Quantum Mechanics, Group Theory, and C_{60}

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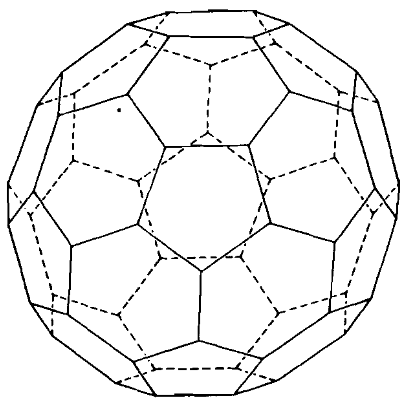
The recent discovery of a new allotropic form of carbon[1] and its production in macroscopic amounts[2] has generated a tremendous amount of research activity in chemistry, physics and material science.[3] Among the areas of current interest are the electronic properties of the fullerenes and this note describes a simple model for the electronic structure of C_{60} that is consistent with recent experimental findings. It is based on the most elementary principles of quantum mechanics and group theory.

After the soccer-ball structure for C_{60} was first suggested in 1985 it became important to obtain as much independent supporting evidence as possible. This came in the areas of nmr, IR, and Raman spectroscopy. The nmr spectrum showed a single resonance indicating 60 equivalent carbon atoms in the structure. The IR spectrum was found to have four lines, while Raman spectroscopy yielded ten lines. The second half of this paper will use group theory to demonstrate that a C_{60} molecule with a soccer-ball structure must have four IR active and ten Raman active vibrational modes.

Electronic Structure

As is well-known C_{60} is a carbon cage consisting of 20 hexagons and 12 pentagons and resembles a soccerball. Removing the leather, but keeping the seams, leaves 60 vertices for the carbon atoms and 90 covalent bonds between them. Actually C_{60} has spheroidal geometry and belongs to the truncated icosahedral symmetry group, I_h. Curly and Smalley, co-discoverers of buckminsterfullerene, have described it as the "roundest molecule that can possibly exist"[4] so the model presented here assumes, initially, that C_{60} is a perfect sphere. Each carbon is sigma bonded to three other carbons using three of its four valence electrons to form these bonds. The remaining electron is considered to be delocalized on the surface of the sphere created by the 60 atom carbon cage.



The quantum mechanical behavior of an individual electron restricted to the surface of a sphere is well-known.[5] Solving Schrödinger's equation for a particle on a sphere yields the spherical harmonic wavefunctions, pictures of which can be found in Atkins' physical chemistry textbook. The energy levels associated with the spherical harmonic states are a function of the radius of the sphere and the angular momentum quantum number.

$$E_L = \frac{h^2}{8\pi^2 m_e R^2} L(L + 1) \qquad (1)$$

Just as the quantum mechanical solution for the one-electron hydrogen atom can be adapted for qualitative treatments of the electronic structure of multi-electron atoms, so the energy level diagram for the electron moving on a sphere can be used to describe the electronic structure of C_{60}. The energy level diagram shown in Figure 1 provides a qualitative description of the electronic structure obtained when one applies the aufbau principle, the Pauli exclusion principle, and Hund's rule to the addition of 60 electrons to the available spherical harmonic energy levels.

h	L = 5	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ __	9.1
g	L = 4	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	6.0
f	L = 3	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	3.6
d	L = 2	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	1.8
p	L = 1	↑↓ ↑↓ ↑↓	0.6
s	L = 0	↑↓	0.0

Figure 1. Sixty electrons placed in the lowest available energy levels according to the aufbau principle, the Pauli exclusion principle, and Hund's rule. The energies for the individual levels shown on the right are in eV and were calculated using equation 1.

As it stands this is not a satisfactory picture because pristine C_{60} is an insulator and has no un-paired electrons. This difficulty is resolved by recalling that C_{60} is not a perfect sphere, but has the lower symmetry of the icosahedral group. Invoking icosahedral symmetry at this point splits the degeneracies of all levels above L = 2. However, initially it is only necessary to examine what happens to the highest occupied level, L = 5, since all other levels are completely filled.

