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An alternative derivation of (almost-) Watson's Hamiltonian•

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Abstract: A derivation of the general wave-mechanical Hamiltonian for non-linear molecules is presented. It is based on the transformation of proper classical (Hamilton) momenta into their wave-mechanical counterparts by means of the Podolsky Transformation in its original form. The result is essentially identical to that obtained by Watson in his milestone paper (J. K. G. Watson, *Mol. Phys.* **15** (1968) 479). While not so elegant as that of the original reference, the way proposed in the present study is conceptually much simpler. This procedure could also be applied to other types of molecular Hamiltonians.

Keywords: Watson's molecular Hamiltonian; classical kinetic energy; Podolsky transformation.

INTRODUCTION

Among the papers I have been forced to understand, there is hardly one I found so difficult as Watson's milestone study[1] in which he simplified the vibration–rotation Hamiltonian for polyatomic molecules, originally derived by Wilson and Howard.[2,3] Just to reproduce five pages of this paper, I needed a whole month, and in order to decipher the extremely complicated formulae in condensed Levi-Civita form, I penned several hundreds of leaves. It seems that other people also had similar problems. I found once in a very serious paper the sentence: "If the Watson's Hamiltonian is correct …". Even Watson himself wrote in his paper, "The simplicity of the final result suggests that it should be obtainable by a less complicated calculation than that described here, I have, however, been unable to find a more direct derivation." As another illustration of the complexity of this study can serve the fact that as Watson needed two years to apply the same procedure for deriving the Hamiltonian for linear polyatomic molecules,[4] some researchers questioned his results,[5] and that Watson's answer to this

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[•] Dedicated to Professor Branislav Nikolić on the occasion of his 70th birthday.

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criticism came only seven years later.[6] Thus, the goal of the present study was to attempt to derive Watson's Hamiltonian in a less elegant but simpler, or at least more straightforward, way.

Separation of variables represents an unavoidable step that precedes every practical *ab initio* handling of the molecular Schrödinger equation, and/or a treatment of the dynamics of molecules. Experimental spectroscopy indicates that molecular spectra can be understood in a good approximation if the existence of several more or less loosely coupled motion modes is supposed. This concept is supported by theoretical considerations. A „normal" molecule has a relatively rigid nuclear skeleton, *i.e*. the nuclei are held at nearly constant mutual distances. More precisely, the changes of these distances (molecular vibrations) are small compared to the average values of the distances. These average distances determine the equilibrium structure of the molecule. The electrons can be imagined as the constituents of an electron cloud tied to the nuclear skeleton. As a whole, the molecule translates and rotates in space.

There are two main approaches for construction of the wave-mechanical Hamiltonian.[7] In the "first" one (a), the wave-mechanical operator is first derived in terms of Cartesian derivatives and subsequently, these derivatives are replaced by the derivatives with respect to appropriately chosen (typically curvilinear) coordinates, or by some impulses (momenta) not conjugate to any coordinates. This can be represented schematically as

$$E\left(\dot{X}\right)\to H\left(P_X\right)\to \hat{H}\left(\hat{P}_X\right)\to \hat{H}\left(\hat{P}_q\right) \tag{1}$$

where $\hat{P}_X = -i\hbar\partial/\partial X$, but in general, $\hat{P}_q \neq -i\hbar\partial/\partial q$. In the "second" approach (b), one derives first the classical Hamiltonian in terms of (classical) impulses conjugate to chosen non-Cartesian coordinates and only after that are these impulses replaced by the corresponding wave-mechanical operators:

$$E\left(\dot{X}\right)\to E\left(\dot{q}\right)\to H\left(P_q\right)\to \hat{H}\left(\hat{P}_q\right) \tag{2}$$

This alternate way was invented by Podolsky and it is called the Podolsky transformation.[8] Sometimes, Hamiltonians are even derived in terms of momenta not conjugate to any coordinates (such momenta are not "true momenta" in the sense of the Hamilton formalism).[1,3,4]

WILSON–WATSON'S HAMILTONIAN

Only the construction of the kinetic energy part of the Hamiltonian will be considered. The transformation of the potential energy is trivial since it only depends on the distances between the particles (electrons and nuclei) and these are invariant to changes in coordinate frames.

An isolated polyatomic molecule composed of S (>2) nuclei $A,B,...,S$, and N electrons, $1,...\mu,...,N$, with non-linear equilibrium geometry, is considered and handled in the non-relativistic approximation. When summing over electrons, Greek letters, $\mu,\nu,...$ will be used. The nuclear masses will be denoted by $m_A,...,m_S$, and the electron mass by m_e. The total mass of the nuclei is denoted by M_n, and the mass of the molecule by M ($M = M_n + Nm_e$). One starts with a space-fixed coordinate system (SFS). A disadvantage of this is that all the molecular motion modes are mixed in it. For this reason, the Hamiltonian is transformed to the coordinate system with the axes parallel to those of the SFS and the origin coinciding with the center of mass of the molecule (including both the nuclei and electrons, $MCMS$). This transformation serves to separate off the translational motions of the molecule. A consequence of the introduction of three center of mass coordinates is that one remains with $3(S+N)-3$ linearly independent particle coordinates in the $MCMS$. Thus a set of redundant coordinates, say those of the nucleus A, is eliminated, and they are expressed as linear combinations of the coordinates of the other nuclei ($B,...,S$).

The $MCMS$ has two drawbacks: First, in the $MCMS$, the coordinates of the nuclei and electrons are (indeed weakly, $\sim m_e / M_n$) coupled. Secondly, contrary to the situation with the nuclear skeleton, which has at any moment a definite structure (it determines the „geometry“ of the molecule), the „electron cloud“ cannot be associated with any simple geometric structure. For these reasons, the positions of all particles are related to the center of mass of the nuclei (*NCMS*). Since the axes of all three mentioned coordinate systems are mutually parallel, the transformation of the kinetic energy expressions is relatively simple and can be realized separately for X,Y and Z coordinates. The position vectors of the nuclei in the *NCMS* will be denoted by $\left(\vec{R}_A\right),\vec{R}_B,...,\vec{R}_S$ and that of the μ^{th} electron by $\vec{R}_\mu$ ($\mu = 1,2,...,N$).

The classical kinetic energy in the velocity form in the *NCMS* is:[7]

$$\begin{aligned} T = T_n + T_e = \frac{1}{2}\sum_{K=B}^{S} m_K\left(\dot{X}_K^2 + \dot{Y}_K^2 + \dot{Z}_K^2\right) + \\ + \frac{1}{2m_A}\sum_{K=B}^{S}\sum_{L=B}^{S} m_K m_L\left(\dot{X}_K\dot{X}_L + \dot{Y}_K\dot{Y}_L + \dot{Z}_K\dot{Z}_L\right) + \\ + \frac{1}{2}m_e\sum_{\mu=1}^{N}\left(\dot{X}_\mu^2 + \dot{Y}_\mu^2 + \dot{Z}_\mu^2\right) - \frac{m_e^2}{2M}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\dot{X}_\mu\dot{X}_\nu + \dot{Y}_\mu\dot{Y}_\nu + \dot{Z}_\mu\dot{Z}_\nu\right) \end{aligned} \tag{3}$$

where $\dot{X}_K \equiv \mathrm{d}X_K / \mathrm{d}t$ *etc*. are time derivatives of the coordinates. The corresponding wave-mechanical operator is:

$$\hat{T}=\hat{T}_n+\hat{T}_e=-\frac{\hbar^2}{2}\sum_{K=B}^{S}\frac{1}{m_K}\left(\frac{\partial^2}{\partial X_K^2}+\frac{\partial^2}{\partial Y_K^2}+\frac{\partial^2}{\partial Z_K^2}\right)+$$
$$+\frac{\hbar^2}{2M_n}\sum_{K=B}^{S}\sum_{L=B}^{S}\left(\frac{\partial^2}{\partial X_K\partial X_L}+\frac{\partial^2}{\partial Y_K\partial Y_L}+\frac{\partial^2}{\partial Z_K\partial Z_L}\right)- \tag{4}$$
$$-\frac{\hbar^2}{2m_e}\sum_{\mu=1}^{N}\left(\frac{\partial^2}{\partial X_\mu^2}+\frac{\partial^2}{\partial Y_\mu^2}+\frac{\partial^2}{\partial Z_\mu^2}\right)-\frac{\hbar^2}{2M_n}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\frac{\partial^2}{\partial X_\mu\partial X_\nu}+\frac{\partial^2}{\partial Y_\mu\partial Y_\nu}+\frac{\partial^2}{\partial Z_\mu\partial Z_\nu}\right)$$

Since the translational motion is of no interest, from now on, as a rule, the terms „space-fixed coordinate system“ and „nuclear center of mass system“ will be used as synonyms. In this way, the distinction between these two systems (having parallel corresponding axes), on the one hand, and the molecule-fixed coordinate system (MFS) that follows the rotation of the molecule (this is just going to be introduced), on the other hand, will be more clearly expressed.

The form of the kinetic energy operator (4) is not yet optimal because in it, the vibrational and rotational coordinates of the nuclei are completely mixed (they are hidden in Cartesian coordinates). Thus, the rotational motion of the molecule will now be separated, as well as possible, from vibrations of the nuclei. In order to accomplish this, a coordinate system is introduced with the origin in the $NCMS$ but with the axes x, y, and z differently oriented than those of the $SFS\,/\,NCMS$. The unit vectors along the x-, y- and z-axes are denoted by $\vec{i}$, $\vec{j}$ and $\vec{k}$, and the unit vectors along the space-fixed axes X, Y and Z by $\vec{I}, \vec{J}$ and $\vec{K}$. The position vector of the i th particle in the SFS will be denoted in the general case (nucleus or electron) by $\vec{R}_k$. Its components are X_k, Y_k and Z_k. For the same position vector in the MFS, the symbol $\vec{r}_k$ will be used. The components of $\vec{r}_k$ are x_k, y_k and z_k. Since both the coordinate frames have the same origin, $\vec{R}_k=\vec{r}_k$, that is:

$$\vec{R}_k\equiv X_k\vec{I}+Y_k\vec{J}+Z_k\vec{K}=x_k\vec{i}+y_k\vec{j}+z_k\vec{k}\equiv\vec{r}_k \tag{5}$$

For derivation of the classical Hamiltonian and the angular momentum, the time derivative of this (these) vector(s) is (are) required. One can differentiate both in the SFS and MFS. When the differentiation is realized by an observer in the SFS, symbols like $\dot{\vec{R}}_k, \dot{\vec{r}}_k$ will be used and for differentiation within the MFS, $\mathring{\vec{R}}_k, \mathring{\vec{r}}_k$. Differentiating in the SFS, $\vec{R}_k$, *i.e.*, the radius-vector with the components along the SFS -axes, one obtains:

$$\dot{\vec{R}}_k=\left(\dot{X}_k\vec{I}+\dot{Y}_k\vec{J}+\dot{Z}_k\vec{K}\right)+\left(X_k\dot{\vec{I}}+Y_k\dot{\vec{J}}+Z_k\dot{\vec{K}}\right)=\dot{X}_k\vec{I}+\dot{Y}_k\vec{J}+\dot{Z}_k\vec{K} \tag{6}$$

because the unit vectors $\vec{I},\vec{J},\vec{K}$ do not change in time ($\dot{\vec{I}}=0,\dot{\vec{J}}=0,\dot{\vec{K}}=0$). However, if the same vector is differentiated in the SFS, but expressed in terms of the components along the MFS -axes, it has to be taken into account that for the observer in the *SFS* not only do the components of the vector (x_k, y_k, z_k) change, but also the unit vectors $\vec{i}, \vec{j}, \vec{k}$. Thus:

$$\dot{\vec{r}}_k = \left(\dot{x}_k \vec{i} + \dot{y}_k \vec{j} + \dot{z}_k \vec{k} \right) + \left(x_k \dot{\vec{i}} + y_k \dot{\vec{j}} + z_k \dot{\vec{k}} \right) \tag{7}$$

