

Nonrelativistic Hamiltonian in the principal central moving axes for N -particle system

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This paper is concerned with derivation of a complete Hamiltonian and its rovibronic part containing no anomalous (singular) coefficients like $I_\alpha/2(I_\beta - I_\gamma)^2$ by the square components of the orbital angular momentum for an N -particle system. The work consists of two parts. In the first part the reasons for appearance of the anomalies (in earlier papers [1,2] as well as in more recent ones [4–9]) are analyzed and a general procedure of removing the singularities is proposed through the correct consideration of both determination of the angular momentum and mutual displacements of the particles. The complete description of transition from laboratory variables to molecular ones including non-holonomic coordinates is presented. In the second part the explicit expressions of the Hamiltonians are obtained through the use of tensor methods. The first of them is as follows:

$$H = \frac{1}{2M} \sum_{\alpha} P_{\alpha} P_{\alpha} + \sum_{\alpha} \frac{1}{2I_{\alpha}} L_{\alpha} L_{\alpha} + \frac{1}{2} \sum_j \sum_k g^{jk} p_j p_k - i\hbar \sum_{\alpha} \frac{1}{I_{\alpha}} W_1^{\alpha} L_{\alpha} - i\hbar \sum_k W_2^k p_k + U.$$

Here P_{α} , L_{α} , p_k are the components of the total momentum, the angular momentum and momenta of internal motion.

KEY WORDS: complete and rovibronic Hamiltonians, laboratory and molecular infinitesimal variables, dynamic and deformation rotations of the principal axes, fundamental tensors, coefficients of connectedness, object of anholonomy, Jacobians of transformations

1. Introduction

Even in the first papers [1,2] dedicated to the successive derivation of the kinetic energy operator for polyatomic molecules (N -particle systems) in the principal central moving axes, the coefficients by the square of components of the angular momentum having the form

$$\frac{I_{\alpha}}{2(I_{\beta} - I_{\gamma})^2} \tag{1}$$

were obtained unlike the commonly used $1/2I_\alpha$, (α, β, γ) – cyclic permutation (x, y, z) . In [3], which initiated speculation (1), Van Vleck upheld the validity of the formula

$$H_{\text{rot}} = \sum_{\alpha} \frac{(P_{\alpha} - \zeta_{\alpha})^2}{2I_{\alpha}}, \quad \alpha = x, y, z, \quad (2)$$

for the rotational part of the kinetic energy operator; here P_{α} –components of the total angular momentum with respect to the principal axes, ζ_{α} – components of vibrational angular momentum. To prove impossibility of appearance of anomalous expressions (1) he considered a simple hypothetical two-dimensional system with a special set of variables. Selecting perturbation and using the second order perturbation theory Van Vleck [3] showed that the appearance of expressions like (1) could be avoided in this model problem. Discussion of more realistic three-dimensional problems considered in [1,2] was qualitative in nature and as to precise calculations Van Vleck [3] noticed:

This calculation might not be easy to make explicitly, due to the clumsy, unsymmetrical nature of the coordinates, but can only lead to (2), at least when the moments of inertia are unequal, since we have proved by means of Eckart’s coordinates that (2) then is inevitable.

Hence in [3] the possibility of avoiding singularities (1) in the rotational part of the kinetic energy operator was shown, but there was no successive derivation of the molecular Hamiltonian in the principal central axes (PCA) without such singularities.

Meanwhile, the (PCA) as a moving frame are widely used in the nuclear theory. The total description and references can be found in [4,5]. Extended and consecutive examination of introducing these axes as well as of using them in the theory of molecules is presented in [6]. The papers [7–9] should be mentioned as those wherein the successive derivation of the molecular Hamiltonians in the PCA of inertia was performed. To our opinion the most surprising general result of [4–9] is that the rotational part of all Hamiltonians contains singularities (1) like in [1,2]. Stability of appearance of the anomalous expressions in the works of different authors testifies to the fact that a general important factor leading to the anomaly is not taken into account. The analysis made leads us to conclude that this factor is the existence of two different reasons for rotation of PCA of a system of particles interacting by means of force fields and having no rigid constraints with respect to the laboratory frame of reference. One of these rotations (let us call it “dynamics”) is completely determined by the angular momentum. The other one has no connection with the angular momentum, but it is connected with redistribution of mass in the system (“additional” or “deformation” rotation). If these rotations are separated exactly (accurately) then the anomalous expressions (1) do not arise in derivation of the Hamiltonian that is shown below.

In fact there are two parts in this paper. In the first one (sections 2–6) equations of transformations which connect the laboratory and the moving frames of reference are obtained through the well-known method in mechanics [10] – that of infinitesimal variables. In the second part (sections 7–11) the Hamiltonian is derived by using tensor methods.

2. Preliminaries

2.1. The system of particles. The systems of reference

A molecule is considered to be a system of N kinematically unrelated particles without explicit separation of electrons and nuclei. Two right-handed Cartesian coordinate systems are introduced: a laboratory one (inertial, fixed) and a molecular one (noninertial, moving). Each system is defined by the origin and the frame of vectors:

$$(O; \vec{i}_*, \vec{j}_*, \vec{k}_*), \quad (O^c; \vec{i}, \vec{j}, \vec{k}) \quad (3)$$

for the laboratory and the molecular system, respectively. Here O^c is the center of mass of the molecule. The following aggregates of indices denoting

- numbers of the particles: $\tau, \eta, \mu = 1, 2, \dots, 3N$,
- projections on the moving axes: $\alpha, \beta, \gamma = x, y, z$,
- numbers of internal (see below) variables: $j, k, l = 1, 2, \dots, 3N - 6$,

are used.

In the laboratory and the molecular systems a configuration of the molecule is defined by the sets of radius-vectors

$$\{O; \vec{r}_*^\tau\}_1^N, \quad \{O^c; \vec{r}^\tau\}_1^N, \quad (4)$$

respectively.

It is evident that

$$\vec{r}_*^\tau = \vec{R}_c + \vec{r}^\tau, \quad \vec{R}_c = \frac{1}{M} \sum_{\tau} m_{\tau} \vec{r}_*^\tau, \quad M = \sum_{\tau} m_{\tau}, \quad (5)$$

where m_{τ} – mass of τ th particle.

Projections on the moving axis $O^c X$ are

$$r_*^{\tau x} = \vec{r}_*^\tau \cdot \vec{i}, \quad r^{\tau x} = \vec{r}^\tau \cdot \vec{i}. \quad (6)$$

For the other moving axes formulae are analogous.

The condition of the center of mass of the system of the particles and conditions of the axes being principal have form

$$\sum_{\tau} m_{\tau} \vec{r}^\tau = 0; \quad \sum_{\tau} m_{\tau} r^{\tau\alpha} r^{\tau\beta} = 0, \quad \alpha \neq \beta. \quad (7)$$

2.2. Operators of projections of orbital angular momentum on the moving axes

Eulerian angles φ, θ, χ and operators of projections of the orbital angular momentum L_{α} ($\alpha = x, y, z$) on the moving axes are defined in the same way as in [11],

$$\begin{aligned}
L_x &= -i\hbar \left[-\frac{\cos \chi}{\sin \theta} \frac{\partial}{\partial \varphi} + \sin \chi \frac{\partial}{\partial \theta} + \cot \theta \cos \chi \frac{\partial}{\partial \chi} \right], \\
L_y &= -i\hbar \left[\frac{\sin \chi}{\sin \theta} \frac{\partial}{\partial \varphi} + \cos \chi \frac{\partial}{\partial \theta} - \cot \theta \sin \chi \frac{\partial}{\partial \chi} \right], \\
L_z &= -i\hbar \frac{\partial}{\partial \chi}.
\end{aligned} \tag{8}$$

The same expression can be found in [4, Vol. 1] and in [12]. Respective projections of angular velocity on the moving axes are as follows:

$$\begin{aligned}
\omega^x &= -\dot{\varphi} \sin \theta \cos \chi + \dot{\theta} \sin \chi, \\
\omega^y &= \dot{\varphi} \sin \theta \sin \chi + \dot{\theta} \cos \chi, \\
\omega^z &= \dot{\varphi} \cos \theta + \dot{\chi}.
\end{aligned} \tag{9}$$

In analytical mechanics the values ω^α ($\alpha = x, y, z$) are treated as quasi-velocities [13]. Multiplication (9) by the element of time dt leads to the values called differentials of quasi-coordinates [13]

$$\begin{aligned}
d\tilde{\omega}^x &= -\sin \theta \cos \chi d\varphi + \sin \chi d\theta, \\
d\tilde{\omega}^y &= \sin \theta \sin \chi d\varphi + \cos \chi d\theta, \\
d\tilde{\omega}^z &= \cos \theta d\varphi + d\chi,
\end{aligned} \tag{10}$$

although there are no generalized coordinates in terms of Lagrange which satisfy (10). In [14] more convenient term for these values is used – non-holonomic components of an object or non-holonomic (infinitesimal) coordinates. We will follow this term for

$$d\tilde{\omega}^\alpha = \omega^\alpha dt, \quad \alpha = x, y, z. \tag{11}$$

Using (8) and (10) it can be shown [15], that operators of projections of the orbital angular momentum on the moving axes (8) have the form

$$L_\alpha = -i\hbar \frac{\partial}{\partial \tilde{\omega}^\alpha}, \quad \alpha = x, y, z. \tag{12}$$

3. Infinitesimal stages and independent variables

Motion of the system of the particles is considered to be a sequence of infinitesimal stages with duration of dt . Each stage is limited to the initial and to the final configuration of the particles, these configurations having their PCA. The continuity conditions of the particles are valid:

- the initial configuration of a stage is the final one for the previous stage, the final configuration of a stage is the initial one for the subsequent stage;
- the PCA of the initial configuration are transformed to the analogous ones of the final configuration.

The initial configurations are represented in (4).

3.1. Infinitesimal independent variables

In the laboratory frame of reference these variables are a set of infinitesimal changes in the radius-vectors of the particles:

$$\{\mathbf{d}\vec{r}_*^{\tau}\}_1^N \equiv \{\mathbf{d}r_*^{\tau x}, \mathbf{d}r_*^{\tau y}, \mathbf{d}r_*^{\tau z}\}_1^N,$$

while making transition from the initial configuration (4) to the final one

$$\{O; \vec{r}_*^{\tau} + \mathbf{d}\vec{r}_*^{\tau}\}_1^N. \quad (13)$$

In the moving frame of reference the infinitesimal variables are classified into three groups:

- the changes in the radius-vectors of the center of mass (5)

$$\mathbf{d}\vec{R}_c = \frac{1}{M} \sum_{\tau} m_{\tau} \mathbf{d}\vec{r}_*^{\tau}, \quad \mathbf{d}R_c^{\alpha} = \frac{1}{M} \sum_{\tau} m_{\tau} \mathbf{d}r_*^{\tau\alpha}, \quad \alpha = x, y, z, \quad (14)$$

while making transition from the initial configuration to the final one;

- the differentials $d\xi^j$ ($j = 1, 2, \dots, 3N - 6$) of the internal molecular variables ξ^j which are invariant with respect to translations and rotations, these variables define mutual location of the particles of a molecule;
- the non-holonomic rotations (11)

$$\{\mathbf{d}\tilde{\omega}^x, \mathbf{d}\tilde{\omega}^y, \mathbf{d}\tilde{\omega}^z\} \equiv \mathbf{d}\tilde{\omega},$$

which transform the PCA of the initial configuration to the analogous axes of the final one. As this takes place, $\mathbf{d}\tilde{\omega}^{\alpha}$ must comply with the definition (12), i.e., include only dynamic rotation of the axes. It is the operation that is essential for eliminating the singularities (1) and it will be considered later.

