Lie-algebra contraction approach to problems of molecular symmetry: The double-potential-minimum problem

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The applicability of an approach to the calculation of tunneling splittings in a one-dimensional potential with symmetrically disposed minima is presented. The method is based on the concept of contraction of a Lie algebra [Mol. Phys. **93**, 441 (1998)], recently extended to encompass the case where more than one symmetry-related minima is present. The method is validated against highly precise published calculations using other approaches and also against the tunneling energy levels of lower inversion vibrational levels in NH_3.

I. INTRODUCTION

The calculation of the energy levels of a particle moving in a potential field possessing symmetry-related minima is a venerable and classic problem of quantum mechanics, with Hund probably the first to provide a qualitative description of the one-dimensional case [1]. This system is illustrated in Fig. 1. The quantitative solution to this problem is often presented as a standard application of the Wentzel-Kramers-Brillouin (WKB) method [2], although, as pointed out by Garg [3], the textbook exposition given by Landau and Lifshitz [4] does not in fact provide a numerically correct formulation. Other approaches of an essentially perturbation character have been advanced by Rosen and Morse [5], Swalen and Ibers [6], and Harmony [7], among others. More recently, the so-called "instanton" approach has been adapted to provide splitting formulas [8,9].

The accurate calculation of very small inversion splittings has recently assumed renewed significance in the light of attempts to identify the origin of chiral preferences in naturally occurring molecules such as amino acids. Factors such as the electroweak interaction have been adduced and sophisticated calculations carried out to demonstrate potentially measurable energy splittings in suitable molecules [10]. For practical spectroscopists, the principal focus of many calculations has been the determination of the height of the energy barrier separating the minima; however, as we shall demonstrate below, this is not the most significant factor influencing the magnitude of splittings.

We have recently shown that the concept of contraction of a Lie algebra, first developed by Inönü and Wigner [11] and Saletan [12], may be extended to the case of multiple symmetry-related minima by means of an appropriate many-to-one variable transformation (Ref. [13], hereafter called I). Resolution of states otherwise lost in this transformation is accomplished by casting the original Hamiltonian to act within manifolds of differing discrete symmetries before transformation; after transformation, this leads to a different Hamiltonian for each manifold. While the basis of this method was laid out in I, numerical results were not explored in detail. In the present work, we show that the method does indeed provide a simple and accurate approach to the calculation of inversion splittings. We also compare with previ-ously published calculations, verify (or otherwise) approximate limiting formulas reported in the literature, and apply the method to the familiar case of the ammonia molecule.

II. APPLICATION OF THE LIE ALGEBRA CONTRACTION METHOD

The general form of a potential function exhibiting symmetrical minima at $x = \pm c$, of the sort illustrated in Fig. 1, may be written

$$V(x) = f(x^2 - c^2), \qquad (1)$$

where the coefficient of the linear term $(x^2 - c^2)$ in the Taylor series expansion of f is constrained to zero. By far the most widely investigated case is limited to a quadratic term in $(x^2 - c^2)$ [14–17], although a few studies of the quadratic plus inverted Gaussian form have been reported. In I, we showed that the quartic Hamiltonian (we set $m = \hbar = 1$ to yield unitless energies to facilitate comparison with the results of others workers)
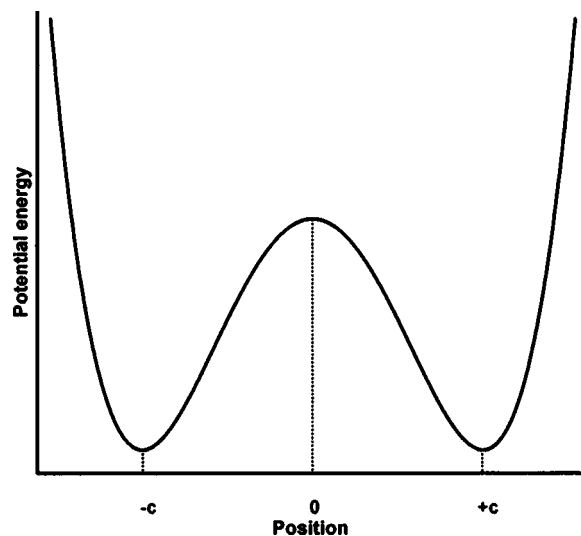

