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Ensemble averages of exponential quadratic phonon operators

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Abstract. Operator disentangling, the evaluation of matrix elements in the coordinate representation, and a matrix technique are all useful for calculating ensemble averages of exponential quadratic phonon operators. Examples are presented using all three techniques, and their respective merits are discussed.

1. Introduction

Exponential operators are of widespread occurrence in quantum physics, and a comprehensive account of their properties has been given by Wilcox (1967). The exponents can often be expressed as functions of two operators having a c-number commutator:

$$[P, Q] = cI, \tag{1}$$

where I is the identity operator. Quadratic functions of this type are common, for example in the density operator $e^{-\beta H}$ formed from a Hamiltonian H in which P and Q are boson annihilation and creation operators ($\beta = 1/kT$).

In recent work on exciton diffusion with quadratic exciton–phonon coupling (Munn and Silbey 1978), we have employed a canonical transformation with an exponent quadratic in phonon operators. Exponential operators like this have then to be averaged over the thermal phonon ensemble. Techniques for evaluating such averages of exponential linear operators are described in various places (Wilcox 1967, Messiah 1959, Grover and Silbey 1970), but for quadratic operators we were unable to find information on comparable techniques. We therefore devised our own methods using a combination of operator-disentangling (Witschel 1975) and coordinate-momentum (Feynman 1972) techniques. Subsequently our attention was drawn to the matrix technique of Balian and Brézin (1969), which is well suited to calculating the required averages. Since the techniques and results are of wider application than our transport work, we present here the evaluation of averages of selected exponential quadratic operators using all three techniques.

2. Techniques

2.1 Operator disentangling

The operator-disentangling technique is essentially a normal-ordering procedure. The exponent we shall mostly use is $\gamma(a^{\dagger 2}-a^2)$ (Munn and Silbey 1978), where $a^\dagger$ and a are operators with $[a, a^\dagger]=I$. Now a^2, $a^{\dagger 2}$ and their commutator form a closed set under commutation (a Lie algebra):

$$[a^2, a^{\dagger 2}]=2(a^\dagger a+aa^\dagger)=4(a^\dagger a+\tfrac{1}{2}), \tag{2}$$

$$[a^2, a^\dagger a]=2a^2, \tag{3}$$

$$[a^{\dagger 2}, a^\dagger a]=-2a^{\dagger 2}. \tag{4}$$

Then the operators $A=a^{\dagger 2}$, $B=-a^2$ and $C=4(a^\dagger a+\frac{1}{2})$ satisfy

$$[A, B]=C; \qquad [A, C]=-bA; \qquad [B, C]=bB \tag{5}$$

with $b=8$. For operators of this sort, Witschel (1975) gives the result

$$\exp[\gamma(A+B)]=\exp(FB)\exp(GC)\exp(FA) \tag{6}$$

where

$$F=(2/b)^{1/2}\tanh[\gamma(b/2)^{1/2}], \tag{7}$$

$$G=(2/b)\ln\cosh[\gamma(b/2)^{1/2}]. \tag{8}$$

Making the appropriate identifications, we find

$$\begin{aligned}\theta &\equiv \exp[\gamma(a^{\dagger 2}-a^2)]\\ &=\exp(-\tfrac{1}{2}a^2\tanh 2\gamma)\exp[(a^\dagger a+\tfrac{1}{2})\ln\cosh 2\gamma]\exp(\tfrac{1}{2}a^{\dagger 2}\tanh 2\gamma).\end{aligned} \tag{9}$$

Alternatively, we may set $A=-a^2$, $B=a^{\dagger 2}$ and $C=-4(a^\dagger a+\frac{1}{2})$ and still satisfy equation (5), obtaining

$$\begin{aligned}\theta &\equiv \exp[\gamma(a^{\dagger 2}-a^2)]\\ &=\exp(\tfrac{1}{2}a^{\dagger 2}\tanh 2\gamma)\exp[-(a^\dagger a+\tfrac{1}{2})\ln\cosh 2\gamma]\exp(-\tfrac{1}{2}a^2\tanh 2\gamma).\end{aligned} \tag{10}$$

Other, less symmetrical, forms of equations (9) and (10) can be obtained in which the middle exponential is moved to the first or last place, but these forms offer no further advantages in the thermal averaging. The averaging proceeds by inserting complete sets of phonon states in the occupation-number representation between successive exponential operators.

