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# Matrix elements of $p^k$ in the Morse oscillator basis

Małgorzata Bancewicz
Instytut Fizyki, Politechnika Poznańska, Piotrowo 3, 60-965 Poznań, Poland

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**Abstract.** Formulae for the matrix elements of $p^k$ in the Morse oscillator basis are derived in the $p$-representation. Explicit expressions are given for $k = 1, 2, 3$ and 4.

## 1. Introduction

In 1929 Morse proposed a model potential to describe the vibrational levels of diatomic molecules [1]. Since then this potential, known as the Morse potential, has proved useful for a wide variety of spectroscopic problems. Some matrix elements for Morse states have been studied by several authors [2–5]. For powers of momentum $p$, one can find in the literature expressions for the $k = 1$ and $k = 2$ matrix elements [6]. The authors used these for calculating eigenvalues of the rotation–vibration Hamiltonian for symmetric-triangular $X_3$ molecules. Recently, the evaluation of diagonal matrix elements of powers of momentum appeared to be necessary in the calculations of moments of the density distribution of vibrational levels [7]. Vibrational spectra composed of many densely packed energy levels are uniquely suited to being described by statistical methods. When the number of levels is very large, then some information about the general shape of the spectrum is required rather than its detailed structure and very often this is only possible. However, even in systems where the individual levels and their quantum descriptions are known, statistical methods are of interest because they reveal new features of the system and are helpful for a more complete understanding. Having obtained analytical expressions for moments, one can investigate how the density of vibrational levels depends on coupling between bonds and on the molecular structure.

In this work formulae for the matrix elements of powers of momentum in the Morse oscillator basis are derived. Calculations are performed in the momentum representation. This method allows one to obtain simple analytical expressions for the matrix elements, both in the diagonal and off-diagonal cases.

The paper is organized as follows. In section 2 the Morse eigenfunctions in the momentum representation are obtained. Then, in section 3, expressions for the matrix elements of powers of momentum are derived. Relevant formulae which allow us to evaluate all integrals and sums found in the expressions for the matrix elements are collected in the appendix.

## 2. Morse eigenfunctions in the $p$-representation

The Morse potential has the form

$$V(r) = D\exp[-2\alpha(r - r_e)] - 2D\exp[-\alpha(r - r_e)] \tag{1}$$

  

where $D$ is the bond energy and $\alpha$ is the anharmonicity constant.

The eigenfunctions of the discrete states of the Morse potential, $\psi_n(r)$, are given as

$$\psi_n(r) = N_n \exp\left[-\frac{z}{2}\right] z^{b_n/2} L_n^{b_n}(z) \tag{2}$$

where

$$N_n = \left(\frac{\alpha b_n n!}{\Gamma(b_n + n + 1)}\right)^{1/2} \tag{3}$$

$$z = 2\beta \exp[-\alpha(r - r_e)] \tag{4}$$

$$b_n = 2\beta - 2n - 1 \tag{5}$$

$$\beta = \frac{1}{\alpha\hbar}\sqrt{2\mu D} \tag{6}$$

and where $\mu$ is the reduced mass of the bond. The generalized Laguerre polynomial $L_n^{b_n}(z)$ in equation (2) can be given by [8]

$$L_n^{b_n}(z) = \sum_{l=0}^{n} \binom{n + b_n}{n - l} \frac{(-z)^l}{l!}. \tag{7}$$

A suitable representation for calculation of the matrix elements of momentum $p$ is the $p$-representation. The action of the momentum operator on a function in the $p$-representation reduces to a multiplication by $p$. In order to find the Morse eigenfunction in the $p$-representation, $\psi(p)$, one has to calculate the Fourier transform of the eigenfunction $\psi(r)$. For the $n$th eigenfunction we have [9]

$$\psi_n(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ip(r-r_e)/\hbar} \psi_n(r)\, dr. \tag{8}$$

From equation (4) one easily finds $r - r_e = (\ln 2\beta)/\alpha - (\ln z)/\alpha$ and $dr = -dz/\alpha z$. With these, equation (8) can also be written as

$$\psi_n(p) = \frac{(2\beta)^{-ip/\hbar\alpha}}{\sqrt{2\pi\hbar}\alpha} N_n \int_0^{\infty} e^{-z/2} z^{(ip/\hbar\alpha)+(b_n/2)-1} L_n^{b_n}(z) dz. \tag{9}$$

