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Diatomic Potential Functions Derived from Accurate Fits to Vibrational Energy Levels Using Algebraic Theory

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Algebraic theory is used to fit the set of bound vibrational energy levels of H_2 and its isotopomers, up to the dissociation limit and to an accuracy of within 1 cm^{-1} in each case. Coordinate space potential functions are constructed from these algebraic Hamiltonians, and the limitations of the algebraic approach are assessed.

1. Introduction

Algebraic methods have been applied to problems in molecular physics for a number of years, with applications extending from one- and three-dimensional treatments of diatomic molecules to the coupled vibrational and rotational motions of triatomic and higher polyatomic molecules. Comprehensive reviews of the algebraic approach have recently been published.[1−3]

The simplest problem to which algebraic theory has been applied is the one-dimensional vibrational motion of a diatomic molecule,[4,5] and this may be considered as a testing ground for the basic algebraic approach. However, despite the fact that fits of algebraic Hamiltonians to diatomic vibrational energy levels have been made previously, quantitative accuracy was not achieved. Such accuracy is necessary if the algebraic Hamiltonians which generate fits to vibrational spectra are to be used subsequently in the construction of potential energy functions in coordinate space. Although well-known techniques exist for the inversion of spectroscopic data[6] to generate diatomic potential functions,[7] it is appropriate to study the applicability of the algebraic approach in this regard because of its capability of extension to polyatomic species for which the link between spectrum and potential by conventional methods is more difficult to achieve. To date, ab initio calculations have been used to calculate potential energy surfaces for triatomic molecules with spectroscopic accuracy,[8] and vibrationally excited states of small polyatomic molecules have been analyzed by canonical Van Vleck perturbation theory.[9]

We shall demonstrate here that the full set of bound energy levels of a diatomic molecule, up to the dissociation limit, can be represented by the eigenvalues of an algebraic Hamiltonian. The resultant Hamiltonian can then be related to a coordinate space potential function representing the one-dimensional vibrational motion of the diatomic molecule.

The present paper is structured as follows. In the next section, we review the algebraic theory appropriate to the one-dimensional treatment of the vibrational motion of diatomic molecules and show how it relates to the vibrational energy level spectrum. By including both linear as well as quadratic Casimir invariants of the dynamical symmetry associated with the O(2) subgroup of U(2), we are able to introduce the flexibility required to provide accurate fits to the vibrational levels of H_2 and its isotopomers HD and D_2. In section 3, we relate the linear Casimir invariant of O(2) to the square root of the Morse oscillator Hamiltonian in one dimension; the quadratic Casimir of O(2) is related to the Morse Hamiltonian itself.[4,5] Removal of the momentum-dependent terms permits the identification of a potential function which is essentially a power series in the square root of the Morse potential function. The potentials derived for the various isotopomers are found to correspond to approximately the same value of well depth. It is shown that a minor modification to a previously proposed scheme for the construction of potential functions from algebraic Hamiltonians is capable of generating identical results, which offers the possibility of extension to more complex systems. The paper concludes with an assessment of the strengths and weaknesses of the algebraic approach in generating potential functions from accurate fits to spectral data.

2. Algebraic Theory of Diatomic Molecules

Background Theory. Stretching vibrations in algebraic theory can be described in terms of U(2), the unitary Lie algebra in two dimensions.[4,5] This algebra can be represented in terms of Casimir invariant operators of the algebra and subalgebras which correspond to a particular dynamical symmetry chain. Expansion of an algebraic Hamiltonian in terms of the Casimir invariant operators of the algebra and its subalgebras leads to energy eigenvalues which can be written down by inspection using the known eigenvalues of these Casimir invariants with respect to the appropriate basis set.

The U(2) algebra may be realized in terms of two boson creation and annihilation operators, with generators $t^\dagger t$, $s^\dagger s$, $t^\dagger s$, and $s^\dagger t$ with where the (number) operator

$$\hat{N} = t^\dagger t + s^\dagger s \equiv \hat{n}_t + \hat{n}_s \tag{1}$$

is the Casimir invariant of U(2) and characterizes its irreducible representation.