On the other hand, if the same vector is differentiated within the *MFS* , one obtains:

$$\mathring{\vec{r}}_k = \left(\mathring{x}_k \vec{i} + \mathring{y}_k \vec{j} + \mathring{z}_k \vec{k} \right) + \left(x_k \mathring{\vec{i}} + y_k \mathring{\vec{j}} + z_k \mathring{\vec{k}} \right) = \dot{x}_k \vec{i} + \dot{y}_k \vec{j} + \dot{z}_k \vec{k} \tag{8}$$

The expression on the right-hand side follows from the fact that for the observer in the MFS, the unit vectors $\vec{i}, \vec{j}, \vec{k}$ are at rest ($\mathring{\vec{i}} = \mathring{\vec{j}} = \mathring{\vec{k}} = 0$), and in the non-relativistic approximation, time is the same in all coordinate frames, *i.e.*, $\mathring{x}_k = \dot{x}_k$ *etc*., as for all scalar quantities.

The *MFS* is chosen so that it rotates together with the nuclear skeleton of the molecule, *i.e.*, the coordinate system itself takes over (as completely as possible) the molecular rotations, while (ideally) the only kind of motion of the nuclei within it represent vibrations. The orientation of the *MFS*-axes with respect to the axes of the *SFS* is usually defined by means of Euler angles φ, θ, χ . They are certain functions of the nuclear coordinates. In this way, the number of linearly independent nuclear coordinates in the *MFS* will be reduced to $3S-6$. Let us assume that the coordinates of nucleus *B* are eliminated by the relations $\xi_B = f_{\xi_B}(x_C, ..., z_S)$, where $\xi = x, y, z$. Besides, there are $3N$ electronic coordinates, $x_\alpha, y_\alpha, z_\alpha$, $..., x_N, y_N, z_N$. Thus, there are the following two sets of $3(S+N)-3$ coordinates: a) *NCMS*: $\vec{R}_B, ..., \vec{R}_S$, $\vec{R}_1, ..., \vec{R}_\mu, ..., \vec{R}_N$ and b) *MFS*: $\varphi, \theta, \chi, \vec{r}_C, ...,$ $\vec{r}_S, \vec{r}_1, ..., \vec{r}_\mu, ..., \vec{r}_N$. They are related by:

$$\varphi = f_\varphi(X_B, ..., Z_S), \quad \theta = f_\theta(X_B, ..., Z_S), \quad \chi = f_\chi(X_B, ..., Z_S),$$

$$\begin{pmatrix} x_n \\ y_n \\ z_n \end{pmatrix} = \begin{pmatrix} \lambda_{xX}(X_B, ..., Z_S) & \lambda_{xY}(X_B, ..., Z_S) & \lambda_{xZ}(X_B, ..., Z_S) \\ \lambda_{yX}(X_B, ..., Z_S) & \lambda_{yY}(X_B, ..., Z_S) & \lambda_{yZ}(X_B, ..., Z_S) \\ \lambda_{zX}(X_B, ..., Z_S) & \lambda_{zY}(X_B, ..., Z_S) & \lambda_{zZ}(X_B, ..., Z_S) \end{pmatrix} \begin{pmatrix} X_n \\ Y_n \\ Z_n \end{pmatrix} \tag{9}$$

$$n = C, ..., S, 1, ..., N$$

and, reversely,

$$\begin{pmatrix} X_n \\ Y_n \\ Z_n \end{pmatrix} = \begin{pmatrix} \lambda_{Xx}(\varphi,\theta,\chi) & \lambda_{Xy}(\varphi,\theta,\chi) & \lambda_{Xz}(\varphi,\theta,\chi) \\ \lambda_{Yx}(\varphi,\theta,\chi) & \lambda_{Yy}(\varphi,\theta,\chi) & \lambda_{Yz}(\varphi,\theta,\chi) \\ \lambda_{Zx}(\varphi,\theta,\chi) & \lambda_{Zy}(\varphi,\theta,\chi) & \lambda_{Zz}(\varphi,\theta,\chi) \end{pmatrix} \begin{pmatrix} x_n \\ y_n \\ z_n \end{pmatrix}$$

$$n = B,\dots,S,1,\dots,N \qquad (10)$$

$$\left\{ x_B = f_{x_B}(x_C,\dots,z_S), \quad y_B = f_{y_B}(x_C,\dots,z_S), \quad z_B = f_{z_B}(x_C,\dots,z_S) \right\},$$

where the coefficients λ_{Xx}=[$\lambda_{xX} = \vec{i}\cdot\vec{I} = \cos(x,X)$], λ_{Xy}=[$\lambda_{yX} = \vec{j}\cdot\vec{I} = \cos(y,X)$] expressed in terms of the Euler angles φ,θ,χ are:

$$\lambda_{xX} = \cos\varphi\cos\theta\cos\chi - \sin\varphi\sin\chi,\ \lambda_{xY} = \sin\varphi\cos\theta\cos\chi + \cos\varphi\sin\chi,$$

$$\lambda_{xZ} = -\sin\theta\cos\chi$$

$$\lambda_{yX} = -\cos\varphi\cos\theta\sin\chi - \sin\varphi\cos\chi,\ \lambda_{yY} = -\sin\varphi\cos\theta\sin\chi + \cos\varphi\cos\chi, \quad (11)$$

$$\lambda_{yZ} = \sin\theta\sin\chi$$

$$\lambda_{zX} = \cos\varphi\sin\theta,\ \lambda_{zY} = \sin\varphi\sin\theta,\ \lambda_{zZ} = \cos\theta$$

The transformations (10) look completely symmetric with respect to the nuclei and electrons, but in fact, they are not. Since the coefficients $\lambda_{xX},\dots,\lambda_{zZ}$ (*via* the Euler angles φ,θ,χ) are determined (solely) by the positions of the nuclei, the relationship between electronic coordinates in the *SFS* and *MFS* is just an orthogonal linear transformation involving constant coefficients. On the other hand, the transformation of the coordinates of the nuclei is not linear.

The number of linearly independent nuclear coordinates in the *MFS*, $3S-6$, is just necessary and sufficient to define unambiguously the form of the nuclear skeleton. In praxis, the Cartesian coordinates $x_C, y_C, z_C, \dots, x_S, y_S, z_S$ of the nuclei will not be used but rather some "internal coordinates", which determine the positions of the nuclei with respect to one another. These can be chosen in a pure geometric way, such that they represent the bond lengths, the angles between bonds, *etc*. In this paper, however, instead of them, appropriate linear combinations of the displacements of the Cartesian coordinates of the nuclei from their equilibrium positions measured in the *MFS*, the "normal coordinates" $Q_1, Q_2, \dots, Q_{3S-6}$, will be used.

It is easy to show that the form of the electronic part of the kinetic energy operator (4), when carried out *via* the "first way" is not changed during the transition to the *MFS*, *i.e.*, that it becomes:

$$\hat{T}_e = -\frac{\hbar^2}{2m_e}\sum_{\mu=1}^{N}\left(\frac{\partial^2}{\partial x_\mu^2} + \frac{\partial^2}{\partial y_\mu^2} + \frac{\partial^2}{\partial z_\mu^2}\right) - \\ -\frac{\hbar^2}{2M_n}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\frac{\partial^2}{\partial x_\mu \partial x_\nu} + \frac{\partial^2}{\partial y_\mu \partial y_\nu} + \frac{\partial^2}{\partial z_\mu \partial z_\nu}\right) \qquad (12)$$

The invariance of the electronic kinetic energy operator is a consequence of the fact that the transformation matrix (9) is only a function of the nuclear coordinates. The transformation of the nuclear kinetic energy operator is much more complex. For example, the first derivative with respect to the coordinate X_K transforms into:

$$\begin{gathered}\frac{\partial}{\partial X_K} \rightarrow \frac{\partial \varphi}{\partial X_K}\frac{\partial}{\partial \varphi} + \frac{\partial \theta}{\partial X_K}\frac{\partial}{\partial \theta} + \frac{\partial \chi}{\partial X_K}\frac{\partial}{\partial \chi} + \sum_{i=1}^{3S-6}\frac{\partial Q_I}{\partial X_K}\frac{\partial}{\partial Q_I} + \\ + \sum_{\mu=1}^{N}\left(\frac{\partial x_\mu}{\partial X_K}\frac{\partial}{\partial x_\mu} + \frac{\partial y_\mu}{\partial X_K}\frac{\partial}{\partial y_\mu} + \frac{\partial z_\mu}{\partial X_K}\frac{\partial}{\partial z_\mu}\right)\end{gathered} \tag{13}$$

Nothing on the right-hand side vanishes automatically. Not only the Euler angles and normal coordinates, but even the electronic coordinates x_μ, y_μ, z_μ, *via* the elements λ_{xX} ,... of the transformation matrix in Eq. (9) are functions (moreover, very complicated) of the coordinate X_K . The last sum on the right-hand side of Eq. (13) will introduce into the expression for $\partial / \partial X_K$ also derivatives of the electronic coordinates in the *MFS*. The same conclusions hold for the second derivatives. This means that the transformation whose role was to separate the rotations from vibrations introduces a coupling between nuclear and electronic coordinates in the kinetic energy operator. The above analysis of the structure of Eq. (13) shows that a derivation of the expression for $\hat{T}_n$ in the *MFS* in the way applied for transformation of $\hat{T}_e$ into (12) would be very difficult. For this reason, it is more convenient to use instead the "second way" (b).

