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C_{60} fullerene as a pseudoatom of the icosahedral symmetry

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Contents

I.	Introduction	729
II.	Unique features of the electronic structure and spectra of icosahedral systems	731
III.	Expansion of molecular orbitals of C_{60} fullerene in terms of spherical harmonics	738
IV.	The method of multipole interactions	742
V.	The energy spectrum of many-electron terms. Hund's rules	745
VI.	Electronic and optical transitions	750
VII.	Conclusion	753

Abstract. Unique features of the electronic structure and spectra of the C_{60} (I_h) fullerene and its ions related to the icosahedral symmetry are discussed. The so-called 'accidental' degeneracy of terms in the open electron shells g^N and h^N (corresponding to four- and fivefold degeneracy of molecular orbitals, respectively) and the abnormal ('non-Bethe') splitting of terms in the h^N configuration are considered. The need to describe these terms arises in studies of ionized and excited states of the C_{60} molecule and its derivatives. A novel approach to the description of $C_{60}^{m\pm}$ ions based on representation of the C_{60} (I_h) fullerene as a (pseudo)atom of icosahedral symmetry is considered in detail. The approach involves an expansion of the molecular orbitals of C_{60} in terms of the atomic orbitals centred at the origin (at the centre of the C_{60} molecule) and a multipole expansion of the electron repulsion. The energy spectra of the fullerene and $C_{60}^{m\pm}$ ions, the magnetic moments and optical dipole transitions are considered. The results obtained are compared with those of *ab initio* calculations and with the available experimental data. The bibliography includes 119 references.

I. Introduction

Since its discovery in 1985,[1] the molecule of C_{60} fullerene has attracted the attention of researchers working in different areas of chemistry and physics. There is a wealth of experimental and theoretical studies, as well as a number of reviews and monographs[2–8] concerned with investigations of this unique molecule and its derivatives (endofullerenes, fullerides, *etc*.). Nowadays there exists a whole branch of physical organic chemistry called 'the chemistry of fullerenes'. Particular interest of quantum chemists in this molecule is first of all due to its high symmetry. Indeed, the symmetry group of the C_{60} fullerene is the icosahedral group I_h, the highest among all known molecular (finite) symmetry groups. A distinctive feature of icosahedral molecules is the appearance of new types of electron shells (electronic configurations) g^N and h^N with the fourfold and fivefold degeneracy, respectively; they are not met in systems of lower symmetry and characterized by a number of unusual features.

A neutral C_{60} molecule has a closed electronic shell; this essentially simplifies the theoretical description of the system because many problems can be solved in the one-electron approximation. Complicated theoretical problems arise in studies of ionized and excited states of C_{60} and compounds based on C_{60}, where charge (one or more electrons) transfer from the highest occupied molecular orbital (HOMO) of the symmetry h_u to the lowest unoccupied molecular orbital (LUMO) of the symmetry t_{1u} occurs. Charge transfer to C_{60} is typical of alkali metal fullerides A_nC_{60}, where A = K, Rb, Cs ($n = 1-6$). In such systems, we deal with the open shell problem when a number of equivalent electrons (the electronic configurations t^N, g^N and h^N) occupy the shell only partly. This is an essentially many-electron problem, which is considered in this review. Research on the electronic properties of C_{60}^{n-} molecular anions is, in particular, necessary to understand such phenomena as polymerization, metal–insulator transitions, as well as magnetic ordering and superconductivity observed in the A_nC_{60} compounds.[4–8] In addition, many-electron effects become significant in the description of the optical spectra of neutral C_{60} molecule.[9,10] The results of *ab initio* quantum chemical studies have shown that even in this case we are still far from exact identification of spectral bands.[11] At the same time, many phenomena can be under-

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stood on the qualitative level (and sometimes be characterized quantitatively) within the framework of a simple model which treats the fullerene C_{60} as a pseudoatom of icosahedral symmetry.[12]

The plan of the review is as follows. A short Introduction (Section I) is followed by consideration of the unique features of the electronic spectra of icosahedral systems with the open shells g^N and h^N based on the theory of 'integral invariants' (Section II). In Section III, we introduce the angular dependence of the h_u, t_{1u} and t_{1g} molecular shells, which are used in the method of multipole many-electron interactions (Section IV). This formalism is then used to describe various charge states of C_{60}, *viz.*, its anions C_{60}^{n-} and cations C_{60}^{m+} (Section V). In that Section, we also disclose the relationship between the theory of integral invariants and the theory of multipole expansion, show the calculated energy spectra and magnetic moments, discuss Hund's rules and compare our results with those obtained in other calculations. Section VI concerns the dipole transitions of C_{60}^{2-} and C_{60}^{3-} and the optical spectrum of neutral C_{60} molecule. In Section VII, we formulate the key conclusions that follow from the studies of the $C_{60}^{n\pm}$ molecular ions.

1. The discovery of the C_{60} molecule: an outline

Carbon clusters now called fullerenes were discovered in the second half of the 1980s.[13] The discovery itself is a result of collaboration of two research groups working in different fields of science.[8] The first group included astrophysicists and spectroscopists headed by Kroto and studied the IR spectra of interstellar carbon clusters.[14,15] The second group headed by Smalley synthesized carbon structures by laser vaporization of carbon.[16] Of all clusters produced, the structure comprising 60 carbon atoms (a buckminsterfullerene) was immediately discovered.[1] This is just that highly symmetric cage structure now called the C_{60} molecule.

The structure of a truncated icosahedron was chosen for the buckminsterfullerene (or, simply, a bucky ball) molecule based on the experimentally observed stability of its electronic structure rather than the criterion for high molecular symmetry. Indeed, in this structure each atom is tetravalent, which is typical of the carbon atom. All four valence electrons are involved in chemical bonding, namely, one s- and two p-electrons are hybridized (sp^2-hybridization) to form three σ-bonds which thus form the cage of the C_{60} molecule. The remaining p-electron participates in the formation of a weaker π-bond. Note that the structure of a truncated icosahedron not necessarily leads to equal bond lengths. Indeed, experiments revealed two types of chemical bonds between carbon atoms in the C_{60} molecule. Phenomenologically, they are called 'double' and 'single' bonds. It should be noted that all sixty atoms in the molecule remain equivalent and each atom forms one double bond (R_6 = 1.404 Å) and two single bonds (R_5 = 1.448 Å),[17–19] with its neighbours (Fig. 1). The molecular symmetry group of C_{60} (icosahedral group), I_h, includes 120 symmetry operations.[8] (Unlike I_h, the symmetry group I does not include inversion and the number of symmetry operations is thus restricted to 60.) It is the high symmetry that is responsible for a nearly spherical shape of the molecule and the main reason for making the soccer ball in the shape of a truncated icosahedron.

A truncated icosahedron has sixty vertices and ninety edges. Twenty faces represent irregular hexagons (with threefold symmetry axes) and twelve faces represent regular pentagons (with fivefold symmetry axes). Before the discovery of the C_{60} molecule, the solid state physicists paid little attention to the icosahedral point groups I and I_h because they were considered exotic.

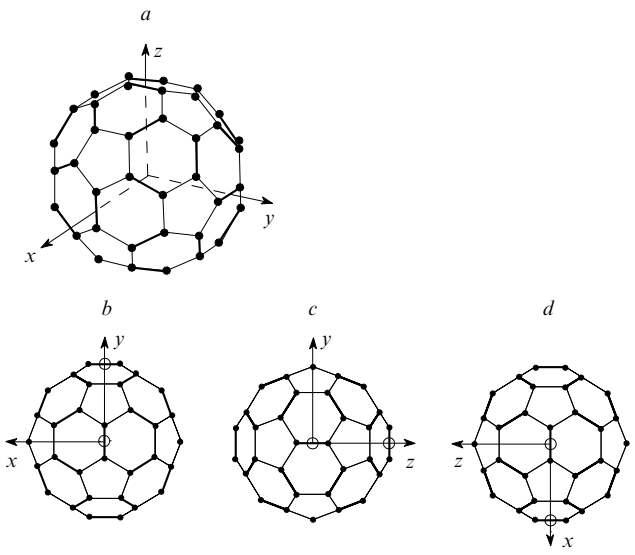


Figure 1. Standard orientation of the C_{60} molecule.
Three-dimensional image (*a*), three projections on the coordinate planes: *xy* (*b*), *yz* (*c*) and *zx* (*d*). The C−C bonds are shown by thin lines, the C=C bonds are shown by thick lines. The third axis crosses the double bond at the midpoint (open circle). This axis of coordinates is simultaneously the molecular twofold axis and the coordinate planes are the mirror planes.

The year 1990 was marked by a breakthrough in the fullerene science. Krätschmer, Huffman and their collaborators succeeded to synthesize macroscopic amounts of C_{60} and C_{70} crystals.[20,21] Earlier, C_{60} and C_{70} were studied only by mass spectrometry in the gas phase.[22] Krätschmer and Huffman called the C_{60} and C_{70} crystals fullerites. These are molecular solids where the C_{60} (or C_{70}) molecules occupy corresponding lattice sites. The method of production of C_{60} and C_{70} developed by Krätschmer and Huffman has played a significant role in the studies of these molecules and their crystals and served a basis for further discoveries.

Fullerites can be doped. Doping results in compounds called fullerides, of which C_{60} crystals doped with alkali metal atoms have been best studied. Rare-earth metal, iodine and oxygen atoms can also play the role of dopants.[5] At present, the family of experimentally produced and investigated fullerides A_nC_{60} includes compounds with n = 1–4, 6 and 10.[23–29] The ability of the molecular crystal C_{60} to form compounds with other atoms (dopants) is, in particular, due to the presence (or absence) of free interstitial space between the relatively large C_{60} molecules. Among alkali C_{60} fullerides, mention may be made of the compounds with the stoichiometry A_3C_{60} (A = Na, K, Rb or Cs). They are best known for their superconducting properties and relatively high superconducting transition temperatures (T_c).[30] However, alkali metal fullerides exhibit not only superconductivity, but also metal–insulator transitions, polymerization, phase transitions and magnetic anomalies.[2,5–8]

2. The problem of description of the electronic structure of many-electron C_{60}^{n-} anions and C_{60}^{m+} cations

Alkaline-earth metal fullerides A_nC_{60} can be treated as ionic molecular crystals. A key distinctive feature of such systems consists in charge transfer from the alkaline-earth metal atom to the fullerene C_{60}. Experimentally, charge transfer is substantiated by measuring the Knight shifts in metallic fullerides.[31, 32] Therefore, the lattice sites are in fact occupied by C_{60}^{n-} molecular anions rather than neutral C_{60} molecules. In a vast majority of compounds based on fullerenes, the C_{60}^{n-} anion behaves as an individual element (quasi-element, or a quasi-atom).[6]

Thus, to understand the physicochemical properties of A_nC_{60}, one first of all should study the electronic properties of C_{60}^{n-}. Note that some difficulties arise in the interpretation of experimental data (*e.g.*, the Knight shifts in charged fullerenes[33, 34]) or when comparing the optical bands and theoretical energy spectra. To overcome such difficulties, an independent theoretical analysis is required. The main goal of this review is to contribute to the solution of this difficult problem. It should also be noted that in the general case ($n \neq 1$) we assume a many-electron problem where an open electron shell contains n equivalent electrons.[12, 35, 36] The case of neutral molecules is simpler because it is treated within the framework of the one-electron approximation. Earlier calculations of the fullerene molecule were based on the Hückel model.[37–39]

Typically, C_{60} is an electron acceptor. This complicates the search for a compound in which this molecule could bear a positive charge. Difficulties in the chemical oxidation of fullerenes were discussed in a review by Reed and Bolskar.[33] Nevertheless, formation of the cation C_{60}^{2+} from the compounds $(AsF_6)_2C_{60}$ and $(SbF_6)C_{60}$ was stated.[40–42] We thus have to describe the many-electron spectra of the C_{60}^{m+} molecular cations ($m = 2, 3, \ldots, 8$). This problem is also considered in this review. The determination of the structure of the electronic spectra of C_{60}^{m+} is not only of practical interest, but also a nontrivial theoretical problem[43–62] taking account of unusually high (fivefold) degeneration multiplicity of the molecular h_u-shell and the corresponding vibronic (Jahn–Teller) interactions.

In this review, the C_{60} molecule and corresponding molecular ions are treated as having the icosahedral symmetry, *i.e.*, it is assumed that the sixty carbon nuclei have the same coordinates as in the neutral C_{60} molecule. For the Jahn–Teller problem,[53–64] *viz.*, vibronic distortions of the geometry of C_{60}^{m+} or C_{60}^{n-}, the energies and functions considered below play the role of the initial and unavoidably necessary approximation. For instance, a vibronic mode is active if $[\Gamma_{el}]^2$ includes Γ_{vib}.[63, 64] Here Γ_{el} is the irreducible representation (symmetry) of the ground electronic state and Γ_{vib} is the symmetry of the corresponding vibrational mode. Thus, even in this stage of analysis one should know the symmetry of the molecular electronic levels. In addition, there are grounds to believe that the static Jahn–Teller effect in C_{60}^{-} is rather weak and the situation can generally be characterized as a dynamic effect with the molecule retaining on average its icosahedral symmetry. Experimentally, distortions of carbon–carbon bonds in C_{60} were observed only in a neutron diffraction study[65] of AC_{60} (A = Rb, Cs) crystals upon formation of a chain comprising C_{60} monomers. In other cases, the C_{60} molecules retained their shape and vibronic interactions in them were estimated at 0.1–0.2 eV. In the text below we will show that the splittings of the highest and the lowest electronic terms are a few times larger than these values. It follows that in this case the Jahn–Teller effect can be studied in the approximation of weak (or medium-strength) vibronic interaction.[64]

II. Unique features of the electronic structure and spectra of icosahedral systems

A distinctive feature of the systems with icosahedral symmetry is the appearance of new types of electronic conUfigurations, g^N and h^N, which have no analogues in systems of lower symmetry. The problems arising in the theoretical description of such systems have attracted much attention of researchers from different scientific schools. In this Section we briefly outline the main approaches to solution of these problems and present some results to illustrate new ideas and problems that arose in the course of analysis of the systems in question.

1. The theory of integral invariants

Important results were obtained within the framework of a novel group-theoretical approach, namely, the theory of 'integral invariants' developed by Plakhutin[43–50] to analyze the spectra of electronic states in highly symmetric molecular systems with degenerate open shells configurations γ^N (γ = e, t, g, h; N is the number of electrons). The theory is based on the representation of two-electron repulsion integrals

$$\langle i,j|\,k,l\rangle = \int \phi_i^*(1)\phi_j(1)\frac{1}{r_{12}}\phi_k^*(2)\phi_l(2)\mathrm{d}v_1\mathrm{d}v_2$$

(numbers 1 and 2 enumerate electrons and r_{12} is the interelectron distance) in degenerate molecular orbitals (ϕ_i, ϕ_j, ϕ_k, $\phi_l \in \gamma$) and the energies of the $^{2S+1}\Gamma$ terms ($2S+1$ is the spin multiplicity and Γ is the irreducible representation) arising from the configuration γ^N in terms of the 'integral invariants' $H^k(\gamma\gamma)$

$$\langle i,j|\,k,l\rangle = \sum_k \alpha^{(k)}(i,j,k,l) \times H^k(\gamma\gamma), \quad (1)$$

$$E\left(^{2S+1}\Gamma,\gamma^N\right) = \sum_k c^{(k)}\left(^{2S+1}\Gamma,\gamma^N\right) \times H^k(\gamma\gamma), \quad (2)$$

where $\alpha^{(k)}(i,j,k,l)$ and $c^{(k)}\left(^{2S+1}\Gamma,\gamma^N\right)$ are the coefficients of expansion. The energy parameters $H^k(\gamma\gamma)$ called 'integral invariants'[43] are molecular analogues to the Slater integrals[66] $F^k(ll)$ for the atomic shell l (l = s, p, d, ...) while the expansions (1) and (2) are analogous to the classical expansions of the electron repulsion integrals in degenerate atomic orbitals and the energies of the atomic states $\left(^{2S+1}\mathrm{L},l^N\right)$ in terms of the Staler integrals (or, which is equivalent in this case, in terms of the Racah parameters[67] A_{ll}, B_{ll}, ...).

The number of terms in the expansions (1) and (2), *i.e.*, the number of integral invariants, which is denoted below by $L_{\gamma,\Omega}$, is the fundamental characteristic of the electron shell γ and the point symmetry group Ω. These numbers for all molecular symmetry groups and electron shells are listed in Table 1. The methods for construction of integral invariants $H^k(\gamma\gamma)$ in the form of combinations of symmetry-unique electron repulsion integrals and the methods for calculations of the coefficients in Eqns (1) and (2) have been documented.[44, 45, 49] A more general approach to calculations of the state coefficients $c^{(k)}\left(2S+1\Gamma,\gamma^N\right)$ for icosahe-

Table 1. Numbers of integral invariants $H^k(\gamma\gamma)$ for systems with the open electron shell γ^N.

Point symmetry groups (Ω)	γ^N	dim γ	Number of invariants ($L_{\gamma,\Omega}$)
Finite groups [a]			
Tetragonal groups (D_{4h}, C_{4v}, D_{2d}) and irreducible representations e_k in the groups D_{4kh} and D_{2kd} at $k = 2, 3, ...$	e^N	2	3
All groups having a two-dimensional irreducible representation, except the tetragonal groups	e^N, π^N	2	2
Cubic groups (T_d, O, O_h)	t^N	3	3
Icosahedral groups (I, I_h)	t^N	3	2
	g^N	4	3
	h^N	5	5
Continuous groups [b]			
Atom [group of three-dimensional rotations $O^+(3)$] with the configuration l^N ($l = p, d, ...$)	p^N	3	2
	d^N	5	3
Orthogonal group $O^+(4)$	$(10)^N$	4	2
Orthogonal group $O^+(5)$	$(10)^N$	5	2

[a] Data taken from Ref. 43.
[b] Data for the atom were taken from Ref. 66; data for the groups $O^+(4)$ and $O^+(5)$ were taken from Refs 44 and 48.

dral systems based on the unitary group theory was more recently proposed by Judd and Lo.[68]

The energy $E\left({}^{2S+1}\Gamma, \gamma^N\right)$ defined by Eqn (2) is only one part of the total energy of the term, which corresponds to inter-electron repulsion in the open shell. Within the framework of the monoconfigurational approximation, underlying both the theory of integral invariants and the Slater–Racah atomic theory, the total electronic energy of the term is given by

$$E_{\text{total}}\left({}^{2S+1}\Gamma, \gamma^N\right) = E\left({}^{2S+1}\Gamma, \gamma^N\right) + E_{\text{rest}}(\gamma N). \tag{3}$$

The corresponding expressions for the addends in the right side of Eqn (3) are defined within the framework of the restricted open-shell Hartree–Fock (ROHF) method,[69]

$$E\left({}^{2S+1}\Gamma, \gamma^N\right) = f^2 \sum_m \sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn}), \tag{4}$$

$$E_{\text{rest}}(\gamma^N) = 2\sum_k H_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl}) + \\ + 2f\left[\sum_m H_{mm} + \sum_k \sum_m (2J_{km} - K_{km})\right], \tag{5}$$

where $f = N/(2\dim\gamma)$ is the occupation number of the open shell γ^N; the subscripts m, n and k, l refer to the orbitals of the open and closed shells, respectively; $\dim\gamma$ is the dimension of the irreducible representation γ; and a_{mn} and b_{mn} are the coefficients characterizing the term and configuration.

A comparison of expressions (2) and (3)–(5) shows that the total electronic energies of all terms present in the configuration γ^N differ from $E\left({}^{2S+1}\Gamma, \gamma^N\right)$ [see Eqns (2) and (4)] by the additive constant $E_{\text{rest}}(\gamma^N)$. (This is valid if the energies of all terms were calculated using the same molecular orbitals.) Note also that Eqns (2) and (4) give two substantially different (but equivalent) definitions of the energy $E\left({}^{2S+1}\Gamma, \gamma^N\right)$. This allows one to use the ROHF method for independent checkout of the results obtained using the theory of integral invariants [47, 70, 71] (see also the text below).

2. The energy spectra of states in the configuration g^N (I, I_h)

An analysis of the spectra of states in the icosahedral systems with the electronic configurations t^N, g^N and h^N using the theory of integral invariants led to unexpected results. The results obtained [43, 47, 48] for the configuration g^N are listed in Tables 2 and 3.