2.2 Coordinate representation

The coordinate-momentum technique depends on the expression (Feynman 1972) for the matrix elements of the density operator ρ for a linear harmonic oscillator in the coordinate representation:

$$\langle q|\rho|q'\rangle=\left(\frac{\omega}{2\pi\hbar\sinh 2x}\right)^{1/2}\exp\left(\frac{-\omega}{2\hbar\sinh 2x}[(q^2+q'^2)\cosh 2x-2qq']\right), \tag{11}$$

where $x=\frac{1}{2}\beta\hbar\omega$. Here q is the mass-weighted coordinate, so that the Hamiltonian is

$$H=\tfrac{1}{2}(\omega^2q^2+p^2), \tag{12}$$

where p is the momentum conjugate to q, $-i\hbar\mathrm{d}/\mathrm{d}q$. An alternative form of equation (11) is

$$\langle q|\rho|q'\rangle = \left(\frac{\omega}{2\pi\hbar\sinh 2x}\right)^{1/2}\exp\left(\frac{-\omega}{4\hbar}[(q+q')^2\tanh x+(q-q')^2\coth x]\right). \tag{13}$$

In this technique, averaging again proceeds by inserting complete sets between successive operators. The exponential quadratic operator still depends on $\mathrm{d}/\mathrm{d}q$ but by suitable manipulations its matrix elements can be derived. Then the thermal average is obtained as a multiple Gaussian integral which can be evaluated directly.

2.3 Matrix representation

In the matrix technique, an exponential quadratic operator $\mathcal{T}$ is written as

$$\mathcal{T} = \exp \tfrac{1}{2}\boldsymbol{\alpha}\mathbf{S}\boldsymbol{\alpha}, \tag{14}$$

where $\boldsymbol{\alpha} = (a, a^{\dagger})$ and the matrix $\mathbf{S}$ is symmetric. This operator is represented by the matrix

$$[\mathcal{T}] = \exp \boldsymbol{\tau}\mathbf{S}, \tag{15}$$

where

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{16}$$

Thus if $\mathcal{T}_3 = \mathcal{T}_1\mathcal{T}_2$, $\mathcal{T}_3$ is represented by the matrix $[\mathcal{T}_3] = [\mathcal{T}_1][\mathcal{T}_2]$ (Balian and Brézin 1969). The representative matrix satisfies

$$[\mathcal{T}]\boldsymbol{\tau}[\tilde{\mathcal{T}}] = \boldsymbol{\tau}. \tag{17}$$

In particular, the density operator for the linear harmonic oscillator,

$$\rho = \exp[-x(aa^{\dagger}+a^{\dagger}a)], \tag{18}$$

is represented by

$$[\rho] = \exp\left[\boldsymbol{\tau}\begin{pmatrix} 0 & -2x \\ -2x & 0 \end{pmatrix}\right] = \begin{pmatrix} e^{-2x} & 0 \\ 0 & e^{2x} \end{pmatrix}. \tag{19}$$

For the thermal averages we require the trace of the operator, given by

$$\mathrm{Tr}\,\mathcal{T} = \sum_{v}\langle v|\mathcal{T}|v\rangle, \tag{20}$$

where the state $|v\rangle$ is an eigenstate belonging to the eigenvalue v of the number operator $a^{\dagger}a$. The trace is invariant under a canonical transformation and so can be evaluated by a transformation which brings $\mathcal{T}$ into the form (18), for which

$$\mathrm{Tr}\,\mathcal{T} = e^{-x}/(1-e^{-2x}). \tag{21}$$

The same transformation brings $[\mathcal{T}]$ into the diagonal form (19). It is then necessary to express $\mathrm{Tr}\,\mathcal{T}$ in terms of some invariant of $[\mathcal{T}]$. It can be verified that this is achieved by the relation

$$\mathrm{Tr}\,\mathcal{T} = [-\det([\mathcal{T}]-\mathbf{I})]^{-1/2}. \tag{22}$$

