

## Ground states of large icosahedral fullerenes

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(Received 21 July 1992)

The ground states for large icosahedral fullerenes and for  $C_{60}^n$  molecular ions ( $-6 \leq n \leq +1$ ) are treated starting from full rotational symmetry and the use of Hund's rule. Treating the icosahedral symmetry as a subgroup of the full rotational group, the icosahedral symmetry of these molecular states is introduced. A method to calculate the electronic structures for the icosahedral molecules and ions is formulated for large fullerenes using a spherical harmonic expansion on a sphere, and the calculated results for  $C_{60}$  are compared with molecular orbital calculations.

The molecular nature of the Raman and infrared spectra of  $C_{60}$  and its doped phases stimulates this investigation of the nature of the ground states for the class of neutral icosahedral fullerenes and for the various ions that are prepared either by ionization from the gas phase or by intercalation of  $C_{60}$  in the solid phase by alkali metals. In this paper we present a general approach based on group-theoretical arguments to find the symmetries of the ground states for general (including large) icosahedral fullerenes and for  $C_{60}^{n\pm}$  molecular ions. In this approach we consider the fullerenes to be of approximately spherical shape, allowing the use of spherical harmonics to classify the electronic configurations. Hund's rule is applied to find the quantum numbers for  $S$ ,  $L$ , and  $J$  for the ground-state configurations allowed by the Pauli principle. The icosahedral symmetry is then introduced as a symmetry-lowering effect, treating the icosahedral groups  $I_h$  and  $I$  as subgroups of the full rotational group. Two limiting cases are considered explicitly depending on whether the icosahedral perturbation is small or large compared with the electron-electron interaction. Using this general approach it is possible to identify fullerenes that are especially stable because they are already stable before the icosahedral symmetry-lowering perturbation is applied. We also show which ground states should have the largest magnetic moments, and compare predictions to experimental findings.<sup>1,2</sup>

For this group-theoretical treatment, it is more convergent to calculate the electronic structure of a large molecule by a spherical harmonic expansion than by localized atomic orbitals. The comparison between the spherical harmonic method for  $C_{60}$   $\pi$ -electron states is made with the first principles calculations of Saito, Oshiyama, and Miyamoto using norm-conserving pseudopotential molecular orbital (MO) calculations with Gaussian basis functions.<sup>3,4</sup>

Consider first the various icosahedral fullerenes  $C_N$  that can be constructed (see Table I).<sup>5</sup> Since each ver-

tex on a fullerene connects a carbon atom (having four valence electrons) to three other carbon atoms, we can assign one available  $\pi$  electron to each carbon atom. We can then form electronic configurations from these  $\pi$  electrons as shown in Table I, by assigning  $2(2\ell + 1)$  of these electrons to each angular momentum state and using the conventional notation  $s, p, d, f, g, h, i, k, l, m, n, o, q, r, t, \dots$  for angular momentum states  $\ell = 0, 1, 2, \dots$ . For each of the electronic configurations, we then apply Hund's rule to get the ground-state quantum numbers  $S, L, J$  listed in Table I. Of particular interest are the special fullerenes  $C_{60}$ ,  $C_{180}$ , and  $C_{420}$  which form  $J = 0$  ground states even when we only consider spherical symmetry. The high stability of these  $J = 0$  molecules is further enhanced by the symmetry-lowering effect, yielding highly stable molecules. In the icosahedral fullerenes, closed shells for  $\ell = \ell_{\max}$  occur very rarely as indicated in the footnote of Table I.

Open-shell structures may be easily distorted by symmetry-lowering interactions. The relative magnitudes of the configurational interaction and the icosahedral (or other symmetry-lowering) splitting determine the most convergent approach to calculations of the electronic structure. If the icosahedral perturbation is large and the electron-electron interactions are small, then the most appropriate scheme is the application of the icosahedral perturbation first to split the large  $\ell$  values and then to formulate the many-electron levels from the icosahedrally split states (low spin state in Table II). If, on the other hand, the electron correlation effects are much larger than the icosahedral splittings, then one should form the multiplet states first and then apply the weak icosahedral perturbation later (high spin state in Table II). We illustrate both of these approaches in Table II which lists the levels of the various  $C_{60}^{n\pm}$  molecular ions formed from  $C_{60}$ .

