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FROM HARMONIC TO ANHARMONIC OSCILLATORS

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Abstract

The algebraic approach to quantum mechanics is briefly reviewed. The role of oscillator realizations is discussed. Applications to vibrations of complex molecules are presented.

1 Introduction

In recent years, a formulation of quantum mechanics, called algebraic theory, has been put forward, in which any quantum mechanical problem is mapped onto an algebraic structure following the logic scheme shown in Fig. 1.

Quantum Mechanical System

$\Downarrow$

Algebraic structure $\begin{cases} \text{Lie algebras} \\ \text{Graded Lie algebras} \\ \text{Infinite dimensional (Kac-Moody) algebras} \\ \text{q-deformed (Hopf) algebras} \\ \ldots \end{cases}$

$\Downarrow$

Observables $\begin{cases} \text{Energies} \\ \text{Transition rates} \\ \ldots \end{cases}$

$\Downarrow$

Experiment

Fig.1. Logic scheme of algebraic theory.

In implementing algebraic theory, it has been found to be very useful to make use of oscillator representations. In this contribution, I will briefly review the use of oscillators in algebraic theory.

2 Oscillators in ν dimensions

I begin with the (trivial) example of the one-dimensional harmonic oscillator. In the algebraic theory this case is described by the introduction of the Heisenberg algebra [1]

$$H(2) : \quad a,\ a^{\dagger},\ 1,\ a^{\dagger}a \tag{2.1}$$

Table I shows the parallelism between the usual treatment in terms of differential operators (Schrödinger equation) and the algebraic approach. This case is well known and does not require further explanation.

I consider instead the (non-trivial) example of the one-dimensional anharmonic Morse oscillator. The differential approach requires the solution of the eigenvalue problem

$$H\,\psi = E\,\psi \quad ,$$

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x) \quad ,$$

$$V(x) = D[1 - \exp(-\beta x)]^2 \quad . \tag{2.2}$$

The solution of the eigenvalue problem produces wave functions

$$\psi_v(x) = N_v\, z^{\eta - v}\, e^{-\frac{z}{2} + \frac{1}{2}x\beta}\, L_v^{2\eta-2v-1}(z) \tag{2.3}$$

where N_v is a normalization and $L(z)$ denotes a Laguerre polynomial. Also

Table I. Differential and algebraic treatment of the one dimensional harmonic oscillator.

Differential approach	Algebraic approach
$H = \frac{1}{2}(p^2 + x^2) =$	$a = \frac{1}{\sqrt{2}}(x + \frac{d}{dx})$
$= \frac{1}{2}\left[-\frac{d^2}{dx^2} + x^2\right]$	$a^\dagger = \frac{1}{\sqrt{2}}(x - \frac{d}{dx})$
$H\psi_n = E_n \psi_n$	$[a, a^\dagger] = 1$
	$H = (a^\dagger a + \frac{1}{2})$
$E_n = (n + \frac{1}{2})$	$E_n = (n + \frac{1}{2})$
$u_0(x) = \pi^{-\frac{1}{4}} e^{-\frac{1}{2}x^2}$	$\vert 0\rangle$
$u_n(x) = \left[\pi^{-\frac{1}{2}} 2^n n!\right]^{-\frac{1}{2}} (x - \frac{d}{dx})^n e^{-\frac{1}{2}x^2}$	$\vert n\rangle = (n!)^{-\frac{1}{2}} (a^\dagger)^n \vert 0\rangle$
$I_{nn'} = \int_{-\infty}^{+\infty} u_{n'}(x) f(x, \frac{d}{dx}) u_n(x)\, dx$	$I_{nn'} = \langle n'\vert f(a, a^\dagger)\vert n\rangle$

$$z = 2\eta\, e^{-\beta x} \quad ; \quad \eta = \frac{1}{\hbar\beta}\sqrt{2\mu D} \quad ; \quad v = 0, 1, \ldots, \eta - \frac{1}{2} \qquad (2.4)$$

The eigenvalues are

$$E(v) = 2\hbar\beta\sqrt{\frac{D}{2\mu}}\,(v+\tfrac{1}{2}) - \frac{1}{2}\frac{\hbar^2\beta^2}{\mu}(v+\tfrac{1}{2})^2 \quad . \tag{2.5}$$

The mass μ, strength of interaction D and range β have been put explicitly in Eqs. (2.2)-(2.5), while they were deleted in Table I.

