Molecular terms, magnetic moments and optical transitions of molecular ions $C_{60}^{m\pm}$

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Starting from a multipole expansion of intra-molecular Coulomb interactions, we present configuration interaction calculations of the molecular energy terms of the hole configurations $(h^\pm)^m$, $m = 2 - 5$, of $C_{60}^+$ cations, of the electron configurations $t^{1u}_u$, $n = 2 - 4$, of the $C_{60}^-$ anions, and of the exciton configurations $(h^+_u t^{1u}_u)$, $(h^+_u t^{1g}_u)$ of the neutral $C_{60}$ molecule. The ground state of $C_{60}^-$ is either $3\,T_{1g}$ or $1\,A_g$, depending on the energy separation between $t_{1g}$ and $t_{1u}$ levels. There are three close ($\approx 0.03 \, \text{eV}$) low lying triplets $3\,T_{1g}$, $3\,G_u$, $3\,T_{2g}$ for $C_{60}^+$, and three quartets $4\,T_{1u}$, $4\,G_u$, $4\,T_{2u}$ for $C_{60}^+$, which can be subjected to the Jahn-Teller effect. The number of low lying nearly degenerate states in largest for $m = 3$ holes. We have calculated the magnetic moments of the hole and electron configurations and found that they are independent of molecular orientation in respect to an external magnetic field. The coupling of spin and orbital momenta differs from the atomic case. We analyze the electronic dipolar transitions $(t_{1u})^2 \rightarrow t_{1u} t_{1g}$ and $(t_{1u})^3 \rightarrow (t_{1u})^2 t_{1g}$ for $C_{60}^+$ and $C_{60}^-$. Three optical absorption lines ($4\,T_{1g} \rightarrow 3\,H_u$, $3\,T_{1u}$, $3\,A_u$) are found for the ground level of $C_{60}^+$ and only one line ($4\,A_u \rightarrow 4\,T_{1g}$) for the ground state of $C_{60}^-$. We compare our results with the experimental data for $C_{60}^+$ in solutions and with earlier theoretical studies.

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I. INTRODUCTION

The physics and chemistry of fullerenes is full of surprises. After almost ten years of intensive theoretical and experimental work, unexpected discoveries of ferromagnetic polymerized $C_{60}$\(\ddagger\) as well as superconductivity in hole doped pristine $C_{60}$\(\S\) and in lattice-expanded $C_{60}$\(\S\) raise new questions about the electronic structure of the $C_{60}$ molecule and its molecular ions. Using the field-effect doping techniques, it has been shown that high transition temperatures are achieved for the case of three holes per the $C_{60}$ molecule\(\S\), when many electron effects come into play. Motivated by these new experimental findings, here we present a calculation of the electronic structure of few holes of $C_{60}^{m\pm}$. Our second goal is to study the molecular term picture of the $C_{60}^-$ anion ($n = 2, 3, 4$), which behaves as a quasi-element in a vast majority of ionic compounds\(\S\). When $C_{60}^{m\pm}$ units are in a solid, additional inter-molecular interactions superimposed on the intra-molecular ones should be taken into account and a realistic theory of solids should treat both kinds of interactions on equal footing. Therefore, the consideration of intra- molecular correlations should be a necessary ingredient of a many electron theory aiming to describe superconductivity, magnetic properties or a metal-insulator transition\(\S\). The problem is also a challenge from experimental point of view\(\S\). In the present paper we will give quantitative results on the many electron terms and magnetic moments of $C_{60}^{m\pm}$ and $C_{60}^{n\pm}$.

While the one-electronic structure of the neutral $C_{60}$ molecule is known for many years\(\dagger\) (in fact, even before the actual discovery of the Buckminsterfullerene\(\dagger\)) the case of two or three electrons (holes) on the degenerate $t_{1u}$ or $h_u$ shell requires a special treatment. Then the two ($n = 2$) or three ($n = 3$) electrons (holes) are equivalent and should be treated on equal footing. Such kind of situation is very typical for atoms with open electron shells. When an atom has two or more valence electrons on orbitally degenerate states (like $p$, $d$ or $f$) its energy spectrum can be very complex reflecting the electronic degrees of freedom. There exist empirical observations known as Hund’s rules, which prescribe the occupation of the orbitals, but those are just consequences of the atomic theory of many electron states formulated by Condon and Shortley long ago\(\dagger\). The real driving force behind the term splitting is the Coulomb repulsion of the valence electrons. While in atoms electronic energy levels are split due to the multipolar Coulomb intra-atomic interactions, in the case of $C_{60}$ we deal with the intra-molecular ones.

Here we present an approach which was inspired by the theory of many electron atomic states\(\dagger\). It is also an extension of our original method of multipole expansion for electronic states\(\dagger\). It is worth mentioning that our treatment should not be confused with an ordinary single-determinant Hartree-Fock calculation which does not take into account the intra-molecular correlations and the molecular term structure is overlooked. We will see (Sec. III) that in our approach each basis function represents a Slater determinant, and the solution is found as their linear combination. As such, the method corresponds to a many determinant treatment or configuration interaction (CI). Therefore, the approach is a genuine many electron one as long as we limit ourselves to the relevant orbital space ($h_u$, $t_{1u}$ or $t_{1g}$). To our knowledge, in the literature there are only two calculations.

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concerning the electronic structure of negatively charged C_{60}^- molecular ions, reported by Negri et al. [16], and by Saito et al. [17]. In the latter work, however, the assignment of excitations with molecular terms is done only for the neutral molecule (\(n = 0\)).

In the present paper we assume that the molecule has the icosahedral symmetry. If one wants to consider a distortion of C_{60}^- or C_{60}^+, the computed energy levels and their eigenvectors can be used as a starting point for the description of the Jahn-Teller effect in these systems. Indeed, the electron-phonon (or vibronic) coupling occurs if \(\Gamma_{el}\) contains \(\Gamma_{vib}\) [23, 24]. Here \(\Gamma_{el}\) is the symmetry of the electronic molecular term under consideration, while \(\Gamma_{vib}\) is the symmetry of a vibrational normal mode. It is evident then that for a meaningful analysis of the vibrational coupling and the resultant Jahn-Teller distortion, one has to know the symmetry of the corresponding electronic terms, that is the issue of the present study. In addition, now it has been realized that the Jahn-Teller effect for C_{60}^- is rather weak, and the situation is probably best described as dynamic [24], where the molecule on average retains its icosahedral symmetry. The vibronic coupling for C_{60}^+ is not so well investigated, but estimated as \(\sim 0.1 - 0.2\) eV. We will see that the energy span of the hole configurations a few times exceeds this value. Therefore, if there is a static Jahn-Teller effect for C_{60}^+, it can be treated in the limit of weak or intermediate coupling, leading to a more complex picture where the molecular terms are subjected to further splitting [24, 25].

Since the C_{60} molecule reveals nontrivial degeneracies and peculiarities, its term structure has been studied by group-theoretical methods [26, 27, 28, 29, 30]. The analysis was focused on the symmetry and number of terms for \(g^N (N = 1 - 7)\) [26] and \(h^N (N = 1 - 9)\) [27, 28, 29, 30] configurations, but by itself it can not give a quantitative picture of the splittings. Where our approach overlaps with the group-theoretical one, our findings are in agreement with the latter.

The paper comprises the following sections. First (Sec. II), we introduce the angular dependencies of \(h_u, t_{1u}\) and \(t_{1g}\) functions. Next (Sec. III), we describe our method of treating multipole Coulomb correlations for many electrons. Then we apply it to hole- and excitonic configurations of the C_{60} molecule, Sec. IV. In Sec. V we give the resultant energy spectra and compare our calculations with those of Negri et al. [16] for C_{60}^- . In Sec. VI we compute magnetic moments, in Sec. VII optical lines and line strengths for the electron dipolar transitions of \(C_{60}^2^-\) and \(C_{60}^-\). Finally, we give our conclusions in Sec. VIII.

II. ANGULAR DEPENDENCE OF MOLECULAR ORBITALS

The neutral C_{60} molecule has the highest molecular point group (\(I_h\)). Expanding its density in multipoles one finds that nontrivial angular dependencies are given by the symmetry adapted functions (SAFs) [31] of \(A_{1g}\) symmetry with the lowest components characterized by \(l = 6, l = 10\) and \(l = 12\) [32, 33]. That makes the C_{60} fullerene the most spherical molecule among the others. Owing to such unique symmetry, the parentage of \(\pi\)-molecular orbitals in spherical harmonics can be clearly traced [3]. For lowest occupied \(\pi\)-levels of the neutral molecule we have \(a_g (l = 0), b_u (l = 1), h_g (l = 2), t_{2u} (l = 3), h_u (l = 3), g_y (l = 4), h_y (l = 4)\) and \(h_u (l = 5)\). The corresponding molecular states accommodate 60 electrons and the seven electron shells are completely filled. Then the generalized Unsöld theorem [34] ensures that the resulting electron density of the \(\pi\)-states has full (or unit) icosahedral symmetry \(A_{1g}\). (Here and below we use capital letters for the irreducible representations (irreps) of density and small letters for the irreps of electron wave functions.)

Due to the direct correspondence between these \(\pi\)-shells and the molecular orbital index \(l\), one can immediately find out an orbital part for a given \(\pi\)-state in the same way as we know the orbital parts of \(s, p, d\) and \(f\) electrons in an atom. Therefore, the type of an irreducible representation \((a, t_1, t_2, g\) and \(h)\) and the orbital index \(l\) uniquely determine the angular dependence of the molecular orbitals. The angular functions are called spherical harmonics adapted for the icosahedral group \(I_h\). Such symmetry adapted functions (SAFs) were tabulated by Cohan in Ref. [32] for all \(l \leq 14\). (Unfortunately, Cohan worked with unnormalized spherical harmonics so that it requires some efforts to express SAFs in conventional spherical harmonics \(Y_{l}^{m}\).) In particular for the highest occupied molecular orbital (HOMO) \(h_u (l = 5)\) one has

\[
\psi(h_u) = \sqrt{\frac{7}{10}} Y_{5}^{1,s}, \quad (2.1a)
\]

\[
\psi(h_u) = Y_{5}^{1,c} + \sqrt{\frac{3}{10}} Y_{5}^{4,c}, \quad (2.1b)
\]

\[
\psi(h_u) = Y_{5}^{1,s} - \sqrt{\frac{3}{10}} Y_{5}^{4,s}, \quad (2.1c)
\]

\[
\psi(h_u) = \sqrt{\frac{2}{5}} Y_{5}^{2,c} + \sqrt{\frac{3}{5}} Y_{5}^{3,c}, \quad (2.1d)
\]

\[
\psi(h_u) = \sqrt{\frac{2}{5}} Y_{5}^{2,s} - \sqrt{\frac{3}{5}} Y_{5}^{3,s}. \quad (2.1e)
\]

Here the normalized real spherical harmonics are defined with the phase convention of Ref. [33] and the orientation of the C_{60} molecule corresponds to the choice of the \(z\) axis as one of 12 fivefold axes and the \(y\) axis as one of the twofold axes perpendicular to \(z\) [32]. We call this position of C_{60} the orientation of Cohan. In order to transform the molecule to the standard orientation [35] where molecular twofold axes lie along the Cartesian \(x, y\) and \(z\) direction one has to rotate the molecule anticlockwise about the \(y\) axis by an angle \(\beta = \arccos(2/\sqrt{10 + 2\sqrt{5}}) \approx 58.28^\circ\) [4]. Each of the \(h_u\) orbital function then is expressed in terms of \(Y_{7}^\tau\), where \(\tau\) stands for \(m = 0\) or \((m, c), (m, s)\)
of real spherical harmonics (Appendix B). In the following we will work with the molecule in the orientation of Cohan. (Of course, the results are independent of the choice of the molecular orientation.)