These results can be extended to sets of N different pairs of operators a_i and $a_i^\dagger$ by writing $\boldsymbol{\alpha} = (a_1, \ldots a_N, a_1^\dagger, \ldots a_N^\dagger)$ and taking the elements of $\boldsymbol{\tau}$ in equation (16) to be the null and unit matrices of order N. The result (17) shows that the diagonalised matrix $[\mathscr{T}]$ then takes the form $\mathrm{diag}(T_1, \ldots T_N, T_1^{-1}, \ldots T_N^{-1})$, and leads to the general result

$$\mathrm{Tr}\,\mathscr{T} = [(-1)^N \det([\mathscr{T}] - \mathbf{1})]^{-1/2}. \tag{23}$$

3. Results

3.1. Calculation of $\langle\theta\rangle$

3.1.1. Operator disentangling. We first calculate the average $\langle\theta\rangle$, where θ is the operator in equations (9) and (10), from

$$\langle\theta\rangle = (1-y)\sum_{v=0}^{\infty} y^v \langle v|\theta|v\rangle, \tag{24}$$

where $y = \mathrm{e}^{-2x}$. The required matrix elements are obtained from

$$\sum_{r,s=0}^{\infty} \frac{(-1)^r f^{r+s}}{r!s!} \langle v|a^{2r}\, \mathrm{e}^{g(a^+a+\frac{1}{2})} a^{+2s}|v\rangle, \tag{25}$$

where $f = \frac{1}{2}\tanh 2\gamma$ and $g = \ln\cosh 2\gamma$; equation (9) is used rather than equation (10) because restrictions on the summation variable are not then necessary (any number of phonons can be created, but not annihilated). Using the results

$$a^{+2s}|v\rangle = [(v+1)_{2s}]^{1/2}|v+2s\rangle \tag{26}$$

$$\langle v|a^{2r} = \langle v+2r|[(v+1)_{2r}]^{1/2}, \tag{27}$$

where (Sneddon 1966)

$$(\alpha)_r = \alpha(\alpha+1)\ldots(\alpha+r-1) \tag{28}$$

$$= \Gamma(\alpha+r)/\Gamma(\alpha) \tag{29}$$

with $\Gamma(z)$ the gamma function, we find

$$\langle v|\theta|v\rangle = (\cosh 2\gamma)^{v+\frac{1}{2}} \sum_{r=0}^{\infty} \frac{(v+1)_{2r}}{(r!)^2}(-\tfrac{1}{4}\sinh^2 2\gamma)^r. \tag{30}$$

Using the duplication formula for the gamma function (Sneddon 1966) we obtain

$$(v+1)_{2r} = 4^r(\tfrac{1}{2}v+\tfrac{1}{2})_r(\tfrac{1}{2}v+1)_r, \tag{31}$$

whence equation (30) becomes

$$\langle v|\theta|v\rangle = (\cosh 2\gamma)^{v+\frac{1}{2}}\, {}_2F_1(\tfrac{1}{2}v+\tfrac{1}{2}, \tfrac{1}{2}v+1; 1; -\sinh^2 2\gamma). \tag{32}$$

The hypergeometric function in equation (32) can be written as a Legendre function (Abramowitz and Stegun 1967, formula 15.4.11), leading to

$$\langle v|\theta|v\rangle = (\cosh 2\gamma)^{-1/2} P_v(1/\cosh 2\gamma). \tag{33}$$

Equation (24) then gives the generating function for the Legendre functions, with the final result

$$\langle\theta\rangle = \{1+2\sinh^2\gamma[n^2+(n+1)^2]\}^{-1/2}, \tag{34}$$

where

$$n = y/(1-y) \tag{35}$$

is the average phonon occupation number. The same result is obtained without going through any special functions if the order of the summations is reversed. This derivation uses the alternative to equation (31)

$$(v+1)_{2r} = (2r+1)_v(2r)!/v! \tag{36}$$

and the result

$$\sum_v (\alpha)_v z^v/v! = (1-z)^{-\alpha}, \tag{37}$$

followed by use of equation (31) for $v=0$, where $(1)_r = r!$.

