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 $^{13}$C$^{16}$O is studied as a way to test the results obtained for different potentials in connection with their ability to model the anharmonicity.

PACS number(s): 31.15.—p, 03.65.Ca, 33.20.Tp, 33.20.Ea

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 vibrational 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

$$\psi_{jv}(x) = \langle x|j,v \rangle = N_{jv}^{-1/2} F(y) P_{v}^{(j)}(y),$$

$$v = 0, 1, 2, \ldots, j - 1,$$  \hspace{1cm} (1)

where $y$ is an arbitrary function of $x$ (the physical coordinate) well behaved in the region of interest $(x_{\text{min}}, x_{\text{Max}})$ (continuous, single valued, finite, and monotonically increasing or decreasing). The values of $y$ at the extremes of this region are $(y_{0}, y_{1})$. $N_{jv}^{-1/2}$ is a normalization constant, $F(y)$ is an arbitrary function of $y$, and $P_{v}^{(j)}(y)$ is a polynomial of order $v$ in $y$. The label $j$ is associated with the potential depth.

The orthogonality of the eigenfunctions implies that

$$\int_{x_{\text{Min}}}^{x_{\text{Max}}} dx \psi_{jv}(x) \psi_{jv'}(x) = \delta_{v,v'},$$  \hspace{1cm} (2)

which, changing variables, leads to

\[\int_{x_{\text{Min}}}^{x_{\text{Max}}} dx \psi_{jv}(x) \psi_{jv'}(x) = \delta_{v,v'},\]
\[
\int_{y_0}^{y_1} dy \omega(y) P_j^{(v)}(y) P_{j'}^{(u)}(y) = N_{jv} \delta_{v,v'}, \tag{3}
\]

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

Consequently, the set \( \{P_j^{(v)}(y); v=0,1,\ldots,j-1\} \) 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 \( P_j^{(v)}(y) \) 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:
\[
\sum_{v=0}^{j-1} \frac{1}{N_{jv}} P_j^{(v)}(y) P_{j'}^{(u)}(z) = \frac{k_{j-1}}{k_j N_{jj-1}} P_j^{(v)}(y) P_{j'}^{(u)}(z) - P_j^{(v)}(z) P_{j'}^{(u)}(y), \tag{5}
\]

where \( k_v \) is the coefficient of the term of order \( v \) in the explicit form of the polynomial \( P_j^{(v)}(y) \). It is worth noticing here that the polynomial \( P_j^{(v)}(y) \) 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 \( P_j^{(v)}(y) \) by \( y - y_s \), where \( y_s, s=1,\ldots,j \) are the \( j \) roots of \( P_j^{(v)}(y) \).

These polynomials are constructed by making \( z = y_s \) in Eq. (5):
\[
Q_j^{(s)}(y) = \sum_{v=0}^{j-1} \frac{1}{N_{jv}} P_j^{(v)}(y) P_{j-s}^{(v)}(y_s), \tag{6}
\]

Alternatively they can be expressed as
\[
Q_j^{(s)}(y) = \frac{k_{j-1}}{k_j N_{jj-1}} P_j^{(s)}(y) P_{j-s}^{(s)}(y_s) \prod_{l \neq s} (y - y_l). \tag{7}
\]

The limit \( y = y_s \) gives
\[
Q_j^{(s)}(y) = \sum_{v=0}^{j-1} \frac{1}{N_{jv}} [P_j^{(v)}(y_s)]^2 = \frac{k_{j-1}}{k_j N_{jj-1}} g_0(y_s) [P_{j-s}^{(s)}(y_s)]^2, \tag{8}
\]

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),

\[
g_2(y) \frac{d}{dy} P_j^{(v)}(y) = g_1(y) P_j^{(v)}(y) + g_0(y) P_{j-1}^{(v)}(y). \tag{9}
\]

These new polynomials are orthogonal with respect to the weight function \( \omega(y) \) [8]:
\[
\int_{y_0}^{y_1} dy \omega(y) Q_j^{(s)}(y) Q_{j-1}^{(s')} (y) = \delta_{ss'} N_{jv}. \tag{10}
\]

These \( Q_j^{(s)}(y) \) polynomials can be used, as shown in Ref. [8], to define quadratures for the integrals
\[
\int_{y_0}^{y_1} dy \omega(y) F(y) = \sum_{s=1}^{j} F(y_s) w_j + R_j, \tag{11}
\]

where \( F(y) \) is any function of \( y \) and \( w_j \) are weight factors given by
\[
w_j = [Q_j^{(s)}(y_s)]^{-1}. \tag{12}
\]

