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A reflective unitary transformation for phonon-assisted quantum transport

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Abstract. A class of unitary transformations of reflective character is proposed for multimode quantum transport systems. The simplest of these is discussed in detail. To optimise the transformation parameters, a new variational principle is introduced which is based on the definition of a positive definite 'measure of non-diagonality' for each state. The optimised transformation removes the leading order of non-diagonality in the phonon coupling strength D (from D^0 to D^{-2} for $D^2 \gg 1$ and from D^2 to D^4 for $D^2 \ll 1$). In this manner the basic shortcoming of quantum diffusion systems, which is the dominating non-diagonality between energetically far-off states, is drastically reduced.

1. Introduction

Phonon-assisted quantum transport has been theoretically studied by many workers (Holstein 1959, Pirc *et al* 1966, Dick 1968, 1977, Flynn and Stoneham 1970, Sander and Shore 1971, Kagan and Klinger 1974, Wagner 1979, Teichler and Seeger 1981, Kuhn and Wagner 1981, Junker and Wagner 1983). In all these attempts a procedure has been chosen, which directly or indirectly amounts to a golden rule (GR) description of the transportive transition rates.

However, the straightforward application of the Fermi GR in quantum transport problems raises some serious questions. Firstly, it should be remembered that any kind of decay in quantum mechanics very sensitively depends on the choice of the initial state. It is the spectral breadth of the projection of the initial state onto the exact eigenfunctions which defines the decay constant. In optical problems frequently the initial state can be prepared as a single eigenstate of some zero-order Hamiltonian H_0, which is the starting prerequisite for the GR description. However, in quantum transport problems an experimental preparation of this kind is not achievable. Therefore, theoretically one eventually has to revert to an initial state in the sense of a Kubo formalism.

Secondly, a basic presupposition of the GR is the requirement that the transition matrix elements between energetically far-distant states of H_0 do not strongly exceed those between equi-energetic ones. However that is just not warranted in quantum diffusion.

Thirdly, there is a strange hierarchical peculiarity in phonon-assisted particle transfer problems. It is a fact that first-order (and all odd-order) results display a Debye-Waller screening, whereas second-order (and all even-order) results do not,

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whence for strong enough particle-phonon coupling second-order may exceed first-order. Since theoretical decay evolves from a combination of first- and second-order, the question arises of whether Debye-Waller screening is partially absent in the decay constant.

In a previous paper (Wagner 1984a), henceforth referred to as I, a Kubo response approach to the occupational decay has been presented. In this approach the occupational decay is characterised by an oscillatory transport coefficient ω_0 and a damping constant Γ_0. It has been shown in I that the Fulton-Gouterman transformation (1961) has a fundamental bearing on quantum transport and allows for exact general statements about the transport quantities ω_0, Γ_0. It is proven that in the limit of a small transitive parameter Δ both ω_0 and Γ_0 depend linearly on Δ. It is further shown that the temperature behaviour of ω_0, Γ_0 is different in the one-, few-, and many-mode cases ($N \gg 1$).

As regards the many-mode case ($N \gg 1$) which, of course, is the physically most relevant one, it turned out that the *hierarchical property* $D_k \sim N^{-1/2}$ of the phonon coupling constants D_k (mode k) has a great impact on the results. Thus, it was shown in I that the linear Δ-behaviour of Γ_0 is of order N^{-1} and accordingly fades away in the limit $N \gg 1$. This fact is somewhat pleasing, since a linear Δ-behaviour would have been a demanding overthrow of the commonly accepted behaviour $\Gamma_0 \sim \Delta^2$. Since in the transport path considered in I there was no direct influence of second-order perturbation theory onto Γ_0, it was suspected that a possible Δ^2-behaviour would result from a combination of first- and third-order perturbation theory, and the general formula for this effect was given. Yet an explicit calculation had the outcome that the suspected kind of Δ^2-behaviour of Γ_0 again is only of order N^{-1}.

Now, in I we have considered only those state combinations $\{m\}^{(+)} \leftrightarrow \{n\}^{(-)}$ between the two Fulton-Gouterman quasi-continua for which the phonon quantum numbers are identical, $m_k^{(+)} = n_k^{(-)}$. It is clear, however, that in the same spectral region we also have those state combinations for which the phonon numbers are only globally conserved, $\Sigma_k m_k^{(+)} = \Sigma_k n^{(-)}$. It is these additional combinations which provide the decisive spectral breadth $\Gamma \sim \Delta^2$. However, in the multimode case, a perturbative type of calculation beyond first-order is not achievable, whence an alternative diagonalisation procedure is desirable. It is the purpose of this article to introduce a reflective type of a unitary transformation, which is to be applied to the residual vibrational problem ensuing from the Fulton-Gouterman transformation, and which displays good diagonalisation properties.

2. Two-site model and Fulton–Gouterman transformation

For lucidity we consider a two-site model (see I) with the Hamiltonian

$$H = H_L + \sigma_z \sum_k \Omega_k D_k Q_k + \Delta\sigma_x \tag{1}$$

where the phonon Hamiltonian is taken in the form ($\hbar = 1$)

$$H_L = \tfrac{1}{2} \sum_k \Omega_k [P_k^2 + Q_k^2], \qquad [Q_k, P_{k'}] = \mathrm{i}\delta_{kk'} \tag{2}$$

and where a spin-$\frac{1}{2}$ description is employed for the two sites of the tunnelling particle ($\sigma_z = \frac{1}{2}(c_1^+ c_1 - c_2^+ c_2)$, $\sigma_x = \frac{1}{2}(c_1^+ c_2 + c_2^+ c_1)$, $\sigma_y = \frac{1}{2}\mathrm{i}(c_1^+ c_2 - c_2^+ c_1)$). It is this model which may be viewed as the archetype of a theoretical model describing phonon-assisted

transport and has been studied by many researchers (Holstein 1959, Pirc *et al* 1966, Dick 1968, 1977, Flynn and Stoneham 1970, Sander and Shore 1971, Kagan and Klinger 1974, Wagner 1979, Teichler and Seeger 1981, Kuhn and Wagner 1981, Junker and Wagner 1983).

We want to consider a many-mode system $N \gg 1$ (N = number of lattice modes), where the tunnel-phonon coupling constants D_k are of order $N^{-1/2}$, but such that

$$D^2 \equiv \sum_k D_k^2 = \mathrm{O}(1) \tag{3a}$$

whereas

$$\sum_k D_k^4 = \mathrm{O}(N^{-1}). \tag{3b}$$

Hamiltonian (1) may be diagonalised with respect to the pseudospin subsystem by means of the symmetrised ansatz

$$\psi^{(\mathrm{p})} = 2^{-1/2}[|1\rangle\Phi^{(\mathrm{p})}(Q) + p|2\rangle G\Phi^{(\mathrm{p})}(Q)], \qquad p = \pm 1 \tag{4}$$

where $|1\rangle$ and $|2\rangle$ denote the two spin states (i.e. the 'two sites' of the tunnelling particle), $\sigma_z|1\rangle = |1\rangle/2$, $\sigma_z|2\rangle = -|2\rangle/2$, and where $G(P_k, Q_k)$ is a reflection operator,

$$GQ_k = -Q_k G, \qquad G^2 = 1, \qquad G^+ = G \tag{5a}$$

$$G\Phi(Q) = \Phi(-Q), \tag{5b}$$

which may be taken in the explicit form

$$G = \prod_k G_k(P_k, Q_k) = \prod_k \exp[\tfrac{1}{2}\mathrm{i}\pi(P_k^2 + Q_k^2 - 1)]. \tag{6}$$

