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O. L. Kapitanchuk [a] & O. V. Shramko [a]

[a] Bogolyubov Institute for Theoretical Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine

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Modeling of Monophotonic Excitation Spectra of Icosahedral C_{60} Fullerene

O. L. Kapitanchuk and O. V. Shramko
Bogolyubov Institute for Theoretical Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine

The monophotonic excitation spectrum of C_{60} fullerene is calculated in the framework of the extended Hubbard model by a symmetry adapted configuration interaction method with realistic electron correlation potential. The parameters of interelectronic potentialare optimized for C_{60} fullerene with respect to the consistency of calculated dipole-active transitions with experimental absorption spectra in the spectral range of 2–6 eV. A quantitative criterion and an original optimization procedure are proposed taking the relative importance of both spectral characteristics, transition energies and intensities, into account. A contradictory character is found in the case of the simultaneous consistence of both spectral characteristics. In view of the obtained results, the origin of the low-frequency peak in the C_{60} absorption spectra is discussed.

Keywords: configuration interaction; electron correlation; fullerene C_{60}; monoexcitation spectra; quantum-chemical calculations

INTRODUCTION

Last two decades, much attention has been attracted to the study of optical properties of C_{60} fullerene as an active element for nano-scale optical devices [1]: limiters, switches, etc. On this way, two important sources are considered to give us the authentic information about the C_{60} spectral characteristics: the absorption spectra measurements [2] and quantum-mechanical calculations [3]. The constant feedback between experiment and theory is a fundamental point in obtaining a convincing identification of the excited states of fullerenes.

This work was done in the close collaboration with Prof. V. A. Kuprievich.

Address correspondence to O. L. Kapitanchuk, Bogolyubov Institute for Theoretical Physics of the National Academy of Sciences of Ukraine, 14-B Metrolohichna Str., Kyiv, 03680, Ukraine. E-mail: oleksiy@kapitanchuk.com

The absorption spectrum of C_{60} is mainly defined by its electronic structure and unique cage symmetry that leads to a high degeneracy of electronic states and symmetry-allowed transitions. The large C_{60} cage is characterized by an enormous number of electronic excited states, which leads to insuperable computational difficulties. The calculations of the energies and oscillator strengths of the lower excited states have been performed in several works [4–7], but, in all of them, some approximations were made due to the large size of the molecule. These calculations were limited in the numbers of excited configurations and were essentially based on semiempirical models QCFF/PI, CNDO/S, INDO/S, and on the configuration interaction (CI) or time dependent DFT treatments. Analyzing the results of the various authors, it appears that calculations can give nearly realistic descriptions of the lowest electronic states only, and the theoretical models need the further specification and the proper consideration of the electron correlation effects and cage symmetry features.

Because of the structural specificity and a large size of fullerenes, the three-dimensional quasi–π–electron model is commonly used to treat the effects of electron–electron (*e–e*) interactions. By essence, one deals with a spatial modification of the widespread Pariser–Parr–Pople (or extended Hubbard) model for the conjugate molecular systems. In its applications to carbon clusters, the crucial point is the choice of the *e–e* potential consistent with a realistic physical picture of *e–e* interactions in the systems with specific multiatom structure. A number of *e–e* parametrizations available in the literature [8–11] differ by magnitudes of the on-site potential and by the shape of the distance dependence for intersite interactions.

The aim of this work is to investigate the influence of the electron correlation strength and the shape of *e-e* potentials on the low-energy electronic spectra of icosahedral C_{60} fullerene. The spectrum of C_{60} is calculated in the framework of the extended Hubbard model by the symmetry adapted configuration interaction method using a reduced set of monoexcitations. The electron correlation potential in this approach is parameterized by the Ohno functional modified by Harigaya and Abe [13], where the dielectric screening of a long-distance electron–electron interaction of the Coulomb type is introduced via an independent parameter. It allows one to scale the Hamiltonian persisting only two optimized values: the Hubbard one-center parameter determining a magnitude of the overall *e–e* interaction and the screening parameter that defines the contribution of a long–range interaction. Finally, the both values are optimized for C_{60} fullerene with respect to the consistency of calculated dipole-active transitions with the experimental absorption spectrum in the low-energy spectroscopic range of 2–6 eV.

