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The linear combination of vibrational wave functions (LCVW) method in a Morse–Gaussian double well molecular potential

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The linear combinations of harmonic oscillator wave functions (LCWV) method is proposed to solve the Schrödinger equation, for a particle of a mass μ moving in a one dimensional double-well potential field, in which, the energy barrier has a gaussian shape. The general double well potential, whether symmetric or not, is constructed from appropriate combinations of Morse-like potentials and a Gaussian function and the problem is solved variationally, using as trial functions, linear combinations of harmonic oscillator wave functions (LCWV) centered at the two minima. The relevant matrix elements are calculated using the Harmonic Oscillator Tensor (HOT) technique. A generalization to multiple well problems is also advanced.

KEY WORDS: LCVW, double-well potential

1. Introduction

Beside the value that in itself has the determination of the energy level pattern in quantum mechanical problems, in particular when the potential energy function shows several minima, the knowledge of analytic wave functions in these cases is useful to analyze other phenomena such as the computation of Franck–Condon factors and quantum mechanical tunneling, among others.

In this work, we construct the general one dimensional double minima potential energy function using a combination of Morse-like potentials plus a Gaussian function, as given in equation (1)

$$V(x) = B(1 - e^{-bx})^2 + B(D + e^{+bx})^2 + Ae^{-ax^2}. \tag{1}$$

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There, the coefficients **a, b, A, B** and **D** are constant parameters and can be chosen in a convenient way to generate double well potentials of a variety of shapes. As an example, if we chose $\mathbf{D} = -1$, we obtain sets of symmetric double well functions, such as the one shown in figure 1, in which case **A** is the height of the barrier and the parameter **a** is simply related to the width of the barrier. Choosing negative values of $|\mathbf{D}| \geqslant 1$, sets of unsymmetrical potential double well functions can be obtained, such as the one depicted in figure 2.

In any case, the position of the maximum and the two minima as well as the curvature of the potential at these two minima, can be analytically evaluated.

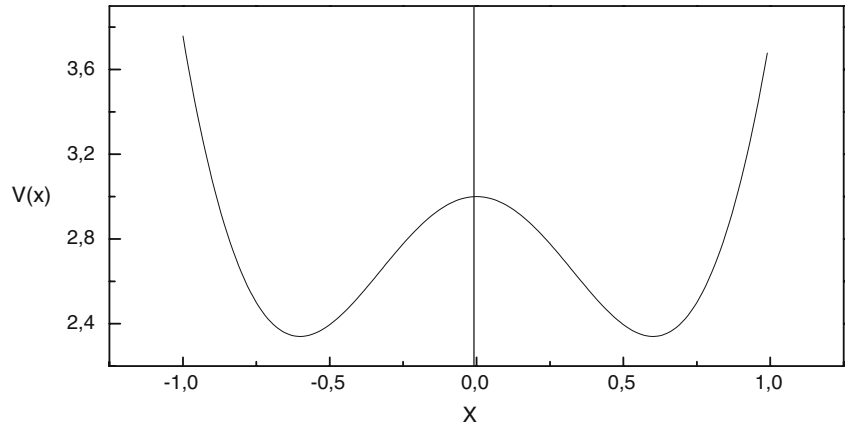

Figure 1. A symmetrical Morse-Gaussian potential function.

