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Formalism of the displaced squeezed Fock states for variational calculations of highly excited ro-vibrational levels: Diatomic molecules

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A set of displaced squeezed number states is proposed as trial wave functions in variational calculations of ro-vibrational energy levels of diatomic molecules. By employing the ladder-operator formalism, we construct such states as well as an algebraic Hamiltonian expressed in terms of normal-ordered boson operators. We also show that this algebraic Hamiltonian can be expanded in terms of pseudoladder operators $\tilde{a}(\lambda,\kappa)$ and $\tilde{a}^{\dagger}(\lambda,\kappa)$ obtained via a generalized Bogoliubov transformation. In this case, the Hamiltonian matrix is built using the usual Fock basis set and the coherence and squeezing parameters λ and κ are optimized variationally. The convergence of the variational calculations is largely improved when using the displaced squeezed number states instead of the usual Fock ones. A class of generalized displaced squeezed number states is also considered, and some numerical applications are given.

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I. INTRODUCTION

It is becoming increasingly common to perform accurate data reductions of high-resolution spectra of diatomic molecules using eigensolutions of the radial Schrödinger equation (see Refs. [1–6], for example, and references therein). For a wide variety of cases, especially for molecules with a small reduced mass, a simultaneous modeling of data for several isotopomers and predictions of ro-vibrational excited states lying near dissociation require an account of Born-Oppenheimer breakdown (BOB) effects in the Hamiltonian [7]. In most spectroscopic papers, the resolution of the one-dimensional radial equation was carried out by using two different approaches. The first one is a numerical approach based on the Cooley-Cashion-Zare algorithm [8] implemented, for example, in the computer program LEVEL [9]. The other one is an algebraic approach based on the hypervirial perturbation theory [1]. So it seemed to us natural and necessary to develop an alternative algebraic technique of solving the radial Schrödinger equation independently of the perturbational and numerical methods currently used in the literature.

This paper is the first of a series of articles which deal with the calculation of very excited ro-vibrational energy levels in di- and polyatomic systems using techniques generally encountered in other fields than spectroscopy. The object of the present paper is focused on the study of ro-vibrational molecular quantum states of diatomic molecules.

Basically there exists three nonperturbative approaches adapted to such calculations: (i) direct numerical solutions of the radial Schrödinger equation obtained through Numerov-Cooley-type methods, as mentioned above. Such methods are essentially exact, but remain difficult to extend to polyatomic systems where complicated kinetic energy terms are involved. (ii) Because no restrictions exist on the form of the kinetic and potential energy terms, the variational method is known to provide an efficient tool for global spectra calculations in atomic and molecular physics. In its simplest form, it approximates the ground-state energy E_0 of a Hamiltonian H by the stationary value of the expectation value $\varepsilon[\Psi]$:

$$\varepsilon[\Psi] = \frac{\langle\Psi_{\text{trial}}|H|\Psi_{\text{trial}}\rangle}{\langle\Psi_{\text{trial}}|\Psi_{\text{trial}}\rangle}, \tag{1}$$

where Ψ_{trial} is a trial wave function which contains a few undetermined (variation) parameters further fixed at the values making the variation $\delta\varepsilon=0$. $\varepsilon[\Psi]$ is a functional since its value will depend on the form of the function Ψ. Employing the Ritz variational approach, the trial wave function is built in terms of an expansion in a finite number of primitive zeroth-order eigenfunctions ϕ_v of a simpler related problem. The ansatz is thus written as

$$\Psi_{\text{trial}} = \sum_{v=0}^{N_{max}} c_v \phi_v(r;p_1,p_2,\ldots), \tag{2}$$

where c_v and $p_1,p_2,\ldots$ are linear and nonlinear parameters, respectively. In our case, r is just the internuclear distance between atoms A and B for an AB molecule. Note that no restrictions exist on the form of the primitive basis set. In practice, one has to determine N_{max} such that ε approaches the exact energy, which is totally reached as $N_{max}\to\infty$. Although this method is conceptionnally very general, it usually requires numerical evaluations of the matrix elements $\langle\phi_{v'}|H|\phi_v\rangle$, which may lead to a loss of precision. (iii) A third approach consists in combining efficient algebraic techniques with accurate variational calculations. The loss of precision may thus be overcome by evaluating the matrix elements analytically and in a faster way. But unlike the traditionnal variational calculations, the problem is then to find a set of relevant primitive functions ϕ_v associated with a known algebra.

In this paper, we are concerned with the latter method. To achieve this end, the radial Hamiltonian $H(r)$ is transformed with the aid of second quantization as $H(a^{\dagger},a)$. In a first

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approximation, the Hamiltonian can be written as H_0+H', where H_0 is simply the harmonic-oscillator system which possesses the Heisenberg-Weyl (HW) h_4 dynamical symmetry [10]. In this case, it becomes quite natural to take the Fock eigenstates $|v\rangle$ of the number operator $a^\dagger a$ as primitive wave functions and to treat H' variationally [11]. However, when the Hamiltonian H' is a strong nonlinear function of the generators of the dynamical group with a high anharmonicity, the exact solutions of Eq. (1) are in general very difficult to obtain, and even to approach. This is because the convergence of the variational calculations is often dramatically slow near the dissociation limit when using the Fock states. To get rid of such limitations, one has to find a more appropriate basis of primitive functions which keeps the possibility to calculate $\langle \phi_{v'}|H|\phi_v\rangle$ analytically.

In this context, the use of the *coherent states* (CSs) [10,12] and *squeezed states* (SSs) [13–15] of the harmonic oscillator for the calculation of molecular vibration-rotation energy levels turns out to be more advantageous than that of the usual Fock states. CSs and SSs are found in almost every paper on modern quantum optics and are often discussed theoretically in many other domains. The Glauber CSs are defined as the eigenstates of the annihilation operator a while the SSs are vacuum states of the pseudoannihilation operator $b=ua+va^\dagger$ (with $|u|^2-|v|^2=1$) obtained via a Bogoliubov transformation (BT) [16], which preserves the commutation relations. Taking such states either separately or combined together leading to the so-called *displaced squeezed states* (DSSs) [15] or *squeezed coherent states* (SCSs) [14] states, as trial wave functions we obtain generally a very good approximation for the solution of the ground state. In this case, the coherence and/or squeezing parameters λ and ξ, which enable one to vary the centering and the opening of the Gaussian wave functions, respectively, play the role of variational parameters and are thus adjusted by minimizing the expectation value $\varepsilon[\Psi]$. In order to take into account excited rotation-vibration energy levels, more general states must be considered as trial wave functions. Since CSs and SSs are also described by unitary HW and SU(1, 1) displacement operators $D(\lambda)$ and $S(\xi)$ on the vaccum oscillator state, respectively, a more general construction can be obtained by applying these displacement operators to states $|\phi\rangle$ different from the vaccum state. For our problem, we simply choose the special case where $|\phi\rangle=|v\rangle$ and only consider the displaced squeezed number or Fock states (DSFSs) [17] defined with the ordering $DS|v\rangle$. This class of algebraic states generalizes the DSSs, the squeezed number states (SNSs) [18], and the displaced Fock states (DFSs) [19], which are thus viewed as particular cases.

High-resolution spectroscopic investigations (accuracy $\sim 10^{-3}-10^{-5}$ cm^{-1} from infrared to microwave spectra) of very excited ro-vibrational energy levels of diatomics using DSFSs have never been carried out to our knowledge. That is why the main purpose of this paper is to calculate all the observed transition in diatomic molecules at the desired accuracy and to show that the two-parameter DSFSs are much more flexible when reaching the dissociation limit than the Fock states. Contrariwise, we will also point out that when investigating high-excited states, the DSFSs are not appropriate to describe the first lower states. As a first attempt, we will suggest to introduce a class of wave functions on the basis of the harmonic oscillator (HO) ones, but with a better local picture describing low, medium, and high v states.

The plan of this paper is as follows. First, the algebraic derivation of the diatomic Hamiltonian from potential terms taken from the literature is given. Thus the DSFSs are defined for our problem using the HW and SU(1, 1) group structures. In a next subsection, a more general zeroth-order quadratic ro-vibrational Hamiltonian H_0', which possesses the h_6 dynamical symmetry, is defined as usual from a generalized BT. Then, some useful matrix elements and expectation values are given by k-fold application of the BT for the calculation of the Hamiltonian matrix. In the last section we apply the previous formalism to three diatomic systems (^{12}C^{16}O, ^{7}Li$_2$, and ^{20}Ca [20]) whose spectroscopic data range is very wide. The convergence and reliability of the DSFSs will be compared to those of the usual Fock states, and the results will be discussed. Finally, generalized DSFSs will be also introduced before to conclude.

II. EXTENDED HO WAVE FUNCTIONS AND DISPLACED SQUEEZING OPERATORS

A. Algebraic radial Hamiltonian

For our purposes, we consider the one-dimensional Schrödinger equation for the calculation of vibration-rotation energy levels of a diatomic molecule in its ground electronic state. The model is described by the Hamiltonian [7]

$$H(\hat{p},r,\mathcal{J})=[1+\beta(r)]\frac{\hat{p}^2}{2\mu}+B(r)[1+\alpha(r)]\mathcal{J}^2+U(r), \quad (3)$$

where $U(r)=U_{\mathrm{BO}}(r)+\Delta U^{\mathrm{ad}}(r)$ includes the Born-Oppenheimer potential and the mass-dependent adiabatic contribution, respectively, and $dU(r_e)/dr|_{r_e}\neq 0$. r is the internuclear distance between the two atoms, $\hat{p}=-i\hbar d/dr$ is the corresponding momentum, and μ is the reduced mass. Concerning the rotational part, we consider the dimensionless operator $\mathcal{J}^2\equiv \mathbf{J}^2/\hbar^2$ with the rotational eigenvalues $J(J+1)$ and $B(r)=\hbar^2/2\mu r^2$, $B(r_e)$ being the equilibrium rotational constant. Finally $\alpha(r)$ and $\beta(r)$ are nonadiabatic rotational and vibrational BOB functions which describe the interactions with excited electronic states. Note that the Hamiltonian (3) does not have a fully Hermitian form because of $\beta(r)$, but for most of the practical applications, this term will be either reduced to a constant or not employed; that is, the non-Hermitian part vanishes. The former case ($\beta=\beta_0$) just consists of a change of the vibrational reduced mass as $\mu\rightarrow\mu/(1+\beta_0)$, while the latter case ($\beta=0$) will be considered here in all the following.

