

The Parity of Rotational Levels

TAKESHI OKA

Division of Physics, National Research Council of Canada, Ottawa, Ontario, Canada

The parity of rotational levels of polyatomic molecules is discussed by using the permutation-inversion group of Longuet-Higgins.

1. INTRODUCTION

Together with the quantum number F for the total angular momentum, the parity, which specifies the symmetry of a wavefunction with respect to space inversion, is a rigorous quantum number for a molecule in free space. This is because the symmetry leading to these quantum numbers is based on properties of space rather than of molecules.

The parity of rotational levels for diatomic molecules has been well discussed and used in the theory of various molecular interactions (1, 2, 3). However, for polyatomic molecules this is not sufficiently done. The only references, to the author's knowledge, in which the parity of polyatomic molecules is discussed or used extensively are the text book by Herzberg (4) and that by Landau and Lifshitz (5). In the present paper the parity of rotational levels of polyatomic molecules will be discussed by using the permutation-inversion group of Longuet-Higgins (6). The results are the same as those of Landau and Lifshitz (5) but we believe the logic used in the derivation of parity is clearer. We limit the discussion to the rotational levels in a totally symmetric vibronic state because the extension to other states is straightforward. Also, up to Section 4, we consider only "rigid" molecules, rigid in the sense that the nuclear displacements from the equilibrium positions are small compared with internuclear distances.

2. MOLECULES (I)

Using the permutation-inversion group, "rigid" molecules are classified into three categories: molecules (I) for which the group includes the inversion operator E^* ; molecules (II) for which the group does not include E^* but includes permutation-inversion operations [such as $(12)^*$]; and molecules (III) for which the group does not include sense reversing operations at all. The molecules (III) possess stereoisomers and the discussion of parity is irrelevant for them (5).

The molecules (I) comprise all linear and planar molecules. The assignment of parity for this type of molecules is simple and is given in Herzberg's books (4). By using the permutation-inversion group, the rotational levels are classified according to irreducible representations; then the symmetry with respect to E^* gives the parity of the level.

The E^* operation is equivalent to a plane reflection of vibronic variables in a molecule-fixed coordinate system and 180° rotation around the axis perpendicular to the plane (1, 7); therefore, the parity of rotational levels of molecules (I) in a totally symmetric vibronic state is determined by whether the angular momentum quantum number along the axis which is perpendicular to the plane of reflection is even or odd. Thus for a linear molecule the parity is even or odd according to $(-1)^J$, and for a planar asymmetric top molecule, for which the rotational levels are specified by $J_{K_a K_c}$, the parity is determined by $(-1)^{K_c}$ regardless of J and K_a .

3. MOLECULES (II)

The molecules (II) comprise all "rigid" molecules except linear and planar molecules and molecules with stereoisomers. Since a permutation-inversion operation [such as (12)*] simultaneously permutes nuclei and inverts space, the discussion of parity for this type of molecules is interwoven with that of spin symmetry. When Longuet-Higgins says that the exclusion principle is non-committal about the permutation-inversion operations such as (12)* since they do not *merely* permute identical nuclei, the parity consideration is lost. Since space inversion is a rigorous symmetry operation on the total wavefunction, we can extend Longuet-Higgins' treatment and consider the operation of (12)* (or any odd permutation of fermions plus inversion) on the total wavefunction.

A total wavefunction corresponding to + parity changes sign under an odd permutation of fermions plus inversion, whereas that corresponding to - parity does not change sign. The reverse is the case for bosons. When this consideration is introduced, we can assign parity to rotational levels.

As an example of molecules (II), let us consider the CH_4 molecule. The molecule has a group of 24 permutation-inversion operations E , $8(123)$, $3(12)(34)$, $6(1423)^*$, and $6(12)^*$. According to Longuet-Higgins (6) the symmetry of the total wavefunction has to be considered by applying the Pauli principle to the first three classes of operations E , $8(123)$ and $3(12)(34)$, but the operations $6(1423)^*$ and $6(12)^*$ are noncommittal; the total wavefunction then has to be of either A_1 or A_2 symmetry. However, the extension of Longuet-Higgins' treatment introduced in this paper indicates that we can consider the operation of $6(1423)^*$ and $6(12)^*$ on the total wavefunctions and obtain the following results: *the total wavefunction is of either A_2 symmetry with + parity or of A_1 symmetry with - parity.* This statement about the total wavefunction is rigorous.