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

With the help of the \( Q_j^{(s)}(y) \) polynomials, configuration localized states in the configuration space can be defined as
\[
\phi_{js}(x) = \langle x|CL;j,s \rangle = w_{js}^{1/2} \omega(y) Q_j^{(s)}(y). \tag{13}
\]

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
\[
|CL;j,s\rangle = \sum_{v=0}^{j-1} \langle j,v|CL;j,s\rangle |j,v\rangle, \tag{14}
\]

and the overlap factors can be computed from the definition of the CLS’s and the polynomials \( Q_j^{(s)}(y) \), giving
\[
\langle j,v|CL;j,s\rangle = w_{js}^{1/2} N_{jv}^{1/2} P_j^{(v)}(y_s). \tag{15}
\]

The CLS’s have the following properties.

(1) Orthogonality:
\[
\langle CL;j,s|CL;j,s' \rangle = \delta_{s,s'}, \tag{16}
\]

which stems directly from the orthogonality of the \( Q_j^{(s)}(y) \) polynomials.

(2) Matrix elements of \( y \):
\[
\langle CL;j,s|y|CL;j,l\rangle = \int_{y_0}^{y_1} dy \omega(y) w_{j;js}^{1/2} w_{j;jl}^{1/2} Q_j^{(s)}(y) y Q_j^{(l)}(y) = y_s \delta_{s,l}. \tag{17}
\]

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 \( P_j^{(v)}(y) \) times a polynomial of order less than \( j \).

(3) Matrix elements of an arbitrary function of \( y \):
\[ \langle \text{CLS}; j, s | G(y) | \text{CLS}; j, l \rangle = \int_{y_0}^{y_1} dy \omega(y) w_{jj}^{1/2} w_{jj}^{1/2} Q_j^{(s)}(y) G(y) Q_j^{(l)}(y) \approx G(y_s) \delta_{s, r} + R_j. \] (18)

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

(4) Matrix elements of the momentum \( p \):

\[ \langle \text{CLS}; j, s | p | \text{CLS}; j, l \rangle = \frac{i \hbar}{2} \frac{1}{y_s - y_l} \left[ \sqrt{w_{jj} / w_{jj}} \left( \frac{dy}{dx} \right)_{y_s}^{y_l} + \sqrt{w_{jj} / w_{jj}} \left( \frac{dy}{dx} \right)_{y_l}^{y_s} \right] \] (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 \( \langle \text{CLS}; j, s | p | \text{CLS}; j, l \rangle \) can be expressed as

\[ \langle \text{CLS}; j, s | p | \text{CLS}; j, l \rangle = \int_{y_{\text{min}}}^{y_{\text{max}}} dx \phi_j(x) \frac{d \phi_j(x)}{dx} = \frac{i \hbar}{2} \int_{y_{\text{min}}}^{y_{\text{max}}} dx \left[ \phi_j(x) \left( \frac{d \phi_j(x)}{dx} \right) - \phi_j(x) \left( \frac{d \phi_j(x)}{dx} \right) \right], \] (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:

\[ \langle \text{CLS}; j, s | p | \text{CLS}; j, l \rangle \approx \frac{i \hbar}{2} \left[ \sqrt{w_{jj} / w_{jj}} \left( \frac{dy}{dx} \right)_{y_s}^{y_l} \left( \frac{dQ_j^{(s)}(y)}{dy} \right)_{y_s}^{y_l} - \sqrt{w_{jj} / w_{jj}} \left( \frac{dy}{dx} \right)_{y_l}^{y_s} \left( \frac{dQ_j^{(s)}(y)}{dy} \right)_{y_l}^{y_s} \right]. \] (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

\[ \left( \frac{dQ_j^{(s)}(y)}{dy} \right)_{y_s}^{y_l} = \left( k_{j-1} \frac{P_j^{(s)}(y_s)}{N_{j-1}} \right) \prod_{i \neq s} (y - y_i) \]

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

\[ H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \lambda^2. \] (23)

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

\[ \psi_{j \mu}(x) = N_{j \mu}^{-1/2} \exp \left( -\frac{x^2}{2} \right) H_{\mu}(x); \quad \mu = 0, \ldots, j - 1, \] (24)

where \( H_{\mu}(x) \) 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 \( H_{\mu}(y) \).

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 (PT) potentials.

