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Harmonic oscillator tensors. III: Efficient algorithms for evaluating matrix elements of vibrational operators

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Succinct expressions for the matrix elements of various vibrational operators have been derived in the basis of the nondegenerate harmonic oscillator. Among these are the matrix elements of $q^k e^{\lambda q}$, $q^k \sin^l(\mu q)$, $q^k \cos^l(\mu q)$, $q^k \sinh^l(\mu q)$ and $q^k \cosh^l(\mu q)$, which are found to be dependent upon two quantities and their derivatives. Furthermore, the derivative property of the commutator is used to obtain an explicit expression for the derivatives of an operator in terms of its nested commutator with the conjugate momentum. It may be applied to any of the above cases to obtain the matrix representatives of expressions such as the mixed products $\sin^l(\mu q)\cos^{l-m}(\mu q)$, for example. In addition, a simple expression for $1/q$ is given and its derivatives may be evaluated by this commutator technique. Also the matrix elements of a Gaussian-type operator $q^k e^{\lambda q^2}$ has been evaluated.

1. Introduction

In his treatment of the harmonic oscillator problem, Dirac [3] employed the factorization method (cf. [5] for a general exposition of this topic) to the well-known creation and annihilation operators,

$$a^\dagger = (q - \mathrm{i}p)/\sqrt{2}, \qquad a = (q + \mathrm{i}p)/\sqrt{2}, \tag{1}$$

respectively. Here q represents the dimensionless displacement coordinate of the oscillator and p its conjugate momentum. These ladder operators have a simple stepping action on an eigenket $|v\rangle$ of the harmonic oscillator, namely,

$$(a^\dagger)^n|v\rangle = \left[\frac{(v+n)!}{v!}\right]^{1/2}|v+n\rangle, \qquad a^n|v\rangle = \left[\frac{v!}{(v-n)!}\right]^{1/2}|v-n\rangle. \tag{2}$$

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The set $\{a, a^\dagger, \mathcal{I}\}$, in which $\mathcal{I}$ denotes the identity operator, is a basis for a Lie algebra whose binary product is commutation. With equations (2) it may be shown that the sole nonvanishing commutator of the set is the fundamental Lie product,

$$[a, a^\dagger] = \mathcal{I}. \tag{3}$$

This particular algebra is called a Heisenberg Lie algebra and is denoted by LAH.

By using equation (3) it is possible to demonstrate [6] that the operators,

$$J_+ = -\tfrac{1}{2}a^\dagger a^\dagger, \qquad J_0 = \tfrac{1}{4}(aa^\dagger + a^\dagger a), \qquad J_- = \tfrac{1}{2}aa, \tag{4}$$

comprise the basis of a Lie algebra of the special unitary group in two dimensions, LASU(2), having the usual behavior under commutation,

$$[J_0, J_\pm] = \pm J_\pm, \qquad [J_+, J_-] = 2J_0. \tag{5}$$

Furthermore, is was shown that the superoperators,

$$\mathcal{J}_\alpha = [J_\alpha,\ ], \quad \alpha = +, 0, -, \tag{6}$$

lead directly to irreducible tensors. The components of an irreducible tensor of rank l was shown to be expressible in the three equivalent forms,

$$T_{lm} = \binom{2l}{l \pm m}^{-1/2} \big\{(a^\dagger)^{l+m} a^{l-m}\big\}, \tag{7a}$$

$$T_{lm} = \binom{2l}{l \pm m}^{1/2} \sum_{\alpha=0}^{l-|m|} \frac{\alpha!}{2^\alpha} \binom{l+m}{\alpha} \binom{l-m}{\alpha} (a^\dagger)^{l+m-\alpha} a^{l-m-\alpha}, \tag{7b}$$

$$T_{lm} = \binom{2l}{l \pm m}^{1/2} \sum_{\alpha=0}^{l-|m|} (-)^\alpha \frac{\alpha!}{2^\alpha} \binom{l+m}{\alpha} \binom{l-m}{\alpha} a^{l-m-\alpha} (a^\dagger)^{l+m-\alpha}. \tag{7c}$$

The braces in equation (7a) denote the symmetric sum of the product contained therein. These harmonic oscillator tensors (HOTs) satisfy the normal relations for the components of an irreducible tensor, viz.,

$$\mathcal{J}_\pm T_{lm} = \sqrt{(l \mp m)(l \pm m + 1)}\, T_{l,m\pm1}, \qquad \mathcal{J}_0 T_{lm} = m T_{lm}. \tag{8}$$

Their construction stems from the realization that the creation and annihilation operators are the maximal and minimal components, respectively, of a tensor of rank $1/2$. Their practical utility lies in the fact that, as irreducible tensors, they are linearly independent by definition and therefore they eliminate the host of linear independences among the monomials of products of creation and annihilation operators.

By analyzing the symmetry properties of the harmonic oscillator, it was seen that the matrix elements of the HOT components reduce to an analog of the Wigner–Eckart theorem [7]. As in the Wigner–Eckart case, the final expression displays a conservation of angular momentum along the axis of quantization. The use of these ideas adopted from the elementary theory of angular momentum led to the determination of general expressions for the matrix elements of several vibrational operators in terms of the Clebsch–Gordan coefficients or Wigner $3j$-symbols [7]. However, it turns out that there exist even simpler analytical expressions for these matrix elements. This article is devoted to their derivation and disclosure.

2. Forms containing q and p

Reid and Brändas [11] derived an expression for the matrix elements of positive integer powers of the dimensionless displacement coordinate q by using the generator of the Hermite polynomials. An angular momentum expression for these matrix elements has also been obtained [7]. Here we shall make use of angular momentum techniques to arrive at simple expressions.

The inverse transformation of equations (1) leads to

$$\begin{aligned} q^{2L} &= \left(\frac{1}{2}\right)^L (a^\dagger + a)^{2L} = \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} \left\{(a^\dagger)^{L+M} a^{L-M}\right\} \\ &= \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} \binom{2L}{L \pm M}^{1/2} T_{LM}, \quad L = 0, 1/2, 1, \ldots, \end{aligned} \tag{9}$$

and the last equality follows from equation (7a). Successive application of the lowering operator $\mathcal{J}_-$ to the principal component of a HOT of rank L gives

$$\begin{aligned} T_{LM} &= \left[\frac{(L+M)!}{(2L)!(L-M)!}\right]^{1/2} \mathcal{J}_-^{L-M} T_{LL} \\ &= \left[\frac{(L+M)!}{(2L)!(L-M)!}\right]^{1/2} \sum_{n=0}^{L-M} (-)^n \binom{L-M}{n} J_-^{L-M-n} T_{LL} J_-^n, \end{aligned} \tag{10}$$

where the second equality results from the expansion of the commutator. Substitution of this result into equation (9) yields

$$q^{2L} = \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} \frac{1}{(L-M)!} \sum_{n=0}^{L-M} (-)^n \binom{L-M}{n} J_-^{L-M-n} T_{LL} J_-^n. \tag{11}$$