In algebraic theory, the one-dimensional Morse oscillator can be dealt with by introducing [2] the Lie algebra U(2), composed of four elements F_+, F_-, F_0, N. The Hamiltonian can be written as

$$H = AC \quad ; \quad C = F_0^{\,2} - N^2 \quad , \tag{2.6}$$

where C is the Casimir operator of the O(2) subalgebra of U(2). The eigenvalues are

$$E(m) = A(m^2 - N^2) \quad , \ m = N, N-2, \ldots, 1 \text{ or } 0 \ (N\text{=odd or even}). \tag{2.7}$$

With the change of variable $v = (N-m)/2$ one has

$$E(v) = -\,4A(Nv - v^2) \quad ,$$
$$v = 0, 1, \ldots, \frac{N}{2} \text{ or } \frac{N}{2} - \frac{1}{2} \qquad (N\text{= even or odd}) \quad , \tag{2.8}$$

which are the eigenvalues of the Morse oscillator, Eq. (2.5). The eigenstates can be written as

$$\left|\begin{array}{ccc} U(2) & \supset & O(2) \\ \downarrow & & \downarrow \\ N & & v \end{array}\right\rangle \tag{2.9}$$

and intensities can be computed by taking matrix elements of operators

$$\langle N,v'|\hat{T}|N,v\rangle \tag{2.10}$$

As a result, all calculations for anharmonic oscillators can be done very easily.

An oscillator realization of U(2) is provided by the Jordan-Schwinger construction in terms of two boson operators σ, τ and their adjoints $\sigma^\dagger, \tau^\dagger$. The algebra is

$$U(2) : \tau^\dagger\sigma,\ \sigma^\dagger\tau,\ \tau^\dagger\tau,\ \sigma^\dagger\sigma \quad . \tag{2.11}$$

Incidentally, in the oscillator realization the harmonic oscillator appears as a contraction of the anharmonic oscillator, obtained by letting

$$\begin{aligned} &N \to \infty \quad , \quad N_\sigma \to \infty \quad , \\ &\tau^\dagger\sigma \to \sqrt{N_\sigma}\,\tau^\dagger \quad , \quad \sigma^\dagger\tau \to \sqrt{N_\sigma}\,\tau \quad , \\ &\tau^\dagger\tau \to \tau^\dagger\tau \quad , \quad \sigma^\dagger\sigma \to N_\sigma \quad . \end{aligned} \tag{2.12}$$

Thus, by adding one extra dimension (with the constraint N=const) one can treat, within the same framework, both harmonic and anharmonic oscillators. The anharmonic Morse oscillator in one dimension is related to the harmonic oscillator in two dimensions.

The same situation occurs in any number of dimensions. For example, in three dimensions, one introduces four boson operators [3,4]

$$\begin{aligned} &b^\dagger_\alpha = \sigma^\dagger \ , \ \pi^\dagger_\mu \ (\mu=0,\pm1) \quad ; \quad \alpha=1,\ldots,4 \quad ; \\ &b_\alpha = \sigma \ , \ \pi_\mu \ (\mu=0,\pm1) \quad ; \quad \alpha=1,\ldots,4 \quad ; \end{aligned} \tag{2.13}$$

divided into a scalar σ and a vector π_μ. The bilinear products $b^\dagger_\alpha b_\beta$ generate the Lie algebra U(4)

$$\mathcal{G}: \quad G_{\alpha\beta} = b^{\dagger}_{\alpha} b_{\beta} \quad . \tag{2.14}$$

The contracted form of U(4) is the oscillator algebra in three dimensions, H(4).

In three dimensions the situation is even richer than in one dimension, since the algebra of U(4) can be reduced in two ways:

$$U(4) \begin{array}{l} \nearrow \; U(3) \supset O(3) \supset O(2) \quad , \quad (I) \quad , \\ \searrow \; O(4) \supset O(3) \supset O(2) \quad , \quad (II) \quad , \end{array} \tag{2.15}$$

corresponding to spherical (I) and deformed situations (II). In one dimension we have

$$U(2) \begin{array}{l} \nearrow \; U(1) \\ \searrow \; O(2) \end{array} \quad , \tag{2.16}$$

but $U(1) \approx O(2)$ and therefore the spherical and deformed coincide.