As the laboratory variables are independent, the following equalities take place

$$\frac{\partial r_*^{\tau\alpha}}{\partial r_*^{\eta\beta}} = \delta_{\eta}^{\tau} \delta_{\beta}^{\alpha}; \quad \tau, \eta = 1, 2, \dots, N; \quad \alpha, \beta = x, y, z \quad (15)$$

($\delta_{\eta}^{\tau}, \delta_{\beta}^{\alpha}$ – Kronecker symbols), and for the molecular variables in different groups we have

$$\frac{\partial R_c^{\alpha}}{\partial R_c^{\beta}} = \delta_{\beta}^{\alpha}, \quad \frac{\partial \tilde{\omega}^{\alpha}}{\partial \tilde{\omega}^{\beta}} = \delta_{\beta}^{\alpha}, \quad \frac{\partial \xi^j}{\partial \xi^k} = \delta_k^j. \quad (16)$$

Derivatives of coordinates from different groups are equal to zero.

It is convenient to write general relations among the laboratory and the molecular variables in the form

$$\mathbf{d}R_c^{\alpha} = \sum_{\tau} \sum_{\beta} A_{\tau\beta}^{R\alpha} \mathbf{d}r_*^{\tau\beta}, \quad \mathbf{d}\tilde{\omega}^{\alpha} = \sum_{\tau} \sum_{\beta} A_{\tau\beta}^{\omega\alpha} \mathbf{d}r_*^{\tau\beta}, \quad \mathbf{d}\xi^j = \sum_{\tau} \sum_{\beta} A_{\tau\beta}^j \mathbf{d}r_*^{\tau\beta}, \quad (17)$$

$$d\vec{r}_*^{\tau\alpha} = \sum_{\beta} B_{R\beta}^{\tau\alpha} dR_c^{\beta} + \sum_{\beta} B_{\omega\beta}^{\tau\alpha} d\tilde{\omega}^{\beta} + \sum_k B_k^{\tau\alpha} d\xi^k. \quad (18)$$

The coefficients from (17), (18) are determined later. Hereafter only the infinitesimal variables are used and the term ‘‘infinitesimal’’ is often omitted if its usage is clear.

4. Transition to the final configuration in the moving axes

In the laboratory and the moving frames of reference the initial configurations are represented in (4), and the final configuration (13) is in the laboratory frame of reference.

The theorem of motion addition is represented as

$$d\vec{r}_*^{\tau} = d\vec{R}_c + d\tilde{\omega} \times \vec{r}^{\tau} + d\vec{r}^{\tau}, \quad d\vec{r}^{\tau} = \sum_k \vec{C}_k^{\tau} d\xi^k \quad (19)$$

and it follows from the theorem of velocity addition in relative motion [10,13]

$$\vec{V}_*^{\tau} = \vec{V}_c + \vec{\omega} \times \vec{r}^{\tau} + \vec{V}^{\tau},$$

where \vec{V}_*^{τ} , \vec{V}^{τ} – the velocities of the τ th particle with respect to the laboratory and the moving frames of reference, respectively. From this it is inferred that the final configuration has the form

$$\{O_f^c; \vec{r}_f^{\tau}\}_1^N = \{O_f^c; \vec{r}^{\tau} + d\tilde{\omega} \times \vec{r}^{\tau} + d\vec{r}^{\tau}\}_1^N \quad (20)$$

in the moving frames of reference. In so doing the axes $(O^c; \vec{i}, \vec{j}, \vec{k})$, (3), are shifted to $d\vec{R}^c$ and rotated on $d\tilde{\omega}$, are transformed to

$$(O_f^c; \vec{i}_f, \vec{j}_f, \vec{k}_f) = (O_f^c; \vec{i} + d\tilde{\omega} \times \vec{i}, \vec{j} + d\tilde{\omega} \times \vec{j}, \vec{k} + d\tilde{\omega} \times \vec{k}), \quad (21)$$

which are the central ones. But, generally speaking, they are not the principal ones for the final configuration (20). Making an additional rotation (21) on $d\vec{\Phi}$, we obtain the final modified axes

$$(O_f^c; \vec{i}_{fm}, \vec{j}_{fm}, \vec{k}_{fm}) = (O_f^c; \vec{i}_f + d\vec{\Phi} \times \vec{i}_f, \vec{j}_f + d\vec{\Phi} \times \vec{j}_f, \vec{k}_f + d\vec{\Phi} \times \vec{k}_f). \quad (22)$$

Like (21) they are central, and they can be transformed to the principal axes for the final configuration, if the following equalities (analogous to (7)) are satisfied

$$\begin{aligned} \sum_{\tau} m_{\tau} (\vec{r}_f^{\tau} \cdot \vec{i}_{fm}) (\vec{r}_f^{\tau} \cdot \vec{j}_{fm}) &= 0, & \sum_{\tau} m_{\tau} (\vec{r}_f^{\tau} \cdot \vec{j}_{fm}) (\vec{r}_f^{\tau} \cdot \vec{k}_{fm}) &= 0, \\ \sum_{\tau} m_{\tau} (\vec{r}_f^{\tau} \cdot \vec{k}_{fm}) (\vec{r}_f^{\tau} \cdot \vec{i}_{fm}) &= 0. \end{aligned}$$

Substituting corresponding expressions from (20)–(22) and restricting oneself to infinitesimal quantities up to the second order we obtain

$$d\Phi^{\alpha} = -\frac{1}{I_{\beta} - I_{\gamma}} \sum_{\tau} m_{\tau} (r^{\tau\beta} dr^{\tau\gamma} + r^{\tau\gamma} dr^{\tau\beta}), \quad (23)$$

here the set of indices (α, β, γ) is a cyclic permutation of (x, y, z) . Taking into account the second equality from (19) one can see that $d\Phi^\alpha$ depends only on mutual displacements of the particles $d\xi^j$, $j = 1, 2, \dots, 3N - 6$, and does not depend on $d\vec{R}_c$ and $d\vec{\omega}$.

Thus the additional rotation of the axes (21) on the angle $d\vec{\Phi}$ (additional, deformation rotation) makes them the PCA (22) of the final configuration (20). This transition is a “passive” form of transformation (alias) [12]. It can be replaced with “active” form (alibi) by rotating the configuration (20) on the angle $(-d\vec{\Phi})$ without changing the axes (21). Limiting oneself to infinitesimal quantities of the first order this leads to the modified final configuration

$$\{O_f^c; \vec{r}_{fm}^\tau\}_1^N = \{O_f^c; \vec{r}^\tau + d\vec{\omega} \times \vec{r}^\tau + d\vec{r}^\tau - d\vec{\Phi} \times \vec{r}^\tau\}_1^N, \quad (24)$$

for which the axes (21) are PCA. In so doing the theorem of motion addition (19) is also modified and has the form

$$d\vec{r}_*^\tau = d\vec{R}_c + d\vec{\omega} \times \vec{r}^\tau + d\vec{r}^\tau - d\vec{\Phi} \times \vec{r}^\tau. \quad (25)$$

It is the two latter equalities that are the basis for further transformations. But the dynamic rotation $d\vec{\omega}$ is not determined yet, and presence of $d\vec{\Phi}$ is, in accordance with (23) the source of singularities (1). Let us consider these questions.

5. Determination and refinement of rotations

In (25) we make the following transformations: $d\vec{R}_c$ is carried over to the left side, then vector product of $m_\tau \vec{r}^\tau$ and both sides of the equalities is calculated and, finally, sum over τ is performed. This leads to

$$\sum_\tau m_\tau \vec{r}^\tau \times (d\vec{r}_*^\tau - d\vec{R}_c) = \sum_\tau m_\tau \vec{r}^\tau \times (d\vec{\omega} \times \vec{r}^\tau) + \sum_\tau m_\tau \vec{r}^\tau \times (d\vec{r}^\tau - d\vec{\Phi} \times \vec{r}^\tau). \quad (26)$$

Dividing both sides of (26) by dt we have

$$\sum_\tau m_\tau \vec{r}^\tau \times \left(\frac{d\vec{r}_*^\tau}{dt} - \frac{d\vec{R}_c}{dt} \right) = \sum_\tau m_\tau \vec{r}^\tau \times (\vec{\omega} \times \vec{r}^\tau) + \sum_\tau m_\tau \vec{r}^\tau \times \left(\frac{d\vec{r}^\tau}{dt} - \frac{d\vec{\Phi}}{dt} \times \vec{r}^\tau \right), \quad (27)$$

(11) being taken into account. The left side expression is the classical orbital angular momentum of N -particle system with respect to the center of mass O^c of this system [10,13]. In the right side the second sum depends only on velocities of relative motion $d\xi^j/dt$ (see the second addend in (19) and a remark in connection with (23)). Therefore, the orbital angular momentum of the system of particles has to be completely determined with the angular velocities $\vec{\omega}$ in the first addend in the right side (27), i.e.,

$$\sum_\tau m_\tau \vec{r}^\tau \times \left(\frac{d\vec{r}_*^\tau}{dt} - \frac{d\vec{R}_c}{dt} \right) = \sum_\tau m_\tau \vec{r}^\tau \times (\vec{\omega} \times \vec{r}^\tau).$$

Multiplying both sides by dt , we obtain an equation for determination of the dynamic rotation $d\tilde{\omega}$

$$\sum_{\tau} m_{\tau} \vec{r}^{\tau} \times (d\vec{r}_{*}^{\tau} - d\vec{R}_c) = \sum_{\tau} m_{\tau} \vec{r}^{\tau} \times (d\tilde{\omega} \times \vec{r}^{\tau}). \quad (28)$$

After substituting it in (26), one obtains an equation for refinement of the rotation $d\vec{\Phi}$

$$\sum_{\tau} m_{\tau} \vec{r}^{\tau} \times d\vec{r}^{\tau} = \sum_{\tau} m_{\tau} \vec{r}^{\tau} \times (d\vec{\Phi} \times \vec{r}^{\tau}). \quad (29)$$

5.1. Expressions of components of the dynamic rotation in the moving frame of reference

If one takes into consideration the first equality from (7) then

$$\sum_{\tau} m_{\tau} \vec{r}^{\tau} \times d\vec{R}_c = \left(\sum_{\tau} m_{\tau} \vec{r}^{\tau} \right) \times \frac{1}{M} \sum_{\eta} m_{\eta} d\vec{r}_{*}^{\eta} = 0,$$

and (28) can be rewritten in the form

$$\sum_{\tau} m_{\tau} \vec{r}^{\tau} \times d\vec{r}_{*}^{\tau} = \sum_{\tau} m_{\tau} \vec{r}^{\tau} \times (d\tilde{\omega} \times \vec{r}^{\tau}). \quad (30)$$

