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# Jahn–Teller Instability of Correlated $C_{60}$ Anions

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*The results of calculations on static Jahn-Teller ground state splittings inicosahedral $C_{60}^{N-}$ $(N = 1, \ldots, 4)$ fullerene anions with different types of electron-electron interaction are presented. Multielectron states of anions are determined within a quasy-π-electronic model configuration interaction (CI) method for two active spaces of $t_{1u}$ and $t_{1u}+t_{1g}$ molecular orbitals. Electron–lattice interaction is taken into account over a linear dependence of the neighbor site resonance integrals on the correspondent length change. The results show that, in opposition to the case of short-range electron repulsion, long-range electron correlation can significantly change the features of the Jahn–Teller splitting.*

**Keywords:** configuration interaction method; fullerene; Jahn–Teller splitting

## INTRODUCTION

Strong electron–phonon interaction and high icosahedral symmetry play an important role in the formation of physical properties in $C_{60}$–based materials. In particular, this interaction is supposed to be responsible for superconductivity of alkali-doped fullerides [1] with fullerenes being in $C_{60}^{N-}$ multicharged anion forms. The lowest unoccupied $t_{1u}$ molecular orbital in fullerene anions becomes partially filled by electrons that, according to group-theoretic analysis can interact with some vibrational modes only. Such an electron-lattice interaction in fullerene can lead to a splitting of electronic terms resulting in the Jahn–Teller (JT) effect, where the orbital triplet interacts with a five-fold distortion mode $(t_{1u} \otimes H_g)$. Moreover, there are eight $H_g$ modes of very different frequencies, all of which should be included in the JT coupling producing an extra complication.

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Another respect motivating our investigation consists in that the $t_{1u}$ orbital adopting extra electrons is not well separated in the one-electron energy spectrum. The next unoccupied orbital above $t_{1u}$ is $t_{1g}$, and it is rather close in energy. Basing on this fact, the ordering of terms different from the Hund ordering is obtained for the $C_{60}$ anion ground states derived from the accounting of the two-orbital active space [2–4].

The available investigations of the JT problem in fullerene structures (for bibliography, see [5]) have been mainly made in single-orbital models neglecting electron correlation that can significantly modify the properties of a multielectron system, closely related to the JT distortion. We report here the results of calculations of static JT ground state splittings in multicharged fullerene anions with different models of electron-electron (*e-e*) interaction.

## MODEL AND METHOD

The calculations of the low-energy electronic states of $C_{60}^{N-}$ anions are performed in the framework of a quasi-$\pi$-electron model defined by the extended Hubbard Hamiltonian

$$H = -\sum_{mn\sigma} t_{mn} a^{+}_{m\sigma} a_{n\sigma} + \frac{1}{2}\sum_{mn} U_{mn} n_m n_n - \frac{1}{2}\sum_{m} U_{mm} n_m, \qquad (1)$$

where the operator $a^{+}_{m\sigma}(a_{m\sigma})$ creates (annihilates) an electron with spin $\sigma = \{\uparrow, \downarrow\}$ at site $m$, $n_m = a^{+}_{m\uparrow} a_{m\uparrow} + a^{+}_{m\downarrow} a_{m\downarrow}$. The electron hopping and interelectron repulsion integrals are denoted by $t_{mn}$ and $U_{mn}$, respectively. For all $C_{60}$ anions we use the same icosahedral geometry based on bond lengths $r_{mn} = 1.45$ Å and 1.40 Å in pentagons and hexagons [6], respectively.

The calculations are performed with *e-e* potentials of two different types. The first type takes into account both the short-range and the long-range interactions with the Coulomb-law decay at a large intersite length $r_{mn}$. This potential is defined by the well-known Ohno formula as $U_{mn} = 11.13\left[1 + (0.77308\, r_{mn})^2\right]^{-1/2}$ specified for carbon atoms (here and below, energies are measured in eV and lengths in Å). The second type of *e-e* interaction is described by the Hubbard potential $U_{mn} = U\delta_{mn}$ that accounts the electron repulsion at the same site only. The calculations within the Hubbard model are performed with two $U$ values, $U = 5$ and 10 eV. The particular case of $U = 0$ corresponds to the model of independent electrons (the Huckel model).