Hence, the matrix element between two vibrational states, $2j'$ and $2j$, where $j', j = 0, 1/2, 1, 3/2, \ldots$, is

$$\begin{aligned} \left\langle 2j' \middle| q^{2L} \middle| 2j \right\rangle = \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} \frac{(-)^{L-M}}{(L-M)!} \sum_{n=0}^{L-M} \binom{L-M}{n} \\ \times \left\langle J_+^{L-M-n}(2j') \middle| T_{LL} J_-^n \middle| 2j \right\rangle, \end{aligned} \tag{12}$$

after invoking the turnover rule while taking into account the fact that J_+ and J_- are an antiadjoint pair [cf. equations (4)]. On the other hand, the definitions (4) and equations (2) show that

$$J_+^n|2j'\rangle = \left(-\frac{1}{2}\right)^n \left[\frac{(2j'+2n)!}{(2j')!}\right]^{1/2} |2j'+2n\rangle \tag{13a}$$

and

$$J_-^n|2j\rangle = \left(\frac{1}{2}\right)^n \left[\frac{(2j)!}{(2j-2n)!}\right]^{1/2} |2j-2n\rangle. \tag{13b}$$

Thus, equation (12) becomes

$$\begin{aligned}\left\langle 2j'\middle|q^{2L}\middle|2j\right\rangle = {} & \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} \left(\frac{1}{2}\right)^{L-M} \frac{1}{(L-M)!} \sum_{n=0}^{L-M} (-)^n \binom{L-M}{n} \\ & \times \left[\frac{(2j'+2L-2M-2n)!}{(2j')!} \frac{(2j)!}{(2j-2n)!}\right]^{1/2} \\ & \times \left\langle 2j'+2L-2M-2n\middle|T_{LL}\middle|2j-2n\right\rangle.\end{aligned} \tag{14}$$

By equations (7a) and (2)

$$T_{LL}|2j-2n\rangle = \left[\frac{(2j+2L-2n)!}{(2j-2n)!}\right]^{1/2} |2j+2L-2n\rangle, \tag{15}$$

so that the orthonormality of the harmonic oscillator states imposes the constraint $j' = j + M$ or $M = j' - j \leqslant L$ and yields the final expression,

$$\begin{aligned}\left\langle 2j'\middle|q^{2L}\middle|2j\right\rangle = {} & \left[1+(-)^{2L+2j+2j'}\right] \left(\frac{1}{2}\right)^{2L+j-j'+1} \frac{(2L)!}{(L+j-j')!} \left[\frac{(2j)!}{(2j')!}\right]^{1/2} \\ & \times \sum_{n=0}^{L+j-j'} (-)^n \binom{L+j-j'}{n} \binom{2L+2j-2n}{2L}.\end{aligned} \tag{16}$$

Half the first factor has been appended to ensure that parity is conserved. Notice that the condition $j' - j \leqslant L$ is automatically satisfied by the factorials. It is also noteworthy that for $L = 0$ the series on the right side vanishes unless $j = j'$, but in that case the right side is unity, in agreement with the orthonormality of the harmonic oscillator states.

Previously [6] it has been shown that

$$p^{2L} = \left(\frac{1}{2}\right)^L \sum_{M=-L}^{L} (-)^{2L-M} \binom{2L}{L \pm M}^{1/2} T_{LM}, \quad L = 0, 1/2, 1, \ldots . \tag{17}$$

Comparison with equation (9) shows that the two equations differ by the phase factor $(-)^{2L-M}$. If then follows from the constraint on M that

$$\left\langle 2j' \middle| p^{2L} \middle| 2j \right\rangle = (-)^{2L+j-j'} \left\langle 2j' \middle| q^{2L} \middle| 2j \right\rangle. \tag{18}$$

One may also obtain the matrix elements of mixed products of q and p. Using equations (9) and (17) along with (10) gives rise to

$$\begin{aligned} q^{2l}p^{2L} = {} & \left(\frac{1}{2}\right)^{l+L} \sum_{m=-l}^{l} \sum_{M=-L}^{L} \frac{(-)^{L-M}}{(l-m)!(L-M)!} \\ & \times \sum_{n=0}^{l-m} \sum_{N=0}^{L-M} (-)^{n+N} \binom{l-m}{n} \binom{L-M}{N} J_-^{l-m-n} T_{ll} J_-^{L-M-N+n} T_{LL} J_-^{n}. \end{aligned} \tag{19}$$

However, the equations (2), (4) and (7) show that

$$\begin{aligned} & J_-^{l-m-n} T_{ll} J_-^{L-M-N+n} T_{LL} J_-^{n} |2j\rangle \\ & \quad = \left(\frac{1}{2}\right)^{l-m+L-M} (2l)!(2L)! \binom{2j-2N+2L}{2L} \binom{2j+2M-2n+2l}{2l} \\ & \qquad \times \left[\frac{(2j)!}{(2j+2M+2m)!}\right]^{1/2} |2j+2M+2m\rangle. \end{aligned} \tag{20}$$

Thus, the matrix elements of the mixed products are given by

$$\begin{aligned} \left\langle 2j' \middle| q^{2l}p^{2L} \middle| 2j \right\rangle = {} & \frac{1}{2}\left[1+(-)^{2j'+2l+2L+2j}\right] \left(\frac{1}{2}\right)^{2l+2L+j-j'} \\ & \times (2l)!(2L)! \left[\frac{(2j)!}{(2j')!}\right]^{1/2} \sum_{m=-l}^{l} \frac{(-)^{L+m+j-j'}}{(l-m)!(L+m+j-j')!} \\ & \times \sum_{n=0}^{l-m} (-)^n \binom{l-m}{n} \binom{2j'-2m-2n+2l}{2l} \\ & \times \sum_{N=0}^{L+m+j-j'} (-)^N \binom{L+m+j-j'}{N} \binom{2j-2N+2L}{2L}, \end{aligned} \tag{21}$$

where the summation over M has been constrained by the orthonormality of the vibrational states, i.e., $j' = j + M + m$. We have chosen the standard form of a monomial in which all q's precede all p's because all monomials of degree $2l + 2L$ may be reduced to this standard form by the basic commutation relation

$$[q, p] = \mathrm{i}\mathcal{I}. \tag{22}$$

Notice that a parity factor has been appended to this result in order to avoid the computation unless the parity constraint holds. It is also readily shown that for $L = 0$, equation (21) reduces to equation (16).

