A symmetry assisted approach to multidimensional vibronic problem: theoretical background and some chemical applications

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The classical treatment of the nuclear motion is invalid (despite the difference in masses of electrons and nuclei) in the region of crossover of the terms or, more commonly, when we are dealing with the orbitally degenerate or pseudo degenerate levels. To overcome significant limitations implied by the adiabatic approximation, we propose a symmetry-adapted approach aimed to the accurate solution of the quantum-mechanical (dynamic) vibronic problem in large scale molecular systems. The algorithm for the solution of the eigen-problem with a huge Hilbert space takes full advantage of the point symmetry arguments. Applying the successive coupling of the bosonic creation operators, we introduce complex irreducible tensors that can be referred to as multivibronic operators. The generated vibrational basis is coupled to the electronic one to get the symmetry adapted electron-vibrational basis within which the full matrix of the Hamiltonian is blocked to maximum extent according to the irreducible representations of the point group. The approach allows to treat optical and thermodynamic properties of the nanoscale multilevel vibronic system, such as mixed-valence molecules and impurity centers in crystals. The developed technique is applied to consideration of 2e-reduced mixed-valence dodecanuclear Keggin anion in which the electronic pair is delocalized over twelve sites, tetrameric systems in which two mobile electrons are employed to encode binary information in molecular quantum cellular automata, complex organic systems exhibiting unusual intervalence optical vibronically assisted absorption.

Acknowledgements: Support from Russian Science Foundation (No. 20-13-00374) and the Ministry of Science and Higher Education (creation of the Lab. of Molecular Magnetic Nanomaterials at IPCP, No. 14.W03.31.0001) is acknowledged.