

Matrix elements for powers of x -dependent operators for the hyperbolic Pöschl–Teller potentials

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys. A: Math. Theor. 42 165209

(<http://iopscience.iop.org/1751-8121/42/16/165209>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.153

The article was downloaded on 03/06/2010 at 07:37

Please note that [terms and conditions apply](#).

Matrix elements for powers of x -dependent operators for the hyperbolic Pöschl–Teller potentials

M Rey¹ and F Michélot²

¹ Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, BP 1039, F-51687, Reims Cedex 2, France

² Institut Carnot de Bourgogne, UMR CNRS 5209, BP 47870, F-21078 Dijon, France

E-mail: michael.rey@univ-reims.fr and francoise.michelot@u-bourgogne.fr

Received 9 February 2009, in final form 10 March 2009

Published 31 March 2009

Online at stacks.iop.org/JPhysA/42/165209

Abstract

Analytical matrix elements of the position operator x^n ($n > 0$) and of the first- and second-order differential operators are derived using the eigenfunctions of two hyperbolic Pöschl–Teller potentials. These general relations are written in closed form and calculated from the properties of the integral powers of hypergeometric series. Additionally, an explicit expression is derived for the successive derivatives of the Beta function. Convergence and reliability of these results will be discussed and an application to the calculation of the rovibrational energy spectrum of CO will be considered.

PACS numbers: 02.30.Gp, 03.65.Ge, 31.15.xt

1. Introduction

Considerable interest has been devoted to the Morse and Kratzer potentials as exactly solvable models describing anharmonic molecular vibrations associated with stretching modes [1, 2]. Due to their relative simplicity, the corresponding matrix elements have been widely considered and derived either numerically, analytically or algebraically in different ways for many years [3–8]. Concerning the bending motions and/or out-of-plane modes, another exactly solvable model, namely the hyperbolic modified Pöschl–Teller (MPT) potential, may be considered and seen as a better alternative than the usual harmonic oscillator. For this potential, matrix elements of the natural variable $u = \tanh(\alpha x)$ and of the differential operators d/dx and d^2/dx^2 have also been derived [9–11] with the same techniques as those used for the Morse and Kratzer oscillators. There exist other formulations for Pöschl–Teller-type potentials which are exactly solvable for both the bound and scattering states. In this work, we are interested in the bound states of the second Pöschl–Teller (SPT) potential, which contains the MPT as a special case. As for the MPT potential, its solutions have been studied in the Lie-algebraic framework involving non-compact Lie dynamical symmetries [12–14] and we anticipate that

the eigenfunctions are expressed by means of the ${}_2F_1$ Gauss hypergeometric functions. Despite its importance for scattering [15] and exact path integral treatments [16], the SPT potential has not attracted much attention, compared to the Morse potential, in molecular physics with bound-state problems. However, we should just mention that for diatomic molecules it has been successfully employed in some earlier works in detailed comparative studies of empirical potential energy functions [17–19] and also used to calculate Franck–Condon factors, photodissociation cross sections and some matrix elements of vibrational transitions [20–24]. In addition, its energy eigenvalues were determined semiclassically in [25]. It is also worth noting that interest in this potential is twofold. First, depending on the values of the parameters, we can select either the discrete or the continuous energy spectrum emerging from the Casimir operators of different representations [12, 13]. Second, unlike the Morse potential, the SPT potential possesses a realistic internuclear behaviour as $x \rightarrow 0$.

To perform well-adapted and efficient variational calculations, we first need to compute the matrix elements of various quantities. In this work, we have determined, for both MPT and SPT potentials, closed analytical expressions of the matrix elements for arbitrary positive powers of the operator x^n as well as for the differential operators d/dx and d^2/dx^2 . All the calculations were based on the properties of the hypergeometric series and of their integral powers [26]. Additionally, these properties allowed us to derive an explicit expression for the successive derivatives of the Beta function. Several applications may involve x^n -type operators such as, for instance, the rovibrational Hamiltonian for semirigid molecules written in normal coordinates [27]. To keep our general expressions compact, intermediate quantities based on infinite series were introduced. But as for practical applications, the arguments involved in the summations are large enough, it will be shown that the series converge quite rapidly at the desired accuracy on 64 bits processors and without rounding off errors. This is not the case in general when performing numerical integrations whose accuracy is rapidly spoiled as n and the vibrational quantum numbers v increase.

As an illustration, the general matrix elements derived from the SPT eigenfunctions have been used to calculate variationally the rovibrational energy spectrum of the CO molecule in its ground electronic state. More generally, applications to bending and stretching vibrations in polyatomic molecules could also be considered using the MPT and SPT potentials, respectively. This will be considered in a forthcoming study.

2. The modified Pöschl–Teller potential

2.1. Eigensolutions and symmetry

The one-dimensional Schrödinger equation (SE) for the modified Pöschl–Teller potential is written as [28–30]

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} - \frac{D}{\cosh^2(\alpha x)} \right] \Psi_v^j(x) = E_v \Psi_v^j(x), \quad x \in (-\infty, +\infty), \quad (1)$$

where D is the depth of the well in energy units, μ the reduced mass and α a scaling parameter related to the potential range. The x variable corresponds to the relative physical displacement from the equilibrium position. This potential can be appropriate for the description of bending molecular vibrations. As usual [10], the natural variable $u = \tanh(\alpha x)$ is introduced for convenience.

The eigensolutions of the SE for this potential are now well established and are given by [11]

$$\Psi_v^j(u) = N_v^j (1 - u^2)^{\frac{j-v}{2}} C_v^{j+1/2-v}(u), \quad (2)$$

where $C_v^\beta(u)$ are the Gegenbauer orthogonal polynomials, N_v^j stands for the normalization constant and j is connected to the potential depth as

$$N_v^j = \sqrt{\frac{\alpha v! \Gamma(j - v + 1/2)}{\pi^{1/2} \Gamma(j - v) (2j - 2v + 1)_v}}, \quad j(j + 1) = \frac{2\mu D}{\alpha^2 \hbar^2}, \quad (3)$$

where $(a)_n = a(a+1) \cdots (a+n-1)$ is the Pochhammer symbol. Note that due to the connection between the one-dimensional MPT eigenfunctions (2) and the states $|[N0], j = \frac{N}{2}, m = v - j\rangle$ associated with $U(2) \supset SU(2) \supset SO(2)$, j also labels the irreducible representations of the corresponding Lie algebra $su(2)$ [11, 31]. Thus it can be shown that the expected maximum number of quanta is $v_{\max} = [j]$ where $[j]$ means the integer part of j . However it must be noted that from the $2j + 1$ bound states of the MPT, only $[j] + 1$ are normalizable, meaning that the eigenfunctions (2) are associated with only one branch ($m < 0$) of the $su(2)$ representations. Since this potential possesses both bound and unbound states and as recently claimed by Aldaya *et al* [32, 33], the correct dynamical symmetry for the MPT is not $SU(2)$ in this case but the non-compact dynamical group $SO(2, 1) (\approx SL(2, \mathfrak{R}) \approx SU(1, 1))$ [12]. The associated algebra contains compact and non-compact generators allowing us to describe discrete and continuous spectra, respectively.

Throughout the paper we shall prefer to work with a more convenient coordinate system. So introducing the dimensionless coordinate $\bar{x} = x/x_e$, the associated SE (1) is written

$$\left[-\frac{d^2}{d\bar{x}^2} - \frac{\bar{\alpha}^2 j(j + 1)}{\cosh^2(\bar{\alpha}\bar{x})} \right] \Psi_v^j(\bar{x}) = \bar{E}_v^{\text{MPT}} \Psi_v^j(\bar{x}), \quad (4)$$

where we have defined

$$\bar{\alpha} = \alpha x_e, \quad \bar{E}_v^{\text{MPT}} = \frac{2\mu x_e^2}{\hbar^2} E_v,$$

and we set now $u = \tanh(\bar{\alpha}\bar{x})$. The energy eigenvalues are given by [11]

$$\bar{E}_v^{\text{MPT}} = -\bar{\alpha}^2 (j - v)^2, \quad v = 0, 1, \dots, [j]. \quad (5)$$

In this case, the variable \bar{x} may correspond to a dimensionless normal coordinate of vibration ($\equiv q$) associated for instance with a bending mode.

2.2. Matrix elements $\langle \bar{x}^n \rangle_{v'v}$ and $\langle d/d\bar{x} \rangle_{v'v}$ between the MPT wavefunctions

Let us first start with the evaluation of the integral

$$\begin{aligned} {}^{(p)}\mathcal{O}_{v'v} &= \int_{-\infty}^{+\infty} \Psi_{v'}^j(\bar{x}) [\cosh(\bar{\alpha}\bar{x}) + \sinh(\bar{\alpha}\bar{x})]^p \Psi_v^j(\bar{x}) d\bar{x}, \\ &= \frac{1}{\bar{\alpha}} \int_{-1}^{+1} \Psi_{v'}^j(u) (1 + u)^p (1 - u^2)^{-p/2-1} \Psi_v^j(u) du. \end{aligned} \quad (6)$$

Expressing the Gegenbauer polynomials as ${}_2F_1$ hypergeometric series [34, 35]

$$C_v^{(\beta)}(u) = \frac{(2\beta)_v}{v!} {}_2F_1 \left(-v, 2\beta + v; \beta + \frac{1}{2}; \frac{1 - u}{2} \right), \quad (7)$$

with (if w integer)

$${}_pF_q \left(\begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix}; y \right) = \sum_{k=0}^l \frac{(a_1)_k \cdots (a_p)_k}{(b_1)_k \cdots (b_q)_k} \frac{y^k}{k!} \begin{cases} l = w & \text{if } a_i = -w, \\ l = \infty & \text{otherwise,} \end{cases} \quad (8)$$

the integral (6), with appropriate integration variables, is written

$$\begin{aligned}
 {}^{(p)}\mathcal{O}_{v'v} &= \frac{N_v^j N_{v'}^j (\beta_v)_v (\beta_{v'})_{v'}}{\bar{\alpha} v! v'!} \sum_{k=0}^v \sum_{k'=0}^{v'} (2)^{2j-(v+v')-1} \\
 &\times \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j-v'+1)_{k'}}{(j-v+1)_k (j-v'+1)_{k'} k! k'!} \\
 &\times \int_0^1 u^{j-\frac{v+v'}{2}+\frac{p}{2}-1} (1-u)^{j-\frac{v+v'}{2}-\frac{p}{2}-1+k+k'} du, \tag{9}
 \end{aligned}$$

with $\beta_v = 2j - 2v + 1$ and ${}^{(0)}\mathcal{O}_{v'v} = \delta_{v'v}$.

