CORRELATION DIAGRAM FOR RIGID AND NONRIGID THREE-BODY SYSTEMS

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We consider the relation between energy level patterns of rigid structures and those of systems in which the particle motions are uncorrelated. Defining an ideal model system of the non-rigid limit for N identical particles, we exhibit the correlation diagram connecting this limit to an ideal rigid system for $N = 3$. States of the two limits are related in a simple manner. Vibration—rotation levels for three identical spin-0 and spin-1/2 particles are classified explicitly, according to their quantum numbers in both limits.

Several problems in chemical physics press us to understand the pattern of vibration—rotation energy levels in semi-rigid structures: the spectra of "fluxional" molecules (both conventional species such as PF_5 and van der Waals molecules such as the HF dimer), and the energy level density patterns in condensation nuclei as a function of the number of particles in the cluster are two obvious examples. It would be helpful if we could relate the pattern of vibration—rotation energy levels to the degree of rigidity or nonrigidity of an n-body system. Calculations of specific systems have been carried out, based on model potentials [1,2], toward a general formulation of that problem. We present a method to construct an energy level correlation diagram between two limiting structures. One is a nearly-rigid polyhedron, thoroughly described by the conventional picture of a molecule undergoing rigid-body rotations and small-amplitude vibrations. The other limit is a cohesive system of independent particles, like a liquid drop model. The abscissa of the correlation diagram corresponds to a variable parameter as yet unspecified, measuring the degree of rigidity. (The selection of the parameter will be discussed in later communications.) The principle of our approach is to idealize both limits in ways that raise their symmetry by putting aside all non-essential differences among levels — these idealized high-symmetry conditions can always be removed by well-known conventional methods — and then connecting the two high-symmetry limits by the established rules connecting representations of related groups. In this report, we apply the method to the simplest nontrivial case, the three-body problem.

The Hartree—Fock model obviously describes the independent particle limit. Small deviations from independent particle motion may be treated by well-known procedures such as configuration interaction or many-body perturbation theory. Deviations from rigid molecule behavior may be treated by the method of Dalton [3]. This method and its natural extensions assume that different permutational and chiral isomers or different geometries transform among themselves by large-amplitude motions, which have frequencies low compared to vibrational and rotational frequencies of the molecule in its center of mass.

We idealize the non-rigid limit to be a system of N identical particles with pairwise attractive harmonic interactions, so that

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N} K(r_i - r_j)^2 . \tag{1}$$

In the center of mass frame this hamiltonian can be rearranged to give $(3N - 3)$ degenerate normal modes [4]. The symmetry group is known to be $SU(3N - 3)$ [5], and the eigenfunctions are bases for irreducible representations of $SU(3N - 3)$ which are symmetric under permutations of oscillator quanta. The degeneracy of the level with ν quanta in n oscillators is [6]

$$g_\nu = (n + \nu - 1)!/\nu!(n - 1)! . \tag{2}$$

One may correlate states of this highly symmetric oscillator model to systems with lower symmetry subject to the kinematic requirement of definite orbital angular momentum J, parity π, and permutational symmetry Γ_N^i. For enumerating states of given L and Γ_N^i in a particular level, the chain

$$SU(3N - 3) \supset SU(3) \times SU(N - 1)$$

is convenient [5], since SU(3) has O(3) as a subgroup and SU($N - 1$) has the permutation group as a subgroup. The symmetry of the SU($3N - 3$) model may be broken according to this chain or any other deemed applicable to an actual physical system. The nature of the correlation in a several-body system can be inferred from comparison of the actual spectrum with the patterns associated with alternative symmetry-breaking schemes and their associated subgroup chains of SU($3N - 3$). Here we do not investigate slight breaking of SU($3N - 3$) but treat the correlation to the rigid limit for $N = 3$, the triangular molecule.