Table 3 presents the coefficients $c^{(k)}\left({}^{2S+1}\Gamma, \gamma^N\right)$ in the energy expansion (2) for $N = 2$, 3, 4 and 8. For the systems with $4 < N < 8$ in which the open shell is more than half-filled the coefficients $c^{(k)}$ of Eqn (2) are calculated using the general expression [50]

$$c^{(k)}\left({}^{2S+1}\Gamma, \gamma^{2\dim\gamma - N}\right) = c^{(k)}\left({}^{2S+1}\Gamma, \gamma^N\right) + \\ + (1 - 2f_N) \times c^{(k)}\left({}^1\text{A}, \gamma^{2\dim\gamma}\right), \tag{6}$$

where $\left({}^1\text{A}, \gamma^{2\dim\gamma}\right)$ is the totally symmetric term ^{1}A in the closed shell $\gamma^{2\dim\gamma}$ (here $2\dim\gamma = N_{\max}$ is the maximum possible number of electrons in the configuration γ^N) and $f_N = N/(2\dim\gamma)$ is the occupation number for the configuration γ^N. At $N = 1$, all coefficients $c^{(k)}\left({}^{2S+1}\Gamma, \gamma^1\right)$ are zero by definition.

To gain a better insight into the structure of the g^N-spectrum (see Table 3), we will compare it with that of the spectrum of states arising from the 'parent' electronic configuration. In this connection, some remarks are required. When analyzing the spectrum of electronic states in a molecule (ion) with a degenerate open shell γ^N (γ = e, t,

Table 2. Integrals of inter-electron interaction $\langle i,j\,|\,k,l\rangle$ in fourfold degenerate (real) icosahedral g-orbitals of 'conventional' representation.[47]

Integral	$H^0(gg)$	$H^1(gg)$	$H^2(gg)$
$J_{11} = J_{22} = J_{33}$	1	+3	+9/4
J_{44}	1	+3	−15/4
$J_{12} = J_{13} = J_{23}$	1	−1	−7/4
$J_{14} = J_{24} = J_{34}$	1	−1	+5/4
$K_{12} = K_{13} = K_{23}$	0	+2	−7/4
$K_{14} = K_{24} = K_{34}$	0	+2	+5/4
$\sum_i \sum_j (2J_{ij} - K_{ij})$	28	−36	0
$\langle 1,2\,|\,3,4\rangle = \langle 1,3\,|\,2,4\rangle = \langle 1,4\,|\,2,3\rangle$	0	0	$-\sqrt{45}/4$

Notes. 1. Numbers in this Table are the coefficients $\alpha^{(k)}$ (k = 0, 1, 2) in Eqn (1). 2. The definition of the g-orbitals of 'standard' presentation and their general forms are available from Refs 47 and 48. 3. From each group of symmetry-equivalent integrals, *e.g.*, $\langle 1,2\,|\,3,4\rangle = \langle 1,2\,|\,4,3\rangle = \langle 2,1\,|\,3,4\rangle = \langle 2,1\,|\,4,3\rangle = \langle 3,4\,|\,1,2\rangle = ...$, we list only one with unique symmetry. All three-index integrals of the types $\langle i,j\,|\,k,k\rangle$ and $\langle i,j\,|\,k,i\rangle$, as well as the two-index integrals different from the Coulomb and exchange integrals are zero.

Table 3. Energies of the terms $^{2S+1}\Gamma$ in the configurations g^N, expressed in terms of the integral invariants $H^k(gg)$.[43,47]

Term	$H^0(gg)$	$H^1(gg)$	$H^2(gg)$
Configuration g^2			
$^3\mathbf{T}_1$	1	−3	0
$^3\mathbf{T}_2$	1	−3	0
^{1}H	1	+1	+4
^{1}G	1	+1	−5
^{1}A	1	+9	0
Configuration g^3			
^{4}G	3	−9	0
$^2H_{(1)}$	3	−3	−6
$^2H_{(2)}$	3	−3	+6
^{2}G	3	+3	0
$^2\mathbf{T}_1$	3	−3	0
$^2\mathbf{T}_2$	3	−3	0
Configuration g^4			
^{5}A	6	−18	0
^{3}H	6	−10	−4
^{3}G	6	−10	+5
$^3\mathbf{T}_1$	6	−6	0
$^3\mathbf{T}_2$	6	−6	0
$^1H_{(1)}$	6	−6	−6
$^1H_{(2)}$	6	−6	+6
$^1H_{(3)}$	6	−2	+4
^{1}G	6	−2	−5
^{1}A	6	+6	0
Configuration g^8			
^{1}A	28	−36	0

Notes. 1. The numbers in this Table represent the coefficients $c^{(k)}$ ($k = 0, 1, 2$) in Eqn (2). 2. The right subscript in parentheses in the notations of the terms $^{2S+1}H_{(i)}$ enumerates the multiple (repeated) terms of the same symmetry. The off-diagonal matrix elements of the Hamiltonian between the wave functions of these terms are always zero. The degenerate terms are given in semi-bold.

g, h), it is usually compared with the spectrum of states arising in a system of higher symmetry, which has a corresponding (parent) electronic configuration λ^N. Both configurations are characterized by the same dimension of the electronic shell, *i.e.*, $\dim\lambda = \dim\gamma$, while the number of terms arising from the configuration λ^N is smaller than that for the configuration γ^N. In this case, the terms of the configuration γ^N are treated as arising upon splitting of the parent λ^N-terms. When considering icosahedral structures (I, I_h) with the electronic configurations t^N and h^N, the parent systems are atoms with the configurations p^N and d^N, respectively.[72,73]

The fourfold degenerate icosahedral electronic shell g ($\dim g = 4$) is a unique shell in the sense that it has no analogues in real molecular (atomic) systems (see Table 1). Based on the group-theoretical considerations,[73] it is natural to choose the quadruply degenerate irreducible representation in the orthogonal group $O^+(4)$, which is denoted by (10), as the parent for the shell g. [All irreducible representations in the group $O^+(4)$ are denoted by $(\mu_1\mu_2)$, where μ_1 and μ_2 are integers.[73]]

The electronic configuration $(10)^N$ in the group $O^+(4)$ is a parent configuration for the icosahedral configuration g^N. In the text below, the terms arising from the configuration $(10)^N$ are denoted as $^{2S+1}(\mu_1\mu_2)$ or, in a more general form, as $\left[^{2S+1}(\mu_1\mu_2), (10)^N\right]$. Symmetry reduction

$$O^+(4) \longrightarrow (I, I_h)$$

causes the terms $^{2S+1}(\mu_1\mu_2)$ to split and transform to the terms of the configuration g^N

$$\left[^{2S+1}(\mu_1\mu_2), (10)^N\right] \longrightarrow \left(^{2S+1}\Gamma_1, g^N\right) + \left(^{2S+1}\Gamma_2, g^N\right) + \ldots . \quad (7)$$

Table 4 presents the overall pattern of the splitting of terms.[48] As can be seen, all terms arising from the configuration g^N (I, I_h) are related to the corresponding (parent) terms from the configuration $(10)^N$ in the orthogonal group $O^+(4)$. For instance, the terms ^{1}H and ^{1}G of the configuration g^2 have a degree of degeneracy of 5 and 4,

Table 4. Reduction of states of the orthogonal group $O^+(4)$ on icosahedral subgroups (I, I_h) and the expansions (2) for the terms from the group $O^+(4)$.[48,73]

N	Terms of the $(10)^N$ configuration in the group $O^+(4)$			Terms of the g^N (I, I_h) configuration	$H^0(10,10)$	$H^1(10,10)$
	spin	$(\mu_1\,\mu_2)$	dim $(\mu_1\,\mu_2)$			
2	1	(11)	6	$^3T_1 + {}^3T_2$	1	−3
	0	(20)	9	$^1H + {}^1G$	1	+1
	0	(00)	1	^{1}A	1	+9
3	3/2	(10)	4	^{4}G	3	−9
	1/2	(21)	16	$^2H_{(1)} + {}^2H_{(2)} + {}^2T_1 + {}^2T_2$	3	−3
	1/2	(10)	4	^{2}G	3	+3
4	2	(00)	1	^{5}A	6	−18
	1	(20)	9	$^3H + {}^3G$	6	−10
	1	(11)	6	$^3T_1 + {}^3T_2$	6	−6
	0	(22)	10	$^1H_{(1)} + {}^1H_{(2)}$	6	−6
	0	(20)	9	$^1H_{(3)} + {}^1G$	6	−2
	0	(00)	1	^{1}A	6	+6

Notes. 1. Recall that $(\mu_1\mu_2)$ is a conventioal notation of irreducible representations in the group $O^+(4)$; $\dim(\mu_1\mu_2)$ is the dimension of the representation $(\mu_1\mu_2)$. 2. The invariants for the fourfold degenerate representation (10) in the orthogonal group $O^+(4)$ are denoted by $H^k(10,10)$, where $k = 0, 1$ (see also Table 1).

respectively. They can be considered as a result of the splitting of the ninefold degenerate term $^1(20)$ arising from the parent configuration $(10)^2$:

$$\left[^1(20), (10)^2\right] \longrightarrow \left(^1\mathrm{H}, \mathrm{g}^2\right) + \left(^1\mathrm{G}, \mathrm{g}^2\right). \tag{8}$$

By and large, five different terms in the configuration g^2 (see Table 3) are divided into three groups depending on their origin (see Table 4). Analogously, ten terms from the configuration g^4 belong to six different groups. Figure 2 presents a detailed pattern of the splitting of terms for $N = 2$ constructed using the energy values (splitting parameters) taken from Tables 3 and 4.

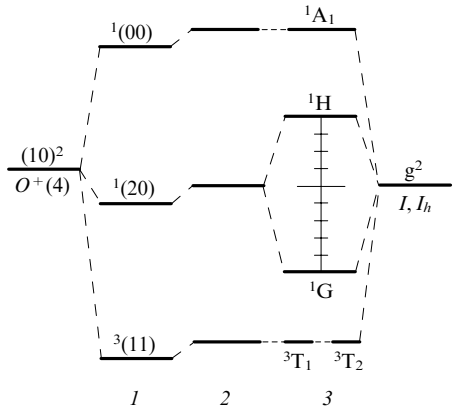


Figure 2. Splitting of terms emerging from the electronic configuration $(10)^2$ in the orthogonal group $O^+(4)$ in electrostatic field of icosahedral symmetry (I, I_h).
Energies of terms in the $(10)^2$ configuration (see Table 4) (*1*); shift of energy levels due to the totally symmetric components of electrostatic field of icosahedral symmetry (*2*); and energies of terms in the g^2 configuration (see Table 3).

3. The splitting of terms

Splittings of terms, similar to those shown in Fig. 2, are well known in the ligand field theory.[72, 74] Additional data on the splitting of terms, obtained within the theory of integral invariants,[44, 47] give novel information and allow one to relate the splitting of terms due to symmetry reduction to the number of integral invariants,[43] a fundamental characteristic of the electron shell. We will consider the issue taking the published data[47, 48] for the configuration g^N (see Tables 1, 3 and 4) as an example.

Two genealogically related electronic configurations λ^N and γ^N, considered in relation to the splitting of terms with conservation of the shell dimension ($\dim\lambda = \dim\gamma$), are characterized by different numbers of invariants (see Table 1)

$$L_{\lambda,\Omega(\lambda)} < L_{\gamma,\Omega(\gamma)}, \tag{9}$$

where $\Omega(\lambda)$ and $\Omega(\gamma)$ are the two point symmetry groups which include the corresponding irreducible representations λ and γ. Thus, the splitting of terms upon symmetry reduction ($\lambda^N \to \gamma^N$) is immediately related to the change in the number of invariants, the number of invariants being a fundamental characteristic of the electronic shell (in addition to the shell dimension).

The two configurations in question, $(10)^N \to g^N$, are characterized by the numbers of invariants equal to 2 and 3, respectively (see Table 1). For better understanding of the interrelation between the number of invariants and the term splitting, we will consider the coefficients $c^{(k)}$ in the expansion (2) for the energy of the g^N-terms originating from the same parent $(10)^N$-term (the corresponding groups of the g^N-terms are listed in Table 4). From the data of Table 3 it follows that all g^N-terms within the same group are characterized by the same coefficients $c^{(0)}$ and $c^{(1)}$. For instance, these coefficients for all g^2-terms arising from the parent term $\left[^1(20), (10)^2\right]$ are

$$c^{(0)}\left(^1\mathrm{H}, \mathrm{g}^2\right) = c^{(0)}\left(^1\mathrm{G}, \mathrm{g}^2\right) = 1, \tag{10}$$

$$c^{(1)}\left(^1\mathrm{H}, \mathrm{g}^2\right) = \mathrm{c}^{(1)}\left(^1\mathrm{G}, \mathrm{g}^2\right) = 1.$$

Also, from relationships (10) it follows that the mean energy of all terms emerging from the same parent term,

$$E_{\mathrm{av}} = \frac{5E\left(^1\mathrm{H}, \mathrm{g}^2\right) + 4E\left(^1\mathrm{G}, \mathrm{g}^2\right)}{9} = \tag{11}$$

$$= H^0(gg) + H^1(gg) + 0 \times H^2(gg)$$

is characterized by the same coefficients $c^{(0)}$ and $c^{(1)}$ specific to the individual (split) terms in Eqn (10).

Two results of crucial importance follow from the relations (10) and (11). Let us compare the mean energy of the group of the split terms with the energy of the corresponding parent term $\left[^1(20), (10)^2\right]$ expressed in terms of the invariants $H^k(10, 10)$ (see Table 4),

$$\left[^1(20), (10)^2\right] = H^0(10, 10) + H^1(10, 10). \tag{12}$$

As can be seen, the coefficients $c^{(0)}$ and $c^{(1)}$, specific to the split g^2-terms [see Eqn (10)] and to their mean energy [see Eqn (11)], are equal to the corresponding coefficients [$c^{(0)}$ and $c^{(1)}$] in the expression for the energy of the parent term (12).

Therefore, the coefficients $c^{(0)}$ and $c^{(1)}$ in the expansion (2) for the energy of the g^N-term characterize the origin of this term. [Strictly speaking, only the $c^{(1)}$ coefficient is characteristic because, by definition, $c^{(0)}\left(^{2S+1}\Gamma, \gamma^N\right) = N(N-1)/2$ depends only on the number of electrons in the configuration γ^N]. Emphasize that the relationships for the $c^{(0)}$ and $c^{(1)}$ coefficients under discussion are of general character in the theory of integral invariants[75] and are thus applicable to all genealogically related configurations $\lambda^N \to \gamma^N$ for which $L_{\gamma,\Omega} = 3$, *i.e.*, for γ = e, t, g (see Table 1).

The next result of paramount importance, which is immediately related to the problem of the splitting of terms, is that the coefficient $c^{(2)}$ corresponding to the mean energy of the group of split terms [see Eqn (11)] is zero

$$c^{(2)}(E_{\mathrm{av}}) = 0. \tag{13}$$

From this it follows that the coefficient $c^{(2)}\left(^{2S+1}\Gamma, \gamma^N\right)$ specific to the individual term $\left(^{2S+1}\Gamma, \gamma^N\right)$ characterizes its position on the energy scale relative to the 'centre of gravity' (mean energy) of all γ^N-terms emerging from the same parent term [see Eqn (11)]. In the energy parameters, the position of the term relative to the 'centre of gravity' is governed by the quantity $c^{(2)} \times H^2(\gamma\gamma)$.

By and large, relations (10)–(13) describe the splitting of terms (see Fig. 2) as follows. On going from the $O^+(4)$ symmetry group to the icosahedral groups (I, I_h) the splitting of terms from the configuration $(10)^2$ can formally be represented by a two-step process whose stages are denoted in Fig. 2 by the numbers '*2*' and '*3*'. They correspond to consecutive inclusion of different components of the electrostatic field of icosahedral symmetry. [Detailed treatment of these field components, *viz*., components of the multipole expansion, and their relation to the integral invariants $H^k(\gamma\gamma)$ is given in the next Sections of the review.]

In the first (intermediate) stage *2*, all terms of the configuration $(10)^2$ undergo a shift but remain unsplit. The shift is due to the action of the components of electrostatic field of icosahedral symmetry, which do not cause splitting. Within the framework of the theory of integral invariants, the inclusion of these components corresponds to a change (re-definition) of the integral invariants $H^k(\gamma\gamma)$ with $k = 0$ and $k = 1$ (Refs 44 and 75). As applied to the process $(10)^N \rightarrow g^N$ under examination, this corresponds to the re-definition of the invariants $H^k(10, 10)$,

$$\begin{aligned} H^0(10,10) &\longrightarrow H^0(gg), \\ H^1(10,10) &\longrightarrow H^1(gg). \end{aligned} \tag{14}$$

This leads to changes in the energies of all $(10)^N$-terms. For instance, the energy of the $\left[^1(20), (10)^2\right]$ term [see Eqn (12)] becomes equal to E_{av} [see Eqn (11)].

In the second stage *3* (see Fig. 2), the remaining components of the electrostatic field, responsible for the splitting of terms are taken into account. Their contributions to the term energy are described by the invariant $H^2(gg)$ which has no analogue among the invariants $H^k(10, 10)$ (where $k = 0$, 1), *i.e*., within the framework of the theory of integral invariants the splitting of terms is immediately related to the change in the number of invariants.[44]

Note that formal division of the splitting of terms into two steps is commonly accepted in the literature (see, *e.g*., a corresponding discussion within the framework of the ligand field theory [74]). In the theory of integral invariants, this operation is natural in the sense that all energy levels (see Fig. 2) are exactly defined mathematically [see Eqns (10)–(14)]. It is important to exactly determine the energy level corresponding to the 'centre of gravity' of the split γ^N-terms. The 'centre of gravity' is determined by the three coefficients $\left\{c^{(0)}, c^{(1)}, c^{(2)} = 0\right\}$, where $\left\{c^{(0)}, c^{(1)}, c^{(2)}\right\}$ are the coefficients characterizing the individual γ^N-term.

Such a determination is very important because it immediately leads to a fundamental condition for the splitting of terms in electrostatic field first derived by Bethe.[72] According to this condition, terms are split in such a manner that the 'centres of gravity' retain their positions. From Eqn (13) it follows (see also Fig. 2) that the position of the 'centre of gravity' differs from the energy level of the parent term defined by Eqn (12).

4. 'Accidental' degeneracy of terms

An analysis of the energy spectrum of states in the configuration g^N (see Table 3) using relations (10)–(13) revealed a number of specific features, which were previously reported only for the atomic l^N-spectra.[66, 76] Among them, the most interesting and unexpected is the degeneracy of the g^N-terms of different spatial symmetry established by Plakhutin,[43]

$$E\left(^{2S+1}\mathrm{T}_1, g^N\right) = E\left(^{2S+1}\mathrm{T}_2, g^N\right) \tag{15}$$

at $N = 2-6$. Such a degeneracy usually called 'accidental' degeneracy is very rare to meet. Prior to Plakhutin's study,[43] the only example of this type of degeneracy was that of atomic terms in the configuration d^3

$$E\left(^2\mathrm{H}, d^3\right) = E\left(^2\mathrm{P}, d^3\right), \tag{16}$$

known since the 1930s.[76]

At present, it is believed that 'accidental' degeneracy is only possible in highly symmetric systems; however, the corresponding lowest symmetry threshold is unknown. The reasons for the degeneracy (16) were unclear for long; however, based on some theoretical results, *e.g*., the degeneracy of atomic terms (16) at any choice of the central field established by Judd,[77] it was assumed that 'accidental' degeneracy can only occur in atoms (or, generally, in systems of continuous symmetry having axes of rotation of an infinite order).