Ansatz (4) is equivalent to the Fulton-Gouterman transformation $H = U_{\mathrm{FG}}^+ H U_{\mathrm{FG}}$, where

$$U_{\mathrm{FG}} = 2^{-1/2}[\tfrac{1}{2} + \mathrm{i}\sigma_y](1 - G) + 2^{-1/2}[\sigma_z + \sigma_x](1 + G). \tag{7}$$

For more details about the background of this tranformation we refer to the original work of Fulton and Gouterman (1961) and to two recent papers of the author (Wagner 1984b, c). In this manner the original Schrödinger equation is reduced to the vibrational eigenvalue problems

$$H^{(\mathrm{p})}\Phi_{\{m\}}^{(\mathrm{p})}(Q) = E_{\{m\}}^{(\mathrm{p})}\Phi_{\{m\}}^{(\mathrm{p})}(Q), \qquad p = \pm 1 \tag{8}$$

where $\{m\}$ is the N-tuple of vibrational quantum numbers $\{m\} = \{m_1, m_2, \ldots\}$, and where

$$H^{(\mathrm{p})} = H_{\mathrm{L}} + H_{\mathrm{D}} + W \tag{9}$$

$$H_{\mathrm{D}} = \tfrac{1}{2}\sum_k \Omega_k D_k Q_k, \qquad W = \tfrac{1}{2}p\Delta G(P, Q). \tag{10a, b}$$

In a Kubo (1957) description of transport the migration of a particle from one site to the other is given by the occupational decay function (see I):

$$\langle\sigma_z\rangle_t = F_{\mathrm{ext}} \int_{-\infty}^{+\infty} \mathrm{d}\omega \exp(-\mathrm{i}\omega t) R(\omega) \tag{11}$$

where $R(\omega)$ is the spectral function of the Mori correlation function,

$$R(\omega)=\tfrac{1}{2}Z(T)^{-1}\sum_{\{m\}}\sum_{\{n\}}|\langle\Phi_m^{(+)}|\Phi_m^{(-)}\rangle|^2\exp[-\tfrac{1}{2}\beta(E_m^{(+)}+E_n^{(-)})]$$
$$\times\{\sinh[\tfrac{1}{2}\beta(E_{\{n\}}^{(-)}-E_{\{m\}}^{(+)})]/(E_{\{n\}}^{(-)}-E_{\{m\}}^{(+)})\}$$
$$\times[\delta(\omega-(E_{\{n\}}^{(-)}-E_{\{m\}}^{(+)}))+\delta(\omega+(E_{\{n\}}^{(-)}-E_{\{m\}}^{(+)}))], \tag{12}$$

Z being the partition function,

$$Z(T)\equiv\operatorname{Tr}\mathrm{e}^{-\beta H}=\sum_{\{m\}}(\mathrm{e}^{-\beta E_{\{m\}}^{(+)}}+\mathrm{e}^{-\beta E_{\{m\}}^{(-)}}),\qquad \beta=1/k_{\mathrm{B}}T. \tag{13}$$

In this manner all characteristic transport quantities can be derived from the knowledge of the set of vibrational eigenfunctions $\Phi_{\{m\}}^{(\pm)}$ and eigenvalues $E_{\{m\}}^{(\pm)}$.

3. Debye–Waller peculiarity

For simplicity we consider the one-mode version of (8),

$$[\tfrac{1}{2}\Omega(P^2+Q^2)+DQ]+\tfrac{1}{2}p\Delta G]\Phi_m^{(\mathrm{p})}=E_m^{(\mathrm{p})}\Phi_m^{(\mathrm{p})}. \tag{14}$$

The zero-order ($\Delta=0$) eigenfunctions of this equation are the displaced oscillator functions

$$|m\rangle=\Phi_m^{(\mathrm{o})}(Q+D/2) \tag{15}$$

with eigenvalues

$$E_m^{(\mathrm{o})}=\Omega(m+\tfrac{1}{2})-\tfrac{1}{8}\Omega D^2 \tag{16}$$

and the first-order correction yields

$$E_m^{(\mathrm{p},1)}=\tfrac{1}{2}p\Delta\langle m|G|m\rangle. \tag{17}$$

The reflection operator G affects the displaced oscillatory functions in the following way

$$G|m\rangle=(-1)^m\Phi_m^{(\mathrm{o})}(Q-D/2), \tag{18}$$

whence $\langle m|G|m\rangle$ are oscillatory overlap integrals ('Franck-Condon' integrals; namely e.g. Wagner 1959),

$$(-1)^m\langle m|G|n\rangle\equiv\int_{-\infty}^{+\infty}\Phi_m^{(\mathrm{o})}(Q+D/2)\Phi_n^{(\mathrm{o})}(Q-D/2)\,\mathrm{d}Q. \tag{19}$$

Specifically we have

$$(-1)^m\langle m|G|m\rangle=\exp(-D^2/4)L_m^0(D^2/2) \tag{19a}$$
$$(-1)^{m+1}\langle m|G|m+1\rangle=-D[2(m+1)]^{-1/2}\exp(-D^2/4)L_m^1(D^2/2) \tag{19b}$$
$$(-1)^{m-1}\langle m|G|m-1\rangle=D(2m)^{-1/2}\exp(-D^2/4)L_{m-1}^1(D^2/?) \tag{19c}$$
$$(-1)^{m-1}\langle m+1|G|m-1\rangle=(-1)^{m+1}\langle m-1|G|m+1\rangle \tag{19d}$$
$$=(D^2/2)[m(m+1)]^{-1/2}L_{m-1}^2(D^2/2)$$
$$\langle m|G|0\rangle=D^m(2^m m!)^{-1/2}\exp(-D^2/4) \tag{19e}$$

where $L_m^{\alpha}(Z)$ is the Laguerre polynomial

$$L_m^{\alpha}(z) = \sum_{n=0}^{\infty} (-1)^n \binom{m+\alpha}{m-n} \frac{z^n}{n!}, \qquad L_m^0 \equiv L_m. \tag{20}$$

To obtain a simple hint for the device of a non-perturbative procedure (unitary transformation) we calculate the second-order correction to the ground-state energy,

$$\begin{aligned} E_0^{(\mathrm{p},2)} &= -(\tfrac{1}{2}p\Delta)^2 \sum_{n(\neq 0)}^{\infty} \frac{\langle n|G|0\rangle^2}{\Omega n} \\ &= -\frac{1}{4}\frac{\Delta^2}{\Omega} \exp(-D^2/2) \sum_{n=1}^{\infty} \left(\frac{D^2}{2}\right)^n \frac{1}{n \cdot n!} \end{aligned} \tag{21}$$

where formula (19*e*) has been used. Employing now

$$\begin{aligned} \mathrm{Ei}(z) &= \gamma + \ln z + \sum_{n=1}^{\infty} \frac{z^n}{n \cdot n!} \qquad \text{for } z > 0, \\ &= \tfrac{1}{2} \mathrm{e}^z [1 + z^{-1} + \mathrm{O}(z^{-2})] \qquad \text{for } z \gg 1, \end{aligned} \tag{22}$$

where $\mathrm{Ei}(z)$ is the exponential integral and γ the Eulerian number, we have

$$E_0^{(\mathrm{p},2)} = -(\Delta^2/2\Omega D^2)[1 + \mathrm{O}(D^{-2})] \qquad \text{for } D^2 \gg 1. \tag{23}$$