We form the various entries in Table II for the  $C_{60}^n$  molecular ions for  $-6 \leq n \leq +1$ . On the left side

TABLE I. Spherical ball approximation for the  $\pi$  molecular orbitals for icosahedral fullerenes.

$C_{N_{m,n}}$	$(m,n)^a$	Sym.	$\ell_{\max}^b$	$n_{\text{tot}}^c$	$n_v^d$	Full configuration	$S^e$	$L^e$	$J^e$	Icosahedral symmetry
$C_{20}$	(1, 0)	$I_h$	3	32	2	$s^2 p^6 d^{10} f^2$	1	5	4	$G_g, H_g$
$C_{60}$	(1, 1)	$I_h$	5	72	10	$s^2 p^6 d^{10} f^{14} g^{18} h^{10}$	5	5	0	$A_g$
$C_{80}$	(2, 0)	$I_h$	6	96	8	$s^2 p^6 d^{10} \dots h^{22} i^8$	4	20	16	$A_g, 2F_{1g}, F_{2g}, 2G_g, 3H_g$
$C_{140}$	(2, 1)	$I$	8	162	12	$s^2 p^6 d^{10} \dots k^{30} l^{12}$	6	30	24	$A, 2F_1, 2F_2, 4G, 4H$
$C_{180}$	(3, 0)	$I_h$	9	200	18	$s^2 p^6 d^{10} \dots l^{34} m^{18}$	9	9	0	$A_g$
$C_{240}$	(2, 2)	$I_h$	10	242	40	$s^2 p^6 d^{10} \dots m^{38} n^{40}$	1	19	20	$A_g, 2F_{1g}, 2F_{2g}, 2G_g, 4H_g$
$C_{260}$	(3, 1)	$I$	11	288	18	$s^2 p^6 d^{10} \dots n^{42} o^{18}$	9	45	36	$2A, 4F_1, 3F_2, 5G, 6H$

<sup>a</sup>Note that icosahedral symmetry requires  $N = 20(n^2 + m^2 + nm)$  where  $n, m$  are integers (Ref. 5). From the  $(m, n)$  values, the symmetries are  $I_h$  (for  $m = n$ , or  $mn = 0$ ) and  $I$  [for all other  $(m, n)$ ]. Group theory notation is from Ref. 6.

<sup>b</sup> $\ell_{\max}$  represents the maximum value of the angular momentum for the HOMO.

<sup>c</sup> $n_{\text{tot}} = 2(\ell_{\max} + 1)^2$  is the number of electrons needed for a filled shell.

<sup>d</sup> $n_v$  represents the number of valence electrons. The smallest possible  $N_{m,n}$  for a  $C_{N_{m,n}}$  icosahedral fullerene with a closed-shell configuration, i.e.,  $n_v = 0$  ( $S = 0, L = 0, J = 0$ ), has  $N_{m,n} = 275\,467\,380$ ;  $(m, n) = (2192, 2093)$ , and  $\ell_{\max} = 11\,735$ .

<sup>e</sup> $S, L, J$  values for the ground state are given according to Hund's rule.

of Table II we list the configurations in full rotational symmetry, the ground state  $S, L$ , and  $J$  from Hund's rule and the irreducible representations of the icosahedral group corresponding to each ground-state  $J$  value. On the right-hand side of the table we list the electronic configuration in icosahedral symmetry for the HOMO-LUMO levels, give the term symmetries and  $J$  values for the ground states, and in the last column we list the corresponding icosahedral irreducible representations of all the  $J$  values of the multiplet. The hyperfine-split state corresponding to Hund's rule is explicitly flagged. Since the spin-orbit coupling for carbon is very small<sup>8</sup> such hyperfine structure could only be observed in high-resolution experiments.

Recent measurements of the magnetic properties of Cs-

doped  $C_{60}$  (Ref. 1) show anomalous behavior which implies that the molecular ions have magnetic dipole moments. The maximum magnetic moment is observed at  $C_{60}^{4-}$  ( $x = 4$  for  $Cs_x C_{60}$ ), which is consistent with the molecular ion ground states listed on the right-hand side of Table II where the maximum  $J = 2$  also occurs at  $C_{60}^{4-}$ . For acceptor-doped  $C_{60}$ , maximum  $J$  value occurs for the +3 ion (not shown in the table).