The discovery of 'accidental' degeneracy (15) in icosahedral systems [43] was more recently characterized as 'striking discovery'.[68] It became a challenge to theory and gave an impetus to research in this field. The role of a 'costimulus' was played by another Plakhutin's report [44] on the 'accidental' degeneracy revealed in the analysis of the energy spectrum of states in the icosahedral configuration h^3,

$$E\left[^2\mathrm{T}_1(a), h^3\right] = E\left[^2\mathrm{T}_2(a), h^3\right]. \tag{17}$$

A distinctive feature of this degeneracy consists in its unusual relation to the degeneracy of atomic terms (16) in the parent configuration d^3. To clarify the issue, Table 5 lists the total energy spectrum of states for the configurations d^3 (atom) and h^3 (I, I_h).[44, 45]

Now we will make some remarks. According to group theory,[73] the terms of the atomic configuration d^3 are related to the corresponding terms of the icosahedral configuration h^3 as follows:

$$\begin{aligned} d^3 &\longrightarrow h^3, \\ ^2\mathrm{P}(3) &\longrightarrow {}^2\mathrm{T}_1(3), \\ ^2\mathrm{H}(11) &\longrightarrow {}^2\mathrm{T}_1(3) + {}^2\mathrm{T}_2(3) + {}^2\mathrm{H}(5), \\ ^2\mathrm{F}(7) &\longrightarrow {}^2\mathrm{T}_2(3) + {}^2\mathrm{G}(4), \end{aligned} \tag{18}$$

where the numbers in parentheses denote the degrees of degeneracy of the terms (ignoring spin). Thus, the terms $^2\mathrm{T}_1(h^3)$ and $^2\mathrm{T}_2(h^3)$ appearing in Eqn (17) emerge as a result of splitting of the atomic terms ^{2}P, ^{2}H and ^{2}F from the configuration d^3. From relations (18) it follows that there are two terms $^2\mathrm{T}_1$, which are denoted in Table 5 as $^2\mathrm{T}_1(a)$ and $^2\mathrm{T}_1(b)$, and two terms $^2\mathrm{T}_2$ denoted as $^2\mathrm{T}_2(a)$ and $^2\mathrm{T}_2(b)$.

From the data of Table 1, the numbers of invariants $L_{\gamma,\Omega}$ for the quintuply degenerate atomic (d) and icosahedral (h) shells are [43, 66]

$$L_{\mathrm{d},\,O^+(3)} = 3, \quad L_{\mathrm{h},\,(I,I_h)} = 5, \tag{19}$$

i.e., the energies of the d^N-terms are described by three invariants (the Racah parameters A_{dd}, B_{dd} and C_{dd}, see Table 5) while the energies of the h^N-terms are described by five invariants $H^k(hh)$. The degeneracy of the h^3-terms [see Eqn (17)] is due to the fact that all five coefficients $c^{(k)}$ for the term $^2\mathrm{T}_1(a)$ are equal to the corresponding coefficients

Table 5. Energies of terms emerging from the atomic configuration d^3 and icosahedral configuration h^3, expressed using the Racah parameters (A_{dd}, B_{dd}, C_{dd}) and the integral invariants $H^k(hh)$, respectively.[44–46]

Atomic (parent) term $\left({}^{2S+1}\mathrm{L}, \mathrm{d}^3\right)$	dim L	Icosahedral term $\left({}^{2S+1}\Gamma, \mathrm{h}^3\right)$	$\frac{A_{dd}}{H^0(hh)}$	$\frac{B_{dd}}{H^1(hh)}$	$\frac{C_{dd}}{H^2(hh)}$	$\frac{-}{H^3(hh)}$	$\frac{-}{H^4(hh)}$
^{4}F	7	^{4}G	3	−15	0	−15	−3
^{4}F	7	^{4}T$_2$	3	−15	0	−15	+4
^{4}P	3	^{4}T$_1$	3	0	0	+35	0
^{2}H,^{2}P	11, 3	**^{2}T$_1$(a)**	3	−6	3	−5	−1
^{2}H,^{2}P	11, 3	^{2}T$_1$(b)	3	−6	3	0	+7
^{2}H	11	**^{2}T$_2$(a)**	3	−6	3	−5	−1
^{2}F	7	^{2}T$_2$(b)	3	9	3	+50	+3
^{2}G	9	^{2}G$_{(1)}$	3	−11	3	−95/4	+4
^{2}F	7	^{2}G$_{(2)}$	3	+9	3	175/4	+0
^{2}G	9	^{2}H$_{(1)}$	3	−11	3	−122/7	−31/35
^{2}H	11	^{2}H$_{(2)}$	3	−6	3	−4	3/5
^{2}D$_{(2)}$	5	^{2}H$_{(3)}$	3	+3	3	185/7	9/7
^{2}D$_{(1)}$	5	^{2}H$_{(4)}$	3	+7	7	+15	+3

Notes. 1. Numbers in the last five columns represent the coefficients $c^{(k)}$ in Eqn (2) for the energy of the $\left({}^{2S+1}\Gamma, \mathrm{h}^3\right)$-terms. The first three coefficients $\left[c^{(0)}, c^{(1)}, c^{(2)}\right]$ also determine the energies of the corresponding (parent) atomic states expressed in terms of the Racah parameters A_{dd}, B_{dd}, C_{dd}.

2. The degenerate terms are given in bold. The multiple terms ^{2}T$_1$ and ^{2}T$_2$ have zero off-diagonal Hamiltonian matrix elements, *i.e.*, $\left\langle {}^2\mathrm{T}_1(a)|\hat{H}|{}^2\mathrm{T}_1(b)\right\rangle = \left\langle {}^2\mathrm{T}_2(a)|\hat{H}|{}^2\mathrm{T}_2(b)\right\rangle = 0$.

3. The right subscript in parentheses in the notation of the atomic $\left[{}^2\mathrm{D}_{(i)}\right]$ and molecular $\left[{}^2\mathrm{G}_{(i)}, {}^2\mathrm{H}_{(i)}\right]$ terms enumerates the multiple terms for which the off-diagonal Hamiltonian matrix elements taken between them differ from zero. These matrix elements were reported in Refs 45 and 46.

for the term ^{2}T$_2(a)$ (see Table 5). Note also that the first three out of five coefficients [*i.e.*, $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$] are equal to the coefficients in the expansion of the energy of the corresponding parent d^N-term in terms of the Racah parameters [this follows from the definition of the coefficients $c^{(k)}$ for the h^N-term[45]]; therefore, these three coefficients also characterize the origin of the icosahedral h^N-term.

A specific feature of the degeneracy (17) consists in that the data of Table 5 do not allow one to determine which of the terms ^{2}T$_1$ [*i.e.*, ^{2}T$_1(a)$ or ^{2}T$_1(b)$] emerges from the atomic term ^{2}P and which of them originates from the term ^{2}H, because these atomic terms are degenerate [see Eqn (16)].

Subsequent analysis[44] of the origin of the terms ^{2}T$_1(a)$ and ^{2}T$_1(b)$ led to quite interesting results. It was found that each component of the wave function of the triply degenerate atomic term ^{2}P is related to the corresponding components of the wave functions of the icosahedral terms ^{2}T$_1(a)$ and ^{2}T$_1(b)$ as follows:[44,45]

$$\Psi({}^2\mathrm{P}, \mathrm{d}^3) \longrightarrow \sqrt{\frac{5}{7}}\Psi\left[{}^2\mathrm{T}_1(a), \mathrm{h}^3\right] + \sqrt{\frac{2}{7}}\Psi\left[{}^2\mathrm{T}_1(b), \mathrm{h}^3\right]. \quad (20)$$

On going to the icosahedral symmetry, eleven degenerate wave functions, which describe the term ^{2}H, are divided into three groups of functions corresponding to the terms ^{2}T$_1$, ^{2}T$_2$ and ^{2}H [see relations (18)]. The functions corresponding to the term ^{2}T$_1$ take the form[44,45]

$$\Psi\left({}^2\mathrm{H}, \mathrm{d}^3\right) \longrightarrow \sqrt{\frac{2}{7}}\Psi\left[{}^2\mathrm{T}_1(a), \mathrm{h}^3\right] - \sqrt{\frac{5}{7}}\Psi\left[{}^2\mathrm{T}_1(b), \mathrm{h}^3\right]. \quad (21)$$

A fundamentally important consequence of relationships (20) and (21) is as follows: the degeneracy of the atomic d^3-terms (16) and the degeneracy of the icosahedral h^3-terms (17) *are not accidental*. Indeed, in the case of genuine accidental degeneracy (physically, it is equivalent to the lack of degeneracy) one should get a one-to-one correspondence between the wave functions of the atomic (parent) term ^{2}P and the corresponding *one and only one icosahedral* term ^{2}T$_1$ instead of relatioship (20).†

Taking into account the peculiarity of 'accidental' degeneracy and the lack of clarity in the understanding of physics of this phenomenon, the degeneracies (15) and (17) were checked out independently by direct quantum chemical calculations of real and model icosahedral structures with the corresponding electronic configuration.[47,70,71] The degeneracy of the g^N-terms (15) was checked taking the molecule C_{20} and the ions C_{20}^{n-} (n = 1, 2) with the configurations g^2, g^3 and g^4, respectively, as examples.[47,70] The test systems to verify the degeneracy of the h^3- (h^7-) terms [see expression (17)] included[71] the fullerene cation C_{60}^{3+} with the configuration h_u^7 and a number of metalloendofullerenes M@C_{60} with the configurations h_g^3 and h_g^7. Calculations of these systems were carried out by two *ab initio* methods, ROHF and the full configuration interaction in the restricted active space (FCI RAS) method. In the latter case, the active space included all electrons and orbitals of the corresponding open shell γ^N while the other two shells

† Note also that, although the numerical values of the coefficients in relationship (20) are unambiguously determined from analysis of the wave functions, the origin and physical sense of such values, as $\sqrt{5/7}$ and $\sqrt{2/7}$, remain unclear.[44,45]

(the closed and virtual one) were 'frozen'. Physically, this approach corresponds to the monoconfigurational approximation.[47, 78] These results of calculations substantiated the degeneracy of terms in the icosahedral g^N- and h^3-systems, which was first established [43, 44] within the framework of the theory of integral invariants.

The problem of 'accidental' degeneracy for the three cases mentioned above [see Eqns (15)–(17)] was comprehensively treated in a series of studies by Judd and Lo reported in 1999.[68, 79, 80] They showed that this degeneracy is not accidental, being due to fundamental reasons of symmetry character.

Without dwelling on mathematical details of the analysis [68, 79, 80] based on the unitary group theory, mention may be made that the degeneracy of the terms T_1 and T_2 in the icosahedral configurations g^N and h^3 is due to additional (hidden) symmetry elements in the groups I and I_h, namely, permutation of six axes of rotation of the fifth order (C_5). Such permutations do not change the molecular structure but can not be achieved using conventional symmetry operations in the groups I and I_h; however, their consideration is natural in the joint analysis of these groups and groups of higher symmetry. Within the framework of this approach, the symmetry of the (degenerate) permutations in question can be related to the symmetry of the icosahedral terms in Eqns (15) and (17).

Some consequences from the analysis by Judd and Lo are noteworthy. First, the group-theoretical approach (Refs 68, 79 and 80) is implicitly based on the monoconfigurational approximation. From this it follows that the degeneracy of states in Eqns (15) and (17) is an exact (rigorously proved) result only within the framework of the monoconfigurational approximation.

Next, although comprehensive, an analysis by Judd and Lo provides no general solution to the problem of 'accidental' degeneracy. There is a number of systems with 'accidentally' degenerate terms of different *spin* (not spatial) symmetry. An example is provided by the degeneracy of two terms of a linear molecule of $D_{\infty h}$ symmetry,[81]

$$E\left({}^1\Sigma_u^-, \pi_u^3\,\pi_g^1\right) = E\left({}^3\Sigma_u^-, \pi_u^3\,\pi_g^1\right). \tag{22}$$

Yet another example is the degeneracy of terms in the configuration $(10)^N$ in the orthogonal group $O^+(4)$ (see above and Ref. 48)

$$E\left[{}^1(22), (10)^4\right] = E\left[{}^3(11), (10)^4\right], \tag{23}$$

(see Table 4). To the best of our knowledge, such types of degeneracy have not been analyzed n the literature so far.

Note that, in addition to 'accidental' degeneracy of terms [see Eqns (15) and (17)], the energy spectra of the g^N and h^N states exhibit some other features. In particular, from the data of Table 3 it follows that the absolute value of the energy gap between the terms $\left({}^{2S+1}\mathrm{H}, g^N\right)$ and $\left({}^{2S+1}\mathrm{G}, g^N\right)$ is the same for different configurations g^N, but changes its sign depending on the number of electrons N and on the multiplicity $(2S+1)$:[48, 68]

$$\begin{aligned} E\left({}^1\mathrm{H}, g^2\right) - E\left({}^1\mathrm{G}, g^2\right) &= +9\,H^2(gg), \\ E\left({}^3\mathrm{H}, g^4\right) - E\left({}^3\mathrm{G}, g^4\right) &= -9\,H^2(gg), \\ E\left({}^1\mathrm{H}, g^4\right) - E\left({}^1\mathrm{G}, g^4\right) &= +9\,H^2(gg). \end{aligned} \tag{24}$$

Such an alternation of the sign of the energy gap was earlier known only for atoms (*e.g.*, for the pair of terms ^{4}F and ^{4}P in the configurations d^3 and d^5).[66, 76] In the case of atoms, interest in this type of alternation is due to the fact that in some sense it contradicts the second Hund's rule,[82] according to which the term with the largest orbital quantum number L is characterized by the lowest energy among all terms with the same spin multiplicity. The sign alternation of the energy gap between the atomic terms ^{4}F and ^{4}P means that the term with the larger L (*i.e.*, the term ^{4}F) can lie on the energy scale either higher or lower than the term ^{4}P. For systems of finite symmetry, an analogue to the atomic term with the larger L is the term $^{2S+1}\Gamma$ characterized by the larger dimension of the irreducible representation Γ.

Note also that, in contrast to 'accidental' degeneracy [see Eqns (15) and (17)], alternation of the type (24) was also found in molecular systems of lower symmetry, *e.g.*, in the configuration t^N in cubic systems (T_d and O_h symmetry).[75]

5. Anomalous ('non-Bethe') splitting of terms

As shown above, the general structure of the energy spectra of the g^N- and h^N-states established within the framework of the theory of integral invariants [43–50] is confirmed independently by different methods. In this Section we will consider a number of unsolved problems in the theory of integral invariants and related difficulties in the interpretation of some predictions of this theory. One such problem is related to analysis of the splitting of the sevenfold degenerate atomic term $\left({}^{2S+1}\mathrm{F}, d^N\right)$ in the icosahedral field,

$$\left({}^{2S+1}\mathrm{F}, d^N\right) \longrightarrow \left({}^{2S+1}\mathrm{T}_2, h^N\right) + \left({}^{2S+1}\mathrm{G}, h^N\right). \tag{25}$$

The theory of integral invariants predicts an anomalous character of this splitting at $N = 5$ (Table 6). From the data of Table 6 it follows that the splitting of atomic terms $\left({}^{2S+1}\mathrm{F}, d^N\right)$ occurs on the invariant $H^4(hh)$. [More rigorously, the splitting in question is due to those components of icosahedral electrostatic field , whose contribution to the energies of the split h^N-terms is given by $c^{(4)} \times H^4(hh)$.] According to the general principle of the splitting of terms in electrostatic field,[72] the mean energy ('centre of gravity') of the split terms is conserved [see also Eqn (13) and the

Table 6. Anomalous splitting of the atomic terms $\left({}^{2S+1}\mathrm{F}, d^N\right)$ in icosahedral field.[45, 46]

N	d^N	h^N (I, I_h)	$\frac{A_{dd}}{H^0(hh)}$	$\frac{B_{dd}}{H^1(hh)}$	$\frac{C_{dd}}{H^2(hh)}$	$\frac{-}{H^3(hh)}$	$\frac{-}{H^4(hh)}$
2	^{3}F	^{3}G	1	–8	0	–15	–3
		^{3}T$_2$	1	–8	0	–15	+4
3	^{4}F	^{4}G	3	–15	0	–15	–3
		^{4}T$_2$	3	–15	0	–15	+4
5	^{4}F	^{4}G$_{(2)}$	10	–13	7	30	**+6**
		^{4}T$_2$	10	–13	7	30	**−1**

Note. The configuration h^5 includes two terms of the same symmetry ^{4}G (dim G = 4), namely, ^{4}G$_{(1)}$ and ^{4}G$_{(2)}$. The former emerges from the atomic term ^{4}G (d^5) with the degree of degeneracy dim G = 9 while the latter emerges from the term ^{4}F (d^5). The icosahedral terms ^{4}G$_{(1)}$ and ^{4}G$_{(2)}$ have a zero off-diagonal matrix element of the Hamiltonian, *i.e.*, $\left\langle {}^4\mathrm{G}_{(1)} \middle| \hat{H} \middle| {}^4\mathrm{G}_{(2)} \right\rangle = 0$.

corresponding text]. As applied to the case under examination [splitting (25)], the mean energy of the split terms $^{2S+1}T_2$ and ^{2S+1}G [denoted below as $E_{av}(N)$] is

$$E_{av}(N) = \frac{3\,E\left(^{2S+1}T_2, h^N\right) + 4\,E\left(^{2S+1}G, h^N\right)}{7}, \qquad (26)$$

where the coefficients 3, 4 and 7 are the degree of degeneracy of the corresponding terms. Since the splitting of terms occurs on the invariant $H^4(hh)$, the position of the terms $^{2S+1}T_2$ and ^{2S+1}G on the energy scale relative to the mean energy (26) is determined by the corresponding coefficients $c^{(4)}$, which should meet the condition

$$c^{(4)}[E_{av}(N)] = \frac{3\,c^{(4)}\left(^{2S+1}T_2, h^N\right) + 4\,c^{(4)}\left(^{2S+1}G, h^N\right)}{7} = 0. \qquad (27)$$

From the data of Table 6 it follows that the condition (27) is satisfied at $N = 2$ and 3 and is not satisfied at $N = 5$ for which one has

$$c^{(4)}\left[E_{av}(5)\right] = \frac{3(-1) + 4(+6)}{7} = 3. \qquad (28)$$

This means that the actual position of the 'centre of gravity' of the split terms $^{2S+1}T_2$ and ^{2S+1}G on the energy scale differs from that predicted by theory.

This paradoxical result first obtained in Ref. 45 was called a *'non-Bethe' splitting*.[50] Since the physical meaning of this splitting is unclear, attempts to validate it by independent methods were made.

The energy spectrum of h^N-states similar to those mentioned above (see Tables 5 and 6) was obtained in a more recent study.[83] It seemed natural to use the data [83] to validate the equality (28). Unfortunately, a direct comparison of the two data arrays [45, 83] did not lead to a better insight into the result (28). Moreover, this comparison showed that the energy spectrum [83] *is not symmetry-reduced*. Taking account of a crucial importance of this point to the theory of integral invariants, we will dwell on it in more detail. The invariants $H^k(hh)$ and the Racah parameters (see Table 5 and 6) are related as follows:

$$\begin{aligned} H^0(hh) &\longrightarrow A_{dd}, \qquad (29)\\ H^1(hh) &\longrightarrow B_{dd},\\ H^2(hh) &\longrightarrow C_{dd},\\ H^3(hh) &\longrightarrow 0,\\ H^4(hh) &\longrightarrow 0. \end{aligned}$$

The last two rows show that at $k = 3$ and 4 the invariants $H^k(hh)$ are characteristic of the irreducible representation h (I, I_h) only and have no analogues (vanish) in the atom.

In Ref. 83, energies of the h^N-terms were also expressed in terms of some parameters which we denote here as T_k ($k = 1-5$) (see Table 8 in Ref. 83). First, we mention that the energies of terms were calculated [83] relative to the mean energy of the configuration; therefore, the parameter T_1 and the corresponding contribution to the energy of the term [83] did not appear explicitly (a similar definition of the state energy was earlier used by Slater [66]). The interrelation between the molecular parameters T_k and the atomic Racah parameters or Slater integrals $F^k(dd)$ was not discussed in Ref. 83; nevertheless, it can be established using the expressions for the energy derived by the authors of that study. For instance, the energy difference between the terms $^3G\,(h^2)$ and $^3T_2\,(h^2)$ was reported to be $(5\,T_2 - 5\,T_4 + 3\sqrt{5}\,T_5)/6$.[83] Since these terms originate from the same atomic term $^3F\ (d^2)$, in estimating its energy (in terms of T_k) the energy difference mentioned above should be equal to zero. Using this and similar conditions, the following relationships between T_k and the Racah parameters were derived:

$$\begin{aligned} T_1 &\longrightarrow 5\,A_{dd} + 7\,C_{dd}, \qquad (30)\\ T_2 &\longrightarrow 2\,C_{dd},\\ T_3 &\longrightarrow 5\,B_{dd} + 2\,C_{dd},\\ T_4 &\longrightarrow 9\,B_{dd} + 2\,C_{dd},\\ T_5 &\longrightarrow 3\sqrt{5}\,B_{dd}. \end{aligned}$$

These expressions clearly demonstrate that the parameters T_k (Ref. 83) are not characteristic of icosahedral symmetry (in other words, they are not symmetry-reduced). Because of this, the results [83] cannot be used for analysis of the splitting of atomic d^N-terms in the icosahedral field.

