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Thermoelectric Power due to small-polaron
hopping motion in disordered systems.

Abstract

We believe that a Generalized Molecular Crystal Model should be used for the study of the thermoelectric power in circumstances in which small-polaron hopping motion is believed to prevail. In our approach we consider a pair of neighbouring molecular sites, g and g' with energy disorder Δg_g . These two sites, being non-equivalent energetically, will affect the small-polaron's binding energy. Assuming that the stiffness of the lattice is unaltered, the difference in the binding energy means a difference in the electron-lattice interaction parameters. In addition we consider the presence of a weak, externally applied electric field E , which will be the driving force for the system.

The Peltier coefficient, Π , under isothermal conditions is evaluated from linear response theory (Kubo theory) for a small-polaron hopping between these two sites. Then from Onsager's relation, $\Pi = \alpha T$, the expression for the thermoelectric power for the two-site system, $\alpha_{gg'}$, is obtained.

The general results are applied to various regimes of physical interest, namely the weak-coupling, and the strong-

coupling regime, at low, and high temperatures.

Finally, using the expressions for the thermoelectric power associated with any pair of sites, the thermoelectric power of the material is evaluated using percolation-theoretic considerations for the high, and low-temperature small-polaron hopping regime.

Comparison with other theories is made, and various conclusions are given.

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Thermoelectric Power due to
small - polaron hopping motion
in disordered systems.

A thesis presented by

Georgios P. Triberis

to the

University of St. Andrews

in application for the Degree of

Doctor of Philosophy.

May 1980

Th 9517

To my Wife.

Declaration

The accompanying thesis is my own composition. It is based on work carried out by me and no part of it has previously been presented in application for a Higher Degree.

Georgios P. Triberis

Certificate

I certify that the conditions of the Ordinance and
Regulations have been fulfilled.

Research Supervisor

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Introduction

Despite numerous measurements of the thermoelectric power of amorphous semiconductors, narrow band materials, oxides and ferrites, in circumstances in which small-polaron hopping motion is believed to prevail, the formulation of a theory of the thermoelectric power is confronted by serious difficulties arising from the lack of a generally accepted approach to this problem. An indisputable expression for the energy of transport, in the case of a small-polaron conductor, does not, as far as we know, seem to exist. It is the purpose of this thesis to give a consistent theory appropriate for this case.

A review of the experimental situation, and the earlier theoretical efforts concerning the thermoelectric power problem is presented in Chapters 1 and 2, respectively. Some basic ideas on Thermodynamics and Thermoelectricity are given in Chapter 3.

We believe that a Generalized Molecular Crystal Model (G.M.C.M.) applicable to a more realistic situation should be used for the study of the thermoelectric power. In our approach we consider a pair of neighbouring molecular lattice sites, $\underline{g}$ and $\underline{g}'$, with energy disorder. These two sites, being non-equivalent energetically, will affect the small-polaron's binding energy in the sense that, the lower the local electronic energy, the more localized the electronic

wave function will be and consequently the larger its binding energy. Assuming that the stiffness of the lattice is unaltered, the difference in binding energy means a difference in the electron-lattice interaction parameter.

In addition to the above assumptions, we consider the presence of a weak externally applied electric field $\underline{E}$, which will be the driving force for the system.

A Review of the M.C.M. is presented in Chapter 4. The Generalization of the M.C.M. is given in Chapter 5.

The Chapters 1-5 constitute PART I of the present thesis.

In part II, consisting of Chapters 6-8, the Peltier coefficient, Π , under isothermal conditions is evaluated from linear response theory (Kubo theory) for a small-polaron hopping between two energetically inequivalent sites of the G.M.C.M. Then, from Onsager's relation, $\Pi = \alpha T$, we obtain the expression for the thermoelectric power, $\propto \mathfrak{g}\mathfrak{g}'$. Specifically, in Chapter 6 the general expressions for the transport coefficients, $\underline{L}_{\mathfrak{g}\mathfrak{g}'}^{(1)}$, and $\underline{L}_{\mathfrak{g}\mathfrak{g}'}^{(2)}$, are evaluated for a small-polaron hopping from a site $\underline{g}$ to a nearest neighbouring site $\underline{g}'$. In Chapter 7 we evaluate the expressions for these coefficients in the weak-dispersion limit. In Chapter 8 the expressions for the net transport coefficients $\underline{L}^{(1)}$, and $\underline{L}^{(2)}$, are obtained.

In Part III, consisting of Chapters 9-12, the general results, obtained in Part II, are applied to special cases. Thus, in Chapters 9 and 10 we consider the case of the strong-coupling at high and low temperature, respectively. In Chapters 11, and 12 we consider the case of the weak-coupling regime at high, and low temperature, respectively. For all these

cases the expression for the thermoelectric power is obtained.

In Part IV, Chapters 13-16, armed with the expressions for the thermoelectric power associated with any pair of sites derived in Part III, we calculate the macroscopic thermoelectric power of the material using percolation theoretic considerations. Specifically, in Chapter 13, the percolation treatment of the conductivity in the low-temperature hopping regime is considered. In Chapter 14, a review of the earlier percolation-theoretic considerations on the thermoelectric power problem is presented. In Chapter 15, the percolation treatment of the thermoelectric power due to small-polaron hopping motion in the low-temperature regime is given. In Chapter 16, the percolation treatment of the conductivity and the thermoelectric power in the high-temperature small-polaron hopping regime is considered.

Finally, in Part V, consisting of Chapter 17, comparison with other theories is made, and various conclusions are given.

Chapter 1

Experimental situation concerning the thermoelectric power due to small- polaron hopping motion.

The thermoelectric power in the small-polaron hopping regime is of considerable practical interest. The comparison between theory and experiment allows a direct determination of the drift mobility of charge carriers that are mobile and participate in the electrical conduction process. Therefore the combination of resistivity(ρ) and thermoelectric power(α) data in principle allows the determination of the drift mobility (μ) and its temperature dependence. Complications in the estimate of μ 's behaviour arise due to other parameters that determine α , viz. the density of states of the conduction(or valence for holes) level and the energy of transfer.

V.W. Bogomolov, et al. (1), (2), (3) investigated the drift mobility, Hall mobility, optical absorption, and thermoelectric power of TiO_2 . From a detailed comparison of the results of these investigations interpreted according to small-polaron theory, they give convincing evidence of small-polaron transport in TiO_2 .

The result of the investigations of the drift mobility

Chapter 1

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The result of the investigations of the drift mobility

is shown in fig(1), (taken from ref. (1)). The curve of the drift mobility has a minimum at $T = 300^\circ\text{K}$, which is characteristic of small-polarons⁽⁵⁾, and which suggests that the hopping transport mechanism dominates at $T > 300^\circ\text{K}$.

The frequency dependence of the absorption coefficient of TiO_2 doped with Nb is shown in fig(2) (taken from ref. (2)). A peak centered at energy $\hbar\omega = 0.8\text{eV}$ is indicated. This agrees well with the theoretical prediction^{(6), (7)} according to which the peak occurs at $\hbar\omega = 4E_a$, where E_a is the activation energy. Indeed, for $\hbar\omega = 0.8\text{eV}$ it follows that $E_a = 0.2\text{eV}$ which is the actual value of the activation energy found experimentally. The temperature dependence of this peak is in good agreement with the theory^{(2), (3)}.

The observed thermoelectric power of TiO_2 is well described by the Morin formula⁽⁸⁾

$$\alpha = \frac{k}{e} \ln \left\{ \frac{n}{N-n} \right\} \quad (1.1)$$

where n is the concentration of the charge carriers and N the concentration of the sites.

Fig (3) (taken from ref.(1)), shows the dependence of $\frac{\alpha e}{k}$ on $\log \epsilon$. The dashed lines show the dependence according to the Morin equation. It should be noted, that the relation (1.1) holds for any non-degenerate system for which the contribution due to the transport of energy may be neglected.

Fig. 1.

Fig. 2.

Fig. 3. Dependence of $\alpha e/k$, the relative thermoelectric power of TiO_2 , on $\log \sigma$ ($\Omega^{-1} \cdot \text{cm}^{-1}$). 1-4) Data obtained in the present work on vacuum-reduced samples (T , $^{\circ}\text{K}$: 1) 300; 2) 200; 3) 143; 4) 100). The line I was plotted from the equation $\alpha_I e/k = \ln(2 \cdot 3.2 \cdot 10^{22}/n)$ and refers to points obtained on samples with c axis situated perpendicular to the temperature gradient. The current carrier concentration, n , was determined with the condition $\mu_I = 0.16 \text{ cm}^2/\text{V} \cdot \text{sec}$ at 300°K . The line II was plotted from the equation $\alpha_{II} e/k = \ln(1.53 \cdot 6.4 \cdot 10^{22}/n)$ and refers to points obtained on samples with c axis situated parallel to the temperature gradient. Mobility at room temperature was calculated to be $\mu_c = 0.57 \text{ cm}^2/\text{V} \cdot \text{sec}$ (the ratio of lattice constants for TiO_2 is $a/c = 1.53$). 5-7) Data obtained in [4], to be referred to the line I; 5) reduced in a vacuum; 6) reduced in a vacuum with added Al; 7) doped with Li. The solid line separates points referring to different sample orientations.

Crevecoeur and de Wit⁽⁹⁾ measured the resistivity and the thermoelectric power of different $\text{Li}_x \text{Mn}_{1-x} \text{O}$ samples, with x in the range $3 \cdot 10^{-4} < x < 5 \cdot 10^{-2}$. As a function of temperature, figs (4), and (5), they observed different activation energies as determined from ρ and α data. In fact for MnO (0.1 at% Li), $W(\alpha) = 0.2 \text{ eV}$ (200 - 1,000)°K whereas $W(\rho) = 0.5 \text{ eV}$ (200 - 400)°K. Here, W is the activation energy of the movement of holes through the lattice. From this, Crevecoeur and de Wit have concluded that the drift mobility of holes in MnO , which already proved to be exceptionally small at high temperatures ($\mu_D \cong 0.01 \text{ cm}^2/\text{V} \cdot \text{sec}$ at 1,200°K), decreases roughly exponentially when the temperature is lowered from 1,000 to 200°K.

They also noted the following:

- (1) The difference in slope is found in single and polycrystalline samples.
- (2) The presence of thin isolating layers between the grains of the polycrystalline samples does not appear from a.c. measurements.
- (3) Thin conducting layers between grains or on the surface of the crystals, having a conductivity comparable to that of the bulk, are improbable because of the high specific resistivity of Mn_2O_3 .

These workers concluded that the different behaviour of $\log \rho$ and α as function of temperature is an intrinsic property of MnO and has not to be ascribed to inhomogeneities (barrier,

second phases etc).

Also arguments that transport is determined by a single type of charge carriers, specifically holes, were given. Thus p-type conduction in MnO seems to be effected by thermally activated hopping of small-polarons. They ascribe the small-polaron character of holes in MnO to an extra interaction between hole and lattice vibrations brought about by the Jahn-Teller deformation of the Mn^{3+} ion and the surrounding octahedron of neighbouring O^{2-} ions.

Comparing ρ and α data they take the thermoelectric power, α , for holes, to be given by

$$\alpha = \frac{k}{e} \left(\ln \frac{N_v}{p} + A \right), \quad (1.2)$$

where N_v is the density of states of the valence band or level, p the concentration of free holes, and A the transport term connected with the kinetic energy of holes.

On the other hand

$$\rho = \frac{1}{pe\mu} \quad (1.3)$$

The temperature dependence of μ can be determined by subtracting $\log \rho$ from α :

$$\frac{e\alpha}{2.3k} - \log \rho = \log (eN_v e^A) + \log \mu, \quad (1.4)$$

as the first term on r.h.s. of equ.(1.4) is taken to be nearly temperature independent.

A mobility increasing rapidly with temperature is given by the small-polaron theory⁽¹⁰⁾, which predicts that μ is proportional to $T^{-3/2} \exp (-W/kT)$, where W is the activation energy for holes. Thus, equ.(1.4) becomes

$$\frac{e\alpha}{2.3k} - \log \rho - \frac{3}{2} \log \frac{1}{T} = \log (e N_v e^A) - \frac{1}{2.3k} W \left(\frac{1}{T} \right). \quad (1.5)$$

Plotting $\frac{e\alpha}{2.3k} - \log \rho - \frac{3}{2} \log \frac{10^3}{T}$ versus $\frac{10^3}{T}$,

fig.(6), the activation energy W from the slope, and the value for $\log (e N_v e^A)$ is obtained. For $A=1$, N_v comes near the number of Mn ions per cm^3 ($= 0.4 \times 10^{21}$).

We thus see that the density of states is affected by the actual choice of the numerical value for A and that the prediction of its value from first principles is a matter of some importance.

Fig. 4. Log resistivity as a function of reciprocal temperature for MnO containing different amounts of Li. ● Single crystal; ○ 0.03 at per cent Li; □ 0.1 at per cent Li; ● 5 at per cent Li.

Fig. 5. Thermoelectric power in units $(2.3k/e)$ vs. reciprocal temperature of MnO containing different amounts of Li. Markings as in Fig. 1.

Fig. 6. Temperature dependence of the difference between the thermoelectric power in units $(2.3k/e)$ and log resistivity after correction for $T^{3/2}$. In the small polaron theory the slope of this plot gives the activation energy of the hopping process. To obtain the mobility one has to subtract $\{\log(eN_0eA) - 3/2 \log 1000/T\}$ from the value of the ordinate. Markings as in Fig. 4.

Seager, Emin, and Quinn⁽¹¹⁾ proposed a small-polaron conduction model in certain As - based chalcogenide glasses. According to these workers, the question of small-polaron formation in chalcogenide glasses is not at variance with the knowledge that has been obtained from studies of low mobility ($\mu \leq 1 \text{ cm}^2/\text{Vsec}$) crystalline systems⁽¹²⁾. In addition, according to them the presence of disorder in non-crystalline compounds generally tends to impede the coherent propagation of an excess carrier through the lattice⁽¹³⁾. Furthermore, since holes appear to be more mobile than electrons in a variety of crystalline chalcogenide materials in which the electrons are believed to be self-trapped (orthorhombic sulfur⁽¹⁴⁾ and As_4S_4 ⁽¹⁵⁾, for example), it is not unreasonable to suspect that self-trapped holes would be more mobile than self-trapped electrons in amorphous chalcogenide substances, as well. Thus, hole like small-polarons might be expected in these materials.

For support of their hypothesis, they discussed their measurements of the electrical conductivity, thermoelectric power, figs (7), (8), (9), and (10), and Hall mobility of some of those glasses.

Taking the general formula for the thermoelectric power to be

$$\alpha = \frac{k}{e} \left(\frac{E_\alpha}{kT} + A \right), \quad (1.6)$$

where E_α is the activation energy derived from thermoelectric power measurements (being the energy required to gen-

erate these carriers), and A the additional contribution to the thermoelectric power due to the energy of transport, they found:

For:

(1) As - Te - I Glasses

p-type thermoelectric power

$\propto -1/T$ linear, with

$E_{\alpha} = 0.16$ and 0.27 for 2- and 20-at%

iodine compositions ($T > 260^{\circ}\text{K}$),

A between 4 and 5.

(2) As - Te - Ge Glasses

p-type thermoelectric power

$\propto -1/T$ linear, with

$E_{\alpha} = 0.24$ and 0.29 eV for $\text{As}_{50}\text{Te}_{80}\text{Ge}_{20}$, $\text{As}_{50}\text{Te}_{45}\text{Ge}_{5}$,

$A \approx 4$.

(3) As - Te Glasses

p-type thermoelectric power

$\propto -1/T$ linear, with

$E_{\alpha} = 0.25 \text{ eV}$, $A \approx 4$ (for, $\text{As}_{50}\text{Te}_{50}$).

The above results, for example for (1), and give:

$$\frac{E_{\alpha}}{kT} = \frac{0.16 \text{ eV}}{8.617 \times 10^{-5} \times 300 \text{ eV}} \approx 6,$$

which is comparable with the value of $A=4$, for this case.

Thus we see that, due to energy of transport, a significant additional contribution to the thermoelectric power can be obtained.

FIG. 7. Conductivity vs temperature in the As-Te-I glasses.

FIG. 8. Seebeck coefficient vs temperature in the As-Te-I glasses.

FIG. 9. Conductivity vs temperature in the As-Te-Ge glasses.

FIG. 10. Seebeck coefficient vs temperature in the As-Te-Ge glasses.

Chapter 2

Earlier theoretical efforts on the thermoelectric power problem.

The formulation of a theory of the thermoelectric power is confronted by serious difficulties arising from the lack of a generally accepted approach to this problem. The absence of an energy of transport term throughout a series of calculations of the thermoelectric power was based upon unsuitable or simplified models or assumptions.

F. J. Morin ^{(8), (16)}, in 1954, analysing the results of the measurements of the electrical conductivities and the thermoelectric powers of $\alpha\text{-Fe}_2\text{O}_3$ and NiO, had arrived at the conclusion that the mobilities of the carriers of the crystals have a strong temperature dependency. This should be described in terms of activation energies for the transport of the carriers. Morin had analysed his data in terms of conventional semiconductor theory. Assuming that the energy of transport term is negligible and that both electrons and holes are involved, the expression obtained for the thermoelectric power is

$$\alpha = \frac{1}{qT} \frac{[\sigma_p \mu - \sigma_n (E_g - \mu)]}{\sigma_p + \sigma_n}, \quad (2.1)$$

where σ_p, σ_n are the partial conductivities for holes and electrons respectively, E_g is the distance from the top of filled band to the bottom of conduction band, μ is the Fermi

level, and q is the absolute electric charge.

M. Tsuji⁽¹⁷⁾, in 1959, derived a formula for the thermoelectric power of a crystal in which carriers are tightly bound to ions and the jump of a carrier from one ion to another needs an activation energy. He claimed that Morin's analysis was not consistent and suggested that Morin's $\sigma_p \mu$ and $\sigma_n(E_g - \mu)$ terms should be replaced by $\sigma_p(Q_p^* + \mu)$ and $\sigma_n(Q_n^* + E_g - \mu)$ respectively. Thus, he obtained the result

$$\alpha = \frac{1}{qT} \frac{[\sigma_p(Q_p^* + \mu) - \sigma_n(Q_n^* + E_g - \mu)]}{\sigma_p + \sigma_n}. \quad (2.2)$$

Here, Q_p^* , Q_n^* are the activation energies of a hole and an electron, respectively, given by

$$Q_p^* = -k \frac{d \ln W_p}{d(1/T)}, \quad Q_n^* = -k \frac{d \ln W_n}{d(1/T)}, \quad (2.3)$$

W_p , W_n being the probabilities of the jump. No reason was given why the energy of transport Q^* might be equal to the activation energy.

R.R. Heikes⁽¹⁸⁾ in 1961, studied the conduction mechanism of narrow band semiconductors, from thermodynamical considerations. He considered the thermoelectric power, α , given by

$$\alpha = \frac{S^*}{q}, \quad (2.4)$$

where S^* is the entropy carried per particle under isothermal conditions. This is given by $S^* = (J_s/J_e)_{\nabla T=0}$, where J_s is the entropy flux and J_e is the particle flux. Further, from the definition of the energy flux, the

entropy flux is given by

$$J_s = \frac{(W - \tilde{\mu} J_e)}{T}, \quad (2.5)$$

where W is the total energy crossing a unit plane, $\tilde{\mu}$ is the electrochemical potential per particle given by $\tilde{\mu} = \mu - q\phi$, ϕ being the electrical potential, it follows that

$$S^* = \frac{(U^* - \mu)}{T}, \quad (2.6)$$

where U^* is defined as

$$U^* = \left[\frac{W}{J_e} - q\phi \right]_{\sigma_T=0}. \quad (2.7)$$

In other words U^* is the total energy, except electrical, carried per charge carried in an isothermal region. Here it is seen that the quantity $(U^* - \mu)$ is the Peltier heat per particle. The calculation of α therefore reduces to a determination of U^* and μ .

The latter quantity is simply the change in free energy of the system upon adding an additional charge carrier. Heikes found it to be given by

$$\mu = -kT \ln \frac{c}{1-c} + \Delta G_R. \quad (2.8)$$

Here c is the concentration of carriers, ΔG_R is the amount of work done against an external agency when the lattice is allowed to relax around the site where the carrier resides, and $k \ln \frac{c}{1-c}$ is the entropy of mixing when we add a charge carrier to the system with the restriction that the system is held rigid.

To determine v^* the isothermal transfer of a particle from site(1) to site(2) is considered. In order to effect this transfer an amount of work W must be done at site(1). Further, to maintain the region isothermal, heat Q must be added. To evaluate W , Heikes used the following model. He assumed that the free energy of activation is a function of the local force constants and atomic displacements. The force constant at a site possessing a carrier is denoted by κ , while the force constant at an empty site is denoted by κ' . The equilibrium positions of the atoms surrounding an empty site are taken as the zero displacement. On this simple model a carrier will transfer whenever the atomic displacements surrounding the two sites are equal.

When the electron is on site(1) the configuration of the site is described by x_0 , and the energy of the site is $\frac{1}{2} \kappa x_0^2$. When the electron is to jump on site(2) the configuration for both sites is characterized by x_c . Then a work $\frac{1}{2} \kappa (x_0 - x_c)^2$ is required on site(1). After the electron's jump on site(2), site(1) relaxes to the configuration $x = 0$ (now the force constant is κ' for the empty, now, site(1)). Thus an energy $\frac{1}{2} \kappa' x_c^2$ will be given to the system from the relaxation of site(1). The system has also received an amount of energy $\frac{1}{2} \kappa x_0^2$ from the relaxation of site(1) from the configuration $x=0$ to $x=x_0$ when the electron was first placed on site (1). Thus the total work w done on site(1) is

$$W = \frac{1}{2} \kappa (x_0 - x_c)^2 - \frac{1}{2} \kappa' x_c^2 - \frac{1}{2} \kappa x_0^2. \quad (2.9)$$

Then he considered the situation in which the electron

and site(1) are in the configuration x_0 and site (2) in a configuration $x=0$. The energy required to have a coincidence event, i.e. $x_1 = x_2 = x_c$, may be written

$$E = \frac{1}{2} k (x_0 - x_c)^2 + \frac{1}{2} k' x_c^2 . \quad (2.10)$$

Clearly x_c must be such to minimize E . This value is

$$x_c = \frac{x_0}{\{1 + (\frac{k'}{k})\}} . \quad (2.11)$$

Thus he obtained

$$W = \Delta G_R \frac{(k^2 + 3kk')}{(k + k')} , \quad (2.12)$$

where

$$\Delta G_R = \frac{1}{2} k x_0^2 . \quad (2.13)$$

Now, since this is an isothermal process the work w done on the system is equal to the increase in free energy. Therefore, $\Delta G = -T \frac{dW}{dT}$, and assuming that $\frac{k'}{k}$ is independent of temperature and using the first law of thermodynamics he obtained

$$U^* = \Delta H_R \frac{(k^2 + 3kk')}{(k + k')^2} , \quad (2.14)$$

from which

$$U^* - \mu = \Delta H_R \frac{(k^2 + 3kk')}{(k + k')^2} + kT \ln \frac{c}{1-c} - \Delta \quad (2.15)$$

and thus,

$$\alpha = \left(\frac{\kappa}{q} \right) \left\{ \frac{\Delta H_R}{\kappa T} \frac{(\kappa^2 + 3\kappa\kappa')}{(\kappa + \kappa')^2} + \ln \frac{C}{1-C} - \frac{\Delta G_R}{\kappa T} \right\} \quad (2.16)$$

It is seen that if $\kappa' \approx \kappa$ the coefficient of $\frac{\Delta H_R}{\kappa T}$ equals 1. Furthermore for $\kappa' > \kappa$ the coefficient of $\frac{\Delta H_R}{\kappa T}$ remains of the order of unity. Thus unless κ is significantly larger than κ' , the thermoelectric power is rather insensitive to $\frac{\kappa'}{\kappa}$. If the coefficient of $\frac{\Delta H_R}{\kappa T}$ is taken of order unity then

$$\alpha = \left(\frac{\kappa}{q} \right) \left\{ \ln \frac{C}{1-C} + A \right\} \quad (2.17)$$

where $A = \frac{\Delta S_R}{\kappa}$, is the change in the entropy of a lattice site due to the presence of an electron.

I.G. Austin and N.F. Mott⁽¹⁹⁾, in 1969, assuming that the entropy change comes from a change of the site's vibrational frequency, found an approximate value for A in the range 0.1-0.2. Further, Austin and Mott studied the small-polaron motion in a molecular lattice. They considered 2 identical molecules (1) and (2), and introduced configurational coordinates q_1, q_2 to describe (say) the inter-nuclear distance in each molecule. The energy of either molecule without addition of an electron is Aq_1^2, Aq_2^2 . If the energy of an extra electron placed in molecule (1) for a given value of q_1 is $-Bq_1$, relative to some arbitrary zero, then the energy of molecule (1) with an electron in it is

$$Aq_1^2 - Bq_1 \quad (2.18)$$

which is a minimum when $q_1 = q_0$, where

$$q_0 = \frac{B}{2A} . \quad (2.19)$$

This energy (the polaron energy) can then be written $-w_p$ where

$$w_p = A q_0^2 . \quad (2.20)$$

If an electron is to jump from one molecule to another the configurational parameters q_1, q_2 must be such that the electron's energy is the same in either molecule thus

$$B_{q_1} = B_{q_2} , \quad (2.21)$$

so that $q_1 = q_2$. The energies required to distort molecules (1) and (2) to configurations in which $q_1 = q_2 = q$ are

$$w_1 = A (q_0 - q)^2 , \text{ and } w_2 = A q^2 , \quad (2.22)$$

which add up to a total energy w_H given by

$$w_H = A (q_0 - q)^2 + A q^2 . \quad (2.23)$$

This is a minimum when

$$q = \frac{1}{2} q_0 . \quad (2.24)$$

Thus,

$$w_H = \frac{1}{2} A q_0^2 + \frac{1}{2} w_p . \quad (2.25)$$

It follows that

$$w_1 = w_2 = \frac{w_H}{2} . \quad (2.26)$$

Thus we see that the activation energy for hopping is equally divided between the two sites. The probability per unit time that an electron jumps from one molecule

to the other is given by $\exp(-w_h/kT)$. In the above case the two sites had the same force constant A , the same electron-lattice interaction parameter B , and there was no energy disorder between the two sites, i.e. $w_D = 0$.

Then, they examined the case where some random field in the solid separates the energies on the two centers by w_D . In this case, if the electron is initially on molecule(2), the energies required to produce a coincidence event, are

$$w_1 = A q_1^2, \quad \text{and} \quad w_2 = A (q_0 - q_2)^2. \quad (2.27)$$

The condition for a jump to take place now takes the form

$$w_D = B q_1 - B q_2. \quad (2.28)$$

The energies w_1, w_2 add up to a total energy $w = w_1 + w_2$ which is a minimum when

$$q_2 = \frac{q_0}{2} - \frac{w_D}{B}. \quad (2.29)$$

Then the activation energy for hopping, w , in the presence of disorder, is given by

$$w = w_h + \frac{1}{2} w_D, \quad (2.30)$$

where $w_h = \frac{1}{2} A q_0^2$. It follows that

$$w_1 = w_2 = \frac{w}{2}. \quad (2.31)$$

Thus, we see that even in the presence of disorder the activation energy is equally divided between the two sites. For this case the probabilities per unit time that an electron jumps upwards or downwards are dif-

ferent and are given by $e \propto \rho [- (w_H + \frac{w_D}{2}) / kT]$,
and $e \propto \rho [- (w_H - \frac{w_D}{2}) / kT]$, (2.32)
respectively.

A simple extension of the above model shows that in absence of disorder assuming that the force constants A are different for each of the two molecules, i.e. $\frac{A_2}{A_1} = \theta \neq 1$, then the fraction β of the total hopping energy expended at the site (2), initially containing the electron is given by $(1 + \theta)^{-1} \neq \frac{1}{2}$, i.e. the activation energy for hopping is not divided equally between the two sites, as before.

Indeed, for this case the condition for a jump to occur is

$$B q_1 = B q_2, \quad (2.33)$$

from which

$$q_1 = q_2 = q. \quad (2.34)$$

Further the energies required to distort the two molecules to the above configuration are

$$w_1 = A_1 q^2, \quad (2.35)$$

$$w_2 = A_2 (q_2 - q_0)^2, \quad (2.36)$$

added up to

$$w_H = w_1 + w_2. \quad (2.37)$$

This is a minimum when

$$q = q_0 \frac{A_2}{A_1 + A_2}. \quad (2.38)$$

Then,

$$W_1 = A_1 q_0^2 \left(\frac{A_2}{A_1 + A_2} \right)^2, \quad (2.39)$$

$$W_2 = A_2 q_0^2 \left(\frac{A_1}{A_1 + A_2} \right)^2, \quad (2.40)$$

and

$$W_H = \frac{A_1 A_2}{(A_1 + A_2)} q_0^2. \quad (2.41)$$

Thus,

$$\beta = \frac{W_2}{W_H} = \frac{A_1}{A_1 + A_2} = (1 + \theta)^{-1}. \quad (2.42)$$

Now, let us suppose that, in absence of disorder, the two sites have the same force constants A , but different electron-lattice interaction parameters $B_1 \neq B_2$. Assuming that the electron resides on site (1) the condition for a jump to occur is given by

$$B_1 q_1 = B_2 q_2. \quad (2.43)$$

The energies required to produce such a state are

$$W_1 = A (q_0 - q_1)^2, \quad (2.44)$$

and

$$W_2 = A q_2^2, \quad (2.45)$$

which add up to an activation energy for hopping

$$W = W_1 + W_2. \quad (2.46)$$

This is a minimum when

$$q_1 = q_0 \frac{1}{1 + \left(\frac{B_1}{B_2} \right)^2}. \quad (2.47)$$

Defining

$$\mathcal{J} \equiv \left(\frac{B_2}{B_1} \right)^2, \quad (2.48)$$

we find

$$w_1 = A q_0^2 \frac{1}{(1+\lambda)^2} , \quad (2.49)$$

$$w_2 = A q_0^2 \frac{\lambda}{(1+\lambda)^2} , \quad (2.50)$$

and

$$w = A q_0^2 \frac{1}{(1+\lambda)} . \quad (2.51)$$

Thus,

$$\beta = \frac{w_1}{w} = (1 + \lambda)^{-1} . \quad (2.52)$$

Summarizing, we may say that in the simple classical cases the existence of disorder alone does not affect the equal division of the total activation energy between the two sites for a hopping to occur but affects the probabilities for a jump to occur in one or the other direction. On the other hand a difference in the force constants or the electron-lattice interaction parameters leads to an unequal division of the total activation energy between the two sites for a jump to occur.

In ref.9. Austin & Mott also considered the case of an electron localized on site (1) a distance r apart from site (2), with $w_D=0$, in the presence of an electric field. For this case the probability that an electron hops in the direction of the field (taken from site (1) to site (2)) is

$$P_{(1 \rightarrow 2)} = C \exp \left\{ - \frac{(w_H - \frac{1}{2} e r F)}{k T} \right\} , \quad (2.53)$$

and in the opposite direction

$$P_{(2 \rightarrow 1)} = c \exp \left\{ - \frac{(W_H + \frac{1}{2} e r F)}{k T} \right\} \quad (2.54)$$

The net jump probability is then

$$P_{net} = P_{(1 \rightarrow 2)} - P_{(2 \rightarrow 1)} = 2 c \exp \left(- \frac{W_H}{k T} \right) \sinh \left(\frac{e r F}{k T} \right), \quad (2.55)$$

which for small field gives a net current

$$j_{net} = \left(\frac{e r F}{k T} \right) n c \exp \left(- \frac{W_H}{k T} \right), \quad (2.56)$$

where n is the concentration of carriers.

Next they considered the effect of temperature on the intermolecular hopping probability. They assumed that the total activation energy is not divided equally between the two sites. They supposed that the site initially containing the electron requires a fraction β of the total energy. Thus, if in addition to the applied field there exists a temperature gradient across the crystal giving temperatures $T - \frac{\delta T}{2}$, and $T + \frac{\delta T}{2}$, to sites 1 and 2, respectively, then

$$P_{(1 \rightarrow 2)} = c \exp \left\{ - \frac{\beta W}{k (T + \frac{1}{2} \delta T)} \right\} \exp \left\{ - \frac{(1 - \beta) W}{k (T - \frac{1}{2} \delta T)} \right\}. \quad (2.57)$$

This, for small temperature gradient reduces to

$$P_{(1 \rightarrow 2)} = c \exp \left(- \frac{W}{k T} \right) \left\{ 1 - (1 - 2\beta) \frac{\delta T}{2 T} \right\}, \quad (2.58)$$

where $W = W_H - \frac{1}{2} e r F$. For the reverse direction

$$P_{(2 \rightarrow 1)} = c \exp \left[- \left(\frac{w'}{k_T} \right) \left\{ 1 + (1-2\beta) \frac{\delta T}{2T} \right\} \right], \quad (2.59)$$

where

$$w' = w_H + \frac{1}{2} e r F. \quad (2.60)$$

Thus, the net jump probability is given by

$$P_{net} = c \left\{ \frac{e r F}{k_T} + (1-\beta) \frac{w_H}{k_T} \frac{r}{T} \frac{dT}{dx} \right\} \exp \left(- \frac{w_H}{k_T} \right), \quad (2.61)$$

and the net current is given by

$$j_{net} = n e r c \left\{ \frac{e r F}{k_T} + (1-2\beta) \frac{w_H}{k_T} \frac{r}{T} \frac{dT}{dx} \right\} \exp \left(- \frac{w_H}{k_T} \right). \quad (2.62)$$

Now, taking the diffusion current given by

$$j_{dif.} = e D \frac{dn}{dx}, \quad (2.63)$$

where

$$D = c r^2 \exp \left(- \frac{w_H}{k_T} \right), \quad (2.64)$$

and

$$\frac{dn}{dx} = n \frac{\partial(E_F/k_T)}{\partial x}, \quad (2.65)$$

where the Fermi energy is measured from the bottom of the polaron well, and equating j_{net} and $j_{dif.}$ they obtained

$$e F = \left\{ \frac{E_F}{k_T} - (1-2\beta) \frac{w_H}{T} \right\} \frac{dT}{dx}, \quad (2.66)$$

from which

$$\alpha = \left(\frac{k}{e} \right) \left\{ \frac{E_F}{k_T} - A \right\}, \quad (2.67)$$

where

$$A = \frac{w_H}{k_T} (1-2\beta). \quad (2.68)$$

Thus, if $\beta = \frac{1}{2}$, i.e. if the hopping energy is equally divided then $A=0$ and there is no extra contribution to the thermopower. For the case in which the force constants of the two sites are different (or the electron-lattice interaction parameters are different) and $\frac{A_2}{A_1} = \theta \neq 1$, then $\beta = (1+\theta)^{-1}$, then

$$A = \frac{W_H}{K_T} \frac{(1-\theta)}{(1+\theta)} \quad (2.69)$$

M.M.Chadda and A.P.B.Sinha⁽²⁰⁾, in 1963, investigated the thermoelectric properties of low mobility semiconductors in which the charge carriers are localized and the electrical conduction takes place through their hopping motion. The heat of transport Q^* and the energy lowering Φ , due to the polarization of the lattice were taken to be related by the expression

$$Q^* = \Phi_h - \Phi_c \quad (2.70)$$

where Φ_h and Φ_c are the components of the binding energy due to polarizations associated with the hot and cold parts of the semiconductor, respectively. They finally obtained the result,

$$\alpha = \frac{1}{qT} \left\{ E - \mu + \beta (\Delta E) \right\} \quad (2.71)$$

where $(E - \mu)$ is the energy required to free the carrier into the conducting state, ΔE is the activation energy associated with the jumping process and $\beta = Q^*/\Delta E$. Since there is a continuous temperature gradient across the specimen, it is unclear why the heat of transport is associated with the difference of the binding energies between the "hot" and "cold"

ends of the specimen. Even accepting this notion, however, they did not say how Φ varied with temperature.

The first microscopic calculation of the thermoelectric power was given by K.D. Schotte⁽²¹⁾, in 1966. The aim of the publication was to give the calculation of the thermoelectric power for the small-polaron hopping regime.

The underlying assumption was a strong coupling between the electrons of a narrow band semiconductor and the crystal polar modes. If the magnitude of the coupling energy is greater than the width of the band, this results in the formation of a polaron, i.e. an electron trapped by the potential of the lattice deformation which itself produces.

The starting point was a localized electron at a definite lattice point, which influences the dynamics of the surrounding lattice. In the language of perturbation theory, the localized additional charge, together with the lattice deformation which it causes, is the state of the system in zeroth order approximation. Then in the next approximation one considers the small but finite tunneling probability to the neighbouring sites, i.e. the resonance integral which is small compared to the strong electron-phonon coupling. Further one assumes that the charges are not influenced in the temperature range considered by the doping mechanism, and that their number is small enough to avoid noticeable mutual interactions.

Using Kubo's relations for the transport coefficients, the Molecular Crystal Model, introduced by T. Holstein⁽¹⁰⁾, and following Lang and Firsov's⁽²²⁾ perturbation method, in the high temperature regime he obtained for the thermoelectric

power the expression

$$\alpha = - \frac{1}{|q| T} \mu . \quad (2.72)$$

The physical feature of interest which can be learned from this result is the absence of an energy of transport term. K. Schotte had obtained this result assuming that the lattice sites on which the electron resides were energetically equivalent and that the coupling strength between the lattice and the electron was the same on every lattice site. The electron-lattice coupling strength is expressed through the electron energy $E(x_n)$ of an isolated "molecular-ion", i.e. of the system of the electron and an isolated molecule. We consider a lattice with molecular lattice sites, where, in conformance with the standard theory of the electron - lattice interaction, a linear approximation is made, namely $E(x_n) = -Ax_n$ where, the constant A characterizing the strength of the coupling, called from now on "electron-lattice interaction parameter", was the same for the electron on every lattice site. In the classical regime, each hop of a small-polaron is associated with a "coincidence event". Explicitly for a carrier to hop, the electronic energy level associated with an occupied site must momentarily coincide with a corresponding local electronic energy level on a neighbouring unoccupied site. The local electronic energy levels are a function of the lattice vibrational coordinates, so that the coincidence event occurs when

$$\epsilon_p(0) - A_p x_p = \epsilon_{p'}(0) - A_{p'} x_{p'} , \quad (2.73)$$

where $\epsilon_p(0)$, $\epsilon_{p'}(0)$ is the energy of a carrier on site p or p' , respectively, if the atoms of the material are constrained to remain at their carrier free equilibrium positions.

A_p , $A_{p'}$ are the electron-lattice interaction parameters for the electron interacting with the site p or p' respectively; p' is a neighbouring site, i.e. $p' = p+1$ for a one-dimensional molecular chain, $\epsilon_p(0) \neq \epsilon_{p'}(0) \neq 0$ and $A_p \neq A_{p'}$, generally.

K. Schotte assumed $\epsilon_p(0) = \epsilon_{p'}(0)$ and $A_p = A_{p'} = A$. This "ordered" situation has the result that the energy required to distort the two neighbouring molecules (activation energy for hopping) to a configuration for which a hop can occur is equally divided between the two sites, the displacement configuration at the initial site being equal to that for the final site. In other words the sum over the energies of all the phonons emitted in this process is equal to the sum over the energies of all the phonons absorbed. In that case, obviously energy will not be transported.

However, the situation becomes more complicated when we consider a more realistic model in which, in addition to energy disorder $\epsilon_p(0) \neq \epsilon_{p'}(0) \neq 0$, we introduce disorder in the local electron-lattice interaction parameters i.e. $A_p \neq A_{p'}$.

The consequence of these assumptions is that the distortional energies associated with two neighbouring sites are no longer equal and considerations which will be presented in this thesis lead to a non-zero transfer contribution to the thermoelectric power associated with a small-polaron hop.

In 1975, D. Emin⁽²³⁾ presented an approach for the calculation of the thermoelectric power associated with phonon

assisted hopping motion between inequivalent sites ($\Delta_{pp'} = \epsilon_{p'} - \epsilon_p \neq 0$), p and p' , having different electron-lattice interaction parameters, $A_p \neq A_{p'}$. In obtaining his result, it was assumed that the two neighbouring sites p and p' were at local temperature $T_p = T + \Delta T_p$, and $T_{p'} = T + \Delta T_{p'}$, respectively (microscopic temperature gradient approximation). The imposition of a temperature gradient tends to induce currents to flow between the two sites. To calculate the emf associated with this current flow and hence the thermoelectric power, one can compute the gradient of the electrochemical potential needed to completely offset this current. To have a temperature gradient existing between the two sites, without there being a net flow of charge, requires both a redistribution of charge (relative to that at equilibrium) and the establishment of a potential difference, $V_{p'p}$ between the two sites. On the other hand, the net particle current associated with motion between these two sites, $I(p \rightarrow p')$, is given by a difference between the current associated with a particle motion from site p to site p' and that associated with a particle's motion from site p' to site p .

These features were taken into account in order to obtain the general expression for the thermoelectric power which reads

$$\alpha_{pp'} = \frac{1}{qT} \left[\frac{1}{2} (\epsilon_p + \epsilon_{p'}) + E_T^{pp'} - \mu \right], \quad (2.74)$$

where $\alpha_{pp'}$ is the thermoelectric power associated with a hop from site p to site p' , ϵ_p and $\epsilon_{p'}$ are, respectively, the equilibrium energies of the system when the electron

occupies site p or p' , and q is the charge of the carrier, $-|e|$. The quantity $E_T^{pp'}$ is the energy (Peltier heat) transported with an electron's hop from site p to p' . It is given by

$$E_T^{pp'} = kT^2 \left[\frac{\partial \ln(R_{pp'}/R_{p'p})}{\partial T_p} + \frac{\partial \ln(R_{pp'}/R_{p'p})}{\partial T_{p'}} \right] \Delta_{pp'}^{\circ}, \quad (2.75)$$

which after considerable manipulation takes the form

$$E_T^{pp'} = \frac{1}{2} \Delta_{pp'}^{\circ} \frac{(\Gamma_p - \Gamma_{p'})}{(\Gamma_p + \Gamma_{p'})}. \quad (2.76)$$

Here, $R_{pp'}$ is the elemental nonadiabatic jump rate for a charge carrier hopping from site p to p' , $\Delta_{pp'}^{\circ}$ is the energy difference between a carrier occupying site p' and p in thermal equilibrium, Γ_p and $\Gamma_{p'}$ are the "effective electron-lattice coupling strengths" associated with a carrier at sites p and p' , respectively. These are given by

$$\Gamma_p \equiv \sum_{\mathbf{k}} |\gamma_p(\mathbf{k})|^2 \hbar \omega_{\mathbf{k}} W_{\mathbf{k}}(\Delta_{pp'}^{\circ}) \operatorname{csch}\left(\frac{\hbar \omega_{\mathbf{k}}}{2kT}\right), \quad (2.77)$$

$$\text{with } W_{\mathbf{k}}(\Delta_{pp'}^{\circ}) \equiv \int_{-\infty}^{\infty} dt e^{F(t)} \sin\left(\Delta_{pp'}^{\circ} \frac{t}{\hbar}\right) \sin \omega_{\mathbf{k}} t, \quad (2.78)$$

$$\text{and } F(t) \equiv \sum_{\mathbf{k}} [|\gamma_p(\mathbf{k})|^2 + |\gamma_{p'}(\mathbf{k})|^2] \operatorname{csch}\left(\frac{\hbar \omega_{\mathbf{k}}}{2kT}\right) \cos \omega_{\mathbf{k}} t. \quad (2.79)$$

The expression for $\Gamma_{p'}$ is analogous to that for Γ_p , with $|\gamma_{p'}(\mathbf{k})|$ replacing $|\gamma_p(\mathbf{k})|$. The derivation of eqs. (2.74), and (2.75) is given in Appendix A2.

This is, in fact, the only microscopic calculation up to the time when this thesis was written which predicts an additional part to the thermoelectric power due to the transport of energy.

However, the imposition of Emin's microscopic temperature gradient assumption seems "artificial", given no prescription to calculate the local temperatures T_p and T_p' and may or may not be justified. That is to say, the electronic states are taken to be coupled to two separate phonon baths at temperatures T_p and T_p' . This is plausible if the intersite separation is larger than the phonon mean free path, but is clearly questionable on a microscopic level.

Appendix A2

Derivation of Emin's expression for the thermoelectric power

We consider the case of a carrier hopping between a state associated with a site p and another state associated with a different site p' . To simplify matters only a single electronic state will be identified with each site index. The net particle current associated with motion between these two sites, $I_{(p \rightarrow p')}$ is given by the difference between the current associated with a particle's motion from site p to site p' and that associated with a particle's motion from site p' to site p :

$$I_{(p \rightarrow p')} = f_p (1 - f_{p'}) R_{pp'} - f_{p'} (1 - f_p) R_{p'p}, \quad (A2.1)$$

where the probability of site p being occupied is denoted as f_p and the probability of site p' being vacant is denoted by $1 - f_{p'}$. f_p is the rate characterizing a phonon-assisted hop from site p to site p' . In equilibrium no current will flow and the factors in equ.(A2.1) will be given by their equilibrium values, henceforth denoted by the superscript zero.

D.Emin, in order to calculate the thermoelectric power he considered the situation of an arbitrarily small temperature gradient across the material. This means that he ascribed different temperatures, T_p and $T_{p'}$ to the two sites p and p' ;

the electronic states are to be viewed as being coupled to two separate phonon baths.

The imposition of a temperature gradient will tend to induce current to flow between the two sites. To calculate the emf associated with this current flow, and hence the thermoelectric power one can compute the gradient of the electrochemical potential needed to completely offset this current flow, (i.e. in the steady state $I(p \rightarrow p') = 0$) To have a temperature gradient existing between the two sites without there being a net flow of charge requires both a redistribution of charge (relative to that at equilibrium) and the establishment of a potential difference, $V_{p'p}$, between the two sites.

Taking these features into account, one writes, for the equilibrium,

$$p_p^0 = 1 / [\exp \{ (\epsilon_p - \mu) / kT \} + 1] , \quad (A2.2)$$

$$\Delta_{p'p}^0 = \epsilon_{p'} - \epsilon_p , \quad (A2.3)$$

where ϵ_p and $\epsilon_{p'}$ are, respectively, the equilibrium energies of the system when the electron occupies site p or p' , and μ is the true (equilibrium) chemical potential. For the steady-state,

$$p_p = 1 / [\exp \{ (\epsilon_p - \mu_p) / kT \} + 1] , \quad (A2.4)$$

$$\Delta_{p'p} = \Delta_{p'p}^0 + V_{p'p} , \quad (A2.5)$$

where

$$\mu_p = \mu + d\mu_p , \quad (A2.6)$$

is the quasi chemical potential associated with the steady-state carrier occupancy of site p, and

$$T_p = T + dT_p . \quad (A2.7)$$

Thus, $f_p = f_p(T, \mu_p)$, from which expanding we obtain

$$f_p - f_p^0 = \left(\frac{\partial f_p}{\partial T_p} \right)_T dT_p + \left(\frac{\partial f_p}{\partial \mu_p} \right)_T d\mu_p \equiv \Delta f_p . \quad (A2.8)$$

On the other hand, $R_{pp'} = R_{pp'}(\Delta_{p'p}, T_p, T_{p'})$, from which

$$\begin{aligned} R_{pp'} - R_{pp'}^0 &= \left(\frac{\partial R_{pp'}}{\partial \Delta_{p'p}} \right)_{\Delta_{p'p}^0} V_{p'p} + \left(\frac{\partial R_{pp'}}{\partial T_p} \right)_T dT_p \\ &+ \left(\frac{\partial R_{pp'}}{\partial T_{p'}} \right)_T dT_{p'} \equiv \Delta R_{pp'} . \end{aligned} \quad (A2.9)$$

Thus,

$$I_{(p \leftrightarrow p')} = 0 = f_p(1 - f_{p'}) R_{pp'} - f_{p'}(1 - f_p) R_{p'p} , \quad (A2.10)$$

or using equs. (A2.8), (A2.9), equ. (A2.10) becomes

$$0 = (f_p^0 + \Delta f_p) [(1 - f_{p'}^0) - \Delta f_{p'}] (R_{pp'}^0 + \Delta R_{pp'}) - (p \leftrightarrow p') , \quad (A2.11)$$

where $(p \leftrightarrow p')$ stands for the same expression given by the first term of the r.h.s. of equ. (A2.11) interchanging p and p'. Using the detailed balance condition $R_{p'p}^0 / R_{pp'}^0$

$= f_p^0 (1 - f_{p'}^0) / f_{p'}^0 (1 - f_p^0) = \exp(\Delta_{p'p} / kT)$, and equ. (A2.8), then equ. (A2.11) becomes

$$\begin{aligned}
 0 = & \frac{1}{f_P^0 (1 - f_P^0)} \left[\left(\frac{\partial f_P}{\partial T_P} \right)_T dT_P + \left(\frac{\partial f_P}{\partial \mu_P} \right)_T d\mu_P \right] \\
 & + \frac{1}{R_{PP'}^0} \left[\left(\frac{\partial R_{PP'}}{\partial \Delta_{PP'}} \right)_{\Delta_{PP'}^0} V_{PP'} + \left(\frac{\partial R_{PP'}}{\partial T_P} \right)_T dT_P \right. \\
 & \left. + \left(\frac{\partial R_{PP'}}{\partial T_{P'}} \right)_T dT_{P'} \right] - (P \leftrightarrow P'). \quad (A2.12)
 \end{aligned}$$

But,

$$\left(\frac{\partial f_P}{\partial \mu_P} \right)_\mu = f_P^0 (1 - f_P^0) \frac{1}{kT}, \quad (A2.13)$$

and

$$\left(\frac{\partial f_P}{\partial T_P} \right)_T = f_P^0 (1 - f_P^0) \frac{(\epsilon_P - \mu)}{kT^2}. \quad (A2.14)$$

Substituting equs. (A2.13), and (A2.14), into equ. (A2.12), we finally obtain

$$\begin{aligned}
 d\mu_{P'} - d\mu_P = & \frac{1}{T} \left\{ \frac{\epsilon_P + \epsilon_{P'}}{2} - \mu + kT^2 \left[\frac{\partial \ln(R_{PP'}/R_{PP})}{\partial T_P} \right. \right. \\
 & \left. \left. + \frac{\partial \ln(R_{PP'}/R_{PP'})}{\partial T_{P'}} \right]_{T, \Delta_{PP'}^0} \right\} (dT_P - dT_{P'}), \quad (A2.15)
 \end{aligned}$$

from which

$$\begin{aligned}
 \frac{\mu_{P'} - \mu_P}{T_P - T_{P'}} = & \frac{d\mu_{P'} - d\mu_P}{dT_P - dT_{P'}} \equiv q \alpha_{PP'} \\
 = & \frac{1}{T} \left[\frac{1}{2} (\epsilon_P + \epsilon_{P'}) + E_{T, \Delta_{PP'}^0} - \mu \right] \quad (A2.16)
 \end{aligned}$$

where

$$E_T^{PP'} = kT^2 \left[\frac{\partial \ln(R_{PP'}/R_{PP})}{\partial T_P} + \frac{\partial \ln(R_{PP'}/R_{PP'})}{\partial T_{P'}} \right]_{T, \Delta_{PP}^{\circ}} \quad (A2.17)$$

Equations (A2.16), and (A2.17) are the text eqs. (2.74), and (2.75) respectively.

Chapter 3

Thermodynamics and Thermoelectricity.

In this chapter, irreversible thermodynamics will be developed in a form suitable for studying thermoelectric phenomena, with eventual application to problems of particular interest to the present thesis.

The thermoelectric phenomena are processes in which currents are created by fields, i.e. by the action of forces. Consider a group of fluxes J_i and their related conjugate forces X_i . For instance, electric current is a flux and electrical potential gradient is its related force. The simplest assumption to make at this point is that the flux is simply proportional to the corresponding force (e.g. Ohm's law, Fick's law). Thus

$$J_i = L_i X_i \quad . \quad (3.1)$$

However, it is well known that a temperature gradient (the force related to heat flow) can induce a particle current in addition to a heat current. Thus, in general, equ. (3.1) is not adequate. In order to make the theory more general, the fluxes will be assumed to be connected to the forces by a linear relation. Then one has

$$J_i = \sum_{j=1}^N L_{ij} X_j \quad . \quad (3.2)$$

To be even more general, quadratic terms in the forces could be included; however, at present thesis, irreversible thermodynamics is limited to a linear theory. The diagonal terms of the matrix L_{ij} represent parameters such as electrical conductivity. The off-diagonal elements are a measure of the interaction of the various fluxes. For example, the experimental fact that a temperature gradient can induce particle flow, in addition to the normal heat flow, is taken care of by an off-diagonal term.

The phenomenological relations in the form of equ. (3.2) are not of much use because of the N^2 independent coefficients. Thus the coefficients relating the i th flux to the forces have no relationship to the coefficients for the j th flux. Onsager's contribution to the theory⁽²⁴⁾ consisted in showing that if the J_i and X_i are chosen in a certain way, the matrix L_{ij} is symmetric. The symmetry of this matrix then serves to connect the various fluxes.