By using the formula of double vector product [16], we obtain

$$\sum_{\tau} m_{\tau} \vec{r}^{\tau} \times d\vec{r}_{*}^{\tau} = \sum_{\tau} m_{\tau} [d\tilde{\omega}(\vec{r}^{\tau} \cdot \vec{r}^{\tau}) - \vec{r}^{\tau}(\vec{r}^{\tau} \cdot d\tilde{\omega})].$$

Going to the projections on the PCA of the initial configuration $O^c; \vec{i}, \vec{j}, \vec{k}$ (see (3)) and taking into account (7), we have

$$\sum_{\tau} m_{\tau} (\vec{r}^{\tau} \times d\vec{r}_{*}^{\tau})^{\alpha} = d\tilde{\omega}^{\alpha} \sum_{\tau} m_{\tau} [(r^{\tau})^2 - (r^{\tau\alpha})^2].$$

As the principal moments of inertia of the initial configuration of the particles are

$$I_{\alpha} = \sum_{\tau} m_{\tau} [(r^{\tau})^2 - (r^{\tau\alpha})^2], \quad \alpha = x, y, z, \quad (31)$$

then the final expressions of the components of the dynamic rotation are as follows

$$d\tilde{\omega}^{\alpha} = \frac{1}{I_{\alpha}} \cdot \sum_{\tau} m_{\tau} (\vec{r}^{\tau} \times d\vec{r}_{*}^{\tau})^{\alpha} = \frac{1}{I_{\alpha}} \sum_{\tau} m_{\tau} \sum_{\beta} \sum_{\gamma} \varepsilon_{\alpha\beta\gamma} r^{\tau\beta} dr_{*}^{\tau\gamma}, \quad \alpha = x, y, z, \quad (32)$$

here $\varepsilon_{\alpha\beta\gamma}$ – the symbol of Levi–Civita [16]. In what follows I_{α} is defined by (31).

5.2. The second variant of the additional rotation of the axes and theorems of motion addition

The first variant is (23), the second one is obtained from (29). If (29) and (30) are compared, then it is clear that the former is obtained from the latter with substitutions $d\vec{\omega} \rightarrow d\vec{\Phi}$ and $d\vec{r}_*^\tau \rightarrow d\vec{r}^\tau$. Therefore, making these substitutions we have the second variant of the additional rotation

$$d\Phi^\alpha = \frac{1}{I_\alpha} \cdot \sum_\tau m_\tau (\vec{r}^\tau \times d\vec{r}^\tau)^\alpha = \frac{1}{I_\alpha} \sum_\tau m_\tau \sum_\beta \sum_\gamma \varepsilon_{\alpha\beta\gamma} r^{\tau\beta} dr^{\tau\gamma}, \quad \alpha = x, y, z. \quad (33)$$

This expression like (32) contains no the singularities that allows one to derive a hamiltonian without anomalous expressions (1) in the rotational part of the kinetic energy operator. It is these expressions that are used thereafter. Turning to the modified theorem of motion addition (25) and denoting

$$d\vec{R}^\tau = d\vec{r}^\tau - d\vec{\Phi} \times \vec{r}^\tau, \quad (34)$$

we obtain

$$d\vec{r}_*^\tau = d\vec{R}^\tau + d\vec{\omega} \times \vec{r}^\tau + d\vec{R}^\tau, \quad dr_*^{\tau\alpha} = dR_c^\alpha + (d\vec{\omega} \times \vec{r}^\tau)^\alpha + dR^{\tau\alpha}, \quad (35)$$

$$\tau = 1, 2, \dots, N; \quad \alpha = x, y, z.$$

The final modified configuration (24) is

$$\{O_f^c; \vec{r}_{fm}^\tau\}_1^N = \{O_f^c; \vec{r}^\tau + d\vec{\omega} \times \vec{r}^\tau + d\vec{R}^\tau\}.$$

Rewriting (34) as

$$dR^{\tau\alpha} = dr^{\tau\alpha} - (d\Phi^\beta r^{\tau\gamma} - d\Phi^\gamma r^{\tau\beta}),$$

and taking into consideration (33) and the second equality from (19) we have after the transformation

$$dR^{\tau\alpha} = \sum_k \left\{ \sum_\eta \left(\delta_\eta^\tau - r^{\tau\beta} \frac{m_\eta}{I_\gamma} r^{\eta\beta} - r^{\tau\gamma} \frac{m_\eta}{I_\beta} r^{\eta\gamma} \right) C_k^{\eta\alpha} + \sum_\eta \left(r^{\tau\beta} \frac{m_\eta}{I_\gamma} r^{\eta\alpha} \right) C_k^{\eta\beta} + \sum_\eta \left(r^{\tau\gamma} \frac{m_\eta}{I_\beta} r^{\eta\alpha} \right) C_k^{\eta\gamma} \right\} d\xi^k, \quad (36)$$

$\tau = 1, 2, \dots, N; \quad \alpha = x, y, z; \quad (\alpha, \beta, \gamma)$ is a cyclic permutation of (x, y, z) . One can see that $dR^{\tau\alpha}$ is a function of the internal variables $d\xi^k$ ($k = 1, 2, \dots, 3N - 6$), and comparison of (35) with (18) leads to

$$dR^{\tau\alpha} = \sum_k B_k^{\tau\alpha} d\xi^k. \quad (37)$$

Correlating (36) with (37) and taking into consideration the fact that $d\xi^k$ are independent, we have

$$B_k^{\tau\alpha} = \sum_{\eta} \left(\delta_{\eta}^{\tau} - r^{\tau\beta} \frac{m_{\eta}}{I_{\gamma}} r^{\eta\beta} - r^{\tau\gamma} \frac{m_{\eta}}{I_{\beta}} r^{\eta\gamma} \right) C_k^{\eta\alpha} + \sum_{\eta} \left(r^{\tau\beta} \frac{m_{\eta}}{I_{\gamma}} r^{\eta\alpha} \right) C_k^{\eta\beta} + \sum_{\eta} \left(r^{\tau\gamma} \frac{m_{\eta}}{I_{\beta}} r^{\eta\alpha} \right) C_k^{\eta\gamma}, \quad (38)$$

$k = 1, 2, \dots, 3N - 6$; $\tau = 1, 2, \dots, N$; $\alpha = x, y, z$; (α, β, γ) is a cyclic permutation of (x, y, z) . Now the modified theorem of motion addition (35) has the form

$$dr_*^{\tau\alpha} = dR_c^{\alpha} + \sum_{\beta} \sum_{\gamma} \varepsilon_{\alpha\beta\gamma} d\tilde{\omega}^{\beta} r^{\tau\gamma} + \sum_k B_k^{\tau\alpha} d\xi^k, \quad \tau = 1, 2, \dots, N; \alpha = x, y, z. \quad (39)$$

6. Coefficients of transformations and conditions being satisfied by them

The coefficients of transformations (17) are found from definitions both (14), (32)

$$A_{\tau\beta}^{R\alpha} = \frac{m_{\tau}}{M} \delta_{\beta}^{\alpha}, \quad M = \sum_{\eta} m_{\eta}; \quad A_{\tau\beta}^{\omega\alpha} = \frac{1}{I_{\alpha}} \sum_{\gamma} \varepsilon_{\alpha\gamma\beta} r^{\tau\gamma} \quad (40)$$

and definition of $d\xi^k$ as a differential of a function $\xi^j = \xi^j(r_*^{\tau\gamma})$, i.e.,

$$A_{\tau\alpha}^j = \frac{\partial \xi^j}{\partial r_*^{\tau\alpha}}. \quad (41)$$

Two types of transformation coefficients (18) are evaluated through comparing with (39)

$$B_{R\beta}^{\tau\alpha} = \delta_{\beta}^{\alpha}, \quad B_{\omega\beta}^{\tau\alpha} = \sum_{\gamma} \varepsilon_{\alpha\gamma\beta} r^{\tau\gamma}, \quad (42)$$

and another one is written similarly to (41)

$$B_k^{\tau\alpha} = \frac{\partial r_*^{\tau\alpha}}{\partial \xi^k}.$$

But it is impossible to use the latter equality for determination of $B_k^{\tau\alpha}$, because dependence of $r_*^{\tau\alpha}$ on ξ^k is unknown. Therefore, we use the fact that the laboratory variables (15) are independent and the well-known formula for derivatives [17]

$$\frac{\partial r_*^{\tau\alpha}}{\partial r_*^{\eta\beta}} = \sum_{\gamma} \frac{\partial r_*^{\tau\alpha}}{\partial R_c^{\gamma}} \frac{\partial R_c^{\gamma}}{\partial r_*^{\eta\beta}} + \sum_{\gamma} \frac{\partial r_*^{\tau\alpha}}{\partial \tilde{\omega}^{\gamma}} \frac{\partial \tilde{\omega}^{\gamma}}{\partial r_*^{\eta\beta}} + \sum_{\gamma} \frac{\partial r_*^{\tau\alpha}}{\partial \xi^k} \frac{\partial \xi^k}{\partial r_*^{\eta\beta}}.$$

If one replaces the derivatives with corresponding transformation coefficients (17), (18) in the right side and compares newly obtained equality with (15), then the following equation takes place

$$\sum_{\gamma} B_{R\gamma}^{\tau\alpha} A_{\eta\beta}^{R\gamma} + \sum_{\gamma} B_{\omega\gamma}^{\tau\alpha} A_{\eta\beta}^{\omega\gamma} + \sum_k B_k^{\tau\alpha} A_{\eta\beta}^k = \delta_{\eta}^{\tau} \delta_{\beta}^{\alpha}. \quad (43)$$

After substituting (40) and (42) in this equation we have a formula which determines the third sum in the left side. It is convenient to rewrite it as two equalities:

- if in (43) $\alpha = \beta$ then

$$\sum_k B_k^{\tau\alpha} A_{\eta\alpha}^k = \delta_{\eta}^{\tau} - \frac{m_{\eta}}{M} - m_{\eta} \left[\frac{r^{\tau\beta} r^{\eta\beta}}{I_{\gamma}} + \frac{r^{\tau\gamma} r^{\eta\gamma}}{I_{\beta}} \right]; \quad (44)$$

- if in (43) $\alpha \neq \beta$ then

$$\sum_k B_k^{\tau\alpha} A_{\eta\beta}^k = m_{\eta} \frac{r^{\tau\beta} r^{\eta\alpha}}{I_{\gamma}}. \quad (45)$$

In (43), (45) (α, β, γ) can be considered as the cyclic permutation (x, y, z) , though it is possible to use conditions $\alpha \neq \beta, \beta \neq \gamma, \gamma \neq \alpha; \alpha, \beta, \gamma = x, y, z$ in this case.