<table>
<thead>
<tr>
<th></th>
<th>HO</th>
<th>Morse</th>
<th>PT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y )</td>
<td>( x )</td>
<td>( (2j+1)^{-1} \exp(x_M) )</td>
<td>( \sin(x_H) )</td>
</tr>
<tr>
<td>((y_0, y_1))</td>
<td>((-\infty, \infty))</td>
<td>((0, \infty))</td>
<td>((-\infty, \infty))</td>
</tr>
<tr>
<td>( N_{jv} )</td>
<td>(\sqrt{\pi} 2^v v!)</td>
<td>( (2j-v)! )</td>
<td>( (2j-v)! )</td>
</tr>
<tr>
<td>( F(y) )</td>
<td>( \exp(-\frac{y^2}{2}) )</td>
<td>( y^{-\frac{1}{2}} \exp\left(-\frac{1}{2y}\right) )</td>
<td>( (1+y^2)^{-j/2} )</td>
</tr>
<tr>
<td>( T^{(j)}_v(y) )</td>
<td>( H_v(y) )</td>
<td>( T^{(j)}_v(y) )</td>
<td>( R^{(j)}_v(y) )</td>
</tr>
<tr>
<td>( \alpha(y) )</td>
<td>( \exp(-y^2) )</td>
<td>( y^{-2j-1} \exp\left(-\frac{1}{y}\right) )</td>
<td>( (1+y^2)^{-j(j+1/2)} )</td>
</tr>
<tr>
<td>( Q^{(j)}_v(y) )</td>
<td>( \frac{H_{j-1}(y_x)}{\sqrt{\pi} 2^{(j-1)!} y-y_x} )</td>
<td>( \frac{(j+1)T^{(j)}_{j-1}(y_x)}{2} T^{(j)}_v(y) )</td>
<td>( \frac{-1}{y-y_x} ) R^{(j)}_v(y)</td>
</tr>
<tr>
<td>( w_{jv} )</td>
<td>( \frac{\sqrt{\pi} 2^{(j-1)!}}{2j} [H_{j-1}(y_x)]^{-2} )</td>
<td>( \frac{y_s L^{(1)}<em>{j-1}(1/y_s)}{j L^{(0)}</em>{j-1}(1/y_s)} [T^{(j)}_{j-1}(y_x)]^{-2} )</td>
<td>( 2(1+y^2)[R^{(j)}_{j-1}(y_x)]^{-2} )</td>
</tr>
</tbody>
</table>

*These are the roots of \( T^{(j)}_v(y) \).

\[
V(x) = D\left[1 - \exp(-x_M)^2\right], \quad (25)
\]

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 \(\beta\) is the inverse of the range of the potential,

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

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

\[
\Psi_{jv}(z) = N_{jv}^{-1/2} \exp\left(-\frac{z}{2}\right) z^{j-v} L^{(2j-2v)}_v(z), \quad (27)
\]

where \(N_{jv}\) is a normalization constant, \(z = (2j + 1) \exp(-x_M)\) is the Morse variable, and \(L^{(p)}_v(z)\) 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

\[
\Psi_{jv}(y) = N_{jv}^{-1/2} y^{-j} \exp\left(-\frac{1}{2y}\right) y^v L^{(2j-2v)}_v(1/y). \quad (28)
\]

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

\[
T^{(j)}_v(y) = y^v L^{(2j-2v)}_v(1/y). \quad (29)
\]
The fact that they are polynomials in \( y \) can be seen easily since \( L_n^{(2j-2v)}(1/y) \) 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 \( L_n^{(2j-2v)}(1/y) \) but in reversed order [e.g., the coefficient of the term of order \( n \) in \( T^{(j)}_v(1/y) \) is the coefficient of order \( v - n \) in \( L_n^{(2j-2v)}(1/y) \)]. The properties of polynomials \( T^{(j)}_v(y) \) are discussed in Appendix A. In terms of these polynomials, the Morse wave functions are written as

\[
\Psi_{jv}(y) = N_{jv}^{-1/2} y^{-j} \exp \left( -\frac{1}{2y} T^{(j)}_v(1/y) \right),
\]

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 \( \phi_{jv}(y) \) 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 function \( V(x) = \exp(-x_M) \) can be written as

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

where \(-D\) is the value of the potential at its minimum. The variable \( x_{PT} = x(r - r_e) \) is related to the separation \( r - r_e \) from the equilibrium position. The parameter \( \alpha \) 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, in the Morse case, the coordinate \( x_{PT} \) can be written as

\[
x_{PT} = \frac{1}{\sqrt{j + 1/2}} x.
\]
In Appendix B it is demonstrated that with this variable a new class of orthogonal polynomials \( v_j \) is a normalization constant, \( y = \tanh(x_{PT}) \), 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,

\[
y = \sinh(x_{PT}) = \frac{z}{\sqrt{1 - z^2}}.
\]

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

\[
P_v^{(j-v)}(z) = (1 + y^2)^{-\frac{j}{2}} \mathcal{R}_v^{(j)}(y).
\]

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

\[
\Psi_{jv}(y) = \mathcal{N}_v^{j-1/2} (1 + y^2)^{-j/2} \mathcal{R}_v^{(j)}(y).
\]

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 \( P_s(y) \) are the Legendre polynomials and \( P_s^{(1)}(y) \) 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 \( y = y_c \) vanishing for the rest of the roots of \( \mathcal{R}_v^{(j)}(y) \).