There exists an efficient numerical method based on the Cooley-Cashion-Zare algorithm [8] for solving the one-dimensional radial equation $H\Psi=E\Psi$. But although such powerful numerical technique gives very accurate results for one-dimensional systems, its extension to polyatomic molecules remains to our knowledge an unsolved issue. Moreover, the evaluation of multidimensional integrals encountered in matrix element calculations for polyatomic molecules may also involve complex numerical problems.

Although this paper is devoted only to a one-dimensional problem, we keep in mind that our final aim is to extend this work as generally as possible to polyatomics.

A relevant way for performing analytical calculations consists in expanding the radial Hamiltonian (3) in a polynomial form to further apply the second-quantization formulation. Throughout this study, we will first assume that $U(r)$ and $\alpha(r)$ can both be expressed as a ξ polynomial in the vinicity of the equilibrium internuclear distance r_e, $\xi=(r-r_e)/r_e$ being the Dunham variable. $B(r)$ can also be locally expanded in terms of ξ, so we finally write

$$U(r)=\sum_{n=1}^{d_{max}}\frac{1}{n!}f_n\xi^n,\qquad \frac{1}{r^2}=\frac{1}{r_e^2}(1-2\xi+3\xi^2-\cdots). \tag{4}$$

The first step consists in converting the radial Hamiltonian $H=H(\hat{p},r,\mathcal{J})$ to

$$H(p,q,J)=\sum_{s=0,1}\sum_{m}\sum_{u=0,1}\gamma_{smu}p^{2s}q^m[J(J+1)]^u, \tag{5}$$

using dimensionless normal coordinates $q=\gamma^{-1}\xi$ and corresponding conjugate momentum $p=-id/dq$ with $\gamma=\sqrt{2B(r_e)/\omega_e}$ and $m=u=0$ if $s=1$ in Eq. (5). The harmonic frequency $\omega_e=(1/2\pi c r_e)\sqrt{f_2/\mu}$, the equilibrium rotational constant $B(r_e)/hc$, and the energy of the system E/hc are all expressed in wave-number units. Because of adiabatic and nonadiabatic contributions, the oscillator frequency ω_e used here will differ slightly (deviation $<0.1\%$) from the usual BO frequency $\omega_e^{\mathrm{BO}}\equiv\sqrt{d^2U_{\mathrm{BO}}(r)/dr^2|_{r_e}/\mu}$.

In a second step, we consider the Heisenberg-Weyl algebra h_3 [21] generated by the set of usual boson operators $\{a,a^\dagger,I\}$ satisfying $[a,a^\dagger]=I$. The h_4 algebra is obtained with the introduction of the number operator $\hat{v}=a^\dagger a$. Now following either the iterative procedure of Ref. [11] or the formula of Refs. [22] given here in Sec. II D, any arbitrary powers $q^m=(a^\dagger+a)^m/2^{m/2}$ can be expressed in a normal-ordering expansion so that the second-quantized form of Hamiltonian (3) is finally given by

$$H=\frac{1}{2}\sum_{n\leqslant m}\sum_{u=0,1}C_{mnu}\{a^{\dagger m}a^n+a^{\dagger n}a^m\}[J(J+1)]^u. \tag{6}$$

Let us write now $H=H_0+H'$ where $H_0=\omega_e(\hat{v}+1/2)$ simply corresponds to the harmonic oscillator. Note that $\omega_e\neq C_{110}$ because of contributions coming from anharmonic terms q^{2k}. At this stage, it becomes quite natural to choose the Fock eigenstates $|v\rangle$ of H_0 as primitive functions in Eq. (2). However, as has been well established for a long time, the eigensolutions of Eq. (6) are rather difficult to obtain variationally for levels lying near dissociation when using such states, particularly if highly anharmonic terms are involved in the Hamiltonian. More flexible primitive functions are thus required for a variational treatment.

We start with the extended harmonic oscillator functions

$$\Phi_v(q;\lambda,\kappa)=\mathcal{N}_vH_v[\kappa(q-\lambda)]e^{-[\kappa^2(q-\lambda)^2/2]}\quad(\lambda,\kappa\ \text{real}), \tag{7}$$

as an initial primitive trial wave-function set for solving the eigenvalue problem associated with Eq. (5). $H_v(x)$ is an Hermite polynomial, the normalization factor is $\mathcal{N}_v=\sqrt{\kappa/\pi^{1/2}2^v v!}$, and (λ,κ) are variational parameters which control the shift and width of the wave functions, respectively, and are optimized within the stationary conditions $\partial\varepsilon([\Psi])/\partial\lambda=\partial\varepsilon([\Psi])/\partial\kappa=0$. Using the trial wave functions (7), the energy eigenvalues of the Hamiltonian (5) can be easily obtained within a numerical procedure using standard Gaussian quadrature routines [11]; it was pointed out in this last reference that the convergence of the variational calculations was largely improved when varying (λ,κ) from their reference values—i.e., from the usual harmonic oscillator values ($\lambda=0$, $\kappa=1$). Note that similar wave functions have also been used in the evaluation of Frank-Condon overlap integrals [23].

To take fully advantage of the ladder-operator formalism as used in Eq. (6), some algebraic tools generally encountered in quantum optics are to be considered.

B. Displaced squeezed number states as a primitive basis set for variational calculations

1. Transformed boson operators

An elegant manner for obtaining wave functions (7) is first to scale the q coordinate and then to displace the result as $\Phi_v(q)\rightarrow\Phi_v(q;\kappa)\rightarrow\Phi_v(q;\lambda,\kappa)=\exp[-i\lambda p]\Phi_v(q;\kappa)$. It has been established for a long time that a normalized function $\Phi_v(q)$ defined on the relevant Hilbert space—that is, the harmonic oscillator functions for our problem—can be used to construct the wave functions $\Phi_v(q;\kappa)$ by means of a scaling transformation [24,25]. This yields

$$\Phi_v(q;\lambda,\kappa)=e^{-i\lambda p}\kappa^{1/2}\Phi_v(\kappa q)=e^{-i\lambda p}e^{i(\ln\kappa/2)(qp+pq)}\Phi_v(q). \tag{8}$$

Similarly, the momentum representation wave functions will be transformed as $\Phi_v(p;\kappa)=\Phi_v(\kappa^{-1}p)$ since p commutes with $\exp[-i\lambda p]$.

Now we consider an appropriate way for defining the transformed states (8) by means of relevant operators. Within the associated Fock space, the states (8) are just DSFSs ($\lambda,\kappa\in\mathbb{R}$) [13–15,17]:

$$|v;\lambda,\kappa\rangle=D(\lambda)S(\kappa)|v\rangle=U(\lambda,\kappa)|v\rangle, \tag{9}$$

and $\langle q|v;\lambda,\kappa\rangle=\Phi_v(q;\lambda,\kappa)$. In Eq. (9), $D(\lambda)$ is the standard unitary displacement operator [10,12,19,26,27],

$$D(\lambda)=\exp\left[\frac{\lambda}{\sqrt{2}}(a^\dagger-a)\right], \tag{10}$$

with coherence parameter $\lambda/\sqrt{2}$, and is an element of the Heisenberg-Weyl group H_3, while $S(\kappa)$ is the squeeze operator [12,14,27,28],

$$S(\kappa)=\exp\left[-\frac{\beta}{2}(a^{\dagger 2}-a^2)\right], \tag{11}$$

with squeezing parameter $\beta=\ln\kappa$. This operator has the SU(1,1) group structure, which is the most elementary noncompact Lie group widely used in quantum optics. It is easily seen from Eqs. (10) and (11) that $U(\lambda,1)^\dagger=U(\lambda,1)^{-1}$

$=U(-\lambda,1)$ and $U(0,\kappa)^\dagger=U(0,\kappa)^{-1}=U(0,\kappa^{-1})$. Let us also point out that the ordering of D and S in U is unitarily equivalent and amounts only to a change of the parameters—that is, $S(\kappa)D(\lambda)\Phi_v(q)\rightarrow\Phi_v(\kappa q-\lambda)$.

Alternatively, we may build generalized displaced squeezed boson operators $\tilde{a}=U^\dagger aU$ and $\tilde{a}^\dagger=U^\dagger a^\dagger U$ which are mathematically convenient, in particular for the calculations of matrix elements. Using the well-known Baker-Campbell-Hausdorff (BCH) formula, we get

$$\tilde{a}(\lambda,\kappa)=a\cosh\beta-a^\dagger\sinh\beta+\frac{\lambda}{\sqrt{2}}I,$$

$$\tilde{a}^\dagger(\lambda,\kappa)=-a\sinh\beta+a^\dagger\cosh\beta+\frac{\lambda}{\sqrt{2}}I, \tag{12}$$

or similarly

$$\tilde{a}(\lambda,\kappa)=\kappa^{-1}\hat{X}_1+i\kappa\hat{X}_2+\frac{\lambda}{\sqrt{2}}I,$$

$$\tilde{a}^\dagger(\lambda,\kappa)=\kappa^{-1}\hat{X}_1-i\kappa\hat{X}_2+\frac{\lambda}{\sqrt{2}}I, \tag{13}$$

which is nothing but the usual linear canonical Bogoliubov transformation with $[\tilde{a}(\lambda,\kappa),\tilde{a}^\dagger(\lambda,\kappa)]=I$ [16] with the added $\lambda\sqrt{2}$ term. The quantum states are thus deformed without changing the algebra. $\hat{X}_1=(a+a^\dagger)/2$ and $\hat{X}_2=(a-a^\dagger)/2i$ are the fundamental quadrature operators. The DSSs are eigenstates of the squeezed annihilation operator,

$$\tilde{a}(0,\kappa^{-1})|\lambda,\kappa\rangle=\frac{\kappa\lambda}{\sqrt{2}}|\lambda,\kappa\rangle, \tag{14}$$

and the coherent squeezed number states (9) can be obtained with the generalized displaced squeezed boson operators through

$$|v;\lambda,\kappa\rangle=\frac{\tilde{a}^{+v}(-\kappa\lambda,\kappa^{-1})}{\sqrt{v!}}|\lambda,\kappa\rangle. \tag{15}$$

As $U(\lambda,\kappa)$ is unitary, the transformed rotation-vibration Hamiltonian (6) is simply given by

$$\tilde{H}(a,a^\dagger;\lambda,\kappa)\rightarrow U^\dagger H(a,a^\dagger)U=H(\tilde{a},\tilde{a}^\dagger) \tag{16}$$

and will be considered in all the following.