From now on, the derivation presented in Wilson's book[3] is closely followed It is easy to show that the classical expression for the kinetic energy of the nuclei from Eq. (3) equals:

$$T_n = \frac{1}{2}\sum_{K=A}^{S} m_K\left(\dot{\vec{R}}_K \cdot \dot{\vec{R}}_K\right) = \frac{1}{2}\sum_{K=A}^{S} m_K\left(\dot{X}_K^2 + \dot{Y}_K^2 + \dot{Z}_K^2\right) \tag{14}$$

under the condition:

$$\sum_{K=A}^{S} m_K \vec{R}_K = 0 \tag{15}$$

The following notations are used: $\vec{R}_K$ is the position vector and $\dot{\vec{R}}_K$ the velocity vector of the nucleus K in the *SFS* (more precisely, in the *NCMS*) *i.e.*, the vector whose components are measured along the axes of the *SFS*; $\vec{r}_K$ is the position vector, and $\vec{r}_K^{\,0}$ the equilibrium position vector in the *MFS*; $\Delta\vec{r}_K$ represents the (vibrational) displacement of the nucleus *K* with respect to its equilibrium value and $\vec{r}_K$ is the velocity of the nucleus measured in the *MFS*. The time derivatives of the radius-vector $\vec{r}_K$ as measured in the *SFS* and in the *MFS* rotating with an angular velocity $\vec{\omega}$, respectively, are connected by the relation:

$$\dot{\vec{r}}_K = \overset{\circ}{\vec{r}}_K + \vec{\omega} \times \vec{r}_K \tag{16}$$

The first term on the right-hand side describes the change in time of the vector $\vec{r}_K$ within the *MFS*, and the second term the effect of rotation of this system on the change of $\vec{r}_K$ as measured in the *SFS*. As stated above, the orientation of the *MFS* is determined by the values of the Euler angles φ, θ and χ, chosen in such a way that the relative displacements of the nuclei with respect to one another (vibrations) be minimally coupled with the rotations of the nuclear skeleton. Note that the components of the angular velocity, $\omega_x, \omega_y, \omega_z$, are not „true“ velocities in the sense that they do not represent time derivatives of the corresponding coordinates – they can be expressed as linear combinations of time derivatives of the Euler angles.

Complete separation of the vibrational from the rotational coordinates would be possible if the “vibrational angular momentum”:

$$\vec{J}_v = \sum_{K=A}^{S} m_K \left(\vec{r}_K \times \overset{\circ}{\vec{r}}_K \right) \tag{17}$$

in the *MFS* were vanishing. It turns out, however, that the three scalar equations, $\vec{J}_{vx} = 0, \vec{J}_{vy} = 0,$ and $\vec{J}_{vz} = 0$ do not enable the determination of the values of φ, θ, and χ such that the corresponding vectors $\{\vec{r}_K\}$ and $\{\overset{\circ}{\vec{r}}_K\}$ fulfill the condition $\vec{J}_v = 0$. The best that can be done in trying to separate vibrations from rotations is to replace the condition $\vec{J}_v = 0$ by:

$$\sum_{K=A}^{S} m_K (\vec{r}_K^{\,0} \times \overset{\circ}{\vec{r}}_K) = 0 \tag{18}$$

The quantity on the left-hand side of (18) differs from (17) in that the instantaneous position vectors $\vec{r}_K$ (which appear in $\vec{J}_v$) are replaced by their equilibrium counterparts, $\vec{r}_K^{\,0}$ – the difference between them tends to zero when the nuclei undergo small-amplitude (“infinitesimal”) vibrations. Since the vibrations are commonly characterized by small amplitudes, the condition (18) ensures, as a rule, good separation of the rotations from the vibrational degrees of freedom. It is easy to show that expression (18) can be obtained by differentiating the Eckart condition:[9]

$$\sum_{K=A}^{S} m_K (\vec{r}_K^{\,0} \times \vec{r}_K) = 0 \tag{19}$$

Inserting the expression (16) for the nuclear velocity in (14), replacing $\vec{r}_K$ by $\vec{r}_K^{\,0} + \Delta\vec{r}_K$, taking into account (19), and expanding the vector quantities into their scalar components, one obtains for the classical kinetic energy of the nuclei the expression:

$$\begin{gathered}
T_n = \frac{1}{2}\sum_{K=A}^{S} m_K \left(\dot{\vec{R}}_K \cdot \dot{\vec{R}}_K\right) = \\
= \frac{1}{2} I_{xx}\omega_x^2 + \frac{1}{2} I_{yy}\omega_y^2 + \frac{1}{2} I_{zz}\omega_z^2 + I_{xy}\omega_x\omega_y + I_{yz}\omega_y\omega_z + I_{zx}\omega_z\omega_x + \\
+\omega_x \sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_x + \omega_y \sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_y + \\
+\omega_z \sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_z + \frac{1}{2}\sum_{K=A}^{S} m_K \left(\overset{\circ}{\vec{r}}_K\right)
\end{gathered} \tag{20}$$

where:

$$\begin{gathered}
I_{xx} \equiv \sum_{K=A}^{S} m_K \left(y_K^2 + z_K^2\right), \quad I_{yy} \equiv \sum_{K=A}^{S} m_K \left(z_K^2 + x_K^2\right), \quad I_{zz} \equiv \sum_{K=A}^{S} m_K \left(x_K^2 + y_K^2\right), \\
I_{xy} = I_{yx} = -\sum_{K=A}^{S} m_K x_K y_K, \quad I_{yz} = I_{zy} = -\sum_{K=A}^{S} m_K y_K z_K, \quad I_{zx} = I_{xz} = -\sum_{K=A}^{S} m_K z_K x_K
\end{gathered} \tag{21}$$

are the instantaneous moments and products of inertia. Note that these quantities are not constant but are functions of the nuclear positions, which change in the course of vibrations.

The expression (20) for the kinetic energy of the nuclei consists of three parts. In the first one appear the moments and products of inertia and the components of the angular velocity vector $\vec{\omega}$, and this part describes the rotational motion of the molecule as a whole. The last term on the right-hand side of (20) involves (besides the nuclear masses) only the velocities of the nuclei moving in the *MFS*, and thus represents the vibrational kinetic energy. In the middle term appear both the angular velocity and velocities within the *MFS*; it describes the coupling between the rotations and vibrations. The appearance of this term is a consequence of defining the orientation of the *MFS* axes by means of the conditions (18), instead of equating (17) to zero.

The most convenient way to describe the molecular vibrations is based on the use of the normal coordinates, $Q_1,\ldots,Q_i,\ldots,Q_{3S-6}$. Actually, their form is not known at this stage, because they can be determined only after the introduction of the Born–Oppenheimer approximation[10] and solving the electronic Schrödinger equation at various nuclear arrangements around the equilibrium molecular geometry. Only the fact that these coordinate do exist can be used at this moment. By summing, the normal coordinates are denoted by lowercase Latin subscripts i, j. They are connected with the Cartesian displacement coordinates, $\Delta x_K, \Delta y_K, \Delta z_K$, by the linear relations:

$$\begin{gathered}\sqrt{m_K}\,\Delta x_K = \sum_{i=1}^{3S-6} l_{xK,i} Q_i,\ \sqrt{m_K}\,\Delta y_K = \sum_{i=1}^{3S-6} l_{yK,i} Q_i, \\ \sqrt{m_K}\,\Delta z_K = \sum_{I=1}^{3S-6} l_{zK,i} Q_i, \quad K = 1,\dots,S\end{gathered} \tag{22}$$

where the (constant) coefficients $l_{xK,i}, l_{yK,i}, l_{zK,i}$ are chosen such that the normal coordinates simultaneously reduce the expressions for the kinetic energy and the quadratic part of the potential energy of vibrations to the sums of quadratic terms:

$$T_v = \frac{1}{2}\sum_{i=1}^{3S-6} \dot{Q}_i^2, \quad V = \frac{1}{2}\sum_{i=1}^{3S-6} \lambda_i Q_i^2 \tag{23}$$

Expressed in terms of the normal coordinates, the terms coupling vibrations with rotations are:

$$\begin{gathered}\sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_x = \sum_{i=1}^{3S-6} \Im_i \dot{Q}_i \\ \sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_y = \sum_{i=1}^{3S-6} \Re_i \dot{Q}_i \\ \sum_{K=A}^{S} m_K (\Delta\vec{r}_K \times \overset{\circ}{\vec{r}}_K)_z = \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i\end{gathered} \tag{24}$$

where:

$$\begin{gathered}\Im_i = \sum_{j=1}^{3S-6}\left[\sum_{K=A}^{S}\left(l_{yK,j} l_{zK,i} - l_{zK,j} l_{yK,i}\right)\right] Q_j \equiv \sum_{j=1}^{3S-6} \zeta_{ji}^{x} Q_j, \\ \Re_i = \sum_{j=1}^{3S-6}\left[\sum_{K=A}^{S}\left(l_{zK,j} l_{xK,i} - l_{xK,j} l_{zK,i}\right)\right] Q_j \equiv \sum_{j=1}^{3S-6} \zeta_{ji}^{y} Q_j, \\ \aleph_i = \sum_{j=1}^{3S-6}\left[\sum_{K=A}^{S}\left(l_{xK,j} l_{zK,i} - l_{yK,j} l_{xK,i}\right)\right] Q_j \equiv \sum_{j=1}^{3S-6} \zeta_{ji}^{z} Q_j\end{gathered} \tag{25}$$

are linear combinations of the normal coordinates. Inserting (24) into (20), one obtains:

$$\begin{aligned} T_n = {} & \frac{1}{2} I_{xx}\omega_x^2 + \frac{1}{2} I_{yy}\omega_y^2 + \frac{1}{2} I_{zz}\omega_z^2 + I_{xy}\omega_x\omega_y + I_{yz}\omega_y\omega_z + I_{zx}\omega_z\omega_x \\ & + \omega_x \sum_{i=1}^{3S-6} \Im_i \dot{Q}_i + \omega_y \sum_{i=1}^{3S-6} \Re_i \dot{Q}_i + \omega_z \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i + \frac{1}{2} \sum_{i=1}^{3S-6} \dot{Q}_i^2 \end{aligned} \tag{26}$$

Equation (26) is the kinetic energy of the nuclei in terms of the coordinates and velocities.

In order to obtain the Hamiltonian, the velocities $\omega_x, \omega_y, \omega_z$ and $\dot{Q}_i = \overset{\circ}{Q}_i$ have to be replaced by impulses. The impulse, P_i, canonically conjugate to the normal coordinate Q_i, is:

$$P_i = \frac{\partial T_n}{\partial \dot{Q}_i} = \dot{Q}_i + \Im_i \omega_x + \Re_i \omega_y + \aleph_i \omega_z \tag{27}$$

First, in expression (26), the components of the angular velocity $\vec{\omega}$ are replaced by the components of the nuclear angular momentum $\vec{R}$:

$$\vec{R} = \sum_{K=A}^{S} m_K (\vec{r}_K \times \dot{\vec{r}}_K) = \sum_{K=A}^{S} m_K (\vec{r}_K \times \overset{\circ}{\vec{r}}_K) + \sum_{K=A}^{S} m_K \left[\vec{r}_K \times (\vec{\omega} \times \vec{r}_K) \right] \tag{28}$$

along the axes of the MFS:

$$\begin{aligned} R_x &= I_{xx}\omega_x + I_{xy}\omega_y + I_{xz}\omega_z + \sum_{i=1}^{3S-6} \Im_i \dot{Q}_i = \frac{\partial T_n}{\partial \omega_x}, \\ R_y &= I_{yx}\omega_x + I_{yy}\omega_y + I_{yz}\omega_z + \sum_{i=1}^{3S-6} \Re_i \dot{Q}_i = \frac{\partial T_n}{\partial \omega_y}, \\ R_z &= I_{zx}\omega_x + I_{zy}\omega_y + I_{zz}\omega_z + \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i = \frac{\partial T_n}{\partial \omega_z}. \end{aligned} \tag{29}$$