FIG. 1. General form of the potential energy discussed in this work.

$$H = -\tfrac{1}{2}\frac{d^2}{dx^2} + \tfrac{1}{8}(x^2 - c^2)^2 \qquad (2)$$

may be usefully reexpressed in terms of the variable

$$y = \frac{x^2 - c^2}{2\sqrt{c}} \qquad (3)$$

to yield the forms

$$H_\pm = -\tfrac{1}{2}\left\{ c\left(\frac{d^2}{dy^2} - y^2\right) + \frac{1}{\sqrt{c}}\left(2\frac{d}{dy}y\frac{d}{dy} \mp \frac{d}{dy}\right)\right\}. \qquad (4)$$

In Eq. (4), the two forms $H_\pm$ operate within manifolds of states of even and odd parity in x, respectively, thus accommodating this distinction that is otherwise lost in the two-to-one mapping of x onto y. The form H_+ arises from direct transformation of Eq. (2) according to Eq. (3). The second form in Eq. (4) arises from allowing Eq. (2) to operate within the manifold of odd parity, defined by functions of the form $xf(x^2)$; after transformation, this yields H_-. Effectively, this corresponds to transformation of Eq. (2) by $(1/x)Hx$. This formulation therefore provides explicitly for the tunneling splitting of such states as well as the anharmonicity associated with a quartic or higher potential. Furthermore, it is readily apparent from the c dependence of Eq. (4) that both splitting and anharmonic effects become negligible in the limit of very large c (separation between the minima), as we would anticipate. If necessary, Eq. (4) may be further generalized by expansion of $V(y)$ in Eq. (1) as a Taylor series and incorporating the coefficient of the leading term in y^2 into the usual scaling for y.

This approach may be contrasted with more conventional methods, where states from all symmetry manifolds must be included in calculations to provide accurate results; the reason is, of course, that any recasting of the Hamiltonian (2) in a linear form centered around one or other minimum obscures the inversion symmetry. The second advantage of our transformation is that Eq. (4) provides a natural framework for calculation within the well-known $g(0,1)$ algebra, isomorphic with familiar harmonic oscillator algebra h_4 [18]. Since all operator effects in common Lie algebras are known, it is unnecessary to derive them afresh for any particular application. In I, we showed that the above process can be viewed as a contraction of the global symmetry of the harmonic oscillator (including inversion symmetry) onto the local symmetry of the immediate neighborhood of *both* potential minima simultaneously. Effectively, this constitutes a contraction of continuous elements of symmetry onto a potential minimum combined with a many-to-one homomorphic mapping of discrete elements (inversion, exchange of identical particles) onto the identity. It is, of course, the concept of contraction onto the local symmetry of a *single* minimum that underlies our intuitive understanding of molecular structure, enantiomeric forms, etc.

Numerical evaluation of the eigenvalues of Eq. (4) requires the identification of a suitable basis set and the corresponding operator effects. At first sight, it might appear that standard harmonic oscillator (normalized Hermite polynomial times Gaussian) functions of y are appropriate, combined with standard operator actions [19]. However, this is not the case; while such functions are orthonormal on the interval $(-\infty, +\infty)$, from the definition of y in Eq. (3) we see that its range is restricted to $\left(-\tfrac{1}{2}\sqrt{c}c, +\infty\right)$. Thus the matrix elements of Eq. (4) in the harmonic oscillator basis set would have to account for this. This leads to very complex expressions, and it is more convenient to acknowledge this fact at the outset and work with a more tractable nonorthonormal set. We have chosen the closely related set

$$|n\rangle = \frac{y^n e^{-y^2/2}}{\sqrt{n!}}, \qquad (5)$$

within which operator actions are simply

$$y|n\rangle = \sqrt{(n+1)}|n+1\rangle, \quad \frac{d}{dy}|n\rangle = \sqrt{n}|n-1\rangle - \sqrt{(n+1)}|n+1\rangle. \qquad (6)$$