It has been suggested [3] that in general any quantum mechanical problem in ν space dimensions can be written in terms of the unitary algebra $U(\nu+1)$. The harmonic oscillator in ν dimensions can be obtained from $U(\nu+1)$ by a limiting procedure leading to $H(\nu+1)$. The Heisenberg algebra $H(\nu+1)$ contains $U(\nu)$, the degeneracy algebra of the ν dimensional harmonic oscillator. The anharmonic oscillator and the deformed anahrmonic roto-oscillator can all be obtained from $U(\nu+1)$. These results allow one to do <u>anharmonic</u> analysis of spectral problems in a way as simple as that of <u>harmonic</u> analysis.

3 Coupled oscillators in ν dimensions

In most problems in physics, one often encounters coupled systems. In algebraic theory, the coupling of physical systems corresponds to the coupling of algebras. Oscillator realizations are particularly useful here and, as a simple example, I will discuss the case of coupled one-dimensional anharmonic oscillators. The algebraic structure of the system is the direct sum of the individual U(2) algebras

$$\mathcal{G} = \sum_{i=1}^{n} \oplus U_i(2) \quad , \tag{3.1}$$

where the sum extends over the number of oscillators, n. An oscillator realization can be done in terms of boson operators $\tau^\dagger_i$, $\sigma^\dagger_i$, τ_i, σ_i. Each algebra $U_i(2)$ is

$$U_i(2) : \tau_i^\dagger\sigma_i, \; \sigma_i^\dagger\tau_i, \; \tau_i^\dagger\tau_i, \; \sigma_i^\dagger\sigma_i \quad . \tag{3.2}$$

Coupled harmonic oscillators can be obtained as before by eliminating the σ_i bosons, as in Eq. (2.12).

In the last year, algebraic models of coupled anharmonic oscillators have been used extensively in order to provide a realistic description of the vibrations of complex molecules [5]. In general, the algebraic Hamiltonian of coupled oscillators is written as

$$H = \sum_{i=1}^{n} h_i + \sum_{i<j=1}^{n} V_{ij} \tag{3.3}$$

where

$$h_i = A_i \; C_i \tag{3.4}$$

The operators C_i are the Casimir operators of the $O_i(2)$ algebras and h_i has eigenvalues

$$\epsilon_i = A_i(m_i^2 - N_i^2) = -4A_i(N_i v_i - v_i^2) \tag{3.5}$$

The couplings V_{ij} depend on the problem under consideration. Two types of couplings are usually considered: (i) diagonal couplings (Casimir couplings) and (ii) non-diagonal couplings (Majorana couplings). In the product basis, labelled by the quantum numbers of each $U_i(2) \supset O_i(2)$ algebra, the matrix elements of the Casimir couplings are given by

$$\langle N_i v_i ; N_j , v_j \mid C_{ij} \mid N_i , v_i ; N_j , v_j \rangle = \\ = 4\left[(v_i+v_j)^2-(v_i+v_j)(N_i+N_j)\right] - \left(\frac{N_i+N_j}{N_i}\right)4\left[v_i{}^2-v_iN_i\right] - \left(\frac{N_i+N_j}{N_j}\right)4\left[v_j{}^2-v_jN_j\right] , \tag{3.6}$$

while the matrix elements of the Majorana couplings are given by:

$$\begin{aligned} &\langle N_i , v_i ; N_j , v_j \mid M_{ij} \mid N_i , v_i ; N_j , v_j \rangle = v_iN_j + v_jN_i - 2v_iv_j , \\ &\langle N_i , v_i+1 ; N_j , v_j-1 \mid M_{ij} \mid N_i , v_i ; N_j , v_j \rangle = - \sqrt{v_j(v_i+1)(N_i-v_i)(N_j-v_j+1)} , \\ &\langle N_i , v_i-1 ; N_j , v_j+1 \mid M_{ij} \mid N_i v_i ; N_j v_j \rangle = - \sqrt{v_i(v_j+1)(N_j-v_j)(N_i-v_i+1)} . \end{aligned} \tag{3.7}$$

As an example of application of these models consider the case of the benzene molecule, C_6H_6, (Fig.2).
This molecule has 12 atoms and thus $36-6=30$ independent vibrations. A conventional treatments of this molecule in terms of coupled differential equations is rather complicated. On the other side, an algebraic treatment is feasible, since the Hamiltonian, expressed in terms of algebraic operators, can be easily diagonalized.

