OPTICS AND SPECTROSCOPY

DETERMINATION OF THE ENERGY LEVELS OF TOTAL AND INTERNAL ROTATION OF ARBITRARY POLYATOMIC MOLECULES WITH A SINGLE INTERNAL ROTATION AXIS

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An algorithm is developed for calculating the eigenvalues of the Hamiltonian operator in the case of asymmetric—asymmetric molecules with a common axis of internal rotation, taking into account the total and internal rotation of these molecules. The algorithm is based on the Ritz variational method. A program is written for reducing a symmetric band matrix to tridiagonal form with subsequent diagonalization of the resulting matrix.

We have previously (see, e.g., [1-4]) investigated the quantum-mechanical problem of determining the eigenvalues and wave eigenfunctions of internal rotation of asymmetric—asymmetric molecules containing a rigid core with a spinning top attached to it.

The objective of the present study is to analyze simultaneously the total and internal rotation of molecules of the indicated class, to construct the quantum-mechanical Hamiltonian of these molecules, and to develop an algorithm for determining their energy levels.

We introduce the following coordinate frames:

- \( o_1 x_1 y_1 z_1 \) — the laboratory Cartesian frame with origin at the center of mass of the molecule; we denote the dihedral angle of rotation of the top relative to the core by \( \tau \);
- \( o_1 x'y'z' \) — a frame whose axes coincide with the principal axes of inertia of the molecule; we denote by \( \alpha, \beta, \) and \( \gamma \) the Euler angles of the \( o_1 x'y'z' \) frame relative to the laboratory frame \( o_1 x_1 y_1 z_1 \);
- \( oxyz \) — a frame rigidly attached to the core of the molecule, its \( z \) axis aligned with the internal rotation axis, and the \( xoy \) plane containing the center of mass of the molecule.

We adopt \( \alpha, \beta, \gamma, \) and \( \tau \) as generalized coordinates, since they completely determine the position of every atom in the laboratory frame.

We have previously [5] derived an expression for the kinetic energy of the investigated molecules in the form

\[
2T = I_{x'}^{-1}(\tau) L_{x'}^2 + I_{y'}^{-1}(\tau) L_{y'}^2 + I_{z'}^{-1}(\tau) L_{z'}^2 + S_{44}^{-1}(\tau) p_4^2,
\]

where \( I_{x'}^{-1}(\tau), I_{y'}^{-1}(\tau), \) and \( I_{z'}^{-1}(\tau) \) are the reciprocal moments of inertia of the molecule, referred to the principal axes, \( L_{x'}, \ L_{y'}, \) and \( L_{z'} \) are the projections of the angular momentum on to the principal axes of inertia, \( p_4 \) is the generalized momentum, and \( S_{44} \) is the generalized moment of inertia of internal rotation.

We express \( 2T \) in terms of the generalized coordinates \( \alpha, \beta, \gamma, \) and \( \tau \), rewriting Eq. (1) in the form

\[
2T = I_x \Omega_x^2 + I_y \Omega_y^2 + I_z \Omega_z^2 + S_{44}^{-1} p_4^2.
\]

The components \( \Omega_{x'}, \Omega_{y'}, \text{ and } \Omega_{z'} \) of the instantaneous angular velocity \( \Omega \) in the \( o_1 x'y'z' \) frame, corresponding to the angular momentum \( (L_{x'}, L_{y'}, L_{z'}) \), are expressed in terms of the Euler angles:

\[
[\Omega]_{o_1 x'y'z'} = A (\alpha \beta \tau),
\]

where

\[
A = \begin{pmatrix}
-\cos \gamma \sin \beta & \sin \gamma & 0 \\
\sin \gamma \sin \beta & \cos \gamma & 0 \\
\cos \beta & 0 & 1
\end{pmatrix}
\]

(see, e.g., [6]).

We introduce the symmetric matrix

\[
G = \begin{pmatrix}
A & 0 & 0 \\
0 & A & 0 \\
0 & 0 & A
\end{pmatrix}
\]

and write Eq. (2) in the form

\[
2T = (\alpha \beta \tau) G (\alpha \beta \tau).
\]

We denote

\[
\hat{\alpha} = \dot{q}_1, \quad \hat{\beta} = \dot{q}_2, \quad \hat{\tau} = \dot{q}_3, \quad \hat{\tau} = \dot{q}_4,
\]

whereupon

\[
2T = \sum_{i,j=1}^{4} G_{ij} \dot{q}_i \dot{q}_j.
\]

Transforming to the generalized momenta \( p_i \) (\( i = 1, 2, 3, 4 \)) conjugate to the generalized coordinates \( q_i \) and introducing the matrix \( g = \| g_{ij} \| \) as the inverse of \( G \) [see Eq. (5)], we obtain

\[
2T = (p_1 p_2 p_3 p_4) g (p_1 p_2 p_3 p_4).
\]

We use the Podol'skii transformation [7] to change to the quantum-mechanical representation of the kinetic energy operator of the given class of molecules for the case of their total and internal rotation:

\[
\hat{T} = -\frac{\hbar^2}{2} \frac{1}{\sin^2 \beta} \sum_{i=1}^{3} \frac{\partial}{\partial q_i} \sqrt{\sin^2 \beta} g_{ii} \frac{\partial}{\partial q_i} + \hbar f(\gamma)^{1/2} \frac{\partial}{\partial \gamma} (f(\gamma)^{-1/2} S_{44}^{-1} \frac{\partial}{\partial \gamma} f(\gamma)^{1/2}).
\]

We now express the operator \( \hat{T} \) in terms of the projection operators \( \hat{L}_{x'}, \hat{L}_{y'}, \text{ and } \hat{L}_{z'} \) of the molecular angular momentum onto the principal axes of inertia (axes of the \( o_1 x'y'z' \) frame).

It is evident from a comparison of (1) and (10) that the sum \( \sum_{x=1}^{3} \hat{L}_{x'}^{2} \hat{L}_{z'}^{2} \) in (1) corresponds to a quantum operator of the form

\[
-\hbar^2 \frac{1}{\sin^2 \beta} \sum_{i=1}^{3} \frac{\partial}{\partial q_i} \sqrt{\sin^2 \beta} g_{ij} \frac{\partial}{\partial q_i}.
\]