The general secular equation for the extraction of the eigenvalues λ within a set of nonorthogonal basis functions reads

$$|\mathbf{H} - \mathbf{S}\lambda| = 0, \qquad (7)$$

where $H_{ij} = \langle i|H|j\rangle$ and the symmetrical overlap matrix $S_{ij} = \langle i|j\rangle$. This is readily reduced to a computationally more convenient form by noting that

$$H_{ij} = \langle i|H|j\rangle = \sum_k \langle i|A_{kj}|k\rangle = \sum_k S_{ik}A_{kj} \text{ or } \mathbf{H} = \mathbf{S}\cdot\mathbf{A}. \qquad (8)$$

In Eq. (8), $\mathbf{A}$ is the "operator action" matrix of the Hamiltonian H in Eq. (4) on a suitable basis set. $\mathbf{S}$ is nonsingular (since the basis functions are chosen to be linearly independent), so that Eq. (7) reduces to

$$|\mathbf{A} - \lambda\mathbf{1}| = 0, \qquad (9)$$

with $\mathbf{1}$ the identity matrix. The complication of calculating overlap integrals is thus avoided entirely, and the problem is reduced to one of evaluating the operator action matrix $\mathbf{A}$; this is straightforwardly accomplished using Eq. (6), and the results are listed in Table I. However, $\mathbf{A}$ is not symmetric, necessitating the computation of eigenvalues through less familiar methods, as described below.

TABLE I. Operator action matrices $A_\pm$ for the Hamiltonians (4).

Element	Operator action
$A_{n,n}$	$c(n+1/2)$
$A_{n,n-2}$	$-1/2c\sqrt{n(n-1)}$
$A_{n,n-1}$	$-1/\sqrt{c}\sqrt{n(n\mp 1/2)}$
$A_{n,n+1}$	$1/\sqrt{c}\sqrt{(n+1)(2n+2\mp 1/2)}$
$A_{n,n+3}$	$-1/\sqrt{c}\sqrt{(n+1)(n+2)(n+3)}$

III. COMPUTATIONAL DETAILS

An interactive program incorporating the analysis described above was written in Visual Basic. The program pro-

TABLE II. Lowest two eigenvalues of Eq. (4) for various basis sizes for $c=10$. All entries in cm^{-1} relative to $n_2=0+$. Vibrational levels labeled by inversion vibration quantum number n_2 and parity. Observations weighted by experimental uncertainties. Reference [15] gives $-615.020\,090\,902\,757\,816\,566\,22$ and $-615.020\,090\,902\,757\,816\,565\,01$, respectively.

N	E_0	E_1
20	$-615.020\,091\,024\,276$	$-615.020\,090\,894\,909$
25	$-615.020\,090\,941\,919$	$-615.020\,090\,952\,915$
30	$-615.020\,090\,904\,113$	$-615.020\,090\,905\,460$
35	$-615.020\,090\,902\,744$	$-615.020\,090\,902\,865$
40	$-615.020\,090\,902\,751$	$-615.020\,090\,902\,756$
45	$-615.020\,090\,902\,756$	$-615.020\,090\,902\,757$
50	$-615.020\,090\,902\,758$	$-615.020\,090\,902\,758$

vides for variable matrix (basis set) size; it also allows for a variety of potential forms and parameters, especially the quadratic of Eq. (2) and the harmonic oscillator+Gaussian barrier model. Routines for balancing and reducing the nonsymmetrical matrices and for the extraction of real eigenvalues were adapted from the FORTRAN recipes BALANCE, ELMHES, and HQR described in the standard work of Press *et al.* [20]. Nonsymmetrical matrices may have complex eigenvalues and care must be taken to avoid false identifications in any predicted results. For the purposes of determining the best values of parameters from the observed experimental data for NH$_3$ as reported here, a standard iterative damped linear least-squares fitting procedure was also implemented. Results are reported to the limit of double precision in machine accuracy (approximately 15 significant figures).

