Journal of Mathematical Chemistry 22 (1997) 255–257

Note

A proof of the equivalence of two formulas for the matrix elements of the Morse potential

Daniel A. Morales

Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela

Received 22 January 1997; revised 15 October 1997

Two important formulas for the matrix elements of the Morse potential are shown to be equivalent. The proof rests on certain theorems relating generalized hypergeometric functions of unit argument.

The Morse potential [3] and its matrix elements are frequently used in model calculations in spectroscopy, molecular scattering, and in some other fields. It is given by

$$V(r) = D\big(\exp(-2au) - 2\exp(-au)\big), \quad u = r - r_0, \tag{1}$$

where D is the well-depth, r_0 is the equilibrium position, and a is a range parameter.

For the matrix element

$$\langle m|\exp(-\beta au)|n\rangle \equiv \int_{-\infty}^{\infty} \psi_m^* \exp(-\beta au)\psi_n \,\mathrm{d}u, \quad \beta = 0, 1, 2, \ldots, \tag{2}$$

Rosen [4] and Vasan–Cross [6] evaluated directly the integral which resulted after substitution of the eigenfunction ψ_j in equation (2) and found

$$\begin{aligned}\langle m|\exp(-\beta au)|n\rangle &= \frac{(-1)^{n+m}}{K^\beta}\left[\frac{b_1 b_2 m!\Gamma(K-m)}{n!\Gamma(K-n)}\right]^{1/2} \\ &\quad\times \sum_{j=0}^{m} \frac{(-1)^j \Gamma(n+\beta-j)\Gamma(K-n-1+\beta-j)}{j!(m-j)!\Gamma(K-m-j)\Gamma(\beta-j)},\end{aligned} \tag{3}$$

where $b_1 = K - 2n - 1$, $b_2 = K - 2m - 1$, and $K = 2\sqrt{2D}/a$.

On the other hand, Berrondo et al. [1], using the fact that the Morse potential is equivalent to a two-dimensional harmonic oscillator, obtained the following expression for the matrix element:

$$\langle m|\exp(-\beta au)|n\rangle = \frac{(-1)^{n+m}}{K^\beta}\left[\frac{b_1 b_2 m!\Gamma(K-m)}{n!\Gamma(K-n)}\right]^{1/2}$$

$$\times \frac{n!}{\Gamma(K-m)} \sum_{j=0}^{m} \binom{\beta-1-n+m}{j} \binom{\beta-1+n-m}{\beta-1-j}$$
$$\times \frac{\Gamma(K-n-1+\beta-j)}{\Gamma(m-j+1)}. \tag{4}$$

Even though it has been shown that for particular values of β both formulas give the same results, although they are not equal term by term, up to now nobody has shown in general that (3) and (4) are completely equivalent [1,2]. It is the purpose of this note to show that equivalence by relying on certain theorems associated with generalized hypergeometric functions of unit argument.

Our proof starts as follows. Equation (3) can be written as

$$\langle m|\exp(-\beta au)|n\rangle$$
$$= \frac{(-1)^{n+m}}{K^\beta}\left[\frac{b_1 b_2 m!\Gamma(K-m)}{n!\Gamma(K-n)}\right]^{1/2} \frac{\Gamma(n+\beta)\Gamma(K-n-1+\beta)}{\Gamma(m+1)\Gamma(K-m)\Gamma(\beta)}$$
$$\times {}_3F_2(-m, 1-K+m, 1-\beta; 1-n-\beta, 2-K+n-\beta; 1), \tag{5}$$

where ${}_3F_2(a_1, a_2, a_3; b_1, b_2; z)$ is a generalized hypergeometric function defined by [5]

$${}_3F_2(a_1, a_2, a_3; b_1, b_2; z) = \sum_{j=0}^{\infty} \frac{(a_1)_j (a_2)_j (a_3)_j}{(b_1)_j (b_2)_j} \frac{z^j}{j!} \tag{6}$$

with

$$(a)_m = a(a+1)(a+2)(a+3)\cdots(a+m-1) = \frac{\Gamma(a+m)}{\Gamma(a)}, \tag{7}$$

