Quantum description of a rotating and vibrating molecule

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A rigorous quantum description of molecular dynamics with a particular emphasis on internal observables is developed accounting explicitly for kinetic couplings between nuclei and electrons. Rotational modes are treated in a genuinely quantum framework by defining a molecular orientation operator. Canonical rotational commutation relations are established explicitly. Moreover, physical constraints are imposed on the observables in order to define the state of a molecular system located in the neighborhood of the ground state defined by the equilibrium condition.

I. INTRODUCTION

The dynamics of quantum molecular systems has been studied analytically and numerically for decades. Molecular rotations are usually characterised by Euler angles and kinetic couplings between nuclei and electrons are neglected. However, in order to make a precise quantum description of molecular dynamics, these couplings have to be taken explicitly into account, which leads to quantum deviations in the commutation relations. It is also important to recognise that the notion of a molecular reference frame is inconsistent with quantum physics, due to nonlocality. For the same reason, the orientation of a molecule cannot be described simply using Euler angles as in a classical framework. In order to treat rotational states of molecular systems in a genuine quantum framework, the orientation and rotation of a molecule has to be described using operators. This is done in this article.

Rotational states of molecular systems are currently of great interest. For example, in small molecular systems at low temperature, the rotational degrees of freedom play an important role since they can be distinguished experimentally from the vibrational degrees of freedom. Due to technological improvement, the distinction between these degrees of freedom became increasingly important in the last decade. Rotating atoms \[5\], rotating molecules \[6,7\], rotating trapped Bose-Einstein condensates \[8\] and even rotating microgyroscopes \[9\] are currently studied experimentally and are attracting much attention. For example, physisorbed \(H_2\), HD and D\(_2\) on a substrate at low temperature form a honeycomb lattice and rotational spectroscopy revealed a resonance width of \(H_2\) twice as large as the resonance widths of HD and D\(_2\) \[3\]. The theoretical explanation requires a rigorous quantum formalism with a genuine quantum treatment of molecular rotations.

A semi-classical approach is commonly used for the description of molecular dynamics \[10,11\]. An important shortcoming of such an approach is that it requires the rotational states to be in an eigenstate, thus imposing severe restrictions on the dynamics. Rotational states play an important role for low temperature spectroscopy \[2\], for THz spectroscopy \[13\], for molecular magnetism \[14\] and for molecular superrotors \[15\]. In order to establish a genuine quantum description of rotational molecular states, a molecular rotation operator has to be introduced.

Here, we develop a rigorous quantum description of molecule with a particular emphasis on internal observables. In this description, the vibrational and rotational modes are described by operators associated to the deformation and orientation of the molecule. The set of internal observables is related explicitly to the set of observables associated to nuclei and electrons through a rotation operator. The internal observables are chosen in order to satisfy canonical commutation relations in translation and rotation. Moreover, in order to define the state of a molecular system, physical constraints need to be imposed on the observables. In fact, the amplitudes of the vibrational modes of a molecular system have to be sufficiently small.

The structure of this publication is the following. In Sec. \[II\] we formally describe the dynamics of a system of \(N\) nuclei and \(n\) electrons. In Sec. \[III\] we define the internal observables in order to obtain canonical commutation relations in translation and rotation. Sec. \[IV\] is devoted to the description of the dynamics of the molecular system in terms of the internal observables. Finally, in Sec. \[V\] we determine the equilibrium conditions that define the molecular ground state and we define explicitly the angular frequency of the vibrational modes of the molecular system.

II. QUANTUM DESCRIPTION OF A SYSTEM OF \(N\) NUCLEI AND \(n\) ELECTRONS

The quantum dynamics of a molecular system consisting of \(N\) nuclei and \(n\) electrons is obtained from the classical dynamics by applying the “correspondence principle”. The Hilbert subspaces describing the nuclei and the electrons are denoted \(\mathcal{H}_N\) and \(\mathcal{H}_e\) respectively. The Hilbert space describing the whole system is expressed as,

\[
\mathcal{H} = \mathcal{H}_N \otimes \mathcal{H}_e.
\]
To investigate the molecular kinematics, it is not restrictive to assume that the nuclei are \( N \) discernible particles denoted by an index \( \mu = 1, \ldots, N \). These particles have a mass \( M_\mu \), an electric charges \( Z_\mu (-e) \) and a spin \( S_\mu \).