3.1.2. Coordinate representation. In the coordinate-momentum representation,

$$a^{\dagger 2} - a^2 = \mathrm{i}(pq+qp)\hbar \tag{38}$$

$$= 1 + 2q\,\mathrm{d}/\mathrm{d}q, \tag{39}$$

so that

$$\theta = \mathrm{e}^{\gamma}\exp(2\gamma q\ \mathrm{d}/\mathrm{d}q). \tag{40}$$

We calculate $\langle\theta\rangle$ from

$$\langle\theta\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}q_1\mathrm{d}q_2\langle q_1|\rho|q_2\rangle\langle q_2|\theta|q_1\rangle/\mathrm{Tr}\,\rho, \tag{41}$$

where from equation (23) we obtain

$$\mathrm{Tr}\,\rho = \int_{-\infty}^{\infty}\mathrm{d}q\langle q|\rho|q\rangle = \frac{1}{2\sinh x}. \tag{42}$$

The matrix elements of θ follow by using the result (Wilcox 1967)

$$\exp(2\gamma\mathrm{d}/\mathrm{d}q)\phi(q) = \phi(\mathrm{e}^{2\gamma}q) \tag{43}$$

with $|q_1\rangle = \delta(q-q_1)$, whence

$$\langle q_2|\theta|q_1\rangle = \mathrm{e}^{\gamma}\delta(\mathrm{e}^{2\gamma}q_2 - q_1). \tag{44}$$

We then have

$$\langle\theta\rangle = 2\,\mathrm{e}^{\gamma}\sinh x\int_{-\infty}^{\infty}\mathrm{d}q\langle\mathrm{e}^{2\gamma}q|\rho|q\rangle, \tag{45}$$

which with equation (11) can be evaluated to give

$$\langle\theta\rangle = 2q\mathrm{e}^{\gamma}\sinh x[(\mathrm{e}^{4\gamma}+1)\cosh 2x - 2]^{-1/2}. \tag{46}$$

Using the results

$$2\sinh x = [n(n+1)]^{-1/2}, \tag{47}$$

$$2\cosh 2x = [n^2+(n+1)^2]/n(n+1), \tag{48}$$

we reduce equation (46) to the required expression (34).

3.1.3. Matrix representation. From equation (15), θ can be represented by the matrix

$$[\theta] = \exp\left[\tau\begin{pmatrix} -2\gamma & 0 \\ 0 & 2\gamma \end{pmatrix}\right] = \begin{pmatrix} \cosh 2\gamma & \sinh 2\gamma \\ \sinh 2\gamma & \cosh 2\gamma \end{pmatrix}. \tag{49}$$

Thus from equation (22)

$$\langle\theta\rangle = \mathrm{Tr}(\rho\theta)/\mathrm{Tr}\rho \tag{50}$$

$$= \left(\frac{\det([\rho][\theta]-\mathbf{I})}{\det([\rho]-\mathbf{I})}\right)^{-1/2}. \tag{51}$$

Using $[\rho]$ from equation (19) we find

$$\det([\rho][\theta]-\mathbf{I}) = 2(1-\cosh 2\gamma\cosh 2x) \tag{52}$$

$$\det([\rho]-\mathbf{I}) = 2(1-\cosh 2x). \tag{53}$$

Substitution in equation (51) and use of equation (48) yield the result (34).

