\omega_0$ is text equation (10.23),

$$W_{T=0}=\frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p}I_{a,0}^{2}\exp(-2S)\{A_0(p_a)+2\sum_{n=1}^{\infty}A_n(p_a)\}. \tag{A10.1.1}$$

Now, if E_M'' is the coupling of the electron to the local mode,

$$E_M''=\frac{\alpha^2\Delta y^2}{2}\hbar\omega_0, \tag{A10.1.2}$$

then

$$I_{a,0}^{2}=\left(\frac{E_M''}{\hbar\omega_0}\right)^a\exp\left(-\frac{E_M''}{\hbar\omega_0}\right)\frac{1}{a!}. \tag{A10.1.3}$$

If E_M' is the coupling of the electron to the crystalline modes, then

$$E_M'=\sum_k\frac{\alpha_k^2\Delta q_k^2}{2}\hbar\omega_k. \tag{A10.1.4}$$

Now, $A_n(p_a)$ where, $p_a=\dfrac{\Delta E-a\hbar\omega_2}{\hbar\omega_0}=\dfrac{p\hbar\omega_0-a\hbar\omega_0}{\hbar\omega_0}=(p-a)$

becomes

$$A_n(p-a)=\left[\frac{E_M'}{\hbar\omega_0}J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p-a}\exp\left[-\frac{E_M'}{\hbar\omega_0}\right]\frac{1}{(p-a)!}. \tag{A10.1.4}$$

Hence, substituting (A10,1,3) and (A10,1,4) into (A10,1,1) we obtain

$$W_{T=0}=\frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p}\left(\frac{E_M''}{\hbar\omega_0}\right)^a\exp\left(-\frac{E_M''}{\hbar\omega_0}\right)\frac{1}{a!}\exp\left(\frac{-E_M''}{\hbar\omega_0}\right)\left(\frac{E_M'}{\hbar\omega_0}\right)^{p-a}\frac{1}{(p-a)!} \tag{A10.1.5}$$
$$\times\left\{1+2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_b}{\omega_0}\right)\right]^{p-a}\right\}.$$

Considering only the first term of (A10,1,5) we have

$$W_{T=0}\cong\frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left[-\frac{(E_M'+E_M'')}{\hbar\omega_0}\right]\left(\frac{E_M'}{\hbar\omega_0}\right)^p\sum_{a=0}^{p}\left(\frac{E_M''}{E_M'}\right)^a\frac{1}{a!(p-a)!}. \tag{A10.1.6}$$

Now we will write the total coupling of the electron to the lattice both local and crystalline modes as,

$$E_M=E_M'+E_M''. \tag{A10.1.7}$$

Thus, performing the summation in (A10.1.6) we obtain for $W_{T=0}$,

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\left(\frac{E_M'}{\hbar\omega_0}\right)^p\left(1+\frac{E_M''}{E_M'}\right)^p\frac{1}{p!}, \tag{A10.1.8}$$

which is

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\left(\frac{E_M'+E_M''}{\hbar\omega_0}\right)^p\frac{1}{p!},$$

which is

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left(-\frac{E_M}{\hbar\omega_0}\right)\left(\frac{E_M}{\hbar\omega_0}\right)^p\frac{1}{p!}. \tag{A10.1.9}$$

This is text equation (10.24).

APPENDIX A10.2

Calculation of transition rate $W_{T=0}$ when $\omega_2 = 2\omega_0$ and $\Delta E = p\hbar\omega_2$.

In this case, the transition rate is given by text equation (10.27),

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p} I_{a,0}^2 \exp(-2S)\left\{A_0[2(p-a)] + 2\sum_{n=1}^{\infty} A_n[2(p-a)]\right\}.$$

Now,

$$I_{a,0}^2 = \left(\frac{E_M''}{\hbar\omega_2}\right)^a \exp\left(-\frac{E_M''}{\hbar\omega_2}\right)\frac{1}{a!} \qquad \text{(A10.2,2)}$$

while,

$$A_n[2(p-a)] = \left[\frac{E_M'}{\hbar\omega_0} J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)\right]^{2(p-a)} \exp\left[-\frac{E_M'}{\hbar\omega_0}\right]\frac{1}{[2(p-a)]!}. \qquad \text{(A10.2,3)}$$