The symbol \( e \) represents the electronic electric charge including its sign and \( Z_\mu \) denotes the atomic number of the nucleus \( \mu \).

The Hilbert subspace \( \mathcal{H}_e \) associated to the electrons is assumed to be isomorphic to the tensor product of a one-electron Hilbert spaces, i.e.

\[
\mathcal{H}_e \sim (L^2(\mathbb{R}^3, \mathbb{C}) \otimes \mathbb{C})^n \sim L^2(\mathbb{R}^{3n}, \mathbb{C}^{2n}).
\]

In fact, the Hilbert spaces describing the electrons are totally antisymmetric subspaces of \( \mathcal{H}_e \). For a molecular system, the contribution of the overlap integrals between the nuclei is negligible. Thus, we do not need to take into account explicitly the fermionic nature of the nuclei.

The position, momentum and spin observables of the nuclei \( \mu \) are characterized respectively by the self-adjoint operators \( R_\mu \otimes 1_e, \quad P_\mu \otimes 1_e, \quad \text{and} \quad S_\mu \otimes 1_e \), where \( \mu = 1, \ldots, N \), acting trivially on the Hilbert subspace \( \mathcal{H}_e \) associated to the electrons. The components of the operators \( R_\mu \) and \( P_\mu \) acting on the Hilbert subspace \( \mathcal{H}_N \) satisfy the canonical commutation relations, i.e.

\[
[e_j \cdot P_\mu, \quad e^k \cdot R_\nu] = -ih \delta_{\mu\nu} (e_j \times e_k) \mathbb{1}_N,
\]

and the components of the operator \( S_\mu \) satisfy the canonical commutation relation, i.e.

\[
[e_j \cdot S_\mu, \quad e_k \cdot S_\nu] = ih \delta_{\mu\nu} (e_j \times e_k) \mathbb{1}_N.
\]

The other commutation relations are trivial, i.e.

\[
[e_j \cdot \mathbf{r}_\mu, \quad e^k \cdot \mathbf{r}_\nu] = 0,
\]

\[
[e_j \cdot P_\mu, \quad e_k \cdot P_\nu] = 0,
\]

\[
[e_j \cdot \mathbf{r}_\mu, \quad e_k \cdot S_\nu] = 0,
\]

\[
[e_j \cdot P_\mu, \quad e_k \cdot S_\nu] = 0.
\]

In order to discuss the dynamics of an electrically neutral molecular system composed of \( N \) nuclei and \( n \) electrons, we implicitly assume that

\[
\sum_{\mu=1}^N Z_\mu = n.
\]

In a non-relativistic framework, we restrict our analysis to instantaneous electromagnetic interactions between the particles, i.e. the electrons and the nuclei. In this framework, the Hamiltonian governing the evolution reads,

\[
H = H_N \otimes 1_e + 1_N \otimes H_e + H_{N-e},
\]

where the Hamiltonians \( H_N \) and \( H_e \) associated to the nuclei and electrons are defined respectively as,

\[
H_N = \sum_{\mu=1}^N \frac{P_\mu^2}{2M_\mu} + V_{N-N} + V_{N}^{SO},
\]

\[
H_e = \sum_{\nu=1}^n \frac{P_\nu^2}{2m} + V_{e-e} + V_{e}^{SO},
\]

where \( m \) is the mass of an electron, \( V_{N}^{SO} \) is the nuclear spin-orbit coupling due to the interaction between the spin and the orbital angular momentum of the nuclei and \( V_{e}^{SO} \) is the electronic spin-orbit coupling due to the interaction between the spin and the orbital angular momentum of the electrons. The Coulomb potentials \( V_{N-N} \) and \( V_{e-e} \) are respectively defined as,

\[
V_{N-N} = \frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^N \frac{Z_\mu Z_\nu}{\|R_\mu - R_\nu\|},
\]

\[
V_{e-e} = \frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^n \frac{1}{\|\mathbf{r}_\mu - \mathbf{r}_\nu\|},
\]

where \( \varepsilon_0 \) is the vacuum dielectric constant. The interaction Hamiltonian \( H_{N-e} \) appearing in the definition describes the interaction between the nuclei and the electrons. It is defined as,

\[
H_{N-e} = V_{N-N} + V_{N}^{SO}.
\]

