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A local–normal description of vibrational excitations of pyramidal molecules in terms of Morse oscillators

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Abstract

A general description of vibrational excitations of pyramidal molecules in both local and normal representations is presented. This study is restricted to the case when no tunneling motion is allowed. The Hamiltonian is first written in terms of curvilinear internal coordinates. The Wilson's **G** matrix as well as the potential are expanded in terms of Morse variables, which allows the identification of a set of six Morse oscillators as zeroth-order Hamiltonian. An algebraic realization of the Hamiltonian is obtained by introducing a linear expansion of the coordinates and momenta in terms of creation and annihilation operators of Morse functions. This algebraic realization provides in natural form the representation of the Hamiltonian in terms of local interactions. The normal interactions are constructed by successive couplings of tensors defined as linear combinations of the ladder operators. The matrix transformation between the local and normal interactions is obtained for the complete Hamiltonian. This analysis provides the spectroscopic parameters in both local and normal schemes in explicit form as functions of the force constants and structure parameters. To exemplify, the analysis of the vibrational excitations of stibine and arsine is presented. Force constants as well as the corresponding x, K relations are given. A comparison with the results obtained using the $U(v+1)$ unitary group approach is included.

Keywords: Local model; Force constants; Vibrational excitations; Local–normal relations; Pyramidal molecules; Stibine; Arsine; Unitary approach

1. Introduction

The method of studying vibrational excitations of molecules may depend on the size of the system. In general the description of vibrational excitations may be carried out in terms of Cartesian or internal coordinates. Cartesian coordinates have the advantage that the kinetic energy is diagonal, but rotational and translational degrees of freedom must be identified to be removed. On the other hand the use of internal coordinates allows translations and rotations to be excluded from the outset and provides a natural way to introduce coordinates to describe non-rigid molecules [1,2]. In this case, however, cross terms in the kinetic energies appear, together with the momentum-independent contribution. An additional disadvantage of dealing with internal coordinates is the appearance of redundant coordinates in high-symmetry systems. In spite of the presence of these problems, for small and medium size molecules internal coordinates are preferred. The reason falls in the physical meaning of the force constants involved in the Taylor expansion of the potential [3–5]. In view of these difficulties medium size molecules present a challenge to any calculation where, in cases of high symmetry, group theoretical methods may play a significant role [6].

A vibrational description in terms of internal coordinates leads in natural form to a local mode description of the system. Since several decades ago, local mode models have become relevant because they allow highly excited vibrational states to be characterized; they convey more insight into the nature of the eigenfunctions than the traditional approach of Darling–Dennison [7–10]. Local behavior is manifested by patterns with close degeneracies [11], easily noticed in systems with large differences in atomic

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masses, and nicely explained with the simplest version of the local theory [12]. The basic idea of the local models consists in expressing the Hamiltonian in terms of a zeroth-order Hamiltonian corresponding of a set of non-interacting oscillators (associated with the local coordinates) coupled by kinetic and potential energy terms. The significance of this theory, however, took time to be recognized due to the success of Darling and Dennison in describing the overtones of H_2O by means of a normal mode effective Hamiltonian [13]. After this work it passed a further quarter of a century before the concept of local mode approach was reintroduced [14–17].

Because both local and normal schemes are able to describe a given system, *i.e.* water molecule, special attention was paid to find the connection between these approaches. Among the first efforts stands out Lehmann's work, where the relation between the local harmonically coupled anharmonic oscillator (HCAO) model for two equivalent oscillators and the equivalent normal mode model was established [18]. Later on the corresponding analysis was carried out for three and four equivalent oscillators arising in the cases of NH_3, CH_4, C_2H_4 and C_3H_4, using perturbation theory [19,20]. In general a molecule behaves neither in the strictly local or normal limits, but somewhere in between. However, near the local limit only a small number of parameters is needed to obtain a reasonable description, while the translation to the normal realization involves a considerable higher number of parameters, albeit with some constraints whose number is determined by the number of parameters involved in the fit. The term "x, K relations" was coined to describe these interrelationships among the normal mode parameters implied by the local description. A particularly convenient way to obtain the x, K relations consists in introducing bosonic creation/annihilation operators [21,22]. In the framework of this scheme Baggott [23] showed, for the case of H_2O molecule, that using symmetry adapted combinations of shift operators the relationship between both schemes may be obtained in a more general manner. This approach was applied for the case of the stretching degrees of freedom of pyramidal and tetrahedral molecules to obtain the general relation between the local and normal spectroscopic parameters of the Hamiltonian when interactions up to quartic order are considered [24].

Because of the relevance of the shift operators to establish in a simple form the relationship between the local and normal schemes, the use of algebraic techniques seems to be the natural approach to deal with this problem [25–27]. An algebraic approach deals with the kinetic and potential energies simultaneously and consequently the spectroscopic parameters involve both structure and potential force constants. It is possible to establish the normal–local transformation in terms of effective Hamiltonians, but in such case a minimum of experimental energies is needed to fix the parameters. When this is not possible, *ab initio* results may be invoked to fix some of the parameters [28,29]. In any case it is thus convenient and necessary to obtain, within the framework of a given algebraic approach, the general relations with explicit expressions of the spectroscopic parameters as functions of the structure and force constants. Clearly this requirement is relatively easy to be satisfied for the harmonic oscillator basis, but here we are interested in going beyond this approximation by considering Morse oscillators since they more accurate reflect the main physical properties of a pure local bond. In this case the corresponding algebraic methods are based on the $su(2)$ algebra where the correspondence between the generators and the creation and annihilation operators of the Morse and/or Pöschl–Teller (PT) functions has been established [30–32]. These potentials can be treated in a unified form, due to their connection with the $su(2)$ generators. However, which potential is appropriate for a given local oscillator depends on the symmetry of the potential. In our case of pyramidal molecules without inversion we shall associate the stretching and bending coordinates with Morse potentials, since in both cases that potential reflects the appropriate asymmetry. The PT potential is used for the symmetrical out-of-plane modes [33]. Hence, in the zeroth-order local approximation the Hamiltonian is described by six independent Morse oscillators. The interaction potential is obtained by inserting the realization of the coordinates and momenta in terms of creation and annihilation operators for the Morse functions in the linear approximation. On the other hand the normal mode scheme is obtained by introducing symmetry adapted tensors expanded in terms of the same ladder operators, which by successive couplings permits to express all the interactions up to any order. The goal of this work consists in obtaining the transformation matrix between the local and the normal mode schemes starting with the Hamiltonian in configuration space taking interactions up to quartic order. In this way the spectroscopic parameters are given explicitly in both schemes in terms of the structure and force constants. Our study is constrained to polyad preservation systems. As examples the vibrational description of stibine and arsine molecules are presented and the corresponding x, K relations are obtained. The results are compared with an algebraic description based on the $U(v+1)$ unitary group approach [34,35].

This paper is organized as follows: the vibrational Hamiltonian for pyramidal molecules in configuration space is presented in Section 2. In Section 3 the algebraic realization of the coordinates and momenta in terms of the creation/annihilation operators of the Morse potential is given. In the same section the local algebraic realization of the Hamiltonian for pyramidal molecules is established. Section 4 is devoted to establish the interactions in the normal representation as well as their relation with the local interactions. The symmetry adapted basis used to diagonalize the Hamiltonian is presented in Section 5. In Section 6 the stibine and arsine systems are studied and their corresponding x, K relations are established. In addition these results are compared with the description in terms of the