IV. NUMERICAL RESULTS AND DISCUSSION

In the first instance, the accuracy and performance of the approach outlined above were validated against previously published results obtained with other methods. A number of authors have calculated the eigenvalues of Eq. (2) for the equivalent of $c=10$ at increasing levels of precision, and we have chosen this value for initial testing. As shown in Table II, the lowest two eigenvalues converge to machine accuracy at a matrix dimension of 50, and no splitting is detectable at this level. In our method, of course, the ground-state tunneling splitting between positive- and negative-parity states is the difference between the lowest eigenvalues for H_+ and H_-, respectively. It is noteworthy that false splittings are calculated below convergence. These results agree with those presented by Balsa *et al.* [14] [to 12 significant figures (SF's)], Arias de Saavedra and Buendia [16] (16 SF's), Witwit and Killingbeck [17] (20 SF's), and Hodgson and Varshni [15] (23 SF's); moreover, the last of these confirmed that tunneling splitting is not observable until the 21st SF. However, the number of basis functions and the computation time required in our formulation are considerably smaller; the most accurate calculations of Hodgson and Varshni [15], for example, required 7–10 iterations of an infinite Taylor series expansion, while Witwit and Killingbeck [17] required a 25th-order perturbation expression.

A number of approximate formulas, usually based on WKB or perturbation approaches, have been advanced for the calculation of tunneling splittings. However, there does not seem to have been a systematic evaluation of these formulas against exact numerical calculations. According to the recent review of Garg [3], the splitting of the lowest pair of levels in terms of our parameter c is given by

$$\Delta E \propto c^{5/2} e^{-c^{3/2}/3}. \tag{10}$$

This form differs slightly from that given by Garg [3], who defines the Hamiltonian to contain $-d^2/dx^2$ rather than $-\frac{1}{2}d^2/dx^2$; moreover, we have eliminated the dependence on other factors (such as mass) to facilitate comparison with the results of other authors. We have calculated the splitting using our approach for various values of c, and these results are listed in Table III. In Fig. 2, we show results determined with the use of Eq. (10) as a function of the true values calculated as above. As the splittings calculated cover a range of 11 orders of magnitude, a log-log plot has been used. As may be observed, the correlation coefficient R^2 of this plot is 0.999 999 5 for values of $c^2 \geqslant 6$, for which a trend line has been plotted; deviations at smaller values of c^2 are clearly apparent in the inset of the figure. Evidently, then, the WKB formulation provides an excellent description of very small splittings, as expected, but cannot be applied to practical cases (such as that of NH$_3$ discussed below) where splittings are larger. A similar result comes from application of the instanton model Eq. (2) [3,8,9].

V. APPLICATION TO NH$_3$

There is a large body of experimental [21–24] and theoretical [2,7,25–29] work on the inversion doubling of the vibrational levels of NH$_3$ and its isotopic variants. Much of this work has focused on the determination of the height of the barrier to inversion and to the *ab initio* calculation of inversion potentials capable of reproducing all observed data. In the most recent investigations, Rajamaki, Miani, and Halonen [29] calculated a full six-dimensional potential energy surface (covering all vibrational modes) and were able to fit vibrational levels up to $4\nu_2$ for a range of isotopes with an average deviation of 4.64 cm^{-1}. These calculations confirmed the experimental evidence of extensive Fermi and Coriolis interactions, and are further complicated by coordinate dependence of the reduced mass for the inversion vibrational normal mode. Bearing these factors in mind, we have attempted to fit only the lower ($n_2 \leqslant 1$) vibrational levels for the five isotopic variants investigated, using a simple one-dimensional potential expression; it must be emphasized again that this is unlikely to reproduce higher-order effects. We modify the Hamiltonian (2) to feature explicitly the reduced mass μ and the two potential parameters described by Garg [3]:

$$H = -\frac{1}{2\mu}\frac{d^2}{dx^2} + \frac{V_0(x^2-c^2)^2}{c^4}. \tag{11}$$

Now the inversion barrier height is V_0, and the limiting single-well harmonic oscillator frequency is $\sqrt{8V_0/\mu c^2}$. The