The Coulomb potential \( V_{N-N} \) between the nuclei and the electrons is defined as,

\[
V_{N-N} = -\frac{e^2}{4\pi \varepsilon_0} \sum_{\mu=1}^N \sum_{\nu=1}^n \frac{Z_\mu}{\|R_\mu \otimes 1_e - 1_N \otimes \mathbf{r}_\nu\|},
\]

\[
\mathbf{r}_\nu = \mathbf{r}_\nu - \mathbf{r}_\nu.
\]
and \( V_{SO} \) is the spin-orbit coupling due to the interaction between the spin of the electrons and the orbital angular momentum of the nuclei and to the interaction between the spin of the nuclei and the orbital angular momentum of the electrons. As usual in molecular physics, the effects of the magnetic field produced by the motion of the particles are neglected.

### III. Internal Observables of the Molecular System

The description of molecular dynamics in a classical framework would be much simpler than in a quantum framework since in the former a rest frame could be attached easily to the physical system. In quantum physics, the approach is slightly different because observables are described mathematically by operators, which implies that there exists no rest frame and no centre of mass frame associated to the molecular system. However, even in the absence of a centre of mass frame, the position and momentum observables of the centre of mass can be expressed mathematically as self-adjoint operators. This enables us to define other position and momentum observables with respect to the centre of mass. We shall refer to them as “relative” position and momentum observables because they are the quantum equivalent of the classical relative position and momentum variables defined with respect to the center of mass frame. Then, using a rotation operator, we define the “rest” position and momentum observables, which are the quantum equivalent of the classical position and momentum variables defined in the molecular rest frame. Finally, the “rest” position and momentum observables are recast in terms of internal observables characterizing the vibrational, rotational and electronic degrees of freedom.

Applying the correspondence principle, the position, momentum and angular momentum observables associated to the center of mass are respectively given by the self-adjoint operators,

\[
\mathcal{Q} = \frac{1}{\mathcal{M}} \left( \sum_{\mu=1}^{N} \mathcal{M}_\mu \, R_\mu \otimes \mathbb{1}_e + \sum_{\nu=1}^{n} \mathbb{1}_N \otimes m \, r_\nu \right),
\]

\[
\mathcal{P} = \sum_{\mu=1}^{N} P_\mu \otimes \mathbb{1}_e + \sum_{\nu=1}^{n} \mathbb{1}_N \otimes p_\nu,
\]

where \( \mathcal{M} \) stands for the total mass of the molecule, i.e.

\[
\mathcal{M} = M + n m,
\]

and \( M \) represents the total mass of the nuclei, i.e.

\[
M = \sum_{\mu=1}^{N} \mathcal{M}_\mu.
\]

The commutation relations (2) and (5) imply that the operators \( \mathcal{P} \) and \( \mathcal{Q} \) satisfy the commutation relations,

\[
\left[ e_j \cdot \mathcal{P}, e^k \cdot \mathcal{Q} \right] = -i \hbar \left( e_j \cdot e^k \right) \mathbb{1}.
\]

Now we define the “relative” position operators \( R_\mu' \) and \( r_\nu' \), and the “relative” momentum operators \( P_\mu' \) and \( p_\nu' \). The “relative” position operators \( R_\mu' \) and \( r_\nu' \) are related to the position operators \( R_\mu \) and \( r_\nu \) by,

\[
R_\mu' = R_\mu \otimes \mathbb{1}_e - \mathcal{Q},
\]

\[
r_\nu' = 1_N \otimes r_\nu - \mathcal{Q}.
\]

