Matrix Elements of the Lorentzian Term

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Recursion formulae for the matrix elements of the Lorentzian term $1/(C^2+q^2)$ as well as $1/(C^2+q^2)^2$, on the basis of harmonic oscillator eigenfunctions, are obtained. A practical application where these formulae would be useful is discussed.

1. Introduction

Recursion relations to obtain the matrix elements of the Gaussian operator $e^{-\beta q^2}$ were given by several authors [1–4]. But for the Lorentzian term $1/(C^2+q^2)$, Johns [5] has made the empirical observation that its matrix elements are obtained by simply inverting the matrix of the operator (C^2+q^2). Recursion relations for a number of functions [not including $1/(C^2+q^2)$] in terms of the eigenfunctions ψ_{vl} of a two-dimensional harmonic oscillator were given by Ullán and Ferester [6]. In this note, we shall present a simple technique to generate the matrix elements of the Lorentzian term in the representation of the harmonic oscillator and discuss one of its applications. These matrix elements are useful in double minimum problems where the potential function may be conveniently represented by a perturbed harmonic oscillator with a Lorentzian barrier

$$V(q) = \tfrac{1}{2} K q^2 + K_B/(C^2+q^2)\,. \tag{1}$$

K, K_B and C^2 are potential constants and q is a dimensionless coordinate.

The $(m,n)^{\text{th}}$ matrix element of the operator $1/(C^2+q^2)$ is defined by

$$L_{m,n} \equiv \left\langle m \left| \frac{1}{C^2+q^2} \right| n \right\rangle = \int_{-\infty}^{\infty} \frac{\psi_m^*(q)\,\psi_n(q)\,\mathrm{d}q}{C^2+q^2} \tag{2}$$

where

$$\psi_n(q) = \frac{1}{(2^n\, n!\, \pi^{1/2})^{1/2}} H_n(q)\, e^{-q^2/2}\,. \tag{3}$$

$H_n(q)$ is the n^{th} Hermite polynomial [7] and q is related to the normal coordinate Q by

$$q = (\gamma^0)^{1/2} Q\,. \tag{4}$$

γ^0 is the scaling factor given by $\gamma^0 = 4\pi^2 c\,\nu^0/h$ and ν^0 is the fundamental frequency of the unperturbed harmonic oscillator. The assumption that the matrix of $1/(C^2+q^2)$ is the inverse of the matrix of (C^2+q^2) rests on the following premise [5]. Taking the matrix elements on both sides of the identity

$$(C^2+q^2)\,\frac{1}{(C^2+q^2)} = 1$$

we have

$$\sum_j \langle m \mid C^2+q^2 \mid j\rangle \left\langle j \left| \frac{1}{C^2+q^2} \right| n \right\rangle = \delta_{m,n}\,. \tag{5}$$

For a given m, j can only take the three values m, $m \pm 2$, eventhough the summation, in principle, extends over a complete set of functions. Relation (5) is strictly valid, if the complete set includes an infinite number of functions. Now assuming that any arbitrary function of a double minimum potential can be expressed as a linear combination of only $(N+1)$ harmonic oscillator functions, (which in fact is the condition for the completeness of $N+1$ functions) we have

$$\Phi = \sum_{n=0}^{N} a_n\, \psi_n(q)\,. \tag{6}$$

Thus Eq. (5) takes the approximate form

$$\sum_j \langle m \mid C^2+q^2 \mid j\rangle \left\langle j \left| \frac{1}{C^2+q^2} \right| n \right\rangle \cong \delta_{m,n}\,. \tag{7}$$

The fact that the matrix of $1/(C^2+q^2)$ is the inverse of the matrix of (C^2+q^2) is valid to the same extent that relation (7) is valid.