The method of choosing the fluxes and the forces will now be discussed. In order to determine the forces and the fluxes, we need to know the rate of internal generation of entropy, Θ . To commence with, it may be noted that the law of conservation of energy can be expressed in the form

(rate of increase of energy of the system)

$$+(\text{rate of passage of energy out of the system})=0. \quad (3.3)$$

The sum of the two terms is zero because energy can not be created. With regard to entropy, however, the position is different, for it is a function which increases continually in natural processes, or, in brief, it is produced. The corresponding equation for entropy thus requires an additional term, which is the rate of its generation within the system. Thus

$$\begin{aligned} & \text{(rate of increase of entropy of the system)} \\ & + \text{(rate of outflow of entropy)} \\ & = \text{(rate of internal generation of entropy)}. \end{aligned} \quad (3.4)$$

According to the second law of thermodynamics, this last term can only be positive, or, in the limiting case of reversible changes, zero. It is always to be borne in mind that the entropy is not a conserved quantity; it is essentially a mathematical function which, for a closed system not at equilibrium, has the property of increasing in the forward direction of time, as it is normally experienced. The essence of the second law of thermodynamics is that the great variety of observed changes in the world, as time goes forward, can all be interpreted by the use of a single function. These changes are reflected by the increase of the entropy.

It is the quantity on the right hand side of equ. (3.4) that is of interest in the Onsager's theory. Onsager shows that this quantity, designated by Θ , can always be written

as a sum of terms each representing a single irreversible process. Further, each term may be considered to be of the form (flux) $\times$ (force). Onsager now proves that if the forces and the fluxes are chosen so that⁽¹⁾

$$\Theta = \sum_i J_i x_i, \quad (3.5)$$

where

$$x_i = \frac{X_i}{T}, \quad (3.6)$$

and a linear theory is taken, then the fluxes may be written

$$J_i = \sum_j L_{ij} X_j \quad (3.7)$$

where L_{ij} is a symmetric matrix. It is important to note that this is true only if the theory is restricted to a linear one.

The above procedure will now be carried out for the

(i) The symbols used in the literature are very confused. In the present Chapter the J_i and X_i have the same significance as in Onsager. De Groot⁽²⁵⁾ uses the symbol X for the quantity here denoted x . In the present the only departure from Onsager's nomenclature is the use of the symbol Θ for the rate of creation of entropy per unit volume. Onsager used the quantity Φ , equal to half of this rate, i.e. $\Phi = \frac{\Theta}{2}$. The present Θ is the same as is used by Meixner.

particular case related to the thermoelectric problem; that is, the entropy production will be calculated of a system of charged particles, of charge q . The entropy change which occurs in the irreversible processes is calculated by the use of the following "thermodynamic identity"

$$dU = Tds - pdV + \mu dn \quad (3.8)$$

where U is the internal energy, S is the entropy, μ is the chemical potential and n is the number of moles of the carrier. This equation has often been regarded as being valid only for a reversible change. On the other hand, the entropy is a function of state and its change, dS , is entirely determined by the changes dU , dV and dn . The equation is thus quite correctly applied to any type of change, provided that the values of T , p and μ which are used in the equation are those which prevail in the system itself, and not in its environment.

For a system of unit volume equ.(3.8) can be transformed to

$$dU = Tds + \mu dc$$

or

$$ds = (dU - \mu dc) / T, \quad (3.9)$$

where

U = internal energy/vol.

S = entropy/vol.

c = concentration of carriers/vol.

From equ. (3.9) ⁽ⁱⁱ⁾ we obtain

$$\frac{ds}{dt} = \left(\frac{1}{T}\right) \left(\frac{dU}{dt}\right) - \left(\frac{\mu}{T}\right) \left(\frac{dc}{dt}\right). \quad (3.10)$$

This expression can be put into the form of equ.(3.4) if the rate of change of energy and concentration can be expressed in terms of energy flux and particle flux. Defining a vector $\underline{u}$ as the energy current density, conservation of energy gives

$$\frac{dU}{dt} + \nabla \cdot \underline{u} = 0. \quad (3.11)$$

In a similar manner, defining the particle current density $\underline{j}/q$, $\underline{j}$ being the charge current density, conservation of matter gives

$$\frac{dc}{dt} + \nabla \cdot \left(\frac{\underline{j}}{q}\right) = 0. \quad (3.12)$$

Hence,

$$\frac{ds}{dt} = -\left(\frac{1}{T}\right) \nabla \cdot \underline{u} + \left(\frac{\mu}{T}\right) \nabla \cdot \frac{\underline{j}}{q}$$

or

$$\frac{ds}{dt} + \nabla \cdot \left[\left(\underline{u} - \mu \frac{\underline{j}}{q} \right) / T \right] = \underline{u} \cdot \nabla \left(\frac{1}{T} \right) - \frac{\underline{j}}{q} \cdot \nabla \left(\frac{\mu}{T} \right). \quad (3.13)$$

(ii) In Ref (25) it has been shown that equ.(3.9) has a meaning in a non-equilibrium system. As long as the gradients are small, the entropy depends only on local T, p and n.

It is now convenient to define

$$\underline{j}_s = \frac{1}{T} \left(\underline{u} - \mu \frac{\underline{j}}{q} \right) \quad , \quad (3.14)$$

as the entropy current density. Using this definition, equ. (3.13) can be written

$$\frac{ds}{dt} + \nabla \cdot \underline{j}_s = \Theta \quad . \quad (3.15)$$

This equation is of the same form as equ. (3.11) which is the equation of continuity of energy, except for the additional term Θ . Equation (3.15) may thus be regarded as a continuity relation for entropy, in which $\frac{ds}{dt}$ is the rate of increase of entropy, $\text{div} \underline{j}_s$ is the rate of outflow of entropy and Θ is the rate of internal creation of entropy, all referred to unit volume.

Equation (3.13) can also be written as

$$\Theta = \frac{ds}{dt} + \frac{1}{T} \left[\nabla \cdot \underline{u} - \frac{\mu}{q} \nabla \cdot \underline{j} - \frac{\underline{j}}{q} \cdot \nabla \mu \right] + \left(\underline{u} - \mu \frac{\underline{j}}{q} \right) \cdot \nabla \left(\frac{1}{T} \right) . \quad (3.16)$$

On the other hand, since a current $\underline{j}$ in an electric field $\underline{E}$ generates joule heat $\underline{j} \cdot \underline{E}$ the energy balance is

$$\frac{\partial w}{\partial t} + \nabla \cdot \underline{u} = (\underline{j} \cdot \underline{E}) \quad (3.17)$$

where w is the energy density, and $\underline{u}$ is the energy current density.

In the steady state, $\frac{\partial s}{\partial t} = 0$, $\frac{\partial w}{\partial t} = 0$, $\frac{\partial \epsilon}{\partial t} = 0$ thus from equs (3.12), (3.17),

$$\underline{\nabla} \cdot \underline{j} = 0 \quad , \quad \underline{\nabla} \cdot \underline{u} = (\underline{j} \cdot \underline{E}) \quad (3.18)$$

Using equs. (3.18), equ.(3.16) becomes

$$\Theta = \frac{1}{T} \left[\underline{j} \cdot \left(\underline{E} - \frac{1}{q} \underline{\nabla} \mu \right) \right] - \left(\underline{u} - \mu \frac{\underline{j}}{q} \right) \frac{1}{T^2} \underline{\nabla} T \quad (3.19)$$

Apart from the electrical current density $\underline{j}$, the expression⁽²⁶⁾

$$\underline{Q} = \underline{u} - \mu \frac{\underline{j}}{q} \quad (3.20)$$

occurs as further current and it must, obviously, be interpreted as the heat current density. Using equ. (3.20), equ. (3.19) can be written as

$$\Theta = \frac{\underline{j} \cdot \left(\underline{E} - \frac{1}{q} \underline{\nabla} \mu \right)}{T} - \underline{Q} \cdot \frac{\underline{\nabla} T}{T^2} \quad (3.21)$$

Equation (3.19) can also be written as

$$\Theta = \frac{1}{T} \left\{ \underline{j} \cdot \left(\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right) - \underline{u} \cdot \frac{\underline{\nabla} T}{T} \right\} \quad (3.22)$$

Comparing equ.(3.22) with equs.(3.5), (3.6) we see that we can take $\underline{j}$, $\underline{u}$ as fluxes, and $\left(\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right)$, $-\frac{\underline{\nabla} T}{T}$ as the corresponding forces. Then from equ. (3.7), follows that

$$\underline{j} = L^{(1)} \left[\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right] - L^{(2)} \frac{\underline{\nabla} T}{T} \quad , \quad (3.23)$$

$$\underline{u} = L^{(3)} \left[\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right] - L^{(4)} \frac{\underline{\nabla} T}{T} \quad (3.24)$$

Equations (3.23), and (3.24) can be inverted to read

$$\underline{E} = L^{(1)-1} \underline{j} + \frac{1}{q} L \nabla T + \frac{1}{q} \nabla \mu, \quad (3.25)$$

$$\underline{u} = \pi \underline{j} - \kappa \nabla T + \frac{1}{q} \mu \underline{j}, \quad (3.26)$$

where

$$L = \frac{(q L^{(1)-1} L^{(2)} - \mu)}{T}, \quad (3.27)$$

the Peltier coefficient, π is given by

$$\pi = \frac{1}{q} (q L^{(1)-1} L^{(3)} - \mu), \quad (3.28)$$

and the thermal conductivity, κ , is given by

$$\kappa = \frac{(L^{(4)} - L^{(1)-1} L^{(3)} L^{(2)})}{T}. \quad (3.29)$$

From equs. (3.27), (3.28),

$$T L = q \pi.$$

The Peltier coefficient is also given by

$$\pi = \frac{Q}{j}. \quad (3.30)$$

Finally the thermoelectric power, α , is given by

$$\alpha = \frac{L}{q} = \frac{\pi}{T} = \frac{Q}{T j}. \quad (3.31)$$

The derivation of the expressions for π and κ is given in Appendix A3.

The transport coefficients $L^{(1)}$, $L^{(2)}$, $L^{(3)}$, $L^{(4)}$, have been independently evaluated by H.Mori⁽²⁷⁾, and Kubo et al⁽²⁸⁾, and are given by

$$L^{(1)} = \int_0^\infty dt \int_0^\beta d\lambda \langle j(-i\hbar\lambda) j(t) \rangle, \quad (3.32)$$

and

$$L^{(2)} = \int_0^\infty dt \int_0^\beta d\lambda \langle j(-i\hbar\lambda) u(t) \rangle. \quad (3.33)$$

Because of the fact that $L_{ik} = L_{ki}$, in the absence of a magnetic field when $L_{ik}(-H) = L_{ki}(H)$, $L^{(1)} = L^{(3)}$, and $L^{(2)} = L^{(4)}$. The symbol $\langle \dots \rangle$ means the average over the canonical equilibrium ensemble, $\beta = 1/kT$ and the operators $j(t)$, $j(-i\hbar\lambda)$, $u(t)$ are taken in the interaction picture given by

$$B(t) = \exp\left[\left(-\frac{it}{\hbar}\right) H_0\right] B \exp\left[\left(-\frac{i\lambda}{\hbar}\right) H_0\right], \quad (3.34)$$

where H_0 is the unperturbed Hamiltonian of the system.

Thus, in order to find the thermoelectric power, α , it is necessary to evaluate the transport coefficients, i.e. the integrals of the correlation functions appearing in equs. (3.32), and (3.33) for the specific system under study.

Appendix A3

Derivation of the expressions for the Peltier coefficient, Π , and the thermal conductivity, κ .

Let us recall the text equations (3.23), and (3.24),

$$\underline{j} = L^{(1)} \left[\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right] - L^{(2)} \frac{\underline{\nabla} T}{T}, \quad (A3.1)$$

$$\underline{\mu} = L^{(3)} \left[\underline{E} - \frac{T}{q} \underline{\nabla} \left(\frac{\mu}{T} \right) \right] - L^{(4)} \frac{\underline{\nabla} T}{T}. \quad (A3.2)$$

From (A3.1) follows

$$\begin{aligned} \underline{E} &= L^{(1)-1} \underline{j} - \frac{\mu}{q} \frac{\underline{\nabla} T}{T} + L^{(1)-1} L^{(2)} \frac{\underline{\nabla} T}{T} + \frac{1}{q} \underline{\nabla} \mu \\ &= L^{(1)-1} \underline{j} + \frac{(q L^{(1)-1} L^{(2)} - \mu)}{T} \underline{\nabla} T + \frac{1}{q} \underline{\nabla} \mu. \end{aligned} \quad (A3.3)$$

Defining

$$L \equiv \frac{(q L^{(1)-1} L^{(2)} - \mu)}{T}, \quad (A3.4)$$

we have

$$\underline{E} = L^{(1)-1} \underline{j} + \frac{1}{q} L \underline{\nabla} T + \frac{1}{q} \underline{\nabla} \mu. \quad (A3.5)$$

Equations (A3.4), and (A3.5) are the text equs. (3.25), and (3.27), respectively.

Substituting $\underline{E}$ from equ. (A3.5) into equ. (A3.2), we obtain

$$\begin{aligned}\underline{u} &= L^{(3)} \left\{ L^{(1)-1} \underline{j} + L^{(1)-1} L^{(2)} \frac{\nabla T}{T} - \frac{\mu}{q} \frac{\nabla T}{T} \right. \\ &\quad \left. + \frac{1}{q} \nabla \mu - \frac{T}{q} \nabla \left(\frac{\mu}{T} \right) \right\} - L^{(4)} \frac{\nabla T}{T} \\ &= L^{(3)} L^{(1)-1} \underline{j} - \frac{(L^{(4)} - L^{(1)-1} L^{(3)} L^{(2)})}{T} \nabla T . \quad (A3.6)\end{aligned}$$

Defining

$$\kappa \equiv \frac{(L^{(4)} - L^{(1)-1} L^{(3)} L^{(2)})}{T} , \quad (A3.7)$$

equ. (A3.6) becomes

$$\underline{u} = L^{(3)} L^{(1)-1} \underline{j} - \kappa \nabla T . \quad (A3.8)$$

This can be written as

$$\begin{aligned}\underline{u} &= L^{(3)} L^{(1)-1} \underline{j} - \frac{1}{q} \mu \underline{j} + \frac{1}{q} \mu \underline{j} - \kappa \nabla T \\ &= \frac{1}{q} (q L^{(3)} L^{(1)-1} - \mu) \underline{j} - \kappa \nabla T + \frac{1}{q} \mu \underline{j} \quad (A3.9)\end{aligned}$$

Defining

$$\pi \equiv \frac{1}{q} (q L^{(3)} L^{(1)-1} - \mu) , \quad (A3.10)$$

equ. (A3.9) becomes

$$\underline{u} = \pi \underline{j} - \kappa \nabla T + \frac{1}{q} \mu \underline{j} . \quad (A3.11)$$

Eqs. (A3.7), (A3.10), and (A3.11) are the text eqs. (3.29), (3.28), and (3.26), respectively.

For $\nabla T = 0$ (Peltier effect), equ. (A3.11) becomes

$$\underline{u} = \pi j + \frac{1}{q} \mu j$$

or

$$\pi = \frac{(\underline{u} - \mu \frac{j}{q})}{j} \quad , \quad (A3.12)$$

and using the fact that

$$\underline{u} - \mu \frac{j}{q} = Q \quad ,$$

(cf. text equ. 5.20), equ. (A3.12) becomes

$$\pi = \frac{Q}{j} \quad , \quad (A3.13)$$

which is the text equ. (3.30).

Chapter 4

The Molecular Crystal Model (M.C.M.)

Probably the most important physical concept of the polaron problem is that of "self-trapping" of the electron. Qualitatively, this may be understood as follows. Let us imagine that an electron is momentarily fixed at some lattice site of a crystal. As a result of the electron-lattice interaction the surrounding lattice particles will be displaced to new equilibrium positions; according to general mechanical principle the "induced" displacements will be such as to provide a potential "well" for the electron. If the "well" is sufficiently deep, the electron will occupy a bound state and will be unable to move unless accompanied by the "well", that is to say, by the induced lattice deformation. The unit consisting of the electron together with its induced lattice deformation is called the "polaron". If the carrier is essentially confined to a single site⁽ⁱ⁾ it is referred to as "small-polaron".

T. Holstein⁽¹⁰⁾ had proposed a theoretical model for

(i) In the case in which the linear dimensions of the polaron are sufficiently large compared to a lattice spacing it is referred to as "large-polaron".

small-polaron motion which incorporated, in simplified form, the physical features of the problem. This is the so-called "Molecular Crystal Model" (M.C.M.). A brief review of this model will now be given.

In the absence of the electron, the system consists of N identical diatomic molecules, whose orientations of centers of gravity are fixed, but whose internuclear separations are allowed to vary. The "lattice-vibrations" thus consist of the vibrations of the individual internuclear separations. Thus each molecule, in addition to be labelled by its position, $\underline{\ell}$, is characterized by a configurational coordinate, $x_{\underline{\ell}}$, which represents the deviation of the atoms of the molecule from their equilibrium configuration.

If the potential energy curve of an individual molecule be assumed parabolic, the lattice Hamiltonian, H_L , reads

$$H_L = \sum_{\underline{\ell}} \left(\frac{1}{2M} P_{\underline{\ell}}^2 + \frac{1}{2} M \omega_0^2 x_{\underline{\ell}}^2 + \frac{1}{2} \sum_{\underline{h}} M \omega_1^2 x_{\underline{\ell}} x_{\underline{\ell}+\underline{h}} \right), \quad (4.1)$$

where M is the molecular mass, $P_{\underline{\ell}} = -i\hbar \frac{\partial}{\partial x_{\underline{\ell}}}$ is the associated canonical momentum, ω_0 is the harmonic oscillator frequency associated with the configurational coordinate of the isolated molecule. The vector $\underline{h}$ indexes the nearest neighbors, $\underline{\ell}+\underline{h}$, of an arbitrary site, $\underline{\ell}$, and the final term couples neighbor molecules and gives rise to dispersion of the lattice vibration frequency.

The motion of the electron in the molecular-crystal medium described above, can be formulated in terms of the tight-binding approximation. In analogy with the corresponding

treatment for atomic sites, one assumes that the one-electron potential may be written as a sum of "molecular" potentials, viz.

$$V(\underline{r}, \dots, \underline{x}_\ell, \dots) = \sum_{\ell} U(\underline{r} - \underline{\ell}; \underline{x}_\ell) , \quad (4.2)$$

where $\underline{r}$ is the electron's position vector, and $U(\underline{r} - \underline{\ell}; \underline{x}_\ell)$ is the contribution to the electronic potential of the molecule with position vector $\underline{\ell}$. This potential depends on the deformation parameter of the molecule at $\underline{\ell}$, $\underline{x}_\ell$; it is this feature which embodies the electron-lattice interaction.

The electron's kinetic energy is, $\frac{1}{2m} (-i\hbar \nabla_r)^2$, where m is the electronic mass; thus the electron's Hamiltonian H_e , reads,

$$H_e = -\frac{\hbar^2}{2m} \nabla_r^2 + \sum_{\ell} U(\underline{r} - \underline{\ell}; \underline{x}_\ell) . \quad (4.3)$$

The basic electron wave functions, $\phi(\underline{r} - \underline{\ell}, \underline{x}_\ell)$, appropriate to the tight-binding approximation, are obtained as solutions of the Schrödinger equation

$$H_e \phi(\underline{r} - \underline{\ell}, \underline{x}_\ell) = E(\underline{x}_\ell) \phi(\underline{r} - \underline{\ell}, \underline{x}_\ell) , \quad (4.4)$$

with eigenvalue $E(\underline{x}_\ell)$ which is the energy of an electron on an isolated molecule depending upon the local internuclear displacement coordinate.

The total wave function of the system, $\Psi(\underline{r}, \dots, \underline{x}_\ell, \dots; t)$, whose Hamiltonian is $\{H_L + H_e\}$ can be written as a linear

superposition of these local electronic wave functions, i.e.

$$\Psi(r, \dots, x_l, \dots; t) = \sum_l \alpha(l, \dots, x_l, \dots; t) \phi(r-l, x_l). \quad (4.5)$$

The coefficients $\alpha(l, \dots, x_l, \dots; t)$ are found, within the standard tight-binding approximation, to be given by the solutions of the coupled equations⁽ⁱⁱ⁾:

$$i\hbar \frac{\partial \alpha(l, \dots, x_l, \dots; t)}{\partial t} = \left[H_l + E(x_l) + W(l, \dots, x_l, \dots) \right] \alpha(l, \dots, x_l, \dots; t) + \sum_h J_h \alpha_{l+h} \quad (4.6)$$

In conformance with the standard concepts of molecular theory $E(x_l)$ is to be regarded as a function of the internuclear displacement coordinate of the molecule and it is given by

$$E(x_l) = \epsilon_l(0) - A x_l, \quad (4.7)$$

where $\epsilon_l(0)$ is the energy of the electron at the particular lattice site l if the atoms are constrained not to be displaced in response to its presence. $W(l, \dots, x_l, \dots)$ represents

(ii) The proof of equ.(4.5), as well as the derivation of the expressions for $E(x_l)$, $W(l, \dots, x_l, \dots)$ and J_h is given in Appendix I ref(10).

the contribution to $E(x_l)$ due to the presence of the other molecules and it is given by

$$W(l, \dots, x_l, \dots) \equiv \int \left[|\phi(r-l, x_l)|^2 \sum_{b \neq l} U(r-b; x_b) \right] dV. \quad (4.8)$$

Finally, the J_b are the transfer integrals of tight-binding theory, depending on the ϕ of typical neighbor sites, $l, l+h$, and are, hence, functions of the internuclear coordinates x_l , and x_{l+h} of these sites. They are given by

$$J_b(x_l, x_{l+h}) \equiv \int \phi^*(r-l, x_l) U(r-l; x_l) \phi(r-l-h, x_{l+h}) dV. \quad (4.9)$$

In proceeding further, a number of simplifications were introduced. There are:

(a) The neglect of the energies, $W(l, \dots, x_l, \dots)$.

The physical significance of this is that, when the electron is localized on a given molecular site, the perturbation of its energy due to the potential of other molecules is assumed small, an assumption which is appropriate to the tight-binding case. Its employment has the effect of restricting the x -dependence of the energy of the localized electron to a single coordinate, x_l , that of the occupied site. In fact, we neglect the x_l -dependence of $W(l, \dots, x_l, \dots)$, and thus $W=W(0)$. For a crystal $W(0)$ is the same for all sites and thus can be neglected. This restriction appears to be a special feature of the molecular crystal model; in particular, it does not apply to the real situation, in which the energy of a localized electron depends upon lattice displacements at

a number of more or less neighboring sites. However, at the present time, it is not at all established whether this difference is significant, as far as physical results are concerned. In fact the point of view of the present studies is that such questions will be best answered by a systematic consideration of various hypothetical cases, starting with the simplest. In this spirit $W(l, \dots, x_l, \dots)$ will be neglected.

(b) The neglect of the x -dependence of the $J_2(x_l, x_{l+h})$.

This simplification means that the $J_2(x_l, x_{l+h})$ are all to be taken equal to a simple constant, $-J$. In principle, the J do depend on the x mainly via the local wave functions, $\Phi(r-l; x_l)$; however the primary physical property of the J , as it will be seen later on, is their order of magnitude relative to other energies. Hence, their x -dependence will be neglected.

(c) The x -dependence of $E(x_l)$ is taken to be linear, i.e.

$$E(x_l) = -A x_l, \quad (4.10)$$

where A is a constant which characterizes the electron-lattice coupling strength ("electron lattice interaction parameter"). The sign has been chosen negative and the additive energy constant $\epsilon_l(0)$ (c.f. equ. (4.7.) being set equal to zero, for an ordered system, both in the interest of notational convenience.

With the simplifications discussed above the "equation of motion" (4.6) reduces to

$$i\hbar \frac{\partial}{\partial t} [\alpha(\underline{l}, \dots, x_{\underline{l}}, \dots; t)] = \left\{ \sum_{\underline{b}} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_{\underline{b}}^2} + \frac{1}{2} M \omega_0^2 x_{\underline{b}}^2 + \frac{1}{2} \sum_{\underline{h}} M \omega_1^2 x_{\underline{b}} x_{\underline{b}+\underline{h}} \right) - A x_{\underline{l}} \right\}$$

$$\alpha(\underline{l}, \dots, x_{\underline{l}}, \dots; t) = J \sum_{\underline{h}} \alpha_{\underline{l}+\underline{h}} \quad , \quad (4.11)$$

or expressing the vibrational coordinates, $x_{\underline{l}}$, in terms of the normal-mode coordinates of the host crystal, by the transformation

$$x_{\underline{l}} = \left(\frac{2}{N} \right)^{1/2} \sum_{\underline{k}} q_{\underline{k}} \sin \left(\underline{k} \cdot \underline{l} + \frac{\pi}{4} \right) \quad , \quad (4.12)$$

equ. (3.11) becomes

$$i\hbar \frac{\partial}{\partial t} [\alpha(\underline{l}, \dots, x_{\underline{l}}, \dots; t)] = \sum_{\underline{k}} \left\{ \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{\underline{k}}^2} + \frac{1}{2} M \omega_{\underline{k}}^2 q_{\underline{k}}^2 \right) - \left(\frac{2}{N} \right)^{1/2} A q_{\underline{k}} \sin \left(\underline{k} \cdot \underline{l} + \frac{\pi}{4} \right) \right\}$$

$$\alpha(\underline{l}, \dots, q_{\underline{k}}, \dots; t) = J \sum_{\underline{h}} \alpha_{\underline{l}+\underline{h}} \quad , \quad (4.13)$$

where $\omega_{\underline{k}}$ is the normal-mode frequency. The consequent relationship between $\omega_{\underline{k}}$ and its associated wave vector, $\underline{k}$, i.e. the dispersion relation⁽ⁱⁱⁱ⁾, is given by

$$\omega_{\underline{k}}^2 = \omega_0^2 + \omega_1^2 \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \quad , \quad (4.14)$$

(iii) The standard approximation of replacing the vibrational frequency by a simple frequency (Einstein model), yields to meaningless results for the M.C.M.⁽¹⁰⁾

where $\kappa = 2\pi\lambda/N$, the integer λ lying in the range $-\frac{1}{2}(N-1) \leq \lambda \leq \frac{1}{2}(N-1)$.

For sufficiently small values of the transfer integrals^(iv) equ.(4.11) may be solved perturbatively in powers of J . In zeroth order the carrier is restricted to a single site with the molecule of the occupied site deforming in response to its presence. The zeroth order wave function is obtained by setting $J=0$ in equ.(4.13). The zeroth-order eigenfunctions are then seen to have the form

$$\alpha_{\underline{l}}^{(g)}(\dots q_{\underline{k}} \dots) = \delta_{\underline{l}, \underline{g}} \chi^{(g)}(\dots q_{\underline{k}} \dots) \quad , \quad (4.15)$$

where $\delta_{\underline{l}, \underline{g}}$ is the Kronecker delta and where $\chi^{(g)}$ satisfies the equation

$$E \chi^{(g)} = \sum_{\underline{k}} \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_{\underline{k}}^2} + \frac{1}{2} M \omega_{\underline{k}}^2 q_{\underline{k}}^2 - \left(\frac{2}{N}\right)^{1/2} A q_{\underline{k}} \sin\left(\underline{k} \cdot \underline{g} + \frac{\pi}{4}\right) \right] \chi^{(g)}. \quad (4.16)$$

The square bracket of equ. (4.16) represents a system of

(iv) As pointed out in Ref.(10), the small-polaron condition $J < E_a$ is not sufficient for the applicability of the jump-perturbation approximation. Rather a more stringent condition $\eta_2 = J / (\hbar \omega_0)^{1/2} (\kappa T E_a)^{1/4} < 1$ where E_a is the activation energy, is required for the case $T > T_t = \frac{\Theta_D}{2}$, Θ_D being Debye temperature.

independent harmonic oscillators, with equilibrium points

$$q_k^{(g)} = \left(\frac{2}{N}\right)^{1/2} \frac{A}{M \omega_k^2} \sin \left(k \cdot g + \frac{\pi}{4} \right) . \quad (4.17)$$

Then, one readily obtains the eigenfunctions and eigenvalues of (4.16),

$$\chi_{\dots n_k \dots}^{(g)} (\dots q_k \dots) = \prod_k \phi_{n_k} \left[\left(\frac{M \omega_k}{\hbar} \right)^{1/2} (q_k - q_k^{(g)}) \right] , \quad (4.18)$$

and

$$E_{\dots n_k \dots} = \sum_k \hbar \omega_k \left(n_k + \frac{1}{2} \right) - E_b , \quad (4.19)$$

where

$$\phi_{n_k}(z) = \left(2^{n_k} n_k! \pi^{1/2} \right)^{-1/2} \exp \left(-\frac{z^2}{2} \right) H_{n_k}(z) \quad (4.20)$$

are the normalized harmonic oscillator eigenfunctions (the $H_{n_k}(z)$ being Hermite polynomials), and

$$E_b = \left(\frac{1}{N} \right) \sum_k \frac{A^2}{2 M \omega_k^2} \quad (4.21)$$

is the small-polaron binding energy. Finally from equs. (4.15) and (4.18), one has for the zeroth-order eigenstates of the total system,

$$\alpha_{g, \dots n_k \dots}(\underline{l}, \dots q_k \dots) = \delta_{\underline{l}, g} \prod_k \phi_{n_k} \left[\left(\frac{M \omega_k}{\hbar} \right)^{1/2} (q_k - q_k^{(g)}) \right] . \quad (4.22)$$

The perturbation development proceeds according to the standard time-perturbation theory. The total wave function of equ. (4.13) is expanded in the interaction picture in the

representation of the zeroth-order eigenstates provided by equ. (4.22). Thus the wave function of the system takes the form:

$$\alpha(\underline{\ell}, \dots, q_k, \dots; t) = \sum_{\underline{g}', \dots, n_k'} C(\underline{g}', \dots, n_k'; t) \alpha_{\underline{g}', \dots, n_k'}(\underline{\ell}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\dots, n_k'}\right]. \quad (4.23)$$

The C are then found to obey the equation

$$i\hbar \frac{\partial}{\partial t} C(\underline{g}, \{n_k\}; t) = \sum_{\underline{g}', \{n_k'\}} \langle \underline{g}, \{n_k\} | V | \underline{g}', \{n_k'\} \rangle C(\underline{g}', \{n_k'\}; t) \exp\left[\left(\frac{it}{\hbar}\right) (E_{\{n_k\}} - E_{\{n_k'\}})\right], \quad (4.24)$$

where $\{n_k\}$, $\{n_k'\}$, represent the totality of the vibrational quantum numbers $(\dots, n_k, \dots)$, $(\dots, n_k', \dots)$, respectively, and $\langle \underline{g}, \{n_k\} | V | \underline{g}', \{n_k'\} \rangle$ are the basic matrix elements of the perturbation i.e. of the J-proportional term of equ.(4.13). They are different from zero only if $\underline{g}$, $\underline{g}'$ are nearest neighbor sites. Their explicit form is given by

$$\begin{aligned} \langle \underline{g}', \{n_k'\} | V | \underline{g}, \{n_k\} \rangle = & -J \sum_{\underline{h}} \delta_{\underline{g}', \underline{g} + \underline{h}} \prod_k \left\{ \left[1 - \left(\frac{u}{N}\right) \left(n_k + \frac{1}{2}\right) \gamma_{\underline{k}, \underline{h}} \cos^2 \left[\underline{k} \cdot \left(\underline{g} + \frac{\underline{h}}{2}\right) + \frac{n}{4} \right] \right] \delta_{n_k', n_k} \right. \\ & \left. + \left[\left(\frac{g}{N}\right)^{1/2} \epsilon_{\underline{k}, \underline{h}} \gamma_{\underline{k}, \underline{h}}^{1/2} \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2} }{2} \right)^{1/2} \cos \left[\underline{k} \cdot \left(\underline{g} + \frac{\underline{h}}{2}\right) + \frac{n}{4} \right] \right] \delta_{n_k', n_k \pm 1} \right\}, \end{aligned} \quad (4.25)$$

where $\epsilon_{\underline{k}, \underline{h}}$ is equal to ± 1 according to whether $\underline{k} \cdot \underline{h} (\geq) 0$, and $\gamma_{\underline{k}, \underline{h}}$ are the characteristic coupling constants of the theory, given by

$$\gamma_{\underline{k}, \underline{h}} = \frac{A^2}{2 M \omega_k^2 \hbar \omega_k} \left[1 - \cos(\underline{k} \cdot \underline{h}) \right]. \quad (4.26)$$

Chapter 5

Generalization of the M.C.M.

The Molecular Crystal Model, as described in the previous Chapter, is suitable for an "ordered" situation in which all the lattice sites are energetically equivalent ($\epsilon_g(0) = \epsilon_{g'}(0) = 0$) and the coupling strength of the electron-lattice interaction is the same ($A_g = A_{g'} = A$) for the electron residing on every lattice site. This simplified situation, as we have already explained in Chapter 2, is the cause of the lack of an energy of transport term, contributing to the thermoelectric power.

We believe that a Generalized M.C.M. (G.M.C.M.) applicable to a more realistic situation should be used as a theoretical model for the study of the thermoelectric power. In our approach we consider a pair of neighbouring molecular lattice sites, g and g' , with energy disorder. By this we mean that the local electronic energies $\epsilon_g(0)$, $\epsilon_{g'}(0)$ are no longer equal but they have a finite difference $\Delta_{gg'}(0) = \epsilon_{g'}(0) - \epsilon_g(0)$. These two sites being non-equivalent energetically will affect the small-polaron's binding energy in the sense that, the lower the local electronic energy the more localized the electronic wave function will be and consequently the larger its binding energy. Assuming that the stiffness of the lattice is unaltered, the difference in the binding energy means

a difference in the electron-lattice interaction parameter, i.e. $\epsilon_g(x_g) = \epsilon_g(0) - A_g x_g$ and $\epsilon_{g'}(x_{g'}) = \epsilon_{g'}(0) - A_{g'} x_{g'}$ with $A_g \neq A_{g'}$. As it will be clear from the following, Holstein's M.C.M. follows as a special case from the Generalized M.C.M.

In addition to the above assumptions we consider the presence of a weak, externally applied, electric field $\underline{E}$, which will be the driving force for the system. In this way Emin's assumption of a temperature gradient is no longer necessary, and the Peltier coefficient π , under isothermal conditions, can be evaluated. Then, from Onsager's relation, $\pi = \alpha T$, we obtain the expression for the thermoelectric power, α .

The free-field basic equation of motion, for the G.M.C.M., reads

$$i\hbar \frac{\partial}{\partial t} [\alpha(\underline{\ell}, \dots q_k \dots; t)] = \sum_k \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} M \omega_k^2 q_k^2 - \left(\frac{2}{N}\right)^{1/2} A_{\underline{\ell}} q_k \sin(k \cdot \underline{\ell} + \frac{\pi}{4}) + \epsilon_{\underline{\ell}}(0) \right] \alpha(\underline{\ell}, \dots q_k \dots; t) - J \sum_{\underline{h}} \alpha_{\underline{\ell}+\underline{h}}. \quad (5.1)$$

As before, the zeroth-order wave equation is obtained by setting $J=0$ in equ. (5.1). The zeroth order eigenstates have the form

$$\alpha_{\underline{\ell}}^{(g)}(\dots q_k \dots) = \delta_{\underline{\ell}, \underline{g}} \chi^{(g)}(\dots q_k \dots), \quad (5.2)$$

where $\chi^{(g)}$ satisfies the equation

$$E \chi^{(g)} = \sum_k \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} M \omega_k^2 q_k^2 - \left(\frac{2}{N}\right)^{1/2} A_g q_k \sin(k \cdot \underline{g} + \frac{\pi}{4}) + \epsilon_g(0) \right] \chi^{(g)}. \quad (5.3)$$

Now, here, the electron-lattice interaction parameter and the local electronic energy, $\epsilon_g \neq 0$, are different for the carrier on each lattice site, and are taken explicitly into account. Equation (5.3) can be written as

$$E \chi^{(g)} = \sum_k \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} M \omega_k^2 \left\{ q_k - \frac{A_g}{M \omega_k^2} \left(\frac{2}{N} \right)^{1/2} \sin \left(k \cdot g + \frac{n}{4} \right) \right\} - \frac{A_g^2}{2M \omega_k^2} \left(\frac{2}{N} \right) \sin^2 \left(k \cdot g + \frac{n}{4} \right) + \epsilon_g(0) \right] \chi^{(g)}, \quad (5.4)$$

which represents a system of independent harmonic oscillators with equilibrium points

$$q_k^{(g)} = \frac{A_g}{M \omega_k^2} \left(\frac{2}{N} \right)^{1/2} \sin \left(k \cdot g + \frac{n}{4} \right), \quad (5.5)$$

where the site dependence appears not only through the trigonometric term but also through the site dependence of the A.

The eigenfunctions and eigenvalues of equ.(5.4) are given by

$$\chi_{\{n_k\}}^{(g)} (\dots q_k \dots) = \prod_k \Phi_{n_k} \left[\left(\frac{M \omega_k}{\hbar} \right)^{1/2} \left(q_k - q_k^{(g)} \right) \right], \quad (5.6)$$

and

$$E_{g, \{n_k\}} = \epsilon_g(0) - E_b(g) + \sum_k \hbar \omega_k \left(n_k + \frac{1}{2} \right), \quad (5.7)$$

where

$$E_b(g) = \left(\frac{1}{N} \right) \sum_k \frac{A_g^2}{2M \omega_k^2} \quad (5.8)$$

is the small-polaron binding energy, which in turn is site dependent. We thus see that the small-polaron energy as expressed via equ.(5.7) becomes site dependent.

The jump-perturbation approximation, in which the

J - proportional term of equ.(5.1) is treated as a small perturbation, gives for the wave functions of the system

$$\alpha(\underline{\ell}, \dots, q_k, \dots; t) = \sum_{\underline{g}, \{n_k\}} C(\underline{g}', \{n_k'\}; t) \cdot \\ = \alpha_{\underline{g}', \{n_k'\}}(\underline{\ell}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_k'\}}\right], \quad (5.9)$$

where $E_{\underline{g}', \{n_k'\}}$ is given by equ.(5.7) for $\underline{g}'$ and $\{n_k'\}$. The equation which the C , in equ.(5.9), obey can be found as follows. Inserting equ.(5.0) into equ.(5.1) we obtain

$$i\hbar \frac{\partial}{\partial t} \left[\sum_{\underline{g}, \{n_k\}} C(\underline{g}', \{n_k'\}; t) \alpha_{\underline{g}', \{n_k'\}}(\underline{\ell}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_k'\}}\right] \right] \\ = \mathcal{H}_0 \left[\sum_{\underline{g}, \{n_k\}} C(\underline{g}', \{n_k'\}; t) \alpha_{\underline{g}', \{n_k'\}}(\underline{\ell}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_k'\}}\right] \right] \\ - J \sum_{\underline{h}} \left[\sum_{\underline{g}, \{n_k\}} C(\underline{g}', \{n_k'\}; t) \alpha_{\underline{g}', \{n_k'\}}(\underline{\ell} + \underline{h}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_k'\}}\right] \right], \quad (5.10)$$

where $\mathcal{H}_0$ is the unperturbed ($J=0$) free-field, Hamiltonian of the system. Multiplying both sides on the left by $\alpha_{\underline{g}, \{n_k\}}(\underline{\ell}, \dots, q_k, \dots)$ and integrating with respect to the vibrational coordinates q_k and using the fact that,

$$\alpha_{\underline{g}, \{n_k\}}(\underline{\ell}, \dots, q_k, \dots) = \delta_{\underline{\ell}, \underline{g}} \prod_k \Phi_{n_k} \left[\left(\frac{M \omega_k}{\hbar} \right)^{1/2} (q_k - q_k^{(g)}) \right], \quad (5.11)$$

as well as orthogonality relations of the form

$$\int_{-\infty}^{\infty} \delta_{\underline{g}, \underline{g}'} \phi_{n_{\underline{g}}} \left[\left(\frac{M\omega_{\underline{g}}}{\hbar} \right)^{1/2} (q_{\underline{g}} - q_{\underline{g}}^{(g')}) \right] \phi_{n'_{\underline{g}}} \left[\left(\frac{M\omega_{\underline{g}}}{\hbar} \right)^{1/2} (q_{\underline{g}} - q_{\underline{g}}^{(g')}) \right] dq_{\underline{g}} = \frac{1}{(M\omega_{\underline{g}}/\hbar)^{1/2}} \delta_{n_{\underline{g}}, n'_{\underline{g}}} \quad (5.12)$$

we obtain the equation which the C of equ.(5.9) obey, and that is

$$i\hbar \frac{\partial}{\partial t} [C(\underline{g}, \{n_{\underline{g}}\}; t)] = \sum_{\underline{g}', \{n'_{\underline{g}}\}} \langle \underline{g}', \{n'_{\underline{g}}\} | V | \underline{g}, \{n_{\underline{g}}\} \rangle C(\underline{g}', \{n'_{\underline{g}}\}; t) \exp \left[\left(\frac{i}{\hbar} \right) (E_{\underline{g}, \{n_{\underline{g}}\}} - E_{\underline{g}', \{n'_{\underline{g}}\}}) t \right] \quad (5.13)$$

where $\langle \underline{g}', \{n'_{\underline{g}}\} | V | \underline{g}, \{n_{\underline{g}}\} \rangle$ are the matrix elements of the overlap part of the Hamiltonian i.e. the matrix elements of the perturbation (the V -proportional term of equ.(5.1)) and are given by

$$\begin{aligned} \langle \underline{g}', \{n'_{\underline{g}}\} | V | \underline{g}, \{n_{\underline{g}}\} \rangle = & -J \sum_{\underline{g}} \delta_{\underline{g}', \underline{g}+\underline{h}} \prod_{\underline{k}} \left[\int_{-\infty}^{\infty} \phi_{n_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(g)}) \right] \right. \\ & \left. \times \phi_{n'_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(g')}) \right] \left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} dq_{\underline{k}} \right] \quad (5.14) \end{aligned}$$

The details of the calculations are given in Appendix A5.a.

We shall now proceed in the evaluation of the matrix elements of the overlap part of the Hamiltonian, given by equ.(5.14). For this generalized case the displaced harmonic oscillator equilibrium points for the two sites $\underline{g}, \underline{g}'$ are expressed as

$$q_k^{(g)} = \left(\frac{2}{\omega_k}\right)^{1/2} \frac{A_g}{M\omega_k^2} \sin(k \cdot q + \frac{\pi}{4}) , \quad (5.15)$$

$$q_k^{(g')} = \left(\frac{2}{\omega_k}\right)^{1/2} \frac{A_{g'}}{M\omega_k^2} \sin(k \cdot q' + \frac{\pi}{4}) ,$$

where $A_g \neq A_{g'}$. The normalized harmonic oscillator eigenfunctions $\phi_{n_k}(z)$, where $z \equiv \left(\frac{M\omega_k}{\hbar}\right)^{1/2} (q_k - q_k^{(g)})$, are of the form

$$\phi_{n_k}(z) = (2^{n_k} n_k! \pi^{1/2})^{-1/2} \exp(-\frac{z^2}{2}) H_{n_k}(z) . \quad (5.16)$$

Using the recursion relations obeyed by the Hermite polynomials $H_{n_k}(z)$,

$$H'_{n_k}(z) = 2 n_k H_{n_k-1}(z) , \quad (5.17)$$

$$H_{n_k+1}(z) = 2z H_{n_k}(z) - 2 n_k H_{n_k-1}(z) ,$$

we can evaluate the derivative of $\phi_{n_k}(z)$ with respect to z ,

$$\frac{\partial \phi_{n_k}(z)}{\partial z} = \left(\frac{n_k}{2}\right)^{1/2} \phi_{n_k-1}(z) - \left(\frac{n_k+1}{2}\right)^{1/2} \phi_{n_k+1}(z) . \quad (5.18)$$

In this way the first derivative of the eigenfunctions of the system, characterized by the quantum number n_k , is expressed in terms of eigenfunctions characterized by quantum numbers (n_k-1) and (n_k+1) . Now we define

$$\left(\frac{M\omega_k}{\hbar}\right)^{1/2} \equiv \alpha_k , \quad \alpha_k (q_k - q_k^{(g)}) \equiv u_k \rightarrow dq_k = du_k / \alpha_k ,$$

and

$$\alpha_k (q_k^{(g')} - q_k^{(g)}) \equiv \hbar_k , \quad (5.19)$$

then

$$\alpha_k (q_k - q_k^{(g)}) = u_k + \alpha_k q_k^{(g')} - \alpha_k q_k^{(g)} = u_k + \hbar_k .$$

Thus, the expression (5.14) for the overlap part becomes

$$\langle g', n' | V | g, n \rangle = -J \sum_{\underline{h}} \delta_{g', g+h} \prod_{\underline{x}} \left[\int_{-\infty}^{\infty} \phi_{n'_{\underline{x}}}(u_{\underline{x}}) \phi_{n_{\underline{x}}}(u_{\underline{x}} + h_{\underline{x}}) du_{\underline{x}} \right], \quad (5.20)$$

where $n' \equiv \{n'_{\underline{x}}\}$, $n \equiv \{n_{\underline{x}}\}$ is the totality of the vibrational quantum numbers, $(\dots n'_{\underline{x}} \dots)$, and $(\dots n_{\underline{x}} \dots)$, respectively.

In order to evaluate the integral

$$\int_{-\infty}^{\infty} \phi_{n'_{\underline{x}}}(u_{\underline{x}}) \phi_{n_{\underline{x}}}(u_{\underline{x}} + h_{\underline{x}}) du_{\underline{x}} \quad (5.21)$$

we expand $\phi_{n_{\underline{x}}}(u_{\underline{x}} + h_{\underline{x}})$ in power series in $h_{\underline{x}}$ and we obtain

$$\int_{-\infty}^{\infty} \phi_{n'_{\underline{x}}}(u_{\underline{x}}) \left[\phi_{n_{\underline{x}}}(u_{\underline{x}}) + \phi'_{n_{\underline{x}}}(u_{\underline{x}}) h_{\underline{x}} + \frac{\phi''_{n_{\underline{x}}}(u_{\underline{x}})}{2} h_{\underline{x}}^2 \right] du_{\underline{x}}, \quad (5.22)$$

taking into account terms of order up to $(\frac{1}{N})$. The second derivative of $\phi_{n_{\underline{x}}}(u_{\underline{x}})$, using equ. (5.18) can be expressed as

$$\begin{aligned} \phi''_{n_{\underline{x}}}(u_{\underline{x}}) = & \left(\frac{n_{\underline{x}}}{2} \right)^{1/2} \left\{ \left(\frac{n_{\underline{x}}-1}{2} \right)^{1/2} \phi_{n_{\underline{x}}-2}(u_{\underline{x}}) - \left(\frac{n_{\underline{x}}}{2} \right)^{1/2} \phi_{n_{\underline{x}}}(u_{\underline{x}}) \right\} \\ & - \left(\frac{n_{\underline{x}}+1}{2} \right)^{1/2} \left\{ \left(\frac{n_{\underline{x}}+1}{2} \right)^{1/2} \phi_{n_{\underline{x}}}(u_{\underline{x}}) - \left(\frac{n_{\underline{x}}+2}{2} \right)^{1/2} \phi_{n_{\underline{x}}+2}(u_{\underline{x}}) \right\}, \end{aligned} \quad (5.23)$$

and after direct substitution of eqs. (5.18), (5.23) into equ. (5.22), and using the orthogonality relations, given before, the integral (5.22) results in

$$\begin{aligned} & \int_{-\infty}^{\infty} \phi_{n'_{\underline{x}}}(u_{\underline{x}}) \phi_{n_{\underline{x}}}(u_{\underline{x}} + h_{\underline{x}}) du_{\underline{x}} \\ &= \left[1 - \frac{1}{2} \left(n_{\underline{x}} + \frac{1}{2} \right) h_{\underline{x}}^2 \right] \delta_{n'_{\underline{x}}, n_{\underline{x}}} \\ & \mp \left(\frac{n_{\underline{x}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} h_{\underline{x}} \delta_{n'_{\underline{x}}, n_{\underline{x}} \pm 1} \end{aligned}$$

$$+ \left(\frac{n_k + \frac{1}{2} \pm \frac{3}{2}}{2} \right)^{1/2} \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \frac{\hbar_k^2}{2} \delta_{n_k', n_k \pm 2} \quad (5.24)$$

Substituting equ.(5.24) into equ.(5.20) we obtain

$$\langle g', n' | V | g, n \rangle = - \sum_k \delta_{g', g+k} \prod_k \left\{ \left[1 - \frac{1}{2} (n_k + \frac{1}{2}) \hbar_k^2 \right] \delta_{n_k', n_k} \right. \\ \left. + \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \hbar_k \delta_{n_k', n_k \pm 1} \right\}, \quad (5.25)$$

where the terms for which the quantum numbers change by 2 are turn out to be unimportant⁽¹⁰⁾.

The details of the calculations are given in Appendix A5.b.

From equ.(5.25) it is clear that in order to find the explicit expression for the matrix elements of the overlap part of the Hamiltonian we have to evaluate $\hbar_k^2$ for the general case in which $A_g \neq A_{g'}$. Recalling equ.(5.19)

$$\hbar_k \equiv \alpha_k (q_k^{(g')} - q_k^{(g)}) = \left(\frac{1}{N} \right)^{1/2} \frac{2}{2^{1/2} M^{1/2} \omega_k (\hbar \omega_k)^{1/2}} \left\{ A_{g'} \sin(k \cdot g' + \frac{\pi}{4}) - A_g \sin(k \cdot g + \frac{\pi}{4}) \right\}. \quad (5.26)$$

After some trigonometric manipulations, given in Appendix A5.c, we find

$$\hbar_k^2 = \left(\frac{2}{N} \right) \frac{1}{2 M \omega_k^2 (\hbar \omega_k)} \left\{ A_{g'}^2 (1 - \lambda \sin(2k \cdot g')) + A_g^2 (1 - \lambda \sin(2k \cdot g)) \right. \\ \left. - 2 A_g A_{g'} [\cos(k \cdot h) - \lambda \sin(k \cdot (g + g'))] \right\}, \quad (5.27)$$

where $\lambda = \mp 1$ according to whether $\underline{k} \cdot \underline{h}$ is positive or negative, respectively. Substituting equs. (5.26), (5.27) into equ. (5.25), we obtain

$$\begin{aligned} \langle \underline{g}', n' | v | \underline{g}, n \rangle = & -J \sum_{\underline{h}} \delta_{\underline{g}', \underline{g}+\underline{h}} \prod_{\underline{k}} \left\{ \left[1 - \left(\frac{1}{N} \right) \left(n_{\underline{k}} + \frac{1}{2} \right) \frac{1}{2 M \omega_{\underline{k}}^2 (\hbar \omega_{\underline{k}})} \right. \right. \\ & \times \left\{ A_{\underline{g}+\underline{h}}^2 [1 - \lambda \sin(2 \underline{k} \cdot (\underline{g}+\underline{h}))] + A_{\underline{g}}^2 [1 - \lambda \sin(2 \underline{k} \cdot \underline{g})] \right. \\ & \left. \left. - 2 A_{\underline{g}} A_{\underline{g}+\underline{h}} [\cos(\underline{k} \cdot \underline{h}) - \lambda \sin(2 \underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2}))] \right\} \right\} \delta_{n_{\underline{k}}, n_{\underline{k}}} \\ & \mp \left(\frac{4}{N} \right)^{1/2} \left(\frac{n_{\underline{k}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \frac{1}{2^{1/2} M^{1/2} \omega_{\underline{k}} (\hbar \omega_{\underline{k}})^{1/2}} \\ & \times \left\{ A_{\underline{g}+\underline{h}} \sin[\underline{k} \cdot (\underline{g}+\underline{h}) + \frac{\pi}{4}] - A_{\underline{g}} \sin(\underline{k} \cdot \underline{g} + \frac{\pi}{4}) \right\} \delta_{n_{\underline{k}}, n_{\underline{k}} \pm 1}, \end{aligned} \quad (5.28)$$

where $\underline{g}'$ has been replaced by $\underline{g}' = \underline{g} + \underline{h}$.

In Appendix (A5.c) it is proved that the usual expression for the matrix elements of the overlap part of the Hamiltonian, given by Holstein, (c.f. equ. (4.25)), for the case of equal electron lattice interaction parameters in an "ordered" situation, follows from our general expression, equ. (5.28), as a special case.

Appendix A5.a

Derivation of the overlap part of the G.M.C.M. Hamiltonian.