2. Particular cases: Coherent and squeezed states

In quantum optics, one usually meets squeezing of the Glauber CSs [12], which are referred to as DSSs [29],

$$|\lambda,\kappa\rangle=U(\lambda,\kappa)|0\rangle, \tag{17}$$

but there does not exist, to our knowledge, any practical spectroscopic study involving state (9) or (17); that is why this work is worth being done. The Glauber CSs $|\lambda\rangle=D(\lambda)|0\rangle$ are just the special case of vanishing squeezing parameter β. Note that the coherent states should be strictly written as $|\lambda/\sqrt{2}\rangle$, but will be simply written $|\lambda\rangle$ in all the following for convenience. We thus have $a|\lambda\rangle=\lambda/\sqrt{2}|\lambda\rangle$.

It is also well known that more general CSs can be associated with particular irreducible representations of various Lie groups and can be generated from appropriate displacement operators. The SU(1,1) group structure of the squeezing operator can be fairly easily seen by considering the two-photon single-mode realization of the corresponding su(1,1) Lie algebra [28,30,31]:

$$K_+=\frac{1}{2}a^{\dagger 2},\quad K_-=\frac{1}{2}a^2,\quad K_3=\frac{1}{2}\left(a^\dagger a+\frac{1}{2}\right). \tag{18}$$

The generators $\{K_\pm,K_3\}$ satisfy the usual commutation rules $[K_3,K_\pm]=\pm K_\pm$ and $[K_+,K_-]=-2K_3$. The Casimir operator $K^2=K_3^2-(K_+K_-+K_-K_+)/2$ and K_3 satisfy $K^2|k,\ell\rangle=k(k-1)|k,\ell\rangle$, $K_3|k,\ell\rangle=(\ell+k)|k,\ell\rangle$ $(\ell=0,1,2,\ldots)$, $|k,\ell\rangle$ being a complete orthonormal basis of su(1,1) characterized by the Bargmann index k labeling the irreducible representations. In this case, the squeezing operator is written as $S(\kappa)=\exp[-\beta(K_+-K_-)]$ and $S(\kappa)^\dagger$ allows one to generate Perelomov SU(1,1) coherent states [32]:

$$|k,\rho\rangle_P=\exp[\beta(K_+-K_-)]|k,0\rangle$$
$$=(1-\rho^2)^k\sum_{\ell=0}^{\infty}\sqrt{\frac{\Gamma(2k+\ell)}{\ell!\Gamma(2k)}}\rho^\ell|k,\ell\rangle, \tag{19}$$

where $\rho=(\kappa^2-1)/(\kappa^2+1)$. For the realization (18), the Casimir operator is $K^2=-3/16$, and therefore, $k=1/4$ (for even $v=2\ell$ Fock states) and $k=3/4$ (for odd $v=2\ell+1$ Fock states) and thus the harmonic oscillator Fock space is isomorphic to the direct sum $D^+_{1/4}\oplus D^+_{3/4}$ [31].

C. "Two-quantum" model for the rotation-vibration Hamiltonian

1. J-independent model

A more suitable zeroth-order model than that given below Eq. (6) is of considerable interest in all problems of molecular physics, in particular in spectroscopic models. If we take

$$H_0'=C_{110}a^\dagger a+\frac{C_{100}}{2}(a^\dagger+a)+\frac{C_{200}}{2}(a^{\dagger 2}+a^2)+C_{000}, \tag{20}$$

we encounter the two-photon algebra [33] h_6 spanned by $\{a,a^\dagger,a^2,a^{\dagger 2},a^\dagger a,I\}$. H_0' being Hermitian it can be diagonalized through a unitary transformation which is an element of the corresponding Lie group H_6 [10]. Let us consider

$$TH_0'T^{-1}=S(\zeta)^\dagger D(\theta)^\dagger H_0'D(\theta)S(\zeta),$$

With

$$\theta=-\frac{C_{100}}{\sqrt{2}(C_{110}+C_{200})}, \tag{21}$$

the linear terms $(a^\dagger+a)$ are canceled, which gives

$$\tilde{H}_0'=D(\theta)^\dagger H'D(\theta)=2C_{110}K_3+C_{200}(K_++K_-)+\delta,$$

with

$$\delta = C_{000} - \frac{C_{110}}{2} - \frac{C_{100}^2}{4(C_{110}+C_{200})}.$$

Likewise, knowing that under an SU(1,1) transformation $S(\zeta)=\exp[-\zeta(K_+-K_-)]$ we have

$$S(\zeta)^\dagger K_3 S(\zeta) = \cosh 2\zeta K_3 - \frac{1}{2}\sinh 2\zeta[K_+ + K_-],$$

$$S(\zeta)^\dagger [K_+ + K_-] S(\zeta) = -2\sinh 2\zeta K_3 + \cosh 2\zeta[K_+ + K_-], \tag{22}$$

we can remove the remaining off-diagonal terms, which leads to

$$\tilde{\tilde{H}}_0' = T H_0' T^{-1} = 2\Omega K_3 + \delta, \tag{23}$$

with Ω and ζ given by

$$\zeta = -\frac{1}{4}\ln\left[\frac{C_{110}-C_{200}}{C_{110}+C_{200}}\right],$$

$$\Omega = \sqrt{C_{110}^2 - C_{200}^2}. \tag{24}$$

Within the Fock basis

$$|v\rangle \equiv |k,\ell\rangle, \quad \ell = \left[\frac{v}{2}\right], \quad k = 1/4, 3/4,$$

we thus have the eigenvalues

$$E_v \equiv E_{\ell,k} = 2\Omega(\ell + k) + \delta = \Omega\left(v + \frac{1}{2}\right) + \delta. \tag{25}$$

The eigenstates of H_0' [Eq. (20)] are obtained with

$$|\tilde{\Psi}_v\rangle = D(\theta)S(\zeta)|k,\ell\rangle \equiv |v;\theta,e^{\zeta}\rangle,$$

which simply correspond to DSFSs with particular (C-dependent) values of coherence and squeezing parameters.

Alternatively they may be written in the coordinate representation as

$$\tilde{\Psi}_v(q) = \frac{e^{\zeta/2}}{\sqrt{\pi^{1/2}2^v v!}} H_v[e^{\zeta}(q-\theta)] e^{[-e^{2\zeta}(q-\theta)^2/2]}. \tag{26}$$

We note that the preceding transformation applied to the elementary boson operators gives

$$\tilde{\tilde{a}}(\theta,\zeta) = S(\zeta)^\dagger D(\theta)^\dagger a D(\theta) S(\zeta) = \cosh\zeta a - \sinh\zeta a^\dagger + \frac{\theta}{\sqrt{2}} I,$$

where the first two terms may be associated with the usual Bogoliubov transformation [16]

$$\tilde{a}(\mu,\nu) = \mu a + \nu a^\dagger \quad (\mu^2 - \nu^2 = 1),$$

with, in our case,

$$\mu = \pm\frac{C_{200}}{\sqrt{2(C_{110}\Omega - \Omega^2)}},$$

$$\nu = \mp\sqrt{\frac{C_{110}-\Omega}{2\Omega}},$$

$$\mu - \nu = \exp(\zeta). \tag{27}$$

It will be shown in a forthcoming paper that the diagonal Hamiltonian (23) can be taken as a zeroth-order model in a perturbative treatment involving higher-order contact transformations and effective models. The wave functions (26) should also be suitable in a variational calculation and could be used as trial wave functions. Calculations should converge *a priori* faster for smaller basis sets than those made with the conventional Fock states.

2. *J*-dependent model

The introduction of the molecular rotation is readily carried out with the change

$$C_{ij0} \to C_{ij}'(J) = C_{ij0} + C_{ij1}J(J+1) \tag{28}$$

in Eq. (20). Consequently, all the terms previously defined become

$$|v;\theta,e^{\zeta}\rangle \to |v;\theta(J),e^{\zeta(J)}\rangle,$$

$$E_v \to E_v(J),$$

$$\delta,\Omega \to \delta(J),\Omega(J),$$

$$\tilde{a}(\mu,\nu) \to \tilde{a}(\mu_J,\nu_J),$$

$$\tilde{\Psi}_v(q) \to \tilde{\Psi}_v^J(q).$$

In the limit $C_{00}'(J) \to C_{11}'(J)/2$ and $C_{10}'(J) \to 0$ ($\theta(J) \to 0$) with $J=0$, the results given by Sohn and Swanson [34] are completely recovered.

To conclude this section we note that the construction of a "2n-quantum Hamiltonian" could also be considered using a special class of nonlinear BT as proposed in [35]; the exact diagonalization of such a Hamiltonian is then only feasible under suitable constraints on the $C_{ij}'(J)$ parameters.