2. Method

To obtain the required recursion relation, we note initially that since q commutes with any function of q we have the commutation relation

$$\left[\frac{1}{C^2+q^2}\,,\ q\right] = 0\,. \tag{8}$$

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The only non-zero matrix elements of q being

$$\langle n \mid q \mid n \pm 1 \rangle = (n + \tfrac{1}{2} \pm \tfrac{1}{2})^{1/2}/2^{1/2} \qquad (9)$$

we see that the $(m, n)^{\text{th}}$ matrix element of the commutator in (8) yields

$$\sum^{+,-} [L_{m,n\pm 1} \langle n \pm 1 \mid q \mid n \rangle - \langle m \mid q \mid m \pm 1 \rangle L_{m\pm 1,n}] = 0\,. \qquad (10)$$

The summation in the above includes terms with + and − signs. This reduces to the recursion formula

$$(m+1)^{1/2} L_{m+1,n} + m^{1/2} L_{m-1,n} = (n+1)^{1/2} L_{m,n+1} + n^{1/2} L_{m,n-1} \qquad (11)$$

when relations (9) are used in (10). Replacing $(m+1)$ by m in the above, we have

$$L_{m,n} = \left(\frac{n+1}{m}\right)^{1/2} L_{m-1,n+1} + \left(\frac{n}{m}\right)^{1/2} L_{m-1,n-1} - \left(\frac{m-1}{m}\right)^{1/2} L_{m-2,n}\,. \qquad (12)$$

During evaluation of the elements $L_{m,n}$ from (12), matrix elements with negative subscripts are set to zero. Since the matrix L is symmetric, it is only necessary to obtain the elements $L_{m,n}$ for, say, $n \geqq m$. We also note from (2) that $L_{m,n} \neq 0$, only when the integrand is an even function of q, i. e. $m+n$ is even.

From the recurrence relation (12), it is now obvious that when the elements $L_{0,n}$ in the first row of L are known, the rest of the elements can be generated row by row. In obtaining the values $L_{0,n}$, we make use of the following standard integrals [9].

$$\int_0^\infty q^{2n} e^{-q^2} \, dq = \frac{1 \cdot 3 \cdot 5 \ldots (2n-1)}{2^{n+1}} \pi^{1/2}, \qquad (13)$$

$$1/(C^2 + q^2) = \int_0^\infty e^{-t(C^2+q^2)} \, dt\,, \qquad (14)$$

$$\int_0^\infty e^{-a^2 q^2} \, dq = \pi^{1/2}/2\,a\,, \qquad (15)$$

$$(2/\pi^{1/2}) \int_0^x e^{-q^2} \, dq = \operatorname{erf}(x)\,; \qquad (16)$$

$\operatorname{erf}(x)$ is an error function of x.

The first row elements $L_{0,n}$ of the matrix L are given by

$$L_{0,n} = \frac{1}{(2^n \cdot n!\,\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{H_n(q)\, e^{-q^2} \, dq}{C^2 + q^2}\,. \qquad (17)$$

$H_n(q)$ is given by the series [8]

$$H_n(q) = (2q)^n - \frac{n(n-1)}{1!}(2q)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!}(2q)^{n-4} - \ldots \qquad (18)$$

Since n is even, the above expansion has $(\tfrac{1}{2}n + 1)$ terms and it is only necessary for our purpose to know how to evaluate

$$I_n = \int_{-\infty}^{\infty} \frac{q^n e^{-q^2} \, dq}{C^2 + q^2} \quad (n \text{ even}) \qquad (19)$$

$$= -C^2 I_{n-2} + \int_{-\infty}^{\infty} q^{n-2} e^{-q^2} \, dq \qquad (20)$$

$$= -C^2 I_{n-2} + \frac{1 \cdot 3 \cdot 5 \ldots (n-3)}{2^{(n/2-1)}} \pi^{1/2}\,. \qquad (21)$$

This result follows from (13) and is valid for $n = 4, 6 \ldots$ $L_{0,n}$ is now given by

$$L_{0,n} = \frac{1}{(2^n\, n!\,\pi)^{1/2}} \left[2^n I_n - \frac{n(n-1)}{1!} 2^{n-2} I_{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!} 2^{n-4} I_{n-4} - \ldots \right]. \qquad (22)$$