The last line in equation (9) can be evaluated analytically using the generalized integral representation [36] (if $\text{Re}(c) > \text{Re}(b) > 0$)

$$\int_0^1 t^{b-1} (1-t)^{c-b-1} (1-yt^q)^{-a} dt = \frac{\Gamma(b)\Gamma(c-b)}{\Gamma(c)} {}_{q+1}F_q \left(\begin{matrix} a, \frac{b}{q}, \frac{b+1}{q}, \dots, \frac{b+q-1}{q} \\ \frac{c}{q}, \frac{c+1}{q}, \dots, \frac{c+q-1}{q} \end{matrix}; y \right), \tag{10}$$

where we have chosen $b = j - \frac{v+v'}{2} + \frac{p}{2}$, $y = 1$, $q = 1$, $a = 0$ and $c = 2j - (v + v') + k + k'$. So, setting

$$q \equiv q(v, v') = j - \frac{v+v'}{2}, \quad q' \equiv q'(v, v', k', k) = q + k + k', \tag{11}$$

we finally arrive for the matrix elements (6) at the result

$$\begin{aligned}
 {}^{(p)}\mathcal{O}_{v'v} &= \frac{N_v^j N_{v'}^j (\beta_v)_v (\beta_{v'})_{v'}}{\bar{\alpha} v! v'!} \sum_{k=0}^v \sum_{k'=0}^{v'} (2)^{2j-(v+v')-1} \\
 &\times \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j-v'+1)_{k'}}{(j-v+1)_k (j-v'+1)_{k'} k! k'!} B\left(q + \frac{p}{2}, q' - \frac{p}{2}\right), \tag{12}
 \end{aligned}$$

with, in the case where j is integer

$$v + v' < 2j - p + 2(k + k'), \tag{13}$$

and where $B(x, y) = \Gamma(x)\Gamma(y) / \Gamma(x + y)$ is the Beta function. Let us mention that it would have been certainly more advantageous to note that the last line in (9) is simply the integral representation of the Beta function. However, it seemed to us necessary to define the more general integral representation (10) since it will be considered for further calculations.

From equations (6) and (12), we can easily derive the matrix elements $\langle \bar{x} \rangle_{v'v}$ of \bar{x} as

$$\text{MPT } \tilde{X}_{v'v}^{j(1)} = \int_{-\infty}^{+\infty} \Psi_{v'}^j(\bar{x}) \bar{x} \Psi_v^j(\bar{x}) d\bar{x} = \frac{1}{\bar{\alpha}} \left. \frac{d^{(p)}\mathcal{O}_{v'v}}{dp} \right|_{p=0}, \tag{14}$$

leading to

$$\begin{aligned}
 \text{MPT } \tilde{X}_{v'v}^{j(1)} &= \frac{N_v^j N_{v'}^j (\beta_v)_v (\beta_{v'})_{v'}}{2\bar{\alpha}^2 v! v'!} \sum_{k=0}^v \sum_{k'=0}^{v'} (2)^{2j-(v+v')-1} \\
 &\times \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j-v'+1)_{k'}}{(j-v+1)_k (j-v'+1)_{k'} k! k'!}, \\
 &\times B(q, q') [\psi(q) - \psi(q')]. \tag{15}
 \end{aligned}$$

Note that these matrix elements are nonvanishing only for $v + v'$ odd and that ψ 's are the digamma functions.

- Matrix elements $\langle \bar{x}^n \rangle_{v'v}$ for arbitrary powers $n > 0$ can be calculated from the generalization of equation (14) by evaluating the n th derivative

$$\text{MPT } \tilde{X}_{v'v}^{j(n)} = \int_{-\infty}^{+\infty} \Psi_{v'}^j(\bar{x}) \bar{x}^n \Psi_v^j(\bar{x}) d\bar{x} = \frac{1}{\bar{\alpha}^n} \left. \frac{d^{n(p)} \mathcal{O}_{v'v}}{dp^n} \right|_{p=0}, \tag{16}$$

which will involve polygamma functions $\psi^{(n-1)}$ —with $\psi^{(0)} \equiv \psi$ the digamma function—defined as [34]

$$\psi^{(n-1)}(z) = (-1)^n (n-1)! \sum_{k=0}^{\infty} (z+k)^{-n}. \tag{17}$$

In this case, $\text{MPT } \tilde{X}_{v'v}^{j(n)}$ are simply expressed as

$$\begin{aligned} \text{MPT } \tilde{X}_{v'v}^{j(n)} &= \frac{N_v^j N_{v'}^j (\beta_v)_v (\beta_{v'})_{v'}}{\bar{\alpha}^{n+1} v! v'!} \sum_{k=0}^v \sum_{k'=0}^{v'} (2)^{2j-(v+v')-1} \\ &\times \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j-v'+1)_{k'}}{(j-v+1)_k (j-v'+1)_{k'} k! k'!} \mathcal{B}_{k'k}^{(n)}(v', v), \end{aligned} \tag{18}$$

with

$$\mathcal{B}_{k'k}^{(n)}(v', v) = \left. \frac{d^n B(q + \frac{p}{2}, q' - \frac{p}{2})}{dp^n} \right|_{p=0}. \tag{19}$$

Using the Leibniz rule for the n th derivative of a product with respect to p , we write

$$\mathcal{B}_{k'k}^{(n)}(v', v) = \sum_{r=0}^n \binom{n}{r} \left. \frac{\Gamma^{(r)}(q + \frac{p}{2}) \Gamma^{(n-r)}(q' - \frac{p}{2})}{\Gamma(q + q')} \right|_{p=0}, \tag{20}$$

where the s th derivative of the gamma function can be written in symbolic notations as

$$\begin{aligned} \Gamma^{(s)}\left(z \pm \frac{p}{a}\right) \Big|_{p=0} &= \frac{(\pm 1)^s}{a^s} \Gamma(z) \sum_{m_0 m_1 \dots m_{s-1}} g_{m_0 m_1 \dots m_{s-1}} \\ &\times [\psi^{(0)}(z)]^{m_0} [\psi^{(1)}(z)]^{m_1} \dots [\psi^{(s-1)}(z)]^{m_{s-1}} \end{aligned} \tag{21}$$

with the additional conditions

$$m_0 + m_1 + \dots + m_{s-1} \leq s, \quad m_0 + 2m_1 + \dots + sm_{s-1} = s,$$

so that

$$\mathcal{B}_{k'k}^{(n)}(v', v) = \frac{B(q, q')}{2^n} \sum_{r=0}^n \binom{n}{r} (-1)^{n-r} \mathcal{F}[\psi^{(w)}(q), \psi^{(w')}(q')]. \tag{22}$$

Here \mathcal{F} is a function, involving power products of $\psi^{(w)}(q)$ and $\psi^{(w')}(q')$, to be determined. But calculations of (20) or (22) for arbitrary positive powers n , which amounts to evaluate the successive derivatives (21) of gamma, is not an easy task. This is because, to our knowledge, no direct calculation gives the g coefficients in a trivial way. However, this task may be carried out rather efficiently using symbolic computer programs such as Maple. In any case, we will present an alternative procedure in section 2.3 for computing equation (20) without knowing explicitly the successive derivatives of gamma.

Let us consider just the $n = 2$ and $n = 3$ cases to illustrate this method by computing the g coefficients ‘by hand’. Then, $\text{MPT } \tilde{X}_{v'v}^{j(2)}$ and $\text{MPT } \tilde{X}_{v'v}^{j(3)}$ are easily derived from (20) with

$$\mathcal{B}_{k'k}^{(2)}(v', v) = \frac{B(q, q')}{4} [\psi^{(1)}(q) + \psi^{(1)}(q') + \psi(q)^2 + \psi(q')^2 - 2\psi(q)\psi(q')], \tag{23}$$

and

$$\begin{aligned} \mathcal{B}_{k'k}^{(3)}(v', v) = & \frac{B(q, q')}{8} [\psi^{(2)}(q) - \psi^{(2)}(q') + 3\psi^{(1)}(q)\psi(q) \\ & - 3\psi^{(1)}(q)\psi(q') + 3\psi^{(1)}(q')\psi(q) - 3\psi^{(1)}(q)\psi(q') \\ & + \psi(q)^3 - \psi(q')^3 + 3\psi(q)\psi(q')^2 - 3\psi(q)^2\psi(q')], \end{aligned} \quad (24)$$

respectively.