Although U(2) possesses two dynamical symmetry chains, namely

$$\mathrm{U}(2) \supset \mathrm{U}(1) \tag{2}$$

$$\mathrm{U}(2) \supset \mathrm{O}(2) \tag{3}$$

the latter (O(2)) chain has been shown to be particularly appropriate for the treatment of anharmonic vibrational motion in diatomic molecules,[4,5] although it is known that the two subalgebras O(2) and U(1) are themselves isomorphic.[1]

For the O(2) chain, the relevant quantum numbers are N and σ, the eigenvalues of the Casimir invariant (number operator) $\hat{N}$ of U(2) and the linear Casimir invariant operator

$$\hat{\sigma} = (t^\dagger s + s^\dagger t) \tag{4}$$

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of O(2), respectively. The quantum number N takes integer values and the quantum number σ takes $N + 1$ values, ranging in steps of 2 from N to $-N$.

If we carry out a rotation to new operators S and T via the transformations

$$S = (s + t)/\sqrt{2} \qquad T = (s - t)/\sqrt{2} \tag{5}$$

with corresponding definitions for the conjugate operators $S^\dagger$ and $T^\dagger$, then the linear Casimir invariant of O(2) can be expressed in the form

$$s^\dagger t + t^\dagger s = S^\dagger S - T^\dagger T \equiv \hat{N} - 2T^\dagger T \tag{6}$$

where we have used the boson conservation relation $s^\dagger s + t^\dagger t = S^\dagger S + T^\dagger T = \hat{N}$. The eigenvalues of $T^\dagger T$ are equivalent to those of $(N - \sigma)/2$ and will be denoted by v, which ranges from 0 to N.

The eigenstates of the O(2) chain may be defined in terms of the quantum numbers N and v and denoted by $|Nv\rangle$, where

$$\hat{N}|Nv\rangle = N|Nv\rangle \tag{7}$$

$$\hat{\sigma}|Nv\rangle = \sigma|Nv\rangle \tag{8}$$

and

$$T^\dagger T|Nv\rangle = v|Nv\rangle \tag{9}$$

These eigenstates $|Nv\rangle$ can be expressed in terms of the two-dimensional harmonic oscillator basis of Schwinger,[10] which allows ladder operators to be constructed. These ladder operators have been discussed in detail elsewhere[11] and compared with those arising from the U(1) dynamical symmetry chain of U(2).

Algebraic Hamiltonians have generally been written in terms of the quadratic Casimir invariant of O(2), $\hat{\sigma}^2$, with eigenvalues $(N - 2v)^2$, which occur in degenerate pairs (except for the particular case where $v = N/2$, for even N, which is nondegenerate). The permitted values of v, the vibrational quantum number, then range from 0 to $N/2$ when N is even and from 0 to $(N - 1)/2$ when N is odd, respectively.

A general algebraic Hamiltonian based on the quadratic Casimir invariant of O(2) is

$$\hat{H} = A_0 + A_2 C_2[\mathrm{O}(2)] \tag{10}$$

where $C_2[\mathrm{O}(2)] = (s^\dagger t + t^\dagger s)^2$ and A_0 and A_2 are constants. Note that A_0 subsumes the Casimir invariant of U(2), which is a constant. Then, from eqs 6 and 9,

$$\begin{aligned}\hat{H}|Nv\rangle &= [A_0 + A_2(N - 2T^\dagger T)^2]|Nv\rangle \equiv E_v|Nv\rangle \\ &= [A_0 + A_2 N^2 - 4A_2 v(N - v)]|Nv\rangle \end{aligned} \tag{11}$$

where the label N has been omitted from the energy eigenvalues.

This may be compared with the familiar vibrational energy expression of Dunham[12] (measuring energies from the $v = 0$ level)

$$E_v = \omega_0 v - \omega_0 x_0 v^2 \tag{12}$$

where ω_0 and $\omega_0 x_0$ represent the vibrational wavenumber and anharmonicity correction (the left-hand side should correctly read E_v/hc). This allows us to make the identifications $\omega_0 = -4A_2N$ and $-\omega_0 x_0 = 4A_2$ so that $A_2 = -\omega_0 x_0/4$ and $N = 1/x_0$.

