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Matrix elements of *u* and *p* for the modified Pöschl–Teller potential

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Abstract

Closed analytical expressions in terms of a single sum are obtained for the matrix elements of the momentum and the natural variable $u = \tanh(\alpha x)$ in the basis of the modified Pöschl–Teller (MPT) bound eigenstates. These matrix elements are first expressed in terms of Franck–Condon factors, which thereafter are substituted for analytic expressions. Expansions of the variables p and u in terms of creation and annihilation operators associated with the MPT bound eigenfunctions are also presented.

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1. Introduction

The modified Pöschl–Teller (MPT) potential [1, 2] belongs to the solvable potential family [3]. It is given by

$$V(x) = -\frac{\hbar^2\alpha^2}{2\mu}\frac{j(j+1)}{\cosh^2(\alpha x)} \tag{1}$$

where $j > 0$ is connected to the potential depth, α is related to the range of the potential, μ is the reduced mass of the system and x is the physical displacement variable. This potential together with the Morse potential represent the most studied anharmonic potentials. A remarkable property of these potentials is that the $su(2)$ algebra constitutes a dynamical algebra for the discrete part of their spectra [4].

In a local description of molecular vibrational excitations, the Hamiltonian is expanded in terms of internal variables. The energy levels are thus obtained variationally by diagonalizing the Hamiltonian in a basis, which is usually chosen as the tensorial product of Morse or MPT functions. Expressions of the matrix elements of the operators involved in the expansion of the Hamiltonian are thus necessary to carry out the theoretical analysis. For the MPT case, the matrix elements of u and $\hat{p}$ can be calculated in a straightforward way in terms of a double sum [5]. However, this procedure when applied to highly excited states is time consuming and leads to numerical errors. In this paper we obtain closed analytic expressions for the matrix elements of the momentum $\hat{p}$ and the natural coordinate u in terms of a single sum.

Using the ladder operators associated with the potential group approach, in section 2 we express the matrix elements of $\hat{p}$ and u in terms of Franck–Condon factors whose analytical expressions in terms of a single sum have been obtained for different depths but equal parameters α [6]. In addition, in section 3 we present the expansion of these operators, $\hat{p}$ and u, in terms of creation and annihilation operators associated with the MPT bound states. This expansion turns out to be relevant in the description of molecular vibrations when the polyad breaking is intended to be taken into account in a systematic way [8]. In section 4 a summary is presented.

2. Matrix elements

All the background on the MPT relevant for the following discussion can be found in [7]. In particular, the solution of the Schrödinger equation associated with the potential (1) is given by

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

where $C_v^\lambda(u)$ are the Gegenbauer polynomials and N_v^j is the normalization constant.

We start considering the following matrix elements for the MPT functions:

$$\left\langle \Psi_{v'}^{j'} \middle| \frac{u}{\alpha} \middle| \Psi_v^j \right\rangle \qquad \text{and} \qquad \left\langle \Psi_{v'}^{j'} \middle| \hat{p} \middle| \Psi_v^j \right\rangle \tag{3}$$

where $u = \tanh(\alpha x)$ and the momentum $\hat{p}$ is given by

$$\hat{p} = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} = -\mathrm{i}\hbar\alpha(1-u^2)\frac{\mathrm{d}}{\mathrm{d}u}. \tag{4}$$

In the expansion of the Hamiltonian in terms of internal coordinates the variable u is preferred to x, for the same reason the Morse variable $y = 1 - \mathrm{e}^{-\beta x}$ is used to expand the Hamiltonian [9]. In both cases the expansions in terms of x diverge for large displacement, while the variables y and u remain finite. We should note that in the limit of small displacements $\lim_{x\to 0} u/\alpha = x$, which explains the convenience of calculating u/α instead of u. In order to compute the matrix elements (3), we shall first express them in terms of Franck–Condon factors. To achieve this goal we need to introduce the ladder operators associated with the potential group approach [10]. In this framework we look for operators that shift the number of quanta as well as the potential parameter j. Applying the operator $(1-u^2)\frac{\mathrm{d}}{\mathrm{d}u}$ to (2), and using the recurrence relation