- In order to calculate the matrix elements of the corresponding momentum operator $\bar{p} = -i\text{d}/\text{d}\bar{x} = -i\bar{\alpha}(1 - u^2)\text{d}/\text{d}u$, we need to take into account the recurrence relations for the Gegenbauer polynomials [34]

$$\begin{aligned} \frac{\text{d}C_v^\lambda(u)}{\text{d}u} &= 2\lambda C_{v-1}^{\lambda+1}(u), \\ uC_v^\lambda(u) &= C_{v-1}^\lambda(u) + \frac{v+1}{2(\lambda-1)}C_{v+1}^{\lambda-1}(u), \end{aligned} \quad (25)$$

so that the matrix elements

$$\text{MPT } \tilde{P}_{v'v}^{j(1)} = \int_{-\infty}^{+\infty} \Psi_{v'}^j(\bar{x}) \bar{p} \Psi_v^j(\bar{x}) \text{d}\bar{x}, \quad (26)$$

are expressed as

$$\begin{aligned} \text{MPT } \tilde{P}_{v'v}^{j(1)} = i\bar{\alpha} \left\{ (j-v) \left[\left(\frac{N_v^j}{N_{v+1}^j} \right) \frac{(v+1)}{2j-2v-1} {}^{(-1)}\mathcal{I}_{v',v+1}^{j,j} + \left(\frac{N_v^j}{N_{v-1}^{j-1}} \right) {}^{(0)}\mathcal{I}_{v',v-1}^{j,j-1} \right] \right. \\ \left. - \left(\frac{N_v^j}{N_{v-1}^j} \right) (2j-2v+1) {}^{(-1)}\mathcal{I}_{v',v-1}^{j,j} \right\}. \end{aligned} \quad (27)$$

In this last expression, we have introduced the following integral representation:

$${}^{(p)}\mathcal{I}_{v',v}^{j,j} = \frac{N_v^j N_{v'}^{j'}}{\bar{\alpha}} \int_{-1}^1 (1-u^2)^{\frac{j+j'}{2} - \frac{v+v'}{2} - p/2 - 1} C_{v'}^{(j'-v'+\frac{1}{2})}(u) C_v^{(j-v+\frac{1}{2})}(u) \text{d}u \quad (28)$$

which is written in a closed form as

$$\begin{aligned} {}^{(p)}\mathcal{I}_{v',v}^{j,j} = & \frac{N_v^j N_{v'}^{j'} (\beta_v)_v (\beta_{v'})_{v'}}{\bar{\alpha} v! v'!} \sum_{k=0}^v \sum_{k'=0}^{v'} (2)^{j+j'-(v+v')-p-1} \\ & \times B\left(\frac{j+j'}{2} - \frac{v+v'}{2} - \frac{p}{2}, \frac{j+j'}{2} - \frac{v+v'}{2} - \frac{p}{2} + k + k'\right) \\ & \times \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j'-v'+1)_{k'}}{(j-v+1)_k (j'-v'+1)_{k'} k! k'}, \end{aligned} \quad (29)$$

where $\Delta v = v - v'$ is odd. Note that ${}^{(p)}\mathcal{I}_{v',v}^{j,j}$ is a particular case of the more general integrals ${}^{(p,p')} \mathcal{I}_{v',v}^{j',j}$ defined in equation (A.3).

At this stage, we can simply note that the integrals ${}^{(p)}\mathcal{I}_{v',v}^{j,j}$ correspond to the matrix elements $\langle \Psi_{v'}^j | \cosh^p(\bar{\alpha}\bar{x}) | \Psi_v^j \rangle$ while the overlap integrals ${}^{(0)}\mathcal{I}_{v',v-1}^{j,j-1}$ are proportional to the Franck–Condon factors $\langle \Psi_{v'}^j | \Psi_{v-1}^{j-1} \rangle$ between two potentials whose depths are characterized by j and $j - 1$, respectively.

Thus, the calculation of the matrix elements of the MPT potential is reduced to

$$\langle \Psi_{v'}^j | -\frac{\bar{\alpha}^2 j(j+1)}{\cosh^2(\bar{\alpha}\bar{x})} | \Psi_v^j \rangle = -\bar{\alpha}^2 j(j+1) {}^{(-2)}\mathcal{I}_{v',v}^{j,j}. \quad (30)$$

For practical applications, we only need to evaluate matrix elements of \tilde{p}^2 which can be deduced from the eigenvalue equation (4) and from (30). In that case, we simply have

$${}^{\text{MPT}}\tilde{P}_{v',v}^{j(2)} \equiv \langle \Psi_{v'}^j | \tilde{p}^2 | \Psi_v^j \rangle = -\tilde{\alpha}^2 \{ (j-v)^2 \delta_{v',v} - j(j+1)^{(-2)} \mathcal{T}_{v',v}^{j,j} \}. \quad (31)$$

Using results (15) and (27) and from the basic definition of the bosonic operators a^+ and a , we can easily deduce the actions of the latters on the modified Pöschl–Teller eigenfunctions (2)

$$\begin{aligned} \langle \Psi_{v+l}^j | a | \Psi_v^j \rangle &= \frac{1}{\sqrt{2}} ({}^{\text{MPT}}\tilde{X}_{v+l,v}^{j(1)} + i {}^{\text{MPT}}\tilde{P}_{v+l,v}^{j(1)}) \\ \langle \Psi_{v+l}^j | a^+ | \Psi_v^j \rangle &= \frac{1}{\sqrt{2}} ({}^{\text{MPT}}\tilde{X}_{v+l,v}^{j(1)} - i {}^{\text{MPT}}\tilde{P}_{v+l,v}^{j(1)}), \quad l = \pm 1, \pm 3, \dots \end{aligned} \quad (32)$$

These last expressions generalize those found in many textbooks of quantum mechanics for the harmonic oscillator.

2.3. Alternative calculation of matrix elements $\langle \tilde{x}^n \rangle_{v'v}$

An alternative procedure can be used for deriving the matrix elements ${}^{\text{MPT}}\tilde{X}_{v',v}^{j(n)}$ of the operator \tilde{x}^n . It consists in the calculation of the desired expressions directly from equation (9) instead of (12) and in the derivation of the former with respect to p . Before considering the general case, let us focus on the $n = 1$ case as a first illustration.

Using the (q, q') variables defined in (11), we must calculate integrals with argument of the type $u^{q-1}(1-u)^{q'-1} \ln u/(1-u)$. To get rid of this problem, the logarithm function can be identified as two ${}_2F_1$ hypergeometric functions

$$\ln\left(\frac{u}{1-u}\right) = u {}_2F_1\left(\begin{matrix} 1, 1 \\ 2 \end{matrix}; u\right) - (1-u) {}_2F_1\left(\begin{matrix} 1, 1 \\ 2 \end{matrix}; 1-u\right), \quad (33)$$

and using the very useful integral representation [35]

$${}_{p+1}F_{q+1}\left(\begin{matrix} v, a_1, \dots, a_p \\ \mu + v, b_1, \dots, b_q \end{matrix}; y\right) = \frac{\Gamma(\mu + v)}{\Gamma(\mu)\Gamma(v)} \int_0^1 (1-t)^{\mu-1} t^{v-1} {}_pF_q\left(\begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix}; yt\right) dt, \quad (34)$$

we obtain another closed form for the desired matrix elements

$$\begin{aligned} {}^{\text{MPT}}\tilde{X}_{v',v}^{j(1)} &= \frac{2^{2j-(v+v')-2} N_v^j N_{v'}^j (\beta_v)_v (\beta_{v'})_{v'}}{\tilde{\alpha}^2 v! v'!} \\ &\times \sum_{k=0}^v \sum_{k'=0}^{v'} \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j-v'+1)_{k'}}{\Gamma(q+q'+1)(j-v+1)_k (j-v'+1)_{k'} k! k'!} \\ &\times \left[\Gamma(q+1)\Gamma(q') {}_3F_2\left(\begin{matrix} q+1, 1, 1 \\ q+q'+1, 2 \end{matrix}; 1\right) \right. \\ &\left. - \Gamma(q)\Gamma(q'+1) {}_3F_2\left(\begin{matrix} q'+1, 1, 1 \\ q+q'+1, 2 \end{matrix}; 1\right) \right]. \end{aligned} \quad (35)$$

Consider now another useful result, as a special case of ${}_3F_2(\alpha, 1, n+1; \beta, n+2; 1)$ [37]

$${}_3F_2\left(\begin{matrix} \alpha, 1, 1 \\ \beta, 2 \end{matrix}; 1\right) = \frac{\Gamma(\alpha)\Gamma(\beta-1)}{\Gamma(\alpha-1)\Gamma(\beta)} [\psi(\alpha-1) - \psi(\alpha-\beta)], \quad (36)$$

which does not appear in any tables of standard textbooks and which comes from a more general result (see equation (7.4.4.11) of [38]). So it can be shown, after substituting (36) into (35), that the form (15) can be recovered.

Concerning the general case $\langle \bar{x}^n \rangle_{v'v}$, we must evaluate the n th derivative of the integrals in equation (9) which is nothing but the function $\mathcal{B}_{k'k}^{(n)}(v', v)$ defined in (20). So the integral representation of expression (20) is given by

$$\mathcal{B}_{k'k}^{(n)}(v', v) = \int_0^1 u^{q-1} (1-u)^{q'-1} \left[\frac{1}{2} \ln \left(\frac{u}{1-u} \right) \right]^n du. \tag{37}$$

In order to compute this integral from (33) we have considered the following expansion for integral powers of the hypergeometric functions [26]:

$$\left[{}_2F_1 \left(\begin{matrix} 1, 1 \\ 2 \end{matrix}; z \right) \right]^n = n! \sum_{m=0}^{\infty} \frac{z^m}{m+n} t_m^{n-1}(1), \tag{38}$$

where t 's are recursively defined coefficients [26]

$$t_m^n(a) = \sum_{k=0}^m \frac{1}{k+na} t_k^{n-1}(a),$$

with $t_0^n(a) = 1/(n!a^n)$, $t_m^0(a) = 1$ and $t_k^1(a) = \psi(k+1+a) - \psi(a)$.

Using all the results above and after some algebra, we can straightforwardly check that

$$\begin{aligned} \mathcal{B}_{k'k}^{(n)}(v', v) &= \frac{n!}{2^n} \sum_{r=0}^n (-1)^{n-r} \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \frac{t_m^{r-1}(1) t_{m'}^{n-r-1}(1)}{(m+r)(m'+n-r)} \\ &\times B(q+r+m, q'+n-r+m'), \end{aligned} \tag{39}$$

with $t_m^{\sigma-1}(1)/(m+\sigma) = 1$ and $m = 0$ if $\sigma = 0$. So, the matrix elements $\text{MPT} \tilde{X}_{v'v}^{j(n)}$ are easily deduced from (18). We thus obtain a closed expression for the successive derivatives of the beta function. In order to make comparison with (22), we write equation (39) in a more convenient form

$$\begin{aligned} \mathcal{B}_{k'k}^{(n)}(v', v) &= \frac{B(q, q')}{2^n} \sum_{r=0}^n \binom{n}{r} (-1)^{n-r} r!(n-r)! \\ &\times \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \frac{t_m^{r-1}(1) t_{m'}^{n-r-1}(1)}{(m+r)(m'+n-r)} \frac{(q)_{m+r} (q')_{m'+n-r}}{(q+q')_{m+m'+n}}, \end{aligned} \tag{40}$$

where the two infinite sums in (40) may correspond to the \mathcal{F} function in (22) involving successive products of polygamma functions. Unlike expressions (20) or (22), we can compute the matrix elements $\text{MPT} \tilde{X}_{v'v}^{j(n)}$ directly from (39) or (40) without using explicitly the gamma function and its successive derivatives. Just consider the $n = 2$ case to illustrate the method.