D. Matrix elements and expectation values

We establish now explicit relations for the matrix elements of the Hamiltonian (6) between two displaced squeezed number states, which amounts to calculating matrix elements of Eq. (16) in the usual Fock space. For example, the matrix representation of the pseudoannihilation and creation operators is deduced from Eq. (12),

$$\langle v'|\tilde{a}(\lambda,\kappa)|v\rangle = \frac{(\kappa+\kappa^{-1})}{2}\sqrt{v}\,\delta_{v',v-1} + \frac{(-\kappa+\kappa^{-1})}{2}\sqrt{v+1}\,\delta_{v',v+1} + \frac{\lambda}{\sqrt{2}}\delta_{v',v},$$

$$\langle v'|\tilde{a}^\dagger(\lambda,\kappa)|v\rangle = \frac{(-\kappa+\kappa^{-1})}{2}\sqrt{v}\,\delta_{v',v-1} + \frac{(\kappa+\kappa^{-1})}{2}\sqrt{v+1}\,\delta_{v',v+1} + \frac{\lambda}{\sqrt{2}}\delta_{v',v}, \tag{29}$$

and generalizes the usual matrix elements of a and $a^\dagger$ found in many textbooks of quantum mechanics. Arbitrary powers of this matrix representation are generated by m-fold application of the BT to $a^\dagger$ and to its Hermitian conjugate. We first calculate $(a^\dagger+\lambda/\sqrt{2})^m$ and then apply the squeezing transformation to obtain

$$\begin{aligned}\tilde{a}^{\dagger m}(\lambda,\kappa) &= \sum_{k=0}^{m}\binom{m}{k}\left(\frac{\lambda}{\sqrt{2}}\right)^k S^\dagger(\kappa)a^{\dagger m-k}S(\kappa)\\ &= \sum_{k=0}^{m}\binom{m}{k}\left(\frac{\lambda}{\sqrt{2}}\right)^k f_{(k-m)/2}(\eta)[a^\dagger+\eta a]^{m-k}, \quad (30)\end{aligned}$$

where $f_j(\eta)$ are c-number factors defined by

$$f_j(\eta) = (1-\eta^2)^j \quad \text{with } \eta = -(\kappa^2-1)/(\kappa^2+1). \quad (31)$$

The powers of the transformed operators can be expressed in normally ordered form using the mathematical formulas of Refs. [22]:

$$\begin{aligned}\tilde{a}^{\dagger m}(\lambda,\kappa) = \sum_{k=0}^{m}\sum_{l=0}^{[(m-k)/2]}\sum_{M=0}^{p}\binom{m}{k}\left(\frac{\lambda}{\sqrt{2}}\right)^k\\ \times f_{(k-m)/2}(\eta)d^{m-k}_{M,p-M}(\eta)a^{\dagger M}a^{p-M}, \quad (32)\end{aligned}$$

with $p=m-k-2l$ and $d^{e}_{g,f}(\eta)$ given by

$$d^{e}_{g,f}(\eta) = \frac{e!}{g!f!(e-g-f)!!}\eta^{(e-g+f)/2}. \quad (33)$$

Next using [36]

$$a^r a^{\dagger m} = \sum_{h=0}^{\min(r,m)}\frac{m^h r^h}{h!}a^{+m-h}a^{r-h}, \quad (34)$$

with $x^{\underline{y}}=x(x-1)(x-2)\cdots(x-y+1)=x!/(x-y)!$, the products $\tilde{a}^{\dagger m}(\lambda,\kappa)\tilde{a}^{r}(\lambda,\kappa)$ are also written in normally ordered form as

$$\begin{aligned}\tilde{a}^{\dagger m}(\lambda,\kappa)\tilde{a}^{r}(\lambda,\kappa) = \sum_{k,l,M}\sum_{k',l',M'}\binom{m}{k}\binom{r}{k'}\\ \times\left(\frac{\lambda}{\sqrt{2}}\right)^{k+k'} f_{(k-m)/2}(\eta)f_{(k'-r)/2}(\eta)\\ \times d^{m-k}_{M,p-M}(\eta)d^{r-k'}_{M',p'-M'}(\eta)\\ \times\sum_h\frac{(p'-M')^h(p-M)^h}{h!}a^{\dagger\sigma'-h}a^{\sigma-h}.\end{aligned} \quad (35)$$

From this normally ordered form, we note that the transformed Hamiltonian (16) can be cast in a form similar to Eq. (6) as

$$\tilde{H}(\lambda,\kappa) = \sum_{r\leqslant m}\tilde{C}'_{mr}(J;\lambda,\kappa)\{a^{\dagger m}a^n + a^{\dagger n}a^m\}, \quad (36)$$

where the (λ,κ) dependence appears in the coefficients of the expansion that is $\tilde{C}'=f(\lambda,\kappa)C'$.

For our purposes, the needed matrix elements

$$A^{m,r}_{v,v'}(\lambda,\kappa) = \langle v'|\tilde{a}^{\dagger m}(\lambda,\kappa)\tilde{a}^{r}(\lambda,\kappa)|v\rangle \quad (37)$$

are then readily obtained in the form

$$\begin{aligned}A^{m,r}_{v,v'}(\lambda,\kappa) = \sum_{k,l,M}\sum_{k',l',M'}\binom{m}{k}\binom{r}{k'}\left(\frac{\lambda}{\sqrt{2}}\right)^{k+k'}\\ \times f_{(k-m)/2}(\eta)f_{(k'-r)/2}(\eta)d^{m-k}_{M,p-M}(\eta)d^{r-k'}_{M',p'-M'}(\eta)\\ \times\sum_h\frac{(p'-M')^{\underline{h}}(p-M)^{\underline{h}}}{h!}\\ \times\begin{cases}(v^{\underline{\sigma-h}})(v'^{\underline{\sigma'-\sigma}})^{1/2}(\sigma'\geqslant\sigma),\\ (v'^{\underline{\sigma'-h}})(v^{\underline{\sigma-\sigma'}})^{1/2}(\sigma'\leqslant\sigma),\end{cases}\end{aligned} \quad (38)$$

with

$$v' = v+\sigma'-\sigma, \quad p' = r-k'-2l',$$

$$\sigma = p-M+M', \quad \sigma' = p'-M'+M,$$

$$0\leqslant h\leqslant\min(p-M,p'-M').$$

Although these matrix elements are computed analytically in a fairly straightforward manner, much computational efforts are required when high m and r values (say, $m>60$) are involved. One way to reduce these computational efforts would be to apply a series of completeness relations on Eq. (37). We can rewrite

$$A^{m,r}_{v,v'}(\lambda,\kappa) = \sum_{v'',v''',v''''}A^{m-1,0}_{v''',v'}A^{0,r-1}_{v'''',v''}A^{1,0}_{v'',v'''}A^{0,1}_{v,v''''}, \quad (39)$$

and all the matrix elements are thus calculated recursively from $A^{1,0}_{v'',v'''}(\lambda,\kappa)$ and $A^{0,1}_{v,v''''}(\lambda,\kappa)$ defined in Eq. (29), with selection rules $v''''=v$, $v\pm1$, $v'''=v''$, $v''\pm1$, $v''=v''''$, $v''''\pm1,\dots,v''''\pm(r-1)$, and $v'=v'''$, $v'''\pm1,\dots,v'''\pm(m-1)$. However, except for some extreme cases encountered in few diatomic systems, expression (38) is well suited for pratical applications and particularly for polyatomic molecules involving reasonable values of (m,r). In this work, the calculations of the Hamiltonian matrix took only few seconds per set (λ,κ) on a standard PC.

The optimal values (λ_J,κ_J) have to be found numerically in order to minimize the energies E_{vJ} resulting from the diagonalization, for each J, of the Hamiltonian matrix

$$\tilde{H}_{vv'} = \sum_{r\leqslant m}\frac{C'_{mr}(J)}{2}[A^{m,r}_{v,v'}(\lambda_J,\kappa_J)+A^{r,m}_{v,v'}(\lambda_J,\kappa_J)]. \quad (40)$$

This amounts to solving the linear system $\partial E_{vJ}/\partial\lambda = \partial E_{vJ}/\partial\kappa = 0$. Once these values are determined, we generally obtain all the expected eigenvalues with the desired accuracy. The latter will depend on external parameters, such as, for example, the truncation of the polynomial expansion (4) of the potential as well as the truncation of the Hamiltonian matrix—that is, the size of the basis. In other words, for each value of N_{max} in Eq. (2) giving the dimension of the basis, it will correspond a different set (λ_J,κ_J).

The displaced squeezed vacuum state (17) can also be used as a two-parameters trial wave function to find the expectation value of the ground-state energy of the diatomic Hamiltonian. One thus obtains the best approximation for the solution of the vibrational ground state E_{0J} without diagonalizing any matrix. Imposing the condition $\sigma = h = \sigma'$ in Eq. (35), we get

$$\begin{aligned}\varepsilon_J(\lambda,\kappa) &= \langle \lambda,\kappa | H | \lambda,\kappa \rangle \\ &= \sum_{r \leqslant m} \frac{C'_{mr}(J)}{2} [A^{m,r}_{0,0}(\lambda,\kappa) + A^{r,m}_{0,0}(\lambda,\kappa)] \\ &= \sum_{r \leqslant m} C'_{mr}(J) \sum_{k,l} \sum_{k',l'} \binom{m}{k} \binom{r}{k'} \left(\frac{\lambda}{\sqrt{2}}\right)^{k+k'} \\ &\quad \times f_{(k-m)/2}(\eta) f_{(k'-r)/2}(\eta) \\ &\quad \times \frac{(m-k)!(r-k')!}{p!2l!!2l'!!} \eta^{(m+r-k-k'-l-l')}, \end{aligned} \qquad (41)$$

with $p = p' \geqslant 0$, which reduces to

$$\varepsilon_J(\lambda) = \sum_{r \leqslant m} \sum_{s=0,1} C_{mrs} \left(\frac{\lambda}{\sqrt{2}}\right)^{m+r} [J(J+1)]^s, \qquad (42)$$

as $\kappa \to 1$ $(\eta \to 0)$. The set of optimized values, found with the aid of the Hellmann-Feynman theorem, for instance, will be denoted by (λ'_J, κ'_J), and the states $|v; \lambda'_J, \kappa'_J\rangle$ may also serve as a trial basis set in a variational calculation.