The lowest unoccupied molecular $t_{1u}$ orbital (LUMO) corresponds to $l = 5$ and has the following three angular components in Cohan’s orientation of $C_{60}$:

$$
\psi_1(t_{1u}) = \frac{6}{\sqrt{50}} Y_{5}^{0} + \sqrt{\frac{7}{25}} Y_{5}^{5,c},
$$

$$
\psi_2(t_{1u}) = \sqrt{\frac{3}{10}} Y_{5}^{1,c} - \sqrt{\frac{7}{10}} Y_{5}^{4,c},
$$

$$
\psi_3(t_{1u}) = \sqrt{\frac{3}{10}} Y_{5}^{1,s} + \sqrt{\frac{7}{10}} Y_{5}^{4,s}.
$$

The angular parts of $t_{1u}$, LUMO have been derived before in Refs. [14] and [15]. In the standard orientation of $C_{60}$ they are given by Table I of Ref. [14]. The LUMO-HOMO energy gap is about 2.7 eV [16, 39].

Finally, at an energy about 1.15 eV [16, 39] above LUMO one finds the molecular $t_{1g}$ level with $l = 6$ (LUMO+1). In the orientation of Cohan the angular parts are given by

$$
\psi_1(t_{1g}) = Y_{6}^{5,s},
$$

$$
\psi_2(t_{1g}) = \sqrt{\frac{3}{16}} Y_{6}^{1,c} - \sqrt{\frac{1}{16}} Y_{6}^{4,c} + \sqrt{\frac{3}{8}} Y_{6}^{6,c},
$$

$$
\psi_3(t_{1g}) = \sqrt{\frac{3}{16}} Y_{6}^{1,s} + \sqrt{\frac{1}{16}} Y_{6}^{4,s} + \sqrt{\frac{3}{8}} Y_{6}^{6,s}.
$$

\[3.1\]

III. METHOD OF CALCULATION

Our method of multipole expansion of the Coulomb interaction has been reported before in [11, 14]. Here we extend it and apply to the case of the $C_{60}$ molecule with the icosahedral symmetry. In the following we consider in detail the case of two and three $t_{1u}$ electrons. Starting with a pair of electrons we will give a special attention to the procedure of adding one extra $t_{1u}$ electron to the pair. In the same way one can add a fourth electron to the group of three electrons and etc. Therefore, our main goal of treating $n$ electrons can be reached by adding one electron after another.

Since the estimated one-electron spin-orbit coupling is negligible (~ 0.16 cm$^{-1}$) [36], we are working in the “LS (Russsell-Saunders)” molecular approximation. (The spin-orbit coupling is a single particle operator and in principle can be included in the calculation [15].) We start with a pair of $t_{1u}$ electrons and label the two-electron basis ket-vectors by a single index $f$ which incorporates a pair of one-electron indices $(i_1, i_2)$,

$$
|f\rangle = |i_1; i_2\rangle.
$$

The indices $i = (k, s_z)$ stand for the $t_{1u}$ orbitals ($k = 1, 2, 3$) and the spin projection quantum number. The corresponding basis wave functions are

$$
\langle \vec{r}', \vec{r}'|f\rangle = \langle \vec{r}'|i_1\rangle \cdot \langle \vec{r}'|i_2\rangle,
$$

where $\langle \vec{r}|i\rangle = R(r)(\hat{n}|i\rangle$. Here $R$ is the radial component of the $t_{1u}$ molecular orbitals (MO), $\hat{n}$ stands for polar angles $\Omega = (\Theta, \phi)$. There are six orientational $t_{1u}$ vectors (or spin-orbitals) $(\hat{n}|i\rangle$ (i.e. $i = 1 - 6$),

$$
\langle \hat{n}|i\rangle = \psi_{k}(\hat{n}) u_{s}(s_z).
$$

Here $\psi_{k}$ are the three $t_{1u}$ MOs as given by Eqs. (2.2a-c) for the Cohan’s orientation of $C_{60}$, $u_{s}$ is the spin function ($s = \pm$) for the spin projections $s_{z} = \pm 1/2$ on the $z$-axis.

The order of indices in (3.1) and (3.2) is important if we associate the first electron with the state $i_1$ while the second with the state $i_2$. From the dynamical equivalence of the electrons we can permute the spin-orbitals of the state $|i_2; i_1\rangle$ to the standard order, Eq. (3.1), by using

$$
|i_2; i_1\rangle = -|i_1; i_2\rangle,
$$

since it requires the interchange of the two electrons. In order to describe the same quantum state we will use the basis vectors (3.1) where $i_1 > i_2$ and apply Eq. (3.1) when needed. (Alternatively, one can use the standard procedure of antisymmetrization of the basis vectors (3.1).)

Thus, our basis (3.1) consists of $(6 \times 5)/2 = 15$ different vectors $|f\rangle$.

In the following we will study the intra-molecular correlations of electrons within a formalism based on a multipole expansion of the Coulomb potential between two electrons (charge $e = -1$),

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

The multipole expansion in terms of real spherical harmonics $Y_{l}^{m,s}$ and $Y_{l}^{m,c}$ (we use the phase convention and the definitions of Ref. [11]) reads:

$$
V(\vec{r}', \vec{r}) = \sum_{l,m,s} v_l(r, r') Y_{l}^{m,s}(\vec{n}) Y_{l}^{m,s}(\vec{n}'),
$$

where $\tau$ stands for $m = 0$, $(m,c)$ or $(m,s)$ of the real spherical harmonics and

$$
v_l(r, r') = \left(\frac{r_{l}}{r_{c}^{l+1}}\right)^{4\pi} \frac{4\pi}{2l + 1},
$$

with $r_{c} = \max(r, r')$, $r_{c} = \min(r, r')$.

The direct matrix elements for the intra-molecular Coulomb interactions are obtained if we consider the $i_1 \rightarrow j_1$ transitions for the first electron and the $i_2 \rightarrow j_2$ transitions for the second (we recall that $i_1 > i_2$ and $j_1 > j_2$). We label this two-electron transition by the index $a_2 = 1$. Starting from Eq. (3.4) we obtain

$$
\langle I|V(\vec{r}', \vec{r}')|J\rangle_{Coul} = \sum_{l,\tau} v_l c_{l,\tau}(i_1 j_1) c_{l,\tau}(i_2 j_2),
$$

(3.8)
where

\[ v_l = \int dr \, r^2 \int dr' \, r'^2 R^2(r) R^2(r') v_l(r, r') \]  \hspace{1cm} (3.9)

accounts for the average radial dependence. The transition matrix elements \( c_{l\tau} \) are defined by

\[ c_{l\tau}(ij) = \int d\Omega \, (i|\tilde{n}) Y_l^\tau(\tilde{n}) \langle \tilde{n}|j \rangle. \]  \hspace{1cm} (3.10)

The other possibility is to consider the transitions \( i_1 \to j_2 \) for the first electron and the transitions \( i_2 \to j_1 \) for the second. We label it by the index \( a_2 = 2 \). This gives the exchange interaction and then we use (3.4) to return to the standard order of the spin-orbitals. We find

\[ \langle J'|V(r', r'')|J \rangle_{\text{exch}} = -\sum_{l,\tau} \sum_{i,j} v_l c_{l\tau}(i j_2 j_1) c_{l\tau}(i j_1 j_2), \]  \hspace{1cm} (3.11)

where \( v_l \) again is given by Eq. (3.9) and the coefficients \( c_{l\tau} \) by Eq. (3.10). We observe that in the basis with the real \( t_{1u} \) orbitals, and with the real spherical harmonics \( Y_l^\tau \), the coefficients \( c_{l\tau} \) are real.

We start with the spherically symmetric term \((l = 0)\) corresponding to the trivial function \( Y_0^0 = 1/\sqrt{4\pi} \). The coefficients \( c_{l\tau} \) in (3.10) become diagonal, \( c_{l=0}(ij) = 1/\sqrt{4\pi} \delta_{ij} \). In considering the other contributions (with \( l > 0 \)) we take advantage of the selection rules imposed by the coefficients \( c_{l\tau} \), Eq. (3.11). First of all, we notice that the coefficients \( c_{l\tau} \) are diagonal in terms of spin components \( u_s \). Secondly, the odd values of \( l \) are excluded due to the parity of the integrand in (3.10), and from the theory of addition of angular momenta we know that \( l_{\text{max}} = 10 \). From these observations we conclude that \( l = 0, 2, 4, 6, 8 \) and 10. Earlier the coefficients \( c_{l\tau} \) have been used for the description of the crystal field of \( \text{C}_{60} \) in Ref. [4]. By adding (3.11) to (3.8) we obtain

\[ \langle I|V(r', r'')|J \rangle = U_0 \delta(I, J) + v_2 c_2(I|J) + v_4 c_4(I|J) \\
+ v_6 c_6(I|J) + v_8 c_8(I|J) + v_{10} c_{10}(I|J), \]  \hspace{1cm} (3.12)

where \( U_0 = v_0/4\pi \) is the Hubbard repulsion, \( \delta \) the Kronecker symbol, and

\[ c(I|J) = \sum_{l,\tau} c_{l\tau}(i_j 1 j_1) c_{l\tau}(i_2 j_2) \\
- c_{l\tau}(i_1 j_2) c_{l\tau}(i_2 j_1). \]  \hspace{1cm} (3.13)

We have studied the secular problem for the 15 \( \times \) 15 matrix of intra-molecular interactions and obtained 15 energy levels \( E_p[t_{1u}^2] \) \((p = 1 - 15)\),

\[ E_p[t_{1u}^2] = U_0 + v_2 \lambda_2(p) + v_4 \lambda_4(p) \\
+ v_6 \lambda_6(p) + v_8 \lambda_8(p) + v_{10} \lambda_{10}(p), \]  \hspace{1cm} (3.14)

where \( \lambda_i(p) \) are numerical constants (called “integral” or “molecular invariants” in Refs. [24, 27, 28, 29]). They are quoted in Table I. The 15 levels of (3.14) form three distinct terms, i.e. a 9-fold degenerate \( \{t_{1u}^2; 2\} \) and a 5-fold degenerate \( \{t_{1u}^2; 3\} \) and a single-level term \( \{t_{1u}^2; 3\} \). The symmetry between the four electrons and the two holes within the \( t_{1u} \) LUMO configuration implies \( \lambda_i(t_{1u}^4; p) = \lambda_i(t_{1u}^6; p) \), \( p = 1 - 15 \). Therefore, Eq. (3.14) holds also for the case of four \( t_{1u}^4 \) electrons if we write \( 6U_0 \) in place of \( U_0 \). In order to study the splitting quantitatively, one has to calculate the radial integrals \( v_l \), Eq. (3.9). We leave this calculation for next section and now move on to the case of three \( t_{1u} \) electrons.