As pointed out in [39], useful representations will naturally appear by transforming the inner finite sums in the t 's to infinite ones. For example, for $n = 2$ we write

$$\begin{aligned} t_m^1(1) &= \psi(m+2) - \psi(1) = \sum_{h=0}^m \frac{1}{h+1}, \\ &= (m+1) \sum_{h=0}^{\infty} \frac{1}{(h+1)(h+m+2)}. \end{aligned}$$

$t_m^1(1)$ being expressed as an infinite sum, we can finally derive the following result:

$$\begin{aligned} \mathcal{B}_{k'k}^{(2)}(v', v) &= T(q-1, q'-1) + T(q'-1, q-1) \\ &- \frac{B(q+1, q'+1)}{2} \sum_{m=0}^{\infty} \frac{(q'+1)_m}{(q+q'+2)_m (m+1)} \\ &\times {}_3F_2 \left(\begin{matrix} 1, 1, q+1 \\ 2, q+q'+2+m \end{matrix}; 1 \right), \end{aligned} \tag{41}$$

Table 1. Comparison between symbolic and numerical calculations for selected $\mathcal{B}_{k'k}^{(n)}(v', v)$ values for $(v, v') = (k, k') = (20, 20)$ and $j = 100$ (see equation (11)).

Equation	(20)	m_{\max}	(39)
$n = 2$ ($\times 10^{-62}$)		10	0.914 948 526
		40	0.921 511 543
	0.921 511 676	50	0.921 511 676
$n = 20$ ($\times 10^{-71}$)		40	0.098 700 268
		100	0.103 901 412
	0.103 901 414	120	0.103 901 414
$n = 30$ ($\times 10^{-75}$)		50	0.144 072 068
		100	0.176 269 202
	0.176 275 523	150	0.176 275 523

where we have defined

$$T(x, y) = \frac{B(x + 1, y + 3)}{4} \sum_{h=0}^{\infty} \frac{1}{(h + 1)(h + 2)} {}_4F_3 \left(\begin{matrix} 2, 2, y + 3, h + 2 \\ 3, h + 3, x + y + 4 \end{matrix}; 1 \right).$$

We can conclude that this result, though it seems different compared to (23), is fully equivalent once the hypergeometric functions are simplified.

Although complex analytical expressions could also be derived for $n > 2$, either from (20) or (39), it seems more advantageous to calculate numerically all the matrix elements directly from equations (39) and (18). Nowadays, the 64 bit computer programs enable us to compute such expressions at any level of accuracy. Practically, the two infinite series involved in (39) or (40) are truncated at certain values, say $m_{\max 1}$ and $m_{\max 2}$, respectively, where we set $m_{\max 1} = m_{\max 2} = m_{\max}$. An illustrative example is presented in table 1 for both methods. In this table, we compare the $\mathcal{B}_{k'k}^{(n)}(v', v)$ values obtained from (20) with symbolic calculations using Maple with those obtained numerically from (39) at different m_{\max} using the Fortran compiler. Only some selected values are given in this table, for $n = 2, 20$ and 30 and for $(v, v') = (k, k') = (20, 20)$ and $j = 100$ in (11). Concerning the numerical details, the recursive t coefficients have been determined using the definition of the digamma function for integer values [34], namely $\psi(n) = \sum_{k=1}^{n-1} k^{-1} - \gamma$ with $\gamma = -\psi(1)$ the Euler constant. To compute the gamma functions appearing in beta, we have employed the Lanczos approximation [40] using an 11 term expansion which provides an accuracy of 13 significant digits for all real numbers. As illustrated in table 1, the purely numerical calculations converge quite rapidly and are very similar to those obtained with equation (20). Note that Maple, though very accurate, becomes quite time consuming as (n, v, v', k, k') increase.

Some other numerical details about the convergence and computation of the matrix elements $\langle \bar{x}^n \rangle_{v'v}$ will be presented in section 3.2 for the second Pöschl–Teller potential.

3. The second Pöschl–Teller potential

3.1. Eigensolutions and symmetry

We now extend the previous MPT potential by adding a repulsive term at the origin and thus consider the second Pöschl–Teller potential [15, 28]. The dimensionless SPT equation is written as

$$\left[-\frac{d^2}{d\bar{x}^2} - \bar{\alpha}^2 \left(\frac{\lambda(\lambda + 1)}{\cosh^2(\bar{\alpha}\bar{x})} - \frac{\kappa(\kappa - 1)}{\sinh^2(\bar{\alpha}\bar{x})} \right) \right] \Psi_v^{(j,\kappa)}(\bar{x}) = \bar{E}_v^{\text{SPT}} \Psi_v^{(j,\kappa)}(\bar{x}), \quad (42)$$

with $\bar{x} \in [0, +\infty)$ and λ, κ are two strength parameters. Since we are only interested in the bound states, we may assume $\lambda > \kappa > 1$ throughout this section. The equilibrium position is given by

$$\bar{x}_{eq} = \frac{1}{\bar{\alpha}} \operatorname{arctanh} \left[\left(\frac{\kappa(\kappa - 1)}{\lambda(\lambda + 1)} \right)^{1/4} \right]. \quad (43)$$

As described in section 4, this potential can be used to calculate diatomic molecular energy spectra. More generally, although it is more common to choose potentials such as Morse or Kratzer [1, 2], it could also be used to describe stretching molecular vibrations in polyatomic systems. Unlike the Morse potential, the nonphysical region corresponding to $\bar{x} < 0$ is not included which thus allows us to characterize the true internuclear behaviour. Moreover, the SPT potential seems to be quite flexible since it possesses 3 parameters against 2 for the Morse potential $V_{\text{Morse}}(\bar{x}) = D[1 - \exp(-\beta\bar{x})]^2$.

During the past, this non-symmetrical system has been solved in different manners, e.g. using one of the oldest approach—the factorization method [41]—the algebraic approach [13, 14] and more recently one based on supersymmetry for shape invariant potentials [42]. In particular, this system exhibits very interesting properties involving an inherent symmetry associated with the non-compact Lie algebra $so(2, 1) \approx su(1, 1)$ [13]. The potential algebra was assigned to $so(2, 2)$ [12] locally isomorphic to $su(1, 1) \oplus su(1, 1)$. In that case, the generators connect eigenstates with the same energy but with different potentials. In addition, Quesne [14] has considered the enveloping algebra $sl(4, \mathfrak{R})$ as dynamical potential algebra and showed in particular that one of its generators can connect eigenstates corresponding to the same potential but with different v values.

As we are only interested in the negative-energy bound states, it has been shown that, in this case, the solution of (42) can be expressed in terms of the $SU(1, 1)$ Bargmann functions [43]—the analytical continuation of the Wigner functions for $SU(2)$ —corresponding to the positive discrete series $D_k^+(k = \frac{1}{2}, 1, \frac{1}{2}, 2, \dots)$. Following [14], the normalized eigenfunctions are given by

$$\Psi_v^{\lambda, \kappa}(\bar{x}) = [(2k - 1)\bar{\alpha} \sinh(2\bar{\alpha}\bar{x})]^{1/2} v_{m'm}^k(2\bar{\alpha}\bar{x}), \quad (44)$$

where the $SU(1, 1)$ Bargmann matrices are

$$\begin{aligned} v_{m'm}^k(\beta) &= \left[\binom{m' - k}{m - k} \binom{m' + k - 1}{m + k - 1} \right]^{1/2} \\ &\times [\sinh(\beta/2)]^{m' - m} [\cosh(\beta/2)]^{-m' - m} \\ &\times {}_2F_1 \left(\begin{matrix} k - m, 1 - m - k \\ m' - m + 1 \end{matrix}; -\sinh^2(\beta/2) \right), \end{aligned} \quad (45)$$

with the auxiliary quantum numbers m, m' related to κ, λ as

$$\kappa = m' - m + \frac{1}{2}, \quad \lambda = m' + m - \frac{1}{2}, \quad k = m - v,$$

with $m' > m + \frac{1}{2} > 1$.

Finally, the eigenstates are written

$$\Psi_v^{\lambda, \kappa}(\bar{x}) = N_v^{\lambda, \kappa} [\sinh(\bar{\alpha}\bar{x})]^\kappa [\cosh(\bar{\alpha}\bar{x})]^{-\lambda} {}_2F_1 \left(\begin{matrix} -v, \kappa - \lambda + v \\ \kappa + \frac{1}{2} \end{matrix}; -w^2 \right) \quad (46)$$

with $w = \sinh(\bar{\alpha}\bar{x})$ and

$$N_v^{\lambda, \kappa} = \left[2\bar{\alpha}(\lambda - \kappa - 2v) \binom{\kappa + v - \frac{1}{2}}{v} \binom{\lambda - v - \frac{1}{2}}{\lambda - \kappa - v} \right]^{1/2}.$$

The associated eigenvalues are written as [13, 14]

$$\bar{E}_v^{\text{SPT}} = -\bar{\alpha}^2(\lambda - \kappa - 2v)^2, \quad v = 0, 1, \dots, [(\lambda - \kappa)/2]. \tag{47}$$

To conclude this subsection, we would like to mention that the solutions (46) of the SPT are connected with the eigenfunctions of the Laplace–Beltrami operator on the hyperboloid $x_1^2 + x_2^2 - x_3^2 - x_4^2 = \rho^2 > 0$ [12].