The total second-order ground-state result thus reads

$$E_0^{(\mathrm{p})} = E_0^{(\mathrm{o})} + \tfrac{1}{2}p\Delta \exp(-D^2/4) - (\Delta^2/2\Omega D^2)[1 + \mathrm{O}(D^{-2})] + \mathrm{O}(\Delta^3). \tag{24}$$

The strange peculiarity of result (21) is that the first-order term displays a Debye-Waller screening $\exp(-D^2/4)$, whereas the Debye-Waller screening is absent in second-order.

For our further understanding it is even more elusive to consider the first-order-corrected ground-state eigenfunction

$$\Phi_0^{(\mathrm{p})} = \Phi_0^{(\mathrm{o})}(Q + D/2) + \Delta\Phi_0^{(\mathrm{p})} \tag{25}$$

where

$$\Delta\Phi_0^{(\mathrm{p})} = p\frac{\Delta}{2\Omega} \exp(-D^2/4) \sum_{m(\neq 0)} \Phi_m^{(\mathrm{o})}(Q + D/2) \frac{1}{m\sqrt{m!}} \left(\frac{D}{\sqrt{2}}\right)^m + \mathrm{O}(\Delta^2) \tag{26}$$

and where use has been made of formula (19*e*). The weight of the addition $\Delta\Phi_0^{(\mathrm{p})}$ is given by the scalar product

$$\langle \Delta\Phi_0^{(\mathrm{p})} | \Delta\Phi_0^{(\mathrm{p})} \rangle = \left(\frac{\Delta}{2\Omega}\right)^2 \exp(-D^2/2) \sum_{m(\neq 0)} \frac{1}{m^2 m!} \left(\frac{D^2}{2}\right)^m + \mathrm{O}(\Delta^3) \tag{27}$$

which by use of relation (22) in the strong coupling case $D \gg 1$ can be shown to have the asymptotic form:

$$\langle \Delta\Phi_0^{(\mathrm{p})} | \Delta\Phi_0^{(\mathrm{p})} \rangle = (\Delta/2\Omega)^2 (D^2/2)\{1 + \mathrm{O}[\exp(-D^2/2)]\} + \mathrm{O}(\Delta^3) \tag{28}$$

which again displays the fading away of Debye-Waller screening. $\Delta\Phi_0^{(\mathrm{p})}$ is located around $Q = +D/2$, which can be seen by projecting it onto $\Phi_0^{(\mathrm{o})}(Q - D/2)$,

$$\langle \Delta\Phi_0 | \Phi_0^{(\mathrm{o})}(Q - D/2) \rangle = p\frac{\Delta}{2\Omega} \exp(-D^2/2) \sum_{m(\neq 0)} \frac{1}{m \cdot m!} \left(\frac{D^2}{2}\right)^m + \mathrm{O}(\Delta^2) \tag{29}$$

where again use has been made of formula (19*e*). In the limit $D^2 \gg 1$ this reads

$$\langle \Delta\Phi_0^{(p)} | \Phi_0^{(o)}(Q - D/2) \rangle = p(\Delta/2\Omega)(D^2/2)^{-1}\{1 + O[\exp(-D^2/2)]\} + O(\Delta^2) \tag{30}$$

which is the square root of (28). We thus conclude

$$\Delta\Phi_0^{(p)} = p(\Delta/2\Omega)(D^2/2)^{-1}\Phi_0^{(o)}(Q - D/2) + O\left(\frac{\Delta}{\Omega}\frac{\exp(-D^2/2)}{D^2}\right). \tag{31}$$

In this manner it turns out that $\Delta\Phi_0$ is a diminished (by a factor $\Delta/D^2\Omega$), but not a Debye-Waller screened mirror image of the zero-order wavefunction. It is this result which makes it suggestive to introduce the unitary transformation which is used in the next section. In passing we note that result (31) can be extracted from the work of Shore and Sander (1973), although they have not stated it in this explicit form.

4. A general reflective transformation

Since in the multimode case straightforward perturbation theory requires the handling of intricate combinatorial problems both for the eigenvalues as well as for the eigenfunctions of (8), we have to seek for other means to solve this eigenvalue problem beyond the first order. It turns out that unitary transformations can be devised by means of which we can achieve the solution of (8) to arbitrary degrees of accuracy. We only consider the most simple class of these, which is characterised by the unitary operator

$$U = \exp S, \qquad S^+ = -S \tag{32}$$

$$S = [\lambda_u(P, Q) + i\lambda_g(P, Q)]G(P, Q) \tag{33}$$

where $\lambda_u(P, Q)$ is a real odd ('ungerade') and $\lambda_g(P, Q)$ a real even ('gerade') Hermitian function of the operators P_k, Q_k,

$$G\lambda_u = -\lambda_u G, \qquad G\lambda_g = \lambda_g G \tag{34}$$

$$\lambda_u(P, Q)^+ = \lambda_u(P, Q), \qquad \lambda_g(P, Q)^+ = \lambda_g(P, Q).$$

Then

$$S^2 = -[\lambda_u + i\lambda_g][\lambda_u - i\lambda_g] = (\lambda_u^2 + \lambda_g^2 + i[\lambda_g, \lambda_u]) \tag{35}$$

and we introduce the notation

$$\Lambda = [(\lambda_u + i\lambda_g)(\lambda_u - i\lambda_g)]^{1/2} = -[\lambda_u^2 + \lambda_g^2 + i[\lambda_g, \lambda_u]]^{1/2}. \tag{36}$$

The unitary operator (32) then assumes the form

$$U = \cos\Lambda + \Lambda^{-1}(\sin\Lambda)S. \tag{37}$$

If any specific choice of the functions λ_u, λ_g turns out to be a suitable one, the diagonal part of the transformed Hamiltonian $U^+H^{(p)}U$ will be a good representative of $H^{(p)}$, which is tantamount to the statement that $\Phi_{\{m\}}^{(o)}(Q_k + D_k/2)$ is a 'good' eigenfunction of $U^+H^{(p)}U$,

$$\Phi_{\{m\}}^{(o)}(Q_k + D_k/2) = U^+\Phi_{\{m\}}^{(p)} \tag{38a}$$

and hence

$$\Phi^{(p)}_{\{m\}} = U\Phi^{(o)}_{\{m\}}(Q_k + D_k/2)$$
$$= (\cos\Lambda)\Phi^{(o)}_{\{m\}}(Q_k + D_k/2) + (-1)^{\Sigma_k m_k}(\Lambda^{-1}\sin\Lambda)(\lambda_u + i\lambda_g)\Phi^{(o)}_{\{m\}}(Q_k - D_k/2) \tag{38b}$$

is a good eigenfunction of $H^{(p)}$ itself. From this expression we recognise that the transformation adds to the original oscillatory function which is localised around $Q_k = -D_k/2$, a second term which is localised around $Q_k = D_k/2$. It is this fact which has been the motivation for introducing the transformation, since the perturbative term W (namely, equation (10*b*)) also has the property of adding a mirror image contribution to the wavefunction.

