

Configuration localized wave functions: General formalism and applications to vibrational spectroscopy of diatomic molecules

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A general formalism for constructing configuration localized states for one-dimensional potentials is presented. It allows the evaluation of accurate approximations to the vibrational matrix elements of the momentum operator and of arbitrary functions of the coordinate. The formalism is applied to three potentials of interest in molecular physics: the harmonic oscillator, Morse, and Pöschl-Teller potentials. Quadratures specifically designed for each potential are used. The infrared vibrational spectrum of $^{12}\text{C}^{16}\text{O}$ is studied as a way to test the results obtained for different potentials in connection with their ability to model the anharmonicity.

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I. INTRODUCTION

Traditional approaches to molecular vibrational spectroscopy rely on the harmonic approximation, though it is well known that a parabolic potential is a rather poor approximation to the interatomic interaction in a diatomic molecule (e.g., it does not allow dissociation). On one hand, when one explores a few states at the bottom of the potential well, that approximation has been proven to be reasonable. On the other hand, the use of anharmonic potentials, which better represent the interatomic interaction, implies greater difficulty. Consequently, the harmonic potential has been the usual reference in molecular physics. However, in the last few years the improvement of experimental techniques has led to the exploration of higher excitation energies in the interatomic potential well [1]. This allows analysis of states where the anharmonicity may be a necessary ingredient (e.g., local modes [2,3]). Consequently, realistic anharmonic potentials that could be a reference for the study of the anharmonicity role should be investigated in detail.

In this paper an approximate analytic method to treat vibrational bound states of one-dimensional potentials (harmonic as well as anharmonic) is presented. The method is based on the introduction of a basis of states that are particular linear combinations of the eigenstates of the potential. They have the property of localizing the system wave functions in configuration space [4], allowing the derivation of closed analytic expressions for the matrix elements of all relevant operators. In a previous paper [4], the method was presented for the particular case of the Morse potential [5]. In the present paper the formalism is generalized. While the Morse potential is revisited, two other potentials of interest in molecular physics are worked out: the harmonic oscillator and the Pöschl-Teller potential [6]. In the Morse potential case the approach presented is somewhat different from that discussed in Ref. [4], although the main ideas are the same. Differences between the two cases will be discussed in the following when appropriate. The formalism developed provides a tool to study in detail anharmonic behavior in vibra-

tional molecular spectroscopy. An application to the study of the carbon monoxide infrared vibrational spectrum is presented, where the model and the sensitivity of the data to the analysis with different potentials are assessed.

The paper is structured as follows. In Sec. II, the general formalism of configuration localized states (CLS's) for a one-dimensional potential well is presented. In Sec. III this general formalism is applied to the harmonic oscillator, Morse, and Pöschl-Teller potentials. Section IV is devoted to testing the model in a realistic case, computing vibrational dipole moment matrix elements for the CO molecule and comparing them with experimental results. Finally, a summary and conclusions are presented in Sec. V.

II. CONFIGURATION LOCALIZED STATES: GENERAL FORMALISM

The starting point are the j bound eigenstates of a one-dimensional potential. The cases considered are those in which the wave function can be written as

$$\psi_{jv}(x) = \langle x | j, v \rangle = \mathcal{N}_{jv}^{-1/2} F(y) \mathcal{P}_v^{(j)}(y),$$

$$v = 0, 1, 2, \dots, j-1, \quad (1)$$

where y is an arbitrary function of x (the physical coordinate) well behaved in the region of interest ($x_{\min}, x_{\max}$) (continuous, single valued, finite, and monotonically increasing or decreasing). The values of y at the extremes of this region are (y_0, y_1). $\mathcal{N}_{jv}^{-1/2}$ is a normalization constant, $F(y)$ is an arbitrary function of y , and $\mathcal{P}_v^{(j)}(y)$ is a polynomial of order v in y . The label j is associated with the potential depth.

The orthogonality of the eigenfunctions implies that

$$\int_{x_{\min}}^{x_{\max}} dx \psi_{jv}(x) \psi_{jv'}(x) = \delta_{v,v'}, \quad (2)$$

which, changing variables, leads to

$$\int_{y_0}^{y_1} dy \omega(y) \mathcal{P}_v^{(j)}(y) \mathcal{P}_{v'}^{(j)}(y) = \mathcal{N}_{jv} \delta_{v,v'}, \quad (3)$$

where

$$\omega(y) = \frac{[F(y)]^2}{dy/dx}. \quad (4)$$

Consequently, the set $\{\mathcal{P}_v^{(j)}(y); v=0,1,\dots,j-1\}$ is a family of j orthogonal polynomials in the interval $y_0 \leq y \leq y_1$ with respect to the weight function $\omega(y)$. If $\omega(y)$ is the weight function for a family of the tabulated orthogonal polynomials $f_v(y)$ (see, e.g., Ref. [7]) then the polynomials $\mathcal{P}_v^{(j)}(y)$ are just $f_v(y)$ up to a normalization constant.

Since we are treating orthogonal polynomials the Christoffel-Darboux formula [7] (p. 785) can be applied:

$$\begin{aligned} \sum_{v=0}^{j-1} \frac{1}{\mathcal{N}_{jv}} \mathcal{P}_v^{(j)}(y) \mathcal{P}_v^{(j)}(z) \\ = \frac{k_{j-1}}{k_j \mathcal{N}_{jj-1}} \frac{\mathcal{P}_j^{(j)}(y) \mathcal{P}_{j-1}^{(j)}(z) - \mathcal{P}_j^{(j)}(z) \mathcal{P}_{j-1}^{(j)}(y)}{y - z}, \end{aligned} \quad (5)$$

where k_v is the coefficient of the term of order v in the explicit form of the polynomial $\mathcal{P}_v^{(j)}(y)$. It is worth noticing here that the polynomial $\mathcal{P}_j^{(j)}(y)$ will not be normalizable in general, but it is defined by its orthogonality with respect to the others with $v < j$. Making use of this relation a new set of j polynomials of order $j-1$ can be defined dividing $\mathcal{P}_j^{(j)}(y)$ by $y - y_s$, where y_s ($s=1, \dots, j$) are the j roots of $\mathcal{P}_j^{(j)}(y)$. These polynomials are constructed by making $z = y_s$ in Eq. (5):

$$\begin{aligned} Q_{j-1}^{(s)}(y) &= \sum_{v=0}^{j-1} \frac{1}{\mathcal{N}_{jv}} \mathcal{P}_v^{(j)}(y) \mathcal{P}_v^{(j)}(y_s) \\ &= \frac{k_{j-1}}{k_j \mathcal{N}_{jj-1}} \frac{\mathcal{P}_j^{(j)}(y) \mathcal{P}_{j-1}^{(j)}(y_s)}{y - y_s}, \quad s=1, \dots, j. \end{aligned} \quad (6)$$

Alternatively they can be expressed as

$$Q_{j-1}^{(s)}(y) = \left(\frac{k_{j-1} \mathcal{P}_{j-1}^{(j)}(y_s)}{\mathcal{N}_{jj-1}} \right) \prod_{i \neq s} (y - y_i). \quad (7)$$