In the case of the  $C_{60}$  solid, the band width of the  $F_{1u}$  band ( $\sim 0.4$  eV) (Ref. 3) is compatible with the electron-electron interaction in a molecule ( $\sim 0.5$  eV).<sup>9</sup> The competition between the itinerant and localized nature of electrons in doped  $M_x C_{60}$  depends on  $x$ , and up to  $x = 1$  the metallic nature of the itinerant electrons will be dominant, as is observed in the maximum Pauli

TABLE II. Various Pauli-allowed states associated with the ground-state configurations for the icosahedral  $C_{60}^{n\pm}$  ions.

$n$	High spin state			Icosahedral symmetry <sup>b</sup>	Low spin state		
	$S^a$	$L^a$	$J^a$		Config.	$I_h$ state <sup>c</sup>	Hyperfine structure
6-	3	15	18 <sup>d</sup>	$A_g, F_{1g}, 2F_{2g}, 3G_g, 3H_g$	$h_u^{10} f_{1u}^6$	$^1A_g(J=0)^d$	$A_g^d$
5-	7/2	14	35/2 <sup>d</sup>	$\Gamma_6^-, \Gamma_7^-, 2\Gamma_8^-, 4\Gamma_9^-$	$h_u^{10} f_{1u}^5$	$^2F_{1u}(J=3/2)^d$	$\Gamma_6^-, \Gamma_8^-^d$
4-	4	12	16 <sup>d</sup>	$A_g, 2F_{1g}, F_{2g}, 2G_g, 3H_g$	$h_u^{10} f_{1u}^4$	$^1A_g$ $^3F_{1g}(J=2)^d$ $^1H_g$	$A_g$ $A_g, F_{1g}, H_g^d$ $H_g$
3-	9/2	9	27/2 <sup>d</sup>	$\Gamma_7^-, 2\Gamma_8^-, 3\Gamma_9^-$	$h_u^{10} f_{1u}^3$	$^4A_u(J=3/2)^d$ $^2F_{1u}$ $^2H_u$	$\Gamma_8^-^d$ $\Gamma_6^-, \Gamma_8^-$ $\Gamma_8^-, \Gamma_9^-$
2-	5	5	10 <sup>d</sup>	$A_g, F_{1g}, F_{2g}, G_g, 2H_g$	$h_u^{10} f_{1u}^2$	$^1A_g$ $^3F_{1g}(J=0)^d$ $^1H_g$	$A_g$ $A_g, F_{1g}, H_g$ $H_g$
1-	11/2	0	11/2 <sup>d</sup>	$\Gamma_6^-, \Gamma_8^-, \Gamma_9^-$	$h_u^{10} f_{1u}^1$	$^2F_{1u}(J=1/2)^d$	$\Gamma_6^-^d, \Gamma_8^-$
0	5	5	0 <sup>d</sup>	$A_g$	$h_u^{10}$	$^1A_g(J=0)^d$	$A_g^d$
1+	9/2	9	9/2 <sup>d</sup>	$\Gamma_8^-, \Gamma_9^-$	$h_u^9$	$^2H_u(J=5/2)^d$	$\Gamma_8^-, \Gamma_9^-^d$

<sup>a</sup>We list only the state  $S = n/2$  of maximum spin multiplicity, and  $L$  and  $S$  for the Hund's rule ground state.

<sup>b</sup>The notation for the irreducible representations is from Ref. 6 and for the double-group representations is that of Ref. 7.

<sup>c</sup>All Pauli-allowed states are listed in terms of irreducible representations of  $I_h$  and the spin degeneracy.  $J$  values for Hund's rule are listed explicitly.