3.2. Calculation of $\langle\theta^\dagger(t)\theta\rangle$

The second average we calculate is $\langle\theta^\dagger(t)\theta\rangle$, where

$$\theta^\dagger(t) = \exp[-\gamma(a^{\dagger 2}\,e^{2i\omega t} - a^2\,e^{-2i\omega t})]. \tag{54}$$

3.2.1. Operator disentangling. Using equation (9) to disentangle $\theta^\dagger(t)$ and equation (10) to disentangle θ, we can write

$$\theta^\dagger(t)\theta = \exp(fa^2\,e^{-2i\omega t})\exp(ga^\dagger a)\exp[-fa^{\dagger 2}(e^{2i\omega t}-1)]\exp(-ga^\dagger a)\exp(-fa^2). \tag{55}$$

Using the alternatives (9) and (10) allows us to combine the terms in $a^{\dagger 2}$. From the cyclic property of the trace and the result (Wilcox 1967)

$$e^{-\lambda a^\dagger a}\phi(a) = \phi(e^\lambda a), \tag{56}$$

the required average can be written as

$$\langle\theta^\dagger(t)\theta\rangle = (1-y)\sum_v (\cosh 2\gamma)^{-v}\langle v|\exp(Xa^2)\exp(Ya^\dagger a)\exp(Za^{\dagger 2})|v\rangle, \tag{57}$$

where

$$X = f(y^{-2}\,e^{-2i\omega t}-1), \tag{58}$$

$$Y = g - \beta\hbar\omega, \tag{59}$$

$$Z = -f(e^{2i\omega t}-1). \tag{60}$$

The matrix elements are now of the same form as in equation (25) and can be evaluated in the same way. After some re-arrangement, the final result can be written as

$$\langle\theta^\dagger(t)\theta\rangle=\{1+\sinh^2 2\gamma[n^2(1-e^{2i\omega t})+(n+1)^2(1-e^{-2i\omega t})]\}^{-1/2}. \tag{61}$$

3.2.2. Coordinate representation. For this technique we write

$$\langle\theta^\dagger(t)\theta\rangle=\mathrm{Tr}[e^{-(\beta-it/\hbar)H}\theta^\dagger\, e^{-itH/\hbar}\theta]/\mathrm{Tr}\rho \tag{62}$$

and use equations (42) and (44) to find

$$\langle\theta^\dagger(t)\theta\rangle=2\sinh x\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}q_1\,\mathrm{d}q_2\langle q_1\,e^{-2\gamma}|e^{-(\beta-it/\hbar)H}|q_2\rangle\langle q_2\,e^{2\gamma}|e^{-itH/\hbar}|q_1\rangle. \tag{63}$$

The matrix elements are given by equation (11), with suitable re-interpretation of x, leading to

$$\langle\theta^\dagger(t)\theta\rangle=2\sinh x/\pi(\sinh 2x'\sinh 2i\omega t)^{1/2}$$

$$\times\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}q_1\,\mathrm{d}q_2\exp[-(a_{11}q_1^2+2a_{12}q_1q_2+a_{22}q_2^2)], \tag{64}$$

where $x'=x-\frac{1}{2}i\omega t$ and

$$a_{11}=e^{-4\gamma}\coth 2x'+\coth 2i\omega t \tag{65}$$

$$a_{22}=\coth 2x'+e^{4\gamma}\coth 2i\omega t \tag{66}$$

$$a_{12}=-(e^{-2\gamma}\,\mathrm{cosech}\,2x'+e^{2\gamma}\,\mathrm{cosech}\,2i\omega t). \tag{67}$$

Now multiple Gaussian integrals are directly evaluated as (Friedman 1956)

$$\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\mathrm{d}q_1\ldots\mathrm{d}q_n\exp\Big(-\sum_{i,j=1}^{n}A_{ij}q_iq_j\Big)=\Big(\frac{\pi^n}{\det\mathbf{A}}\Big)^{1/2}. \tag{68}$$

After lengthy algebra, equations (64)–(68) yield the previous result (61) for $\langle\theta^\dagger(t)\theta\rangle$.