III. APPLICATIONS: THE RO-VIBRATIONAL SPECTRA OF $^{12}C^{16}O$, $^{7}Li_2$, AND $^{20}Ca_2$

A. Displaced squeezed Fock states for fixed values of coherence and squeezing parameters

In this part, we are interested in applications of the general method described above. For that, we consider the following set of diatomic molecules $\{^{12}C^{16}O, ^{7}Li_2, ^{20}Ca_2\}$ whose spectroscopic data span respectively 75.10%, 99.90%, and 99.92% of the X electronic ground-state well depths which correspond to vibrational states $v \leqslant 41$, $v \leqslant 39$, and $v \leqslant 37$, respectively [20]. The J values range from 0 up to 133 for the CO molecule. Thus, all these species turn out to be very good candidates for testing the convergence and reliability of the variational calculations with the appropriate displaced squeezed basis (9) for a given value of λ and κ. Our calculations will be compared to those obtained with the Cooley-Cashion-Zare method [8], implemented in the Le Roy's computer program LEVEL [9].

Fully analytical potential functions, adiabatic and nonadiabatic ones, were determined in Ref. [20] for these species by a direct-potential-fit approach based on the conventional wave-function propagator method. We use these functions as input data for our algebraic variational calculations. The increasing availability of high-quality data for levels lying very close to the dissociation challenges the accuracy of very sophisticated models. These latter ensure a qualitatively correct long-range behavior even beyond the range of observed data. A detailed description of all terms involved in the models is beyond the scope of the present paper; we will simply give here a brief example of a model employed in the literature.

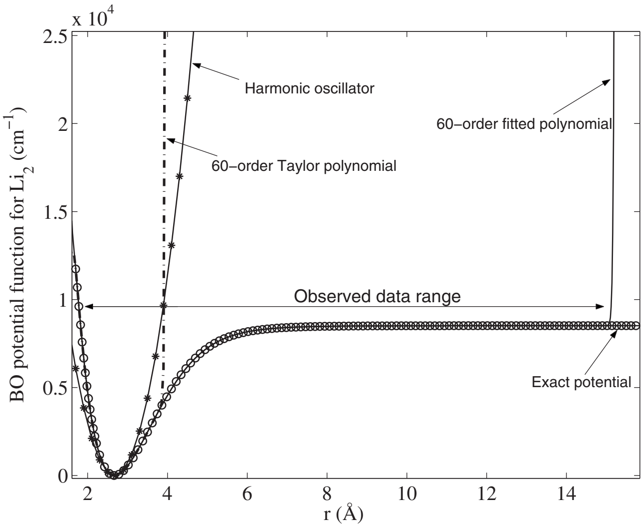

FIG. 1. Born-Oppenheimer potential energy curves for Li_2. The exact form of the potential (circles), the fitted Dunham potential (solid line), the Taylor polynomial potential (stars), and the harmonic-oscillator potential (dashed line) are plotted.

One of the BO potential functions we use for CO is the Morse–Lennard-Jones potential [20]

$$U_{\mathrm{BO}}(r) = D_e \left[1 - \left(\frac{r_e}{r}\right)^n e^{-\phi(r)z} \right]^2, \qquad (43)$$

where $z = 2(r - r_e)/(r + r_e)$, n is the inverse power of the leading term in the long-range expansion, and the $\phi(r)$ function is expressed as

$$\phi(r) = f_{sw}(r) \sum_{m=0} \phi_m z^m + [1 - f_{sw}(r)]\phi(\infty). \qquad (44)$$

The switching function $f_{sw}(r) = (e^{\delta(r - r_x)} + 1)^{-1}$ cares about the behavior of $\phi(r)$ and damps it beyond the range of the data until the specified limit $\phi(\infty) = \ln(2D_e r_e^n / C_n)/2$. C_n is a leading coefficient, δ the damping parameter, and r_x the distance at which the switching function turns on. The detailed form of the functions $\Delta U^{\mathrm{ad}}(r)$ and $\alpha(r)$ can also be found in Ref. [20]. Note that adiabatic and BOB functions are not considered for Ca_2.

For high vibrational states lying near dissociation, the Taylor expansion of the potential functions like Eq. (43) could suffer from some convergence problems (see Fig. 1). So we found it is more suitable to fit "exact" BO and BOB functions by a d_{max}-order Dunham polynomial, this approximation still enabling us to apply the technique described in Sec. II A and get the form Eq. (4). We have thus checked that by increasing d_{max} in Eq. (4), we were able to reproduce very accurately (better than 10^{-5} cm^{-1}) the exact BO and BOB functions in the ranges sampled by experimental data and also to ensure a *wall* by using a truncation at a positive term (see Fig. 1, for example) to get rid of spurious minima. Indeed, such spurious minima are not critical for Cooley-Cashion-Zare algorithms if they lie far from the equilibrium structure, but can cause difficulties for accurate variational calculations. Finally, we obtained a ξ polynomial with d_{max}

equal, respectively, to 46, 60, and 58 for $^{12}C^{16}O$, $^{7}Li_2$, and $^{20}Ca_2$, while the term $1/r^2$ was expanded by a 70th-order Taylor polynomial for the three species, employing the MAPLE processor.

Applying the procedure given in Sec. II A, we can write the algebraic rovibrational Hamiltonian associated with a BO potential energy curve for each molecule. As an illustration, we get the Hamiltonian (6) for CO (with truncated digits) as

$$\begin{aligned} H^{CO} = {} & 2196.912a^{\dagger}a + 1091.840 - 135.246(a^{\dagger} + a) + 1.937\mathcal{J}^2 \\ & + 13.187(a^{\dagger 2} + a^2) - 133.556(a^{\dagger 2}a + a^{\dagger}a^2) + \cdots \\ & + 3.826 \times 10^{-68}(a^{\dagger 46} + a^{46}) \\ & + 6.211 \times 10^{-69}(a^{\dagger 46} + a^{46})\mathcal{J}^2. \end{aligned} \tag{45}$$

We next perform a variational calculation using the matrix elements (38). Calculations have been carried out with the four following primitive functions: (i) the eigenstates $|v\rangle$ of the harmonic oscillator ($\lambda=0$, $\kappa=1$), (ii) the eigenstates $|v;\theta,e^{\zeta}\rangle$, Eq. (26), of the quadratic "two-quantum" Hamiltonian, (iii) the displaced squeezed states $|v;\lambda,\kappa\rangle$, Eq. (9), with coherence and squeezing parameters (λ_J,κ_J) optimized variationally from Eq. (38), and (iv) the displaced squeezed states $|v;\lambda,\kappa\rangle$, Eq. (9), with coherence and squeezing parameters (λ'_J,κ'_J) optimized variationally from the expectation value (41).

Taking the ro-vibrational energies E_{vJ}^{LEVEL} obtained from the wave-function propagator method implemented in LEVEL as the reference values, the quality of our various results was measured by

$$\sigma_{rms} = \sqrt{\frac{1}{N}\sum_{v,J}[E_{vJ}^{\mathrm{var}} - E_{vJ}^{\mathrm{LEVEL}}]^2}. \tag{46}$$

N is the total number of energy levels and E_{vJ}^{var} are the rovibrational energies resulting from the diagonalization of the Hamiltonian (6). The numerical calculation was performed with an integration mesh-size of 0.0001 Å to ensure that error in the derived eigenvalues was as negligible as possible.

As an example, let us focus our discussion on the $^{12}C^{16}O$ isotopologue. As illustrated in Fig. 2, the optimized values (λ_0,κ_0) are found to be those of the minimum of the σ_{rms} surface plotted in the (λ,κ) space, where we have truncated the basis at $N_{max}=100$ and considered all observed energy levels for $v \leqslant 41$ ($J=0$). We thus get ($\lambda_0=6.02$, $\kappa_0=0.852$), which corresponds to the wave function, in the r representation,

$$\Phi_v(r) = \mathcal{N}H_v\left(\sqrt{\frac{m\omega_*}{\hbar}}(r-r_*)\right)e^{-(m\omega_*/2\hbar)(r-r_*)^2}, \tag{47}$$

with

$$\omega_* = \kappa_0^2\omega_e = 1459.46985\ \mathrm{cm}^{-1},$$

$$r_* = r_e + r_e\lambda_0\gamma = 1.414769\ \text{Å}. \tag{48}$$

In other words, the use of DSFSs amounts to changing the equilibrium distance and the harmonic frequency of the HO wave functions, compared to the initial values given in Table I. On that account, for those who use standard numerical approaches with the calculation of integrals, the wave functions (47) are suitable for the determination of highly excited levels and to improve drastically the convergence of the calculations at high v values.

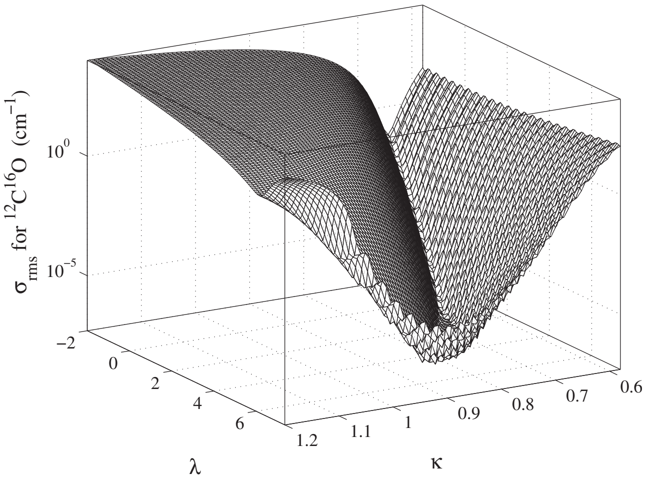

FIG. 2. rms error surface plotted in the space of coherence and squeezing variational parameters for $^{12}C^{16}O$.

Using Eqs. (21) and (24) and the form (45), the quadratic Hamiltonian (20) is diagonalized with the parameters [$\theta(0)=0.086$, $e^{\zeta(0)}=1.006$], which corresponds to another set (ω_*,r_*) according to Eq. (48), while the expectation value Eq. (41) is minimized with the set ($\lambda'_0=0.0876$, $\kappa'_0=0.9986$),

TABLE I. Optimization of the coherence and squeezed variational parameters for $^{12}C^{16}O$, $^{7}Li_2$, and $^{20}Ca_2$ and for $J=0$. These values minimize the rms error (46).