When dealing only with the nuclei, as now, these quantities equal the components J_x, J_y, J_z of the total angular momentum (also involving electronic contributions). Using Eq. (27), one derives

$$\begin{aligned} R_x - p_x &= I'_{xx}\,\omega_x + I'_{xy}\,\omega_y + I'_{xz}\,\omega_z, \\ R_y - p_y &= I'_{yx}\,\omega_x + I'_{yy}\,\omega_y + I'_{yz}\,\omega_z, \\ R_z - p_z &= I'_{zx}\,\omega_x + I'_{zy}\,\omega_y + I'_{zz}\,\omega_z. \end{aligned} \tag{30}$$

where:

$$p_x = \sum_{i=1}^{3S-6} \Im_i P_i, \quad p_y = \sum_{i=1}^{3S-6} \Re_i P_i, \quad p_z = \sum_{i=1}^{3S-6} \aleph_i P_i \tag{31}$$

are “vibrational angular momenta”, and the quantities, defined as:

$$I'_{xx} \equiv I_{xx} - \sum_{i=1}^{3S-6} \Im_i^2\,, \quad I'_{yy} \equiv I_{yy} - \sum_{i=1}^{3S-6} \Re_i^2\,, \quad I'_{zz} \equiv I_{zz} - \sum_{i=1}^{3S-6} \aleph_i^2\,,$$
$$I'_{xy} \equiv I_{xy} - \sum_{i=1}^{3S-6} \Im_i \Re_i\,, \quad I'_{yz} \equiv I_{yz} - \sum_{i=1}^{3S-6} \Re_i \aleph_i\,, \quad I'_{zx} \equiv I_{zx} - \sum_{i=1}^{3S-6} \aleph_i \Im_i\,, \tag{32}$$

reduce, in the case of small-amplitude vibrations, to the instantaneous moments and products of inertia. To eliminate from the expressions (26) and (28) the components of the angular velocity, the transformation inverse to (30) is required:

$$\begin{aligned}
\omega_x &= \mu_{xx}(R_x - p_x) + \mu_{xy}(R_y - p_y) + \mu_{xz}(R_z - p_z),\\
\omega_y &= \mu_{yx}(R_x - p_x) + \mu_{yy}(R_y - p_y) + \mu_{yz}(R_z - p_z),\\
\omega_z &= \mu_{zx}(R_x - p_x) + \mu_{zy}(R_y - p_y) + \mu_{zz}(R_z - p_z).
\end{aligned} \tag{33}$$

The coefficients $\mu_{\alpha\beta} = \mu_{\beta\alpha}$ $(\alpha, \beta = x, y$ or $z)$ are elements of the matrix inverse to the matrix with elements $I'_{\alpha\beta}$. $\mu_{\alpha\beta}$ are only the functions of the normal coordinates. Using the relations (27)–(33), expression (26) can be transformed into:

$$T_n = \frac{1}{2} \sum_{\gamma=x}^{z} \sum_{\delta=x}^{z} \mu_{\gamma\delta}(R_\gamma - p_\gamma)(R_\delta - p_\delta) + \frac{1}{2} \sum_{i=1}^{3S-6} P_i^2 \tag{34}$$

PODOLSKY TRANSFORMATION

Equation (34) represents the classical expression for the kinetic energy of nuclei in terms of the momenta P_i conjugate to the normal coordinates, the vibrational angular momenta, p_x, p_y, p_z, and the nuclear angular momenta R_x, R_y, R_z. The construction of the corresponding wave-mechanical operator is, however, not trivial for two reasons. First, curvilinear coordinates (Euler angles) are being dealt with, and secondly, the momenta R_x, R_y, R_z are (in general) not conjugate to any concrete coordinates. The first problem was solved by Podolsky.[8]

Suppose that one has M generalized (in the general case non-Cartesian) coordinates, $q_1, q_2, ..., q_M$. In all cases of present interest, the classical kinetic energy will be homogeneous quadratic functions of generalized velocities:

$$T = \frac{1}{2} \sum_{m=1}^{M} \sum_{n=1}^{M} T_{mn}(q_1, q_2, ..., q_M)\dot{q}_m \dot{q}_n \tag{35}$$

The coefficients $T_{mn}\,(= T_{nm})$ depend, in general, on generalized coordinates. The relationship between the generalized velocities and the impulses conjugate to the coordinates $q_1, q_2, ..., q_M$ are:

$$p_n = \frac{\partial T}{\partial \dot{q}_n} = \sum_{m=1}^{M} T_{mn}(q_1, q_2, \ldots, q_M)\dot{q}_m\,, \qquad n = 1, \ldots, M \tag{36}$$

The relations inverse to (36) are:

$$\dot{q}_n = \sum_{m=1}^{n} g_{mn}(q_1, q_2, \ldots, q_M)p_m\,, \qquad n = 1, \ldots, M \tag{37}$$

where $g_{mn} = g_{nm}$ are elements of the matrix inverse to the matrix $\{T_{mn}\}$, $g_{mn} = (T^{-1})_{mn}$. Inserting the expressions (37) for $\dot{q}_n$ into (35), one obtains the classical kinetic energy in impulse form:

$$T = \frac{1}{2}\sum_{m=1}^{M}\sum_{n=1}^{M} g_{mn}\left(q_1, q_2, \ldots, q_M\right)p_m p_n \tag{38}$$

If an attempt is made to construct the corresponding wave-mechanical operator by replacing the impulses in expression (38) with the corresponding operators, problems are encountered. Since the impulse operators do not in general commute with the coefficients g_{mn} (because these depend on the coordinates), it is not possible based on (38) to conclude which is the correct ordering of the quantities on the right-hand side. If one worked instead with Cartesian coordinates (or any other „rectilinear“ coordinates as, *e.g.*, the normal coordinates), the expansion coefficients would be constant, and since the impulse operators associated with different coordinates or particles commute, one would directly obtain the wave-mechanical kinetic energy operator as:

$$\hat{T} = \frac{1}{2}\sum_{m=1}^{M}\sum_{n=1}^{M} g_{mn}\hat{p}_m\hat{p}_n = -\frac{\hbar^2}{2}\sum_{m=1}^{M}\sum_{n=1}^{M} g_{mn}\frac{\partial^2}{\partial q_m \partial q_n} \tag{39}$$

Podolsky showed that it is nevertheless possible, without intermediate use of Cartesian coordinates, to construct the wave-mechanical Hamiltonian that corresponds to the classical expression (38) if this classical expression is first appropriately symmetrized:

$$T \equiv \frac{1}{2}g^{1/4}\sum_{m=1}^{M}\sum_{n=1}^{M} p_m g^{-1/2} g_{mn} p_n g^{1/4} \tag{40}$$

This leads to the operator in the form:

$$\hat{T}=\frac{1}{2}s_q^{-1/2}g^{1/4}\left\{\sum_{m=1}^{M}\sum_{n=1}^{M}\hat{p}_m g^{-1/2}g_{mn}\hat{p}_n\right\}g^{1/4}s_q^{1/2}=$$
$$=-\frac{\hbar^2}{2}s_q^{-1/2}g^{1/4}\left\{\sum_{m=1}^{M}\sum_{n=1}^{M}\frac{\partial}{\partial q_m}g^{-1/2}g_{mn}\frac{\partial}{\partial q_n}\right\}g^{1/4}s_q^{1/2} \tag{41}$$

By g is denoted the determinant with elements g_{mn}, and s_q is a conveniently chosen weight factor (in general a function of the coordinates) of the volume (integration) element, $dV = dq_1dq_2...dq_M \equiv s_q\Pi_{n=1}^{M}dq_n$. In the expression (41), the operators act onto everything on their right-hand sides (including, of course, the wave function). The operator (41) can be transformed so that the differential operators only act on the wave function:

$$\hat{T}\equiv\hat{T}^{(2)}+\hat{T}^{(1)}+\hat{T}^{(0)}=-\frac{\hbar^2}{2}\sum_{m=1}^{M}\sum_{n=1}^{M}g_{mn}\frac{\partial^2}{\partial q_m\partial q_n}-$$
$$-\frac{\hbar^2}{2}\sum_{m=1}^{M}\left[\sum_{n=1}^{M}\left(\frac{\partial g_{mn}}{\partial q_n}+\frac{g_{mn}}{s_q}\frac{\partial s_q}{\partial q_n}\right)\right]\frac{\partial}{\partial q_m}-$$
$$-\frac{\hbar^2}{8}\sum_{m=1}^{M}\sum_{n=1}^{M}\{\frac{1}{g}\left(\frac{\partial g_{mn}}{\partial q_n}\frac{\partial g}{\partial q_n}+g_{mn}\frac{\partial^2 g}{\partial q_m\partial q_n}\right)+$$
$$+\frac{2}{s_q}\left(\frac{\partial g_{mn}}{\partial q_n}\frac{\partial s_q}{\partial q_m}+g_{mn}\frac{\partial^2 s_q}{\partial q_m\partial q_n}\right)-\frac{g_{mn}}{s_q^2}\frac{\partial s_q}{\partial q_m}\frac{\partial s_q}{\partial q_n}\} \tag{42}$$

Note that the kinetic energy operator in curvilinear coordinates (unlike the operator in Cartesian coordinates, which is a homogenous quadratic form of derivatives) also involves terms linear in derivatives and a constant (*i.e.*, not containing any derivatives) term. Both the linear and constant terms are completely determined by the expansion coefficients of the quadratic part. In a special, but quite common case, when $g=J^{-2}$ and $s_q=J$, where J is the Jacobian of the transformation from Cartesian into non-Cartesian coordinates, $\hat{T}^{(0)}=0$.

The Podolsky transformation in its original version covers the cases when all momenta are conjugate to the corresponding, in general curvilinear, coordinates. However, sometimes it is more convenient to use the momenta, such as the components of the angular momentum, which are not conjugate to any coordinates. These quantities are called quasi-momenta. This topic was investigated by Wilson and Howard[2,3] and later more generally by Watson;[1,4] they showed that the wave-mechanical Hamiltonian could be expressed in terms of the operators corresponding to quasi-momenta, provided that some special conditions are fulfilled.