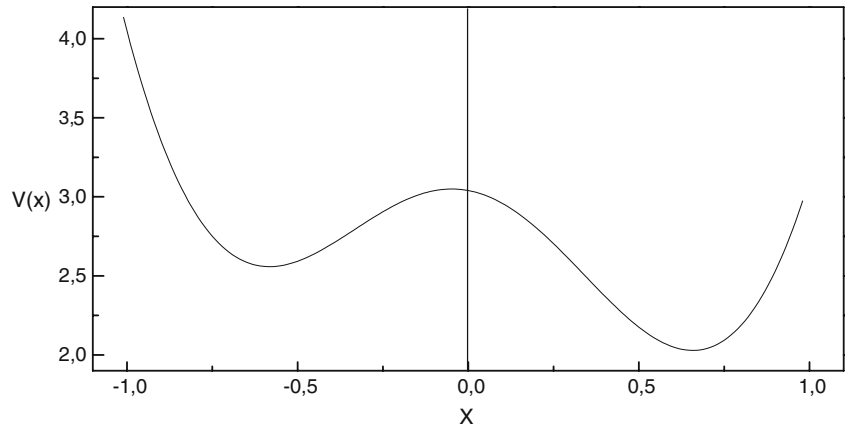

Figure 2. An unsymmetrical Morse-Gaussian potential function.

As an example, the extreme points in a symmetric double well potential, are the solutions of the equation

$$4Bb\left(\cosh(bx)+\sinh(2bx)\right)+2(C-1)Bbe^{bx}-2aAx^{-ax^2}=0.$$

These are easily solved with the help of any symbolic algebra program, such as Maple [3]. The same is true for the evaluation of the curvature at the respective minima.

The Harmonic Oscillator (HO) functions, used in the present work, are defined by the parameter $\alpha=\sqrt{\frac{k}{\mu}}$, where μ is the reduced mass and κ the force constant or the curvature $\left(\partial^2 V/\partial x^2\right)_0$ of the harmonic potential.

$$\Psi_n(x)=\left[\frac{1}{2^n n!}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}} H_n(x)e^{-\frac{1}{2}\alpha x^2}=N_n H_n(x)e^{-\frac{1}{2}\alpha x^2}. \tag{2}$$

2. Method

It seems appropriate to address the problem of solving the Schrödinger equation for a particle of mass μ moving in a potential field that exhibits multiple minima, such as the one shown in figure 1, by taking linear combinations of vibrational wave functions (LCWV) [2] centered at each one of these minima, a method rooted in the molecular orbital theory. The best of such combinations would be those made up by the solutions for each well as if they were independent from each other. These solutions, in turn, are usually found in terms of HO functions. In this work, we will use linear combinations of M displaced HO centered at each of one these N minima.

$$\Psi(x)=\sum_{i=0}^{M}\sum_{k=1}^{N} C_i(k)\Psi_i(x_k). \tag{3}$$

In equation (3), Ψ_i is the ith vibrational wave function centered at the kth minimum, x_k represents the variable whose origin is located at that minimum and the $C_i(k)$ are linear variational coefficients to be found, as in molecular orbital theory, by solving the appropriate secular equation

$$\left|\left\langle i\left|\hat{H}\right|j\right\rangle-\lambda\left\langle i|j\right\rangle\right|=0. \tag{4}$$

In the present work, we will develop the working equations for both, the unsymmetrical, whose minima are located at $x=+c_1$ and $x=-c_2$, as well as the symmetrical double well potential, where the minima are located at $x=\pm c$. In this case several simplifications occur.

For simplicity, we assume that x is already a dimensionless variable and the Hamiltonian is written as

$$\hat{H} = -\nabla_x^2 + \frac{2}{\kappa}\theta^{-1}V(x), \tag{5}$$

where the energy factor for this dimensionless Hamiltonian is $\hbar^2/2\mu\theta$ and is defined with the help of $\theta = \sqrt{\frac{\hbar^2}{\kappa\mu}}$.

The displaced HO wave functions, centered at $x_1 = +c$ and $x_2 = -c$, expressed in terms of the variable x, used to described the potential function, are then

$$\Psi_n(x \pm c) = N_n H_n(x \pm c) e^{-\frac{1}{2}\alpha(x\pm c)^2}, \tag{6}$$

where N_n is the normalization constant of equation (2). As it will be apparent later in the handling and evaluation of matrix elements for the vibrational operators, it is convenient to have these functions referred to the origin $x = 0$, therefore, with the help of Runge's addition theorem for the Hermite polynomials [1,8], we can write

$$\Psi_n(x \pm c) = N_n \frac{e^{-\frac{c^2}{2}}}{\sqrt{2^n}} \sum_{k=0}^{n} \binom{n}{k} H_{n-k}(\sqrt{2}c) H_k(\sqrt{2}x) e^{-\frac{1}{2}x^2 \mp cx} \tag{7}$$

in this manner, all displaced functions can be referred to a single common origin. We note that the new variable for the Hermite polynomials is now $\xi = \sqrt{2}x$.

