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Structure of matrix perturbation coefficients for anharmonic oscillators

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Abstract. For perturbed harmonic oscillators, a hypervirial recurrence relation is examined to discover the positions of vanishing elements in the matrix perturbation coefficients (MPCs) of the $x^N(\lambda)$ matrices. It is found that only certain families of elements in the MPCs can be evaluated from the recurrence relation.

1. Introduction

In a recent paper, Clarke (1985) presented an algorithm for the calculation of perturbation series for the transition moments $\langle m|x|n\rangle$ of the Hamiltonian operator in one dimension

$$H = -\alpha D^2 + \mu x^2 + \lambda x^{2\nu}. \tag{1}$$

The calculation rested on a structural law for the matrix perturbation coefficients (MPCs) of the $x(\lambda)$ matrix, which gave the positions of vanishing elements in these coefficients. The law for the $x(\lambda)$ matrix (with $\nu = 2$) required no proof in this context. For the purpose of the calculation it could be regarded as a postulate which acquired validity through the consequent agreement of the calculated $\langle m|x|n\rangle$ perturbation series with results obtained from variational calculations. However, the law asserted in this paper was more general than that demanded by the calculation and consequently stands in need of proof. Although this had been achieved when the transition moment algorithm was in preparation, a much simpler demonstration has since been found.

For the general Hamiltonian

$$H = -\alpha D^2 + \mu x^2 + \lambda \sum_{t=2}^{\nu} A_t x^{2t} \tag{2}$$

we shall prove that matrix elements in the γth order MPCs of $x^{2h+1}(\lambda)$ vanish for eigenstate indices m, n which satisfy

$$|m-n| \neq 2s+1 \qquad s = 0, 1, \ldots, h+\gamma(\nu-1) \qquad h, \gamma \geq 0 \qquad \nu \geq 2.$$

This structural law is of interest not only for its mathematical simplicity. In anharmonic oscillator calculations involving sums over products of MPC elements, the law realises its practical value by converting infinite sums into finite ones through the exclusion of known vanishing elements.

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2. Hypervirial recurrence relation

The hypervirial recurrence relation derived by Clarke (1985) is based on the Hamiltonian (1) and involves perturbation series representations for the $\langle m|x^k|n\rangle$ elements and the energies E_m so that

$$x^k(\lambda) = \sum_{i=0}^{\infty} Q_i^k \lambda^i \tag{3}$$

$$E_{mn}^{+}(\lambda) = \sum_{i=0}^{\infty} E_i^{+} \lambda^i \tag{4}$$

$$E_{mn}^{-}(\lambda) = \sum_{i=0}^{\infty} E_i^{-} \lambda^i \tag{5}$$

where $E_i^+ = (E_m + E_n)_i$ and $E_i^- = (E_m - E_n)_i$. If we now consider the more general Hamiltonian (2) and regard only the odd power moments ($k = 2h+1$) we arrive at the relation

$$\begin{aligned}
4\alpha\mu[(m-n)^2 - (2h+1)^2]Q_\gamma^{2h+1} \\
&= 4\alpha(2h+1)\sum_{t=2}^{\nu} A_t(2h+t)Q_{\gamma-1}^{2(h+t)-1} - 4\alpha h(2h+1)\sum_{i+j=\gamma-1} E_{i+1}^{+} Q_j^{2h-1} \\
&\quad - \sum_{u=0}^{\gamma-1}\sum_{r+s=\gamma-u} E_r^- E_s^- Q_u^{2h+1} - 4\alpha^2 h(h-1)(4h^2-1)Q_\gamma^{2h-3} \\
&\quad - 4\alpha h(2h+1)E_0^+ Q_\gamma^{2h-1}.
\end{aligned} \tag{6}$$

The positions of the vanishing elements in the Q matrices will be determined by the function

$$\Delta(m, n, 2h+1) = [(m-n)^2 - (2h+1)^2]. \tag{7}$$

This function appears on the left-hand side of (6) and depends on the eigenstate indices m, n and the recursion index h. We can see that by considering the possibilities $|m-n| = 2h+1$ and $|m-n| \neq 2h+1$ there are four possible conclusions we can reach about $\langle m|Q_\gamma^{2h+1}|n\rangle$ depending on the vanishing or non-vanishing of the right-hand side of (6);

(i) defined and undetermined ($\Delta = 0$, RHS $= 0$);
(ii) undefined ($\Delta = 0$, RHS $\neq 0$);
(iii) vanishing ($\Delta \neq 0$, RHS $= 0$);
(iv) defined and determinable ($\Delta \neq 0$, RHS $\neq 0$).