The basic, field free equation of motion reads

$$i\hbar \frac{\partial}{\partial t} [\alpha(\underline{l}, \dots, q_k, \dots; t)] = \sum_k \left[\left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} M \omega_k^2 q_k^2 \right) - \left(\frac{2}{N} \right)^{1/2} A_l q_k \sin(\underline{k} \cdot \underline{l} + \frac{\pi}{4}) + \epsilon_l(0) \right] \alpha(\underline{l}, \dots, q_k, \dots; t) - J \sum_b \alpha_{l+b} . \quad (A5.a.1)$$

The present treatment is based on the so called jump-perturbation approximation. The perturbation development proceeds according to the standard time-dependent perturbation theory. The total wave function of equ. (A5.a.1) is expanded in the interaction picture in the representation of the zeroth-order eigenstates provided by the text equs. (5.2), and (5.6). Thus

$$\alpha(\underline{l}, \dots, q_k, \dots; t) = \sum_{g', \{n_k'\}} c(g', \{n_k'\}; t) \alpha_{g', \{n_k'\}}(\underline{l}, \dots, q_k, \dots) \exp\left[\left(-\frac{it}{\hbar}\right) E_{g', \{n_k'\}}\right] . \quad (A5.a.2)$$

Inserting equ. (A5.a.2) into equ. (A5.a.1), we get, for the left hand side, the following expression

$$i\hbar \frac{\partial}{\partial t} \left[\sum_{\underline{g}', \{n_{\underline{u}}'\}} C(\underline{g}', \{n_{\underline{u}}'\}; t) \alpha_{\underline{g}', \{n_{\underline{u}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \exp \left[\left(-\frac{it}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \right] \right] .$$

(A5.a.3)

Multiplying the expression (A5.a.3) on the left by $\alpha_{\underline{g}, \{n_{\underline{u}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots)$ and integrating with respect to the vibrational coordinates $q_{\underline{k}}$, we obtain

$$\begin{aligned} & i\hbar \frac{\partial}{\partial t} \left[\sum_{\underline{g}', \{n_{\underline{u}}'\}} C(\underline{g}', \{n_{\underline{u}}'\}; t) \left\{ \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{u}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{u}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \right\} \right. \\ & \quad \left. \times \exp \left[\left(-\frac{it}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \right] \right] \\ &= i\hbar \sum_{\underline{g}', \{n_{\underline{u}}'\}} \exp \left[\left(-\frac{it}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \right] \frac{\partial C(\underline{g}', \{n_{\underline{u}}'\}; t)}{\partial t} \\ & \quad \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{u}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{u}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \\ &+ i\hbar \sum_{\underline{g}', \{n_{\underline{u}}'\}} C(\underline{g}', \{n_{\underline{u}}'\}; t) \left(-\frac{i}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \exp \left[\left(-\frac{it}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \right] \\ & \quad \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{u}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{u}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} . \quad (A5.a.4) \end{aligned}$$

Proceeding in the same way, for the right hand side of equ. (A5.a.1), we obtain the expression

$$\begin{aligned} & \sum_{\underline{g}', \{n_{\underline{u}}'\}} C(\underline{g}', \{n_{\underline{u}}'\}; t) E_{\underline{g}', \{n_{\underline{u}}'\}} \exp \left[\left(-\frac{it}{\hbar} \right) E_{\underline{g}', \{n_{\underline{u}}'\}} \right] \\ & \quad \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{u}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{u}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \end{aligned}$$

$$-J \sum_{\underline{h}} \left[\sum_{\underline{g}', \{n_{\underline{h}}'\}} c(\underline{g}', \{n_{\underline{h}}'\}; t) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{h}}'\}}\right] \right. \\ \left. \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{h}}'\}}(\underline{\ell} + \underline{h}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \right] \quad (\text{A5.a.5})$$

Equating the expressions (A5.a.4), and (A5.a.5) we obtain

$$i\hbar \sum_{\underline{g}', \{n_{\underline{h}}'\}} \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{h}}'\}}\right] \frac{\partial c(\underline{g}', \{n_{\underline{h}}'\}; t)}{\partial t} \\ \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{h}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \\ + \sum_{\underline{g}', \{n_{\underline{h}}'\}} c(\underline{g}', \{n_{\underline{h}}'\}; t) E_{\underline{g}', \{n_{\underline{h}}'\}} \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{h}}'\}}\right] \\ \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{h}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \\ = \sum_{\underline{g}', \{n_{\underline{h}}'\}} c(\underline{g}', \{n_{\underline{h}}'\}; t) E_{\underline{g}', \{n_{\underline{h}}'\}} \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{h}}'\}}\right] \\ \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{h}}'\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \\ -J \sum_{\underline{h}} \left[\sum_{\underline{g}', \{n_{\underline{h}}'\}} c(\underline{g}', \{n_{\underline{h}}'\}; t) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{h}}'\}}\right] \right. \\ \left. \int_{-\infty}^{\infty} \alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) \alpha_{\underline{g}', \{n_{\underline{h}}'\}}(\underline{\ell} + \underline{h}, \dots, q_{\underline{k}} \dots) dq_{\underline{k}} \right] \quad (\text{A5.a.6})$$

Substituting the expression for $\alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots)$ given by

$$\alpha_{\underline{g}, \{n_{\underline{h}}\}}(\underline{\ell}, \dots, q_{\underline{k}} \dots) = \delta_{\underline{\ell}, \underline{g}} \prod_{\underline{k}} \phi_{n_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g})}) \right], \quad (\text{A5.a.7})$$

into equ. (A5.a.6), we obtain

$$\begin{aligned}
 & i\hbar \sum_{\underline{g}', \{n_{\underline{u}}'\}} \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{u}}'\}}\right] \frac{\partial C(\underline{g}, \{n_{\underline{u}}\}; t)}{\partial t} \\
 & \int_{-\infty}^{\infty} \delta_{\underline{g}, \underline{g}'} \left(\prod_{\underline{k}} \phi_{n_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g})}) \right] \right) \delta_{\underline{g}, \underline{g}'} \left(\prod_{\underline{k}} \phi_{n_{\underline{k}}'} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g}')}) \right] \right) dq_{\underline{k}} \\
 & = -J \sum_{\underline{h}} \left[\sum_{\underline{g}', \{n_{\underline{u}}'\}} C(\underline{g}', \{n_{\underline{u}}'\}; t) \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}', \{n_{\underline{u}}'\}}\right] \right. \\
 & \left. \int_{-\infty}^{\infty} \delta_{\underline{g}, \underline{g}'} \left(\prod_{\underline{k}} \phi_{n_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g})}) \right] \right) \delta_{\underline{g}+\underline{h}, \underline{g}'} \left(\prod_{\underline{k}} \phi_{n_{\underline{k}}'} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g}')}) \right] \right) dq_{\underline{k}} \right. \\
 & \left. \right] \quad (A5.a.8)
 \end{aligned}$$

Taking into account the orthogonality relations given by the text equation (5.12), equ. (A5.a.8) becomes

$$\begin{aligned}
 & i\hbar \frac{\partial C(\underline{g}, \{n_{\underline{u}}\}; t)}{\partial t} \exp\left[\left(-\frac{it}{\hbar}\right) E_{\underline{g}, \{n_{\underline{u}}\}}\right] \left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} \\
 & = -J \sum_{\underline{g}', \{n_{\underline{u}}'\}} \left\{ \left[\sum_{\underline{h}} \delta_{\underline{g}, \underline{g}+\underline{h}} \prod_{\underline{k}} \int_{-\infty}^{\infty} \phi_{n_{\underline{k}}} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g})}) \right] \phi_{n_{\underline{k}}'} \left[\left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} (q_{\underline{k}} - q_{\underline{k}}^{(\underline{g}')}) \right] dq_{\underline{k}} \right] \right. \\
 & \left. \left(\frac{M\omega_{\underline{k}}}{\hbar} \right)^{1/2} C(\underline{g}', \{n_{\underline{u}}'\}; t) \exp\left[\left(-\frac{it}{\hbar}\right) (E_{\underline{g}, \{n_{\underline{u}}\}} - E_{\underline{g}', \{n_{\underline{u}}'\}})\right] \right\} . \\
 & \quad (A5.a.9)
 \end{aligned}$$

Calling

$$\langle q', \{n'_k\} | V | q, \{n_k\} \rangle = -J \sum_k \delta_{q', q+k} \prod_k \int_{-\infty}^{\infty} \phi_{n_k} \left[\left(\frac{m\omega_k}{\hbar} \right)^{1/2} (q_k - q_k^{(q)}) \right] \\ \times \phi'_{n'_k} \left[\left(\frac{m\omega_k}{\hbar} \right)^{1/2} (q_k - q_k^{(q')}) \right] dq_k, \quad (A5.a.10)$$

the overlap part of the Hamiltonian, then

$$i\hbar \frac{\partial C(q, \{n_k\}; t)}{\partial t} = \sum_{q', \{n'_k\}} \langle q', \{n'_k\} | V | q, \{n_k\} \rangle C(q', \{n'_k\}; t) \exp \left[\left(\frac{it}{\hbar} \right) (E_{q, \{n_k\}} - E_{q', \{n'_k\}}) \right]. \quad (A5.a.11)$$

Equations (A5.a.10), and (A5.a.11) are the text equs. (5.14) and (5.13), respectively.

Appendix A5.b.

Evaluation of the matrix elements of the overlap part.

As has been shown in Appendix A5.a., the matrix elements of the overlap part of the Hamiltonian are given by

$$\langle g', n' | V | g, n \rangle = -J \sum_{\mathbf{h}} \delta_{g', g+\mathbf{h}} \prod_{\mathbf{z}} \left[\int_{-\infty}^{\infty} \phi_{n_{\mathbf{z}}} \left[\left(\frac{m\omega_{\mathbf{z}}}{\hbar} \right)^{1/2} (q_{\mathbf{z}} - q_{\mathbf{z}}^{(g)}) \right] \phi_{n'_{\mathbf{z}}} \left[\left(\frac{m\omega_{\mathbf{z}}}{\hbar} \right)^{1/2} (q_{\mathbf{z}} - q_{\mathbf{z}}^{(g')}) \right] \left(\frac{m\omega_{\mathbf{z}}}{\hbar} \right)^{1/2} dq_{\mathbf{z}} \right] . \quad (\text{A5.b.1})$$

Here, the displaced harmonic oscillator equilibrium points $q_{\mathbf{z}}^{(g)}$, $q_{\mathbf{z}}^{(g')}$ for the sites g, g' , respectively, are given by the text equ.(5.15). The normalized harmonic oscillator eigenfunctions, $\phi_{n_{\mathbf{z}}}(z)$ are given by the text equ.(5.16) in terms of the Hermite polynomials $H_{n_{\mathbf{z}}}(z)$ which obey the recursion relations given by the text equ.(5.17).

Using these relations we can evaluate the derivative of the eigenfunction $\phi_{n_{\mathbf{z}}}(z)$ in the following way. Let us define for convenience the coefficient $(2^{n_{\mathbf{z}}} n_{\mathbf{z}}! \pi^{1/2})^{-1/2} \equiv \vartheta_{n_{\mathbf{z}}}$.

Then

$$\begin{aligned} \frac{\partial \phi_{n_{\mathbf{z}}}(z)}{\partial z} &= \vartheta_{n_{\mathbf{z}}} \left\{ \exp\left(-\frac{z^2}{2}\right) H'_{n_{\mathbf{z}}}(z) + H_{n_{\mathbf{z}}}(z) (-z) \exp\left(-\frac{z^2}{2}\right) \right\} \\ &= \vartheta_{n_{\mathbf{z}}} \left\{ \exp\left(-\frac{z^2}{2}\right) [2n_{\mathbf{z}} H_{n_{\mathbf{z}}-1}(z)] + H_{n_{\mathbf{z}}}(z) (-z) \exp\left(-\frac{z^2}{2}\right) \right\} \end{aligned}$$

$$\begin{aligned}
 &= 2n_x \vartheta_{n_x} \exp(-\frac{z^2}{2}) H_{n_x-1}(z) - z H_{n_x} \exp(-\frac{z^2}{2}) \vartheta_{n_x} \\
 &= 2n_x \vartheta_{n_x} \exp(-\frac{z^2}{2}) H_{n_x-1}(z) - n_x \vartheta_{n_x} H_{n_x-1}(z) \exp(-\frac{z^2}{2}) \\
 &\quad - \vartheta_{n_x} \frac{H_{n_x+1}(z)}{2} \exp(-\frac{z^2}{2}) \\
 &= \vartheta_{n_x} n_x \exp(-\frac{z^2}{2}) H_{n_x-1}(z) \\
 &\quad - \frac{\vartheta_{n_x}}{2} \exp(-\frac{z^2}{2}) H_{n_x+1}(z) \\
 &= (2^{n_x-1} (n_x-1)! n^{1/2})^{-1/2} (2n_x)^{-1/2} n_x \exp(-\frac{z^2}{2}) H_{n_x-1}(z) \\
 &\quad - (2^{n_x+1} (n_x+1)! \pi^{1/2})^{-1/2} 2^{1/2} (n_x+1)^{1/2} 2^{-1} \exp(-\frac{z^2}{2}) H_{n_x+1}(z) ,
 \end{aligned}$$

or

$$\frac{\partial \phi_{n_x}(z)}{\partial z} = \left(\frac{n_x}{2}\right)^{1/2} \phi_{n_x-1}(z) - \left(\frac{n_x+1}{2}\right)^{1/2} \phi_{n_x+1}(z) .$$

(A5.b.2)

Equation (A5.b.2) is the text equ. (5.18). Now using the definitions given by the text eqs. (5.19), the expression (A5.b.1) for the overlap part becomes

$$\langle g', n' | v | g, n \rangle = -J \sum_h \delta_{g', g+h} \prod_k \left[\int_{-\infty}^{\infty} \phi'_{n'_k}(u_k) \phi_{n_k}(u_k + h_k) du_k \right] .$$

(A5.b.3)

Let us now evaluate the integral

$$\int_{-\infty}^{\infty} \phi'_{n'_k}(u_k) \phi_{n_k}(u_k + h_k) du_k .$$

(A5.b.4)

Expanding $\phi_{n_k}(u_k + h_k)$ in power series in h_k we get

$$\int_{-\infty}^{\infty} \phi_{n_{\pm}}'(u_{\pm}) \left[\phi_{n_{\pm}}(u_{\pm}) + \phi_{n_{\pm}}'(u_{\pm}) h_{\pm} + \frac{\phi_{n_{\pm}}''(u_{\pm})}{2} h_{\pm}^2 \right] du_{\pm} \quad (\text{A5.b.5})$$

taking into account terms of order up to $(\frac{1}{N})$. Now taking the derivative of $\phi_{n_{\pm}}'(z)$ given by equ. (A5.b.2), we obtain

$$\begin{aligned} \phi_{n_{\pm}}''(u_{\pm}) &= \{ \phi_{n_{\pm}}'(u_{\pm}) \}' = \left\{ \left(\frac{n_{\pm}}{2} \right)^{1/2} \phi_{n_{\pm}-1}(u_{\pm}) - \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \phi_{n_{\pm}+1}(u_{\pm}) \right\} \\ &= \left(\frac{n_{\pm}}{2} \right)^{1/2} \left\{ \left(\frac{n_{\pm}-1}{2} \right)^{1/2} \phi_{n_{\pm}-2}(u_{\pm}) - \left(\frac{n_{\pm}}{2} \right)^{1/2} \phi_{n_{\pm}}(u_{\pm}) \right\} \\ &\quad - \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \left\{ \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \phi_{n_{\pm}}(u_{\pm}) - \left(\frac{n_{\pm}+2}{2} \right)^{1/2} \phi_{n_{\pm}+2}(u_{\pm}) \right\}. \end{aligned} \quad (\text{A5.b.6})$$

Substituting $\phi_{n_{\pm}}'(u_{\pm})$ from equ. (A5.b.2), and $\phi_{n_{\pm}}''(u_{\pm})$ from equ. (A5.b.6), into the integral (A5.b.5), we obtain

$$\begin{aligned} \int_{-\infty}^{\infty} \phi_{n_{\pm}}'(u_{\pm}) \left\{ \phi_{n_{\pm}}(u_{\pm}) + \left(\frac{n_{\pm}}{2} \right)^{1/2} \phi_{n_{\pm}-1}(u_{\pm}) h_{\pm} - \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \phi_{n_{\pm}+1}(u_{\pm}) h_{\pm} \right. \\ \left. + \left(\frac{n_{\pm}}{2} \right)^{1/2} \left(\frac{n_{\pm}-1}{2} \right)^{1/2} \phi_{n_{\pm}-2}(u_{\pm}) \frac{h_{\pm}^2}{2} - \left(\frac{n_{\pm}}{2} \right)^{1/2} \left(\frac{n_{\pm}}{2} \right)^{1/2} \phi_{n_{\pm}}(u_{\pm}) \frac{h_{\pm}^2}{2} \right. \\ \left. - \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \phi_{n_{\pm}}(u_{\pm}) \frac{h_{\pm}^2}{2} + \left(\frac{n_{\pm}+1}{2} \right)^{1/2} \left(\frac{n_{\pm}+2}{2} \right)^{1/2} \phi_{n_{\pm}+2}(u_{\pm}) \frac{h_{\pm}^2}{2} \right\} du_{\pm}. \end{aligned}$$

Now, combining some terms, the above expression is reduced to

$$\begin{aligned} \int_{-\infty}^{\infty} \phi_{n_{\pm}}'(u_{\pm}) \left\{ \left[1 - \frac{1}{2} \left(n_{\pm} + \frac{1}{2} \right) h_{\pm}^2 \right] \phi_{n_{\pm}}(u_{\pm}) \right. \\ \left. + \left(\frac{n_{\pm}}{2} \right)^{1/2} h_{\pm} \phi_{n_{\pm}-1}(u_{\pm}) \right. \end{aligned}$$

$$\begin{aligned}
 & - \left(\frac{n_k+1}{2} \right)^{1/2} h_k \phi_{n_k+1}(u_k) \\
 & + \left(\frac{n_k}{2} \right)^{1/2} \left(\frac{n_k-1}{2} \right)^{1/2} \frac{h_k^2}{2} \phi_{n_k-2}(u_k) \\
 & + \left(\frac{n_k+1}{2} \right)^{1/2} \left(\frac{n_k+2}{2} \right)^{1/2} \frac{h_k^2}{2} \phi_{n_k+2}(u_k) \} du_k .
 \end{aligned}
 \tag{A5.b.7}$$

Because of the fact that the eigenfunctions of the system are expressed in terms of the Hermite polynomials, they satisfy the orthonormality relation

$$\begin{aligned}
 & \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \phi_{n_k}(u_k) du_k \\
 & = \int_{-\infty}^{\infty} \left(2^{n'_k} n'_k! \pi^{1/2} \right)^{-1/2} \exp\left(-\frac{u_k^2}{2}\right) H_{n'_k}(u_k) \\
 & \quad \times \left(2^{n_k} n_k! \pi^{1/2} \right)^{-1/2} \exp\left(-\frac{u_k^2}{2}\right) H_{n_k}(u_k) du_k = \delta_{n'_k, n_k} .
 \end{aligned}
 \tag{A5.b.8}$$

Using, the above proved orthonormality condition in equ. (A5.b.7), we obtain

$$\begin{aligned}
 & \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \left\{ \left[1 - \frac{1}{2} \left(n_k + \frac{1}{2} \right) h_k^2 \right] \right\} \phi_{n_k}(u_k) du_k \\
 & + \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \left\{ \left(\frac{n_k}{2} \right)^{1/2} h_k \right\} \phi_{n_k-1}(u_k) du_k \\
 & + \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \left\{ - \left(\frac{n_k+1}{2} \right)^{1/2} h_k \right\} \phi_{n_k+1}(u_k) du_k
 \end{aligned}$$

$$\begin{aligned}
 & + \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \left\{ \left(\frac{n_k}{2} \right)^{1/2} \left(\frac{n_k-1}{2} \right)^{1/2} \frac{h_k^2}{2} \right\} \phi_{n_k-2}(u_k) du_k \\
 & + \int_{-\infty}^{\infty} \phi_{n'_k}(u_k) \left\{ \left(\frac{n_k+1}{2} \right)^{1/2} \left(\frac{n_k+2}{2} \right)^{1/2} \frac{h_k^2}{2} \right\} \phi_{n_k+2}(u_k) du_k \\
 & = \left[1 - \frac{1}{2} \left(n_k + \frac{1}{2} \right) h_k^2 \right] \delta_{n'_k, n_k} + \left(\frac{n_k}{2} \right)^{1/2} h_k \delta_{n'_k, n_k-1} - \left(\frac{n_k+1}{2} \right)^{1/2} h_k \delta_{n'_k, n_k+1} \\
 & + \left(\frac{n_k}{2} \right)^{1/2} \left(\frac{n_k-1}{2} \right)^{1/2} \frac{h_k^2}{2} \delta_{n'_k, n_k-2} + \left(\frac{n_k}{2} \right)^{1/2} \left(\frac{n_k+2}{2} \right)^{1/2} \frac{h_k^2}{2} \delta_{n'_k, n_k+2},
 \end{aligned}$$

or combining some terms,

$$\begin{aligned}
 & = \left[1 - \frac{1}{2} \left(n_k + \frac{1}{2} \right) h_k^2 \right] \delta_{n'_k, n_k} \\
 & \mp \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} h_k \delta_{n'_k, n_k \pm 1}, \tag{A5.b.9}
 \end{aligned}$$

where the terms for which the quantum numbers change by 2 are omitted as unimportant. Substituting equ.(A5.b.9) into equ. (A5.b.1), we obtain

$$\begin{aligned}
 \langle g', n' | v | g, n \rangle & = - \mathcal{J} \sum_k \delta_{g', g+k} \prod_k \left\{ \left[1 - \frac{1}{2} \left(n_k + \frac{1}{2} \right) h_k^2 \right] \delta_{n'_k, n_k} \right. \\
 & \left. \mp \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} h_k \delta_{n'_k, n_k \pm 1} \right\}. \tag{A5.b.10}
 \end{aligned}$$

Equation (A5.b.10) is the text equ.(5.25).

In the following Chapter 6 we shall need the expression for $|\langle g', n' | v | g, n \rangle|^2$. This comes straightforward from the

already evaluated expression $\langle g', n' | V | g, n \rangle$, as follows

$$|\langle g', n' | V | g, n \rangle|^2 = J^2 \sum_{\underline{h}} \delta_{g', g+h} \prod_{\underline{k}} \left\{ \left[1 - \frac{1}{2} (n_{\underline{k}} + \frac{1}{2}) h_{\underline{k}}^2 \right] \delta_{n'_{\underline{k}}, n_{\underline{k}}} \right. \\ \left. + \left(\frac{n_{\underline{k}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} h_{\underline{k}} \delta_{n'_{\underline{k}}, n_{\underline{k}} \pm 1} \right\}^2$$

$$= J^2 \sum_{\underline{h}} \delta_{g', g+h} \prod_{\underline{k}} \left\{ \left[1 - (n_{\underline{k}} + \frac{1}{2}) h_{\underline{k}}^2 \right] \delta_{n'_{\underline{k}}, n_{\underline{k}}} + \left(\frac{n_{\underline{k}}}{2} \right) h_{\underline{k}}^2 \delta_{n'_{\underline{k}}, n_{\underline{k}}-1} + \left(\frac{n_{\underline{k}}+1}{2} \right) h_{\underline{k}}^2 \delta_{n'_{\underline{k}}, n_{\underline{k}}+1} \right\}. \\ \text{(A5.b.11)}$$

where only terms of the order $(\frac{1}{N})$ have been retained.

Appendix A5.c.

Final expression for the matrix elements of the overlap part.

We shall evaluate equ.(A5.b.10) for the general case in which $A_{\underline{g}} \neq A_{\underline{g}'}$. We recall the text equ.(5.26)

$$\begin{aligned} h_{\underline{k}} &\equiv \alpha_{\underline{k}} (q_{\underline{k}}^{(\underline{g})} - q_{\underline{k}}^{(\underline{g}')}) \\ &= \left(\frac{L}{N}\right)^{1/2} \frac{2}{2^{1/2} M^{1/2} \omega_{\underline{k}} (\hbar \omega_{\underline{k}})^{1/2}} \left\{ A_{\underline{g}'} \sin(\underline{k} \cdot \underline{g}' + \frac{n}{4}) - A_{\underline{g}} \sin(\underline{k} \cdot \underline{g} + \frac{n}{4}) \right\}, \end{aligned} \quad (\text{A5.c.1})$$

or

$$h_{\underline{k}}^2 = \left(\frac{4}{N}\right) \frac{1}{2 M \omega_{\underline{k}}^2 (\hbar \omega_{\underline{k}})} \left\{ A_{\underline{g}'} \sin(\underline{k} \cdot \underline{g}' + \frac{n}{4}) - A_{\underline{g}} \sin(\underline{k} \cdot \underline{g} + \frac{n}{4}) \right\}^2. \quad (\text{A5.c.2})$$

Let us evaluate the square of the term in brackets

$$\begin{aligned} &\left\{ A_{\underline{g}'} \sin(\underline{k} \cdot \underline{g}' + \frac{n}{4}) - A_{\underline{g}} \sin(\underline{k} \cdot \underline{g} + \frac{n}{4}) \right\}^2 \\ &= A_{\underline{g}'}^2 \sin^2(\underline{k} \cdot \underline{g}' + \frac{n}{4}) + A_{\underline{g}}^2 \sin^2(\underline{k} \cdot \underline{g} + \frac{n}{4}) \\ &\quad - 2 A_{\underline{g}} A_{\underline{g}'} \sin(\underline{k} \cdot \underline{g}' + \frac{n}{4}) \sin(\underline{k} \cdot \underline{g} + \frac{n}{4}) . \end{aligned} \quad (\text{A5.c.3})$$

Using the trigonometric identities

$$2 \sin x \sin y = \cos(x-y) - \cos(x+y) ,$$

$$\cos(\pm\theta + \frac{\pi}{2}) = \mp \sin\theta, \quad (0 \leq \theta \leq \frac{\pi}{2}) ,$$

and having in mind that $\underline{q}' = \underline{q} + \underline{h}$, we obtain

$$2 \sin(\underline{k} \cdot \underline{q}' + \frac{\pi}{4}) \sin(\underline{k} \cdot \underline{q} + \frac{\pi}{4}) = \cos(\underline{k} \cdot \underline{h}) - \lambda \sin[\underline{k} \cdot (\underline{q} + \underline{q}')] ,$$

$$\sin^2(\underline{k} \cdot \underline{q}' + \frac{\pi}{4}) = \frac{1}{2} \{ 1 - \lambda \sin 2 \underline{k} \cdot \underline{q}' \} , \quad (\text{A5.c.4})$$

$$\sin^2(\underline{k} \cdot \underline{q} + \frac{\pi}{4}) = \frac{1}{2} \{ 1 - \lambda \sin 2 \underline{k} \cdot \underline{q} \} ,$$

where $\lambda = \pm 1$ according to whether $\underline{k} \cdot \underline{h}$ is positive or negative, respectively. Substituting equs. (A5.c.4) into equ. (A5.c.2), we obtain

$$\begin{aligned} \bar{H}_{\underline{k}}^2 = & \left(\frac{2}{N} \right) \frac{1}{2 M \omega_{\underline{k}}^2 (\hbar \omega_{\underline{k}})} \left\{ A_{\underline{q}'}^2 (1 - \lambda \sin 2 \underline{k} \cdot \underline{q}') + A_{\underline{q}}^2 (1 - \lambda \sin 2 \underline{k} \cdot \underline{q}) \right. \\ & \left. - 2 A_{\underline{q}} A_{\underline{q}'} [\cos \underline{k} \cdot \underline{h} - \lambda \sin \{ \underline{k} \cdot (\underline{q} + \underline{q}') \}] \right\} . \end{aligned} \quad (\text{A5.c.5})$$

Thus, the equ. (A5.b.10) for the overlap part becomes

$$\begin{aligned} \langle \underline{q}', n' | V | \underline{q}, n \rangle = & -J \sum_{\underline{h}} \delta_{\underline{q}', \underline{q} + \underline{h}} \prod_{\underline{k}} \left\{ \left[1 - \left(\frac{1}{N} \right) \left(n_{\underline{k}} + \frac{1}{2} \right) \frac{1}{2 M \omega_{\underline{k}}^2 (\hbar \omega_{\underline{k}})} \right. \right. \\ & \left. \left\{ A_{\underline{q} + \underline{h}}^2 (1 - \lambda \sin [2 \underline{k} \cdot (\underline{q} + \underline{h})]) + A_{\underline{q}}^2 (1 - \lambda \sin 2 \underline{k} \cdot \underline{q}) \right. \right. \\ & \left. \left. - 2 A_{\underline{q}} A_{\underline{q} + \underline{h}} [\cos \underline{k} \cdot \underline{h} - \lambda \sin (2 \underline{k} \cdot (\underline{q} + \frac{\underline{h}}{2}))] \right\} \right] \delta_{n_{\underline{k}}, n_{\underline{k}} \pm 1} \\ & \mp \left(\frac{1}{N} \right)^{1/2} \left(\frac{n_{\underline{k}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \frac{1}{2^{1/2} M^{1/2} \omega_{\underline{k}} (\hbar \omega_{\underline{k}})^{1/2}} \\ & \left. \left\{ A_{\underline{q} + \underline{h}} \sin [\underline{k} \cdot (\underline{q} + \underline{h}) + \frac{\pi}{4}] - A_{\underline{q}} \sin (\underline{k} \cdot \underline{q} + \frac{\pi}{4}) \right\} \delta_{n_{\underline{k}}, n_{\underline{k}} \pm 1} \right\} , \end{aligned} \quad (\text{A5.c.6})$$

where g' has been replaced $g+h$.

The usual expression for the matrix elements of the overlap part of the Hamiltonian, given by Holstein, (cf. text equ.(4.25), for the case of equal electron-lattice interaction parameters, follows from our general expression (A5.c.6) as a special case. Indeed, for $A_g = A_{g+h} \equiv A$,

$$\begin{aligned}
 & A_{g+h}^2 (1 - \lambda \sin 2\underline{k} \cdot (\underline{g} + \underline{h})) + A_g^2 (1 - \lambda \sin 2\underline{k} \cdot \underline{g}) \\
 & - 2 A_g A_{g+h} \left\{ \cos \underline{k} \cdot \underline{h} - \lambda \sin \left(2\underline{k} \cdot \left(\underline{g} + \frac{\underline{h}}{2} \right) \right) \right\} \\
 & = A^2 + A^2 - 2 A^2 \cos \underline{k} \cdot \underline{h} \pm A^2 \sin(2\underline{k} \cdot (\underline{g} + \underline{h})) \\
 & \pm A^2 \sin 2\underline{k} \cdot \underline{g} \mp 2 A^2 \sin(2\underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2})) \\
 & = 2 A^2 (1 - \cos \underline{k} \cdot \underline{h}) \pm A^2 \{ \sin(2\underline{k} \cdot (\underline{g} + \underline{h})) \\
 & + \sin 2\underline{k} \cdot \underline{g} \} \mp 2 A^2 \sin(2\underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2})) \\
 & = 2 A^2 (1 - \cos \underline{k} \cdot \underline{h}) \mp 2 A^2 \sin[2\underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2})] (1 - \cos \underline{k} \cdot \underline{h}) \\
 & = 2 A^2 (1 - \cos \underline{k} \cdot \underline{h}) \left\{ 1 + \cos \left[2\underline{k} \cdot \left(\underline{g} + \frac{\underline{h}}{2} \right) + \frac{\pi}{2} \right] \right\} \\
 & = 4 A^2 (1 - \cos \underline{k} \cdot \underline{h}) \cos^2 \left[\underline{k} \cdot \left(\underline{g} + \frac{\underline{h}}{2} \right) + \frac{\pi}{4} \right] . \quad (A5.c.7)
 \end{aligned}$$

On the other hand,

$$\begin{aligned}
 & A_{\underline{g}+\underline{h}} \sin \left\{ \underline{k} \cdot (\underline{g} + \underline{h}) + \frac{n}{4} \right\} - A_{\underline{g}} \sin \left(\underline{k} \cdot \underline{g} + \frac{n}{4} \right) \\
 &= 2A \cos \left\{ \underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2}) + \frac{n}{4} \right\} \sin \frac{\underline{k} \cdot \underline{h}}{2} \\
 &= 2^{1/2} \epsilon_{\underline{k} \cdot \underline{h}} (1 - \cos \underline{k} \cdot \underline{h})^{1/2} \cos \left\{ \underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2}) + \frac{n}{4} \right\}, \quad (\text{A5.c.8})
 \end{aligned}$$

where $\epsilon_{\underline{k} \cdot \underline{h}} = \pm 1$ according to whether $\underline{k} \cdot \underline{h} (\pi)$. Substituting equs. (A5.c.7), and (A5.c.8) into equ. (A5.c.6), and defining

$$\gamma_{\underline{k} \cdot \underline{h}} = \frac{A^2}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} [1 - \cos(\underline{k} \cdot \underline{h})],$$

we obtain

$$\begin{aligned}
 \langle \underline{g}', n' | V | \underline{g}, n \rangle &= -J \sum_{\underline{h}} \delta_{\underline{g}', \underline{g} + \underline{h}} \prod_{\underline{k}} \left\{ \left[1 - \left(\frac{4}{N} \right) \left(n_{\underline{k}} + \frac{1}{2} \right) \right. \right. \\
 &\quad \left. \left. \times \gamma_{\underline{k} \cdot \underline{h}} \cos^2 \left\{ \underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2}) + \frac{n}{4} \right\} \right] \delta_{n'_{\underline{k}}, n_{\underline{k}}} \right. \\
 &\quad \left. \mp \left[\left(\frac{8}{N} \right)^{1/2} \epsilon_{\underline{k} \cdot \underline{h}} \gamma_{\underline{k} \cdot \underline{h}}^{1/2} \left(\frac{n_{\underline{k}} + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \cos \left\{ \underline{k} \cdot (\underline{g} + \frac{\underline{h}}{2}) + \frac{n}{4} \right\} \right] \delta_{n'_{\underline{k}}, n_{\underline{k}} \pm 1} \right\}, \\
 &\hspace{15em} (\text{A5.c.9})
 \end{aligned}$$

which is exactly the expression obtained by Holstein (cf. text equ. (4.25)), for the case of equal electron-lattice interaction parameters.

Part II

Thermoelectric Power due to
small-polaron hopping motion

Chapter 6

General expressions for the transport coefficients for a two-site jump.

Having generalized the M.C.M. in a more realistic form suitable for the study of the thermoelectric power, and having given the thermodynamical origin of thermoelectricity, we are now in a position to study the thermoelectric power problem. We start from the situation in which the small-polaron hops between two energetically inequivalent sites which have different electron-lattice interaction parameters but where the stiffness of the lattice sites remains unaltered.

This situation, although "microscopic", contains all the physical features of the problem. Then, once having derived an expression for the thermoelectric power associated with any pair of sites, the macroscopic thermoelectric power of a material can be calculated using percolation-theoretic considerations.

From thermodynamical considerations, given before, the heat current density operator, Q , is expressed as

$$Q = u - \mu \frac{j}{q} \quad (6.1)$$

where u is the energy current density operator, given by

$$u = \frac{vH + Hv}{2} \quad (6.2)$$

Here, v is the small-polaron velocity operator, H is the Hamiltonian of the system, with matrix elements

$$\langle m | H | n \rangle = \langle m | H_0 + V | n \rangle = E_n \delta_{mn} + \langle m | V | n \rangle \quad (6.3)$$

where $|n\rangle \equiv |g, \{n_k\}\rangle$ are the eigenstates of H , H_0 is the zeroth-order (i.e. $J=0$) Hamiltonian with corresponding eigenvalues

$$E_n = E_{g, \{n_k\}} = \epsilon_g(0) - E_b(g) + \sum_k \hbar \omega_k (n_k + \frac{1}{2}) \quad (6.4)$$

and V is the overlap part of the Hamiltonian. The matrix elements of V , for the G.M.C.M., are given by

$$\begin{aligned} \langle m | V | n \rangle &= \langle g', \{n'_k\} | V | g, \{n_k\} \rangle \\ &= -J \sum_h \delta_{g', g+h} \prod_k \left\{ \left[1 - \left(\frac{1}{N}\right) \left(n_k + \frac{1}{2}\right) \frac{1}{2M\omega_k^2 (\hbar\omega_k)} \right. \right. \\ &\quad \left. \left\{ A_{g+h}^2 [1 - \lambda \sin(2k \cdot (g+h))] + A_g^2 [1 - \lambda \sin 2k \cdot g] \right. \right. \\ &\quad \left. \left. - 2 A_g A_{g+h} [\cos k \cdot h - \lambda \sin(2k \cdot (g + \frac{h}{2}))] \right\} \right\} \delta_{n'_k, n_k} \\ &\quad \mp \left(\frac{4}{N}\right) \left(\frac{n_k + \frac{1}{2} \pm \frac{1}{2}}{2}\right)^{1/2} \frac{1}{2^{1/2} M^{1/2} \omega_k (\hbar\omega_k)^{1/2}} \\ &\quad \left\{ A_{g+h} \sin[k \cdot (g+h) + \frac{\pi}{4}] - A_g (k \cdot g + \frac{\pi}{4}) \right\} \delta_{n'_k, n_k \pm 1}. \end{aligned} \quad (6.5)$$

Further, in equ.(6.1), j is the charge current density operator

(i.e. $\frac{j}{q}$ is the particle current density operator), μ is the chemical potential in thermal equilibrium, and q is the carrier's charge. For an electron, $q = -|e|$.

In Chapter 3, the thermoelectric power, was defined as

$$\alpha \equiv \frac{L}{q} = \frac{\pi}{T} = \frac{1}{q} (q L^{(1)} - L^{(2)} - \mu) , \quad (6.6)$$

where

$$L^{(1)} = \int_0^\infty dt \int_0^\beta d\lambda \langle j(-i\hbar\lambda) j(t) \rangle , \quad (6.7)$$

and

$$L^{(2)} = \int_0^\infty dt \int_0^\beta d\lambda \langle j(-i\hbar\lambda) u(t) \rangle . \quad (6.8)$$

Here, $\langle \dots \rangle$ means the thermal average, given by

$$\langle A \rangle = \frac{1}{Z} \sum_n \exp(-\beta E_n) A , \quad (6.9)$$

where $Z = \sum_n \exp(-\beta E_n)$ is the canonical partition function of the system, E_n is defined by equ. (6.4), and $\beta = \frac{1}{kT}$. The operators $j(-i\hbar\lambda)$, $j(t)$, and $u(t)$ appearing in eqs. (6.7), and (6.8) are taken in the interaction picture to be of the general form

$$B(t) = \exp\left[\left(-\frac{it}{\hbar}\right) H_0\right] B \exp\left[\left(\frac{it}{\hbar}\right) H_0\right] \quad (6.10)$$

From the above expressions, it is clear that what is actually evaluated is the Peltier coefficient π under isothermal conditions. Then, from Onsager's relation, $\pi = \alpha T$, we obtain the expression for the thermoelectric power, α . In this way, we

avoid the problem of having to incorporate a temperature gradient on a microscopic scale.

To this end we evaluate the coefficients $L^{(1)}$, and $L^{(2)}$, given by equs. (6.7), and (6.8) for a given pair of sites which are energetically inequivalent, under isothermal conditions. The electron-lattice interaction parameter is assumed to be different for the electron residing on different sites, resulting in different small-polaron binding energies for each lattice site, as described in Chapter 5, where the Generalized M.C.M. was introduced.

In order to evaluate the coefficient $L^{(2)}$, we first have to evaluate the thermal average $\langle j(-i\hbar\lambda) u(t) \rangle$. According to equ. (6.9),

$$\langle j(-i\hbar\lambda) u(t) \rangle = \frac{1}{Z} \sum_n \exp(-\beta E_n) j(-i\hbar\lambda) u(t) , \quad (6.11)$$

where ⁽ⁱ⁾

$$j(-i\hbar\lambda) = n_c q v(-i\hbar\lambda) , \quad (6.12)$$

and

$$u(t) = \frac{[v(t)H(t) + H(t)v(t)]}{2} , \quad (6.13)$$

where n_c is the charge carrier density. The meaning of the other quantities has been given before.

Substituting equs. (6.12), (6.13) into equ. (6.11), using equ. (6.3), and expressing the operators in the interaction

(i) This assumes n_c independent, non-interacting small-polarons.

picture according to equ.(6.10), we obtain

$$\langle j(-i\hbar\lambda)u(t) \rangle = \langle j(-i\hbar\lambda)u(t) \rangle_1 + \langle j(-i\hbar\lambda)u(t) \rangle_2, \quad (6.14)$$

where

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_1 &\equiv q n_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right) \\ &\quad \exp[(E_n - E_m)\lambda] |\langle n|v|m \rangle|^2 \exp\left[(-\frac{it}{\hbar})(E_n - E_m)\right], \end{aligned} \quad (6.15)$$

and

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_2 &\equiv \frac{q n_c}{2} \frac{1}{Z} \sum_{nm\ell} \exp(-\beta E_n) \exp[(E_n - E_m)\lambda] \\ &\quad \exp\left[(-\frac{it}{\hbar})(E_n - E_m)\right] \{ \langle n|v|m \rangle \langle m|v|\ell \rangle \langle \ell|V|n \rangle \\ &\quad + \langle n|v|m \rangle \langle m|V|\ell \rangle \langle \ell|v|n \rangle \}. \end{aligned} \quad (6.16)$$

But (30),

$$\langle n|v|m \rangle = \langle \underline{g}, \{n_k\} | v | \underline{g}', \{n'_k\} \rangle = \left(\frac{i}{\hbar} \right) \langle n|V|m \rangle (\underline{g} - \underline{g}'). \quad (6.17)$$

Substituting equ.(6.17) into equ.(6.16), we obtain

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_2 &= \frac{q n_c}{2} \frac{1}{Z} \sum_{nm\ell} \exp(-\beta E_n) \exp[(E_n - E_m)\lambda] \\ &\quad \exp\left[(-\frac{it}{\hbar})(E_n - E_m)\right] \left(\frac{i}{\hbar} \right)^2 \{ \langle n|V|m \rangle \langle m|V|\ell \rangle \langle \ell|V|n \rangle \\ &\quad [- (\underline{g} - \underline{g}')^2] \}. \end{aligned} \quad (6.18)$$

But, $\langle n|V|m \rangle \propto J$ (cf. equ.(5.28)) where J is the transfer integral.

Thus $\langle j(-i\hbar\lambda)u(t) \rangle_2 \propto J^3$, which is negligible in lowest order in

J in the jump-perturbation approximation. Thus,

$$\langle j(-i\hbar\lambda) u(t) \rangle_2 \simeq 0. \quad (6.19)$$

Then, equ. (6.15) reduces to

$$\begin{aligned} \langle j(-i\hbar\lambda) u(t) \rangle &= \langle j(-i\hbar\lambda) u(t) \rangle_1 \\ &= q \eta_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right) \\ &\quad \exp[(E_n - E_m)\lambda] | \langle n | u | m \rangle |^2 \\ &\quad \exp \left[\left(-\frac{it}{\hbar} \right) (E_n - E_m) \right]. \end{aligned} \quad (6.20)$$

The details of the above calculations are given in Appendix A6.a.

Emin⁽²⁹⁾ has evaluated the thermal average $\langle j(-i\hbar\lambda) j(t) \rangle$. We recall here his result, the proof of which is given in Appendix A6.b, for completeness. The expression for $\langle j(-i\hbar\lambda) j(t) \rangle$ is given by

$$\begin{aligned} \langle j(-i\hbar\lambda) j(t) \rangle &= q^2 \eta_c \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_m \exp[(E_n - E_m)\lambda] \\ &\quad \exp \left[\left(-\frac{it}{\hbar} \right) (E_n - E_m) \right] | \langle n | u | m \rangle |^2. \end{aligned} \quad (6.21)$$

Having now obtained the general expressions for the thermal averages of $j(-i\hbar\lambda) u(t)$, and $j(-i\hbar\lambda) j(t)$, given by

equs. (6.20) and (6.21), respectively, we are in position to proceed to the evaluation of the coefficients $L^{(2)}$, and $L^{(1)}$ given by equs. (6.8), and (6.7), respectively. Substituting equ.(6.20) into equ.(6.8), and performing the λ -integration, we obtain

$$\begin{aligned}
 L^{(2)} &= q n_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right) |\langle n | v | m \rangle|^2 \\
 &\quad \left[\frac{\exp[\beta(E_n - E_m) - 1]}{E_n - E_m} \right] \int_0^\infty \exp\left[(-\frac{it}{\hbar})(E_n - E_m)\right] dt \\
 &= q n_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right) |\langle n | v | m \rangle|^2 \\
 &\quad \left[\frac{\exp[\beta(E_n - E_m) - 1]}{E_n - E_m} \right] F_{n,m}, \quad (6.22)
 \end{aligned}$$

where

$$\begin{aligned}
 F_{n,m} &= \frac{1}{2} \lim_{\tau \rightarrow \infty} \int_0^\tau dt \left\{ \exp\left[(-\frac{it}{\hbar})(E_n - E_m)\right] + c.c. \right\} \\
 &= \lim_{\tau \rightarrow \infty} \left\{ \frac{t}{E_n - E_m} \sin\left[\frac{(E_n - E_m)\tau}{\hbar}\right] \right\} \\
 &= \pi \hbar \delta(E_n - E_m). \quad (6.23)
 \end{aligned}$$

Employing the δ -character of $F_{n,m}$ in equ.(6.22), one readily obtains

$$L^{(2)} = q n_c \beta \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right) |\langle n | v | m \rangle|^2 F_{n,m}. \quad (6.24)$$

Now, let us take $\langle n | \equiv \langle \underline{g}, \{n_{\underline{x}}\} |$, $|m\rangle \equiv | \underline{g}', \{n'_{\underline{x}}\} \rangle$, where the sites $\underline{g}, \underline{g}'$ are fixed and $\{n_{\underline{x}}\}, \{n'_{\underline{x}}\}$ are the totality of the vibrational quantum numbers $\{\dots n_{\underline{x}} \dots\}, \{\dots n'_{\underline{x}} \dots\}$ when the carrier is localized on site $\underline{g}$ or $\underline{g}'$, respectively. From equ. (6.24) we evaluate $L_{\underline{g}\underline{g}'}^{(2)}$, which stands for $L^{(2)}$ when a small-polaron hops from site $\underline{g}$ to site $\underline{g}'$.

$$L_{\underline{g}\underline{g}'}^{(2)} = \frac{1}{\tau} \sum_{\{n'_{\underline{x}}\}} \left(\frac{E_{\underline{g}, \{n_{\underline{x}}\}} + E_{\underline{g}', \{n'_{\underline{x}}\}}}{2} \right) | \langle \underline{g}', \{n'_{\underline{x}}\} | v | \underline{g}, \{n_{\underline{x}}\} \rangle |^2 F_{(\underline{g}, \{n_{\underline{x}}\}), (\underline{g}', \{n'_{\underline{x}}\})} >, \quad (6.25)$$

where the outer brackets denote a thermal average over the set of phonon occupation numbers, $\{\dots n_{\underline{x}} \dots\}$, and

$$\begin{aligned} F_{(\underline{g}, \{n_{\underline{x}}\}), (\underline{g}', \{n'_{\underline{x}}\})} &= \frac{1}{2} \lim_{\tau \rightarrow \infty} \int_0^\tau dt \{ \exp [(\frac{it}{\hbar}) \Delta \underline{g}'\underline{g}] \\ &\quad \exp [(-\frac{it}{\hbar}) \sum_{\underline{k}} \hbar \omega_{\underline{k}} (n_{\underline{k}} - n'_{\underline{k}})] + c.c. \} \\ &= \frac{1}{2} \lim_{\tau \rightarrow \infty} \int_{-\tau}^\tau dt \{ \exp [(\frac{it}{\hbar}) \Delta \underline{g}'\underline{g}] \\ &\quad \exp [(-\frac{it}{\hbar}) \sum_{\underline{k}} \hbar \omega_{\underline{k}} (n_{\underline{k}} - n'_{\underline{k}})] \}, \end{aligned} \quad (6.26)$$

where

$$\Delta \underline{g}'\underline{g} = [\epsilon_{\underline{g}'}(0) - E_b(\underline{g}')] - [\epsilon_{\underline{g}}(0) - E_b(\underline{g})]. \quad (6.27)$$

In order to obtain equ. (6.26), the expression for the eigenvalues $E_n = E_{\underline{g}, \{n_{\underline{x}}\}}$, given by equ. (6.24) has been used. Substi-

tuting equ. (6.26) into equ. (6.25), and using equ. (6.24) we obtain

$$L_{\underline{g}\underline{g}'}^{(2)} = L_{(1),\underline{g}\underline{g}'}^{(2)} + L_{(2),\underline{g}\underline{g}'}^{(2)}, \quad (6.28)$$

where

$$L_{(1),\underline{g}\underline{g}'}^{(2)} = \frac{q n_c \beta}{2} \frac{\tilde{E}(\underline{g}, \underline{g}')}{2} < \sum_{\{n_k'\}} | \langle \underline{g}', \{n_k'\} | \underline{v} | \underline{g}, \{n_k\} \rangle |^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n_k') \right] \rangle, \quad (6.29)$$

and

$$L_{(2),\underline{g}\underline{g}'}^{(2)} = \frac{q n_c \beta}{2} < \sum_{\{n_k'\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n_k' + 1) | \langle \underline{g}', \{n_k'\} | \underline{v} | \underline{g}, \{n_k\} \rangle |^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n_k') \right] \rangle, \quad (6.30)$$

where

$$\tilde{E}(\underline{g}, \underline{g}') = \frac{[E_{\underline{g}}(0) - E_b(\underline{g})] + [E_{\underline{g}'}(0) - E_b(\underline{g}')] }{2} \quad (6.31)$$

is the mean energy of the two-site system. Proceeding in the same way for the coefficient $L_{\underline{g}\underline{g}'}^{(1)}$ we find

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta}{2} < \sum_{\{n_k'\}} | \langle \underline{g}', \{n_k'\} | \underline{v} | \underline{g}, \{n_k\} \rangle |^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n_k') \right] \rangle. \quad (6.32)$$

Using the result obtained for the coefficient $L_{\underline{g}\underline{g}'}^{(1)}$ equ.

(6.29) can be written as

$$L_{(1), \underline{g} \underline{g}'}^{(2)} = \frac{1}{\underline{g}} \tilde{E}(\underline{g}, \underline{g}') L_{\underline{g} \underline{g}'}^{(1)} \quad (6.33)$$

Now we proceed to the evaluation of $L_{(2), \underline{g} \underline{g}'}^{(2)}$, given by equ. (6.30). Using the expression⁽³⁰⁾

$$\begin{aligned} | \langle \underline{g}', \{n'_k\} | \hat{V} | \underline{g}, \{n_k\} \rangle |^2 &= \left(\frac{1}{\hbar} \right)^2 \alpha^2 | \langle \underline{g}', \{n'_k\} | \hat{V} | \underline{g}, \{n_k\} \rangle |^2 \\ &= \left(\frac{J}{\hbar} \right)^2 \alpha^2 \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \delta_{n'_k, n_k} + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k-1} \right. \\ &\quad \left. + \left(\frac{n_k+1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k+1} \right\} \quad (6.34) \end{aligned}$$

obtained in Appendix (A5.b), (cf. equ. (A5.b.11)), where

$$\begin{aligned} \hbar_k^2 &= \frac{1}{2 M \omega_k^2 \hbar \omega_k} \left(\frac{2}{N} \right) \left\{ A_{\underline{g}'}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g}')) + A_{\underline{g}}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g})) \right. \\ &\quad \left. - 2 A_{\underline{g}} A_{\underline{g}'} [\cos(\underline{k} \cdot \underline{h}) - \lambda \sin[\underline{k} \cdot (\underline{g} + \underline{g}')]] \right\} \quad (6.35) \end{aligned}$$

equ. (6.30) can be written as

$$\begin{aligned} L_{(2), \underline{g} \underline{g}'}^{(2)} &= \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g} \underline{g}'} \right] \\ &\quad < \sum_{\{n'_k\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n'_k + 1) \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \delta_{n'_k, n_k} \right. \\ &\quad \left. + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k-1} + \left(\frac{n_k+1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k+1} \right\} \\ &\quad \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n'_k) \right] >. \quad (6.36) \end{aligned}$$

After considerable manipulation, given in Appendix A6.c.,
equ. (6.36) finally becomes

$$\begin{aligned}
 L_{(2), g g'}^{(2)} &= \frac{q n_c \beta \alpha^2}{2} \left[\sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{B \hbar \omega_{\underline{k}}}{2} \right] \left(\frac{J}{\hbar} \right)^2 \\
 &\quad \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g g' \right] \exp [-S'(\underline{k})] \\
 &\quad \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] \\
 &\quad + \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g g' \right] \\
 &\quad \left\{ \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \cos \omega_{\underline{k}} t \right\} \\
 &\quad \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] \\
 &\quad + \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g g' \right] \\
 &\quad \left\{ i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{B \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \sin \omega_{\underline{k}} t \right\} \\
 &\quad \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] , \quad (6.37)
 \end{aligned}$$

where

$$\begin{aligned}
 S'(\underline{k}) &\equiv \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \coth \frac{B \hbar \omega_{\underline{k}}}{2} , \\
 F_1'(\underline{k}, t) &\equiv \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t , \\
 F_2'(\underline{k}, t) &\equiv \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \sin \omega_{\underline{k}} t .
 \end{aligned}$$

At this stage of calculations the coefficient $L_{\underline{g}\underline{g}'}^{(1)}$ is given by

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \\ \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] . \quad (6.39)$$

The proof of equ.(6.39) is given in Appendix A6.d., for completeness.