<sup>d</sup>Hund's rule ground state.

susceptibility at  $x = 1$ .<sup>1</sup>

In  $C_{60}$  the crystal-field splitting between the  $H_u$  and  $F_{1u}$  levels ( $\sim 1.9$  eV) is much larger than the electron-electron interaction and thus low spin states are appropriate. However, in a large fullerene, the atomic potential modulation is expanded to high  $\ell$  values and the energy gap decreases with increasing radius. Thus the high-spin state would be expected to be the preferred representation for the large fullerenes. In both cases,  $\pi$  electrons in fullerenes are well represented by a large wave-function amplitude on a ball. Following the group-theoretical treatment of symmetry lowering from spherical to icosahedral symmetry, we have developed a spherical harmonic expansion for a surface with spherical symmetry and for icosahedral symmetry. Although we only show the one-electron states of  $C_{60}$ , the same procedure can be applied to larger fullerenes and their multiplet structure.<sup>10</sup>

First we solve the model quantum-mechanical problem for the  $C_{60}$   $\pi$ -electrons treating them as free electrons bounded in a spherical square-well potential  $V(r)$  written as

$$V(r) = \begin{cases} -V_0 & (|r_0 - r| < r_w/2) \\ 0 & \text{otherwise.} \end{cases} \quad (1)$$

Here  $V_0$ ,  $r_0$ , and  $r_w$  are the depth, center, and width of the spherical well. Connecting analytical solutions of real and imaginary spherical Bessel functions of  $\ell$ th order for angular momentum  $\ell$  at the boundary of the well, we obtain the bound states in the well. Using reasonable choices of the parameters for  $C_{60}$ , that is,  $V_0 = 10$  eV,  $r_0 = 4.05$  Å, and  $r_w = 3.5$  Å, we find that nodeless radial wave functions up to  $\ell = 8$  have a lower energy than the corresponding excited states whose radial functions have nodes. All irreducible representations of the  $\pi$ -electron MO's of  $C_{60}$  in  $I_h$  symmetry ( $A_g + F_{1g} + F_{2g} + 2G_g + 3H_g + 2F_{1u} + 2F_{2u} + 2G_u + 2H_u$ ) are included in the spherical harmonics through  $\ell = 8$ . Thus it is sufficient to consider only nodeless wave functions for the electronic states. In this case the angular part of the wave function, which is expressed in spherical harmonics, has a special meaning, which corresponds to determining the molecular-orbital coefficients in the tight-binding approximation. Considering only the nodeless radial wave functions which are localized in the well, the energy-level differences corresponding to different  $\ell$  values come mainly from the centrifugal force of the angular momentum and are proportional to  $\ell(\ell+1)/r_0^2$ . The spherical approximation improves with increasing radius  $r_0$ .

The phenomenological one-electron Hamiltonian for icosahedral molecules can be simplified by introducing the angular momentum operator. The Hamiltonian consists of a spherical term  $\mathcal{H}_0$  and an icosahedral perturbation  $\mathcal{H}_{I_h}$ , which is suggested by Harter and Reimer<sup>11</sup> for obtaining the rotational and vibrational states of  $C_{60}$ ,

$$\mathcal{H}_i = \mathcal{H}_0 + \mathcal{H}_{I_h}. \quad (2)$$

Here  $\mathcal{H}_0$  is approximated by

$$\mathcal{H}_0 = B_0 + B_2\ell^2 + \dots \quad (3)$$

in which  $B_2$  denotes the repulsive potential associated

with the angular momentum and has the approximate value of  $\sim (\hbar^2/2m)\ell(\ell+1)/r_0^2$ . The icosahedral perturbation  $\mathcal{H}_{I_h}$  is expanded in terms of the  $I_h$ -invariant, irreducible tensor form of sixth and tenth rank,

$$\mathcal{H}_{I_h} \sim t_6 T^{(6)} + t_{10} T^{(10)} + \dots, \quad (4)$$

where  $T^{(\ell)}$  is given by

$$T^{(6)} = \left[ \frac{\sqrt{11}}{5} T_0^6 + \frac{\sqrt{7}}{5} (T_5^6 - T_{-5}^6) \right] \quad (5)$$

and

$$T^{(10)} = \left[ \frac{\sqrt{3 \times 13 \times 19}}{75} T_0^{10} + \frac{\sqrt{11 \times 19}}{25} (T_5^{10} - T_{-5}^{10}) - \frac{\sqrt{3 \times 11 \times 17}}{75} (T_{10}^{10} + T_{-10}^{10}) \right], \quad (6)$$