In the present case, the quasi-momenta are the quantities $\left(R_\gamma - p_\gamma\right)$. It can be shown that the components of the total angular momentum, J_x, J_y, J_z, along the *MFS* axes, being in the present case equal to the components of the angular momentum of the nuclei, R_x, R_y, R_z, are related to the impulses $p_\varphi, p_\theta, p_\chi$, conjugate to the Euler angles:

$$p_\varphi = \frac{\partial T}{\partial \dot{\varphi}}, \quad p_\theta = \frac{\partial T}{\partial \dot{\theta}}, \quad p_\chi = \frac{\partial T}{\partial \dot{\chi}} \tag{43}$$

by:[7,11]

$$\begin{aligned} J_x &= -\frac{\cos\chi}{\sin\theta}\cdot p_\varphi + \sin\chi\cdot p_\theta + \cot\theta\cos\chi\cdot p_\chi, \\ J_y &= \frac{\sin\chi}{\sin\theta}\cdot p_\varphi + \cos\chi\cdot p_\theta - \cot\theta\sin\chi\cdot p_\chi, \\ J_z &= p_\chi \end{aligned} \tag{44}$$

Note that the relations (44) are valid independently of whether the electronic coordinates are related to the *SFS* or *MFS*, whereas the expressions on the right-hand side equal to R_x, R_y, R_z, respectively, are only valid when the electronic coordinates are left in the *SFS*. There were some reasons to prefer up to now the symbols R_x, R_y, R_z; but from now on, we skip to J_x, J_y, J_z. It turns out that the transformations (43/44) fulfill the conditions required for application of the generalized Podolsky transformation. The volume element at the integration of the wave functions will be $dV = \sin\theta\cdot d\varphi\cdot d\theta\cdot d\chi\cdot dQ_1 \ldots dQ_{3S-6}$. Therefore, the wave-mechanical operator for the kinetic energy of nuclei, analogous to the general expression (41), is:

$$\begin{aligned} \hat{T}_n = {} & \frac{1}{2}\mu^{\frac{1}{4}}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\left(\hat{J}_\gamma - \hat{p}_\gamma\right)\mu_{\gamma\delta}\mu^{-\frac{1}{2}}\left(\hat{J}_\delta - \hat{p}_\delta\right)\right\}\mu^{\frac{1}{4}} + \\ & + \frac{1}{2}\mu^{\frac{1}{4}}\left\{\sum_{i=1}^{3S-6}\hat{P}_i\mu^{-\frac{1}{2}}\hat{P}_i\right\}\mu^{\frac{1}{4}} \end{aligned} \tag{45}$$

where the wave-mechanical operators $\hat{J}_\gamma$ and $\hat{p}_\gamma$ $(\gamma = x, y, z)$ are obtained by replacing in the expressions (44) and (31), the classical impulses $\hat{p}_q$ $(q = \varphi, \theta, \chi, P_i)$ by the operators $-i\hbar\partial/\partial q$. (Watson[4] claimed that this did not in general hold and that in the present case the correct result was obtained thanks to "a more-or-less fortuitous cancellation" of some terms. I find this statement a little bit severe; the mentioned fortuitous cancellation is actually a direct consequence of the proper choice of the volume element $\mathrm{d}V$).

Watson[1] showed that the expression (45) could be simplified. He derived certain commutation relations, such as:

$$\sum_{\alpha=x}^{z}\left[\hat{p}_{\alpha},\mu_{\alpha\beta}\right]=0 \tag{46}$$

which enabled Eq. (45) to be rearranged into:

$$\begin{aligned}\hat{T}_n&=\frac{1}{2}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\left(\hat{J}_{\gamma}-\hat{p}_{\gamma}\right)\mu_{\gamma\delta}\left(\hat{J}_{\delta}-\hat{p}_{\delta}\right)\right\}+\frac{1}{2}\sum_{i=1}^{3S-6}\hat{P}_i^2-\frac{\hbar^2}{8}\sum_{\gamma=x}^{z}\mu_{\gamma\gamma}=\\&=\frac{1}{2}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\mu_{\gamma\delta}\left(\hat{J}_{\gamma}-\hat{p}_{\gamma}\right)\left(\hat{J}_{\delta}-\hat{p}_{\delta}\right)\right\}+\frac{1}{2}\sum_{i=1}^{3S-6}\hat{P}_i^2-\frac{\hbar^2}{8}\sum_{\gamma=x}^{z}\mu_{\gamma\gamma}\end{aligned} \tag{47}$$

The term $-\left(\hbar^2/8\right)\sum_{\gamma}\mu_{\gamma\gamma}$ can be handled as an additional part of the potential; however, unlike the common potential terms, it depends on the nuclear masses and thus, it is not isotopically invariant.

TRANSFER OF ELECTRONIC COORDINATES INTO A MOLECULE FIXED SYSTEM

Now both the electronic (Eq. (12)) and the nuclear kinetic energy (Eq. (47)) operators, expressed in terms of the desired impulses/momenta, are available. Let us return, however, to Eq. (13) and the text following it: It was concluded that the transformed nuclear kinetic energy operator would be spoiled by electron variables but the operator (47) does not contain them. What has happened? The explanation is the following: the full classical kinetic energy was separated into two parts, which were handled in different ways. The electronic kinetic energy operator was constructed by method (a) (as defined in Introduction), and the kinetic energy operator by method (b). These two methods give identical results when applied to the full kinetic energy, but not always when the classical kinetic energy is separated into its constituent part. Thus, although we started with the classical kinetic energy for nuclei being equivalent to the corresponding quantum mechanical operator in terms of the *NCMS* variables, results identical to those that would have been derived if the problem had been handled using method (a) were not obtained. Since good reasons existed to avoid scheme (a) in the construction of the nuclear kinetic energy operator, now the electronic kinetic energy will be transformed also by method (b). Note that neither Wilson[2,3] nor Watson[1] considered the transfer of the electronic variables into the *MFS*. This topic was handled in the classical paper by Van Vleck,[12] nowadays very difficult to read due to the old-fashioned notation and definition of the Euler angles. A modern presentation can be found in the book by Brown and Carrington.[13] The non-appearance of the electronic coordinates in the operator (47) is explained as being a consequence of the tacit assumption that the angular momentum operator with the components J_x, J_y, J_z, depending only on the Euler angles, does not act on the electron coordinates. However, if the electronic coordinates are defined with respect to the *MFS*-axes, the indirect effect of the operators J_x, J_y, J_z on them (*via* the transformation coefficients expressed in terms of the Euler angles) has to be taken into account. The way chosen herein is more straightforward.

Starting with the classical electronic kinetic energy in velocity form, defined in the *NCMS* (see Eq. (3)):

$$T_e = \frac{1}{2} m_e \sum_{\mu=1}^{N} \left(\dot{\vec{R}}_\mu \cdot \dot{\vec{R}}_\mu \right) - \frac{m_e^2}{2M} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \left(\dot{\vec{R}}_\mu \cdot \dot{\vec{R}}_\nu \right) \tag{48}$$

and substituting $\dot{\vec{R}}_K$ by the expressions analogous to (16), $\dot{\vec{r}}_\mu = \overset{\circ}{\vec{r}}_\mu + \vec{\omega} \times \vec{r}_\mu$, one obtains:

$$\begin{aligned} T_e = {} & \frac{1}{2} I_{xx}^e \omega_x^2 + \frac{1}{2} I_{yy}^e \omega_y^2 + \frac{1}{2} I_{zz}^e \omega_z^2 + I_{xy}^e \omega_x \omega_y + I_{yz}^e \omega_y \omega_z + I_{zx}^e \omega_z \omega_x + \\ & + \omega_x \left[\sum_{\mu=1}^{N} m_e \left(y_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} y_\nu \right) \dot{z}_\mu - \sum_{\mu=1}^{N} m_e \left(z_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} z_\nu \right) \dot{y}_\mu \right] + \\ & + \omega_y \left[\sum_{\mu=1}^{N} m_e \left(z_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} z_\nu \right) \dot{x}_\mu - \sum_{\mu=1}^{N} m_e \left(x_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} x_\nu \right) \dot{z}_\mu \right] + \\ & + \omega_z \left[\sum_{\mu=1}^{N} m_e \left(x_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} x_\nu \right) \dot{y}_\mu - \sum_{\mu=1}^{N} m_e \left(y_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} y_\nu \right) \dot{x}_\mu \right] + \\ & + \frac{1}{2} \sum_{\mu=1}^{N} m_e \dot{x}_\mu \left(\dot{x}_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} \dot{x}_\nu \right) + \frac{1}{2} \sum_{\mu=1}^{N} m_e \dot{y}_\mu \left(\dot{y}_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} \dot{y}_\nu \right) + \\ & + \frac{1}{2} \sum_{\mu=1}^{N} m_e \dot{z}_\mu \left(\dot{z}_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} \dot{z}_\nu \right) \end{aligned} \tag{49}$$

where:

$$\begin{gathered} I_{xx}^e = m_e \sum_{\mu=1}^{N} \left[\left(y_\mu^2 + z_\mu^2 \right) - \frac{m_e}{M} \sum_{\nu=1}^{N} \left(y_\mu y_\nu + z_\mu z_\nu \right) \right], \ldots, \\ I_{zx}^e = -m_e \sum_{\mu=1}^{N} \left[z_\mu x_\mu - \frac{m_e}{M} \sum_{\nu=1}^{N} z_\mu x_\nu \right] \end{gathered} \tag{50}$$

are the electronic moments and products of inertia. (The physical sense of these quantities is less sound than that of their nuclear counterparts but they will not appear in any final result). Adding (49) to (26), one obtains the total classical kinetic energy of the molecule.

The momenta conjugate to the electronic velocities have the form:

$$\begin{aligned}
P_{\mu x} &\equiv \frac{\partial T}{\partial \dot{x}_\mu} = \frac{\partial T_e}{\partial \dot{x}_\mu} = m_e\left(\dot{x}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{x}_\nu\right) + m_e\omega_y\left(z_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} z_\nu\right) - \\
&\qquad - m_e\omega_z\left(y_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} y_\nu\right), \\
P_{\mu y} &\equiv \frac{\partial T}{\partial \dot{y}_\mu} = \frac{\partial T_e}{\partial \dot{y}_\mu} = m_e\left(\dot{y}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{y}_\nu\right) + m_e\omega_z\left(x_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} x_\nu\right) - \\
&\qquad - m_e\omega_x\left(z_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} z_\nu\right), \\
P_{\mu z} &\equiv \frac{\partial T}{\partial \dot{z}_\mu} = \frac{\partial T_e}{\partial \dot{z}_\mu} = m_e\left(\dot{z}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{z}_\mu\right) + m_e\omega_x\left(y_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} y_\nu\right) - \\
&\qquad - m_e\omega_y\left(x_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N} x_\nu\right)
\end{aligned} \tag{51}$$

The electronic momenta associated with the components of the angular velocity are:

$$\begin{aligned}
\frac{\partial T_e}{\partial \omega_x} &\equiv L_x = I^e_{xx}\omega_x + I^e_{xy}\omega_y + I^e_{xz}\omega_z + m_e\sum_{\mu=1}^{N} y_\mu\left(\dot{z}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{z}_\nu\right) - \\
&\qquad - m_e\sum_{\mu=1}^{N} z_\mu\left(\dot{y}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{y}_\nu\right), \\
\frac{\partial T_e}{\partial \omega_y} &\equiv L_y = I^e_{yx}\omega_x + I^e_{yy}\omega_y + I^e_{yz}\omega_z + m_e\sum_{\mu=1}^{N} z_\mu\left(\dot{x}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{x}_\nu\right) - \\
&\qquad - m_e\sum_{\mu=1}^{N} x_\mu\left(\dot{z}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{z}_\nu\right), \\
\frac{\partial T_e}{\partial \omega_z} &\equiv L_z = I^e_{zx}\omega_x + I^e_{zy}\omega_y + I^e_{zz}\omega_z + m_e\sum_{\mu=1}^{N} x_\mu\left(\dot{y}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{y}_\nu\right) - \\
&\qquad - m_e\sum_{\mu=1}^{N} y_\mu\left(\dot{x}_\mu - \frac{m_e}{M}\sum_{\nu=1}^{N}\dot{x}_\nu\right).
\end{aligned} \tag{52}$$