Similarly, the “relative” momentum operators \( P_\mu' \) and \( p_\nu' \) are related to the momentum operators \( P_\mu \) and \( p_\nu \) by,

\[
P_\mu' = P_\mu \otimes \mathbb{1}_e - \frac{M_\mu}{\mathcal{M}} \mathcal{P},
\]

\[
p_\nu' = 1_N \otimes p_\nu - \frac{m}{\mathcal{M}} \mathcal{P}.
\]

The operators \( R_\mu' \), \( P_\mu' \), \( r_\nu' \) and \( p_\nu' \) commute with the operators \( \mathcal{Q} \) and \( \mathcal{P} \). In addition, these operators satisfy the condition,

\[
\sum_{\mu=1}^{N} M_\mu R_\mu' + \sum_{\nu=1}^{n} m \, r_\nu' = 0, \tag{21}
\]

which is a direct consequence of the definitions (14) and (19), and the condition,

\[
\sum_{\mu=1}^{N} P_\mu' + \sum_{\nu=1}^{n} p_\nu' = 0, \tag{22}
\]

which is a direct consequence of the definitions (15) and (20). Now, we can determine some further commutation relations. Clearly the components of the position operator \( R_\mu' \) commute and the components of the position operator \( r_\nu' \) commute as well. The components of the momenta operators \( P_\mu' \) and \( p_\nu' \) commute likewise, i.e.

\[
\left[ e^j \cdot R_\mu', e^k \cdot R_\nu' \right] = 0,
\]

\[
\left[ e_j \cdot P_\mu', e_k \cdot P_\nu' \right] = 0,
\]

\[
\left[ e_j \cdot r_\mu', e_k \cdot r_\nu' \right] = 0,
\]

\[
\left[ e_j \cdot p_\mu', e_k \cdot p_\nu' \right] = 0.
\]

Thus, the only non-trivial commutation relations read,

\[
\left[ e_j \cdot P_\mu', e^k \cdot R_\nu' \right] = -i \hbar \left( e_j \cdot e^k \right) \left( \delta_{\mu\nu} - \frac{M_\mu}{\mathcal{M}} \right) \mathbb{1},
\]

\[
\left[ e_j \cdot P_\mu', e^k \cdot R_\nu' \right] = i \hbar \left( e_j \cdot e^k \right) \frac{m}{\mathcal{M}} \mathbb{1},
\]

\[
\left[ e_j \cdot P_\mu', e^k \cdot r_\nu' \right] = i \hbar \left( e_j \cdot e^k \right) \frac{M_\mu}{\mathcal{M}} \mathbb{1},
\]

\[
\left[ e_j \cdot p_\mu', e^k \cdot r_\nu' \right] = -i \hbar \left( e_j \cdot e^k \right) \left( \delta_{\mu\nu} - \frac{m}{\mathcal{M}} \right) \mathbb{1}.
\]

Now we define the “rest” position operators \( R_\mu'' \) and \( r_\nu'' \), and the “rest” momentum operators \( P_\mu'' \) and \( p_\nu'' \). These operators are related respectively to the operators “relative” \( R_\mu' \), \( r_\nu' \), \( P_\mu' \) and \( p_\nu' \) by a rotation operator \( R(\omega) \).
that is a function of the operator $\omega$ describing the orientation of the molecular system. The rotation operator commutes with the "rest" position operators $R_{\mu}$, $r_{\nu}$, and the "rest" momentum operator $p_{\nu}$, but not with the "rest" momentum operator $p'_{\nu}$ as explained in Appendix [C]. The components of the "rest" position operators $R_{\mu}$ and $r_{\nu}$, are related to the components of the "relative" position operators $R_{\mu}$ and $r_{\nu}$ by,

$$
e^j \cdot R_{\mu} = \left( e^j \cdot R(\omega)^{-1} \cdot e^k \right) \left( e^k \cdot R_{\mu}^j \right),
$$

$$
e^j \cdot r_{\nu} = \left( e^j \cdot R(\omega)^{-1} \cdot e^k \right) \left( e^k \cdot r_{\nu}^j \right).$$