The main advantage of these simple formulae is that they obviate the necessity of evaluating Clebsch–Gordan coefficients.

3. Exponential forms

The matrix elements of the exponential function of q has been determined by Duch [4] and later by one of us ($P.P.$) in terms of the Clebsch–Gordan coefficients [7]. The formula of the latter work is unwieldy because of four nested summations. Here we will see how these matrix elements may be expressed in terms of one summation. By equation (1) the exponential may be expressed as

$$\mathrm{e}^{\lambda q} = \mathrm{e}^{\lambda(a^\dagger + a)/\sqrt{2}} = \mathrm{e}^{\lambda^2/4}\mathrm{e}^{\lambda a^\dagger/\sqrt{2}}\,\mathrm{e}^{\lambda a/\sqrt{2}}, \tag{23}$$

where the second equality is a result of the Baker–Campbell–Hausdorff identity [10],

$$\mathrm{e}^{X+Y} = \mathrm{e}^{-[X,Y]/2}\mathrm{e}^{X}\mathrm{e}^{Y}, \quad \text{if } \big[X,[X,Y]\big] = 0 = \big[Y,[X,Y]\big]. \tag{24}$$

Thus, the matrix elements of the exponential operator are given by

$$\begin{aligned}
\big\langle 2j'\big|\mathrm{e}^{\lambda q}\big|2j\big\rangle &= \mathrm{e}^{\lambda^2/4}\big\langle 2j'\big|\mathrm{e}^{\lambda a^\dagger/\sqrt{2}}\mathrm{e}^{\lambda a/\sqrt{2}}\big|2j\big\rangle \\
&= \mathrm{e}^{\lambda^2/4}\big\langle \mathrm{e}^{\lambda^* a/\sqrt{2}}(2j')\big|\mathrm{e}^{\lambda a/\sqrt{2}}(2j)\big\rangle \\
&= \mathrm{e}^{\lambda^2/4}\sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\frac{1}{n!n'!}\left(\frac{\lambda}{\sqrt{2}}\right)^{n+n'}\big\langle a^n(2j')\big|a^{n'}(2j)\big\rangle \\
&= \mathrm{e}^{\lambda^2/4}\sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\frac{1}{n!n'!}\left(\frac{\lambda}{\sqrt{2}}\right)^{n+n'}\left[\frac{(2j')!}{(2j'-n)!}\,\frac{(2j)!}{(2j-n')!}\right]^{1/2} \\
&\quad \times \big\langle 2j'-n \mid 2j-n'\big\rangle \\
&= \mathrm{e}^{\lambda^2/4}\sqrt{(2j')!(2j)!}\sum_{n=0}^{\infty}\frac{1}{n!(n+2j-2j')!(2j'-n)!}\left(\frac{\lambda}{\sqrt{2}}\right)^{2n+2j-2j'}.
\end{aligned} \tag{25}$$

Here we have used the turnover rule and expanded the exponentials. The orthonormality of the vibrational states requires that $n' = n + 2j - 2j'$. In this way, the two summations are reduced to one. The remaining summation cannot be infinite because of the factorials. Together they require that $2j' - 2j \leqslant n \leqslant 2j'$. Hence, the final expression is

$$\begin{aligned}
\big\langle 2j'\big|\mathrm{e}^{\lambda q}\big|2j\big\rangle &= \sqrt{(2j')!(2j)!} \\
&\quad \times \mathrm{e}^{\lambda^2/4}\sum_{n}^{2j'}\frac{1}{n!(n+2j-2j')!(2j'-n)!}\left(\frac{\lambda}{\sqrt{2}}\right)^{2n+2j-2j'}.
\end{aligned} \tag{26}$$

For $2j' \leqslant 2j$ the lower limit of the summation is 0, while for $2j < 2j'$ it is $2j' - 2j$. Notice that if λ is real, the matrix is real and symmetric, in which case it suffices to evaluate only the upper triangular portion of the matrix and the diagonal elements.

This equation may be used to arrive at the matrix elements of positive integer powers or q times the exponential. Successive differentiation of the left side with respect to λ gives rise to

$$\frac{\mathrm{d}^l}{\mathrm{d}\lambda^l}\langle 2j'|\mathrm{e}^{\lambda q}|2j\rangle = \langle 2j'|q^l \mathrm{e}^{\lambda q}|2j\rangle. \tag{27}$$

The right-hand side of equation (26) may be considered as a product of functions of λ. We write it as

$$f_{2j';2j}(\lambda) = F_{2j';2j} A(\lambda; 1/4) B_{2j';2j}(\lambda; +1), \tag{28a}$$

in which

$$F_{2j';2j} \equiv \sqrt{(2j')!(2j)!}, \tag{28b}$$

$$A(\lambda; a) \equiv \mathrm{e}^{a\lambda^2}, \tag{28c}$$

and

$$B_{2j';2j}(\lambda; \pm 1) \equiv \sum_{n}^{2j'} \frac{(\pm 1)^n}{n!(n+2j-2j')!(2j'-n)!}\left(\frac{\lambda}{\sqrt{2}}\right)^{2n+2j-2j'}. \tag{28d}$$

The lth derivative of the product with respect to λ is

$$f^{(l)}_{2j';2j}(\lambda) = F_{2j';2j} \sum_{k=0}^{l} \binom{l}{k} A^{(k)}(\lambda; 1/4) B^{(l-k)}_{2j';2j}(\lambda; +1). \tag{29}$$

The successive differentiation of $A(\lambda; a)$ yields

$$A^{(k)}(\lambda; a) = \mathrm{e}^{a\lambda^2}\left[(2a\lambda)^k + \sum_{\kappa=1}^{[k/2]} (2\kappa-1)!!\binom{k}{2\kappa}(2a)^\kappa (2a\lambda)^{k-2\kappa}\right]. \tag{30}$$

Here $[k/2] = k/2$ for even values of k and $[k/2] = (k-1)/2$ for odd values of k. Since the powers of λ are always semipositive definite integers, the successive differentiation of $B_{2j';2j}(\lambda; \pm 1)$ gives

$$B^{(m)}_{2j';2j}(\lambda; \pm 1) = m! \sum_{n}^{2j'} \left(\frac{1}{\sqrt{2}}\right)^{2n+2j-2j'} \frac{(\pm 1)^n}{n!(n+2j-2j')!(2j'-n)!} \times \binom{2n+2j-2j'}{m} \lambda^{2n+2j-2j'-m}. \tag{31}$$

The nonzero terms in the summation are those for which $2n + 2j - 2j' \geqslant m$.