The most straightforward way of performing a transformation is by means of the commutator expansion

$$T: A \equiv U^+AU = A + (1/1!)[A, S] + (1/2!)[[A, S], S] + \ldots . \tag{39}$$

This yields for our Hamiltonian constituents

$$T: H^{(p)} = H_L + H_D$$
$$+ \tfrac{1}{2}p\Delta G + (H_L + H_D)(\lambda_u + i\lambda_g)G - (\lambda_u + i\lambda_g)G(H_L + H_D)$$
$$- p\Delta\lambda_u + (1/2!)[(H_L + H_D)\Lambda^2 + \Lambda^2(H_L + H_D)$$
$$+ 2(\lambda_u + i\lambda_g)(H_L + H_D)(\lambda_u - i\lambda_g)] + \text{third-order terms} \tag{40}$$

from which we recognise that all first-order matrix elements by virtue of the reflection operator G will be of an overlap nature and thus display Debye-Waller screening, whereas in the second-order terms the reflective operator, and hence Debye-Waller screening, is absent. Another characteristic which is worth noting is the fact that by virtue of $[W, \lambda_g] = 0$ there is no second-order offspring of W from λ_g. Hence, if $\lambda_u = 0$ and if the parameters of λ_g would have to be fixed in a variational way, there would be no second-order stabilisation of these.

5. The simplest reflective transformation

Henceforth we discuss in more detail the simplest of the class (33) of transformations, which is given by

$$S = \sum_k \alpha_k Q_k G, \qquad U = \cos\left(\sum_k \alpha_k Q_k\right) + \left(\sin\left(\sum_k \alpha_k Q_k\right)\right)G \tag{41}$$

(α_k real), which amounts to the choice

$$\lambda_u = \sum_k \alpha_k Q_k, \qquad \lambda_g = 0. \tag{42}$$

The transformation of the basic operators in $H^{(p)}$ is then given by

$$T: P_k^2 = P_k^2 - 2i\alpha_k P_k G + \alpha_k^2 \tag{43a}$$

$$T: Q_k^2 = Q_k^2 \tag{43b}$$

$$T: Q_k = (\cos 2\lambda_u - \sin 2\lambda_u G)Q_k \tag{43c}$$

$$T: G = \cos 2\lambda_u G - \sin 2\lambda_u \tag{43d}$$

and Hamiltonian (9) itself assumes the transformed form

$$\tilde{H}^{(\mathrm{p})} \equiv T : H^{(\mathrm{p})} = H_{\mathrm{L}} + \tfrac{1}{2}\sum_k \Omega_k(\alpha_k^2 - 2\mathrm{i}\alpha_k P_k G) + \tfrac{1}{2}\sum_k D_k\Omega_k[\cos 2\lambda_{\mathrm{u}} - (\sin 2\lambda_{\mathrm{u}})G]Q_k + \tfrac{1}{2}p\Delta[\cos 2\lambda_{\mathrm{u}}(G - \sin 2\lambda_{\mathrm{u}})] \tag{44}$$

with its one-mode version

$$\tilde{H}^{(\mathrm{p})} = \tfrac{1}{2}\Omega(P^2 + Q^2 + DQ - 2\mathrm{i}\alpha PG + \alpha^2) + \tfrac{1}{2}D\Omega Q[\cos 2\alpha Q + (\sin 2\alpha Q)G] + \tfrac{1}{2}p\Delta[(\cos 2\alpha Q)G - \sin 2\alpha Q]. \tag{44a}$$

It now might seem that it is a hopeless venture to calculate matrix elements of the multi-mode Hamiltonian (44). But this in fact turns out to be more easy than in the single-mode case, if one makes recourse to the hierarchical statements (3*a*, *b*). We demonstrate this procedure for the matrix element $\langle\{m\}|P_kG|\{m\}\rangle$, where

$$|\{m\}\rangle = \prod_k \Phi^{(\mathrm{o})}_{m_k}(Q_k + D_k/2). \tag{45}$$

Then, by means of (19)

$$\langle\{m\}|\mathrm{i}P_kG|\{m\}\rangle = \prod_{k'(\neq k)} (-1)^{m_{k'}} \exp(-D_{k'}^2/4) L_{m_{k'}}(D_{k'}^2/2) \times \tfrac{1}{2}D_k(-1)^{m_k}\exp(-D_k^2/4)[L^1_{m_k-1}(D_k^2/2) + L^1_{m_k}(D_k^2/2)]. \tag{46}$$

The general prescription then will be to neglect all powers beyond the second of each single D_k, since these eventually will lead to summations of the form (3*b*) and hence to contributions of order $(1/N)$. Applying this rule to (46), in the $k' \neq k$ terms we may introduce the replacement

$$L_{m_{k'}}(D_k^2/2) = 1 - m_{k'}D_{k'}^2/2 + \mathrm{O}(D_{k'}^4) = \exp(-\tfrac{1}{2}m_{k'}D_{k'}^2) + \mathrm{O}(D_{k'}^4) \qquad \text{for } k' \neq k \tag{47}$$

and in the k term

$$D_k[L^1_{m_k-1}(D_k^2/2) + L^1_{m_k}(D_k^2/2)] = (2m_k+1)D_k + \mathrm{O}(D_k^3) = (2m_k+1)D_k\exp(-\tfrac{1}{2}m_kD_k^2) + \mathrm{O}(D_k^3). \tag{48}$$

In this manner integral (46) is simplified to

$$\langle\{m\}|\mathrm{i}P_kG|\{m\}\rangle = (m_k + \tfrac{1}{2})D_k\prod_{k'}(-1)^{m_{k'}}\exp[-\tfrac{1}{2}(m_{k'}+\tfrac{1}{2})D_{k'}^2] + \mathrm{O}(N^{-3/2}). \tag{49}$$

