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Mean field for the vibron model: Dipole-moment function of diatomic molecules

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We have investigated the mean-field approach to the vibron model. The link between the algebraic description of molecular vibrations, as described by the vibron model, and the usual variables in configuration space has been used to extract the dipole-moment function of diatomic molecules. A comparison is shown between the vibron-model results and the experimentally derived dipole-moment function for HF.

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Recently, a model based on Lie algebras has received considerable attention. The model, called the vibron model (VM), was originally [1,2] proposed for the treatment of rotational and vibrational degrees of freedom of diatomic molecules. Successively it has been extended to the treatment of vibrational modes of polyatomic molecules [3–9] as well as to the representation of other molecular structure properties [10,11]. As has been the case for an analogous model developed for the treatment of collective excitation of nuclei, the interacting boson model [12], the mean-field approximation has been applied to the VM in order to give a geometrical picture of an otherwise completely abstract approach. This plan, originated by the work of van Roosmalen [13], was extensively explored by Levit and Smilansky [14], Leviatan and Kirson [15], and more recently by Shao and co-workers [16,17].

In this work we will show the relations necessary to go from the VM Hamiltonian to the potential energy surface as well as from the VM dipole operator to the dipole-moment function of single molecular bonds (diatomic molecules). In the case of the potential energy surface, the comparison will be made with one of the most celebrated and simple models for the rovibrational motion of molecular bonds, the Morse potential model (MPM). For the dipole-moment function, the comparison will be made with the up-to-date dipole-moment function derived from a combination of *ab initio* and empirical models.

The determination of the potential affecting the two nuclei of a diatomic molecule as a function of the internuclear distance r can be made using *ab initio* techniques, based on electronic molecular orbital theory. Alternatively, the potential can be determined on the basis of spectroscopic information [Rydberg-Klein-Rees (RKR) methods], occasionally combined with *ab initio* or model potentials. However, in many practical applications, especially when dealing with polyatomic molecular systems, the use of potentials based on phenomenological models is required because of the simplicity with which they can be derived. The Morse potential

$$V(r) = D_e[1 - e^{-a(r-r_e)}]^2 \tag{1}$$

has been widely used for the representation of anharmonic molecular vibrations. Here, D_e is the dissociation energy limit and r_e the equilibrium internuclear distance.

Note that there are three parameters for this model potential: D_e, a, and r_e. One possible method to derive those parameters is to use the molecular constants ω_e, $\omega_e\chi_e$, and B_e, which furnish

$$D_e = \omega_e\chi_e s^2, \qquad a = \frac{1}{s r_e}\sqrt{\frac{D_e}{B_e}}, \tag{2}$$

with $s \equiv \omega_e/2\omega_e\chi_e$. The wave functions are also available for the MPM and, therefore, the matrix elements of common operators can be evaluated either analytically [18,19] or numerically [20].

The vibron model has been proposed [1,2] to represent the vibrational and rotational degrees of freedom of molecular bonds. It is, therefore, a model whose objective is similar to the MPM. However, the VM is based on a very different ground. In fact, it starts from assuming a Hamiltonian written in terms of generators of Lie algebras. In particular the Lie algebra associated with a single molecular bond (e.g., a diatomic molecule) is assumed to be the u(4) Lie algebra. It has been shown that the anharmonic vibrational spectrum of a diatomic molecule can be described by a Hamiltonian which contains only generators of a subalgebra of u(4), namely the o(4) Lie algebra. This situation is referred to as a *dynamic symmetry* for the VM. In fact, the Hamiltonian for a single bond can be written as

$$\hat{H} = \hat{E}_0 + A\mathcal{C}_2[\mathrm{o}(4)] \ , \tag{3}$$

where $\hat{E}_0$ is a term containing only conserved quantities and A is a parameter to be fixed as described below. The operator $\mathcal{C}_2[\mathrm{o}(4)]$ is the quadratic Casimir invariant of the o(4) algebra. The energy spectrum obtained from this Hamiltonian is altogether equivalent to the MPM spectrum and can be written directly since the eigenvalues of Casimir invariants are known analytically [1,2]. Just as in the case of the MPM, the parameters entering the VM can be derived from the molecular constants

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$$A = -\frac{\omega_e \chi_e}{4}, \qquad N = \left[\frac{\omega_e}{\omega_e \chi_e} - 2\right]_{\text{int}} . \tag{4}$$

N is the total number of bosons; E_0 is the eigenvalue of the $\hat{E}_0$ operator and serves only to define the zero point of the energy spectrum, and therefore it is not to be considered as a parameter of the model.