The limit $y = y_s$ gives

$$\begin{aligned} Q_{j-1}^{(s)}(y_s) &= \sum_{v=0}^{j-1} \frac{1}{\mathcal{N}_{jv}} [\mathcal{P}_v^{(j)}(y_s)]^2 \\ &= \frac{k_{j-1}}{k_j \mathcal{N}_{jj-1}} \frac{g_0(y_s)}{g_2(y_s)} [\mathcal{P}_{j-1}^{(j)}(y_s)]^2, \end{aligned} \quad (8)$$

where $g_0(y)$ and $g_2(y)$ can be obtained from the differential relation of the corresponding orthogonal polynomial (see [7], Table 22.8, for tabulated polynomials),

$$g_2(y) \frac{d}{dy} \mathcal{P}_j^{(j)}(y) = g_1(y) \mathcal{P}_j^{(j)}(y) + g_0(y) \mathcal{P}_{j-1}^{(j)}(y). \quad (9)$$

These new polynomials are orthogonal with respect to the weight function $\omega(y)$ [8]:

$$\int_{y_0}^{y_1} dy \omega(y) Q_{j-1}^{(s)}(y) Q_{j-1}^{(s')}(y) = Q_{j-1}^{(s)}(y_s) \delta_{s,s'}. \quad (10)$$

These $Q_{j-1}^{(s)}(y)$ polynomials can be used, as shown in Ref. [8], to define quadratures for the integrals

$$\int_{y_0}^{y_1} dy \omega(y) \mathcal{F}(y) = \sum_{s=1}^j \mathcal{F}(y_s) w_{js} + R_j, \quad (11)$$

where $\mathcal{F}(y)$ is any function of y and w_{js} are weight factors given by

$$w_{js} = [Q_{j-1}^{(s)}(y_s)]^{-1}. \quad (12)$$

In Eq. (11) R_j is the residual, which is proportional to the 2 j derivative of $\mathcal{F}(y)$.

With the help of the $Q_{j-1}^{(s)}(y)$ polynomials, configuration localized states in the configuration space can be defined as

$$\phi_{js}(x) = \langle x | \text{CL}; j, s \rangle = w_{js}^{1/2} F(y) Q_{j-1}^{(s)}(y). \quad (13)$$

The name of these states comes from the fact that they are strongly localized around $y = y_s$. In addition, the wave function $\phi_{js}(x)$ vanishes at all the points y_l for $l \neq s$. The states can be written in terms of the original eigenstates given in Eq. (1) as

$$| \text{CL}; j, s \rangle = \sum_{v=0}^{j-1} \langle j, v | \text{CL}; j, s \rangle | j, v \rangle, \quad (14)$$

and the overlap factors can be computed from the definition of the CLS's and the polynomials $Q_{j-1}^{(s)}(y)$, giving

$$\langle j, v | \text{CL}; j, s \rangle = w_{js}^{1/2} \mathcal{N}_{jv}^{-1/2} \mathcal{P}_v^{(j)}(y_s). \quad (15)$$

The CLS's have the following properties.

(1) Orthogonality:

$$\langle \text{CL}; j, s | \text{CL}; j, s' \rangle = \delta_{s,s'}, \quad (16)$$

which stems directly from the orthogonality of the $Q_{j-1}^{(s)}(y)$ polynomials.

(2) Matrix elements of y :

$$\begin{aligned} \langle \text{CL}; j, s | y | \text{CL}; j, l \rangle &= \int_{y_0}^{y_1} dy \omega(y) w_{js}^{1/2} w_{jl}^{1/2} Q_{j-1}^{(s)}(y) y Q_{j-1}^{(l)}(y) \\ &= y_s \delta_{s,l}. \end{aligned} \quad (17)$$

This can be proved by writing $y = (y - y_s) + y_s$. Integration of the factor $(y - y_s)$ cancels because it involves an integral of $\mathcal{P}_j^{(j)}(y)$ times a polynomial of order less than j .

(3) Matrix elements of an arbitrary function of y :

$$\begin{aligned}
& \langle \text{CL}; j, s | G(y) | \text{CL}; j, l \rangle \\
&= \int_{y_0}^{y_1} dy \omega(y) w_{js}^{1/2} w_{jl}^{1/2} Q_{j-1}^{(s)}(y) G(y) Q_{j-1}^{(l)}(y) \\
&\approx G(y_s) \delta_{s,l} + R_j.
\end{aligned} \tag{18}$$

This result can be obtained by using integration by quadratures (11) noticing that the CLS $\phi_{js}(x)$ vanishes at all the points of the quadrature except at $y=y_s$. The residual R_j is proportional to the $2j$ derivative of the function $Q_{j-1}^{(s)}(y)G(y)Q_{j-1}^{(l)}(y)$, which depends on the second derivative of the function $G(y)$.

(4) Matrix elements of the momentum p :

$$\begin{aligned}
\langle \text{CL}; j, s | p | \text{CL}; j, l \rangle &\approx \frac{i\hbar}{2} \frac{1}{y_s - y_l} \left[\sqrt{\frac{w_{jl}}{w_{js}}} \frac{\mathcal{P}_{j-1}^{(j)}(y_l)}{\mathcal{P}_{j-1}^{(j)}(y_s)} \left(\frac{dy}{dx} \right)_{y_s} \right. \\
&\quad \left. + \sqrt{\frac{w_{js}}{w_{jl}}} \frac{\mathcal{P}_{j-1}^{(j)}(y_s)}{\mathcal{P}_{j-1}^{(j)}(y_l)} \left(\frac{dy}{dx} \right)_{y_l} \right]
\end{aligned} \tag{19}$$

for $s \neq l$.

The diagonal matrix elements in the CLS basis vanish. This is the case for any basis of wave functions that are real in configuration space. To derive this formula we use the fact that the matrix elements $\langle \text{CL}; j, s | p | \text{CL}; j, l \rangle$ can be expressed as

$$\begin{aligned}
& \langle \text{CL}; j, s | p | \text{CL}; j, l \rangle \\
&= \int_{x_{\min}}^{x_{\max}} dx \phi_{js}(x) p \phi_{jl}(x) \\
&= \frac{i\hbar}{2} \int_{x_{\min}}^{x_{\max}} dx \left[\phi_{js}(x) \left(\frac{d\phi_{jl}(x)}{dx} \right) - \phi_{jl}(x) \left(\frac{d\phi_{js}(x)}{dx} \right) \right],
\end{aligned} \tag{20}$$

where the integral has been written in a symmetrical form and integrated by parts. It is clear that the diagonal matrix elements vanish. From now on, only the case $s \neq l$ is considered. Expressing the integral and the derivative in terms of the variable y and evaluating the integral by quadratures, the following expression is obtained:

$$\begin{aligned}
\langle \text{CL}; j, s | p | \text{CL}; j, l \rangle &\approx \frac{i\hbar}{2} \left[\sqrt{\frac{w_{jl}}{w_{js}}} \left(\frac{dy}{dx} \right)_{y_s} \left(\frac{dQ_{j-1}^{(l)}(y)}{dy} \right)_{y_s} \right. \\
&\quad \left. - \sqrt{\frac{w_{js}}{w_{jl}}} \left(\frac{dy}{dx} \right)_{y_l} \left(\frac{dQ_{j-1}^{(s)}(y)}{dy} \right)_{y_l} \right].
\end{aligned} \tag{21}$$