To initiate the process of recursion, we now need to know I_0 and I_2. I_0 is given by

$$I_0 = \int_{-\infty}^{\infty} \frac{e^{-q^2} \, dq}{C^2 + q^2}\,. \qquad (23)$$

Replicing $1/(C^2 + q^2)$ in the above by the integral on the right-side of (14), we have *

$$I_0 = \int_0^\infty e^{-C^2 t} \, dt \int_{-\infty}^{\infty} e^{-(1+t) q^2} \, dq = \pi^{1/2} \int_0^\infty \frac{e^{-C^2 t} \, dt}{(1+t)^{1/2}}\,. \qquad (24)$$

This result follows when we make use of (15). Now setting $y = (1+t)^{1/2}$ in (24), we have

$$I_0 = 2\,\pi^{1/2} e^{C^2} \int_1^\infty e^{-C^2 y^2} \, dy$$

$$= 2\,\pi^{1/2} e^{C^2} [\int_0^\infty e^{-C^2 y^2} \, dy - \int_0^1 e^{-C^2 y^2} \, dy]$$

$$= 2\,\pi^{1/2} e^{C^2} \left[\frac{\pi^{1/2}}{2C} - \frac{1}{C} \int_0^C e^{-x^2} \, dx \right]$$

$$= (\pi e^{C^2}/C)\,[1 - \operatorname{erf}(C)] \qquad (25)$$

where use is made of (15) and (16). The error function in (25) is usually available as a built-in computer library routine similar to $\sin(x)$, e^x etc.

* I thank Dr. J. D. Talman for suggesting this important step.

Its evaluation, even otherwise, is simple. It can be obtained to the desired accuracy from

$$\operatorname{erf}(C) = \frac{2}{\pi^{1/2}} \left(C - \frac{C^3}{3} + \frac{C^5}{5.2!} - \frac{C^7}{7.3!} + \dots \right). \tag{26}$$

I_2 is given by

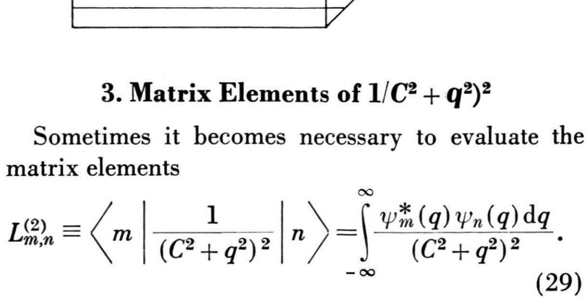
$$I_2 = \int_{-\infty}^{\infty} \frac{q^2 e^{-q^2} \mathrm{d}q}{C^2 + q^2} = \int_{-\infty}^{\infty} e^{-q^2} \mathrm{d}q - C^2 I_0 = \pi^{1/2} - C^2 I_0 . \tag{27}$$

Thus to obtain the required matrix elements in (2): (i) first evaluate I_0 and then I_2 from (25) and (27) respectively, (ii) generate all the values of I_n (n even) from (21), (iii) evaluate the $(\frac{1}{2} n + 1)$ terms in (22) to obtain $L_{0,n}$ for a given n, (iv) calculate all the elements $L_{0,n}$ in the first row of the matrix L in (2) (alternate ones are zero) and (v) using the recursion formula (12) generate all the elements $L_{m,n}$ ($n \geqq m$) of L in the second and successive rows.