To validate the result (28), direct ROHF and FCI-RAS quantum chemical calculations of appropriate icosahedral structures including metalloendofullerenes M@C_{60}, where M = Cr, Mn, Fe, and their ions with the electronic configuration h_g^5 were carried out.[71] However, an analysis of the results obtained in Ref. 71 showed that no splitting of the d^N-terms of the central atom occurs with a real geometry of metalloendofullerenes ($R_{M-C} = 3.54$ Å) because the electrostatic field induced on the metal atom by the fullerene sphere is too weak. A very small splitting is predicted only upon strong compression of the fullerene ($R_{M-C} = 2.5$ Å); however, its value (about 1 cm^{-1}) is of the order of the overall error of quantum chemical calculations.

Summing up, although the result (28) was reported [45] more than a decade ago, no convincing proofs or rejections are available as yet and the possibility for 'non-Bethe' splitting to occur is still a moot question.

III. Expansion of molecular orbitals of C_{60} fullerene in terms of spherical harmonics

This Section concerns the expansion of π-molecular orbitals of C_{60} fullerene in terms of spherical harmonics. It is accepted that the largest contributions to the highest occupied molecular orbital h_u and to the lowest unoccupied molecular orbital t_{1u} come from the components with the orbital index $l = 5$. Indeed, a one-to-one correspondence between the molecular shells and the orbital angular number l was used in some studies of C_{60} (see, *e.g.*, Refs 12, 52 and 84–88). However, the applicability of this approximation was assessed only recently.[89] In the text below we consider how can the approximation $l = 5$ be derived within the framework of the Hückel model.[37, 38] As a result, we derive simple analytical angular dependences for HOMO, LUMO and LUMO + 1, which then will be used in the following calculations.

1. Molecular orbitals of C_{60} in the Hückel model

The Hückel model treats only π-electrons and ignores σ-electrons (so-called σ – π-separability). Nevertheless, the model correctly predicts the order and degeneracy of molecular orbitals, and gives a reasonable evaluation of the one-electron energy spectrum (in units of the integral β)

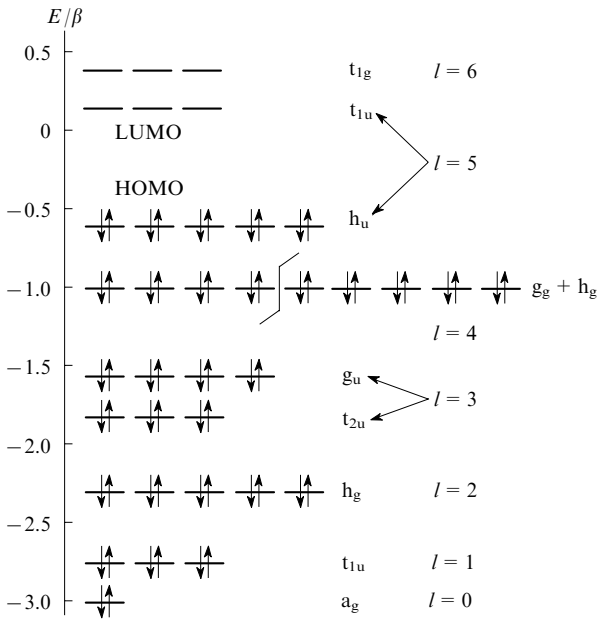


Figure 3. One-electron (π) energy spectrum of C_{60} fullerene first calculated by Bochvar and Galpern.[37]
Each molecular shell corresponds to an irreducible representation (a, t_1, t_2, g, h) in the icosahedral group I_h. In addition, each π shell can to a first approximation be ascribed an orbital index l (see text). The levels g_g and h_g have equal energies because only one value of the transfer integral β is allowed. Taking into account different bond lengths and, correspondingly, integrals $\beta_1 \neq \beta_2$ this degeneracy is removed.

(Fig. 3).[37,38] Interestingly, the pioneering calculation of the one-electron spectrum of C_{60} molecule by the Hückel method was reported by Bochvar and Galpern[37] in 1973, long before the discovery of this molecule. Subsequent more accurate calculations[38,39] within the framework of the same Hückel model or *ab initio* Hartree–Fock calculations (see Table 7) confirmed the order of the upper-lying valence π-shells.

Table 7. One-electron energies (E_{MO}) of the electron shells of C_{60} in the Hartree–Fock method in the vicinity of LUMO–HOMO.[11]

MO	Number	Symmetry	E_{MO}/eV
LUMO+2	187–189	$7t_{2u}$	1.150
LUMO+1	184–186	$3t_{1g}$	0.947
LUMO	181–183	$7t_{1u}$	−0.817
HOMO	176–180	$6h_u$	−7.834
HOMO−1	171–175	$10h_g$	−9.627
HOMO−2	167–170	$6g_g$	−9.890
HOMO−3	163–166	$6g_u$	−12.589
HOMO−4	160–162	$6t_{2u}$	−13.050

Note. Obtained with the aug-cc-pVTZ basis set[90] (no *f*-functions); the C–C bond lengths are 1.4507 and 1.3906 Å;[91] the total energy of the molecule is −61832.1625 eV.

In the one-electron spectrum of C_{60} (see Fig. 3) each π-shell corresponds to a particular orbital number l. Indeed, as was repeatedly mentioned above, the C_{60} molecule possesses the highest molecular symmetry, *viz*., icosahedral symmetry I_h. Therefore, expansion of the electron density of the C_{60} molecule in a multipole series in terms of symmetrized spherical harmonics[92] gives that, except a trivial (but significant) spherical contribution with $L = 0$, other components have smaller magnitudes but are characterized by unusually large multipole moments, *viz*., $L = 6$, 10 and 12.[93–95] This means that the C_{60} molecule is spherical to a very high accuracy. It is due to this fact that the π-molecular orbitals should almost unambiguously be characterized by a particular orbital number l. Thus, the following correspondence between l and π-levels is established in a neutral molecule as the occupation of the π-shell increases with increasing l (see Fig. 3):

π-Level	$1a_g$	$1t_{1u}$	$1h_g$	$1t_{2u}$	$1g_u$	$1g_g$	$2h_g$	$1h_u$
l	0	1	2	3	3	4	4	5

Note that sixty π-electrons completely fill the eight electron shells and, in accordance with the generalized Unsöld theorem,[96] the electron density possesses a complete (unitary) symmetry of icosahedral group, *viz*., the A_{1g} representation. Then, the LUMO $2t_{1u}$ corresponds to $l = 5$ and, eventually, the next unoccupied orbital (LUMO+1) $1t_{1g}$ is characterized by $l = 6$. Although this scheme seems to be reasonable and realistic, the accuracy of this approximation is unknown. Therefore, in the text below the problem of the correspondence between the electronic level and the orbital number l will be solved in another manner, using the calculated eigenvectors of the Hückel model.[89]

Consider the eigenvectors of molecular orbitals in the Hückel model in the form of a matrix C^i_μ, where the superscript i enumerates the molecular orbitals ψ_i and the subscript μ enumerates atomic p-orbitals (*i.e*., $\mu = 1-60$). Correspondingly, one has

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{60} C^i_\mu \chi_\mu(\mathbf{r}). \tag{31}$$

The eigenvectors C^i_μ are found by diagonalization of the 60×60 Hückel matrix $H_{\mu,\nu}$ ($\mu, \nu = 1-60$). In the local polar system of coordinates, each atomic orbital $\chi_\mu(\mathbf{r}')$ is specified by the angular dependence $Y^{m=0}_{l=1}(\theta', \varphi')$. The local axis z' passes from the centre of fullerene (0,0,0) through the nucleus (or centre) of the μth carbon atom of radius $r_{C_{60}} = 3.55$ Å (Fig. 4). The corresponding atomic function

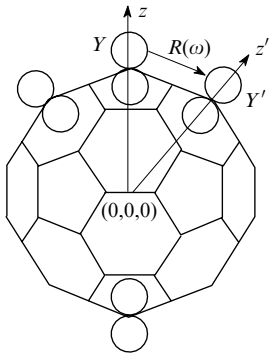


Figure 4. Fullerene C_{60} and atomic p_z-orbitals (angular dependence $Y^{m=0}_{l=1}$).
First, the function $Y^{m=0}_{l=1}(\theta,\varphi)$ aligned along the z axis is expanded in terms of spherical harmonics centred at the origin (0,0,0). Then, this function is rotated towards each carbon atomic nucleus μ ($\mu = 1-60$) (for details, see text).
$Y^{m=0}_{l=1}(\theta',\varphi') = R(\omega_\mu) Y^0_1(\theta,\varphi)$ $(z \to z')$.

χ_μ is defined as the product of the angular component $Y_{l=1}^{m=0}(\theta', \varphi')$ by the radial component $u(r)$

$$\chi_\mu(\mathbf{r}) = u(r)\, Y_1^0(\theta, \varphi). \tag{32}$$

The normalization condition has the form:

$$\int_0^\infty u^2(r) r^2 \mathrm{d}r = 1.$$

To a first approximation, the function $u(r)$ can be determined by simple atomic calculations within the framework of the density functional theory (DFT) in the local density approximation (LDA).

2. Expansion of molecular orbitals in terms of spherical harmonics

Our goal is to expand sixty atomic orbitals χ_μ in terms of spherical harmonics centred at the point (0,0,0), which is also the centre of the molecule of C_{60} fullerene (see Fig. 4) and to derive, using the eigenvectors C_μ^i, an expansion in terms of spherical harmonics for all molecular orbitals. We begin with the solution of an auxiliary problem and consider an atomic orbital v of a carbon atom with the coordinates $(0,0,r_{C_{60}})$. Note that this atomic orbital is aligned along the z axis. Let us expand χ_v in terms of spherical harmonics centred at the point (0,0,0)

$$\chi_v(\mathbf{r}) = \sum_{l=0}^{\infty} u_l(r)\, Y_l^0(\theta, \varphi). \tag{33}$$

The normalization condition is as follows:

$$\sum_{l=0}^{\infty} \int_0^\infty u_l^2(r) r^2 \mathrm{d}r = 1;$$

$u_l(r)$ can be calculated using expression (A7a) in Ref. 86; the necessary details of the computational procedure are reported in the Appendix A in that study. Below we will show that the molecular orbitals of the types h_u (HOMO) and t_{1u} (LUMO) can be described using only a few functions $u_l(r)$, namely, those with $l = 5$ and 7.

Consider the transformation properties of the spherical harmonics $Y_{l=1}^{m=0}$. We are interested in the changes in the expansion (33) provided that the function χ_v is rotated to one out of sixty nuclei of carbon atoms C_μ using rotations by three Euler angles (see Fig. 4). Since the centre of rotation is at the point (0,0,0), this p-function before and after rotation is aligned along the radius of the fullerene. The operator of rotation by three Euler angles $R(\alpha,\beta,\gamma)$ (Ref. 92) transforms the spherical harmonic $Y_l^m(\theta, \varphi)$ to another function $Y_l'^m(\theta, \varphi)$, which can be expanded in terms of fixed (untransformed) spherical harmonics $Y_l^n(\theta, \varphi)$, where $-l \leqslant n \leqslant l$ (Ref. 92)

$$R(\alpha,\beta,\gamma)\, Y_l^m(\theta, \varphi) = \sum_{n=-l}^{l} D_{n,m}^l(\alpha,\beta,\gamma)\, Y_l^n(\theta, \varphi), \tag{34}$$

where $D_{n,m}^l(\alpha,\beta,\gamma)$ are the Wigner functions (or matrices). Note that here and below the expression for the spherical harmonics has the phase factor as defined according to Bradley and Cracknell.[92] This definition differs from that given in Ref. 68. We will also use an abbreviated notation of three Euler angles $\omega = (\alpha,\beta,\gamma)$. Taking account of Eqn (33), the expansion (31) can be re-written:

$$\psi_i(r,\theta,\varphi) = \sum_{\mu=1}^{60} C_\mu^i \sum_{l=0}^{\infty} u_l(r) R(\omega_\mu)\, Y_l^0(\theta, \varphi). \tag{35}$$

Thus, we only have to find $R(\omega_\mu) Y_1^0(\theta, \varphi)$. In a particular case Y_l^0, the general expression for the Wigner D-functions [92] is reduced to

$$D_{n,0}^l(\alpha,\beta,\gamma) = D_{n,0}^l(\beta,\gamma) = \sqrt{\frac{4\pi}{2l+1}}\, Y_l^0(\theta, \varphi)^*.$$

This expression is simpler than relationship (34) because it depends only on two angles only. Thus one gets

$$R(\alpha,\beta,\gamma)\, Y_l^0(\theta, \varphi) = \sqrt{\frac{4\pi}{2l+1}} \left(Y_l^0(\omega_1)\, Y_l^0(\theta, \varphi) + \right. \tag{36}$$

$$\left. + \sum_{n=1}^{l} \left[Y_l^{n,\mathrm{c}}(\omega_1)\, Y_l^{n,\mathrm{c}}(\theta, \varphi) + Y_l^{n,\mathrm{s}}(\omega_1)\, Y_l^{n,s}(\theta, \varphi) \right] \right),$$

where $\omega_1 = (\beta,\gamma)$ and $Y_l^{n,\mathrm{c}}$ and $Y_l^{n,\mathrm{s}}$ are the real spherical harmonics. If the z axis of the function Y_1^0 is aligned along the z' axis specified by the polar angles $(\theta_\mu, \varphi_\mu)$ (these angles also specify the polar coordinates of the nucleus C_μ), one gets $\beta = \theta_\mu$, $\gamma = \varphi_\mu$.

The C_{60} molecule contains sixty carbon atoms whose nuclei have the coordinates $(\theta_\mu, \varphi_\mu)$; therefore, from Eqns (35) and (36) one gets

$$\psi_i(r,\theta,\varphi) = \sum_{l=0}^{\infty} u_l(r) \sum_{\tau} a_{l,\tau}^i\, Y_l^\tau(\theta, \varphi),$$

where $a_{l,\tau}^i$ are the coefficients of the expansion

$$a_{l,\tau}^i = \sqrt{\frac{4\pi}{2l+1}} \sum_{\mu=1}^{60} Y_l^\tau(\theta_\mu, \varphi_\mu) C_\mu^i.$$

Here $\tau = (n,\mathrm{c})$ or (n,s), $n = 0-l$, and C_μ^i are the coefficients of the expansion of the molecular orbital i in the Hückel model.[37,38] The coefficients $a_{l,\tau}^i$ contain detailed information on the expansion and the symmetry of molecular orbitals; but they are composed of many τ-components. Therefore, it is convenient to use the integral quantity

$$g_l^i = \sqrt{\sum_{\tau} (a_{l,\tau}^i)^2}, \tag{37}$$

which characterizes the partial contribution of the components with the same orbital index l. The quantities g_l^i for all π-molecular orbitals calculated in Ref. 89, as well as the coefficients characterizing the partial contributions of the radial component

$$W_l = \int_0^\infty u_l^2(r) r^2 \mathrm{d}r,$$

are listed in Table 8. From group-theoretical considerations it follows that many coefficients g_l^i are zero. The data of Table 8 excellently confirm the appearance of the zero values for the relevant molecular orbitals.

Table 8. Partial l-contributions g_l^i (Hückel model) and the radial contributions W_l to the π-orbitals of C_{60}.[89]

i	Orbital	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$	$l=6$	$l=7$	$l=8$	$l=9$	$l=10$
Partial contributions g_l^i											
1	a_g						0.33465				1.92725
2–4	t_{1u}	4.47159				0.28060		0.20204		1.38664	
5–9	h_g		3.45823		0.37860		0.11346		1.22369		1.06693
10–12	t_{2u}			3.05156		0.19911		0.93154		0.62854	
13–16	g_u			2.82811				1.42396		1.09570	
17–21	g_g				2.47387		1.61285		0.20391		0.84758
22–25	h_g		0.20086		2.59756		1.12223		1.01239		0.51642
26–30	h_u					2.84819		0.20663		0.10719	
31–33	t_{1u}	0.07011				2.13126		1.69637		0.74664	
34–36	t_{1g}						2.67686				0.95258
Radial contributions W_l		0.12230	0.14122	0.13435	0.11717	0.09695	0.07738	0.06027	0.04624	0.03518	0.02667

Note. Empty cells correspond to zero values.

The radial dependence $u(r)$ in Eqn (32) was determined in the self-consistent DFT LDA calculations of carbon atom (configuration s^2p^2). Also, the radial dependence of the electron density for fullerene C_{60} was derived.[97]

3. Analytical expressions for angular dependence

The nonzero coefficients g_l^i (see Table 8) exactly meet the selection rules for the orbital index l in the icosahedral group.[93] The data of Table 2 show that the most important components of the HOMO (h_u) and LUMO (t_{1u}) are described by $l=5$. Also, the radial contributions W_l decreases with an increase in l (except for $l=1$ and 2), so the contributions with $l=7$ and 9 are less important than that with $l=5$. The calculated radial dependences $u_l(r)$ ($l=5-7$) are shown in Fig. 5. By simultaneously taking into account g_l^i and W_l ($l\leqslant 10$), one gets the following partial contributions to h_u: 0.276 ($l=5$), 0.012 ($l=7$) and 0.004 ($l=9$). Correspondingly, for t_{1u} one gets 0.207 ($l=5$), 0.102 ($l=7$), 0.026 ($l=9$), 0.009 ($l=1$). Note that the sums of the contributions differ from unity, being equal to 0.292 (HOMO) and 0.344 (LUMO). This is due to nonorthogonality of the initial basis functions χ_μ [see Eqn (32)] in the Hückel model. To exclude the nonorthogonality effects, the molecular orbitals should be renormalized to unity for all contributions $l\leqslant 10$. One gets that the component with $l=5$ amounts to 94% of HOMO and to 60% of LUMO. Thus, HOMO can be characterized by only one radial component with $l=5$ (see Fig. 5). For LUMO, the component with $l=5$ also makes the major contribution; the next in magnitude contribution ($l=7$) is 30%.

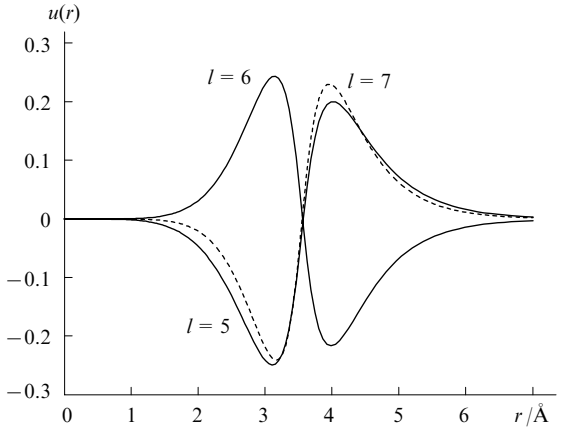


Figure 5. Radial dependence of the fullerene π-wave function obtained using the Hückel model and normalized to unity.
The shells are described using the radial components with $l=5$ (h_u); $l=5$ and 7 (t_{1u}) and $l=6$ (t_{1g}). The curves intercept at a C_{60} fullerene radius of 3.55 Å.

Considering only the contributions with $l=5$ to the HOMO and LUMO, the angular dependences for these shells can be written analytically. We recall that the molecular wave function has the form

$$\psi(\mathbf{r}) = u(r)\phi(\theta,\varphi).$$

Using the group-theoretical approach, only the angular component $\phi(\theta,\varphi)$ is analyzed because the radial component $u(r)$ is invariant to all symmetry operations. Therefore, in the text below we will discuss the angular function $\phi=\phi(\theta,\varphi)$ assuming any radial component. Explicit expressions for the functions ϕ as representations of the icosahedral group in the form of spherical harmonics were first derived by Cohan.[93] These functions are called symmetry adapted spherical harmonics of the group I_h; they were tabulated for all $l\leqslant 14$.[93] Unfortunately, the functions were not normalized in that study; this makes operations with them difficult. Taking into account the normalizing factor, these functions can be expressed using conventional real spherical harmonics $Y_l^\tau(\theta,\varphi)$ [$\tau=0$; (m,c) or (m,s)]. From this point on, in this Section the polar angles in the function designations will be omitted for brevity. In particular, for the HOMO h_u with $l=5$ one gets

$$\phi_1(h_u) = Y_5^{5,s}, \tag{38}$$

$$\phi_2(h_u) = \sqrt{\frac{7}{10}}Y_5^{1,c} + \sqrt{\frac{3}{10}}Y_5^{4,c}, \tag{39}$$

$$\phi_3(h_u) = \sqrt{\frac{7}{10}}Y_5^{1,s} - \sqrt{\frac{3}{10}}Y_5^{4,s}, \tag{40}$$

$$\phi_4(h_u) = \sqrt{\frac{2}{5}}Y_5^{2,c} + \sqrt{\frac{3}{5}}Y_5^{3,c}, \tag{41}$$

$$\phi_5(h_u) = \sqrt{\frac{2}{5}}Y_5^{2,s} - \sqrt{\frac{3}{5}}Y_5^{3,s}. \tag{42}$$

In this case, the C_{60} molecule is oriented in such a manner that its z axis coincides with one of the six fivefold axes of rotation and the molecular y axis coincides with one twofold axis passing perpendicular to the z axis. This orientation of the molecule will be called the Cohan orientation.[93] To obtain a standard molecular orientation (see Fig. 1), where three twofold axes match the x, y and z axes of a Cartesian system of coordinates, the molecule should be rotated by the angle β about the y axis (Ref. 51)

$$\beta = \arccos\left(2\sqrt{10+2\sqrt{5}}\right) \approx 58.28^\circ.$$

Each function of the orbital h_u is expressed through Y_5^τ. In the following, it is assumed that the molecule is in Cohan's orientation, although the final results (energy spectrum, *etc*.) are of course independent of the choice of orientation.