where  $T_m^\ell$  is the  $m$ th component of the irreducible tensor operator  $T^{(\ell)}$  of  $\ell$ th rank. When we only consider the splitting of the energy levels in a space of  $\{\ell=\text{const}\}$ ,  $T^{(\ell)}$  can be expressed by operators of angular momentum called equivalent operators.<sup>12</sup> However, since the icosahedral perturbation  $\mathcal{H}_{I_h}$  mixes spaces for different  $\ell$ 's, we directly calculate the matrix elements of  $T^{(k)}$  as shown below. For basis functions, we use spherical harmonics,  $Y_{\ell m}$ . The basis function in the space  $\{\ell=\text{const}\}$  is easily decomposed into irreducible representations of the icosahedral group by solving an eigenvalue problem of equivalent operators of  $T^{(6)}$  in  $\{\ell=\text{const}\}$ . Icosahedrally invariant tensors for higher rank  $\ell$  appear for  $\ell = 12, 16, 18, \dots$  whose coefficients are the same as those of the basis functions of  $\ell$  in the  $A_g$  irreducible representation. Thus an invariant tensor of any rank can be generated from  $T^{(6)}$ .

To get explicit solutions we have diagonalized the phenomenological Hamiltonian equation (2) numerically in the space of  $\ell \leq 8$ . The parameters  $B_0$  and  $B_2$  and  $t_6$  and  $t_{10}$  are fitted to reproduce low  $\ell$  states in the first-principles MO calculation by Saito and Oshiyama.<sup>4</sup> The parameters  $B_0$  and  $B_2$  are most sensitive to the  $\ell = 0, 1$ , and 2 states since the  $I_h$  perturbation does not act within the space of  $\{\ell = \text{const}\}$  for  $\ell = 0, 1$ , and 2. The expansion of Eq. (6) in  $T^{(\ell)}$  is performed using the potential of the molecule. Here we roughly estimate the ratio  $t_{10}/t_6$  by calculating the  $\ell$  and  $m$  components of the structure factor of the atomic coordinates  $r_i, \theta_i, \phi_i$  for  $i = 1, \dots, N$  as an approximation

$$S_m^\ell = - \sum_{i=1}^N Y_{\ell m}(\theta_i, \phi_i), \quad (7)$$

where the minus sign arises from the attractive potential and  $S^{(\ell)}$  is defined by substituting  $S_m^\ell$  for  $T_q^k$  in Eqs. (5) and (6) since the same nonzero  $S_m^\ell$  and  $T_q^k$  appear in the  $I_h$  invariant form. In Table III we show for comparison the coefficients  $S^{(6)}$ ,  $S^{(10)}$ , and the higher-order coefficient  $S^{(12)}$  for the icosahedral fullerenes  $C_{60}$ ,  $C_{80}$ , and  $C_{140}$ . The parameter  $B_2$  is estimated to be  $\sim (\hbar^2/2m)[\ell(\ell+1)/r_N^2]$ , where  $r_N$  denotes the radius of  $C_N$ . The absolute value of the perturbation  $\mathcal{H}_{I_h}$  is the only parameter to be determined when we fix the ratio of the  $S^{(\ell)}$  terms. From Table III, we see that the perturbation of tenth order is dominant in  $C_{60}$  (Ref. 13)

TABLE III. Values of  $S^{(\ell)}$  (dimensionless) for  $C_N$  icosahedral fullerenes.

Parameter	$N = 60$	$N = 80$	$N = 140$
$S^{(6)}$	2.44	2.05	5.04
$S^{(10)}$	-19.44	9.72	1.31
$S^{(12)}$	-7.09	-25.71	8.07

and of twelfth order is dominant for  $C_{80}$ . On the other hand, the higher-order terms,  $T^{(2\ell)}$ , do not affect the electronic states within the same  $\ell$  space that have smaller  $\ell$  values. Thus the electronic properties will eventually become free-electron-like, i.e., solutions of  $\mathcal{H}_0$ , when the radius of the icosahedral molecule becomes very large.