In a similar way we find the other relevant overlap integrals

$$\langle\{m\}|Q_k^{2\mu+1}G|\{m\}\rangle = 0 \tag{50a}$$

$$\left\langle\{m\}\middle|\left(\sum_k 2\alpha_kQ_k\right)^{2\mu}G\middle|\{m\}\right\rangle = (2\mu-1)!!\left[4\sum_k \alpha_k^2(m_k+\tfrac{1}{2})\right]^{\mu}\mathscr{L} + \mathrm{O}\left(\frac{1}{N}\right) \tag{50b}$$

$$\left\langle \{m\} \middle| Q_k \left(\sum_{k'} 2\alpha_{k'} Q_{k'} \right)^{2\mu+1} \middle| \{m\} \right\rangle$$

$$= 2\alpha_k (m_k + \tfrac{1}{2})(2\mu+1)!! \left[4 \sum_k \alpha_{k'}^2 (m_{k'} + \tfrac{1}{2}) \right]^{\mu} \mathscr{L} + \mathrm{O}(N^{-3/2}) \tag{50c}$$

where the abbreviation

$$\mathscr{L} = \prod_k (-1)^{m_k} \exp[-\tfrac{1}{2}(m_k + \tfrac{1}{2}) D_k^2] \tag{51}$$

has been used. We now turn to the regular, which is 'non-overlap', integrals,

$$\langle \{m\} | (Q_k + D_k/2)^{2\mu+1} | \{m\} \rangle = 0 \tag{52a}$$

$$\left\langle \{m\} \middle| \left[\sum_k 2\alpha_k (Q_k + D_k/2) \right]^{2\mu} \middle| \{m\} \right\rangle = (2\mu - 1)!! \left(4 \sum_k \alpha_k^2 (m_k + \tfrac{1}{2}) \right)^{\mu} + \mathrm{O}\left(\frac{1}{N} \right) \tag{52b}$$

$$\left\langle \{m\} \middle| (Q_k + D_k/2) \left(2 \sum_{k'} \alpha_{k'} (Q_{k'} + D_{k'}/2) \right)^{2\mu+1} \middle| \{m\} \right\rangle$$

$$= 2\alpha_k (m_k + \tfrac{1}{2})(2\mu+1)!! \left(4 \sum_{k'} \alpha_{k'}^2 (m_{k'} + \tfrac{1}{2}) \right)^{\mu} + \mathrm{O}(N^{-3/2}). \tag{52c}$$

In this way the energy expectation value of the transformed Hamiltonian (44) is found to be

$$\langle \{m\} | \tilde{H}^{(\mathrm{p})} | \{m\} \rangle = E_{\{m\}}^{(\mathrm{o})} + \tfrac{1}{2} \sum_k \Omega_k \alpha_k^2$$

$$+ \tfrac{1}{4} \sum_k D_k^2 \Omega_k \left(1 - A \cos \sum_{k'} \alpha_{k'} D_{k'} \right) - \sum_k \alpha_k D_k \Omega_k (m_k + \tfrac{1}{2}) \mathscr{L}[1 - A]$$

$$+ \left(\sum_k \alpha_k D_k \Omega_k (m_k + \tfrac{1}{2}) + \tfrac{1}{2} p \Delta \right) A \sin \sum_k \alpha_{k'} D_{k'}$$

$$+ \tfrac{1}{2} p \Delta \mathscr{L} A + \mathrm{O}\left(\frac{1}{N} \right) \tag{53}$$

where the abbreviations

$$E_{(m)}^{(\mathrm{o})} = \sum_k \Omega_k [(m_k + \tfrac{1}{2}) - \tfrac{1}{8} D_k^2] \tag{54}$$

$$A = \exp \left[-2 \sum_k \alpha_k^2 (m_k + \tfrac{1}{2}) \right] \tag{55}$$

have been used.

We mention that the hierarchical device used in this section for the many-mode case ($N \gg 1$, namely (3*a*, *b*)) also may be fruitfully applied to the matrix elements of other operators, and also in the non-diagonal situation $\{m\} \neq \{n\}$.

Astonishingly enough the one-mode version of the expectation values and matrix elements cannot be given in a similarly simple closed form. Thus, the single-mode version of (53) is written in its series representation

$$\langle m | \tilde{H}^{(\mathrm{p})} | m \rangle = E_m^{(\mathrm{o})} + \tfrac{1}{2} p \Delta (-1)^m \exp(-D^2/4) L_m(D^2/2)$$

$$+ \tfrac{1}{2} \alpha^2 \Omega + \alpha^2 D^2 \Omega [\tfrac{3}{2}(m + \tfrac{1}{2}) + (D/2)^2] + \tfrac{1}{2} p \Delta \alpha D + \mathrm{O}(\Delta^3) \tag{53a}$$

which is derived from (44*a*).

6. Ground-state minimisation

There are several possibilities of finding criteria for the 'goodness' of a unitary transformation. The most straightforward criterion is the decrease of the ground state of the diagonal part of the transformed Hamiltonian. From (53) we derive for the ground state

$$\begin{aligned} E_0^{(p)} = E_0^{(o)} &+ \tfrac{1}{2}\sum_k \Omega_k \alpha_k^2 \\ &+ \tfrac{1}{4}\sum_k D_k^2 \Omega_k \left[1 - \exp\left(-\sum_{k'} \alpha_{k'}^2\right) \cos \sum_{k''} \alpha_{k''} D_{k''}\right] \\ &- \tfrac{1}{2}\sum_k \alpha_k D_k \Omega_k \exp\left(-\sum_{k'} D_{k'}^2/4\right)\left[1 - \exp\left(-\sum_{k''} \alpha_{k''}^2\right)\right] \\ &+ \tfrac{1}{2}\left(\sum_k \alpha_k D_k \Omega_k + p\Delta\right) \exp\left(-\sum_{k'} \alpha_{k'}^2\right) \sin \sum_{k''} \alpha_{k''} D_{k''} \\ &+ \tfrac{1}{2} p\Delta \exp\left(-\sum_k (D_k^2/4 + \alpha_k^2)\right) + O\left(\frac{1}{N}\right). \end{aligned} \tag{56}$$

Minimisation with respect to α_k evolves in

$$\begin{aligned} \alpha_k \Bigg[&\Omega_k + \tfrac{1}{2}\sum_{k'} D_{k'}^2 \Omega_{k'} \exp\left(-\sum_{k''} \alpha_{k''}^2\right) \cos \sum_{k'''} \alpha_{k'''} D_{k'''} \\ &- \sum \alpha_{k'} D_{k'} \Omega_{k'} \exp\left(-\sum_{k''} (D_{k''}^2/4 + \alpha_{k''}^2)\right) \\ &- \left(\tfrac{1}{2}\sum_{k'} \alpha_{k'} D_{k'} \Omega_{k'} + \tfrac{1}{2} p\Delta\right) \exp\left(-\sum_{k'} \alpha_{k'}^2\right) \sin \sum \alpha_{k''} D_{k''} \\ &- p\Delta \exp\left(-\sum_{k'} (D_{k'}^2/4 + \alpha_{k'}^2)\right)\Bigg] \\ &+ \tfrac{1}{4} D_k \sum_{k'} D_{k'}^2 \Omega_{k'} \exp\left(-\sum_{k''} \alpha_{k''}^2\right) \sin \sum_{k'''} \alpha_{k'''} D_{k'''} \\ &- \tfrac{1}{2} D_k \Omega_k \exp\left(-\sum_{k'} D_{k'}^2/4\right)\left[1 - \exp\left(-\sum_{k''} \alpha_{k''}^2\right)\right] \\ &- \tfrac{1}{2} D_k \Omega_k \exp\left(-\sum_{k'} \alpha_{k'}^2\right) \sin \sum_{k''} \alpha_{k''} D_{k''} \\ &+ D_k \left(\tfrac{1}{2}\sum_{k'} \alpha_{k'} D_{k'} \Omega_{k'} + \tfrac{1}{2} p\Delta\right) \exp\left(-\sum_{k''} \alpha_{k''}^2\right) \cos \sum_{k'''} \alpha_{k'''} D_{k'''} \\ &+ O\left(\frac{1}{N}\right) = 0. \end{aligned} \tag{57}$$