(25)

The components of the "rest" momentum operators $P_{\mu}$ and $p'_{\nu}$ are related to the "relative" position operators $P_{\mu}$ and $p'_{\nu}$ by,

$$e^j \cdot P_{\mu}^k = \frac{1}{2} \left\{ e^k \cdot R(\omega) \cdot e_j, e_j \cdot P_{\mu}^k \right\},
$$

$$e^j \cdot p'_{\nu} = \left( e^k \cdot R(\omega) \cdot e_j \right) \left( e^k \cdot p'_{\nu} \right).$$

(26)

where the brackets $\{,\}$ denote an anticommutator accounting for the fact that the rotation operator $R(\omega)$ does not commute with the position operator $P_{\mu}$ of the nuclei.

The self-adjoint molecular orientation operator $\omega$ is fully determined by the position operators $R_{\mu}$ and $r_{\nu}$. Thus, the components of $\omega$ satisfy the trivial commutation relations,

$$[ e^j \cdot \omega, e^k \cdot \omega ] = 0.$$  

(27)

The orientation operator $\omega$ belongs to the rotation algebra and it is related to the rotation operator $R(\omega)$ that belongs to the rotation group by exponentiation, i.e.

$$R(\omega) = \exp (\omega \cdot G),$$

(28)

taking into account the commutation relation (27) of the components of the orientation operator $\omega$. The elements of the rotation group have to satisfy the orthogonality condition, i.e.

$$R(\omega)^T \cdot R(\omega) = 1,$$

(29)

which implies that $R(\omega)^T = R(\omega)^{-1}$ and in turn that,

$$G^T = -G.$$  

(30)

where the components of the vector $G$ are rank-2 tensors that are generators of the rotation group acting on $\mathbb{R}^3$. The action of the rotation group is locally defined as,

$$(e_j \cdot G) x = e_j \times x,$$  

(31)

which implies that the generators $G$ of the rotation in $\mathbb{R}^3$ verify the well known commutation relations

$$[ e_j \cdot G, e_k \cdot G ] = (e_j \times e_k) \cdot G.$$  

(32)

The operators $n_{(j)} (\omega)$ are Killing vectors [16] of the rotation algebra that are defined in terms of the rotation operator $R(\omega)$ and the rotation generators as,

$$R(\omega)^{-1} \cdot (e_j \cdot \partial_{\omega}) R(\omega) = n_{(j)} (\omega) \cdot G.$$  

(33)

The dual operator $m^{(k)} (\omega)$ satisfies the duality condition,

$$n_{(j)} (\omega) \cdot m^{(k)} (\omega) = e_j \cdot e^k.$$  

(34)

As shown in Appendix A, the Killing form [17] associated to the rotation group is given by,

$$n_{(j)} (\omega) \cdot n_{(k)} (\omega) = e_j \cdot \left( P_\omega + A (1 - P_\omega) \right) \cdot e_k,$$  

(35)

where the projector $P_\omega$ and the scalar $A$ are respectively defined as,

$$P_\omega = \frac{\omega \cdot \omega}{||\omega||^2},$$

$$A = \left( \frac{2}{||\omega||^2} \sin \frac{||\omega||}{2} \right)^2.$$  

(36)

According to the definition (36), in the limit of an infinitesimal rotation, i.e. $||\omega|| \rightarrow 0$, the scalar $A \rightarrow 1$, which implies that,

$$\lim_{||\omega|| \rightarrow 0} n_{(j)} (\omega) = e_j \cdot 1,$$

$$\lim_{||\omega|| \rightarrow 0} m^{(k)} (\omega) = e^k \cdot 1.$$  

(37)

The operators $n_{(j)} (\omega)$ and $m^{(k)} (\omega)$ determine the structure of the rotation algebra.