![FIG. 3. Configuration localized states \( \Phi_{v}(x) \) for a j = 10 Pöschl-Teller oscillator.](image-url)

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

\[
\Psi_{jv}(z) = \mathcal{N}_v^{j-1/2} P_v^{(j-v)}(z),
\]

where \( \mathcal{N}_v^j \) is a normalization constant, \( z = \tanh(x_{PT}) \), and \( P_s^{(p)}(y) \) are the associated Legendre functions. These states can be written as

\[
\Psi_{jv}(y) = \mathcal{N}_v^{j-1/2} (1 + y^2)^{-j/2} \mathcal{R}_v^{(j)}(y).
\]

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 \( \hbar \alpha \), 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 diatomic Morse 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 \( \text{CO} \) 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>
<thead>
<tr>
<th>( v ) ( \backslash ) ( v' )</th>
<th>( v + 1 )</th>
<th>( v + 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact</td>
<td>CLS approx.</td>
<td>Exact</td>
</tr>
<tr>
<td>0</td>
<td>-0.3322</td>
<td>-0.3312</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>3</td>
<td>-1.0403</td>
<td>-1.3244</td>
</tr>
</tbody>
</table>
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. 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

$$R_{\nu} = \langle \Psi_\nu | \hat{\mu} | \Psi_{\nu'} \rangle = \int_0^\infty \Psi_\nu^*(r) \mu(r) \Psi_{\nu'}(r) r^2 dr,$$

(37)

where $\Psi_\nu(r)$ 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

$$R_{\nu} = \sum_{j=1}^{j} \langle j, \nu | \text{CLS}_j, s \rangle \mu(r_j) \langle \text{CLS}_j, s | j, \nu' \rangle.$$

(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 or as an ab initio calculation. In the present work an analytical dipole moment function taken from the literature 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 ($r_e = 1.1279$ Å) 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

$$E_1 = 2143.407 \text{ cm}^{-1}, \quad E_2 = 4260.279 \text{ cm}^{-1}.$$  

(39)

thus the spectroscopic parameters $\omega_c$ and $\omega_c x_c$ are

$$E_v = \omega_c (v + 1/2) - \omega_c x_c (v + 1/2)^2,$$

$$\omega_c = 2169.94 \text{ cm}^{-1},$$

$$\omega_c x_c = 13.2675 \text{ cm}^{-1}.$$  

(40)

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

$$2j + 1 = \frac{\omega_c}{\omega_c x_c} = 163.55.$$  

(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 $\beta$ value, with the result $\beta = 2.327$ Å$^{-1}$. Once the $\mu(r_j)$ 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.
In order to reflect the quality of the results obtained in Fig. 5, Fig. 6 shows the corresponding errors. The quantity plotted is

\[ x_{v\rightarrow v'} = \frac{R^2_{\text{theor}}(v\rightarrow v') - R^2_{\text{exp}}(v\rightarrow v')}{\sigma_{\text{exp}}(v\rightarrow v')} \]

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

\[ \sigma_{\text{exp}}(v\rightarrow v') = \sigma_{\text{exp}}(0\rightarrow 1) \sqrt{\frac{R^2_{\text{exp}}(v\rightarrow v')}{R^2_{\text{exp}}(0\rightarrow 1)}}. \]

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

\[ x = 21.004(r - r_e), \]

where \( r \) is given in Å and \( r_e \) is the equilibrium position. The statistical errors \( x_{v\rightarrow v'} \) 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.