We shall form (i), (ii), (iv) into two groups: the defined values D, (i), (iv) which are either given to the recurrence relation as initial values (i), or are recursively determined from given values (iv); and the undefined values U, (ii), which the recurrence relation cannot determine. This distinction shall be carried through our structural analysis since it will be of use later to know the positions of the defined (knowable) elements in order to arrive at a recurrence relation for them. These considerations reduce the possible conclusions about Q_γ^{2h+1} to

(*a*) vanishing;
(*b*) defined—D;
(*c*) undefined—U.

Representing quantities in this way for a structural analysis of Q_γ^{2h+1} renders attention to constants in (6) superfluous so long as we adhere to the 'Q-convention'

$$Q_\gamma^{2h+1}=0 \qquad \gamma, 2h+1<0. \tag{8}$$

This embodies the vanishing of these constants and at the same time gives the condition of the existence of the Q matrices. Since the multiplication of the Q matrices by defined constants has no effect on the status of the matrix elements—i.e. vanishing, defined, or undefined—we can absorb the constants into the matrices and write (6) in the form

$$\Delta(m, n, 2h+1)Q_\gamma^{2h+1} = \sum_{t=2}^{\nu} Q_{\gamma-1}^{2(h+t)-1} + \sum_{j=0}^{\gamma-1} Q_j^{2h-1} + \sum_{u=0}^{\gamma-1} Q_u^{2h+1} + Q_\gamma^{2h-3} + Q_\gamma^{2h-1}. \tag{9}$$

Our next task is to investigate the type of results arising from (9).

3. Form of results

The recurrence relation operates by selecting eigenstates m, n and running up the h from $h=0$ at each γ in ascending order beginning at $\gamma=0$. The Q_γ^{2h+1} elements obtained in this way depend on given zeroth-order elements and are substituted back into (6) to support the later calculations.

For example at $h=0$, $\gamma=0$ we have

$$\Delta(m, n, 1)Q_0^1=0 \tag{10}$$

having made use of the Q-convention (8). Q_0^1 is the x matrix of the pure harmonic oscillator. The possibilities $|m-n|=1$ and $|m-n|\neq 1$ lead through equations (7) and (10) to the result

$$Q_0^1 = D\delta_{m,n\pm 1}. \tag{11}$$

Equation (11) informs us that the matrix elements of Q_0^1 vanish when $|m-n|\neq 1$. For brevity, we shall rewrite the Kronecker delta $\delta_{m,n\pm(2h+1)}$ as δ_{2h+1}.

Advancing h to $h=1$ in (9) gives

$$\Delta(m, n, 3)Q_0^3 = D\delta_1 \tag{12}$$

so that the alternatives $|m-n|=3$, and $|m-n|\neq 3$ give the result

$$Q_0^3 = D\delta_1 + D\delta_3. \tag{13}$$

Continuing in this way, we expect all zeroth order Q_0^{2h+1} matrices to contain only defined quantities.

If we choose $h=1$ in the first order ($\gamma=1$) and examine only how the second and third terms on the right-hand side of (9) are modified by the Δ function, we have, after substitution of previous results, the solution

$$Q_1^3 = (D\delta_1) + (D\delta_1 + U\delta_3). \tag{14}$$

Of course, other terms containing both defined and undefined quantities will appear in (14), so before proceeding further we must set up some rules of addition for these quantities in order to express our results as briefly as possible.