In view of the hexagonal geometry of benzene, in the coupling terms $\sum_{ij}V_{ij}$, one can have three types of couplings: (I) first neighbor couplings, (II) second neighbor couplings and (III) third neighbor couplings. The algebraic Hamiltonian appropriate to benzene can be written as

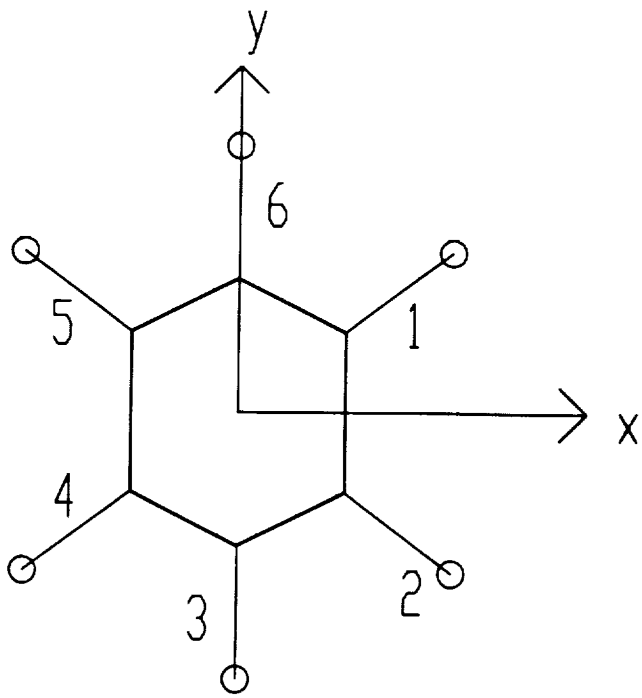

Fig.2. The benzene molecule.

$$H = A_H C + A_{HH} C' + \lambda_{HH}^{(I)} S^{(I)} + \lambda_{HH}^{(II)} S^{(II)} + \lambda_{HH}^{(III)} S^{(III)} , \quad (3.8)$$

where

$$A_i = A_{HH} \; ; \; A_{ij} = A_{HH} \; ; \; \lambda_{ij} = \lambda_{HH} ,$$

$$C = \sum_i C_i , \quad C' = \sum_{i<j} C_{ij} , \quad (3.9)$$

and the three operators $S^{(I)}$, $S^{(II)}$ and $S^{(III)}$ (called symmetry adapter operators) are given by:

$$S^{(I)} = \sum_{i<j} c'_{ij} M_{ij} , \quad S^{(II)} = \sum_{i<j} c''_{ij} M_{ij} , \quad S^{(III)} = \sum_{i<j} c'''_{ij} M_{ij} ,$$

$$c'_{12} = c'_{23} = c'_{34} = c'_{45} = c'_{56} = c'_{16} , \quad c'_{13} = c'_{24} = c'_{35} = c'_{46} = c'_{15} = c'_{26} = 0 , \quad c'_{14} = c'_{25} = c'_{36} = 0;$$

$$c''_{12}=c''_{23}=c''_{34}=c''_{45}=c''_{56}=c''_{16}=0, \quad c''_{13}=c''_{24}=c''_{35}=c''_{46}=c''_{15}=c''_{26}=0, \quad c''_{14}=c''_{25}=c''_{36}=0;$$

$$c'''_{12}=c'''_{23}=c'''_{34}=c'''_{45}=c'''_{56}=c'''_{16}=0, \quad c'''_{13}=c'''_{24}=c'''_{35}=c'''_{46}=c'''_{15}=c'''_{26}=0,$$

$$c'''_{14}=c'''_{25}=c'''_{36}=1 \quad . \tag{3.10}$$

It is important to note that the use of algebraic oscillator realizations solves another crucial problem in the theory of molecules, that is the construction of states that transform according to irreducible representations of point groups (For C_6H_6, the point group is $\mathcal{D}_{6h}$). For this reason the operators $S^{(I)}$, $S^{(II)}$ and $S^{(III)}$, whose diagonalization produces states that transform as irreducible representations, have been called symmetry adapter operators [5,6]. The role of these operators in the representation theory of finite groups will be discussed elsewhere [7]. They can be constructed for any finite group and provide an oscillator (or boson) realization of finite groups (a new and very important mathematical result).