From this equation the coefficients α_k may be determined for any value of the transitive coupling constant Δ. There is no practical difficulty in performing this computation if the distribution of phonon coupling constants D_k is known. We will not pursue this further at this place, but turn to the one-mode case, since it will be interesting to find

out whether we are able to reproduce results (21) and (23). From (53*a*) the one-mode version of the ground state is found to be

$$E_0^{(p)} = E_0^{(o)} + \tfrac{1}{2}p\Delta\, e^{-D^2/4} + \tfrac{1}{2}\Omega\alpha^2\{1 + D^2[(\tfrac{3}{2} + (\tfrac{1}{2}D)^2]\} + \tfrac{1}{2}p\Delta\alpha D + O(\Delta^3). \tag{56a}$$

Minimisation with respect to α yields

$$\alpha\Omega = -\tfrac{1}{2}p\Delta D\{1 + D^2[\tfrac{3}{2} + (\tfrac{1}{2}D)^2]\}^{-1} + O(\Delta^2). \tag{57a}$$

Inserting this in (56*a*) we find

$$E_0^{(p)} = E_0^{(o)} + \tfrac{1}{2}p\Delta \exp(-D^2/4) - \tfrac{1}{8}\frac{(p\Delta D)^2}{\Omega}\{1 + D^2[\tfrac{3}{2} + (\tfrac{1}{2}D^2)^2]\}^{-1} + O(\Delta^3). \tag{58}$$

Comparing this with results (21) and (23) we observe that the *exact* second-order results are reproduced in *both limiting cases* $D^2 \ll 1$ and $D^2 \gg 1$. Thus our transformation is 'good' for the ground state.

7. Measures of non-diagonality

A possibility to optimise the transformation with respect to excited states would be the minimisation of the free energy. For this and similar procedures we refer to a forthcoming book by the author (1985).

Here we want to introduce an even more specific variational procedure for the excited states. If we, quite generally, have a Hamiltonian of the form

$$H = H_0 + W \tag{59}$$

and consider the 'non-diagonality' of a state $\{|\alpha\rangle, E_\alpha^{(o)}\}$ of H_0, we may characterise the non-diagonality by

$$M_\alpha^{(nd)} = \sum_{\beta(\neq\alpha)} |\langle\alpha|W|\beta\rangle|^2 \tag{60}$$

where $\{|\beta\rangle, E_\beta^{(o)}\}$ are the other eigenstates of H_0. The closure property then yields

$$M_\alpha^{(nd)} = \langle\alpha|W^2|\alpha\rangle - \langle\alpha|W|\alpha\rangle^2. \tag{60a}$$

We also may define the 'mean position' $\mu_\alpha^{(nd)}$ of the non-diagonality by

$$\mu_\alpha^{(nd)} = (M_\alpha^{(nd)})^{-1} \sum_{\beta(\neq\alpha)} |\langle\alpha|W|\beta\rangle|^2 E_\beta^{(o)}$$

$$= (M_\alpha^{(nd)})^{-1}(\langle\alpha|WH_0W|\alpha\rangle - E_\alpha^{(o)}\langle\alpha|W|\alpha\rangle^2) \tag{61}$$

and the 'mean deviation' $\delta_\alpha^{(nd)}$ from $\mu_\alpha^{(nd)}$ by

$$\delta_\alpha^{(nd)^2} + \mu_\alpha^{(nd)^2} = (M_0^{(nd)})^{-1} \sum_{\beta(\neq\alpha)} E_\beta^{(o)^2} |\langle\alpha|W|\beta\rangle|^2$$

$$= (M_\alpha^{(nd)})^{-1}[\langle\alpha|WH_0^2W|\alpha\rangle - E_\alpha^{(o)^2}\langle\alpha|W|\alpha\rangle^2]. \tag{62}$$

Let us consider these quantities for our original Hamiltonian (9), for which we choose $H_0 = H_L + H_D$. Then we arrive at

$$M_{\{m\}}^{(nd)} = (\tfrac{1}{2}p\Delta)^2(1 - \mathscr{L}^2) \tag{63}$$

which in the strong-coupling case $\Sigma_k D_k^2 \gg 1$ reads

$$M_{\{m\}}^{(nd)} = \tfrac{1}{4}(p\Delta)^2 \tag{63a}$$

and in the weak-coupling limit $\Sigma_k D^2 \ll 1$

$$M_{\{m\}}^{(\mathrm{nd})} = \tfrac{1}{4}(p\Delta)^2 \sum_k D_k^2(m_k + \tfrac{1}{2}). \tag{63b}$$

Further

$$\mu_{\{m\}}^{(\mathrm{nd})} = E_{\{m\}}^{(\mathrm{o})} + \tfrac{1}{2}\sum_k \Omega_k D_k^2 (1 - \mathscr{L}^2)^{-1} \tag{64}$$

with its extremal coupling forms

$$\mu_{\{m\}}^{(\mathrm{nd})} = E_{\{m\}}^{(\mathrm{o})} + \tfrac{1}{2}\sum_k \Omega_k D_k^2 \qquad \text{for} \sum D_k^2 \gg 1 \tag{64a}$$

and

$$\mu_{\{m\}}^{(\mathrm{nd})} = E_{\{m\}}^{(\mathrm{o})} + \tfrac{1}{2}\sum_k \Omega_k D_k^2 \Big(\sum_k D_k^2(m_k + \tfrac{1}{2})\Big)^{-1} \qquad \text{for} \sum_k D_k^2 \ll 1. \tag{64b}$$

And finally

$$(\delta_{\{m\}}^{(\mathrm{nd})})^2 = (1 - \mathscr{L}^2)^{-1}\left[\sum_k \Omega_k^2 D_k^2(m_k + \tfrac{1}{2}) - \Big(\tfrac{1}{2}\sum_k \Omega_k D_k^2\Big)^2 \frac{\mathscr{L}^2}{1 - \mathscr{L}^2}\right] \tag{65}$$

with its special versions

$$(\delta_{\{m\}}^{(\mathrm{nd})})^2 = \sum_k \Omega_k^2 D_k^2(m_k + \tfrac{1}{2}) \qquad \text{for} \sum_k D_k^2 \gg 1 \tag{65a}$$

$$(\delta_{\{m\}}^{(\mathrm{nd})})^2 = \left[\sum_k \Omega_k^2 D_k^2(m_k + \tfrac{1}{2}) - \Big(\tfrac{1}{2}\sum_k \Omega_k D_k^2\Big)^2 \times \Big(\sum_k D_k^2(m_k + \tfrac{1}{2})\Big)^{-1}\right]\Big(\sum_k D_k^2(m_k + \tfrac{1}{2})\Big)^{-1} \qquad \text{for} \sum_k D_k^2 \ll 1. \tag{65b}$$

The mean position $\mu_{\{m\}}^{(\mathrm{nd})}$ of the non-diagonality indicates whether energetically far off states are more strongly coupled to each other than energetically adjacent ones. From (64) we conclude that, in particular in the strong phonon coupling case ($\Sigma_k D_k^2 \gg 1$), each state $\{m\}$ displays its dominant matrix elements to energetically elevated states, $E_{\{n\}}^{(\mathrm{o})} > E_{\{m\}}^{(\mathrm{o})}$.