The elements in the second row of L corresponding to $m = 1$ cannot be obtained directly from (12). But by noting that $L_{-1,n} = 0$, we see that they can be generated from

$$L_{1,n} = (n+1)^{1/2} L_{0,n+1} + n^{1/2} L_{0,n-1} . \tag{28}$$

It may also be noted that to evaluate the $(N+1)$ elements in the last row, we need to obtain $(2N+1)$ elements in the first row, $2N$ elements in the second row and so on (see figure below)



3. Matrix Elements of $1/C^2 + q^2)^2$

Sometimes it becomes necessary to evaluate the matrix elements

$$L^{(2)}_{m,n} \equiv \left\langle m \left| \frac{1}{(C^2 + q^2)^2} \right| n \right\rangle = \int_{-\infty}^{\infty} \frac{\psi_m^*(q) \psi_n(q) \mathrm{d}q}{(C^2 + q^2)^2} . \tag{29}$$

This can easily be accomplished by expressing $L^{(2)}_{m,n}$ in terms of I_n. Denoting J_n by

$$J_n = \int_{-\infty}^{\infty} \frac{q^n e^{-q^2} \mathrm{d}q}{(C^2 + q^2)^2} \tag{30}$$

we have

$$L^{(2)}_{0,n} = \frac{1}{(2^n n! \, \pi)^{1/2}} \Big[2^n J_n - \frac{n(n-1)}{1!} 2^{n-2} J_{n-2} + \frac{n(n-1)(n-2)(n-3)}{2!} \cdot 2^{n-4} J_{n-4} - \dots \Big]. \tag{31}$$

Expressing $-2q/(C^2 + q^2)^2$ as the derivative of $1/(C^2 + q^2)$, integrating (30) by parts and rearranging the terms, we can obtain J_n as

$$J_n = \tfrac{1}{2} (n-1) I_{n-2} - I_n . \tag{32}$$

Formulae (21), (32) and (31) together with (12) and (28) enable us to evaluate the elements $L^{(2)}_{m,n}$. In (12) and (28), $L_{m,n}$ has of course to be replaced by $L^{(2)}_{m,n}$

4. Application

Let us consider the one-dimensional Schrödinger's equation $H(q)\,\Psi = E\,\Psi$ with the Hamiltonian

$$H(q) = \tfrac{1}{2} h \nu^0 [p^2 + K q^2 + K_{\mathrm{B}}/(C^2 + q^2)] . \tag{33}$$

The potential function in H is a harmonic oscillator perturbed by a Lorentzian barrier with constants K, K_{B} and C^2. p is the momentum conjugate to the dimensionless coordinate q and ν^0 is the scaling factor with the dimensions of cm^{-1}. The matrix elements of (33) are usually set up using the eigenfunctions $\psi_n(q)$ of $H^0 = \frac{1}{2} h \nu^0 (p^2 + q^2)$ as the basis functions and the solutions of the Schrödinger's equation are obtained by diagonalizing the resulting Hamiltonian matrix. But in the case of the above one-dimensional problem, it is strictly not necessary to employ this procedure. A much simpler and more elegant numerical integration technique by Cooley [10] can be adopted. But when it is required to calculate the energy levels of a two-dimensional Schrödinger's equation with a Hamiltonian [12]

$$\begin{aligned} H(q_1, q_2) = {} & \tfrac{1}{2} h \nu_1{}^0 (p_1{}^2 + K_1 q_1{}^2) \\ & + \tfrac{1}{2} h \nu_2{}^0 [p_2{}^2 + K_2 q_2{}^2 + K_{\mathrm{B}}/(C^2 + q_2{}^2)] \\ & + \tfrac{1}{2} h (\nu_1{}^0 \nu_2{}^0)^{1/2} K_{12} f(q_1, q_2) , \end{aligned} \tag{34}$$

it is necessary and convenient to set up the Hamiltonian matrix using the products of functions $\psi_{v_1} \times \psi_{v_2}$ as the basis and diagonalize it.