	$^{12}C^{16}O$	$^{7}Li_2$	$^{20}Ca_2$	Eqs.
v_{max}	41	39	37	
r_e (Å) [20]	1.1282294764	2.67299391	4.27781	
ω_e (cm^{-1})	2170.53815	351.39670	64.96459	
$B(r_e)$ (cm^{-1})	1.93160	0.67257	0.04610	
λ_0[a]	6.02	12.90	13.91	(40)
κ_0[a]	0.852	0.450	0.480	(40)
r_* (Å)	1.414769	4.806403	6.519588	(48)
ω_* (cm^{-1})	1459.46985	71.15783	14.96766	(48)
σ_{rms} (cm^{-1})	1.20×10^{-6}	1.32×10^{-4}	6.50×10^{-4}	
λ'_0	0.0876	0.0890	0.1330	(41)
κ'_0	0.9986	0.9979	0.9955	(41)
$\varepsilon_0(\lambda'_0,\kappa'_0)$ (cm^{-1})	1083.52642	175.32604	32.33101	(41)
E_{00}^{var} (cm^{-1})[b]	1081.77148	175.01953	32.20582	
$\theta(0)$	0.0860	0.0872	0.1275	(21)
$\mu_0-\nu_0$	1.0060	1.0057	1.0126	(27)
$\zeta(0)$	0.0060	0.0058	0.0126	(24)

[a] Value optimized for $N_{max}=100$ for $^{12}C^{16}O$, $N_{max}=300$ for $^{7}Li_2$, and $N_{max}=340$ for $^{20}Ca_2$. The optimization was made for $J=0$.

[b] Value found from (λ_0,κ_0).

TABLE II. Convergence of the ro-vibrational energy levels for $^{12}C^{16}O$ and $^{7}Li_2$ using the displaced squeezed Fock states $|v;\lambda_0,\kappa_0\rangle$ optimized variationally (upper panel) and given in Table I. Calculations using the Fock states $|v;0,1\rangle$ up to v_{max} are also specified (lower panel). See the text for the description of the global and local pictures.

	$^{12}C^{16}O$				$^{7}Li_2$	
	DSFS basis				DSFS basis	
	Global picture		*Local* picture		*Global* picture	
N_{max}	$\lambda_0=6.02,\ \kappa_0=0.852$		$\lambda=0.001,\ \kappa=0.962$	N_{max}	$\lambda_0=12.90,\ \kappa_0=0.450$	
	$v=0,\ J=0$	$v=0,\ J=20$	$v=0,\ J=0$		$v=0,\ J=0$	$v=0,\ J=20$
5	9538.020968	10163.972324	1081.773397	10	2362.045862	2532.986828
10	4360.610839	5060.566215	1081.771485	20	268.024152	530.032666
20	1143.601831	1942.646501	1081.771485	40	175.086815	454.359267
30	1081.772619	1888.155164	1081.771485	50	175.021484	454.295886
40	1081.771485	1888.154311	1081.771485	70	175.019530	454.293806
E_{vJ}^{LEVEL}	1081.771486	1888.154311	1081.771486	E_{vJ}^{LEVEL}	175.019522	454.293819
			$\lambda=1.052,\ \kappa=0.948$			
	$v=10,\ J=0$	$v=10,\ J=30$	$v=10,\ J=0$		$v=10,\ J=0$	$v=10,\ J=20$
20	31197.154999	32339.073341	21331.205310	20	7298.603128	7385.820135
30	23279.207453	24645.716569	21331.139696	50	3851.169128	4094.184995
40	21335.687716	22953.342538	21331.139694	70	3457.898062	3693.510040
50	21331.140958	22951.089651	21331.139694	100	3395.867385	3643.385034
60	21331.139695	22951.088504	21331.139694	140	3395.742878	3643.262751
E_{vJ}^{LEVEL}	21331.139694	22951.088504	21331.139694	E_{vJ}^{LEVEL}	3395.742860	3643.263024
			$\lambda=4.05,\ \kappa=0.9$			
	$v=30,\ J=0$	$v=30,\ J=40$	$v=30,\ J=0$		$v=30,\ J=0$	$v=30,\ J=20$
50	55162.126214	57264.780143	54173.779320	100	8113.060912	8204.268980
60	54207.613995	56457.181441	54166.505399	150	7868.266972	8010.251409
70	54166.654668	56442.677222	54166.495591	180	7864.033406	8007.376132
80	54166.495741	56442.596796	54166.495587	200	7863.966210	8007.352517
90	54166.495588	56442.596693	54166.495587	220	7863.964636	8007.351897
E_{vJ}^{LEVEL}	54166.495586	56442.596691	54166.495586	E_{vJ}^{LEVEL}	7863.964680	8007.354987
			$\lambda=\lambda_0,\ \kappa=\kappa_0$			
	$v=41,\ J=0$	$v=41,\ J=5$	$v=41,\ J=0$		$v=39,\ J=0$	$v=39,\ J=5$
70	68059.074025	68095.004704	68059.074025	120	8525.200199	8528.212432
80	68042.569222	68078.645976	68042.569222	180	8508.634137	8511.264012
90	68042.486662	68078.565724	68042.486662	220	8508.575793	8511.058678
100	68042.486321	68078.565388	68042.486321	300	8508.565558	8511.037021
E_{vJ}^{LEVEL}	68042.486322	68078.565381	68042.486322	E_{vJ}^{LEVEL}	8508.565168	8511.034769
	Harmonic-oscillator basis				Harmonic-oscillator basis	
	$\lambda=0,\ \kappa=1$				$\lambda=0,\ \kappa=1$	
	$v=41,\ J=0$	$v=41,\ J=5$			$v=39,\ J=0$	$v=39,\ J=5$
280	68042.486322	68078.565390		1400	8508.715629	8511.225679

which are both, as expected, very close to the harmonic set ($\lambda=0$, $\kappa=1$). The same procedure was applied for $J=0$ to Li_2 and Ca_2, and the results are given in Table I. Note that the three parameters sets (λ_0,κ_0) given in this table have been determined with a *global* optimization—that is, by minimizing the quantity $(\Sigma_v E_{v0})/N$ considering the energy levels E_{v0} for all observed levels ($v=0,\ldots,v_{max}$). This assumption is due to the variational nature of the basis truncation, which makes *a priori* all eigenvalues E_{vJ} lower. Some examples of convergences of rovibrational energy levels using these global sets are given in Table II. We see that the differences between our calculations and those obtained with standard

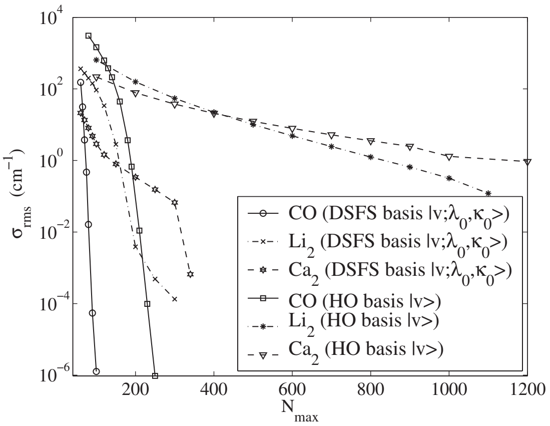

FIG. 3. Convergence of the vibrational energy levels using either the DSFS or HO basis set. λ_0 and κ_0 are given in Table I.

integro-differential procedures are more pronounced when increasing the v values for very anharmonic potentials such as Li_2, but remain in all cases below the experimental accuracy. As also pointed out in this table, the convergence of calculations is significantly enhanced (by a factor of 3 and more) according as we use the displaced squeezed Fock states or not. See, for example, the last lines of Table II, which correspond to calculations made with the standard Fock states, and also Fig. 3. Although the convergence is faster when using the displaced squeezed Fock states with parameters optimized globally, the calculation of energies with these states for low and medium v numbers is less efficient compared to those made with the usual Fock states. One way to circumvent this problem is, for example, the determination of coherence and squeezing parameters for each v—that is, to *locally* optimize these parameters. Tables II and III give the set (λ_0,κ_0) for different values of v, and we thus see that, for a given level E_{vJ}, the convergence is largely improved for low and medium v numbers if we compare the results given in Tables II and III. A preliminary analysis according to this *local* picture will be considered in Sec. III B.

Let us compare now the convergence of our calculations when using either state $|v\rangle$, $|v;\lambda_0',\kappa_0'\rangle$, or $|v;\theta,e^{\zeta}\rangle$. As indicated in Table IV for $^{20}Ca_2$, the use of the states which minimize the expectation value (41) as well as the eigenfunctions of the quadratic Hamiltonian (20) have not brought much improvement compared to the calculations with the eigenkets of the harmonic oscillator, except when the Hamiltonian matrix is truncated at low v values. Most probably this means that terms $a^{\dagger m}a^n$ with high degrees (m,n) are not important for low v, while their contributions become significant and more important than that of the quadratic terms when v increases. In other words, the use of the eigenfunctions $|v;\theta,e^{\zeta}\rangle$ should be most useful in Hamiltonian models involving terms $a^{\dagger m}a^n$ with relatively small values of (m,n)—that is, for most of the algebraic models. An illustration will be given in a forthcoming paper dedicated to the ladder-operator formalism in triatomics.

TABLE III. Optimization of the coherence and squeezed parameters for $^{12}C^{16}O$ and for a given energy level E_{v0}. Unlike the *global* optimization given in Table I, a *local* optimization is carried out here for a specific energy level.

v	N_{max}	(λ_0,κ_0)	E_{v0}
0	8	(0.001,0.962)	1081.771491
5	15	(0.360,0.954)	11533.993809
10	25	(1.052,0.948)	21331.139767
15	35	(1.720,0.942)	30482.676880
20	48	(2.640,0.934)	38998.862852
25	60	(3.240,0.914)	46890.194455
30	75	(4.050,0.900)	54166.495587
35	90	(4.950,0.880)	60835.616497
41	100	(6.020,0.852)	68042.486322

TABLE IV. Comparison of vibrational energy convergences for $^{20}Ca_2$ using the Fock states, the displaced squeezed Fock states optimized within the ground-state expectation value, and the eigenfunctions of the quadratic Hamiltonian (20).