TABLE 1: Fits to the Set of Bound Vibrational Energy Levels of H_2, HD, and D_2 with Expansion to Power p of the Quadratic Casimir Invariant of O(2)[a]

molecule	value of p	v_{max}	N_{opt}	rms deviation	ω_0	$\omega_0 x_0$	D_0
H_2	1	17	34	138.1	4423	130.1	36 325
H_2	2	16	32	58.8	4140	74.2	36 049
H_2	3	15	31	24.6	4339	158.8	36 128
H_2	expt				4284	123.4	36 118
HD	1	19	39	177.3	3864	99.0	36 651
HD	2	18	36	88.2	3507	37.3	36 258
HD	3	17	35	38.2	3867	160.2	36 450
HD	expt				3726	93.3	36 405
D_2	1	24	48	194.8	3152	65.7	36 925
D_2	2	22	45	79.4	2920	32.0	36 637
D_2	3	22	45	68.9	3026	57.4	36 724
D_2	expt				3058	63.2	36 748

[a] The experimental values refer to those corresponding to the data of Le Roy[13] used as input. The optimal value of N and maximum value of vibrational quantum number observed are given in each case. The root-mean-square deviation, ω_0, $\omega_0 x_0$, and D_0 are quoted in cm^{-1}.

Hence, in the particular case of O(2) dynamical symmetry, with restriction to the quadratic Casimir invariant, the quantum number (vibron number) N is equal to the inverse of the anharmonicity constant x_0. However, the dissociation limit corresponds to $-4A_2N^2 \equiv \omega_0/4x_0$, which is also dependent on the value of N. The N dependence of both the vibrational constants and the dissociation energy has implications for the ability of the quadratic Casimir invariant of O(2) to provide a fit to the full set of bound vibrational levels of a diatomic molecule, since N must necessarily be a constant.

Expansion in Powers of the Quadratic Casimir of O(2). Accurate vibration−rotation energy levels of H_2 and its isotopomers have been generated by Le Roy,[13,14] the former reference using relativistically corrected potential energy curves and the latter using more accurate recent data and extending the calculations to include the tritium isotopes. Since we are primarily interested in illustrating the ability of the algebraic approach to treat such systems, we shall focus on the extensive vibrational data of Le Roy[13] for H_2, HD, and D_2 (measured relative to zero of energy at the appropriate dissociation limit).

We attempt to fit the vibrational energy levels to an algebraic Hamiltonian expressed as a power series in the quadratic Casimir invariant of O(2), in the form

$$\hat{H} = \sum_{k=0}^{p} A_{2k} C_2[\mathrm{O}(2)]^k \tag{13}$$

The energy eigenvalues of this algebraic Hamiltonian with respect to the basis $|Nv\rangle$ in which the Casimir invariant of O(2) is diagonal may be written down by inspection as

$$E_v = \sum_{k=0}^{p} A_{2k}(N - 2v)^{2k} \tag{14}$$

The results for $p = 1$, 2, and 3, leading to expansions up to the sixth power in vibrational quantum number v, are shown in Table 1 for H_2, HD, and D_2. Although the spectral fits do improve with increasing number of terms as expected, the values of vibrational constants vary somewhat erratically as a consequence of fixed interrelationships involving the various powers of vibrational quantum number arising from the terms $(N - 2v)^{2k}$. In addition, the series becomes seriously affected by numerical instability when further terms are included in the expansion.

The number of predicted bound vibrational levels is found initially to be in excess of the observed maximum values of vibrational quantum number (14, 17, and 22 for H_2, HD, and D_2, respectively), but an improved description occurs as higher terms are included in the expansion.

The dissociation energy is determined from the relation

$$D_0 = -\sum_{k=0}^{p} A_{2k} N^{2k} \tag{15}$$

and the experimental values can be seen to be reasonably well described by the three-term expansion in each case. The values of vibrational energies provided by Le Roy[13] are with respect to an energy zero located at the dissociation limit for each molecule so the value of D_0 is equivalent to the negative of the energy of the $v = 0$ vibrational level.