In this Chapter we derived the general expressions for the transport coefficients $L_{\underline{g}\underline{g}'}^{(1)}$ and $L_{\underline{g}\underline{g}'}^{(2)}$, when a small-polaron hops from a site $\underline{g}$ to a nearest neighbouring site $\underline{g}'$ of a G.M.C.M. We found that they are given by

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \\ \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] , \quad (6.40)$$

and

$$L_{\underline{g}\underline{g}'}^{(2)} = \frac{1}{q} \tilde{E}(\underline{g}, \underline{g}') L_{\underline{g}\underline{g}'}^{(1)} \\ + \frac{q n_c \beta \alpha^2}{2} \left[\sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \right] \left(\frac{J}{\hbar} \right)^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right] \exp [-S'(\underline{k})] \\ \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] \\ + \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}\underline{g}'} \right]$$

$$\begin{aligned}
 & \left\{ \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \cos \omega_{\underline{k}} t \right\} \\
 & \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] \\
 & + \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{i t}{\hbar} \right) \Delta_{\underline{g}' \underline{g}} \right] \\
 & \left\{ i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \hbar \frac{\beta \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \sin \omega_{\underline{k}} t \right\} \\
 & \exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] , \quad (6.41)
 \end{aligned}$$

where $\tilde{E}(\underline{g}, \underline{g}')$, $\Delta_{\underline{g}' \underline{g}}$ are given by equs. (6.31), (6.27), respectively, and $S'(\underline{k})$, $F_1'(\underline{k}, t)$, $F_2'(\underline{k}, t)$ are given by equs. (6.38). In the next Chapter we shall use these expressions for the transport coefficients in order to derive their form in the weak-dispersion limit.

Appendix A6.a.

Evaluation of the thermal average $\langle j(-i\hbar\lambda)u(t) \rangle$.

According to the text equ.(6.9), the thermal average $\langle j(-i\hbar\lambda)u(t) \rangle$ is given by

$$\langle j(-i\hbar\lambda)u(t) \rangle = \frac{1}{Z} \sum_n \exp(-\beta E_n) j(-i\hbar\lambda)u(t), \quad (\text{A6.a.1})$$

where $Z = \sum_n \exp(-\beta E_n)$ is the canonical partition function of the system, E_n is defined by the text equ. (6.4), $\beta = 1/kT$; $j(-i\hbar\lambda)$ is given by

$$j(-i\hbar\lambda) = n_c q v(-i\hbar\lambda), \quad (\text{A6.a.2})$$

and

$$u(t) = \frac{[v(t)H(t) + H(t)v(t)]}{2}, \quad (\text{A6.a.3})$$

where v is the small-polaron velocity operator, q is the carrier's charge, n_c is the charge carrier density, $u(t)$ is the energy current density operator and H is the Hamiltonian of the system. All the operators are taken in the interaction

picture given by the text equ.(6.10). Substituting equs. (A6.a.2), and (A6.a.3) into equ.(A6.a.1), we obtain

$$\begin{aligned} \langle j(-i\hbar\lambda) u(t) \rangle &= \frac{q\eta_c}{2} \langle v(-i\hbar\lambda) [v(t)H(t) + H(t)v(t)] \rangle - \\ &= \frac{q\eta_c}{2} \langle v(-i\hbar\lambda) v(t) H(t) \rangle \\ &+ \frac{q\eta_c}{2} \langle v(-i\hbar\lambda) H(t) v(t) \rangle . \quad (\text{A6.a.4}) \end{aligned}$$

Taking explicitly the thermal average in equ. (A6.a.4),

$$\begin{aligned} \langle j(-i\hbar\lambda) u(t) \rangle &= \frac{q\eta_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \\ &\langle n | \exp\left[\frac{iH}{\hbar}(-i\hbar\lambda)\right] v \exp\left[\left(-\frac{iH}{\hbar}\right)(-i\hbar\lambda)\right] \\ &\exp\left(\frac{iHt}{\hbar}\right) v \exp\left(-\frac{iHt}{\hbar}\right) \exp\left(\frac{iHt}{\hbar}\right) H \exp\left(-\frac{iHt}{\hbar}\right) | n \rangle \\ &+ \frac{q\eta_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \\ &\langle n | \exp\left[\frac{iH}{\hbar}(-i\hbar\lambda)\right] v \exp\left[\left(-\frac{iH}{\hbar}\right)(-i\hbar\lambda)\right] \\ &\exp\left(\frac{iHt}{\hbar}\right) H \exp\left(-\frac{iHt}{\hbar}\right) \exp\left(\frac{iHt}{\hbar}\right) v \exp\left(-\frac{iHt}{\hbar}\right) | n \rangle, \end{aligned}$$

(A6.a.5)

where $\langle n | \equiv \langle q, \{n_x\} |$ are the eigenstates of H , which has matrix elements given by

$$\langle m | H | n \rangle = \langle m | H_0 + V | n \rangle = E_n \delta_{mn} + \langle m | V | n \rangle .$$

(A6.a.6)

Here, H_0 is the zeroth-order (i.e. $J=0$) Hamiltonian, with corresponding eigenvalues

$$E_n = E_{g, \{n_k\}} = \epsilon_g(0) - E_b(g) + \sum_k \hbar \omega_k (n_k + \frac{1}{2}), \quad (A6.a.7)$$

and $\langle m | V | n \rangle$ are the matrix elements of the overlap part of the Hamiltonian, where vibrational as well as electronic overlap are included. The analytic expression for $\langle m | V | n \rangle$ is given by the text equ.(6.5).

Then equ. (A6.a.5) becomes

$$\langle j(-i\hbar\lambda) u(t) \rangle = \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_{m\ell} \langle n | \exp(H\lambda)$$

$$v \exp(-H\lambda) | m \rangle \langle m | \exp(\frac{iHt}{\hbar}) v \exp(-\frac{iHt}{\hbar}) | \ell \rangle$$

$$\langle \ell | \exp(\frac{iHt}{\hbar}) H \exp(-\frac{iHt}{\hbar}) | n \rangle$$

$$+ \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_{m\ell} \langle n | \exp(H\lambda)$$

$$v \exp(-H\lambda) | m \rangle \langle m | \exp(\frac{iHt}{\hbar}) H \exp(-\frac{iHt}{\hbar}) | \ell \rangle$$

$$\langle \ell | \exp(\frac{iHt}{\hbar}) v \exp(-\frac{iHt}{\hbar}) | n \rangle$$

$$= \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_m \exp[(E_n - E_m)\lambda]$$

$$\langle n | v | m \rangle \exp[(-\frac{it}{\hbar})(E_n - E_m)] \langle m | v | n \rangle E_n$$

$$+ \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_{m\ell} \exp[(E_n - E_m)\lambda]$$

$$\langle n|v|m\rangle \exp\left[\left(-\frac{it}{\hbar}\right)(E_\ell - E_m)\right] \langle m|v|\ell\rangle$$

$$\exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_\ell)\right] \langle \ell|v|n\rangle$$

$$+ \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_{m\ell} \exp[(E_n - E_m)\lambda]$$

$$\langle n|v|m\rangle \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] E_m \langle m|v|\ell\rangle$$

$$+ \frac{q n_c}{2} \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_{m\ell} \exp[(E_n - E_m)\lambda]$$

$$\langle n|v|m\rangle \exp\left[\left(-\frac{it}{\hbar}\right)(E_\ell - E_m)\right] \langle m|v|\ell\rangle$$

$$\exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_\ell)\right] \langle \ell|v|n\rangle$$

$$= \langle j(-i\hbar\lambda)u(t) \rangle_1 + \langle j(-i\hbar\lambda)u(t) \rangle_2,$$

where

(A6.a.8)

$$\langle j(-i\hbar\lambda)u(t) \rangle_1 = \frac{q n_c}{2} \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right)$$

$$|\langle n|v|m\rangle|^2 \exp[(E_n - E_m)\lambda]$$

$$\exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right], \quad (\text{A6.a.9})$$

and

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_2 &= \frac{q n_c}{2} \frac{1}{Z} \sum_{nml} \exp(-\beta E_n) \exp[(E_n - E_m)\lambda] \\ &\quad \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] \{ \langle n|v|m\rangle \langle m|v|l\rangle \\ &\quad \langle l|v|n\rangle + \langle n|v|m\rangle \langle m|v|l\rangle \langle l|v|n\rangle \}. \end{aligned} \quad (A6.a.10)$$

Using the fact that

$$\langle n|v|m\rangle \equiv \langle \underline{g}, \{n_k\} | v | \underline{g}', \{n'_k\} \rangle = \left(\frac{i}{\hbar}\right) \langle n|v|m\rangle (g - g'),$$

equ. (A6.a.10) can be written as

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_2 &= \frac{q n_c}{2} \frac{1}{Z} \sum_{nml} \exp(-\beta E_n) \exp[(E_n - E_m)\lambda] \\ &\quad \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] \\ &\quad \left(\frac{i}{\hbar}\right)^2 \{ \langle n|v|m\rangle (g - g') \langle m|v|l\rangle (g - g'') \langle l|v|n\rangle \\ &\quad + \langle n|v|m\rangle (g - g') \langle m|v|l\rangle \langle l|v|n\rangle (g'' - g) \}, \end{aligned} \quad (A6.a.11)$$

where $\langle n| \equiv \langle \underline{g}, \{n_k\} |$, $\langle m| \equiv \langle \underline{g}', \{n'_k\} |$, and $\langle l| \equiv \langle \underline{g}'', \{n''_k\} |$. Finally, equ. (A6.a.11) becomes

$$\begin{aligned} \langle j(-i\hbar\lambda)u(t) \rangle_2 &= \frac{q n_c}{2} \frac{1}{Z} \sum_{nml} \exp(-\beta E_n) \exp[(E_n - E_m)\lambda] \\ &\quad \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] \\ &\quad \langle n|v|m\rangle \langle m|v|l\rangle \langle l|v|n\rangle [-(g - g')^2]. \end{aligned} \quad (A6.a.12)$$

But $\langle n|V|m \rangle \propto J$ where J is the transfer integral. Thus

$$\langle j(-i\hbar\lambda)u(t) \rangle_2 \propto J^3, \quad (\text{A6.a.13})$$

which is negligible in lowest order in J , in the jump-perturbation approximation, i.e. $\langle j(-i\hbar\lambda)u(t) \rangle_2 \approx 0$.

Then equ. (A6.a.8) reduces to

$$\langle j(-i\hbar\lambda)u(t) \rangle = \langle j(-i\hbar\lambda)u(t) \rangle_1$$

$$= q n_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) \left(\frac{E_n + E_m}{2} \right)$$

$$\exp[(E_n - E_m)\lambda] |\langle n|v|m \rangle|^2 \exp\left[-\frac{it}{\hbar}(E_n - E_m)\right].$$

(A6.a.14)

Equation (A6.a.14) is the text equ. (6.20).

Appendix A6.b.

Evaluation of the thermal average $\langle j(-i\hbar\lambda) j(t) \rangle$.

According to the text equ. (6.9), the thermal average $\langle j(-i\hbar\lambda) j(t) \rangle$ is given by

$$\langle j(-i\hbar\lambda) j(t) \rangle = \frac{1}{Z} \sum_n \exp(-\beta E_n) j(-i\hbar\lambda) j(t) .$$

(A6.b.1)

Taking into account the text equs. (6.12), and (6.10), equ. (A6.b.1) can be written as

$$\langle j(-i\hbar\lambda) j(t) \rangle = q^2 n_c \frac{1}{Z} \sum_n \exp(-\beta E_n)$$

$$\langle n | \exp(H\lambda) v \exp(-H\lambda)$$

$$\exp\left(\frac{iHt}{\hbar}\right) v \exp\left(-\frac{iHt}{\hbar}\right) |n\rangle$$

$$= q^2 n_c \frac{1}{Z} \sum_n \exp(-\beta E_n)$$

$$\sum_m \exp[(E_n - E_m)\lambda] \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] |\langle n | v | m \rangle|^2,$$

(A6.b.2)

where the text equ. (6.3) has been taken into account.

Equation (A6.b.2) is the text equ.(6.21).

Appendix A6.c.

Evaluation of the coefficient $L_{(2), \underline{g} \underline{g}'}^{(2)}$.

According to the text equ. (6.30),

$$L_{(2), \underline{g} \underline{g}'}^{(2)} = \frac{q n_c \beta}{2} < \sum_{\{n_k'\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n_k' + 1) | < \underline{g}', \{n_k'\} | v | \underline{g}, \{n_k\} > |^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta \underline{g} \underline{g}'\right] \exp\left[\left(-\frac{it}{\hbar}\right) \sum_k \hbar \omega_k (n_k - n_k')\right] >, \quad (A6.c.1)$$

where

$$\Delta \underline{g} \underline{g}' = [\epsilon_{\underline{g}'}(0) - E_b(\underline{g}')] - [\epsilon_{\underline{g}}(0) - E_b(\underline{g})], \quad (A6.c.2)$$

$$| < \underline{g}', \{n_k'\} | v | \underline{g}, \{n_k\} > |^2 = \left(\frac{1}{\hbar}\right)^2 \alpha^2 | < \underline{g}', \{n_k'\} | V | \underline{g}, \{n_k\} > |^2 \\ = \left(\frac{J}{\hbar}\right)^2 \alpha^2 \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2}\right) \hbar_k^2 \right] \delta_{n_k', n_k} + \left(\frac{n_k}{2}\right) \hbar_k^2 \delta_{n_k', n_k-1} \right. \\ \left. + \left(\frac{n_k+1}{2}\right) \hbar_k^2 \delta_{n_k', n_k+1} \right\}. \quad (A6.c.3)$$

Here,

$$\hbar_k^2 = \frac{1}{2M\omega_k^2 \hbar \omega_k} \left(\frac{2}{N}\right) \left\{ A_{\underline{g}'}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g}')) \right. \\ \left. + A_{\underline{g}}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g})) - 2 A_{\underline{g}} A_{\underline{g}'} [\cos(\underline{k} \cdot \underline{h}) - \lambda \sin(\underline{k} \cdot (\underline{g} + \underline{g}'))] \right\}, \quad (A6.c.4)$$

where $\lambda = \mp 1$ according to whether $\underline{k} \cdot \underline{h}$ is positive or

negative, respectively, and N is the total number of lattice sites.

Substituting equ. (A6.c.3) into equ. (A6.c.1), we obtain

$$L_{(2), g g'}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g' g \right]$$

$$\left\langle \sum_{\{n'_k\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n'_k + 1) \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \delta_{n'_k, n_k} \right. \right.$$

$$\left. \left. + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k - 1} + \left(\frac{n_k + 1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k + 1} \right\} \right.$$

$$\left. \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n'_k) \right] \right\rangle . \quad (\text{A6.c.5})$$

Equation (A6.c.5) is the text equ. (6.36).

Let us examine the term in the brackets $\langle \dots \rangle$ of equ. (A6.c.5):

$$\sum_{\{n'_k\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n'_k + 1) \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \delta_{n'_k, n_k} \right.$$

$$\left. + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k - 1} + \left(\frac{n_k + 1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k + 1} \right\} \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n'_k) \right]$$

$$= \sum_{\{n'_k\}} \sum_k \frac{\hbar \omega_k}{2} (n_k + n'_k + 1) \prod_k \left\{ 1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k} \right.$$

$$\left. + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k - 1} + \left(\frac{n_k + 1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k + 1} \right\} \exp(-it) \omega_k (n_k - n'_k) \} .$$

(A6.c.6)

Defining

$$\left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \equiv A_{k, n_k} ,$$

$$\left(\frac{n_k}{2}\right) \hbar \omega_k \equiv B_{k, n_k} \quad , \quad \left(\frac{n_k+1}{2}\right) \hbar \omega_k \equiv C_{k, n_k} \quad ,$$

(A6.c.7)

$$\frac{\hbar \omega_k}{2} (n_k + n'_k + 1) \equiv \alpha_{k, n_k} \quad ,$$

$$(A_{k, n_k} \delta_{n'_k, n_k} + B_{k, n_k} \delta_{n'_k, n_k-1} + C_{k, n_k} \delta_{n'_k, n_k+1}) \exp[(-it) \omega_k (n_k - n'_k)] \equiv b_{k, n_k} \quad ,$$

and summing on k equ. (A6.c.6) becomes

$$\begin{aligned} & \sum_{\{n'_k\}} \left[\left\{ \frac{\hbar \omega_{k_1}}{2} (n_{k_1} + n'_{k_1} + 1) + \frac{\hbar \omega_{k_2}}{2} (n_{k_2} + n'_{k_2} + 1) + \dots \right\} \right. \\ & \quad \left\{ (A_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}} + B_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}-1} + C_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}+1}) \right. \\ & \quad \left. \exp[(-it) \omega_{k_1} (n_{k_1} - n'_{k_1})] \right\} \\ & \quad \left\{ (A_{k_2, n_{k_2}} \delta_{n'_{k_2}, n_{k_2}} + B_{k_2, n_{k_2}} \delta_{n'_{k_2}, n_{k_2}-1} + C_{k_2, n_{k_2}} \delta_{n'_{k_2}, n_{k_2}+1}) \right. \\ & \quad \left. \exp[(-it) \omega_{k_2} (n_{k_2} - n'_{k_2})] \right\} \\ & \quad \left. \dots \dots \dots \right] \end{aligned}$$

$$\begin{aligned} = & \sum_{\{n'_k\}} \left[\frac{\hbar \omega_{k_1}}{2} (n_{k_1} + n'_{k_1} + 1) \left\{ (A_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}} + B_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}-1} \right. \right. \\ & \left. \left. + C_{k_1, n_{k_1}} \delta_{n'_{k_1}, n_{k_1}+1}) \exp[(-it) \omega_{k_1} (n_{k_1} - n'_{k_1})] \right\} \right. \end{aligned}$$

$$\{ (A_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}} + B_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}-1} + C_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}+1})$$

$$\exp[(-it) \omega_{\underline{k}_2} (n_{\underline{k}_2} - n'_{\underline{k}_2})] \}$$

$$+ \{ (A_{\underline{k}_1, n_{\underline{k}_1}} \delta_{n'_{\underline{k}_1}, n_{\underline{k}_1}} + B_{\underline{k}_1, n_{\underline{k}_1}} \delta_{n'_{\underline{k}_1}, n_{\underline{k}_1}-1} + C_{\underline{k}_1, n_{\underline{k}_1}} \delta_{n'_{\underline{k}_1}, n_{\underline{k}_1}+1})$$

$$\exp[(-it) \omega_{\underline{k}_1} (n_{\underline{k}_1} - n'_{\underline{k}_1})] \}$$

$$\frac{\hbar \omega_{\underline{k}_2}}{2} (n_{\underline{k}_2} + n'_{\underline{k}_2} + 1) \} \{ (A_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}} + B_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}-1}$$

$$+ C_{\underline{k}_2, n_{\underline{k}_2}} \delta_{n'_{\underline{k}_2}, n_{\underline{k}_2}+1}) \exp[(-it) \omega_{\underline{k}_2} (n_{\underline{k}_2} - n'_{\underline{k}_2})] \}$$

$$= \sum_{n_{\underline{k}_1}} \alpha_{\underline{k}_1, n_{\underline{k}_1}} b_{\underline{k}_1, n_{\underline{k}_1}} \sum_{n_{\underline{k}_2}} b_{\underline{k}_2, n_{\underline{k}_2}} \sum_{n_{\underline{k}_3}} b_{\underline{k}_3, n_{\underline{k}_3}} \dots$$

$$+ \sum_{n_{\underline{k}_1}} b_{\underline{k}_1, n_{\underline{k}_1}} \sum_{n_{\underline{k}_2}} \alpha_{\underline{k}_2, n_{\underline{k}_2}} b_{\underline{k}_2, n_{\underline{k}_2}} \sum_{n_{\underline{k}_3}} b_{\underline{k}_3, n_{\underline{k}_3}} \dots + \dots$$

$$= \sum_{\underline{k}} \sum_{n_{\underline{k}}} \alpha_{\underline{k}, n_{\underline{k}}} b_{\underline{k}, n_{\underline{k}}} \prod_{\underline{k} \neq \underline{k}} b_{\underline{k}, n_{\underline{k}}} \quad (A6.c.8)$$

Substituting equ. (A6.c.8) into equ. (A6.c.5) we obtain

$$L_{(2), \underline{g} \underline{g}'}^{(2)} = \frac{q n_c B \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar} \right) \Delta \underline{g}' \underline{g} \right]$$

$$< \sum_{\underline{k}} \left[\sum_{n_{\underline{k}}} \frac{\hbar \omega_{\underline{k}}}{2} (n_{\underline{k}} + n'_{\underline{k}} + 1) \{ [1 - (n_{\underline{k}} + \frac{1}{2}) \hbar \underline{k}]^2 \} \delta_{n'_{\underline{k}}, n_{\underline{k}}} \right]$$

$$+ \left(\frac{n_{\underline{k}}}{2} \right) \hbar_{\underline{k}}^2 \delta_{n'_{\underline{k}}, n_{\underline{k}}-1} + \left(\frac{n_{\underline{k}}+1}{2} \right) \hbar_{\underline{k}}^2 \delta_{n'_{\underline{k}}, n_{\underline{k}}+1} \} \exp[(-it)\omega_{\underline{k}}(n_{\underline{k}}-n'_{\underline{k}})]$$

$$\prod_{\tilde{\underline{k}} \neq \underline{k}} \left[\left\{ \left(1 - (n_{\tilde{\underline{k}}} + \frac{1}{2}) \hbar_{\tilde{\underline{k}}}^2 \right) \delta_{n'_{\tilde{\underline{k}}}, n_{\tilde{\underline{k}}}} + \left(\frac{n_{\tilde{\underline{k}}}}{2} \right) \hbar_{\tilde{\underline{k}}}^2 \delta_{n'_{\tilde{\underline{k}}}, n_{\tilde{\underline{k}}}-1} \right. \right.$$

$$\left. + \left(\frac{n_{\tilde{\underline{k}}}+1}{2} \right) \hbar_{\tilde{\underline{k}}}^2 \delta_{n'_{\tilde{\underline{k}}}, n_{\tilde{\underline{k}}}+1} \right\} \exp[(-it)\omega_{\tilde{\underline{k}}}(n_{\tilde{\underline{k}}}-n'_{\tilde{\underline{k}}})] \right] > .$$

(A6.c.9)

Now, let us define

$$\hbar_{\underline{k}}^2 = \frac{1}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(\frac{1}{N} \right) \left[A_{\underline{g}'}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g}')) \right.$$

$$\left. + A_{\underline{g}}^2 (1 - \lambda \sin(2\underline{k} \cdot \underline{g})) - 2 A_{\underline{g}} A_{\underline{g}'} \{ \cos(\underline{k} \cdot \underline{h}) - \lambda \sin(\underline{k} \cdot (\underline{g} + \underline{g}')) \} \right]$$

$$\equiv 2 F(\underline{k}) .$$

(A6.c.10)

Then

$$L_{(2), \underline{g} \underline{g}'}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g} \underline{g}'} \right]$$

$$< \sum_{\underline{k}} \left\{ \hbar \omega_{\underline{k}} (n_{\underline{k}} + \frac{1}{2}) \left[1 - (2n_{\underline{k}} + 1) F(\underline{k}) \right] \right.$$

$$\left. + \hbar \omega_{\underline{k}} n_{\underline{k}}^2 F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + \hbar \omega_{\underline{k}} (n_{\underline{k}}+1)^2 F(\underline{k}) \exp(i\omega_{\underline{k}} t) \right\}$$

$$\prod_{\tilde{\underline{k}} \neq \underline{k}} \left[1 - (2n_{\tilde{\underline{k}}} + 1) F(\tilde{\underline{k}}) + n_{\tilde{\underline{k}}} F(\tilde{\underline{k}}) \exp(-i\omega_{\tilde{\underline{k}}} t) \right.$$

$$\left. + (n_{\tilde{\underline{k}}}+1) F(\tilde{\underline{k}}) \exp(i\omega_{\tilde{\underline{k}}} t) \right] > . \quad (\text{A6.c.11})$$

Let us evaluate the expression in bracket $\langle \dots \rangle$.

$$\sum_{\underline{k}} \{ \dots \} \prod_{\substack{\underline{k} \\ \underline{k} \neq \underline{k}}} [\dots]$$

$$= \sum_{\underline{k}} \left\{ \frac{\hbar \omega_{\underline{k}} \left\{ (n_{\underline{k}} + \frac{1}{2}) [1 - (2n_{\underline{k}} + 1) F(\underline{k})] + n_{\underline{k}}^2 F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + (n_{\underline{k}} + 1)^2 F(\underline{k}) \exp(i\omega_{\underline{k}} t) \right\}}{1 - (2n_{\underline{k}} + 1) F(\underline{k}) + n_{\underline{k}} F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + (n_{\underline{k}} + 1) F(\underline{k}) \exp(i\omega_{\underline{k}} t)} \right\}$$

$$\prod_{\underline{k}} [1 - (2n_{\underline{k}} + 1) F(\underline{k}) + n_{\underline{k}} F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + (n_{\underline{k}} + 1) F(\underline{k}) \exp(i\omega_{\underline{k}} t)].$$

(A6.c.12)

Let us define

$$W(\underline{k}, n_{\underline{k}}, t) \equiv (n_{\underline{k}} + \frac{1}{2}) [1 - (2n_{\underline{k}} + 1) F(\underline{k})] + n_{\underline{k}}^2 F(\underline{k}) \exp(-i\omega_{\underline{k}} t)$$

$$+ (n_{\underline{k}} + 1)^2 F(\underline{k}) \exp(i\omega_{\underline{k}} t)$$

$$= (n_{\underline{k}} + \frac{1}{2}) [1 - (2n_{\underline{k}} + 1) F(\underline{k})$$

$$+ (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t]$$

$$+ i (n_{\underline{k}} + \frac{1}{2}) F(\underline{k}) \sin \omega_{\underline{k}} t + \frac{1}{2} F(\underline{k}) \cos \omega_{\underline{k}} t, \quad (A6.c.13)$$

and

$$D(\underline{k}, n_{\underline{k}}, t) \equiv 1 - (2n_{\underline{k}} + 1) F(\underline{k}) + n_{\underline{k}} F(\underline{k}) \exp(-i\omega_{\underline{k}} t)$$

$$+ (n_{\underline{k}} + 1) F(\underline{k}) \exp(i\omega_{\underline{k}} t)$$

$$= 1 - (2n_{\underline{k}} + 1) F(\underline{k}) + (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t.$$

(A6.c.14)

Dividing equ. (A6.c.13) by equ. (A6.c.14), we obtain

$$\begin{aligned} & \frac{W(\underline{k}, n_{\underline{k}}, t)}{D(\underline{k}, n_{\underline{k}}, t)} \\ &= \frac{(n_{\underline{k}} + \frac{1}{2}) [1 - (2n_{\underline{k}} + 1) F(\underline{k})] + n_{\underline{k}}^2 F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + (n_{\underline{k}} + 1)^2 F(\underline{k}) \exp(i\omega_{\underline{k}} t)}{1 - (2n_{\underline{k}} + 1) F(\underline{k}) + n_{\underline{k}} F(\underline{k}) \exp(-i\omega_{\underline{k}} t) + (n_{\underline{k}} + 1) F(\underline{k}) \exp(i\omega_{\underline{k}} t)} \\ &= \frac{(n_{\underline{k}} + \frac{1}{2}) \{ 1 - (2n_{\underline{k}} + 1) F(\underline{k}) + (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t \}}{1 - (2n_{\underline{k}} + 1) F(\underline{k}) + (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t} \\ &+ \frac{i (n_{\underline{k}} + \frac{1}{2}) F(\underline{k}) \sin \omega_{\underline{k}} t + \frac{1}{2} F(\underline{k}) \cos \omega_{\underline{k}} t}{1 - (2n_{\underline{k}} + 1) F(\underline{k}) + (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t} = (n_{\underline{k}} + \frac{1}{2}) + \frac{1}{2} \frac{1}{i\omega_{\underline{k}}} \frac{\partial D(\underline{k}, n_{\underline{k}}, t)}{\partial t} \cdot \end{aligned}$$

(A6.c.15)

Substituting equ. (A6.c.15) into equ. (A6.c.12), we obtain

$$\begin{aligned} & \sum_{\underline{k}} \{ \dots \} \prod_{\underline{k} + \underline{k}} [\dots] \\ &= \sum_{\underline{k}} \hbar \omega_{\underline{k}} \left\{ (n_{\underline{k}} + \frac{1}{2}) + \frac{1}{2} \frac{1}{i\omega_{\underline{k}}} \frac{\partial D(\underline{k}, n_{\underline{k}}, t)}{\partial t} \right\} \prod_{\underline{k}} D(\underline{k}, n_{\underline{k}}, t) . \end{aligned}$$

(A6.c.16)

Then equ. (A6.c.11) becomes

$$\begin{aligned} L_{(2), g'g'}^{(2)} &= \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{g'g'} \right] \\ &\langle \sum_{\underline{k}} \hbar \omega_{\underline{k}} \left\{ (n_{\underline{k}} + \frac{1}{2}) + \frac{1}{2} \frac{1}{i\omega_{\underline{k}}} \frac{\partial D(\underline{k}, n_{\underline{k}}, t)}{\partial t} \right\} \prod_{\underline{k}} D(\underline{k}, n_{\underline{k}}, t) \rangle \end{aligned}$$

$$= \frac{q n_c B \alpha^2}{2} \left(-\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{i t}{\hbar} \right) \Delta g' g \right]$$

$$\left\langle \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \left\{ (2n_{\underline{k}} + 1) + \frac{1}{i\omega_{\underline{k}} t} \frac{d}{dt} \ln D(\underline{k}, n_{\underline{k}}, t) \right\} \prod_{\underline{k}} D(\underline{k}, n_{\underline{k}}, t) \right\rangle, \quad (\text{A6.c.17})$$

where $D(\underline{k}, n_{\underline{k}}, t)$ is given by equ. (A6.c.14) as

$$D(\underline{k}, n_{\underline{k}}, t) = 1 - F(\underline{k}) \{ (2n_{\underline{k}} + 1) - (2n_{\underline{k}} + 1) \cos \omega_{\underline{k}} t - i \sin \omega_{\underline{k}} t \}.$$

Using the fact that

$$F(\underline{k}) = \frac{J_{\underline{k}}^2}{2} \propto \left(\frac{1}{N} \right),$$

(c.f. equ. (A6.c.10)),

$$D(\underline{k}, n_{\underline{k}}, t) = \exp \left\{ -F(\underline{k}) [(2n_{\underline{k}} + 1) - (2n_{\underline{k}} + 1) \cos \omega_{\underline{k}} t - i \sin \omega_{\underline{k}} t] \right\}.$$

If we define

$$S(\underline{k}, n_{\underline{k}}) \equiv \frac{1}{2} (2n_{\underline{k}} + 1) F(\underline{k}),$$

$$F_1(\underline{k}, n_{\underline{k}}, t) \equiv (2n_{\underline{k}} + 1) F(\underline{k}) \cos \omega_{\underline{k}} t, \quad (\text{A6.c.18})$$

$$F_2(\underline{k}, t) \equiv F(\underline{k}) \sin \omega_{\underline{k}} t,$$

then

$$D(\underline{k}, n_{\underline{k}}, t) = \exp[-2S(\underline{k}, n_{\underline{k}})] \exp[F_1(\underline{k}, n_{\underline{k}}, t)] \exp[iF_2(\underline{k}, t)].$$

(A6.c.19)

From equ. (A6.c.19) we obtain

$$\ln D(\underline{k}, n_{\underline{k}}, t) = -2 S(\underline{k}, n_{\underline{k}}) + F_1(\underline{k}, n_{\underline{k}}, t) + i F_2(\underline{k}, t),$$

and using equs. (A6.c.18), we obtain

$$\frac{d}{dt} \ln D(\underline{k}, n_{\underline{k}}, t) = -(2n_{\underline{k}} + 1) F(\underline{k}) \omega_{\underline{k}} \sin \omega_{\underline{k}} t + i F(\underline{k}) \omega_{\underline{k}} \cos \omega_{\underline{k}} t.$$

Thus,

$$\frac{1}{i\omega_{\underline{k}} t} \frac{d}{dt} \ln D(\underline{k}, n_{\underline{k}}, t) = F(\underline{k}) [\cos \omega_{\underline{k}} t + i (2n_{\underline{k}} + 1) \sin \omega_{\underline{k}} t]. \quad (\text{A6.c.20})$$

Substituting the above equation into equ. (A6.c.17), we obtain

$$L_{(12), g'g}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g'g \right]$$

$$\left\{ \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \langle (2n_{\underline{k}} + 1) \rangle \prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle \right.$$

$$+ \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g'g \right]$$

$$\left\{ \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} F(\underline{k}) \cos \omega_{\underline{k}} t \right\} \prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle$$

$$+ \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g'g \right]$$

$$\left\{ \sum_{\underline{k}} i \frac{\hbar \omega_{\underline{k}}}{2} \langle (2n_{\underline{k}} + 1) \rangle F(\underline{k}) \sin \omega_{\underline{k}} t \right\} \prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle.$$

(A6.c.21)

Now, we shall proceed to the evaluation of the thermal averages $\langle (2n_k + 1) \rangle$ and $\langle D(k, n_k, t) \rangle$ appearing in equ. (A6.c.21)

$$\langle (2n_k + 1) \rangle = 2\langle n_k \rangle + 1 = 2 \frac{1}{\exp(\beta \hbar \omega_k) - 1} = \coth \frac{\beta \hbar \omega_k}{2}. \quad (\text{A6.c.22})$$

$$\begin{aligned} \langle D(k, n_k, t) \rangle &= \langle \exp[-2S(k, n_k)] \exp[F_1(k, n_k, t)] \exp[iF_2(k, t)] \rangle \\ &= \langle \exp\{-F(k)[(2n_k + 1) - (2n_k + 1)\cos\omega_k t - i\sin\omega_k t]\} \rangle. \end{aligned} \quad (\text{A6.c.23})$$

Before performing the thermal averages, let us evaluate the fluctuations of $D(k, n_k, t)$ about $\langle D(k, n_k, t) \rangle$.

$$\begin{aligned} &\langle [D(k, n_k, t) - \langle D(k, n_k, t) \rangle]^2 \rangle \\ &= \langle D^2(k, n_k, t) \rangle - \langle D(k, n_k, t) \rangle^2 \\ &= \langle (\exp[-F(k)\{(2n_k + 1) - (2n_k + 1)\cos\omega_k t - i\sin\omega_k t\}])^2 \rangle \\ &\quad - \langle \exp[-F(k)\{(2n_k + 1) - (2n_k + 1)\cos\omega_k t - i\sin\omega_k t\}] \rangle^2 \\ &= \langle 1 - 2F(k)\{(2n_k + 1) - (2n_k + 1)\cos\omega_k t - i\sin\omega_k t\} \rangle \\ &\quad - \langle 1 - F(k)\{(2n_k + 1) - (2n_k + 1)\cos\omega_k t - i\sin\omega_k t\} \rangle^2 \\ &= -[F(k)]^2 \{ \langle (2n_k + 1) \rangle - \langle (2n_k + 1) \rangle \cos\omega_k t - i\sin\omega_k t \}^2 \propto \left(\frac{1}{N}\right)^2 \end{aligned} \quad (\text{A6.c.24})$$

because from equ. (A6.c.10), $F(\underline{k}) \propto \frac{1}{N}$. Thus, the fluctuations of $D(\underline{k}, n_{\underline{k}}, t)$ about $\langle D(\underline{k}, n_{\underline{k}}, t) \rangle$ are negligible.

According to the above statement, equ. (A6.c.23) can be written as

$$\langle D(\underline{k}, n_{\underline{k}}, t) \rangle = \exp[-F(\underline{k}) \{ \langle (2n_{\underline{k}} + 1) \rangle - \langle (2n_{\underline{k}} + 1) \rangle \cos \omega_{\underline{k}} t - i \sin \omega_{\underline{k}} t \}],$$

and using equ. (A6.c.22),

$$\langle D(\underline{k}, n_{\underline{k}}, t) \rangle = 1 - F(\underline{k}) \left[\coth \frac{\beta \hbar \omega_{\underline{k}}}{2} - \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t - i \sin \omega_{\underline{k}} t \right].$$

(A6.c.25)

Then,

$$\prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle$$

$$= \prod_{\underline{k}} \left\{ 1 - F(\underline{k}) \left[\coth \frac{\beta \hbar \omega_{\underline{k}}}{2} - \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t - i \sin \omega_{\underline{k}} t \right] \right\}$$

$$= \exp \left\{ \sum_{\underline{k}} \left[-F(\underline{k}) \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} + F(\underline{k}) \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t \right] \right\}. \quad (\text{A6.c.26})$$

We shall now proceed to find a more simplified form for the expression $\sum_{\underline{k}} [\dots]$ appearing in equ. (A6.c.26). According to equ. (A6.c.10),

$$F(\underline{k}) \equiv \frac{\hbar^2}{2} = \left(\frac{1}{N}\right) \frac{1}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left[A_{\underline{g}'}^2 (1 - \lambda \sin(\underline{k} \cdot \underline{g}')) + A_{\underline{g}}^2 (1 - \lambda \sin(\underline{k} \cdot \underline{g})) - 2 A_{\underline{g}} A_{\underline{g}'} \{ \cos \underline{k} \cdot \underline{h} - \lambda \sin(\underline{k} \cdot (\underline{g} + \underline{g}')) \} \right], \quad (A6.c.10)$$

where $\lambda = \mp 1$ according to whether $\underline{k} \cdot \underline{h}$ is positive or negative respectively. Substituting equ. (A6.c.10) into the expression $\sum_{\underline{k}} [\dots]$, equ. (A6.c.26), we obtain

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{1}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left[A_{\underline{g}'}^2 (1 - \lambda \sin(\underline{k} \cdot \underline{g}')) + A_{\underline{g}}^2 (1 - \lambda \sin(\underline{k} \cdot \underline{g})) - 2 A_{\underline{g}} A_{\underline{g}'} \{ \cos(\underline{k} \cdot \underline{h}) - \lambda \sin(\underline{k} \cdot (\underline{g} + \underline{g}')) \} \right] \left[-\coth \frac{B\hbar\omega_{\underline{k}}}{2} + \coth \frac{B\hbar\omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i \sin \omega_{\underline{k}} t \right]. \quad (A6.c.27)$$

Defining

$$\left[-\coth \frac{B\hbar\omega_{\underline{k}}}{2} + \coth \frac{B\hbar\omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i \sin \omega_{\underline{k}} t \right] \equiv B(\omega_{\underline{k}}, t)$$

and summing over $\pm \underline{k}$ the expression (A6.c.27) becomes

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \{ \dots \} = \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{1}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}'}^2 + A_{\underline{g}}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) B(\omega_{\underline{k}}, t), \quad (A6.c.28)$$

where account has been taken of the fact that $\omega_{-\underline{k}} = \omega_{\underline{k}}$. According to equ. (A6.c.28)

$$\begin{aligned}
 & \sum_{\underline{k}} \left\{ -F(\underline{k}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} + F(\underline{k}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t \right\} \\
 &= \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \\
 & \quad \left[-\coth \frac{B \hbar \omega_{\underline{k}}}{2} + \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i \sin \omega_{\underline{k}} t \right] \\
 &= -\left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \\
 & \quad + \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t \\
 & \quad + i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \sin \omega_{\underline{k}} t .
 \end{aligned}$$

(A6.c.29)

Defining

$$\begin{aligned}
 & \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \equiv S'(\underline{k}) , \\
 & \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t \equiv F_1'(\underline{k}, t) , \\
 & \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos \underline{k} \cdot \underline{h}) \sin \omega_{\underline{k}} t \equiv F_2'(\underline{k}, t) ,
 \end{aligned}$$

(A6.c.30)

equ. (A6.c.29) takes the form

$$\sum_{\underline{k}} \left\{ -F(\underline{k}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} + F(\underline{k}) \coth \frac{B \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t + i F(\underline{k}) \sin \omega_{\underline{k}} t \right\}$$

$$= -S'(\underline{k}) + F_1'(\underline{k}, t) + i F_2'(\underline{k}, t) \quad . \quad (A6.c.31)$$

Substituting equ. (A6.c.31) into equ. (A6.c.26), we obtain

$$\prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle = \exp[-S'(\underline{k})] \exp[F_1'(\underline{k}, t)] \exp[i F_2'(\underline{k}, t)], \quad (A6.c.32)$$

where the quantities appearing in the exponents are defined by equs. (A6.30).

Using the definition of $F(\underline{k})$, given by equ. (A6.c.10), and equ. (A6.c.22), some other expressions, appearing in equ. (A6.c.21), can be written as

$$\begin{aligned} & \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} F(\underline{k}) \cos \omega_{\underline{k}} t \\ &= \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h}) \right) \cos \omega_{\underline{k}} t, \end{aligned} \quad (A6.c.33)$$

$$\begin{aligned} & \sum_{\underline{k}} i \frac{\hbar \omega_{\underline{k}}}{2} \langle (2 n_{\underline{k}} + 1) \rangle F(\underline{k}) \sin \omega_{\underline{k}} t \\ &= i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{B \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \\ & \quad \left(A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h}) \right) \sin \omega_{\underline{k}} t \quad . \end{aligned} \quad (A6.c.34)$$

Using equs. (A6.c.22), (A6.c.32), and (A6.c.34), equ. (A6.c.21) becomes finally

$$L_{(2),g,g'}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \left[\sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \hbar \frac{\beta \hbar \omega_{\underline{k}}}{2} \right] \left(\frac{T}{\hbar} \right)^2$$

$$\lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g' g \right] \exp [-S'(\underline{k})]$$

$$\cdot \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)]$$

$$+ \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g' g \right]$$

$$\left\{ \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(A_{g'}^2 + A_g^2 - 2 A_g A_{g'} \cos(\underline{k} \cdot \underline{h}) \right) \cos \omega_{\underline{k}} t \right\}$$

$$\exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)]$$

$$+ \frac{q n_c \beta \alpha^2}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g' g \right]$$

$$\left\{ i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(A_{g'}^2 + A_g^2 - 2 A_g A_{g'} \cos(\underline{k} \cdot \underline{h}) \right) \sin \omega_{\underline{k}} t \right\}$$

$$\exp [-S'(\underline{k})] \exp [F_1'(\underline{k}, t)] \exp [i F_2'(\underline{k}, t)] , \quad (A6.c.35)$$

where $S'(\underline{k})$, $F_1'(\underline{k}, t)$ and $F_2'(\underline{k}, t)$ are defined by equs. (A6.c.30). Equation (A6.c.35) is the text equ. (6.37).

Appendix A6.d.

Evaluation of the coefficient $L_{gg'}^{(1)}$.

According to the text equ.(6.21), the proof of which we have given in Appendix A6.b., the thermal average $\langle j(-i\hbar\lambda)j(t) \rangle$ is given by

$$\langle j(-i\hbar\lambda)j(t) \rangle = q^2 n_c \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_m \exp[(E_n - E_m)\lambda] \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] |\langle n|v|m \rangle|^2. \quad (\text{A6.d.1})$$

Substituting equ.(A6.d.1) into the text equ.(6.7), and performing the λ -integration, we obtain

$$\begin{aligned} L^{(1)} &= q^2 n_c \frac{1}{Z} \sum_n \exp(-\beta E_n) \sum_m |\langle n|v|m \rangle|^2 \left[\frac{\exp[\beta(E_n - E_m) - 1]}{E_n - E_m} \right] \\ &\quad \int_0^\infty dt \exp\left[\left(-\frac{it}{\hbar}\right)(E_n - E_m)\right] \\ &= q^2 n_c \frac{1}{Z} \sum_{nm} \exp(-\beta E_n) |\langle n|v|m \rangle|^2 \\ &\quad \left[\frac{\exp[\beta(E_n - E_m) - 1]}{E_n - E_m} \right] F_{n,m}, \end{aligned} \quad (\text{A6.d.2})$$

where $F_{n,m}$ is given by the text equ.(6.23). Employing the

δ -character of $F_{n,m}$ in equ. (A6.d.2), and taking $\langle n | \equiv \langle \underline{g}, \{n_k\} |$, $|m\rangle \equiv | \underline{g}', \{n'_k\} \rangle$, where the sites $\underline{g}, \underline{g}'$ are fixed, as described in Chapter 6, we can evaluate $L_{\underline{g}\underline{g}'}^{(1)}$ from equ. (A6.d.2). $L_{\underline{g}\underline{g}'}^{(1)}$ stands for $L^{(1)}$, when a small-polaron hops from site $\underline{g}$ to site $\underline{g}'$. We find

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta}{2} \left\langle \sum_{\{n_k\}} | \langle \underline{g}', \{n'_k\} | v | \underline{g}, \{n_k\} \rangle |^2 \right. \\ \left. \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}'\underline{g}} \right] \exp \left[\left(-\frac{it}{\hbar} \right) \sum_k \hbar \omega_k (n_k - n'_k) \right] \right\rangle. \quad (\text{A6.d.3})$$

Equation (A6.d.3) is the text equ. (6.32). Now, recalling the text equ. (6.34),

$$| \langle \underline{g}', \{n'_k\} | v | \underline{g}, \{n_k\} \rangle |^2 = \left(\frac{J}{\hbar} \right)^2 \alpha^2 \prod_k \left\{ \left[1 - \left(n_k + \frac{1}{2} \right) \hbar_k^2 \right] \delta_{n'_k, n_k} \right. \\ \left. + \left(\frac{n_k}{2} \right) \hbar_k^2 \delta_{n'_k, n_k - 1} + \left(\frac{n_k + 1}{2} \right) \hbar_k^2 \delta_{n'_k, n_k + 1} \right\}, \quad (\text{A6.d.4})$$

and equ. (A6.c.10),

$$\hbar_k^2 \equiv 2 F(k), \quad (\text{A6.d.5})$$

equ. (A6.d.3) becomes

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}'\underline{g}} \right] \\ \prod_k \langle D(k, n_k, t) \rangle, \quad (\text{A6.d.6})$$

where $\prod_k \langle D(k, n_k, t) \rangle$ is given by equ. (A6.c.32) as

$$\prod_{\underline{k}} \langle D(\underline{k}, n_{\underline{k}}, t) \rangle = \exp[-S'(\underline{k})] \exp[F_1'(\underline{k}, t)] \exp[i F_2'(\underline{k}, t)],$$

(A6.d.7)

where $S'(\underline{k})$, $F_1'(\underline{k}, t)$, and $F_2'(\underline{k}, t)$ are given by equs. (6.38).
Substituting equ. (A6.d.6), we obtain

$$L_{\underline{g}\underline{g}'}^{(1)} = \frac{q^2 n_c \beta \alpha^2}{2} \left(\frac{J}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta \underline{g}' \underline{g} \right]$$

$$\exp[-S'(\underline{k})] \exp[F_1'(\underline{k}, t)] \exp[i F_2'(\underline{k}, t)].$$

(A6.d.8)

Equation (A6.d.8) is the text equ. (6.39).

Chapter 7

Evaluation of the transport coefficients in the weak-dispersion limit.

In the previous Chapter, we found the general expressions for the transport coefficients $L_{\underline{g}\underline{g}'}^{(2)}$, and $L_{\underline{g}\underline{g}'}^{(1)}$. Now, we shall proceed to the evaluation of these coefficients in the weak-dispersion limit, using the general expressions previously obtained. In the weak-dispersion limit the dispersion relation

$$\omega_{\underline{k}}^2 = \omega_0^2 + \omega_L^2 \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \quad , \quad (7.1)$$

becomes

$$\omega_{\underline{k}} = \omega_0 + \omega_b \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \quad , \quad (7.2)$$

where

$$\omega_b \equiv \frac{\omega_L^2}{\omega_0^2} \quad , \quad (7.3)$$

and

$$\omega_L \ll \omega_0 \quad . \quad (7.4)$$

In this limit, $S'(\underline{k})$, $F_1'(\underline{k}, t)$, $F_2'(\underline{k}, t)$, given generally by equs. (6.38), become

$$S' \equiv \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} , \quad (7.5)$$

$$\begin{aligned} F_1'(\underline{k}, t) &\equiv \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} \left(\frac{1}{N} \right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \\ &- \frac{2 A_{\underline{g}} A_{\underline{g}'}}{2 M \omega_0^2 \hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} \left(\frac{1}{N} \right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \cos \omega_{\underline{k}} t , \end{aligned} \quad (7.6)$$

$$\begin{aligned} F_2'(\underline{k}, t) &\equiv \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \left(\frac{1}{N} \right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \\ &- \frac{2 A_{\underline{g}} A_{\underline{g}'}}{2 M \omega_0^2 \hbar \omega_0} \left(\frac{1}{N} \right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \sin \omega_{\underline{k}} t , \end{aligned} \quad (7.7)$$

where

$$E_b(\underline{g}) = \frac{A_{\underline{g}}^2}{2 M \omega_0^2} , \quad E_b(\underline{g}') = \frac{A_{\underline{g}'}^2}{2 M \omega_0^2} . \quad (7.8)$$

Details are given in Appendix A7.a. Also we prove there that

$$\left(\frac{1}{N} \right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \approx J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x ,$$

$$\left(\frac{1}{N} \right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \approx J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x , \quad (7.9)$$

$$\left(\frac{1}{N} \right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \cos(\underline{k} \cdot \underline{h}) \approx 0 ,$$

$$\left(\frac{1}{N} \right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \cos(\underline{k} \cdot \underline{h}) \approx 0 ,$$

where $x = \omega_0 t$, and $J_0(\frac{\omega_b}{\omega_0} x)$ is a Bessel function of zeroth order.

Using equs. (7.9), the expressions for $F_1'(\underline{k}, t)$, and $F_2'(\underline{k}, t)$, become

$$F_1(t) = \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0} x\right) \cos x, \quad (7.10)$$

$$F_2(t) = \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} J_0\left(\frac{\omega_b}{\omega_0} x\right) \sin x. \quad (7.11)$$

On the other hand, using equs. (7.9), and equs. (7.8),

$$\begin{aligned} \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \cos \omega_{\underline{k}} t \\ = \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2} J_0\left(\frac{\omega_b}{\omega_0} x\right) \cos x, \end{aligned} \quad (7.12)$$

and

$$\begin{aligned} i \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \sin \omega_{\underline{k}} t \\ = i \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2} \coth \frac{\beta \hbar \omega_0}{2} J_0\left(\frac{\omega_b}{\omega_0} x\right) \sin x. \end{aligned} \quad (7.13)$$

Details are given in Appendix A7.8.

Now, substituting the quantities appearing in equ. (6.37) by their weak-dispersion form, we obtain

$$\begin{aligned} L_{(2), \underline{g} \underline{g}'}^{(2)} = \frac{q n_c \beta a^2}{2} N \frac{\hbar \omega_0}{2} \coth \frac{\beta \hbar \omega_0}{2} \left(\frac{J}{\hbar}\right)^2 \\ \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{i t}{\hbar}\right) A_{\underline{g} \underline{g}'}\right] \exp(-S) \exp[F_1(t)] \exp[i F_2(t)] \end{aligned}$$

$$+ \frac{q n_c B \alpha^2}{2} \tilde{E}_b(\underline{g}, \underline{g}') \left(\frac{T}{\hbar} \right)^2$$

$$\lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}'\underline{g}} \right] J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x \exp(-S) \exp[F_1(t)] \exp[iF_2(t)]$$

$$+ i \frac{q n_c B \alpha^2}{2} \tilde{E}_b(\underline{g}, \underline{g}') \coth \frac{B \hbar \omega_0}{2} \left(\frac{T}{\hbar} \right)^2$$

$$\lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}'\underline{g}} \right] J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x \exp(-S)$$

$$\exp[F_1(t)] \exp[iF_2(t)] \quad , \quad (7.14)$$

where

$$\tilde{E}_b(\underline{g}, \underline{g}') \equiv \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2} \quad , \quad (7.15)$$

is the mean binding energy of the two-site system.

In this limit the coefficient $L_{\underline{g}\underline{g}'}^{(1)}$, given by equ.(6.39), readily takes the form

$$L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c B \alpha^2 R_{\underline{g}\underline{g}'} \quad , \quad (7.16)$$

where

$$R_{\underline{g}\underline{g}'} = \frac{1}{2} \left(\frac{T}{\hbar} \right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta_{\underline{g}'\underline{g}} \right] \exp(-S) \exp[F_1(t)] \exp[iF_2(t)] \quad , \quad (7.17)$$

is the rate for a hop from g to g' .