This expression will be exact if dy/dx is a linear function of y . Using the definition of the Q polynomials from Eq. (7) and computing the corresponding derivatives we obtain

$$\begin{aligned}
\left(\frac{dQ_{j-1}^{(s)}(y)}{dy} \right)_{y_l} &= \left(\frac{k_{j-1} \mathcal{P}_{j-1}^{(j)}(y_s)}{\mathcal{N}_{jj-1}} \right) \prod_{i \neq l, s} (y - y_i) \\
&= \frac{Q_{j-1}^{(l)}(y_l)}{y_l - y_s} \frac{\mathcal{P}_{j-1}^{(j)}(y_s)}{\mathcal{P}_{j-1}^{(j)}(y_l)}.
\end{aligned} \tag{22}$$

Substituting this last expression in Eq. (21) the stated result in Eq. (19) is obtained.

III. CLS's FOR ONE-DIMENSIONAL POTENTIALS OF RELEVANCE IN MOLECULAR PHYSICS

In this section the formalism presented in the preceding section is applied to three potentials of relevance in molecular physics.

A. Truncated harmonic oscillator

By a truncated harmonic oscillator we mean a truncation of the model space to a finite number of the lowest harmonic oscillator states. In this case the starting point is the first j states of a harmonic oscillator with Hamiltonian

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} x^2. \tag{23}$$

The dimensionless variable $x = (r - r_e)/a_0$ is introduced, where $a_0 = \sqrt{\hbar/\mu\omega}$ is the oscillator length, r is the physical coordinate, and r_e is the equilibrium position. The solutions for the one-dimensional (1D) harmonic oscillator are

$$\psi_{jv}(x) = \mathcal{N}_{jv}^{-1/2} \exp\left(-\frac{x^2}{2}\right) H_v(x); \quad v = 0, \dots, j-1, \tag{24}$$

where $H_v(x)$ are the Hermite polynomials. This set of j wave functions has the form required to apply the described procedure to form the CLS's. This case is particularly simple since $y=x$. In Table I the relevant information to build the CLS's for the truncated harmonic oscillator is shown under the label HO. In Fig. 1 the CLS states for a truncated harmonic oscillator with $j=10$ are shown. They are distributed symmetrically with respect to the origin and each CLS wave function is concentrated around a point $y=y_s$, vanishing for the rest of the roots of $H_j(y)$.

For the harmonic oscillator the vibrational matrix elements of the coordinate x and the momentum p calculated by using the corresponding CLS are exact due to the quadrature used. This has been checked by comparing the CLS results with numerical ones obtained by integration with harmonic oscillator wave functions.

B. Morse potential

This case was presented previously in Ref. [4] using a different quadrature. Here the CLS's for a Morse potential are reconstructed following the formalism presented above. The Morse potential can be written as

TABLE I. Relevant information to construct CLS's for harmonic oscillator (HO), Morse, and Pöschl-Teller (P-T) potentials.

	HO	Morse	P-T
y	x	$(2j+1)^{-1} \exp(x_M)$	$\sinh(x_{PT})$
(y_0, y_1)	$(-\infty, \infty)$	$(0, \infty)$	$(-\infty, \infty)$
$\mathcal{N}_{jv}$	$\sqrt{\pi} 2^v v!$	$\frac{(2j-v)!}{(2j-2v)v!}$	$\frac{(2j-v)!}{(j-v)v!}$
$F(y)$	$\exp\left(-\frac{y^2}{2}\right)$	$y^{-j} \exp\left(-\frac{1}{2y}\right)$	$(1+y^2)^{-j/2}$
$\mathcal{P}_v^{(j)}(y)$	$H_v(y)$	$\mathcal{T}_v^{(j)}(y)$	$\mathcal{R}_v^{(j)}(y)$
y_s	$H_j(y)$ roots	Inverse of $L_j(y)$ roots ^a	$\mathcal{R}_j^{(j)}(y)$ roots
k_j, k_{j-1}	$2^j, 2^{j-1}$	$1, \frac{j(j+1)}{2}$	$1, -\frac{j(j+1)}{2}$
$\frac{g_2(y)}{g_0(y)}$	$\frac{1}{2j}$	$\frac{y L_{j-1}^{(1)}(1/y)}{j L_{j-1}^{(0)}(1/y)}$	$-1-y^2$
$\omega(y)$	$\exp(-y^2)$	$y^{-2j-1} \exp\left(-\frac{1}{y}\right)$	$(1+y^2)^{-(j+1/2)}$
$Q_{j-1}^{(s)}(y)$	$\frac{H_{j-1}(y_s)}{\sqrt{\pi} 2^j (j-1)!} \frac{H_j(y)}{y-y_s}$	$\frac{(j+1) \mathcal{T}_{j-1}^{(j)}(y_s)}{2} \frac{\mathcal{T}_j^{(j)}(y)}{y-y_s}$	$-\mathcal{R}_{j-1}^{(j)}(y_s) \frac{\mathcal{R}_j^{(j)}(y)}{y-y_s}$
w_{js}	$\frac{\sqrt{\pi} 2^j (j-1)!}{2j} [H_{j-1}(y_s)]^{-2}$	$\frac{y_s L_{j-1}^{(1)}(1/y_s)}{j L_{j-1}^{(0)}(1/y_s)} [\mathcal{T}_{j-1}^{(j)}(y_s)]^{-2}$	$2(1+y_s^2) [\mathcal{R}_{j-1}^{(j)}(y_s)]^{-2}$

^aThese are the roots of $\mathcal{T}_j^{(j)}(y)$.

$$V(x) = D\{[1 - \exp(-x_M)]^2 - 1\}, \quad (25)$$

where $-D$ is the value of the potential at its minimum and $x_M = \beta(r - r_e)$ is related to the separation from the equilibrium position (r_e). The parameter β is the inverse of the range of the potential,

$$\beta = \frac{1}{\sqrt{j+1/2} a_0}, \quad (26)$$

where the parameter a_0 is the oscillator length for a parabolic approximation to the Morse potential. The coordinate x_M can be written in terms of the harmonic oscillator coordinate x as $x_M = (1/\sqrt{j+1/2})x$.

