

# Electronic and vibrational properties of the C<sub>60</sub> molecule

F. Alonso-Marroquin and J. Giraldo

*Departamento de Física, Universidad Nacional de Colombia, Apartado aéreo 67904, Santafé de Bogotá, Colombia*

A. Calles

*Facultad de Ciencias, Universidad Nacional Autónoma de México, 041510 México, D.F., Mexico*

J.J. Castro

*Departamento de Física, Centro de Investigación y Estudios Avanzados, Instituto Politécnico Nacional  
Apartado postal 14740, 07000 México, D.F., Mexico*

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We have studied the electronic and vibrational properties of the C<sub>60</sub> molecule by means of simplified models where only a few parameters are adjusted to experimental data. For the electronic part we use an independent electron model with a central Morse potential corrected by splitting the spherical degeneracy by properly including the icosahedral symmetry given rise to the LUMO and HOMO states. The vibrational spectra is obtained by solving the corresponding secular equation using a Born-Mayer type potential with two parameters adjusted to Raman and IR spectra. The results of our model are compared with some of the best *ab initio* calculations, phenomenological models and experimental data. We found in general a good agreement for the vibrational spectrum particularly for the high frequency part. Since in our model contains only two parameters we are not able to reproduce accurately the whole spectra. The main contribution of this model is its simplicity to extract most of the gross features of the C<sub>60</sub> molecule without cumbersome computation.

**Keywords:** Fullerenes; C<sub>60</sub> molecule; electron spectra; vibrational spectrum

En el presente trabajo se estudian propiedades electrónicas y vibracionales de la molécula de C<sub>60</sub> por medio de modelos semi-empíricos sencillos que utilizan pocos parámetros para ajustar a datos experimentales. Para la parte electrónica se usa un modelo de partícula independiente, usando un potencial de Morse, con simetría esférica la cual se corrige para incluir la simetría icosaedrál y así obtener los estados LUMO y HOMO. Por otro lado, el espectro vibracional se obtiene resolviendo la ecuación secular de la matriz dinámica usando potenciales tipo Born-Mayer, entre cada par de átomos, con sólo dos parámetros que se utilizan para ajustar a experimentos Raman e infrarrojo. Los resultados se comparan con cálculos de primeros principios, otros modelos fenomenológicos y datos experimentales. Se encuentra un buen acuerdo de nuestro modelo con datos experimentales sobre todo para la región de altas frecuencias. Sin embargo, no se reproduce con exactitud todo el espectro vibracional debido a que sólo hay 2 parámetros para ajustar. La principal contribución del trabajo es que se obtienen aspectos importantes de propiedades del C<sub>60</sub> de una manera sencilla que no implica una computación exhaustiva.

**Descriptores:** Fullerenos; molécula de C<sub>60</sub>; espectro electrónico; espectro vibracional

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## 1. introduction

The discovery of fullerenes and the method for their production in gram quantities have stimulated a great deal of experimental and theoretical work. Within the whole family of fullerenes, C<sub>60</sub> is the most studied system mainly due to its interesting physical and chemical properties. These are partially a result of the high symmetry of the molecule. The truncated icosahedral structure of the C<sub>60</sub> molecule raises interesting questions regarding its electronic structure and vibrational properties. Therefore the study of the molecule itself is a natural starting point in order to understand other members of the fullerene family in their molecular and solid forms.

In the study of the electronic and vibrational properties some authors have emphasized the distinction between the  $\pi$  (delocalized) and  $\sigma$  (localized) electrons and the spherical

character of the molecular wave [1, 2]. For the understanding of the vibrational spectra different models have been used in the literature ranging from *ab initio* calculations to phenomenological models to determine the force constants. In this work we have taken the second approach to study both the electronic and vibrational properties of the C<sub>60</sub> molecule. It is based on a phenomenological model that allows, in a very simple and direct way, to extract some of the main features of this complex system. The paper is organized as follows: In Sect. 2 we present the spherical model for the electronic structure which corresponds to the zero order approximation for the electronic wave function. In Sect. 3 we discuss the effect on the electronic wave function of breaking the spherical symmetry by taking into account the icosahedral symmetry. Sect. 4 contains a summary of the model that we used for the study of the vibrational properties. The conclusions and the discussion of the results are included in Sect. 5.