In order to compute the matrix elements needed in equation (4), it is necessary to rewrite the kinetic energy operator $\hat{T}(x)$, the potential energy operator $\hat{V}(x)$ of equation (1) and the HO functions of equation (7) in terms of the variable ξ. These are:

$$\hat{V}(x) = B(1 - e^{-\frac{b}{\sqrt{2}}\xi})^2 + B(-D + e^{+\frac{b}{\sqrt{2}}\xi})^2 + Ae^{-\frac{1}{2}a\xi^2} \tag{8a}$$

$$\hat{T}(x) = -\left(\nabla_\xi^2\right) \tag{8b}$$

and

$$\begin{aligned}\Psi_n(x \pm c) &= N_n \frac{e^{-\frac{c^2}{2}}}{\sqrt{2^n}} \sum_{k=0}^{n} K_c(n,k) H_k(\xi) e^{-\frac{1}{2}\xi^2} e^{+\frac{1}{4}\xi^2 \mp \frac{c}{\sqrt{2}}\xi} \\ &= N_n \frac{e^{-\frac{c^2}{2}}}{\sqrt{2^n}} \sum_{k=0}^{n} K_c(n,k) \Psi_k(\xi) e^{+\frac{1}{4}\xi^2 \mp \frac{c}{\sqrt{2}}\xi},\end{aligned} \tag{9}$$

where, to simplify the notation, we have called

$$K_c(n,k) = \binom{n}{k} H_{n-k}(\sqrt{2}c) \times \begin{cases} 1 & \text{when (x + c)} \\ (-1)^{n-k} & \text{when (x - c)} \end{cases}.$$

3. Overlap matrix elements

Overlap matrix elements between displaced HO on the same center are zero by orthogonality and will not be considered here. The nonzero matrix elements arise between functions on different centers. Thus, bearing in mind the equalities given in (9), one can write the general overlap matrix element for the unsymmetrical case as:

$$\langle \Psi_n(x+c_1)|\Psi_m(x-c_2)\rangle = \frac{N_n N_m e^{-\frac{1}{2}(c_1^2+c_2^2)}}{\sqrt{2^{n+m}}} \sum_{i=0}^{n} K_{c_1}(n,i) \sum_{j=0}^{m} K_{c_2}(m,j) \times \left\langle \Psi_i(\xi)|e^{+\frac{1}{2}\xi^2+\frac{1}{\sqrt{2}}(c_1-c_2)\xi}|\Psi_j(\xi)\right\rangle. \tag{10}$$

For the symmetrical case, where $c_1 = c_2 = c$, we find some simplifications, thus

$$\langle \Psi_n(x+c)|\Psi_m(x-c)\rangle = \frac{N_n N_m e^{-c^2}}{\sqrt{2^{n+m}}} \sum_{i=0}^{n} K_c(n,i) \sum_{j=0}^{m} K_c(m,j) \left\langle \Psi_i(\xi)|e^{+\frac{1}{2}\xi^2}|\Psi_j(\xi)\right\rangle. \tag{11}$$

The evaluation of the last integral in equations (10) and (11) will be discussed later in a more general context.

4. Energy matrix elements

Energy matrix elements are usually divided in two categories. Those between displaced HO on the same center and those between displaced HO on different centers, but even though we are referring all functions to a common origin, they are treated separately for convenience.