4. Rules of addition

There are three fundamental rules of addition for defined and undefined quantities which require no proof and serve as axioms;

$$D\delta_{2s+1}+D\delta_{2s+1}=D\delta_{2s+1} \tag{15}$$

$$D\delta_{2s+1}+U\delta_{2s+1}=U\delta_{2s+1} \tag{16}$$

$$U\delta_{2s+1}+U\delta_{2s+1}=U\delta_{2s+1}. \tag{17}$$

Only the form of the quantity is of interest here without regard for particular quantities. It follows from these axioms that

$$\sum_{s=0}^{\alpha} D\delta_{2s+1}+\sum_{s=0}^{\beta} D\delta_{2s+1}=\sum_{s=0}^{\alpha} D\delta_{2s+1} \tag{18}$$

$$\sum_{s=0}^{\alpha} U\delta_{2s+1}+\sum_{s=0}^{\beta} D\delta_{2s+1}=\sum_{s=0}^{\alpha} U\delta_{2s+1} \tag{19}$$

$$\sum_{s=0}^{\alpha} U\delta_{2s+1}+\sum_{s=0}^{\beta} U\delta_{2s+1}=\sum_{s=0}^{\alpha} U\delta_{2s+1} \tag{20}$$

for $\alpha \geqslant \beta$ and also

$$\left(\sum_{s=0}^{\alpha} U\delta_{2s+1}+\sum_{s=\alpha+1}^{\beta} D\delta_{2s+1}\right)+\left(\sum_{s=0}^{\alpha'} U\delta_{2s+1}+\sum_{s=\alpha'+1}^{\beta'} D\delta_{2s+1}\right)$$
$$=\left(\sum_{s=0}^{\alpha} U\delta_{2s+1}+\sum_{s=\alpha+1}^{\beta} D\delta_{2s+1}\right) \qquad \beta \geqslant \beta',\ \alpha \geqslant \alpha'. \tag{21}$$

Now that sufficient ground has been prepared, the place has arrived to find the structure of the general Q_γ^{2h+1}.

5. Structure of Q_γ^{2h+1}

We advance the postulate that the structure of Q_γ^{2h+1} for the Hamiltonian (2) is given by

$$Q_\gamma^{2h+1}=\sum_{s=0}^{h+(\gamma-1)(\nu-1)} U\delta_{2s+1}+\sum_{s'=h+(\gamma-1)(\nu-1)+1}^{h+\gamma(\nu-1)} D\delta_{2s'+1}. \tag{22}$$

In accordance with our expectations from § 3 about the zeroth-order Q matrices ($\gamma=0$), the convention is to be adopted in (22) that at $\gamma=0$ the sum over s vanishes and the sum containing the defined quantities commences from $s'=0$. (If we had not distinguished between defined and undefined quantities we would only have had one sum in (22), with limits $p=0$ and $p=h+\gamma(\nu-1)$, and the convention for $\gamma=0$ would have been unnecessary.) The terms on the right-hand side of (9) can be represented according to (22);

$$\sum_{t=2}^{\nu} Q_{\gamma-1}^{2(h+t)-1}=\sum_{t=2}^{\nu}\left(\sum_{s=0}^{X} U\delta_{2s+1}+\sum_{s'=Y}^{Z} D\delta_{2s'+1}\right) \tag{23}$$

where

$$X = h + (\gamma - 1)(\nu - 1) + (t - \nu)$$

$$Y = h + (\gamma - 1)(\nu - 1) + (t - \nu) + 1$$

$$Z = h + \gamma(\nu - 1) + (t - \nu)$$

$$\sum_{j=0}^{\gamma-1} Q_j^{2h-1} = \sum_{j=0}^{\gamma-1} \left(\sum_{s=0}^{h+(j-1)(\nu-1)-1} U\delta_{2s+1} + \sum_{s'=h+(j-1)(\nu-1)}^{h+j(\nu-1)-1} D\delta_{2s'+1} \right) \tag{24}$$

$$\sum_{u=0}^{\gamma-1} Q_u^{2h+1} = \sum_{u=0}^{\gamma-1} \left(\sum_{s=0}^{h+(u-1)(\nu-1)} U\delta_{2s+1} + \sum_{s'=h+(u-1)(\nu-1)+1}^{h+u(\nu-1)} D\delta_{2s'+1} \right) \tag{25}$$