Using traditional group theoretical methods[6], it can be shown that the L = 5 spherical harmonics transform under the rotations of the icosahedral symmetry group as shown in the last row of the icosahedral character table shown below. The behavior of the spherical harmonics under the rotations of the icosahedral group is given by

$$\chi(C_\alpha) = \frac{\sin(L + \frac{1}{2})\alpha}{\sin\frac{\alpha}{2}} \tag{2}$$

I_h	E	12 C_5	12 C_5^2	20 C_3	15 C_2
A	1	1	1	1	1
T_1	3	1.618	-.618	0	-1
T_2	3	-.618	1.618	0	-1
G	4	-1	-1	1	0
H	5	0	0	-1	1
L = 5	11	1	1	-1	-1

It is easy to show that this reducible representation is a linear combination of the five-fold degenerate H_u, an the two three-fold degenergate, T_{1u} and T_{2u} irreducible representations of the icosahedral group. Group theory doesn't predict the order of the levels, but Figure 2 shows that if the five-fold degenerate level is placed lowest , an energy level diagram that captures the essentials of the known electronic structure of C_{60} is obtained.[7,8] This assignment is consistent with HOMO, LUMO, and LUMO+1 levels of the Huckel molecular orbital calculation on C_{60}.[8,9] In addition, if the splittings of the L = 3 and L = 4 states are also examined in the manner outlined above, the complete energy level diagram for the π-electrons of C_{60} shown in Figure 3 is obtained. This set of π-electron levels is qualitatively consistent with the results of an ab initio calculation based on the pseudopotential local density method.[10]

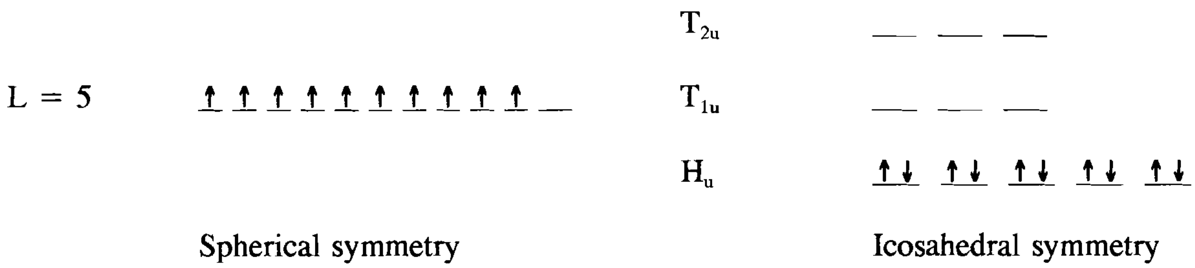


Figure 2. The splitting of the L = 5 energy level under icosahedral symmetry.