To determine the multi-electron states of Hamiltonian (1) for negatively charged ions of icosahedral $C_{60}$-fullerene, the configuration-interaction (CI) method based on Hartree-Fock orbitals is used.

The wave functions are defined by CI expansions in terms of all single-determinant functions in the active space involving three lowest vacant $t_{1u}$ MOs or three next $t_{1g}$ MOs in addition. In the case of the three-orbital space (we denote it as CI3), all $N$ extra electrons can be described by a degenerate single configuration $(t_{1u})^N$ only, but in the six-orbital space (CI6) – by all additional configurations $(t_{1u})^m(t_{1g})^{N-m}$, $N \geq m \geq 1$, thus realizing a correlation extension of the single-configuration approach. According to the variational principle, the ground state energy is associated with the lowest eigenvalue of the correspondent CI matrix.

The electron–lattice interaction is introduced in the framework of the Su–Schrieffer–Heeger model [7] by a linear dependence of the *neighbour* site hopping integrals $t_{mn}$ on the correspondent bond-length change (deformations) $q_{mn}$ with the interaction parameter $t_1$,

$$t_{mn}(q_{mn}) = t^0_{mn} - t_1 q_{mn}, \tag{2}$$

where $t^0_{mn}$-hopping parameter with the values of 2.5 eV for shorter bonds and smaller by factor of 1.1 for longer bonds of fullerene in the absence of bond deformations.

In the framework of the adiabatic approach, the electron energy of the system $E_{el}$ in the $\psi$ state is determined as a mean energy of Hamiltonian (1) accounting for relation (2), where $q_{mn}$ deformations are considered as variable parameters. The full energy of the system includes also the elastic lattice energy $E_{latt}$,

$$E_{tot} = E_{el} + E_{latt}, \quad E_{el} = \langle\psi|H|\psi\rangle, \quad E_{latt} = (W/2)\sum_{m>n} q^2_{mn}. \tag{3}$$

We use the value $50\,\text{eV}/\text{Å}^2$ for the vibronic constant $W$, and the parameter $t_1$ is varied in the range of 1–10 eV/Å starting from the larger values (as the reference estimations, the values $W = 47\,\text{eV}/\text{Å}^2$ and $t_1 = 4.3\,\text{eV}/\text{Å}$ are obtained for polyacethylene [8]).

To associate bond deformations $q_{mn}$ with a particular symmetry type of normal vibrations, the new variables $y_k$ realizing a basis of the irreducible representations of the icosahedral group are introduced. The orthogonal matrix of the transformation of $y_k$ to $q_{mn}$ with elements $B^k_{mn}$ is obtained with the use of the group-theoretic technique of projection operators. As a result, the set of $q_{mn}$ restricted by some selected irreducible representations, whose set is denoted as $\Lambda$, is

expressed in terms of the variables $y_k$ as

$$q_{mn} = \sum_{k \in \Lambda} B^k_{mn} y_k. \tag{4}$$

An equilibrium structure of the system is determined by the full minimization of $E_{\text{tot}}$ in respect of the electron variables (both molecular orbitals and CI coefficients) and the lattice variables $y_k$ by their step-by-step optimization to achieve the self-consistence. The self-consistent set of the variables obtained in this manner always corresponds to the stable state realizing the minimum of full energy, at least, a local one. Choosing different initial approximations for the deformations, one can obtain either symmetric stable state with no deformations or one or more stable states with a reduced symmetry if the distortions are more favorable by energy.

To exclude the $A_g$ deformation components that do not break the symmetry of the fullerene skeleton, we keep the $A_g$ variables $y_k$ equal to zero. Analyzing the transformation matrix, one can see that the neglecting of $A_g$ deformations is equivalent to the additional condition of shorter and longer bonds mean lengths keeping separately.