Let the generic operator $\hat{O}$, in turn, represent the Kinetic energy or the Potential energy operator, then for the unsymmetrical problem

$$\begin{aligned}\left\langle \Psi_n(x\pm c_1)|\hat{O}(x)|\Psi_m(x\pm c_2)\right\rangle = {} & \frac{N_n N_m e^{-\frac{1}{2}(c_1^2+c_2^2)}}{\sqrt{2^{n+m}}} \sum_{i=0}^{n} K_{c_1}(n,i) \sum_{j=0}^{m} K_{c_2}(m,j) \\ & \times \left\langle H_i(\sqrt{2}x)e^{-\frac{1}{2}x^2\mp c_1 x}|\hat{O}(x)|H_j(\sqrt{2}x)e^{-\frac{1}{2}x^2\mp c_2 x}\right\rangle \\ = {} & \frac{N_n N_m e^{-\frac{1}{2}(c_1^2+c_2^2)}}{\sqrt{2^{n+m}}} \sum_{i=0}^{n} K_{c_1}(n,i) \\ & \sum_{j=0}^{m} K_{c_2}(m,j) \times \left\langle \Psi_i(\xi)|F_{\pm}(c_1) g \hat{O}(\xi) F_{\pm}(c_2)|\Psi_j(\xi)\right\rangle.\end{aligned} \tag{12}$$

The symmetrical case becomes

$$\left\langle \Psi_n(x \pm c)|\hat{O}(x)|\Psi_m(x \pm c)\right\rangle = \frac{N_n N_m e^{-c^2}}{\sqrt{2^{n+m}}} \sum_{i=0}^{n} K_c(n,i) \sum_{j=0}^{m} K_c(m,j) \left\langle \Psi_i(\xi)|F_{\pm}(c) g\hat{O}(\xi) F_{\pm}(c)|\Psi_j(\xi)\right\rangle. \tag{13}$$

In equations (12) and (13) we have called $F_{\pm}(c) = e^{+\frac{1}{4}\xi^2 \mp \frac{c}{\sqrt{2}}\xi}$ in order to simplify the long expression obtained there. Also, **g** is the factor arising, if any, after transforming the operator $\hat{O}$ from *x-coordinate* to ξ-*coordinate*.

5. Kinetic energy matrix elements

The kinetic energy operator, written in terms of the dimensionless momentum operator $\hat{p} = -i\frac{d}{d\xi} = -i\sqrt{2}\frac{d}{d\xi}$, is then $g\hat{T} = -\frac{d^2}{d\xi^2}$.
In what follows, in the operator $F_{\pm}(c_1) g\hat{O}(\xi) F_{\pm}(c_2)$ of equation (12), we will combine upper with upper and lower with lower signs to avoid confusion. Replacing the value of $\hat{T}$ and, after performing the corresponding derivatives, we find for this operator:

(a) For *off-site* matrix elements, where the signs cross-combine between them (functions centered at different minima), we have for the unsymmetrical case

$$-F_{\pm}(c_1)\frac{d^2}{d\xi^2}F_{\mp}(c_2) = F_{\pm}(c_1)F_{\mp}(c_2)\left\{\left(-\frac{1}{4}\xi^2 \pm \frac{1}{\sqrt{2}}c_2\xi - \frac{c_2^2-1}{2}\right) + \left(\xi \mp \sqrt{2}c_2\right)\frac{d}{d\xi} - \frac{d^2}{d\xi^2}\right\}, \tag{14}$$

where we have called

$$F_{\pm}(c_1)F_{\mp}(c_2) = \exp\left(\frac{1}{2}\xi^2 \mp \frac{1}{\sqrt{2}}(c_1 - c_2)\xi\right) \tag{15}$$

and for a symmetrical double well potential, where $c_1 = c_2 = c$ equation (14) becomes

$$-F_{\pm}(c)\frac{d^2}{d\xi^2}F_{\mp}(c) = e^{\frac{1}{2}\xi^2}\left\{\left(-\frac{1}{4}\xi^2 \pm \frac{1}{\sqrt{2}}c\xi - \frac{c^2-1}{2}\right) + \left(\xi \mp \sqrt{2}c\right)\frac{d}{d\xi} - \frac{d^2}{d\xi^2}\right\}. \tag{16}$$