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

\[ x_{PT} = 2.327(r - r_e), \]

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.
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 than the Morse oscillator CLS’s could provide for these calculations. It is worth noting that the polynomials \( T_{v}^{(j)}(y) \) have the same coefficients as the Laguerre \( L_{2j}^{(2\gamma-2\alpha)}(y) \) but in reversed order; thus the independent term in \( L_{2j}^{(2\gamma-2\alpha)}(y) \) corresponds to the power \( y^{\gamma} \) in \( T_{v}^{(j)}(y) \). From the orthonormality of the wave function (30) the following orthogonality relation for the \( T_{v}^{(j)}(y) \) polynomials can be derived:

\[
\int_{0}^{\infty}dy y^{-2j-1}e^{-\beta y}T_{v}^{(j)}(y)T_{v'}^{(j)}(y) = N_{j\beta} \delta_{v,v'}. \quad (A2)
\]

Thus the \( T_{v}^{(j)}(y) \) are orthogonal polynomials in the interval \([0,\infty]\) with weight function \( \omega(y) = y^{-2j+1}e^{-\beta y} \) and normalization \( N_{j\beta} \). The values of \( k_{j} \) and \( k_{j-1} \) can be derived in a straightforward way from the information on Laguerre polynomials [7].

\[
k_{j} = 1, \quad (A3)
\]

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

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

\[
g_{2}(y) \frac{d}{dy}T_{v}^{(j)}(y) = g_{1}(y)T_{v}^{(j)}(y) + g_{0}(y)T_{v}^{(j-1)}(y), \quad (A5)
\]

with

\[
g_{2}(y) = \sum_{i=0}^{j-1} (-1)^{j+i-1} \binom{j-1}{i} \frac{j!}{(j-i)!} y^{i} = (j-1)!y^{j}L_{j-1}^{(1)}(1/y), \quad (A6)
\]
\[ g_j(y) = \sum_{i=0}^{j-1} (-1)^{j-i+1} \binom{j-1}{i} \frac{j!}{(j-i-1)!} y^i \]
\[ g_0(y) = \sum_{i=0}^{j-1} (-1)^{j+i-1} \binom{j-1}{i} \frac{j!}{(j-i-1)!} y^i \]
\[ = j! y^{-j-1} L_{j+1}^{(0)}(1/y), \quad (A7) \]
\[ = j! y^{-j-1} L_{j+1}^{(0)}(1/y), \quad (A8) \]

**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),
\[ \mathcal{R}_v^{(j)}(y) = (1 + y^2)^{j/2} P_{j-v}^{(j-v)}(z). \quad (B1) \]
We use the definition of the associated Legendre function,
\[ P_{j-v}^{(j-v)}(z) = (-1)^{j-v}(1-z^2)^{(j-v)/2} \frac{d^{j-v} P_j(z)}{dz^{j-v}}, \quad (B2) \]
where \( P_j(z) \) is the Legendre polynomial which can be written as
\[ P_j(z) = \sum_{n=0}^{\lfloor j/2 \rfloor} C_j^{(n)} z^{j-2n}. \quad (B3) \]

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
\[ \mathcal{R}_v^{(j)}(y) = (-1)^{j-v} \sum_{n=0}^{\lfloor v/2 \rfloor} C_j^{(n)} \binom{j-2n}{v-2n} y^{v-2n}(1 + y^2)^n, \quad (B4) \]
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 \( \omega(y) = (1 + y^2)^{-j/2} \) gives
\[ \int_{-\infty}^{\infty} (1 + y^2)^{-j/2} \mathcal{R}_v^{(j)}(y) \mathcal{R}_{v'}^{(j)}(y) dy = \mathcal{N}_{v,v'} \delta_{v,v'}, \quad (B5) \]
where \( \mathcal{N}_{v,v'} = (2j-v)!/(j-v)\nu! \). It is worth noting that the polynomial \( \mathcal{R}_v^{(j)}(y) \) is orthogonal to all the others even if it cannot be normalized. The coefficients of \( y^j \) in \( \mathcal{R}_v^{(j)}(y) \) and of \( y^{j-1} \) in \( \mathcal{R}_{v-1}^{(j)}(y) \) are easily obtained by using Eq. (B4) and Eq. (B3):
\[ k_j = P_j(1) = 1, \quad (B6) \]
\[ k_{j-1} = -P_j(1) = -\frac{j(j+1)}{2}. \quad (B7) \]

Direct computation gives the differential relation of the \( \mathcal{R}_v^{(j)} \) polynomials,
\[ g_2(y) \frac{d}{dy} \mathcal{R}_v^{(j)}(y) = g_1(y) \mathcal{R}_v^{(j)}(y) + g_0(y) \mathcal{R}_{v-1}^{(j)}(y), \quad (B8) \]
with
\[ g_2(y) = 1 + y^2, \quad (B9) \]
\[ g_1(y) = jy, \quad (B10) \]
\[ g_0(y) = -1. \quad (B11) \]