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

A. A. Vinogradov and V. N. Vinogradova

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

$$2T = I_x^{-1}(\tau) L_x^2 + I_y^{-1}(\tau) L_y^2 + I_z^{-1}(\tau) L_z^2 + S_{\text{int}}(\tau) p^2, \quad (1)$$

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, $p_\tau$ is the generalized momentum, and $S_{\text{int}}$ 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

$$2T = I_x \Omega_x^2 + I_y \Omega_y^2 + I_z \Omega_z^2 + S_{\text{int}} \dot{\tau}^2. \quad (2)$$
The components $\Omega_{x'}$, $\Omega_{y'}$, and $\Omega_{z'}$ of the instantaneous angular velocity $\Omega$ in the $O_{x'y'z'}$ frame, corresponding to the angular momentum $(L_{x'}, L_{y'}, L_{z'})$, are expressed in terms of the Euler angles:
\[
[\Omega]_{O_{x'y'z'}} = A \left( \alpha \beta \gamma \right),
\]
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
\[
2T = (\alpha \beta \gamma \dot{\alpha} \dot{\beta} \dot{\gamma}) G (\alpha \beta \gamma \dot{\alpha} \dot{\beta} \dot{\gamma}).
\]
We denote
\[
\dot{\alpha} = \dot{q}_1, \quad \dot{\beta} = \dot{q}_2, \quad \dot{\gamma} = \dot{q}_3, \quad \dot{\tau} = \dot{q}_4,
\]
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:
\[
\hat{T} = \frac{1}{2} \hbar^2 \left( \frac{1}{\sin^2 \beta} \sum_{i,j=1}^{3} \frac{\partial}{\partial q_i} \sqrt{\sin^2 \beta} g_{ij} \frac{\partial}{\partial q_j} + \right.
\]
\[
+ f(\varepsilon)^{1/4} \frac{\partial}{\partial \varepsilon} f(\varepsilon)^{-1/2} S^{-1} \frac{\partial}{\partial \varepsilon} f(\varepsilon)^{1/4} \right).
\]

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

It is evident from a comparison of (1) and (10) that the sum $\sum_{k=1}^{3} \hat{L}_{x} \hat{L}_{z}$ in (1) corresponds to a quantum operator of the form
\[
- \hbar^2 \left( \frac{1}{\sin^2 \beta} \sum_{i,j=1}^{3} \frac{\partial}{\partial q_i} \sqrt{\sin^2 \beta} g_{ij} \frac{\partial}{\partial q_j} \right).
\]