(b) For *in-site* diagonal matrix elements, whether the well is symmetric or not, the operator is:

$$-F_{\pm}(c)\frac{d^2}{d\xi^2}F_{\pm}(c) = e^{\frac{1}{2}\xi^2\mp\sqrt{2}c\xi}\left\{\left(-\frac{1}{4}\xi^2 \mp \frac{1}{\sqrt{2}}c\xi - \frac{c^2-1}{2}\right) + \left(\xi \pm \sqrt{2}c\right)\frac{d}{d\xi} - \frac{d^2}{d\xi^2}\right\}. \quad (17)$$

On the other hand, considering that

$$\frac{d}{d\xi} = ip = \frac{1}{\sqrt{2}}(a - a^+)$$

and that

$$\frac{d^2}{d\xi^2} = -\frac{1}{2}\left(a^2 - aa^+ - a^+a + (a^+)^2\right),$$

where a and a^+ are the annihilation and creation operators, respectively, the various terms arising in the bracket at the right hand side of equation (12), when the operator $\hat{O}$ is the kinetic energy operator $\hat{T}$, in self explanatory notation, are:

(a) For *off-site* matrix elements

$$\left\langle \Psi_i(\xi)|F_{\pm}(c_1)gT(\xi)F_{\mp}(c_2)|\Psi_j(\xi)\right\rangle = M^{(0)}_{i,j} + \frac{1}{\sqrt{2}}\left\{\sqrt{(j+1)}M^{(1)}_{i,j+1} - \sqrt{j}M^{(1)}_{i,j-1}\right\}$$
$$-\frac{1}{2}\left\{\sqrt{j(j-1)}M^{(2)}_{i,j-2} - (2j+1)M^{(2)}_{i,j} + \sqrt{(j+1)(j+2)}M^{(2)}_{i,j+2}\right\}, \quad (18)$$

where, to simplify the expression, we have called the matrix elements

$$M^{(0)}_{i,j} = \left\langle i\left|(-\tfrac{1}{4}\xi^2 \pm \tfrac{1}{\sqrt{2}}c_2\xi - \tfrac{c_2^2-1}{2})F_{\pm}(c_1)F_{\mp}(c_2)\right|j\right\rangle$$
$$M^{(1)}_{i,j} = \left\langle i\left|(\xi \mp \sqrt{2}c_2)F_{\pm}(c_1)F_{\mp}(c_2)\right|j\right\rangle \quad (19)$$
$$M^{(2)}_{i,j} = \langle i\,|F_{\pm}(c_1)F_{\mp}(c_2)|\,j\rangle\,.$$

In equations (19) again we have for an unsymmetrical double well,

$$F_{\pm}(c_1)F_{\mp}(c_2) = \exp\left(\frac{1}{2}\xi^2 \mp \frac{1}{\sqrt{2}}(c_1 - c_2)\xi\right) \quad (20)$$

or for the symmetrical case

$$F_{\pm}(c)F_{\mp}(c) = \exp\left(\tfrac{1}{2}\xi^2\right)$$

(b) For *in-site* matrix elements (whether symmetric or not), the matrix elements of equations (19) become

$$\begin{aligned} M_{i,j}^{(0)} &= \left\langle i \left| (-\tfrac{1}{4}\xi^2 \pm \tfrac{1}{\sqrt{2}}c\xi - \tfrac{c^2-1}{2}) F_{\pm}(c) F_{\pm}(c) \right| j \right\rangle \\ M_{i,j}^{(1)} &= \left\langle i \left| (\xi \mp \sqrt{2}c) F_{\pm}(c) F_{\pm}(c) \right| j \right\rangle \\ M_{i,j}^{(2)} &= \langle i \,| F_{\pm}(c) F_{\pm}(c) |\, j \rangle \end{aligned} \tag{21}$$

and, where $F_{\pm}(c)F_{\pm}(c) = \exp\left(\frac{1}{2}\xi^2 \mp \sqrt{2}c\xi\right)$.