For the SU(6) oscillator model for 3 particles,

Table 1
Decomposition of SU(6) non-rigid limit states under O(3) and S_3. The three left columns give the number of quanta ν, the parity π, and the degeneracy g_ν of each energy level up to $\nu = 8$. The upper integer in each entry in the main table is $g_{\nu J} = n\Gamma_3^S + n\Gamma_3^A + 2n\Gamma_3^M$; the lower triplet is $n\Gamma_3^S$, $n\Gamma_3^A$, $n\Gamma_3^M$, where S, A, M refer to symmetric, antisymmetric, and mixed under S_3, so $g_3 = 56 = 3 \times 6 + 5 \times 2 + 7 \times 4 = \Sigma_J (2J + 1)g_{3,J}$. The "staircases" partition the states into sets which correlate in fig. 1 to rovibrational manifolds built on ideal rigid limit vibrational levels α. States labelled e and o correlate to even and odd values of $|K|$

ν	π	g_ν	J=0	J=1	J=2	J=3	J=4	J=5	J=6	J=7	J=8
0	+	1	1e 1,0,0								
1	−	6		2o 0,0,1							
2	+	21	3e 1,0,1	1e 0,1,0	3e 1,0,1						
3	−	56		6o 1,1,2	2o 0,0,1	4o 1,1,1					
4	+	126	6e 2,0,2	3e 0,1,1	9e 2,1,3	3e 0,1,1	5e 1,0,2				
5	−	252		12o 2,2,4	6o 1,1,2	12o 2,2,4	4o 1,1,1	6o 1,1,2			
6	+	462	10e 3,1,3	6e 0,2,2	18e 4,2,6	9e 1,2,3	15e 3,2,5	5e 0,1,2	7e 2,1,2		
7	−	792		20o 3,3,7	12o 2,2,4	24o 4,4,8	12o 2,2,4	18o 3,3,6	6o 1,1,2	8o 1,1,3	
8	+	1287	15e 4,1,5	10e 1,3,3	30e 6,4,10	18e 2,4,6	30e 6,4,10	15e 2,3,5	21e 4,3,7	7e 1,2,2	9e 2,1,3
			α_{-4}		α_{-3}		α_{-2}	α_{-1}		α_{-0}	

table 1 gives degeneracies up to $\nu = 8$ and the number of times given values of L and Γ_3^i occur within each level. This much information was first presented in a table in a paper by Karl and Obryk [7]. We also give the parity $\pi = (-1)^\nu$. This table has several striking regularities, which are exploited below and which will be discussed fully in a separate publication.

As the rigid limit it is useful to focus on the vibrating equilateral triangle top, at first in the circumstance in which all three normal modes are degenerate. The D_{3h} symmetry of the equilateral triangle requires degeneracy of only two normal modes, and our temporary assumption of triple degeneracy will be realized only for special molecular hamiltonians which may be considered "ideal". The condition for triple degeneracy is that the vibrational secular polynominal and its first two derivatives be zero simultaneously; for the general equilateral triangle, only the first two derivatives are zero at one of the roots. The left side of fig. 1 indicates the correlation from the ideal system to the general case. Further correlation to isosceles or scalene triangle geometry may be done according to the methods of ref. [3].

The spectrum consists of rovibrational states specified by α, J, and $|K|$, denoting the number of vibrational quanta, angular momentum, and its projection along the symmetry axis. The equilateral triangle is an oblate symmetric top with energy levels dependent on $|K|$. For convenience in the following, we ignore this $|K|$ dependence with no loss of generality. With these assumptions the energy of the (α, J) level is given by

$$E_{\alpha J} = \kappa(n + 1/2) + AJ(J + 1) \qquad (3)$$

and the degeneracy by

$$g_{\alpha J} = [(\alpha + 2)!/2\alpha!] \ (2J + 1)^2 . \qquad (4)$$

Eq. (4) is obtained using eq. (2) with $\nu = 3$, bearing in mind eq. (3) and the degeneracy of a spherical top with respect to space-fixed as well as body-fixed axes [8]. Table 2 enumerates the occurrence of J^π and Γ_3^i for rovibrational levels (α, J). States labelled e and o are those with even and odd values of $|K|$. This information is determined according to the methods in ref. [9].