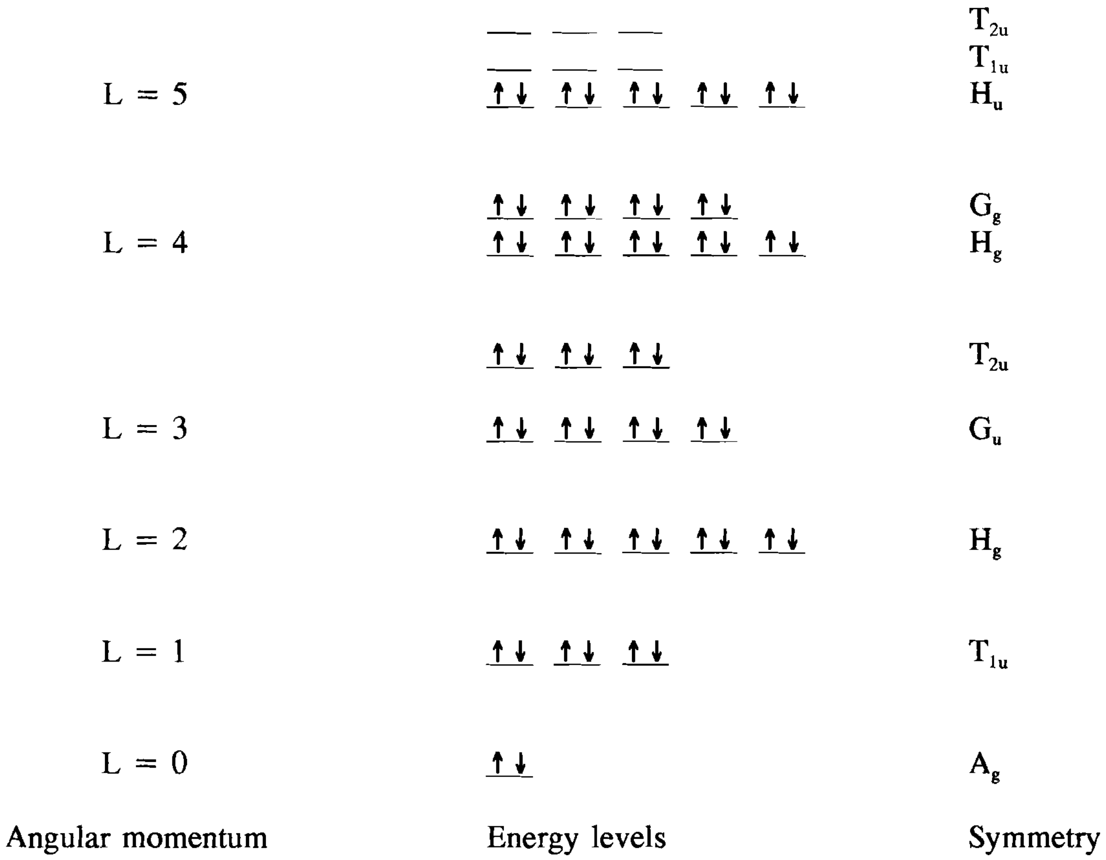


Figure 3. A complete energy level diagram for the π-electrons of C_{60} showing the splitting of the relevant angular momentum states under icosahedral symmetry.

The HOMO-LUMO energy gap is known to be 1.5 eV. However, the HOMO -> LUMO electronic transition is optically forbidden. Because H_u level is full, $(H_u)^{10}$, the ground electronic state has A_g symmetry. The first excited state $(H_u)^9(T_{1u})^1$ produces the reducible representation shown in the table below. This is obbtained by taking the direct product of the H_u and T_{1u} irreducible representations ($H_u x T_{1u}$). The reducible representation of the second excited state, $(H_u)^9(T_{1g})^1$ is also shown in the table. It is important to note that both excited states are 15-fold degenerate.

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^2$	$20S_6$	15σ
H_uT_{1u}	15	0	0	0	-15	15	0	0	0	-15
H_uT_{1g}	15	0	0	0	-15	-15	0	0	0	15

Employing the usual methods it is not difficult to show that the first and second excited electronic configurations contain the following irreducible representations.

$$(H_u)^9(T_{1u})^1 \rightarrow T_{1g} + T_{2g} + G_g + H_g$$

$$(H_u)^9(T_{1g})^1 \rightarrow T_{1u} + T_{2u} + G_u + H_u$$

Thus, it can be seen that the excited electronic configurations each give rise to four excited states. In order for a transition to any of these states from the ground state to be allowed, the transition probability integral $\int \Psi_i \, \mu \, \Psi_f \, d\tau$ must be non-zero. For this integral to be non-zero the direct product of the irreducible representations for the ground electronic state, the electric dipole operator, and the excited electronic state must contain the totally symmetric irreducible representation A_g. Because the ground state itself has A_g symmetry and the electric dipole operator has T_{1u} symmetry, only an excited state with T_{1u} symmetry will lead to a direct product which contains the A_g irreducible representation.

Inspection of the irreducible representations for the first and second exited electronic configurations shows that only the second excited electronic configuration contains the T_{1u} irreducible representation. Thus, while the HOMO → LUMO transition is forbidden, the HOMO → LUMO+1transition is allowed. This result is consistent with the visible spectrum of the free molecule.[9]

A further comment on the magnitude of the HOMO-LUMO gap might be made at this point. The energies of the spherical harmonic states shown in Figure 1 were calculated using equation (1) and a value of 710 pm for the diameter of the carbon cage. At the L = 5 level the energy difference between adjacent states is 3.1 and 3.6 eV. While the model doesn't provide a detailed quantitative analysis of the splitting of the L = 5 level, using reasonable assumptions one can obtain a value for the HOMO-LUMO gap that is "in the ball park."

In summary, this analysis provides a simple interpretation of the fact that C_{60} is an insulator. The model also provides low-lying, un-occupied orbitals to form conduction bands and receive electrons from donors such as potassium. Furthermore, the fact that the LUMO is triply degenerate is consistent with the experimental evidence that K_3C_{60} is a conductor and K_6C_{60} is an insulator.[7] While this simple model is not a rival to the more sophisticated molecular orbital or band theory calculations, it does provide the non-specialist with an appealing and simple alternative.