Let us introduce

$$G^{jk} = \sum_{\tau} m_{\tau}^{-1} \sum_{\alpha} A_{\tau\alpha}^j A_{\tau\alpha}^k = \sum_{\tau} m_{\tau}^{-1} \vec{A}_{\tau}^j \cdot \vec{A}_{\tau}^k, \quad (46)$$

$$G_{kl} = \sum_{\eta} m_{\eta} \sum_{\alpha} B_k^{\tau\beta} B_l^{\tau\beta} = \sum_{\eta} m_{\eta} \vec{B}_k^{\tau} \cdot \vec{B}_l^{\tau}. \quad (47)$$

It is clear that $G^{jk} = G^{kj}, G_{kl} = G_{lk}$. Using (44), (45) one can show that (46), (47) satisfy the relationships

$$\sum_k G_{jk} G^{kl} = \delta_j^l; \quad j, l = 1, 2, \dots, 3N - 6, \quad (48)$$

$$B_j^{\eta\alpha} = m_{\eta}^{-1} \sum_k G_{jk} A_{\eta\alpha}^k; \quad \eta = 1, 2, \dots, N; \alpha = x, y, z, \quad (49)$$

$$A_{\tau\alpha}^j = m_{\tau} \sum_k G^{jk} B_k^{\tau\alpha}; \quad \tau = 1, 2, \dots, N; \alpha = x, y, z. \quad (50)$$

The equality (48) shows that the values (46), (47) are reciprocal; (49), (50) allow one to represent $B_i^{\eta\alpha}$ as functions of $A_{\eta\alpha}^k$ and vice versa. The way of determination of $B_j^{\eta\alpha}$ from (18) is as follows:

- if $A_{\tau\alpha}^j$ are known from (41), then G^{jk} are found from (46);
- (48) defines G_{jk} ;
- in accordance with (49) $B_k^{\eta\alpha}$ are determined;
- (50) enables one to check precision of determination of $B_j^{\eta\alpha}$.

Thus determination of coefficients transformations (17), (18) is completed. But the coefficients $C_k^{\tau\alpha}$ (the second equality in (19)) are not determined yet. To solve this problem the equalities (38) which for every fixed $k = 1, 2, \dots, 3N - 6$ are convenient to write in the form

$$\begin{aligned} & \sum_{\eta} \left(\delta_{\eta}^{\tau} - r^{\tau y} \frac{m_{\eta}}{I_z} r^{\eta y} - r^{\tau z} \frac{m_{\eta}}{I_y} r^{\eta z} \right) C_k^{\eta x} + \left(r^{\tau y} \frac{m_{\eta}}{I_z} r^{\eta x} \right) C_k^{\eta y} \\ & + \sum_{\eta} \left(r^{\tau z} \frac{m_{\eta}}{I_y} r^{\eta x} \right) C_k^{\eta z} = B_k^{\tau x}, \quad \tau = 1, 2, \dots, N; \\ & \sum_{\eta} \left(r^{\tau x} \frac{m_{\eta}}{I_z} r^{\eta y} \right) C_k^{\eta x} + \sum_{\eta} \left(\delta_{\eta}^{\tau} - r^{\tau z} \frac{m_{\eta}}{I_x} r^{\eta z} - r^{\tau x} \frac{m_{\eta}}{I_z} r^{\eta x} \right) C_k^{\eta y} \\ & + \sum_{\eta} \left(r^{\tau z} \frac{m_{\eta}}{I_x} r^{\eta y} \right) C_k^{\eta z} = B_k^{\tau y}, \quad \tau = 1, 2, \dots, N; \\ & \sum_{\eta} \left(r^{\tau x} \frac{m_{\eta}}{I_y} r^{\eta z} \right) C_k^{\eta x} + \sum_{\eta} \left(r^{\tau y} \frac{m_{\eta}}{I_x} r^{\eta z} \right) C_k^{\eta y} \\ & + \sum_{\eta} \left(\delta_{\eta}^{\tau} - r^{\tau x} \frac{m_{\eta}}{I_y} r^{\eta x} - r^{\tau y} \frac{m_{\eta}}{I_x} r^{\eta y} \right) C_k^{\eta z} = B_k^{\tau z}, \quad \tau = 1, 2, \dots, N \end{aligned}$$

are used. By correlating the system coefficients with (44), (45) we obtain the final system of equalities for determination of $C_k^{\eta\alpha}$ by means of the coefficients of transformations (17), (18)

$$\begin{aligned} & \sum_{\eta} \left(\sum_j B_j^{\tau x} A_{\eta x}^j + \frac{m_{\eta}}{M} \right) C_k^{\eta x} + \sum_{\eta} \left(\sum_j B_j^{\tau x} A_{\eta y}^j \right) C_k^{\eta y} + \sum_{\eta} \left(\sum_j B_j^{\tau x} A_{\eta z}^j \right) C_k^{\eta z} = B_k^{\tau x}, \\ & \tau = 1, 2, \dots, N; \\ & \sum_{\eta} \left(\sum_j B_j^{\tau y} A_{\eta x}^j \right) C_k^{\eta x} + \sum_{\eta} \left(\sum_j B_j^{\tau y} A_{\eta y}^j + \frac{m_{\eta}}{M} \right) C_k^{\eta y} + \sum_{\eta} \left(\sum_j B_j^{\tau y} A_{\eta z}^j \right) C_k^{\eta z} = B_k^{\tau y}, \\ & \tau = 1, 2, \dots, N; \\ & \sum_{\eta} \left(\sum_j B_j^{\tau z} A_{\eta x}^j \right) C_k^{\eta x} + \sum_{\eta} \left(\sum_j B_j^{\tau z} A_{\eta y}^j \right) C_k^{\eta y} + \sum_{\eta} \left(\sum_j B_j^{\tau z} A_{\eta z}^j + \frac{m_{\eta}}{M} \right) C_k^{\eta z} = B_k^{\tau z}, \\ & \tau = 1, 2, \dots, N, \end{aligned} \tag{51}$$

for every fixed $k = 1, 2, \dots, 3N - 6$. Methods of solving such systems of equations can be found in [18,19]. In conclusion of this section we write out additional relationships

(omitting proof) wherein the coefficients of transformations (17), (18) are included. In so doing the starting point is (16) as well.

$$\begin{aligned}
\sum_{\tau} \vec{A}_{\tau}^j &= 0, & \text{i.e.,} & \sum_{\tau} A_{\tau\alpha}^j = 0, \\
\sum_{\tau} (\vec{r}^{\tau} \times \vec{A}_{\tau}^j) &= 0, & \text{i.e.,} & \sum_{\tau} (\vec{r}^{\tau} \times \vec{A}_{\tau}^j)^{\alpha} = 0, \\
\sum_{\tau} m_{\tau} \vec{B}_{\tau}^j &= 0, & \text{i.e.,} & \sum_{\tau} m_{\tau} B_j^{\tau\alpha} = 0, \\
\sum_{\tau} m_{\tau} (\vec{r}^{\tau} \times \vec{B}_{\tau}^j) &= 0, & \text{i.e.,} & \sum_{\tau} m_{\tau} (\vec{r}^{\tau} \times \vec{B}_{\tau}^j)^{\alpha} = 0, \\
\sum_{\tau} \vec{A}_{\tau}^j \cdot \vec{B}_{\tau}^k &= \sum_{\tau} \sum_{\alpha} A_{\tau\alpha}^j B_k^{\tau\alpha} = \delta_k^j.
\end{aligned} \tag{52}$$

There are equalities, part of them was obtained in the previous sections:

$$\begin{aligned}
d\vec{R}^{\tau} &= \sum_k \vec{B}_k^{\tau} d\xi^k, & \sum_{\tau} m_{\tau} d\vec{R}^{\tau} &= 0, & \sum_{\tau} m_{\tau} (\vec{r}^{\tau} \times d\vec{R}^{\tau}) &= 0, \\
d\vec{r}^{\tau} &= \sum_k \vec{C}_k^{\tau} d\xi^k, & \sum_{\tau} m_{\tau} d\vec{r}^{\tau} &= 0, & \sum_{\tau} m_{\tau} \vec{C}_k^{\tau} &= 0, \\
&& \sum_{\tau} \vec{A}_{\tau}^j \cdot \vec{C}_k^{\tau} &= \delta_k^j.
\end{aligned} \tag{53}$$

It should be noted that the next to last equality in (53) allows one to omit the addend m_{τ}/M in parentheses of the equation (51). This enables us to rewrite these equations in a compact form

$$\sum_{\eta} \sum_{\gamma} \left(\sum_j B_j^{\tau\alpha} A_{\eta\gamma}^j \right) C_k^{\eta\gamma} = B_k^{\tau\alpha}, \quad \tau = 1, 2, \dots, N, \quad \alpha = x, y, z; \tag{54}$$

for every $k = 1, 2, \dots, 3N - 6$.

7. Operators of the kinetic energy in Cartesian and generalized coordinates

Let us introduce projections of radius vectors of the particles in the laboratory system \vec{r}_*^{τ} (4), (5) on these axes (3) (the first expression)

$$r_{**}^{\tau x} = \vec{r}_*^{\tau} \cdot \vec{i}_*, \quad r_{**}^{\tau y} = \vec{r}_*^{\tau} \cdot \vec{j}_*, \quad r_{**}^{\tau z} = \vec{r}_*^{\tau} \cdot \vec{k}_*. \tag{55}$$

These projections are different from those of these vectors on axes of the moving system (3) (the second expression)

$$r_*^{\tau x} = \vec{r}_*^{\tau} \cdot \vec{l}, \quad r_*^{\tau y} = \vec{r}_*^{\tau} \cdot \vec{j}, \quad r_*^{\tau z} = \vec{r}_*^{\tau} \cdot \vec{k}, \tag{56}$$

which are used (6) in the first part of the paper.

In the laboratory axes the kinetic energy operator acting on an absolute scalar – a wavefunction ψ – has the form

$$T\psi = -\frac{\hbar^2}{2} \sum_{\tau} m_{\tau}^{-1} \sum_{\alpha} \frac{\partial}{\partial r_{**}^{\tau\alpha}} \frac{\partial}{\partial r_{**}^{\tau\alpha}} \psi. \quad (57)$$

By analogy with (55), (56) mass-weighted Cartesian coordinates are introduced

$$\begin{aligned} \rho_{**}^{\tau x} &= m_{\tau}^{1/2} \vec{r}_{*}^{\tau} \cdot \vec{i}_{*} = m_{\tau}^{1/2} r_{**}^{\tau x}, & \text{etc.}, \\ \rho_{*}^{\tau x} &= m_{\tau}^{1/2} \vec{r}_{*}^{\tau} \cdot \vec{i} = m_{\tau}^{1/2} r_{*}^{\tau x}, & \text{etc.} \end{aligned} \quad (58)$$

Then (57) is

$$T\psi = -\frac{\hbar^2}{2} \sum_{\tau} \sum_{\alpha} \frac{\partial}{\partial \rho_{**}^{\tau\alpha}} \frac{\partial}{\partial \rho_{**}^{\tau\alpha}} \psi. \quad (59)$$