Expansion in Powers of the Linear Casimir of O(2). All previous fits to diatomic vibrational energy levels in terms of the O(2) chain have considered expansions in terms of the quadratic Casimir of O(2).[1,3,4] Higher order orthogonal groups do not possess linear Casimir invariants, and this has been used as an argument against the inclusion of the first-order Casimir invariant of O(2) in the algebraic Hamiltonian.

However, we note from eq 11 that the coefficients of the linear and quadratic powers of the vibrational quantum number are related through N. This interrelationship would be removed if we introduced the linear Casimir of O(2), based on the expansion

$$\hat{H} = A_0 + A_1 C_1[\mathrm{O}(2)] + A_2 C_2[\mathrm{O}(2)] \tag{16}$$

so that

$$E_v = A_0 + A_1(N - 2v) + A_2(N - 2v)^2 \tag{17}$$

The coefficients of the linear and quadratic powers of vibrational quantum number are now decoupled from each other, and the energy eigenvalues no longer depend on the precise value of N since only three independent coefficients are required.

With inclusion of the linear Casimir invariant of O(2), the analogues of eqs 13 and 14 are

$$\hat{H} = \sum_{k=0}^{p} A_k C_1[\mathrm{O}(2)]^k \tag{18}$$

and

$$E_v = \sum_{k=0}^{p} A_k (N - 2v)^k \tag{19}$$

The results for $p = 2-6$, up to and including the sixth power of the vibrational quantum number, are shown in Table 2 for H_2, HD, and D_2. Note that convergence is achieved when the expansion in the vibrational quantum number is truncated at the sixth power, with a root-mean-square deviation of less than 0.5 cm^{-1}. In fact, the fits to the individual levels are observed to lie within 1 cm^{-1} of the values provided as input with maximum deviations of 0.7, 0.6, and 1.0 cm^{-1} for H_2, HD, and D_2, respectively.

A number of features should be noted. Although the highest bound level in H_2 (corresponding to $v = 14$) lies 139 cm^{-1} below the dissociation limit, a further (spurious) level appears in the fit at 22.2 cm^{-1} below the dissociation limit. The highest vibrational levels in HD ($v = 17$) and D_2 ($v = 21$) lie 2.5 and 1.1 cm^{-1} below their respective dissociation limits, and no further bound states are observed in the fits to the vibrational levels for those molecules.

TABLE 2: Fits to the Set of Bound Vibrational Energy Levels of H_2, HD, and D_2 with Expansion to Power p of the Linear Casimir Invariant of O(2)[a]

molecule	value of p	$v_{\max}$	rms deviation	ω_0	$\omega_0 x_0$	D_0
H_2	2	17	134.6	4399	128.2	36 279
H_2	3	16	46.4	4166	85.3	36 056
H_2	4	15	7.99	4275	114.8	36 126
H_2	5	15	3.58	4289	123.2	36 120
H_2	6	15	0.30	4284	123.4	36 118
H_2	expt			4284	123.4	36 118
HD	2	20	176.7	3855	98.5	36 630
HD	3	18	61.0	3596	59.3	36 316
HD	4	17	11.4	3758	105.2	36 419
HD	5	17	2.3	3712	84.2	36 403
HD	6	17	0.38	3726	93.3	36 405
HD	expt			3726	93.3	36 405
D_2	2	24	176.4	3162	65.7	36 982
D_2	3	24	61.3	2947	39.4	36 650
D_2	4	21	11.5	3084	70.5	36 764
D_2	5	21	2.3	3045	56.2	36 745
D_2	6	21	0.46	3058	63.2	36 749
D_2	expt			3058	63.2	36 748

[a] The experimental values refer to those corresponding to the data of Le Roy[13] used as input. The root-mean-square deviation, ω_0, $\omega_0 x_0$, and D_0 are quoted in cm^{-1}.

Since all powers of vibrational quantum number, up to and including the sixth power, are free to vary independently in the expansion, the fits to the vibrational energy levels are independent of the precise value of quantum number N, but the value of N should be consistent with the number of bound vibrational levels ($(N + 2)/2$ for N even and $(N + 1)/2$ for N odd).