Using the relations (25), the condition (21) is recast as,

$$\sum_{\mu=1}^{N} M_\mu R_{\mu} + \sum_{\nu=1}^{n} m \cdot r_{\nu} = 0.$$  

(38)

Similarly, using the relations (26), the condition (22) is recast as,

$$\sum_{\mu=1}^{N} P_{\mu} + \sum_{\nu=1}^{n} p'_{\nu} = 0.$$  

(39)

Now, we can introduce operators characterizing the internal observables of the quantum molecular system. First, we introduce the scalar operators $Q^\alpha$, where $\alpha = 1, \ldots, 3N - 6$, characterizing the amplitude of the vibrational modes of the $N$ nuclei. Second, we introduce the vectorial operators $q_{(\nu)}$ related to the relative position of the electrons respectively. The "rest" position operator $R_{\mu}^0$ is expressed in terms of the scalar operators $Q^\alpha$ and the vectorial operators $q_{(\nu)}$ as,

$$R_{\mu}^0 = R_{\mu}^0 \cdot \mathbb{1} + \frac{1}{\sqrt{M}} Q^\alpha X_{\mu \alpha} - \frac{m}{M} \sum_{\nu, \nu' = 1}^{n} A_{\nu \nu'} q_{(\nu')}.$$  

(40)
where we used Einstein’s implicit summation convention for the vibrational modes α. The relation (10) yields a kinetic coupling between the “rest” position operators of the nuclei and electrons. The “rest” position operator \( r''_\nu \) is expressed in terms of the position operators \( q_{(\nu')} \) as,

\[
r''_\nu = \sum_{\nu'=1}^{n} A_{\nu\nu'} q_{(\nu')} ,
\]

where the matrix elements \( A_{\nu\nu'} \) and \( A^{-1}_{\nu\nu'} \) are defined as,

\[
A_{\nu\nu'} = \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{M/M_0} - 1 \right) ,
\]

\[
A^{-1}_{\nu\nu'} = \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{M/M_0} - 1 \right) .
\]

Similarly, the “rest” momentum operator \( P''_\mu \) is expressed in terms of the scalar operators \( P_\alpha \), the vector operators \( p_{(\nu')} \) and the angular velocity pseudo-vectorial operator \( \Omega \) as,

\[
P''_\mu = \Omega \times \left( M_\mu R''_\mu^{(0)} \right) + \sqrt{M_\mu} P_\alpha X''_\mu \left( \frac{M}{M_\mu} \right) \sum_{\nu'=1}^{n} A_{\nu\nu'} p_{(\nu')} .
\]

The relation (43) yields a kinetic coupling between the “rest” momentum operators of the nuclei and electrons. The “rest” momentum operator \( p''_\nu \) is expressed in terms of the momentum operators \( p_{(\nu')} \) as,

\[
p''_\nu = \sum_{\nu'=1}^{n} A_{\nu\nu'} p_{(\nu')} .
\]

Note that the definition of the matrix elements \( A_{\nu\nu'} \) is not unique. However, the particular choice made in relation (42) leads to canonical commutation relations between the electronic position operator \( q_{(\nu')} \) and the electronic momentum operator \( p_{(\nu')} \).

The vector set \( \{ X_{\mu\alpha} \} \) is the orthonormal basis characterizing the vibrational modes and the vector set \( \{ X'_{\mu} \} \) is the dual orthonormal basis, i.e.

\[
\sum_{\mu=1}^{N} X_{\mu\alpha} \cdot X'_{\mu} = \delta_{\alpha}^\beta .
\]

The vectors \( R''_\mu^{(0)} \) correspond to the equilibrium configurations of the nuclei. In order for the identities (40) and (41) to satisfy the condition (38) and for the identities (43) and (44) to satisfy the condition (39), we need to impose conditions on the vectors \( R''_\mu^{(0)} \) and \( X_{\mu\alpha} \). First, we choose the origin of the coordinate system such that it coincides with the center of mass, i.e.

\[
\sum_{\mu=1}^{N} M_\mu R''_\mu^{(0)} = 0 .
\]

Then, we require the deformation modes of the molecule to preserve the momentum, i.e.