To a first approximation, the lowest unoccupied molecular orbital of the t_{1u} symmetry is described by the $l = 5$ component, which has the following angular dependences:

$$\phi_1(t_{1u};1) = \frac{6}{\sqrt{50}}Y_5^0 + \sqrt{\frac{7}{25}}Y_5^{5,c}, \tag{43}$$

$$\phi_2(t_{1u};1) = \sqrt{\frac{3}{10}}Y_5^{1,c} - \sqrt{\frac{7}{10}}Y_5^{4,c}, \tag{44}$$

$$\phi_3(t_{1u};1) = \sqrt{\frac{3}{10}}Y_5^{1,s} + \sqrt{\frac{7}{10}}Y_5^{4,s}, \tag{45}$$

These expressions for t_{1u} were used in Refs 51 and 62. The angular components for the standard orientation of the C_{60} molecule can be found in the literature (see Table 1 in Ref. 51). The second ($l = 7$) component of this LUMO is described as follows:

$$\phi_1(t_{1u};2) = \frac{1}{5}\sqrt{\frac{77}{5}}Y_7^0 + \frac{4}{5}\sqrt{\frac{3}{5}}Y_7^{5,c}, \tag{46}$$

$$\phi_2(t_{1u};2) = \frac{2}{5}\sqrt{\frac{11}{5}}Y_7^{1,c} - \frac{1}{5}\sqrt{\frac{3}{5}}Y_7^{4,c} + \frac{1}{5}\sqrt{\frac{78}{5}}Y_7^{6,c}, \tag{47}$$

$$\phi_3(t_{1u};2) = \frac{2}{5}\sqrt{\frac{11}{5}}Y_7^{1,s} + \frac{1}{5}\sqrt{\frac{3}{5}}Y_7^{4,s} + \frac{1}{5}\sqrt{\frac{78}{5}}Y_7^{6,s}. \tag{48}$$

The next molecular orbital (LUMO + 1) belongs to the irreducible representation t_{1g} with $l = 6$ and its angular components are as follows:

$$\phi_1(t_{1g}) = Y_6^{5,s}, \tag{49}$$

$$\phi_2(t_{1g}) = \sqrt{\frac{11}{2}}\,\frac{\sqrt{3}}{5}\,Y_6^{1,c} - \sqrt{\frac{11}{2}}\,\frac{1}{5}\,Y_6^{4,c} + \frac{\sqrt{3}}{5}\,Y_6^{6,c}, \tag{50}$$

$$\phi_3(t_{1g}) = \sqrt{\frac{11}{2}}\,\frac{\sqrt{3}}{5}\,Y_6^{1,s} + \sqrt{\frac{11}{2}}\,\frac{1}{5}\,Y_6^{4,s} + \frac{\sqrt{3}}{5}\,Y_6^{6,s}. \tag{51}$$

Expressions (38)–(45) and (49)–(51) were widely used in the studies [12, 51, 86, 87] where the fullerene was treated as a pseudoatom of icosahedral symmetry. It was shown [11, 83, 98] that the energy spectrum obtained in the approximation '$l = 5$' for the HOMO and LUMO is in good agreement with that obtained from the first-principle calculations involving no approximations (38)–(45).

IV. The method of multipole interactions

The electronic energy spectrum of C_{60} molecular ions can be studied by conventional quantum chemistry methods. However, a set of sixty atoms is a rather large quantum system. Therefore, the first calculations of fullerene C_{60} were carried out by either semiempirical or the DFT LDA method.[84, 85, 98–102] More accurate *ab initio* calculations were performed only recently.[11, 83] As an alternative, an original method [12, 103] of investigation of many-electron C_{60} molecular ions using molecular orbitals in the pseudoatom model (see Section III.3) was also developed. It is described in this Section. Note that an interesting approach to the problem of multipole interactions inside the fullerene sphere was proposed [104] and an original one-electron method of linearized spherical waves for spherical clusters including fullerenes was formulated.[105, 106] However, in the following we focus on many-electron effects.

1. The computational scheme for multipole interaction (in t_{1u} shell)

Consider the case for a few t_{1u}-electrons in detail. First, we describe multipole interaction experienced by two electrons and then add yet another t_{1u}-electron and analyze all changes in this new system. By analogy, we can add a next electron to the three-electron system, *etc*., until the number of electrons reaches a specified value n. This makes it possible to obtain the general sotition to the problem. We recall that for the t_{1u}-shell one has $n = 1-6$. Since in this case the spin–orbit interaction is very weak (0.16 cm^{-1}, Ref. 62), we used the so-called LS (or the Russell–Saunders) approximation. Actually, this is not very important because the spin–orbit interaction is the one-electron operator, which can be included in the computational scheme [103] without significant difficulties.

We will characterize the two-electron t_{1u}-states by a basis ket vector I comprising two one-electron indices (i_1, i_2),

$$|I\rangle = |i_1, i_2\rangle. \tag{52}$$

The indices $i = (k, s_z)$ enumerate the t_{1u}-orbitals (k = 1, 2, 3 is the orbital degeneracy) and the spin projection on the z axis. The corresponding two-electron wave functions are expressed through the one-electron functions in a conventional manner

$$\langle \mathbf{r}, \mathbf{r}'|I\rangle = \langle \mathbf{r}|i_1\rangle\langle \mathbf{r}'|i_2\rangle,$$

where

$$\langle \mathbf{r}|i\rangle = u(r)\langle \hat{n}|i\rangle.$$

Here u is the radial component of the molecular orbital t_{1u}, which is independent of the index i, and $\langle \hat{n}|i\rangle$ is the angular component of this molecular orbital. The symbol $\hat{n}$ denotes two angles in the polar system of coordinates, *viz*., $\Omega = (\theta, \varphi)$. Thus, one gets a total of six vectors of t_{1u}-states (or spin-orbitals) $\langle \hat{n}|i\rangle$,

$$\langle \hat{n}|i\rangle = \phi_k(\hat{n})\sigma_s(s_z). \tag{53}$$

Here ϕ_k are the three angular t_{1u}-components described by Eqns (43)–(45) and σ_s is the spin function ($s = \pm$) for the spin projections on the z axis($s_z = \pm 1/2$).

We enunrate the two-electron states by an index i running from 1 to 6. The relative position of the indices in Eqn (52) becomes important if the state i_1 is attributed to

the first electron while the state i_2 is attributed to the second electron. In accordance with the dynamic equivalence of electrons, having changed the order of the spin-orbitals of a state, *i.e.*, $|i_2, i_1\rangle$, one gets

$$|i_2, i_1\rangle = -|i_1, i_2\rangle, \tag{54}$$

because this operation requires the permutation of two electrons. The independent states are described by the vectors (52) with $i_1 > i_2$; otherwise, expression (54) will be used.‡ Thus, our basis set includes $(6\times 5)/2 = 15$ different vectors of states $|I\rangle$.

In the two-electron basis set $|I\rangle$ we calculate the matrix elements of intramolecular Coulomb repulsion between two electrons (in the atomic system of units, the electron charge e equals -1),

$$V(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{55}$$

In terms of the real spherical harmonics Y_l^0, $Y_l^{m,c}$ and $Y_l^{m,s}$ the Coulomb repulsion can be written as a multipole expansion

$$V(\mathbf{r},\mathbf{r}') = \sum_{l,\tau} v_l(r,r') Y_l^\tau(\hat{n}) Y_l^\tau(\hat{n}'), \tag{56}$$

where

$$v_l(r,r') = \frac{r_<^l}{r_>^{(l+1)}} \frac{4pi}{2l+1}. \tag{57}$$

Here $r_> = \max(r,r')$ is the larger of two radii and $r_< = \min(r,r')$ is the smaller of them.

The matrix elements of the direct Coulomb interaction will be calculated for the transitions $i_1 \to j_1$ (first electron) and $i_2 \to j_2$ (second electron) and we recall that $i_1 > i_2$ and $j_1 > j_2$. This type of two-electron transitions will be labelled by the index $a_2 = 1$. From Eqn (56) one gets

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{\text{coul}} = \sum_{l,\tau} v_l c_{l,\tau}(i_1 j_1) c_{l,\tau}(i_2 j_2), \tag{58}$$

where the integral

$$v_l = \int \mathrm{d}r r^2 \int \mathrm{d}r' r'^2 u^2(r) u^2(r') v_l(r,r') \tag{59}$$

gives the effective radial averaging and is independent of the angular components. These integrals describing a strength of two-electron Coulomb operators [68, 79, 80] are analogous to the Slater (or Condon–Shortley) integrals in the classical theory of atomic shells.[76] The matrix elements of the transition ($c_{l,\tau}$) are given by

$$c_{l,\tau}(ij) = \int \langle i|\hat{n}\rangle Y_l^\tau(\hat{n}) \langle \hat{n}|j\rangle \mathrm{d}\Omega. \tag{60}$$

In turn, they are independent of the radial components.

There is also yet another type of electronic transitions, *viz.*, $i_1 \to j_2$ for the first electron and $i_2 \to j_1$ for the second electron. These transitions will be denoted by the index $a_2 = 2$; they lead to exchange interaction. To return to a conventional order of spin-orbitals, one can use relationship (54) and thus gets

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle^{\text{exch}} = -\sum_{l,\tau} v_l c_{l,\tau}(i_1 j_2) c_{l,\tau}(i_2 j_1). \tag{61}$$

Here v_l are still described by expression (59) and the coefficients $c_{l,\tau}$ are described by Eqn (60). With real angular functions t_{1u} and the real spherical harmonics Y_l^τ, the coefficients $c_{l,\tau}$ are also real.

Now consider the spherically symmetric component ($l = 0$) of the Coulomb expansion which is described by a trivial angular function

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}.$$

In this case, the coefficients $c_{l,\tau}$ in Eqn (60) become the diagonal coefficients with respect to the indices i and j

$$c_{l=0}(ij) = \frac{1}{\sqrt{4\pi}} \delta_{ij},$$

where δ is the Kronecker delta.

In the analysis of the coefficients $c_{l,\tau}$ with the other multipolar components (with $l > 0$) we use the selection rules [see expression (60)]. First, all coefficients $c_{l,\tau}$ are diagonal coefficients in terms of the spin components u_s. Second, all odd values of l vanish [from the parity of the integrand in formula (60)]. In addition, from the theory of the addition of angular momenta one gets $l_{\max} = 10$. It follows that nonzero coefficients are possible for $l = 0$, 2, 4, 6, 8 and 10. Note that the coefficients $c_{l,\tau}$ were first used for calculations of the crystal field C_{60}^-.[51, 52] Having added Eqns (61) and (58), one gets

$$\langle I|V(\mathbf{r},\mathbf{r}')|J\rangle = U_0\delta(I,J) + v_2 c_2(I,J) + v_4 c_4(I,J) + \tag{62}$$
$$+ v_6 c_6(I,J) + v_8 c_8(I,J) + v_{10} c_{10}(I,J),$$

where

$$U_0 = \frac{v_0}{4\pi}$$

is the so-called Hubbard repulsion, and

$$c_l(I,J) = \sum_\tau \left[c_{l,\tau}(i_1 j_1) c_{l,\tau}(i_2 j_2) - c_{l,\tau}(i_1 j_2) c_{l,\tau}(i_2 j_1)\right]. \tag{63}$$

Now we have the 15×15 matrix of the intramolecular interaction. Diagonalizing it we obtain the fifteen energy levels $E_p[t_{1u}^2]$ ($p = 1-15$), which we write in the form

$$E_p[t_{1u}^2] = U_0 + v_2\lambda_2(p) + v_4\lambda_4(p) + \tag{64}$$
$$+ v_6\lambda_6(p) + v_8\lambda_8(p) + v_{10}\lambda_{10}(p).$$

A salient feature of Eqn (64) is that the energy spectrum can be found for any set of radial integrals v_l ($l = 2$, 4, 6, 8, 10). To this end, one should first construct the matrix $c_l(I,J)$ of dimension 15×15 using Eqn (63) and then diagonalize it for each l value. The coefficients obtained after diagonlization are labelled $\lambda_l(p)$ (Table 9).

Fifteen energy levels (64) are grouped into three different terms, namely, the ninefold degenerate (t_{1u}^2; 1), the fivefold degenerate (t_{1u}^2; 2) and a singlet term (t_{1u}^2; 3).

‡ One can also work in the space of Slater determinants where antisymmetrization is taken into account explicitly.

Table 9. Coefficients $\lambda_l(p) \times 10^3$ for the electronic molecular configurations t_{1u}^2 ($p = 1-15$) and t_{1u}^3 ($p = 1-20$).

Term	p	Degeneracy	$l = 2$	$l = 4$	$l = 6$	$l = 8$	$l = 10$
Configuration t_{1u}^2							
$^3T_{1g}$	1–9	9	−2.943	−21.190	21.817	−39.706	−37.556
^1H_g	10–14	5	0.589	4.238	23.596	7.941	11.641
^1A_g	15	1	5.886	42.379	26.265	79.413	85.436
Configuration t_{1u}^3							
^4A_u	1–4	4	−8.829	−63.568	65.450	−119.119	−112.667
^2H_u	5–14	10	−3.532	−25.427	68.119	−47.648	−38.872
$^2T_{1u}$	15–20	6	0	0	69.898	0	10.324

(Here the notation t_{1u}^2 means that the t_{1u}-shell is occupied by two equivalent electrons.) From group-theoretical analysis it follows that the same splitting is observed for two holes,[50] *i.e.*, there is a conditional electron–hole symmetry within the same shell. In Section V.3, we will discuss this symmetry in more detail. If we are interested only in energy splitting then one can take that $\lambda_l(t_{1u}^4; p) = \lambda_l(t_{1u}^2; p)$, $p = 1-15$, thereby ignoring a certain shift of the levels (Plakhutin shift, see Refs 35 and 50). Then Eqn (64) holds also for the case of four t_{1u}-electrons (two holes). To obtain the numerical value of the splitting, one should first evaluate the radial integrals v_l [see expression (59)].

Next we will consider the case of three t_{1u}-electrons. For three t_{1u}-electrons (configuration t_{1u}^3), one gets $6 \times 5 \times 4/3! = 20$ basis ket vectors

$$|I'\rangle = |i_1, i_2, i_3\rangle,$$

where $i_1 > i_2 > i_3$. Now the Coulomb intramolecular interaction can be written as the sum of three two-electron terms

$$V^{(3)} = V(\mathbf{r}_1, \mathbf{r}_2) + V(\mathbf{r}_1, \mathbf{r}_3) + V(\mathbf{r}_2, \mathbf{r}_3), \tag{65}$$

where each term $V(\mathbf{r}_a, \mathbf{r}_b)$ is expanded in the multipole series (56), (57). When calculating the matrix element $\langle I'|V^{(3)}|J'\rangle$, one should consider all possible combinations of the one-electron indices in I' and J' (electronic transitions). This requires permutation analysis of all electrons.[12, 36, 103] In the text below we will illustrate the main principle of such an analysis, namely, how to reduce the case of three electrons to the case of two electrons.

Note that only three transitions are possible for the third electron: $i_3 \to j_3$, $i_3 \to j_2$ and $i_3 \to j_1$; they will be denoted by the index a_3 ($a_3 = 1$, 2 and 3). From anticommutation relations it follows that the parity of these transitions (P_3) is +1, −1 and +1, respectively. For each transition, one can consider 'sub-cases' related to transitions of the two remaining t_{1u}-electrons. Denote their final states as j'_1 and j'_2. (For instance, if $a_3 = 1$, the indices are j_1 and j_2; if $a_3 = 2$, the indices are j_1 and j_3; and if $a_3 = 3$, the indices are j_2 and j_3.) However, the two-electron transitions were considered in detail when we analyzed the configuration t_{1u}^2 (see above). We know that there are only two such transitions:

$$i_1 \to j'_1,\ i_2 \to j'_2 \text{ at } a_2 = 1,$$

$$i_1 \to j'_2,\ i_2 \to j'_1 \text{ at } a_2 = 2.$$

The parities of the first and second transitions are $P_2 = +1$ and $P_2 = -1$, respectively. Thus, three-electron transitions are described by two indices (a_3, a_2), where $a_3 = 1-3$ and $a_2 = 1$, 2.

Generally, n electronic transitions are classified using $(n-1)$ indices $(a_n, a_{n-1}, a_{n-2}, \ldots, a_2)$, where $a_k = 1, 2, \ldots, k$. The parity of three-electron transitions (a_3, a_2) is given by

$$P = P_3(a_3)P_2(a_2),$$

in the general case, one has

$$P = P_n(a_n)P_{n-1}(a_{n-1}) \ldots P_2(a_2).$$

The total number of transitions for three t_{1u}-electrons is $3 \times 2 = 6$ (for the general case, $n!$). For the contribution of each transition to the matrix element $V^{(3)}$ [see Eqn (65)], we get

$$\langle I'|V^{(3)}|J'\rangle^{(a_3,a_2)} = \\ = P_3(a_3)P_2(a_2) \sum_{l,\tau} v_l c_{l,\tau}(i_1, j'_1) c_{l,\tau}(i_2, j'_2) \delta(i_3, j_{a_3}) + p.i.$$

Here *p.i.* denote other pair Coulomb interactions $V(r_a, r_b)$. In the case of three electrons, one gets three such terms [see Eqn (65)]. The first of them is given explicitly while the other two terms can be obtained by replacing $c_{l,\tau}(i_1, j'_1)c_{l,\tau}(i_2, j'_2)\delta(i_3, j_{a_3})$ by $c_{l,\tau}(i_1, j'_1)c_{l,\tau}(i_3, j_{a_3})\delta(i_2, j'_2)$ and $c_{l,\tau}(i_2, j'_2)c_{l,\tau}(i_3, j_{a_3})\delta(i_1, j'_1)$ (the parity of the transitions remains unchanged). For n electrons, there are $n(n-1)/2$ different pair interactions. As a result, for the matrix element $\langle I,'|V^{(3)}|J'\rangle$ we have

$$\left\langle I'|V^{(3)}|J'\right\rangle = \sum_{a_3=1}^{3} \sum_{a_2=1}^{2} \left\langle I'|V^{(3)}|J'\right\rangle^{(a_3,a_2)}.$$

As in the case of two electrons, we then diagonalize the 20×20 matrix of repulsion. The energy of the configuration t_{1u}^3 is given by:

$$E_{p'}[t_{1u}^3] = 3U_0 + \sum_{l=2}^{10} v_l \lambda_l(p'). \tag{66}$$

here, as before, summation is performed only over the even l, $p' = 1-20$, the coefficients λ_l are listed in Table 9. The energy levels are grouped into three terms, *viz.*, a fourfold degenerate (t_{1u}^3; 1) (ground state), a tenfold degenerate (t_{1u}^3; 2) and a sixfold degenerate (t_{1u}^3; 3).