Let us now proceed to the evaluation of the terms involved in equ. (7.4). In order to gain physical insight into the meaning of the first term, let us evaluate the quantity $N \frac{\hbar \omega_0}{2} \coth \frac{\beta \hbar \omega_0}{2}$ in the high-temperature limit, $\hbar \omega_0 \ll kT$. In this limit $N \frac{\hbar \omega_0}{2} \coth \frac{\beta \hbar \omega_0}{2} = N kT$. We notice that this quantity is the thermally averaged lattice energy. This is just

$$\left\langle \sum_{\mathbf{k}} \frac{\hbar \omega_{\mathbf{k}}}{2} (n_{\mathbf{k}} + n'_{\mathbf{k}} + 1) \right\rangle = \sum_{\mathbf{k}} \frac{\hbar \omega_{\mathbf{k}}}{2} \langle (2n_{\mathbf{k}} + 1) \rangle = N kT, \quad (7.18)$$

for $n_{\mathbf{k}} = n'_{\mathbf{k}}$ (diagonal transitions), and the weak dispersion classical limit. The remaining part of the first term of equ. (7.14), apart from a constant, is recognized as the small-polaron jump rate $R_{g \underline{g}}$ (c.f. equ. (7.17)). Thus, the thermally averaged lattice energy, which corresponds to diagonal transitions ($n_{\mathbf{k}} = n'_{\mathbf{k}}$), seems to be transported in a site jump with a rate equal to the small-polaron's.

The remaining terms in equ. (7.14) correspond to the energy which is transported due to the change of the vibrational quantum numbers $n_{\mathbf{k}}, n'_{\mathbf{k}}$ by ± 1 (non-diagonal transitions).

In the ordinary conductivity theory for the hopping regime, the vibrational quantum numbers $n_{\mathbf{k}}, n'_{\mathbf{k}}$ appear only in the exponentials and terms which correspond to diagonal transitions ($n_{\mathbf{k}} = n'_{\mathbf{k}}$) are eliminated^{(10), (29)}. In the expression for the energy of transport, a $n_{\mathbf{k}}, n'_{\mathbf{k}}$ -dependence appears in the prefactors of the exponentials, as well. Thus, terms in which the prefactors are diagonal, must also be eliminated. Physically,

these terms represent the background thermal energy of the lattice, which is not transported and thus, it is not of our interest. Their inclusion arises from the formulation of the problem in which the small-polaron energy spectrum, equ. (5.7), includes the lattice vibrational energy of the entire specimen. Rather we are interested in the energy which is transported in excess of this background energy and this is given by the last two terms of equ. (7.14), alone.

Thus,

$$L_{(2), \underline{g} \underline{g}'}^{(2)} = L_{(3), \underline{g} \underline{g}'}^{(2)} + L_{(4), \underline{g} \underline{g}'}^{(2)}, \quad (7.19)$$

where

$$L_{(3), \underline{g} \underline{g}'}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \tilde{E}_b(\underline{g}, \underline{g}') \left(\frac{T}{\hbar}\right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta \underline{g} \underline{g}'\right]$$

$$J_0\left(\frac{\omega_b}{\omega_0} x\right) \cos x \exp(-\mathcal{S}) \exp[F_1(t)] \exp[i F_2(t)], \quad (7.20)$$

and

$$L_{(4), \underline{g} \underline{g}'}^{(2)} = i \frac{q n_c \beta \alpha^2}{2} \tilde{E}_b(\underline{g}, \underline{g}') \coth \frac{\beta \hbar \omega_0}{2} \left(\frac{T}{\hbar}\right)^2 \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta \underline{g} \underline{g}'\right] J_0\left(\frac{\omega_b}{\omega_0} x\right) \sin x \exp(-\mathcal{S}) \exp[F_1(t)] \exp[i F_2(t)]. \quad (7.21)$$

In order to evaluate the integral of the form

$$I_{(3)} = \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta \underline{g} \underline{g}'\right] J_0\left(\frac{\omega_b}{\omega_0} x\right) \cos x \exp(-\mathcal{S}) \exp[F_1(t)] \exp[i F_2(t)], \quad (7.22)$$

we follow Emin ⁽²⁹⁾ and rewrite it as a sum of integrals, each of which is characterized by a time domain of a single vibrational period, $\frac{2\pi}{\omega_0}$. Within this time interval, $I_0(\frac{\omega_0}{\omega_0}x)$ is almost constant provided that $\frac{\omega_0}{\omega_0} \ll 1$. Writing A_n as the appropriate constant value of $J(\frac{\omega_0}{\omega_0} 2\pi n)$ in a time domain of a single vibrational period, $\frac{2\pi}{\omega_0}$ corresponding to the n -th integral, $t_n = \frac{2\pi n}{\omega_0}$, after some manipulation, given in Appendix A7.6, we obtain

$$I_{(3)} = I_{(3)}^{(1)} + I_{(3)}^{(2)}, \quad (7.23)$$

where

$$\begin{aligned} I_{(3)}^{(1)} = & \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(\alpha_n \cos x) \\ & \cos [\alpha'_n \sin x + (b-1)x] \cos 2\pi n(b-1) \\ & + \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(\alpha_n \cos x) \\ & \cos [\alpha'_n \sin x + (b+1)x] \cos 2\pi n(b+1), \quad (7.24) \end{aligned}$$

and

$$\begin{aligned} I_{(3)}^{(2)} = & \frac{i}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(\alpha_n \cos x) \\ & [\alpha'_n \sin x + (b-1)x] \cos 2\pi n(b-1) \\ & + \frac{i}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(\alpha_n \cos x) \\ & \sin [\alpha'_n \sin x + (b+1)x] \cos 2\pi n(b+1), \quad (7.25) \end{aligned}$$

where

$$b \equiv \frac{\Delta g' g}{\hbar \omega_0}, \quad (7.26)$$

$$\alpha_n \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} A_n, \quad (7.27)$$

$$\alpha'_n \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} A_n. \quad (7.28)$$

The integrals appearing in eqs. (7.24), and (7.25) are of the general form⁽³¹⁾

$$\begin{aligned} & \int_{-\pi}^{\pi} \exp(r \cos x + s \sin x) \cos(mx - \lambda \cos x - \mu \sin x) dx \\ &= \pi [(r-\mu)^2 + (s+\lambda)^2]^{-m/2} \left\{ (A+iB)^{m/2} I_m(\sqrt{C-iD}) \right. \\ & \quad \left. + (A-iB)^{m/2} I_m(\sqrt{C+iD}) \right\}, \quad (7.29) \end{aligned}$$

and

$$\begin{aligned} & \int_{-\pi}^{\pi} \exp(r \cos x + s \sin x) \sin(mx - \lambda \cos x - \mu \sin x) dx \\ &= -i\pi [(r-\mu)^2 + (s+\lambda)^2]^{-m/2} \left\{ (A+iB)^{m/2} I_m(\sqrt{C-iD}) \right. \\ & \quad \left. - (A-iB)^{m/2} I_m(\sqrt{C+iD}) \right\}, \quad (7.30) \end{aligned}$$

where

$$A = r^2 - s^2 + \lambda^2 - \mu^2, \quad B = 2(rs + \lambda\mu), \quad (r-\mu)^2 + (s+\lambda)^2 > 0, \quad (7.31)$$

$$C = r^2 + s^2 - \lambda^2 - \mu^2, \quad D = 2(r\lambda + s\mu), \quad m = 1, 2, \dots$$

I_m is the modified Bessel function of order m . Using the results (7.29), and (7.30) in our case, where $B = D = 0$, we obtain

$$I_{(3)}^{(1)} = \left(\frac{\pi}{\omega_0} \right) \exp(-S) [\exp(-\beta \hbar \omega_0)]^{\frac{(b-1)}{2}}$$

$$\lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\omega_0 \tau / 2\hbar} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(\underline{g}, \underline{g}')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2n\eta(b-1)$$

$$+ \left(\frac{n}{\omega_0} \right) \exp(-s) \left[\exp(-\beta \hbar \omega_0) \right]^{\frac{(b+1)}{2}}$$

$$\lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(q, q')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b+1), \quad (7.32)$$

and

$$I_{(3)}^{(2)} = 0. \quad (7.33)$$

Thus,

$$I_{(3)} = I_{(3)}^{(1)}, \quad (7.34)$$

where $I_{(3)}^{(1)}$ is given by equ. (7.32). The details of the calculations are given in Appendix A7.b.

Finally, substituting the expression for $I_{(3)}$ into equ. (7.20), after some manipulation, given in Appendix (A7.c), we obtain

$$L_{(3), q, q'}^{(2)} = \frac{q n_c \beta \alpha^2}{2} \tilde{E}_b(q, q') \left(\frac{n}{\omega_0} \right) \left(\frac{\tau}{\hbar} \right)^2$$

$$\exp \left[- \frac{2 \tilde{E}_b(q, q')}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right] \exp \left(- \frac{\Delta q' q}{2 k T} \right)$$

$$\left\{ \exp \left(\frac{\hbar \omega_0}{2 k T} \right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(q, q')}{\hbar \omega_0} \right. \right.$$

$$\left. A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b-1)$$

$$\begin{aligned}
 & + \exp\left(-\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\pi}}^{\frac{\omega_0\tau}{2\pi}} A_n I_{(b+1)} \left\{ \frac{2\tilde{E}_b(\underline{g}, \underline{g}')}{\hbar\omega_0} \right. \\
 & \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b+1) \Big\} .
 \end{aligned}
 \tag{7.35}$$

Proceeding in a similar way, we can evaluate $L_{(4)}^{(2)}$ given by equ. (7.21). Details are given in Appendices A7.c. and A7.d. The result is

$$\begin{aligned}
 L_{(4)}^{(2)}, \underline{g}\underline{g}' &= \frac{q\pi_c \beta \alpha^2}{2} \tilde{E}_b(\underline{g}, \underline{g}') \left(\frac{n}{\omega_0}\right) \coth \frac{B\hbar\omega_0}{2} \left(\frac{T}{\hbar}\right)^2 \\
 & \exp\left[-\frac{2\tilde{E}_b(\underline{g}, \underline{g}')}{\hbar\omega_0} \coth \frac{B\hbar\omega_0}{2}\right] \exp\left(-\frac{\Delta \underline{g}'\underline{g}}{2kT}\right) \\
 & \left\{ \exp\left(-\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\pi}}^{\frac{\omega_0\tau}{2\pi}} A_n I_{(b+1)} \left\{ \frac{2\tilde{E}_b(\underline{g}, \underline{g}')}{\hbar\omega_0} \right. \right. \\
 & \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b+1) \right. \\
 & \left. - \exp\left(\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\pi}}^{\frac{\omega_0\tau}{2\pi}} A_n I_{(b-1)} \left\{ \frac{2\tilde{E}_b(\underline{g}, \underline{g}')}{\hbar\omega_0} \right. \right. \\
 & \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b-1) \right\} .
 \end{aligned}
 \tag{7.36}$$

Recalling equ. (7.19),

$$L_{(2)}^{(2)}, \underline{g}\underline{g}' = L_{(3)}^{(2)}, \underline{g}\underline{g}' + L_{(4)}^{(2)}, \underline{g}\underline{g}' . \tag{7.37}$$

Substituting equs. (7.35), and (7.36) into equ. (7.37), we obtain the final expression for the coefficient $L_{(2)}^{(2)}, \underline{g}\underline{g}'$,

$$\begin{aligned}
 L_{(2), \underline{g} \underline{g}'}^{(2)} &= q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left(- \frac{\Delta g' g}{2 k T} \right) \\
 &\quad \exp \left[- \frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right] \\
 &\quad \left\{ \exp \left(\frac{\hbar \omega_0}{2 k T} \right) \left(1 - \coth \frac{\beta \hbar \omega_0}{2} \right) \sum_{n=-\infty}^{\infty} A_n I_{(b-1)} \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} \right. \right. \\
 &\quad \left. \left. A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2 \pi n (b-1) \right. \\
 &\quad \left. + \exp \left(- \frac{\hbar \omega_0}{2 k T} \right) \left(1 + \coth \frac{\beta \hbar \omega_0}{2} \right) \sum_{n=-\infty}^{\infty} A_n I_{(b+1)} \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} \right. \right. \\
 &\quad \left. \left. A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2 \pi n (b+1) \right\} ,
 \end{aligned}
 \tag{7.38}$$

where

$$\epsilon_2 \equiv \frac{\tilde{E}_b(\underline{g}, \underline{g}')}{2} .
 \tag{7.39}$$

Recalling equ. (6.28),

$$L_{\underline{g} \underline{g}'}^{(2)} = L_{(1), \underline{g} \underline{g}'}^{(2)} + L_{(2), \underline{g} \underline{g}'}^{(2)} ,
 \tag{7.40}$$

where $L_{(1), \underline{g} \underline{g}'}^{(2)}$ is given by equ. (6.33),

$$L_{(1), \underline{g} \underline{g}'}^{(2)} = \frac{1}{q} \tilde{E}(\underline{g}, \underline{g}') L_{\underline{g} \underline{g}'}^{(1)} ,
 \tag{7.41}$$

and $L_{\underline{g} \underline{g}'}^{(1)}$, at this stage of calculations, is given by

$$L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \exp \left(- \frac{\Delta \underline{g}\underline{g}'}{2kT} \right)$$

$$\exp \left[- \frac{4\epsilon_2}{\hbar\omega_0} \coth \frac{B\hbar\omega_0}{2} \right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4\epsilon_2}{\hbar\omega_0} A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n b, \quad (7.42)$$

where $b \equiv \Delta \underline{g}\underline{g}' / \hbar\omega_0$ is an integer.

In this Chapter we derived the expressions for the transport coefficient $L_{\underline{g}\underline{g}'}^{(2)}$ in the weak-dispersion limit, when a small-polaron hops from a site $\underline{g}$ to a nearest neighbouring site $\underline{g}'$ of a G.M.C.M. We also gave the result, at this stage of calculations, for the transport coefficient $L_{\underline{g}\underline{g}'}^{(1)}$ obtained by Emin⁽²⁹⁾. Thus, the expressions which give, for this case, the transport coefficients $L_{\underline{g}\underline{g}'}^{(1)}$ and $L_{\underline{g}\underline{g}'}^{(2)}$ are

$$L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \exp \left(- \frac{\Delta \underline{g}\underline{g}'}{2kT} \right) \exp \left[- \frac{4\epsilon_2}{\hbar\omega_0} \coth \frac{B\hbar\omega_0}{2} \right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4\epsilon_2}{\hbar\omega_0} A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n b, \quad (7.43)$$

and

$$L_{\underline{g}\underline{g}'}^{(2)} = \frac{1}{q} \tilde{E}(\underline{g}, \underline{g}') L_{\underline{g}\underline{g}'}^{(1)}$$

$$+ q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left(- \frac{\Delta \underline{g}\underline{g}'}{2kT} \right) \exp \left[- \frac{4\epsilon_2}{\hbar\omega_0} \coth \frac{B\hbar\omega_0}{2} \right]$$

$$\left\{ \exp \left(\frac{\hbar\omega_0}{2kT} \right) (1 - \coth \frac{B\hbar\omega_0}{2}) \sum_{n=-\infty}^{\infty} A_n I_{(b-1)} \left\{ \frac{4\epsilon_2}{\hbar\omega_0} A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b-1) \right.$$

$$\left. + \exp \left(- \frac{\hbar\omega_0}{2kT} \right) (1 + \coth \frac{B\hbar\omega_0}{2}) \sum_{n=-\infty}^{\infty} A_n I_{(b+1)} \left\{ \frac{4\epsilon_2}{\hbar\omega_0} A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b+1) \right\}.$$

(7.44)

In the next Chapter we shall use these expressions in order to evaluate the transport coefficients for the reverse hop, i.e. from site $\underline{g}'$ to $\underline{g}$ and then the net transport coefficients $L^{(1)}$ and $L^{(2)}$ for a small-polaron jumping between these two sites. These will be the required expressions for the transport coefficients which are necessary in order to evaluate the thermoelectric power associated with the process under consideration.

Appendix A7.a.

The weak-dispersion limit approximation.

In Chapter 4., where the M.C.M. is described, the phonon dispersion relation is given by

$$\omega_{\underline{k}}^2 = \omega_0^2 + \omega_1^2 \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) , \quad (\text{A7.a.1})$$

where $\underline{k} = 2\pi\lambda/N$, the integer λ lying in the range $-\frac{1}{2}(N-1) \leq \lambda \leq \frac{1}{2}(N-1)$. Thus,

$$\omega_{\underline{k}} = \omega_0 \left[1 + \left(\frac{\omega_1}{\omega_0} \right)^2 \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \right]^{1/2} ,$$

which, in the weak-dispersion limit ($\omega_1 \ll \omega_0$), takes the form

$$\omega_{\underline{k}} \approx \omega_0 \left[1 + \frac{1}{2} \left(\frac{\omega_1}{\omega_0} \right)^2 \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \right] .$$

This can be written in the form

$$\omega_{\underline{k}} \approx \omega_0 + \omega_b \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) , \quad (\text{A7.a.2})$$

where

$$\omega_b \equiv \frac{\omega_1^2}{2\omega_0} . \quad (\text{A7.a.3})$$

In the present context the weak-dispersion limit is then

$$\frac{\omega_b}{\omega_0} = \frac{1}{2} \left(\frac{\omega_1}{\omega_0} \right)^2 \ll 1. \quad (\text{A7.a.4})$$

In this limit, equs. (6.38) can be written in a more simple form as follows

$$\begin{aligned} S'(\underline{k}) &\equiv \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{1}{2M\omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \\ &= \left(\frac{1}{N} \right) \frac{1}{2M\omega_0^2 \hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \sum_{\underline{k}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \\ &= \left(\frac{1}{N} \right) \frac{1}{2M\omega_0^2 \hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \sum_{\underline{k}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2) \\ &\quad - \left(\frac{1}{N} \right) \frac{1}{2M\omega_0^2 \hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} 2A_{\underline{g}} A_{\underline{g}'} \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}). \quad (\text{A7.a.5}) \end{aligned}$$

But if $\underline{h}$ is a unit vector, $\sum_{\underline{k}} e^{i\underline{k} \cdot \underline{h}} = 0$, for $\underline{h} \neq 0$, or $\sum_{\underline{k}} e^{i\underline{k} \cdot \underline{h}} = \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) + i \sum_{\underline{k}} \sin(\underline{k} \cdot \underline{h}) = 0$. Then, $\sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) = 0$. Thus equ. (A7.a.5) becomes

$$S' = \frac{(A_{\underline{g}}^2 + A_{\underline{g}'}^2)}{2M\omega_0^2 \hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} = \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2}, \quad (\text{A7.a.6})$$

where

$$E_b(\underline{g}) = \frac{A_{\underline{g}}^2}{2M\omega_0^2}, \quad (\text{A7.a.7})$$

is the binding energy, in the weak-dispersion limit, for a carrier residing on site $\underline{g}$.

In the same way

$$\begin{aligned}
 F_1'(\underline{k}, t) &\equiv \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \coth \hbar \frac{\beta \hbar \omega_{\underline{k}}}{2} \cos \omega_{\underline{k}} t \\
 &= \frac{(A_{\underline{g}}^2 + A_{\underline{g}'}^2)}{2 M \omega_0^2 \hbar \omega_0} \coth \hbar \frac{\beta \hbar \omega_0}{2} \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \\
 &\quad - \frac{2 A_{\underline{g}} A_{\underline{g}'}}{2 M \omega_0^2 \hbar \omega_0} \coth \hbar \frac{\beta \hbar \omega_0}{2} \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \cos \omega_{\underline{k}} t, \quad (\text{A7.a.8})
 \end{aligned}$$

and

$$\begin{aligned}
 F_2'(\underline{k}, t) &\equiv \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} (A_{\underline{g}'}^2 + A_{\underline{g}}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h})) \sin \omega_{\underline{k}} t \\
 &= \frac{(A_{\underline{g}}^2 + A_{\underline{g}'}^2)}{2 M \omega_0^2 \hbar \omega_0} \left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \\
 &\quad - \frac{2 A_{\underline{g}} A_{\underline{g}'}}{2 M \omega_0^2 \hbar \omega_0} \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \sin \omega_{\underline{k}} t. \quad (\text{A7.a.9})
 \end{aligned}$$

Let us now evaluate the expressions

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t, \quad \left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t$$

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \cos \omega_{\underline{k}} t, \quad \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos(\underline{k} \cdot \underline{h}) \sin \omega_{\underline{k}} t,$$

in the weak-dispersion limit. In this limit, using equ.

(A7.a.2),

$$\begin{aligned}
 \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t &\rightarrow \frac{1}{2\pi} \int_{-\pi}^{\pi} \cos [\omega_0 t + \omega_b t \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h})] d(\underline{k} \cdot \underline{h}) \\
 &= \frac{\cos \omega_0 t}{2\pi} \int_{-\pi}^{\pi} \cos [\omega_b (t) \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h})] d(\underline{k} \cdot \underline{h})
 \end{aligned}$$

$$= \frac{\sin \omega_0 t}{2\pi} \int_{-\pi}^{\pi} \sin \left[\omega_b(t) \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \right] d(\underline{k} \cdot \underline{h}) \quad . \quad (\text{A7.a.10})$$

But (32),

$$\begin{aligned} \cos \left[\omega_b t \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \right] &= J_0(\omega_b t) \\ &+ 2 \sum_{p=1}^{\infty} (-1)^p J_p(\omega_b t) \sum_{\underline{h}} \cos 2p(\underline{k} \cdot \underline{h}), \end{aligned} \quad (\text{A7.a.11})$$

$$\sin \left[\omega_b t \sum_{\underline{h}} \cos(\underline{k} \cdot \underline{h}) \right] = 2 \sum_{p=0}^{\infty} (-1)^p J_{p+1}(\omega_b t)$$

$$\sum_{\underline{h}} \cos [(2p+1)\underline{k} \cdot \underline{h}],$$

where J_0, J_p are Bessel functions of order zero and p , respectively. Thus

$$\begin{aligned} \left(\frac{1}{N} \right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t &\approx \frac{\cos \omega_0 t}{2\pi} J_0(\omega_b t) \int_{-\pi}^{\pi} d(\underline{k} \cdot \underline{h}) \\ &+ \frac{\cos \omega_0 t}{2\pi} 2 \sum_{p=1}^{\infty} (-1)^p J_{p+1}(\omega_b t) \int_{-\pi}^{\pi} \sum_{\underline{h}} \cos [(2p+1)(\underline{k} \cdot \underline{h})] d(\underline{k} \cdot \underline{h}) \\ &- \frac{\sin \omega_0 t}{2\pi} 2 \sum_{p=1}^{\infty} (-1)^p J_{p+1}(\omega_b t) \int_{-\pi}^{\pi} \sum_{\underline{h}} \cos [(2p+1)(\underline{k} \cdot \underline{h})] d(\underline{k} \cdot \underline{h}). \end{aligned} \quad (\text{A7.a.12})$$

Now,

$$\int_{-\pi}^{\pi} \sum_{\underline{h}} \cos [2p(\underline{k} \cdot \underline{h})] d(\underline{k} \cdot \underline{h}) = \frac{1}{2p} \sum_{\underline{h}} \sin 2p(\underline{k} \cdot \underline{h}) \Big|_{-\pi}^{\pi} = 0.$$

Thus, equ. (A7.a.12) becomes

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \approx \frac{\cos \omega_0 t}{2\pi} J_0(\omega_b t) 2\pi$$

or, defining

$$\omega_b t \equiv x, \quad (A7.a.13)$$

we obtain

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \approx J_0\left(\frac{\omega_b}{\omega_0} x\right) \cos x. \quad (A7.a.14)$$

Using the result (A7.a.14) we may also derive an expression for $\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t$, as follows

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t = -\frac{d}{dt} \left\{ \left(\frac{1}{N}\right) \sum_{\underline{k}} \frac{1}{\omega_{\underline{k}}} \cos \omega_{\underline{k}} t \right\}. \quad (A7.a.15)$$

In the weak-dispersion limit, equ. (A7.a.15) becomes.

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \approx \left(\frac{1}{\omega_0}\right) \left\{ -\frac{d}{dt} \left[\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \right] \right\}.$$

Using equ. (A7.a.14),

$$\begin{aligned} \left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t &\approx \left(\frac{1}{\omega_0}\right) \left\{ -\frac{d}{dt} \left[J_0(\omega_b t) \cos \omega_0 t \right] \right\} \\ &= \left(\frac{1}{\omega_0}\right) \left\{ -J_0'(\omega_b t) \omega_b \cos \omega_0 t - J_0(\omega_b t) (-\omega_0 \sin \omega_0 t) \right\} \end{aligned} \quad (A7.a.16)$$

In the weak-dispersion limit, $\frac{\omega_b}{\omega_0} \ll 1$, the first term of the r.h.s. of equ. (A7.a.16) is negligible. Thus

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \cong J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x . \quad (\text{A7.a.17})$$

Proceeding in the same way, we obtain, in the weak-dispersion limit,

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \cos (\underline{k} \cdot \underline{h}) \cong 0 , \quad (\text{A7.a.18})$$

and

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \cos (\underline{k} \cdot \underline{h}) \cong 0 . \quad (\text{A7.a.19})$$

Thus, in summary, we have shown that, in the weak-dispersion limit,

$$\begin{aligned} \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t &\cong J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x , \\ \left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t &\cong J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x , \\ \left(\frac{1}{N}\right) \sum_{\underline{k}} \cos \omega_{\underline{k}} t \cos (\underline{k} \cdot \underline{h}) &\cong 0 , \end{aligned} \quad (\text{A7.a.20})$$

$$\left(\frac{1}{N}\right) \sum_{\underline{k}} \sin \omega_{\underline{k}} t \cos (\underline{k} \cdot \underline{h}) \cong 0 ,$$

where $x = \omega_0 t$. Equations (A7.a.20) are the text equs. (7.9).

Now, using equs. (A7.a.20), equ. (A7.a.8) and equ. (A7.a.9), become

$$\begin{aligned} F_1(t) &\equiv \frac{(A_{\underline{g}}^2 + A_{\underline{g}'}^2)}{2 M \omega_0^2 \hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x \\ &= \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x , \end{aligned} \quad (\text{A7.a.21})$$

and

$$F_2(t) \equiv \frac{(A_{\underline{g}}^2 + A_{\underline{g}'}^2)}{2 M \omega_0^2 \hbar \omega_0} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x$$

$$= \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{\hbar \omega_0} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x, \quad (A7.a.22)$$

where $E_b(\underline{g})$ is given by

$$E_b(\underline{g}) = \frac{A_{\underline{g}}^2}{2 M \omega_0^2} \quad (A7.a.23)$$

Equations (A7.a.21), (A7.a.22) are the text equs (7.10), (7.11) respectively.

On the other hand, using equs. (A7.a.20), and (A7.a.23),

$$\begin{aligned} & \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h}) \right) \cos \omega_{\underline{k}} t \\ &= \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x, \end{aligned} \quad (A7.a.24)$$

and

$$\begin{aligned} & i \left(\frac{1}{N} \right) \sum_{\underline{k}} \frac{\hbar \omega_{\underline{k}}}{2} \coth \frac{\beta \hbar \omega_{\underline{k}}}{2} \frac{1}{2 M \omega_{\underline{k}}^2 \hbar \omega_{\underline{k}}} \left(A_{\underline{g}}^2 + A_{\underline{g}'}^2 - 2 A_{\underline{g}} A_{\underline{g}'} \cos(\underline{k} \cdot \underline{h}) \right) \sin \omega_{\underline{k}} t \\ &= i \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2} \coth \frac{\beta \hbar \omega_0}{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x. \end{aligned} \quad (A7.a.25)$$

Equations (A7.a.24), (A7.a.25) are the text equs. (7.12), and (7.13), respectively.

Appendix A7.b.

Evaluation of some useful integrals.

Here we shall give the details of the evaluation of some useful integrals, involved in the text eqs. (7.20), and (7.21). Let us first evaluate the integral

$$I_{(3)} \equiv \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{\hbar} \right) \Delta g' g \right] J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x \\ \exp(-S) \exp[F_1(t)] \exp[iF_2(t)] \quad , \quad (A7.b.1)$$

given in the text by equ. (7.22), and where

$$x \equiv \omega_0 t \quad ,$$

$$F_1(t) \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \cos x \equiv \tilde{\alpha}_n \cos x \quad , \quad (A7.b.2)$$

$$F_2(t) \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \sin x \equiv \tilde{\alpha}'_n \sin x \quad , \quad (A7.b.3)$$

and

$$S \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \quad . \quad (A7.b.4)$$

Here $\tilde{\alpha}_n$, $\tilde{\alpha}'_n$ are defined by

$$\tilde{\alpha}_n \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} J_0 \left(\frac{\omega_b}{\omega_0} x \right) \quad , \quad (A7.b.5)$$

and

$$\tilde{\alpha}'_n = \frac{[E_b(\underline{q}) + E_b(\underline{q}')] }{\frac{1}{2} \omega_0} J_0\left(\frac{\omega_b}{\omega_0} x\right) . \quad (\text{A7.b.6})$$

We shall rewrite $I_{(3)}$ as a sum of integrals, each of which is characterized by a time domain of a single vibrational period, $\frac{2\pi}{\omega_0}$. Within this time interval, $J_0(\frac{\omega_b}{\omega_0} x)$, and consequently $\tilde{\alpha}_n, \tilde{\alpha}'_n$ are almost constant provided that $\omega_b/\omega_0 \ll 1$. Let us then write A_n as the appropriate constant value of $J(\frac{\omega_b}{\omega_0} 2\pi n)$ in a time domain of a single vibrational period $\frac{2\pi}{\omega_0}$ corresponding to the n-th integral, $t_n = \frac{2\pi n}{\omega_0}$. Explicitly we write

$$\lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \longrightarrow \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} \left(\frac{1}{\omega_0}\right) \int_{n(2\pi-1)}^{n(2\pi+1)} dx . \quad (\text{A7.b.7})$$

The lower and upper values of x for the lower and upper values of n are

$$dx \left| \begin{array}{l} \pi(2n+1) \longrightarrow \pi\left(2\frac{\omega_0 \tau}{2\pi} + 1\right) = \omega_0 \tau + \pi = \omega_0 \left(\tau + \frac{n}{\omega_0}\right) \\ \pi(2n-1) \longrightarrow \pi\left(-2\frac{\omega_0 \tau}{2\pi} - 1\right) = -\omega_0 \tau - \pi = -\omega_0 \left(\tau + \frac{n}{\omega_0}\right) \end{array} \right.$$

and taking into account that $dt = \frac{dx}{\omega_0}$,

$dt \left| \begin{array}{l} (\tau + \frac{n}{\omega_0}) \\ -(\tau + \frac{n}{\omega_0}) \end{array} \right.$, from which it is clear that each integral in the sum is characterized by a single vibrational period, $2\pi/\omega_0$. For convenience τ is taken to be an integral number of vibrational periods, i.e. $\frac{\omega_0 \tau}{2\pi}$ is an integer.

Hence we write

$$\begin{aligned}
 I_{(3)} &= \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} \left(\frac{1}{\omega_0} \right) \int_{n(2\pi-1)}^{n(2\pi+1)} \{ dx \exp[i(\alpha'_n \sin x + \frac{\Delta g' g}{\hbar \omega_0} x)] \\
 &\quad \cos x A_n \exp(\alpha_n \cos x) \} \\
 &= \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{n(2\pi-1)}^{n(2\pi+1)} \{ dx \exp(\alpha_n \cos x) \\
 &\quad \cos [\alpha'_n \sin x + bx] \cos x \} \\
 &+ i \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{n(2\pi-1)}^{n(2\pi+1)} \{ dx \exp(\alpha_n \cos x) \\
 &\quad \sin [\alpha'_n \sin x + bx] \cos x \} ,
 \end{aligned}
 \tag{A7.b.8}$$

where

$$\alpha_n \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} A_n , \tag{A7.b.9}$$

$$\alpha'_n \equiv \frac{[E_b(g) + E_b(g')]}{\hbar \omega_0} A_n , \tag{A7.b.10}$$

and

$$b \equiv \frac{\Delta g' g}{\hbar \omega_0} . \tag{A7.b.11}$$

Now,

$$\begin{aligned}
 &\cos [\alpha'_n \sin x + bx] \cos x \\
 &= \frac{1}{2} \{ \cos [\alpha'_n \sin x + (b-1)x] + \cos [\alpha'_n \sin x + (b+1)x] \} ,
 \end{aligned}
 \tag{A7.b.12}$$

$$\begin{aligned}
 &\sin [\alpha'_n \sin x + bx] \cos x \\
 &= \frac{1}{2} \{ \sin [\alpha'_n \sin x + (b-1)x] + \sin [\alpha'_n \sin x + (b+1)x] \} .
 \end{aligned}
 \tag{A7.b.13}$$

Taking into account equs. (A7.b.12), (A7.b.13), and changing

the limits of integration from $[n(2\pi-1), \pi(2\pi+1)]$ to $[-n, n]$

by $x \rightarrow x + 2\pi n$ equ. (A7.b.8) becomes

$$I_{(3)} = I_{(3)}^{(1)} + I_{(3)}^{(2)} \quad , \quad (A7.b.14)$$

where

$$I_{(3)}^{(1)} = \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\cos [a'_n \sin x + (b-1)x] \cos 2\pi n(b-1)$$

$$+ \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\cos [a'_n \sin x + (b+1)x] \cos 2\pi n(b+1) \quad ,$$

(A7.b.15)

and

$$I_{(3)}^{(2)} = \frac{i}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\sin [a'_n \sin x + (b-1)x] \cos 2\pi n(b-1)$$

$$+ \frac{i}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\sin [a'_n \sin x + (b+1)x] \cos 2\pi n(b+1) \quad .$$

(A7.b.16)

Equations (A7.b.15), and (A7.b.16) are the text equs. (7.24)

and (7.25), respectively.

Let us now proceed to the evaluation of the integral $I_{(3)}^{(1)}$ given by equ. (A7.b.15). The integrals appearing in equ. (A7.b.15) are of the general form

$$\int_{-n}^n \exp(r \cos x + s \sin x) \cos(m x - \lambda \cos x - \mu \sin x) dx$$

$$= \pi [(r-\mu)^2 + (s+\lambda)^2]^{-m/2} \{ (A+iB)^{m/2} I_m(\sqrt{C-iD})$$

$$+ (A-iB)^{m/2} I_m(\sqrt{C+iD}) \},$$

where

(A7.b.17)

$$A = r^2 - s^2 + \lambda^2 - \mu^2, \quad B = 2(rs + \lambda\mu), \quad (r-\mu)^2 + (s+\lambda)^2 > 0,$$

(A7.b.18)

$$C = r^2 + s^2 - \lambda^2 - \mu^2, \quad D = 2(r\lambda + s\mu), \quad m = 1, 2, \dots,$$

(A7.b.19)

where I_m is a modified Bessel function of order m .

In our case, equ. (A7.b.15),

$$r = \alpha_n, \quad s = 0, \quad m = (b-1), (b+1), \quad \lambda = 0, \quad \mu = -\alpha'_n,$$

$$A = \alpha_n^2 - \alpha_n'^2, \quad B = 0, \quad (\alpha_n + \alpha_n')^2 > 0,$$

(A7.b.20)

$$C = \alpha_n^2 - \alpha_n'^2, \quad D = 0, \quad (b-1), (b+1) = 1, 2, \dots$$

Thus, using the result given by equ. (A7.b.17) with parameters given by eqs. (A7.b.20), we obtain

$$\frac{1}{2} \int_{-n}^n dx \exp(\alpha_n \cos x) \cos[\alpha_n' \sin x + (b-1)x]$$

$$= \pi \left[\frac{\alpha_n \mp \alpha_n'}{\alpha_n \pm \alpha_n'} \right]^{\frac{|b-1|}{2}} I_{(b-1)}[\sqrt{\alpha_n^2 - \alpha_n'^2}],$$

(A7.b.21)

where the $\pm$ sign refers to the sign of b . Using eqs.

(7.27), (7.28),

$$\left[\frac{\alpha_n \mp \alpha'_n}{\alpha_n \pm \alpha'_n} \right]^{\frac{|b-1|}{2}} = \left\{ \frac{\frac{[E_b(\underline{q}) + E_b(\underline{q}')] \coth \frac{\beta \hbar \omega_0}{2}}{\hbar \omega_0} A_n \mp \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n}{\hbar \omega_0}}{\frac{[E_b(\underline{q}) + E_b(\underline{q}')] \coth \frac{\beta \hbar \omega_0}{2}}{\hbar \omega_0} A_n \pm \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n}{\hbar \omega_0}} \right\}^{\frac{|b-1|}{2}}$$

$$= \left\{ \frac{\coth \frac{\beta \hbar \omega_0}{2} \mp 1}{\coth \frac{\beta \hbar \omega_0}{2} \pm 1} \right\}^{\frac{|b-1|}{2}} = \left\{ \frac{\coth \frac{\beta \hbar \omega_0}{2} - 1}{\coth \frac{\beta \hbar \omega_0}{2} + 1} \right\}^{\frac{|b-1|}{2}} = [\exp(-\beta \hbar \omega_0)]^{(b-1)/2}, \quad (\text{A7.b.22})$$

$$\sqrt{\alpha_n^2 - \alpha'^2} = \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n}{\hbar \omega_0} \sqrt{\left[\coth \frac{\beta \hbar \omega_0}{2} \right]^2 - 1}$$

$$= \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n}{\hbar \omega_0} \operatorname{csch} \frac{\beta \hbar \omega_0}{2}. \quad (\text{A7.b.23})$$

Substituting equs. (A7.b.22), (A7.b.23) into equ. (A7.b.21), we obtain

$$\frac{1}{2} \int_{-n}^n dx \exp(\alpha_n \cos x) \cos [\alpha'_n \sin x + (b-1)x]$$

$$= \pi [\exp(-\beta \hbar \omega_0)]^{\frac{(b-1)}{2}} I_{(b-1)} \left\{ \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2}}{\hbar \omega_0} \right\}. \quad (\text{A7.b.24})$$

Similarly

$$\frac{1}{2} \int_{-n}^n dx \exp(\alpha_n \cos x) \cos [\alpha'_n \sin x + (b+1)x]$$

$$= \pi [\exp(-\beta \hbar \omega_0)]^{\frac{(b+1)}{2}} I_{(b+1)} \left\{ \frac{[E_b(\underline{q}) + E_b(\underline{q}')] A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2}}{\hbar \omega_0} \right\}. \quad (\text{A7.b.25})$$

Substituting equs. (A7.b.24), (A7.b.25) into equ. (A7.b.15), we obtain

$$I_{(3)}^{(1)} = \left(\frac{n}{\omega_0}\right) \exp(-s) [\exp(-\beta \hbar \omega_0)]^{(b-1)/2}$$

$$\begin{aligned} & \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(\underline{g}, \underline{g}')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b-1) \\ & + \left(\frac{n}{\omega_0}\right) \exp(-s) [\exp(-\beta \hbar \omega_0)]^{(b+1)/2} \\ & \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(\underline{g}, \underline{g}')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b+1), \end{aligned}$$

(A7.b.26)

where

$$\tilde{E}_b(\underline{g}, \underline{g}') = \frac{[E_b(\underline{g}) + E_b(\underline{g}')] }{2}, \quad (A7.b.27)$$

Equation (A7.b.26) is the text equ. (7.32).

In order to evaluate the integral $I_{(3)}^{(2)}$ given by equ. (A7.b.16), we notice that the integrals appearing in this equ. are of the general form

$$\begin{aligned} & \int_{-\pi}^{\pi} \exp(r \cos x + s \sin x) \sin(m x - \lambda \cos x - \mu \sin x) dx \\ & = -i \pi [(r - \mu)^2 + (s + \lambda)^2]^{-m/2} \left\{ (A + i B)^{m/2} I_m(\sqrt{C - i D}) \right. \\ & \quad \left. - (A - i B)^{m/2} I_m(\sqrt{C + i D}) \right\}, \end{aligned}$$

(A7.b.28)

where the parameters are given by equs. (A7.b.19). In our case, $B = D = 0$, equs. (A7.b.20), and thus from equ. (A7.b.28) it follows that the value of each of the integrals in

equ. (A7.b.16) is zero. Thus

$$I_{(3)}^{(2)} = 0 \quad (A7.b.29)$$

Equation (A7.b.29) is the text equ. (7.33).

Substituting the expressions for $I_{(3)}^{(1)}$, equ. (A7.b.26), and $I_{(3)}^{(2)}$, equ. (A7.b.29), into equ. (A7.b.14), we obtain

$$I_{(3)} = I_{(3)}^{(1)} \quad (A7.b.30)$$

where $I_{(3)}^{(1)}$ is given by equ. (A7.b.26). Equation (A7.b.30) is the text equ. (7.34).

Let us now evaluate the integral

$$I_{(4)} = i \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp \left[\left(\frac{it}{h} \right) \Delta g' g \right] J_0 \left(\frac{\omega_0}{\omega_0} x \right) \sin x$$

$$\exp(-S) \exp[F_1(t)] \exp[iF_2(t)] \quad (A7.b.31)$$

which appears in the text equ. (7.21). The various symbols have been already defined. Proceeding as before, $I_{(4)}$ can be written as

$$I_{(4)} = I_{(4)}^{(1)} - I_{(4)}^{(2)} \quad (A7.b.32)$$

where

$$I_{(4)}^{(1)} = i \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\sin[\alpha'_n \sin x + (b+1)x] \cos 2\pi n(b+1)$$

$$- i \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-S) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x)$$

$$\sin[\alpha'_n \sin x + (b-1)x] \cos 2\pi n(b-1) \quad (A7.b.33)$$

and

$$\begin{aligned}
 I_{(4)}^{(2)} &= \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-s) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x) \\
 &\quad \cos [a'_n \sin x + (b-1)x] \cos 2\pi n(b-1) \\
 &- \frac{1}{2} \left(\frac{1}{\omega_0} \right) \exp(-s) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n \int_{-n}^n dx \exp(a_n \cos x) \\
 &\quad \cos [a'_n \sin x + (b+1)x] \cos 2\pi n(b+1), \quad (A7.b.34)
 \end{aligned}$$

where the parameters involved have been already defined.

The integrals which appear in equ. (A7.b.33) are of the same form as those which appear in $I_{(3)}^{(2)}$. Thus, in the same way we obtain

$$I_{(4)}^{(1)} = 0. \quad (A7.b.35)$$

The integrals which appear in equ. (A7.b.34) are of the same form of those which appear in $I_{(3)}^{(1)}$. Thus in the same way we obtain

$$\begin{aligned}
 I_{(4)}^{(2)} &= \left(\frac{n}{\omega_0} \right) \exp(-s) [\exp(-\beta \hbar \omega_0)]^{(b-1)/2} \\
 &\quad \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(q, q')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b-1) \\
 &- \left(\frac{n}{\omega_0} \right) \exp(-s) [\exp(-\beta \hbar \omega_0)]^{(b+1)/2} \\
 &\quad \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\frac{\omega_0 \tau}{2\pi}} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(q, q')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b+1). \quad (A7.b.36)
 \end{aligned}$$

Substituting the expressions for $I_{(u)}^{(u)}$, equ. (A7.b.35), and $I_{(u)}^{(2)}$, equ. (A7.b.36), into equ. (A7.b.32), we obtain

$$I_{(u)} = - I_{(u)}^{(2)} \quad , \quad (A7.b.37)$$

where $I_{(u)}^{(2)}$ is given by equ. (A7.b.36).

Thus, in this Appendix we have evaluated the integrals

$$\begin{aligned} I_{(3)} &\equiv \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta g' g\right] T_0\left(\frac{\omega_0}{\omega_0} x\right) \cos x \\ &\quad \exp(-S') \exp[F_1(t)] \exp[iF_2(t)] \\ &= \left(\frac{n}{\omega_0}\right) \exp(-S') [\exp(-\beta \hbar \omega_0)]^{(b-1)/2} \\ &\quad \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b-1) \\ &\quad + \left(\frac{n}{\omega_0}\right) \exp(-S') [\exp(-\beta \hbar \omega_0)]^{(b+1)/2} \\ &\quad \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b+1), \end{aligned} \quad (A7.b.38)$$

in terms of which the coefficient $L_{(3)}^{(2)}, g, g'$ is expressed, and

$$I_{(4)} \equiv i \lim_{\tau \rightarrow \infty} \int_{-\tau}^{\tau} dt \exp\left[\left(\frac{it}{\hbar}\right) \Delta g' g\right] J_0\left(\frac{\omega_b}{\omega_0} x\right) \sin x$$

$$\exp(-S) \exp[F_1(t)] \exp[iF_2(t)]$$

$$= \left(\frac{n}{\omega_0}\right) \exp(-S) [\exp(-\beta \hbar \omega_0)]^{(b+1)/2}$$

$$\lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b+1)$$

$$- \left(\frac{n}{\omega_0}\right) \exp(-S) [\exp(-\beta \hbar \omega_0)]^{(b-1)/2}$$

$$\lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\pi}}^{\omega_0 \tau / 2\pi} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n(b-1),$$

(A7.b.39)

in terms of which the coefficient $L_{(4), g' g}^{(2)}$ is expressed.

Appendix A7.c.

Evaluation of the coefficient $L_{(3)}^{(2)}, g, g'$.

Substituting equ. (A7.b.38) into the text equ. (7.20), we obtain

$$L_{(3)}^{(2)}, g, g' = \frac{q n_c \beta a^2}{2} \tilde{E}_b(g, g') \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2$$

$$\exp \left[- \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right]$$

$$\left\{ [\exp(-\beta \hbar \omega_0)]^{(b-1)/2} \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \right. \right.$$

$$A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \left. \right\} \cos 2\pi n(b-1)$$

$$+ [\exp(-\beta \hbar \omega_0)]^{(b+1)/2} \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \right.$$

$$A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \left. \right\} \cos 2\pi n(b+1) \left. \right\}. \quad (\text{A7.c.1})$$

We recall here that

$$b \equiv \frac{\Delta g' g}{\hbar \omega_0},$$

(A7.c.2)

$$[\exp(-\beta \hbar \omega_0)]^{(b \pm 1)/2} = \exp \left(- \frac{\Delta g' g}{2 k T} \right) \exp \left(\pm \frac{\hbar \omega_0}{2 k T} \right).$$

Using equ. (A7.c.2), equ. (A7.c.1) becomes

$$L_{(3)}^{(2)}, g, g' = \frac{q n_c \beta a^2}{2} \tilde{E}_b(g, g') \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2$$

$$\exp \left[- \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right] \exp \left(- \frac{\Delta g' g}{2 k T} \right)$$

$$\left\{ \exp\left(\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\hbar}}^{\frac{\omega_0\tau}{2\hbar}} A_n I_{(b-1)} \right\} \frac{2\tilde{E}_b(\underline{q}, \underline{q}')}{\hbar\omega_0}$$

$$A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \left\{ \cos 2\pi n(b-1) \right.$$

$$\left. + \exp\left(-\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\hbar}}^{\frac{\omega_0\tau}{2\hbar}} A_n I_{(b+1)} \right\} \frac{2\tilde{E}_b(\underline{q}, \underline{q}')}{\hbar\omega_0}$$

$$A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \left\{ \cos 2\pi n(b+1) \right\} .$$

Equation(A7.c.3) is the text equ.(7.35).

(A7.c.3)

Appendix A7.d

Evaluation of the coefficient $L_{(4),g,g'}^{(2)}$.

Substituting equ. (A7.b.39) into the text equ. (7.21), we obtain

$$L_{(4),g,g'}^{(2)} = \frac{q n_c B a^2}{2} \tilde{E}_b(g, g') \left(\frac{n}{\omega_0} \right) \coth \frac{B \hbar \omega_0}{2} \left(\frac{T}{\hbar} \right)^2$$

$$\exp \left[- \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} \right]$$

$$\left\{ [\exp(-\beta \hbar \omega_0)]^{(b+1)/2} \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b+1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \right. \right.$$

$$A_n \operatorname{csch} \frac{B \hbar \omega_0}{2} \left. \right\} \cos 2n\pi(b+1)$$

$$- [\exp(-\beta \hbar \omega_0)]^{(b-1)/2} \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0 \tau}{2\hbar}}^{\frac{\omega_0 \tau}{2\hbar}} A_n I_{(b-1)} \left\{ \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \right.$$

$$A_n \operatorname{csch} \frac{B \hbar \omega_0}{2} \left. \right\} \cos 2n\pi(b-1) \left. \right\}.$$

(A7.d.1)

Using equ. (A7.c.2), equ. (A7.d.1) becomes

$$L_{(4),g,g'}^{(2)} = \frac{q n_c B a^2}{2} \tilde{E}_b(g, g') \left(\frac{n}{\omega_0} \right) \coth \frac{B \hbar \omega_0}{2} \left(\frac{T}{\hbar} \right)^2$$

$$\exp \left[- \frac{2 \tilde{E}_b(g, g')}{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} \right] \exp \left(- \frac{4g'g}{2kT} \right)$$

$$\left\{ \exp\left(-\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\hbar}}^{\frac{\omega_0\tau}{2\hbar}} A_n I_{(b+1)} \left\{ \frac{2\tilde{E}_b(q, q')}{\hbar\omega_0} \right. \right. \\ \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b+1) \right.$$

$$\left. - \exp\left(\frac{\hbar\omega_0}{2kT}\right) \lim_{\tau \rightarrow \infty} \sum_{n=-\frac{\omega_0\tau}{2\hbar}}^{\frac{\omega_0\tau}{2\hbar}} A_n I_{(b-1)} \left\{ \frac{2\tilde{E}_b(q, q')}{\hbar\omega_0} \right. \right. \\ \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b-1) \right\}.$$

Equation (A7.d.2) is the text equ. (7.36) .

(A7.d.2)

Chapter 8.

Evaluation of the net transport coefficients.

In the previous Chapter we evaluated the transport coefficients $L_{g'g}^{(1)}$, and $L_{gg'}^{(2)}$, in the weak-dispersion limit, when a small-polaron hops from a site g to a nearest neighbouring site g' . Following exactly the same procedure we can evaluate the transport coefficients $L_{g'g}^{(1)}$, and $L_{gg'}^{(2)}$ for the reverse hop from the site g' to the site g . The only difference is that, for the reverse hop, the disorder energy will be $\Delta_{gg'} = -\Delta_{g'g}$.

We find,

$$L_{g'g}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{J}{\hbar} \right)^2 \exp \left(\frac{\Delta_{g'g}}{2 k T} \right)$$

$$\exp \left[- \frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2 \pi n b . \quad (8.1)$$

and

$$L_{g'g}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{g'g}^{(1)}$$

$$+ q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{J}{\hbar} \right)^2 \epsilon_2 \exp \left(\frac{\Delta_{g'g}}{2 k T} \right)$$

$$\exp \left[- \frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right]$$

$$\begin{aligned}
 & \left\{ \exp\left(-\frac{\hbar\omega_0}{2kT}\right) \left(1 + \coth h \frac{B\hbar\omega_0}{2}\right) \sum_{n=-\infty}^{\infty} A_n I_{(b-1)} \left\{ \frac{4\epsilon_2}{\hbar\omega_0} \right. \right. \\
 & \qquad \qquad \qquad \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b-1) \right\} \\
 & + \exp\left(\frac{\hbar\omega_0}{2kT}\right) \left(1 - \coth h \frac{B\hbar\omega_0}{2}\right) \sum_{n=-\infty}^{\infty} A_n I_{(b+1)} \left\{ \frac{4\epsilon_2}{\hbar\omega_0} \right. \\
 & \qquad \qquad \qquad \left. \left. A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n(b+1) \right\}. \quad (8.2)
 \end{aligned}$$

Now we are able to evaluate the net transport coefficients $L^{(1)}$, $L^{(2)}$ for a small-polaron hopping between the two sites g , and g' . They are given by

$$L^{(1)} = L_{g'g}^{(1)} - L_{gg'}^{(1)}, \quad (8.3)$$

and

$$L^{(2)} = L_{g'g}^{(2)} - L_{gg'}^{(2)}. \quad (8.4)$$

Substituting $L_{g'g}^{(1)}$, and $L_{gg'}^{(1)}$, given by equs. (7.44), and (8.1), respectively, into equ. (8.3), we obtain

$$\begin{aligned}
 L^{(1)} &= -q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0}\right) \left(\frac{T}{\hbar}\right)^2 \\
 & \exp \left[-\frac{4\epsilon_2}{\hbar\omega_0} \coth h \frac{B\hbar\omega_0}{2} \right] \sinh \frac{\Delta g'g}{2kT} \\
 & \sum_{n=-\infty}^{\infty} I_b \left\{ \frac{4\epsilon_2}{\hbar\omega_0} A_n \operatorname{csch} \frac{B\hbar\omega_0}{2} \right\} \cos 2\pi n b. \quad (8.5)
 \end{aligned}$$

Substituting $L_{g'g}^{(2)}$, and $L_{gg'}^{(2)}$, given by equs. (7.44), and (8.2), respectively, into equ. (8.4), we obtain

$$L^{(2)} = \frac{1}{q} \tilde{E}(g, g') L^{(1)}$$

$$\begin{aligned}
 & + q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left[- \frac{4\epsilon_2}{\hbar \omega_0} \coth \frac{B \hbar \omega_0}{2} \right] \\
 & \left\{ \exp \left(- \frac{\Delta g' g}{2 k T} \right) \exp \left(\frac{\hbar \omega_0}{2 k T} \right) \left(1 - \coth \frac{B \hbar \omega_0}{2} \right) \right. \\
 & \quad \left. - \exp \left(\frac{\Delta g' g}{2 k T} \right) \exp \left(- \frac{\hbar \omega_0}{2 k T} \right) \left(1 + \coth \frac{B \hbar \omega_0}{2} \right) \right\} \\
 & \sum_{n=-\infty}^{\infty} A_n I_{(b-1)} \left\{ \frac{4\epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{B \hbar \omega_0}{2} \right\} \cos 2\pi n (b-1) \\
 & + \left[\exp \left(- \frac{\Delta g' g}{2 k T} \right) \exp \left(- \frac{\hbar \omega_0}{2 k T} \right) \left(1 + \coth \frac{B \hbar \omega_0}{2} \right) \right. \\
 & \quad \left. - \exp \left(\frac{\Delta g' g}{2 k T} \right) \exp \left(\frac{\hbar \omega_0}{2 k T} \right) \left(1 - \coth \frac{B \hbar \omega_0}{2} \right) \right] \\
 & \sum_{n=-\infty}^{\infty} A_n I_{(b+1)} \left\{ \frac{4\epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{B \hbar \omega_0}{2} \right\} \cos 2\pi n (b+1) \} . \quad (8.6)
 \end{aligned}$$

Now, having evaluated the net transport coefficients $L^{(1)}$, and $L^{(2)}$, given by equs. (8.5), and (8.6), respectively, direct substitution into equ. (6.6), which we recall here

$$\alpha_{g, g'} = \frac{1}{q T} \left(q L^{(1)-1} L^{(2)} - \gamma \right) \quad (8.7)$$

gives us the expression for the thermoelectric power, associated with a small-polaron hop between the two sites g , and g' . In the following Part III, this expression, equ. (8.7.), with $L^{(1)}$, $L^{(2)}$ given by equs. (8.5), and (8.6), respectively, will be used to evaluate the thermoelectric power in a two-site jump for the various regimes of coupling and temperature of physical interest.