3.2. Matrix elements $\langle \bar{x}^n \rangle_{v'v}$ and $\langle d/d\bar{x} \rangle_{v'v}$ between the SPT wavefunctions

Following the same procedure as in the previous section, we first evaluate, through the change of variable $u = \tanh(\bar{\alpha}\bar{x})$, the integral

$$\begin{aligned} {}^{(p)}\mathcal{O}_{v'v} &= \int_0^{+\infty} \Psi_{v'}^{\lambda,\kappa}(\bar{x}) [\cosh(\bar{\alpha}\bar{x}) + \sinh(\bar{\alpha}\bar{x})]^p \Psi_v^{\lambda,\kappa}(\bar{x}) d\bar{x}, \\ &= \frac{1}{\bar{\alpha}} \int_0^1 \Psi_{v'}^{\lambda,\kappa}(u)(1+u)^p(1-u^2)^{-p/2-1} \Psi_v^{\lambda,\kappa}(u) du, \end{aligned} \tag{48}$$

which can be expressed as

$$\begin{aligned} {}^{(p)}\mathcal{O}_{v'v} &= \frac{N_v^{\lambda,\kappa} N_{v'}^{\lambda,\kappa}}{\bar{\alpha}} \sum_{s=0}^v \sum_{s'=0}^{v'} \frac{(-1)^{s+s'} (-v)_s (-v')_{s'} (\gamma_v)_s (\gamma_{v'})_{s'}}{(\kappa + \frac{1}{2})_s (\kappa + \frac{1}{2})_{s'} s! s'!} \\ &\quad \times \int_0^1 (u)^{2\kappa+2(s+s')} (1-u)^{\sigma_{ss'}-p/2} (1+u)^{\sigma_{ss'}+p/2} du, \end{aligned} \tag{49}$$

with $\gamma_v = \kappa - \lambda + v$ ($\gamma_v, \gamma_{v'} < 0$) and $\sigma_{ss'} = \lambda - \kappa - (s + s') - 1$.

From equation (10) and using the properties of the ${}_2F_1(z)$ Gauss hypergeometric functions at $z = -1$, we finally arrive at the result

$$\begin{aligned} {}^{(p)}\mathcal{O}_{v'v} &= \frac{N_v^{\lambda,\kappa} N_{v'}^{\lambda,\kappa}}{\bar{\alpha}} \sum_{s,s'} \frac{(-1)^{s+s'} (-v)_s (-v')_{s'} (\gamma_v)_s (\gamma_{v'})_{s'}}{(\kappa + \frac{1}{2})_s (\kappa + \frac{1}{2})_{s'} s! s'!} \\ &\quad \times \frac{\Gamma(2\kappa + 2(s + s') + 1) \Gamma(\sigma_{ss'} - p/2 + 1)}{4^{2-\sigma_{ss'}} \Gamma(2\lambda)} \\ &\quad \times \sum_{j=0}^p \binom{p}{j} \frac{\Gamma(\lambda + j/2)}{\Gamma(\kappa + s + s' + 1 + (j - p)/2)}. \end{aligned} \tag{50}$$

Unfortunately, the differentiation of this last equation with respect to p is very difficult because of the p -dependent sum. So we can proceed exactly as in section 2.3 by evaluating the matrix elements $\langle \bar{x}^n \rangle_{v'v}$ from equations (14) and (49). To this end, the logarithm function arising from the derivative with respect to p is expressed as

$$\ln\left(\frac{1+u}{1-u}\right) = 2u {}_2F_1\left(\frac{1}{2}, 1; \frac{3}{2}; u^2\right), \tag{51}$$

and the integral representation (34), with appropriate integration variables, is considered. That finally leads to

$$\begin{aligned} \text{SPT } \tilde{X}_{v'v}^{\lambda,\kappa(1)} &= \frac{N_v^{\lambda,\kappa} N_{v'}^{\lambda,\kappa}}{2\bar{\alpha}^2} \sum_{s=0}^v \sum_{s'=0}^{v'} \frac{(-1)^{s+s'} (-v)_s (-v')_{s'} (\gamma_v)_s (\gamma_{v'})_{s'}}{(\kappa + \frac{1}{2})_s (\kappa + \frac{1}{2})_{s'} s! s'!} \\ &\quad \times B(\sigma_{ss'} + 1, \kappa + s + s' + 1) {}_3F_2\left(\frac{1}{2}, 1, \kappa + s + s' + 1; \frac{3}{2}, \lambda + 1; 1\right), \end{aligned} \tag{52}$$

with $\Delta v = 0, \pm 1, \pm 2 \dots$ and with the additional condition $\lambda - \kappa - s - s' > 0$. Note that this latter condition ensures that the ${}_3F_2$ series of unit argument

$$\frac{\Gamma(\kappa + s + s' + 1)}{\Gamma(\lambda + 1)} {}_3F_2 \left(\begin{matrix} \frac{1}{2}, 1, \kappa + s + s' + 1 \\ \frac{3}{2}, \lambda + 1 \end{matrix}; 1 \right) = \sum_{k=0}^{\infty} \frac{1}{2k+1} \frac{(\kappa + s + s' + k)!}{(\lambda + k)!}$$

is convergent and then numerically stable and computable at the desired accuracy even if the convergence will be slower and slower as $\kappa + s + s' \rightarrow \lambda$. It also turns out that this series can be evaluated in a closed form making some assumptions. Indeed further simplifications occur when assuming $(\lambda - \kappa)/2 = V_m$ integer. Setting $r = 2V_m - s - s' > 0$, the ${}_3F_2(1)$ series can be thus rearranged as [37]

$${}_3F_2 \left(\begin{matrix} \frac{1}{2}, 1, \lambda - r + 1 \\ \frac{3}{2}, \lambda + 1 \end{matrix}; 1 \right) = \frac{\Gamma(\lambda + 1)\Gamma(\lambda - r + \frac{1}{2})[\psi(\lambda - r + 1) - \psi(\frac{1}{2})]}{2\Gamma(\lambda - r + 1)\Gamma(\lambda + \frac{1}{2})} + \frac{\Gamma(\lambda + 1)\Gamma(\frac{1}{2} - \lambda)}{2} \sum_{l=0}^{r-2} \frac{(-1)^l}{(r-l-1)\Gamma(r-l)\Gamma(\frac{3}{2} - \lambda + l)}$$

which is a special case of a known result (see equation (7.4.4.11) of [38]). Note that we have $\psi(\frac{1}{2}) = -\gamma - 2 \ln 2$.

- Concerning the calculation of $\langle \bar{x}^n \rangle_{v'v}$, we have to evaluate now integrals of the type

$$\mathcal{M}_{ss'}^{(n)} = \int_0^1 u^{2\kappa+2(s+s')} (1-u^2)^{\sigma_{ss'}} \left[\frac{1}{2} \ln \left(\frac{1-u}{1+u} \right) \right]^n du. \tag{53}$$

From the method described in section 2.3 as well as from results of [26], we can integrate (53) to obtain a series representation

$$\mathcal{M}_{ss'}^{(n)} = \sum_{m=0}^{\infty} \frac{n!}{2^n} \frac{t_m^{n-1}(\frac{1}{2})}{2m+n} B \left(\sigma_{ss'} + 1, \kappa + s + s' + m + \frac{n+1}{2} \right), \tag{54}$$

which finally leads to

$$\text{SPT } \tilde{X}_{v'v}^{\lambda, \kappa(n)} = \frac{N_v^{\lambda, \kappa} N_{v'}^{\lambda, \kappa}}{\bar{\alpha}^{n+1}} \sum_{s=0}^v \sum_{s'=0}^{v'} (-1)^{s+s'} \frac{(-v)_s (-v')_{s'} (\gamma_v)_s (\gamma_{v'})_{s'}}{(\kappa + \frac{1}{2})_s (\kappa + \frac{1}{2})_{s'} s! s'!} \mathcal{M}_{ss'}^{(n)}. \tag{55}$$

Two illustrative examples are now considered for the $n = 2$ and $n = 3$ cases. To derive $\text{SPT } \tilde{X}_{v'v}^{\lambda, \kappa(2)}$ and $\text{SPT } \tilde{X}_{v'v}^{\lambda, \kappa(3)}$, we first need to find the expressions of $\mathcal{M}_{ss'}^{(2)}$ and $\mathcal{M}_{ss'}^{(3)}$, respectively. For the $n = 2$ case, one has

$$\mathcal{M}_{ss'}^{(2)} = \frac{1}{4} \sum_{m=0}^{\infty} \frac{t_m^1(\frac{1}{2})}{m+1} B \left(\sigma_{ss'} + 1, \kappa + s + s' + m + \frac{3}{2} \right). \tag{56}$$

As already pointed out in section 2.3, to generate useful representations for successive and increasing values of n , the inner finite sums that appear in the coefficients $t_m^n(a)$ must be transformed to infinite ones. For example, we note that for $n = 2$

$$\begin{aligned} t_m^1 \left(\frac{1}{2} \right) &= \psi \left(m + \frac{3}{2} \right) - \psi \left(\frac{1}{2} \right) = \sum_{h=0}^m \frac{1}{h + \frac{1}{2}}, \\ &= (m+1) \sum_{h=0}^{\infty} \frac{1}{(h + \frac{1}{2})(h + m + \frac{3}{2})}. \end{aligned}$$

Table 2. Convergence of the matrix elements $\text{SPT} \tilde{X}_{v'v}^{\lambda,\kappa(n)}$ for $n = 2, 10$ and 26 as a function of m_{\max} (see the text) and with $\lambda = 248, \kappa = 80$ and $\bar{\alpha} = 0.0546$ (see equation (68)).