By equations (27) and (29) the final expression is

$$\langle 2j'|q^l \mathrm{e}^{\lambda q}|2j\rangle = F_{2j';2j} \sum_{k=0}^{l} \binom{l}{k} A^{(k)}(\lambda; 1/4) B^{(l-k)}_{2j';2j}(\lambda; +1), \tag{32}$$

where the derivatives $A^{(k)}(\lambda;1/4)$ and $B^{(l-k)}_{2j';2j}(\lambda;\pm 1)$ are given by equations (30) and (31), respectively. The above algorithm to generate the matrix elements of this operator is much simpler than that given in [7] because in that case there are six nested summations, among which the three innermost require the evaluation of Clebsch–Gordan coefficients. Notice that for $l = 0$ it reduces to equation (25), so that it naturally includes that case. On the other hand, if $\lambda = 0$, all the derivatives vanish, except for the case in which $k = 0 = l$. In this case the definitions of A and $B_{2j';2j}$ show that the right side becomes unity when $2j' = 2j$.

4. Forms containing sine and cosine functions

Equation (25) is also useful for obtaining the matrix elements of the sine and cosine functions. For $\lambda = \pm \mathrm{i}\mu$, where μ is a real scalar, the Euler formulae give:

$$\begin{aligned}
\langle 2j' | \sin(\mu q) | 2j \rangle &= \frac{\mathrm{i}}{2} \langle 2j' | \mathrm{e}^{-\mathrm{i}\mu q} - \mathrm{e}^{\mathrm{i}\mu q} | 2j \rangle \\
&= \frac{\mathrm{i}}{2} F_{2j';2j} \mathrm{e}^{-\mu^2/4} \sum_{n=0}^{\infty} \frac{1}{n!(n+2j-2j')!(2j'-n)!} \\
&\quad \times \left[\left(-\mathrm{i}\frac{\mu}{\sqrt{2}} \right)^{2n+2j-2j'} - \left(\mathrm{i}\frac{\mu}{\sqrt{2}} \right)^{2n+2j-2j'} \right] \\
&= \frac{\mathrm{i}}{2} F_{2j';2j} \mathrm{e}^{-\mu^2/4} \sum_{n=0}^{\infty} \frac{1}{n!(n+2j-2j')!(2j'-n)!} \\
&\quad \times \left(\frac{\mu^2}{2} \right)^{n+j-j'} \left[(-\mathrm{i})^{2n+2j-2j'} - (\mathrm{i})^{2n+2j-2j'} \right] \\
&= \frac{\mathrm{i}}{2} \left[(-\mathrm{i})^{2j-2j'} - (\mathrm{i})^{2j-2j'} \right] F_{2j';2j} \mathrm{e}^{-\mu^2/4} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-)^n}{n!(n+2j-2j')!(2j'-n)!} \left(\frac{\mu^2}{2} \right)^{n+j-j'} \\
&= \frac{\mathrm{i}^{2j-2j'+1}}{2} \left[(-)^{2j-2j'} - 1 \right] F_{2j';2j} \mathrm{e}^{-\mu^2/4} \\
&\quad \times \sum_{n=0}^{\infty} \frac{(-)^n}{n!(n+2j-2j')!(2j'-n)!} \left(\frac{\mu^2}{2} \right)^{n+j-j'} \\
&= -\frac{1}{2} \left[1 + (-)^{2j-2j'+1} \right] (-)^{(2j-2j'+1)/2} F_{2j';2j} \mathrm{e}^{-\mu^2/4}
\end{aligned}$$

$$\times \sum_{n=0}^{2j'} \frac{(-)^n}{n!(n+2j-2j')!(2j'-n)!} \left(\frac{\mu^2}{2}\right)^{n+j-j'}$$

$$= -\frac{1}{2}\left[1+(-)^{2j-2j'+1}\right](-)^{(2j-2j'+1)/2} F_{2j';2j} \times A(\mu;-1/4) B_{2j';2j}(\mu;-1) \tag{33}$$

for $2j' \leqslant 2j$. In the final expression we have made use of the definitions (26c) and (28d) and taken cognizance of the fact that the matrix is real and symmetric. Notice that the rule for the conservation of parity is an inherent property of this result.

In a similar manner it is found that for $2j' \leqslant 2j$

$$\begin{aligned}\langle 2j' | \cos(\mu q) | 2j \rangle &= \frac{1}{2}\langle 2j' | \mathrm{e}^{-\mathrm{i}\mu q} + \mathrm{e}^{\mathrm{i}\mu q} | 2j \rangle \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right](-)^{(2j-2j')/2} \\ &\quad \times F_{2j';2j} A(\mu;-1/4) B_{2j';2j}(\mu;-1),\end{aligned} \tag{34}$$

$$\begin{aligned}\langle 2j' | \sinh(\mu q) | 2j \rangle &= \frac{1}{2}\langle 2j' | \mathrm{e}^{\mu q} - \mathrm{e}^{-\mu q} | 2j \rangle \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right] F_{2j';2j} A(\mu;1/4) B_{2j';2j}(\mu;+1) \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right]\langle 2j' | \mathrm{e}^{\mu q} | 2j \rangle,\end{aligned} \tag{35}$$

$$\begin{aligned}\langle 2j' | \cosh(\mu q) | 2j \rangle &= \frac{1}{2}\langle 2j' | \mathrm{e}^{\mu q} + \mathrm{e}^{-\mu q} | 2j \rangle \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right] F_{2j';2j} A(\mu;1/4) B_{2j';2j}(\mu;+1) \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right]\langle 2j' | \mathrm{e}^{\mu q} | 2j \rangle.\end{aligned} \tag{36}$$

The first factors in these equations reflect the parity restriction of these matrix elements. Casting them in terms of A and B shows how closely they are related to each other, a particularly simplifying feature when programming them.

The successive differentiation of equations (33) through (36) with respect to μ gives the relations

$$\begin{aligned}\langle 2j' | q^{2k} \sin(\mu q) | 2j \rangle &= (-)^k \frac{\mathrm{d}^{2k}}{\mathrm{d}\mu^{2k}} \langle 2j' | \sin(\mu q) | 2j \rangle \\ &= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right](-)^{(2j-2j'+1)/2}(-)^{k+1} F_{2j';2j} \\ &\quad \times \sum_{\kappa=0}^{2k} \binom{2k}{\kappa} A^{(\kappa)}(\mu;-1/4) B^{(2k-\kappa)}_{2j';2j}(\mu;-1),\end{aligned} \tag{37a}$$