TABLE III. Ground-state tunneling splitting for increasing c. All entries in cm^{-1} relative to $n_2=0+$. Vibrational levels labeled by inversion vibration quantum number n_2 and parity. Observations weighted by experimental uncertainties.

c^2	ΔE (this work)	ΔE [14]	ΔE [15]	ΔE [16]
1	2.176 883 196 929	2.176 883 196 93		2.176 883 196 928 590
2	1.575 242 049 577	1.575 242 049 58		
3	0.971 155 373 166			
4	0.462 427 958 058	0.462 427 958 06		
5	0.159 467 398 951	0.159 467 398 95	0.159 467 398 950 594	0.159 467 398 950 592
6	0.041 398 003 493			
7	0.008 652 983 823	0.008 652 983 82		
8	0.001 516 375 423			
9	0.000 227 908 229			
10	0.000 029 818 548	0.000 029 818 5		0.000 029 818 547 95
11	0.000 003 433 299			
12	0.000 000 350 848			
13	0.000 000 032 038			
14	0.000 000 002 630			
15	0.000 000 000 196	0.000 000 000 2		0.000 000 000 196 06
16	0.000 000 000 013			

reduced mass μ is dependent on the masses of the hydrogen atoms, m_H, and nitrogen atom, m_N, as well as the angle γ between the N-H bond and the threefold symmetry axis [30]:

$$\mu = \frac{3m_H\{m_N + 3m_H \sin^2(\gamma - 90\,°)\}}{m_N + 3m_H}. \tag{12}$$

It therefore varies during the inversion motion in a manner that depends on the definition of the inversion coordinate. For NH_3, for example, μ ranges between approximately 3.00 and 2.47 amu as γ runs from 0° to 90°. However, for the simple fitting of the lower levels described here, we have fixed μ at that calculated for the experimentally determined equilibrium value [31] of γ of 112.14°. With these limitations in mind, we found that the Hamiltonian (11) reproduces the experimental data shown in Table IV with a rms deviation of 2.6 times the experimental uncertainties (weightings have been set at 0.1 cm^{-1} for the ground-state splittings and 1 cm^{-1} for $n_2=1$). The barrier height V_0 was found to be 1984 cm^{-1}, with a standard deviation of 2 cm^{-1}, and the relative minimum separation c is 0.0721(1). Very little improvement was found on extending the potential to harmonic+Gaussian or any other form.

The most comparable analysis is the early work of Swalen and Ibers [6], who fitted all observed levels of NH_3 and ND_3 with a harmonic oscillator+Gaussian barrier. They found a potential barrier of 2020 cm^{-1}; for this same set of levels, we find a barrier of 2012 cm^{-1}. More recently, Spirko and Kraemer [32] have found isotope-dependent effective barriers varying between 2023 cm^{-1} for NH_3 and 1946 cm^{-1} for NT_3, using the so-called nonrigid invertor Hamiltonian (where the N-H bond length varies during the inversion motion) [21]. High-level *ab initio* calculations have generally predicted values within ±100 cm^{-1} of the rigid invertor (fixed N-H bond length) figure of 1874 cm^{-1} [29]. The results of the contracted Hamiltonian approach are very similar to those found using other methods, clear assurance of the validity of the approach in a practical sense.
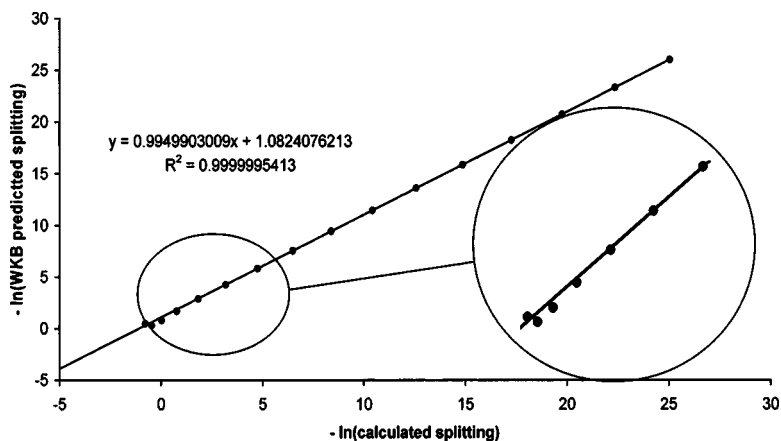

FIG. 2. Log-log plot of the ground-state tunneling splitting calculated using the WKB formula of Eq. (10) as a function of the true values of Table III. The correlation line shown is that for all but the lowest four values; note the deviation for large splittings at the lower end of the plot shown in the inset.