3.2.3. Matrix representation. The operator $\theta^\dagger(t)$ is represented by the matrix

$$[\theta^\dagger(t)]=\exp\left[\tau\begin{pmatrix}2\gamma\,e^{-2i\omega t} & 0\\ 0 & -2\gamma\,e^{2i\omega t}\end{pmatrix}\right] \tag{69}$$

$$=\begin{pmatrix}\cosh 2\gamma & -e^{2i\omega t}\sinh 2\gamma\\ -e^{-2i\omega t}\sinh 2\gamma & \cosh 2\gamma\end{pmatrix}. \tag{70}$$

With equation (49) for $[\theta]$ this yields the matrix representation

$$[\theta^\dagger(t)\theta]=\begin{pmatrix}1-A_+\sinh^2 2\gamma & A_+\sinh 2\gamma\cosh 2\gamma\\ A_-\sinh 2\gamma\cosh 2\gamma & 1-A_-\sinh^2 2\gamma\end{pmatrix}, \tag{71}$$

where

$$A_\pm=1-e^{\pm 2i\omega t}. \tag{72}$$

This leads to the result

$$\det([\rho\theta^\dagger(t)\theta]-\mathbf{I})=2-2\cosh 2x-\sinh^2 2\gamma(e^{2x}A_-+e^{-2x}A_+) \tag{73}$$

which with equation (53) can be manipulated to give $\langle\theta^\dagger(t)\theta\rangle$ in the form (61).

3.3. Calculations for a dimer

In our work on exciton transport in a molecular crystal lattice (Munn and Silbey 1978), the calculation of the foregoing averages serves mainly as a guide to more complicated calculations. In particular, it is necessary to consider operators defined for different sites in the crystal, averaged over a band of phonon states in order to obtain ergodic behaviour and hence diffusive transport at long times. These calculations can be illustrated by the evaluation of averages like those above but for a dimer consisting of a pair of identical molecules labelled 1 and 2.

If there is no vibrational coupling between the sites (Einstein limit), the average breaks up into a product of averages for individual sites having the forms already deduced. When there is coupling, the average is conveniently taken over the dimer oscillator eigenstates with frequencies ω_+ and ω_-, corresponding to new operators

$$a_\pm = 2^{-1/2}(a_1 \pm a_2). \tag{74}$$

Then we find

$$\theta_1^\dagger \theta_2 = \exp 2\gamma(a_+^\dagger a_-^\dagger - a_+ a_-). \tag{75}$$

3.3.1. Calculation of $\langle \theta_1^\dagger \theta_2 \rangle$. The average $\langle \theta_1^\dagger \theta_2 \rangle$ corresponds to the band-narrowing factor e^{-S} in conventional small-polaron theory (Holstein 1959). It is evaluated by *operator disentangling* using the fact that the operators $A = a_+^\dagger a_-^\dagger$, $B = -a_+ a_-$ and $C = a_+^\dagger a_+ + a_-^\dagger a_- + 1$ satisfy equation (5) with $b = 2$. The evaluation then proceeds like that of $\langle \theta \rangle$. The analogue of equation (24) involves a sum over states $|v_+, v_-\rangle$, where it again proves more convenient to evaluate this sum before the sum over r. The result is

$$\langle \theta_1^\dagger \theta_2 \rangle = \{1 + 2\sinh^2 \gamma[n_+ n_- + (n_+ + 1)(n_- + 1)]\}^{-1}, \tag{76}$$

which reduces to $\langle \theta \rangle^2$ as n_+ and n_- each tend to n.

In this case, the *coordinate-representation technique* is at a disadvantage, because it gives a square root of a complicated expression which, as equation (76) shows, has to reduce after lengthy algebra to a perfect square.