Taking into account (50) and (51), Eqs. (52) can be transformed into:

$$\begin{gathered}\frac{\partial T_e}{\partial \omega_x} = \sum_{\mu=1}^{N}\left(y_\mu P_{\mu z} - z_\mu P_{\mu y}\right) = L_x\,, \quad \frac{\partial T_e}{\partial \omega_y} = \sum_{\mu=1}^{N}\left(z_\mu P_{\mu x} - x_\mu P_{\mu z}\right) = L_y\,, \\ \frac{\partial T_e}{\partial \omega_z} = \sum_{\mu=1}^{N}\left(x_\mu P_{\mu y} - y_\mu P_{\mu x}\right) = L_z\end{gathered} \tag{53}$$

Thus, by summing R_x, R_y, R_z and L_x, L_y, L_z, one has, based on Eq. (30):

$$\begin{aligned} J_x &= \frac{\partial T}{\partial \omega_x} = \frac{\partial T_n}{\partial \omega_x} + \frac{\partial T_e}{\partial \omega_x} = R_x + L_x = \\ &= I'_{xx}\,\omega_x + I'_{xy}\,\omega_y + I'_{zx}\,\omega_z + p_x + L_x\,, \\ J_y &= \frac{\partial T}{\partial \omega_y} = \frac{\partial T_n}{\partial \omega_y} + \frac{\partial T_e}{\partial \omega_y} = R_y + L_y = \\ &= I'_{xy}\,\omega_x + I'_{yy}\,\omega_y + I'_{yz}\,\omega_z + p_y + L_y\,, \\ J_z &= \frac{\partial T}{\partial \omega_z} = \frac{\partial T_n}{\partial \omega_z} + \frac{\partial T_e}{\partial \omega_z} = R_z + L_z = \\ &= I'_{zx}\,\omega_x + I'_{yz}\,\omega_y + I'_{zz}\,\omega_z + p_z + L_z \end{aligned} \tag{54}$$

Using the above relations and Eqs. (26), (27), (31) and (32), one obtains for the total kinetic energy:

$$\begin{aligned} T_n + T_e = {} & \frac{1}{2} I'_{xx}\,\omega_x^2 + \frac{1}{2} I'_{yy}\,\omega_y^2 + \frac{1}{2} I'_{zz}\,\omega_z^2 + I'_{xy}\,\omega_x\omega_y + I'_{yz}\,\omega_y\omega_z + \\ & + I'_{zx}\,\omega_z\omega_x + \frac{1}{2}\sum_{i=1}^{2S-6} P_i^2 + \frac{1}{2m_e}\sum_{\mu=1}^{N}\left(P_{\mu x}^2 + P_{\mu y}^2 + P_{\mu z}^2\right) + \\ & + \frac{1}{2M_n}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(P_{\mu x}P_{\nu x} + P_{\mu y}P_{\nu y} + P_{\mu z}P_{\nu z}\right) \end{aligned} \tag{55}$$

Note that the electronic moments of inertia have disappeared. From Eq. (54), one has:

$$\begin{aligned} J_x - p_x - L_x &= I'_{xx}\,\omega_x + I'_{xy}\,\omega_y + I'_{zx}\,\omega_z\,, \\ J_y - p_y - L_y &= I'_{xy}\,\omega_x + I'_{yy}\,\omega_y + I'_{yz}\,\omega_z\,, \\ J_z - p_z - L_z &= I'_{zx}\,\omega_x + I'_{zy}\,\omega_y + I'_{zz}\,\omega_z \end{aligned} \tag{56}$$

It follows:

$$T_n + T_e = \frac{1}{2}\left(J_x - p_x - L_x\right)\omega_x + \frac{1}{2}\left(J_y - p_y - L_y\right)\omega_y + \\ + \frac{1}{2}\left(J_z - p_z - L_z\right)\omega_z + \frac{1}{2}\sum_{i=1}^{2S-6} P_i^2 + \frac{1}{2m_e}\sum_{\mu=1}^{N}\left(P_{\mu x}^2 + P_{\mu y}^2 + P_{\mu z}^2\right) + \\ + \frac{1}{2M_n}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(P_{\mu x}P_{\nu x} + P_{\mu y}P_{\nu y} + P_{\mu z}P_{\nu z}\right) \tag{57}$$

The transformation inverse to (56) is:

$$\begin{aligned} \omega_x &= \mu_{xx}\left(J_x - p_x - L_x\right) + \mu_{xy}\left(J_y - p_y - L_y\right) + \mu_{zx}\left(J_z - p_z - L_z\right), \\ \omega_y &= \mu_{xy}\left(J_x - p_x - L_x\right) + \mu_{yy}\left(J_y - p_y - L_y\right) + \mu_{yz}\left(J_z - p_z - L_z\right), \\ \omega_z &= \mu_{zx}\left(J_x - p_x - L_x\right) + \mu_{yz}\left(J_y - p_y - L_y\right) + \mu_{zz}\left(J_z - p_z - L_z\right) \end{aligned} \tag{58}$$

Inserting the expressions (58) for $\omega_x, \omega_y, \omega_z$ into Eq. (57), one obtains:

$$T_n + T_e = \frac{1}{2}\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\mu_{\gamma\delta}\left(J_\gamma - p_\gamma - L_\gamma\right)\left(J_\delta - p_\delta - L_\delta\right) + \\ + \frac{1}{2}\sum_{i=1}^{2S-6} P_i^2 + \frac{1}{2m_e}\sum_{\mu=1}^{N}\left(P_{\mu x}^2 + P_{\mu y}^2 + P_{\mu z}^2\right) + \\ + \frac{1}{2M_n}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(P_{\mu x}P_{\nu x} + P_{\mu y}P_{\nu y} + P_{\mu z}P_{\nu z}\right) \tag{59}$$

Thus, as predicted, the electronic coordinates (*via* the electronic angular momentum) have crept into the nuclear kinetic energy (first sum on the right-hand side). This expression differs from the Wilson one, Eq. (34), due to presence of the last two terms representing the electronic kinetic energy, and by the substitution:

$$\begin{aligned} R_x - p_x &\to J_x - L_x - p_x, \\ R_y - p_y &\to J_y - L_y - p_y, \\ R_z - p_z &\to J_z - L_z - p_z \end{aligned} \tag{60}$$

in the rotation part of the kinetic energy. If the electron spin variables were also defined in the MFS, the expression on the right-hand side of Eq. (60) would be replaced by $J_\xi - L_\xi - p_\xi - S_\xi$ ($\xi = x, y, z$). Since L_x, L_y, L_z only involve the electronic variables, and the coefficients $\mu_{\gamma\delta}$ only depend on the normal coordinates, one could now proceed in the same way as Watson.[1] The final result for the total kinetic energy operator would be analogous to (47):

$$\begin{aligned}\hat{T} = \hat{T}_n + \hat{T}_e = \frac{1}{2}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\mu_{\gamma\delta}\left(\hat{J}_\gamma - \hat{L}_\gamma - \hat{p}_\gamma\right)\left(\hat{J}_\delta - \hat{L}_\delta - \hat{p}_\delta\right)\right\} + \\ + \frac{1}{2}\sum_{i=1}^{3S-6}\hat{P}_i^2 - \frac{\hbar^2}{8}\sum_{\gamma=x}^{z}\mu_{\gamma\gamma} + \frac{1}{2m_e}\sum_{\mu=1}^{N}\left(\hat{P}_{\mu x}^2 + \hat{P}_{\mu y}^2 + \hat{P}_{\mu z}^2\right) - \\ - \frac{1}{2m_e}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\hat{P}_{\mu x}\hat{P}_{\nu x} + \hat{P}_{\mu y}\hat{P}_{\nu y} + \hat{P}_{\mu z}\hat{P}_{\nu z}\right)\end{aligned} \tag{61}$$

The last two terms (sums) on the right-hand side of Eq. (61) represent the kinetic energy operator of electrons. The result (60) will be used to simplify the derivation of the total kinetic energy operator. Only T_n, will be explicitly transformed and later the fact that the components of the electronic angular momentum, L_x, L_y, L_z, enter the kinetic energy operator in the same way as those of the vibrational (p_x, p_y, p_z) one will be used.

DERIVATION OF THE HAMILTONIAN WITHOUT USE OF QUASI-MOMENTA

Now several relations will be derived that will be required later. First, the time derivatives of the elements λ_{xX} ,… can be expressed in terms of these elements and the time derivatives of the Euler angles:

$$\dot{\lambda}_{xX} = -\lambda_{xY}\dot{\varphi} - \lambda_{zX}\cos\chi\cdot\dot{\theta} + \lambda_{yX}\dot{\chi}, \ldots, \quad \dot{\lambda}_{zZ} = -\sin\theta\cdot\dot{\theta} \tag{62}$$

The time derivatives $\dot{\vec{i}}, \dot{\vec{j}}, \dot{\vec{k}}$ are expressible in terms of the unit vectors $\vec{i}, \vec{j}, \vec{k}$ themselves:

$$\begin{aligned}\dot{\vec{i}} &= \left(\lambda_{zZ}\dot{\varphi} + \dot{\chi}\right)\vec{j} + \left(-\lambda_{yZ}\dot{\varphi} - \cos\chi\cdot\dot{\theta}\right)\vec{k}, \\ \dot{\vec{j}} &= \left(-\lambda_{zZ}\cdot\dot{\varphi} - \dot{\chi}\right)\vec{i} + \left(\lambda_{xZ}\dot{\varphi} + \sin\chi\cdot\dot{\theta}\right)\vec{k}, \\ \dot{\vec{k}} &= \left(\lambda_{yZ}\dot{\varphi} + \cos\chi\cdot\dot{\theta}\right)\vec{i} + \left(-\lambda_{xZ}\dot{\varphi} - \sin\chi\cdot\dot{\theta}\right)\vec{j}\end{aligned} \tag{63}$$

Using (62) and (63), one can rewrite Eqs. (6) and (7) in the form:

$$\begin{aligned}\dot{\vec{R}}_i = \dot{\vec{r}}_i = \left[\dot{x}_i + \left(-\lambda_{zZ}\dot{\varphi} - \dot{\chi}\right)y_i + \left(\lambda_{yZ}\dot{\varphi} + \cos\chi\cdot\dot{\theta}\right)z_i\right]\vec{i} + \\ + \left[\dot{y}_i + \left(\lambda_{zZ}\dot{\varphi} + \dot{\chi}\right)x_i + \left(-\lambda_{xZ}\dot{\varphi} - \sin\chi\cdot\dot{\theta}\right)z_i\right]\vec{j} + \\ + \left[\dot{z}_i + \left(-\lambda_{yZ}\dot{\varphi} - \cos\chi\cdot\dot{\theta}\right)x_i + \left(\lambda_{xZ}\dot{\varphi} + \sin\chi\cdot\dot{\theta}\right)y_i\right]\vec{k}\end{aligned} \tag{64}$$