The bound eigenstates of the Morse Hamiltonian are written as

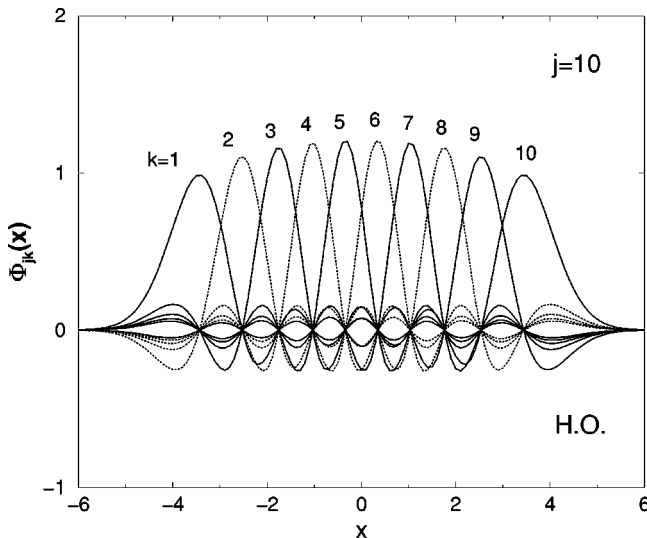
$$\Psi_{jv}(z) = \mathcal{N}_{jv}^{-1/2} \exp\left(-\frac{z}{2}\right) z^{j-v} L_v^{(2j-2v)}(z), \quad (27)$$

where $\mathcal{N}_{jv}$ is a normalization constant, $z = (2j+1)\exp(-x_M)$ is the Morse variable, and $L_s^{(p)}(z)$ are the generalized Laguerre polynomials of degree s and order p . To attain the form required to define CLS's, we rewrite the wave function in terms of a new variable $y = 1/z$ as

$$\Psi_{jv}(y) = \mathcal{N}_{jv}^{-1/2} y^{-j} \exp\left(-\frac{1}{2y}\right) y^v L_v^{(2j-2v)}(1/y). \quad (28)$$

A set of orthogonal polynomials $\{\mathcal{T}_v^{(j)}(y); v=0, 1, \dots, j-1\}$ in the variable $y = 1/z = (2j+1)^{-1} \exp(x_M)$ is defined as

$$\mathcal{T}_v^{(j)}(y) = y^v L_v^{(2j-2v)}(1/y). \quad (29)$$

FIG. 1. Configuration localized states $\Phi_{jk}(x)$ for a $j=10$ truncated harmonic oscillator.

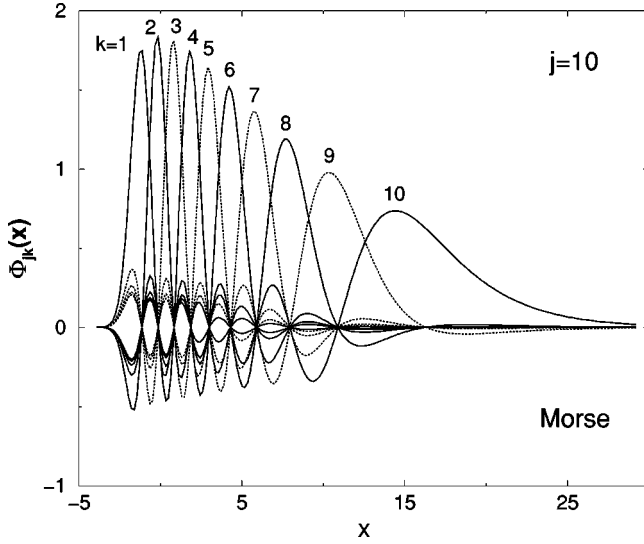


FIG. 2. Configuration localized states $\Phi_{jk}(x)$ for a $j=10$ Morse oscillator.

The fact that they are polynomials in y can be seen easily since $L_v^{(2j-2v)}(1/y)$ is a polynomial of order v in $1/y$ and multiplying this by y^v gives a polynomial of order v in y . The coefficients of this polynomial are those of $L_v^{(2j-2v)}(1/y)$ but in reversed order [e.g., the coefficient of the term of order n in $\mathcal{T}_v^{(j)}(y)$ is the coefficient of order $v-n$ in $L_v^{(2j-2v)}(y)$]. The properties of polynomials $\mathcal{T}_v^{(j)}(y)$ are discussed in Appendix A. In terms of these polynomials, the Morse wave functions are written as

$$\Psi_{jv}(y) = \mathcal{N}_{jv}^{-1/2} y^{-j} \exp\left(-\frac{1}{2y}\right) \mathcal{T}_v^{(j)}(y), \quad (30)$$

which have the form required to construct the CLS's. In Table I the relevant information to build the CLS's for the Morse oscillator is shown under the label Morse. In Fig. 2 the CLS states for a Morse oscillator with $j=10$ are shown. They are distributed asymmetrically with respect to the origin as expected. Each wave function $\phi_{js}(y)$ is concentrated at specific values of $y=y_s$, and vanishes for the rest of the inverse of the roots of $L_j(y)$.

It is remarkable that the nature of the quadrature presented (as well as the quadrature of Ref. [4]) is such that the matrix elements of the momentum operator are exact. This is because the derivative of the variable y with respect to the coordinate dy/dx_M is a linear function of y . The agreement between the CLS's and numerical results has been checked. This is not the case for the coordinate x_M , a nonlinear function of y , even though the results obtained by using CLS's provide a good approximation to the numerical results. In Table II numerical results for the matrix elements of x_M are compared with the results obtained by the present quadrature and that of Ref. [4] for the case $j=5$. Even for this very unfavorable case the approximation is correct and the main differences are concentrated in the least bound state. In both cases the approximation improves with increasing j . A comment on the differences between the quadratures used in Ref.

TABLE II. Matrix elements of the operator x_M in a Morse potential with $j=5$. Successive entries correspond to the exact calculation integrating with the Morse eigenfunctions (first line), an approximate calculation using CLS's defined in Ref. [4] (second line), and the approximate calculation using the CLS's defined in this paper (third line).

$v \setminus v'$	0	1	2	3	4
0	0.1461	0.3143	-0.0722	0.0275	-0.0129
	0.1461	0.3146	-0.0730	0.0290	-0.0146
	0.1469	0.3116	-0.0662	0.0181	-0.0030
1		0.4934	0.4666	-0.1361	0.0582
		0.4920	0.4706	-0.1440	0.0683
		0.5031	0.4437	-0.0979	0.0157
2			0.9596	0.6000	-0.2004
			0.9468	0.6299	-0.2453
			1.0176	0.4933	-0.0691
3				1.6513	0.7127
				1.5646	0.8886
				1.8785	0.3731
4					2.9251
					2.2608
					3.6559

[4] and in this paper is in order here. The quadrature presented in Ref. [4] is such that it provides the exact result for the matrix elements of the function $z = \exp(-x_M)$ while the quadrature presented in this work gives the exact values of the matrix elements of the function $y = \exp(x_M)$. The fact that the quadrature of Ref. [4] provides a better approximation for the matrix elements of x_M indicates simply that $x_M(z) = -\log(z)$ is better expanded by a polynomial expression than $x_M(y) = \log(y)$ in the region where the Morse wave functions are relevant. However, for realistic values of j in molecular physics (for instance, $j=81$ for the $^{12}\text{C}^{16}\text{O}$ molecule treated in the next section) both quadratures are extremely accurate.