## RESULTS AND DISCUSSION

The performed calculations of $C_{60}^{N-}$ anions with $N = 1, 2, 3, 4$ in the absence of deformations show that, in the framework of the single-configuration approach CI3, the symmetry of ground states for all anions is determined by the Hund's rules. Namely, the ground states $^2T_{1u}$ ($N = 1$), $^3T_{1g}$ ($N = 2, 4$), and $^4A_u$ ($N = 3$) have really the highest multiplicity for a given $N$ and the highest degeneracy for a fixed multiplicity. These characteristics are also the same when the electron correlation is taken into account. However, the exceptional case is presented by a dianion obtained with a long-range potential for which the CI6 approach predicts the ground state of $A_g$ symmetry with an energy lower than that of the $^3T_{1g}$ Hund's state by 0.15 eV at $t_1 = 5$. The correlation expansion of the active space provides a significant decrease of the ground state energy with the Ohno potential only. This decrease has nearly the same values in both cases–with deformation and without it, and is equal to 0.32, 0.72, and 0.89 eV for $N = 2, 3, 4$, respectively.

The results of our calculation with electron-vibration interaction show that indeed only $A_g$ and $H_g$ symmetry components affect the ground-state energies of anions. These normal vibration modes are conformed to the Jahn-Teller active modes of the known group-theoretic data. A deformation of the $A_g$ type does not affect the

JT splitting keeping the icosahedral symmetry of the system. So, in our further consideration, we use a deformation of the $H_g$ symmetry type only, projecting out all other symmetry types. For each of four *e-e* interactions each procedure of electron-deformation iterations is performed with a symmetric initial approximation and is repeated with an symmetric one. One of the obtained patterns of the bond-deformation distribution over the fullerene sphere is shown in Figure 1. This discrete distribution corresponds to the continual Jahn–Teller distortion picture presented in Figure 1(a) in [9].

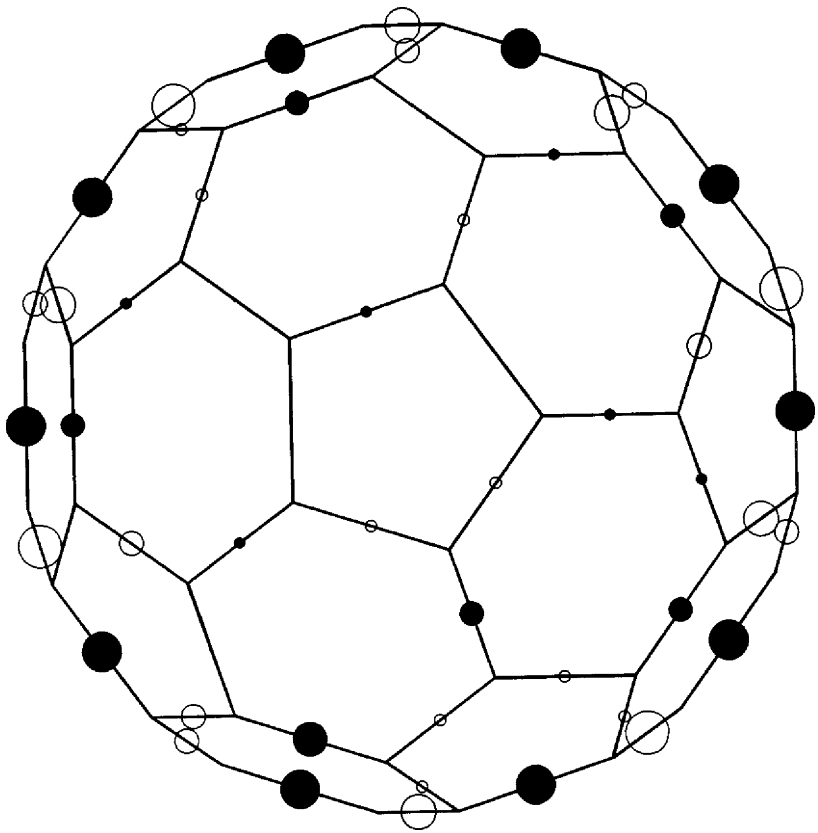

**FIGURE 1** Distribution of bond deformations in the Huckel $^3T_{1g}$ state of a fullerene dianion. Shortened and elongated bonds are denoted by bright and dark circles, respectively. The circle diameters are proportional to the bond-length changes by absolute values.