This classification scheme of electronic transitions can be used to calculate the matrix elements of any one-electron operator A. This group includes the operator of electron–

nuclear interactions, crystal field, external magnetic field, spin–orbit interaction and the electronic dipole operator. The main difference from the preceding case (the pair electronic interaction) is that only one electron interacts and integration over other variables gives the Kronecker delta. For instance, for three t_{1u}-electrons one gets

$$A = A_1 + A_2 + A_3,$$

where A_k refers to the kth electron. For each 'sub-case' (a_3, a_2) one has

$$\langle I'|A|J'\rangle^{(a_3,a_2)} = P_3(a_3)P_2(a_2)\sum_{l,\tau}\langle i_1|A_1|j'_1\rangle\delta(i_2,j'_2)\delta(i_3,j_{a_3}) + c.p.$$

Here '*c.p.*' denotes the other two contributions, which can be obtained from the first contribution by cyclic permutation of the indices, *i.e.*, $i_1 \to i_2 \to i_3$ and $j'_1 \to j'_2 \to j'_{a_3}$. In the general case of n electrons, there are n terms for each matrix element $\langle I'|A|J'\rangle^{(a_n,a_n-1,\ldots,a_2)}$.

Summing up, it is worth mentioning that the rotation or inversion (R) operator of the group I_h acts on all electrons simultaneously. Therefore, it has the form

$$R = R_n R_{n-1} \ldots R_1,$$

where R_k is the corresponding one-electron operator.

To calculate the many-electron matrix operators, we again use the classification scheme mentioned above. For instance, in the case of three t_{1u}-electrons one gets

$$\langle I|R|J\rangle = \sum_{a_3=1}^{3}\sum_{a_2=1}^{2}\langle I|R|J\rangle^{(a_3,a_2)},$$

where

$$\langle I|R|J\rangle^{(a_3,a_2)} = P^{(a_3,a_2)}\langle i_1|R_1|j'_1\rangle\langle i_2|R_1|j'_2\rangle\langle i_3|R_1|j'_{a_3}\rangle.$$

These expressions were used to determine the character of molecular terms in order to establish to which irreducible representation they belong. Note that the orbital component is transformed as an irreducible representation of the group I_h, whereas the spin component is transformed as a single (t_{1u}^2) or a double (t_{1u}^3) representation of the group $SO(3)$ depending on the parity ($2S$). The resultant molecular terms of C_{60} are labelled as $^{2S+1}\Gamma$, where $2S+1$ is the spin multiplicity and Γ is an irreducible representation of the group I_h.[8,43,68,80]

The molecular terms are $^3T_{1g}$, ^1H_g, ^1A_g for the t_{1u}^2 configuration and ^4A_u, ^2H_u, $^2T_{1u}$ for the t_{1u}^3 configuration (see Table 9).

2. Other ionic configurations

In the partially filled HOMO level instead of electronic states it is more convenient to consider complementary hole configurations $(h_u^+)^m = h_u^{10-m}$ ($m = 2-5$). Such hole states occur in C_{60}^{m+} cations. [The C_{60}^{2+} cation is, in particular, formed in the compounds $(AsF_6)_2C_{60}$ and $(SbF_6)C_{60}$.[40–42]] In the atomic theory a configuration with m holes within the same shell is considered equivalent to the corresponding electron configuration.[76] The same also holds for the molecular ions C_{60}^{m+}, although with some differences (see Section V.3 below). The important finding is that the term splitting of an m hole $(h_u^+)^m$ configuration is equal to the corresponding electronic (h_u^m) term splitting, although the absolute values of energies are of course different. Since we are mainly interested in the splitting of terms, in the following we will use this conditional equivalence. Below discussing the hole configuration $(h_u^+)^m$ we consider it equivalent to the corresponding electron configuration h_u^m.

In determining the basis functions we will take into account the fact that the index i_{h_u} runs from 1 to 10 [the fivefold degeneracy is due to the orbital index, see expressions (38)–(42)] and the twofold degeneracy is due to the spin). As a result, for the energy of terms one gets

$$E_p[h_u^m] = E_0 + \sum_{l=2}^{10} v_l \mu_l^{(m)}(p), \tag{67}$$

where summation is performed over even l values and E_0 is the average configuration energy, which is of no concern for us. The coefficients $\mu_l^{(m)}(p)$ characterize the symmetry of the molecular term. Their values for the case of two electrons (holes) are listed in Table 10; for other cases, they can be found in Ref. 12. These coefficients are analogous to λ_l for the t_{1u} electronic terms. We recall that the electron configurations h_u^2 and h_u^3 correspond to the hole configurations $(h_u^+)^2$ and $(h_u^+)^3$, respectively. It was found that some of these coefficients depend on v_l, which was not observed in the case of t_{1u}^2 or t_{1u}^3 (see Table 9). The dependence appears because in the energy spectrum there are few terms of the same symmetry. For h_u^2, these are two ^1H_g levels while for h_u^3, these are four ^2H_u and two ^2G_u levels. In Plakhutin's approach, these coefficients correspond to off-diagonal matrix elements (see Tables 2 and 3 in Ref. 45). The appearance of ambiguously defined coefficients μ_l means that the calculation of the term splitting (67) is no longer reduced to independent computations of v_l and μ_l. The 'accidental' degeneracy of the $^2T_{1u}$ and $^2T_{2u}$ levels of the h_u^3 configuration was considered in Section II.4.

Table 10. Coefficients $\mu_l(p) \times 10^3$ for the molecular configuration h_u^2.

Term	Degeneracy	$l=2$	$l=4$	$l=6$	$l=8$	$l=10$
$^3T_{1g}$	9	−25.702	−4.238	−8.063	−30.424	−11.151
^3G_g	12	−18.835	−4.238	−35.245	−2.015	−19.244
$^3T_{2g}$	9	−10.987	−39.553	11.212	−28.746	−11.503
^1G_g	4	−18.050	0.471	29.597	13.426	11.721
^1A_g	1	74.162	59.330	57.274	74.228	136.987
^1H_g	5	−18.492[a]	0.471[a]	−12.595[a]	29.970[a]	6.970[a]
^1H_g	5	55.180[a]	16.951[a]	8.429[a]	−18.442[a]	64.255[a]

[a] These coefficients depend on the integrals v_l (see text for details).

In addition to the hole configurations $(h_u^+)^m$, excited configurations $t_{1u}t_{1g}$ and $t_{1u}^2t_{1g}$ were also studied[12,36] because they are used for calculating the electronic dipole transitions $t_{1u}^2 \to t_{1u}t_{1g}$ and $t_{1u}^3 \to t_{1u}^2t_{1g}$ in the anions C_{60}^{2-} and C_{60}^{3-}. The exciton configurations of neutral molecule were calculated in Ref. 11.

V. The energy spectrum of many-electron terms. Hund's rules

1. The splitting energies

To calculate the splittings of molecular terms, one should calculate the radial integrals v_l using expression (59), which requires the radial component $u(r)$ of molecular orbitals. This can be done using the radial functions $u_l(r)$ ($l = 5, 6, 7$) derived within the framework of the Hückel model (see

Section III, Fig. 5). In addition to $u_l(r)$, we will use three model functions $u(r)$.[12, 36] The first model (I) is the most rough and has the form

$$u(r) = \frac{\delta(r - r_{C_{60}})}{r^2}, \tag{68}$$

where δ is the delta function and $r_{C_{60}} = 3.55$ Å is the radius of a sphere passing through the carbon nuclei of the C_{60} molecule. As a result, one gets for v_l

$$v_l = \frac{4\pi}{2l+1}\,\frac{1}{r_{C_{60}}}. \tag{69}$$

The second model (II) uses the exponentially decreasing function of the Slater-orbital type

$$u(r) = C\exp\left(-\sqrt{|E|}\;|r - r_{C_{60}}|\right), \tag{70}$$

where C is found from the normalization condition and $E = -5.863$ eV is the one-electron energy of the p_z-AO calculated by the DFT LDA method. (This dependence is obtained for the p_z-AO in the long distance limit.)

In the third model (III), one has

$$u(r) = C' R_{p_z}\left(|r - r_{C_{60}}|\right), \tag{71}$$

where C' is the normalizing factor and R_{p_z} is the radial component of the p_z-AO. This component was calculated numerically for the carbon atom in the DFT LDA approximation [12] (for the v_l values, see Table 11). Noteworthy are the close values of the parameters v_l calculated using the models II and III. The values of the parameters v_l obtained using model I are much larger due to strong radial contraction (delta function). Thus, model I can be used to roughly estimate the parameters v_l. The models II and III, as well as the Hückel model (in Table 11, it is denoted as $l = 5$) are realistic and correct. In the Hückel model, the functions $u_l(r)$ are more diffuse than the $u(r)$ functions in the models II and III; this leads to somewhat smaller v_l values (Fig. 6). Note that, unlike the functions $u_l(r)$ ($l = 5$, 6, 7), the radial components $u(r)$ in the models II and III are independent of l. By and large, the v_l values obtained in the models II, III and $l = 5$ give good description of the energy spectrum of the C_{60} molecule. Below, we demonstrate this by comparing with the results of quantum chemical calculations.

Table 11. Molecular integrals v_l (eV) calculated for three models of the dependence $u(r)$ [12] and in the Hückel model ($l = 5$, 6, 7).

Model	$l = 2$	$l = 4$	$l = 6$	$l = 8$	$l = 10$	$l = 12$
I	10.195	5.664	3.921	2.998	2.427	2.039
II	6.919	3.064	1.752	1.137	0.797	0.589
III	6.798	2.965	1.673	1.074	0.747	0.550
$\boldsymbol{l} = 5$	5.941	2.439	1.327	0.834	0.574	0.419
$\boldsymbol{l} = 6$	6.087	2.542	1.399	0.885	0.611	0.448
$\boldsymbol{l} = 7$	6.254	2.656	1.476	0.941	0.652	0.480
Model	$l = 1$	$l = 3$	$l = 5$	$l = 7$	$l = 9$	$l = 11$
I	16.991	7.282	4.634	3.398	2.683	2.216
II	13.145	4.390	2.270	1.395	0.944	0.681
III	13.018	4.279	2.181	1.324	0.889	0.637
$\boldsymbol{l} = 5$	11.874	3.615	1.758	1.038	0.686	0.487
$\boldsymbol{l} = 6$	12.013	3.740	1.843	1.098	0.729	0.520
$\boldsymbol{l} = 7$	12.204	3.878	1.937	1.163	0.777	0.556

Note. For $\boldsymbol{l} = 7$, the extra values are $v_{l=13} = 0.418$ and $v_{l=14} = 0.368$ eV.

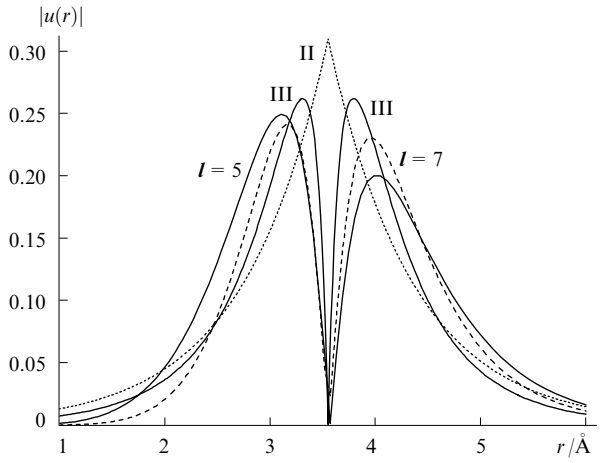


Figure 6. Absolute values of model radial dependences for the π-molecular orbitals of C_{60} fullerene.
The radial dependences in models II and III (for all l-components) were used in Refs 12 and 36. The components with $\boldsymbol{l} = 5$, 6, 7, obtained using the Hückel model are discussed in this review. The point $u(r) = 0$ corresponds to the radius of C_{60} fullerene (3.55 Å).

Now, one can calculate the energy spectra for the configurations t_{1u}^2 and t_{1u}^3 (Table 12) using Eqns (64) and (66). Note that the molecular terms of these configurations are to some extent similar to the atomic terms of the configurations p^2 (^{3}P, ^{1}D, ^{1}S) and p^3 (^{4}S, ^{2}D, ^{2}P), respectively.[76] This is due to the fact that the angular functions $Y_1^{1,c}$, $Y_1^{1,s}$ and Y_1^0 representing the p_x-, p_y- and p_z-AOs, respectively, belong also to the irreducible representation t_{1u} in the group I_h.[93] The models II and III give an almost equal overall splitting of 0.5 eV for the configurations t_{1u}^2 and t_{1u}^3. (The overall splitting is the energy difference between the highest and the lowest energy levels in the group.) This is smaller than the overall splitting of 0.75 eV obtained for the configurations t_{1g}^2 and t_{1g}^3 (Ref. 12).

The splittings for the hole configurations $(h_u^+)^m$ are listed in Tables 13 and 14. In the models II and III, the overall splittings for $(h_u^+)^2$ and $(h_u^+)^3$ is about 1.2 eV. This is much

Table 12. Energies and degeneracies (in parentheses) of molecular terms (eV) of the t_{1u}^2 and t_{1u}^3 electron configurations.

Model, method	Configuration t_{1u}^2			Configuration t_{1u}^3		
	$^3T_{1g}$ (9)	^1H_g (5)	^1A_g (1)	^4A_u (4)	^2H_u (10)	$^2T_{1u}$ (6)
I	−0.225	0.225	0.898	−0.674	0.0	0.449
II	−0.0995	0.0995	0.398	−0.298	0.0	0.199
III	−0.095	0.095	0.380	−0.285	0.0	0.191
$\boldsymbol{l} = 5$	−0.0765	0.0765	0.306	−0.230	0.0	0.154
CAS CI [a]	−0.095	0.095	0.380	−0.285	0.0	0.190

Note. Data for models I – III were taken from Ref. 12. The model $\boldsymbol{l} = 5$ corresponds to the radial dependence obtained using the Hückel model. [a] The method of configuration interaction in complete active space.

Table 13. Energies (eV) of electronic molecular terms $(h_u^+)^2$ calculated using the models II and III (see Ref. 12), the Hückel model with $l = 5$, CAS CI is the method of configuration interaction in complete active space.

Term	Degeneracy	II	III	$l = 5$	CAS CI
$^3T_{1g}$	9	−0.154	−0.150	−0.128	−0.132
^3G_g	12	−0.129	−0.124	−0.104	−0.119
$^3T_{2g}$	9	−0.125	−0.121	−0.099	−0.125
^1G_g	4	0.047	0.043	0.029	0.047
^1H_g	5	0.054	0.050	0.035	0.053
^1H_g	5	0.504	0.494	0.427	0.460
^1A_g	1	1.083	1.050	0.880	0.999

Table 14. Energies (eV) of electronic molecular terms $(h_u^+)^3$ calculated using the models II and III (Ref. 12), the Hückel model with $l = 5$, CAS CI is the method of configuration interaction in complete active space.

Term	Degeneracy	II	III	$l = 5$	CAS CI
$^4T_{1u}$	12	−0.425	−0.412	−0.348	−0.382
^4G_u	16	−0.400	−0.387	−0.324	−0.369
$^4T_{2u}$	12	−0.396	−0.383	−0.320	−0.375
$^2T_{2u}$	6	−0.148	−0.148	−0.137	−0.122
^2H_u	10	−0.132	−0.132	−0.122	−0.112
$^2T_{1u}$	6	−0.119	−0.119	−0.109	−0.114
^2H_u	10	−0.114	−0.114	−0.105	−0.106
^2G_u	8	0.205	0.200	0.171	0.189
$^2T_{1u} + {}^2T_{2u}$ (see [a])	12	0.217	0.213	0.183	0.198
^2H_u	10	0.438	0.430	0.374	0.399
^2G_u	8	0.442	0.434	0.378	0.400
^2H_u	10	0.813	0.789	0.661	0.750

[a] The level $(^2T_{1u} + {}^2T_{2u})$ corresponds to the 'accidental' degeneracy of two terms (see Section II.4).

larger than for the electron configurations t_{1u}^n and t_{1g}^n. In two cases, *viz*., four and three h_u-holes, the overall splitting is twice as large as this value (nearly 2.4 eV).[12] The hole terms are also characterized by the presence of many levels in the vicinity of the ground state. In all cases, the first Hund rule [63, 82] is met, *i.e*., the term of the ground electronic state has the highest spin multiplicity.

The energy splittings (or energy differences) of various configurations are shown in Tables 12–14. The absolute value of this energy requires calculations of the energy of repulsion of the spherically symmetric component and, in addition, all one-electron contributions including the energies of inner electron shells; this goes beyond the scope of this review. However, in some cases we will estimate the energy difference between two configurations using the one-electron energy difference between two levels. For instance, excitation of one t_{1u}-electron to the t_{1g} level causes its one-electron energy to increase by about 1.153 eV (Ref. 33)

$$\Delta\varepsilon_1 = \varepsilon(t_{1g}) - \varepsilon(t_{1u}) \approx 1.153 \text{ eV}. \quad (72)$$

This energy difference is due to the interaction of one valence electron with the carbon atomic nuclei and inner σ- and π-electrons. Thus, a comparison of, *e.g*., the absolute energy t_{1g}^2 with the energy t_{1u}^2 shows that the former should be increased by $2\Delta\varepsilon_1$. The energies of the three-electron configurations t_{1u}^3 and t_{1g}^3 should be increased by $3\Delta\varepsilon_1$. Analogously, excitation of one electron from the h_u to the t_{1u} shell increases the one-electron energy [33] by

$$\Delta\varepsilon_2 = \varepsilon(t_{1u}) - \varepsilon(h_u) \approx 2.69 \text{ eV}.$$

The quantity $\Delta\varepsilon_2$ can be used to correct the energy difference between the t_{1u} and h_u configurations.

The molecular terms of two configurations $t_{1u}t_{1g}$ and $t_{1u}^2t_{1g}$, playing an important role in calculations of the dipole optical transitions from the configurations t_{1u}^2 and t_{1u}^3 can be found in the literature.[12] In both cases, a t_{1u}-electron goes to the higher t_{1g} shell. Therefore, the energies of these configurations should be increased by $\Delta\varepsilon_1$ in comparison with the energies of t_{1u}^2 and t_{1u}^3. Interestingly, the configurations t_{1u}^2 and $t_{1u}t_{1g}$, as well as t_{1u}^3 and $t_{1u}^2t_{1g}$ are characterized by different parity of states. This means no interaction between them.

2. First Hund's rule for the ground state

As mentioned above, the first Hund rule for the ground state is met in all cases considered so far (see Tables 12–14);[12] in other words, the ground state has the highest spin multiplicity.[63, 82] However, our theoretical analysis is reduced to the active space of one molecular shell (t_{1u}, t_{1g} or h_u). If two terms have the same parity and symmetry, a configuration interaction may occur between them, *e.g*., the interaction between the t_{1u}^2 and t_{1g}^2 levels having the same total parity. Excitation of two electrons from the t_{1u} level to the t_{1g} level is accompanied by an increase in the one-electron energy by $2\Delta\varepsilon_1 \approx 2.3$ eV [see Eqn (72)]. This large difference between the centres of configurations favours a decrease in the interactions between distant levels. The effect of $\Delta\varepsilon_1$ on the energy of the configuration interaction between t_{1u}^2 and t_{1g}^2 was studied.[12] Calculations were carried out with allowance for the interactions between two $^3T_{1g}$ terms, two ^1H_g levels and two ^1A_g levels at different $\Delta\varepsilon_1$ values. As earlier, the method of multipole expansion of the Coulomb repulsion (see Section IV) was used. It was found that the terms are grouped in two energy intervals. The lower interval includes the molecular terms of mainly the t_{1u}^2-configuration, whereas the upper interval mainly includes those of the t_{1g}^2-configuration. The energies of the three low-lying terms calculated at different $\Delta\varepsilon_1$ values (in this case, $\Delta\varepsilon_1$ is treated as an independent parameter) are shown in Fig. 7.

Interestingly, the spin triplet $^3T_{1g}$ crosses the spin singlet ^1A_g at 0.58 eV; this is followed by inversion of the terms. Thus, the spin-singlet term ^1A_g is the ground state term at $\Delta\varepsilon_1 < 0.58$ eV, whereas the spin triplet term $^3T_{1g}$ is the ground-state term at $\Delta\varepsilon_1 > 0.58$ eV. The data shown in Fig. 7 explain why the calculations by Negri *et al*.[102] led to the ^1A_g ground state for the C_{60}^{2-} molecular ion. The main reason is a small difference between the one-electron energies of the t_{1g} and t_{1u} shells [see Eqn (72)]. Indeed, $\Delta\varepsilon_1 = 0.64$ eV [102] is nearly two times smaller than a value of 1.153 eV obtained as an experimental estinate [33] for C_{60}^-. The low-lying shell t_{1g} leads to overestimation of the configuration mixing $^1A_g[t_{1u}^2] - {}^1A_g[t_{1g}^2]$ and decreases in the energy of the ^1A_g term below the $^3T_{1g}$ level.

