Thematic Section: Theoretical Research. **Full Paper**
Subsection: Mathematical and Quantum Chemistry. *Reference Object Identifier* – ROI: jbc-01/18-54-4-29
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/18-54-4-29
Submitted on March 13, 2018.

A new form of the Hamiltonian for calculating the electron-vibrational-rotational spectra of polyatomic molecules

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Keywords: quantum theory of molecules, molecular spectra, electron-vibrational-rotational states, Hamiltonian.

Abstract

It is shown that in the case of small vibrations, the Hamiltonian for the general vibrational-rotational problem can be constructed in a form analogous to the Hamiltonian in the problem of harmonic vibrations of polyatomic molecules. Instead of solving two different problems for vibrations and rotations, as is usually done, it is suggested to formulate a single problem in a common coordinate space. The conventional coordinates used in the theory of molecular vibrations are introduced for molecular deformations and three additional coordinates are introduced for rotations. These coordinates describe the rotations of the molecule as a whole around the axes, for which it is natural to choose the principal axes of inertia for the equilibrium geometry.

Expressions for the elements of the matrix B, which define relations between the rates of change of the introduced rotational coordinates and the Cartesian velocities of the atoms, are obtained. This makes it possible to form a single matrix of kinematic coefficients and, after simultaneous diagonalizations of two quadratic forms corresponding to the kinetic and potential parts of the Hamiltonian, to obtain an expression for the energy levels of vibrational-rotational motions. This expression completely coincides with that in the problem only about vibrations, and allows us to calculate the frequencies of a single vibrational-rotational spectrum without separating rotations from vibrations.

The result obtained is important not only in itself, but also provides the possibility of setting up a general problem of the energy levels of a polyatomic molecule without separation into electronic, vibrational and rotational ones. The general expression for the energy levels of the electron-vibrational-rotational states of the molecule in the adiabatic approximation is obtained.

The entire computational procedure is very simple, which makes it possible to carry out calculations for large molecules.

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