MODEL AND METHOD

Model Hamiltonian for C_{60}

A fullerene molecule is described in the framework of the 60-center quasi–π–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 $\sigma = \{\uparrow, \downarrow\}$ on site m, $n_m = a^{+}_{m\uparrow} a_{m\uparrow} + a^{+}_{m\downarrow} a_{m\downarrow}$, and t_{mn} and U_{mn} are hopping (resonance) and electron-repulsion integrals, respectively. Assuming the icosahedral geometry for C_{60}, for the bond lengths $r_{mn} = 1.40$ Å (in hexagons between pentagons) and 1.45 Å (in pentagons) [12], t_{mn} are set as $t_0 = 2.5$ eV and $t_1 = t_0/1.1$, respectively, the rest of t_{mn} are neglected.

The dependence of the *e–e* repulsion potential on the distance is parameterized by the modified Ohno functional [13], where the dielectric screening of a long-distance electron–electron interaction of the Coulomb type is introduced via the independent parameter V so that

$$U(r_{mn}) = \frac{1}{\sqrt{\left(\frac{1}{U}\right)^2 + \left(\frac{r_{mn}}{r_0 V}\right)^2}} = \frac{U}{\sqrt{1 + \left(Q\frac{r_{mn}}{r_0}\right)^2}}, \quad Q = \frac{U}{V}, \qquad (2)$$

where r_{mn} – distance between m and n sites, $U = U(0)$ – one-site repulsion magnitude, r_0 – average bond length ($r_0 = 1.43$ Å was taken in calculations), Q – a new independent parameter.

Definition of the Electronic States

For the ground state of neutral C_{60}, the Hartree–Fock state and self-consistent molecular orbitals are determined using the self-consistence procedure [14,15] that supports the preassigned irreducible representations {A,T_1,T_2,G,H} of the icosahedral group $I_h = I \times C_s$ for orbitals. We have

$$|\Psi_{HF}\rangle = \prod_{k=1}^{30} A_{k\uparrow}{}^{+} A^{+}_{k\downarrow} |0\rangle, \qquad (3)$$

where the molecular operator $A_{i\sigma}$ is determined as the orthogonal transformation of atomic operators:

$$A^{+}_{i\sigma} = \sum_{m} C_{mi} a^{+}_{m\sigma}, \sum_{m} C_{mi} C_{mj} = \delta_{ij}. \qquad (4)$$

The C_{mi} coefficients of the transformation matrix are defined through the Hartree–Fock energy minimization approach for 30 doubly occupied molecular orbitals. The obtained self-consistent molecular wave functions are referred to irreducible representations of the icosahedral group I_h as eigenfunctions of the full-symmetry Fock operator.

We are concentrated here on the mono-photonic excitations that correspond to the most intensive absorption bands in the low-energy region. The excited states of Hamiltonian (1) are determined using the CI method [9,15] as a superposition of singly-excited configurations that describe the electron-hole pairs in the Hartree–Fock ground state

$$|\Psi_{ku}\rangle = (A^+_{u\uparrow}A_{k\uparrow} + A^+_{u\downarrow}A_{k\downarrow})|\Psi_{HF}\rangle, \tag{5}$$

where «+» sign corresponds to the singlet states with allowed transitions with fixed multiplicity (here and below, u, v indices are used for electrons, and k, l – for holes).

In this formalism, the CI matrix elements of Hamiltonian (1) look as

$$\langle\Psi_{ku}|H|\Psi_{lv}\rangle = \delta_{ku}\delta_{lv}(\varepsilon_u - \varepsilon_k) + 2(ku|lv) - (kl|uv), \tag{6}$$

where ε_u and ε_k – self-consistent eigenvalues of the Fock operator (one-electron energies), $(ij|kl)$ – two-electron integrals that describe the Coulomb interaction of ij and kl electron distributions,

$$(ij|kl) = \sum_{mn} C_{mi}C_{mj}U_{mn}C_{nk}C_{nl}. \tag{7}$$

A full set of electron-hole pairs includes about 900 states defined by formula (5), which rqeuires to diagonalize the huge CI matrix. To simplify the computational problem, the symmetry approach [9,15] is used in calculations. The inclusion of the high icosahedral symmetry of the C_{60} atomic skeleton reduces the initial CI matrix to that of the advantageous block-diagonal form, where each block corresponds to a fixed irreducible representation. On the other hand, since all dipole-allowed transitions are associated with transfers into odd states [3] only, the size of the CI matrix is finally reduced to 195×195. The dipole transitions from the ground state of C_{60} are allowed only for the states of T_1 symmetry and are characterized by the orbital momentum $L = 1$. So, based on the calculated transition moments, the oscillator strengths are associated with the intensities of experimental lines in the C_{60} absorption spectrum.