Based on Eq. (64), for the classical nuclear energy, the following expression was derived:

$$
\begin{aligned}
T_n &= \frac{1}{2}\sum_{K=A}^{S} m_K \left(\dot{\vec{R}}_K \cdot \dot{\vec{R}}_K\right) = \frac{1}{2}\sum_{K=A}^{S} m_K \left(\dot{\vec{r}}_K \cdot \dot{\vec{r}}_K\right) = \frac{1}{2}\sum_{i=1}^{3S-6} \dot{Q}_i^2 + \\
&+ \sum_{i=1}^{3S-6} \left(\lambda_{xZ}\Im_i + \lambda_{yZ}\Re_i + \lambda_{zZ}\aleph_i\right)\dot{Q}_i\dot{\varphi} + \sum_{i=1}^{3S-6} \left(\Im_i \sin\chi + \Re_i \cos\chi\right)\dot{Q}_i\dot{\theta} + \\
&+ \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i \dot{\chi} + \frac{1}{2}[\lambda_{xZ}^2 I_{yy} + \lambda_{yZ}^2 I_{xx} + \lambda_{zZ}^2 I_{zz} + 2\lambda_{xZ}\lambda_{yZ} I_{xy} + \\
&+ 2\lambda_{yZ}\lambda_{zZ} I_{yz} + 2\lambda_{xZ}\lambda_{zZ} I_{zx}]\dot{\varphi}^2 + \frac{1}{2}[I_{xx}\sin^2\chi + I_{yy}\cos^2\chi + \qquad (65) \\
&+ 2I_{xy}\sin\chi\cos\chi]\dot{\theta}^2 + \frac{1}{2}I_{zz}\dot{\chi}^2 + [\left(\lambda_{xZ}I_{xx} + \lambda_{yZ}I_{xy} + \lambda_{zZ}I_{xz}\right)\sin\chi + \\
&+ \left(\lambda_{xZ}I_{yx} + \lambda_{yZ}I_{yy} + \lambda_{zZ}I_{yZ}\right)\cos\chi]\dot{\varphi}\dot{\theta} + [\lambda_{xZ}I_{zx} + \lambda_{yZ}I_{zy} + \\
&+ \lambda_{zZ}I_{zz}]\dot{\varphi}\dot{\chi} + \left[I_{yz}\cos\chi + I_{zx}\sin\chi\right]\dot{\theta}\dot{\chi}
\end{aligned}
$$

where by means of the relations (22), the Cartesian coordinates and their time derivatives are replaced by the normal coordinates and their derivatives:

$$
\begin{aligned}
\sum_{K=A}^{S} m_K \left(y_K \dot{z}_K - z_K \dot{y}_K\right) &= \sum_{i=1}^{3S-6} \Im_i \dot{Q}_i, \\
\sum_{K=A}^{S} m_K \left(z_K \dot{x}_K - x_K \dot{z}_K\right) &= \sum_{i=1}^{3S-6} \Re_i \dot{Q}_i, \qquad (66) \\
\sum_{K=A}^{S} m_K \left(x_K \dot{y}_K - y_K \dot{x}_K\right) &= \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i
\end{aligned}
$$

These relations, when accompanied by the Eckart condition (17), are equivalent to (24). The momenta conjugate to the coordinates are:

$$
\begin{aligned}
P_i &\equiv \frac{\partial T}{\partial \dot{Q}_i} = \dot{Q}_i + \left[\lambda_{xZ}\Im_i + \lambda_{yZ}\Re_i + \lambda_{zZ}\aleph_i\right]\dot{\varphi} + \left[\Im_i \sin\chi + \Re_i \cos\chi\right]\dot{\theta} + \aleph_i \cdot \dot{\chi} \\
p_\varphi &\equiv \frac{\partial T}{\partial \dot{\varphi}} = \sum_{i=1}^{3S-6} \left(\lambda_{xZ}\Im_i + \lambda_{yZ}\Re_i + \lambda_{zZ}\aleph_i\right)\dot{Q}_i \\
&\left[\lambda_{xZ}^2 I_{yy} + \lambda_{yZ}^2 I_{xx} + \lambda_{zZ}^2 I_{zz} + 2\lambda_{xZ}\lambda_{yZ} I_{xy} + 2\lambda_{yZ}\lambda_{zZ} I_{yz} + 2\lambda_{xZ}\lambda_{zZ} I_{zx}\right]\dot{\varphi} + \qquad (67) \\
&+ \left[\left(\lambda_{xZ}I_{xx} + \lambda_{yZ}I_{xy} + \lambda_{zZ}I_{xz}\right)\sin\chi + \left(\lambda_{xZ}I_{yx} + \lambda_{yZ}I_{yy} + \lambda_{zZ}I_{yZ}\right)\cos\chi\right]\dot{\theta} + \\
&+ \left[\lambda_{xZ}I_{zx} + \lambda_{yZ}I_{zy} + \lambda_{zZ}I_{zz}\right]\dot{\chi},
\end{aligned}
$$

$$
\begin{aligned}
p_\theta \equiv \frac{\partial T}{\partial \dot{\theta}} = & \sum_{i=1}^{3S-6} \left(\Im_i \sin\chi + \Re_i \cos\chi \right) \dot{Q}_i + \\
& + \left[\left(\lambda_{xZ} I_{xx} + \lambda_{yZ} I_{xy} + \lambda_{zZ} I_{xz} \right) \sin\chi + \left(\lambda_{xZ} I_{xy} + \lambda_{yZ} I_{yy} + \lambda_{zZ} I_{yz} \right) \cos\chi \right] \dot{\varphi} + \\
& + \left[I_{xx} \sin^2\chi + I_{yy} \cos^2\chi + 2 I_{xy} \sin\chi \cos\chi \right] \dot{\theta} + \left[I_{xz} \sin\chi + I_{yz} \cos\chi \right] \dot{\chi}, \\
p_\chi \equiv \frac{\partial T}{\partial \dot{\chi}} = & \sum_{i=1}^{3S-6} \aleph_i \dot{Q}_i + \left[\lambda_{xZ} I_{xz} + \lambda_{yZ} I_{yz} + \lambda_{zZ} I_{zz} \right] \dot{\varphi} + \\
& + \left[I_{yz} \cos\chi + I_{zx} \sin\chi \right] \dot{\theta} + I_{zz} \dot{\chi}
\end{aligned}
$$

The transformation inverse to (67) is a concrete case of the relations (37) with $\dot{q}_n = \dot{Q}_1, \ldots, \dot{Q}_{3S-6}, \dot{\varphi}, \dot{\theta}, \dot{\chi}$, and $p_m = P_1, \ldots, P_{3S-6}, p_\varphi, p_\theta, p_\chi$, where the coefficients g_{mn} are:

$$
\begin{aligned}
g_{Q_iQ_j} &= \delta_{ij} + \Xi_{ix} \Im_j + \Xi_{iy} \Re_j + \Xi_{iz} \aleph_j \\
g_{Q_i\varphi} &= \Xi_{ix} \frac{\cos\chi}{\sin\theta} - \Xi_{iy} \frac{\sin\chi}{\sin\theta} \\
g_{Q_i\theta} &= -\Xi_{ix} \sin\chi - \Xi_{iy} \cos\chi \\
g_{Q_i\chi} &= -\Xi_{ix} \cot\theta \cos\chi + \Xi_{iy} \cot\theta \sin\chi - \Xi_{iz} \\
g_{\varphi\varphi} &= \mu_{xx} \frac{\cos^2\chi}{\sin^2\theta} + \mu_{yy} \frac{\sin^2\chi}{\sin^2\theta} - 2\mu_{xy} \frac{\sin\chi\cos\chi}{\sin^2\theta} \\
g_{\theta\theta} &= \mu_{xx} \sin^2\chi + \mu_{yy} \cos^2\chi + 2\mu_{xy} \sin\chi\cos\chi \\
g_{\chi\chi} &= \left(\mu_{xx} \cos^2\chi + \mu_{yy} \sin^2\chi - 2\mu_{xy} \sin\chi\cos\chi \right) \cot^2\theta + \\
&\quad + 2\left(\mu_{zx} \cos\chi - \mu_{yz} \sin\chi \right) \cot\theta + \mu_{zz} \\
g_{\varphi\theta} &= \left(\mu_{yy} - \mu_{xx} \right) \frac{\sin\chi\cos\chi}{\sin\theta} - \mu_{xy} \frac{\cos^2\chi - \sin^2\chi}{\sin\theta} \\
g_{\varphi\chi} &= -\mu_{xx} \frac{\cos\theta\cos^2\chi}{\sin^2\theta} - \mu_{yy} \frac{\cos\theta\sin^2\chi}{\sin^2\theta} + \\
&\quad + 2\mu_{xy} \frac{\cos\theta\sin\chi\cos\chi}{\sin^2\theta} + \mu_{yz} \frac{\sin\chi}{\sin\theta} - \mu_{zx} \frac{\cos\chi}{\sin\theta} \\
g_{\theta\chi} &= \left(\mu_{xx} - \mu_{yy} \right) \cot\theta \sin\chi\cos\chi + \\
&\quad + \mu_{xy} \cot\theta \left(\cos^2\chi - \sin^2\chi \right) + \mu_{yz} \cos\chi + \mu_{zx} \sin\chi
\end{aligned} \tag{68}
$$

with:

$$
\begin{gathered}
\Xi_{ix} \equiv \mu_{xx} \Im_i + \mu_{xy} \Re_i + \mu_{xz} \aleph_i, \quad \Xi_{iy} \equiv \mu_{yx} \Im_i + \mu_{yy} \Re_i + \mu_{yz} \aleph_i, \\
\Xi_{iz} \equiv \mu_{zx} \Im_i + \mu_{zy} \Re_i + \mu_{zz} \aleph_i
\end{gathered} \tag{69}
$$

The determinant of the matrix with elements g_{mn} is:

$$g=\frac{\mu_{xx}\mu_{yy}\mu_{zz}-\mu_{xx}\mu_{yz}^2-\mu_{yy}\mu_{zx}^2-\mu_{zz}\mu_{xy}^2+2\mu_{xy}\mu_{yz}\mu_{zx}}{\sin^2\theta}g= \\ =\mu(Q_1,Q_2,Q_3)\sin^{-2}\theta \tag{70}$$

The coefficients (68) determine the classical kinetic energy of the nuclei and at the same time the quadratic part of the corresponding wave-mechanical operator (42):

$$\hat{T}_n^{(2)}=-\frac{\hbar^2}{2}\sum_{m=1}^{3S-3}\sum_{n=1}^{3S-3}g_{mn}\frac{\partial^2}{\partial q_m\partial q_n},\qquad m,n=Q_1,\ldots,Q_{3S-6},\varphi,\theta,\chi \tag{71}$$