$$Q_\gamma^{2h-3} = \sum_{s=0}^{h+(\gamma-1)(\nu-1)-2} U\delta_{2s+1} + \sum_{s'=h+(\gamma-1)(\nu-1)-1}^{h+\gamma(\nu-1)-2} D\delta_{2s'+1} \tag{26}$$

$$Q_\gamma^{2h-1} = \sum_{s=0}^{h+(\gamma-1)(\nu-1)-1} U\delta_{2s+1} + \sum_{s'=h+(\gamma-1)(\nu-1)}^{h+\gamma(\nu-1)-1} D\delta_{2s'+1}. \tag{27}$$

The aim is to prove that the sum of the terms in (9), given by equations (23)-(27), reduces to (22) thereby validating the postulate.

Equations (23)-(25) can be simplified. If we consider (23) for $\gamma \geq 1$ the sum over t reduces to one term (at $t = \nu$) through repeated use of (18) and (21). We then have

$$\sum_{t=2}^{\nu} Q_{\gamma-1}^{2(h+t)-1} = \left(\sum_{s=0}^{h+(\gamma-1)(\nu-1)} U\delta_{2s+1} + \sum_{s'=h+(\gamma-1)(\nu-1)+1}^{h+\gamma(\nu-1)} D\delta_{2s'+1} \right). \tag{23a}$$

Similarly, taking note of the convention tied up with (22), equations (24) and (25) become

$$\sum_{j=0}^{\gamma-1} Q_j^{2h-1} = \left(\sum_{s=0}^{h+(\gamma-2)(\nu-1)-1} U\delta_{2s+1} + \sum_{s'=h+(\gamma-2)(\nu-1)}^{h+(\gamma-1)(\nu-1)-1} D\delta_{2s'+1} \right) \tag{24a}$$

$$\sum_{u=0}^{\gamma-1} Q_u^{2h+1} = \left(\sum_{s=0}^{h+(\gamma-2)(\nu-1)} U\delta_{2s+1} + \sum_{s'=h+(\gamma-2)(\nu-1)+1}^{h+(\gamma-1)(\nu-1)} D\delta_{2s'+1} \right) \tag{25a}$$

so that we find, as we did with (23), that the term corresponding to the upper limit of the sum over the Q matrices dominates and absorbs the other terms.

We shall now prove the validity of the postulate (22) for the three cases $\gamma = 0$, $\gamma = 1$, $\gamma \geq 2$. At $\gamma = 0$, the convention relating to (22) leaves (9) as

$$\Delta(m, n, 2h+1) Q_0^{2h+1} = \sum_{s'=0}^{h-2} D\delta_{2s'+1} + \sum_{s'=0}^{h-1} D\delta_{2s'+1}. \tag{28}$$

Use of (18) and subsequent determination of Q_0^{2h+1} by the Δ function gives

$$Q_0^{2h+1} = \sum_{s=0}^{h} D\delta_{2s+1} \tag{29}$$

which validates (22) at $\gamma = 0$.

Setting $\gamma=1$ in (9) produces

$$\begin{aligned}\Delta(m,n,2h+1)Q_1^{2h+1} &= \left(\sum_{s=0}^{h} U\delta_{2s+1}+\sum_{s'=h+1}^{h+\nu-1} D\delta_{2s'+1}\right)+\left(\sum_{s'=0}^{h-1} D\delta_{2s'+1}\right)\\ &\quad+\left(\sum_{s'=0}^{h} D\delta_{2s'+1}\right)+\left(\sum_{s=0}^{h-2} U\delta_{2s+1}+\sum_{s'=h-1}^{h+\nu-3} D\delta_{2s'+1}\right)\\ &\quad+\left(\sum_{s=0}^{h-1} U\delta_{2s+1}+\sum_{s'=h}^{h+\nu-2} D\delta_{2s'+1}\right). \qquad (30)\end{aligned}$$