Part III

Specific applications

Chapter 9

Evaluation of the thermoelectric power in the strong-coupling and high-temperature regime.

In this Chapter, we shall apply the general results, obtained in Chapter 8 for the transport coefficients $L^{(1)}$, $L^{(2)}$ and the thermoelectric power $\alpha_{g,g'}$ to the high-temperature case $\hbar\omega_0 \ll kT$, in which the hops are characterized by the absorption and emission of many phonons. The coupling between the charge carrier and the lattice is taken to be strong, i.e. $\frac{4\epsilon_2}{\hbar\omega_0} \gg 1$.

Here, and in the following sections, it will be assumed that the conditions are such that the principal contribution to the n -summation is made by the $n=0$ term. In this case $A_n = A_0 = 1$. Specifically, the condition⁽²⁹⁾ which must be satisfied is $\frac{(2\pi)^2}{8} \left(\frac{\omega_b}{\omega_0}\right)^2 \left(\frac{2\tilde{E}_b(g,g')}{\hbar\omega_0}\right) \left(\coth \frac{8\hbar\omega_0}{2}\right) \gg 1$, which in the high-temperature regime, $\hbar\omega_0 \ll kT$, may be written as $(2\pi)^2 \left(\frac{\omega_b}{\omega_0}\right)^2 \left(\frac{\epsilon_2}{\hbar\omega_0} - \frac{kT}{\hbar\omega_0}\right) \gg 1$.

At sufficiently high-temperatures, the argument of the Bessel functions of the $n=0$ term is very large, provided that $\frac{4\epsilon_2}{\hbar\omega_0}$ is large enough (strong-coupling). Thus we can use the large-argument approximation of the Bessel function, which generally reads⁽³²⁾,

$$I_p(z) \approx \frac{\exp(z)}{\sqrt{2\pi z}} \left\{ 1 - \frac{p-1}{8z} \right\}, \quad (9.1)$$

for fixed ρ , $|z|$ large, and $\mu = 4\rho^2$.

Applying the expansion (9.1) on the Bessel functions which appear in equ. (8.6), we obtain.

$$I_{(b \pm 1)} \left\{ \frac{4\epsilon_2}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \right\} = \frac{\exp \left\{ \frac{4\epsilon_2}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \right\}}{\sqrt{2\pi \frac{4\epsilon_2}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2}}} \left\{ 1 - \frac{4(b \pm 1)^2 - 1}{8 \frac{4\epsilon_2}{\hbar\omega_0} \operatorname{csch} \frac{\beta\hbar\omega_0}{2}} \right\}, \quad (9.2)$$

An analogous expression holds for I_b , appearing in equ. (8.5).

On the other hand, in the high-temperature limit, the trigonometric functions, appearing in eqs. (8.5), (8.6), can be approximated by

$$\operatorname{csch} \frac{\beta\hbar\omega_0}{2} \cong \frac{2}{\beta\hbar\omega_0} - \frac{\beta\hbar\omega_0}{12},$$

and

$$\coth \frac{\beta\hbar\omega_0}{2} \cong \frac{2}{\beta\hbar\omega_0} + \frac{\beta\hbar\omega_0}{6}.$$

(9.3)

Further, the terms of the form $\exp(\pm \hbar\omega_0/2kT)$ can be approximated as

$$\exp\left(\pm \frac{\hbar\omega_0}{2kT}\right) \cong 1 \pm \frac{\hbar\omega_0}{2kT}. \quad (9.4)$$

Substituting the expressions given by eqs. (9.2), (9.3), and (9.4), into eqs. (8.5), and (8.6), after some straightforward algebra, we obtain.

$$L_{s.h.}^{(1)} = -q^2 \pi_c \beta \alpha^2 \left(\frac{J^2}{\hbar} \right) \sqrt{\frac{\pi}{4\epsilon_2 kT}}$$

$$\exp\left(-\frac{\epsilon_2}{kT}\right) \exp\left(-\frac{\Delta g^2}{16\epsilon_2 kT}\right) \sinh\left(\frac{\Delta g^2}{2kT}\right), \quad (9.5)$$

and

$$L_{s.h.}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{s.h.}^{(1)} + q n_c \beta \alpha^2 \left(\frac{T^2}{h} \right) \sqrt{\frac{\pi}{4\epsilon_2 kT}} \exp\left(-\frac{\epsilon_2}{kT}\right) \left(-\frac{\Delta g'g}{2}\right) \cosh\left(\frac{\Delta g'g}{2kT}\right) \quad (9.6)$$

Here, the symbol $L_{s.h.}$ stands for L at the strong-coupling (s), and high-temperature(h) regime.

Now, substituting eqs. (9.5), (9.6) into the general expression for the thermoelectric power

$$\alpha_{g,g'}^{s.h.} = \frac{1}{qT} \left(q L_{s.h.}^{(1)} - \mu \right), \quad (9.7)$$

$$\alpha_{g,g'}^{s.h.} = \frac{1}{qT} \left\{ q \left[\frac{\frac{1}{q} \tilde{E}(g, g') L_{s.h.}^{(1)}}{L_{s.h.}^{(1)}} + \frac{q n_c \beta \alpha^2 \left(\frac{T^2}{h} \right) \sqrt{\frac{\pi}{4\epsilon_2 kT}} \exp\left(-\frac{\epsilon_2}{kT}\right) \left(-\frac{\Delta g'g}{2}\right) \cosh\left(\frac{\Delta g'g}{2kT}\right)}{-q^2 n_c \beta \alpha^2 \left(\frac{T^2}{h} \right) \sqrt{\frac{\pi}{4\epsilon_2 kT}} \exp\left(-\frac{\epsilon_2}{kT}\right) \exp\left(-\frac{\Delta g'g}{16\epsilon_2 kT}\right) \sinh\left(\frac{\Delta g'g}{2kT}\right)} - \mu \right] \right\},$$

we obtain the expression for the thermoelectric power for a small-polaron hop between sites g , and g' , $\alpha_{g,g'}^{s.h.}$, in the strong-coupling and high-temperature regime

$$\alpha_{g,g'}^{s.h.} = \frac{1}{qT} \left[\tilde{E}(g, g') + E_{T,s.h.}^{g,g'} - \mu \right], \quad (9.8)$$

where

$$E_{T,s.h.}^{g,g'} \equiv \frac{\Delta g'g}{2} \coth \frac{\Delta g'g}{2kT} \exp\left(\frac{\Delta g'g}{16\epsilon_2 kT}\right), \quad (9.9)$$

is the additional heat of transport part to the thermoelectric power. Recalling equ. (6.31),

$$\tilde{E}(\underline{q}, \underline{q}') \equiv \frac{[\epsilon_{\underline{q}}(0) - E_b(\underline{q})] + [\epsilon_{\underline{q}'}(0) - E_b(\underline{q}')]}{2}, \quad (9.10)$$

is the mean energy of the two site system.

Equation (9.8) can also be written in terms of the coefficient $A_{\underline{q}, \underline{q}'}^{s.h.}$, as

$$\alpha_{\underline{q}, \underline{q}'}^{s.h.} = \left(\frac{\kappa}{q}\right) \left[\frac{\tilde{E}(\underline{q}, \underline{q}') - \mu}{kT} + A_{\underline{q}, \underline{q}'}^{s.h.} \right], \quad (9.11)$$

where

$$A_{\underline{q}, \underline{q}'}^{s.h.} = \frac{\Delta_{\underline{q}, \underline{q}}}{2kT} \coth \frac{\Delta_{\underline{q}, \underline{q}}}{2kT} \exp\left(-\frac{\Delta_{\underline{q}, \underline{q}}^2}{16\epsilon_2 kT}\right). \quad (9.12)$$

The variation of the coefficient $A_{\underline{q}, \underline{q}'}^{s.h.}$ with respect to the disorder energy $\Delta_{\underline{q}, \underline{q}}$ in the range $[0.02 - 0.1] \text{ eV}$, for a temperature range $[200 - 800]^\circ \text{K}$, is presented in fig. 11. The argument used to choose the numerical values of the parameters involved in a consistent way ($\Delta_{\underline{q}, \underline{q}} \equiv E_b(\underline{q}) - E_b(\underline{q}')$, $E_b(\underline{q}) = 0.2 \text{ eV}$), is presented in Appendix A9.

Fig. 11. The variation of the coefficient A'_{gg} with respect to the energy disorder $\Delta g'g$ in the range (200-800) °K.

Appendix A9.

The "polaronic character" of the energy disorder.

In order to choose the numerical values of the parameters involved in our expression for the additional part of the thermoelectric power, (c.f. equ. (9.12)), and thus to obtain a numerical estimate for the coefficient A, the following approximate procedure has been used.

The disorder energy is given by

$$\Delta_{\underline{g}'\underline{g}} = [\epsilon_{\underline{g}'}(0) - \epsilon_{\underline{g}}(0)] + [E_b(\underline{g}) - E_b(\underline{g}')] , \quad (\text{A9.1})$$

for a pair of sites $\underline{g}, \underline{g}'$, such that, $\epsilon_{\underline{g}'}(0) > \epsilon_{\underline{g}}(0)$. Using the relation between binding energy and radius of the localized state⁽²¹⁾

$$\frac{E_b(\underline{g})}{E_b(\underline{g}')} = \left(\frac{r_{\underline{g}'}}{r_{\underline{g}}} \right)^3 , \quad (\text{A9.2})$$

where $r_{\underline{g}}, r_{\underline{g}'}$ are the radii of the localized states for the sites $\underline{g}, \underline{g}'$, respectively, and further assuming that the Anderson-Lukes formula⁽³³⁾

$$r = \frac{c}{(E_c - E)^x} , \quad (\text{A9.3})$$

is valid for all E, we find that

$$[\epsilon_{\underline{g}'}(0) - \epsilon_{\underline{g}}(0)] = \Delta_{\underline{g}'\underline{g}} - E_b(\underline{g}') \left\{ \left[\frac{\Delta_{\underline{g}'\underline{g}}}{(E_c - E_{\underline{g}'})} + 1 \right]^{3x} - 1 \right\} , \quad (\text{A9.4})$$

where $E_{\underline{g}'}$ is the total electronic energy of the site $\underline{g}'$.

For representative values of the parameters involved in equ.

(A9.4), $\alpha = 0.6$, $\Delta g'g = 0.1 \text{ eV}$, $E_b(g') = 0.25 \text{ eV}$, and for $E_c - E_{g'}$

in a range $[0.4 - 0.5] \text{ eV}$ we find that for $E_c - E_{g'} = 0.5 \text{ eV}$,

$[\epsilon_{g'}(0) - \epsilon_g(0)] = 0.003 \text{ eV}$, while $[E_b(g) - E_b(g')] = 0.097 \text{ eV}$

i.e. $[E_b(g) - E_b(g')] \approx 32 [\epsilon_{g'}(0) - \epsilon_g(0)]$.

Thus, $[\epsilon_{g'}(0) - \epsilon_g(0)]$ can be considered negligibly small compared to $[E_b(g) - E_b(g')]$, and we can write

$$\Delta g'g \approx [E_b(g) - E_b(g')] \quad (A9.5)$$

Thus $E_b(g)$ can be estimated for given values of $\Delta g'g$ and $E_b(g')$.

The results do not change appreciably if instead of the above approximation we use actual numerical values for all the parameters involved, i.e. $\Delta g'g$, $E_b(g')$ and $E_b(g)$.

Chapter 10

Evaluation of the thermoelectric power in the strong-coupling and low-temperature regime.

In this Chapter, we consider another small-polaron hopping regime of physical interest, the strong-coupling $\frac{4\epsilon_2}{\hbar\omega_0} \gg 1$, and low-temperature, $\hbar\omega_0 \gg kT$, regime. We shall find the limiting form of the expressions for the transport coefficients, $L^{(1)}$, $L^{(2)}$, and the thermoelectric power $\alpha_{g,g'}$ for this case. In this limit the hops upwards in energy are characterized by an absorption of $|\Delta_{g,g'}|/\hbar\omega_0$ phonons. The hops downwards in energy are characterized by the carrier's spontaneous emission of that number of phonons which is needed to comply with the requirement of energy conservation.

The above statements can be easily verified from the expression for the jump rate, or, equivalently from the expression for the transport coefficient $L^{(1)}$. This, as well as the expression for the transport coefficient $L^{(2)}$, can be obtained from the general expressions, given by eqs. (7.43) (7.44), by taking the low-temperature limit of the quantities involved.

Because of the definition of the low-temperature regime, i.e. $\hbar\omega_0 \gg kT$, the argument of the Bessel functions is very small, so that, we can use the small-argument approximation of the Bessel function, which generally reads ⁽³²⁾

$$I_p(z) = \frac{\left(\frac{z}{2}\right)^{|p|}}{(|p|)!} \quad (10.1)$$

Applying the expansion(10.1) to the Bessel functions which appear in equs. (8.5), (8.6), and using the approximations,

$$\operatorname{csch} \frac{\beta \hbar \omega_0}{2} \approx 2 \exp\left(-\frac{\beta \hbar \omega_0}{2}\right),$$

and

$$\coth \frac{\beta \hbar \omega_0}{2} \approx 1,$$

(10.2)

for the trigonometric functions in the low-temperature limit, we obtain

$$\begin{aligned} I_{(b \pm 1)} & \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \\ &= \frac{\left[\frac{1}{2} - \frac{4 \epsilon_2}{\hbar \omega_0} 2 \exp\left(-\frac{\beta \hbar \omega_0}{2}\right) \right] \left| \frac{\Delta g' g}{\hbar \omega_0} \pm 1 \right|}{\left(\left| \frac{\Delta g' g}{\hbar \omega_0} \pm 1 \right| \right)!} \\ &= \exp\left\{ -\frac{|\Delta g' g \pm \hbar \omega_0|}{2 k T} \right\} \frac{\left[\frac{4 \epsilon_2}{\hbar \omega_0} \right]^{\frac{|\Delta g' g \pm \hbar \omega_0|}{\hbar \omega_0}}}{\left(\left| \frac{\Delta g' g \pm \hbar \omega_0}{\hbar \omega_0} \right| \right)!}, \quad (10.3) \end{aligned}$$

where only the $n=0$, $A_n=A_0=1$, contribution has been considered.

A similar expression holds for the I_b Bessel function.

Thus, substituting equs. (10.2), (10.3), into equs. (8.5), (8.6), after some algebra, details of which are given in Appendix A10.a., and A10.b., we finally obtain

$$L_{s.l.}^{(1)} = -q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right)!} \left[1 - \exp\left(-\frac{\Delta g'g}{kT}\right) \right]^2, \quad (10.4)$$

and

$$L_{s.l.}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{s.l.}^{(1)}$$

$$- 2q n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)!}$$

$$\left\{ -\exp\left[-\frac{1}{kT}(\Delta g'g + \hbar\omega_0)\right] \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} + \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} \right\}. \quad (10.5)$$

The symbol $L_{s.l.}$ stands for L at the strong-coupling(s) and low-temperature(l) regime.

Now, substituting equs. (10.4), and (10.5) into the general expressions for the thermoelectric power

$$\alpha_{g,g'}^{s.l.} = \frac{1}{qT} \left(q L_{s.l.}^{(1)-1} L_{s.l.}^{(2)} - \mu \right), \quad (10.6)$$

$$\alpha_{g,g'}^{s.l.} = \frac{1}{qT} \left\{ q \left[\frac{\frac{1}{q} \tilde{E}(g, g') L_{s.l.}^{(1)}}{L_{s.l.}^{(1)}} \right. \right.$$

$$+ \frac{2q n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \epsilon_2 \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)!} \left\{ \exp\left[-\frac{1}{kT}(\Delta g'g + \hbar\omega_0)\right] \frac{\frac{4\epsilon_2}{\hbar\omega_0}}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} - \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} \right\}$$

$$+ \frac{q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)! \left(\frac{\Delta g'g}{\hbar\omega_0} \right)} \left\{ \exp\left(-\frac{\Delta g'g}{kT}\right) - 1 \right\}$$

$$\left. - \mu \right\}$$

$$\begin{aligned}
 &= \frac{1}{qT} \left\{ \tilde{E}(\underline{g}, \underline{g}') + \frac{2\epsilon_2 \left\{ \exp\left[-\frac{1}{kT}(\Delta g'g + \hbar\omega_0)\right] \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0}\right)}{\left(\frac{\Delta g'g}{\hbar\omega_0}\right)\left(\frac{\Delta g'g}{\hbar\omega_0} + 1\right)} - \left(\frac{4\epsilon_2}{\hbar\omega_0}\right)^{-1} \right\}}{\frac{1}{\left(\frac{\Delta g'g}{\hbar\omega_0}\right)} \left[\exp\left(-\frac{\Delta g'g}{kT}\right) - 1 \right]} \right. \\
 &\quad \left. - \mu \right\} \\
 &= \frac{1}{qT} \left\{ \tilde{E}(\underline{g}, \underline{g}') - \frac{8\epsilon_2^2}{(\Delta g'g + \hbar\omega_0)} \frac{\exp\left[-\frac{(\Delta g'g + \hbar\omega_0)}{kT}\right]}{\left[1 - \exp\left(-\frac{\Delta g'g}{kT}\right)\right]} \right. \\
 &\quad \left. + \left(\frac{\Delta g'g}{2}\right) \frac{1}{\left[1 - \exp\left(-\frac{\Delta g'g}{kT}\right)\right]} - \mu \right\},
 \end{aligned}$$

we obtain the expression for the thermoelectric power for a small-polaron hop between sites $\underline{g}$ and $\underline{g}'$, $\alpha_{\underline{g}, \underline{g}'}^{s.l.}$, in the strong-coupling and low-temperature regime,

$$\alpha_{\underline{g}, \underline{g}'}^{s.l.} = \frac{1}{qT} \left[\tilde{E}(\underline{g}, \underline{g}') + E_{\tau, s.l.}^{\underline{g}, \underline{g}'} - \mu \right], \quad (10.7)$$

where

$$\begin{aligned}
 E_{\tau, s.l.}^{\underline{g}, \underline{g}'} &\equiv \left(\frac{\Delta g'g}{2}\right) \frac{1}{\left[1 - \exp\left(-\frac{\Delta g'g}{kT}\right)\right]} \\
 &\quad - \frac{8\epsilon_2^2}{(\Delta g'g + \hbar\omega_0)} \frac{\exp\left[-\frac{(\Delta g'g + \hbar\omega_0)}{kT}\right]}{\left[1 - \exp\left(-\frac{\Delta g'g}{kT}\right)\right]} \quad (10.8)
 \end{aligned}$$

is the additional heat of transport part to the thermoelectric

power.

Equation (10.8) can also be written in terms of the coefficient $A_{\underline{g},\underline{g}'}^{s.l.}$ as

$$\alpha_{\underline{g},\underline{g}'}^{s.l.} = \left(\frac{\kappa}{q} \right) \left[\frac{\tilde{E}(\underline{g},\underline{g}') - \mu}{\kappa \tau} + A_{\underline{g},\underline{g}'}^{s.l.} \right], \quad (10.9)$$

where

$$A_{\underline{g},\underline{g}'}^{s.l.} = \left(\frac{\Delta \underline{g}' \underline{g}}{2 \kappa \tau} \right) \frac{1}{[1 - \exp(-\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})]} - \frac{8 \epsilon_2^2}{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)} \frac{\exp[-\frac{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)}{\kappa \tau}]}{[1 - \exp(-\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})]}. \quad (10.10)$$

N.B.: The exponential terms arise from the Bose-Einstein distribution function $N(\Delta \underline{g}' \underline{g})$ which for an upward hop reads

$$N(\Delta \underline{g}' \underline{g}) = 1 / [\exp(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau}) - 1] = \exp[-(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})] / \{1 - \exp[-(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})]\}$$

while for a downward hop,

$$N(\Delta \underline{g}' \underline{g}) + 1 = \exp(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau}) / [\exp(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau}) - 1] = 1 / \{1 - \exp[-(\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})]\}.$$

Observing equ. (10.8) we notice that the main contribution to the additional heat of transport part of the thermoelectric power $E_{\tau, s.l.}^{\underline{g}, \underline{g}'}$ comes from the first term. The reason is that at sufficiently low-temperatures, the expression $[1 - \exp(-\frac{\Delta \underline{g}' \underline{g}}{\kappa \tau})]$ can be approximated by 1, thus equ. (10.8) can be written as

$$E_{\tau, s.l.}^{\underline{g}, \underline{g}'} = \frac{\Delta \underline{g}' \underline{g}}{2} - \frac{8 \epsilon_2^2}{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)} \exp\left[-\frac{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)}{\kappa \tau}\right]. \quad (10.11)$$

On the other hand, for the same **limiting** case,

$$\frac{\Delta_{2,2}}{2} \gg \frac{8\epsilon_z^2}{(\Delta_{2,2} + \hbar\omega_0)} \exp\left[-\frac{(\Delta_{2,2} + \hbar\omega_0)}{kT}\right], \quad (10.12)$$

even if the coupling is strong, $\frac{4\epsilon_z}{\hbar\omega_0} \gg 1$, because of the strong exponential dependence on the temperature of the r.h.s. term of the inequality (10.12) again by definition of the low-temperature regime.

Note that the main contribution, $A_{2,2} = \frac{\Delta_{2,2}}{2kT}$ for this case agrees with the strong-coupling, high-temperature case at the lowest temperature possible, namely $kT \gg \hbar\omega_0$. Hence, with

$$\Delta_{2,2}/\hbar\omega_0 > 1, \text{ we get } A_{2,2} \rightarrow \frac{\Delta_{2,2}}{2kT}.$$

The variation of the coefficient $A_{2,2}^{s.l.}$ with respect to the disorder energy $\Delta_{2,2}$ in the range $[0.02 - 0.1] \text{ eV}$, and the temperature, $T = 10, 15, 20 \text{ }^\circ\text{K}$, is presented in fig.12.

Fig. 12. The variation of the coefficient $A_{g,2}^{s.l.}$ with respect to the energy disorder $\Delta_{g,2}$ in the range (10-20)°K.

Appendix A10.a.

Evaluation of the coefficient $L_{gg}^{(1)}$.

Substituting the text equs. (10.2),

$$\operatorname{csch} \frac{\beta \hbar \omega_0}{2} \cong 2 \exp\left(-\frac{\beta \hbar \omega_0}{2}\right),$$

and

$$\coth \frac{\beta \hbar \omega_0}{2} \cong 1,$$

(A10.a.1)

into the text equ. (7.43),

$$L_{gg}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0}\right) \left(\frac{\gamma}{\hbar}\right)^2 \exp\left(-\frac{\Delta g' g}{2 K T}\right) \\ \exp\left[-\frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2}\right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2 \pi n b, \quad (\text{A10.a.2})$$

and expanding the Bessel function according to the text equ. (10.1).

$$I_b \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \\ = \exp\left\{-\frac{|\Delta g' g|}{2 K T}\right\} \frac{\left[\frac{4 \epsilon_2}{\hbar \omega_0}\right] \frac{|\Delta g' g|}{\hbar \omega_0}}{\left(\left|\frac{\Delta g' g}{\hbar \omega_0}\right|\right)!}, \quad (\text{A10.a.3})$$

equ. (A10.a.2) becomes

$$s.l. L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \gamma \exp \left(- \frac{2\epsilon_2}{\hbar \omega_0} \right)}{\hbar \omega_0} \right]^2$$

$$\exp \left\{ - \frac{1}{2\kappa T} \left[\Delta_{\underline{g}\underline{g}'} + |\Delta_{\underline{g}\underline{g}'}| \right] \right\} \frac{\left[\frac{4\epsilon_2}{\hbar \omega_0} \right]^{\frac{|\Delta_{\underline{g}\underline{g}'}|}{\hbar \omega_0}}}{\left(\frac{|\Delta_{\underline{g}\underline{g}'}|}{\hbar \omega_0} \right)!} , \quad (A10.a.4)$$

where only the $n=0$, $A_n = A_0 = 1$, contribution has been considered.

Taking into account the fact that $\frac{\Delta_{\underline{g}\underline{g}'}}{\hbar \omega_0} \equiv b = 1, 2, 3, \dots$, we obtain, for an upwards hop,

$$s.l. L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \gamma \exp \left(- \frac{2\epsilon_2}{\hbar \omega_0} \right)}{\hbar \omega_0} \right]^2$$

$$\exp \left(- \frac{\Delta_{\underline{g}\underline{g}'}}{\kappa T} \right) \frac{\left[\frac{4\epsilon_2}{\hbar \omega_0} \right]^{\frac{\Delta_{\underline{g}\underline{g}'}}{\hbar \omega_0}}}{\left(\frac{\Delta_{\underline{g}\underline{g}'}}{\hbar \omega_0} \right)!} . \quad (A10.a.5)$$

From equ. (A10.a.5) it becomes clear that for a hop upward in energy by an amount $\Delta_{\underline{g}\underline{g}'}$ the carrier must absorb $\Delta_{\underline{g}\underline{g}'}/\hbar \omega_0$ phonons. This accounts for proportionality of $s.l. L_{\underline{g}\underline{g}'}^{(1)}$ to both $\exp(-\Delta_{\underline{g}\underline{g}'}/\kappa T)$ and to $(4\epsilon_2/\hbar \omega_0)^{\Delta_{\underline{g}\underline{g}'}/\hbar \omega_0}$.

For the reverse (downwards) hop, applying the above approximations to the text equ. (8.1), we obtain

$$s.l. L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \gamma \exp \left(- \frac{2\epsilon_2}{\hbar \omega_0} \right)}{\hbar \omega_0} \right]^2$$

$$\frac{\left[\frac{4\epsilon_2}{\hbar \omega_0} \right]^{\frac{\Delta_{\underline{g}\underline{g}'}}{\hbar \omega_0}}}{\left(\frac{\Delta_{\underline{g}\underline{g}'}}{\hbar \omega_0} \right)!} . \quad (A10.a.6)$$

From equ. (A10.a.6) we conclude that for a hop downward in energy by an amount $\Delta_{g'g} = -\Delta_{g'g}$, the dominant process, in the low-temperature and strong-coupling limit, is the carrier's spontaneous emission of that number of phonons which is needed to comply with the requirement of energy conservation. As a result $^{s.l.}L_{g'g}^{(1)}$ is temperature-independent at sufficiently low temperatures while remaining proportional to $(4\epsilon_2 / \hbar\omega_0) \frac{\Delta_{g'g}}{\hbar\omega_0}$. It should be noted that the rate characterizing the phonon emission processes, can, when $\frac{\Delta_{g'g}}{\hbar\omega_0} < \frac{4\epsilon_2}{\hbar\omega_0}$ increase with an increase in the energy disparity between the initial and final electronic states, provided that $4\epsilon_2 / \hbar\omega_0 > 1$.

Thus, the statements given in the beginning of this Chapter become clear.

Now, substituting $^{s.l.}L_{g'g}^{(1)}$ from equ. (A10.a.5), and from equ. (A10.a.6) into the text equ. (8.3),

$$L_{s.l.}^{(1)} = ^{s.l.}L_{g'g}^{(1)} - ^{s.l.}L_{g'g}^{(1)}, \quad (\text{A10.a.7})$$

we obtain

$$L_{s.l.}^{(1)} = -q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{\pi} \right) \left[\frac{\pi T \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right) \frac{\Delta_{g'g}}{\hbar\omega_0}}{\left(\frac{\Delta_{g'g}}{\hbar\omega_0} \right)!} \left[1 - \exp\left(-\frac{\Delta_{g'g}}{kT}\right) \right]. \quad (\text{A10.a.8})$$

Equation (A10.a.8) is the text equ. (10.4).

Appendix A10.b.

Evaluation of the coefficient $L_{s.l.}^{(2)}$.

Substituting the text equs.(10.2), into the text equ. (7.44), and using the expansion of the Bessel functions involved according to the text equ.(10.3), we obtain

$$s.l. L_{g g'}^{(2)} = \frac{1}{g} \tilde{E}(g, g') s.l. L_{g g'}^{(1)} + 2 g n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp(-\frac{2\epsilon_2}{\hbar \omega_0})}{\hbar \omega_0} \right]^2 \epsilon_2 \exp \left\{ -\frac{1}{2kT} [(\Delta g' g + \hbar \omega_0) + |\Delta g' g + \hbar \omega_0|] \right\} \frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{|\Delta g' g + \hbar \omega_0|}{\hbar \omega_0}}}{\left(\frac{|\Delta g' g + \hbar \omega_0|}{\hbar \omega_0} \right)!} \quad (A10.b.1)$$

Taking into account the fact that $\Delta g' g / \hbar \omega_0 \equiv b = 1, 2, 3, \dots$, we obtain, for an upwards hop,

$$s.l. L_{g g'}^{(2)} = \frac{1}{g} \tilde{E}(g, g') s.l. L_{g g'}^{(1)} + 2 g n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp(-\frac{2\epsilon_2}{\hbar \omega_0})}{\hbar \omega_0} \right]^2 \epsilon_2 \exp \left\{ -\frac{1}{2kT} (\Delta g' g + \hbar \omega_0) \right\} \frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\left(\frac{\Delta g' g}{\hbar \omega_0} + 1 \right)}}{\left(\frac{\Delta g' g}{\hbar \omega_0} + 1 \right)!}, \quad (A10.b.2)$$

where $s.l. L_{g g'}^{(1)}$ is given by equ.(A10.a.5).

For the reverse(downwards)hop, applying the above approximations to the text equ.(8.2), we obtain

$$s.l. L_{g'g}^{(1)} = \frac{1}{q} \bar{E}(g, g') s.l. L_{g'g}^{(1)}$$

$$+ 2q n_c \beta \alpha^2 \left(\frac{\omega_0}{\pi} \right) \left[\frac{\pi \exp \left(-\frac{2\epsilon_2}{\hbar\omega_0} \right)}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\exp \left\{ -\frac{1}{2\kappa T} [-\Delta g'g + \hbar\omega_0 + |\Delta g'g - \hbar\omega_0|] \right\} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{|\Delta g'g - \hbar\omega_0|}{\hbar\omega_0}}}{\left(\frac{|\Delta g'g - \hbar\omega_0|}{\hbar\omega_0} \right)!}, \quad (A10.b.3)$$

Using the fact that $\Delta g'g / \hbar\omega_0 = 1, 2, 3, \dots$, equ. (A10.b.3) becomes

$$s.l. L_{g'g}^{(2)} = \frac{1}{q} \bar{E}(g, g') s.l. L_{g'g}^{(1)}$$

$$+ 2q n_c \beta \alpha^2 \left(\frac{\omega_0}{\pi} \right) \left[\frac{\pi \exp \left(-\frac{2\epsilon_2}{\hbar\omega_0} \right)}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)!}, \quad (A10.b.4)$$

where $s.l. L_{g'g}^{(1)}$ is given by equ. (A10.a.6).

As we mentioned examining the coefficient $s.l. L_{g'g}^{(1)}$, the same remarks are to be made here; i.e. in the phonon emission process, and when $\frac{\Delta g'g}{\hbar\omega_0} - 1 < \frac{4\epsilon_2}{\hbar\omega_0}$, the coefficient $s.l. L_{g'g}^{(1)}$ increases with an increase of the energy disparity $\Delta g'g$.

Now, substituting $s.l. L_{g'g}^{(2)}$, from equ. (A10.b.2), and $s.l. L_{g'g}^{(2)}$, from equ. (A10.b.4) into the text equ. (8.4)

$$L_{s.l.}^{(2)} = s.l. L_{g'g}^{(2)} - s.l. L_{g'g}^{(2)}, \quad (A10.b.5)$$

we obtain

$$L_{s.l.}^{(2)} = \frac{1}{q} \tilde{E}(q, q') L_{s.l.}^{(1)}$$

$$- 2 q n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp \left(- \frac{2 \epsilon_z}{\hbar \omega_0} \right)}{\hbar \omega_0} \right]^2 \epsilon_z$$

$$\frac{\left(\frac{4 \epsilon_z}{\hbar \omega_0} \right) \frac{\Delta q' q}{\hbar \omega_0}}{\left(\frac{\Delta q' q}{\hbar \omega_0} - 1 \right)!}$$

$$\left\{ - \exp \left[- \frac{1}{kT} (\Delta q' q + \hbar \omega_0) \right] \frac{\left(\frac{4 \epsilon_z}{\hbar \omega_0} \right)}{\left(\frac{\Delta q' q}{\hbar \omega_0} \right) \left(\frac{\Delta q' q}{\hbar \omega_0} + 1 \right)} + \left(\frac{4 \epsilon_z}{\hbar \omega_0} \right)^{-1} \right\} .$$

(A10.b.6)

where $L_{s.l.}^{(1)}$ is given by the text equ. (10.4). Equation (A10.b.6) is the text equ. (10.5).

Chapter 11

Evaluation of the thermoelectric power in the weak-coupling and high-temperature regime.

In this Chapter, we shall apply the general results, obtained in Chapter 8, for the transport coefficients $L^{(1)}$, $L^{(2)}$, and the thermoelectric power $\alpha_{g.g'}$ to the weak-coupling, $4\epsilon_z/\hbar\omega_0 \ll 1$, and high-temperature, $\hbar\omega_0 \ll kT$, regime. The weak-coupling case is arbitrarily defined⁽²⁹⁾ as being the circumstance in which the argument of the Bessel functions involved in the expressions for the coefficients $L^{(1)}$, and $L^{(2)}$ is much less than unity even when $kT \gg \hbar\omega_0$.

In the weak-coupling case the Bessel function may be replaced by its small-argument approximation,

$$I_p(z) = \frac{\left(\frac{z}{2}\right)^{|p|}}{(|p|)!} \quad (11.1)$$

On the other hand, in this limit, the trigonometric functions, and the exponentials can be approximated as follows

$$\operatorname{csch} \frac{\beta \hbar \omega_0}{2} \cong \frac{2}{\beta \hbar \omega_0} - \frac{\beta \hbar \omega_0}{12} ,$$

$$\coth \frac{\beta \hbar \omega_0}{2} \cong \frac{2}{\beta \hbar \omega_0} + \frac{\beta \hbar \omega_0}{6} ,$$

(11.2)

$$\exp \left[- \frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right] \cong 1 ,$$

$$\exp \left[\pm \frac{\beta \hbar \omega_0}{2} \right] \cong 1 \pm \frac{\beta \hbar \omega_0}{2} .$$

Thus,

$$\exp \left(\pm \frac{\beta \hbar \omega_0}{2} \right) \left(1 \pm \coth \frac{\beta \hbar \omega_0}{2} \right) \cong \mp \frac{2}{\beta \hbar \omega_0} \pm \frac{\beta \hbar \omega_0}{2} . \quad (11.3)$$

Applying the expansion (11.1) to the Bessel functions which appear in eqs. (8.5), (8.6), and using the approximations (11.2), in the weak-coupling limit $\frac{4 \epsilon_2}{\hbar \omega_0} \ll 1$, we obtain

$$I_{(b \pm 1)} = \left(\frac{k_T}{\hbar \omega_0} \right)^{\left| \frac{\Delta g_2}{\hbar \omega_0} \pm 1 \right|} \frac{\left(-\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{\left| \frac{\Delta g_2}{\hbar \omega_0} \pm 1 \right|}}{\left(\left| \frac{\Delta g_2}{\hbar \omega_0} \pm 1 \right| \right)!} , \quad (11.4)$$

where, as before, we have assumed that sufficient dispersion exists so that the major contribution arises from the $n=0$ term of the n -summation. An analogous expression holds for the I_b Bessel function.

Thus, substituting eqs. (11.2), (11.3), (11.4) into eqs. (8.5), (8.6), after some algebra, details of which are given in Appendix A11.a, and A11.b., we finally obtain

$$L_{w.h.}^{(1)} = -2q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}}{\left(\frac{\Delta g'g}{\hbar \omega_0} \right)!} \sinh h \frac{\Delta g'g}{2KT}, \quad (11.5)$$

and

$$L_{w.h.}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{w.h.}^{(1)}$$

$$- 4q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}} \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}}{\left(\frac{\Delta g'g}{\hbar \omega_0} - 1 \right)!}$$

$$\left\{ - \frac{\left(\frac{KT}{\hbar \omega_0} \right)^2 \left(\frac{4\epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar \omega_0} \right) \left(\frac{\Delta g'g}{\hbar \omega_0} + 1 \right)} + \left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{-1} \right\} \cosh h \frac{\Delta g'g}{2KT}. \quad (11.6)$$

Here, the symbol $L_{w.h.}$ stands for L at the weak-coupling (w), and high-temperature (h) regime.

Now, substituting eqs. (11.5), (11.6) into the general expression for the thermoelectric power

$$\alpha_{g,g'}^{w.h.} = \frac{1}{qT} \left(q L_{w.h.}^{(1)-1} L_{w.h.}^{(2)} - \mu \right), \quad (11.7)$$

$$\alpha_{\underline{g}, \underline{g}'}^{w.h.} = \frac{1}{qT} \left\{ q \left[\frac{\frac{1}{q} \tilde{E}(\underline{g}, \underline{g}') L_{s.h.}^{(1)}}{L_{s.h.}^{(1)}} \right] \right.$$

$$+ \frac{4 q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g' g}{\hbar \omega_0}} \epsilon_2 \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta g' g}{\hbar \omega_0}}}{\left(\frac{\Delta g' g}{\hbar \omega_0} - 1 \right)!} \left\{ \frac{\left(\frac{KT}{\hbar \omega_0} \right)^2 \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta g' g}{\hbar \omega_0} \right) \left(\frac{\Delta g' g}{\hbar \omega_0} + 1 \right)} - \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{-1} \right\} \cosh \frac{\Delta g' g}{2KT}$$

$$- 2 q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g' g}{\hbar \omega_0}} \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta g' g}{\hbar \omega_0}}}{\left(\frac{\Delta g' g}{\hbar \omega_0} \right)!} \sinh \frac{\Delta g' g}{2KT}$$

$$- \mu \left. \right\}$$

$$= \frac{1}{qT} \left\{ \tilde{E}(\underline{g}, \underline{g}') + \frac{2 \epsilon_2 \coth \frac{\Delta g' g}{2KT}}{\frac{1}{\left(\frac{\Delta g' g}{\hbar \omega_0} \right)}} \left\{ \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right) - \frac{\left(\frac{KT}{\hbar \omega_0} \right)^2 \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta g' g}{\hbar \omega_0} \right) \left(\frac{\Delta g' g}{\hbar \omega_0} + 1 \right)} \right\} - \mu \right\}$$

$$= \frac{1}{qT} \left[\tilde{E}(\underline{g}, \underline{g}') + \left\{ \frac{\Delta g' g}{2} - \frac{1}{2} \frac{\frac{(4 \epsilon_2)^2}{\hbar \omega_0} \left(\frac{KT}{\hbar \omega_0} \right)^2}{\left(\frac{\Delta g' g}{\hbar \omega_0} + 1 \right)} \right\} \coth \frac{\Delta g' g}{2KT} - \mu \right],$$

we obtain the expression for the thermoelectric power for a small-polaron hop between sites $\underline{g}$, and $\underline{g}'$, $\alpha_{\underline{g}, \underline{g}'}^{w.h.}$ in the

weak-coupling and high temperature regime,

$$\alpha_{\underline{g}, \underline{g}'}^{\text{w.h.}} = \frac{1}{qT} \left[\tilde{E}(\underline{g}, \underline{g}') + E_{\tau, \text{w.h.}}^{\underline{g}, \underline{g}'} - \mu \right], \quad (11.8)$$

where

$$E_{\tau, \text{w.h.}}^{\underline{g}, \underline{g}'} \equiv \frac{\Delta \underline{g}, \underline{g}'}{2} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T} - \frac{1}{2} \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^2 (kT)^2 \frac{1}{(\Delta \underline{g}, \underline{g}' + \hbar \omega_0)} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T}, \quad (11.9)$$

is the additional heat of transport part to the thermoelectric power. $\tilde{E}(\underline{g}, \underline{g}')$ is the mean energy of the two site system.

Equation (11.8) can also be written in terms of the coefficient $A_{\underline{g}, \underline{g}'}^{\text{w.h.}}$, as

$$\alpha_{\underline{g}, \underline{g}'}^{\text{w.h.}} = \left(\frac{k}{q} \right) \left[\frac{\tilde{E}(\underline{g}, \underline{g}') - \mu}{kT} + A_{\underline{g}, \underline{g}'}^{\text{w.h.}} \right], \quad (11.10)$$

where

$$A_{\underline{g}, \underline{g}'}^{\text{w.h.}} = \frac{\Delta \underline{g}, \underline{g}'}{2 k T} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T} - \frac{1}{2} \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^2 (kT)^2 \frac{1}{(\Delta \underline{g}, \underline{g}' + \hbar \omega_0)} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T}. \quad (11.11)$$

Observing equ. (11.9) we notice that the main contribution to the additional heat of transport part to the thermoelectric power, $E_{\tau, \text{w.h.}}^{\underline{g}, \underline{g}'}$, comes from the first term. The reason is that

$$\frac{\Delta \underline{g}, \underline{g}'}{2} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T} \gg \frac{1}{2} \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^2 (kT)^2 \frac{1}{(\Delta \underline{g}, \underline{g}' + \hbar \omega_0)} \coth \frac{\Delta \underline{g}, \underline{g}'}{2 k T}, \quad (11.12)$$

even at high-T, because the coupling is weak, $\frac{4 \epsilon_2}{\hbar \omega_0} \ll 1$.

Appendix A11.a

Evaluation of the coefficient $L_{\omega_0}^{(1)}$

Substituting the text equs. (11.2), and (11.3)

$$\operatorname{csch} \frac{\beta \hbar \omega_0}{2} \cong \frac{2}{\beta \hbar \omega_0} - \frac{\beta \hbar \omega_0}{2} ,$$

$$\coth \frac{\beta \hbar \omega_0}{2} \cong \frac{2}{\beta \hbar \omega_0} + \frac{\beta \hbar \omega_0}{6} ,$$

(A11.a.1)

$$\exp \left(- \frac{4\epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right) \cong 1 ,$$

$$\exp \left(\pm \frac{\beta \hbar \omega_0}{2} \right) \cong 1 \pm \frac{\beta \hbar \omega_0}{2} ,$$

$$\exp \left(\pm \frac{\beta \hbar \omega_0}{2} \right) \left(1 \mp \coth \frac{\beta \hbar \omega_0}{2} \right) \cong \mp \frac{2}{\beta \hbar \omega_0} \pm \frac{\beta \hbar \omega_0}{2} ,$$

(A11.a.2)

into the text equ. (7.43),

$$L_{\underline{g}\underline{g}}^{(1)} = q^2 n_c \beta a^2 \left(\frac{n}{\omega_0} \right) \left(\frac{\gamma}{\hbar} \right)^2 \exp \left(- \frac{\Delta \underline{g} \underline{g}}{2 k T} \right)$$

$$\exp \left[- \frac{4\epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2} \right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4\epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2\pi n b , \quad (\text{A11.a.3})$$

and expanding the Bessel function according to the text equ. (10.1),

$$I_b \left\{ \frac{4\epsilon_2}{\hbar\omega_0} \csc h \frac{\beta \hbar\omega_0}{2} \right\} = \left(\frac{K T}{\hbar\omega_0} \right)^{\frac{|\Delta g'g|}{\hbar\omega_0}} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{|\Delta g'g|}{\hbar\omega_0}}}{\left(\frac{|\Delta g'g|}{\hbar\omega_0} \right)!}, \quad (A11.a.4)$$

equ. (A11.a.3) becomes

$$w.h. L_{g'g}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{K T}{\hbar\omega_0} \right)^{\frac{|\Delta g'g|}{\hbar\omega_0}} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{|\Delta g'g|}{\hbar\omega_0}}}{\left(\frac{|\Delta g'g|}{\hbar\omega_0} \right)!} \exp \left(- \frac{\Delta g'g}{2 K T} \right), \quad (A11.a.5)$$

where only the $n=0$, $A_n = A_0 = 1$, contribution has been considered.

Taking into account the fact that $(\Delta g'g / \hbar\omega_0) \equiv b = 1, 2, 3, \dots$, we obtain, for an upwards hop,

$$w.h. L_{g'g}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{K T}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right)!} \exp \left(- \frac{\Delta g'g}{2 K T} \right). \quad (A11.a.6)$$

For the reverse (downwards) hop applying the above approximations to the text equ. (8.1), we obtain

$${}^{w.h.}L_{g'g}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{J}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}} \frac{\left(\frac{4\epsilon_z}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}}{\left(\frac{\Delta g'g}{\hbar \omega_0} \right)!} \exp \left(- \frac{\Delta g'g}{2KT} \right) . \quad (A11.a.7)$$

Now, substituting ${}^{w.h.}L_{g'g}^{(1)}$, from equ. (A11.a.6), and ${}^{w.h.}L_{g'g}^{(1)}$, from equ. (A11.a.7) into the text equ. (8.3),

$$L_{w.h.}^{(1)} = {}^{w.h.}L_{g'g}^{(1)} - {}^{w.h.}L_{g'g}^{(1)} \quad (A11.a.8)$$

we obtain,

$$L_{w.h.}^{(1)} = - 2 q^2 n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{J}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}} \frac{\left(\frac{4\epsilon_z}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}}{\left(\frac{\Delta g'g}{\hbar \omega_0} \right)!} \sinh \frac{\Delta g'g}{\hbar \omega_0} . \quad (A11.a.9)$$

Equation (A11.a.9) is the text equ. (11.5).

Appendix A11.b.

Evaluation of the coefficient $L_{\omega, \omega'}^{(2)}$

Substituting the text equs. (11.2), (11.3), and (11.4) into the text equ. (7.44), for an upwards hop, we obtain

$$\begin{aligned}
 w.h. L_{\underline{g} \underline{g}'}^{(2)} &= \frac{1}{\underline{g}} \tilde{E}(\underline{g}, \underline{g}') L_{\underline{g} \underline{g}'}^{(1)} \\
 &+ \underline{g} n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{2 k T} \right) \\
 &\left(\frac{k T}{\hbar \omega_0} \right)^{\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0}} \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0}}}{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0} - 1 \right)!} \\
 &\left\{ - 2 \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{-1} + \left(\frac{k T}{\hbar \omega_0} \right)^{-2} \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{-1} + \frac{2 \left(\frac{k T}{\hbar \omega_0} \right)^2 \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0} \right) \left(\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0} + 1 \right)} \right. \\
 &\left. - \frac{1}{2} \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0} \right) \left(\frac{\Delta \underline{g}' \underline{g}}{\hbar \omega_0} + 1 \right)} \right\} .
 \end{aligned}
 \tag{A11.b.1}$$

In the weak-coupling, $\frac{4 \epsilon_2}{\hbar \omega_0} \ll 1$, and high-temperature

$kT \gg \hbar\omega_0$, limit, we can also approximate

$$\frac{1}{2} \left(\frac{kT}{\hbar\omega_0} \right)^{-1} \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} \cong 0 ,$$

and

(A11.b.2)

$$\frac{1}{2} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} \cong 0 .$$

Then, equ. (A11.b.1) becomes

$${}^{w.h.} L_{\underline{g}\underline{g}'}^{(2)} = \frac{1}{\underline{g}} \tilde{E}(\underline{g}, \underline{g}') {}^{w.h.} L_{\underline{g}\underline{g}'}^{(1)}$$

$$+ \underline{g} n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left(- \frac{\Delta g'g}{2kT} \right)$$

$$\left(\frac{kT}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}} \left\{ -2 \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} + \frac{2 \left(\frac{kT}{\hbar\omega_0} \right)^2 \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} \right\} ,$$

(A11.b.3)

where ${}^{w.h.} L_{\underline{g}\underline{g}'}^{(1)}$ is given by equ. (A11.a.6).

For the reverse (downwards) hop, applying the above approximations to the text equ. (8.2), we obtain

$${}^{w.h.} L_{\underline{g}'\underline{g}}^{(2)} = \frac{1}{\underline{g}'} \tilde{E}(\underline{g}', \underline{g}) {}^{w.h.} L_{\underline{g}'\underline{g}}^{(1)}$$

$$+ \underline{g}' n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \epsilon_2 \exp \left(\frac{\Delta g'g}{2kT} \right)$$

$$\left(\frac{kT}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}} \left\{ 2 \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} - \frac{2 \left(\frac{kT}{\hbar\omega_0} \right)^2 \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} \right\} ,$$

(A11.b.4)

where ${}^{w.h.} L_{\underline{q}, \underline{q}}^{(1)}$ is given by equ. (A11.a.7).

Now, substituting ${}^{w.h.} L_{\underline{q}, \underline{q}'}^{(2)}$, from equ. (A11.b.3), and ${}^{w.h.} L_{\underline{q}', \underline{q}}^{(2)}$, from equ. (A11.b.4) into the text equ. (8.4)

$$L_{w.h.}^{(2)} = {}^{w.h.} L_{\underline{q}, \underline{q}'}^{(2)} - {}^{w.h.} L_{\underline{q}', \underline{q}}^{(2)}, \quad (A11.b.5)$$

we obtain

$$L_{w.h.}^{(2)} = \frac{1}{f} \tilde{E}(\underline{q}, \underline{q}') L_{w.h.}^{(1)}$$

$$= 4q n_c \beta \alpha^2 \left(\frac{n}{\omega_0} \right) \left(\frac{T}{\hbar} \right)^2 \left(\frac{KT}{\hbar \omega_0} \right)^{\frac{\Delta \underline{q}' \underline{q}}{\hbar \omega_0}} \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta \underline{q}' \underline{q}}{\hbar \omega_0}}}{\left(\frac{\Delta \underline{q}' \underline{q}}{\hbar \omega_0} - 1 \right)!}$$

$$\left\{ - \frac{\left(\frac{KT}{\hbar \omega_0} \right)^2 \left(\frac{4\epsilon_2}{\hbar \omega_0} \right)}{\left(\frac{\Delta \underline{q}' \underline{q}}{\hbar \omega_0} \right) \left(\frac{\Delta \underline{q}' \underline{q}}{\hbar \omega_0} + 1 \right)} + \left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{-1} \right\} \cosh \frac{\Delta \underline{q}' \underline{q}}{2KT},$$

(A11.b.6)

where $L_{w.h.}^{(1)}$ is given by the text equ. (11.5). Equation (A11.b.6) is the text equ. (11.6).

Chapter 12

Evaluation of the thermoelectric power in the weak-coupling and low-temperature regime.

In this Chapter, we consider another small-polaron hopping regime of physical interest, the weak-coupling, $\frac{4\epsilon_2}{\kappa\omega_0} \ll 1$, and low-temperature, $\hbar\omega_0 \gg kT$, regime. We shall find the limiting form of the expressions for the transport coefficients $L^{(1)}$, $L^{(2)}$, and the thermoelectric power, $\alpha_{\frac{1}{2}, \frac{1}{2}}$, for this case.

