

Kapitanchuk O.L. Symmetry approaches in the studies of correlated multi-electron states of C₆₀ fullerene and fullerides. – Manuscript. – 121 p.

Thesis for a candidate's degree (equivalent to PH.D.) by speciality 01.04.02 – theoretical physics. – Bogolyubov Institute for Theoretical Physics of NAS of Ukraine, Kiev, 2004.

The thesis deals with theoretical study of electronic processes in icosahedral C₆₀ fullerene ions and fullerides taking into account electron correlation and molecular symmetry. These fullerene C₆₀-based compounds are considered as promising active organic materials for various nanoelectronic devices. Their unique physical properties are mostly determined by their form, icosahedral symmetry, causing high degeneracy of levels, and by strong electron–electron (*e–e*) and electron–lattice interactions. In particular, these interactions are supposed to be responsible for superconductivity of fullerides with fullerenes being in multi-charged anion forms. The fullerene crystals are molecular crystals with small interunits hopping and strong *e–e* correlation inside the charged C₆₀ molecules, which electronic structure principally determines main physical processes in fullerene solids.

The method that successively takes full advantage of symmetry relations between molecular integrals and matrix elements of configurational interaction (CI) defined on symmetry molecular orbitals is elaborated. Using symmetry-similarity principle within the model with two-center *e–e* interaction a simple technique is elaborated enabling to represent each integral of complete set as an expansion of a few independent integrals. For icosahedral C₆₀ fullerene basis orbitals for all irreducible representation are obtained with simple algebraic coefficients and the symmetry transformation matrices are constructed numerically in the form enabling to avoid round-off errors. The computer programs are developed for the straightforward determination of molecular integral and energy invariant expansions in mathematically rigorous form. The results of symmetry-adapted CI calculations for C₆₀ ions with the charges from –4 to +2 are obtained. Two different CI active spaces built on *h_u* highest occupied molecular orbital and *t_{1u}+t_{1g}* lowest unoccupied molecular orbitals are considered for fullerene cations and anions, respectively. The obtained energy functionals involve only five (six) independent integrals instead of 120 (231) ones, respectively, in the general case, thus, enabling to perform the simple full-CI calculations of multi-charged ions within the corresponding orbital spaces. Multi-electron states of C₆₀ ions are calculated within the spatial π -electron model with four different parametrizations for *e–e* potentials known in literature, with some of them that take into account polarization of carbon atoms of fullerene. The manifestation of electron correlation in the ion excitation spectra and correlation functions are discussed in the relation to *e–e* potential shape. As it is shown, all above *e–e* potentials predict similar energy–charge dependencies of parabolic form. In particular, the results show the essential role of Coulomb long-range interactions and electron correlations to predict the observed order of ground-state energies of C₆₀ fullerene anions, thus, suggesting

the restricted applicability of Hubbard model and one-electron approaches for the calculations of many-electron states of fullerenes and fullerides.

The influence of the range of electron correlation potentials on Jahn-Teller ground state splittings in icosahedral C_{60}^{-N} ($N=1, \dots, 4$) fullerene anions is investigated in the framework of Su–Schrieffer–Heeger model. Results of CI calculations showed that, opposite to the case of short-range electron repulsion, long-range electron correlation could significantly change features of Jahn-Teller splitting. Influence of the active space expansion from three t_{1u} orbitals to six $t_{1u}+t_{1g}$ ones on long-range electron repulsion is shown as change of ground state multiplicity in distorted fullerene dianion. Correlation effectively damps electron–lattice interaction favouring the electron delocalization, thus, destabilizing deformations.

Basing on the obtained ground state energies of fullerene ions and the evaluation of the Madelung energy, the energetics of A_3C_{60} crystals ($A=\{Li, Na, K, Rb\}$) in different charge states of the subunits is considered with varied screenings of $e-e$ potentials inside and outside of fullerene cages. Screening areas are specified where a partial metal-fullerene electron transfer turns to be more preferable than complete. An original model is proposed to describe the distribution between two-dimensional layers of C_{60} fullerite of electrons or holes, injected by external electric field in structure of field effect transistor. The electron repulsion is taken into account with direct use of the evaluated energies of multicharged C_{60} ions. The problem is solved both for the electrons and holes in the unique way. An exponential charge density dropping with the crystal depth increase is predicted. Relative charge distribution between the layers turns to be independent on the total amount of the injected charges. A top layer is shown to accumulate 3/4 and 2/3 charges in the case of electron and hole injection, respectively. In general, charge-localization degree on crystal surface turns to be essentially different from that known in the literature.

Key words: high-symmetry molecules, icosahedral symmetry, C_{60} fullerene ions, electron correlation, configurational interaction, many-electron states, Jahn-Teller effect, charge distribution.