In order to study the link between the algebraic models and the usual models based on geometrical variables, we need to go into some detail of the boson realization of the Lie algebras entering the VM. The boson realization of the u(4) algebra has been utilized since the introduction of the VM [1]. The concept of mean field for the VM was introduced subsequently [13–17].

The boson realization of the Lie algebras entering the VM Hamiltonian can be done by introducing a scalar boson s carrying angular momentum and parity $l^\pi = 0^+$ and a dipole (or vector) boson p carrying angular momentum and parity $l^\pi = 1^-$. All the operators and Casimir invariants can then be written in terms of creation and annihilation operators for these two kinds of bosons. For example, the Casimir invariant of o(4) is written as

$$\mathcal{C}_2[\mathrm{o}(4)] = \hat{\mathbf{D}} \cdot \hat{\mathbf{D}} + \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \ , \tag{5}$$

where

$$\hat{D}_\mu = [p^\dagger \times s + s^\dagger \times \tilde{p}]^{(1)}_\mu, \qquad \mu = 0, \pm 1 \ , \tag{6}$$

and

$$\hat{J}_\mu = -\sqrt{2}[p^\dagger \times \tilde{p}]^{(1)}_\mu, \qquad \mu = 0, \pm 1. \tag{7}$$

Here, the creation $s^\dagger, p^\dagger_{\mu=0,\pm1}$ and annihilation $s, p_{\mu=0,\pm1}$ operators for s and p bosons have been introduced together with the usual conventions [3] for scalar ($\cdot$) and tensor ($\times$) products and for the conjugations $\tilde{s} = s$, $\tilde{p}_\mu = (-)^\mu p_{-\mu}$. The number operators for s and p bosons take the usual forms

$$\hat{n}_s = s^\dagger \cdot s, \quad \hat{n}_p = p^\dagger \cdot \tilde{p} \ , \tag{8}$$

and consequently the operator for the total number of bosons is just $\hat{N} = \hat{n}_s + \hat{n}_p$. All the terms in the VM Hamiltonian are number conserving; it follows that $\hat{N}$ is diagonal in any representation of u(4) and its eigenvalue is equal to N.

Following the line of Ref. [15] we will introduce now the mean field for the VM. The N-boson system generates a mean field within which the N bosons move. The four eigenstates of the mean field furnish an approximate representation for the N-boson system. It can be shown that the boson condensate which the bosons occupy can be constructed as the application of a linear combination of single-boson operators depending only on one real parameter ρ. It can be expressed by

$$\mid \rho; N\rangle = \frac{1}{\sqrt{N!}} (b_c^\dagger)^N \mid 0\rangle. \tag{9}$$

The boson condensate is therefore constructed by the multiple application of the creation operator

$$b_c^\dagger(\rho) \equiv \frac{1}{\sqrt{1+\rho^2}}(s^\dagger + \rho p_0^\dagger) \tag{10}$$

on the boson vacuum. The energy surface is given by the expectation value of the Hamiltonian in the boson condensate,

$$\begin{aligned} E(\rho) &\equiv \langle \rho; N \mid \hat{H} \mid \rho; N\rangle \\ &= E_1 + 4AN(N-1)\frac{\rho^2}{(1+\rho^2)^2}. \end{aligned} \tag{11}$$

In this equation, E_1 can be fixed by the condition $E(\rho = 1) = 0$. In fact, $\rho = 1$ is a minimum of the energy surface and, as will become apparent below, it should correspond to the minimum of the potential energy at the equilibrium distance.

Up to this point, no correspondence has been given between the parameter ρ and the geometrical variables of the molecules. There have been some previous suggestions that this parameter should be related to the internuclear distance for diatomic bonds [15–17] but no clear relation was shown. We propose here that the relation between the parameter ρ and the internuclear distance r in a diatomic molecule is given by

$$a(r - r_e) = -\ln \frac{2\rho^2}{1+\rho^2} \ , \tag{12}$$

where a is the MPM parameter given above and r_e the internuclear equilibrium distance. Thus, the relation (12) provides the mapping of the parameter ρ into the geometrical variable r. It is clear that defining $y \equiv a(r - r_e)$ as $\rho \in [0, \infty)$ then $y \in (\infty, -\ln 2]$. Using the transformation (12) it is easy to derive the energy surface as a function of the geometrical variable r,