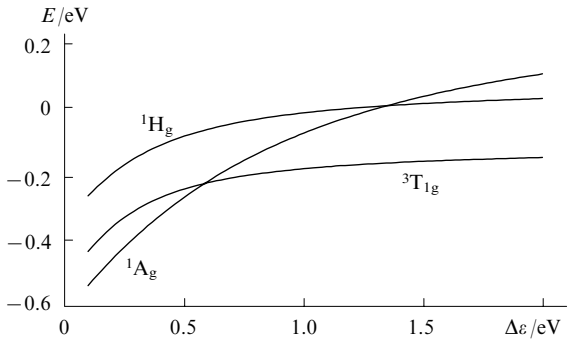


Figure 7. Energies of three low-lying electron levels of interacting configurations $t_{1u}^2 + t_{1g}^2$ plotted *vs.* $\Delta\varepsilon_1$ (energy difference between the one-electron levels t_{1g} and t_{1u} within the pseudoatom model of C_{60}).[12] The ground state is the spin singlet ^1A_g at $\Delta\varepsilon_1 < 0.58$ eV and the spin triplet $^3T_{1g}$ at $\Delta\varepsilon_1 > 0.58$ eV. In the latter case, the first Hund rule is met.

This result was validated by *ab initio* Hartree–Fock calculations with the configuration interaction in the complete active space including two molecular shells, t_{1u} and t_{1g} (LUMO and LUMO + 1). Using the AlgoQMT software [107] and the molecular orbitals of neutral fullerene (in the Dunning aug-cc-pVTZ basis set [90] with no *f*-functions and in the resolution of the identity approximation,[108] in the auxiliary basis set [11] HCNO.001), one gets

$$E(^1A_g) - E(^3T_{1g}) = 0.056\ \text{eV},$$

$$E(^1H_g) - E(^3T_{1g}) = 0.170\ \text{eV}.$$

Further enlargement of the active space to 11 electron shells of C_{60} (from the LUMO to the LUMO + 10 inclusive) causes no changes in the order of the molecular terms

$$E(^1A_g) - E(^3T_{1g}) = 0.073\ \text{eV},$$

$$E(^1H_g) - E(^3T_{1g}) = 0.096\ \text{eV}.$$

This means that the ground state of C_{60}^{2-} remains the $^3T_{1g}$ spin triplet, which exactly obeys Hund's rule.

At the same time, calculations for the three-electron configuration (C_{60}^{3-}) in a large active space revealed a change in the symmetry of the ground-state term. In the active space including the t_{1u} shell (see Table 12) the ground-state corresponds to the ^4A_u level. The situation holds for the active space of the t_{1u} and t_{1g} shells (LUMO and LUMO + 1)

$$E(^2H_u) - E(^4A_u) = 0.352\ \text{eV},$$

$$E(^2T_{1u}) - E(^4A_u) = 0.370\ \text{eV}.$$

However, in the extended active space including four electron shells (from LUMO to LUMO + 3 inclusive), the ground state corresponds to the $^4T_{1u}$ level. The next are the $^2T_{1u}$ and ^4H_u levels (0.014 and 0.029 eV, respectively). Note in this case the ground-state term also has the highest spin multiplicity in accordance with the first Hund rule. Nevertheless, the change in the ground state from ^4A_u to $^4T_{1u}$ is quite unexpected. This result directly affects the character of the optical transitions in C_{60}^{3-} (see below Section VI.2).

3. Fundamental characteristics of the multipole expansion and their relation to the theory of integral invariants

A general expression for the energies of individual terms in the configuration γ^N (γ = t, g, h), obtained by the method of multipole expansion, takes the form [12, 50]

$$E\left(^{2S+1}\Gamma, \gamma^N\right) = \sum_l v_l \times \lambda_l\left(^{2S+1}\Gamma, \gamma^N\right), \tag{73}$$

In particular, the expression (64) for the energies of terms in the icosahedral configuration t^2 is transformed to (73) if [12, 50]

$$U_0 = v_0 \times \lambda_0\left(^{2S+1}\Gamma, t^2\right).$$

By definition, the energy (73) is a part of the total energy accounting for the electron Coulomb interaction within the open shell γ^N, and, therefore, it exactly corresponds to the energy defined in the theory of integral invariants [see Eqn (2)].

This allows one to relate the coefficients $\lambda_l\left(^{2S+1}\Gamma, \gamma^N\right)$ and $c^{(k)}\left(^{2S+1}\Gamma, \gamma^N\right)$ to the corresponding energy characteristics v_l and $H^k(\gamma\gamma)$ appeared in Eqns (73) and (2).

By definition, the quantities v_l and $H^k(\gamma\gamma)$ are independent of the state (term) of the system and characterize only the electron shell γ. All information on the state $\left(^{2S+1}\Gamma, \gamma^N\right)$ is contained in the coefficients $\lambda_l\left(^{2S+1}\Gamma, \gamma^N\right)$ and $c^{(k)}\left(^{2S+1}\Gamma, \gamma^N\right)$, which are denoted in the text below as λ_l and $c^{(k)}$ for brevity. A fundamental difference between λ_l and $c^{(k)}$ is that the former depends also on the multipole expansion number l, *i.e.*, the coefficients λ_l are functions of two different physical characteristics. Plakhutin [50] proposed a direct procedure for separation of these two dependences, which involves representation of the coefficients λ_l in the form

$$\lambda_l\left(^{2S+1}\Gamma, \gamma^N\right) = \sum_k \beta_l^{(k)} \times c^{(k)}\left(^{2S+1}\Gamma, \gamma^N\right), \tag{74}$$

where $\beta_l^{(k)}$ are some new coefficients to be discussed below. Having substituted expression (74) into Eqn (73) and compared it with Eqn (2), one gets the relation between the corresponding energy characteristics:[50]

$$H^k(\gamma\gamma) = \sum_l \beta_l^{(k)} v_l\,. \tag{75}$$

From this it follows that the coefficients $\beta_l^{(k)}$ are independent of the state under study and only characterize the electronic shell γ (γ = t, g, h) and the components of the multipole expansion l (l = 0, 1, 2, ...).

From the group-theoretical standpoint this result means that it is the coefficients $\beta_l^{(k)}$ that are the fundamental (symmetry-reduced) characteristics of the multipole expansion, whereas λ_l (main coefficients of the multipole expansion method [12]) are composite quantities. The fundamental character of the coefficients $\beta_l^{(k)}$ was demonstrated [50] for the configuration t_{1u}^N (I_h). In that study, it was found that the invariants $H^k(t_{1u}t_{1u})$ (k = 0, 1) are related to the corresponding characteristics of the multipole expansion:

$$H^0(t_{1u}t_{1u}) = \beta_0^{(0)} v_0 + \beta_6^{(0)} v_6 + \beta_{10}^{(0)} v_{10}\,, \tag{76}$$

$$H^1(t_{1u}t_{1u}) = \sum_{l=0}^{10} \beta_l^{(1)} v_l$$

[all coefficients $\beta_l^{(0)}$ with $l = 1-5$ and $l = 7-9$ in this case are zero from symmetry considerations]. Clearly, the invariant $H^0(t_{1u}t_{1u})$ corresponds to the totally symmetric part of the multipole expansion with the $l = 0$, 6, and 10 components. In the theory of multipole expansion this information is contained in the coefficients $\beta_l^{(k)}$ and Eqn (76) illustrates this statement.

Expressions (74)–(76) relate the key characteristics of the method of multipole expansion to those of the theory of integral invariants. Using these relations and the known expansion of two-electron integrals in terms of the integral invariants [see Eqn (1)], one can also derive a direct relation between these invariants and the main characteristics of the multipole expansion $[v_l$ and $\beta_l^{(k)}]$. In our case $\gamma = t_{1u}$ (I_h), the expansion of the two-electron integrals has the form:[50]

$$J_{mm} = H^0(t_{1u}t_{1u}) + 4H^1(t_{1u}t_{1u}), \tag{77}$$

$$J_{mn} = H^0(t_{1u}t_{1u}) - H^1(t_{1u}t_{1u}),\ m \neq n,$$

$$K_{mn} = H^1(t_{1u}t_{1u}),\ m \neq n,$$

where the indices m, n = 1, 2, 3 enumerate the t_{1u} orbitals.

Applying the results of the theory of integral invariants to the method of multipole expansion, one can also relate the coefficients λ_l for the terms of the configuration γ^N to the corresponding coefficients for the terms of the complementary configuration

$$\gamma^{N_{\max}-N} \equiv \gamma^{2\dim\gamma-N},$$

where $N_{\max} = 2\dim\gamma$ is the maximum number of electrons which can be accommodated on the close γ^N shell. This relation has the form [50]

$$\lambda_l\left({}^{2S+1}\Gamma, \gamma^{2\dim\gamma-N}\right) = \lambda_l\left({}^{2S+1}\Gamma, \gamma^N\right) + \tag{78}$$
$$+ (1-2f_N) \times \lambda_l({}^1\mathrm{A}, \gamma^{2\dim\gamma}),$$

[here we use the same notations as in Eqn (6)].

From Eqn (78) it follows with certainty that the energy gap between any two terms of the configuration γ^N (*e.g.*, the terms ${}^{2S_1+1}\Gamma_1$ and ${}^{2S_2+1}\Gamma_2$) calculated using Eqn (73) equals the energy gap between two corresponding terms in the 'hole' configuration $\gamma^{2\dim\gamma-N}$, *i.e.*,

$$E\left({}^{2S_1+1}\Gamma_1, \gamma^{2\dim\gamma-N}\right) - E\left({}^{2S_2+1}\Gamma_2, \gamma^{2\dim\gamma-N}\right) = \tag{79}$$
$$= E\left({}^{2S_1+1}\Gamma_1, \gamma^N\right) - E\left({}^{2S_2+1}\Gamma_2, \gamma^N\right).$$

This result confirms the correctness of the splitting values [12] between the terms of the hole configuration h_u^{10-N} in C_{60} cations calculated assuming equal coefficients λ_l for the corresponding terms in the electronic (γ^N) and hole$\left(\gamma^{N_{\max}-N}\right)$ configurations.

Summing up, the method of multipole expansion[12] developed to describe various physical characteristics of fullerene ions is deeply related to other known approaches including the theory of integral invariants [44] and the ROHF method.[69] For systems with one open shell (γ^N configuration), this interrelation explicitly follows from the equivalence of the expressions for energy [see Eqns (2), (4) and (73)] and also from the detailed correspondence between other characteristics of these methods [see Eqns (74)–(77)].[50]

This relation also hihlights a number of unsolved theoretical problems in the method of multipole expansion. Among them, the most important is to carry out the first-principle calculations of the fundamental characteristic of the method, *viz.*, the coefficients $\beta_l^{(k)}$. At present, these coefficients are defined implicitly [50] *via* the coefficients λ_l and $c^{(k)}$ [see Eqn (74)].

4. The magnetic moments

The open shells of $C_{60}^{m\pm}$ molecular ions have nonzero magnetic moments. To calculate then within the framework of the C_{60} pseudoatom model, the initial many-electron Coulomb interaction $V(r,r')$ should be augmented with the magnetic interaction of electrons in an external magnetic field H:

$$V_{\mathrm{mag}} = -M_z H, \tag{80}$$

where

$$M_z = \sum_{k=1}^{n} M_z(k)$$

is the sum of the one-electron contributions with

$$\mathbf{M}(k) = \mu_{\mathrm{B}}\left[\mathbf{L}(k) + 2\mathbf{S}(k)\right]. \tag{81}$$

Here μ_{B} is the Bohr magneton, $\mathbf{L}$ is the orbital momentum, $\mathbf{S}$ is the spin momentum, the index k runs from 1 to n for electrons and from 1 to m for holes. The magnetic moment [see Eqn (81)] belongs to the group of one-electron operators (see above, Section IV.1). Using the electron density matrix $\langle I|V_{\mathrm{mag}}|J\rangle$, one can express the matrix elements of the one-particle operator through $\langle i|M_z|j\rangle$.

In turn, expressions for the one-particle matrix elements of the spin moment are known.[63] They are independent of the molecular orientation.

To calculate the orbital momentum, we will first of all consider the C_{60} fullerene in the Cohan orientation.[93] For real spherical harmonics, one has

$$L_z Y_l^{m,\mathrm{c}} = \mathrm{i}m Y_l^{m,\mathrm{s}},$$

$$L_z Y_l^{m,\mathrm{s}} = -\mathrm{i}m Y_l^{m,\mathrm{c}},$$

where m is the azimuthal quantum number. Taking into account these relationships for the orbital momenta of the t_{1u} states [Eqns (43)–(45)], one gets

$$\langle t_{1u}, 2|L_z|t_{1u}, 3\rangle = 2.5\mathrm{i}$$

and the corresponding expression for the complex conjugate. Other matrix elements of L_z are equal to zero. (From this point on, all magnetic moments are given in Bohr magnetons.) For the h_u states [see Eqns (38)–(42)], one gets

$$\langle h_u, 2|L_z|h_u, 3\rangle = \frac{\mathrm{i}}{2},$$

$$\langle h_u, 4|L_z|h_u, 5\rangle = \mathrm{i}$$

and the corresponding expressions for the complex conjugates (other are zero).

The magnetic properties of the C_{60} molecule in an external field can be determined in two manners. One of them involves active rotation of the molecule as a three-dimensional object provided that the magnetic field is always aligned to the z axis and the molecular position is

specified by three Euler angles $\omega = (\alpha, \beta, \gamma,)$. In the second approach, the molecular orientation remains unchanged while the direction of the magnetic field is changed. In this case, one should use the matrix elements for all three components of the orbital momentum.

Having calculated the matrix elements V_{mag}, we diagonalize the matrix

$$H = \sum_{a,b} V(\mathbf{r}_a, \mathbf{r}_b) + V_{\text{mag}}(a).$$

The molecular degeneracies are removed and one can determine the magnetic moment of each sublevel p using the formula

$$M(p) = \langle p|M_z|p\rangle, \tag{82}$$

where $|p\rangle$ is the corresponding eigenvector.

Consider the ground state of a system with two t_{1u}-electrons (holes), *i.e.*, the term $^3T_{1g}$. Its spin multiplicity is 3 and the number of spatial components is also 3; therefore, the overall degeneracy is 9, *i.e.*, one has $p = 1-9$. In accordance with Eqn (82), one gets nine values of the magnetic moment

$$M = 0;\ \pm 0.5;\ \pm 2;\ \pm 2.5;\ \pm 4.5.$$

By analogy, for the ^1H_g term one gets

$$M = 0;\ \pm 2.5;\ \pm 5;$$

for the term ^1A_g, the spin and orbital momenta are zero or

$$M = 0.$$

For the three-electron system one has

$$M = \pm 1;\ \pm 3 \text{ (ground state } ^4A_u);$$

for the term ^2H_u one has

$$M = \pm 1;\ \pm 1.5;\ \pm 3.5;\ \pm 4;\ \pm 6;$$

for the term $^2T_{1u}$ one has

$$M = \pm 1;\ \pm 1.5;\ \pm 3.5.$$

From the M values (see above) it follows that the coupling scheme of the orbital and spin moments differs from that used in the atomic case.

In the case of configuration interaction, one also deals with changes in the magnetic moments. In Section V.2, we have considered the mixing of the configurations t_{1u}^2 and t_{1g}^2 of C_{60}^{2-} anion. It was found [12] that in this case the magnetic moments of the ground-state term $^3T_{1g}$ can be written as follows:

$$M = 0;\ \pm g;\ \pm 2;\ \pm(2+g);\ \pm(4+g). \tag{83}$$

When no mixing occurs (the case of the $^3T_{1g}$ term of the configuration t_{1u}^2), the M values are calculated using formula (83) assuming that $g = 0.5$. Generally, the parameter g depends on $\Delta\varepsilon_1$.[12]

The magnetic moments of the hole configurations $(h_u^+)^m$, where $m = 2-5$, were reported in Ref. 12. Usually, the magnetic moments are described by a relation similar to expression (83), although in some cases one should use two different parameters g, *i.e.*, g_1 and g_2.[12] For instance, the magnetic moments of the term 1^2H_u of the configuration $(h_u^+)^3$ are given by:

$$M = \pm(g_1; g_2; 1; 2-g_2; 2-g_1),$$

$$g_1 = 0.6529,\ g_2 = 0.8265.$$

Interestingly, the magnetic moments are independent of the molecular orientation. This holds for both shells, t_{1u} and h_u, so most likely, a group-theoretical explanation for this fact is possible. We will try to clarify the situation taking a single t_{1u}-electron in a magnetic field as an example. Consider the extermal magnetic field **H** applied along the direction $\mathbf{n} = \mathbf{H}/H$. Then

$$n_x = \sin\theta\cos\varphi,$$

$$n_y = \sin\theta\sin\varphi,$$

$$n_z = \cos\theta,$$

$$V_{\text{mag}} = \mathbf{HL} = HL_n.$$

The matrix L_n is given by

$$L_n = n_x L_x + n_y L_y + n_z L_z.$$

Having calculated the matrix elements, from Eqns (43)–(45) for the three components of t_{1u} one gets

$$L_n = \begin{pmatrix} 0 & -M_0 n_y \mathrm{i} & M_0 n_x \mathrm{i} \\ M_0 n_y \mathrm{i} & 0 & M_0 n_z \mathrm{i} \\ -M_0 n_x \mathrm{i} & -M_0 n_z \mathrm{i} & 0 \end{pmatrix},$$

where $M_0 = 2.5\ \mu_B$. As before, the magnetic moments are determined by diagonalization of the matrix L_n. One gets $M = 0$ and $M = \pm 2.5\ \mu_B$ for any direction **H**. A similar result is obtained for one h_u-electron (hole). In this case, the magnetic moments are equal to $0; \pm 1/2; \pm 1\ \mu_B$ for any direction **H**. This result for a single electron possibly predetermines the independence of the magnetic moments of molecular rotation also in the many-electron case.

VI. Electronic and optical transitions

In this Section we consider the electronic dipole and corresponding optical transitions of C_{60}^{n-} and neutral C_{60} molecule. First of all, mention should be made that such description is incomplete because it ignores vibronic interactions (so-called Herzberg–Teller interactions [109]), which can indirectly change the symmetry of the initial and final states.[8, 109] In the following, we will consider only the electronic of this complicated problem.

1. Molecular ions C_{60}^{2-} and C_{60}^{3-}

Optical transitions occur if the expectation value of the electronic dipole operator **P** differs from zero. The operator of the electric dipole moment

$$\mathbf{P} = -\mathrm{e}\sum_i \mathbf{r}_i \tag{84}$$

is odd with respect to inversion. It follows that the matrix element **P** is zero for the same-parity states. Therefore, all spectral lines due to the dipole radiation of an electron are only observed for the transitions involving parity changes (Lapport rule [76]). As applied to the molecular ions C_{60}^{2-} and C_{60}^{3-}, this means that one should consider the following transitions:

$$t_{1u}^2 \to t_{1u}t_{1g}, \tag{85}$$

$$t_{1u}^3 \to t_{1u}^2 t_{1g}.$$

The intensity of a transition line from the level A to the level B is given [76] by

$$I(A,B) = N(a)\mathrm{h}\nu\,\frac{64\pi^4\sigma^3}{3\mathrm{h}}S(A,B),$$

where $N(a)$ is the number of C_{60}^{n-} ions in the state a,

$$\nu = \frac{E_A - E_B}{\mathrm{h}}$$

is the line frequency and $\sigma = \mathrm{h}\nu/c$ is the wavenumber. The line strength $S(A,B)$ is found from the equation

$$S(A,B) = \sum_{a,b}\left|\langle a|\mathbf{P}|b\rangle\right|^2. \quad (86)$$

Then, we will calculate the $S(A,B)$ values for the transitions (85). The matrix elements of the dipole operator are given by:

$$\langle a|\mathbf{P}|b\rangle = \sum_{I,J}\langle a|I\rangle\langle I|\mathbf{P}|J'\rangle\langle J,'|b\rangle,$$

where $|I\rangle$ and $|J'\rangle$ are the basis states of the configurations t_{1u}^2 and $t_{1u}t_{1g}$, respectively, and $\langle a|I\rangle$ and $\langle b|J'\rangle$ are the eigenvectors of the levels a and b, respectively. Since we deal with the one-electron operator (84), the expression for $\langle I|\mathbf{P}|J'\rangle$ can be derived using the method considered in Section IV. We recall that $\langle I| = \langle i_{u1}, i_{u2}|$, where i_{u1} and i_{u2} ($i_{u1} > i_{u2}$) are the indices which enumerate the six states t_{1u}, and $|I'\rangle = |j_u, j_g\rangle$ [see Eqn (52)]. From the parity of the states it follows that the nonzero matrix elements should have the form $\langle i_u|\mathbf{P}|j_g\rangle$. They can be calculated using the procedure from Section IV.1 and having separated two components, angular and radial, in explicit form. (For details, see Ref. 12.) If the eigenvectors and eigenvalues of t_{1u}^2 and $t_{1u}t_{1g}$ are known, one can calculate the line strengths using Eqn (86). The results obtained are listed in Tables 15 (pseudoatom model) and 16 (are configuration interactions).