Substituting (A10.2,2) and (A10,2,3) into (A10.2.1) we obtain

$$W_{T=0} = \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left[-\left(\frac{E_M''}{\hbar\omega_2} + \frac{E_M'}{\hbar\omega_0}\right)\right]\sum_{a=0}^{p}\left(\frac{E_M''}{\hbar\omega_2}\right)^a\left(\frac{E_M'}{\hbar\omega_0}\right)^{2(p-a)}\frac{1}{a!\,[2(p-a)]!}$$
$$\times\left\{1 + 2\sum_{n=1}^{\infty}\left[J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)\right]^{2(p-a)}\right\}. \qquad \text{(A10.2,4)}$$

Taking only the first term in this series

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left[-\left(\frac{E_M''}{\hbar\omega_2} + \frac{E_M'}{\hbar\omega_0}\right)\right]\left(\frac{E_M'}{\hbar\omega_0}\right)^{2p}\sum_{a=0}^{p}\left[\frac{E_M''}{2\hbar\omega_0}\,\frac{(\hbar\omega_0)^2}{E_M'}\right]^a\frac{1}{a!\,[2(p-a)]!}. \qquad \text{(A10.2.5)}$$

We may express this in terms of a Hermite polynomial of imaginary argument

$$\frac{1}{u^t\,t!}H_t(u) = \sum_{a=0}^{\frac{1}{2}t}\frac{1}{(-2u^2)^a(t-2a)!\,a!}, \qquad \text{(A10,2.6)}$$

$$W_{T=0} \cong \frac{2\pi|K|^2}{\hbar^2\omega_0}\exp\left[-\left(\frac{E_M''}{\hbar\omega_2} + \frac{E_M'}{\hbar\omega_0}\right)\right]\left(\frac{E_M'}{\hbar\omega_0}\right)^{2p}\frac{1}{\left[\frac{iE_M'}{(E_M''\hbar\omega_0)^{1/2}}\right]^{2p}}\frac{1}{2p!}H_{2p}\left[\frac{iE_M'}{(E_M''\hbar\omega_0)^{1/2}}\right]. \qquad \text{(A10.2.7)}$$

This is text equation (10.28).

APPENDIX A10.3

Calculation of Temperature Dependence of Transition Rates in the Weak Coupling Limit.

The general expression for the transition rate is given by text equation (10,21)

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0 Z_\ell}\sum_a\sum_r I^2_{r+a,r}\exp[-\beta\hbar\omega_2 r]\exp(-2S)$$
$$\times\{A_0(p_a+\Delta_a)+2\sum_{n=1}^{\infty}A_n(p_a+\Delta_a)\cos 2\pi n\Delta_a\}. \quad (A10.3.1)$$

As in Appendix A11.2, we will simplify the calculations by choosing

$\Delta E = p\hbar\omega_2$ and $\omega_2 = 2\omega_0$.

In this case

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_a\left(\sum_r I^2_{r+a,r}\exp[-\beta\hbar\omega_2 r]Z_\ell^{-1}\right)\exp(-2S)$$
$$\times\{A_0[2(p-a)]+2\sum_{n=1}^{\infty}A_n[2(p-a)]\}. \quad (A10.3.2)$$

In the weak coupling limit, $\frac{E_M'}{\hbar\omega_0} \ll 1$ and $\frac{E_M''}{\hbar\omega_0} \ll 1$.

Now, in the weak coupling limit $\frac{E_M''}{\hbar\omega_0} \ll 1$ we have shown in Chapter 3 [Appendix A3.] that

$$\sum_{r=0}^{\infty} I^2_{r+a,r}\exp[-\beta\hbar\omega_2 r]Z_\ell^{-1} = \exp\left(-\frac{E_M''}{\hbar\omega_2}\right)\left[\frac{E_M''}{\hbar\omega_2}\{1+N(\omega_2)\}\right]^a\frac{1}{a!}$$

where $N(\omega_2)$ is the thermal probability of occupation of the local mode,

$$N(\omega_2) = \frac{1}{e^{\beta\hbar\omega_2}-1}.$$

Substituting (A10,3.3) into (A10,3.2) we obtain

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p}\exp\left(-\frac{E_M''}{\hbar\omega_2}\right)\left[\frac{E_M''}{\hbar\omega_2}\{1+N(\omega_2)\}\right]^a\frac{1}{a!}\exp\left(-\frac{E_M'}{\hbar\omega_0}\right)$$
$$\times\{A_0[2(p-a)]+2\sum_{n=1}^{\infty}A_n[2(p-a)]\}. \quad (A10,3,4)$$

In the weak coupling limit $\frac{E_M'}{\hbar\omega_0} \ll 1$, we have shown in Chapter 8 [Appendix A8, 7]

$$A_n[2(p-a)] = \left[\frac{E_M'}{\hbar\omega_0}J_0\left(2\pi n\frac{\omega_p}{\omega_0}\right)(1+N(\omega_0))\right]^{2(p-a)}\frac{1}{[2(p-a)]!}. \quad (A10,3,5)$$