Although Table 2 displays the vibrational constants ω_0, it is a straightforward matter to rearrange the energy expression, eq 19, as a power series in $(v + 1/2)$. The coefficent of the linear term then represents the familiar vibrational constant ω_e, with predicted values of 4408.4, 3820.1, and 3122.0 cm^{-1} for H_2, HD, and D_2, respectively. The true vibrational constants are expected to scale with reduced mass μ as $\mu^{-1/2}$, and if we multiply the above values by $\mu^{1/2}$, we find the numerical results 3117.2, 3119.1, and 3122.0, respectively, showing that the expected dependence on reduced mass is obeyed to within a good approximation.

3. Coordinate Realization of Algebraic Hamiltonians

Here, we consider the realization of the Hamiltonians corresponding to the O(2) dynamical symmetry in terms of a coordinate space representation.[1,15] This enables potential functions to be extracted from the algebraic procedure.

In the case U(2) ⊃ O(2), it has been demonstrated previously[15,16] that the quadratic Casimir invariant of O(2) can be related to the Hamiltonian corresponding to a one-dimensional Morse oscillator. We shall summarize the main steps of the argument here since the results are of significance in the present context, although it should be stressed that this particular approach is restricted to the subalgebra O(2) of U(2).

Applying the transformations

$$s = (i/\sqrt{2})(x + ip_x) \qquad t = (1/\sqrt{2})(y + ip_y) \tag{20}$$

to the quadratic Casimir invariant of O(2)) gives

$$(s^{\dagger}t + t^{\dagger}s)^2 = (xp_y - yp_x)^2 = (-i\partial/\partial\phi)^2 \equiv \hat{L}^2 \tag{21}$$

where $\hat{L}$ is the angular momentum operator, and we have transformed to polar coordinates via $x = \rho \cos \phi$ and $y = \rho \sin \phi$. The Hamiltonian for the O(2) chain then becomes (we drop the constant term A_0 for convenience)

$$\hat{H} = A_2(s^\dagger t + t^\dagger s)^2 = A_2\hat{L}^2 \tag{22}$$

with eigenvalues $A_2(N - 2v)^2$. Since the two-dimensional harmonic oscillator Hamiltonian can be expressed in polar coordinates as

$$\hat{H}_{\text{osc}} = -\frac{\partial^2}{\partial\rho^2} - \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\hat{L}^2}{\rho^2} + \rho^2 \tag{23}$$

with eigenvalues given by $2(N + 1)$, we have, from eqs 22 and 23,

$$\hat{H} = A_2\left(\rho^2\frac{\partial^2}{\partial\rho^2} + \rho\frac{\partial}{\partial\rho} - ((N+1) - \rho^2)^2 + (N+1)^2\right) \tag{24}$$

This result depends on the fact that the chosen basis is the two-dimensional harmonic oscillator basis of Schwinger.[10]

Transformation to the one-dimensional variable y via $\rho = (N + 1)^{1/2} \exp(-y/2)$ gives

$$\hat{H} = -4A_2\left(-\frac{d^2}{dy^2} + ((N+1)/2)^2(1 - e^{-y})^2 - ((N+1)/2)^2\right) \tag{25}$$

This represents the Hamiltonian of a one-dimensional Morse oscillator with well depth parameter $(N + 1)/2$, corresponding to Int $(N/2 + 1)$ bound vibrational levels. The eigenvalues of this Hamiltonian are given by (compare eq 11)

$$E_v = -4A_2[-((N+1)/2 - v - 1/2)^2] \equiv A_2N^2 - 4A_2Nv + 4A_2v^2 \tag{26}$$

Note from eqs 25 and 26 that the well depth is given by $D_e = -A_2(N + 1)^2$. The dissociation energy is given by $D_0 = -A_2N^2$.

The realization of the quadratic Casimir invariant of O(2) in terms of the Hamiltonian corresponding to the one-dimensional Morse oscillator shows that the inclusion of the linear Casimir in the Hamiltonian for the O(2) dynamical symmetry chain would result in a term involving the square root of the Morse oscillator Hamiltonian.

It is of interest to note in this connection that an expansion in fifth and higher powers of the square root of the Morse potential was first proposed by Dunham[12] and forms the basis for the extensive series of papers by Huffaker[17] on the perturbed Morse oscillator potential. However, it should be noted that the square root dependence arising naturally within the algebraic approach involves the form of Morse potential which vanishes at infinite separation, whereas that of Dunham refers to the form which is zero at equilibrium, at the foot of the potential well.