When the common factor $(-\hbar^2/2)$ is not considered then the rest of (59) is multiparticle Laplacian – the sum of three-dimensional operators

$$\sum_{\alpha} \frac{\partial}{\partial \rho_{**}^{\tau\alpha}} \frac{\partial}{\partial \rho_{**}^{\tau\alpha}} \psi, \quad \tau = 1, 2, \dots, N,$$

acting on ψ . As was shown in [20, chapter 1], the form of Laplacian is invariant with respect to transition from one Cartesian coordinate system to another, (i.e., from the first system in (3) to the second one) since

$$\text{div grad } \psi = \nabla^2 \psi = \frac{1}{h_1 h_2 h_3} \sum_{n=1}^3 \frac{\partial}{\partial \zeta_n} \left[\frac{h_1 h_2 h_3}{h_n^2} \frac{\partial \psi}{\partial \zeta_n} \right],$$

all Lamé coefficients $h_n = 1$. Therefore, (59) can be rewritten as the multiparticle Laplacian acting on the absolute scalar ψ ,

$$-\frac{2}{\hbar^2} T\psi = \sum_{\tau} \sum_{\alpha} \frac{\partial}{\partial \rho_{*}^{\tau\alpha}} \frac{\partial}{\partial \rho_{*}^{\tau\alpha}} \psi = \sum_{\tau} \sum_{\alpha} \sum_{\eta} \sum_{\beta} \delta_{\tau}^{\eta} \delta_{\alpha}^{\beta} \frac{\partial}{\partial \rho_{*}^{\tau\alpha}} \frac{\partial}{\partial \rho_{*}^{\eta\beta}} \psi, \quad (60)$$

which is expressed through the mass-weighted laboratory variables (58). On the other hand, this operator can be written by using generalized coordinates $\{x^p\}_1^{3N}$ like in [16],

$$\begin{aligned} \nabla^2 \psi &\equiv g^{ps} \nabla_p \nabla_s \psi \equiv g^{ps} \nabla_s \frac{\partial \psi}{\partial x^s} \equiv g^{ps} \left(\frac{\partial^2 \psi}{\partial x^p \partial x^s} - \Gamma_{ps}^h \frac{\partial \psi}{\partial x^h} \right) \\ &\equiv \frac{1}{\sqrt{|g|}} \frac{\partial}{\partial x^p} \left(g^{ps} \sqrt{|g|} \frac{\partial \psi}{\partial x^s} \right), \end{aligned} \quad (61)$$

where ∇_s – covariant derivative, the summation being taken over recurring indices. In applications the last expression is often used, but we will use next to the last. In this formula g^{ps} is the contravariant metric (fundamental) tensor [14] which is inverse to the

covariant one g_{ps} ; Γ_{ps}^h – coefficients of affine connectedness [14]. $\Gamma_{ps}^t = 0$ for the mass-weighted laboratory variables relating to Cartesian axes. For the molecular generalized variables including non-holonomic ones these coefficients have the form [14]

$$\Gamma_{ps}^h = \left\{ \begin{array}{c} h \\ ps \end{array} \right\} = \Omega_{ps}^{\cdot h} + g_{pv} g^{hu} \Omega_{su}^{\cdot v} + g_{sv} g^{hu} \Omega_{pu}^{\cdot v}. \quad (62)$$

Here, in addition to the fundamental tensors, $\left\{ \begin{array}{c} h \\ ps \end{array} \right\}$ – Christoffel symbol, $\Omega_{ps}^{\cdot h}$ – an object of anholonomy. For our problem it is necessary to substitute all variables from $\{x^p\}_1^{3N}$ for those used in the sections 2–6, with additional substitution the laboratory variables for the mass-weighted ones (58). In the process of transformation equations (17), (18) have the form

$$dR_c^{\alpha} = \sum_{\tau} \sum_{\beta} (m_{\tau}^{-1/2} A_{\tau\beta}^{R\alpha}) d\rho_*^{\tau\beta}, \quad d\tilde{\omega}^{\alpha} = \sum_{\tau} \sum_{\beta} (m_{\tau}^{-1/2} A_{\tau\beta}^{\omega\alpha}) d\rho_*^{\tau\beta}, \quad (63)$$

$$d\xi^j = \sum_{\tau} \sum_{\beta} (m_{\tau}^{-1/2} A_{\tau\beta}^j) d\rho_*^{\tau\beta};$$

$$d\rho_*^{\tau\alpha} = \sum_{\beta} (m_{\tau}^{1/2} B_{R\beta}^{\tau\alpha}) dR_c^{\beta} + \sum_{\beta} (m_{\tau}^{1/2} B_{\omega\beta}^{\tau\alpha}) d\tilde{\omega}^{\beta} + \sum_k (m_{\tau}^{1/2} B_k^{\tau\alpha}) d\xi^k. \quad (64)$$

8. Metric tensors

By using (60), (61), i.e.,

$$-\frac{2}{\hbar^2} T\psi = g^{ps} \left(\frac{\partial^2 \psi}{\partial x^p \partial x^s} - \Gamma_{ps}^h \frac{\partial \psi}{\partial x^h} \right), \quad (65)$$

the summation being taken over recurring indices $p, s, t = 1, 2, \dots, 3N$.

Now one determines the metric tensors expressed in the laboratory and the molecular variables. As was mentioned above $\Gamma_{ps}^t = 0$ for the laboratory variables referring to the Cartesian axes and comparison of (60) and (65) gives the following relations for the mass-weighted variables

$$g^{ps}(\rho_*) \equiv g^{\widehat{\tau\alpha} \widehat{\eta\beta}}(\rho_*) = \delta_{\tau}^{\eta} \delta_{\alpha}^{\beta} = g_{\widehat{\tau\alpha} \widehat{\eta\beta}}(\rho_*) \equiv g_{ps}(\rho_*). \quad (66)$$

Here every $\widehat{\tau\alpha}$ or $\widehat{\eta\beta}$ ($\tau, \eta = 1, 2, \dots, N; \alpha, \beta = x, y, z$) denotes one tensor index which has $3N$ values. If one uses usual Cartesian coordinates $r_*^{\tau\alpha}$ instead of mass-weighted ones it can be shown that

$$\begin{aligned} g^{ps}(r_*) &\equiv g^{\widehat{\tau\alpha} \widehat{\eta\beta}}(r_*) = m_{\tau}^{-1} \delta_{\tau}^{\eta} \delta_{\alpha}^{\beta}, \\ g_{ps}(r_*) &\equiv g_{\widehat{\tau\alpha} \widehat{\eta\beta}}(r_*) = m_{\tau} \delta_{\tau}^{\eta} \delta_{\alpha}^{\beta} \end{aligned} \quad (67)$$

take place (this follows from (58)). When passing from the variables $\{x^p\}_1^{3N}$ to $\{x^{p'}\}_1^{3N}$ the metric tensors are transformed as

$$g^{p's'} = \frac{\partial x^{p'}}{\partial x^p} \frac{\partial x^{s'}}{\partial x^s} g^{ps}, \quad g_{p's'} = \frac{\partial x^p}{\partial x^{p'}} \frac{\partial x^s}{\partial x^{s'}} g_{ps} \quad (68)$$

(the summation is meant). If the metric tensors of our problem written in the laboratory (mass-weighted) variables are represented in (66), then (63), (64) are used to make transformation (68). If the form of the metric tensors expressed in the laboratory non-weighted variables is (67), then (17), (18) are exploited. In both cases the expressions of the metric tensors (after some transformations with the use (16), (52)) are identical. Namely, for $g_{p's'}$ we have

- the components of translational variables

$$g_{\widehat{R}\alpha\widehat{R}\beta} = M\delta_{\alpha\beta}, \quad M = \sum_{\tau} m_{\tau},$$

- the ones of rotational variables

$$g_{\widehat{\omega}\alpha\widehat{\omega}\beta} = I_{\alpha}\delta_{\alpha\beta}, \quad I_{\alpha} = \sum_{\tau} m_{\tau}[(r^{\tau})^2 - (r^{\tau\alpha})^2],$$

- the ones of internal variables

$$g_{jk} = \sum_{\tau} m_{\tau} \sum_{\alpha} B_j^{\tau\alpha} B_k^{\tau\alpha} = \sum_{\tau} m_{\tau} \vec{B}_j^{\tau} \cdot \vec{B}_k^{\tau}, \quad (69)$$

- the ones of variables of mixed types

$$g_{\widehat{R}\alpha\widehat{\omega}\beta} = g_{\widehat{R}\alpha k} = g_{\widehat{\omega}\alpha k} = 0.$$

In a similar manner the components of $g^{p's'}$ are as follows:

$$\begin{aligned} g^{\widehat{R}\alpha\widehat{R}\beta} &= M^{-1}\delta^{\alpha\beta}, \\ g^{\widehat{\omega}\alpha\widehat{\omega}\beta} &= I_{\alpha}^{-1}\delta^{\alpha\beta}, \\ g^{jk} &= \sum_{\tau} m_{\tau}^{-1} \sum_{\alpha} A_{\tau\alpha}^j A_{\tau\alpha}^k = \sum_{\tau} m_{\tau}^{-1} \vec{A}_{\tau}^j \cdot \vec{A}_{\tau}^k. \\ g^{\widehat{R}\alpha\widehat{\omega}\beta} &= g^{\widehat{R}\alpha k} = g^{\widehat{\omega}\alpha k} = 0. \end{aligned} \quad (70)$$

In (69), (70) $\delta_{\alpha\beta} = \delta^{\alpha\beta} = \delta_{\beta}^{\alpha}$ is Kronecker delta and $g_{jk} = G_{jk}$, (47), $g^{jk} = G^{jk}$, (46). It is evident that matrices of the fundamental tensors written in the laboratory variables have the form presented in tables 1 and 2.

9. Expression of Laplacian in molecular non-holonomic variables

9.1. General transformation

Substituting (62) in (65) one obtains

$$\begin{aligned} -\frac{2}{\hbar^2} T\psi &= g^{ps} \frac{\partial^2 \psi}{\partial x^p \partial x^s} - g^{ps} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} \\ &+ g^{ps} \Omega_{ps}^{\cdot h} \frac{\partial \psi}{\partial x^h} - g^{ps} g_{pv} g^{hu} \Omega_{su}^{\cdot v} \frac{\partial \psi}{\partial x^h} - g^{ps} g_{sv} g^{hu} \Omega_{pu}^{\cdot v} \frac{\partial \psi}{\partial x^h} \end{aligned} \quad (71)$$

Table 1
Matrix of the fundamental tensor g_{ps} (a blank cell means zero).

	dR_c^α			$d\tilde{\omega}^\alpha$			$d\xi^j$						
dR_c^α	M												
		M											
			M										
$d\tilde{\omega}^\alpha$				I_x									
					I_y								
						I_z							
$d\xi^j$							g_{11}	g_{12}	g_{13}	g_{14}	\dots		
							g_{21}	g_{22}	g_{23}	g_{24}	\dots		
							g_{31}	g_{32}	g_{33}	g_{34}	\dots		
							g_{41}	g_{42}	g_{43}	g_{44}	\dots		
							\vdots	\vdots	\vdots	\vdots	\ddots		

Table 2
Matrix of the fundamental tensor g^{ps} (a blank cell means zero).