C. Pöschl-Teller potential

The Pöschl-Teller potential can be written as

$$V(x) = -D \frac{1}{\cosh^2[x_{PT}]}, \quad (31)$$

where $-D$ is the value of the potential at its minimum. The variable $x_{PT} = \alpha(r - r_e)$ is related to the separation from the equilibrium position (r_e). The parameter α is the inverse of the range of the potential, $\alpha = 1/\sqrt{j+1/2} a_0$, where a_0 is the oscillator length for the harmonic approximation to the Pöschl-Teller potential. Then, as in the Morse case, the coordinate x_{PT} can be written in terms of the harmonic oscillator coordinate x as

$$x_{PT} = \frac{1}{\sqrt{j+1/2}} x. \quad (32)$$

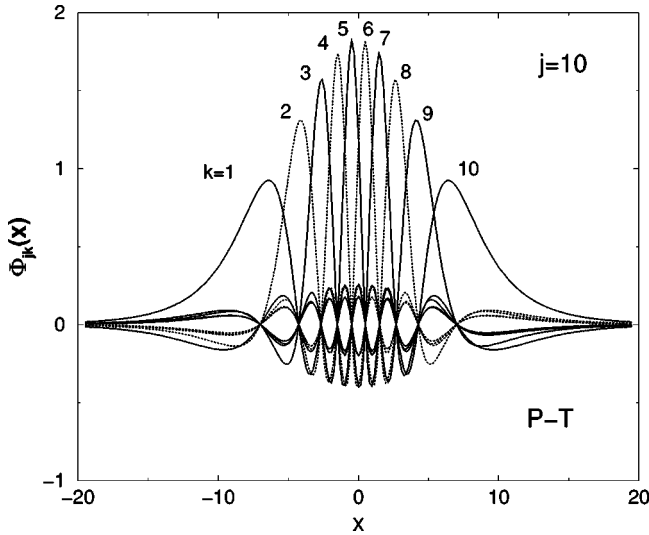


FIG. 3. Configuration localized states $\Phi_{jk}(x)$ for a $j=10$ Pöschl-Teller oscillator.

The bound eigenstates of the Pöschl-Teller Hamiltonian are written as

$$\Psi_{jv}(z) = \mathcal{N}_{jv}^{-1/2} P_j^{(j-v)}(z), \quad (33)$$

where $\mathcal{N}_{jv}$ is a normalization constant, $z = \tanh(x_{PT})$, and $P_s^{(p)}(y)$ are the associated Legendre functions. These states do not have the form required to define CLS's [Eq. (1)] but it can be achieved by defining a new variable,

$$y = \sinh(x_{PT}) = \frac{z}{\sqrt{1-z^2}}. \quad (34)$$

With this variable a new class of orthogonal polynomials $\mathcal{R}_v^{(j)}(y)$ can be defined by

$$P_j^{(j-v)}(z) = (1+y^2)^{-j/2} \mathcal{R}_v^{(j)}(y). \quad (35)$$

In Appendix B it is demonstrated that $\mathcal{R}_v^{(j)}(y)$ are j polynomials of order v ($v=0,1,\dots,j-1$) in the variable y that are orthogonal with respect to the weight function $(1+y^2)^{-(j+1/2)}$. The values of $\mathcal{N}_{jv}$ and k_j are also calculated there. With these new polynomials the Pöschl-Teller wave functions can be written as

$$\Psi_{jv}(y) = \mathcal{N}_{jv}^{-1/2} (1+y^2)^{-j/2} \mathcal{R}_v^{(j)}(y). \quad (36)$$

These states now have the appropriate form to define the CLS's. In Table I the relevant information to build the CLS's for the Pöschl-Teller oscillator is shown under the label P-T. In this table $P_j(y)$ are the Legendre polynomials and $P_j^{(1)}(y)$ the associated Legendre function (see Appendix B). In Fig. 3 the CLS's for a Pöschl-Teller potential with $j=10$ are shown. They are distributed symmetrically with respect to the origin and each wave function is concentrated around a specific value of $y=y_s$ vanishing for the rest of the roots of $\mathcal{R}_j^{(j)}(y)$.

TABLE III. Matrix elements of the operator p in units of $i\hbar\alpha$ in a Pöschl-Teller potential with $j=5$. The exact calculation, integrating with the Pöschl-Teller eigenfunctions, and the approximate calculation using CLS's defined in this paper are presented. Parity conservation implies that Δv has to be odd for the matrix elements of any odd parity operator.

$v \setminus v'$	$v+1$		$v+3$	
	Exact	CLS approx.	Exact	CLS approx.
0	1.4948	1.4944	-0.1744	-0.1701
1	1.8493	1.8529	-0.3032	-0.3229
2	1.8724	1.8557		
3	1.5605	1.6170		

The quadrature presented is such that the matrix elements of the momentum operator are not exact, since $dy/dx_{PT} = \sqrt{1+y^2}$ is not a linear function of y , but it gives a good approximation. In Table III numerically computed matrix elements of p , in units of $i\hbar\alpha$, are compared with the results obtained by using the CLS's presented here in the case of $j=5$. In the case of the coordinate x_{PT} , the results obtained by using CLS's are a good approximation to the numerical results too. In Table IV numerically computed matrix elements of x_{PT} are compared with the results obtained by using the quadrature presented here for the case $j=5$. Again, even for this very unfavorable case, the approximation is good and the main differences are concentrated in the least bound state. As for the Morse potential, the approximation becomes better as j increases.

IV. APPLICATION TO THE DIATOMIC MOLECULE CO

In a previous paper [4] the Morse potential CLS's were used to compute infrared transition matrix elements for the diatomic species HF and DF. In that reference was shown the possibility of computing the intensities once the dipole moment function was known in terms of the internuclear distance. In this section, vibrational dipole matrix elements of the carbon monoxide CO diatomic molecule, in particular, of the isotopomer $^{12}\text{C}^{16}\text{O}$, are computed, assuming different interatomic potentials. It is shown that the experimental data

TABLE IV. Matrix elements of the operator x_{PT} in a Pöschl-Teller potential with $j=5$. The exact calculation, integrating with the Pöschl-Teller eigenfunctions, and the approximate calculation using CLS's defined in this paper are presented. Parity conservation implies that Δv has to be odd for the matrix elements of any odd parity operator.

$v \setminus v'$	$v+1$		$v+3$	
	Exact	CLS approx.	Exact	CLS approx.
0	-0.3322	-0.3312	0.0166	0.0124
1	-0.5284	-0.5386	0.0404	0.0656
2	-0.7490	-0.6865		
3	-1.0403	-1.3244		

are well reproduced by modeling the interatomic interaction with a Morse potential, while major discrepancies are obtained by using harmonic oscillator and Pöschl-Teller potentials. This is not surprising, but the main goal is to provide an example of how CLS's can be a useful tool to study the relevance of different interatomic potentials to describe the anharmonicity in a particular problem.