\[
\sum_{\mu=1}^{N} \sqrt{M_\mu} X_{\mu\alpha} = 0 .
\]

We also require the deformation modes of the molecule to preserve the orbital angular momentum, i.e.

\[
\sum_{\mu=1}^{N} \sqrt{M_\mu} \left( R''_\mu^{(0)} \times X_{\mu\alpha} \right) = 0 .
\]

The constraints (46)-(48) are known as the Eckart conditions (13). Finally, we choose the orientation of the coordinate system such that the inertia tensor of the equilibrium position of the nuclei is diagonal, i.e.

\[
\sum_{\mu=1}^{N} M_\mu \left( e_j \cdot R''_\mu^{(0)} \right) \left( e_k \cdot R''_\mu^{(0)} \right) = 0 .
\]

As shown in Appendix E, the first relation (25) and the physical constraints (46) and (48) determine the rotation operator \( R(\omega) \), i.e.

\[
\sum_{\mu=1}^{N} M_\mu R''_\mu^{(0)} \times \left( R(\omega)^{-1} \right) \cdot R''_\mu^{(0)} = 0 .
\]

To emphasize the physical motivation behind the previous formal development, we consider the classical counterpart of a quantum molecular system. In a classical framework, the classical counterpart of the operatorial relation (50) determines the rest frame of the molecular system. Moreover, the equilibrium configuration of a molecule is given by a vector set \( \{ R''_\mu^{(0)} \} \) describing the position of the nuclei. The condition (46) implies that the centre of mass of the molecule coincides with the origin of the coordinate system and the condition (49) requires the inertial tensor of this molecule to be diagonal with respect to the coordinate system.

The set of orthonormal vectors \( \{ X_{\mu\alpha} \} \) characterize the \( 3N - 6 \) normal deformation modes of the molecule and thus account for the vibrations. The condition (47) implies that the normal deformation modes preserve the momentum of the molecule and the condition (48) requires that these modes also preserve the orbital angular momentum of the molecule. Thus, the deformation modes of the molecule do not generate translations or rotations of the molecule.

The commutation relations (23) and (24) and the transformation laws (25) and (26) imply that the commutation relations between the operators \( R''_\mu^{(0)}, r''_\nu^{(0)} \) and \( p''_\nu \)
are given by,
\[
\begin{align*}
[e_j \cdot R''_{\mu}, e^k \cdot R''_{\nu}] &= 0, \\
[e_j \cdot R''_{\mu}, e^k \cdot R''_{\nu}] &= 0 , \\
[e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu}] &= 0 , \\
[e_j \cdot R''_{\mu}, e^k \cdot P''_{\nu}] &= 0 , \\
[e_j \cdot P''_{\mu}, e^k \cdot R''_{\nu}] &= -i\hbar (e_j \cdot e^k) \left( \delta_{\mu\nu} - \frac{m_{\mu}}{M} \right) .
\end{align*}
\]
(51)

The kinetic couplings \[40\] and \[43\] between the “rest” position and momentum operators of the nuclei and electrons lead to quantum deviations in the commutation relations \[51\], characterised by the mass ratio \( m/M \). These deviations are larger for smaller molecules. For example, for a \( \text{H}_2^+ \) molecule \[19\] : \( m/\mathcal{M} = 2 \cdot 10^{-4} \).

As shown in Appendix \[C\] using the physical identity \[50\] defining the rotation operator, the mathematical identity \[33\] associated to the action of the rotation group, the commutation relation \[23\] and \[24\] and the transformation laws \[25\] and \[26\], the commutation relations between the operators \( R''_{\mu}, P''_{\nu}, R''_{\nu}, \) and \( P''_{\nu} \) are found to be,
\[
\begin{align*}
[e_j \cdot P''_{\mu}, e^k \cdot R''_{\nu}] &= i\hbar \left( e_j \cdot e^k \right) \frac{M_{\mu}}{\mathcal{M}} \mathbb{1} , \\
[e_j \cdot P''_{\mu}, e^k \cdot \omega] &= \left( n_{(j)} (\omega) \times R''_{\nu} \right) , \\
[e_j \cdot P''_{\mu}, e^k \cdot \omega] &= \left( n_{(j)} (\omega) \times P''_{\nu} \right) , \\
[e_j \cdot P''_{\mu}, e^k \cdot R''_{\nu}] &= -i\hbar \left( e_j \cdot e^k \right) \left( \delta_{\mu\nu} - \frac{M_{\mu}}{\mathcal{M}} \right) \mathbb{1} , \\
[e_j \cdot P''_{\mu}, e^k \cdot \omega] &= \left( n_{(j)} (\omega) \times R''_{\nu} \right) ,
\end{align*}
\]
(52)