$$V(r) = E_1 + AN(N-1)[2e^{-a(r-r_e)} - e^{-2a(r-r_e)}] \ , \tag{13}$$

where $E_1 = -AN(N-1)$ satisfies the requirement $V(r_e) = 0$. It is, at this point, possible to make a direct comparison between the mean-field potential of the VM and the Morse potential. The r dependence of the two potentials is the same; at large internuclear distances, while the Morse potential tends to the constant D_e, the VM mean-field potential of Eq. (13) tends to the same value, but only in the limit of large N. In fact, it can immediately be seen that

$$D_e = \frac{{\omega_e}^2}{4\omega_e \chi_e} \approx -AN^2 \ , \tag{14}$$

which is the large r limit of Eq. (13). This situation is not at all surprising since the mean-field approximation is expected to be correct only in the leading order in $1/N$ [13].

In the traditional approaches the dipole-moment function is expressed as a power expansion of type

$$\mu(r) = \sum_{k=0} M_k (r - r_e)^k \ , \tag{15}$$

where all the constants M_k need to be determined empirically from the comparison with the measurable matrix elements $|\langle f \mid \mu(r) \mid i\rangle|^2$. For example, the MPM can be used to derive the initial (i) and final (f) state wave functions and then the constants M_k can be determined by comparison with a proper set of experimental data. It is clear that this is not a *model* for the dipole-moment function itself but a phenomenological representation of the $\mu(r)$. More sophisticated techniques have been developed which are based on the Padé approximants [21] but even though reliable dipole-moment functions can be derived using these methods, no physical model enters in the evaluation of $\mu(r)$.

On the other hand, *ab initio* calculations furnish the most reliable dipole-moment functions for internuclear distances close to the equilibrium position. However, even the sophisticated *ab initio* techniques need to be cured to correctly represent the dipole-moment functions at large separation distances [22].

The dipole operator of the VM has been discussed in detail in Ref. [11]. For transitions in a given vibrational band, it can be identified with the operator $\hat{\mathbf{D}}$ introduced above in Eq. (6),

$$\hat{T}^{E1}_{\mu} = d_0 \hat{D}_{\mu}, \qquad \mu = 0, \pm 1 \tag{16}$$

where d_0 is a parameter to be fixed by the value of the molecular dipole moment. This operator gives the correct matrix elements for the rotational transitions within a given vibrational band. In order to take into account the possibility of transitions between different vibrational bands, additional terms need to be incorporated into the expression for $\hat{\mathbf{T}}^{E1}$. For example, it has been shown [11] that it is possible to reproduce the matrix elements of the dipole operator for several hydrogen halides using an expression of type

$$\hat{T}^{E1}_{\mu} = \frac{1}{2} \sum_{k=0} d_k [e^{\lambda_k \hat{n}_p} \hat{D}_{\mu} + \hat{D}_{\mu} e^{\lambda_k \hat{n}_p}]. \tag{17}$$

In this expression, $\hat{n}_p$ is the p-boson number operator defined above and d_k and λ_k additional parameters to be fixed by comparison with experimental quantities. A few terms may be necessary when treating transitions to very high overtones.

The mean-field approximation (MFA) and the analysis made above allow us to derive the dipole-moment function for the VM. In fact, let us first assume a dipole operator $\hat{\mathbf{T}}^{E1}$ of the kind shown in Eq. (16). Its expectation value in the condensate will be

$$T^{E1}(\rho) \equiv \mu(\rho) = 2Nd_0 \frac{\rho}{1+\rho^2}. \tag{18}$$

Using the mapping provided by Eq. (12) for going from ρ to r we can easily obtain the dipole-moment function of the VM in the mean-field approximation,

$$\mu(r) = T^{E1}(\rho(r)). \tag{19}$$

The result of this calculation is shown in Fig. 1. In the upper part of the figure, the simple function (18) is shown whereas in the lower part the corresponding dipole-moment function is shown as a function of the geometrical variable r. It can be seen that the VM dipole-moment function presents the correct behavior at both the small and large r limits, namely, the dipole moment increases as the internuclear distance increases up to a maximum and then decreases rapidly at very large r. This situation itself is an improvement over the conventional models based on power expansions. In fact those models predict erratic behavior of the dipole-moment function outside the range of a few atomic units in the vicinity of the equilibrium distance. Our calculation also shows that the dipole operator $\hat{\mathbf{D}}$ has the correct physical content besides furnishing the correct matrix elements for rotational transitions.