$$(1-u^2)\frac{\mathrm{d}}{\mathrm{d}u}C_n^\lambda(u) = -(n+1)C_{n+1}^\lambda(u) + (2\lambda+n)uC_n^\lambda(u) \tag{5}$$

we obtain

$$(1-u^2)\frac{\mathrm{d}}{\mathrm{d}u}\Psi_v^j(u) = u(j+1)\Psi_v^j(u) - (v+1)\frac{N_v^j}{N_{v+1}^{j+1}}\Psi_{v+1}^{j+1}(u) \tag{6}$$

where we have introduced the identification

$$\Psi_{v+1}^{j+1}(u) = N_{v+1}^{j+1}(1-u^2)^{\frac{j-v}{2}} C_{v+1}^{j-v+1/2}(u). \tag{7}$$

So, the state $\Psi_{v+1}^{j+1}(u)$ is the bound eigenstate with $v+1$ quanta of a MPT potential whose depth is characterized by $j+1$.

At this point we introduce the following family of operators that depend on a parameter q:

$$\hat{M}_{\pm}(q) = \mp(1-u^2)\frac{\mathrm{d}}{\mathrm{d}u} + qu. \tag{8}$$

They have the remarkable property that they can be expressed in terms of a linear combination of operators $\hat{M}_{\pm}(q')$ with different arguments [7]

$$\hat{M}_{\pm}(q) = \frac{q+q''}{q'+q''}\hat{M}_{\pm}(q') + \frac{q-q'}{q'+q''}\hat{M}_{\mp}(q''). \tag{9}$$

Taking into account the appropriate recurrence relations for the Gegenbauer polynomials, we obtain the action of the operators (8) for particular values of q on the MPT eigenfunctions (2)

$$\hat{M}_{-}(j)\Psi_v^j(u) = \sqrt{v(2j-v)}\,\Psi_{v-1}^{j-1}(u) \tag{10a}$$

$$\hat{M}_{+}(j+1)\Psi_v^j(u) = \sqrt{(v+1)(2j-v+1)}\,\Psi_{v+1}^{j+1}(u). \tag{10b}$$

In terms of the ladder operators (8) the operators $\hat{p}$ and u are given by

$$u = \frac{1}{2q}[\hat{M}_{+}(q) + \hat{M}_{-}(q)] \tag{11a}$$

$$\hat{p} = \frac{\mathrm{i}\hbar\alpha}{2}[\hat{M}_{+}(q) - \hat{M}_{-}(q)]. \tag{11b}$$

If we now substitute (11) into (3) and use (8) with $q = j$, $q' = j+1$ and $q'' = j$, we obtain the following expresions:

$$\left\langle \Psi_{v'}^{j'} \middle| \frac{u}{\alpha} \middle| \Psi_v^j \right\rangle = \frac{1}{\alpha(2j+1)}\left[\sqrt{(v+1)(2j-v+1)}\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v+1}^{j+1} \right\rangle + \sqrt{v(2j-v)}\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v-1}^{j-1} \right\rangle\right] \tag{12a}$$

$$\left\langle \Psi_{v'}^{j'} \middle| \hat{p} \middle| \Psi_v^j \right\rangle = \frac{\mathrm{i}\hbar\alpha}{2j+1}\left[j\sqrt{(v+1)(2j-v+1)}\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v+1}^{j+1} \right\rangle - (j+1)\sqrt{v(2j-v)}\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v-1}^{j-1} \right\rangle\right] \tag{12b}$$

where $v' = v \pm \gamma$, with $\gamma = 1, 3, 5, \ldots$, since both operators are odd. We have thus expressed the matrix elements (3) in terms of the Franck–Condon factors $\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v+1}^{j+1} \right\rangle$ and $\left\langle \Psi_{v'}^{j'} \middle| \Psi_{v-1}^{j-1} \right\rangle$. Recently, the Franck–Condon factors with the same parameter α were calculated in closed form in terms of a single sum [6]. Using the expressions obtained in [6], but keeping the consistency with the phase involved in our wavefunctions and re-arranging the expression in a condensed form, the Franck–Condon factors are given in the cases in which v' and n are both even or odd (otherwise the Franck–Condon factor cancels due to parity) by