and use has been made of the relation

$$(a)_{-n} = \frac{(-1)^n}{(1-a)_n}. \tag{8}$$

Similarly, equation (4) can be written as

$$\langle m|\exp(-\beta au)|n\rangle$$
$$= \frac{(-1)^{n+m}}{K^\beta}\left[\frac{b_1 b_2 m!\Gamma(K-m)}{n!\Gamma(K-n)}\right]^{1/2} \frac{n!}{\Gamma(K-m)} \frac{\Gamma(\beta+n-m)\Gamma(K-n-1+\beta)}{\Gamma(\beta)\Gamma(n-m+1)\Gamma(m+1)}$$
$$\times {}_3F_2(1-\beta+n-m, 1-\beta, -m; n-m+1, 2-K+n-\beta; 1). \tag{9}$$

A relation between the hypergeometric functions occurring in equations (5) and (9) can be found by using interconnecting formulae for ${}_3F_2(1)$ series [5].

Let

$$\alpha_{123} = 1-\beta, \qquad \beta_{40} = 1-n-\beta, \qquad \beta_{50} = 2-K+n-\beta$$

and

$$\alpha_{502} = 1+n+m+\beta-K, \qquad \beta_{50} = 2-K+n-\beta, \qquad \beta_{52} = n+1-m.$$

Then, the ${}_3F_2(1)$ series occurring in equations (5) and (9) can be written in terms of a $F_p(0;4,5)$ function and a $F_n(5;0,2)$ function (see [5] for the general definition of these functions) as

$$F_p(0;4,5) = \frac{1}{\Gamma(\alpha_{123})\Gamma(\beta_{40})\Gamma(\beta_{50})} \times {}_3F_2(-m, 1-K+m, 1-\beta; 1-n-\beta, 2-K+n-\beta; 1) \quad (10)$$

and

$$F_n(5;0,2) = \frac{1}{\Gamma(\alpha_{502})\Gamma(\beta_{50})\Gamma(\beta_{52})} \times {}_3F_2(-m, 1+n-\beta-m, 1-\beta; 2-K+n-\beta, 1+n-m; 1). \quad (11)$$

The relation between $F_p(0;4,5)$ and $F_n(5;0,2)$ is given by [5]

$$F_p(0;4,5) = \frac{(-1)^{\beta-1}\Gamma(\alpha_{025})\Gamma(\alpha_{015})}{\Gamma(\alpha_{123})\Gamma(\alpha_{124})} F_n(5;0,2), \quad (12)$$

where

$$\alpha_{025} = 1+n+m+\beta-K, \qquad \alpha_{124} = -n, \qquad \alpha_{015} = n+\beta-m.$$

From equations (10)–(12) the following identity relating our two ${}_3F_2(1)$ functions follows:

$$\begin{aligned} &{}_3F_2(-m, 1-K+m, 1-\beta; 1-n-\beta, 2-K+n-\beta; 1) \\ &\quad = \frac{n!\Gamma(n+\beta-m)}{\Gamma(n+\beta)\Gamma(n+1-m)} \\ &\quad\quad \times {}_3F_2(-m, 1+n-\beta-m, 1-\beta; 2-K+n-\beta, 1+n-m; 1). \end{aligned} \quad (13)$$

Substitution of equation (13) into (5) yields equation (9). Thus, the proof is done.

References

[1] M. Berrondo, A. Palma and J.L. López-Bonilla, Int. J. Quant. Chem. 31 (1987) 243.
[2] V. Gaftoi, J. López, J. Morales and D. Navarrete, Rev. Mexicana Fis. 36 (1990) 649.
[3] P.M. Morse, Phys. Rev. 34 (1929) 57.
[4] N. Rosen, J. Chem. Phys. 1 (1933) 319.
[5] L.J. Slater, *Generalized Hypergeometric Functions* (Cambridge University Press, Cambridge, 1966).
[6] V.S. Vasan and R.J. Cross, J. Chem. Phys. 78 (1983) 3869.