$$\begin{aligned}\left\langle 2j'\middle|q^{2k-1}\sin(\mu q)\middle|2j\right\rangle &= (-)^k\frac{\mathrm{d}^{2k-1}}{\mathrm{d}\mu^{2k-1}}\left\langle 2j'\middle|\cos(\mu q)\middle|2j\right\rangle\\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right](-)^{(2j-2j')/2}(-)^k F_{2j';2j}\\ &\quad\times\sum_{\kappa=0}^{2k-1}\binom{2k-1}{\kappa}A^{(\kappa)}(\mu;-1/4)B_{2j';2j}^{(2k-\kappa-1)}(\mu;-1),\end{aligned}\tag{37b}$$

$$\begin{aligned}]\left\langle 2j'\middle|q^{2k}\cos(\mu q)\middle|2j\right\rangle &= (-)^k\frac{\mathrm{d}^{2k}}{\mathrm{d}\mu^{2k}}\left\langle 2j'\middle|\cos(\mu q)\middle|2j\right\rangle\\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right](-)^{(2j-2j')/2}(-)^k F_{2j';2j}\\ &\quad\times\sum_{\kappa=0}^{2k}\binom{2k}{\kappa}A^{(\kappa)}(\mu;-1/4)B_{2j';2j}^{(2k-\kappa)}(\mu;-1),\end{aligned}\tag{38a}$$

$$\begin{aligned}\left\langle 2j'\middle|q^{2k-1}\cos(\mu q)\middle|2j\right\rangle &= (-)^{k+1}\frac{\mathrm{d}^{2k-1}}{\mathrm{d}\mu^{2k-1}}\left\langle 2j'\middle|\sin(\mu q)\middle|2j\right\rangle\\ &= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right](-)^{(2j-2j'+1)/2}(-)^k F_{2j';2j}\\ &\quad\times\sum_{\kappa=0}^{2k-1}\binom{2k-1}{\kappa}A^{(\kappa)}(\mu;-1/4)B_{2j';2j}^{(2k-\kappa-1)}(\mu;-1),\end{aligned}\tag{38b}$$

$$\begin{aligned}\left\langle 2j'\middle|q^{2k}\sinh(\mu q)\middle|2j\right\rangle &= \frac{\mathrm{d}^{2k}}{\mathrm{d}\mu^{2k}}\left\langle 2j'\middle|\sinh(\mu q)\middle|2j\right\rangle\\ &= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right]F_{2j';2j}\\ &\quad\times\sum_{\kappa=0}^{2k}\binom{2k}{\kappa}A^{(\kappa)}(\mu;1/4)B_{2j';2j}^{(2k-\kappa)}(\mu;+1),\end{aligned}\tag{39a}$$

$$\begin{aligned}\left\langle 2j'\middle|q^{2k-1}\sinh(\mu q)\middle|2j\right\rangle &= \frac{\mathrm{d}^{2k-1}}{\mathrm{d}\mu^{2k-1}}\left\langle 2j'\middle|\cosh(\mu q)\middle|2j\right\rangle\\ &= \frac{1}{2}\left[1+(-)^{2j-2j'}\right]F_{2j';2j}\\ &\quad\times\sum_{\kappa=0}^{2k-1}\binom{2k-1}{\kappa}A^{(\kappa)}(\mu;1/4)B_{2j';2j}^{(2k-\kappa-1)}(\mu;+1),\end{aligned}\tag{39b}$$

$$\langle 2j'|q^{2k}\cosh(\mu q)|2j\rangle = \frac{\mathrm{d}^{2k}}{\mathrm{d}\mu^{2k}}\langle 2j'|\cosh(\mu q)|2j\rangle$$
$$= \frac{1}{2}\left[1+(-)^{2j-2j'}\right]F_{2j';2j}$$
$$\times \sum_{\kappa=0}^{2k}\binom{2k}{\kappa}A^{(\kappa)}(\mu;1/4)B^{(2k-\kappa)}_{2j';2j}(\mu;+1), \qquad (40a)$$

$$\langle 2j'|q^{2k-1}\cosh(\mu q)|2j\rangle = \frac{\mathrm{d}^{2k-1}}{\mathrm{d}\mu^{2k-1}}\langle 2j'|\sinh(\mu q)|2j\rangle$$
$$= \frac{1}{2}\left[1+(-)^{2j-2j'+1}\right]F_{2j';2j}$$
$$\times \sum_{\kappa=0}^{2k-1}\binom{2k-1}{\kappa}A^{(\kappa)}(\mu;1/4)B^{(2k-\kappa-1)}_{2j';2j}(\mu;+1), \qquad (40b)$$

in which $k = 1, 2, 3, \ldots$. The final expressions are obtained by substituting the appropriate derivatives indicated by equations (33) through (36).

Since q commutes with itself, so do exponents of q. As a consequence, powers of the Euler formulae may be expanded in a binomial series. We have

$$\sin^l(\mu q) = \left(\frac{\mathrm{i}}{2}\right)^l\left[\mathrm{e}^{-\mathrm{i}\mu q}-\mathrm{e}^{\mathrm{i}\mu q}\right]^l$$
$$= \left(\frac{\mathrm{i}}{2}\right)^l\sum_{m=0}^{l}(-)^{l-m}\binom{l}{m}\mathrm{e}^{\mathrm{i}(l-2m)\mu q}$$
$$= \begin{cases} \dfrac{(-)^{l/2}}{2^l}\left\{2\displaystyle\sum_{m=0}^{l/2-1}(-)^m\binom{l}{m}\cos(l-2m)\mu q+(-)^{l/2}\binom{l}{l/2}\right\}, \\ \left(-\dfrac{1}{4}\right)^{(l-1)/2}\displaystyle\sum_{m=0}^{(l-1)/2}(-)^m\binom{l}{m}\sin(l-2m)\mu q, \end{cases} \qquad (41)$$

$$\cos^l(\mu q) = \left(\frac{1}{2}\right)^l\left[\mathrm{e}^{-\mathrm{i}\mu q}+\mathrm{e}^{\mathrm{i}\mu q}\right]^l = \left(\frac{1}{2}\right)^l\sum_{m=0}^{l}\binom{l}{m}\mathrm{e}^{\mathrm{i}(l-2m)\mu q}$$
$$= \begin{cases} \dfrac{1}{2^l}\left\{2\displaystyle\sum_{m=0}^{l/2-1}\binom{l}{m}\cos(l-2m)\mu q+\binom{l}{l/2}\right\}, \\ \dfrac{1}{2^{l-1}}\displaystyle\sum_{m=0}^{(l-1)/2}\binom{l}{m}\cos(l-2m)\mu q, \end{cases} \qquad (42)$$

$$\sinh^l(\mu q) = \left(-\frac{1}{2}\right)^l \left[e^{-\mu q} - e^{\mu q}\right]^l = \left(-\frac{1}{2}\right)^l \sum_{m=0}^{l} (-)^{l-m} \binom{l}{m} e^{(l-2m)\mu q}$$