	dR_c^α			$d\tilde{\omega}^\alpha$			$d\xi^j$						
dR_c^α	M^{-1}												
		M^{-1}											
			M^{-1}										
$d\tilde{\omega}^\alpha$				I_x^{-1}									
					I_y^{-1}								
						I_z^{-1}							
$d\xi^j$							g^{11}	g^{12}	g^{13}	g^{14}	\dots		
							g^{21}	g^{22}	g^{23}	g^{24}	\dots		
							g^{31}	g^{32}	g^{33}	g^{34}	\dots		
							g^{41}	g^{42}	g^{43}	g^{44}	\dots		
							\vdots	\vdots	\vdots	\vdots	\ddots		

(the summation is taken over all recurring indices). Taking into account that $g^{ps} = g^{sp}$ and $\Omega_{ps}^{\cdot h} = -\Omega_{sp}^{\cdot h}$ one has

$$g^{ps} \Omega_{ps}^{\cdot h} \frac{\partial \psi}{\partial x^h} = 0.$$

Changing index p to s and s to p in the fourth addend we obtain

$$-g^{ps} g_{pv} g^{hu} \Omega_{su}^{\cdot v} \frac{\partial \psi}{\partial x^h} = -g^{sp} g_{sv} g^{hu} \Omega_{pu}^{\cdot v} \frac{\partial \psi}{\partial x^h} = -g^{ps} g_{sv} g^{hu} \Omega_{pu}^{\cdot v} \frac{\partial \psi}{\partial x^h},$$

i.e., the fourth and the fifth addends are equal. Since

$$g^{ps} g_{sv} = \delta_v^p,$$

then (71) is

$$-\frac{2}{\hbar^2} T \psi = g^{ps} \frac{\partial^2 \psi}{\partial x^p \partial x^s} - g^{ps} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} - 2g^{hu} \Omega_{pu} \frac{\partial \psi}{\partial x^h}. \quad (72)$$

In accordance with [14] we have expressions for Christoffel symbols

$$\left\{ \begin{matrix} h \\ ps \end{matrix} \right\} = \frac{1}{2} g^{ht} (\partial_p g_{st} + \partial_s g_{pt} - \partial_t g_{ps}) \quad (73)$$

and those for objects of anholonomy

$$\Omega_{ps}^{\cdot h} = A_p^\lambda A_s^\mu \partial_{[\lambda} A_{\mu]}^h. \quad (74)$$

It should be noted that non-holonomic components [14] and derivatives with respect to them are

$$(d\zeta)^h = A_v^h d\zeta^v, \quad \partial_p = A_p^\mu \partial_\mu \quad (h, p = 1, 2, \dots, 3N).$$

In (74) the operation of alternation is

$$\partial_{[\lambda} A_{\mu]}^h = \frac{1}{2} (\partial_\lambda A_\mu^h - \partial_\mu A_\lambda^h).$$

As was mentioned above, the summation is taken over all recurring indices from 1 to $3N$. In what follows we use the summation in an explicit form because it is necessary to distinguish among translation, rotation and internal variables:

$$\sum_{p=1}^{3N} (\dots) = \sum_{\substack{R\alpha \\ (\alpha=x,y,z)}} (\dots) + \sum_{\substack{\omega\alpha \\ (\alpha=x,y,z)}} (\dots) + \sum_{j=1}^{3N-6} (\dots). \quad (75)$$

Let us consider every addend in (72).

9.2. The second addend in (72)

This addend is

$$\begin{aligned} & - \sum_{p=1}^{3N} \sum_{s=1}^{3N} g^{ps} \sum_{h=1}^{3N} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} \\ & = -\frac{1}{2} \sum_{p=1}^{3N} \sum_{s=1}^{3N} g^{ps} \sum_{h=1}^{3N} \sum_{t=1}^{3N} g^{ht} (\partial_p g_{st} + \partial_s g_{pt} - \partial_t g_{ps}) \frac{\partial \psi}{\partial x^h}. \end{aligned} \quad (76)$$

The use of explicit form of the matrices (tables 1 and 2) symplifies the work with numerous sums, while going to the molecular variables in accordance with (75), the right side of (76) is represented as

$$\begin{aligned}
& - \sum_{p=1}^{3N} \sum_{s=1}^{3N} g^{ps} \sum_{h=1}^{3N} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} \\
& = - \frac{1}{2} \sum_{\alpha} g^{\widehat{R\alpha} \widehat{R\alpha}} \sum_{h=1}^{3N} \sum_{t=1}^{3N} g^{ht} (\partial_{\widehat{R\alpha}} g_{\widehat{R\alpha}t} + \partial_{\widehat{R\alpha}} g_{\widehat{R\alpha}t} - \partial_t g_{\widehat{R\alpha} \widehat{R\alpha}}) \frac{\partial \psi}{\partial x^h} \\
& \quad - \frac{1}{2} \sum_{\alpha} g^{\widehat{\omega\alpha} \widehat{\omega\alpha}} \sum_{h=1}^{3N} \sum_{t=1}^{3N} g^{ht} (\partial_{\widehat{\omega\alpha}} g_{\widehat{\omega\alpha}t} + \partial_{\widehat{\omega\alpha}} g_{\widehat{\omega\alpha}t} - \partial_t g_{\widehat{\omega\alpha} \widehat{\omega\alpha}}) \frac{\partial \psi}{\partial x^h} \\
& \quad - \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \sum_{h=1}^{3N} \sum_{t=1}^{3N} g^{ht} (\partial_j g_{kt} + \partial_k g_{jt} - \partial_t g_{jk}) \frac{\partial \psi}{\partial x^h}.
\end{aligned}$$

In parentheses of the first addend only those of $g_{\widehat{R\alpha}t}$ (see table 1) are not equal to zero for which $t = \widehat{R\alpha}$, $g_{\widehat{R\alpha} \widehat{R\alpha}} = M = \text{const}$. Therefore, all derivatives are equal to zero and the first addend is also zero. Similarly in parentheses of the second addend only $g_{\widehat{\omega\alpha} \widehat{\omega\alpha}}$ are not zero, $g_{\widehat{\omega\alpha} \widehat{\omega\alpha}} = I_{\alpha}$, the moments of inertia depending only on the internal variables ξ^j . If one takes into consideration that, in accordance with table 1, $g_{\widehat{R\alpha}j} = g_{\widehat{\omega\alpha}k} = 0$ then we obtain

$$\begin{aligned}
& - \sum_{p=1}^{3N} \sum_{s=1}^{3N} g^{ps} \sum_{h=1}^{3N} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} \\
& = \frac{1}{2} \sum_{\alpha} I_{\alpha}^{-1} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} (\partial_k I_{\alpha}) \frac{\partial \psi}{\partial \xi^j} \\
& \quad - \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \sum_{i=1}^{3N-6} \sum_{l=1}^{3N-6} g^{il} (\partial_j g_{kl} + \partial_k g_{jl} - \partial_l g_{jk}) \frac{\partial \psi}{\partial \xi^i}.
\end{aligned}$$

To simplify these expressions it is necessary to use the relations among variables obtained in the sections 2–6 of this work. In that case the form of the second addend in (72) is

$$\begin{aligned}
& - \sum_{p=1}^{3N} \sum_{s=1}^{3N} g^{ps} \sum_{h=1}^{3N} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} \\
& = \sum_{\alpha} I_{\alpha}^{-1} \sum_j \sum_{\tau} \left\{ \sum_{\beta} r^{\tau\beta} A_{\tau\beta}^j - r^{\tau\alpha} A_{\tau\alpha}^j \right\} \frac{\partial \psi}{\partial \xi^j} \\
& \quad + \sum_i \sum_{\tau} \sum_{\alpha} \sum_{\eta} \sum_{\beta} m_{\tau}^{-1} \left(\sum_j B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^i \frac{\partial \psi}{\partial \xi^i}, \tag{77}
\end{aligned}$$

where $A_{\widehat{\tau\alpha\eta\beta}}^i = \partial^2 \xi^i / (\partial r_*^{\tau\alpha} \partial r_*^{\eta\beta})$.

9.3. The third addend in (72) and sum of the second and the third addends

In the third addend non-zero components of the object of anholonomy are obtained from (74) together with (17), (18)

$$\Omega_{pu}^{\cdot p} = \Omega_{\widehat{\omega\alpha j}}^{\cdot \widehat{\omega\alpha}} = \frac{1}{2I_\alpha} \sum_{\tau} m_{\tau} \left(\sum_{\beta} r^{\tau\beta} B_j^{\tau\beta} - r^{\tau\alpha} B_j^{\tau\alpha} \right),$$

$$\alpha = x, y, z; \quad j = 1, 2, \dots, 3N - 6, \quad (78)$$

(there is no summation over p and $\widehat{\omega\alpha}$ in this formula). The other non-zero components to be used are

$$\Omega_{kj}^{\cdot \widehat{\omega\alpha}} = \frac{1}{I_\alpha} \sum_{\tau} m_{\tau} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} = \frac{1}{I_\alpha} \sum_{\tau} m_{\tau} \sum_{\beta} \sum_{\gamma} \varepsilon_{\alpha\beta\gamma} B_k^{\tau\beta} B_j^{\tau\gamma},$$

$$\alpha = x, y, z; \quad k, j = 1, 2, \dots, 3N - 6. \quad (79)$$

By taking into account (78), the third addend is

$$\begin{aligned} & -2 \sum_{h=1}^{3N} \sum_{u=1}^{3N} \sum_{p=1}^{3N} g^{hu} \Omega_{pu}^{\cdot p} \frac{\partial \psi}{\partial x^h} \\ &= -2 \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \sum_{\alpha} g^{ij} \Omega_{\widehat{\omega\alpha j}}^{\cdot \widehat{\omega\alpha}} \frac{\partial \psi}{\partial \xi^i} \\ &= - \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \sum_{\alpha} g^{ij} I_\alpha^{-1} \sum_{\tau} m_{\tau} \left(\sum_{\beta} r^{\tau\beta} B_j^{\tau\beta} - r^{\tau\alpha} B_j^{\tau\alpha} \right) \frac{\partial \psi}{\partial \xi^i} \\ &= - \sum_{i=1}^{3N-6} \sum_{\alpha} I_\alpha^{-1} \sum_{\tau} \left[\sum_{\beta} r^{\tau\beta} \left(m_{\tau} \sum_{j=1}^{3N-6} g^{ij} B_j^{\tau\beta} \right) - r^{\tau\alpha} \left(m_{\tau} \sum_{j=1}^{3N-6} g^{ij} B_j^{\tau\alpha} \right) \right] \frac{\partial \psi}{\partial \xi^i}. \end{aligned}$$

Comparison of the expression in parentheses and (50) shows that

$$-2 \sum_{h=1}^{3N} \sum_{u=1}^{3N} \sum_{p=1}^{3N} g^{hu} \Omega_{pu}^{\cdot p} \frac{\partial \psi}{\partial x^h} = - \sum_{\alpha} I_\alpha^{-1} \sum_{i=1}^{3N-6} \sum_{\tau} \left(\sum_{\beta} r^{\tau\beta} A_{\tau\beta}^i - r^{\tau\alpha} A_{\tau\alpha}^i \right) \frac{\partial \psi}{\partial \xi^i}.$$

In (72) the sum of the third and the second (77) addends is

$$\begin{aligned} & -g^{ps} \left\{ \begin{matrix} h \\ ps \end{matrix} \right\} \frac{\partial \psi}{\partial x^h} - 2g^{hu} \Omega_{pu}^{\cdot p} \frac{\partial \psi}{\partial x^h} \\ &= \sum_i \left[\sum_{\tau} \sum_{\alpha} \sum_{\eta} \sum_{\beta} m_{\tau}^{-1} \left(\sum_j B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\widehat{\tau\alpha\eta\beta}}^i \right] \frac{\partial \psi}{\partial \xi^i}, \quad (80) \end{aligned}$$

where $A_{\tau\alpha\eta\beta}^i = \partial^2 \xi^i / (\partial r_*^{\tau\alpha} \partial r_*^{\eta\beta})$, in the left side the summation being taken over recurring indices from 1 to $3N$. The expression in parentheses can be transformed in accordance with (44), (45), but there is no necessity to make it.