For the \( t_{1u}^3 \), there are \( 6 \times 5 \times 4/3! = 20 \) basis ket-vectors \( |J \rangle = |i_1 i_2 i_3 \rangle \), where \( i_1 > i_2 > i_3 \). Now for the Coulomb interaction we have a sum of three two-body terms,

\[ V^{(3)} = V(r_1, r_2) + V(r_1, r_3) + V(r_2, r_3), \]  \hspace{1cm} (3.15)

where each \( V(r_a, r_b) \) is given by the multipole expansion (3.6). In considering a matrix element \( \langle J'|V^{(3)}|J \rangle \) we have many subcases which we also call transitions. We sort them out as shown in Fig. 1. It is important to notice that for the third electron there are only three possibilities, i.e. \( i_3 \to j_3, i_3 \to j_2 \) and \( i_3 \to j_1 \), which...
are labeled by $a_3 = 1, 2$ and 3, respectively. From the anticommutation relations we find that the parity ($P_3$) of the transitions are $+1, -1$ and $+1$. Each case leaves possibilities for further transitions of the remaining two $t_{1u}$ electrons. We denote their final states as $j_1'$ and $j_2'$. (For $a_3 = 1$ these indices are $j_1$ and $j_2$; for $a_3 = 2$ $j_1$ and $j_3$, Fig. 1; and for $a_3 = 3$ $j_2$ and $j_3$.) However, the two-electron transitions have been sorted out before when we considered the $t_{1u}$ configuration. In that case there are only two options, ($a_2 = 1$) $t_1 \to j_1'$, $t_2 \to j_2'$, and ($a_2 = 2$) $t_1 \to j_2'$, $t_2 \to j_1'$.

The first has parity $P_2 = +1$, the second $P_2 = -1$.

Therefore, we can classify the transitions by two indices ($a_3, a_2$) where $a_3 = 1 - 3$ and $a_2 = 1, 2$. For a general case of $n$ electrons it is $\langle a_n, a_{n-1}, a_{n-2}, ..., a_2 \rangle$, where $a_k = 1, 2, ..., k$. The parity of an ($a_3, a_2$) transition is $P = P_3(a_3) P_2(a_2)$, for the general case $P = P_3(a_3) P_{n-1}(a_{n-1}) \cdots P_2(a_2)$. The total number of transitions of three $t_{1u}$ electrons is $3 \times 2 = 6$, in general it is $n!$. For each of the subcases we calculate the matrix element of $V^{(3)}$, Eq. (3.15),

$$
\langle I'|V^{(3)}|J'\rangle^{(a_3,a_2)} = P_3(a_3) P_2(a_2) \times \sum_{l,r} v_l c_{l+}(i_1 j_1') c_{l+}(i_2 j_2') \delta(i_3, j_3) + p.i. \tag{3.16}
$$

Here $p.i.$ stands for the other pair Coulomb interactions $V(\mathbf{r}_i, \mathbf{r}_j)$. For three particles there are three terms, Eq. (3.16). The first term is given in Eq. (3.16), two others are found by replacing $c_{l+}(i_1 j_1') c_{l+}(i_2 j_2') \delta(i_3, j_3)$ with $c_{l+}(i_1 j_1') c_{l-}(i_2 j_2) \delta(i_3, j_3')$ and with $c_{l+}(i_1 j_1') c_{l+}(i_2 j_2') \delta(i_3, j_3')$. (The parity of the transitions of course remains the same.) For the general case of $n$ electrons one has $\binom{n}{2}$ different pairs for each $n$-electron transition. (Here $\binom{n}{2}$ is a binomial coefficient.) Finally, the matrix element $\langle I'|V^{(3)}|J'\rangle$ is found as

$$
\langle I'|V^{(3)}|J'\rangle = \sum_{a_3=1}^{3} \sum_{a_2=1}^{2} \langle I'|V^{(3)}|J'\rangle^{(a_3,a_2)}. \tag{3.17}
$$

Having found the matrix elements, we solve a $20 \times 20$ secular problem for $t_{1u}^3$. The energy levels are given by

$$
E_{p'}[t_{1u}^3] = \left( \frac{n^3-3}{2} \right) U_0 + \sum_{l=2}^{10} v_l \lambda_l(p'), \tag{3.18}
$$

where only even values of $l$ occur, $p' = 1 - 20$, and $\lambda_l$ are quoted in Table I. There are three terms, a 4-fold degenerate $\{t_{1u}^3;1\}$ (ground state), a 10-fold degenerate $\{t_{1u}^3;2\}$ and a 6-fold degenerate $\{t_{1u}^3;3\}$, see Table I.

The classification scheme described above is very useful for handling a single-particle interaction $\mathcal{A}$. In particular, the electron coupling to an external magnetic field, the spin-orbit interaction, crystal electric field effects and the electron dipolar operator fall in this class. The main difference from the Coulomb case is that now the interaction occurs to a single electron (represented by an arrow in Fig. 1) while the rest (the other $(n-1)$ electrons, or arrows in Fig. 1) produce $(n-1)$ Kronecker factors. For example, for the three $t_{1u}$ electrons we have

$$
\mathcal{A} = A_1 + A_2 + A_3, \tag{3.19}
$$

where $A_k$ refers to a single electron. For each three-electron subcase ($a_3, a_2$), Fig. 1, we obtain

$$
\langle I'|\mathcal{A}|J'\rangle^{(a_3,a_2)} = P_3(a_3) P_2(a_2) \times \sum_{l,r} (i_1 | A_1 | j_1') \delta(i_2 j_2') \delta(i_3, j_3) + c.p.. \tag{3.20}
$$

c.p. stands for the two other terms obtained from the first by two cyclic permutations, i.e. when $i_1 \to j_2 \to i_3$ and $j_1' \to j_2' \to j_3'$. For the general $n$-electron case there will be $n$ such terms for each matrix element $\langle I'|\mathcal{A}|J'\rangle^{(a_n,a_{n-1},...,a_2)}$.

Finally, we would like to mention that an operator $R$ (rotation or inversion) of the icoshedral group $I_h$ acts on all electrons simultaneously and therefore can be written as $R = R_0 R_{n-1} \cdots R_1$, where $R_k$ stands for the corresponding one-particle operator. The classification scheme again is useful for determining the matrix elements of the transformation in the many electron space. For example, for three $t_{1u}$ electrons we obtain

$$
\langle I|R|J\rangle = \sum_{a_3=1}^{3} \sum_{a_2=1}^{2} \langle I|R|J\rangle^{(a_3,a_2)}, \tag{3.21}
$$

where

$$
\langle I|R|J\rangle^{(a_3,a_2)} = P^{(a_3,a_2)} \langle i_1 | R_1 | j_1' \rangle \langle i_2 | R_2 | j_2' \rangle \langle i_3 | R_3 | j_3' \rangle. \tag{3.22}
$$

Expressions of that type were used to calculate the characters of molecular terms and to identify their symmetry. The orbital part of the many electron wave function transforms as an irrep of $I_h$, while the spin function as a single ($t_{1u}^3$) or double valued ($t_{1u}$) representation of $SO(3)$. Therefore, we classify the molecular terms $2t_{1u}, 2t_{1g}, 2t_{2g}$ by the symbol $2S + 1 \Gamma$, where $2S + 1$ is the spin multiplicity and $\Gamma$ is an irrep of $I_h$. Thus, the molecular terms are $3T_{1g}, \ 1H_{g}, \ 1A_g$ for $t_{1u}$, and $4A_u, 2H_u, 2T_{1u}$ for $t_{1g}$, Table II.

IV. APPLICATION TO OTHER CONFIGURATIONS

Below we apply our method for the hole configurations $(h_{1u}^+)^m$ of $C_{60}^{m+}$ and excitonic configurations $h_{1u}^+ t_{1u}^- h_{1g}^+ t_{1g}^-$ of the neutral molecule. We also consider configurations $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$, because they are important for calculations of electronic dipolar transitions $(t_{1u})^2 \to t_{1u} t_{1g}$ and $(t_{1u})^2 \to (t_{1u})^2 t_{1g}$ of the anions $C_{60}^{2-}$ and $C_{70}^{3-}$.

A. Hole configurations $(h_{1u}^+)^m$ $(m = 2 - 5)$

The treatment of a $m$-hole configuration $(h_{1u}^+)^m$ formally coincides [13] with the analogous electronic case
TABLE II: Coefficients $\mu_i(p) \times 10^3$ for $(h^+_u)^2$. The coefficients marked by (*) are not unique depending on integrals $v_l$, see text for details.

| deg. | $l = 2$ | 4 | 6 | 8 | 10 |
|------|--------|---|---|---|----|
| $^3T_{1u}$ (9) | -25.702 | -4.238 | -8.063 | -30.424 | -11.151 |
| $^3G_u$ (12) | -18.835 | -4.238 | -35.345 | -2.015 | -19.244 |
| $^3T_{2g}$ (9) | -10.987 | -39.553 | 11.212 | -28.746 | -11.503 |
| $^1G_u$ (4) | -18.050 | 0.471 | 29.597 | 13.426 | 11.721 |
| $^1A_u$ (1) | 74.162 | 59.330 | 57.274 | 74.228 | 136.987 |

* $^1H_u$ (5) | -18.492 | 0.471 | -12.595 | 29.970 | 6.970 |
* $^1H_g$ (5) | 55.180 | 16.951 | 8.429 | -18.442 | 64.255 |

TABLE III: Coefficients $\mu_i(p) \times 10^3$ for $(h^+_u)^3$. The coefficients marked by (*) are not unique depending on integrals $v_l$, see text for details.

| deg. | $l = 2$ | 4 | 6 | 8 | 10 |
|------|--------|---|---|---|----|
| $^1G_u$ (16) | -65.916 | -33.903 | -61.552 | -39.129 | -48.232 |
| $^3T_{1u}$ (12) | -62.783 | -33.903 | -34.370 | -67.538 | -40.139 |
| $^3T_{2g} + T_{2g}$ (12) | -48.068 | -69.218 | 15.095 | -65.860 | -40.491 |
| $^3T_{1u} + T_{2g}$ (12) | -0.392 | -5.650 | -30.218 | -13.676 | 30.095 |
| $^3T_{2g}$ (6) | -62.194 | -5.650 | 18.710 | -11.293 | -3.192 |
| $^3T_{1u}$ (6) | -47.480 | -40.966 | 37.985 | -9.615 | -3.544 |

* $^1H_u$ (10) | -60.906 | -41.550 | -63.897 | -30.436 | -12.533 |
* $^2H_u$ (10) | -51.236 | -5.650 | 24.355 | -5.511 | -10.208 |
* $^2H_u$ (10) | 28.220 | 6.121 | -1.637 | 24.146 | 61.563 |
* $^2H_u$ (10) | 45.941 | 44.376 | 58.833 | 54.239 | 108.509 |
* $^3G_u$ (8) | -2.237 | -40.966 | -36.070 | -43.844 | 38.009 |
* $^3G_u$ (8) | 38.730 | 6.121 | 10.229 | -40.794 | 60.323 |