After substitution of the Laguerre polynomial, (9) becomes

$$\psi_n(p) = \frac{(2\beta)^{-ip/\hbar\alpha}}{\sqrt{2\pi\hbar}\alpha} N_n \sum_{l=0}^{n} \binom{n + b_n}{n - l} \frac{(-1)^l}{l!} \int_0^{\infty} e^{-z/2} z^{(ip/\hbar\alpha)+(b_n/2)+l-1}\, dz. \tag{10}$$

The integral in equation (10) is an integral representation of the gamma function

$$\int_0^{\infty} e^{-z/2} z^{(ip/\hbar\alpha)+(b_n/2)+l-1}\, dz = 2^{(ip/\hbar\alpha)+(b_n/2)+l}\, \Gamma\left(\frac{ip}{\hbar\alpha} + \frac{b_n}{2} + l\right). \tag{11}$$

Finally, we get

$$\psi_n(p) = \frac{2^{(b_n/2)-\frac{1}{2}}}{\sqrt{\pi\hbar}\beta^{(ip/\hbar\alpha)}\alpha} N_n \sum_{l=0}^{n} \frac{(-1)^l}{l!} \binom{n + b_n}{n - l} 2^l\, \Gamma\left(\frac{ip}{\hbar\alpha} + \frac{b_n}{2} + l\right). \tag{12}$$

## 3. Matrix elements of $p^k$

In order to give, in the $p$-representation, formulae for the matrix elements, $\langle m|p^k|n\rangle$, of powers of momentum in the Morse oscillator basis one has to calculate the integrals

$$\langle m|p^k|n\rangle = \int_{-\infty}^{\infty} \psi_m(p)^* p^k \psi_n(p)\, dp. \tag{13}$$

For any value of $k$, calculations of these integrals reduce to performing several summations.

### 3.1. Diagonal matrix elements

At first let us note a property of the momentum operator. Generally each power of the $p$ operator is Hermitian. In the coordinate representation in the basis of real functions, matrix elements of odd powers of $p$ are imaginary. Consequently, diagonal matrix elements of odd powers of $p$ must be zero. Of course, the Morse functions obey this rule and

$$\langle n|p^l|n\rangle = 0 \qquad l = 1, 3, 5, \ldots. \tag{14}$$

In the case of the matrix element of the square of momentum one has to evaluate

$$\langle n|p^2|n\rangle = \frac{2^{b_n-1}}{\pi\hbar\alpha^2}N_n^2\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l}2^{l'+l} \times\int_{-\infty}^{\infty}\Gamma\left(\frac{-\mathrm{i}p}{\hbar\alpha}+\frac{b_n}{2}+l'\right)p^2\Gamma\left(\frac{\mathrm{i}p}{\hbar\alpha}+\frac{b_n}{2}+l\right)\mathrm{d}p. \tag{15}$$

From equations (A1) and (A5) of the appendix we obtain

$$\langle n|p^2|n\rangle = \frac{\hbar^2\alpha}{4}N_n^2\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l} \times(b_n+2l'-2l'^2+2l'l)\Gamma(b_n+l'+l). \tag{16}$$

This formula can be further simplified if one notes that according to equations (A8)–(A13) we have

$$\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l}ll'\Gamma(b_n+l'+l) = \frac{n\Gamma(b_n+n+1)}{n!} \tag{17}$$

$$\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l}\Gamma(b_n+l'+l) = \frac{\Gamma(b_n+n+1)}{b_n n!} \tag{18}$$

$$\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l}l'\Gamma(b_n+l'+l) = 0 \tag{19}$$

$$\sum_{l'=0}^{n}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{n+b_n}{n-l'}\binom{n+b_n}{n-l}l'^2\Gamma(b_n+l'+l) = 0. \tag{20}$$