Reduction of (30) with (18) and (19), noting that $\nu\geqslant 2$, followed by reduction with (21) produces

$$\Delta(m,n,2h+1)Q_1^{2h+1}=\sum_{s=0}^{h} U\delta_{2s+1}+\sum_{s'=h+1}^{h+\nu-1} D\delta_{2s'+1}. \qquad (31)$$

Determining Q_1^{2h+1} with the Δ function leaves $U\delta_{2h+1}$ unchanged so that

$$Q_1^{2h+1}=\sum_{s=0}^{h} U\delta_{2s+1}+\sum_{s'=h+1}^{h+\nu-1} D\delta_{2s'+1} \qquad (32)$$

thereby confirming (22) at $\gamma=1$.

Finally, for $\gamma\geqslant 2$ we have $\Delta(m,n,2h+1)Q_\gamma^{2h+1}$ equal to the sum of the terms in (23*a*), (24*a*), (25*a*), (26) and (27). These may be reduced with (21) to give

$$\Delta(m,n,2h+1)Q_\gamma^{2h+1}=\sum_{s=0}^{h+(\gamma-1)(\nu-1)} U\delta_{2s+1}+\sum_{s'=h+(\gamma-1)(\nu-1)+1}^{h+\gamma(\nu-1)} D\delta_{2s'+1}. \qquad (33)$$

This yields the result

$$Q_\gamma^{2h+1}=\sum_{s=0}^{h+(\gamma-1)(\nu-1)} U\delta_{2s+1}+\sum_{s'=h+(\gamma-1)(\nu-1)+1}^{h+\gamma(\nu-1)} D\delta_{2s'+1} \qquad (34)$$

validating the postulate (22) for $\gamma\geqslant 2$. The essence of (22) is that matrix elements in Q_γ^{2h+1}, the MPCs of $x^{2h+1}(\lambda)$, vanish for eigenstates m and n satisfying

$$|m-n|\neq 2s+1 \qquad s=0,1,\ldots,h+\gamma(\nu-1). \qquad (35)$$

For the zeroth-order case ($\gamma=0$), the result (29) is given by Kilpatrick and Sass (1965) who derive the defined zeroth-order elements D in (29) in terms of polynomials in the quantum numbers m and n.

We can provide some independent support for the first-order case ($\gamma=1$) by considering the Rayleigh-Schrödinger series to first order for the perturbed state vector $|n\rangle'$. This is given by

$$|n\rangle'=|n\rangle+\lambda\sum_{m\neq n}|m\rangle\langle m|V|n\rangle(E_m-E_n)^{-1} \qquad (36)$$

where $|m\rangle$ and E_m are respectively unperturbed state vectors and energies. We shall confine our attention to the case where the potential energy is $V=x^4$ ($\nu=2$). After advancing n to $n+5$ in (36) we can form the $\langle n|x|n+5\rangle'$ perturbed element to first order, so that

$$\langle n|x|n+5\rangle' = 0 + \lambda\left(\frac{\langle n|x|n+1\rangle\langle n+1|x^4|n+5\rangle}{(E_{n+1}-E_{n+5})} + \frac{\langle n+5|x|n+4\rangle\langle n+4|x^4|n\rangle}{(E_{n+4}-E_n)}\right) + \dots \tag{37}$$

having observed that the x operator may only link adjacent unperturbed eigenstates. In consequence of this observation, the numerators of each first-order term become $\langle n|x^5|n+5\rangle$. We also note that the energies of adjacent eigenstates of the harmonic oscillator differ by equal amounts, so that

$$(E_{n+1}-E_{n+5}) = -(E_{n+4}-E_n). \tag{38}$$

This gives the vanishing of the first-order term in (37) by cancellation, for $|m-n|=5$, contrary to expectation. Placing $h=0$, $\gamma=1$, $\nu=2$ in (35) shows that the first-order elements $\langle m|Q_1^1|n\rangle$ vanish for $|m-n|\neq 1, 3$, in particular for $|m-n|=5$, in accord with the Rayleigh-Schrödinger result.