$(h^+_u)^n$, i.e., the Coulomb repulsion between holes and between electrons is the same. The only difference concerns the spherically symmetric term (Hubbard $U_0$). Below we count the energy from the level of an empty $h_u$ shell. In constructing the basis functions, one should take into account that the one-hole index $i_{hu}$ changes from one to ten, where the five-fold degeneracy is due to the orbital freedom, Eqs. (2.1a-e), and the two-fold degeneracy due to its spin. As a result we obtain the term energies

$$E_p[h^+_u] = \left(10^{-2}m\right)U_0 + \sum_{l=2}^{10} v_l\mu_l^{(m)}(p), \hspace{1cm} (4.1)$$

where only even values of $l$ occur. The coefficients $\mu_l^{(m)}(p)$ are again molecular invariants. We quote them in Tables II and III for two and three holes, configurations $(h^+_u)^2$ and $(h^+_u)^3$. Some coefficients depend on $v_l$. This did not occur to $i_{1u}^2$ or $i_{1u}^3$, Table I. These coefficients are marked by star (*) in Tables II and III. For them (19) we give values which are calculated with only one parameter $v_l$. For example, $\mu_2^*$ corresponds to the case when $v_{l=2} \neq 0$, while the others are zero, $v_{l=2} = 0$, and etc. Interestingly, the stared terms have off-diagonal matrix elements in the approach of Plakhtin et al. (Tables 2 and 3 of Ref. 30). The appearance of $\mu_l^*$ implies that the computation of energy splittings, Eq. (4.1), can not be separated in two independent evaluations of $v_l$ and $\mu_l$. Finally, we remark that the "accidental" degeneracy of $^2T_{1u}$ and $^2T_{2u}$, states of $(h^+_u)^3$ has been thoroughly studied in Refs. 27, 28, 29, 30.

B. Excitonic configurations $h^+_u t_{1u}$ and $h^+_u t_{1g}$

In order to describe the excitonic configuration $(h^+_u t_{1u})$, we introduce one $h_u$ hole (missing electron in HOMO) and one $t_{1u}$ electron. The basis functions read

$$|J\rangle = |j_{1u}^u; j_{1u}^t\rangle, \hspace{1cm} (4.2)$$

where now there are 10 states of the $h_u$ hole (index $j_{1u}^u$) and 6 states of the $t_{1u}$ electron (index $j_{1u}^t$). The total number of basis functions is 60. The important thing here is that we have to treat exchange differently. If we consider $I$ as the initial state and $|J\rangle = |j_{1u}^u; j_{1u}^t\rangle$ as a final state, then the exchange transition $I \rightarrow J$ is described as two electronic transitions $i_{hu} \rightarrow j_{hu}$ and $j_{hu} \rightarrow i_{hu}$. For the direct Coulomb interaction we consider $i_{hu} \rightarrow j_{hu}$ and $j_{hu} \rightarrow i_{hu}$. In addition, the sign of the direct Coulomb and exchange interactions has to be reversed $\overline{[3]$. That is,

$$v_l(h^+_u t_{1u}) = -v_l(h^+_u t_{1u}), \hspace{1cm} (4.3)$$

for the direct Coulomb (even $l$) and exchange matrices (even $l$ for $(h^+_u t_{1u})$ and odd $l$ for $(h^+_u t_{1g})$). The resulting energy spectrum for both configurations is given by

$$E_p = \Delta \epsilon + \sum_{l} v_{i}^{l}v_{i}(p), \hspace{1cm} (4.4)$$

for $p = 1 - 60$. Here the energy of the closed shell $(h^+_u)^{10}$ is taken as zero and $\Delta \epsilon$ is an energy associated with the promotion of one electron from the $h_u$ level to the $t_{1u}$ level ($\Delta \epsilon = 2.7$ eV) or $t_{1g}$ shell ($\Delta \epsilon = 3.85$ eV) (see also Sec. V). The calculated values of $v_l(p)$ are quoted in Table III for $(h^+_u t_{1u})$ and in Table IV for $(h^+_u t_{1g})$. The coefficients $v_l(p)$ in the Tables correspond to $v_{i}^{l}$ with the plus sign, i.e. $v_{i}^{l} = v_{i} > 0$, where $v_{i}$ are given by Eq. (4.3).
where, as before, the index $i$ are relevant, while for exchange these are odd numbers.

Table VI.

| deg. | $l = 2$ | 4 | 6 | 8 | 10 |
|------|---------|---|---|---|----|
| $^3G_u$ (12) | 21.425 | 0.0 | -19.130 | -5.219 | 18.167 |
| $^3G_u$ (4) | 21.425 | 0.0 | -19.130 | -5.219 | 18.167 |
| $^5H_u$ (15) | 16.834 | -16.204 | 20.434 | 4.128 | 12.320 |
| $^5H_u$ (5) | 16.834 | -16.204 | 20.434 | 4.128 | 12.320 |
| $^3T_{1u}$ (9) | -16.834 | 16.204 | -14.058 | -4.128 | -27.802 |
| $^3T_{1u}$ (3) | -16.834 | 16.204 | -14.058 | -4.128 | -27.802 |
| $^3T_{2u}$ (9) | -39.789 | 10.802 | 21.449 | 4.207 | 55.659 |
| $^3T_{2u}$ (3) | -39.789 | 10.802 | 21.449 | 4.207 | 55.659 |

Table VII.

| deg. | $l = 2$ | 4 | 6 | 8 | 10 |
|------|---------|---|---|---|----|
| $^4H_g$ (20) | -1.413 | -17.949 | 54.714 | -37.446 | -43.636 |
| $^2G_g$ + $^2T_{2g}$ (14) | -2.472 | -2.244 | 53.450 | 3.420 | 2.127 |
| $^4T_{1g}$ (12) | -10.595 | -37.393 | 46.627 | -51.009 | -50.504 |
| $^4A_g$ (4) | 12.360 | 11.218 | 63.844 | -17.102 | -33.333 |
| $^2A_g$ (2) | 12.360 | 11.218 | 63.844 | -17.102 | -33.333 |

* $^4H_g$ (10) | -1.413 | -17.949 | 54.714 | -37.446 | -43.636 |
* $^2H_g$ (10) | 11.301 | 26.923 | 62.580 | 23.765 | 12.429 |
* $^2T_{1g}$ (6) | 17.976 | -30.048 | 42.958 | -12.337 | -4.859 |
* $^2T_{1g}$ (6) | 13.738 | 53.979 | 63.568 | 83.868 | 79.472 |
* $^2T_{1g}$ (6) | -1.413 | -17.949 | 54.714 | -37.446 | -43.636 |

Table VIII.

| deg. | $l = 1$ | 5 | 7 | 9 | 11 |
|------|---------|---|---|---|----|
| $^7H_g$ (20) | -64.274 | -16.775 | -17.407 | -38.347 | -56.201 |
| $^2G_g$ + $^2T_{2g}$ (14) | -32.137 | -4.194 | -8.442 | -14.152 | -23.791 |
| $^4T_{1g}$ (12) | 0.0 | -41.939 | -2.614 | -50.216 | -43.092 |
| $^4A_g$ (4) | -64.274 | -41.939 | -18.975 | -68.476 | -82.056 |
| $^2A_g$ (2) | 32.137 | 20.969 | 9.487 | 34.238 | 41.028 |

* $^7H_g$ (10) | -32.137 | -21.987 | -9.260 | -33.523 | -39.202 |
* $^2H_g$ (10) | 32.137 | 13.599 | 8.738 | 23.480 | 30.584 |
* $^2T_{1g}$ (6) | -64.274 | -41.939 | -14.929 | -33.480 | -46.641 |
* $^2T_{1g}$ (6) | -32.137 | -17.804 | -9.006 | -26.724 | -18.081 |
* $^2T_{1g}$ (6) | 96.411 | 34.578 | 22.366 | 30.075 | 32.867 |

D. Three electron configuration $(t_{1u})^2t_{1g}$

In case of the three-electron $(t_{1u})^2t_{1g}$ configuration, we construct $(6 \times 5/2) \times 6 = 90$ basis vectors

$$|I\rangle = |i_{1u}i_{2u}i_{1g}\rangle.$$  

(4.6)

Here $i_{1u}$ and $i_{2u}$ are indices of the $t_{1u}$ LUMO states, i.e. $i_{1u}, i_{2u} = 1 - 6$ and $i_{1g}$ labels six $t_{1g}$ states ($i_{1g} = 1 - 6$). Since in that case we deal with two equivalent $t_{1u}$ electrons, the basis functions are taken with $i_{1u} > i_{2u}$. The calculated $\lambda_l$ ($p = 1 - 90$) are quoted in Table VII. The important peculiarity of $\lambda_l$ is that as in the case of few holes, Sec. IV-A, the coefficients marked by ($\ast$) in Table VIII (for two $^2H_g$ and three $^2T_{1g}$ terms), exhibit dependence on $v_l$. For these coefficients ($\lambda_l'$) we give values which are calculated with only one parameter $v_l$. For example, $\lambda_0'$ corresponds to a calculation where $v_{l=2} = 0$ and etc.

Another very interesting observation is that the energy of the $^2G_g$ term "accidentally" coincides with the $^2T_{1g}$ states, Table VII. The same feature has been found for the $t_{1u}(t_{1g})^2$ configuration.

V. ENERGY LEVELS

In order to study the splitting quantitatively we calculated the integrals $v_l$ using three models for radial dependence $R$ of $t_{1u}$ MOs. In the first model (I) we assume...
On the other hand, the first model is a rude approximation for an orbital in atomic calculations in local density approximation (LDA).

This one-electron energy difference accounts for the in-

TABLE VIII: Calculated \( v_1 \) for models I, II and III; in eV.

| model | \( l = 2 \) | 4 | 6 | 8 | 10 | 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 |

TABLE IX: Molecular terms and their degeneracies (in parentheses) for \((t_{1u})^2 \) and \((t_{1u})^3 \) calculated with models I, II and III; in eV. \((\frac{1}{2})U_0 \) is zero of energy.

\[
\begin{array}{cccccccc}
3T_{1u} & (t_{1u})^2 & 1H_u & (t_{1u})^3 & 1A_g & (t_{1u})^2 & 2H_u & 2T_{1u} \\
I & -0.275 & 0.175 & 0.848 & -0.824 & -0.150 & 0.299 \\
II & -0.122 & 0.077 & 0.375 & -0.366 & -0.068 & 0.131 \\
III & -0.117 & 0.073 & 0.359 & -0.351 & -0.066 & 0.125 \\
\end{array}
\]

that the \( t_{1u}^2 \) and \( t_{1u}^3 \) energy spectra are the analogue of \( \rho^2 \) (\( 3P\), \( 1D\), \( 1S \)) and \( \rho^3 \) (\( 4S\), \( 2D\), \( 2P \)) terms in atomic physics. This occurs because \( p_x, p_y \) and \( p_z \) orbitals (\( Y_1^1 \), \( Y_1^1 \) and \( Y_1^3 \)) also belong to the \( t_{1u} \) irrep of \( I_h \) \cite{22}. In Table IX as well as in all other Tables of this section \((5) \) the energy associated with the spherically symmetric multipole component (i.e. \((\frac{1}{2})U_0 \) for electrons, \((\frac{10}{2})U_0 \) for holes and \( \Delta \epsilon \) for excitonic configurations) is put to zero.