Optimization of Model Parameters

Three model parameters t, U, and Q that define Hamiltonian (1) and potential (2) are considered as independent parameters in the

optimization approach. Due to the linear dependence of the Hamiltonian on t and U, the wave functions are independent of the scaling of the state energy E_{k} which can be considered as a function of three optimization parameters

$$E_k(t, U, Q) = pE_k(t_0, U_0, Q), \quad t = pt_0, \quad U = pU_0, \quad \forall p. \tag{8}$$

This relation allows us to simplify significantly the procedure of searching the optimal parameter value. So, it is enough to reach a proportionality between calculated and experimental energies and then to perform the renormalization of parameters.

The unified optimization criterion is proposed for the matching of the measured and calculated data of spectral energies and intensities. The set of parameters is found to minimize the deviation of the base experimental a_k and calculated b_k values (energies or intensities), where a_k and b_k are considered as the components of the vectors in the Euclidean space. After the vector normalization, the deviation from the parallelism is described by the root-mean-square criterion

$$\xi = S_{aa}^{-1} \sum_{k=1}^{M} (a_k - pb_k)^2 = 1 + S_{aa}^{-1}(p^2 S_{bb} - 2pS_{ab}), \tag{9}$$

$$S_{aa} = \sum_{k=1}^{M} a_k^2, \quad S_{bb} = \sum_{k=1}^{M} b_k^2, \quad S_{ab} = \sum_{k=1}^{M} a_k b_k, \quad a_k \sim pb_k, \tag{10}$$

where S defines the corresponding scalar products, and p is the coefficient of proportionality.

The value of p that corresponds to the minimum point of ξ is defined from the condition $\mathrm{d}\xi/\mathrm{d}p = 0$ as follows:

$$p = \frac{S_{ab}}{S_{aa}}, \quad \xi = 1 - \frac{S_{ab}^2}{S_{aa} S_{bb}}. \tag{11}$$

In case of the energy optimization, a_k and b_k are associated, respectively, with base experimental spectral energies and calculated transition energies, whereas ξ characterizes the coincidence degree of energy values. Respectively, for the intensity optimization, the heights of lines in the absorption spectrum $\tilde{a}_k$ are compared with obtained oscillator strengths $\tilde{b}_k$ within the corresponding criterion η defined by (11).

RESULTS OF CALCULATIONS

First, we define the main initial data used in the calculations. The symmetry reduction of the interatomic distances (from possible 1830

to 23 different ones) [9] is used to simplify the definition of e–e potentials. As can be seen from Figure 1, the distance dependence of the Harigaya–Abe potential (2) qualitatively differs from the Ohno–Yukava one, $U(r_{mn}) = U \cdot \exp(-ar_{mn})[1 + (U \cdot r_{mn}/e_0^2)^2]^{-1/2}$ [9,16], describing a much steeper descent with distance (as asserted in [13]. In this case, the best correspondence with spectroscopic data is realized for the values $U = 7.2\,\text{eV}$, $Q = 2$). The energy values and the corresponding oscillator strengths are obtained at each point of the 2D parameter grid of 45×50 in size ($U = 3, \ldots, 14\,\text{eV}$, step $= 0.25$; $Q = 0.1, \ldots, 5$, step $= 0.1$) covering the set of standard physical parameters assumed both for fullerenes and for other conjugated systems.