Fig. 1 shows schematically the correlation of rigid and non-rigid limits for the states contained in tables 1 and 2. The correlation is subject to preservation of definite values of J^π and Γ_3^i. We note the very simple
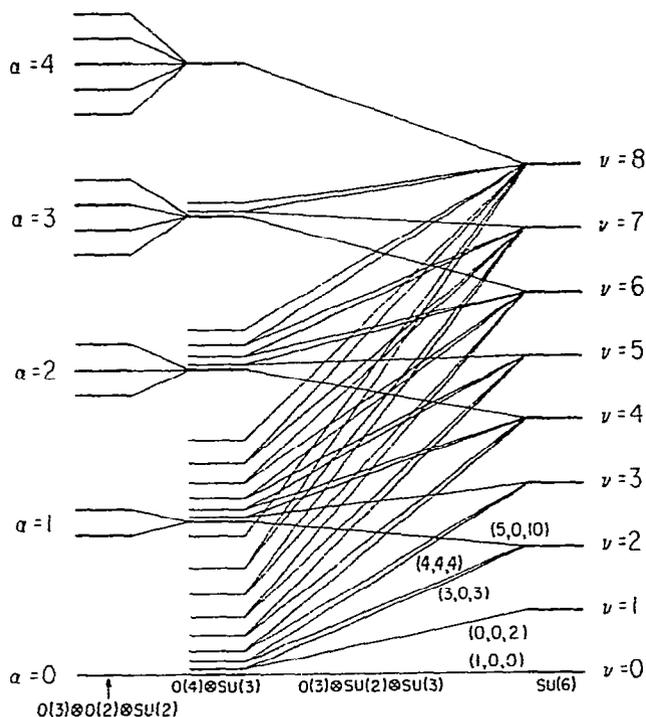
Fig. 1. Correlation diagram for three particles from nonrigid to rigid limits. The spectrum at the extreme right is that of the SU(6) nonrigid limit. The states are correlated to the "ideal" rigid limit spectrum in the middle. The decomposition of some of the states under S_3 is indicated in parentheses. At the extreme left is the set of levels of the general equilateral triangle (only rotational ground state levels are shown) in which only two of the normal modes of vibration are degenerate. The group designations at the bottom of the figure indicate the symmetry appropriate to each region of the correlation diagram.

Table 2

Decomposition of ideal rigid limit states under O(3). Rovibrational levels (α, J) of the ideal rigid limit built on vibrational levels with α quanta up to $(\alpha, J) = (4, 8)$ appear between horizontal lines. Each integer gives the number of occurrences of the J heading the column in a level (α, J). States are labelled e and o according to whether $|K|$ is even or odd. States within one diagonal band correlate as in fig. 1 to non-rigid limit levels having a common value of v. Thus states 6o, 2o, 4o correlate to the level $v = 3$ with $g_v = 56$ of table 1. Decomposition of states under S_3 may be inferred from reference to table 1. Only those states contained in table 1 are partitioned into diagonal bands

	J=0	J=1	J=2	J=3	J=4	J=5	J=6	J=7	J=8
α=0	1e	2o	3e	4o	5e	6o	7e	8o	9e
		1e	2o	3e	4o	5e	6o	7e	8o
α=1	3e	6o	9e	12o	15e	18o	21e	24o	27e
		3e	6o	9e	12o	15e	18o	21e	24o
α=2	6e	12o	18e	24o	30e	36o	42e	48o	54e
		6e	12o	18e	24o	30e	36o	42e	48o
α=3	10e	20o	30e	40o	50e	60o	70e	80o	90e
		10e	20o	30e	40o	50e	60o	70e	80o
α=4	15e	30o	45e	60o	75e	90o	105e	120o	135e

correspondence between states of the two limits. In table 1, all non-rigid oscillator model states in the same diagonal "staircase" correlate to rotational states of the triangle limit built on a single vibrational level α. States of the non-rigid limit labelled e and o correlate to rigid limit states with even and odd values of $|K|$. On the other hand, rigid limit states within each diagonal band of table 2 correlate to a single degenerate oscillator model level v.