6. Potential energy matrix elements

For the potential energy operator of equation (8) upon introduction in equation (12) or (13) and further expansion, we have:

(a) Off-site matrix elements of the asymmetric potential:

$$\begin{aligned} F_{\pm}(c_1)\hat{V}(\xi)\ F_{\mp}(c_2) &= \left\{ 2B - 2B(De^{+\frac{b}{\sqrt{2}}\xi} + e^{-\frac{b}{\sqrt{2}}\xi}) + B(e^{+\sqrt{2}b\xi} + e^{-\sqrt{2}b\xi}) + Ae^{-\frac{1}{2}a\xi^2} \right\} \\ &\quad \times e^{\left[\frac{1}{2}\xi^2 \mp \frac{1}{\sqrt{2}}(c_1 - c_2)\xi\right]} \end{aligned} \tag{22}$$

and for the symmetric double well potential

$$\begin{aligned} F_{\pm}(c)\hat{V}(\xi)F_{\mp}(c) &= \left\{ 2B - 2B(e^{+\frac{b}{\sqrt{2}}\xi} + e^{-\frac{b}{\sqrt{2}}\xi}) + B(e^{+\sqrt{2}b\xi} + e^{-\sqrt{2}b\xi}) + Ae^{-\frac{1}{2}a\xi^2} \right\} e^{\frac{1}{2}\xi^2} \\ &= \left\{ 2B - 4Bcosh\left(\frac{b}{\sqrt{2}}\xi\right) + 2B\cosh(\sqrt{2}b\xi) + Ae^{-\frac{1}{2}a\xi^2} \right\} e^{\frac{1}{2}\xi^2}. \end{aligned} \tag{23}$$

(b) In-site matrix elements, unsymmetrical potential

$$\begin{aligned} F_{\pm}(c)\hat{V}(\xi)F_{\pm}(c) &= \left\{ 2B - 2B(De^{+\frac{b}{\sqrt{2}}\xi} + e^{-\frac{b}{\sqrt{2}}\xi}) + B(e^{+\sqrt{2}b\xi} + e^{-\sqrt{2}b\xi}) + Ae^{-\frac{1}{2}a\xi^2} \right\} e^{\left[\frac{1}{2}\xi^2 \mp \sqrt{2}c\xi\right]} \end{aligned} \tag{24}$$

and for the symmetrical potential

$$F_{\pm}(c)\hat{V}(\xi)F_{\pm}(c) = \left\{ 2B - 4B\cosh\left(\frac{b}{\sqrt{2}}\xi\right) + 2B\cosh(\sqrt{2}b\xi) + Ae^{-\frac{1}{2}a\xi^2} \right\} e^{\left[\frac{1}{2}\xi^2 \mp \sqrt{2}c\xi\right]}. \tag{25}$$

Matrix elements involving the operators of equations (22)–(25) may be evaluated with the help of the formulae given in the Appendix A. This can be achieved using any convenient power expansion of the exponential or hyperbolic functions.

7. Final comments

We have circumscribed in this work to find the vibrational states in a particular double well potential, constructed from combinations of Morse-like potentials and a Gaussian function. It is readily appreciated that the method can be easily extended to any analytic potential function (power series, trigonometric) that shows multiple minima, by taking linear combinations of vibrational functions appropriate to each minima found.

Although the computation of matrix elements using displaced harmonic oscillators may look a little more involved (it is simpler to calculate matrix elements referred to a single origin), the advantages of taking linear combination of vibrational functions that closely describe the physical situation around each minima, largely reduces the basis set needed to be used for any desired accuracy.

Appendix A

Formulas for the computation of matrix elements between harmonic oscillators wave functions for a variety of vibrational operators $\langle\hat{O}\rangle_{ij} = \langle\Psi_i|\hat{O}|\Psi_j\rangle$ have been previously reported[4–7]. The evaluation of these matrix elements make use of the Harmonic Oscillator Tensor technique developed by Palting et al. and arrive to simple expressions that can be put into efficient algorithms. In their work, q represents the coordinate and the ith vibrational wave functions denoted by the ket $|v_i\rangle$. We list some of the formulas useful in our case.

