

Quantum Mechanics, Group Theory, and C₆₀

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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). It has also provided educators with an exciting new vehicle for breathing fresh life into some old, well-established methods and principles. Recently, for example, Boo (4) demonstrated the power of group theory in classifying existing and hypothetical fullerenes by their symmetries. In a similar spirit this note describes a model for the electronic structure of C₆₀ based on the most elementary principles of quantum mechanics and group theory.

Electronic Structure and Behavior

Spherical Harmonic Wavefunctions

In this model the behavior of the 60 π electrons of buckminsterfullerene are described by the spherical harmonic wavefunctions as modified by the icosahedral symmetry of the carbon cage. Ozaki and Takahashi previously presented this model as a zeroth-order approximation on their way to a self-consistent Hückel molecular orbital calculation in the months immediately following the discovery of C₆₀ (5). Because the model is qualitatively consistent with much of the recent research on C₆₀ and because it has great pedagogical appeal, I thought an update might be of interest to the readers of *this Journal*.

As is well-known, C₆₀ resembles a soccerball. Removing the leather, but keeping the seams, we leave 60 vertices for the carbon atoms and 90 covalent bonds between them. Actually C₆₀ has spheroidal geometry and belongs to the truncated icosahedral symmetry group, I_h . Curly and Smalley have described it as the "roundest molecule that can possibly exist" (6) so the model presented here assumes, initially, that C₆₀ is a perfect sphere. Each carbon is σ -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.

Particle on a Sphere

The quantum mechanical behavior of an individual electron restricted to the surface of a sphere is well-known. Solving Schrödinger's equation for a particle on a sphere, we get the spherical harmonic wavefunctions as illustrated, for example, in Atkins' physical chemistry text (7). The energy levels associated with the spherical harmonic states are a function of the radius of the sphere and the angular momentum quantum number.

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

Electronic Structure: Icosahedral Symmetry

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

h	L = 5	$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	9.1
g	L = 4	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	6.0
f	L = 3	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	3.6
d	L = 2	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	1.8
p	L = 1	$\uparrow\downarrow \uparrow\downarrow$	0.6
s	L = 0	$\uparrow\downarrow$	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 the equation.

of C₆₀. 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.

As it stands this is not a satisfactory picture because pristine C₆₀ is an insulator and has no unpaired electrons. This difficulty is resolved by recalling that C₆₀ 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, $L = 5$, because all other levels are completely filled.

With traditional group theoretical methods as outlined (e.g., by Atkins (8)) it can be shown that the $L = 5$ spherical harmonics transform as follows under the rotations of the icosahedral symmetry group.

E	$12 C_5$	$12 C_5^2$	$20 C_3$	$15 C_2$
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 and the two three-fold degenerate T_{1u} and T_{2u} irreducible representations of the icosahedral group. Group theory does not 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 C₆₀ is obtained (9, 10). This assignment is consistent with HOMO, LUMO, and LUMO + 1 levels of the Hückel molecular orbital calculation on C₆₀ (10, 11). 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 C₆₀ 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 (12).

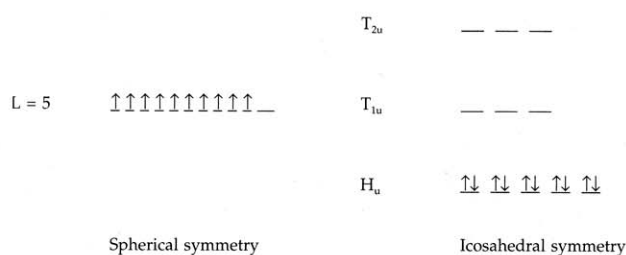


Figure 2. The splitting of the $L = 5$ energy level under icosahedral symmetry.

The HOMO–LUMO Energy Gap

With the usual symmetry arguments it is easy to show that the $H_u \rightarrow T_{1u}$ optical transition is formally forbidden. However, the use of other spectroscopic techniques yields a value of 1.5 eV for the HOMO–LUMO energy gap in solid C_{60} (11). The energies of the spherical harmonic states shown in Figure 1 were calculated using 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. Although the model does not provide a quantitative analysis of the splitting of the $L = 5$ level, with reasonable assumptions one can obtain a value for the HOMO–LUMO gap that is “in the ballpark”.

Summary

This analysis provides a simple interpretation of the fact that C_{60} is an insulator. The model also provides low-lying, unoccupied 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 (11).

Although this simple model is not a rival to the more sophisticated molecular orbital or band theory calculations, it does provide the nonspecialist with an appealing and simple alternative. In his text on molecular quantum mechanics Atkins (8) speaks of the “deep connection between group theory and the quantum mechanics of angular momentum”. It is the author’s opinion that this simple model

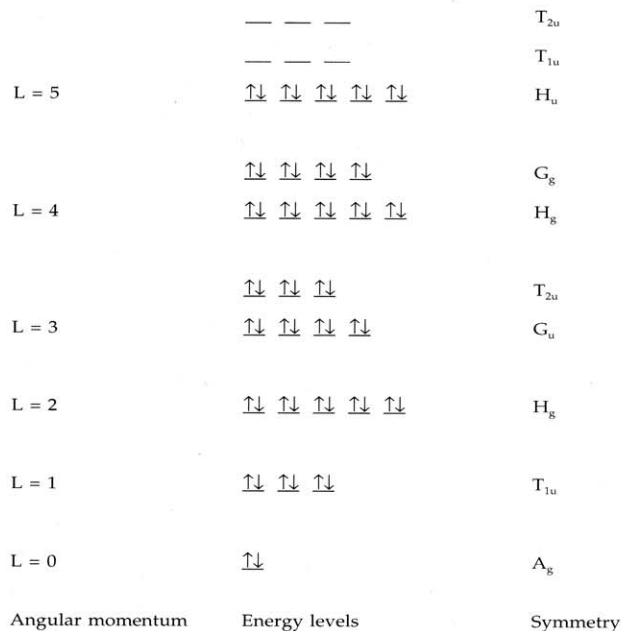


Figure 3. A complete energy-level diagram for the π electrons of C_{60} showing the splitting of the relevant angular momentum states under icosahedral symmetry.

for the electronic structure of C_{60} illustrates that “deep connection”.

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