In the above, merely for illustration, functions of q_1 and q_2 are taken to represent single and double minimum potentials respectively. ν_1 and ν_2 are the frequencies of the two modes with the corresponding harmonic force constants K_1 and K_2. $K_{12} f(q_1, q_2)$ is an interaction term which allows for a possible coupling between the two modes. q_1 and q_2 are the dimensionless coordinates with the corresponding momenta p_1 and p_2. ν_1^0 and ν_2^0 are the scaling factors. $\psi_{v_1}(q_1)$ and $\psi_{v_2}(q_2)$ are the eigenfunctions of two 1-dimensional harmonic oscillators, with the associated quantum numbers v_1 and v_2, satisfying $H_i^0 \psi_{vi} = E_i^0 \psi_{vi}$ where

$$H_i^0 = \tfrac{1}{2} h \nu_i^0 (p_i^2 + q_i^2) \quad (i = 1, 2) . \tag{35}$$

In setting up the matrix elements of the Lorentzian term in (34), the recursion formula given by (12) would be useful. The matrix elements of the rest of the terms in the Hamiltonian (34) are known and are readily available [7]. If we take n_1 basis functions in q_1 and n_2 functions in q_2, the number of product functions $|v_1\rangle \cdot |v_2\rangle$ will be $n_1 \times n_2$. But as far as the Lorentzian term is concerned, since the resulting matrix is symmetric, we need to evaluate only $n_2(n_2+1)/2$ elements of $\langle v_2' | 1/(C^2 + q_2^2) | v_2 \rangle$. The elements of this matrix are then distributed appropriately in the larger $(n_1 n_2 \times n_1 n_2)$ matrix.

We shall now see a pertinent case where matrix elements of the term $1/(C^2 + q^2)^2$ would be required [see formula (29)].

5. Refinement of Force Constants

The five constants K_1, K_2, K_B, C^2 and K_{12} in (34) are usually adjusted so that the calculated values of the transition frequencies $\nu_{nm} [= (E_m - E_n)/h]$ give a least-squares fit with the observed values [11]. The first order corrections ΔK to the five force constants are obtained from

$$\Delta K = (\tilde{J} W J)^{-1} \tilde{J} W \Delta\nu , \tag{36}$$

where $\Delta\nu$ is a column vector of differences between the observed and the calculated frequencies. J is the Jacobian matrix and W is the diagonal weight matrix. They are defined by

$$\Delta K = K_n - K_{n-1} , \qquad \Delta\nu = \nu^{\text{obs}} - \nu^{\text{cal}} , \qquad J_{ij} = \partial\nu_i / \partial K_j \quad \text{and} \quad w_{ii} = 1/\delta_i^2 . \tag{37}$$

K_n is the force constant vector obtained in the n^{th} cycle of the least squares procedure and δ_i is the experimental uncertainty of the i^{th} observed frequency. The elements of J are given as follows:

$$\frac{\partial\nu_{nm}}{\partial K_j} = [\tilde{L} V\{q_j^2\} L]_{mm} - [\tilde{L} V\{q_j^2\} L]_{nn} , \tag{38}$$

$$\frac{\partial\nu_{nm}}{\partial K_B} = \left[\tilde{L} V \left\{\frac{1}{C^2 + q_2^2}\right\} L\right]_{mm} - \left[\tilde{L} V \left\{\frac{1}{C^2 + q_2^2}\right\} L\right]_{nn} , \tag{39}$$

$$\frac{\partial\nu_{nm}}{\partial C^2} = \left[\tilde{L} V \left\{\frac{-K_B}{(C^2 + q_2^2)^2}\right\} L\right]_{mm} - \left[\tilde{L} V \left\{\frac{-K_B}{(C^2 + q_2^2)^2}\right\} L\right]_{nn} \tag{40}$$

and

$$\frac{\partial\nu_{nm}}{\partial K_{12}} = [\tilde{L} V\{f(q_1, q_2)\} L]_{mm} - [\tilde{L} V\{f(q_1, q_2)\} L]_{nn} . \tag{41}$$

Here $V\{X\}$ is the matrix representation of the term X [see (34)], L is the eigenvector matrix of H and $\sim$ represents transpose. Expression (39) involves only the matrix elements of the Lorentzian term $1/(C^2 + q_2^2)$ whereas (40) involves the matrix representation of $1/(C^2 + q_2^2)^2$. It is during the evaluation of (40), that we require the use of special formulae (29) – (32).

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