Vibrational Spectroscopy

To analyze the vibrational modes of C_{60} using group theory it is necessary to determine how the 180 degrees of freedom of the C_{60} molecule transform under the symmetry operations of the I_h group. This is actually quite easily done because the rotations and the inversion symmetry operation move all the carbon atoms and, therefore, have characters of 0. The identity operation leaves all carbons unmoved for a character of 180, while the 15 planes of symmetry contain four carbon atoms each and can be shown to have a character of 4. The model of C_{60} on the first page shows one of these planes. It is perpendicular to the plane of the paper and clearly contains four carbon atoms, two at the top and two at the bottom.

This makes it very easy to decompose the reducible representation, Γ_{tot}, into its irreducible representations by the usual methods. This is summarized in the table on the next two pages. For simplicity only the E and σ symmetry operations are shown, but it must be remembered that there are 120 symmetry operations total. For example, the occurrence of H_g is calculated as follows:

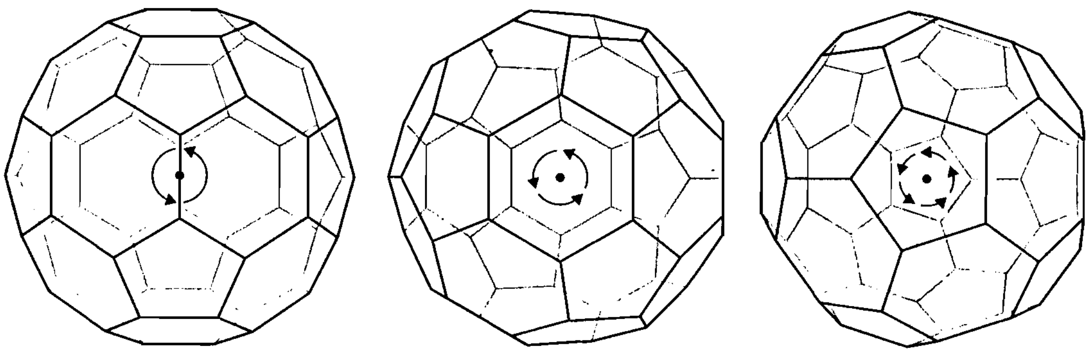
$$\Gamma_{tot} \bullet H_g \;=\; [(1)(180)(5) \;+\; (15)(4)(1)]/120 \;=\; 8$$

After translation and rotation are subtracted from the total, 174 vibrational degrees of freedom remain. However, group theory shows that many vibrational modes are degenerate. In fact, as the table below shows, there are only 46 distinct vibrational frequencies.

$$\Gamma_{vib} = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$$

Of these, the table indicates that only the four triply degenerate T_{1u} modes are IR active while ten vibrational modes (2 A_g + 8 H_g) are Raman active. This analysis is in complete agreement with the experimental measurements[11] and was considered to be crucial evidence in support of the proposed soccer-ball structure for C_{60}.

Several of the rotational axes for C_{60} are shown below to illustrate that they do move all atoms.



I_h	E	15 σ	Occurrence	h = 120
Γ_{xyz}	180	4		
A_g	1	1	2	Raman Active
T_{1g}	3	-1	4	R_x, R_y, R_z
T_{2g}	3	-1	4	
G_g	4	0	6	
H_g	5	1	8	Raman Active
A_u	1	-1	1	
T_{1u}	3	1	5	T_x, T_y, T_z / IR
T_{2u}	3	1	5	
G_u	4	0	6	
H_u	5	-1	7	

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Icosahedral Character Table - Buckminsterfullerene

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	h = 120
A_g	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
T_{1g}	3	1.62	-0.62	0	-1	3	1.62	-0.62	0	-1	R_x,R_y,R_z
T_{2g}	3	-0.62	1.62	0	-1	3	-0.62	1.62	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	xy,xz,yz
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	1.62	-0.62	0	-1	-3	-1.62	0.62	0	1	x, y, z
T_{2u}	3	-0.62	1.62	0	-1	-3	0.62	-1.62	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	
Γ_{atom}	60	0	0	0	0	0	0	0	0	4	
Γ_{tot}	180	0	0	0	0	0	0	0	0	4	$\Gamma_{atom}^{b} \cdot T_{1u}$