It is interesting to compare  $\ell_{\max}$  in Table I and the dominant  $\ell$ , in the expansion of  $T^{(\ell)}$  denoted as  $\ell_{I_h}$ . In the case of  $\ell_{I_h} > 2\ell_{\max}$ , the splitting of the valence states becomes small. Since  $\ell_{I_h}$  increases more quickly than  $\ell_{\max} \sim \sqrt{(N/2)} - 1$  with increasing  $N$  in  $C_N$ , high spin states could occur for larger icosahedral fullerenes, if the electron-electron interaction is larger than the energy level splitting.

Finally we show the calculated results for  $C_{60}$  using this method and show the agreement obtained with MO calculations. For  $\ell \leq \frac{5}{2}$ , all matrix elements of  $\mathcal{H}_{I_h}$  in the space of  $\{\ell = \text{const}\}$  vanish since the icosahedral splitting does not appear until  $\ell = 3$  is reached. There is, however, a small interaction between  $\ell$  and  $\ell \pm 6$  through  $T^{(6)}$ , which gives rise to a perturbation in the energy levels having the form  $B_2\ell(\ell + 1)$ .

The diagonalization of this Hamiltonian gives the eigenvalues listed in Table IV, using the fitting parameters of  $B_0 = -7.40$  eV,  $B_2 = 0.27$  eV,  $t_6 = -1.25$  eV and  $t_{10}$  is determined by the ratio of  $S^{(10)}/S^{(6)}$  from Table III. The comparison between the calculated results of the molecular orbital calculation by Saito, Oshiyama, and Miyamoto<sup>3</sup> and the present work is shown in Table IV. The calculated results reproduce the sequence of irreducible representations and their energy positions well. The only difference in the sequence of irreducible representation between the two calculations occurs for  $h_u(\ell = 7)$  and  $g_g(\ell = 6)$ . The numerical inaccuracy arises from the limited space of  $\ell \leq 8$  terms, neglect of the effect of  $T^{(12)}$  in Eq. (5) and use of  $t_{10}/t_6$  obtained

TABLE IV.  $\pi$ -electron energy states of the  $C_{60}$  Hamiltonian.

$\ell$	Symmetry	Model (eV)	Literature (eV) <sup>a</sup>
0	$a_g$	-7.41	-7.41
1	$f_{1u}$	-6.87	-6.87
2	$h_g$	-5.87	-5.82
3	$f_{2u}$	-4.40	-4.52
3	$g_u$	-4.13	-3.99
4	$h_g$	-2.21	-2.44
4	$g_g$	-2.12	-2.37
5	$h_u$	-0.20	-1.27
5	$f_{1u}$	0.88	0.62
5	$f_{2u}$	1.82	1.59
6	$f_{1g}$	3.38	2.71
6	$h_g$	3.43	2.78
7	$h_u$	5.27	4.15
6	$g_g$	4.92	4.60
7	$g_u$	6.98	5.05
8	$f_{2g}$	7.98	5.47

<sup>a</sup>Reference 2.

from geometrical considerations of the atomic coordinate.

The energy splitting at  $\ell = 3$  is due to the interaction of  $T^{(6)}$ . The reason why the splitting of the  $\ell = 4$  level into  $H_g$  and  $G_g$  levels is smaller than  $\ell = 3$  into  $F_{2u}$  and  $G_u$  is that there is a level crossing of  $H_g$  and  $G_g$  near the optimized parameter for the absolute value of the perturbation when we change the value of  $t_6$ .

Using the one-electron wave function, multiplets of neutral and doped  $C_{60}$  can be calculated. For the neutral  $C_{60}$  molecule, the two-electron excitation is calculated by a configuration interaction method.<sup>9</sup> Although the quantum chemistry approach gives only numerical results, most of the electron-electron interaction may be determined by the geometric factors of the one-electron wave functions. This work will be published in the future.<sup>10</sup>

We sincerely thank Dr. Atsushi Oshiyama for making the numerical data from Ref. 3 available to us. The analytic calculation was performed on the Athena network at MIT using MAPLE. One of the authors (R.S.) acknowledges support from the Ministry of Education, Science and Culture of Japan. We gratefully acknowledge NSF Grant No. DMR88-19896 for support of this research.

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