$$= \begin{cases} \left(-\frac{1}{2}\right)^l \left\{2 \sum_{m=0}^{l/2-1} (-)^m \binom{l}{m} \cosh(l-2m)\mu q + (-)^{l/2} \binom{l}{l/2}\right\}, \\ \left(-\frac{1}{2}\right)^{l-1} \sum_{m=0}^{(l-1)/2} (-)^m \binom{l}{m} \sinh(l-2m)\mu q, \end{cases} \tag{43}$$

$$\cosh^l(\mu q) = \left(\frac{1}{2}\right)^l \left[e^{-\mu q} + e^{\mu q}\right]^l = \left(\frac{1}{2}\right)^l \sum_{m=0}^{l} \binom{l}{m} e^{(l-2m)\mu q}$$

$$= \begin{cases} \left(\frac{1}{2}\right)^l \left\{2 \sum_{m=0}^{l/2-1} \binom{l}{m} \cosh(l-2m)\mu q + \binom{l}{l/2}\right\}, \\ \left(\frac{1}{2}\right)^{l-1} \sum_{m=0}^{(l-1)/2} \binom{l}{m} \cosh(l-2m)\mu q. \end{cases} \tag{44}$$

The upper of these relations are for an even positive definite value of l, while the lower expressions are valid for an odd positive definite l.

Multiplying equations (41) through (44) by q^k, we find the matrix elements

$$\langle 2j'|q^k \sin^l(\mu q)|2j\rangle = \frac{1}{2}\left[1 + (-)^{2j'+k+l+2j}\right]$$

$$\times \begin{cases} \frac{(-)^{l/2}}{2^l} \left\{2 \sum_{m=0}^{l/2-1} (-)^m \binom{l}{m} \langle 2j'|q^k \cos(l-2m)\mu q|2j\rangle \right. \\ \left. \qquad + (-)^{l/2} \binom{l}{l/2} \langle 2j'|q^k|2j\rangle \right\}, \\ \left(-\frac{1}{4}\right)^{(l-1)/2} \sum_{m=0}^{(l-1)/2} (-)^m \binom{l}{m} \langle 2j'|q^k \sin(l-2m)\mu q|2j\rangle, \end{cases} \tag{41}$$

$$\langle 2j'|q^k \cos^l(\mu q)|2j\rangle = \frac{1}{2}\left[1 + (-)^{2j'+k+2j}\right]$$

$$\times \begin{cases} \frac{1}{2^l} \left\{2 \sum_{m=0}^{l/2-1} \binom{l}{m} \langle 2j'|q^k \cos(l-2m)\mu q|2j\rangle + \binom{l}{l/2} \langle 2j'|q^k|2j\rangle \right\}, \\ \frac{1}{2^{l-1}} \sum_{m=0}^{(l-1)/2} \binom{l}{m} \langle 2j'|q^k \cos(l-2m)\mu q|2j\rangle, \end{cases} \tag{42}$$

$$\langle 2j'|q^k \sinh^l(\mu q)|2j\rangle = \frac{1}{2}\left[1+(-)^{2j'+k+l+2j}\right] \times \begin{cases} \left(-\frac{1}{2}\right)^l \left\{2\sum_{m=0}^{l/2-1}(-)^m \binom{l}{m}\langle 2j'|q^k \cosh(l-2m)\mu q|2j\rangle \right. \\ \qquad \left. +(-)^{l/2}\binom{l}{l/2}\langle 2j'|q^k|2j\rangle\right\}, \\ \left(-\frac{1}{2}\right)^{l-1}\sum_{m=0}^{(l-1)/2}(-)^m\binom{l}{m}\langle 2j'|q^k \sinh(l-2m)\mu q|2j\rangle, \end{cases} \tag{43}$$

$$\langle 2j'|q^k \cosh^l(\mu q)|2j\rangle = \frac{1}{2}\left[1+(-)^{2j'+k+2j}\right] \times \begin{cases} \left(\frac{1}{2}\right)^l \left\{2\sum_{m=0}^{l/2-1}\binom{l}{m}\langle 2j'|q^k \cosh(l-2m)\mu q|2j\rangle \right. \\ \qquad \left. +\binom{l}{l/2}\langle 2j'|q^k|2j\rangle\right\}, \\ \left(\frac{1}{2}\right)^{l-1}\sum_{m=0}^{(l-1)/2}\binom{l}{m}\langle 2j'|q^k \cosh(l-2m)\mu q|2j\rangle, \end{cases} \tag{44}$$

where we have appended the appropriate parity constraints. The integrals on the right may be evaluated by equations (16) and (37) through (40). Thus, essentially the functions A and B and their derivatives determine the matrix elements of both exponential forms and these trigonometric forms.

5. The differentiation technique

For an operator O on a vector space, let us consider the commutator,

$$\left[O, f(x)\right]g(x) = O\left[f(x)g(x)\right] - f(x)\left[Og(x)\right]. \tag{45}$$

If the operator possesses the *derivation property*,

$$O\left[f(x)g(x)\right] = \left[Of(x)\right]g(x) + f(x)\left[Og(x)\right], \tag{46}$$

then equation (45) may be written as

$$\left[O, f(x)\right]g(x) = \left[Of(x)\right]g(x). \tag{47}$$

In particular, the commutation relation

$$\mathcal{O}f(x) \equiv \left[O, f(x)\right] = \left[Of(x)\right] \tag{48}$$

obtains whenever the operator O satisfies the derivation property. Repeating this process with $f(x)$ replaced by $[Of(x)]$ gives

$$\mathcal{O}^2 f(x) \equiv \big[O, [O, f(x)]\big] = \big[O^2 f(x)\big], \tag{49}$$

so that in general,

$$\mathcal{O}^n f(x) = \big[O^n f(x)\big]. \tag{50}$$

The expansion of the nested commutators on the left leads to the expression

$$\mathcal{O}^n f(x) = \big[O^n f(x)\big] = \sum_{m=0}^{n} (-)^m \binom{n}{m} O^{n-m} f(x) O^m. \tag{51}$$

In the domain of angular momentum theory Aebersold and Biedenharn [2] pointed out the necessity that the angular momentum operators possess the derivation property in order for wave functions to be considered as irreducible tensors. Indeed, we have previously used the expansion in equation (51) in this context in order to arrive at equation (10), for example.