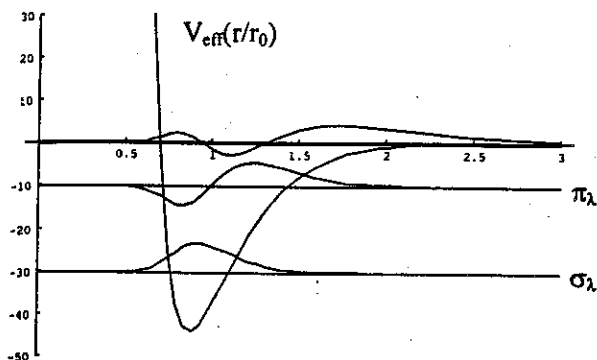


FIGURE 1. Wave functions obtained from the Morse potential employed in the present work.

## 2. Spherical model for the electronic spectra

As a starting model for the electronic spectra of C<sub>60</sub> we consider a system formed by the 240 valence electrons as moving independently in a spherical shell simulated by a Morse potential [3]

$$V_{\text{eff}}(r) = D \left[ 1 + \exp \left( -\frac{r - r_0}{d} \right) \right]^2 - D + \frac{l(l+1)}{2mr^2}. \quad (1)$$

This is the result of approximating the whole electron interaction by a sum of two terms: one attractive arising from the interaction between each electron and the core of the whole molecule (produced by the 360 protons in the carbon nuclei and the 120 electrons in the 1s shell), and one repulsive. The latter is the average of the mutual repulsion between the valence electrons. This central field approximation allows us to make the usual separation between the radial and angular part of the wave function expressing it in terms of the associate Laguerre polynomials and the spherical harmonics [4], labeling the resulting wave functions by three indexes ( $n, l, m$ ). The states with  $n = 0$  (no radial nodes) are occupied by electrons strongly localized between atoms, corresponding therefore to  $\sigma$  electrons, whereas the orbitals with  $n = 1$  correspond to  $\pi$  electrons (Fig. 1). The  $\sigma$  states which will be denoted by  $\sigma l$  will be occupied by 180 electrons ( $l = 9$ ) and the  $\pi l$  states with 60 delocalized electrons ( $l = 5$ ). The Morse potential parameters were fitted by imposing the following conditions:

$$E(\sigma_9) - E(\sigma_0) = 30 \text{ eV},$$

$$E(\pi_5) - E(\pi_0) = 7 \text{ eV},$$

$$E(\pi_5) = -5 \text{ eV},$$

$$E(\pi_5) = E(\sigma_9).$$

The above conditions correspond to the range of energies for the  $\sigma$  electrons, for the  $\pi$  electrons, fit to the electron affinity, and the condition that the highest molecular orbitals for the  $\pi$  and  $\sigma$  electrons coincide, respectively. With this we obtain

TABLE I. Energy levels and occupation numbers of the spherical model.

Niv.	oc.	(eV)	Niv.	oc.	(eV)
$\sigma_9$	18	-5.1	$\pi_5$	10	-5.2
$\sigma_8$	34	-10.6	$\pi_4$	18	-7.7
$\sigma_7$	30	-15.7	$\pi_3$	14	-9.7
$\sigma_6$	26	-20.3	$\pi_2$	10	-11.2
$\sigma_5$	22	-24.3	$\pi_1$	6	-12.3
$\sigma_4$	18	-27.7	$\pi_0$	2	-12.8
$\sigma_3$	14	-30.4	-	-	-
$\sigma_2$	10	-32.5	-	-	-
$\sigma_1$	6	-33.9	-	-	-
$\sigma_0$	2	-34.6	-	-	-

the following parameters:

$$r_0 = 3.15 \text{ \AA},$$

$$D = 49.43 \text{ eV},$$

$$d = 0.86 \text{ \AA},$$

$$m = m_e.$$

The corresponding electronic levels and occupation numbers are shown in Table I.

## 3. Effect of the icosahedral symmetry on the electronic structure

When we take into account the effect of the icosahedral symmetry on the electronic wave function we partially remove the degeneracy found in the spherical approximation discussed in the last section, and the wave function is now expressed in the form:

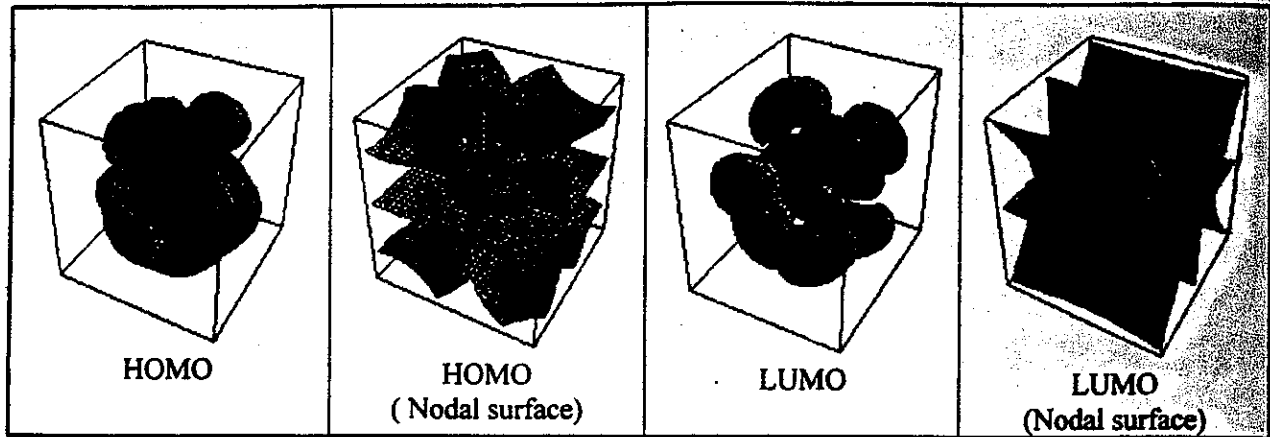
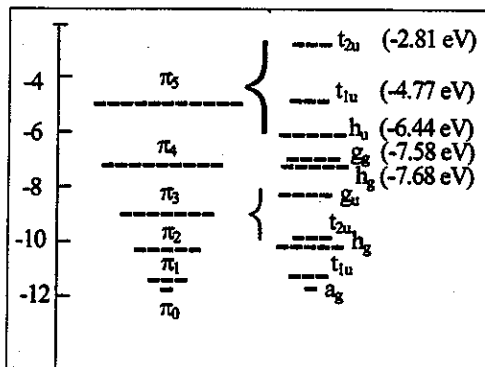
$$\Psi_{n,l,\gamma}(r, \theta, \varphi) = \frac{1}{r} R_{n,l}(r) \Omega_{l,\gamma}(\theta, \varphi). \quad (2)$$

where  $R_{nl}$  is the solution to the Schrodinger equation with the central potential given by Eq. (1). The angular functions  $\Omega_{l,\gamma}$  are now linear combinations of the spherical harmonics with the adapted icosahedral symmetry, and the index  $\gamma$  labels the irreducible representation of the symmetry group. This approximation recovers the main topological properties of the exact molecular orbitals, e.g. the nodal features (cf. Fig. 2). The splitting due to the icosahedral symmetry also allows to obtain the HOMO and LUMO levels. The last energy levels for the  $\sigma$  and  $\pi$  orbitals show the following splitting [1, 2]:

For the molecular electronic configuration we obtain [3]

$$\sigma_9^{18} \pi_5^{10} \rightarrow \sigma_9(g_u^8) \sigma_9(h_u^{10}) \pi_5(h_u^{10}) \pi_5(t_{1u}^0)$$

The Fig. 3 shows this level splitting. Where is evident the gap between the HOMO and LUMO levels.

FIGURE 2. Molecular orbitals of the  $C_{60}$  molecule.FIGURE 3. Energy levels of the  $\pi$  electrons.

#### 4. Vibrational spectra

The  $C_{60}$  molecule possesses 174 vibrational modes which reduces to only 46 distinct eigenfrequencies by the  $I_h$  symmetry. Using the icosahedral group these modes can be classified according to the irreducible representation:  $\Gamma = 2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$ . This leads to 32 silent modes, 10 Raman ( $2A_g + 8H_g$ ) and 4 infrared ( $4T_{1u}$ ). There are in the literature a large number of theoretical models predicting the vibrational spectra and the assignment of some of the vibrational modes which are normally compared with experimental data coming from Raman, infrared, high-resolution electron-energy-loss spectroscopy, and inelastic neutron scattering. In spite of the high symmetry of  $C_{60}$ , since it is a 60 atom molecule, the resulting normal modes of vibration are not easy to visualize. Therefore a proper construction of the eigenvectors is very useful. In order to get good agreement between the model predictions and experimental data it is necessary to have a correct assignment of the experimentally observed modes and an experimental determination of the corresponding eigenvectors. It is a well known fact that it is possible to construct models which