The algebraic Hamiltonians (3.8) allow one to do anharmonic analysis of molecular vibration spectra. One determines the coefficients A_H, A_{HH}, $\lambda^{(I)}{}_{HH}$, $\lambda^{(II)}{}_{HH}$ and $\lambda^{(III)}{}_{HH}$ from some known energies and then computes all the others. This procedure can be applied not only to the molecule C_6H_6, but also to all other molecules obtained by replacing the hydrogen atoms with deuterium atoms [8]. Table II shows some calculated frequencies and infrared intensities in C_6H_6 and C_6D_6. This Table, reproduced from Ref. [8], is shown here as an example of the power of the method which allows a simultaneous calculation of all frequencies and infrared intensities of many molecules. One must note that this is still a small portion of the complete spectrum of benzene, since it describes only the so-called stretching vibrations in which the hydrogen atoms move in a radial direction relative to the carbon skeleton. (Vibrational modes v_7, v_{13}, v_{20} and v_2 in Wilson notation)[8]. A calculation of all the other modes and their combinations has been performed and will appear soon [9].

Table III shows a partial comparison of the calculation with experiment. One may note the close agreement not only for the fundamental vibrations (n=1) but also for the overtones (n=2, n=3). This agreement originates from the use of anharmonic oscillators. Had one used harmonic oscillators the expected frequencies of the n=2 and n=3 modes would have been respectively twice and three

TABLE II. Calculated frequencies[a] and infrared intensities[b] in C_6H_6 and C_6D_6.

	C_6H_6			C_6D_6		
	symm	computed energy	computed IR int.	symm	computed energy	computed IR int.
	$E_{2g}(v_7)$	3056.91		$E_{2g}(v_7)$	2272.03	
n=1	$B_{1u}(v_{13})$	3057.51		$B1_u(v_{13})$	2284.62	
	$E_{1u}(v_{20})$	3065.13	0.16(+2)	$Elu(v_{20})$	2288.94	0.64(+1)
	$A_{1g}(v_2)$	3073.96		$A_{1g}(v_2)$	2303.20	
	A_{1g}	6004.04		A_{1g}	4494.02	
	E_{1u}	6004.40	0.10(+1)	E_{1u}	4497.19	0.42(+0)
	E_{2g}	6004.92		E_{2g}	4497.55	
	B_{1u}	6005.10		B_{1u}	4498.21	
	A_{1g}	6109.49		E_{2g}	4550.04	
	E_{2g}	6110.93		A_{1g}	4556.93	
n=2	E_{1u}	6113.02	0.17(-2)	E_{1u}	4557.10	0.65(-3)
	B_{2u}	6117.07		B_{2u}	4559.26	
	A_{1g}	6118.94		A_{1g}	4571.15	
	E_{2g}	6121.24		E_{2g}	4572.49	
	B_{1u}	6123.40		E_{2g}	4575.46	
	E_{2g}	6125.35		B_{1u}	4579.11	
	E_{1u}	6128.15	0.60(-2)	E_{1u}	4582.29	0.15(-1)
	A_{1g}	6139.40		A_{1g}	4600.31	

[a]All values in cm^{-1}; [b]All values in 10^6 barns/cm.

TABLE III. Experimental frequencies[a] and infrared intensities[b] in C_6H_6 and C_6D_6.