In contrast we now look at the transformed Hamiltonian (44), choosing

$$\tilde{H}_0 = H_{\mathrm{L}} + H_{\mathrm{D}} + \tfrac{1}{2}\sum_k \Omega_k \alpha_k^2 \tag{66a}$$

$$\tilde{W} = \tfrac{1}{2}p\Delta G + \sum_k \alpha_k \Omega_k \Big(-\mathrm{i}P_k + Q_k \sum_{k'} D_{k'} \Omega_{k'} Q_{k'}\Big) G + \mathrm{O}(\Delta^2). \tag{66b}$$

Also in this case the evaluation of the 'measures of non-diagonality' does not pose any difficulty, provided we employ again hierarchical arguments in the way indicated in the preceding section. We then obtain

$$\tilde{M}_{\{m\}}^{(\mathrm{nd})} = (\tfrac{1}{2}p\Delta)^2(1 - \mathscr{L}^2) + p\Delta \sum_k \alpha_k D_k \Omega_k (m_k + \tfrac{1}{2}) + \sum_k \alpha_k^2 \Omega_k^2 (m_k + \tfrac{1}{2}) + \Big(\sum_k \alpha_k D_k \Omega_k (m_k + \tfrac{1}{2})\Big)^2 + \mathrm{O}(\Delta^3). \tag{67}$$

We now introduce as a *criterion for an optimal choice of the transformation* the requirement

$$\delta \tilde{M}^{(\mathrm{nd})}_{\{m\}} = 0 \tag{68}$$

or specifically, in our case

$$(\partial/\partial\alpha_k)\tilde{M}^{(\mathrm{nd})}_{\{m\}} = 0. \tag{69}$$

Applying this to (67) we find

$$\alpha_k \Omega_k = -\tfrac{1}{2} p\Delta \frac{D_k}{1+\Sigma_{k'} D^2_{k'}(m_{k'}+\frac{1}{2})} + \mathrm{O}(\Delta^2). \tag{70}$$

Inserting it in (67) we have

$$\tilde{M}^{(\mathrm{nd})}_{\{m\}} = (\tfrac{1}{2}p\Delta)^2 \Bigg[1 - \exp\Bigg(-\sum_k D^2_k (m_k + \tfrac{1}{2}) \Bigg) - \sum_k D^2_k (m_k+\tfrac{1}{2}) \Bigg(1 + \sum_{k'} D^2_{k'}(m_{k'}+\tfrac{1}{2}) \Bigg)^{-1} \Bigg] + \mathrm{O}(\Delta^3) \tag{71}$$

with its extremal coupling versions

$$\tilde{M}^{(\mathrm{nd})}_{\{m\}} = (\tfrac{1}{2}p\Delta)^2 \Bigg(\sum_k D^2_k (m_k+\tfrac{1}{2}) \Bigg)^{-1} \qquad \text{for } \sum_k D^2_k \gg 1 \tag{71a}$$

$$\tilde{M}^{(\mathrm{nd})}_{\{m\}} = (\tfrac{1}{2}p\Delta)^2 \tfrac{1}{2} \Bigg(\sum_k D^2_k (m_k+\tfrac{1}{2}) \Bigg)^{2} \qquad \text{for } \sum_k D^2_k \ll 1. \tag{71b}$$

We now compare (71*a*) and (71*b*) with the corresponding ones for the untransformed Hamiltonian (namely (63*a*), (63*b*)). We observe that in both extremal coupling cases the non-diagonality has been *drastically reduced.* In the strong coupling case ($\Sigma_k D^2_k \gg 1$) we get an inverse dependence an $\Sigma_k D^2_k (m_k+\frac{1}{2})$ in place of a constant, whereas in the weak coupling case ($\Sigma_k D^2_k \ll 1$) we find proportionality to $[\Sigma_k D^2_k (m_k+\frac{1}{2}))^2$ in place of one to $\Sigma_k D^2_k (m_k+\frac{1}{2})$.

We also briefly present the results for the one-mode case. If we perform the step by step analogues of those above, we find for the non-transformed Hamiltonian

$$M^{(\mathrm{nd})}_m = (\tfrac{1}{2}p\Delta)^2 \{1 - \exp[-D^2(m+\tfrac{1}{2})]\} \tag{72}$$

or

$$M^{(\mathrm{nd})}_m = (\tfrac{1}{2}p\Delta)^2 \qquad \text{for } D^2 \gg 1 \tag{72a}$$

$$M^{(\mathrm{nd})}_m = (\tfrac{1}{2}p\Delta)^2 D^2 (m+\tfrac{1}{2}) \qquad \text{for } D^2 \ll 1. \tag{72b}$$

In contrast we get for the transformed Hamiltonian

$$\tilde{M}^{(\mathrm{nd})}_m = (\tfrac{1}{2}p\Delta)^2 \{1 - \exp[-D^2(m+\tfrac{1}{2})]\} + p\Delta\alpha\Omega D(m+\tfrac{1}{2}+\tfrac{1}{4}D^2) + (\alpha\Omega)^2 (m+\tfrac{1}{2}+D^2(\tfrac{3}{2}m^2+\tfrac{3}{2}m+\tfrac{7}{4})+\tfrac{3}{2}D^4(m+\tfrac{1}{2})+\tfrac{1}{16}D^4) + \mathrm{O}(\Delta^3) \tag{73}$$

from which, after applying the variation (68),

$$\alpha\Omega = -\tfrac{1}{2}p\Delta D \frac{(m+\frac{1}{2}+\frac{1}{4}D^2)}{[m+\frac{1}{2}+D^2(\frac{3}{2}m^2+\frac{3}{2}m+\frac{7}{4})+\frac{3}{2}D^4(m+\frac{1}{2})+\frac{1}{16}D^6]} + \mathrm{O}(\Delta^2) \tag{74}$$

or

$$\alpha\Omega = -2p\Delta/D^3 \qquad \text{for } D^2 \gg 1 \tag{74a}$$

$$\alpha\Omega = -\tfrac{1}{2}p\Delta D \qquad \text{for } D^2 \ll 1. \tag{74b}$$

Inserting this back in (73) leads to

$$\tilde{M}_m^{(\mathrm{nd})} = (\tfrac{1}{2}p\Delta)^2\Bigg(1-\exp(-D^2(m+\tfrac{1}{2})) - D^2\frac{(m+\frac{1}{2}+\frac{1}{4}D^2)^2}{[m+\frac{1}{2}+D^2(\frac{3}{2}m^2+\frac{3}{2}m+\frac{7}{4})+\frac{3}{2}D^4(m+\frac{1}{2})+\frac{1}{16}D^6]}\Bigg)+\mathrm{O}(\Delta^3) \tag{75}$$

or

$$\tilde{M}_m^{(\mathrm{nd})} = (\tfrac{1}{2}p\Delta)^2 20(m+\tfrac{1}{2})/D^2 \qquad \text{for } D^2 \gg 1 \tag{75a}$$

$$\tilde{M}_m^{(\mathrm{nd})} = (\tfrac{1}{2}p\Delta)^2\,\tfrac{9}{8}D^4(m^2+m+1) \qquad \text{for } D^2 \ll 1. \tag{75b}$$

Comparing the last two formulae with (72*a*, *b*) we recognise again the drastic diminution of the non-diagonality. Having a closer look at the transformation parameter α we observe that the 'non-diagonality' variational principle (68) yields a different expression for $\alpha\Omega$ (namely (72)) than the minimisation of the ground-state energy (namely (57*a*)). However, in the limiting cases they respectively become coincident.