The optical transitions (85) for C_{60}^{3-} are considered analogously. One should calculate the matrix elements **P** between the three-electron basis vectors

$$\langle I, t_{1u}^3| = \langle i_1, i_2, i_3|,$$
$$|J, [t_{1u}^2 t_{1g}]\rangle = |j_1, j_2, j_g\rangle.$$

The line strengths thus determined are listed in Tables 17 (pseudoatom model) and 18 (configuration interaction).

Table 15. Energies $E_{ab} = \Delta\varepsilon_1 + \varepsilon_{ab}$ (eV) and line strengths (in arbitrary units) for the electronic transitions $(t_{1u}^2; a) \rightarrow (t_{1u}t_{1g}; b)$ calculated in the pseudoatom model III (Ref. 12).

b	$a = {}^3T_{1g}$		$a = {}^1H_g$		$a = {}^1A_g$	
	ε_{ab}	S	ε_{ab}	S	ε_{ab}	S
^1A_u						
^3H_u	−0.350	0.482				
$^3T_{1u}$	−0.267	0.289				
^1H_u			0.392	0.482		
^3A_u	0.624	0.386				
$^1T_{1u}$			0.609	0.161	0.323	0.129

Note. Here and in Table 17 $\Delta\varepsilon_1$ is the phenomenological one-electron parameter (for details, see text). Listed are only nonzero line strengths, $S(a,b) \neq 0$.

Table 16. Energies (E_{ab}/eV) and oscillator strengths (f) of low-lying electronic transitions $(t_{1u}^2; a) \rightarrow (t_{1u}t_{1g}; b)$ calculated by the method of configuration interaction in the complete active space $t_{1u} + t_{1g}$.

b	$a = {}^3T_{1g}$		$a = {}^1A_g$		$a = {}^1H_g$	
	E_{ab}	f	E_{ab}	f	E_{ab}	f
^1A_u						
^3H_u	1.338	4.256				
$^3T_{1u}$	1.270	4.510				
^1H_u					2.631	7.503
^3A_u	3.063	7.797				
$^1T_{1u}$			2.704	1.208	2.704	5.113

Table 17. Energies $E_{ab} = \Delta\varepsilon_1 + \varepsilon_{ab}$ (eV) and line strengths (in arbitrary units) for the electronic transitions $(t_{1u}^2; a) \rightarrow (t_{1u}t_{1g}; b)$ calculated in the pseudoatom model III (Ref. 12).

b	$a = {}^4A_u$		$a = {}^2H_u$		$a = {}^2T_{1u}$	
	ε_{ab}	S	ε_{ab}	S	ε_{ab}	S
^4H_g						
$^2T_{1g}$			−0.913	0.002	−1.103	$< 10^3$
^2G_g						
$^2G_u + {}^2T_{2u}$			−0.330	0.450		
$^4T_{1g}$	−0.010	0.771				
^2H_g			−0.158	0.120	−0.349	0.205
$^2T_{1g}$			0.058	0.072	−0.132	0.120
^2H_g			0.508	0.683	0.318	0.277
^2A_g					0.589	0.193
$^2T_{1g}$			0.780	0.602	0.920	0.362

Three optical transitions from the ground-state term $^3T_{1g}$ are observed for the C_{60}^{2-} ion (see Table 15)

$$E(^3T_{1g} \rightarrow {}^3H_{1u}) = \Delta\varepsilon_1 - 0.350\ \mathrm{eV},$$
$$E(^3T_{1g} \rightarrow {}^3T_{1u}) = \Delta\varepsilon_1 - 0.267\ \mathrm{eV},$$
$$E(^3T_{1g} \rightarrow {}^3A_u) = \Delta\varepsilon_1 + 0.624\ \mathrm{eV}.$$

For $\Delta\varepsilon_1 = 1.153$ eV [see Eqn (72)], one gets

$$E(^3T_{1g} \rightarrow {}^3H_{1u}) = 0.803\ \mathrm{eV},$$
$$E(^3T_{1g} \rightarrow {}^3T_{1u}) = 0.886\ \mathrm{eV},$$
$$E(^3T_{1g} \rightarrow {}^3A_u) = 1.777\ \mathrm{eV}.$$

These values should be compared with two main transition bands, *viz*., 1.305 (950 nm) and 1.494 eV (830 nm), which were observed in the IR spectra of C_{60} in solution.[33] It follows that the first two transitions can conditionally correspond to the experimental values if one takes a somewhat larger value of $\Delta\varepsilon_1 \approx 1.7$ eV. This is admissible because in the context of Ref. 12 the parameter $\Delta\varepsilon_1$ in Eqn (72) is phenomenological.

The results of calculations by the method of configuration interaction in the complete active space including the $t_{1u} + t_{1g}$ (LUMO and LUMO + 1) molecular orbitals of a neutral C_{60} molecule (Ref. 11) (the Dunning aug-cc-pVTZ basis set[90] without *f*-functions, using expansion of the unitary operator,[108] in the auxiliary basis set[11] HCNO.001) (see Table 16) are in good agreement with the results obtained within the framework of the pseudoatom

model. Thus, the theoretical results agree with the experimental data for C_{60}^{2-}, although the theory predicts a third transition band at 3.063 eV.

Poorer agreement between the results of calculations and experimental data was obtained for the molecular ion C_{60}^{3-}. The pseudoatom model of C_{60} [12] as well as the configuration interaction method in the active space of the t_{1u} (LUMO) or $t_{1u}+t_{1g}$ (LUMO and LUMO + 1) predict the ^4A_u ground state (see Section V.2). Using the data of Table 17, one can find that for the ground state there is only one optical transition, *viz.*, $^4A_u \rightarrow {}^4T_{1g}$. Its energy calculated by the method of configuration interaction (see Table 18) is about 2.2 eV. This contradicts the experimental

Table 18. Energies (E_{ab}/eV) and oscillator strengths (f) of low-lying electronic transitions (t_{1u}^2; a) $\rightarrow$ ($t_{1u}t_{1g}$; b) calculated by the configuration interaction method in the complete active space $t_{1u}+t_{1g}$.

b	$a = {}^4A_u$		$a = {}^2H_u$		$a = {}^2T_{1u}$	
	E_{ab}	f	E_{ab}	f	E_{ab}	f
^4H_g						
$^2T_{1g}$			1.297	0.022	1.297	0.020
^2G_g						
$^2G_u + {}^2T_{2u}$			1.918	3.245		
$^4T_{1g}$	2.197	8.914				
^2H_g			1.725	0.604	1.725	2.048
$^2T_{1g}$			1.937	1.114	1.937	3.192
^2H_g			2.897	11.416	2.897	1.744
^2A_g					3.097	3.480
$^2T_{1g}$			3.708	16.927	3.708	4.037

data, according to which there are three optical bands at 1350 (0.919 eV), 960 (1.292 eV) and 770 nm (1.61 eV).[33] In principle, the $^4A_u \rightarrow {}^4T_{1g}$ line can split under the action of the crystal field, the Jahn–Teller distortion or by the Herzberg–Teller mechanism.[109] However, this splitting ($\sim$0.3 eV) is too large and the initial transition energy (2.2 eV) is rather high. But this can also be explained in some other manner. From Section V.2 it follows that yet another electron level, namely, $^4T_{1u}$, becomes the ground-state level in the large active space. Now the allowed transitions include

$$^4T_{1u} \rightarrow {}^4A_g,$$

$$^4T_{1u} \rightarrow {}^4T_{1g},$$

$$^4T_{1u} \rightarrow {}^4H_g,$$

i.e., the pattern of the optical spectrum fundamentally changes. Probably, elucidation of the nature of the splitting requires additional experimental and theoretical studies.

2. Neutral C_{60} molecule

Interpretation of optical transitions in neutral C_{60} molecule is also complicated. The experimental absorption spectra of C_{60} in argon [10] and n-hexane [9] exhibit three main bands (Fig. 8) in the region below 6 eV (> 200 nm), namely, at 3.78 eV (oscillator strength $f = 0.37$), 4.84 eV ($f = 2.27$) and 5.88 eV ($f = 3.09$). Semiempirical methods of configuration interaction, except the CNDO/S method,[84,85] failed to describe the first band with an energy of 3.78 eV (Table 19). Recent *ab initio* calculations [11] did not improve agreement between the theory and experiment. Rather, it was found that two low-lying transitions $^1A_g \rightarrow {}^1T_{1u}$ are at

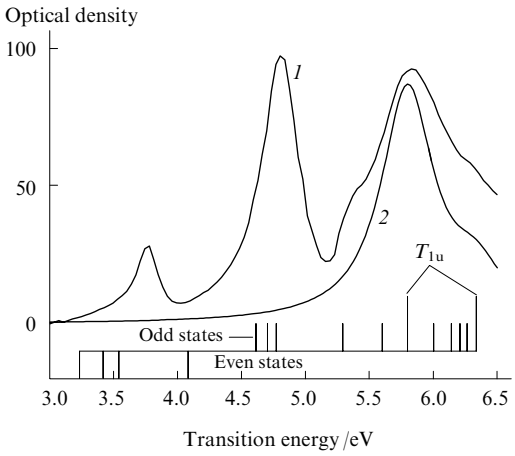


Figure 8. Experimental optical density of C_{60} (in arbitrary units) in n-hexane (*1*)[9] and the calculated energes of singlet excitations of neutral molecule (*2*).[11]
The lower line shows the electronic contributions of two allowed dipole transitions from the ground state level (^1A_g) to two excited $^1T_{1u}$ levels assuming a halfwidth of 0.5 eV.

Table 19. Selected characteristic molecular excitations of neutral molecule C_{60} calculated using the semiempirical models of configuration interaction and ab initio Hartree–Fock method with the configuration interaction.

Term	PPP method, N_{CSF} = 134 (see [100])		QCFF/π method, N_{CSF} = 226 (see [99])	CNDO/S method, N_{CSF} = 900 (see [84,85])	*ab initio* CIS method, N_{CSF} = 2857 (see [11])
	planar	three-dimensional			
1^3T_{2g}	2.456	2.232	2.06		2.549
1^1G_u	3.603	3.381	3.21		4.700
1^1H_u	3.635	3.391	3.15		4.771
1^1T_{1u}	4.227	4.000	4.08	3.40	5.796
2^1T_{1u}	4.750	4.681	4.53	4.06	6.335

Note. 1. Notations of methods are as follows: PPP is the Pariser–Parr–Pople method, QCFF/π is the Quantum-mechanical Consistent Force Field method for π-electrons; CNDO/S is the Complete Neglect of Differential Overlap for Spectroscopy, CIS is the Configuration Interaction with Single excitations. 2. The energies are given in eV; N_{CSF} is the number of configuration functions, 1^3T_{2g} is the lowest excited level of C_{60}.

relatively high energies of 5.8 (214 nm) and 6.3 eV (197 nm) (see Fig. 8). These results were obtained for the configuration interactions with single and double excitatios (42 correlated electrons in the active space of molecular orbitals ranging from 160 to 248).[11] The origin of these transitions is as follows. The first band is due to the excitation from the HOMO to the LUMO + 1 ($6h_u \rightarrow 3t_{1g}$) at 6.44 eV, while the second band appears as a result of transition from the HOMO − 1 to the LUMO ($10h_g \rightarrow 7t_{1u}$) at 6.96 eV. The configuration interaction between these and other $^1T_{1u}$ levels leads to a further decrease in their energies.

Summing up, the *ab initio* calculations [11] carried out taking into account only the electronic mechanism (ignoring vibronic interactions) provide an explanation for the optical band at 5.88 eV only.[10] However, starting with 2.55 eV

(1^3T_{2g}), there is a large number of excited molecular symmetry levels in C_{60} (see Table 19). Therefore, it is possible that the bands at 3.78 and 4.84 eV experimentally observed in the absorption spectrum[9] become optically active only because of mixing with the molecular vibrational modes.[109]

The interpretation of optical transitions in fullerene to some extent resembles the situation with the optical transitions in benzene. Like C_{60}, the first allowed electronic optical transition of the benzene molecule ($^1A_{1g} \rightarrow 1^1E_{1u}$) is at a relatively high energy of about 7 eV. At the same time, there are two low-lying bands at 4.90 (1^1B_{2u}) and 6.20 eV (1^1B_{1u}),[110,111] which are forbidden for the electronic transitions. They appear because of vibronic interaction. Of course, an unambiguous interpretation of the spectra of benzene molecule became possible owing to numerous experimental and theoretical studies. It seems that in the case of the fullerene molecule, we are still in the early stage of such research.

VII. Conclusion

In this review various theoretical approaches for the electronic structure and spectra of the C_{60} (I_h) fullerene and its ions are considered including semiempirical (model), *ab initio* and group-theoretical methods. We mainly focus on various electron states of the icosahedral symmetry, but also discuss some other physical characteristics, such as magnetic moments and intensities of optical transitions, and compare theoretical results with the experimental data.

We have considered the energy spectrum of states produced from the icosahedral electron configurations g^N and h^N (Section II). These configurations, with the fourfold and fivefold degeneracy of molecular orbitals, respectively, have no analogues among systems of lower symmetry and their analysis required elaboration of new approaches[43,68] (see Subsections II.1 and II.4). The pattern of the spectra in question was for the first time obtained within the framework of the theory of 'integral invariants',[43–50] a novel group-theoretical approach (molecular analogue to the Slater–Racah atomic theory). Analysis of the spectra[44,47] revealed a number of unique features including the so-called 'accidental' term degeneracy (see Tables 3 and 5). Subsequent quantum mechanical analysis[68,80] using the spinor representation for the g- and h-orbitals (within the framework of the theory of unitary group) showed that the degeneracy of the g^N- and h^N-terms is not accidental, being due to fundamental reasons of pure symmetry character. Namely, this degeneracy is due to the existence of additional (hidden) symmetry elements in the icosahedral groups (I, I_h).

We have discussed the novel approach[12] to the description of the spectral characteristics of the fullerene molecule and ions occurring in molecular crystals AC_{60} with the open-shell electronic state of C_{60}. The approach is based on the multipole expansion of inter-electron interaction within the open shell γ^N (γ = t, h) and on representation of the energy of electronic states (terms) as the sum of the corresponding multipole contributions (Section IV). The main idea of the approach is to represent the molecular orbitals of fullerene C_{60} as an expansion in terms of atomic orbitals centred at the origin (at the cetnre of the C_{60} molecule) (Section III). As a result the C_{60} fullerene is described as a (pseudo)atom of icosahedral symmetry (I_h).

Using an analogy between the pseudoatom model of C_{60} and the classical Condon–Shortley theory,[76] we considered some practical aspects of application of the multipole expansion to calculations of the many-electron energy spectrum (Section V), the optical transitions and magnetic moments (Section VI). The energy spectra of $C_{60}^{m\pm}$ ions, which were first obtained within the framework of the pseudoatom model,[12] are in good agreement with the results of quantum chemical calculations by the multiconfiguration method of self-consistent field in the complete active space. This comparison was made in Ref. 83. It was found that Hund's rules are valid for the ground state of all open shells. In the case of the t_{1u}^n-configurations the term splitting can be completely described by a single parameter J:

$$E(^1H_g) - E(^3T_{1g}) = 2J,$$
$$E(^1A_g) - E(^1H_g) = 3J,$$
$$E(^2H_u) - E(^4A_u) = 3J,$$
$$E(^2T_{1u}) - E(^2H_u) = 2J.$$

The parameter J can be determined by averaging over the calculated energy differences obtained by different quantum chemical methods (Table 20).

Table 20. Calculated parameters J (10^{-3} eV) determining the splitting of the terms t_{1u}^n of C_{60}^{n-} anion (see text) calculated by different quantum chemical methods.

Method	$n=2$	$n=3$	$n=4$	Average	Ref.
CAS SCF	114.1	113.6	112.7	113.5	83, 112
Restricted configuration interaction	29–146	8–388	8.5–380	15–305	113
MNDO + CI	50	–	–	50	114
INDO + CI	120	185	–	153	115
LDA	–	–	–	32	98
Pseudoatom	99.95	99.95	99.95	99.95	12
Pseudoatom-2	76.7	76.7	76.7	76.7	this work

Notes. 1. Notations of methods: MNDO is the Modified Neglect of Differential Overlap, CI is the Configuration Interaction, INDO is the Intermediate Neglect of Differential Overlap, LDA is the Local Density Approximation (in DFT), CAS SCF is the Complete Active Space Self Consistent Field method. 2. Pseudoatom model-2 refers to the radial dependence with $l = 5$ obtained using the Hückel model (see Fig. 4).

In the case of the hole configurations $(h_u^+)^m = h_u^{10-m}$, the splitting[45] is described by the parameters[83] F_2, F_3, F_4 and F_5. For instance, the splitting between the highest and the lowest levels in the configuration $(h_u^+)^2$ is

$$\frac{4}{3}F_2 + \frac{5}{4}F_3 + \frac{11}{12}F_4 - \frac{\sqrt{5}}{2}F_5 .$$

The effective parameters F calculated by different quantum chemical methods are listed in Table 21. As can be seen, the splitting values predicted by the pseudoatom model[12] are very close to those predicted by the CAS SCF calculations, and this model 'works' better than the DFT LDA approximation.

Table 21. Calculated parameters F_i (10^{-3} eV) determining the splitting of the terms $(h_u^+)^m$ of C_{60}^{m+} cation ($m = 2-8$) calculated by different quantum chemical methods.

Method	F_2	F_3	F_4	$\|F_5\|$	Ref.
LDA	105	155	47	0	98
CAS SCF	193.5	584.2	184.5	2.3	83
Pseudoatom, II	193	640	180	13	12
Pseudoatom, III	185	625	172	13	12

Relations between the experimental and calculated energies of optical transitions have been discussed. For the C_{60}^{2-} anion, two lines ($^3T_{1g} \rightarrow {}^3H_u$ and $^3T_{1g} \rightarrow {}^3T_{1u}$) correspond tentatively to two IR bands at 950 and 830 nm, respectively. However, calculations also predict the third band $^3T_{1g} \rightarrow {}^3A_u$. In the case of C_{60}^{3-} anion, the situation is more complicated. In the active space of the t_{1u} shell, the ground-state term ^4A_u corresponds to a single allowed optical transition $^4A_u \rightarrow {}^4T_{1g}$. However, three bands are observed experimentally.[33] At the same time, in the large active space the ground state of C_{60}^{3-} changes ($^4T_{1u}$), which causes fundamental changes in the whole spectrum.

Thus, agreement between the theoretical and experimental data for fullerene anions is by and large poor. In this connection, mention should be made that at present even the optical absorption spectrum of the neutral C_{60} molecule is far from being completely understood. According to *ab initio* calculations,[11] the first allowed electronic transitions are at relatively high energies, namely, 5.8 and 6.3 eV. It follows that two low-lying optical bands (3.78 and 4.84 eV) should have a vibronic origin.[109] Here, additional studies are required for clarity. It is also desired to obtain a larger array of experimental data for both the fullerene molecule and the C_{60}^{n-} and C_{60}^{m+} ions.

The pseudoatom model [12, 36] offers a number of advantages which can be used to describe fullerene-based compounds. The main point is that sixty carbon atoms are in fact replaced by a single pseudoatom C_{60}. This allows one to focus on the key effects instead of dwelling on insignificant details. For instance, the calculated [87] electron density distribution on C_{60} in the one-dimensional polymer chain comprising fullerene molecules in AC_{60} (A = K, Rb, Cs) is in reasonable agreement with experimental data. Yet another example is provided by the description of the ground singlet state in the molecular complexes $C_{60}-A-C_{60}$ (A = K, Rb, Cs).[86] Three components of t_{1u} [see Eqns (43)–(45)] were used to calculate of the energy band structure in AC_{60}.[116, 117] The pseudoatom model can be combined with the description of C_{60} as a cluster of interacting van der Waals centres [94, 95, 118, 119] to explain more complex physicochemical phenomena.

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