(v', v)	m_{\max}	$n = 2$	m_{\max}	$n = 10$	m_{\max}	$n = 26$
(0, 0)	10	140.590 213 746	10	6.318 025 589	10	($\times 10^{28}$) 2.349 179 558
	20	140.590 424 344	20	6.320 090 941	20	2.434 267 545
	50	140.590 424 350	50	6.320 091 207	50	2.434 449 668
	60	140.590 424 350	60	6.320 091 207	60	2.434 449 668
(10, 30)		($\times 10^{-12}$)				($\times 10^{21}$)
	20	-1.602 495 681	20	-3.687 463 969	20	44.621 (832)
	50	-1.958 673 128	50	-1.986 779 565	50	-0.914 595 903
	80	-1.958 675 387	80	-1.986 549 486	80	-1.135 766 963
	100	-1.958 675 386	100	-1.986 549 380	150	-1.135 493 531
(70, 70)				($\times 10^{16}$)		($\times 10^{43}$)
	100	1746.538 928 659	100	3.124 734 468	100	0.250 (900)
	300	1784.822 200 328	300	5.075 358 079	300	5.295 (528)
	700	1784.670 124 177	700	5.206 553 874	700	8.984 (789)
	1300	1784.671 728 304	1300	5.207 150 209	1300	9.103 983 688
	1700	1784.671 729 074	1700	5.207 150 736	1700	9.104 412 985
	1800	1784.671 729 081	1800	5.207 150 742	2000	9.104 426 556
					2200	9.104 427 680
					2300	9.104 427 852

Interchanging the two infinite sums in (56) and performing convenient transformations, we obtain

$$\mathcal{M}_{ss'}^{(2)} = \frac{B(\sigma_{ss'} + 1, \kappa + s + s' + \frac{3}{2})}{4} \sum_{h=0}^{\infty} \frac{1}{(h + \frac{1}{2})(h + \frac{3}{2})} \times {}_3F_2\left(1, h + \frac{1}{2}, 1, \kappa + s + s' + \frac{3}{2}; h + \frac{5}{2}, \lambda + \frac{3}{2}; 1\right). \tag{57}$$

For the $n = 3$ case, transforming this time the two inner finite sums that appear in $t_m^2(1/2)$ as infinite ones and after a suitable ordering, the $\mathcal{M}_{ss'}^{(3)}$ series becomes

$$\mathcal{M}_{ss'}^{(3)} = \frac{B(\sigma_{ss'} + 1, \kappa + s + s' + 2)}{4} \sum_{h=0}^{\infty} \frac{1}{(h + \frac{1}{2})} \times \sum_{k=0}^{\infty} \frac{1}{(h + k + \frac{3}{2})(h + k + \frac{5}{2})} {}_4F_3\left(\frac{3}{2}, 2, h + k + \frac{5}{2}, 1, \kappa + s + s' + 2; \frac{5}{2}, h + k + \frac{7}{2}, \lambda + 2; 1\right). \tag{58}$$

For the $n \geq 4$ cases, similar but very complex expressions could be derived in the same way. However, all calculations of the matrix elements $\text{SPT} \tilde{X}_{v'v}^{\lambda,\kappa(n)}$ may be carried out numerically directly from (54) and computed with 64 bits of precision on any current PCs without significant loss of precision. For practical applications, the infinite sum in (54) is truncated at a certain value, say m_{\max} . Table 2 gives information to us about the convergence of the $\text{SPT} \tilde{X}_{v'v}^{\lambda,\kappa(n)}$ as a function of m_{\max} for $n = 2, 10$ and 26 and for different (v', v) sets. As highlighted in this table, all matrix elements converge reasonably well—with accuracy $\sim 10^{-7}$ – 10^{-9} —even for very large powers of n and for excited vibrational states v .

- For the calculation of the matrix elements of the momentum operator $\bar{p} = -i\text{d}/\text{d}\bar{x}$

$$\text{SPT } \tilde{P}_{v'v}^{\lambda,\kappa(1)} = \int_0^{+\infty} \Psi_{v'}^{\lambda,\kappa}(\bar{x}) \bar{p} \Psi_v^{\lambda,\kappa}(\bar{x}) \text{d}\bar{x}, \quad (59)$$

the well-known relations for the hypergeometric functions [34] are considered

$$\begin{aligned} \frac{\text{d}}{\text{d}z} {}_2F_1 \left(\begin{matrix} -v, b \\ c \end{matrix}; z \right) &= \frac{(-v)b}{c} {}_2F_1 \left(\begin{matrix} -v+1, b+1 \\ c+1 \end{matrix}; z \right), \\ {}_2F_1 \left(\begin{matrix} -v, b \\ c \end{matrix}; z \right) &= (1-z)^v {}_2F_1 \left(\begin{matrix} -v, c-b \\ c \end{matrix}; \frac{z}{z-1} \right). \end{aligned}$$

So, using the integral representation ${}^{(p,p')}\mathcal{K}_{v',v}^{\lambda,\kappa,\lambda\kappa}$ defined in equation (A.7), we can show that

$$\begin{aligned} \text{SPT } \tilde{P}_{v'v}^{\lambda,\kappa(1)} &= i\bar{\alpha} \left\{ -\kappa^{(-1,-2)} \mathcal{K}_{v',v}^{\lambda\kappa,\lambda\kappa} + (\lambda - \kappa - 2v)^{(1,0)} \mathcal{K}_{v',v}^{\lambda\kappa,\lambda\kappa} \right. \\ &\quad \left. + \left(\frac{N_v^{\lambda,\kappa}}{N_{v-1}^{\lambda,\kappa+1}} \right) \frac{2v(\lambda - v + 1/2)}{\kappa + 1/2} {}^{(0,-1)}\mathcal{K}_{v',v-1}^{\lambda\kappa,\lambda\kappa+1} \right\}, \quad (60) \end{aligned}$$

and $\text{SPT } \tilde{P}_{vv}^{\lambda,\kappa(1)} = 0$.

The matrix elements of \bar{p}^2 are easily deduced from the eigenvalue equation (42) as well as results of appendix A

$$\text{SPT } \tilde{P}_{v'v}^{\lambda,\kappa(2)} = -\bar{\alpha}^2 \left\{ (\lambda - \kappa - 2v)^2 \delta_{v'v} - \lambda(\lambda + 1)^{(0,-2)} \mathcal{K}_{v',v}^{\lambda\kappa,\lambda\kappa} + \kappa(\kappa - 1)^{(-2,-2)} \mathcal{K}_{v',v}^{\lambda\kappa,\lambda\kappa} \right\}. \quad (61)$$

The action of the bosonic operators a^+ and a on the second Pöschl–Teller eigenfunctions (46) are also easily deduced

$$\begin{aligned} \langle \Psi_{v+l}^{\lambda,\kappa} | a | \Psi_v^{\lambda,\kappa} \rangle &= \frac{1}{\sqrt{2}} \left(\text{SPT } \tilde{X}_{v+l,v}^{\lambda,\kappa(1)} + i \text{SPT } \tilde{P}_{v+l,v}^{\lambda,\kappa(1)} \right) \\ \langle \Psi_{v+l}^{\lambda,\kappa} | a^+ | \Psi_v^{\lambda,\kappa} \rangle &= \frac{1}{\sqrt{2}} \left(\text{SPT } \tilde{X}_{v+l,v}^{\lambda,\kappa(1)} - i \text{SPT } \tilde{P}_{v+l,v}^{\lambda,\kappa(1)} \right), \quad (62) \end{aligned}$$

with $l = 0, \pm 1, \pm 2, \dots$

4. Application to the rovibrational energy spectrum of $^{12}\text{C}^{16}\text{O}$

This part intends to apply the general methods described above to the one-dimensional diatomic system $^{12}\text{C}^{16}\text{O}$. Its spectroscopic data span 75.10% of the X electronic ground state which corresponds to vibrational states with $v \leq 41$ [44]. The rotational J values range from 0 to 133. So this molecule turns out to be a very good candidate for testing the validity of the SPT model. To our knowledge, there exists no high-resolution spectroscopic studies for diatomics involving the SPT potential that is why this present work is worth being done.

The Schrödinger equation for the calculation of ro-vibrational energy levels of a diatomic molecule may be written as [45]

$$\left[\frac{\hat{p}^2}{2\mu} + \frac{\hbar^2}{2\mu r^2} [1 + \alpha(r)] \mathcal{J}^2 + U(r) \right] \Psi(r) = E \Psi(r), \quad (63)$$

where $U(r) = U_{\text{BO}}(r) + \Delta U^{\text{ad}}(r)$ includes the Born–Oppenheimer potential and the mass-dependent adiabatic contribution, respectively. r is the internuclear distance between the two atoms and μ the reduced mass. For the rotational part, $\mathcal{J}^2 = J(J+1)$ and $\alpha(r)$ are nonadiabatic

rotational BOB functions describing the interactions with excited electronic states. A detailed description of all these terms can be found in [44].

Following the procedure described in [46, 47], the overall potential $U(r)$ is fitted by a ξ polynomial of order 28—with $\xi = (r - r_e)/r_e$ the Dunham variable—while the term $1/r^2$ is expanded as a 40th-order Taylor ξ -polynomial so that the radial Hamiltonian $H = H(\hat{p}, r, \mathcal{J})$ can be converted to

$$H(p, q, J) = \sum_{s=0,1} \sum_m \sum_{u=0,1} \gamma_{smu} p^{2s} q^m [J(J+1)]^u. \quad (64)$$

Here, q and $p = -i\hbar/dq$ are dimensionless normal coordinates and the corresponding conjugate momentum, respectively, and $m = u = 0$ if $s = 1$ in (64). The normal coordinates are defined from ξ as $q = r_e \sqrt{\mu \omega_e / \hbar} \xi$ where the oscillator frequency $\omega_e = (1/2\pi c r_e) \sqrt{k_e / \mu}$, expressed in cm^{-1} , is determined from the force constant $k_e = d^2U(r)/dr^2|_{r=r_e}$. Note that we have found $\omega_e = 2170.538 \text{ cm}^{-1}$ for $^{12}\text{C}^{16}\text{O}$.

Since the potential $V(q) = H(0, q, 0)$ is centred around the origin $q = 0$, the corresponding wavefunctions (44) must be displaced from the quantity q_0 , that is

$$\Psi_v^{\lambda,\kappa}(q + q_0) = D(q_0) \Psi_v^{\lambda,\kappa}(q) \quad \text{with} \quad D(q_0) = e^{iq_0 p}, \quad (65)$$

where we have defined $q_0 = q_{eq} + q'_0$. Here, the fixed value q_{eq} simply corresponds to the equilibrium value (43) which allows to centre the wavefunctions at $q = 0$ while q'_0 is a free variational parameter. This latter will be adjusted when minimizing the energies E_{vJ} resulting from the diagonalization, for each J , of the Hamiltonian matrix.

Alternatively, instead of using the transformed wavefunctions (65), we may transform the Hamiltonian and consider the initial functions $\Psi_v^{\lambda,\kappa}(q)$. As $D(q_0)$ is unitary, the transformed Hamiltonian is simply given by

$$\tilde{H} = D^\dagger H D = \sum_{s,m,u} \sum_{r=0}^m \binom{m}{r} (-q_0)^r \gamma_{smu} p^{2s} q^{r-m} [J(J+1)]^u, \quad (66)$$

and our aim thus consists in the construction of the corresponding Hamiltonian matrix using the states $\Psi_v^{\lambda,\kappa}(q)$.

