Journal of Mathematical Chemistry 17 (1995) 395–399

A general expression for matrix elements of reciprocal powers of the displacement coordinate q in the harmonic oscillator basis

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Received 27 February 1995

A formula is derived that allows one to determine the matrix elements of an arbitrary integral reciprocal power of the dimensionless displacement coordinate q of the harmonic oscillator from those of q^{-1} in an exact manner. This relation is obtained from the use of the chain rule and irreducible tensors expressed in terms of the creation and annihilation operators of the harmonic oscillator.

To evaluate matrix elements of reciprocal powers of q, the dimensionless displacement coordinate, in the harmonic oscillator basis, it has been rather common in the past to use the back-transformation method resulting from the Hamilton–Cayley theorem [1,2]. Since the harmonic oscillator basis is infinite, this technique is at best approximate, its accuracy depending upon the size of the basis chosen. Here we show how this difficulty may be sidestepped, presenting a way to calculate these matrix elements exactly for an arbitrary inverse power of q.

Given that the matrix elements of q^{-1} may be calculated without difficulty we initiate this procedure by determining them in a brute-force manner. The harmonic oscillator wave functions (or Hermite orthogonal functions) are written as

$$|v\rangle = N_v H_v(q) e^{-q^2/2}\,, \tag{1}$$

where the normalization constant is

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

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

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$$H_v(q) = \sum_{m=0}^{v} h_{vm} q^{v-m} , \tag{3}$$

whose scalar coefficients may be determined by analyzing their tabulations (cf. table 22.1.2 of ref. [3] or eqs. (11)–(23) of ref. [4], for example). We find that

$$h_{vm} = \mathrm{Re}(i^m) 2^{v-m/2} (m-1)!! \binom{v}{m} , \tag{4}$$

where $\mathrm{Re}(i^m)$ denotes the real part of the argument i^m. The desired integral is then easily evaluated:

$$\begin{aligned}
\langle v'|q^{-1}|v\rangle &= N_{v'}N_v \int_{-\infty}^{+\infty} H_{v'}(q)H_v(q)q^{-1}e^{-q^2}dq \\
&= N_{v'}N_v[1+(-)^{v'+v-1}] \int_{-\infty}^{+\infty} H_{v'}(q)H_v(q)q^{-1}e^{-q^2}\, dq \\
&= N_{v'}N_v[1+(-)^{v'+v-1}] \sum_{m'=0}^{v'}\sum_{m=0}^{v} h_{v'm'}h_{vm} \int_0^{\infty} q^{v'+v-m'-m-1}e^{-q^2}\, dq \\
&= \sqrt{\pi}N_{v'}N_v[1+(-)^{v'+v-1}] \sum_{m'=0}^{v'}\sum_{m=0}^{v} h_{v'm'}h_{vm} \frac{(v'+v-m'-m-2)!!}{2^{(v'+v-m'-m+1)/2}} .
\end{aligned} \tag{5}$$

The final form is obtained by eq. (7.4.4) of ref. [3]. The factor immediately following the product of normalization constants is a consequence of parity symmetry. For a general discussion of the symmetry of the harmonic oscillator, see ref. [5].

The next step is to take cognizance of the commutation relation

$$\frac{1}{q^{n+1}} = -\frac{i}{n}\left[p, \frac{1}{q^n}\right] , \tag{6}$$

which arises from the chain rule. Here $p\ (= -i\ d/dq)$ is the momentum conjugate to q. At this juncture it is worthwhile noting that, by starting with $n=1$, one may take matrix elements of both sides of this equation and bootstrap one's way up to the desired reciprocal power of q. Computationally, however, it may prove more convenient to take a direct approach.

Using eq. (6) to successively substitute for the reciprocal power of q in the commutator, we find that at the kth substitution

$$\frac{1}{q^{n+1}} = \frac{(-i)^k(n-k)!}{n!} \mathcal{P}^k \frac{1}{q^{n-k+1}} , \tag{7}$$

where $\mathcal{P}^k$ represents the nested commutation of p with its argument, and k is the depth of the nesting. For $k = n$, eq. (7) becomes

$$\frac{1}{q^{n+1}} = \frac{(-i)^n}{n!}\mathcal{P}^n \frac{1}{q}\,, \tag{8}$$

which in effect evinces the possibility that the matrix elements of the higher reciprocal powers of q may be expressed in terms of those of q^{-1}. To proceed further we note that the nested commutator may be expanded in a binomial series:

$$\frac{1}{q^{n+1}} = \frac{(-i)^n}{n!}\sum_{l=0}^{n}(-)^l\binom{n}{l}p^{n-l}\left(\frac{1}{q}\right)p^l\,, \tag{9}$$

so that the matrix elements we seek are expressible as

$$\langle v'|q^{-n-1}|v\rangle = \frac{(-i)^n}{n!}\frac{[1+(-)^{v'+v-n-1}]}{2} \times \sum_{l=0}^{n}(-)^l\binom{n}{l}\langle p^{n-l}v'|q^{-1}|p^l v\rangle\,. \tag{10}$$

Notice that in the prefactor of the sum we have taken into consideration the parity of the integral on the left. Also in the matrix element on the right we have applied the turnover rule while acknowledging the Hermiticity of p.