In this limit, the Bessel functions may be replaced by their small-argument approximation,

$$I_p(z) = \frac{\left(\frac{z}{2}\right)^{|p|}}{(|p|)!} \quad (12.1)$$

On the other hand, in this limit, the trigonometric functions appearing in our general equations (8.5), (8.6), can be approximated by

$$\csc h \frac{\beta \hbar \omega_0}{2} \cong 2 \exp\left(-\frac{\beta \hbar \omega_0}{2}\right), \quad (12.2)$$

and

$$\coth h \frac{\beta \hbar \omega_0}{2} \cong 1.$$

Applying the expansion (12.1) to the Bessel functions which appear in equs. (8.5) and (8.6), and using the ap-

proximations (12.2), for the trigonometric functions we obtain

$$I_{(b \pm 1)} = \exp \left\{ - \frac{|\Delta g'g + \hbar \omega_0|}{2 k T} \right\} \frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{|\Delta g'g + \hbar \omega_0|}{\hbar \omega_0}}}{\left(\frac{|\Delta g'g + \hbar \omega_0|}{\hbar \omega_0} \right)!} , \quad (12.3)$$

where, as before, we have assumed that sufficient dispersion exists so that the major contribution arises from the $n=0$ term of the n -summation. A similar expression holds for the b -order Bessel function.

Substituting equs. (12.2), and (12.3) into equs. (8.5), (8.6), after some algebra, given in Appendices A12.a., and A12.b, we, finally obtain

$$L_{w.l.}^{(1)} = - q^2 n_c \beta a^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp\left(-\frac{2\epsilon_2}{\hbar \omega_0}\right)}{\hbar \omega_0} \right]^2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar \omega_0} \right)^{\frac{\Delta g'g}{\hbar \omega_0}}}{\left(\frac{\Delta g'g}{\hbar \omega_0} \right)!} \left[1 - \exp\left(-\frac{\Delta g'g}{k T}\right) \right] , \quad (12.4)$$

and

$$L_{w.l.}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{w.l.}^{(1)}$$

$$- 2 q n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi T \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0}\right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1\right)!} \left\{ -\exp\left[-\frac{1}{kT}(\Delta g'g + \hbar\omega_0)\right] \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0}\right)}{\left(\frac{\Delta g'g}{\hbar\omega_0}\right)\left(\frac{\Delta g'g}{\hbar\omega_0} + 1\right)} + \left(\frac{4\epsilon_2}{\hbar\omega_0}\right)^{-1} \right\} . \quad (12.5)$$

The symbol $L_{w.l.}$ stands for L at the weak-coupling (w), and low-temperature (l) regime.

Now, substituting eqs. (12.4), (12.5) into the general expression for the thermoelectric power

$$\alpha_{g, g'}^{w.l.} = \frac{1}{qT} \left(q L_{w.l.}^{(1)-1} L_{w.l.}^{(2)} - \gamma \right), \quad (12.6)$$

we obtain the expression for the thermoelectric power for a small-polaron hop between sites g and g' , $\alpha_{g, g'}^{w.l.}$, in the weak-coupling and low-temperature regime,

$$\alpha_{g, g'}^{w.l.} = \frac{1}{qT} \left[\tilde{E}(g, g') + E_{T, w.l.}^{g, g'} - \gamma \right], \quad (12.7)$$

where

$$E_{\tau, w.l.}^{\underline{g}, \underline{g}'} \equiv \left(\frac{\Delta_{\underline{g}'\underline{g}}}{2} \right) \frac{1}{[1 - \exp(-\frac{\Delta_{\underline{g}'\underline{g}}}{kT})]} - \frac{8\epsilon_2^2}{(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)} \frac{\exp[-\frac{(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)}{kT}]}{[1 - \exp(-\frac{\Delta_{\underline{g}'\underline{g}}}{kT})]}, \quad (12.8)$$

is the additional heat of transport part to the thermoelectric power.

Equation (12.7) can also be written in terms of the coefficient $A_{\underline{g}, \underline{g}'}^{w.l.}$, as

$$\alpha_{\underline{g}, \underline{g}'}^{w.l.} = \left(\frac{k}{q} \right) \left[\frac{\tilde{E}(\underline{g}, \underline{g}') - \mu}{kT} + A_{\underline{g}, \underline{g}'}^{w.l.} \right], \quad (12.9)$$

where

$$A_{\underline{g}, \underline{g}'}^{w.l.} \equiv \left(\frac{\Delta_{\underline{g}'\underline{g}}}{2kT} \right) \frac{1}{[1 - \exp(-\frac{\Delta_{\underline{g}'\underline{g}}}{kT})]} - \frac{8\epsilon_2^2}{kT(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)} \frac{\exp[-\frac{(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)}{kT}]}{[1 - \exp(-\frac{\Delta_{\underline{g}'\underline{g}}}{kT})]}. \quad (12.10)$$

Here, as in Chapter 10, where we consider the strong-coupling and low-temperature case, we can approximate the expression $[1 - \exp(-\frac{\Delta_{\underline{g}'\underline{g}}}{kT})]$ by 1, and the main contribution to $E_{\tau, w.l.}^{\underline{g}, \underline{g}'}$ comes from the first term of the r.h.s. of equ. (12.8), because

$$\frac{\Delta_{\underline{g}'\underline{g}}}{2} \gg \frac{8\epsilon_2^2}{(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)} \exp\left[-\frac{(\Delta_{\underline{g}'\underline{g}} + \hbar\omega_0)}{kT}\right]. \quad (12.11)$$

The reason is, as in Chapter 10, the strong exponential dependence on temperature of the r.h.s. term of the inequality (12.11), and additionally, the weak-coupling condition $\frac{4\epsilon_2}{\hbar\omega_0} \ll 1$, which makes the above inequality stronger than that of Chapter 10.

Appendix A12.a.

Evaluation of the coefficient $L_{\omega, \epsilon}^{(1)}$.

Substituting the text equs. (12.2), and (12.3)

$$\operatorname{csch} \frac{\beta \hbar \omega_0}{2} \cong 2 \exp\left(-\frac{\beta \hbar \omega_0}{2}\right),$$

and

(A12.a.1)

$$\coth \frac{\beta \hbar \omega_0}{2} \cong 1,$$

into the text equ. (7.43),

$$L_{\underline{g} \underline{g}'}^{(1)} = q^2 n_c \beta a^2 \left(\frac{n}{\omega_0}\right) \left(\frac{\gamma}{\hbar}\right)^2 \exp\left(-\frac{\Delta \underline{g} \underline{g}'}{2 k T}\right)$$

$$\exp\left[-\frac{4 \epsilon_2}{\hbar \omega_0} \coth \frac{\beta \hbar \omega_0}{2}\right]$$

$$\sum_{n=-\infty}^{\infty} A_n I_b \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} A_n \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\} \cos 2 \pi n b, \quad (\text{A12.a.2})$$

and expanding the Bessel function according to the text equ. (12.1),

$$I_b \left\{ \frac{4 \epsilon_2}{\hbar \omega_0} \operatorname{csch} \frac{\beta \hbar \omega_0}{2} \right\}$$

$$= \exp\left\{-\frac{|\Delta \underline{g} \underline{g}'|}{2 k T}\right\} \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0}\right) \frac{|\Delta \underline{g} \underline{g}'|}{\hbar \omega_0}}{\left(\left|\frac{\Delta \underline{g} \underline{g}'}{\hbar \omega_0}\right|\right)!}, \quad (\text{A12.a.3})$$

equ. (A12.a.2) becomes

$$w.l. L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2$$

$$\exp\left\{-\frac{1}{2kT} [\Delta \underline{g}'\underline{g} + |\Delta \underline{g}'\underline{g}|]\right\} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0}\right)^{\frac{|\Delta \underline{g}'\underline{g}|}{\hbar\omega_0}}}{\left(\frac{|\Delta \underline{g}'\underline{g}|}{\hbar\omega_0}\right)!},$$

(A12.a.4)

where only the $n=0$, $A_n=A_0=1$, contribution has been considered.

Taking into account the fact that $(\Delta \underline{g}'\underline{g} / \hbar\omega_0) \equiv b = 1, 2, 3, \dots$, we obtain for an upwards hop,

$$w.l. L_{\underline{g}\underline{g}'}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2$$

$$\exp\left\{-\frac{\Delta \underline{g}'\underline{g}}{kT}\right\} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0}\right)^{\frac{\Delta \underline{g}'\underline{g}}{\hbar\omega_0}}}{\left(\frac{\Delta \underline{g}'\underline{g}}{\hbar\omega_0}\right)!}.$$

(A12.a.5)

For the reverse (downwards) hop, applying the above approximations to the text equ. (8.1), we obtain

$$w.l. L_{\underline{g}'\underline{g}}^{(1)} = q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \tau \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right) \frac{\Delta g'g}{\hbar\omega_0}}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right)!} \quad (A12.a.6)$$

Now, substituting $L_{\underline{g}'\underline{g}}^{(1)}$ from equ. (A12.a.5), and $L_{\underline{g}'\underline{g}}^{(2)}$ from equ. (A12.a.6) into the text equ. (8.3)

$$L_{w.l.}^{(1)} = w.l. L_{\underline{g}'\underline{g}}^{(1)} - w.l. L_{\underline{g}'\underline{g}}^{(1)} \quad (A12.a.7)$$

we obtain

$$L_{w.l.}^{(1)} = - q^2 n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \tau \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right) \frac{\Delta g'g}{\hbar\omega_0}}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right)!} \left[1 - \exp\left(-\frac{\Delta g'g}{k\tau}\right) \right] \quad (A12.a.8)$$

Equation (A12.a.8) is the text equ. (12.4).

Appendix A12.b.

Evaluation of the coefficient $L_{w.l.}^{(2)}$.

Substituting the text equs.(12.2), into the text equ. (7.44), and using the expansion of the Bessel functions involved according to the text equ.(12.3), we obtain

$$w.l. L_{\underline{q}\underline{q}'}^{(2)} = \frac{1}{\underline{q}} \tilde{E}(\underline{q}, \underline{q}') w.l. L_{\underline{q}\underline{q}'}^{(1)}$$

$$+ 2 \underline{q} n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi \mathcal{I} \exp \left(- \frac{2 \epsilon_2}{\hbar \omega_0} \right)}{\hbar \omega_0} \right]^2 \epsilon_2$$

$$\exp \left\{ - \frac{1}{2 k T} \left[\Delta \underline{q}' \underline{q} + \hbar \omega_0 + | \Delta \underline{q}' \underline{q} + \hbar \omega_0 | \right] \right\} \frac{\left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^{\frac{| \Delta \underline{q}' \underline{q} + \hbar \omega_0 |}{\hbar \omega_0}}}{\left(\frac{| \Delta \underline{q}' \underline{q} + \hbar \omega_0 |}{\hbar \omega_0} \right)!} ,$$

(A12.b.1)

Taking into account the fact that $(\Delta \underline{q}' \underline{q} / \hbar \omega_0) \equiv b = 1, 2, \dots$, we obtain for an upwards hop,

$$w.l. L_{\underline{g}\underline{g}'}^{(2)} = \frac{1}{\underline{g}} \tilde{E}(\underline{g}, \underline{g}') w.l. L_{\underline{g}\underline{g}}^{(1)}$$

$$+ 2 \underline{g} n_c \beta \alpha^2 \left(\frac{\omega_0}{\pi} \right) \left[\frac{\pi \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\exp \left\{ -\frac{1}{K_T} (\Delta \underline{g}' \underline{g} + \hbar\omega_0) \right\} \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar\omega_0} + 1 \right)}}{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar\omega_0} + 1 \right)!}, \quad (A12.b.2)$$

where $w.l. L_{\underline{g}\underline{g}}^{(1)}$ is given by equ.(A12.a.5).

For the reverse(downwards)hop, applying the above approximations to the text equ.(8.2), we obtain

$$w.l. L_{\underline{g}'\underline{g}}^{(2)} = \frac{1}{\underline{g}'} \tilde{E}(\underline{g}, \underline{g}') w.l. L_{\underline{g}'\underline{g}'}^{(1)}$$

$$+ 2 \underline{g}' n_c \beta \alpha^2 \left(\frac{\omega_0}{\pi} \right) \left[\frac{\pi \exp\left(-\frac{2\epsilon_2}{\hbar\omega_0}\right)}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar\omega_0} - 1 \right)}}{\left(\frac{\Delta \underline{g}' \underline{g}}{\hbar\omega_0} - 1 \right)!}, \quad (A12.b.3)$$

where $w.l. L_{\underline{g}'\underline{g}'}^{(1)}$ is given by equ.(A12.a.6).

Now, substituting $w.l. L_{\underline{g}\underline{g}'}^{(2)}$ from equ.(A12.b.2), and $w.l. L_{\underline{g}'\underline{g}}^{(2)}$ from equ.(A12.b.3) into the text equ.(3.4)

$$L_{w.l.}^{(2)} = w.l. L_{\underline{g}\underline{g}'}^{(2)} - w.l. L_{\underline{g}'\underline{g}}^{(2)}, \quad (A12.b.4)$$

we obtain

$$L_{w.l.}^{(2)} = \frac{1}{q} \tilde{E}(g, g') L_{w.l.}^{(1)}.$$

$$- 2q n_c \beta \alpha^2 \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp(-\frac{2\epsilon_2}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \epsilon_2$$

$$\frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{\frac{\Delta g'g}{\hbar\omega_0}}}{\left(\frac{\Delta g'g}{\hbar\omega_0} - 1 \right)!} \left\{ -\exp \left[-\frac{1}{k_T} (\Delta g'g + \hbar\omega_0) \right] \frac{\left(\frac{4\epsilon_2}{\hbar\omega_0} \right)}{\left(\frac{\Delta g'g}{\hbar\omega_0} \right) \left(\frac{\Delta g'g}{\hbar\omega_0} + 1 \right)} + \left(\frac{4\epsilon_2}{\hbar\omega_0} \right)^{-1} \right\},$$

(A12.b.5)

where $L_{w.l.}^{(1)}$ is given by the text equ.(12.4). Equation (A12.b.5) is the text equ.(12.5).

Summary of the results of Part III

Here, we summarize the results obtained in Part III, where we consider various regimes of coupling and temperature of physical interest.

The thermoelectric power, $\alpha_{\underline{g}, \underline{g}'}$, associated with a small-polaron hop between the two sites $\underline{g}$, and $\underline{g}'$ given by

$$\alpha_{\underline{g}, \underline{g}'} = \frac{1}{qT} (q L^{(1)-1} L^{(2)} - \gamma) , \quad (\text{III.1})$$

was found to be expressible as

$$\alpha_{\underline{g}, \underline{g}'} = \left(\frac{\kappa}{q}\right) \left(\frac{\tilde{E}(\underline{g}, \underline{g}') - \gamma}{kT} + A_{\underline{g}, \underline{g}'} \right). \quad (\text{III.2})$$

Here, $\tilde{E}(\underline{g}, \underline{g}')$ is the mean energy, of the two site system, given by

$$\tilde{E}(\underline{g}, \underline{g}') = \frac{[\epsilon_{\underline{g}}(0) - E_b(\underline{g})] + [\epsilon_{\underline{g}'}(0) - E_b(\underline{g}')] }{2} , \quad (\text{III.3})$$

and the term $\left(\frac{\kappa}{q}\right) A_{\underline{g}, \underline{g}'}$ is the additional part to the thermoelectric power due to the energy of transport. For the various regimes, strong-coupling(s), weak-coupling(w), high-temperature (h), and low-temperature(l), the coefficient $A_{\underline{g}, \underline{g}'}$ was found to be given by

$$A_{\underline{g}, \underline{g}'}^{s.h.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T} \coth \frac{\Delta \underline{g}' \underline{g}}{2 k T} \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{16 \epsilon_2 k T} \right), \quad (\text{III.4})$$

$$A_{\underline{g}, \underline{g}'}^{s.l.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T} \frac{1}{\left[1 - \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{k T} \right) \right]} - \frac{8 \epsilon_2^2}{k T (\Delta \underline{g}' \underline{g} + \hbar \omega_0)} \frac{\exp \left[- \frac{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)}{k T} \right]}{\left[1 - \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{k T} \right) \right]}, \quad (\text{III.5})$$

$$A_{\underline{g}, \underline{g}'}^{w.h.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T} \coth \frac{\Delta \underline{g}' \underline{g}}{2 k T} - \frac{1}{2} \left(\frac{4 \epsilon_2}{\hbar \omega_0} \right)^2 (k T) \frac{1}{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)} \coth \frac{\Delta \underline{g}' \underline{g}}{2 k T}, \quad (\text{III.6})$$

$$A_{\underline{g}, \underline{g}'}^{w.l.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T} \frac{1}{\left[1 - \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{k T} \right) \right]} - \frac{8 \epsilon_2^2}{k T (\Delta \underline{g}' \underline{g} + \hbar \omega_0)} \frac{\exp \left[- \frac{(\Delta \underline{g}' \underline{g} + \hbar \omega_0)}{k T} \right]}{\left[1 - \exp \left(- \frac{\Delta \underline{g}' \underline{g}}{k T} \right) \right]}. \quad (\text{III.7})$$

Taking into account the remarks we made in the previous Chapters of Part III, we can neglect the contribution to the coefficient $A_{\underline{g}, \underline{g}'}$ due to the small negative terms ap-

pearing in equs. (III.5), (III.6), (III.7).

Then we obtain

$$A_{\underline{g}, \underline{g}'}^{s.h.} \approx A_{\underline{g}, \underline{g}'}^{w.h.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T} \coth \frac{\Delta \underline{g}' \underline{g}}{2 k T}, \quad (III.8)$$

and

$$A_{\underline{g}, \underline{g}'}^{s.l.} = A_{\underline{g}, \underline{g}'}^{w.l.} = \frac{\Delta \underline{g}' \underline{g}}{2 k T}. \quad (III.9)$$

From equs. (III.8), (III.9), we conclude that the strength of coupling does not appreciably change the additional part of the thermoelectric power due to the energy of transport. On the other hand, at sufficiently low temperatures $\coth \frac{\Delta \underline{g}' \underline{g}}{2 k T}$ can be approximated by 1 and the expressions for $A_{\underline{g}, \underline{g}'}^{s.l.}$ can be obtained from $A_{\underline{g}, \underline{g}'}^{s.h.}$ taking the low -T limit. Thus the curve $A_{\underline{g}, \underline{g}'}$ versus $1/T$ is continuous as we pass from the high to the low-temperature regime with a departure from linearity when we enter the high-T region (cf. fig 13 for $\Delta \underline{g}' \underline{g} = 0.04 \text{ eV}$),

Having derived the expressions for the thermoelectric power associated with any pair of sites, for the various regimes of coupling and temperature of physical interest, in the following Chapters of Part IV we shall calculate the macroscopic thermoelectric power of the material using percolation-theoretic considerations.

Fig.13. The variation of the coefficient A_{ij} with respect to $\frac{10^3}{T}$ for energy disorder $\Delta_{ij}=0.04$ eV.

Part IV

Percolation-theoretic considerations
for the small-polaron hopping regime.

Chapter 13

Percolation theoretic considerations for the conductivity in the low-temperature regime.

In the low-temperature hopping regime, the expression for the intrinsic transition rate, $\gamma_{\underline{g}\underline{g}'} = \gamma(r_{\underline{g}\underline{g}'}, E_{\underline{g}} - E_{\underline{g}'}),$ for a small-polaron hopping from a site $\underline{g}$ to an empty neighbouring site $\underline{g}'$, a distance $r_{\underline{g}\underline{g}'}$ away, has been found to be given by⁽²⁹⁾ (cf. equs. (A10.a.5), (A10.a.6)).

$$\gamma_{\underline{g}\underline{g}'} = \gamma_0 \exp(-2\alpha r_{\underline{g}\underline{g}'}) \left\{ \begin{array}{l} N(E_{\underline{g}'} - E_{\underline{g}}) = \{ \exp[\beta(E_{\underline{g}'} - E_{\underline{g}})] - 1 \}^{-1} \cong \exp[-\beta(E_{\underline{g}'} - E_{\underline{g}})], \\ \text{for } \beta(E_{\underline{g}'} - E_{\underline{g}}) \gg 1 (\text{absorption}) \end{array} \right. \begin{array}{c} \text{Diagram 1: Energy level } E_{\underline{g}} \text{ with an arrow pointing up to } E_{\underline{g}}'. \end{array}$$

$$\left\{ \begin{array}{l} N(|E_{\underline{g}'} - E_{\underline{g}}|) + 1 = \frac{\exp[\beta(E_{\underline{g}} - E_{\underline{g}'})]}{\exp[\beta(E_{\underline{g}} - E_{\underline{g}'})] - 1} \cong 1, \\ \text{for } \beta(E_{\underline{g}} - E_{\underline{g}'}) \gg 1 (\text{emission}) \end{array} \right. \begin{array}{c} \text{Diagram 2: Energy level } E_{\underline{g}} \text{ with an arrow pointing down to } E_{\underline{g}}'. \end{array}$$

(13.1)

Here,

$$\gamma_0 = \left(\frac{\omega_0}{n} \right) \left[\frac{\pi J \exp(-\frac{2\epsilon_1}{\hbar\omega_0})}{\hbar\omega_0} \right]^2 \frac{\left(\frac{4\epsilon_1}{\hbar\omega_0} \right)^{\frac{\Delta_{g'g}}{\hbar\omega_0}}}{\left(\frac{\Delta_{g'g}}{\hbar\omega_0} \right)!}, \quad (13.2)$$

and

$$E_g = \epsilon_g(0) - E_b(g), \quad (13.3)$$

is the electronic energy of the small-polaron residing on site g and $\Delta_{g'g} = E_{g'} - E_g$. The dominant dependence of $\gamma_{gg'}$ on the distance between the two sites $r_{gg'}$, is taken to be exponential, where α^{-1} is the length which describes the spatial extent of the wave function localized at a single site.

We notice that the expression for $\gamma_{gg'}$ is the same as that used by various workers^{(34), (35), (36), (37)} for the percolation treatment of the d.c. conductivity for the case in which charge is transported via single phonon-induced tunneling of electrons between localized states which are randomly distributed in energy and position. The only difference comes in the expression of the preexponential factor γ_0 . Thus, the electric-current's percolation path is well known. For completeness we review here the case following ref. (34).

Let us denote the jump rate for an electron hopping from a site g to an empty site g' by

$$\gamma_{gg'} = \gamma(r_{gg'}, E_g - E_{g'}), \quad (13.4)$$

where $r_{gg'}$ is the distance between the sites and E_g and

$E_{\underline{g}'}$ are the respective electronic energy levels. The average transition rate from site $\underline{g}$ to site $\underline{g}'$ is then

$$\Gamma_{\underline{g}\underline{g}'}^{\circ} = \langle n_{\underline{g}} (1 - n_{\underline{g}'}) \gamma_{\underline{g}\underline{g}'} \rangle, \quad (13.5)$$

where $\langle \dots \rangle$ denotes the thermal average and $n_{\underline{g}}$ are the occupation numbers of the $\underline{g}$ -th site. We neglect electron-electron interactions except to say that not more than one electron can occupy a single site. Then $\gamma_{\underline{g}\underline{g}'}$ is independent of the occupation numbers and may be removed from the brackets. Furthermore, in thermal equilibrium, the occupation numbers adjacent sites are assumed to be uncorrelated, so that

$$\langle n_{\underline{g}} n_{\underline{g}'} \rangle = \langle n_{\underline{g}} \rangle \langle n_{\underline{g}'} \rangle, \quad (13.6)$$

and

$$\langle n_{\underline{g}} \rangle = n_{\underline{g}}^{\circ} = \left(1 + \exp \frac{E_{\underline{g}}}{kT} \right)^{-1}, \quad (13.7)$$

where the energy $E_{\underline{g}}$ is measured from the Fermi level. Finally, detailed balance requires that in equilibrium,

$$\Gamma_{\underline{g}\underline{g}'}^{\circ} = \Gamma_{\underline{g}'\underline{g}}^{\circ} \quad (13.8)$$

i.e.

$$\gamma_{\underline{g}\underline{g}'} n_{\underline{g}}^{\circ} (1 - n_{\underline{g}'}^{\circ}) = \gamma_{\underline{g}'\underline{g}} n_{\underline{g}'}^{\circ} (1 - n_{\underline{g}}^{\circ}), \quad (13.9)$$

and thus

$$\frac{\gamma_{\underline{g}\underline{g}'}}{\gamma_{\underline{g}'\underline{g}}} = \exp \left[\frac{(E_{\underline{g}} - E_{\underline{g}'})}{kT} \right]. \quad (13.10)$$

We next predict a more detailed form for $\gamma_{\underline{g}\underline{g}'}$. We know

that the dominant dependence of $\gamma_{\underline{g}\underline{g}'}$ on $r_{\underline{g}\underline{g}'}$ must be exponential^{(38), (39)}

$$\gamma_{\underline{g}\underline{g}'} \propto \exp(-2\alpha r_{\underline{g}\underline{g}'}), \quad (13.11)$$

where α^{-1} is a length which describes the spatial extent of the wave function localized at a single site.

For single-phonon assisted hops

$$\gamma_{\underline{g}\underline{g}'} = \gamma_0 \exp(-2\alpha r_{\underline{g}\underline{g}'}) \begin{cases} N(E_{\underline{g}'} - E_{\underline{g}}), & \text{for } E_{\underline{g}'} > E_{\underline{g}} \text{ (abs.)} \\ N(|E_{\underline{g}'} - E_{\underline{g}}|), & \text{for } E_{\underline{g}'} < E_{\underline{g}} \text{ (emis.)} \end{cases} \quad (13.12)$$

where $N(\hbar\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$ is the equilibrium Planck distribution and γ_0 some constant which depends on the electron-phonon coupling strength, the phonon density of states, and other properties of the material but which depends only weakly on the energies $E_{\underline{g}}$ and $E_{\underline{g}'}$ or on $r_{\underline{g}\underline{g}'}$ relative to the exponential factors.

Combining equs. (13.5), (13.7), and (13.12), and assuming KT small compared with all the energies which appear, (justified a posteriori), we find that the value of $\Gamma_{\underline{g}\underline{g}'}^{\circ}$ can be written as

$$\Gamma_{\underline{g}\underline{g}'}^{\circ} = [\Gamma_{\underline{g}\underline{g}}^{\circ}, \Gamma_{\underline{g}'\underline{g}}^{\circ}]^{1/2} = [n_{\underline{g}}^{\circ}(1-n_{\underline{g}}^{\circ})]^{1/2} [n_{\underline{g}'}^{\circ}(1-n_{\underline{g}'}^{\circ})]^{1/2} [\gamma_{\underline{g}\underline{g}'}\gamma_{\underline{g}\underline{g}}]^{1/2},$$

from which,

$$\Gamma_{\underline{g}\underline{g}'}^{\circ} = \gamma_0 \exp[-2\alpha r_{\underline{g}\underline{g}'} - (|E_{\underline{g}}| + |E_{\underline{g}'}| + |E_{\underline{g}} - E_{\underline{g}'}|)/2KT].$$

(13.13)

In the presence of a weak external electric field $\underline{\xi}$ the intrinsic transition rates $\gamma_{g g'}$ will be changed to

$$\gamma_{g g'}(\underline{\xi}) = \gamma_{g g'}(r_{g g'}, E_g - E_{g'} + e \underline{\xi} \cdot \underline{r}) \equiv \gamma_{g g'} + \delta \gamma_{g g'}. \quad (13.14)$$

Also, the occupation numbers will be changed from their equilibrium values n_g^0 to

$$\langle n_g \rangle = n_g^0 + \langle \delta n_g \rangle \equiv [1 + \exp[(E_g - \delta \mu_g)/kT]]^{-1}, \quad (13.15)$$

expressed in terms of changes $\delta \mu_g$ in the local chemical potentials. Then, assuming that $\langle n_g n_{g'} \rangle = \langle n_g \rangle \langle n_{g'} \rangle$ even if $\langle n_g \rangle \neq n_g^0$, we obtain

$$\begin{aligned} \Gamma_{g g'}(\underline{\xi}) &= \langle n_g \rangle \langle 1 - n_{g'} \rangle \gamma_{g g'}(\underline{\xi}) \\ &= (n_g^0 + \langle \delta n_g \rangle) (1 - n_{g'}^0 - \langle \delta n_{g'} \rangle) (\gamma_{g g'} + \delta \gamma_{g g'}), \end{aligned} \quad (13.16)$$

where

$$\gamma_{g g'}(\underline{\xi}) = \gamma_0 \exp(-2\alpha r_{g g'}) \begin{cases} \exp[-(E_{g'} - E_g)/kT] \exp[(q \underline{\xi} \cdot \underline{r}_{g g'})/kT], & \text{for } E_{g'} > E_g, \\ 1, & \text{for } E_{g'} < E_g, \end{cases} \quad (13.17)$$

$$\delta \gamma_{g g'} = \gamma_{g g'}(\underline{\xi}) - \gamma_{g g'}(0) = \begin{cases} \gamma_{g g'}(0) q \underline{\xi} \cdot \underline{r}_{g g'} / kT, & \text{for } E_{g'} > E_g, \\ 0, & \text{for } E_{g'} < E_g, \end{cases} \quad (13.18)$$

$$\langle \delta n_g \rangle = n_g^0 (1 - n_g^0) \delta \mu_g / kT. \quad (13.19)$$

Using equs. (13.16)-(13.19) the average net flow from site g to site g' is given by

$$\Gamma_{\underline{g}\underline{g}'}(\underline{\xi}) - \Gamma_{\underline{g}'\underline{g}}(\underline{\xi}) = \frac{1}{kT} \Gamma_{\underline{g}\underline{g}'}^0 \{ q \underline{\xi} \cdot \underline{r}_{\underline{g}\underline{g}'} + \delta \mu_{\underline{g}} - \delta \mu_{\underline{g}'} \}. \quad (13.20)$$

The quantity in curly brackets is the total electrochemical energy difference,

$$\Delta A_{\underline{g}\underline{g}'} \equiv q \underline{\xi} \cdot \underline{r}_{\underline{g}\underline{g}'} + \delta \mu_{\underline{g}} - \delta \mu_{\underline{g}'}, \quad (13.21)$$

between sites $\underline{g}, \underline{g}'$. The electrochemical potential difference, $\Delta U_{\underline{g}\underline{g}'}$, will be given by

$$\Delta U_{\underline{g}\underline{g}'} = \frac{\Delta A_{\underline{g}\underline{g}'}}{q} = \frac{1}{q} \{ q \underline{\xi} \cdot \underline{r}_{\underline{g}\underline{g}'} + \delta \mu_{\underline{g}} - \delta \mu_{\underline{g}'} \}. \quad (13.22)$$

Thus the average net transition rate from $\underline{g}$ to $\underline{g}'$ is given by

$$\Gamma_{\underline{g}\underline{g}'}(\underline{\xi}) - \Gamma_{\underline{g}'\underline{g}}(\underline{\xi}) = \frac{\Gamma_{\underline{g}\underline{g}'}^0}{kT} q \Delta U_{\underline{g}\underline{g}'}. \quad (13.23)$$

The net current across an area element between $\underline{g}$, and $\underline{g}'$ will be

$$\begin{aligned} \{ \Gamma_{\underline{g}\underline{g}'}(\underline{\xi}) - \Gamma_{\underline{g}'\underline{g}}(\underline{\xi}) \} q &\equiv I(\underline{g} \rightarrow \underline{g}') \\ &= \frac{\Gamma_{\underline{g}\underline{g}'}^0}{kT} q^2 \Delta U_{\underline{g}\underline{g}'} = G_{\underline{g}\underline{g}'} \Delta U_{\underline{g}\underline{g}'} \end{aligned} \quad (13.24)$$

where

$$G_{\underline{g}\underline{g}'} \equiv \frac{q^2}{kT} \Gamma_{\underline{g}\underline{g}'}^0(\underline{r}_{\underline{g}\underline{g}'}, E_{\underline{g}}, E_{\underline{g}'}) \quad (13.25)$$

may be interpreted as a conductance between the two sites.

Using equ. (13.13),

$$G_{\underline{g}\underline{g}'} = \frac{q^2}{kT} \gamma_0 \exp[-2\alpha \underline{r}_{\underline{g}\underline{g}'} - (|E_{\underline{g}}| + |E_{\underline{g}'}| + |E_{\underline{g}} - E_{\underline{g}'}|)/kT]. \quad (13.26)$$

From equ.(13.26), we see that we can associate an impedance (actually a resistance) with the pair of sites , $\underline{g}$, $\underline{g}'$,

$$Z_{\underline{g}\underline{g}'} = G_{\underline{g}\underline{g}'}^{-1} = \frac{kT}{q^2 \Gamma_{\underline{g}\underline{g}'}} \quad (13.27)$$

From equ.(13.13), for small kT , we see that this can be written as

$$Z_{\underline{g}\underline{g}'} = Z_0 \exp(\xi_{\underline{g}\underline{g}'}), \quad (13.28)$$

where

$$Z_0 = \frac{kT}{q^2 \gamma_0}, \quad (13.29)$$

and

$$\xi_{\underline{g}\underline{g}'} = 2\alpha \Gamma_{\underline{g}\underline{g}'} + \frac{E_{\underline{g}\underline{g}'}}{kT}, \quad (13.30)$$

where

$$E_{\underline{g}\underline{g}'} = \frac{1}{2} (|E_{\underline{g}}| + |E_{\underline{g}'}| + |E_{\underline{g}} - E_{\underline{g}'}|) = \begin{cases} E_{\underline{g}'} , & \text{if } E_{\underline{g}'} > E_{\underline{g}} \\ E_{\underline{g}} , & \text{if } E_{\underline{g}'} < E_{\underline{g}} \end{cases} \quad (13.31)$$

Thus, we see that the transport problem is equivalent to a network of randomly located sites connected by impedances $Z_{\underline{g}\underline{g}'}$. The $\delta\mu_{\underline{g}}$ are obtained from the condition that the incoming and outgoing currents be equal at each site (Kirchhoff's first law) and from the condition that the sum of the electrochemical potentials in a closed circuit be equal to the applied voltage (Kirchhoff's second law).

Thus, imagine initially that all the impedances are removed. Then put the smallest impedance (i.e. the one with

the smallest $\xi_{gg'}$), then the next largest impedance, and so on. Eventually a connected cluster is formed which spans the specimen. Say this occurs for $\xi_{gg'} = \xi_c$. Then it is argued that the impedance of the specimen is

$$Z_c = Z_0 \exp(\xi_c). \quad (13.32)$$

The argument for this is that, because of the very wide range of the $Z_{gg'}$ we have three kinds of regions: (1) isolated regions of low impedance $Z_{gg'} \ll Z_c$ which act like short circuits, (2) impedance chains with $Z_{gg'} \gg Z_c$ which act like open circuits, (3) impedances $Z_{gg'} \sim Z_c$ which link together regions (1). Therefore, the macroscopic impedance is determined by Z_c .

The condition $Z_{gg'} \leq Z_c$ or $Z_0 \exp(\xi_{gg'}) \leq Z_c$ can be written as

$$\xi_{gg'} \leq \ln\left(\frac{Z_c}{Z_0}\right) = \xi_c, \quad (13.33)$$

where Z_0 is given by equ. (13.29).

The condition

$$\xi_{gg'} \leq \xi_c, \quad (13.34)$$

using equ. (13.30) can be written as

$$2\alpha r_{gg'} + \frac{E_{gg'}}{kT} \leq \xi_c, \quad (13.35)$$

or

$$\frac{r_{gg'}}{r_m} + \frac{E_{gg'}}{E_m} \leq 1, \quad (13.36)$$

where

$$r_m \equiv \frac{\xi_c}{2\alpha} , \quad (13.37)$$

and

$$E_m \equiv kT\xi_c . \quad (13.38)$$

Thus, the condition $\xi_{gg'} \leq \xi_c$ implies that there is a maximum separation r_m , given by equ. (13.37), so that, impedances with $r_{gg'} > r_m$ are not on the percolation cluster regardless of the value of $E_{gg'}$. There is also a maximum $E_{gg'}$, E_m , given by equ. (13.38), so that impedances with $E_{gg'} > E_m$ are not on the percolation cluster, regardless of the value of $r_{gg'}$.

If we assume that the density of states $N(E)$ is constant over an energy E_m about the Fermi energy μ , then the number of sites per unit volume in this energy range is

$$N_s = 2 N_0 E_m . \quad (13.39)$$

The number of sites in a sphere of radius r_m and in the above energy range is then

$$\begin{aligned} N &= N_s r_m^3 \\ &= 2 N_0 E_m r_m^3 = \frac{1}{4\alpha^3} N_0 \xi_c^4 kT. \end{aligned} \quad (13.40)$$

We require that in order to get percolation across the specimen, the average number of accessible sites N about any chosen site, be some constant. Numerical simulation gives ^{(34) (40)}, $N=2$ to 7 . Thus,

$$\xi_c = \left(\frac{4 N \alpha^3}{N_o k T} \right)^{1/4}, \quad (13.41)$$

and

$$z_c = z_o \exp(\xi_c)$$

which can be written

$$z_c = z_o \exp \left[\left(\frac{T_o}{T} \right) \right] \quad (13.42)$$

where

$$T_o = \frac{4 N \alpha^3}{N_o k} . \quad (13.43)$$

Thus the Mott's $\sigma \propto \exp[-(\frac{T_o}{T})^{1/4}]$ law is obtained. We note that α is in the range 10^7 - 10^8 cm^{-1} , and N_o is of order 10^{19} . Equ. (13.43) gives a T_o of order $10^8 \text{ }^\circ\text{K}$.

Chapter 14

Earlier percolation-theoretic considerations on the thermoelectric power problem.

A lot of work has been done in connection with the thermoelectric power problem in the low-T regime where charge is transported via single phonon-assisted tunneling of electrons between localized states. These are randomly distributed in energy and position and Mott's $T^{-1/4}$ law is valid.

A percolation treatment of the thermoelectric power has been reported by H. Overhof⁽⁴¹⁾. The thermoelectric power α , was calculated from the Peltier coefficient

$$\pi = \frac{\langle q \rangle}{\langle j \rangle} , \quad (14.1)$$

using Onsager's relation

$$\alpha = \frac{\pi}{T} . \quad (14.2)$$

Here $\langle q \rangle$ is the heat current transported by the electrical current $\langle j \rangle$. Denoting the average number of bonds of length r attached to a site with energy E_g , by $n(E_g, f, r)$, he obtains

$$\langle j \rangle = c_1 e \int \int r n(E_g, f, r) n(E_g, r) N(E_g) dE_g dr, \quad (14.3)$$

where f is defined by

$$\begin{aligned} \epsilon_{gg'} &= \epsilon_0 \exp \left\{ -2\alpha r - \frac{|E_g| + |E_{g'}| + |E_g - E_{g'}|}{2kT} \right\} \\ &\equiv \epsilon_0 \exp \left(-\frac{f}{T} \right), \end{aligned} \quad (14.4)$$

C_1 is a function of the network geometry and of the critical conductance, and e the electron's charge; $n(E_g, f)$ is the average number of sites accessible by a bond from a given site at energy E_g , given by

$$\begin{aligned} n(E_g, f) &= \frac{4\pi}{3} \frac{1}{(2T\alpha)^3} \left[\int_0^{E_g} N(E) (f - E_g)^3 dE \right. \\ &\quad \left. + \int_{E_g}^f N(E) (f - E)^3 dE + \int_{f-E_g}^0 N(E) (f - E_g - E)^3 dE \right] \end{aligned} \quad (14.5)$$

where $N(E)$ is the density of states, and α^{-1} the localization length.

The energy transported by a carrier hopping from energy E_g to $E_{g'}$ is assumed to be the arithmetic mean of E_g and $E_{g'}$. Thus he writes

$$q = Q_g + Q_{g'} \quad (14.6)$$

where

$$Q_g = C_1 \iint E_g r n(E_g, f, r) N(E_g) n(E_g, f) dE_g dr. \quad (14.7)$$

$Q_{g'}$ is built up in a similar way averaging the final energies.

Since in variable range hopping near the Fermi energy carriers of positive and negative energies contribute, the main contributions cancel and only a small result due to an asymmetry in the density of states with respect to E_F is expected. For a constant density of states $N(E) = N_0 = \text{const.}$ there is no thermoelectric power because of the electron-hole symmetry. If the leading asymmetric term of $N(E)$ is proportional to E , then, Overhof finds that

$$\alpha \propto T^{1/2} . \quad (14.8)$$

v.v. Kosarev⁽⁴²⁾ studying the thermoelectric power of lightly doped semiconductors, in the region under consideration, starts from a general expression for the thermoelectric power which reads

$$\alpha = \frac{1}{q} \frac{\langle \epsilon \rangle - \psi}{T} . \quad (14.9)$$

The quantity $\langle \epsilon \rangle$ is defined as the average energy along the one-dimensional current paths, predicted by percolation theory, and is given by

$$\langle \epsilon \rangle = \frac{\int N(\epsilon) \epsilon d\epsilon}{\int N(\epsilon) d\epsilon} . \quad (14.10)$$

Here, the integration is performed over an energy range near the Fermi level with a width of order $\omega_0 \approx kT_0 \left(\frac{T}{T_0}\right)^{3/4}$, within which hops occur contributing to the $T^{-1/4}$ law. Again, the elements of the optimal percolation path should

be of resistivity

$$\rho_{gg'} \propto \exp(\xi_{gg'}) \quad (14.11)$$

where

$$\xi_{gg'} = 2\alpha r_{gg'} + \frac{E_{gg'}}{T}, \quad (14.12)$$

lower than a certain critical value $\rho_c \propto \exp(\xi_c)$.

If the density of states above E_F is higher, the average electron jumps are shorter than the average vacancy jumps and, consequently, electrons may have a higher percolation energy so that the overall value of ξ is less than ξ_c . He found that

$$W_{n(p)} = W_0 + (-) \frac{3}{8} W_0^2 \left(\frac{\partial \ln N(\epsilon)}{\partial \epsilon} \right)_{E_F} \quad (14.13)$$

Since the probability of a jump has a sharp maximum at the activation energy W_0 , and since a band width may shift upward and downward relative to μ , the energy $\langle \epsilon \rangle$ should include equiprobable contributions of all the states between $\mu - W_p$ and $\mu + W_n$, and thus

$$\langle \epsilon \rangle - \mu = \frac{\int_{\mu - W_p}^{\mu + W_n} \epsilon N(\epsilon) d\epsilon}{\int_{\mu - W_p}^{\mu + W_n} N(\epsilon) d\epsilon}, \quad (14.14)$$

where $W_{n(p)}$ is given by equ. (14.13). Thus, he obtained

$$\alpha \approx \frac{2}{3} \frac{1}{e} \frac{W_0^2}{T} \left(\frac{\partial \ln N(\epsilon)}{\partial \epsilon} \right)_{\epsilon_F}, \quad (14.15)$$

resulting in

$$\alpha \propto T^{1/2}. \quad (14.16)$$

I.P. Zvyagin⁽⁴³⁾ studying hopping transport in disordered semiconductors, considered the usual model of randomly distributed sites with random energy levels, one localized state being attributed to each site. The rate of phonon-assisted transitions is of the form

$$\gamma_{gg'} = \gamma_0 \exp(-\xi_{gg'}) \quad , \quad (14.17)$$

where $\xi_{gg'}$ is given by equ. (14.12). The total electrochemical potential difference U applied to the sample bounded by the planes $x=0$ and $x=L$ is found to be

$$\begin{aligned} U &= \sum' (V_{gg'} + \delta \mu_{g'} - \delta \mu_g) \\ &= \sum' \gamma_{gg'}^{-1} i_{gg'} + \sum' (x_g E_g - x_{g'} E_{g'}) \frac{d \ln B}{dx} \\ &= i_s \sum' \gamma_{gg'}^{-1} - L E_s \frac{d \ln B}{dx}. \end{aligned} \quad (14.18)$$

Here, $V_{gg'}$ is the difference of electrostatic potentials (multiplied by e) between the points r_g and $r_{g'}$, $i_{gg'}$ is the "hopping current" from the g -th to the g' -th site. The prime means that the sum is taken over the pairs of the adjacent sites of the chain starting near the plane $x=0$

and ending near the opposite plane $x=L$. Thus, when the effective network is taken to consist of non-intersecting chains piercing the system, for such a chain (say, s -th) the value of the "hopping current" $i_{gg'}$ is the same for all the pairs of neighbours, i.e. $i_{gg'} = i_s$, and is given by

$$i_s = \frac{U + L E_s \frac{d \ln \beta}{dx}}{\sum' \gamma_{gg'}^{-1}}, \quad (14.19)$$

where $\beta = \tau^{-1}$.

The current and energy flow densities I_1 and I_2 were found to be given by

$$I_j = Q_{jl} X_l, \quad (14.20)$$

where $j, l = 1, 2$,

$$X_1 = \frac{U}{L}, \quad X_2 = -\frac{d \ln \beta}{dx}, \quad (14.21)$$

and

$$Q_{jl} = e^{-2} \int dE \epsilon(E) E^{j+l-2} \tilde{N}(E). \quad (14.22)$$

Here $\tilde{N}(E)$ is proportional not only to the density of localized states per unit volume, $N(E)$, but also to the probability $P(E)$ that a state of energy E belongs to the effective network; $\epsilon(E)$ is given by

$$\epsilon(E) = e^2 n_s (L^{-1} \sum' \gamma_{gg'}^{-1}), \quad (14.23)$$

where n_s is the average number of chains crossing the unit area of the boundary plane.

The thermoelectric power, α , is given by

$$\alpha = \frac{Q_{12}}{e T Q_{11}} . \quad (14.24)$$

Various regimes of the hopping conduction are known to correspond to various temperature dependences of the conductivity. In the low-T case when the density of states does not change appreciably over the energy interval E_m , and Mott's law is valid, Zvyagin finds

$$\alpha \propto T^{1/2} . \quad (14.25)$$

When the Fermi level is fixed within the mobility gap but outside the region of continuously distributed hopping states (this can be the case when conduction is by hopping within the band tails), using as a model a step-like density of states $N(E) = N_0 \Theta(E - E_c)$, $E_c > 0$, he found that

$$\alpha = \frac{1}{9} \left(\frac{E_c}{T} + A \right) \quad (14.26)$$

where the kinetic term A , in contrast to the band conduction depends on T (although weakly), given by

$$A = \frac{1}{2} \zeta \left(\frac{T_0'}{T} \right)^{1/4} , \quad (14.27)$$

where $\zeta \approx 0.35$, and $T_0' = 2 \times 10^8 \text{ } ^\circ\text{K}$.

Chapter 15

Percolation treatment of the thermoelectric power due to small-polaron hopping notion in the low-temperature regime.

After the historical review given in Chapter 14, let us proceed to our case, i.e. to the percolation treatment of the thermoelectric power for the low-temperature regime.

When a small-polaron hops from a site g to a neighbouring site g' , Peltier heat, $Q_{g,g'}$, under isothermal conditions, is transported along the electric current's path. Then the "microscopic" thermoelectric power, $\alpha_{g,g'}$, associated with this pair of sites, is written

$$\alpha_{g,g'} = \frac{Q_{g,g'}}{q T} \quad (15.1)$$

For our case,

$$Q_{g,g'} = Q_{g,g'}^{s.l.} = \left\{ \frac{(E_g + E_{g'})}{2} - \mu + E_{\tau, s.l.}^{g,g'} \right\}, \quad (15.2)$$

where

$$[_{\tau, s. l.}^{g, g'} \equiv \left(\frac{\Delta g' g}{2} \right) \frac{1}{[1 - \exp(-\frac{\Delta g' g}{k \tau})]} , \quad (15.3)$$

is the additional heat of transport part to the thermoelectric power (c.f. equs, (10.7), (10,8)).

Now, the "macroscopic" thermoelectric power of the material, α , in analogy, will be given by

$$\alpha = \frac{Q}{q \tau} , \quad (15.4)$$

where Q is the Peltier heat which is transported along the electric current's percolation path.

In order to obtain the Peltier heat which is transported, we have to sum the "microscopic" Peltier heat transported via every pair of sites which belong to the percolation path. Using equs (15.1), and (15.4), we see that the sum of the "microscopic" thermoelectric power associated with every pair of sites which belong to the percolation path will be the "macroscopic" thermoelectric power of the material.

At low-temperatures the additional part to the thermoelectric power is given by

$$\left(\frac{k}{q} \right) A_{g, g'}^{\ell} = \left(\frac{k}{q} \right) \frac{\Delta g' g}{2 k \tau} \quad (15.5)$$

Thus, the additional part of the thermoelectric power depends on the difference of the electronic energies, of the two neighbouring sites g , and g' . We also notice that the "microscopic" thermoelectric power, $\alpha_{g,g'}^l$ is independent of $r_{gg'} = r_g - r_{g'}$.

So, in order to sum the "microscopic" thermoelectric power associated with every pair of sites along the percolation path, we have to know the average number of pairs of sites with energy difference Δ , connected with impedances of magnitude Z_m , or less. We denote this quantity by $P(\Delta, Z_m)$.

Then, the thermoelectric power of the material, α , will be given by

$$\alpha_l = \int_0^{\Delta_m} P(\Delta, Z_m) \alpha_{g,g'}^l d\Delta, \quad (15.6)$$

where Δ_m is the maximum value of the disorder energy between two sites belonging to the percolation path. Lack of correlation between successive hops is assumed.

In order to evaluate $P(\Delta, Z_m)$ we consider a distribution of sites with random energies $E_g, E_{g'}$, and separations $r_{gg'}$. Then,

$$P(\Delta, Z_m) = \int_{\text{perc. path}} p(\Delta, r_{gg'} | E) dr_{gg'} dE, \quad (15.7)$$

where $p(\Delta, r_{gg'} | E)$ is the probability density that a site of electronic energy E , ($E = E_g$ or $E_{g'}$), has a neighbour at

distance $r_{gg'}$ with energy difference Δ .

Now, assuming lack of correlation between the distributions of Δ and r , $p(\Delta, r_{gg'} | E_g)$ can be written as a product

$$p(\Delta, r_{gg'} | E) = p(\Delta | E) p(r_{gg'} | E), \quad (15.8)$$

where $p(\Delta | E)$ is the probability density that a site with energy E has a neighbour with energy difference Δ , and $p(r_{gg'} | E)$ denotes the spatial distribution of sites with energy E .

Thus,

$$P(\Delta, z_m) = K \int_{\text{perc. path}} p(\Delta | E) p(r_{gg'} | E) dr_{gg'} dE, \quad (15.9)$$

where K is a normalization factor which is obtained from

$$\int_0^{\Delta_{\max}} P(\Delta, z_m) d\Delta = K \int_0^{\Delta_{\max}} \left\{ \int_{\text{perc. path}} p(\Delta | E) p(r_{gg'} | E) dr_{gg'} dE \right\} d\Delta \quad (15.10)$$

The distribution of $r_{gg'}$ is in practice independent of site energy, and is simply

$$p(r_{gg'} | E) = 4\pi N_s r_{gg'}^2, \quad (15.11)$$

where N_s is the concentration of sites. The probability density $p(\Delta | E)$ is given by

$$P(\Delta_{g,g'} | E_{g'}) N_s^2 = \delta(|E_{g'} - E_g|) N(E_g) N(E_{g'}) \quad (15.12)$$

where $N(E_g)$, $N(E_{g'})$ are the densities of states.

We wish to consider a semiconducting case (not metallic) where the states are on one side of E_F . Because of the random distribution of the sites g and g' , and because of the fact that the electronic energies E_g and $E_{g'}$ are on the same side of E_F (hereafter we will measure all the energies from E_F , i.e. $E_F \equiv \mu \equiv 0$), we can have the following two arrangements

where $E_{\max}$ is the maximum percolation energy which we have already defined in equ. (13.38).

Taking into account the above picture, equ. (15.4) for the thermoelectric power of the material, α_t , using eqs. (15.9), (15.11) and (15.12), can be written

$$\alpha_t = \alpha_t^{(I)} + \alpha_t^{(II)} \quad , \quad (15.13)$$

where

$$\alpha_t^{(I)} = 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{(I)} N(E_{g'} - \Delta_{g,g'}) N(E_g) \alpha_{(I),g,g'}^t \left[\int_0^{r_c^{(I)}} r_{g,g'}^2 dr_{g,g'} \right] dE_{g'} \right\} d\Delta_{g,g'} \quad , \quad (15.14)$$

and

$$\alpha_{\ell}^{(II)} \equiv 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{(II)} N(E_{\underline{g}} - \Delta_{\underline{g}\underline{g}'}) N(E_{\underline{g}}) \alpha_{(II), \underline{g}\underline{g}'}^{\ell} \left[\int_0^{r_c^{(II)}} r_{\underline{g}\underline{g}'}^2 dr_{\underline{g}\underline{g}'} \right] dE_{\underline{g}} \right\} d\Delta_{\underline{g}\underline{g}'}, \quad (15.15)$$

where $\alpha_{(I), \underline{g}\underline{g}'}^{\ell}$ is given by

$$\alpha_{(I), \underline{g}\underline{g}'}^{\ell} = \left(\frac{k}{q} \right) \left\{ \frac{(E_{\underline{g}} + E_{\underline{g}'})}{2kT} + A_{\underline{g}\underline{g}'}^{\ell} \right\}. \quad (15.16)$$

Here, as we've already mentioned, we measure the energies from the Fermi level ($\gamma \equiv 0$), and $A_{\underline{g}\underline{g}'}^{\ell}$ is given by

$$A_{\underline{g}\underline{g}'}^{\ell} = \frac{\Delta_{\underline{g}\underline{g}'}}{2kT}. \quad (15.17)$$

For the arrangement (II), $\alpha_{(II), \underline{g}\underline{g}'}^{\ell}$ can be obtained from the above expressions interchanging $\underline{g}$ with $\underline{g}'$.