Similarly, one can obtain the energy levels of \( t_{1g}^2 \) and \( t_{1g}^3 \), Table IX. Notice that the energy span of \( t_{1u}^2 \) and \( t_{1u}^3 \) configurations is almost the same, \(~0.5 \text{ eV} \), and it is smaller than that of \( t_{1g}^2 \) and \( t_{1g}^3 \) states, \(~0.75 \text{ eV} \). However, the zero of energy in Tables IX and X is different for \( t_{1u}^2 \) and \( t_{1u}^3 \) configurations. When one \( t_{1u} \) electron is promoted to a \( t_{1g} \) state, its energy is increased by \(~1.153 \text{ eV} \), that is,

\[
\Delta \epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u}) \approx 1.153 \text{ eV}.
\] (5.5)

This one-electron energy difference accounts for the interaction of the electron with the carbon nuclei and the “core” like \( \sigma \)- and \( \pi \)-electrons. Therefore, comparing the energy of \((t_{1g})^2 \) with that of \((t_{1u})^2 \) states one should add \( 2 \Delta \epsilon_1 \) to the \((t_{1g})^2 \) values. For the case of three electrons \((t_{1u})^3 \) and \((t_{1g})^3 \) we add \( 3 \Delta \epsilon_1 \) to the \((t_{1g})^3 \) values.

Next, in Tables X and XI we give results for the hole configurations \((h_u)^n \). We observe that the energy span of \((h_u)^2 \) and \((h_u)^3 \), \(~1.2 \text{ eV} \), is almost the same. The magnitude is larger than for electronic \( t_{1u}^2 \) and \( t_{1u}^3 \) configurations, Tables IX and X. Even a larger value of energy splitting, \(~2.4 \text{ eV} \), was obtained for the case of four and five holes, \((h_u)^4 \) and \((h_u)^5 \). Another important observation is that the number of states in a small energy interval \( \Delta \epsilon \sim 0.03 \text{ eV} \) near the ground state is \(30, 40, 25, 6 \) for \( m = 2, 3, 4, 5 \), respectively. This suggests that the configuration of \( m = 3 \) holes is most susceptible
for Jahn-Teller distortions of the C_{60} molecule and hence for hole-phonon coupling which causes superconductivity \[2\].

The results of calculations of excitonic configurations \((h_u^+t_{1u})\) and \((h_u^-t_{1g})\) are quoted in Table XIV. The energy span of \((h_u^+t_{1g})\), \(\sim 1.5\) eV, greatly exceeds that of \((h_u^-t_{1u})\), \(\sim 0.57\) eV. A promotion of one electron to the \(t_{1u}\) shell increases the one-electron energy by the factor \(\Delta \epsilon_2 = \epsilon(t_{1u}) - \epsilon(h_u^-) \approx 2.69\) eV. \[5.6\]

The quantity \(\Delta \epsilon_2\) is called electron affinity of C_{60} and it was measured experimentally \[37\]. It accounts for the energy difference due to the interactions of the electron with the carbon nuclei and the "core" electrons. The value should be taken into account in Eq. (4) (i.e. \(\Delta \epsilon = \Delta \epsilon_1 + \Delta \epsilon_2\)) when \((h_u^+t_{1u})\) is compared with the ground state energy of the neutral molecule. In the case of \((h_u^-t_{1g})\) one should use \(\Delta \epsilon = \Delta \epsilon_1 + \Delta \epsilon_2 = 3.85\) eV in Eq. (5).

The molecular terms for \((t_{1u}t_{1g})\) and \((t_{1u})^2t_{1g}\) are given in Table XIV. The energy span of the excited configurations is relatively large. It is approximately 1.6 eV for \((t_{1u}t_{1g})\) and 2 eV for \((t_{1u})^2t_{1g}\). Since both configurations imply the excitation of one \(t_{1u}\) electron to a \(t_{1g}\) state, we should add \(\Delta \epsilon_1\) to the energies of the \((t_{1u}t_{1g})\) and \((t_{1u})^2t_{1g}\) molecular terms, when we compare them with those of the \((t_{1u})^2\) and \((t_{1u})^3\) configurations. The \((t_{1u})^2\) and \((t_{1u}t_{1g})\) (as well as \((t_{1u})^3\) and \((t_{1u})^2t_{1g}\)) groups of terms are of different parity and thus there is no configuration mixing between them. Therefore, although some two-electron molecular terms of the \((t_{1u})^2\) and \((t_{1u}t_{1g})\) configurations overlap, they do not interact with each other.

The same holds for the \((t_{1u})^3\) and \((t_{1u})^2t_{1g}\) con-
However, there can be a hybridization between terms of the same symmetry of \((t_{1u})^2\) and \((t_{1g})^2\) configurations. The \((t_{1g})^2\) configuration requires promotion of two electrons to the \(t_{1g}\) shell, with a subsequent energy increase of \(2\Delta \epsilon_1 \sim 2.3\) eV. Since the value is relatively large, the hybridization is expected to be weak. In order to study this issue we have carried out calculations where the mixing between the \((t_{1u})^2\) and \((t_{1g})^2\) configurations was allowed. In the calculation we have considered couplings between two \(3T_{1g}\) levels, two \(2H_g\) levels and two \(1A_g\) levels at different values of \(\Delta \epsilon_1\). As before, we have employed the method described in Sec. III. We have found that the energy spectrum separates in two groups. A group at lower energies originates from the former \((t_{1u})^2\) levels, while the other group at higher energies has a large parentage of the \((t_{1u})^2\) states. In Fig. 3 we plot the energies of the three lowest levels as a function of \(\Delta \epsilon_1\). An interesting feature of Fig. 3 is the crossing of the \(3T_{1g}\) triplet with the \(1A_g\) singlet at 0.58 eV with subsequent inversion of their positions. Thus, if \(\Delta \epsilon_1 < 0.58\) eV then the ground state is the \(1A_g\) singlet, while for \(\Delta \epsilon_1 > 0.58\) eV the ground state is the \(3T_{1g}\) triplet. This unusual behavior explains why the \(1A_g\) singlet was reported as the ground state of \(C_{60}^{2-}\) by Negri et al., Ref. [7] (QCFF/\(\pi\) method). From our calculation (Fig. 3) it follows that the reason for this is a small energy difference between \(t_{1g}\) and \(t_{1u}\) states. In Ref. [6,\(\Delta \epsilon_1=0.64\) eV, which is only half of the experimental value of 1.153 eV for \(C_{60}^{2-}\). Such low lying \(t_{1g}\) states lead to an overestimation of the \(1A_g\) \([t_{1u}]^2 - 1A_g [t_{1g}]^2\) configuration mixing and lowering of the bonding \(1A_g\) term below \(3T_{1g}\). The experimental value \(\Delta \epsilon_1=1.153\) eV \([3, 28]\) implies that the ground state is a triplet, as obtained by our calculations and in accordance with Hund’s rules.

**FIG. 3:** Three lowest levels of the coupled \((t_{1u})^2 + (t_{1g})^2\) configurations as a function of \(\Delta \epsilon_1 = \epsilon(t_{1g}) - \epsilon(t_{1u})\). The ground state is the \(1A_g\) singlet for \(\Delta \epsilon_1 < 0.58\) eV, and the \(3T_{1g}\) triplet for \(\Delta \epsilon_1 > 0.58\) eV.

VI. MAGNETIC MOMENTS

In this section we will calculate the magnetic moments of \(C_{60}^{2+}\) for different orientations of the molecule. In a small external magnetic field \(\hat{H}\) we add to a many body Coulomb interaction \(V(\vec{r}, \vec{r}')\), Eq. (3.4), a magnetic term

\[
V_{mag} = -\mathcal{M}_z \cdot H,
\]

where \(\mathcal{M}_z = \sum_{k=1}^{n} M_z(k)\) is a sum of one-electron (one-hole) terms with

\[
\vec{M}(k) = \mu_B (\vec{L}(k) + 2\vec{S}(k)).
\]

Here \(\mu_B\) is the Bohr magneton, \(k = 1 - n\) for electrons and \(k = 1 - m\) for holes. The magnetic moment (6.1) belongs to the class of one-particle operators discussed in Sec. III. Explicitly, for the two-particle case we find

\[
\langle J|V_{mag}|J\rangle = \left[ \langle i|1M_z|j\rangle \delta(i_1j_2) + \langle i_2|2M_z|j_2\rangle \delta(i_1j_1) - \langle i_1|1M_z|j_2\rangle \delta(i_2j_1) - \langle i_2|2M_z|j_1\rangle \delta(i_1j_2) \right] \cdot H,
\]

where \((i|M_z|j)\) stands for the one-particle matrix elements. The generalization of the procedure for a many particle case is given in Sec. III.

The one-particle matrix elements of spin momentum are given by the standard expressions [31, 34]. They are shown to be zero. (Here and below all values of magnetic moments are given in \(\mu_B\).)

We obtain for the orbital momentum of \(t_{1u}\) states

\[
\langle t_{1u}, 2|L_z|t_{1u}, 3\rangle = 2.5i, \quad \langle t_{1u}, 3|L_z|t_{1u}, 2\rangle = -2.5i.
\]

The other matrix elements of \(L_z\) are zero. (Here and below all values of magnetic moments are given in \(\mu_B\).)

In the case of \(h_u\) states we find

\[
\langle h_u, 2|L_z|h_u, 3\rangle = \frac{1}{2}i, \quad \langle h_u, 3|L_z|h_u, 2\rangle = -\frac{1}{2}i, \quad \langle h_u, 4|L_z|h_u, 5\rangle = i, \quad \langle h_u, 5|L_z|h_u, 4\rangle = -i,
\]

and the rest is zero.

There are two equivalent approaches to study the \(C_{60}\) molecule in the magnetic field. The first is to use an active operator \(R(\omega)\), which rotates the molecule as a three-dimensional object. In such case the magnetic field is always directed along the \(z\)-axis, while the position of the molecule is specified by three Euler angles \(\omega = (\alpha, \beta, \gamma)\). In the second case the position of the molecule is fixed but the direction of the magnetic field is changed. In the latter case one has to know the matrix components of the three projections of molecular orbital momentum. Below we have adopted the first approach which is more
familiar to us from our previous study of rotator functions. The advantage is that we are working only with the $z$-component of orbital momentum. The details of the technique are given in Appendices A and B.