In ref. [6] it was shown that one may express powers of the conjugate momentum p in terms of irreducible tensors, viz.,

$$p^l = \left(\frac{1}{\sqrt{2}}\right)^l \sum_{m=-l/2}^{l/2}(-)^{l-m}\binom{l}{l/2\pm m}^{1/2} T_{l/2,m}\,, \tag{11}$$

with the irreducible tensors defined in terms of the creation and annihilation operators of the harmonic oscillator, i.e.,

$$T_{l/2,m} = \binom{l}{l/2\pm m}^{1/2}\sum_{\alpha=0}^{l/2-|m|}\frac{\alpha!}{2^\alpha}\binom{l/2+m}{\alpha}\binom{l/2-m}{\alpha}\cdot \times (a^\dagger)^{l/2+m-\alpha}a^{l/2-m-\alpha}\,. \tag{12}$$

The replacement of the tensor in eq. (11) by (12) then gives

$$p^l = \left(\frac{1}{\sqrt{2}}\right)^l \sum_{m=-l/2}^{l/2}(-)^{l-m}\binom{l}{l/2\pm m}\sum_{\alpha=0}^{l/2-|m|}\frac{\alpha!}{2^\alpha}\binom{l/2+m}{\alpha}\binom{l/2-m}{\alpha}\cdot \times (a^\dagger)^{l/2+m-\alpha}a^{l/2-m-\alpha}\,. \tag{13}$$

Since the action of powers of the creation and annihilation operators on a ket gives

$$a^m|v\rangle = \sqrt{\frac{v!}{(v-m)!}}|v-m\rangle \quad \text{and} \quad (a^\dagger)^m|v\rangle = \sqrt{\frac{(v+m)!}{v!}}|v+m\rangle\,, \tag{14}$$

the action of p^l on the ket $|v\rangle$ is

$$p^l|v\rangle = \sqrt{\frac{v!}{2^l}} \sum_{m=-l/2}^{l/2} (-)^{l-m} \binom{l}{l/2 \pm m} \frac{\sqrt{(v+2m)!}}{(v-l/2+m)!} |v+2m\rangle \times \sum_{\alpha=0}^{l/2-|m|} \frac{1}{2^\alpha} \binom{l/2+m}{\alpha} \binom{l/2-m}{\alpha} \binom{v-l/2+m}{\alpha}^{-1} . \tag{15}$$

Consequently, the substitution of this expression into eq. (10) yields

$$\begin{aligned}\langle v'|q^{-n-1}|v\rangle = {} & \frac{(-i)^n}{n!} \frac{[1+(-)^{v'+v-n-1}]}{2} \sqrt{\frac{v'!v!}{2^n}} \sum_{l=0}^{n} (-)^l \binom{n}{l} \\ & \times \sum_{m'=-(n-l)/2}^{(n-l)/2} \frac{\sqrt{(v'+2m')!}}{[v'-(n-l)/2+m']!} \binom{n-l}{(n-l)/2 \pm m'} \\ & \times \sum_{m=-l/2}^{l/2} \frac{(-)^{n+m'-m}\sqrt{(v+2m)!}}{(v-l/2+m)!} \binom{l}{l/2 \pm m} \langle v'+2m'|q^{-1}|v+2m\rangle \\ & \times \sum_{\alpha'=0}^{(n-l)/2-|m'|} \frac{1}{2^{\alpha'}} \binom{(n-l)/2+m'}{\alpha'} \binom{(n-l)/2-m'}{\alpha'} \\ & \times \binom{v'-(n-l)/2+m'}{\alpha'}^{-1} \\ & \times \sum_{\alpha=0}^{l/2-|m|} \frac{1}{2^\alpha} \binom{l/2+m}{\alpha} \binom{l/2-m}{\alpha} \binom{v-l/2+m}{\alpha}^{-1} ,\end{aligned} \tag{16}$$

where the matrix elements of q^{-1} are given by eq. (5). In arriving at this final form one must exercise a little caution. When substituting for the action of p^{n-l} on the v' in the bra it should be noticed that, while n and l are integers, m' is half-integral. Hence when the phase factor is removed from the bra, the sign of m' changes. The above result is being incorporated into an existing program that calculates a variety of potentials in the harmonic oscillator basis [7].

Acknowledgements

The authors take pleasure in expressing their gratitude to Professor Ying Nan Chiu for his constant moral encouragement. This work was supported by the Chiu Nien-Tai / Liang Yun-Dan Fund and the Chiu Feng-Chia Research Fund.

References

[1] G. Stephenson, *An Introduction to Matrices, Sets and Groups for Sciences Students* (Dover, New York, 1986).
[2] D.F. Zetik and F.A. Matsen, J. Mol. Spec. 24 (1967) 122.
[3] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables* (Dover, New York, 1965).
[4] L. Pauling and E.B. Wilson Jr., *Introduction to Quantum Mechanics with Applications to Chemistry* (Dover, New York, 1935).
[5] P. Palting, Int. J. Quant. Chem. 46 (1993) 257.
[6] P. Palting, Int. J. Quant. Chem. 40 (1991) 457.
[7] S.-T. Lai, P. Palting and Y.-N. Chiu, Computer Phys. Comm. 82 (1994) 221.