It is straightforward to show that the coordinate space (potential) representation of the algebraic Hamiltonian providing the best fit to the vibrational energy levels of H_2 and its isotopomers has the form

$$V(y) = k = \sum_{k=0}^{p} A_k(N+1)^k\, e^{-ky/2}(2 - e^{-y})^{k/2} \tag{27}$$

where we note that the minimum value of V (occurring at $y = 0$) gives the depth of the potential well as

$$D_e = -\sum_{k=0}^{p} A_k(N+1)^k \tag{28}$$

The inverse power dependence of the correct interaction potential at long range[18] precludes an accurate fit to high vibrational levels by a potential of Morse type. We note here that the involvement of the square root term does permit such a fit to high vibrational energy levels up to dissociation but also implies that the potential is defined only for values of the variable y greater than $-\ln 2$, such that the potential lies below the value at dissociation. A similar square root dependence has been introduced previously for a potential describing the coupled stretching vibrations of triatomic molecules.[20]

The difference beween well depth and dissociation energy, the zero-point energy, does depend on the chosen value of N. Table 3 shows how the predicted well depths for H_2, HD, and D_2 compare with the values implied by the vibrational constants arising from the optimal fits to the vibrational energy levels. Note that the values of N in Table 3 are consistent with the observed values of 14, 17, and 21 for $v_{\max}$ for H_2, HD, and D_2, respectively, although the optimal fit for H_2 did yield an additional bound level, as noted in section 2 above.

The largest discrepancy in zero-point energy observed in Table 3 occurs with H_2, which also has the largest energy gap between the highest bound vibrational level and the dissociation limit. A bound vibrational level lies close to the dissociation limit for both HD and D_2, which is consistent with the observation that the relevant integer value of N yields a well depth close to that predicted by the vibrational constants. This restriction to integer values of N represents the only constraint implicit in the algebraic model, provided that the algebraic Hamiltonian is expanded in powers of the linear Casimir invariant of O(2), in order that the coefficients of the various powers of vibrational quantum number may be varied independently. An expansion in powers of the quadratic Casimir invariant of O(2) invokes an additional constraint in that such an expansion is unable to describe independently the various powers of vibrational quantum number appearing in the Dunham energy expansion.

The potentials determined from eq 27 are found to differ slightly, as a consequence of the integer nature of the vibron number N, in conflict with the Born Oppenheimer approximation. In fact, the expansion coefficients in eq 27 are N-dependent, and the potential parameters are not invariant. However, the resultant potentials for HD and D_2 are found to lie close in value over the full range, with maximum deviation of around 50 cm^{-1} (less than 1 kJ mol^{-1}). The deviation between the H_2 and HD potentials is somewhat larger but never exceeds 200 cm^{-1}. This slight discrepancy is to be expected since the H_2 well depth is slightly less well represented relative to those of the other two isotopomers, as noted above.

It should be emphasized that the route from the fit to the energy levels to the coordinate space potential, as described above, is unique to the O(2) subalgebra of U(2). A general procedure for the construction of the classical limit of boson operators involves a coherent state approach,[16,19] and a simplified version of this scheme has been formulated[20] in terms of so-called intensive boson operators first introduced by Gilmore.[21] However, direct application of this latter approach is found to generate a potential function in which the well depth occurs at the same value of energy as the $v = 0$ vibrational level. In other words, the zero-point energy is lost. This deficiency may be rectified by the following minor modification of the previously proposed procedure.[20]

TABLE 3: Predicted Well Depths and Zero-Point Energies for H_2, HD, and D_2 Derived from Optimal Fits to the Vibrational Energy Levels and from the Classical Potentials Using the Appropriate Value of N[a]

	D_0	D_e	E_0	$E_0(N)$	$D_e(N)$
H_2	36 118	38 291	2173	2161 ($N = 29$)	38 279 ($N = 29$)
HD	36 405	38 292	1887	1884 ($N = 34$)	38 289 ($N = 34$)
D_2	36 748	38 294	1546	1544 ($N = 42$)	38 292 ($N = 42$)

[a] All energy values are quoted in cm^{-1}.