In this section we shall look specifically at the derivative itself. Since it is related to the momentum conjugate to q, we may write equation (51) as

$$\mathrm{i}^n \mathfrak{p}^n f(q) = f^{(n)}(q) = \mathrm{i}^n \sum_{m=0}^{n} (-)^m \binom{n}{m} p^{n-m} f(q) p^m. \tag{52}$$

This equation is quite useful because it allows the evaluation of the matrix elements of the derivatives of the functions of q, viz.,

$$\big\langle 2j' \big| f^{(n)}(q) \big| 2j \big\rangle = \mathrm{i}^n \sum_{m=0}^{n} (-)^m \binom{n}{m} \big\langle 2j' \big| p^{n-m} f(q) p^m \big| 2j \big\rangle. \tag{53}$$

To evaluate this relation we first make use of equation (17) to express the integral in the binomial expansion in terms of the HOTs, i.e.,

$$\begin{aligned} &\big\langle 2j' \big| f^{(n)}(q) \big| 2j \big\rangle \\ &\quad = \Big(-\frac{\mathrm{i}}{\sqrt{2}}\Big)^n \sum_{m=0}^{n} (-)^m \binom{n}{m} \sum_{\mu'=-(n-m)/2}^{(n-m)/2} (-)^{-\mu'} \binom{n-m}{(n-m)/2 \pm \mu'}^{1/2} \\ &\qquad \times \sum_{\mu=-m/2}^{m/2} (-)^{-\mu} \binom{m}{m/2 \pm \mu}^{1/2} \big\langle 2j' \big| T_{(n-m)/2,\mu'} f(q) T_{m/2,\mu} \big| 2j \big\rangle. \end{aligned} \tag{54}$$

We then employ equation (10) to relate these HOT components in terms of the principal components and subsequently apply the turnover rule to give

$$\begin{aligned}
&\langle 2j' | f^{(n)}(q) | 2j \rangle \\
&= \left(-\frac{\mathrm{i}}{\sqrt{2}} \right)^n \sum_{m=0}^{n} (-)^m \binom{n}{m} \sum_{\mu'=-(n-m)/2}^{(n-m)/2} \frac{(-)^{(n-m)/2-2\mu'}}{[(n-m)/2-2\mu]!} \sum_{\mu=-m/2}^{m/2} \frac{(-)^{-\mu}}{(m/2-\mu)!} \\
&\times \sum_{\nu'=0}^{(n-m)/2-\mu'} (-)^{\nu'} \binom{(n-m)/2-\mu'}{\nu'} \sum_{\nu=0}^{m/2-\mu} (-)^{\nu} \binom{m/2-\mu}{\nu} \\
&\times \langle J_+^{\nu'} a^{n-m} J_+^{(n-m)/2-\mu'-\nu'}(2j') | f(q) | J_-^{m/2-\mu-\nu} (a^\dagger)^m J_-^{\nu}(2j) \rangle,
\end{aligned} \tag{55}$$

where we have inserted maximal and minimal components of the HOTs as creation and annihilation operators, respectively. We next use equations (4) to likewise express J_+ and J_- in terms of creation and annihilation operators and subsequently apply equations (2) to obtain

$$\begin{aligned}
&\langle 2j' | f^{(n)}(q) | 2j \rangle \\
&= \left(-\frac{\mathrm{i}}{2} \right)^n \sum_{m=0}^{n} (-)^m \binom{n}{m} \sum_{\mu'=-(n-m)/2}^{(n-m)/2} \frac{(-1/2)^{-\mu'}}{[(n-m)/2-2\mu]!} \left[\frac{(2j'-2\mu')!}{(2j')!} \right]^{1/2} \\
&\times \sum_{\mu=-m/2}^{m/2} \frac{(-1/2)^{-\mu}}{(m/2-\mu)!} \left[\frac{(2j)!}{(2j+2\mu)!} \right]^{1/2} \langle 2j'-2\mu' | f(q) | 2j+2\mu \rangle \\
&\times \sum_{\nu'=0}^{(n-m)/2-\mu'} (-)^{\nu'} \binom{(n-m)/2-\mu'}{\nu'} \frac{(2j'+n-m-2\mu'-2\nu')!}{(2j'-2\mu'-2\nu')!} \\
&\times \sum_{\nu=0}^{m/2-\mu} (-)^{\nu} \binom{m/2-\mu}{\nu} \frac{(2j-2\nu+m)!}{(2j-2\nu)!}.
\end{aligned} \tag{56}$$

Finally, we make the substitutions, $\mu' = I' - (n-m)/2$ and $\mu = I - m/2$ to obtain

$$\begin{aligned}
&\langle 2j' | f^{(n)}(q) | 2j \rangle \\
&= \left(\frac{1}{2\sqrt{2}} \right)^n \sum_{m=0}^{n} (-)^m \binom{n}{m} \sum_{I'=0}^{n-m} \frac{(-1/2)^{I'}}{(n-m-I')!} \left[\frac{(2j'-2I'+n-m)!}{(2j')!} \right]^{1/2} \\
&\times \sum_{I=0}^{m} \frac{(-1/2)^{I}}{(m-I)!} \left[\frac{(2j)!}{(2j+2I-m)!} \right]^{1/2} \langle 2j'-2I'+n-m | f(q) | 2j+2I-m \rangle \\
&\times \sum_{\nu'=0}^{n-m-I'} (-)^{\nu'} \binom{n-m-I'}{\nu'} \frac{(2j'+2n-2m-2I'-2\nu')!}{(2j'-2I'+n-m-2\nu')!} \\
&\times \sum_{\nu=0}^{m-I} (-)^{\nu} \binom{m-I}{\nu} \frac{(2j-2\nu+m)!}{(2j-2\nu)!}.
\end{aligned} \tag{57}$$

Previously, equation (53) has been used to determine a general expression for the matrix elements of integral powers of $1/q$ [8]. There the starting integral is that for the operator $1/q$, viz.,

$$\begin{aligned}\langle v'|q^{-1}|v\rangle &= N_{v'}N_v \int_{-\infty}^{+\infty} H_{v'}(q)H_v(q)q^{-1}\mathrm{e}^{-q^2}\,\mathrm{d}q \\ &= \frac{1}{2}\left[1+(-)^{v'+v-1}\right]N_{v'}N_v \int_{-\infty}^{+\infty} H_{v'}(q)H_v(q)q^{-1}\mathrm{e}^{-q^2}\,\mathrm{d}q \\ &= \frac{1}{2}\left[1+(-)^{v'+v-1}\right]N_{v'}N_v \sum_{m'=0}^{v'}\sum_{m=0}^{v}\frac{1}{2}\left[1+(-)^{v'+v-m'-m-1}\right] \\ &\quad\times h_{v'm'}h_{vm}\int_{-\infty}^{+\infty} q^{v'+v-m'-m-1}\mathrm{e}^{-q^2}\,\mathrm{d}q, \end{aligned} \tag{58}$$