In general, a class of functions for Q_γ^{2h+1} with summation limits $s_{\min}=p$ and $s'_{\max}=h+(\gamma-q)(\nu-1)+r$ are valid postulates (where p, q, r are constants), however, only the choice $p, q, r=0$ yields the correct result at $\gamma=0$.

The lower limit of the defined elements may, in general, be $s'_{\min}=h+(\gamma-q')(\nu-1)+r'$ where q', r' are constants. We fix s' in the recursion and select the lowest order ($\gamma=1$) at which the sum over s' for the defined elements is valid. Q_1^{2h+1} is recursively determined by using ascending values of h from $h=0$ and substituting previously calculated results back into the recurrence relation. For Q_1^{2h+1} to be defined we must have $s'>h$ otherwise at some h in the sequence of determinations for Q_1^{2h+1} we have $s'=h$ and Q_1^{2h+1} becomes undefined. It follows that the minimum value of s' for which Q_1^{2h+1} remains defined is $s'_{\min}=h+1$ so that with $\gamma=1$ we have $q', r'=1$. For general γ we then have $s'_{\min}=h+(\gamma-1)(\nu-1)+1$.

We now turn our attention to the defined elements in (22) for $\gamma>0$. These are the elements which conform to the condition

$$|m-n| = 2s'+1 \qquad s' = h+(\gamma-1)(\nu-1)+1, \dots, h+\gamma(\nu-1)$$
$$h\geqslant 0;\ \gamma>0;\ \nu\geqslant 2. \tag{39}$$

Their values can only depend on given zeroth-order elements. This dependence is a property of the recurrence relation (6) which we shall see reduces to a special recurrence relation for the range of s' given by (39).

6. Recurrence relation for defined elements

Equation (39) gives the range of s' for which the recurrence relation (6) yields defined values for elements. By examining equations (23)-(27) we can see which terms in (6) will contribute to the determination of the defined elements of Q_γ^{2h+1}. These are the terms whose defined elements have eigenstate indices m, n which fall within the range of s' given by (39). Since the terms given by (24) and (25) are therefore excluded, the recurrence relation (6) reduces to

$$Q_\gamma^{2h+1}=\mu^{-1}[(2s'+1)^2-(2h+1)^2]^{-1}\bigg((2h+1)\sum_{t=2}^{\nu}(2h+t)Q_{\gamma-1}^{2(h+t)-1}A_t$$

$$-\alpha h(h-1)(4h^2-1)Q_\gamma^{2h-3}-h(2h+1)E_0^+Q_\gamma^{2h-1}\bigg) \tag{40}$$

for $\gamma>0$, $s'=h+(\gamma-1)(\nu-1)+1,\ldots,h+\gamma(\nu-1)$; $\gamma=0$, $s'=0,1,\ldots,h-1$. Provision of appropriate zeroth-order elements permits the deduction of all defined elements of Q_γ^{2h+1} from (40).

7. Even power matrices Q_γ^{2h}

Proceeding along similar lines for the even power matrices Q_γ^{2h}, we arrive at the conclusion that vanishing elements occur for eigenstates m, n satisfying

$$|m-n|\neq 2s \qquad s=0,1,\ldots,h+\gamma(\nu-1) \qquad h,\gamma\geqslant 0,\ \nu\geqslant 2. \tag{41}$$

The recurrence relation for the defined elements becomes

$$Q_\gamma^{2h}=(4\mu)^{-1}(s^2-h^2)^{-1}\bigg(2h\sum_{t=2}^{\nu}(2h+t-1)Q_{\gamma-1}^{2(h+t-1)}A_t$$

$$-\alpha h(h-1)(2h-1)(2h-3)Q_\gamma^{2(h-2)}-h(2h-1)E_0^+Q_\gamma^{2(h-1)}\bigg) \tag{42}$$

for $\gamma=0$, $s=0,1,\ldots,h-1$; $\gamma>0$, $s=0$ and $s=h+(\gamma-1)(\nu-1)+1,\ldots,h+\gamma(\nu-1)$. For the diagonal case $m=n$ $(s=0)$, E_0^+ becomes $2E_0$ and with an appropriate choice of constants we have the relation derived by Swenson and Danforth (1972).

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