In order to assign the parity on individual rotational levels we consider the symmetry of rovibrational wavefunctions, which for CH_4 are classified into A_1 , A_2 , E , F_1 , and F_2 species (8, 4, 5, 9). The classification of rotational levels according to the symmetry of the rovibrational wavefunction is not rigorous when nuclear spin-rotation interaction is considered. However, since the magnitude of nuclear spin-rotation interaction is very small it gives a good approximation. In fact the usefulness of the permutation-inversion group for classifying rovibronic symmetry is based on the very fact that such nuclear spin interaction is very small so that we can consider operations on the coordinate part and on the spin part separately to a good approximation. Using the symmetry of the spin wavefunction which is expressed as $5A_1 + E + 3F_2$ (8, 11) and the underlined statement given above, we find that the A_1 and F_2 rotational levels of CH_4 correspond to - parity and the A_2 and F_1 rotational levels correspond to + parity. The E levels

Table I. Parity of Rotational Levels of "Rigid" Molecules (II)

Symmetry	Example	Total Wavefunction	Spin Wavefunction ^b	Parity ^a	Lowest Level ^a
C _s	PH ₂ D	+A", -A'	3A' +A"	+ A' (A"), A" (A') - A' (A'), A" (A")	+(A"), -(A')
C _{2v}	CH ₂ F ₂	+A ₂ , -A ₁	6A ₁ +4A ₂ +3B ₁ +3B ₂	+ A ₁ (A ₂), A ₁ (A ₁), B ₁ (B ₂), B ₂ (B ₁) - A ₁ (A ₁), A ₂ (A ₂), B ₁ (B ₁), B ₂ (B ₂)	+(A ₂), -(A ₁)
C _{3v}	CH ₃ F	+A ₂ , -A ₁	4A ₁ +2E	+ A ₂ , -A ₁ , ±E	-(A ₁)
	CD ₃ F	+A ₁ , -A ₂	10A ₁ +A ₂ +8E	+ A ₁ (A ₁), A ₂ (A ₂), -A ₁ (A ₂), A ₂ (A ₁), ±E	+(A ₁), -(A ₂)
C _{4v}	XeOF ₄	+B ₂ , -B ₁	6A ₁ +3B ₁ +B ₂ +3E	+ A ₁ (B ₂), A ₂ (B ₁), B ₁ (A ₂), B ₂ (A ₁) - A ₁ (B ₁), A ₂ (B ₂), B ₁ (A ₁), B ₂ (A ₂) ± E	+(B ₂), -(B ₁)
D _{2d}	H ₂ C=C=CH ₂	+B ₁ , -A ₁	6A ₁ +B ₁ +3B ₂ +3E	+ A ₁ (B ₁), A ₂ (B ₂), B ₁ (A ₁) - A ₁ (A ₁), B ₁ (B ₁), B ₂ (B ₂), ±E	+(B ₁), -(A ₁)
T _d	CH ₄	+A ₂ , -A ₁	5A ₁ +3F ₂ +E	+ A ₂ , F ₁ , -A ₁ , F ₂ , ±E	-(A ₁)
	CD ₄	+A ₁ , -A ₂	15A ₁ +6E+3F ₁ +15F ₂	+ A ₁ , F ₁ (F ₁), F ₂ (F ₂), -A ₂ , F ₁ (F ₂), F ₂ (F ₁), ±E	+(A ₁)

(a) The symmetry species in the parentheses indicate symmetry of spin wavefunctions.

(b) Spin weight factors arising from the nuclei which are not involved in permutation symmetry are excluded.

correspond to doubly parity ± because E × E has both A₁ and A₂. This assignment of parity is already given by Landau and Lifshitz (5).

Hougen (12) has discussed the symmetry of rotation-inversion levels of "tunneling" CH₄ using a larger symmetry group in which the E* operation appears explicitly. For such a group the assignment of parity is straightforward as in molecules (I); however, it should be noticed that the unique assignment of parity is possible even if the tunneling is not considered.

The parity is assigned to rotational levels of other molecules (II) in a similar fashion; it is summarized in Table I. The extension of Table I to other molecules and molecules with other nuclei is straightforward. In addition to the space inversion which leads to the parity labels, permutations of identical nuclei are also rigorous symmetry operations. However, since the Pauli exclusion principle has to be satisfied by a total wavefunction, only one species in the classification by using pure permutation operations is allowed. Therefore a total wavefunction is always one of the two species which have the same symmetry for pure permutations but different symmetry for sense reversing operations and thus combine with different parity. When the nuclear spin wavefunction (which has always + parity) has only one of the two species allowed for the total wavefunction (as in CH₃F, CH₄, and CD₄), unique parity is assigned to all non-doubly degenerate levels. If the nuclear spin wavefunction has both species (as in CD₃F, CH₂F₂, XeOF₄, and H₂C=C=CH₂), each rotational level has double parity. However, each parity is assigned to levels with different nuclear spin wavefunctions; therefore, when the nuclear hyperfine structure is resolved under high resolution each component has unique parity. For all the molecules in Table I the doubly degenerate E levels have double parity. However, again under very high resolution, they are split into two components with opposite parity as a result of off-diagonal spin-rotation interaction.