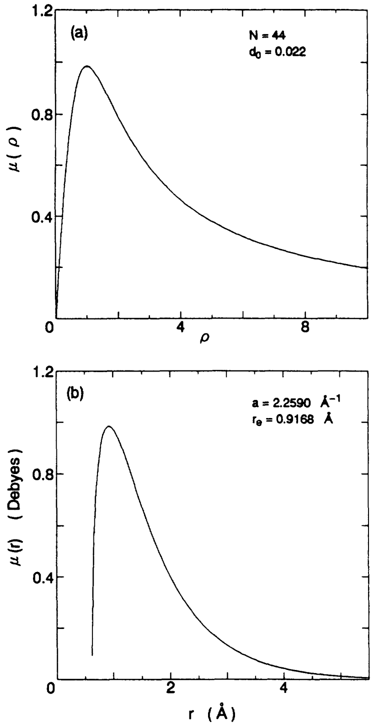

FIG. 1. Dipole-moment functions (a) $\mu(\rho)$ with d_0 in units of Debyes and (b) $\mu(r)$. See the text for explanation.

An improvement of the simple expression for the dipole operator can be obtained using the operator of Eq. (17). In this case the mean-field expression for the dipole-moment function becomes

$$T^{E1}(\rho) = \sum_{k=0} 2Nd_k \frac{\rho}{1+\rho^2} e^{\lambda_k N \frac{\rho^2}{1+\rho^2}}. \tag{20}$$

Again, using Eq. (12) we can evaluated the dipole moment as a function of the internuclear distance.

The results of this calculation are shown in Fig. 2. In this case a comparison is shown with the dipole-moment function of the HF molecule [22]. The data are a combination of experimentally derived quantities (full dots in the figure) and extrapolations based on Padé approximants (crosses). We can see that the maximum of the dipole-moment function moved from the position corresponding to the equilibrium distance (see Fig. 1) to approximately the experimentally derived value. At very large internuclear distances the two models give a noticeable discrepancy. This is due to the fact that the calculations based on phenomenological models, including those shown in Fig. 2, assume a $1/r^4$ dependence of $\mu(r)$ at large r. The operator of Eq. (17), instead, gives a dipole-moment function proportional to $\rho \approx \sqrt{e^{-ar}}$ for large r. Even though not immediately apparent, we can expect that an algebraic operator which gives the same large r behavior can be derived.

The accuracy of the MFA calculation obtained using the operators given in Eq. (17) is comparable with that presented in Ref. [21]. To improve the agreement with the data of Ref. [22], additional terms in the dipole operator can be added.

Our analysis of the VM mean-field approximation showed that the relation given in Eq. (12) allows for a link between the parameter ρ and the geometrical variable r. Thus, the VM boson condensate built as a function of the real parameter ρ can be related to the geometrical configuration of the molecule. As far as the dipole-moment function is concerned, even though the results of the mean-field approximation can be improved by adding more terms in the dipole operator, we can conclude that the VM dipole-moment operator has the proper physical content and that the general trend of the calculations is reliable.

In the simplest case analyzed here, namely, that of a diatomic molecule, the only geometrical variable which has a physical content is the internuclear distance r. It is, however, possible to extend the method to the interpretation of the multiple geometrical variables appearing in the description of polyatomic molecules. In fact, the mean-field approximation to the VM has been already derived for triatomic linear [17] and bent [16] molecules and the present methodology can be extended to treat those cases.

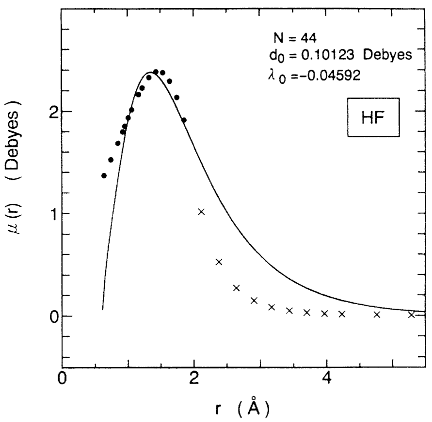

FIG. 2. Dipole-moment functions of HF. The full dots are values derived from the experimental infrared transition matrix elements and the crosses are extrapolation values obtained using the Padé approximants [22]. The solid line is obtained as described in the text.

We hope that our analysis will serve for a more complete understanding of the relations between the abstract algebraic approaches and the traditional approaches based on geometrical variables.

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