where we have used the definitions

$$|v\rangle = N_v H_v(q)\mathrm{e}^{-q^2/2}, \tag{59}$$

in which the normalization constant is

$$N_v = \left[2^v\ v!\ \sqrt{\pi}\right]^{-1/2}, \tag{60}$$

and the $H_v(q)$ are the Hermite polynomials,

$$H_v(q) = \sum_{m=0}^{v} h_{vm}q^{v-m}, \tag{61}$$

whose scalar coefficients may be determined by analyzing their tabulations (cf. table 22.1.2 of reference [1] or equations (11)–(23) of reference [9], for example). We find that

$$h_{v0} = 2^v, \tag{62a}$$

$$h_{vm} = \mathrm{Re}\left(\mathrm{i}^m\right)2^{v-m/2}(m-1)!!\binom{v}{m}, \quad m>0, \tag{62b}$$

where Re(i^m) denotes the real part of the argument i^m. These latter two equations show that m must be an even semipositive definite integer since the Hermite polynomials are real. Integration over the symmetric interval leads to the final expression,

$$\langle v'|q^{-1}|v\rangle = \frac{1}{2}\left[1+(-)^{v'+v-1}\right]\sqrt{\frac{2}{v'!v!}} \tag{63a}$$

$$\times \sum_{m'=0}^{2[v'/2]}\sum_{m=0}^{2[v/2]}\begin{cases} 0, & (v'+v-m'-m-1)\ \text{odd}, \\ g_{v'm'}g_{vm}, & (v'+v-m'-m-1)=0, \\ (v'+v-m'-m-2)!!\,g_{v'm'}g_{vm}, & (v'+v-m'-m-1)\ \text{even}, \end{cases}$$

where the summations over m' and m are restricted to even integers. The g coefficients are defined as

$$g_{v0} = 1, \tag{63b}$$

$$g_{vm} = (-)^{m/2}(m-1)!!\binom{v}{m}, \quad m \text{ even}. \tag{63c}$$

Apart from being a relation that contains a rather large number of summations, the expression for the general derivative of a function (equation (57)) also has some subtle conditions embedded in its structure. Taken together, these features lead us to believe that the practical implementation of taking the derivative of a function to some arbitrary order is perhaps more efficiently carried out by stepwise differentiation. To illustrate the potential pitfalls, we consider the case of a simple first-order derivative.

For $n = 1$, equation (52) leads to

$$\begin{aligned} \langle v | f^{(1)}(q) | v' \rangle &= \mathrm{i}\langle v | [p, f(q)] | v' \rangle \\ &= \frac{1}{\sqrt{2}} \Big[\sqrt{v+1}\langle v+1 | f(q) | v' \rangle - \sqrt{v}\langle v-1 | f(q) | v' \rangle \\ &\quad + \sqrt{v'+1}\langle v | f(q) | v'+1 \rangle - \sqrt{v'}\langle | f(q) | v'-1 \rangle \Big], \end{aligned} \tag{64}$$

where the final result is obtained by using the inverse of equation (1) to determine p in terms of $a^\dagger$ and a, the turnover rule and equations (2). In a practical application of this formula, the matrix elements of the operator $f(q)$ have been previously prepared for the basis, say, $v = 0, 1, \ldots, v_{\max}$. Thus, the matrix representative of $f(q)$ is a matrix of dimension $v_{\max} \times v_{\max}$. However, the creation operator $a^\dagger$ in equation (64) will limit the dimension of $\langle v | f^{(1)}(q) | v' \rangle$ to a basis of size $v_{\max} - 1$, because the ket $|v_{\max} + 1\rangle$ does not exist in the previously prepared basis for $f(q)$. In order to ensure consistencies in precision, one should border the matrix of the derivative by setting the last row and column equal to zero.

Obviously, this caveat should be taken into account each time a derivative is taken, i.e., to evaluate a derivative of nth order this bordering process must be carried out in a sequential manner, thereby rendering a final matrix of $f^{(n)}(q)$ whose last n rows and columns have been set to zero. The remaining $(v_{\max} - n) \times (v_{\max} - n)$ matrix is then a precise expression of the matrix representative of $f^{(n)}(q)$.

6. Gaussian forms

The potential containing a Gaussian multiplied by a monomial may be evaluated in a direct manner. Consider the integral with a semipositive definite integer k,

$$\langle v' | q^k \mathrm{e}^{-\lambda q^2} | v \rangle = N_{v'} N_v \int_{-\infty}^{+\infty} H_{v'}(q) H_v(q) q^k \mathrm{e}^{-(\lambda+1)q^2} \, \mathrm{d}q, \tag{65}$$

for which we have the parity restriction,

$$\begin{aligned}\langle v'|q^k \mathrm{e}^{-\lambda q^2}|v\rangle &= \left[1+(-)^{v'+v+k}\right]N_{v'}N_v \\ &\quad\times \int_0^\infty H_{v'}(q)H_v(q)q^k \mathrm{e}^{-(\lambda+1)q^2}\,\mathrm{d}q \\ &= \left[1+(-)^{v'+v+k}\right]\frac{1}{\sqrt{\pi}}\frac{1}{2^{(v'+v)/2}}\sqrt{\frac{1}{v'!v!}}\sum_{m'=0}^{2[v'/2]}\sum_{m=0}^{2[v/2]} g_{v'm'}g_{vm} \\ &\quad\times 2^{v'+v-(m'+m)/2}\int_0^\infty q^{v'+v-m'-m+k}\mathrm{e}^{-(\lambda+1)q^2}\,\mathrm{d}q,\end{aligned}$$

$$\begin{aligned}\langle v'|q^k \mathrm{e}^{-\lambda q^2}|v\rangle &= \frac{1}{2}\left[1+(-)^{v'+v+k}\right]\sqrt{\frac{1}{2^k v'!v!}} \\ &\quad\times\sum_{m'=0}^{2[v'/2]}\sum_{m=0}^{2[v/2]}\begin{cases}0, \\ g_{v'm'}g_{vm}/\sqrt{\lambda+1}, \\ g_{v'm'}g_{vm}\frac{(v'+v-m'-m+k-1)!!}{(\lambda+1)^{(v'+v-m'-m+k+1)/2}}.\end{cases}\end{aligned} \tag{66}$$

From top to bottom the equalities of equation (66) are for odd, zero and even values of $v'+v-m'-m+k$, respectively. Also the summations over m' and m are carried out in steps of two. To arrive at the final result, use has been made of equations (60)–(63).

7. Summary

There is an increasing literature concerning the evaluation of matrix elements of vibrational operators, stimulated by ongoing studies of the many potentials proffered to better understand the nuclear motion in molecules, be they flexible, non-rigid or floppy in character. Here we have shown that various techniques may be used to facilitate the determination of generalized forms of many such operators. A computer program has been written to evaluate the matrix representatives of all the operators considered in this work and will be published elsewhere.

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