10. The first addend in (72)

Detailed examination of this addend is necessary due to non-zero components of the object of anholonomy (79), since, in accordance with [13], the following relations must take place:

$$\frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} - \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} = 2 \sum_{\alpha} \Omega_{kj}^{\cdot\widehat{\omega}\alpha} \frac{\partial \psi}{\partial \widetilde{\omega}^{\alpha}}; \quad k \neq j, \quad k, j = 1, 2, \dots, 3N - 6. \quad (81)$$

It should be noted that in [13] as well as in other works on analytical mechanics so-called three-indices symbols γ_{ps}^h are in common use instead of objects of anholonomy. These symbols satisfy the relation

$$\gamma_{ps}^h = 2\Omega_{ps}^{\cdot h}.$$

Let us write out the first addend in (72) expressed in the molecular variables, taking into consideration the form of the metric tensor from table 2.

$$g^{ps} \frac{\partial^2 \psi}{\partial x^p \partial x^s} = M^{-1} \sum_{\alpha} \frac{\partial^2 \psi}{\partial R_c^{\alpha} \partial R_c^{\alpha}} + \sum_{\alpha} I_{\alpha}^{-1} \frac{\partial^2 \psi}{\partial \widetilde{\omega}^{\alpha} \partial \widetilde{\omega}^{\alpha}} + \sum_j \sum_k g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k}. \quad (82)$$

In the last term the indices j, k form couples (jk) denoting addends in the sum. Both indices range $1, 2, \dots, 3N - 6$ independently. Let us define them in the following way: when $j = k$ let us denote them $l = 1, 2, \dots, 3N - 6$; in the other cases let it be $j < k$ for every couple, so that $j = 1, 2, \dots, 3N - 7, k = 2, 3, \dots, 3N - 6$. In so doing in (82) the last addend is

$$\begin{aligned} & \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} \\ &= \sum_{l=1}^{3N-6} g^{ll} \frac{\partial^2 \psi}{\partial \xi^l \partial \xi^l} + \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{kj} \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} + \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k}. \end{aligned}$$

Relation (81) is rewritten as

$$\frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} = \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} + 2 \sum_{\alpha} \Omega_{kj}^{\cdot\widehat{\omega}\alpha} \frac{\partial \psi}{\partial \widetilde{\omega}^{\alpha}}, \quad k > j. \quad (83)$$

Substituting it in the previous formula we obtain

$$\begin{aligned}
& \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} \\
&= \sum_{l=1}^{3N-6} g^{ll} \frac{\partial^2 \psi}{\partial \xi^l \partial \xi^l} + 2 \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{kj} \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} \\
&\quad + 2 \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{jk} \sum_{\alpha} \Omega_{kj}^{\omega\alpha} \frac{\partial \psi}{\partial \tilde{\omega}^{\alpha}} \\
&= \sum_{l=1}^{3N-6} g^{ll} \frac{\partial^2 \psi}{\partial \xi^l \partial \xi^l} + 2 \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{kj} \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} \\
&\quad + 2 \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{jk} \sum_{\alpha} \frac{1}{I_{\alpha}} \sum_{\tau=1}^N m_{\tau} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \frac{\partial \psi}{\partial \tilde{\omega}^{\alpha}}. \tag{84}
\end{aligned}$$

As $\vec{B}_k^{\tau} \times \vec{B}_j^{\tau} = 0$ when $j = k$, the condition to $(k > j)$ can be changed to $(k \geq j)$ in the last addend. This leads (84) to the expression

$$\begin{aligned}
& \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} \\
&= \sum_{l=1}^{3N-6} g^{ll} \frac{\partial^2 \psi}{\partial \xi^l \partial \xi^l} + 2 \sum_{k>j}^{3N-6} \sum_{j=1}^{3N-7} g^{jk} \frac{\partial^2 \psi}{\partial \xi^k \partial \xi^j} \\
&\quad + 2 \sum_{\alpha} \frac{1}{I_{\alpha}} \sum_{\tau=1}^N m_{\tau} \left\{ \sum_{k \geq j}^{3N-6} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \right\} \frac{\partial \psi}{\partial \tilde{\omega}^{\alpha}}. \tag{85}
\end{aligned}$$

In the right side of (83) the second addend can be presented as an isolated (the last) addend in the right sides of (84), (85). This allows one to rewrite (85) in the form

$$\begin{aligned}
& \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} \\
&= \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \left(\frac{\partial^2 \psi}{\partial \xi^j \partial \xi^k} \right)_{\text{comm}} \\
&\quad + 2 \sum_{\alpha} \frac{1}{I_{\alpha}} \sum_{\tau=1}^N m_{\tau} \left\{ \sum_{k \geq j}^{3N-6} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \right\} \frac{\partial \psi}{\partial \tilde{\omega}^{\alpha}},
\end{aligned}$$

where $\partial^2\psi/(\partial\xi^j\partial\xi^k) \neq \partial^2\psi/(\partial\xi^k\partial\xi^j)$ in the left side in accordance with (81), (83) and $\partial^2\psi/(\partial\xi^j\partial\xi^k)_{\text{comm}} = \partial^2\psi/(\partial\xi^k\partial\xi^j)_{\text{comm}}$ in the right side. In such a manner, (82), i.e., the first addend in (72), is as follows:

$$g^{ps} \frac{\partial^2\psi}{\partial x^p \partial x^s} = M^{-1} \sum_{\alpha} \frac{\partial^2\psi}{\partial R_c^\alpha \partial R_c^\alpha} + \sum_{\alpha} I_\alpha^{-1} \frac{\partial^2\psi}{\partial \tilde{\omega}^\alpha \partial \tilde{\omega}^\alpha} + \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \left(\frac{\partial^2\psi}{\partial \xi^j \partial \xi^k} \right)_{\text{comm}} + 2 \sum_{\alpha} \frac{1}{I_\alpha} \sum_{\tau=1}^N m_\tau \left\{ \sum_{k \geq j} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^\tau \times \vec{B}_j^\tau)^\alpha \right\} \frac{\partial\psi}{\partial \tilde{\omega}^\alpha}. \quad (86)$$

10.1. Laplacian and Schrödinger equation expressed in the Laboratory variables

Taking into account (80), (86), Laplacian (72) acting on the absolute scalar ψ can be written as

$$-\frac{2}{\hbar^2} T\psi = \frac{1}{M} \sum_{\alpha} \frac{\partial^2\psi}{\partial R_c^\alpha \partial R_c^\alpha} + \sum_{\alpha} I_\alpha^{-1} \frac{\partial^2\psi}{\partial \tilde{\omega}^\alpha \partial \tilde{\omega}^\alpha} + \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \left(\frac{\partial^2\psi}{\partial \xi^j \partial \xi^k} \right)_{\text{comm}} + 2 \sum_{\alpha} \frac{1}{I_\alpha} \sum_{\tau=1}^N m_\tau \left[\sum_{k \geq j} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^\tau \times \vec{B}_j^\tau)^\alpha \right] \frac{\partial\psi}{\partial \tilde{\omega}^\alpha} + \sum_{k=1}^{3N-6} \left[\sum_{\tau=1}^N \sum_{\eta=1}^N \sum_{\alpha} \sum_{\beta} m_\tau^{-1} \left(\sum_{j=1}^{3N-6} B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^k \right] \frac{\partial\psi}{\partial \xi^k}, \quad (87)$$

where $A_{\tau\alpha\eta\beta}^k = \partial^2\xi^k/(\partial r_*^{\tau\alpha} \partial r_*^{\eta\beta})$. The Schrödinger equation is obtained through multiplying both sides of (87) by $(-\hbar^2/2)$ and adding the potential energy function U

$$-\frac{\hbar^2}{2} \left\{ \frac{1}{M} \sum_{\alpha} \frac{\partial^2\psi}{\partial R_c^\alpha \partial R_c^\alpha} + \sum_{\alpha} I_\alpha^{-1} \frac{\partial^2\psi}{\partial \tilde{\omega}^\alpha \partial \tilde{\omega}^\alpha} + \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \left(\frac{\partial^2\psi}{\partial \xi^j \partial \xi^k} \right)_{\text{comm}} + 2 \sum_{\alpha} \frac{1}{I_\alpha} \sum_{\tau=1}^N m_\tau \left[\sum_{k \geq j} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^\tau \times \vec{B}_j^\tau)^\alpha \right] \frac{\partial\psi}{\partial \tilde{\omega}^\alpha} + \sum_{k=1}^{3N-6} \left[\sum_{\tau=1}^N \sum_{\eta=1}^N \sum_{\alpha} \sum_{\beta} m_\tau^{-1} \left(\sum_{j=1}^{3N-6} B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^k \right] \frac{\partial\psi}{\partial \xi^k} \right\} + U\psi = E\psi. \quad (88)$$

Let us represent $-\hbar^2 = (-i\hbar)(-i\hbar)$ and introduce operators

$$P_\alpha = -i\hbar \frac{\partial}{\partial R_c^\alpha}, \quad L_\alpha = -i\hbar \frac{\partial}{\partial \tilde{\omega}^\alpha} \quad (\alpha = x, y, z); \quad (89) \\ p_k = -i\hbar \frac{\partial}{\partial \xi^k}, \quad k = 1, 2, \dots, 3N-6.$$

Then (88) has the form

$$\begin{aligned}
& \left\{ \frac{1}{2M} \sum_{\alpha} P_{c\alpha} P_{c\alpha} + \sum_{\alpha} \frac{1}{2I_{\alpha}} L_{\alpha} L_{\alpha} + \frac{1}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} p_j p_k \right. \\
& - i\hbar \sum_{\alpha} \frac{1}{I_{\alpha}} \sum_{\tau=1}^N m_{\tau} \left[\sum_{k \geq j}^{3N-6} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \right] L_{\alpha} \\
& \left. - \frac{i\hbar}{2} \sum_{k=1}^{3N-6} \left[\sum_{\tau=1}^N \sum_{\alpha} \sum_{\eta=1}^N \sum_{\beta} m_{\tau}^{-1} \left(\sum_{j=1}^{3N-6} B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^k \right] p_k \right\} \\
& + U\psi = E\psi, \tag{90}
\end{aligned}$$

where $i = \sqrt{-1}$. The expression in braces $\{\dots\}$ is the kinetic energy operator T of the nonrelativistic N -particle system in the principal central moving axes. It is evident that the Hamiltonian of this system and the Schrödinger equation (90) are

$$H = T + U, \quad H\psi = E\psi.$$

Restricting oneself to only Coulomb interaction among particles forming a molecule, the potential energy function is

$$U = \frac{1}{4\pi\epsilon_0} \sum_{\eta} \sum_{\tau \neq \eta} \frac{1}{2} \frac{e_{\tau} e_{\eta}}{r^{\tau\eta}}, \tag{91}$$

in nonrelativistic approximation. Here e_{τ} – a charge of τ th particle (with an appropriate sign), $r^{\tau\eta}$ – a distance between the τ th and the η th particles.