In comparing the spectrum of a three-body system with fig. 1 it must be remembered that the only allowed states are those which satisfy Bose or Fermi statistics when both orbital and spin degrees of freedom are taken into account. This restriction may be treated by the standard methods of ref. [8]. For identical spin-0 bosons only the symmetric representations of

S_3 appearing in table 1 are allowed. Three spin-1/2 fermions form an 8-dimensional representation $4S + 2M$ of S_3 (the total spin 3/2 quartet forms the $4S$ and each spin 1/2 doublet forms an M). The allowed states are the A representations from the direct product orbital-spin basis. This information for non-rigid limit boson and fermion systems is presented in tables 3 and 4. The corresponding information for rigid limit states may be determined in the same way.

The introduction of the idealized SU(3N − 3) and O(4) systems simplifies the construction of the correlation diagram, yet allows the pattern to be made more realistic by the introduction of further symmetry-breaking, as, for example, on the left side of fig. 1. To interpret the spectra of real nonrigid molecules, such as the (presumably stable) rare gas triatomics or HCl—Ar, we can use perturbation theory to lower the symmetry of the idealized model at any point along the correlation diagram, or, at the rigid limit, reduce the symmetry group by conventional methods. Symmetry groups are not known for n-body nonrigid clusters, except when the potentials are all pairwise-harmonic, so we cannot carry out such reductions at the nonrigid

Table 3
Allowed non-rigid limit states for identical spin-0 particles.
The integers give the occurrences of a given J for spin-0 particles,
when the statistics of the total wavefunction is taken into account. Here J refers to orbital angular momentum

v	$J=0$	$J=1$	$J=2$	$J=3$	$J=4$	$J=5$	$J=6$	$J=7$	$J=8$
0	1								
1	0	0							
2	1	0	1						
3	0	1	0	1					
4	2	0	2	0	1				
5	0	2	1	2	1	1			
6	3	0	4	1	3	0	2		
7	0	3	2	4	2	3	1	1	
8	4	1	6	2	6	2	4	1	2

Table 4
Allowed non-rigid limit states for identical spin-1/2 particles.
The integers give the occurrences of a given J for spin-1/2
particles, when the statistics of the total wavefunction is
taken into account. Here J refers to orbital angular momentum.
Spin—orbit interaction is neglected

v	$J=0$	$J=1$	$J=2$	$J=3$	$J=4$	$J=5$	$J=6$	$J=7$	$J=8$
0	0								
1	0	2							
2	2	4	2						
3	0	8	2	6					
4	4	6	10	6	4				
5	0	16	8	16	6	8			
6	10	12	20	14	18	8	8		
7	0	26	16	32	16	24	8	10	
8	14	18	36	28	36	22	16	12	10

limit. We can, however, take into account the possibility that the force constants or effective masses differ among the harmonic interactions, by reducing the symmetry from SU($3N - 3$) to a product of SU(M) groups, with the sum of all M's adding to $3N - 3$.

Several questions are raised by our findings. One might hope to find a cogent mathematical formulation of the numerical regularities in tables 1 and 2 and the simple relation between them. Equally tantalizing is the elucidation of the relation, if any, between nuclear vibrational and rotational collective motion in nuclear shell theories such as the Elliott model [10], and that of rigid molecule systems. Finally, the extension of our procedure to systems with $N > 3$ will introduce new complications. In three dimensions, molecules with $N > 3$ have permutational and chiral isomers, since their permutation-inversion groups are larger than their point groups. Therefore the correlation between rigid and non-rigid limits is more complicated than in the case discussed here, and will depend on the dynamics (through the Dalton Q-group) [3], not only on the geometry of the rigid limit.

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