The CO molecule is of great spectroscopic and astrophysical interest. The rovibrational intensities of this molecule have received considerable attention and much work is devoted to their calculation [9–12]. In particular, the experimental data set used in this section is taken from Ref. [9]. The purpose of this work is far from competing with those extensive rovibronic calculations, but, focusing our attention on the purely vibrational problem, we aim to check the CLS's formalism presented and show its applicability. Within the Born-Oppenheimer approximation the vibrational transition intensities for the electronic ground state band are defined by the matrix elements

$$R(v \rightarrow v') = \langle \Psi_v | \hat{\mu} | \Psi_{v'} \rangle = \int_0^\infty \Psi_v^*(r) \mu(r) \Psi_{v'}(r) r^2 dr, \quad (37)$$

where $\Psi_v(r)$ are the vibrational wave functions and $\mu(r)$ is the expectation value of the dipole moment for internuclear distance r and electronic ground state functions.

It is assumed, as in Ref. [4], that the vibrational wave functions can be approximated as the eigenfunctions of a 1D potential (with j bound states) and that the dipole moment function is a well behaved function of the internuclear separation. Using the orthogonality of CLS's and Eq. (18), Eq. (37) can be rewritten as

$$R(v \rightarrow v') \approx \sum_{s=1}^j \langle j, v | \text{CLS}; j, s \rangle \mu(r_s) \langle \text{CLS}; j, s | j, v' \rangle. \quad (38)$$

It is worth noting that the evaluation of this expression is simple, requiring solely the knowledge of the dipole moment function at certain internuclear distances determined by the zeros of the appropriate orthogonal polynomial and the overlap factors defined in Eq. (15).

There are several references that tackle the problem of computing the dipole moment function of the CO molecule, either with a phenomenological approach [13] or as an *ab initio* calculation [14,15]. In the present work an analytical dipole moment function taken from the literature [13] is employed. With this input the vibrational matrix elements of the dipole moment are computed using the CLS's formalism for the different potentials presented. The corresponding results for each potential are then compared with the experimental ones.

The form of the dipole moment function is shown in Fig. 4, where the equilibrium value ($r_e = 1.1279 \text{ \AA}$) has been marked. The CO molecule static dipole moment is small but, as the figure shows, its first derivative is large. This is one of the reasons why the CO spectrum is so widely known. The energies for the fundamental and first overtone are [10]

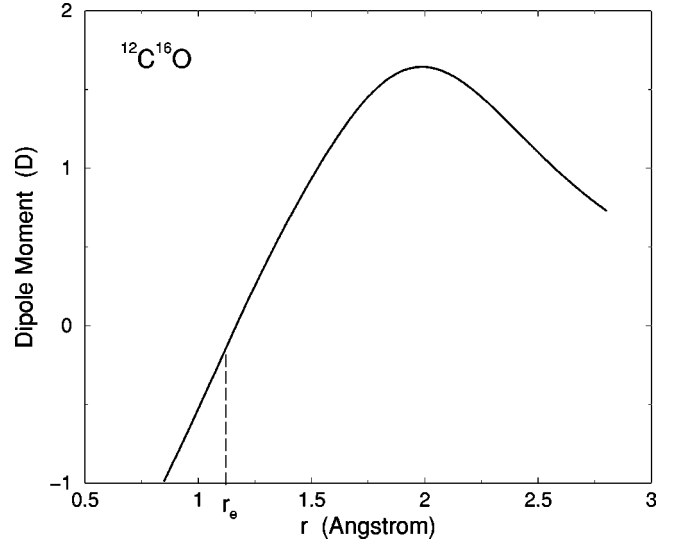


FIG. 4. Phenomenological dipole moment for the $^{12}\text{C}^{16}\text{O}$ molecule from Ref. [13].

$$E_1 = 2143.407 \text{ cm}^{-1}, \quad E_2 = 4260.279 \text{ cm}^{-1}; \quad (39)$$

thus the spectroscopic parameters ω_e and $\omega_e x_e$ are

$$\begin{aligned} E_v &= \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2, \\ \omega_e &= 2169.94 \text{ cm}^{-1}, \\ \omega_e x_e &= 13.2675 \text{ cm}^{-1}. \end{aligned} \quad (40)$$

From these spectroscopic data the corresponding j parameter can be obtained [4]:

$$2j + 1 = \frac{\omega_e}{\omega_e x_e} = 163.55. \quad (41)$$

Thus, the value $j = 81$ has been used to compute the CLS's for the different potentials. Calculations have been carried out for truncated harmonic oscillator, Morse, and Pöschl-Teller potentials. First, the dipole moment function from [13] has to be evaluated at the points corresponding to roots of the polynomials linked to the CLS's for the different potentials. These values are included in Eq. (38) together with the corresponding overlap factors to compute the vibrational matrix elements of the dipole function.

For the Morse oscillator the relation between x_M and the physical coordinate is $x_M = \beta(r - r_e)$ and Eq. (26) can be used to estimate the β value, with the result $\beta = 2.327 \text{ \AA}^{-1}$. Once the $\mu(r_k)$ values are computed, Eq. (38) allows us to obtain the full spectrum. The comparison between computed and experimental [9] values of the square of the dipole moment matrix elements, R^2 , is shown in Fig. 5. The different panels present transitions changing the number of quanta by 0, 1, 2, and 3 units. Good agreement between the experimental and Morse CLS's dipole matrix elements is obtained, the largest discrepancies arising for some $\Delta v = 0$ transitions.

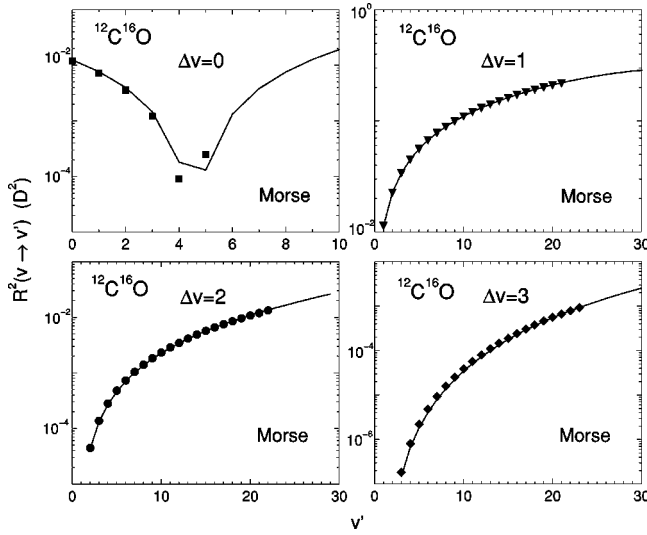


FIG. 5. Experimental and CLS results for the square of the carbon monoxide dipole moment matrix elements, R^2 , expressed in units of D^2 . CLS results are obtained by assuming a Morse type interatomic interaction. Different panels present transitions changing the number of quanta by 0 (top left panel), 1 (top right panel), 2 (bottom left panel), and 3 (bottom right panel) units. Symbols represent the experimental data as taken from Ref. [9]; full lines give the CLS results.