Let us consider first the simplest case of monoanion. A single electron in the degenerate vacant orbital causes the actual JT effect of electron-vibration interaction being independent of the *e-e* potential type. As a result, we obtain the classic picture of $^2T_{1u}$ orbital triplet splitting on the nondegenerate ground term and the doubly degenerate excited one of $E'_{tot}$ and $E''_{tot}$ energies, respectively. In the case of ideal and clean splitting, we have the simple dependence for the electron energy $2E''_{el} = -E'_{el}$. Thus, the shift value of the ground terms is equal to $-3E'_{el}$.

This picture is the same for doubly and quarterly charged anions, whose ground states are characterized by $T_1$ symmetry. As far as the double degeneracy is remained, the symmetry of the fullerene cage is not broken completely but only reduced. Nearly the same values of the ground state splitting for different *e-e* parametrizations and different numbers of extra electrons indicate a predominant influence of the single-electron part of Hamiltonian (1) on a deformation in comparison with the two-electron component.

Some deviations from the typical situation take place for anions with $N = 2$ and $N = 4$ within the Huckel model, when the singlet and triplet ground states coincide without electron-vibration interaction and are splitted with the lower triplet state with minor electron-vibration interaction. However, in the case of the deformed initial approximation, the singlet state becomes the ground one, where the electron-vibration interaction decreases the energy by a factor of four in comparison with the triplet state case. These singlet states are also stable within the Hubbard's model but at small values of $U$ (up to 3 eV). On the contrary, the single stable doublet state with deformations is predicted for a trianion in the vicinity of $U = 0$, whereas the nondeformed spin quartet $^4A_u$ becomes stable at larger $U$.

Now we consider the influence of a correlation expansion of the active space on JT deformations proceeding from the single configurational approximation CI3 to CI6. The calculations showed that this expansion of the Hubbard's model doesn't lead to significant changes of the ground states. An exception occurs with the Ohno potential in the dianion case where the multiplicity of the ground state is changed from the Hund's triplet state to the singlet one. The initial deformations turn to be necessary to obtain a deformed state in the expanded CI space. There is one more qualitative distinction in the deformation behavior connected with a change of the interaction parameter $t_1$. In the reduced CI space, this behavior is typical of the linear effect when the deformation energy descends smoothly by the quadratic law as $t_1$ decreasing to zero. However, as shown in Figure 2, in the case of the two-orbital active space, the descend becomes more abrupt and, at