The linear (in derivatives) part of the wave-mechanical operator (42) corresponding to the choice:

$$g\propto\mu(Q_1,Q_2,Q_3)\sin^{-2}\theta,\quad s_q=\sin\theta \tag{72}$$

where the symbol $\propto$ stands for irrelevant constant factors, is determined by the second term on the right-hand side of Eq. (42), having in the present case the form:

$$\begin{gathered}\hat{T}^{(1)}=-\frac{\hbar^2}{2}\left\{\sum_{i=1}^{3S-6}\left[\sum_{j=1}^{3S-6}\frac{\partial g_{Q_iQ_j}}{\partial Q_j}\right]\frac{\partial}{\partial Q_i}+\right. \\ +[\sum_{j=1}^{3S-6}\frac{\partial g_{Q_j\varphi}}{\partial Q_j}+\frac{\partial g_{\varphi\theta}}{\partial\theta}+g_{\varphi\theta}\cot\theta+\frac{\partial g_{\varphi\chi}}{\partial\chi}]\frac{\partial}{\partial\varphi}+ \\ +[\sum_{j=1}^{3S-6}\frac{\partial g_{Q_j\theta}}{\partial Q_j}+g_{\theta\theta}\cot\theta+\frac{\partial g_{\theta\chi}}{\partial\chi}]\frac{\partial}{\partial\theta} \\ \left.+[\sum_{j=1}^{3S-6}\frac{\partial g_{Q_j\chi}}{\partial Q_j}+\frac{\partial g_{\chi\varphi}}{\partial\varphi}+\frac{\partial g_{\chi\theta}}{\partial\theta}+g_{\chi\theta}\cot\theta+\frac{\partial g_{\chi\chi}}{\partial\chi}]\frac{\partial}{\partial\chi}\right\}\end{gathered} \tag{73}$$

The constant term (with respect to derivatives) from Eq. (42) reduces in the present case to:

$$\begin{gathered}\hat{T}^{(0)}=-\frac{\hbar^2}{8}\sum_{i=1}^{3S-6}\sum_{j=1}^{3S-6}\{\frac{1}{\mu}\left(\frac{\partial g_{Q_iQ_j}}{\partial Q_i}\frac{\partial u}{\partial Q_j}+g_{Q_iQ_j}\frac{\partial^2 u}{\partial Q_i\partial Q_j}\right)- \\ -\frac{5}{4\mu^2}g_{Q_iQ_j}\frac{\partial\mu}{\partial Q_i}\frac{\partial\mu}{\partial Q_j}\}\end{gathered} \tag{74}$$

Using the formulae (68), (31), (44), those for the quantities $\hat{J}_x^2=\hat{J}_x\hat{J}_x$, $\hat{J}_x\hat{J}_y$, $\hat{J}_y\hat{J}_x$,…, which can be derived starting with Eqs. (44), and rearranging, one obtains for the wave-mechanical kinetic energy operator of the nuclei the expression:

$$\hat{T}_n = \frac{1}{2}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\left(\hat{J}_\gamma - \hat{p}_\gamma\right)\mu_{\gamma\delta}\left(\hat{J}_\delta - \hat{p}_\delta\right)\right\} + \frac{1}{2}\sum_{i=1}^{3S-6}\hat{P}_i^2 + \hat{T}^{(0)} \tag{75}$$

The explicit form of $\hat{T}^{(0)}$ is:

$$\begin{aligned}\hat{T}^{(0)} = -\frac{\hbar^2}{8}\Bigg\{&\left[\frac{1}{\left(I"\right)^2}\sum_{i=1}^{3S-6}\left(\frac{\partial I"}{\partial Q_i}\right)^2 - \frac{2}{I"}\sum_{i=1}^{3S-6}\frac{\partial^2 I"}{\partial Q_i^2}\right] + \\ &+\left[\frac{1}{\left(I"\right)^2}\sum_{i=1}^{3S-6}\sum_{j=1}^{3S-6}\frac{\partial I"}{\partial Q_i}\frac{\partial I"}{\partial Q_j} - \frac{2}{I"}\sum_{i=1}^{3S-6}\sum_{j=1}^{3S-6}\frac{\partial^2 I"}{\partial Q_i \partial Q_j}\right]\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\mu_{\gamma\delta} \\ &\sum_{k=1}^{3S-6}\zeta_{ki}^{\gamma}Q_k\sum_{l=1}^{3S-6}\zeta_{lj}^{\delta}Q_l - \\ &-\frac{2}{I"}\sum_{j=1}^{3S-6}\frac{\partial I"}{\partial Q_j}\sum_{i=1}^{3S-6}\sum_{\alpha=x}^{z}\sum_{\beta=x}^{z}\frac{\partial \mu_{\alpha\beta}}{\partial Q_i}\sum_{k=1}^{3S-6}\zeta_{ki}^{\alpha}Q_k\sum_{l=1}^{3S-6}\zeta_{lj}^{\beta}Q_l - \\ &-\frac{2}{I"}\sum_{j=1}^{3S-6}\frac{\partial I"}{\partial Q_j}\sum_{i=1}^{3S-6}\sum_{\alpha=x}^{z}\sum_{\beta=x}^{z}\mu_{\alpha\beta}\zeta_{ij}^{\beta}\sum_{k=1}^{3S-6}\zeta_{ki}^{\alpha}Q_k\end{aligned} \tag{76}$$

where:

$$\begin{aligned}&\mu_{\alpha\beta} = \sum_{\varepsilon=x}^{z}\left(I"^{-1}\right)_{\alpha\varepsilon}I^0{}_{\varepsilon\varepsilon}\left(I"^{-1}\right)_{\varepsilon\beta}, \quad I"_{\alpha\beta} = I_{\alpha\beta}^0\delta_{\alpha\beta} + \frac{1}{2}\sum_{i=1}^{3S-6}a_i^{\alpha\beta}Q_i, \\ &a_i^{\alpha\beta} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_i}\right)_0, \quad \alpha,\beta,\varepsilon = x,y,z\end{aligned} \tag{77}$$

are the quantities introduced by Watson. After some algebra, one finds that:

$$\hat{T}^{(0)} = U_1 + U_2 + U_3 + U_4 \tag{78}$$

where U_1, U_2, U_3, U_4 are the quantities defined by Eqs. (45), (48), (50) and (52) in Watson's paper.[1]

CONCLUSIONS

In the present study, I derived the kinetic energy operator for molecules with non-linear equilibrium geometry in the form (when the electron variables are included *via* Scheme (60)):

$$\begin{aligned}\hat{T}_n = &\frac{1}{2}\left\{\sum_{\gamma=x}^{z}\sum_{\delta=x}^{z}\left(\hat{J}_\gamma - \hat{p}_\gamma - \hat{L}_\gamma\right)\mu_{\gamma\delta}\left(\hat{J}_\delta - \hat{p}_\delta - \hat{L}_\delta\right)\right\} + \\ &+\frac{1}{2}\sum_{i=1}^{3S-6}\hat{P}_i^2 + U_1 + U_2 + U_3 + U_4 + \\ &+\frac{1}{2m_e}\sum_{\mu=1}^{N}\left(\hat{P}_{\mu x}^2 + \hat{P}_{\mu y}^2 + \hat{P}_{\mu z}^2\right) - \\ &-\frac{1}{2m_e}\sum_{\mu=1}^{N}\sum_{\nu=1}^{N}\left(\hat{P}_{\mu x}\hat{P}_{\nu x} + \hat{P}_{\mu y}\hat{P}_{\nu y} + \hat{P}_{\mu z}\hat{P}_{\nu z}\right)\end{aligned} \tag{79}$$

It is almost equal to the Watson's one. "Almost" because I was not able to show in a simple way two things: a) that the coefficients $\mu_{\gamma\delta}$ can also be put before the term $\left(\hat{J}_\gamma - \hat{p}_\gamma - \hat{L}_\gamma\right)$ in the first sum on the right-hand side of Eq. (79), as in the last link of the chain of Eqs. (47) – for doing that, I needed the commutation relations (46) derived by Watson; b) I have not proven that:

$$U_1 + U_2 + U_3 + U_4 = -\left(\hbar^2 / 8\right)\sum_\gamma \mu_{\gamma\gamma}$$

However, I find the expression (79) indeed essentially equal to Watson's one. If one compares it with Wilson's expression (45), it can be seen that the determinant μ, appearing in Eq. (45), is not present in Eq. (79), which is the most important simplification made by Watson. Furthermore, although I did not show that the free term in Eq. (79) is simply:

$$-\left(\hbar^2 / 8\right)\sum_\gamma \mu_{\gamma\gamma}$$

I showed that it represents a small correction of the potential, because according to Eqs. (76) and (77), it involves derivatives (of second and higher order) of the instantaneous moments of inertia. From the point of view of a computer (and *it* solves nowadays every Schrödinger equation), the difference between $U_1 + U_2 + U_3 + U_4$ and $-\left(\hbar^2 / 8\right)\sum_\gamma \mu_{\gamma\gamma}$ is only of esthetical significance. When already speaking about esthetics, let me mention that (not attempting to diminish the achievement of Watson) the middle expression in Eq. (47), being obviously Hermitean, looks nicer than the last one. Thus, I hope that I have shown in a sense that also in the present case "*Omnes viae Romam ducunt*", or, more modestly, when not directly to Rome, than at least "*Romam ad/ante portas*".

A great part of the present study represents in fact compilation of already derived results. I think, however, that the approach applied in Section "Derivation of the Hamiltonian without use of quasi-momenta" has some advantages when compared with that used by Wilson and Watson. The fulfillment of the conditions that allowed the application of the generalized Podolsky transformation to quasi-momenta such as J_x, J_y, J_z might look accidental. As mentioned in the Introduction, the algebraic efforts connected with the application of this approach are tremendous. On the other hand, the only real difficulty in using the approach of the present study consists in inverting the matrix of coefficients appearing in the transformation (67) to obtain the coefficients g_{mn} given in Eq. (68). This looks difficult, because the transformation matrix is of the order $3S-3$ (when only dealing with the nuclei), but in fact it is not so. The final result could be obtained quite easily stepwise: One inverts first the 3×3 matrix involving solely the time derivatives of the Euler angles and the corresponding impulses and, bearing in mind the structure of this transformation, it is not difficult to invert the matrix additionally involving one and two normal coordinates. The jump to the real $(3S-3)\times(3S-3)$ problem is then straightforward. The present procedure becomes very appealing in some other cases, *e.g.*, in the construction of the Hamiltonian for triatomic molecules in terms of a set of internal coordinates (*e.g.*, two bonds and the valence angle, or Jacobi coordinates) and the Euler angles, at various definitions of the *MFS* (*e.g.*, with the axes coinciding with the instantaneous principal moments of inertia). Due to the fact that the nuclear skeleton of triatomic molecules is always planar (or linear), it is even possible to reduce the Podolsky transformation to a 4×4 matrix problem.[14,15]

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ИЗВОД

АЛТЕРНАТИВНО ИЗВОЂЕЊЕ (СКОРО-) ВОТСОНОВОГ ХАМИЛТОНИЈАНА

МИЉЕНКО ПЕРИЋ

Факултет за физичку хемију Универзитета у Београду

Приказано је извођење општег таласномеханичког хамилтонијана за нелинеарне молекуле. Оно се базира на трансформацији Хамилтонових импулса у одговарајуће таласномеханичке операторе помоћу трасформације Подолског. Резултат је суштински идентичан ономе који је извео Вотсон у свом епохалном раду (J. K. G. Watson, *Mol. Phys.* **15** (1968) 479). Мада не тако елегантан као онај из оригиналне референце, пут предложен у овом раду је концептуално много једноставнији. Овај поступак може се примијенити и на извођење других типова хамилтонијана.

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