In order to reflect the quality of the results obtained in Fig. 5, Fig. 6 shows the corresponding errors. The quantity plotted is $\chi_{v \rightarrow v'}$ defined as

$$\chi_{v \rightarrow v'} = \frac{R_{\text{theor}}^2(v \rightarrow v') - R_{\text{expt}}^2(v \rightarrow v')}{\sigma_{\text{expt}}(v \rightarrow v')}, \quad (42)$$

where $\sigma_{\text{expt}}(v \rightarrow v')$ is an estimation of the experimental error of the data that takes into account the Poissonian charac-

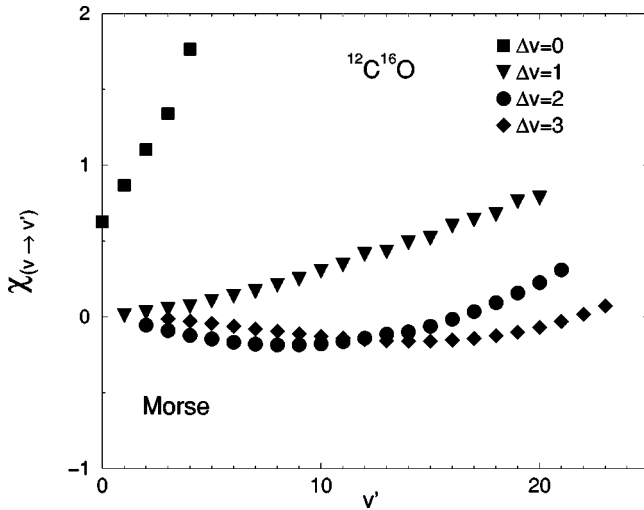


FIG. 6. Statistical errors $\chi_{(v \rightarrow v')}$ (see text) for the square of the dipole moment matrix elements for carbon monoxide. The theoretical calculation corresponds to that presented in Fig. 5 and is performed assuming a Morse potential as interatomic interaction and using the CLS approach.

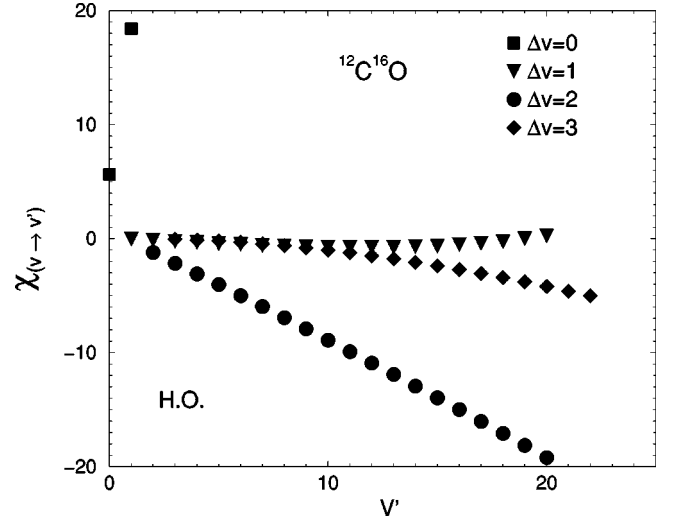


FIG. 7. Statistical errors $\chi_{(v \rightarrow v')}$ (see text) for the square of the dipole moment matrix elements for carbon monoxide. The theoretical calculation is performed assuming a harmonic oscillator potential as interatomic interaction and using the CLS formalism.

ter of the measurement. Thus, the experimental error assigned to the matrix element between states v and v' is related to the experimental error of the transition $0 \rightarrow 1$ by

$$\sigma_{\text{expt}}(v \rightarrow v') = \sigma_{\text{expt}}(0 \rightarrow 1) \sqrt{\frac{R_{\text{expt}}^2(v \rightarrow v')}{R_{\text{expt}}^2(0 \rightarrow 1)}}. \quad (43)$$

In addition, it has been assumed arbitrarily (although this affects only $\chi_{v \rightarrow v'}$, on a global scale) that $\sigma_{\text{expt}}(0 \rightarrow 1)$ is 5% of the experimental value $R_{\text{expt}}^2(0 \rightarrow 1)$. With this definition $\chi_{v \rightarrow v'}$ is a dimensionless quantity.

In order to analyze the sensitivity of the results to the assumed interatomic potential, similar calculations have been done employing CLS's for the truncated harmonic oscillator and anharmonic Pöschl-Teller potentials.

In the harmonic case the relation between the physical coordinate and x is the usual one given in Sec. III, and thus

$$x = 21.004(r - r_e), \quad (44)$$

where r is given in Å and r_e is the equilibrium position. The statistical errors $\chi_{v \rightarrow v'}$ for this calculation are presented in Fig. 7. Be aware of the different scaling on the ordinate axis compared to Fig. 6. The errors are considerably larger, especially for $\Delta v = 0, 2$. It should be noted that some values for $\Delta v = 0$ are out of scale too.

For the Pöschl-Teller case the relation with the physical coordinate is given by Eq. (32),

$$x_{PT} = 2.327(r - r_e), \quad (45)$$

with r assumed to be expressed in Å. The statistical errors for this case are shown in Fig. 8, where again one should notice the different scaling with respect to the Morse case and the large discrepancies that arise in some cases, especially again for $\Delta v = 0, 2$. Some values for $\Delta v = 0$ are out of scale too.

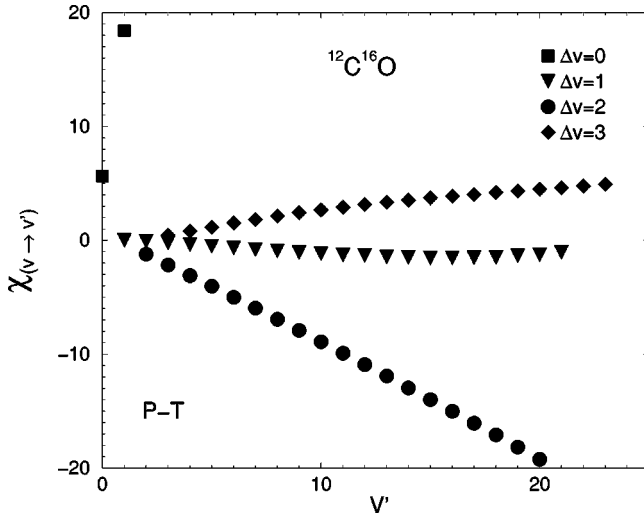


FIG. 8. Same as Fig. 7 but assuming a Pöschl-Teller potential as interatomic interaction.

As expected, the best results are obtained for the Morse calculations, as this potential is closer to a realistic molecular interatomic interaction for a diatomic molecule than the other two cases examined. However, this might not be the case when dealing with polyatomic molecules. For instance, it has been suggested that the bending mode in a triatomic molecule is better represented by a Pöschl-Teller potential [16]. The CLS formalism could help in clarifying which kind of anharmonicity is more relevant. It can be concluded that the CLS formalism allows one to obtain analytical formulas that ease the calculations, and it is sufficiently accurate to discriminate between harmonicity and anharmonicity as well as between different types of anharmonicity (Morse and Pöschl-Teller).