The *matrix technique* for the dimer involves 4×4 matrices. The density operator is represented by

$$[\rho] = \mathrm{diag}(y_+, y_-, y_+^{-1}, y_-^{-1}), \tag{77}$$

where $y_i = \exp(-2x_i)$, and $\theta_1^\dagger \theta_2$ is represented by

$$[\theta_1^\dagger \theta_2] = \begin{pmatrix} \cosh 2\gamma & 0 & 0 & \sinh 2\gamma \\ 0 & \cosh 2\gamma & \sinh 2\gamma & 0 \\ 0 & \sinh 2\gamma & \cosh 2\gamma & 0 \\ \sinh 2\gamma & 0 & 0 & \cosh 2\gamma \end{pmatrix}. \tag{78}$$

The determinant of $([\rho\theta_1^\dagger\theta_2] - \mathbf{I})$ is also 4×4, but interchanging rows and columns reduces it to a product of two 2×2 determinants which is readily expressed as

$$\det([\rho\theta_1^\dagger\theta_2] - \mathbf{I}) = [(1 - y_+)(1 - y_-) + 2\sinh^2 \gamma(1 + y_+ y_-)]^2 / y_+ y_-, \tag{79}$$

while from equation (77)

$$\det([\rho] - \mathbf{I}) = [(1 - y_+)(1 - y_-)]^2 / y_+ y_-. \tag{80}$$

The perfect squares arise naturally here, and lead at once to the result (76).

3.3.3. Calculation of $\langle\theta_1^\dagger(t)\theta_2(t)\theta_2^\dagger\theta_1\rangle$. The *operator-disentangling technique* evaluates this average by combining the methods used for $\langle\theta^\dagger(t)\theta\rangle$ and $\langle\theta_1^\dagger\theta_2\rangle$, with the result

$$\langle\theta_1^\dagger(t)\theta_2(t)\theta_2^\dagger\theta_1\rangle = \{1+\sinh^2 2\gamma[n_+n_-(1-\mathrm{e}^{\mathrm{i}(\omega_++\omega_-)t})+(n_++1)(n_-+1)(1-\mathrm{e}^{-\mathrm{i}(\omega_++\omega_-)t})]\}^{-1}. \tag{81}$$

This reduces correctly to $\langle\theta^\dagger(t)\theta\rangle^2$ in the Einstein limit. It also reduces to equation (76) with γ replaced by 2γ when $\mathrm{e}^{\mathrm{i}(\omega_++\omega_-)t}=-1$, which is the correct result for $\langle(\theta_1^\dagger\theta_2)^2\rangle$ in view of the exponential form of θ.

The *coordinate-representation technique* again suffers from the algebraic disadvantage noted above.

The *matrix technique* is applied straightforwardly. The matrix representing $\theta_2^\dagger\theta_1$ is given by equation (78) with the sign of γ changed, and that representing $\theta_1^\dagger(t)\theta_2(t)$ is given by equation (78) with the upper right 2×2 submatrix multiplied by $\mathrm{e}^{\mathrm{i}(\omega_++\omega_-)t}$ and the lower left submatrix divided by the same factor. The required determinant again factorises into 2×2 determinants, with the result

$$\det([\rho\theta_1^\dagger(t)\theta_2(t)\theta_2^\dagger\theta_1]-\mathbf{I}) = [(1-y_+)(1-y_-)+\sinh^2 2\gamma(B_-+B_+y_+y_-)]^2/y_+y_-, \tag{82}$$

where

$$B_\pm = 1-\mathrm{e}^{\pm\mathrm{i}(\omega_++\omega_-)t}. \tag{83}$$

These expressions with equation (80) readily yield the result (81).

3.3.3. Calculation of $\langle\theta_1\rangle$. The average $\langle\theta_1\rangle$ is not readily calculated by the *operator-disentangling* and *coordinate-representation techniques* because the exponent in θ_1 is a complicated function of the operators $a_\pm$ and $a_\pm^\dagger$. This presents no obstacle in the *matrix technique*. The matrix $\mathbf{S}$ is given by

$$\mathbf{S}=\begin{pmatrix}-\gamma\mathbf{U} & \mathbf{0}\\ \mathbf{0} & \gamma\mathbf{U}\end{pmatrix}, \qquad \mathbf{U}=\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}, \tag{84}$$

with the result that θ_1 is represented by the matrix

$$[\theta_1]=\begin{pmatrix}\mathbf{C} & \mathbf{S}\\ \mathbf{S} & \mathbf{C}\end{pmatrix}; \tag{85}$$

$$\mathbf{C}=\mathbf{I}+\tfrac{1}{2}(\cosh 2\gamma-1)\mathbf{U}; \qquad \mathbf{S}=\tfrac{1}{2}\sinh 2\gamma\mathbf{U}. \tag{86}$$