Let us consider the spectroscopic data that can be used as base values to determine the optimal parameters. In the experimental absorption spectrum of a C_{60} fullerene solution (Fig. 2), most distinguished are the low-energy lines with energies of 3.0, 3.7, 4.7, and 5.7 eV with relative heights of 0.03, 0.3, 1.0, and 0.9, respectively. At the same time due to the reduced interaction with the rare gas environment, the lines of the fullerene spectrum for the gas phase are significantly narrower. Moreover, the 3-eV line is not observed

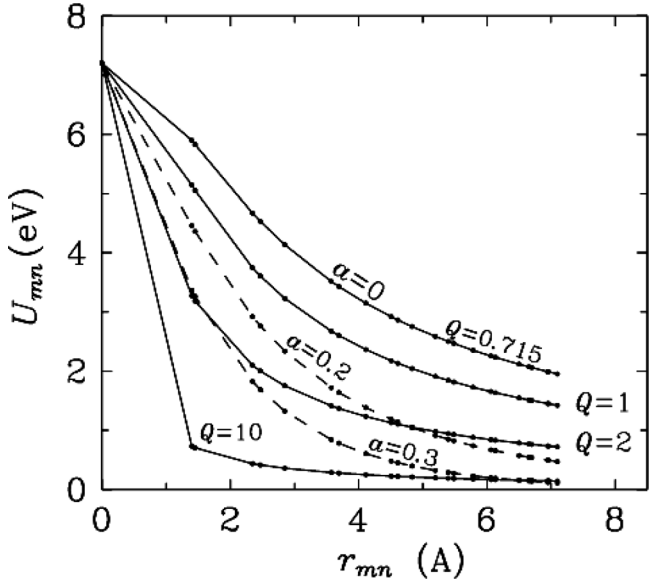

FIGURE 1 Profiles of the Harigaya–Abe (solid lines) and Ohno–Yukava (dashed lines) potentials calculated for different values of the screening parameters Q and a, with $U = 7.2\,\text{eV}$. Points on the curves correspond to the values of potentials for the real distances in C_{60}.

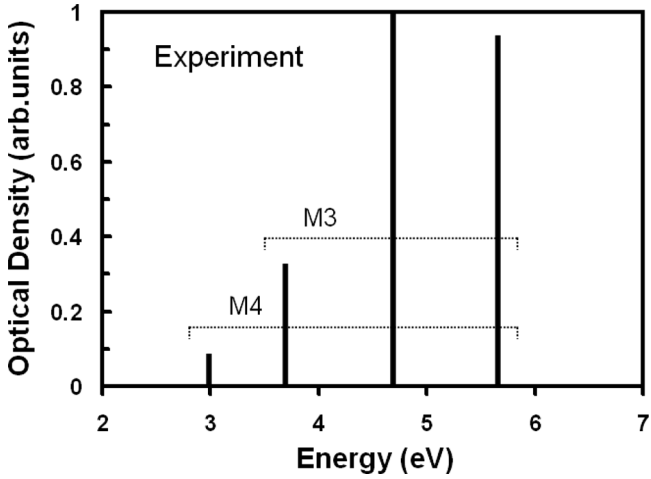

FIGURE 2 Low-energy absorption spectra of a C_{60} fullerene solution [2] used for optimization.

there, and the rest three lines at 3.8, 4.9, and 6.0 eV are shifted to the higher energy region. They are naturally associated with dipole-allowed transfers into excited states of the T_{1u} symmetry, whereas the nature of the 3-eV peak can be referred to the transfers into the states of another symmetry and provided by another mechanism. Thus, the calculated spectral characteristics for T_{1u} transitions are sequentially compared with four peaks (M4 model) or with three peaks (M3 model, excluding the peak at 3 eV) in the experimental spectrum of a fullerene solution (Fig. 2).

The values of optimum criterions ξ and η for energies and intensities were obtained for both models as a result of the comparison of spectroscopic data with the set of tabulated energies and oscillator strengths for each set of the model parameters. As was found, the sets of parameters which define the minimum conditions for ξ and η are significantly different. To clarify this contradiction, we fix the limiting value $\xi_0 = \max(\xi)$ and, from the set of results obtained for $\xi < \xi_0$, find the result with minimal intensity error $\eta_0 = \min(\eta)$. The functional dependences $\eta_0(\xi_0)$ for both M3 and M4 models are presented in Figure 3a together with the corresponding set of model parameters illustrated by Figure 3b,c,d. It is important to note that a range of the obtained values for the criterion ξ_0 is much narrower than the η_0 range. This means that the separate energy optimization problem is naturally easy in comparison with the consistent optimization of both spectral characteristics including also the intensity. A stepwise