Having calculated the matrix elements of $V_{mag}$ as a function of the molecular rotation $\omega$, we diagonalize the matrix $\mathcal{H} = \sum_{a,b} V(\mathbf{r}_a, \mathbf{r}_b) + V_{mag}(\omega)$. The degeneracies of molecular terms are lifted and the magnetic moment of each sublevel $p$ is given by

$$\mathcal{M}(p) = \langle p | \mathcal{M}_z | p \rangle,$$  \hspace{1cm} (6.7)

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

For two electrons (or two $t_{1u}$ holes) we obtain $\mathcal{M}_z = (\pm 4.5, \pm 2.5, \pm 2, \pm 0.5, 0)$ for $^3T_{1g}$ (ground state), while $\mathcal{M}_z(1H_g) = (\pm 5, \pm 2.5, 0)$. In the $^1A_g$ state the spin and the orbital momenta are quenched and $\mathcal{M}_z = 0$. For three electrons we have $\mathcal{M}_z(1A_u) = (\pm 3, \pm 1)$ (the ground term); $\mathcal{M}_z(2H_u) = (\pm 6, \pm 4, \pm 3.5, \pm 1.5, \pm 1)$ and $\mathcal{M}_z(2T_{1u}) = (\pm 3.5, \pm 1.5, \pm 1)$. We immediately conclude that the coupling scheme of orbital and spin momenta is different from the atomic case. In order to clarify this issue we have studied the polarization of spin and orbital momenta separately. By excluding the orbital momentum from Eq. (6.2) we have obtained the results expected from the spin multiplicity index of molecular terms: $2S_z = (\pm 2(3), 0(3))$ for $^3T_{1g}$ (spin triplet state) and $2S_z = 0(5)$ for $^1H_g$ (spin singlet). For $t_{1u}$ we find $2S_z(1A_u) = (\pm 3, \pm 1)$, $2S_z(2H_u) = \pm 1(5)$, and $2S_z(2T_{1u}) = \pm 1(3)$.

In Sec. V we have already discussed the effect of mixing between the $(t_{1u})^2$ and $(t_{1g})^2$ configurations on the energy of the ground state of the $C_{60}^-$ anion. The hybridization affects also the magnetic moments of the $^3T_{1g}$ ground state, which are given by

$$\mathcal{M} = 0, \pm g, \pm 2, \pm (2+g), \pm (4+g).$$ \hspace{1cm} (6.8)

The magnetic moments of the unhybridized $^3T_{1g}$ triplet of the pristine $t_{1u}$ configuration correspond to $g = 0.5$ (dashed line in Fig. 4). The evolution of the $g$-factor as a function of $\Delta \epsilon_1$ is given in Fig. 4.

The results for the hole configurations $(h_u^+)^m$ are quoted in Tables XVIII. In the case of four or five holes the number of molecular terms is too big (27) and we give only magnetic moments for ten lowest states. In general, magnetic moments are described by an expression of the type (18) although in some cases two distinct values of $g$ are required.

Interestingly, we have found that the calculated magnetic moments are independent of the molecular orientation. The conclusion holds for both $t_{1u}$ and $h_u$ shells and we think that there must be a hidden group-theoretical reason behind this. We consider the result as unexpected, because the magnetic moment of a $\pi$ or $\delta$ MO of diatomic molecules is anisotropic in respect to the direction of the magnetic field. From our previous study of $C_{60}$ in a cubic environment it also follows that the crystal field of $C_{60}$ exhibits strong dependence on its orientation [14].

In case of the $C_{60}$ molecule, the orbital $t_{1u}$ (or $h_u$) space of the icosahedral symmetry is greatly reduced in comparison with the 11 dimensional $l = 5$ space of the rotation

![FIG. 4: $g$ for the ground state triplet $^3T_{1g}$ as a function of $\Delta \epsilon_1$, $C_{60}^-$. The corresponding magnetic moments are given by Eq. (6.8).](image)

**TABLE XV: The magnetic moments $\mathcal{M}$ and the orbital momenta $L_z$ of $(h_u^+)^2$, in $\mu_B$.**

| $^3T_{1g}$ | $^3G_u$ | $^3T_{2g}$ | $^1G_g$ | $^1H_g$ | $^1A_u$ |
|-----------|--------|-----------|--------|--------|--------|
| 0: $\pm (1, 3, 4, 5) g$ | $\pm (1, 1, 3, 3, 5, 5) g$ | 0.0, 0, $\pm (1, 1, 1) g$ | $\pm (1, 1, 1, 1) g$ | 2 | 0.8333 $\mathcal{M}$ |
| 0, 0, 0 | 2 | 0.6608 $\mathcal{M}$ | 0.2335 $\mathcal{M}$ | 0.0668 $\mathcal{M}$ | 0 |
| $\pm (1, 2) g$ | $\pm (1, 2) g$ | 0.2335 $\mathcal{M}$ | 0.0668 $\mathcal{M}$ | 0.0668 $\mathcal{M}$ | 0 |
| 0 | 0 | 0 | 0 | 0 | 0 |

**TABLE XVI: Magnetic moments $\mathcal{M}$ of $(h_u^+)^3$, in $\mu_B$. $^2T_{1u}$ and $^2T_{2u}$ states are degenerate.**

| $^4T_{1u}$ | $^4G_u$ | $^4T_{2u}$ | $^2H_u$ | $^2G_u$ | $^2H_u$ |
|-----------|--------|-----------|--------|--------|--------|
| $\pm (1, 2, 3, 5, 6, 7) g$ | $\pm (1, 1, 3, 3, 5, 7, 7) g$ | 1.0 | (g, 1.2 $- g$) | (g, g, 1.2 $- g$) | 1 |
| (g, 1.1 $- g$) | 1.0 | 0.25 | 0.2218, 0.3891 | 0.8983 | 0.5650 |
| (g, 1.2 $- g$) | 0.6529, 0.8265 | 1 |
| (g, g, 2 $- g$, 2 $- g$) | 0.8983 | 1 |
| (0, 1, 2, 3, 4, 4) g | 0.5 |
| 0.9578, 0.9789 | 0.5650 | 0.5 |
TABLE XVII: Magnetic moments $M$ for ten lowest molecular terms of $(h_u^+)^4$, in $\mu_B$.

| $M$ | $g$ |
|-----|-----|
| $^6A_g$ | $\pm(1,3,5,7)g$ | 1.0 |
| $^4H_u$ | $M(4H)$ | 0.533,0,766 |
| $^2H_u$ | $\pm(g_1,g_2,1,2-g_2,2-g_1)$ | 0.873,0,936 |
| $^2G_u$ | $\pm(g_2,2-g_2,2-g)$ | 0.366 |
| $^4H_u$ | $M(4H)$ | 0.866,0,933 |
| $^2G_u$ | $\pm(g_1,g_2,1,2-g_2,2-g)$ | 0.167 |
| $^2A_u$ | $\pm g$ | 1.0 |
| $^2G_u$ | $\pm(g_2,2-g_2,2-g)$ | 0.978 |
| $^2T_{2u}$ | $\pm(1,1,1,3,3,3)$ | 1.0 |
| $^4G_u$ | $\pm(g_1,g_2,1,2-g_2,2-g)$ | 0.5 |

TABLE XVIII: Magnetic moments $M$ for ten lowest molecular terms of $(h_u^+)^5$, in $\mu_B$. $M(4H)$ stands for $\pm(g_1,g_2,1,2-g_2,2-g_1,2+g_2,2+g_2,3-4,g_2,4-g_1)$.

| $M$ | $g$ |
|-----|-----|
| $^6A_u$ | $\pm(1,3,5)g$ | 1.0 |
| $^4H_u$ | $M(4H)$ | 0.533,0,766 |
| $^2H_u$ | $\pm(g_1,g_2,1,2-g_2,2-g_1)$ | 0.873,0,936 |
| $^2G_u$ | $\pm(g_2,2-g_2,2-g)$ | 0.366 |
| $^4H_u$ | $M(4H)$ | 0.866,0,933 |
| $^2G_u$ | $\pm(g_1,g_2,1,2-g_2,2-g)$ | 0.167 |
| $^2A_u$ | $\pm g$ | 1.0 |
| $^2G_u$ | $\pm(g_2,2-g_2,2-g)$ | 0.978 |
| $^2T_{2u}$ | $\pm(1,1,1,3,3,3)$ | 1.0 |
| $^4G_u$ | $\pm(g_1,g_2,1,2-g_2,2-g)$ | 0.5 |

group $SO(3)$. However, this is not accompanied by an anisotropic behavior of orbital momenta.

In order to understand this issue we have considered a simplified case of one electron on the $t_{1u}$ molecular level. Applying $\vec{H}$ in a direction $\vec{n} = \vec{H}/H$, where $n_x = \sin \Omega \cos \phi$, $n_y = \sin \Omega \sin \phi$ and $n_z = \cos \Omega$, we find

$$V_{mag} = \vec{H} \vec{L} = H L_{\vec{n}}.$$  \hfill (6.9)

Here the matrix $L_{\vec{n}}$ is given by

$$L_{\vec{n}} = n_x L_x + n_y L_y + n_z L_z.$$  \hfill (6.10)

By using Eqs. (2.2)-(c) for three $t_{1u}$ MOs, after calculating the matrix elements, we arrive at

$$L_{\vec{n}} = \begin{bmatrix} 0 & M_{0} n_y & M_{0} n_z \\ M_{0} n_y & 0 & M_{0} n_z \\ -M_{0} n_y & -M_{0} n_z & 0 \end{bmatrix},$$  \hfill (6.11)

where $M_0 = 2.5 \mu_B$. The magnetic moments are obtained through the diagonalization of $L_{\vec{n}}$. We find that $M = 0$ and $M = \pm 2.5 \mu_B$ for any direction of $\vec{H}$. The same conclusion is obtained for the case of one $h_u$-electron (or $h_u$—hole). The matrix $L_{\vec{n}}$ then reads

$$L_{\vec{n}} = \begin{bmatrix} 0 & \frac{\sqrt{3}}{2} n_x i & \frac{\sqrt{3}}{2} n_y i \\ \frac{\sqrt{3}}{2} n_y i & 0 & \frac{1}{2} n_z i \frac{1}{2} n_x i \\ \frac{1}{2} n_y i & \frac{1}{2} n_x i & 0 \end{bmatrix}.$$  \hfill (6.12)

The matrix has the same magnetic moments (eigenvalues), which are 0, $\pm 1/2$, $\pm 1$ (in $\mu_B$), for any direction of $\vec{H}$. The reasoning given above is suggestive and we are looking for a full-scale group-theoretical solution to this problem.

VII. ELECTRON OPTICAL TRANSITIONS

In this section we consider only the electronic dipolar transitions and the corresponding optical lines for $C_{60}^-$. The picture is not complete because there exist electron–vibration interactions ("Herzberg-Teller" couplings) which can alter the symmetry of the initial or the final state $[\text{13}]$. Here we omit the electron–vibration couplings and limit ourselves to the electronic part of the problem.

The optically active transitions are associated with a nonzero expectation value of the electron dipolar operator $\vec{P}$. Since the electric-dipole moment,

$$\vec{P} = -e \sum_i \vec{r}_i,$$  \hfill (7.1)

is an odd quantity in respect to the inversion symmetry, it follows that $\vec{P}$ has no matrix components between states of the same parity. Therefore, all spectral lines due to electric-dipole radiation arise from transitions between states of opposite parity (Laporte’s rule) $[\text{13}]$ and the following schemes are relevant for the $C_{60}^-$ and $C_{60}^3$-molecular ions:

$$\begin{align*}
(t_{1u})^2 & \rightarrow t_{1u} t_{1g}, \\
(t_{1u})^3 & \rightarrow (t_{1u})^2 t_{1g}.
\end{align*}$$  \hfill (7.2a,b)

These configurations have been considered already in previous sections, and now we can proceed to calculations of optical transitions.