For the present study, we used the Ritz variational approach and expanded the trial wavefunctions in terms of the functions (44)

$$\Psi_{\text{trial}} = \sum_{v=0}^{V_{\text{max}}} c_v \Psi_v^{\lambda,\kappa}(q; \bar{\alpha}), \quad (67)$$

where we have defined, similarly to q_0 , the quantity $\bar{\alpha} = \bar{\alpha}_0 + \alpha'_0$. Here the λ, κ and $\bar{\alpha}_0$ parameters of the SPT potential (42) are fixed at their initial values determined from the potential shape while the quantity α'_0 is a free nonlinear variational parameter to be adjusted such that $\partial E / \partial \alpha'_0 = 0$. V_{max} is the size of the basis corresponding to the Hamiltonian matrix truncation. Note that the matrix elements of \tilde{H} were built using equations (55) and (61).

The optimization of the variational parameters (α'_0, q'_0) has been carried out on the purely vibrational problem; the procedure is the following. We first define the average quantity $S_v = \sum_v E_{v0} / N$ with $v = 0 \dots N = 41$. Then, for a given value of V_{max} , we vary (α'_0, q'_0) and find the corresponding vibrational energies resulting from the diagonalization of \tilde{H} . The optimized (α'_0, q'_0) set is thus determined in such a way that the average quantity S_v is minimized, meaning that $\partial S_v / \partial \alpha'_0 = \partial S_v / \partial q'_0 = 0$. This is based on the variational nature of the basis truncation, which makes *a priori* all eigenvalues E_{vJ} lower.

For our practical application to the $^{12}\text{C}^{16}\text{O}$ molecule, we have considered the following fixed parameters found from the $V(q)$ potential shape and from (43)

$$V_{\text{max}} = 70, \quad \lambda = 248, \quad \kappa = 80, \quad \bar{\alpha}_0 = 0.0546, \quad q_{eq} = 11.7407. \quad (68)$$

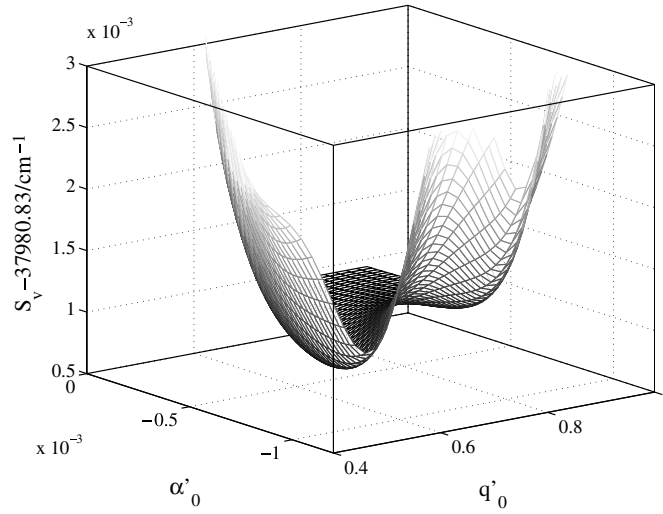


Figure 1. Average quantity $\Delta S_v = S_v - 37980.83$ (see the text) plotted in the space (α'_0, q'_0) of variational parameters for $^{12}\text{C}^{16}\text{O}$ at $V_{\max} = 70$.

For the construction of the matrix elements of q^n , we have set $m_{\max} = 2200$ in (54) to ensure a good convergence for all (n, v', v) sets. For example, the convergence error between $m_{\max} = 2200$ and $m_{\max} = 2500$ for $\text{SPT } \tilde{X}_{70,70}^{\lambda,\kappa(40)}$ is around 10^{-5} which remains below the experimental accuracy.

Finally, the optimized values of (α'_0, q'_0) are those corresponding to the minimum of the surface plotted in figure 1 and built in the space of variational parameters. We thus find

$$\alpha'_0 = -0.000225, \quad q'_0 = 0.74. \quad (69)$$

The corresponding functions $\Psi_v^{\lambda,\kappa}(q + q_0)$ are plotted in figure 2 and are compared to the true eigenfunctions of the transformed Hamiltonian (66). The slight discrepancy for low v -values between $\Psi_v^{\lambda,\kappa}(q + q_0)$ and the true eigenkets is probably due to the shift q'_0 . In fact, since q'_0 has been determined from a global optimization ($\partial S_v / \partial q'_0 = 0$), the functions $\Psi_v^{\lambda,\kappa}(q + q_0)$ are well adapted to describe, *in average*, all the vibrational states but are not necessarily suited to *locally* describe one state in particular. Nevertheless, one can point out on this figure the quite good consistency of the $\Psi_v^{\lambda,\kappa}(q + q_0)$ functions for the overall potential range.

Using the values (69), we are able to compute all energy levels up to $v = 41$ and $J = 133$, corresponding to the experimental data. Some selected calculated values are listed in table 3. We have compared our results to all the observed transitions (downloadable as indicated in [44]) used to generate the potential $U(r)$ from a Direct-Potential-Fit approach (DPF). This approach is based on the numerical solutions of the radial equation; more details concerning this approach can be found in [44].

We have obtained an rms error of 0.0012 cm^{-1} for the 13719 observed transitions of the $^{12}\text{C}^{16}\text{O}$ species. We can compare this value to that obtained from the DPF approach which is exactly the same one. Other studies were carried out in [46, 47] for this molecule using the harmonic oscillator and the displaced squeezed Fock states. Similar results were found using basis-sets truncated at $V_{\max} = 280$ and 100, respectively. We can thus conclude that the PT eigenfunctions (44) are well suited to perform variational calculations for diatomic molecules. It remains to test their validity on polyatomic systems.

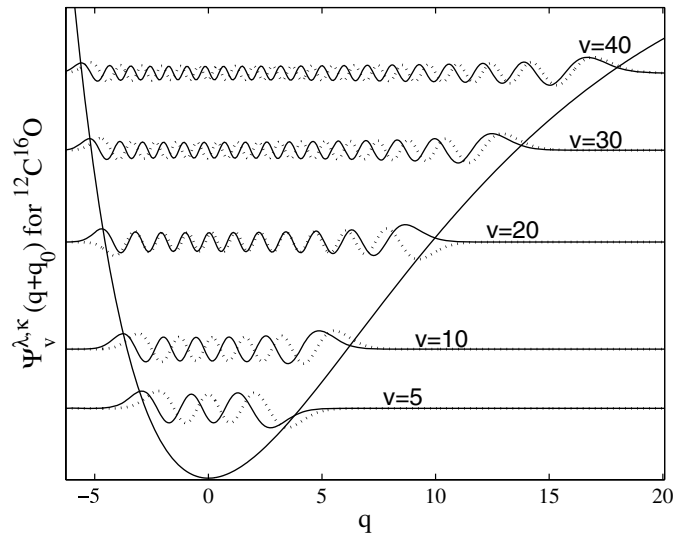


Figure 2. Plot of the wavefunctions $\Psi_v^{\lambda, \kappa}(q + q_0)$ (solid line), equation (44), for $v = 5, 10, 20, 30$ and 40 and with the parameters of equations (68) and (69). The eigenkets of \tilde{H} are also plotted (dotted line) for $V_{\max} = 70$.

Table 3. Selected energy levels E_{vJ} for $^{12}\text{C}^{16}\text{O}$ obtained with $V_{\max} = 70$ and with from the values (68) and (69).

v	J	E_{vJ}	v	J	E_{vJ}
0	0	1081.7714	10	0	21 331.1397
	5	1139.4418		5	21 383.5615
	10	1293.1756		10	21 523.2990
	50	5944.5126		50	25 747.6727
	100	19 880.4991		100	38 360.2886
5	0	11 533.9936	30	0	54 166.4956
	5	11 589.0390		5	54 208.4355
	10	11 735.7727		20	54 752.6237
	50	16 173.5949	40	0	66 901.6768
	100	29 448.1415		5	66 938.3002
				10	67 035.9047

5. Conclusion

In this work, we have established general expressions for the matrix elements of the operators x^n for two hyperbolic Pöschl–Teller potentials. Taking advantage of the analytical properties of hypergeometric series, all the desired expressions have been put in closed forms. Moreover, an analytical expression for the n th derivative of the beta function has been derived. Its values have been computed using symbolic and purely numerical calculations and successfully compared for both methods. Although our compact results involve infinite series, we have verified numerically the good convergence of our matrix elements in a fast way and without loss of precision. These expressions could be now of great interest in molecular physics, and in particular for high-resolution spectroscopic calculations which involve couplings between

bending and stretching vibrations. Rather than describing as usual the stretching modes with Morse oscillators and bending modes with harmonic oscillators, we are now able to treat simultaneously both motions with the MPT and SPT potentials, respectively.