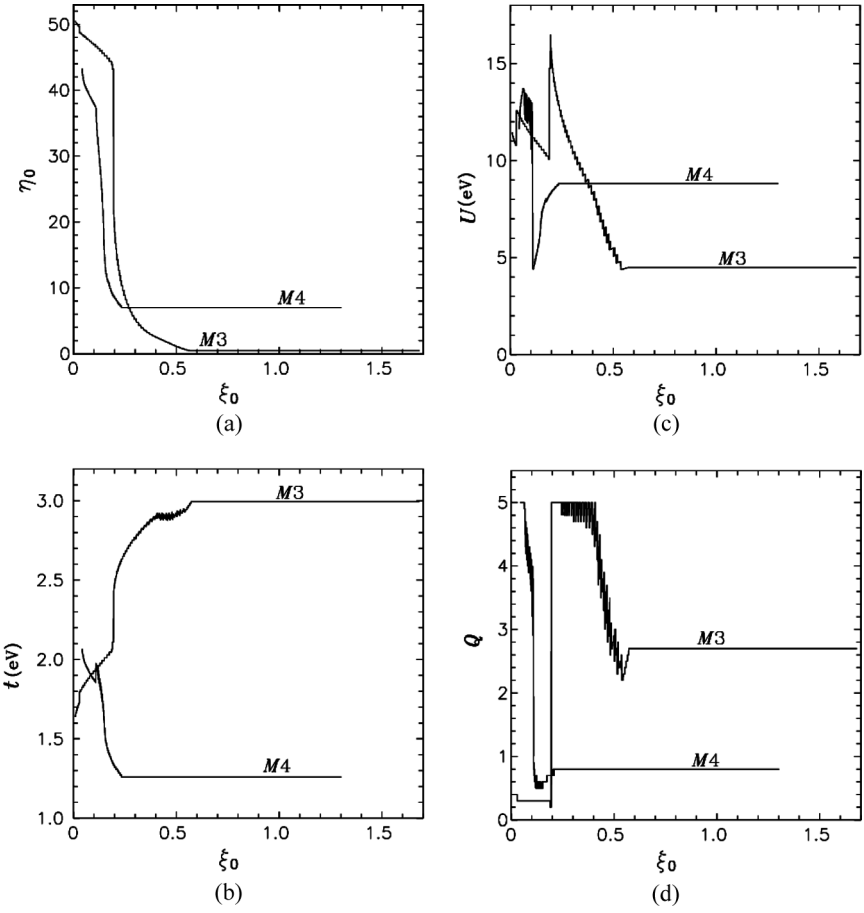

FIGURE 3 Dependences of the acceptable energy error ξ_0 on the optimized characteristics of the C_{60} monoexcitation spectrum. (a) – dependence of η_0 on the optimal error for transition energies $\xi < \xi_0$; (b), (c), (d) – optimal values of the model parameters U, Q, t as a function of ξ_0. The results are presented for two models (M3 and M4) interpreting the spectrum.

character of the curves reflects the discrete change of parameters. The start points of all curves correspond to the optimal energy criterion only when the end points describe the best agreement for intensities. The long horizontal region presented in all plots describes the set of parameters, whose widening does not contain the optimal one. The jump-like changes of the parameters can be associated with the presence of several local minima in the functional dependences of ξ_0 and η_0 on the model parameters.

It is worth noting that the M3 model naturally provides more possibilities for the optimization and gives a better agreement due to the reduced number of base data. So, the nature of the low-energy peak at 3 eV can be related to higher excitations and transfers into the states of a symmetry that differs from T_{1u}.

CONCLUSIONS

We have performed the numerical analysis of the inverse spectral problem for the monoexcitation electronic spectrum of icosahedral C_{60} fullerene within the extended Hubbard model by the symmetry adapted configuration interaction method. A quantitative criterion and an original optimization procedure are proposed by taking the relative importance of both spectral characteristics (transition energies and intensities) into account. A contradictory character is found in case of the simultaneous consistence of both characteristics. The values of model parameters are systematically tabulated in the natural physical range important for a study of conjugated systems. The possible ways to reach a better consistency are: (i) modification of the one-electron part of the model Hamiltonian; (ii) using a more suitable functional form of the electron correlation potential; (iii) including double or higher excitations in the configuration interaction scheme.

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