The normalization factor K is obtained from

$$\begin{aligned} & \int_0^{\Delta_m} P(\Delta_{\underline{g}\underline{g}}, z_m) d\Delta_{\underline{g}\underline{g}} + \int_0^{\Delta_m} P(\Delta_{\underline{g}\underline{g}'}, z_m) d\Delta_{\underline{g}\underline{g}'} \\ &= 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{(I)} N(E_{\underline{g}'} - \Delta_{\underline{g}\underline{g}}) N(E_{\underline{g}'}) \left[\int_0^{r_c^{(I)}} r_{\underline{g}\underline{g}'}^2 dr_{\underline{g}\underline{g}'} \right] dE_{\underline{g}'} \right\} d\Delta_{\underline{g}\underline{g}} \\ &+ 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{(II)} N(E_{\underline{g}} - \Delta_{\underline{g}\underline{g}'}) N(E_{\underline{g}}) \left[\int_0^{r_c^{(II)}} r_{\underline{g}\underline{g}'}^2 dr_{\underline{g}\underline{g}'} \right] dE_{\underline{g}} \right\} d\Delta_{\underline{g}\underline{g}'} = 1. \end{aligned} \quad (15.18)$$

The limits of integration for equs. (15.14), (15.15) are determined as follows:

(I) : $E_m > E_{g'} > E_g > 0$

For fixed $\Delta_{g'g}$, $E_{g'}$ varies from A to B, where $A = \Delta_{g'g}$ and $B = E_m$.

Here the percolation condition (c.f. equ. (13.36))

$$\frac{r_{gg'}}{r_m} + \frac{\frac{1}{2} (|E_g| + |E_{g'}| + |E_g - E_{g'}|)}{E_m} \leq 1 \quad (15.19)$$

becomes

$$\frac{r_{gg'}}{r_m} + \frac{E_{g'}}{E_m} \leq 1. \quad (15.20)$$

Thus,

$$r_{gg'} \leq r_m \left(1 - \frac{E_{g'}}{E_m} \right) \equiv r_c^{(I)}, \quad (15.21)$$

where r_m , and E_m are given by equs. (13.37), and (13.38), which we recall here

$$r_m = \frac{\xi_c}{2\alpha}, \quad (15.22)$$

and

$$E_m = kT \xi_c. \quad (15.23)$$

For fixed $\Delta_{gg'}$, $E_{g'}$ varies from A' to B' , where $A' = \Delta_{gg'}$, and $B' = E_m$.

Here the percolation condition, (equ. (15.19)), becomes

$$\frac{r_{gg'}}{r_m} + \frac{E_g}{E_m} \leq 1, \quad (15.24)$$

from which we obtain

$$r_{gg'} \leq r_m \left(1 - \frac{E_g}{E_m} \right) \equiv r_c^{(II)}. \quad (15.25)$$

Thus, equs. (15.14), (15.15) become

$$\alpha_{\ell}^{(I)} = 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{\Delta_{gg'}}^{E_m} N(E_g - \Delta_{gg'}) N(E_{g'}) \alpha_{(I),g,g'}^{\ell} \left[\int_0^{r_m(1-\frac{E_g}{E_m})} r_{gg'}^2 dr_{gg'} \right] dE_{g'} \right\} d\Delta_{gg'} \quad (15.26)$$

and

$$\alpha_{\ell}^{(II)} = 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{\Delta_{g'g}}^{E_m} N(E_g - \Delta_{g'g}) N(E_g) \alpha_{(II),g'g}^{\ell} \left[\int_0^{r_m(1-\frac{E_g}{E_m})} r_{g'g}^2 dr_{g'g} \right] dE_g \right\} d\Delta_{g'g}. \quad (15.27)$$

Obviously, interchanging g with g' we notice that

$$\alpha_{\ell}^{(I)} = \alpha_{\ell}^{(II)}. \quad (15.28)$$

Thus we can write that

$$\alpha_{\ell} = \alpha_{\ell}^{(I)}, \quad (15.29)$$

with the normalization factor K obtained from

$$\begin{aligned} & \int_0^{\Delta_m} P(\Delta_{g'g}, Z_m) d\Delta_{g'g} \\ &= 4\pi \frac{1}{N_s} K \int_0^{\Delta_m} \left\{ \int_{\Delta_{g'g}}^{E_m} N(E_g - \Delta_{g'g}) N(E_g) \left[\int_0^{r_m(1-\frac{E_g}{E_m})} r_{g'g}^2 dr_{g'g} \right] \right\} d\Delta_{g'g} = 1. \end{aligned} \quad (15.30)$$

instead of equ. (15.18).

Thus, finally the general expression for the thermoelectric power of the material α_{ℓ} for the low-temperature regime, is given by

$$\alpha_l = 4\pi \frac{1}{N_s} k \int_0^{\Delta_m} \left\{ \int_{\Delta_{g'g}}^{\epsilon_m} N(\epsilon_{g'} - \Delta_{g'g}) N(\epsilon_{g'}) \alpha_{g,g'}^l \left[\int_0^{r_m(1-\frac{\epsilon_{g'}}{\epsilon_m})} r_{g'g}^2 dr_{g'g} \right] d\epsilon_{g'} \right\} d\Delta_{g'g}, \quad (15.31)$$

where k is obtained from equ. (15.30), and $\alpha_{g,g'}^l$ is given by equ. (15.16). We notice that the expression for α_l depends on the specific choice of the form of the density of states $N(\epsilon_{g'})$.

Let us now assume, for simplicity, a density of states $N(\epsilon_{g'})$ which is constant over an energy range ϵ_m i.e.

$$N(\epsilon_{g'}) = N(\epsilon_g) \equiv N_0 = \text{const.}, \quad (15.32)$$

where the energy ϵ_m is the maximum energy $\epsilon_{g'g}$ defined by equ. (13.38) as

$$\epsilon_m = kT \xi_c. \quad (15.33)$$

A more appropriate choice of density of states, for the actual physical situation, could be one which takes into account the fact that the deeper in energy states are less "dense", i.e. densities of states of the form

$$N(\epsilon_{g'}) = N_0 + \lambda \epsilon_{g'}, \quad (15.34)$$

or

$$N(\epsilon_{g'}) = \exp(\lambda \epsilon_{g'}), \quad (15.35)$$

where

$$\epsilon_{g'} = \epsilon_{g'}(0) - E_v(g'), \quad (15.36)$$

and $\lambda > 0$. Here we have chosen a constant density of states only in order to simplify the calculations.

Hereafter we shall omit, for convenience, the subscripts $\underline{g}, \underline{g}$ and we shall use the notation α_{mic}^{ℓ} for $\alpha_{\underline{g}, \underline{g}'}^{\ell}$. Now, using equ. (15.32), and noticing that the maximum value of the disorder energy between two sites belonging to the percolation path, Δ_m is equal to E_m equ. (15.31) can be written as

$$\alpha_{\ell} = 4\pi \frac{1}{N_s} K N_0^2 \int_0^{E_m} \left\{ \int_A^{E_m} \alpha_{mic}^{\ell} \left[\int_0^{r_m(1-\frac{E}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (15.37)$$

where E_m is given by equ. (15.33), and $\mathcal{F}_c$ is given by equ. (13.41) as

$$\mathcal{F}_c = \left(\frac{8 N \alpha^3}{N_0 K T} \right)^{1/4}, \quad (15.38)$$

where we have taken into account that the number of sites per unit volume

$$N_s = N_0 E_m, \quad (15.39)$$

instead of $2 N_0 E_m$, (c.f. equ. (13.39)), because our energies are on one side of the Fermi level. The maximum distance r_m is given by equ. (13.37),

$$r_m = \frac{\mathcal{F}_c}{2 \alpha}. \quad (15.40)$$

The normalization factor K is obtained from

$$4\pi \frac{1}{N_s} K N_o^2 \int_0^{E_m} \left\{ \int_\Delta^{E_m} \left[\int_0^{r_m(1-\frac{E}{E_m})} r^2 dr \right] dE \right\} d\Delta = 1, \quad (15.41)$$

and $\alpha_{mic.}^l$, is given by equ.(15.16),

$$\alpha_{mic.}^l = \frac{1}{2qT} \left\{ (2E - \Delta) + \Delta \right\}, \quad (15.42)$$

where the energies are measured from the Fermi level, $\gamma \equiv 0$, and we have expressed E_g in terms of $E_{g'} \equiv E$, and $\Delta_{g'g} \equiv \Delta$, using the fact that $\Delta_{g'g} = E_{g'} - E_g$.

Now, substituting equ.(15.42) into equ.(15.37), we obtain

$$\alpha_\ell = \tilde{\alpha}_\ell + \alpha'_\ell, \quad (15.43)$$

where $\tilde{\alpha}_\ell$ is the macroscopic thermoelectric power due to the main microscopic contribution $\frac{1}{2qT} (2E - \Delta)$, and α'_ℓ is the corresponding quantity due to the additional microscopic contribution $\frac{1}{qT} \left(\frac{\Delta}{2} \right)$. They are given by

$$\tilde{\alpha}_\ell = \frac{4\pi N_o^2 K}{N_s} \frac{1}{2qT} \int_0^{E_m} \left\{ \int_\Delta^{E_m} (2E - \Delta) \left[\int_0^{r_m(1-\frac{E}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (15.44)$$

and

$$\alpha'_l = \frac{4\pi N_o^2 K}{N_s} \frac{1}{2qT} \int_0^{E_m} \left\{ \int_{\Delta}^{E_m} \Delta \left[\int_0^{r_m(1-\frac{E}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (15.45)$$

where the normalization factor is obtained from equ.

(15.41). Performing the integrations, indicated in equ.

(15.41), we obtain

$$K = \frac{15 N_s}{\pi N_o^2 r_m^3 E_m^2} . \quad (15.46)$$

Now, using equ. (15.46) and defining

$$\frac{4\pi N_o^2 K}{2N_s qT} = \left(\frac{30}{qT} \right) \left(\frac{1}{r_m^3 E_m^2} \right) \equiv M, \quad (15.47)$$

equ. (15.44) becomes

$$\tilde{\alpha}_l = M \int_0^{E_m} \left\{ \int_{\Delta}^{E_m} (2E - \Delta) \left[\int_0^{r_m(1-\frac{E}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (15.48)$$

from which, integrating we obtain

$$\tilde{\alpha}_l = M \frac{r_m^3 E_m^3}{120} . \quad (15.49)$$

Substituting M from equ. (15.47) into equ. (15.49), we obtain

$$\tilde{\alpha}_l = \left(\frac{1}{4} \right) \left(\frac{K}{q} \right) \left(\frac{T_o}{T} \right)^{1/4}, \quad (15.50)$$

where equs. (15.33), and (15.38) have been taken into account; T_0 is given by

$$T_0 = \left(\frac{8 N \alpha^3}{N_0 k} \right)^{1/4}. \quad (15.51)$$

Equation (15.50) gives the "macroscopic" thermoelectric power of the material due to the contribution of the main "microscopic" part.

From equ. (15.45), performing the integrations, we obtain

$$\alpha'_e = M \frac{r_m^3 E_m^3}{360}. \quad (15.52)$$

Substituting M from equ. (15.47) into equ. (15.52), and using equs. (15.33), and (15.38), equ. (15.52) becomes

$$\alpha'_e = \left(\frac{1}{12} \right) \left(\frac{k}{q} \right) \left(\frac{T_0}{T} \right)^{1/4}, \quad (15.53)$$

from which

$$A_e = \frac{1}{12} \left(\frac{T_0}{T} \right)^{1/4}. \quad (15.54)$$

Here T_0 is given by equ. (15.51). Equation (15.53) gives the additional part to the "macroscopic" thermoelectric power due to energy of transport.

Substituting equs. (15.50), (15.52) into equ. (15.43), we obtain the thermoelectric power of the material,

$$\alpha_L = \left(-\frac{1}{3}\right) \left(-\frac{k}{q}\right) \left(-\frac{T_0}{T}\right)^{1/4}. \quad (15.55)$$

We notice that the thermoelectric power of the material has the same temperature dependence as the conductivity of the material at low-temperature, i.e. follows the $T^{-1/4}$ law.

Chapter 16

Percolation-theoretic considerations in the high-temperature small-polaron hopping regime.

In the high-temperature, $\hbar\omega_0 \ll kT$, hopping regime, as discussed in Chapter 9, the hops are characterised by the absorption and emission of many phonons. The intrinsic transition rate $\gamma_{\underline{g}\underline{g}'}$ for a small-polaron hopping from a site $\underline{g}$ to an empty nearest neighbouring site $\underline{g}'$, a distance $r_{\underline{g}\underline{g}'}$ away, has been found to be given by⁽²⁹⁾

$$\gamma_{\underline{g}\underline{g}'} = \gamma_0 \exp(-2\alpha r_{\underline{g}\underline{g}'}) \exp\left(-\frac{E_2}{kT}\right) \begin{cases} \exp\left[-\frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT}\right], & \text{for } E_{\underline{g}'} > E_{\underline{g}} \text{ (abs.)} \\ \exp\left[\frac{(E_{\underline{g}} - E_{\underline{g}'})}{2kT}\right], & \text{for } E_{\underline{g}'} < E_{\underline{g}} \text{ (emis.)} \end{cases}$$

(16.1)

Here,

$$\gamma_0 = \left(\frac{J^2}{\hbar} \right) \sqrt{\frac{\pi}{4 \epsilon_2 \kappa T}} \quad , \quad (16.2)$$

$$\epsilon_2 = \frac{E_b(\underline{g}) + E_b(\underline{g}')}{2} \quad , \quad (16.3)$$

and α^{-1} is the spatial extent of the wave function localized at a single site. The dominant dependence of $\gamma_{\underline{g}\underline{g}'}$ on the distance between the two sites, $r_{\underline{g}\underline{g}'}$, is taken to be exponential, and the dependence on the $\exp[-\Delta_{\underline{g}\underline{g}'}^2 / (4 \epsilon_2 \kappa T)]$ term appearing when the coupling is strong, has been neglected because of the much stronger dependence of on the rest exponential terms for an actual variation of the parameters involved. Indeed, the exponential $\exp[-\Delta_{\underline{g}\underline{g}'}^2 / (4 \epsilon_2 \kappa T)]$ term, for representative values of the parameters involved, i.e. $\Delta_{\underline{g}\underline{g}'} = 0.04 \text{ eV}$, $E_b(\underline{g}') = 0.2 \text{ eV}$, $T = [(250 - 800)^\circ \text{K}]$ assuming that the disorder energy is mainly polaronic, takes values which lie between $[0.96 - 0.98]$, while the term $\exp[-(\epsilon_{\underline{g}'} - \epsilon_{\underline{g}}) / \kappa T]$ varies between $[0.39 - 0.74]$, and the term $\exp(-\epsilon_2 / \kappa T)$ varies between $[6 \cdot 10^{-3} - 2 \cdot 10^{-4}]$.

At this stage we notice that for a downward hop the expression for the intrinsic transition rate, for the high-temperature regime (c.f. equ. (16.1)), differs essentially from that we meet in the low temperature case (c.f. equ. (13.1)). The reason is that in the low-temperature regime for a downward hop, the minimum number of phonons, needed to comply with the requirement of energy conservation, are

emitted, while, in the high-temperature regime, for a downward hop, we have emission of many phonons.

Obviously, the detailed balance condition

$$\frac{\gamma_{\underline{g}\underline{g}'}}{\gamma_{\underline{g}'\underline{g}}} = \exp \left[\frac{(E_{\underline{g}} - E_{\underline{g}'})}{kT} \right], \quad (16.4)$$

is satisfied for both cases.

Following ref. (34), for the high-temperature regime, the average transition rate in equilibrium, $\Gamma_{\underline{g}\underline{g}'}^0$, is given by

$$\begin{aligned} \Gamma_{\underline{g}\underline{g}'}^0 &= [\Gamma_{\underline{g}\underline{g}}^0, \Gamma_{\underline{g}'\underline{g}}^0]^{1/2} = [n_{\underline{g}}(1-n_{\underline{g}})]^{1/2} [n_{\underline{g}'}(1-n_{\underline{g}'})]^{1/2} [\gamma_{\underline{g}\underline{g}}\gamma_{\underline{g}'\underline{g}}]^{1/2} \\ &= [n_{\underline{g}}(1-n_{\underline{g}})]^{1/2} [n_{\underline{g}'}(1-n_{\underline{g}'})]^{1/2} \left[\exp \left\{ -\frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT} \right\} \exp \left\{ \frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT} \right\} \right]^{1/2} \\ &\quad \gamma_0 \exp(-2\alpha r_{\underline{g}\underline{g}'}) \exp\left(-\frac{E_{\underline{g}}}{kT}\right), \end{aligned} \quad (16.5)$$

since if $\underline{g} \rightarrow \underline{g}'$ is a transition upward in energy, $\underline{g}' \rightarrow \underline{g}$ must be a transition downward in energy. Here, we notice that because of the difference in the expressions for the intrinsic transition rates between the low-T and high-T regime, for a downward hop, as we mentioned before, the term $\left[\exp \left\{ -\frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT} \right\} \exp \left\{ \frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT} \right\} \right]^{1/2}$ of equ. (16.5) equals 1, and thus we obtain an average transition rate, $\Gamma_{\underline{g}\underline{g}'}^0$, independent of the energy difference, $\Delta_{\underline{g}\underline{g}'}$, of the two-sites. In the single-phonon (low-T) regime instead of the above mentioned term we have the term

$\left[\exp \left\{ - \frac{(E_{g'} - E_g)}{kT} \right\} \right]^{1/2}$, from which a Δg_g -dependence is obtained (c.f. ref. (34), or equ. (13.13)).

Now, assuming that $\beta |E_g| \gg 1$, $\beta |E_{g'}| \gg 1$ we obtain,

$$\left[n_g^0 (1 - n_g^0) \right]^{1/2} \left[n_{g'}^0 (1 - n_{g'}^0) \right]^{1/2} \approx \exp \left[- \frac{(|E_g| + |E_{g'}|)}{2kT} \right]. \quad (16.6)$$

Substituting equ. (16.6) into equ. (16.5), we obtain,

$$\Gamma_{gg'}^0 = \gamma_0 \exp(-2\alpha r_{gg'}) \exp \left[- \frac{1}{2kT} \{ |E_g| + |E_{g'}| + 2\epsilon_2 \} \right], \quad (16.7)$$

where ϵ_2 is defined by equ. (16.3).

In the presence of a weak external electric field $\underline{\xi}$ following exactly the same procedure as in Chapter 13, we obtain

$$\gamma_{gg'}(\underline{\xi}) = \gamma_0 \exp(-2\alpha r_{gg'}) \exp\left(-\frac{\epsilon_2}{kT}\right) \begin{cases} \exp\left[-\frac{(E_{g'} - E_g)}{2kT}\right] \exp\left[\frac{q \underline{\xi} \cdot r_{gg'}}{2kT}\right] \\ \text{for } E_{g'} > E_g, \\ \\ \exp\left[\frac{(E_g - E_{g'})}{2kT}\right] \exp\left[\frac{q \underline{\xi} \cdot r_{gg'}}{2kT}\right] \\ \text{for } E_g < E_{g'}. \end{cases} \quad (16.8)$$

$$\delta \gamma_{\underline{g}\underline{g}'} = \gamma_{\underline{g}\underline{g}'}(\underline{\xi}) - \gamma_{\underline{g}\underline{g}'}(0) = \gamma_0 \exp(-2\alpha r_{\underline{g}\underline{g}'}) \exp\left(-\frac{\underline{\xi}}{kT}\right) \begin{cases} \exp\left[-\frac{(E_{\underline{g}'} - E_{\underline{g}})}{2kT}\right] \frac{q \underline{\xi} \cdot r_{\underline{g}\underline{g}'}}{2kT}, \\ \text{for } E_{\underline{g}'} > E_{\underline{g}}, \\ \\ \exp\left[\frac{(E_{\underline{g}} - E_{\underline{g}'})}{2kT}\right] \frac{q \underline{\xi} \cdot r_{\underline{g}\underline{g}'}}{2kT}, \\ \text{for } E_{\underline{g}'} < E_{\underline{g}}, \end{cases}$$

or

(16.9)

$$\delta \gamma_{\underline{g}\underline{g}'} = \gamma_{\underline{g}\underline{g}'}(0) \frac{q \underline{\xi} \cdot r_{\underline{g}\underline{g}'}}{2kT}, \quad (16.10)$$

where $\gamma_{\underline{g}\underline{g}'}(0)$ is defined by (16.1) according to whether $E_{\underline{g}'} > E_{\underline{g}}$ or $E_{\underline{g}'} < E_{\underline{g}}$. We also have

$$\langle \delta n_{\underline{g}} \rangle = n_{\underline{g}}^0 (1 - n_{\underline{g}}^0) \frac{\delta \mu_{\underline{g}}}{kT}. \quad (16.11)$$

Using equs. (16.1), (16.10), (16.11) and the expression

$$\Gamma_{\underline{g}\underline{g}'}(\underline{\xi}) = (n_{\underline{g}}^0 - \langle \delta n_{\underline{g}} \rangle) (1 - n_{\underline{g}'}^0 - \langle \delta n_{\underline{g}'} \rangle) (\gamma_{\underline{g}\underline{g}'} + \delta \gamma_{\underline{g}\underline{g}'}), \quad (16.12)$$

we obtain the average net flow from site $\underline{g}$ to site $\underline{g}'$,

$$\Gamma_{\underline{g}\underline{g}'}(\underline{\xi}) - \Gamma_{\underline{g}'\underline{g}}(\underline{\xi}) = \frac{1}{kT} \Gamma_{\underline{g}\underline{g}'}^0 \{ q \underline{\xi} \cdot r_{\underline{g}\underline{g}'} + \delta \mu_{\underline{g}} - \delta \mu_{\underline{g}'} \}. \quad (16.13)$$

Using the same arguments as in Chapter 13, we see that the transport problem is equivalent to a network of randomly located sites connected by impedances given by

$$Z_{\underline{g}\underline{g}'} = Z_0 \exp(\xi_{\underline{g}\underline{g}'}), \quad (16.14)$$

where

$$Z_0 = \frac{kT}{q^2 \gamma_0}, \quad (16.15)$$

and

$$\xi_{\underline{q}\underline{q}'} = 2 \propto r_{\underline{q}\underline{q}'} + \frac{E_{\underline{q}\underline{q}'}}{K_T} , \quad (16.16)$$

where

$$E_{\underline{q}\underline{q}'} = \frac{1}{2} \{ |E_{\underline{q}}| + |E_{\underline{q}'}| + 2\epsilon_2 \} . \quad (16.17)$$

As we have already mentioned, $E_{\underline{q}}$ and $E_{\underline{q}'}$ are on the same side of the Fermi level. On the other hand, in Appendix A9. we have shown that we can approximate

$$\Delta_{\underline{q}\underline{q}'} \cong [E_b(\underline{q}) - E_b(\underline{q}')], \quad (16.18)$$

(c.f.equ.(A9.5)). Using this approximation we may write

$$|E_{\underline{q}}| \cong E_b(\underline{q}) , \quad |E_{\underline{q}'}| \cong E_b(\underline{q}') . \quad (16.19)$$

Thus, using equs. (16.19), and (16.3), equ. (16.17) becomes

$$E_{\underline{q}\underline{q}'} = \frac{3}{4} \{ E_b(\underline{q}) + E_b(\underline{q}') \} . \quad (16.20)$$

Then equ. (16.16) becomes

$$\xi_{\underline{q}\underline{q}'} = 2 \propto r_{\underline{q}\underline{q}'} + \frac{\tilde{E}_{\underline{q}\underline{q}'}}{K'_T} , \quad (16.21)$$

where

$$\tilde{E}_{\underline{q}\underline{q}'} = E_b(\underline{q}) + E_b(\underline{q}') , \quad (16.22)$$

and

$$K' = \frac{4}{3} K . \quad (16.23)$$

Hereafter we shall refer to the binding energy as the site energy, and we shall use the symbol E_g instead of $E_b(g)$, for convenience. Thus, the impedances $Z_{gg'}$ are given by equ.(16.14),

$$Z_{gg'} = Z_0 \exp(\xi_{gg'}) ,$$

where

$$\xi_{gg'} = 2\alpha r_{gg'} + \frac{\tilde{E}_{gg'}}{k'T} , \quad (16.24)$$

$$\tilde{E}_{gg'} = E_g + E_{g'} \quad (16.25)$$

and k' is given by equ.(16.23).

Now, we notice that $\xi_{gg'}$ is of the same form as in the low-temperature case (c.f. equ.(13.30)), but the energy dependence of $\xi_{gg'}$ is different from the one given by equ.(13.31), for the low-temperature regime. Here, we have a dependence on both site energies E_g , and $E_{g'}$ and not only on one as in the low-T regime. Using the same argument as before, the condition for percolation reads

$$\xi_{gg'} \leq \xi_c , \quad (16.26)$$

or using equ.(16.24), (16.25), we obtain

$$\frac{r_{gg'}}{r_m} + \frac{E_g}{E_m} + \frac{E_{g'}}{E_m} \leq 1 , \quad (16.27)$$

where

$$r_m = \frac{\xi_c}{2\alpha} , \quad (16.28)$$

and

$$E_m = k' T \xi_c . \quad (16.29)$$

Thus, before discussing the thermoelectric power problem we have to examine the conductivity problem. This study will give us the expression for the maximum separation, r_m , and the maximum energy, E_m , on the percolation path, necessary for the evaluation of the thermoelectric power of the material.

Following ref. (35), the condition for percolation reads

$$P(z_m) = \vartheta , \quad (16.30)$$

where $P(z_m)$ is the average number of impedances of magnitude z_m or less connected to a given site. For we use the value ⁽ⁱ⁾ 1.7. (35)

The function $P(z_m)$ can now be evaluated from the distribution of the random variables E_2, E_2' , and r_{22}' which enter in the expression for z ,

$$\vartheta = \int_{z = \text{const.}} p(E_2, E_2', r_{22}') d r_{22}' d E_2 d E_2', \quad (16.31)$$

where $p(E_2, E_2', r_{22}')$ is the probability density that a site with energy E_2 has a neighbour at distance r_{22}' with energy E_2' . Assuming lack of correlation between successive impedances in a chain, and between the distribu-

(i) The symbol ϑ here stands for α of ref. (35).

tion of r and site energies,

$$N_s^2 p(E_g, E_{g'}, r_{gg'}) = 4\pi N_s r_{gg'}^2 N(E_g) N(E_{g'}), \quad (16.32)$$

for a random distribution of sites. The integration extends over surfaces of constant Z in the $E_g, E_{g'}$ and $r_{gg'}$ space. Specifically the integration extends over surfaces defined by

$$\frac{r_{gg'}}{r_m} + \frac{2E_{g'} - \Delta_{g'g}}{E_m} = 1, \quad (16.33)$$

which are defined from the percolation condition (16.27) substituting E_g by $E_{g'} - \Delta_{g'g}$. Then, equ. (16.31) becomes

$$\int_0^{E_m} \left\{ \int_{\Delta}^{\frac{1}{2}(E_m + \Delta)} \frac{1}{N_s^2} N(E_{g'} - \Delta) N(E_{g'}) \left[\int_0^{r_m \left(1 - \frac{2E_{g'}}{E_m} + \frac{\Delta}{E_m}\right)} 4\pi N_s r^2 dr \right] dE_{g'} \right\} d\Delta = \theta. \quad (16.34)$$

Assuming, for simplicity a constant density of states $N(E_g) = N(E_{g'}) = N_0$, and integrating, we obtain

$$\xi_c = \left(\frac{8.5 N_s'^{1/2} \alpha^{3/2}}{k N_0 T} \right)^{2/5}, \quad (16.35)$$

and

$$Z_c = Z_0 \exp(\xi_c),$$

which can be written as

$$z_c = z_0 \exp \left[\left(\frac{T_0'}{T} \right) \right]^{2/5}, \quad (16.36)$$

where

$$T_0' = \frac{8.5 N_s'^{1/2} \alpha^{3/2}}{k N_0}. \quad (16.37)$$

Thus, a $\sigma \propto \exp[-(T_0'/T)^{2/5}]$ law is obtained for the conductivity, for the case of high-temperature small-polaron hopping regime. We note that for, α in the range $[10^7-10^8] \text{ cm}^{-1}$, N_0 of order 10^{19} , and N_s 10^{16} equ. (16.32) gives a T_0' of order $10^6 \text{ }^\circ\text{K}$.

We also note that, the $T^{-2/5}$ law we derived for the high-T case resembles the $T^{-1/4}$ law for the low-T case, in the sense that they both follow the general formula

$$T^{-\frac{\varepsilon}{\varepsilon+r}} \quad (16.38)$$

where ε is the energy's dimensions (number) involved in the percolation condition, and r the spatial dimensions involved. For the $T^{-1/4}$ law $\varepsilon=1$, (i.e. the energy of a site), and $r=3$, while for the case of $T^{-2/5}$ law, $\varepsilon=2$ (i.e. the energies of two sites), and $r=3$ (c.f. equs. (15.20), and (16.24)).

Let us now proceed to the thermoelectric power

treatment for the high-temperature small-polaron hopping case. Using the notation we've already used in Chapter 15

$$\alpha_h = 4\pi \frac{1}{N_s} K N_o^2 \int_0^{E_m} \left\{ \int_{\Delta}^{\frac{1}{2}(E_m + \Delta)} \alpha_{mic}^h \left[\int_0^{r_m \left(1 - \frac{2E}{E_m} + \frac{\Delta}{E_m}\right)} r^2 dr \right] dE \right\} d\Delta, \quad (16.39)$$

where E_m is given by equ.(16.29),

$$E_m = k' T \xi_c.$$

ξ_c is given by equ.(16.35),

$$\xi_c = \left(\frac{8.5 N_s^{1/2} \alpha^{3/2}}{K N_o T} \right)^{2/5}.$$

The normalization factor K is obtained from

$$4\pi \frac{1}{N_s} K N_o^2 \int_0^{E_m} \left\{ \int_{\Delta}^{\frac{1}{2}(E_m + \Delta)} \left[\int_0^{r_m \left(1 - \frac{2E}{E_m} + \frac{\Delta}{E_m}\right)} r^2 dr \right] dE \right\} d\Delta = \Theta. \quad (16.40)$$

The microscopic thermoelectric power for the high-temperature hopping regime, α_{mic}^h , is given by

$$\alpha_{mic}^h = \left(\frac{K}{q} \right) \left\{ \frac{(2E - \Delta)}{2kT} + \frac{\Delta}{2kT} \coth \frac{\Delta}{2kT} \right\}, \quad (16.41)$$

where the energies are measured from the Fermi energy ($\mu \equiv 0$). For high-T, we can approximate

$$\frac{\Delta}{2kT} \coth \frac{\Delta}{2kT} \approx 1 + \frac{\Delta^2}{12(kT)^2} \quad (16.42)$$

Now, substituting eqs. (16.41), (16.42) into equ. (16.39) we obtain

$$\alpha_h = \tilde{\alpha}_h + \alpha'_h \quad (16.43)$$

where $\tilde{\alpha}_h$ is the macroscopic thermoelectric power due to the main microscopic contribution, $\frac{1}{2qT}(2E-\Delta)$, and α'_h is the corresponding quantity due to the additional microscopic contribution, $(\frac{k}{q})[1 + \frac{\Delta^2}{12(kT)^2}]$. They are given by

$$\tilde{\alpha}_h = \frac{4\pi N_0^2 K}{N_s} \frac{1}{2qT} \int_0^{E_m} \left\{ \int_{\Delta}^{\frac{1}{2}(E_m+\Delta)} (2E-\Delta) \left[\int_0^{r_m(1-\frac{2E}{E_m}+\frac{\Delta}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (16.44)$$

and

$$\alpha'_h = \frac{4\pi N_0^2 K}{N_s} \left(\frac{k}{q}\right) \int_0^{E_m} \left\{ \int_{\Delta}^{\frac{1}{2}(E_m+\Delta)} \left(1 + \frac{\Delta^2}{12(kT)^2}\right) \left[\int_0^{r_m(1-\frac{2E}{E_m}+\frac{\Delta}{E_m})} r^2 dr \right] dE \right\} d\Delta, \quad (16.45)$$

where a constant density of states, as before, is considered. The normalization factor is obtained from equ. (16.40). Performing the integrations, in equ. (15.40), we obtain

$$K = \frac{30 \theta N_s}{\pi N_o^2 r_m^3 E_m^2} . \quad (16.46)$$

Now, using equ. (16.45), and defining

$$\frac{4 \pi N_o^2 K}{2 N_s q \tau} = \left(\frac{60 \theta}{q \tau} \right) \left(\frac{1}{r_m^3 E_m^2} \right) \equiv M , \quad (16.47)$$

equ. (16.44) becomes

$$\tilde{\alpha}_h = M \int_0^{E_m} \left\{ \int_0^{\frac{1}{2}(E_m + \Delta)} (2E - \Delta) \left[\int_0^{r_m \left(1 - \frac{2E}{E_m} + \frac{\Delta}{E_m}\right)} r^2 dr \right] dE \right\} d\Delta , \quad (16.48)$$

from which, integrating we obtain

$$\tilde{\alpha}_h = M \frac{1}{360} r_m^3 E_m^3 . \quad (16.49)$$

Substituting M from equ. (16.47) into equ. (16.48), and using eqs. (16.29), and (16.35), we obtain

$$\tilde{\alpha}_h = 0.38 \left(\frac{K}{q} \right) \left(\frac{\tau_o'}{\tau} \right)^{2/5} , \quad (16.50)$$

where τ_0 is given by equ.(16.37). Equation (16.50) gives the "macroscopic" thermoelectric power of the material due to the contribution of the main "microscopic" part.

From equ.(16.45), integrating we obtain

$$\alpha_h' = \left(\frac{k}{q} \right) \left\{ 1.7 + 10^{-2} \left(\frac{\tau_0'}{\tau} \right)^{4/5} \right\}, \quad (16.51)$$

from which

$$A_h = 1.7 + 10^{-2} \left(\frac{\tau_0'}{\tau} \right)^{4/5}. \quad (16.52)$$

Equation (16.51) gives the additional part to the "macroscopic" thermoelectric power due to energy of transport.

Substituting equs.(16.50), and (16.51) into equ.(16.43), we obtain the thermoelectric power of the material,

$$\alpha_h = \left(\frac{k}{q} \right) \left\{ 0.38 \left(\frac{\tau_0'}{\tau} \right)^{2/5} + 1.7 + 10^{-2} \left(\frac{\tau_0'}{\tau} \right)^{4/5} \right\}. \quad (16.53)$$

Part V

Comparison with other theories-Summary and
Discussion of the Results.

Chapter 17

Comparison with other theories-Summary and Discussion of the Results.

The present thesis can be divided in two main parts. In the first, a theory of the (microscopic) thermoelectric power associated with electronic phonon-assisted hopping motion between energetically inequivalent sites with different electron-lattice interaction parameters has been developed. In the second the (macroscopic) thermoelectric power of the material is evaluated.

Concerning the first part, as we have already mentioned in Chapter 2, the only result, up to now, predicting a finite contribution to the thermoelectric power due to energy transport in the small-polaron hopping regime, is the one given by Emin⁽²³⁾. We evaluated Emin's general expressions, given by the text eqs. (2.14)-(2.17), for the $E_T^{g,g'}$ term, or equivalently for $A_{g,g'} = E_T^{g,g'} / kT$, in the high-temperature, strong coupling and weak-dispersion limit. The calculations lead to the result of the form

$$\alpha_{g,g'}^{s.h.} = \left(\frac{k}{q} \right) \left[\frac{\tilde{E}(g, g')}{kT} - \frac{\mu}{kT} + A_{g,g'}^{s.h.} \right], \quad (17.1)$$

where

$$\tilde{E}(\underline{g}, \underline{g}') = \frac{[\epsilon_{\underline{g}}(0) - E_b(\underline{g})] + [\epsilon_{\underline{g}'}(0) - E_b(\underline{g}')] }{2} \quad (17.2)$$

and

$$A_{\underline{g}, \underline{g}'}^{s.h.} = \left(\frac{\Delta \underline{g}' \underline{g}}{2 k T} \right) \frac{[E_b(\underline{g}) - E_b(\underline{g}')] }{[E_b(\underline{g}) + E_b(\underline{g}')] } . \quad (17.3)$$

In contrast, our theory results in an expression for the thermoelectric power given by equ. (17.1) as well, but where $A_{\underline{g}, \underline{g}'}^{s.h.}$ is given by

$$A_{\underline{g}, \underline{g}'}^{s.h.} = \left(\frac{\Delta \underline{g}' \underline{g}}{2 k T} \right) \coth \frac{\Delta \underline{g}' \underline{g}}{2 k T} \exp \left(- \frac{\Delta^2 \underline{g}' \underline{g}}{16 \epsilon_2 k T} \right) , \quad (17.4)$$

under the same temperature, strength of coupling and dispersion conditions.

Comparing equs. (17.1), (17.3), and (17.4), we can make the following remarks:

(a) For both theories the same main contribution to the thermoelectric power was found; namely $\left(\frac{k}{q} \right) \left[\frac{\tilde{E}(\underline{g}, \underline{g}')}{k T} - \frac{\mu}{k T} \right]$.

(b) In both expressions for the additional part, due to the energy of transport, equs. (17.3), (17.4), the coefficient $A_{\underline{g}, \underline{g}'}^{s.h.}$ depends on the temperature T and on the energy disorder $\Delta \underline{g}' \underline{g}$.

The direct dependence of $A_{\underline{g}, \underline{g}'}^{s.h.}$ given by equ. (17.3),

on the difference of the binding energies of the two sites arises from the fact that the imposition of the local temperature on every lattice site, permits each site to be treated independently. In our theory, in order to avoid this microscopic temperature gradient assumption we treated the system of the two sites as a whole, and thus the direct dependence on the difference of the binding energies does not appear. This difference, for the range of values of the parameters involved, i.e.

$\Delta_{\underline{q}'\underline{q}} = [(0.02 - 0.1) \text{ eV}]$, $E_b = [(0.2 - 0.4) \text{ eV}]$, $T = [(250 - 800)^\circ \text{K}]$, leads to values for $A_{\underline{q}'\underline{q}}^{\text{s.h.}}$, as given by our expression, equ.(17.4), which are larger than those given by Emin's result, equ.(17.3). Specifically, we choose representative values of the parameters, $\Delta_{\underline{q}'\underline{q}} = 0.08 \text{ eV}$, $E_b(\underline{q}') = 0.25 \text{ eV}$, and a temperature range $(250 - 800)^\circ \text{K}$. Assuming that the disorder energy is mainly polaronic, so that $\Delta_{\underline{q}'\underline{q}} = E_b(\underline{q}) - E_b(\underline{q}')$, as shown in Appendix A9, Emin's values for $A_{\underline{q}'\underline{q}}^{\text{s.h.}}$, for values of the parameters as given above, lie between $[0.1 - 0.3]$, while our values lie between $[1 - 3.6]$ (see fig. 11). The above approximation, i.e. the polaronic character of the disorder, was used in order to choose the numerical values of the parameters in a consistent way. However, the results do not change appreciably if instead of the above approximation we use actual numerical values for all the parameters involved, i.e. $\Delta_{\underline{q}'\underline{q}}$, $E_b(\underline{q}')$, and $E_b(\underline{q})$. The two-site result is representative of the macroscopic situation of the system, thus our values are closer to the experimentally

observed values for $A^{(11)}$, which lie between [2-5].

With restriction that $b \equiv \Delta_{g'g} / \hbar\omega_0$ be an integer, an energy-conserving hop can take place with a small number of phonons being emitted or absorbed. If $\Delta_{g'g}$ is not a multiple of $\hbar\omega_0$, and especially in the weak-dispersion limit, processes involving both the absorption and emission of a large number of phonons may be required in order to conserve energy in a hop between sites. In the low-temperature limit such processes would be associated with vanishingly small jump rates compared with the rates for which $\Delta_{g'g} / \hbar\omega_0$ is an integer. With increasing temperature and passage into the (high-temperature) regime in which more than the minimum number of phonons required for energy conservation are involved in a transition, the disparity between the rates with and without $\Delta_{g'g} / \hbar\omega_0$ being an integer is reduced and in the semiclassical limit $(\hbar\omega_0/kT) \rightarrow 0$, the restriction on $\Delta_{g'g}$ is of no consequence. The strong dependence of the (weak-dispersion) low-temperature jump rate on the deviation of $\Delta_{g'g} / \hbar\omega_0$ from integral values is a feature that must, however, be re-examined in a more realistic model for low-temperatures in which a carrier interacts with acoustic as well as optical phonons. On the other hand the restriction that $\Delta_{g'g} / \hbar\omega_0$ be an integer does not permit the use of equ. (17.4) in the limiting case $\Delta_{g'g} = 0$ in order to obtain the value of $A_{g'g}^{s.h.}$. In this connection it should be noted that in the generalized M.C.M., a nonzero disorder

energy ($\Delta_{\underline{g},\underline{g}'} \neq 0$) requires different interaction parameters ($A_{\underline{g}} \neq A_{\underline{g}'}$) for $\epsilon_{\underline{g}}(0) \neq \epsilon_{\underline{g}'}(0)$.

Throughout our calculations we used the weak-dispersion limit. This approximation does not influence the generality of the problem. The only remark which should be made at this point is that the relation⁽²⁸⁾

$$n^2 \frac{(2\pi)}{8} \left(\frac{\omega_b}{\omega_0} \right)^2 \left(\frac{4\epsilon_z}{\hbar\omega_0} \right) \left[\cosh \frac{B\hbar\omega_0}{2} \right] \gg 1, \quad (17.5)$$

must be satisfied in order that the principal contribution of the sum over n arises only from the $n=0$ term.

Thus, under the above assumptions, the microscopic thermoelectric power, for the two-site system, was found to be given by

$$\alpha_{\underline{g},\underline{g}'} = \left(-\frac{k}{q} \right) \left(\frac{\tilde{E}(\underline{g},\underline{g}') - \mu}{kT} + A_{\underline{g},\underline{g}'} \right) \quad (17.6)$$

where

$$\tilde{E}(\underline{g},\underline{g}') = \frac{[\epsilon_{\underline{g}}(0) - E_b(\underline{g})] + [\epsilon_{\underline{g}'}(0) - E_b(\underline{g}')] }{2}, \quad (17.7)$$

and the term $\left(\frac{k}{q} \right) A_{\underline{g},\underline{g}'}$ is the additional part to the thermoelectric power due to the energy of transport. For the various regimes of physical interest, as the strong-coupling(s), weak-coupling(w), high-temperature(h), and low-temperature (l) regime, the coefficient $A_{\underline{g},\underline{g}'}$ was found to be given by

$$A_{\underline{g},\underline{g}'}^{\text{s.h.}} \cong A_{\underline{g},\underline{g}'}^{\text{w.h.}} = \frac{\Delta_{\underline{g},\underline{g}'}}{2kT} \coth \frac{\Delta_{\underline{g},\underline{g}'}}{2kT}, \quad (17.8)$$

and

$$A_{\underline{g},\underline{g}'}^{\text{s.l.}} = A_{\underline{g},\underline{g}'}^{\text{w.l.}} = \frac{\Delta_{\underline{g},\underline{g}'}}{2kT}, \quad (17.9)$$

following the remarks we have made in Part III.

Here we have to notice that our two-site result follows from the given choice of the heat current operator (c.f. equ.(6.2)). This choice seems to give, for $A_{\underline{g}} = A_{\underline{g}'}$ (or $E_{\underline{g}}(\underline{g}) = E_{\underline{g}'}(\underline{g}')$), but $\epsilon_{\underline{g}}(0) \neq \epsilon_{\underline{g}'}(0)$, a result $A_{\underline{g},\underline{g}'}^{\text{s.h.}} \neq 0$ (equ.(17.8)). This does not agree with the classical result^{(18),(19)}, which, for the same situation, predicts $A_{\underline{g},\underline{g}'}^{\text{s.h.}} = 0$.

From equs. (17.8) and (17.9) follows that:

(a) The strength of coupling does not change appreciably the additional part to the thermoelectric power due to energy of transport. It, mainly, depends on the disorder energy, $\Delta_{\underline{g},\underline{g}'}$, and on the temperature.

(b) The main contribution to the additional part,

$A_{\underline{g},\underline{g}'} = \frac{\Delta_{\underline{g},\underline{g}'}}{2kT}$, for the case of low-temperature agrees with the high-temperature case at the lowest temperature possible, namely $kT \geq \hbar\omega_0$. Thus, the curve $A_{\underline{g},\underline{g}'}$ versus $\frac{1}{T}$ is continuous as we pass from the low to the high-temperature regime, with a departure from linearity when we enter the high-temperature region (c.f. fig.13). Quantitatively,

(a) in the high-temperature regime, and specifically in a temperature range $(200-800)^{\circ}\text{K}$, and in a disorder energy range $(0.02-0.1)\text{eV}$, the values of $A_{g,g'}^k$ lie between $[3.6-4]$ (c.f. fig. 11).

(b) In the low-temperature regime, and specifically in a temperature range $(10-20)^{\circ}\text{K}$, and in the same range of disorder energy, the values of $A_{g,g'}^{\ell}$ lie between $[60-58]$ (c.f. fig. 12).

(c) For a fixed value of the disorder energy, for example $\Delta_{g,g'} = 0.04\text{eV}$, and in the temperature region $(26-1000)^{\circ}\text{K}$, the values of $A_{g,g'}$ lie between $[8-4]$ (c.f. fig. 13). Thus, we see that the additional part to the thermoelectric power, $A_{g,g'}$ increases as we lower the temperature, showing a linear dependence on $\frac{1}{T}$ at low-temperatures and non-linear in the high-temperature regime.

In the second part of the thesis using the microscopic results we evaluated the macroscopic thermoelectric power for the low and high-temperature regime. Our method is representative of how to proceed from the two-site result to the macroscopic one, though the latter cannot be correct in detail because the former is not. The choice of a constant density of states has been made only for computational convenience and does not affect the generality of the method. Thus for a constant density of states, and taking, no correlation between successive hops into account we found that

(a) for the low-temperature regime, where the $T^{-1/4}$ law for the conductivity is valid, we found that

$$\alpha_l = \tilde{\alpha}_l + \alpha'_l. \quad (17.10)$$

Here, α_l is the thermoelectric power of the material at low-temperatures, $\tilde{\alpha}_l$ is the thermoelectric power of the material due to the principal microscopic contribution, $(\frac{k}{q})[\frac{E_2 + E_2'}{2kT}]$, $\mu \equiv 0$, and α'_l is the corresponding quantity due to the additional microscopic part $(\frac{k}{q}) \frac{A_2'g}{2kT}$. They are given by

$$\tilde{\alpha}_l = \left(\frac{1}{4}\right) \left(\frac{k}{q}\right) \left(\frac{T_0}{T}\right)^{1/4}, \quad (17.11)$$

and

$$\alpha'_l = \left(\frac{1}{12}\right) \left(\frac{k}{q}\right) \left(\frac{T_0}{T}\right)^{1/4}, \quad (17.12)$$

from which

$$A_l = \left(\frac{1}{12}\right) \left(\frac{T_0}{T}\right)^{1/4}, \quad (17.13)$$

adding up to

$$\alpha_l = \left(\frac{1}{3}\right) \left(\frac{k}{q}\right) \left(\frac{T_0}{T}\right)^{1/4}, \quad (17.14)$$

where T_0 is of the order of $10^8 \text{ }^\circ\text{K}$.

For a temperature range $[10-20]$, the values of A_l lie between $[4.6-3.9]$, resulting to an additional part to the thermoelectric power, α'_l , in a range $[0.4-0.35] \text{ mV/K}$. We notice that the values of A_l are not as large as

those of $A_{g,g'}^{\ell}$ for the same temperature range. The reason is that the maximum disorder energy between two sites belonging to the percolation path, Δ_m , equals the maximum percolation energy, $E_m = kT(\frac{T_0}{T})^{1/4}$. At very low temperatures the values of E_m are much smaller than those we use microscopically, i.e. $\Delta_m \leq E_m < \Delta_{g,g'} = [0.02 - 0.1] \text{ eV}$. Thus, pairs of sites with large energy disorder, which in the microscopic picture at sufficiently low temperatures give large values for $A_{g,g'}^{\ell}$, do not contribute to the macroscopic thermoelectric power because they do not belong to the percolation path, and thus the values of A_{ℓ} are not as large as those of $A_{g,g'}^{\ell}$.

The contribution due to the main part to the thermoelectric power $\tilde{\alpha}_{\ell}$ lie in the range $[1.2 - 1.05] \text{ mV K}^{-1}$; adding up with α_{ℓ}' to a total thermoelectric power, α_{ℓ} , in the range $[1.6 - 1.4] \text{ mV K}^{-1}$.

Thus we see that the additional part to the thermoelectric power due to the energy of transport is comparable with the main contribution.

(b) For the high-temperature regime, $\hbar\omega_0 \ll kT$, the use of the approximation $\coth \frac{\Delta}{2kT} \cong \frac{2kT}{\Delta} + \frac{\Delta^2}{12(kT)^2}$ (c.f. equ. 16.42), for $\Delta \ll 2kT$, has only been made for computational convenience and does not affect the generality of the method. Thus, again, for a constant density of states, we found that the electrical conductivity follows a $T^{-2/5}$ law. Specifically we found that

$$\sigma \propto \exp \left[- \left(\frac{T_0'}{T} \right)^{2/5} \right], \quad (17.15)$$

where T_0' is of the order of $10^6 \text{ }^\circ\text{K}$. This result agrees with the $\tau^{-1/4}$ law, in the sense that they both follow the general formula $\tau^{-\frac{\epsilon}{\epsilon+r}}$, where ϵ is the energy's dimensions (number) involved in the percolation condition, and r the spatial dimensions involved. For the $\tau^{-1/4}$ law, $\epsilon = 1$ (i.e. the energy of a site), and $r = 3$, while for the case of $\tau^{-2/5}$ law, $\epsilon = 2$ (i.e. the energies of two sites), and $r = 3$.

The macroscopic thermoelectric power for the high-temperature regime (h), α_h , was found to be given by

$$\alpha_h = \tilde{\alpha}_h + \alpha_h' , \quad (17.16)$$

where $\tilde{\alpha}_h$ is the thermoelectric power of the material due to the principal microscopic contribution, $(\frac{\kappa}{q}) \left[\frac{E_g + E_g'}{2} \right]$, $\gamma \equiv 0$, and α_h' is the corresponding quantity due to the additional microscopic part, $(\frac{\kappa}{q}) \frac{\Delta g_g}{2\kappa T} \coth h \frac{\Delta g_g'}{2\kappa T}$. At sufficiently high-temperatures they are given by

$$\tilde{\alpha}_h = (0.38) \left(\frac{\kappa}{q} \right) \left(\frac{T_0'}{T} \right)^{2/5} , \quad (17.17)$$

and

$$\alpha_h' = \left(\frac{\kappa}{q} \right) \left\{ 1.7 + 10^{-2} \left(\frac{T_0'}{T} \right)^{4/5} \right\} \quad (17.18)$$

from which

$$A_h = 1.7 + 10^{-2} \left(\frac{T_0'}{T} \right)^{4/5} , \quad (17.19)$$

adding up to

$$\alpha_h = \left(\frac{k}{q} \right) \left\{ (0.38) \left(\frac{T_0'}{T} \right)^{2/5} + 1.7 + 10^{-2} \left(\frac{T_0'}{T} \right)^{4/5} \right\}, \quad (17.20)$$

where T_0' is of the order of 10^6 °K.

For a temperature range [850-1000]°K, consistent with the approximation, given by equ. (16.42), the values of A_h lie between [4.5 - 4.2], resulting in an additional part to the thermoelectric power, α_h' , in the range [0.38 - 0.36] mV K⁻¹. The contribution due to the main part to the thermoelectric power, $\tilde{\alpha}_h$, lies in the range [0.55 - 0.51] mV K⁻¹, adding up with α_h' to a total thermoelectric power, α_h , in the range [0.93 - 0.87] mV K⁻¹.

Thus, we see that the additional part to the thermoelectric power due to the energy of transport is comparable with the main contribution. Comparing our result with the experimentally observed values⁽³²⁾ as we have discussed in Chapter 1, we see that we have a good agreement.

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