N_{max}	$\lambda_0=0$ $\kappa_0=1$	$\lambda_0'=0.1330$ $\kappa_0'=0.9955$	$\theta(0)=0.1275$ $e^{\zeta(0)}=1.0126$
	$v=0$	$v=0$	$v=0$
0	32.900512	32.331006	32.349906
2	32.334539	32.331044	32.331431
5	32.206726	32.206637	32.206696
8	32.205842	32.205839	32.205841
E_{vJ}^{LEVEL}	32.205812		
	$v=5$	$v=5$	$v=5$
5	435.852906	406.233865	401.527491
10	332.154202	329.896046	331.155980
20	325.509342	325.501997	325.506646
25	325.496975	325.496570	325.496725
30	325.496442	325.496440	325.496441
E_{vJ}^{LEVEL}	325.496444		
	$v=20$	$v=20$	$v=20$
30	1330.272873	1301.974360	1319.344726
90	930.561152	927.207647	931.362108
150	906.938558	906.915070	906.951893
170	906.886055	906.884878	906.886898
190	906.883726	906.883680	906.883764
200	906.883656	906.883650	906.883663
E_{vJ}^{LEVEL}	906.883673		

We described above the optimization procedure of the coherence and squeezing parameters for $J=0$, but the same method can easily be applied for finding (λ_J,κ_J) for all $J\neq 0$. To this end, Fig. 4 shows the behavior of $\Delta\lambda_J$, $\Delta\lambda_J'$, $\Delta\theta(J)$ (upper panel) and $\Delta\kappa_J$, $\Delta\kappa_J'$ $\Delta e^{\zeta(J)}$ (lower panel) for $^{12}C^{16}O$ when J increases, with $\Delta X_J=X_J-X_0$. By comparing the values given for each J to those obtained for $J=0$, we can note that these differences are not so important and we can thus assume in a first approximation that the values derived only for $J=0$ can be taken for the calculations of all rovibrational energies (see Table II as an illustration).

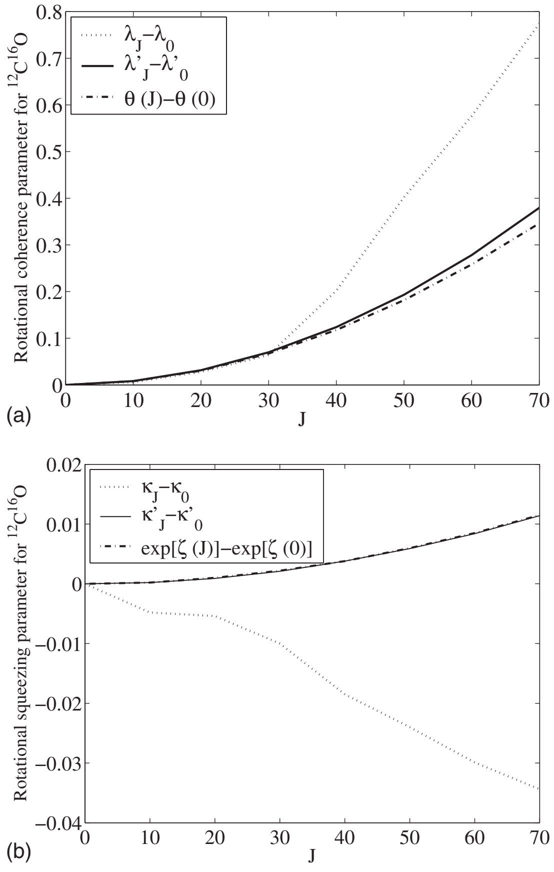

FIG. 4. J dependence of the coherence (upper figure) and squeezed (lower figure) parameters for $^{12}C^{16}O$.

To conclude this section, we have drawn in Fig. 5 the primitive functions $\phi_v(r,\lambda,\kappa)$ in the r representation, for small, medium, and high v. This corroborates the fact mentioned above that the new set of wave functions with ($\lambda \gg 0$, $\kappa \ll 1$) is more suitable for very anharmonic regime and conversely, better adapted to harmonic regime when ($\lambda \simeq 0$, $\kappa \simeq 1$). It is easily seen that the functions $\phi_v(r,\lambda,\kappa)$ are poorly adapted to low v values when using the set (λ_0,κ_0) resulting from the *global* optimization, while those of the standard harmonic oscillator are more suitable. When v increases, this feature is totally inverted. That is why, we thus suggest, in the same spirit as the results given in Tables II and III, that both λ and κ can be chosen to be v-dependent functions—i.e., $\lambda \equiv \lambda(v)$ and $\kappa \equiv \kappa(v)$.

B. Displaced squeezed Fock states for *v*-dependent values of coherence and squeezing parameters

We conclude this work with the effect of scaling and displacing the q coordinate by v-dependent quantities, as suggested above. For our purposes, the normalized trial functions (7) were just replaced with

$$\Phi_v(q;\lambda(v),\kappa(v)) = \sqrt{\frac{\kappa(v)}{\pi^{1/2}2^v v!}}\,H_v(\tilde{q}(v))\,e^{-\tilde{q}(v)^2/2}, \qquad (49)$$

with

$$\tilde{q}(v) = \kappa(v)[q-\lambda(v)].$$

According to Eq. (47), we thus have $\omega_* \equiv \omega(v)$ and $r_* \equiv r_e(v)$. Although such wave functions remain purely harmonic, they should allow a better physical description of the system. Note that the algebraic derivation of such states in terms of a ladder-operator formalism such as Eq. (9) does not seem trivial and exists only in some particularly cases. For example, Matamala and Maldonado [37] have considered the quartic Hamiltonian (5) $H(p,q)=(p^2+q^2)/2+\beta_{040}q^4$ and, after neglecting one term, have found the linear transformation which makes this Hamiltonian diagonal. An explicit analytical formula for $\kappa(v)$ was thus derived, and very good approximate energy eigenvalues for this very simple anharmonic system were obtained [37]. But the anharmonic models we consider here are much more complicated and that is why we will carry out in this part only numerical calculations without making approximations.

Unfortunately the set $\{\Phi_v\}$ is not orthogonal for arbitrary functions $\lambda(v)$ and $\kappa(v)$. We must consider the generalized eigenvalue problem

$$H\underline{c} = \varepsilon S\underline{c} \qquad (50)$$

instead of Eq. (1), where the c's are the expansion coefficients in Eq. (2) and S is the overlap matrix

$$S_{v'v} = \int_{-\infty}^{+\infty} \Phi_{v'}(q;\lambda(v'),\kappa(v'))\Phi_v(q;\lambda(v),\kappa(v))dq, \qquad (51)$$

with $S_{vv}=1$ and which reduces to the unity matrix as λ and κ are constants. Note that Eq. (50) can be solved in a straightforward manner by using standard numerical routines. But the use of nonorthogonal functions is generally not common in all problems of molecular spectroscopy. So we must deal with the problem of eliminating S from Eq. (50). There exists several orthogonalization procedures (at least three: Gram-Schmidt and symmetric and canonical due to Löwdin [38]) for transforming the generalized eigenvalue (50) problem with overlapping basis sets to a standard eigenvalue problem with orthogonal basis. Many of them are used, for instance, in order to orthogonalize a set of orbitals in quantum chemical calculations (see Ref. [39], for example). In such procedures the overlap matrix S, Eq. (51), is transformed to a unit matrix.

For the present study, assuming linearly independent vectors in the basis set, Löwdin's symmetric orthogonalization scheme was used [38]. It consists in transforming the set $\{\Phi_v\}$ into a new one as

$$\tilde{\Phi}_v(q;\lambda(v),\kappa(v)) = \sum_{v'=0}^{N_{max}} X_{v'v}\Phi_{v'}(q;\lambda(v),\kappa(v)), \qquad (52)$$

with

$$\boldsymbol{X} = \boldsymbol{S}^{-1/2} \equiv \boldsymbol{U}\boldsymbol{s}^{-1/2}\boldsymbol{U}^{\dagger}, \qquad (53)$$

where $\boldsymbol{U}$ is the unitary matrix which diagonalizes $\boldsymbol{S}$ and $\boldsymbol{s}$ the diagonal matrix of the corresponding eigenvalues. We thus