4. NONRIGID MOLECULES

The parity is a good quantum number also for nonrigid molecules; the assignment of parity to levels can be done by using permutation-inversion groups. There are nonrigid molecules (I) such as H_2O_2 , NH_3 (4), NH_2NH_2 (6), CH_4 (12), etc., whose permutation-inversion groups contain E^* when internal rotation or inversion of molecules is considered feasible. For these molecules the assignment of irreducible representations to the levels immediately gives the parity of levels. On the other hand, for nonrigid molecules (II) such as CH_3OH , CH_3NH_2 , CH_3CH_3 , etc., whose groups do not involve E^* but permutation-inversion operations such as (12)* and (14)(25)(36)*, etc., we can assign the parity in the same way as we assigned the parity in rigid molecules (II) in the previous section. For example, all levels of the E torsional state of CH_3OH have double parity whereas for the A torsional state the levels with even K_c have $-$ parity and those with odd K_c have $+$ parity.

5. DISCUSSION

The knowledge of the parity of molecular levels does not introduce any new symmetry distinction between energy levels other than those which are already given by using the permutation-inversion group of Longuet-Higgins. Its net effect is to recognize that not all energy levels of a rigidly nonplanar molecule occur in closely spaced inversion doublets, one of $+$ and one of $-$ parity, but often, because of the Pauli exclusion principle, one is missing and the overall wavefunction has unique parity. However, a knowledge of the parities of levels is useful for discussions of intramolecular interactions, interactions with electromagnetic fields, and intermolecular interactions.

Since the parity is a rigorous quantum number for a free molecule, any intramolecular interaction occurs only between states with the same parity (and F). Recognition of this fact simplifies considerably the discussion of off-diagonal spin-rotation interactions and the mixing of different spin modifications (13). For example, the mixing of ortho and para wavefunctions of H_2O and H_2CO occurs only between two levels with $\Delta K_c = \text{even}$ and $\Delta F = 0$, and the mixing in CH_4 occurs only between A_1, F_2, E^- , and between A_2, F_1, E^+ . Since the total angular momentum quantum number F and the parity are the only good quantum numbers for the overall wavefunctions, all the levels with the same F and parity are mixed.

The mixing due to an electric field occurs between levels with different parity and that due to a magnetic field between levels with the same parity; so do the transitions caused by oscillating electromagnetic field. For this reason the Zeeman shift always has a first order component whereas the Stark shift is first order only for levels with double parity. Even for a molecule such as CH_4 , which is nonpolar in the lowest rovibrational state, a vibration-induced (14) or a rotation-induced (15, 16) dipole moment exists and causes a first order Stark effect in the levels with double parity (17). In fact if we neglect the very small splitting of double parity levels due to off-diagonal spin-rotation interaction, all the levels of CH_4 with double parity (with $J \neq 0$) have a first order Stark shift. Molecules with a center of symmetry such as CH_3CH_3 do not possess levels with double parity.

The parity is used also for discussion of intermolecular interactions. A rotational transition caused by weak, long-range interactions obeys "selection rules" similar to the dipole rules (18). In general, if a collision process between two molecules 1 and 2

without accompanying emission or absorption of radiation is considered, there is a rigorous parity relation

$$P_1 P_2 (-1)^L = P_1' P_2' (-1)^{L'},$$

where P_1 and P_2 are the parities of the levels of the colliding molecules 1 and 2 before the collision and P_1' and P_2' are those after the collision. L and L' are the angular momenta of relative motion before and after the collision.

A knowledge of parity will be of use for other molecular interactions such as photo-dissociation or even chemical reactions if details of the interactions are to be studied.

Finally, it is interesting to ask whether *absolute* parity means anything. If molecules are left in an environment with very low temperature and very low density long enough, eventually they will all be in the lowest rotational level. The parity of the lowest level is + for H_2 , CO, HCN, OH, H_2O , H_2CO , whereas it is - for NH_3 , CH_3CN , CH_4 and CH_3OH .

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