show a very good agreement with the whole experimental frequency spectra although the assignment of some of the modes may be wrong. It is worth mentioning that even if all the level assignment is made correctly, the agreement between theory and experiment can be claimed only if the eigenvectors can be verified experimentally; that is when the calculated displacement pattern can be confirmed by experiment. This is important since the displacement pattern of a mode belonging to a symmetry class with a multiplicity bigger than one is not determined by the symmetry alone. There are in the literature a large number of theoretical models for the calculation of the vibrational spectra of  $C_{60}$  which can be generally classified as *ab initio*, semiempirical, and phenomenological methods, going from a free parameter model to others that use parameters determined by fitting experimental data [5-8]. In this section we present the results of a calculation for the vibrational spectra of  $C_{60}$  based on a phenomenological model formed by a Coulomb potential part, representing the repulsion between carbon nuclei and a decaying exponential term simulating the electronic cloud. This is a two parameter model fitted to the highest experimentally reported vibrational mode. The simplicity of this model potential provides an easy and quick calculation for both the normal modes of vibration and eigenvectors for the whole spectra together with their symmetry classification. Here we only present the discussion corresponding to the normal modes, leaving the construction of the eigenvectors and the experimental determination of the displacement pattern for a future work. In Table II we present the results of the calculation of the vibrational spectra together with their symmetry assignment produced by the present model, and compare with those coming from different models and also with the experimental spectra. As it can be seen from this table, the results of this simple model compare quite satisfactorily with the results of more sophisticated models and experimental data. In particular, we can see how the high frequency part of the spectra is very well reproduced by this model having for some states an error of only 2.3%. Note that in our model we did not differentiate between single and double bonds whose effect could be important for

TABLE II. Vibrational spectra of the Raman and IR active modes. The experimental results[6] are compared with previous calculations[7-10] and with our results (last column).

	Exp.[5]	Force constants[6]		Hartree-fock method[7]		Density functional[8]		Quantum mol. dynamics[9]		Born-mayer potential	
$A_g$	491	492	0.2%	540	9.5%	483	1.6%	537	8.9%	613.1	22.1%
	1470	1468	0.1%	1417	3.7%	1529	3.9%	1680	13.3%	1602.42	8.6%
$H_g$	271	269	0.7%	263	3.0%	263	3.0%	249	8.5%	241.91	11.3%
	437	439	0.5%	467	6.6%	432	1.2%	413	5.6%	318.6	31.3%
	710	708	0.3%	739	4.0%	713	0.4%	681	4.2%	377.79	61.1%
	774	492	0.2%	540	9.5%	778	0.5%	845	8.8%	609.53	23.8%
	1099	1102	0.3%	1168	6.1%	1111	1.1%	1209	9.5%	1135.62	3.3%
	1250	1217	2.7%	1214	2.9%	1282	2.5%	1453	15.0%	1314.41	5.0%
$T_{1u}$	1428	1401	1.9%	1422	0.4%	1469	2.8%	1624	12.8%	1393.05	2.5%
	1570	1575	0.3%	1636	4.1%	1598	1.8%	1726	9.5%	1502.81	4.4%
	527	505	4.3%	556	5.4%	533	1.1%	494	6.5%	349.42	40.5%
	577	628	8.5%	540	9.5%	548	5.2%	643	10.8%	395.83	37.2%
	1185	1208	2.1%	1173	0.8%	1214	2.6%	1358	13.8%	1256.06	6.0%
	1428	1450	1.5%	1400	2.0%	1485	3.9%	1641	13.9%	1461.43	2.3%
Discrepancies	-	1.34%	-	4.56%	-	2.26%	-	10.08%	-	18.54%	-

some part of the spectra. The main advantage of the model proposed here is its simplicity in the calculation of the vibrational properties of the Fullerene molecule that permits in an easy and rather straightforward way to study the principal physical characteristics related to the vibrational properties. The close agreement with experimental data and the simplicity of the model suggest the obtainment of reliable eigenvectors that could be used for the electron-phonon interaction.

## 5. Conclusions

We have shown by using a simple phenomenological model how some of the main electronic and vibrational properties of the  $C_{60}$  molecule can be extracted without the necessity of cumbersome calculations. The use of the spherical model for a zero order electronic wave function and the breaking of the spherical symmetry by introducing the icosahedral symmetry

proved to be adequate for reproducing the main features of the electronic properties. In particular it was shown how the symmetry breaking gave rise to energy levels for the  $\pi$  electrons and the appearance of the gap between the LUMO and HOMO states. For the vibrational spectra we have illustrated how the use of a simple phenomenological model for the interaction between carbon atoms is capable of reproducing the main characteristics of the vibrational spectra. By comparing our results for the vibrational spectra with those coming from experimental data and *ab initio* calculations it has been shown how our model can reproduce quite satisfactorily the high frequency part of the vibrational modes. The main advantage of the approach presented here is its simplicity and capability in reproducing the main physical characteristics of the electronic and vibrational states and the gaining of physical insight without the necessity to carry out cumbersome calculations.

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