$$\begin{aligned}
\left\langle \Psi_{v'}^{j'} \middle| \Psi_n^s \right\rangle &= (-1)^{[n/2]} 2^{s-j'} \frac{\Gamma(s-[n/2]+\delta_n)[n/2]!}{\Gamma(j'-[v'/2]+\delta_n)[v'/2]!} \\
&\quad \times \sqrt{(s-n)(j'-v')\frac{v'!\Gamma(2j'-v'+1)}{n!\Gamma(2s-n+1)}} \\
&\quad \times \sum_{k=0}^{[n/2]} \frac{(-1)^k\Gamma(s-k+1/2)}{k!([n/2]-k)!\Gamma(s-[n/2]-k+\delta_n)} \\
&\quad \times \frac{\Gamma((s+j')/2-[v'/2]-k-1+\delta_n)\Gamma((j'-s)/2+1+k)}{\Gamma((s+j')/2+1/2-k)\Gamma((j'-s)/2-[v'/2]+1+k)}
\end{aligned} \tag{13}$$

where $[a]$ is the integer part of a and we have defined the function

$$\delta_n = \frac{1+(-1)^n}{2}. \tag{14}$$

We thus have that $(s, n) = (j+1, v+1)$ for $\langle \Psi_{v'}^{j'} | \Psi_{v+1}^{j+1} \rangle$, and $(s, n) = (j-1, v-1)$ for $\langle \Psi_{v'}^{j'} | \Psi_{v-1}^{j-1} \rangle$. Hence we have arrived at closed analytical expressions in terms of a single sum for the matrix elements (3) when (13) is substituted into (12).

3. Expansions in terms of the ladder operators

In this section we derive the expansions of the natural coordinate u and the momentum $\hat{p}$ in terms of the $su(2)$ generators $\{b^\dagger, b, v\}$ whose action on the wavefunctions is [8]

$$\hat{b}^\dagger \Psi_v^j(u) = \sqrt{(v+1)(1-(v+1)/(2j+1))}\, \Psi_{v+1}^j(u) \tag{15a}$$

$$\hat{b} \Psi_v^j(u) = \sqrt{v(1-v/(2j+1))}\, \Psi_{v-1}^j(u) \tag{15b}$$

$$\hat{v} \Psi_v^j(u) = v \Psi_v^j(u). \tag{15c}$$

Since in the preceding section we have obtained analytical closed expressions for the u and $\hat{p}$ matrix elements, the expansion of u and $\hat{p}$ in terms of $\hat{b}^\dagger$ and $\hat{b}$ is readily obtained by direct comparison with the deduced u and $\hat{p}$ matrix elements (12), (13). The natural coordinate u and the momentum $\hat{p}$ in terms of the creation and annihilation operators defined in (15) [8] are

$$\hat{p} = \frac{\mathrm{i}}{2}\sqrt{2\hbar\mu\omega}\left[g_v^{(1)} \hat{b}^\dagger + \frac{1}{\kappa} g_v^{(3)} (\hat{b}^\dagger)^3 + \frac{1}{\kappa^2} g_v^{(5)} (\hat{b}^\dagger)^5 + O\left(\frac{1}{\kappa^7}\right) - \text{h.c.}\right] \tag{16}$$

and

$$\frac{u}{\alpha} = \sqrt{\frac{\hbar}{2\mu\omega}}\left[f_v^{(1)} \hat{b}^\dagger + \frac{1}{\kappa} f_v^{(3)} (\hat{b}^\dagger)^3 + \frac{1}{\kappa^2} f_v^{(5)} (\hat{b}^\dagger)^5 + O\left(\frac{1}{\kappa^7}\right) + \text{h.c.}\right] \tag{17}$$

where we have introduced the definition $\kappa = 2j+1$. The diagonal operators $f_v^{(i)}$ and $g_v^{(i)}$ are obtained by comparison with the matrix elements (12)