Thus, we obtain

$$W_T = \frac{2\pi|K|^2}{\hbar^2\omega_0}\sum_{a=0}^{p}\exp\left[-\left(\frac{E_M''}{\hbar\omega_2}+\frac{E_M'}{\hbar\omega_0}\right)\right]\left[\frac{E_M''}{\hbar\omega_2}\{1+N(\omega_2)\}\right]^{a}\left[\frac{E_M'}{\hbar\omega_0}\{1+N(\omega_0)\}\right]^{2(p-}$$
$$\times\frac{1}{a!\,[2(p-a)]!}\left\{1+2\sum_{h=1}^{\infty}\left[J_0\left(2\pi h\frac{\omega_h}{\omega_0}\right)\right]^{2(p-a)}\right\}. \qquad \text{(A10.3.6)}$$

This is text equation (10.29).

Conclusions and Suggestions for Future Work

The main contribution of this thesis is the introduction of the Molecular Crystal Model to study the recombination problem. Using both the M.C.M. and the standard S.C.C.M. we have rederived the standard zero temperature [equations (3.21)], and strong coupling, high temperature [equations (3.22), (5.38)] results.

The calculational methods we use in the M.C.M. follow both the formal development of Holstein[1] in Chapter 5 and the more intuitive combinatorial approach followed by Huang Rhys[8] in Chapter 6. The inclusion of finite dispersion in the crystalline modes of vibration is theoretically essential for a sound treatment of radiationless transitions. Otherwise the transition rates are zero unless $\Delta E = p\hbar\omega_0$ and are not well-defined even if this condition is satisfied. In Chapter 8 we have included the effects of weak but finite dispersion in calculating modified transition rates. The relaxation process now occurs for any value of the electronic energy difference ΔE and the transition rates [equations (8.15), (8.22), and (8.33)] are all series in which the first term is the standard transition rate while the higher terms are corrections to this. In Chapter 10 we have incorporated a local mode into the M.C.M. as most electrons at impurity centres in crystals are coupled to both local and lattice modes of vibration. The discussion of recombination rates becomes more qualitative in this chapter but nevertheless an important aspect of the relaxation problem is dealt with.

We have also extended the S.C.C.M. to deal with the situation in which the vibrational mode has different frequencies according to whether the electron is in the ground or excited state. The result originally derived by Hutchisson is obtained. We have also derived, at the absolute zero of temperature, a new form of the energy gap law [equation (4.14)] which may be appropriate for oxygen impurities in GaP.

We now make some suggestions for the ways in which the present work might usefully be extended. First of all, in the calculation of the effect of dispersion on the recombination rates, the relaxation of the weak dispersion condition $\frac{\omega_b}{\omega_0} \ll 1$ would be very helpful. The effect of the electron being coupled to the acoustic modes as well as the optical modes could then be included. We feel that more work might be done on the inclusion of a local mode into the M.C.M. In particular, the determination of the coupling strengths E_M^{1} and E_M^{11} in terms of the linear electron-lattice interaction constants A and the lattice and local mode frequencies ω_0 and ω_2 would be an advance on our work.

In regard to the S.C.C.M., the work we have done considers only harmonic potential energy wells. In the future, attention might be directed towards anharmonic potentials, for example, the Morse potential. On a more fundamental note, the question of energy conservation in the S.C.C.M. might be considered from the point of view of the local mode being coupled to the crystalline modes by anharmonic terms. This type of coupling results in broadening of the S.C.C.M. energy levels which allows relaxation processes to occur for any value of the electronic energy difference. In this model, the electron is directly coupled to the local mode and indirectly coupled to the crystalline modes by the anharmonic terms. In reality electrons on impurity centres are probably coupled directly to local modes and directly and indirectly to crystalline modes in the manner we have just described. Probably the effect of the direct coupling which has already been dealt with in Chapters 8 and 10 is the more important.

This thesis and many of the other publications on non-radiative transitions have neglected the study of the electronic factors

$$\int d\underline{r}\,\varphi_0^*(r,q)\frac{d^2}{dq^2}\varphi_1(r,q) \quad \text{and} \quad \int d\underline{r}\,\varphi_0^*(r,q)\frac{d}{dq}\varphi_1(r,q).$$

These factors are often treated as phenomenological parameters whose magnitude is found experimentally. A fundamental evaluation of these terms would appear to require knowledge of how the electronic wavefunctions actually change as the lattice vibrates, knowledge which is at present lacking.

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