Substituting these results into (16) and taking into account equations (3) and (6) one gets

$$\langle n|p^2|n\rangle = \frac{D\mu}{2\beta^2}(2n+1)b_n. \tag{21}$$

In principle, for any even value of $k$, this procedure can be repeated to give the corresponding matrix element, but as $k$ increases, the complexity of the procedure also increases. The matrix element of the fourth power of momentum derived in this way is as follows

$$\langle n|p^4|n\rangle = \frac{D^2\mu^2}{4\beta^4}(4n^3+6b_nn^2+6n^2+6b_nn+6n+3b_n+2)b_n. \tag{22}$$

### 3.2. Off-diagonal matrix elements

The linear matrix element can be calculated as follows

$$\langle m|p|n\rangle = \frac{2^{(b_m/2)+(b_n/2)-1}}{\pi\hbar\alpha^2}N_mN_n\sum_{l'=0}^{m}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{m+b_m}{m-l'}\binom{n+b_n}{n-l}2^{l'+l} \times\int_{-\infty}^{\infty}\Gamma\left(\frac{-\mathrm{i}p}{\hbar\alpha}+\frac{b_m}{2}+l'\right)p\Gamma\left(\frac{\mathrm{i}p}{\hbar\alpha}+\frac{b_n}{2}+l\right)\mathrm{d}p. \tag{23}$$

Since

$$\langle m|p^k|n\rangle = (-1)^k \langle n|p^k|m\rangle \tag{24}$$

we assume $m > n$ for convenience. Then taking into account equations (A1) and (A4) we obtain

$$\langle m|p|n\rangle = \frac{-\mathrm{i}\hbar}{2} N_m N_n \sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} \times \left(\frac{b_m}{2}+l'\right) \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right). \tag{25}$$

As before, according to (A8), (A9), (A13) and (5) we have

$$\sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} l' \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right) = (-1)^{m-n} \frac{\Gamma(b_m+m+1)}{n!} \tag{26}$$

$$\sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right) = 0. \tag{27}$$

Using these results and equations (3), (5) and (6) one easily finds

$$\langle m|p|n\rangle = (-1)^{m-n-1}\, \mathrm{i} \left(\frac{b_m b_n m!\Gamma(2\beta-m)}{2\beta^2 n!\Gamma(2\beta-n)} \mu D\right)^{1/2} \qquad m > n. \tag{28}$$

The second-order matrix element ($k = 2$) can be calculated in a similar way. Taking into account (A1) and (A5) we have

$$\langle m|p^2|n\rangle = \frac{\hbar^2\alpha}{16} N_m N_n \sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} \times [b_m(2-b_m+b_n) + 4(1+b_n-b_m)l' - 4l'^2 + 8l'l] \times \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right). \tag{29}$$

Now, in order to find simple analytical expressions for the second-order matrix element one has to evaluate another two sums. After some algebraic manipulations and simplifications we obtain from equations (A10)–(A14) and (5)

$$\sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} l'^2 \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right) = (-1)^{m-n} \frac{(b_n^2-4b_m-b_m^2)}{4n!} \Gamma(b_m+m+1) \tag{30}$$

$$\sum_{l'=0}^{m} \sum_{l=0}^{n} \frac{(-1)^{l'+l}}{l'!l!} \binom{m+b_m}{m-l'} \binom{n+b_n}{n-l} l' l \Gamma\left(\frac{b_m}{2}+\frac{b_n}{2}+l'+l\right) = (-1)^{m-n-1} \left[\frac{\Gamma(b_n+n+1)}{(m-1)!} - \frac{\Gamma(b_m+m+1)}{(n-1)!}\right]. \tag{31}$$

After substituting these results and equations (3), (5) and (6) back into (29) the second-order matrix element becomes

$$\langle m|p^2|n\rangle = (-1)^{m-n} \left(\frac{b_m b_n m!\Gamma(2\beta-m)}{4\beta^4 n!\Gamma(2\beta-n)} \mu^2 D^2\right)^{1/2} \times [(m-n)(m+n+1) + 2\beta(1+n-m)] \qquad m > n. \tag{32}$$

In equation (32) the term involving $\Gamma(b_n + n + 1)/(m - 1)!$ has been omitted since it corresponds to the case when $n > m$.