Intensive boson operators may be constructed by dividing the original boson operators by $(N + 1)^{1/2}$ (rather than by $N^{1/2}$), whereby the commutators vanish in the limit of high boson number. The intensive boson operator derived from t is replaced by a complex number whose complex conjugate represents the intensive boson operator derived from $t^\dagger$. The intensive boson operators derived from s and $s^\dagger$ may be eliminated by application of of the boson conservation relation (eq 1) which will then hold to order N^{-1}. The classical limit of the algebraic Hamiltonian (eq 22) then becomes

$$H_{\mathrm{cl}} = A_2(N + 1)^2\, q^2(2 - p^2 - q^2) \tag{29}$$

where the complex number has been expressed in the form $(q + ip)/\sqrt{2}$, where q and p represent position and momentum, respectively. If we assign zero to the momentum variable and replace the variable q by y, defined by the relation $q^2 = \exp(-y)$, the classical potential becomes

$$V(y) = A_2(N + 1)^2\, \mathrm{e}^{-y}(2 - \mathrm{e}^{-y}) \tag{30}$$

which is precisely the result derived previously from the O(2) algebra (cf. the potential term in eq 25). This analysis can be extended to the algebraic Hamiltonian, eq 18, leading to the classical potential function given in eq 27.

This substitution of N by $N + 1$ in the previously proposed method[20] generates a classical potential function whose well depth is consistent with the known value of dissociation energy and includes the zero-point energy.

4. Concluding Remarks

We have demonstrated that the expansion of the algebraic Hamiltonian as a power series in the linear Casimir invariant of the subalgebra O(2) of the algebra U(2) leads to accurate fits to the vibrational energy levels of H_2 and its isotopomers up to the dissociation limit in each case. By restricting attention to a dynamical symmetry chain, no diagonalization is required and the energy expressions can be written down by inspection. The eigenstates are also well defined although they have not been used explicitly in the present analysis.

The coordinate space representation of the algebraic Hamiltonian becomes a power series expansion in half integral powers of the Morse Hamiltonian with a corresponding classical potential expanded in half integral powers of the Morse potential function. We note that a knowledge of the full set of vibrational levels—up to dissociation—was necessary for the construction of a potential function which would accurately represent the highly excited vibrational energy levels. The equilibrium position is not uniquely defined from the algebraic approach, since the variable y is dimensionless, and can be expressed in the form $\alpha(r - r_e)$, where α represents the range parameter and r_e the equilibrium separation, by analogy with the Morse oscillator potential.

The zero-point energy predicted by the model depends on the choice of N, the irreducible representation of U(2). The number of bound levels is $N/2 + 1$ or $(N + 1)/2$, for N even or odd, respectively, leading to predictions for N of 28 (29), 34 (35), and 42 (43), for H_2, HD, and D_2, respectively. The best fits to the zero-point energies predicted by the vibrational constants are 29, 34, and 42, respectively. The potentials arising from the spectral fits should each display the same value of well depth, but this is affected slightly by the constraint that N should be an integer. This is most obvious in the case of H_2, where the well depth appearing in the potential functions differs by some 10 cm^{-1} from that predicted by the vibrational constants, and may be attributed to the fact that the highest bound vibrational level in H_2 lies some 140 cm^{-1} below the dissociation limit.

Potental functions may also—and more generally—be determined by use of intensive boson operators, and it has been demonstrated that the definition of these operators can be adapted, while remaining within the philosophy of an expansion valid to order $1/N$, in order to generate a classical potential which displays the correct value of well depth.

In the absence of this modification, intensive boson operators generate classical potential functions which have the undesirable property that the well depth is identical to the dissociation energy, thereby eliminating the zero-point energy.

In conclusion, we emphasize that we have managed to achieve fits of high accuracy to the vibrational energy levels of diatomic molecules based on an algebraic Hamiltonian for which a well-defined potential function can be identified from a classical Hamiltonian in which the momentum coordinate is put equal to zero. We have also demonstrated the ability of the algebraic approach to provide results of quantitative accuracy for the vibrational energy levels of diatomic molecules without the need to perform explicit diagonalization of the algebraic Hamiltonian itself.

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