(1) Gaussian forms where the operator is $\hat{O} = q^k e^{-\lambda q^2}$ and $-1 < \lambda$ (real), k $= \frac{1}{2}, 1, \frac{3}{2}, \ldots$.

$$\left\langle v_1 \left| q^k e^{-\lambda q^2} \right| v_2 \right\rangle = \frac{1}{2}\left(1 + (-1)^{v_1+v_2+k}\right) \times \sqrt{\frac{1}{2^k v_1! v_2!}} \sum_{m_1=0}^{2\left[\frac{v_1}{2}\right]} \sum_{m_2=0}^{2\left[\frac{v_2}{2}\right]} \begin{cases} 0 \\ \dfrac{g_{v_1 m_1} g_{v_2 m_2}}{\sqrt{\lambda+1}} \\ g_{v_1 m_1} g_{v_2 m_2} \dfrac{(v_1+v_2-m_1-m_2+k-1)!!}{(\lambda+1)^{\frac{1}{2}(v_1+v_2-m_1-m_2+k+1)}}. \end{cases} \tag{A.1}$$

In equation (A.1), from top to bottom, the rightmost coefficients are for odd, zero and even values of $(v_1+v_2-m_1-m_2+k-1)$, respectively. Also, the definition of the g_{vm} coefficient is as follows

$$\begin{aligned} g_{vm} &= 0 && m = \text{odd} \\ g_{v0} &= 1 && m = 0 \\ g_{vm} &= (-1)^{\frac{m}{2}}(m-1)!! \begin{pmatrix} v \\ m \end{pmatrix} && m = \text{even} \end{aligned}.$$

(2) Matrix elements containing powers of the coordinate

$$\langle 2j_1 | q^{2L} | 2j_2 \rangle = \left[1 + (-1)^{2L+2j_2+2j_1}\right] \left(\frac{1}{2}\right)^{2L+j_2-j_1+1} \frac{(2L)!}{(L+j_2-j_1)!} \left[\frac{(2j_2)!}{(2j_1)!}\right] \times \sum_{n=0}^{L+j_2-j_1} (-1)^n \binom{L+j_2-j_1}{n} \binom{2L+2j_2-2n}{2L}. \tag{A.2}$$

(3) Matrix elements involving mixed forms, that is powers of q and exponential of q in the type $q^{\mathrm{L}} e^{\lambda \mathrm{q}}$. In these formulae $\lambda =$ real, and $L = \frac{1}{2}, 1, \frac{3}{2}, \ldots$.

$$\langle 2j_1 | q^L e^{\lambda q} | 2j_2 \rangle = F_{2j_1 2j_2} \sum_{k=0}^{L} \binom{L}{k} A^{(k)}\left(\lambda, \frac{1}{4}\right) B^{L-k}_{2j_1 2j_2}(\lambda, +1) \tag{A.3}$$

$$B^m_{2j_1 2j_2}(\lambda, \pm 1) = m! \sum_{n}^{2j_1} \left(\frac{1}{\sqrt{2}}\right)^{2n+2j_2-2j_1} \frac{(\pm 1)^n}{n!(n+2j_2-2j_1)!(2j_1-n)!} \tag{A.4}$$

$$A^{(k)}(\lambda, a) = e^{a\lambda^2} \left[(2a\lambda)^k + \sum_{i=1}^{\left[\frac{k}{2}\right]} (2i-1)!! \binom{k}{2i} (2a)^i (2a\lambda)^{k-2i} \right], \tag{A.5}$$

Where $\left[\frac{k}{2}\right] = \frac{k}{2}$ for even values of k and $\left[\frac{k}{2}\right] = \frac{(k-1)}{2}$ for odd values of k.

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