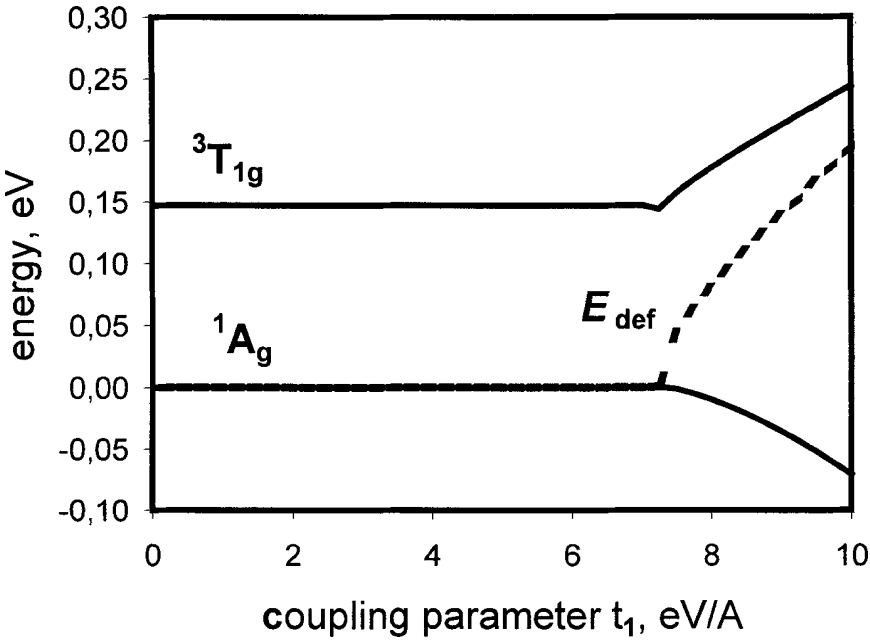


**FIGURE 2** Energies of two lowest multi-electron terms ($^1A_g$, $^3T_{1g}$) vs. electron–lattice coupling parameter $t_1$ calculated for a fullerene dianion with the Ohno potential in the expanded active space CI6.

$t_1 < 7\,\text{eV/Å}$, the deformations fully disappear providing the full-symmetry state.

## CONCLUSION

The expansion of the CI active space plays a crucial role in the realization of the electron-correlation effect that evidently can appear in the case of Coulomb long-range *e-e* potentials only. As shown in [4], the long-range electron repulsion is necessary to predict the observed order of the ground-state energies of $C_{60}$ fullerene anions, thus, suggesting the restricted applicability of the Hubbard model for the calculations of the many-electron states of fullerenes and fullerides. The correlated motion of extra electrons in an anion is characterized by the trend to be separated that leads to some delocalization of the electronic density. Thus, as expected, the correlation should effectively damp the electron–lattice interaction favoring the electron delocalization and destabilizing deformations, the energetic gain of which conversely increases with a greater localization of the electronic

density. This delocalizing effect of electron correlation is pronounced for two extra electrons in $C_{60}^{2-}$ dianion and must be much weaker in $C_{60}^{4-}$ anion with four electrons on the same fullerene sphere. This explains the absence of the correlation reduction of deformations in the case of $C_{60}^{4-}$ and additionally confirms the JT nature of the ground state in the above system. On the whole, the results of our investigations show that, in opposition to the case of short-range electron repulsion, the long-range electron correlation can significantly change features of the Jahn–Teller splitting.

## REFERENCES

[1] Gunnarsson, O. (1997). *Rev. Mod. Phys.*, *69*, 575.
[2] Huang, Y., Okada, M., Fukui, K., Tanaka, K., Aoki, T. H., & Yamabe, T. (1997). *Int. J. Quantum Chem.*, *63*(2), 361.
[3] Negri, F., Orlandi, G., & Zebretto, F. (1992). *J. Am. Chem. Soc.*, *114*(8), 2909.
[4] Kuprievich, V. A., Shramko, O. V., & Kapitanchuk, O. L. (2001). *Mol. Cryst. and Liq. Cryst.*, *361*, 31.
[5] Chancey, C. C. & O'Brien, M. C. M. (1997). *The Jahn–Teller effect in $C_{60}$ and other icosahedral complexes*, Princeton Univ. Press: Princeton.
[6] Yannoni, C. S., Bernier, P. P., Berthune, D. S., Meijer, G., & Salem, J. R. (1991). *J. Am. Chem. Soc.*, *113*(8), 3190.
[7] Su, W. P., Schrieffer, J. R., & Heeger, A. (1980). *J. Phys. Rev. B.*, *22*, 2099.
[8] Ovchinnikov, A. A., Belinskii, A. I., Misurkin, I. A., & Ukrainskii, I. I. (1982). *Int. J. Quantum Chem.*, *22*, 761.
[9] Auerbach, A., Manini, N., & Tosatti, E. (1994). *Phys. Rev. B.*, *49*(18), 12998.