Appendix. Matrix elements $\langle \cosh^n(\bar{\alpha}\bar{x}) \rangle_{v'v}$, $\langle \sinh^n(\bar{\alpha}\bar{x}) \rangle_{v'v}$ and $\langle \tanh^n(\bar{\alpha}\bar{x}) \rangle_{v'v}$

A.1. Matrix elements between the MPT wavefunctions

Let us consider the following integral

$$\begin{aligned} {}^{(p,p')} \mathcal{J}_{v'v}^{j',j} &= \int_{-\infty}^{+\infty} \Psi_{v'}^{j'}(\bar{x}) [\tanh(\bar{\alpha}\bar{x})]^p [\cosh(\bar{\alpha}\bar{x})]^{p'} \Psi_v^j(\bar{x}) d\bar{x}, \\ &= \frac{1}{\bar{\alpha}} \int_{-1}^{+1} \Psi_{v'}^{j'}(u) u^p (1-u^2)^{-p'/2-1} \Psi_v^j(u) du. \end{aligned} \tag{A.1}$$

Such an integral can be cast in the form

$$\begin{aligned} {}^{(p,p')} \mathcal{J}_{v'v}^{j',j} &= \frac{2^{2a'+1} N_v^j N_{v'}^{j'} (\beta_{jv})_v (\beta_{j'v'})_{v'}}{\bar{\alpha} v! v'!} \\ &\times \int_0^1 u^{a'} (1-u)^{a'} (1-2u)^p {}_2F_1 \left(\begin{matrix} -v', 2j' - v' + 1 \\ j' - v' + 1 \end{matrix}; u \right) \\ &\times {}_2F_1 \left(\begin{matrix} -v, 2j - v + 1 \\ j - v + 1 \end{matrix}; u \right) du, \end{aligned} \tag{A.2}$$

with $\beta_{jv} = 2j - 2v + 1$ and $a' = \frac{j'+j}{2} - \frac{v'+v}{2} - \frac{p'}{2} - 1$. Using equation (10), this expression can be written as

$$\begin{aligned} {}^{(p,p')} \mathcal{J}_{v'v}^{j',j} &= \frac{2^{2a'+1} N_v^j N_{v'}^{j'} (\beta_{jv})_v (\beta_{j'v'})_{v'} \Gamma(c-b)}{\bar{\alpha} v! v'!} \\ &\times \sum_{k=0}^v \sum_{k'=0}^{v'} \frac{\Gamma(b)}{\Gamma(c)} \frac{(-v)_k (-v')_{k'} (2j-v+1)_k (2j'-v'+1)_{k'}}{(j-v+1)_k (j'-v'+1)_{k'} k! k'!} \\ &\times {}_2F_1 \left(\begin{matrix} -p, b \\ c \end{matrix}; 2 \right), \end{aligned} \tag{A.3}$$

with $b = a' + k' + k + 1$ and $c = 2a' + k' + k + 2$. For $p = 0$, the integral (29) can be recovered when simplifying the ${}_2F_1(2)$ series and we have in this case Δv even. The condition $c - b > 0$ implies that $p' < 2j - (v' + v)$.

Various matrix elements can be deduced from this closed form which is written in a more compact form than in [9]. For example, we have ($n \in \mathbb{Z}$)

$$\begin{aligned} \langle v' | \tanh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{MPT}} &= {}^{(n,0)} \mathcal{J}_{v'v}^{j,j}, \\ \langle v' | \cosh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{MPT}} &= {}^{(0,n)} \mathcal{J}_{v'v}^{j,j} \equiv {}^{(n)} \mathcal{J}_{v'v}^{j,j} \text{ (see equation (29))}, \\ \langle v' | \sinh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{MPT}} &= {}^{(n,n)} \mathcal{J}_{v'v}^{j,j}. \end{aligned} \tag{A.4}$$

A.2. Matrix elements between the SPT wavefunctions

Let

$${}^{(p,p')} \mathcal{K}_{v'v}^{\lambda',\kappa',\lambda,\kappa} = \int_0^{+\infty} \Psi_{v'}^{\lambda',\kappa'}(\bar{x}) [\tanh(\bar{\alpha}\bar{x})]^p [\cosh(\bar{\alpha}\bar{x})]^{p'} \Psi_v^{\lambda,\kappa}(\bar{x}) d\bar{x}, \tag{A.5}$$

the integral to be evaluated. Performing a suitable change of variable, we write

$${}_{(p,p')} \mathcal{K}_{v'v}^{\lambda',\kappa',\lambda\kappa} = \frac{N_v^{\lambda,\kappa} N_{v'}^{\lambda',\kappa'}}{2\bar{\alpha}} \int_0^1 u^v (1-u)^{\mu-1} \times {}_2F_1\left(-v', \lambda' - v' + \frac{1}{2}; \kappa' + \frac{1}{2}; u\right) {}_2F_1\left(-v, \lambda - v + \frac{1}{2}; \kappa + \frac{1}{2}; u\right) du \tag{A.6}$$

with $v = \frac{\kappa'+\kappa+p-1}{2}$ and $\mu = \frac{\lambda'-\kappa'}{2} + \frac{\lambda-\kappa}{2} - (v'+v) - \frac{p'}{2}$.

Using equation (34) and after some algebraic manipulations, we simply get

$${}_{(p,p')} \mathcal{K}_{v'v}^{\lambda',\kappa',\lambda\kappa} = \frac{N_v^{\lambda,\kappa} N_{v'}^{\lambda',\kappa'}}{2\bar{\alpha}} \sum_{m'=0}^{v'} \frac{(-v')_{m'} (\lambda' - v' + \frac{1}{2})_{m'}}{(\kappa' + \frac{1}{2})_{m'} m'!} \times B(\mu, v + m' + 1) {}_3F_2\left(-v, v + m' + 1, \lambda - v + \frac{1}{2}; \mu + v + m' + 1, \kappa + \frac{1}{2}; 2\right), \tag{A.7}$$

where p' must satisfy the condition $\mu > 0$.

Similarly to the MPT, we have ($n \in \mathbb{Z}$)

$$\begin{aligned} \langle v' | \tanh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{SPT}} &= {}^{(n,0)} \mathcal{K}_{v'v}^{\lambda\kappa,\lambda\kappa}, \\ \langle v' | \cosh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{SPT}} &= {}^{(0,n)} \mathcal{K}_{v'v}^{\lambda\kappa,\lambda\kappa}, \\ \langle v' | \sinh^n(\bar{\alpha}\bar{x}) | v \rangle_{\text{SPT}} &= {}^{(n,n)} \mathcal{K}_{v'v}^{\lambda\kappa,\lambda\kappa}. \end{aligned} \tag{A.8}$$

References

[1] Jensen P 1988 *J. Mol. Spectrosc.* **128** 478
 [2] Requena A, Alacid M, Bastida A and Zúñiga J 1994 *Int. J. Quantum Chem.* **52** 165
 [3] Sage M L 1978 *Chem. Phys.* **35** 375
 [4] Zúñiga J, Hidalgo A, Francés J M and Requena A 1988 *Phys. Rev. A* **38** 4205
 [5] Francés J M, Zúñiga J, Alacid M and Requena A 1989 *J. Chem. Phys.* **90** 5536
 [6] Tuzun R E and Secrest D 1992 *Comput. Phys. Commun.* **70** 362
 [7] Matsumoto A 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 2863
 [8] Dong S H, Lemus R and Frank A 2002 *Int. J. Quantum Chem.* **86** 433
 [9] Zúñiga J, Alacid M, Requena A and Bastida A 1996 *Int. J. Quantum Chem.* **57** 43
 [10] Gomez-Camacho J, Lemus R and Arias J M 2004 *J. Phys. A: Math. Gen.* **37** 5237
 [11] Dong S H and Lemus R 2002 *Int. J. Quantum Chem.* **86** 265
 [12] Wu J and Alhassid Y 1990 *J. Math. Phys.* **31** 557
 [13] Barut A O, Inomata A and Wilson R 1987 *J. Phys. A: Math. Gen.* **20** 4083
 [14] Quesne C 1989 *J. Phys. A: Math. Gen.* **22** 3723
 [15] Frank A and Wolf K B 1985 *J. Math. Phys.* **26** 973
 [16] Grosche C 1989 *J. Phys. A: Math. Gen.* **22** 5073
 [17] Davies M 1949 *J. Chem. Phys.* **17** 374
 [18] Varshni Y P 1957 *Rev. Mod. Phys.* **29** 664
 [19] Steele D, Lippincott E L and Vanderslice J T 1962 *Rev. Mod. Phys.* **34** 239
 [20] Zhirnov N I and Shadrin O P 1967 *Opt. Spectrosc.* **24** 478
 [21] Shadrin O P and Zhirnov N I 1975 *Opt. Spectrosc.* **38** 367
 [22] Khersonskii V K 1977 *Opt. Spectrosc.* **42** 610
 [23] Khersonskii V K 1977 *Opt. Spectrosc.* **43** 19
 [24] Bell K L 1970 *J. Phys. B: At. Mol. Phys.* **3** 1426
 [25] Schiöberg D 1986 *Mol. Phys.* **59** 1123
 [26] Milgram M 2006 *Int. Transforms Special Funct.* **17** 829
 [27] Watson J K G 1968 *Mol. Phys.* **15** 479
 [28] Pöschl G and Teller E Z 1933 *Z. Phys.* **5** 143
 [29] Rosen N and Morse P M 1932 *Phys. Rev.* **42** 210
 [30] Flügge S 1971 *Practical Quantum Mechanics* (Berlin: Springer)

- [31] Lemus R and Bernal R 2002 *Chem. Phys.* **283** 401
- [32] Aldaya V and Guerrero J 2005 *J. Phys. A: Math. Gen.* **38** 6939
- [33] Guerrero J and Aldaya V 2006 *J. Phys. A: Math. Gen.* **39** L267
- [34] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)
- [35] Gradshteyn I S and Ryzhik I M 2007 *Table of Integrals, Series and Products* (New York: Academic)
- [36] Driver K A and Johnston S J 2006 *Elec. Trans. Num. Anal.* **25** 115
- [37] Milgram M 2004 On Some Sums of Digamma and Polygamma functions, arXiv:[math.CA/0406338v1](https://arxiv.org/abs/math.CA/0406338v1)
- [38] Prudnikov A P, Brychkov Yu A and Marichev O I 1990 *More Special Functions (Integrals and Series vol 3)* (New York: Gordon & Breach)
- [39] Milgram M 2005 *Ann. Nucl. Energy* **32** 1167
- [40] Lanczos C 1964 *J. SIAM Numer. Anal. Ser. B* **1** 86
- [41] Infeld L and Hull T E 1951 *Rev. Mod. Phys.* **23** 21
- [42] Lévai G 1994 *J. Phys. A: Math. Gen.* **27** 3809
- [43] Bargmann V 1947 *Ann. Math.* **48** 568
- [44] Coxon J and Hajigeorgiou P G 2004 *J. Chem. Phys.* **121** 2992
- [45] Watson J K G 1980 *J. Mol. Spectrosc.* **80** 411
- [46] Rey M and Tyuterev VI G 2007 *Phys. Chem. Chem. Phys.* **9** 2538
- [47] Rey M, Michelot F and Tyuterev G VI 2008 *Phys. Rev. A* **78** 022511