V. SUMMARY AND CONCLUSIONS

In this paper the general formalism for building configuration localized states is presented. Their properties are analyzed and analytical expressions for the matrix elements of the operators of interest, including the momentum p and a generic function of the coordinate $G(x)$, are computed.

The CLS states are the eigenfunctions of a certain function of the coordinate in the basis formed by the bound states of the appropriate one-dimensional potential. They provide a simple and numerically appropriate tool to face the problem of molecular vibrations and allow one to reach analytical expressions even for anharmonic wells.

The CLS formalism is worked out for three potentials of interest in molecular physics, providing the necessary elements to build the CLS's in each case. Finally, we have applied the formalism presented to a real case, the analysis of the $^{12}\text{C}^{16}\text{O}$ vibrational intensity spectrum. The results obtained through comparison of the calculations carried out with the three examples presented show the sensitivity of the formalism, at the same time reducing the numerical complexity of the problem and providing a valuable tool for these problems. In addition, the CLS's may help in some numerically extensive calculations that make use of a grid of

points where the wave functions are evaluated. In particular, the Morse oscillator CLS's could provide for these calculations a very interesting alternative to the harmonic approach, as the momentum matrix elements are exact due to the quadrature employed.

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APPENDIX A

In this appendix we show that the polynomials $\mathcal{T}_v^{(j)}(y)$ introduced in Eq. (29) are in fact orthogonal polynomials and their standardization and differential relations are deduced. The starting point is Eq. (30) for the Morse eigenfunctions with the redefined variable $y = \exp(x_M)/(2j+1)$, bounded between zero and infinity, and the polynomials

$$\mathcal{T}_v^{(j)}(y) = y^v L_v^{(2j-2v)}(1/y). \quad (\text{A1})$$

It is worth noting that the polynomials $\mathcal{T}_v^{(j)}(y)$ have the same coefficients as the Laguerre $L_v^{(2j-2v)}(y)$ but in reversed order; thus the independent term in $L_v^{(2j-2v)}(y)$ corresponds to the power y^v in $\mathcal{T}_v^{(j)}(y)$. From the orthonormality of the wave function (30) the following orthogonality relation for the $\mathcal{T}_v^{(j)}(y)$ polynomials can be derived:

$$\int_0^\infty dy y^{-2j-1} e^{-1/y} \mathcal{T}_v^{(j)}(y) \mathcal{T}_{v'}^{(j)}(y) = \mathcal{N}_{jv} \delta_{v,v'}. \quad (\text{A2})$$

Thus the $\mathcal{T}_v^{(j)}(y)$ are orthogonal polynomials in the interval $[0, \infty]$ with weight function $\omega(y) = y^{-2j-1} e^{-1/y}$ and normalization $\mathcal{N}_{jv}$. The values of k_j and k_{j-1} can be derived in a straightforward way from the information on Laguerre polynomials [7],

$$k_j = 1, \quad (\text{A3})$$

$$k_{j-1} = \frac{j(j+1)}{2}. \quad (\text{A4})$$

The differential relation of the $\mathcal{T}^{(j)}$ polynomials can be shown to be

$$g_2(y) \frac{d}{dy} \mathcal{T}_j^{(j)}(y) = g_1(y) \mathcal{T}_j^{(j)}(y) + g_0(y) \mathcal{T}_{j-1}^{(j)}(y), \quad (\text{A5})$$

with

$$g_2(y) = y \sum_{i=0}^{j-1} (-1)^{j+i-1} \binom{j-1}{i} \frac{j!}{(j-i)!} y^i \\ = (j-1)! y^j L_{j-1}^{(1)}(1/y), \quad (\text{A6})$$

$$g_1(y) = j \sum_{i=0}^{j-1} (-1)^{j+i-1} \binom{j-1}{i} \frac{j!}{(j-i-1)!} y^i$$

$$= jj! y^{j-1} L_{j-1}^{(0)}(1/y), \quad (\text{A7})$$

$$g_0(y) = \sum_{i=0}^{j-1} (-1)^{j+i-1} \binom{j-1}{i} \frac{j!}{(j-i-1)!} y^i$$

$$= j! y^{j-1} L_{j-1}^{(0)}(1/y). \quad (\text{A8})$$

APPENDIX B

In this appendix it is shown that the functions $\mathcal{R}_v^{(j)}(y)$ introduced in Eq. (35) are in fact orthogonal polynomials and their standardization and differential relations are deduced. The starting point is Eq. (35),

$$\mathcal{R}_v^{(j)}(y) = (1+y^2)^{j/2} P_j^{(j-v)}(z). \quad (\text{B1})$$

We use the definition of the associated Legendre function,

$$P_j^{(j-v)}(z) = (-1)^{j-v} (1-z^2)^{(j-v)/2} \frac{d^{j-v} P_j(z)}{dz^{j-v}}, \quad (\text{B2})$$

where $P_j(z)$ is the Legendre polynomial which can be written as

$$P_j(z) = \sum_{n=0}^{[j/2]} C_n^{(j)} z^{j-2n}. \quad (\text{B3})$$

Taking the corresponding derivatives and using the relation between z and y variables $z^2 = y^2/(1+y^2)$, Eq. (B1) can be rewritten as

$$\mathcal{R}_v^{(j)}(y) = (-1)^{j-v} \sum_{n=0}^{[v/2]} C_n^{(j)} \frac{(j-2n)!}{(v-2n)!} y^{v-2n} (1+y^2)^n, \quad (\text{B4})$$

which shows that $\mathcal{R}_v^{(j)}(y)$ is a polynomial of order v in the variable y . Straightforward computation of the integral of two of these polynomials with weight function $\omega(y) = (1+y^2)^{-(j+1/2)}$ gives

$$\int_{-\infty}^{\infty} (1+y^2)^{-(j+1/2)} \mathcal{R}_v^{(j)}(y) \mathcal{R}_{v'}^{(j)}(y) dy = \mathcal{N}_{jv} \delta_{v,v'}, \quad (\text{B5})$$

where $\mathcal{N}_{jv} = (2j-v)!/(j-v)v!$. It is worth noting that the polynomial $\mathcal{R}_j^{(j)}(y)$ is orthogonal to all the others even if it cannot be normalized. The coefficients of y^j in $\mathcal{R}_j^{(j)}(y)$ and of y^{j-1} in $\mathcal{R}_{j-1}^{(j)}(y)$ are easily obtained by using Eq. (B4) and Eq. (B3):

$$k_j = P_j(1) = 1, \quad (\text{B6})$$

$$k_{j-1} = -P'_j(1) = -\frac{j(j+1)}{2}. \quad (\text{B7})$$

Direct computation gives the differential relation of the $\mathcal{R}^{(j)}$ polynomials,

$$g_2(y) \frac{d}{dy} \mathcal{R}_j^{(j)}(y) = g_1(y) \mathcal{R}_j^{(j)}(y) + g_0(y) \mathcal{R}_{j-1}^{(j)}(y), \quad (\text{B8})$$

with

$$g_2(y) = 1 + y^2, \quad (\text{B9})$$

$$g_1(y) = jy, \quad (\text{B10})$$

$$g_0(y) = -1. \quad (\text{B11})$$

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