For higher-order matrix elements the calculations are similar. However, with an increase of order the calculations leading to simple analytical formulae are more and more complicated. Nevertheless, expressions involving two sums with a certain number of terms can be used in all cases. The application of the same techniques to the third-order matrix element results in

$$\langle m|p^3|n\rangle = (-1)^{m-n}\,\mathrm{i}\left(\frac{b_m b_n m!\Gamma(2\beta - m)}{32\beta^6 n!\Gamma(2\beta - n)}\mu^3 D^3\right)^{1/2}$$
$$\times[m(1+m)(4+m+m^2) + n(1+n)(4+n+n^2) - 2m(1+m)n(1+n)$$
$$+2 + 2\beta(m+n+1)(-4+3m-2m^2-3n-2n^2+4mn)$$
$$+4\beta^2(1-m+n)(2-m+n)] \qquad m > n. \tag{33}$$

To calculate the matrix elements of $p^k$ in the coordinate representation, it is very convenient to start from the relations

$$(E_m - E_n)\langle m|p|n\rangle = \langle m|[H, p]|n\rangle = -\mathrm{i}\hbar\left\langle m\left|\frac{\mathrm{d}V}{\mathrm{d}r}\right|n\right\rangle = \mathrm{i}\hbar D\alpha\beta^{-2}\left\langle m\left|\frac{z^2}{2} - \beta z\right|n\right\rangle \tag{34}$$

$$p^2 = 2\mu[H - V(r)]. \tag{35}$$

However, with an increase in $k$ the corresponding derivations, especially for odd $k$ values, become cumbersome.

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## Appendix

Calculations of the integrals related to the gamma functions can be performed by the method described by Marichev [10]. Accordingly

$$\int_{-\infty}^{\infty}\Gamma(a+\mathrm{i}x)\Gamma(a'-\mathrm{i}x)x^k\,\mathrm{d}x = (-1)^k\frac{2\pi}{\mathrm{i}^k}\Gamma(a+a')\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(a+a')_n(a+n)^k$$
$$= \frac{2\pi}{\mathrm{i}^k}\Gamma(a+a')\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(a+a')_n(a'+n)^k. \tag{A1}$$

The sums in this equation evaluated with the help of the *Mathematica* system are as follows [11],

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(a+a')_n(a+n)^k = 2^{-a-a'}A_k \tag{A2}$$

where

$$A_0 = 1 \tag{A3}$$
$$A_1 = \tfrac{1}{2}(a'-a) \tag{A4}$$
$$A_2 = -\tfrac{1}{4}(a+a') + \tfrac{1}{4}(a-a')^2 \tag{A5}$$
$$A_3 = \tfrac{3}{8}(a'^2-a^2) + \tfrac{1}{8}(a-a')^3 \tag{A6}$$
$$A_4 = \tfrac{1}{8}(a+a') - \tfrac{3}{8}(a+a')(a'-a)^2 + \tfrac{3}{16}(a+a')^2 + \tfrac{1}{16}(a-a')^4. \tag{A7}$$

The sums appearing in the formulae for the matrix elements of powers of momentum ($k = 1, 2, 3$) can be obtained by using the *Mathematica* system and read [11]

$$\sum_{l'=0}^{m}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{m+b'}{m-l'}\binom{n+b}{n-l}\Gamma\left(\frac{b'}{2}+\frac{b}{2}+l'+l\right)$$
$$=\frac{(b'+1)_m\Gamma((b'/2)+(b/2))((b/2)-(b'/2)+1)_n}{m!n!}$$
$$\times{}_3F_2\left(\frac{b'}{2}-\frac{b}{2},\frac{b'}{2}+\frac{b}{2},-m;b'+1,\frac{b'}{2}-\frac{b}{2}-n;1\right) \tag{A8}$$

$$\sum_{l'=0}^{m}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{m+b'}{m-l'}\binom{n+b}{n-l}l'\Gamma\left(\frac{b'}{2}+\frac{b}{2}+l'+l\right)$$
$$=\frac{-\Gamma((b'/2)+(b/2)+1)(b'+2)_{m-1}((b/2)-(b'/2))_n}{(m-1)!n!}$$
$$\times{}_3F_2\left(\frac{b'}{2}-\frac{b}{2}+1,\frac{b'}{2}+\frac{b}{2}+1,1-m;b'+2,\frac{b'}{2}-\frac{b}{2}-n+1;1\right) \tag{A9}$$