11. Jacobian, volume element, rovibronic equation and the Hamiltonian

It is well known (e.g., [17]) that Jacobi matrix for transition from variables x_i ($i = 1, 2, \dots, n$) to functions $F_l(x)$ ($l = 1, 2, \dots, m$) is

$$M = \begin{pmatrix} \frac{\partial F_1}{\partial x_1} & \frac{\partial F_1}{\partial x_2} & \cdots & \frac{\partial F_1}{\partial x_n} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial F_m}{\partial x_1} & \frac{\partial F_m}{\partial x_2} & \cdots & \frac{\partial F_m}{\partial x_n} \end{pmatrix}. \tag{92}$$

If $m = n$ then determinant of (92) is Jacobian to be denoted as $\mathcal{D} = \det M$. In our case, we consider x_i in (92) to be the molecular variables dR_{α}^{α} , $d\tilde{\omega}^{\alpha}$ ($\alpha = x, y, z$); $d\xi^k$ ($k = 1, 2, \dots, 3N - 6$) whereas the laboratory variables $dr_{*}^{\tau\alpha}$ ($\tau = 1, 2, \dots, N$; $\alpha = x, y, z$) play the role of F_l . By using (18) it can be shown that the Jacobi matrix (92) (let it be B) has the form displayed in table 3.

In accordance with (17) the inverse matrix $A = B^{-1}$ is displayed in table 4.

$$\begin{aligned} \mathcal{D} &= [\det(B)\det(B')]^{1/2} = \left[\left(\prod_{\tau=1}^N m_{\tau}^3 / \prod_{\eta=1}^N m_{\eta}^3 \right) \det(B)\det(B') \right]^{1/2} \\ &= \left(\prod_{\eta=1}^N m_{\eta}^3 \right)^{-1/2} [\det(B_1)\det(B')]^{1/2} = \left(\prod_{\eta=1}^N m_{\eta}^3 \right)^{-1/2} [\det(B_1 B')]^{1/2}. \end{aligned}$$

The matrix B_1 results from B table 3 by multiplying every of three rows $dr_*^{\tau\alpha}$ by m_{τ} ($\alpha = x, y, z, \tau = 1, 2, \dots, N$). The product $B_1 B'$ is the matrix depicted in table 1, i.e.,

$$\mathcal{D} = \left(\prod_{\eta=1}^N m_{\eta}^3 \right)^{-1/2} [\det(g_{ps})]^{1/2}.$$

In a similar manner, by using the matrix A from table 4 we obtain

$$\begin{aligned} \mathcal{D} &= [\det(A)\det(A')]^{-1/2} = \left[\left(\prod_{\tau=1}^N m_{\tau}^3 / \prod_{\eta=1}^N m_{\eta}^3 \right) \det(A)\det(A') \right]^{-1/2} \\ &= \left(\prod_{\tau=1}^N m_{\tau}^3 \right)^{-1/2} [\det(A_1 A')]^{1/2} = \left(\prod_{\tau=1}^N m_{\tau}^3 \right)^{-1/2} [\det(g^{ps})]^{-1/2}. \end{aligned}$$

The matrix A_1 results from A by multiplying every of three columns $dr_*^{\eta\alpha}$ by m_{η} , $\eta = 1, 2, \dots, N$. The product $A_1 A'$ coincides with the matrix shown in table 2. Taking into consideration table 1, table 2, the final expression is

$$\mathcal{D} = \left(\frac{M^3}{\prod_{\eta=1}^N m_{\eta}^3} \right)^{1/2} \mathcal{D}', \quad (94)$$

$$\mathcal{D}' = [I_x(\xi)I_y(\xi)I_z(\xi)]^{1/2} \{\det[g_{jk}(\xi)]\}^{1/2} = [I_x(\xi)I_y(\xi)I_z(\xi)]^{1/2} \{\det[g^{jk}(\xi)]\}^{-1/2}. \quad (95)$$

In \mathcal{D}' all variables depend on $\xi^1, \xi^2, \dots, \xi^{3N-6}$, only.

As a function of the laboratory variables the volume element is

$$dV = \prod_{\tau=1}^N dr_*^{\tau x} dr_*^{\tau y} dr_*^{\tau z}$$

and as that of the molecular variables

$$dV = |\mathcal{D}| dR_c^x dR_c^y dR_c^z d\tilde{\omega}^x d\tilde{\omega}^y d\tilde{\omega}^z \prod_{j=1}^N d\xi^j. \quad (96)$$

Let us transform the rotational part of the volume element for going from the non-holonomic variables $d\tilde{\omega}^{\alpha}$ ($\alpha = x, y, z$) to differentials $d\varphi, d\theta, d\chi$ of Euler angles which are the generalized (Lagrangian) variables. To accomplish this it is necessary to find

the Jacobi matrix (92) by using (10), $d\varphi$, $d\theta$, $d\chi$ playing the role x_i . Jacobian of this transformation is

$$\det \begin{pmatrix} -\sin \theta \cos \chi & \sin \chi & 0 \\ \sin \theta \sin \chi & \cos \chi & 0 \\ \cos \theta & 0 & 1 \end{pmatrix} = -\sin \theta.$$

Then

$$d\tilde{\omega}^x d\tilde{\omega}^y d\tilde{\omega}^z = |-\sin \theta| d\varphi d\theta d\chi$$

and the final form of (96) is

$$dV = |\mathcal{D}| dR_c^x dR_c^y dR_c^z \sin \theta d\varphi d\theta d\chi \prod_{j=1}^N d\xi^j. \quad (97)$$

Let us denote

$$R \equiv (R_c^x, R_c^y, R_c^z), \quad \zeta \equiv (\varphi, \theta, \chi), \quad \xi \equiv (\xi^1, \xi^2, \dots, \xi^{3N-6}),$$

for short. In this case, (97) is

$$dV = |\mathcal{D}| dR \sin \theta d\zeta d\xi \quad \text{and} \quad \psi = \psi(R, \zeta, \xi). \quad (98)$$

Scalar product of vectors corresponding ψ is

$$(\psi, \psi) = \int_{(R)} \int_{(\zeta)} \int_{(\xi)} |\mathcal{D}| \overline{\psi}(R, \zeta, \xi) \psi(R, \zeta, \xi) dR \sin \theta d\zeta d\xi. \quad (99)$$

As the normalization condition

$$(\psi, \psi) = 1 \quad (100)$$

should be met then taking into account (94) the expression (99) can be rewritten as

$$(\psi, \psi) = \int_{(R)} \int_{(\zeta)} \int_{(\xi)} |\mathcal{D}'| \overline{\psi}(R, \zeta, \xi) \psi(R, \zeta, \xi) dR \sin \theta d\zeta d\xi, \quad (101)$$

since the fixed multiplier in the right side (94) is included in a normalizing factor in (101). The same result is obtained for non-normalized functions ψ in solving the variational problem based on Rayleigh fraction

$$\frac{(\psi, H\psi)}{(\psi, \psi)},$$

or for approximate representation of the Schrödinger equation as a matrix one on a set of basic functions depending on (R, ζ, ξ) .

The general Schrödinger equation both in coordinate representation (88) and in operator one (90) has some peculiarities:

- the coefficient by the operator $\sum_{\alpha} (\partial/\partial R_c^{\alpha})(\partial/\partial R_c^{\alpha})$ does not depend on coordinates;
- the coefficients by the other differential operators, Jacobian (95) and the function of potential energy U (having form (91) for molecules) do not depend on coordinates of center of mass R_c^{α} ($\alpha = x, y, z$).

This leads to the fact that the complete wavefunction can be represented as

$$\psi(R, \zeta, \xi) = \psi_{\text{trans}}(R)\Psi(\zeta, \xi)$$

and motion of center of mass is separated. Ψ – a rovibronic wavefunction is a solution of the Schrödinger equation

$$\begin{aligned} & -\frac{\hbar^2}{2} \left\{ \sum_{\alpha} \frac{1}{I_{\alpha}} \frac{\partial^2 \Psi}{\partial \tilde{\omega}^{\alpha} \partial \tilde{\omega}^{\alpha}} + \sum_{\alpha} \frac{2}{I_{\alpha}} \sum_{\tau} m_{\tau} \left[\sum_{k \geq j}^{3N-6} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \right] \frac{\partial \Psi}{\partial \tilde{\omega}^{\alpha}} \right. \\ & + \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} g^{jk} \left(\frac{\partial^2 \Psi}{\partial \xi^j \partial \xi^k} \right)_{\text{comm}} \\ & \left. + \sum_{k=1}^{3N-6} \left[\sum_{\tau=1}^N \sum_{\alpha} \sum_{\eta=1}^N \sum_{\beta} m_{\tau}^{-1} \left(\sum_{j=1}^{3N-6} B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^k \right] \frac{\partial \Psi}{\partial \xi^k} \right\} \\ & + U\Psi = \mathcal{E}\Psi, \end{aligned} \quad (102)$$

where \mathcal{E} – an eigenvalue of a rovibronic problem. To obtain corresponding Hamiltonian it is necessary to use (89), that leads to

$$\mathcal{H} = \sum_{\alpha} \frac{1}{2I_{\alpha}} L_{\alpha} L_{\alpha} - i\hbar \sum_{\alpha} \frac{1}{I_{\alpha}} W_1^{\alpha} L_{\alpha} + \frac{1}{2} \sum_j \sum_k g^{jk} p_j p_k - i\hbar \sum_k W_2^k p_k + U, \quad (103)$$

where

$$\begin{aligned} W_1^{\alpha} &= \sum_{\tau} m_{\tau} \left[\sum_{k \geq j}^{3N-6} \sum_{j=1}^{3N-6} g^{jk} (\vec{B}_k^{\tau} \times \vec{B}_j^{\tau})^{\alpha} \right], \\ W_2^k &= \frac{1}{2} \sum_{\tau=1}^N \sum_{\alpha} \sum_{\eta=1}^N \sum_{\beta} m_{\tau}^{-1} \left(\sum_{j=1}^{3N-6} B_j^{\eta\beta} A_{\tau\alpha}^j \right) A_{\tau\alpha\eta\beta}^k. \end{aligned}$$

For the rovibronic problem Jacobian has the form (95), the volume element based on (95) is

$$dV_{\text{rovibron}} = |\mathcal{D}'| \sin \theta d\theta d\varphi d\chi \prod_{j=1}^{3N-6} d\xi^j.$$

In this paper the use of (102), (103) for solving various problems is not considered. We only note that if all terms containing \hbar are omitted in (103) then (103) becomes the

classical expression of rovibronic energy that is consistent with the Bohr correspondence principle.

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