TABLE IV. Fitting of NH_3 vibrational energy levels with Hamiltonian (11). All entries in cm^{-1} relative to $n_2=0+$. Vibrational levels labeled by inversion vibration quantum number n_2 and parity. Observations weighted by experimental uncertainties.

Isotope	n_2	Obs.	Calc.	Obs.-Calc.	Weight
$^{14}NH_3$	0−	0.793	0.519	0.274	0.1
$^{14}NH_3$	1+	932.43	930.76	1.67	1.0
$^{14}NH_3$	1−	968.12	963.53	4.59	1.0
$^{14}ND_3$	0−	0.050	0.021	0.029	0.1
$^{14}ND_3$	1+	745.60	748.58	−2.98	1.0
$^{14}ND_3$	1−	749.15	750.72	−1.57	1.0
$^{15}NH_3$	0−	0.760	0.494	0.266	0.1
$^{15}NH_3$	1+	928.46	927.68	0.78	1.0
$^{15}NH_3$	1−	962.69	959.18	3.51	1.0
$^{14}NT_3$	0−	0.010	0.003	0.007	0.1
$^{14}NT_3$	1+	656.37	658.14	−1.77	1.0
$^{14}NT_3$	1−	657.19	658.47	−1.28	1.0
$^{15}ND_3$	0−	0.050	0.019	0.031	0.1
$^{15}ND_3$	1+	739.53	743.32	−3.79	1.0
$^{15}ND_3$	1−	742.78	745.26	−2.48	1.0

VI. DISCUSSION AND CONCLUSIONS

The results described above confirm that our approach based on a many-to-one homomorphic contraction of a Lie algebra yields valid and practical results for the calculation of energy levels arising from semirigid motions. The method illuminates fundamental philosophical puzzles (where do the elements of global symmetry not apparent in the Born-Oppenheimer picture of molecules go to?), as well as explicitly revealing the origin of energy level splittings through Eq. (4) and allowing for fast and accurate numerical calculation. We have also verified the form of the WKB approximation for very small tunneling splittings, and we have further shown that practical calculations such as the case of NH_3 are easily accomplished.

A number of questions remain. First, the full mathematical consequences and implications of the homomorphic contraction have yet to be explored. It may be that generalizations about the nature of the symmetry groups of molecules exhibiting nonrigid motion can be drawn from the homomorphic mapping. The homomorphism theorem states, for example, that the kernel of the contraction (those elements that map onto the identity of the contracted algebra and therefore do not appear explicitly in the rigid molecule picture) forms an invariant subalgebra of the total algebra. It has been observed by a number of authors, however, that the same statement cannot be made about the corresponding subgroup of the contracted group [33,34]. Second, it appears possible that recipes may be derivable for the determination of *all* possible homomorphically contracted algebras of a given Lie algebra. This would allow, for example, the prediction of all possible equilibrium symmetries derived from a given global symmetry, and permit generalization of the many-to-one mapping exemplified by [3]. While this may be done by inspection for simple systems, interest has recently focused on more exotic species such as the CH_5^+ ion, where possible equilibrium structures are less obvious.[35] Third, it would be useful to draw up simple and practical rules for the derivation of useful results such as nuclear spin statistical weights or spectroscopic selection rules akin to those of traditional rigid molecule point group theory. Finally, it is not obvious whether there are any unforeseen or novel issues relating to electron spin. The algebra of a single spin of $1/2$, for example, is $su(2)$ rather than the $so(3)$ of ordinary objects, and so it is possible that the contraction process will lead to different results. These and other questions will be explored in future work.

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