In atoms there are several additional selection rules which greatly facilitate line assignments. These rules are not developed for the icosahedral symmetry and in the following we have to rely on numerical analysis. The total intensity for the line from level $A$ to level $B$ is given by $[\text{13}]$

$$I(A,B) = N(a) \nu \frac{64 \pi^2 \sigma^3}{3h} S(A,B),$$  \hfill (7.3)

where $N(a)$ is the number of $C_{60}^-$ molecules in state $a$, $\nu = (E_A - E_B)/h$ is the frequency and $\sigma = h \nu / c$ is the
wave number. Finally, $S(A, B)$ is the line strength which is found as

$$S(A, B) = \sum_{ab} |\langle a | \vec{P} | b \rangle|^2. \tag{7.4}$$

The line strength is a very convenient quantity and in the following we calculate $S(A, B)$ for the transitions $\epsilon_{2u}$.

The matrix elements of the dipole operator for the case $\epsilon_{2u}$ read

$$\langle a | \vec{P} | b \rangle = \sum_{I, I'} \langle a | I \rangle \langle I | \vec{P} | J' \rangle \langle J' | b \rangle, \tag{7.5}$$

where $|I\rangle$ and $|J'\rangle$ are the basis states of $(t_{1u})^2$ and $(t_{1u}t_{1g})$, respectively, while $\langle a | I \rangle$ and $\langle b | J' \rangle$ are the eigenvectors corresponding to levels $a$ and $b$. The dipole moment Eq. (7.3) is a one-electron operator, Sec. III. Its matrix elements are given by

$$\langle I | \vec{P} | J' \rangle = \delta(i_{u1}, j_{u}) \langle i_{u2} | \vec{P} | j_{g} \rangle - \langle i_{u1} | \vec{P} | j_{g} \rangle \delta(i_{u2}, j_{u}).$$

We recall that $\langle I \rangle = \langle i_{u1}, i_{u2} \rangle$, where $i_{u1}$ and $i_{u2}$ are indices referring to six $t_{1u}$ states, and $|J'\rangle = |j_{u}, j_{g}\rangle$, Eq. (7.3). From parity consideration it follows that the nonzero matrix elements are of the type $\langle i_{u} | \vec{P} | j_{g} \rangle$. In order to calculate them, we first rewrite $\vec{P}$ in the following form:

$$P_{x} = \sqrt{\frac{4\pi}{3}} r Y_{1}^{0,0}(\hat{r}), \tag{7.6a}$$

$$P_{y} = \sqrt{\frac{4\pi}{3}} r Y_{1}^{0,1}(\hat{r}), \tag{7.6b}$$

$$P_{z} = \sqrt{\frac{4\pi}{3}} r Y_{1}^{0,2}(\hat{r}). \tag{7.6c}$$

Here $Y_{1}^{\tau}$ are real spherical harmonics $[11]$, and as before $r = |\vec{r}|$, while $\hat{r}$ stands for the polar angles ($\Omega, \phi$). Then we find that the one-electron matrix elements of $\vec{P}$ are

$$\langle i_{u} | P_{k} | j_{g} \rangle = \mathcal{V} c_{1, r(k)}(i_{u}, j_{g}), \tag{7.7}$$

where $\tau = (1, c)$, $(1, s)$ or $0$ for $k = x, y$ and $z$, respectively. The quantities $c_{1, r(k)}(i_{u}, j_{g})$ are given by Eq. (3.10) for $l = 1$. In fact, these coefficients have been also used for the calculation of the $(t_{1u} t_{1g})$ and $(t_{1u})^2 t_{1g}$ configurations in Sec. IV and V. Finally, the radial part of Eq. (7.7) reads

$$\mathcal{V} = \sqrt{\frac{4\pi}{3}} \int dr r^3 \mathcal{R}_{1ru}(r) \mathcal{R}_{1tg}(r). \tag{7.8}$$

Since we have already computed the eigenvalues and eigenvectors of $(t_{1u})^2$ and $(t_{1u} t_{1g})$ in Sec. V, we now can calculate the line strengths using equations (7.4), (7.5), (7.6), (7.7) and (7.8). The results are quoted in Table XIX.

### Table XIX: Energies $E_{ab} = \Delta \epsilon_{1} + \epsilon_{ab}$ (in eV) and line strengths (in $\mathcal{V}$) of the transitions $(|t_{1u})^2; a \rangle \rightarrow \{|t_{1u}t_{1g}; b\rangle$, $a = 1 - 3$, $b = 1 - 6$, calculated with the model III. Only transitions with $S(a, b) \neq 0$ are given.

| $(t_{1u}t_{1g}); b\rangle$ | $(t_{1u})^2; a = 3T_{1g}$ | $^1H_{a}$ | $^1A_{a}$ |
|-----------------------------|-----------------|--------|--------|
| $^1A_{u}$                    | $^3H_{u}$       | -0.350 | 0.482  |
| $^2H_{u}$                   | -0.267          | 0.289  |
| $^1H_{u}$                   | 0.392           | 0.482  |
| $^1A_{u}$                    | 0.624           | 0.386  |
| $^2T_{1u}$                  | 0.609           | 0.161  |
| $^1A_{u}$                    | 0.323           | 0.129  |

Similarly, one can treat the optical transitions $[7,24]$ for $C_{60}^{3-}$. Now we consider the matrix elements of $P$ between three-electron basis states $\langle I | (t_{1u})^3 \rangle = \langle i_{1}, i_{2}, i_{3} \rangle$ and $\langle J | (t_{1u}^2 t_{1g}) \rangle = \langle j_{1}, j_{2}, j_{g} \rangle$, and obtain

$$\langle I | \vec{P} | J \rangle =$$

$$\langle i_{1} | \vec{P} | j_{g} \rangle \delta(i_{2}, j_{1}) \delta(i_{3}, j_{2}) - \langle i_{1} | \vec{P} | j_{g} \rangle \delta(i_{2}, j_{2}) \delta(i_{3}, j_{1})$$

$$+ \langle i_{2} | \vec{P} | j_{g} \rangle \delta(i_{1}, j_{1}) \delta(i_{3}, j_{2}) - \langle i_{2} | \vec{P} | j_{g} \rangle \delta(i_{1}, j_{2}) \delta(i_{3}, j_{1})$$

$$+ \langle i_{3} | \vec{P} | j_{g} \rangle \delta(i_{1}, j_{1}) \delta(i_{2}, j_{2}) - \langle i_{3} | \vec{P} | j_{g} \rangle \delta(i_{1}, j_{2}) \delta(i_{2}, j_{1}).$$

Here again, the one-electron matrix elements $\langle i_{u} | \vec{P} | j_{g} \rangle$ are specified by Eq. (7.7). The resulting line strengths are quoted in Table XX.

### Table XX: Energies $E_{ab} = \Delta \epsilon_{1} + \epsilon_{ab}$ (in eV) and line strengths (in $\mathcal{V}$) of the transitions $(|t_{1u})^3; a \rangle \rightarrow \{|t_{1u}t_{1g}; b\rangle$, $a = 1 - 3$, $b = 1 - 10$, calculated with the model III. Only the transitions with $S(a, b) \neq 0$ are given.

| $(t_{1u}^2 t_{1g}); b\rangle$ | $(t_{1u})^3; a = 4A_{u}$ | $^2H_{a}$ | $^2T_{1u}$ |
|-----------------------------|-----------------|--------|--------|
| $^2H_{u}$                   | -0.913           | 0.002  | -1.103 |
| $^2G_{u} + ^2T_{2u}$        | -0.330           | 0.450  |
| $^2T_{1g}$                  | -0.158           | 0.120  |
| $^2T_{1g}$                  | 0.058            | 0.072  |
| $^2T_{1g}$                  | 0.508            | 0.683  |
| $^2T_{1g}$                  | 0.589            | 0.193  |
| $^2T_{1g}$                  | 0.780            | 0.602  |
| $^2T_{1g}$                  | 0.920            | 0.362  |

It follows from Table XIX that for $C_{60}^{3-}$ there are three lines from the ground state $^3T_{1g}$,

$$E(^3T_{1g} \rightarrow ^3H_{u}) = \Delta \epsilon_{1} - 0.350 \text{ eV}, \tag{7.9a}$$

$$E(^3T_{1g} \rightarrow ^3T_{1u}) = \Delta \epsilon_{1} - 0.267 \text{ eV}, \tag{7.9b}$$

$$E(^3T_{1g} \rightarrow ^3A_{u}) = \Delta \epsilon_{1} + 0.624 \text{ eV}. \tag{7.9c}$$

With $\Delta \epsilon_{1} = 1.153 \text{ eV}$, Eq. (5.5), we obtain $E(^3T_{1g} \rightarrow ^3H_{u}) = 0.803 \text{ eV}$, $E(^3T_{1g} \rightarrow ^3T_{1u}) = 0.886 \text{ eV}$ and $E(^3T_{1g} \rightarrow ^3A_{u}) = 1.777 \text{ eV}$. These values should be compared with two dominant bands at 1.305 eV (950 nm)
and 1.494 eV (830 nm) observed by the near-infrared experiments in solutions [1]. We conclude that first two transitions can be tentatively ascribed to the experimental bands if \( \Delta \epsilon_1 \) is taken to be larger, \( \Delta \epsilon_1 \sim 1.7 \) eV. Here it is worth to notice that in our approach \( \Delta \epsilon_1 \) in Eq. (5.5) remains a phenomenological quantity which is not immediately connected with the term splittings. In Ref. [16] the authors have obtained that the ground state of \( C_{60}^- \) is the \(^1\text{A}_g \) singlet. We have shown in Sec. V that this is possible if \( \Delta \epsilon_1 \) is small, see Fig. 3. However, if \(^1\text{A}_g \) is the ground state, then there is only one optical transition \((^1\text{A}_g \rightarrow ^1\text{T}_{1u}) \) at \( \Delta \epsilon_1 + 0.323 \) eV, Table XX and comparison with the experiment becomes even more problematic. We conclude that our calculations are basically in agreement with the experiment for \( C_{60}^- \), although also a third band is expected. The position of the third band however can change due to the effect of configuration mixing discussed in Sec. V.

The situation is less clear for the \( C_{60}^3^- \) molecular ion. Both our calculations and those of Ref. [16] predict that the ground state is the \(^1\text{A}_g \) level. Then from Table XXI we find that the only optical transition allowed by the selection rules is \(^1\text{A}_u \rightarrow ^1\text{T}_{1g} \). This is at variance with the experimental consensus for three dominant bands at 1350, 960 and 770 nm [1]. In principle, the theoretical line \(^1\text{A}_u \rightarrow ^1\text{T}_{1g} \) can be split by the crystal field and Jahn-Teller distortions, but the magnitude of the splitting (\( \sim 0.3 \) eV) seems excessive. The other possibility is if some transitions become allowed through the “Herzberg-Teller” (electron-vibration) mechanism [3]. Further experimental and theoretical investigations are needed to clarify the issue.

VIII. DISCUSSION AND CONCLUSIONS

We have presented an efficient configuration interaction method for many electron (hole) molecular terms of the \( C_{60}^m \) molecular ion. The method is based on the multipole expansion of the Coulomb interactions and takes into account the molecular symmetry. Although there are some similarities with approaches used for treating many electron effects in atomic calculations [3], the technique is novel and original. Crystal electric field effects [14] and the spin-orbit coupling can be easily incorporated in the calculation. The technique can be used for other electron systems.