8. Other reflective transformations

Up to this point we have concentrated on the specific form (41) for the exponent of the reflective transformation. Other forms have not been discussed in any detail up to now. We briefly mention some suggestive other forms.

(a) The momentum analogue of (41) is given by

$$S = \sum_k \alpha_k P_k G,$$
$$U = \cos\Big(\sum_k \alpha_k P_k\Big) + \sin\Big(\sum_k \alpha_k P_k\Big)\cdot G \tag{76}$$

(α_k real), and yields

$$T: P_k^2 = P_k^2 \tag{77a}$$

$$T: Q_k^2 = Q_k^2 + 2\mathrm{i}\alpha_k Q_k G + \alpha_k^2 \tag{77b}$$

$$T: P_k = \Big[\cos\Big(2\sum_k \alpha_k P_k\Big)\cdot -\sin\Big(2\sum_k \alpha_k P_k\Big)\cdot G\Big]P_k \tag{77c}$$

$$T: G = \cos\Big(2\sum_k \alpha_k P_k\Big)\cdot G - \sin\Big(2\sum_k \alpha_k P_k\Big). \tag{77d}$$

Yet one may have some doubts whether this transformation is more suitable than the form (41), since the reflected part of the wavefunction turns purely imaginary and thus

cannot compensate the effect of W,

$$U\Phi^{(o)}_{\{m\}}\left(Q_k+\frac{D_k}{2}\right)=\cosh\left(\sum_k \alpha_k\frac{\partial}{\partial Q_k}\right)\Phi^{(o)}_{\{m\}}(Q_k+D_k/2)$$
$$-\mathrm{i}(-1)^{\Sigma_{k'}m_{k'}}\cdot\sinh\left(\sum_k \alpha_k\frac{\partial}{\partial Q_k}\right)\Phi^{(o)}_{\{m\}}(Q_k-D_k/2). \tag{78}$$

(b) The lowest power 'even' exponential form

$$S=\mathrm{i}\alpha G, \qquad U=\cos\alpha+\mathrm{i}(\sin\alpha)G, \qquad \alpha \text{ real} \tag{79}$$

has the effect

$$T: P_k^2=P_k^2 \tag{80a}$$
$$T: Q_k^2=Q_k^2 \tag{80b}$$
$$T: Q_k=(\cos 2\alpha G-\mathrm{i}\sin 2\alpha)Q \tag{80c}$$
$$T: G=G. \tag{80d}$$

Again, in $U\Phi^{(o)}$ the reflected part is purely imaginary and thus cannot compensate the effect of W.

(c) The second power ('even') exponential forms involve the combinations, $\mathrm{i}P_kP_{k'}G$, $\mathrm{i}Q_kQ_{k'}G$, $\mathrm{i}P_kQ_{k'}G$, from which only the last produces non-imaginary reflections,

$$S=\mathrm{i}\sum_{\substack{kk'\\(k\neq k')}}\alpha_{kk'}Q_kP_{k'}G, \qquad \alpha_{kk'} \text{ real}$$
$$U=\cos\left(\sum_{\substack{kk'\\(k\neq k')}}\alpha_{kk'}Q_kP_{k'}\right)+\mathrm{i}\sin\left(\sum_{\substack{kk'\\(k\neq k')}}\alpha_{kk'}Q_kP_{k'}\right)G \tag{81}$$

and thus

$$U\Phi^{(o)}_{\{m\}}(Q_k+D_k/2)=\cosh\left(\sum_{\substack{k'k''\\(k'\neq k'')}}\alpha_{k'k''}Q_{k'}\left(\frac{\partial}{\partial Q_{k''}}\right)\right)\Phi^{(o)}_{\{m\}}(Q_k+D_k/2)$$
$$-(-1)^{\Sigma m_k}\sinh\left(\sum_{\substack{k'k''\\(k'\neq k'')}}\alpha_{k'k''}Q_{k'}\left(\frac{\partial}{\partial Q_{k''}}\right)\right)\Phi^{(o)}_{\{m\}}(Q_k-D_k/2). \tag{82}$$

This transformation stands a good chance of playing a major role, since it has some capacity to remove the coupling between energetically close lying states, if, for instance, one chooses $\alpha_{kk'}\sim(\Omega_k-\Omega_{k'})^{-1}$. Thus it is a kind of counterpart to our transformation (41), which removes the non-diagonality between energetically distant states.

(d) From the third power forms the peculiar one

$$S=\sum_{\substack{k,k'\\(k\neq k')}}\alpha_{kk'}Q_k(P_{k'}^2+Q_{k'}^2)G \tag{83}$$

seems to offer a chance, if combined with the form (41), to improve the diagonalisation capacity of the latter.

9. Summary

Stimulated by the desire to avoid conventional techniques in the theory of quantum diffusion ('golden rule') we have introduced a class of unitary transformations with a reflective ingredient. We have discussed the most simple of these transformations in some detail, and we have shown that in the many-mode case ($N \gg 1$) *hierarchical relations* can be used to evaluate multimode matrix elements of fully transformed operators in a *closed form*, which is more than what can be done in the one-mode case.

Thereupon we have considered the ground state of the diagonal part of the transformed Hamiltonian and have minimised it with respect to the transformation parameters. In the one-mode case the perturbation theory result is known, whence our result could be compared with it. It turned out that the perturbative result was reproduced in both extremal phonon coupling cases $D \gtrless 1$. In particular it was shown that in the second-order lowering of the ground state the Debye–Waller screening was absent.

Since the ground state lowering is not a good overall criterion for the diagonalising capacity of a transformation, we have defined a *positive definite measure of non-diagonality* for each single base vector of a system. This being done, we have introduced a *new variational principle* for the optimisation of a unitary transformation, and we have applied this principle to our transformation. This allowed for the calculation of the transformation parameters. It then turned out that the 'measure of non-diagonality' was drastically reduced. Specifically, in the strong phonon coupling case ($D^2 = \Sigma_k D_k^2 \gg 1$) it was reduced from a D^0 to a D^{-2} behaviour, whereas in the weak coupling regime ($D^2 \ll 1$) the reduction was from D^2 to D^4.

Finally, we have briefly glanced at a few other special forms of the introduced class of reflective transformations.

It seems that the main virtue of the special form considered here in detail lies in its capacity to remove the domination of non-diagonal matrix elements between states which are energetically far away from each other in favour of an energetic neighbourhood coupling. However, the coupling of a state to its energetic neighbourhood is modified in this manner, and it is this modified coupling distribution which will govern the quantum diffusion. This decay process itself seems to be treatable by means of another special form of the presented class of reflective transformations, but a more detailed discussion is postponed.

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