After some algebraic manipulation, it is found that

$$\mathrm{Tr}([\rho\theta_1]-\mathbf{I})=\{(1-y_+)^2(1-y_-)^2+\sinh^2\gamma[(1-y_+)^2(1-y_-)^2+(1-y_+y_-)^2]\}/y_+y_-, \tag{87}$$

which with equation (80) gives

$$\langle\theta_1\rangle=\{1+\sinh^2\gamma[1+(n_++n_-+1)^2]\}^{-1/2}. \tag{88}$$

This correctly reduces to $\langle\theta\rangle$ in the Einstein limit.

4. Discussion

We have shown how ensemble averages of certain exponential quadratic phonon operators can be calculated in different ways. More general quadratic operator exponents can be treated by extensions of the present methods, which depend on the fact that the density operator ρ is itself an exponential quadratic operator.

The alternative techniques used here have different advantages. Operator disentangling is useful for separating functions of $a^\dagger$ from those of a (or of q from $\mathrm{d}/\mathrm{d}q$), making it easier to write down matrix elements. However, evaluating these matrix elements and carrying out sums over intermediate states to obtain compact expressions may not be easy. From the coordinate matrix elements of the density matrix and manipulations of differential operators, one obtains an integral which gives the required ensemble average directly in terms of a determinant. The disadvantage of this technique is that algebraic evaluation of the determinant may be lengthy.

The matrix technique may be regarded as more fundamental than the other two. For instance, it can be used to derive the operator disentangling formula (Balian and Brézin 1969). Like the coordinate-representation technique, it gives the trace of an operator as the inverse square root of a determinant, but one often less complicated to evaluate algebraically. The strength of the matrix technique lies in the replacement of manipulation of operators by simple multiplication (note that $\exp \boldsymbol{\tau}\mathbf{S}$ is obtained trivially by diagonalising $\boldsymbol{\tau}\mathbf{S}$). One consequence is that the dimer calculations of §3.3 can be readily carried through by the matrix technique without first transforming to the operators $a_\pm$ from a_1 and a_2. The matrix $[\rho]$ then consists of two 2×2 blocks on the diagonal, but for example $[\theta_1]$ is reduced from the sixteen non-zero elements of equation (85) to only six.

In simple cases, more than one of the techniques can be used to confirm the correctness of results. In more complicated cases, obtaining an answer may depend on a judicious application of one technique, alone or in combination with another . For most purposes, the matrix technique is likely to prove the most direct.

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References

Abramowitz M and Stegun I A 1967 *Handbook of Mathematical Functions* (New York: Dover)
Balian R and Brézin E 1969 *Nuovo Cim.* **B 64** 37–55
Feynman R P 1972 *Statistical Mechanics* (Reading, Mass.: Benjamin)
Friedman B 1956 *Principles and Techniques of Applied Mathematics* (New York: Wiley) p107
Grover M K and Silbey R 1970 *J. Chem. Phys.* **52** 2099–108
Holstein T 1959 *Ann. Phys., NY* **8** 343–89
Messiah A 1959 *Quantum Mechanics* vol. 1 (Amsterdam: North-Holland)
Munn R W and Silbey R 1978 *J. Chem. Phys.* **68** 15 March issue
Sneddon I N 1966 *Special Functions of Mathematical Physics and Chemistry* (Edinburgh: Oliver and Boyd)
Wilcox R M 1967 *J. Math. Phys.* **8** 962–82
Witschel W 1975 *J Phys. A: Math. Gen.* **8** 143–55