$$g_v^{(i)} = \kappa^{\frac{(i-1)}{2}} z_v^i \left[\frac{\kappa-1}{\kappa}\sqrt{\frac{(1-v/\kappa)}{1-(v+1)/\kappa}} \langle \Psi_{v+i}^j | \Psi_{v+1}^{j+1} \rangle - \frac{\kappa+1}{\kappa}\sqrt{\frac{v}{v+1}} \langle \Psi_{v+i}^j | \Psi_{v-1}^{j-1} \rangle \right] \tag{18a}$$

$$f_v^{(i)} = \kappa^{\frac{i-1}{2}} z_v^i \left[\sqrt{\frac{(1-v/\kappa)}{(1-(v+1)/\kappa)}} \langle \Psi_{v+i}^j | \Psi_{v+1}^{j+1} \rangle + \sqrt{\frac{v}{(v+1)}} \langle \Psi_{v+i}^j | \Psi_{v-1}^{j-1} \rangle \right] \tag{18b}$$

where we have defined

$$z_v^i = \sqrt{\frac{\kappa^{i-1}}{(v+2)_{i-1}(\kappa-v-i)_{i-1}}} \tag{19}$$

for $i = 1, 3, 5, \ldots$, where $(a)_n$ stands for a Pochhammer symbol. Since equations (18) have a dependence in κ it is not clear that expressions (16) and (17) are expansions in terms of $1/\kappa$. This can be clarified by looking at the harmonic limit of (18). The diagonal operators (18) have the harmonic limit

$$\lim_{\kappa\to\infty} f_v^{(1)} = \lim_{\kappa\to\infty} g_v^{(1)} = 1 \tag{20}$$

$$\lim_{\kappa\to\infty} f_v^{(3)} = \lim_{\kappa\to\infty} g_v^{(3)} = -\tfrac{1}{2} \tag{21}$$

$$\lim_{\kappa\to\infty} f_v^{(5)} = \lim_{\kappa\to\infty} g_v^{(5)} = \tfrac{3}{8} \tag{22}$$

with similar expressions for $f_v^{(i)}$, $g_v^{(i)}$ with $i \geqslant 7$. These results imply that equations (16) and (17) are effectively expansions in terms of powers of the parameter $1/\kappa$ that for large κ are

$$\lim_{\kappa\to\infty} \hat{p} = \frac{\mathrm{i}}{2}\sqrt{2\hbar\mu\omega}[\hat{b}^\dagger - \hat{b}] \tag{23a}$$

$$\lim_{\kappa\to\infty} \frac{\hat{u}}{\alpha} = \sqrt{\frac{\hbar}{2\mu\omega}}[\hat{b}^\dagger + \hat{b}]. \tag{23b}$$

In the harmonic limit $\lim_{\kappa\to\infty} \hat{b}^\dagger = \hat{a}^\dagger$ and $\lim_{\kappa\to\infty} \hat{b} = \hat{a}$ [8], where the operators $\hat{a}^\dagger$ and $\hat{a}$ are the usual creation and annihilation operators for the harmonic functions. This result, together with equation (23), leads to the correct harmonic limit for $\hat{p}$ and u.

4. Summary

In this work we have established the connection between the MPT matrix elements of the $\hat{p}$ and u operators in terms of Franck–Condon factors. Taking advantage of this connection we have written close analytic expressions for these matrix elements in terms of a single sum. The latter has been possible due to the analytic expressions of Franck–Condon factors obtained by Hornburger and Dierckensen [6]. The MPT matrix elements for the momentum and the variable $u = \tanh(\alpha x)$ allow us to improve the calculations involved in the diagonalization of the Hamiltonian. Formulae (12) are expected to be particularly useful when several local oscillators are involved in the vibrational description of a molecular system. For example, the benzene molecule presents 12 out-of-plane local modes which may be modelled with MPT potentials, a fact that makes important any simplification in the calculation of matrix elements.

Expansions of the variables p and u in terms of creation and annihilation operators associated with the MPT bound eigenfunctions are presented. These expansions are given in terms of powers of the parameter $1/\kappa$. This fact provides an approach to include interactions of higher order in a systematic way.

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