We have applied the method for studying molecular terms of electron and hole configurations of \( C_{60}^n/m \) (\( n = 2-4, m = 2-5 \)), and for excitonic configurations \( (h_u^{m}t_{1u}) \) and \( (h_u^{-}t_{1u}) \) of the neutral molecule. In most of the cases the ground state is found to obey Hund’s rules.

Our calculations of the molecular term structure \((t_{1u})^2 \) for \( C_{60}^2^- \) differs from the previous result of Negri et al., Ref. [32]. They have reported that the ground term of \( C_{60}^2^- \) is the \(^3\text{A}_g \) singlet, while we have found that for realistic parameters (\( \Delta \epsilon_1 = 1.15 \) eV [14, 33]) it is the \(^3\text{T}_{1g} \) triplet, in accordance with Hund’s rules. We have shown (Fig. 3 and Sec. V) that the reason for this is that in Ref. [16] the one-electron energy difference between \( t_{1g} \) and \( t_{1u} \) states is too small, \( \Delta \epsilon_1 \sim 0.64 \) eV.

Our results for the \( (h_u^{m})^2 \) hole configuration indicate that there are three very close (\( \sim 0.03 \) eV) low lying molecular triplets of \( ^3\text{T}_{1g}, ^3\text{G}_2 \) and \( ^3\text{T}_2 \) symmetry. The lowest molecular terms for \( (h_u^{m})^3 \) belong to the \( ^4\text{T}_{1u}, ^4\text{G}_u \) and \( ^4\text{T}_2 \) symmetry. The number of states in a small energy interval \( \Delta \epsilon \sim 0.03 \) eV near the ground state is 30, 40, 25, 6 for hole configurations \( (h_u^{m})^m \) with \( m = 2, 3, 4, 5 \), respectively. This suggests that the configuration of \( m = 3 \) holes is most susceptible for Jahn-Teller distortions of the \( C_{60}^- \) molecule and possibly for hole-phonon coupling which causes superconductivity [2].

We have calculated the magnetic moments of the \((t_{1u})^n \) and \( (h_u^{m})^m \) configurations, Sec. VI. The coupling of spin and orbital momenta differs from the Landé \( g \)-factor scheme of atoms. The magnetic moments do not depend on the orientation of the molecule with respect to an external magnetic field. The latter statement was demonstrated explicitly for the case of one \( t_{1u} \) electron and one \( h_u \) hole. We consider this as a group-theoretical puzzle of the icosahedral symmetry. We have also found new “accidental” degeneracy between the \( ^2\text{G}_2 \) and \( ^2\text{T}_2 \) states of the \((t_{1u})^2t_{1g} \) and \((t_{1g})^2t_{1u} \) configurations (Tables VII and XXIV).

Finally, we have studied optical absorption associated with electron dipolar transitions \((t_{1u})^2 \rightarrow (t_{1u}t_{1g}) \) and \((t_{1u})^3 \rightarrow (t_{1u})^2t_{1g} \). For \( C_{60}^- \) we have found that two lines \((^3\text{T}_{1g} \rightarrow ^3\text{H}_u \) and \(^3\text{T}_{1g} \rightarrow ^3\text{T}_{1u} \) can be tentatively ascribed to the two near-infrared dominant bands at 950 and 830 nm. However, in addition a third band \((^3\text{T}_{1g} \rightarrow ^3\text{A}_u \) is expected from the calculation. For \( C_{60}^3^- \) with \(^4\text{A}_u \) as the ground state, we have found that only one electron dipolar transition, \(^4\text{A}_u \rightarrow ^3\text{T}_{1g} \), is allowed. It seems that a better understanding of optical transitions requires a study of the Herzberg-Teller (electron-vibration) effect which is beyond the scope of the present work. We suggest to perform optical experiments for \( C_{60}^- \) and \( C_{60}^3^- \) in the gas phase to obtain more precise and full data on the optical lines which can shed light on the problem of electronic intra-molecular correlations.

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APPENDIX A: \( L_z \) FOR A ROTATED MOLECULE

If the molecule is rotated away, then the MOs of \( t_{1g} \) and \( h_u \) symmetry are given by Eqs. (2.23c) and (2.1a).
e) in the coordinate system \((x', y', z')\) attached to the molecule. The rotated functions can be expanded in terms of real spherical harmonics (RSH) defined in the fixed set of axes \((x, y, z)\). For example, a rotation \(R\) defined by three Euler angles \(\omega = (\alpha, \beta, \gamma)\) transforms 
\[ \psi_1(t_{1u}) = R(\omega) \psi_1(t_{1u}) \]
\[ = \frac{6}{\sqrt{50}} R(\omega) Y^0_5 + \frac{\sqrt{25}}{5} R(\omega) Y^{5,c}_0. \]  
(A1)

Here \(R(\omega) Y^0_5\) and \(R(\omega) Y^{5,c}_0\) defines the rotations of \(Y^0_5\) and \(Y^{5,c}_0\), respectively. The rotated functions can be found from Eqs. (B3), and (B9), quoted in the Appendix B. Analogously, we proceed with the other angular functions of \(t_{1u}\) and \(h_u\) symmetry. In general,
\[ R(\omega) Y^\tau_r = \sum_{\tau'} Y^{\tau'}_r \ U^{l, \tau'}_{\tau, \tau}(\omega). \]  
(A2)

Here \(\tau, \tau' = (m, c), (m, s)\) or 0, and the rotator functions (matrices) \(U^{l, \tau'}_{\tau, \tau}(\omega)\) are specified in Appendix B, Eqs. (B5), (B7), and (B9). Now we are ready to calculate \(L_z \psi'_k(t_{1u})\) \((k = 1 - 3)\) and \(L_z \psi'_k(h_u)\) \((k = 1 - 5)\). By means of Eq. (A4) we obtain
\[ \langle k|L_z|k'\rangle_\omega = i \sum_{m>0} m \ (g(m,c) k g(m,c) k' - g(m,s) k g(m,c) k'), \]  
(A3)

where the functions \(g_{r,k}\) depend on \(\omega\),
\[ g_{m,c}(k) = \alpha(\tau_1) U^l_{m,c}(\tau_1) + \alpha(\tau_2) U^l_{m,c}(\tau_2), \]
\[ g_{m,s}(k) = \alpha(\tau_1) U^l_{m,s}(\tau_1) + \alpha(\tau_2) U^l_{m,s}(\tau_2). \]

Here \(\alpha(\tau)\) stands for the coefficients of expansion of MOs of \(t_{1u}\) and \(h_u\) symmetry in terms of RSH,
\[ \psi_k(\Omega) = \alpha(\tau_1) Y^1_1(\Omega) + \alpha(\tau_2) Y^2_2(\Omega), \]  
(A5)

see Eqs. (2.23c) and (2.13c). For example, for the first MO \((k = 1)\) of \(t_{1u}\) symmetry we have \(\tau_1 = 0, \alpha(\tau_1) = 6/\sqrt{50}\) and \(\tau_2 = (5, c), \alpha(\tau_2) = \sqrt{25/25}\), and etc. The indices \(k, k'\) in (A3) belong to the same molecular shell \((t_{1u} \text{ or } h_u)\), otherwise \(\langle k|L_z|k'\rangle_\omega = 0\). From Eq. (A3) we also conclude that
\[ \langle k|L_z|k\rangle_\omega = 0, \]  
(A6a)
\[ \langle k|L_z|k'\rangle_\omega = (k'|L_z|k\rangle)_{\omega^*}. \]  
(A6b)

The latter condition is a consequence of working with real spherical harmonics, the latter ensures the hermiticity of \(L_z\).

**APPENDIX B: ROTATION OF REAL SPHERICAL HARMONICS**

An active rotation \(R\) is specified by its Euler angles \(\omega = (\alpha, \beta, \gamma)\). It transforms a complex spherical harmonic \(Y^m_r\) to \(Y'^m_r\), where
\[ Y'^m_r = R(\omega) Y^m_r = \sum_n Y^{n}_r D^{l}_{nm}(\omega). \]  
(B1a)

For \(Y'^-m_r\) we have
\[ Y'^-m_r = R(\omega) Y^{-m}_r = \sum_n Y^{n}_r D^{l}_{-n-m}(\omega). \]  
(B1b)

Here \(D^{l}_{nm}\) stands for the Wigner functions given by
\[ D^{l}_{nm}(\alpha, \beta, \gamma) = C_{nm} e^{-i\gamma} d^{l}(\beta)_{nm} e^{-im\alpha}. \]  
(B2)

d\(d^{l}(\beta)_{nm}\) is a reduced matrix element which is a real quantity, and \(C_{nm} = \pm 1\) depending on \(n, m\) (see Eqs. (2.1.6) and (2.1.5) of Refs. 31). From Eq. (B2) and the properties
\[ d^{l}(\beta)_{-n,-m} = (1)^{n+m} d^{l}(\beta)_{nm}, \]
\[ C_{-n,-m} = (1)^{n+m} C_{nm}, \]
we find that
\[ D^{l}_{-n-m} = D^{l}_{nm}(\omega)^{*}. \]  
(B4)

We then combine (B1a) with (B1b) and use Eq. (B4) for deriving the transformation law of real spherical harmonics. After some algebra we find
\[ R Y^{m,c}_{l}(0,(m,c)) + \sum_{n>0} \left( Y^{n,c}_{l}(n,c);(m,c) + Y^{n,s}_{l}(n,s);(m,c) \right), \]  
(B5)

where \(U^{l}_{0,(m,c)} = \sqrt{2} Re D^{l}_{0m,} and \)
\[ U^{l}_{0,(n,c);(m,c)} = Re (D^{l}_{nm} + D^{l}_{n-m}), \]
\[ U^{l}_{0,(n,s);(m,c)} = -Im (D^{l}_{nm} + D^{l}_{n-m}). \]
(B6b)

In Eqs. (B3)-(B6b), and below for clarity we drop the argument \(\omega\). Analogously, rotating \(Y^{m,s}_{l}\) we obtain
\[ R Y^{m,s}_{l}(m,s) + \sum_{n>0} \left( Y^{n,c}_{l}(n,c);(m,s) + Y^{n,s}_{l}(n,s);(m,s) \right), \]  
(B7)

where \(U^{l}_{0,(m,s)} = \sqrt{2} Im D^{l}_{0m,} and \)
\[ U^{l}_{0,(n,c);(m,s)} = Im (D^{l}_{nm} - D^{l}_{n-m}), \]
\[ U^{l}_{0,(n,s);(m,s)} = Re (D^{l}_{nm} - D^{l}_{n-m}). \]
(B8b)

Finally, the rotation of \(Y^{0}_{l}\) yields
\[ R Y^{0}_{l} = Y^{0}_{l} U^{l}_{0,0} + \sum_{n>0} \left( Y^{n,c}_{l}(n,c);0 + Y^{n,s}_{l}(n,s);0 \right), \]  
(B9)

where \(U^{l}_{0,0} = D^{l}_{00}, \ U^{l}_{(n,c);0} = \sqrt{2} Re D^{l}_{n0} and U^{l}_{(n,s);0} = -\sqrt{2} Im D^{l}_{n0}. \)
