

Symmetry approaches in the quantum-mechanical calculations of multielectronic states

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New achievements in the chemical synthesis of novel organic substances and materials of unique structure and physical properties raise specific computational problems in quantum mechanics demanding to consider the electronic structure of multiatomic molecular systems in excited and ionic states beyond one-electron approaches.

The original computer-oriented treatment of high symmetry in quantum chemical calculation of correlated electronic states is reported with emphasis on the symmetry-induced degeneracy of molecular states. The method is essentially based on the theory of symmetry molecular invariants that supposes (i) use of fixed reference symmetry base and (ii) determination of invariant expansions for two-electron integrals and energies. The method successively takes full advantage of the relations between the integrals defined on symmetry molecular orbitals (MO). Using the symmetry-similarity principle within the model of two-center electron - electron interaction a simple computational technique is elaborated enabling to represent each integral from complete set as an expansion of a few independent integrals [1,2].

The technique is specified for the most complicated case of icosahedral (I_h) symmetry which is inherent to fullerene C_{60} . It is considered for (i) the configurations ($t_{1u}+t_{1g}$), the symmetries of two lowest vacant MOs and (ii) for upper occupied h_u -shell. The reference symmetry basis sets (mostly with integer components) are presented enabling to obtain the most results in a mathematically rigorous form thus avoiding round-off errors. Energy functionals for all multiplet states of multi-charged ions are reduced to simple form involving only five (h -shell) or six ($t_{1u}+t_{1g}$ case) independent integrals (instead of 120 or 231, respectively, in the general case) thus enabling to reduce full-CI or multiconfigurational self-consistent-field calculations of multicharged ions within the corresponding orbital spaces [3].

The developed method is applied for the calculations of multielectronic energy spectra and Jahn-Teller splitting in multi-charged C_{60} fullerene ions [3,4].

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