C_6H_6

	Energy				IR Intensity	
	symm.	calc.	obs.	obs-calc	calc.	obs.
	$E_{2g}(v_7)$	3056.91	3056.6	-0.31		
	$B_{1u}(v_{13})$	3057.51	3057	-0.51		
n=1	$E_{1u}(v_{20})$	3065.13	3064.367[c]	-0.763	0.16(+2)	0.16(+2)
	$A_{1g}(v_2)$	3073.96	3073.94	-0.02		
n=2	E_{1u}	6004.40	6006	1.60	0.10(+1)	0.58(+0)
n=3	E_{1u}	8827.53	8827	-0.53	0.51(-1)	0.35(-1)

C_6D_6

	Energy				IR Intensity	
	symm.	calc.	obs.	obs-calc	calc.	obs.
	$E_{2g}(v_7)$	2272.24	2272.5	0.26		
n=1	$B_{1u}(v_{13})$	2284.83	2285	0.17		
	$E_{1u}(v_{20})$	2289.14	2289.3	0.16	0.64(+1)	0.64(+1)
	$A_{1g}(v_2)$	2303.41	2303.44	0.03		
n=2	E_{1u}	4497.60	4497	-0.60	0.42(+0)	0.42(+0)
n=3	E_{1u}	6643.81	6644	0.19	0.22(-1)	0.22(-1)

[a]All values in cm^{-1}; [b]All values in 10^6 barns/cm; [c]deperturbed value.

times those of the fundamental, in disagreement with experiment.

4 Summary

In summary, algebraic theory is an expansion of all operators of physical interest into elements of an algebra, $\mathcal{G}$. For example, the Hamiltonian H can be expanded as

$$H = E_0 + \sum_{\alpha\beta} \epsilon_{\alpha\beta} G_{\alpha\beta} + \frac{1}{2} \sum_{\alpha\beta\gamma\delta} u_{\alpha\beta\gamma\delta} G_{\alpha\beta} G_{\gamma\delta} + \dots$$

$$G_{\alpha\beta} \in \mathcal{G} \quad . \tag{4.1}$$

In implementing algebraic theory an oscillator realization is often useful. The elements of $\mathcal{G}$ are then constructed from boson creation and annihilation operators

$$b_\alpha^\dagger \ , \ b_\alpha \qquad , \qquad \alpha = 1,\dots,\nu+1 \quad . \tag{4.2}$$

The bilinear products

$$G_{\alpha\beta} = b_\alpha^\dagger b_\beta \quad , \tag{4.3}$$

generate the Lie algebras U(ν+1). Within this algebra one can describe both harmonic and anharmonic situations (and isotropic and anisotropic situations).

The oscillators (and algebras) can be coupled. The expansion of the operators is now in terms of the direct sum of algebras $\mathcal{G}_i$,

$$\mathcal{G} = \sum_i \oplus \mathcal{G}_i \quad . \tag{4.4}$$

The oscillator realization is in terms of boson operators

$$b^{\dagger}_{\alpha i} \quad , \quad b_{\alpha i} \qquad ; \ \alpha = 1,\ldots,\nu+1 \quad ; \quad i = 1,\ldots,n \quad . \tag{4.5}$$

The index α provides a treatment of continuous symmetries (space index). The index i provides a treatment of discrete symmetries (oscillator index).

5 Conclusions

Algebraic theory is a powerful tool to deal with complex spectroscopic problems. Oscillator realizations of this theory have proven to be very useful in the analysis of several physical situations. In particular, the extension of harmonic to anharmonic analysis has led to a new and deeper understanding of the spectra of complex molecules.

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References

1. For a review, see, B.G. Wybourne, "Classical Groups for Physicists", J. Wiley and Sons, New York, 1974, p. 286.
2. See, Y. Alhassid, F. Gürsey and F. Iachello, Ann. Phys. (N.Y.) **148**, 346 (1983).
3. F. Iachello, Chem. Phys. Lett. **78**, 581 (1981).
4. F. Iachello and R.D. Levine, J. Chem. Phys. **77**, 3046 (1982).
5. F. Iachello and S. Oss, Phys. Rev. Lett. **66**, 2976 (1991); Chem. Phys. Lett. **187**, 500 (1991).
6. A. Frank and R. Lemus, Phys. Rev. Lett. **68**, 413 (1992).
7. F. Iachello, to be published.
8. F. Iachello and S. Oss, J. Mol. Spectrosc. **153**, 225 (1992).
9. F. Iachello and S. Oss, to be published.