$$\sum_{l'=0}^{m}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{m+b'}{m-l'}\binom{n+b}{n-l}l'l\Gamma\left(\frac{b'}{2}+\frac{b}{2}+l'+l\right)$$
$$=\frac{\Gamma((b'/2)+(b/2)+2)(b'+2)_{m-1}((b/2)-(b'/2))_{n-1}}{(m-1)!(n-1)!}$$
$$\times{}_3F_2\left(\frac{b'}{2}-\frac{b}{2}+1,\frac{b'}{2}+\frac{b}{2}+2,1-m;b'+2,\frac{b'}{2}-\frac{b}{2}-n+2;1\right) \tag{A10}$$

$$\sum_{l'=0}^{m}\sum_{l=0}^{n}\frac{(-1)^{l'+l}}{l'!l!}\binom{m+b'}{m-l'}\binom{n+b}{n-l}l'^2\Gamma\left(\frac{b'}{2}+\frac{b}{2}+l'+l\right)$$
$$=\frac{-\Gamma((b'/2)+(b/2)+1)(b'+3)_{m-2}((b/2)-(b'/2))_{n-1}}{4(m-1)!(n-1)!}$$
$$\times\left[2(b'+2)(b-b'+2n-2)\times{}_3F_2\left(\frac{b'}{2}-\frac{b}{2}+1,\frac{b'}{2}+\frac{b}{2}+1,1-m;b'\right.\right.$$
$$\left.+2,\frac{b'}{2}-\frac{b}{2}-n+1;1\right)+(2-b'-b)(2+b-b')(m-1)$$
$$\left.\times{}_3F_2\left(\frac{b'}{2}-\frac{b}{2}+2,\frac{b'}{2}+\frac{b}{2}+2,2-m;b'+3,\frac{b'}{2}-\frac{b}{2}-n+2;1\right)\right]. \tag{A11}$$

The confluent hypergeometric function ${}_3F_2$ in these equations is defined by [8]

$$ {}_3F_2(a,b,c;d,e;1)=\sum_{i=0}^{\infty}\frac{(a)_i(b)_i(c)_i}{(d)_i(e)_i i!}. \tag{A12}$$

If one of the parameters in the numerator is equal to another one in the denominator then this function reduces to [8]

$$ {}_2F_1(a,b;c;1)=\sum_{i=0}^{\infty}\frac{(a)_i(b)_i}{(c)_i i!}=\frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)}. \tag{A13}$$

Another property of the hypergeometric function ${}_3F_2$ useful in our calculations is [8]

$$ {}_3F_2(-n,a,b;a+1,b-n-1;1)=\frac{n!a}{(1-b)_{n+1}}\left[\frac{(1+a-b)_{n+1}}{(a)_{n+1}}-1\right]. \tag{A14}$$

## References

[1] Morse P M 1929 *Phys. Rev.* **34** 57
[2] Gallas J A C 1980 *Phys. Rev.* A **21** 1829
[3] Elsum I R and Gordon R G 1982 *J. Chem. Phys.* **76** 5452
[4] Vasan V S and Cross R J 1983 *J. Chem. Phys.* **78** 3869
[5] Matsumoto A 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 2863
[6] Špirko V, Jensen P, Bunker P R and Čejchan A 1985 *J. Mol. Spectrosc.* **112** 183
[7] Bancewicz M 1996 *Chem. Phys.* **203** 93
[8] Prudnikov A P, Brichkov Y A and Marichev O I 1986 *Integrals and Series. Supplement* (Moscow: Science) (in Russian)
[9] Messiah A 1970 *Quantum Mechanics* (Amsterdam: North-Holland)
[10] Marichev O I 1978 *Method of Calculation of Special Function Integrals* (Minsk: Science and Technology) (in Russian)
[11] Wolfram S 1991 *Mathematica: a System for doing Mathematics by Computer* (Redwood City, CA: Addison-Wesley)