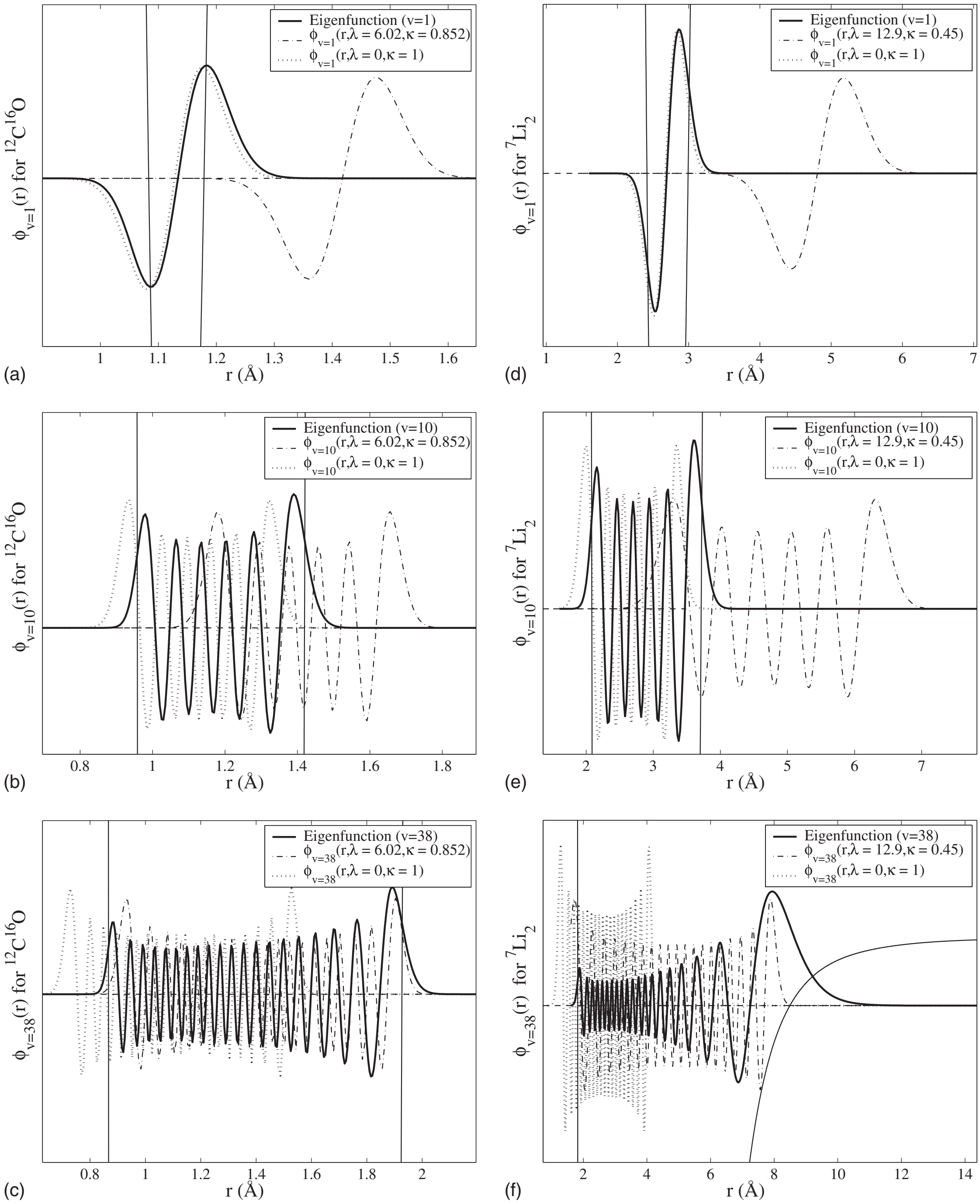

FIG. 5. Comparison between the eigenfunctions, the extended Gaussian wave functions $\phi_v(r;\lambda,\kappa)$, Eq. (7), and the harmonic wavefunctions $\phi_v(r;0,1)$ in the r representation for $v=1$, $v=10$, and $v=38$. The three left figures correspond to $^{12}C^{16}O$, and the three right ones correspond to $^7Li_2$.

have $\langle \tilde{\Phi}_{v'} | \tilde{\Phi}_v \rangle = \delta_{v'v}$, which amounts to solving a standard eigenvalue problem using the new set $\{\tilde{\Phi}_v\}$.

All our numerical calculations were performed using quadruple-precision floating-point FORTRAN programs for high-accurate evaluations of integrals such as Eq. (51) involving high v values. For practical applications, a polynomial form for the trial functions $\lambda(v)$ and $\kappa(v)$ was chosen:

$$\lambda(v) = \sum_{i=0} \lambda_i v^i, \quad \kappa(v) = \sum_{i=0} \kappa_i v^i. \tag{54}$$

As an illustration, some preliminary calculations were performed on $^{12}C^{16}O$ and $^7Li_2$ whose extended Gaussian wave functions $\phi_v(q;\lambda,\kappa)$, Eq. (7), in Fig. 5 clearly show unconsistencies for the calculations of the energy levels in the bottom of the potential wells. It seems quite obvious from Fig. 5

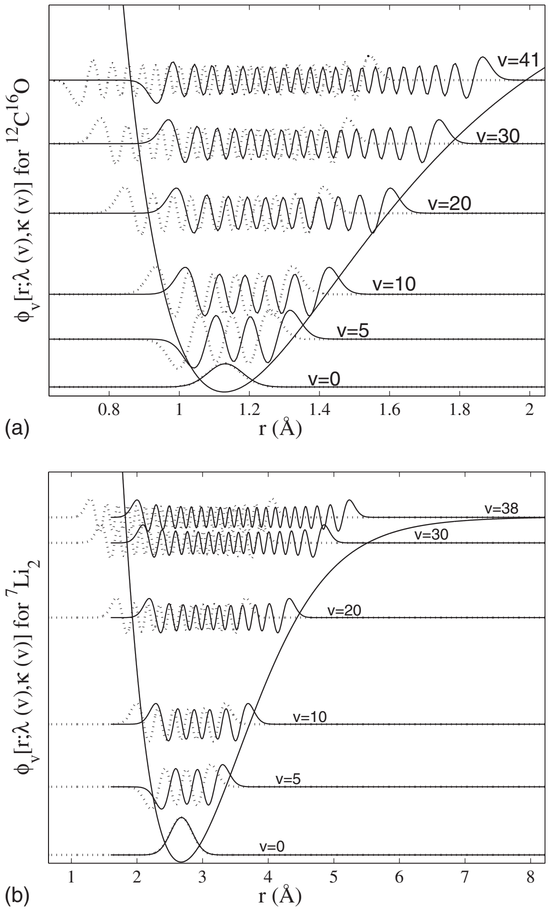

FIG. 6. Form of the generalized displaced squeezed wave functions (49) (solid line) compared to the eigenkets of the harmonic oscillator (dotted line). These wave functions are given for $^{12}C^{16}O$ (upper figure) and $^{7}Li_2$ (lower figure) with the parameter sets (55) and (56), respectively.

that the wave functions must be centered at different values $r_e(v) \geqslant r_e$ with $r_e(v+1) > r_e(v)$ and must be dilated—that is, $\omega(v+1) < \omega(v)$—with increasing energy levels E_v.

The optimization of the variational parameters (λ_i, κ_i) values for $^{12}C^{16}O$ was carried out by truncating the Hamiltonian matrix at $N_{max}=90$. We obtained the following set of generalized coherence and squeezing parameters:

$$\lambda_0^{CO} = 7 \times 10^{-2}, \quad \lambda_1^{CO} = 0.2076, \quad \lambda_2^{CO} = -1.7 \times 10^{-2},$$

$$\kappa_0^{CO} = 0.965, \quad \kappa_1^{CO} = -1.75 \times 10^{-3}, \tag{55}$$

with an rms error of $\sigma_{rms} = 1.61 \times 10^{-5}$ cm^{-1} up to $v=41$. In Fig. 6 (upper figure) we have plotted the generalized nonorthogonal wave functions (49) in the r representation as well as the usual harmonic-oscillator wave functions for different values of v. Apparently we can conclude that such generalized displaced squeezed wave functions are good compromises between the standard ones defined in Eq. (7) or Eq. (47) and those of the harmonic oscillator with ($\lambda=0$, $\kappa=1$). Indeed, they behave more correctly for low, medium, and high v values. Concerning $^{7}Li_2$, because of the large computational efforts required during the numerical integral evaluations, only some first prelimimary tests were carried out by truncating the Hamiltonian matrix at $N_{max}=170$. We get the set

$$\lambda_0^{Li_2} = 3 \times 10^{-2}, \quad \lambda_1^{Li_2} = 0.205, \quad \lambda_2^{Li_2} = -1.66 \times 10^{-2},$$

$$\lambda_3^{Li_2} = 5.4 \times 10^{-6},$$

$$\kappa_0^{Li_2} = 0.9998, \quad \kappa_1^{Li_2} = -3.72 \times 10^{-3}, \tag{56}$$

with $\sigma_{rms} = 0.089$ cm^{-1} up to $v=39$. Comparatively, we obtain, for the same N_{max}, the σ_{rms} errors of 0.7 cm^{-1} and 241.1 cm^{-1} using the sets (λ_0, κ_0) (see Table I) and ($\lambda=0$, $\kappa=1$), respectively. Apparently, as shown in Fig. 6 (lower figure), for the very anharmonic part of the potential (say, for $v>30$) the distribution of the generalized wave functions (49) is not broadened enough. This could be explained by the use of the simple linear model for $\kappa(v)$, which turns out to be thus not sufficient for describing states lying near the dissociation. In this case, more sophisticated models for $\kappa(v)$ and probably for $\lambda(v)$ should be required. This study is beyond the scope of the present work.

IV. CONCLUSION

In this paper, we describe a method for calculating the entire set of ro-vibrational energy levels for a diatomic molecule at the spectroscopic accuracy. To achieve this end, the displaced squeezed Fock states encountered in modern quantum optics and related fields have been used as physical ansatz in the variational principle. The coherence and squeezing parameters λ and κ have been optimized and found in this way for $^{12}C^{16}O$, $^{7}Li_2$, and ^{20}Ca. Note also that within the ladder-operator formalism most of the methods we have used for constructing the Hamiltonian matrix are algebraic ones. We thus conclude that the convergence of our variational calculations was significantly improved when using such states instead of the usual Fock ones. Although much improvement was achieved, the use of one single set of displaced squeezed Fock states remains poorly adapted to the study of lower molecular states when making a global calculation—that is when optimizing the set of parameters for all energy levels. For instance, if we assume the basis $|v;\lambda_0,\kappa_0\rangle$ to be well suited for the calculation of energy levels near dissociation, then this basis will not be appropriate for lower states. This can be simply explained because the effective constants r_* and ω_* resulting from the displacement and the scaling of the initial basis are far from their true equilibrium values. Therefore, the wave functions (47) will also be far from the expected eigenstates as well as the harmonic-oscillator ones, for low v values. Consequently unlike the case of the harmonic oscillator, the couplings between the lower states will be very strong, but will decrease with increasing energies.

This lack of consistency has been partially removed by introducing a class of displaced squeezed wave functions where the coherence and squeezing parameters are now v dependent or, similarly, $r_e \equiv r_e(v)$ and $\omega_e \equiv \omega_e(v)$. As the unitary displacement operator approach is difficult to apply in this case, only some numerical preliminary calculations were carried out in this work. Finally, the use of such generalized wave functions gave results similar to the standard DSFSs, but with a more clear physical meaning.

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