The kinetic couplings \[40\] and \[43\] between the “rest” position and momentum operators of the nuclei and electrons lead to quantum deviation in the commutation relations \[52\], characterised by the mass ratio \( M_{\mu}/\mathcal{M} \). These deviations are larger for smaller molecules. For example, for a \( \text{H}_2^+ \) molecule \[19\] : \( M_{\mu}/\mathcal{M} = 0.33 \). Moreover, the fact that molecular rotations are treated in a genuine quantum framework leads to other quantum deviations in the commutation relations \[52\]. These deviations are proportional to the commutator of the “rest” momentum operator \( P''_{\nu} \) and the molecular orientation operator \( \omega \).

The internal observables are described by the scalar operators \( Q^\alpha, P_\alpha \), the vectorial operators \( q_{(\nu)}, p_{(\nu)} \), and the pseudo-vectorial operators \( \Omega \) and \( \omega \). As shown in Appendix \[D\] the inversion of the definitions \[10, 11, 13, 14\] yields explicit expressions for the internal observables \( Q^\alpha, P_\alpha, q_{(\nu)}, p_{(\nu)} \), i.e.
\[
Q^\alpha = \sum_{\mu=1}^{N} \sqrt{\mathcal{M}_\mu} X^\alpha_{\mu} \left( R''_{\mu} - R''_{\mu}^{(0)} \right) , \\
P_\alpha = \sum_{\mu=1}^{N} \left( \frac{1}{\mathcal{M}_\mu} - \frac{1}{\mathcal{M}} \right) \left( R_{\mu} \cdot X_{\mu} \cdot P''_{\mu} \right) , \\
q_{(\nu)} = \sum_{\nu'=1}^{n} \left( \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{\mathcal{M}} - 1 \right) \right) r''_{\nu} , \\
p_{(\nu)} = \sum_{\nu'=1}^{n} \left( \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{\mathcal{M}} - 1 \right) \right) p''_{\nu} .
\]
(53)

The components of the inertia tensorial operator \( I(Q^\cdot) \) are defined as,
\[
e_k \cdot I(Q^\cdot) \cdot e_\ell = (e_k \cdot l_0 \cdot e_\ell) \mathbb{1} + Q^\alpha (e_k \cdot l_\alpha \cdot e_\ell) ,
\]
(54)

where the dot in the argument of the operator \( I(Q^\cdot) \) refers to all the vibrational modes. The first term on the RHS of the definition \[54\], i.e.
\[
e_k \cdot l_0 \cdot e_\ell = \sum_{\mu=1}^{N} M_{\mu} \left( e_k \times R''_{\mu}^{(0)} \right) \cdot \left( e_\ell \times R''_{\mu}^{(0)} \right) ,
\]
(55)

\[
= \sum_{\mu=1}^{N} M_{\mu} \left( R''_{\mu}^{(0)} \cdot (e_k \cdot e_\ell) - \left( e_k \cdot R''_{\mu}^{(0)} \right) \left( e_\ell \cdot R''_{\mu}^{(0)} \right) \right) ,
\]
is required to be diagonal with respect to the rotating molecular system according to the constraint \[49\], i.e.
\[
e_k \cdot l_0 \cdot e_\ell = (e_k \cdot l_0 \cdot e_k) (e_k \cdot e_\ell) \\
= \sum_{\mu=1}^{N} M_{\mu} \left( R''_{\mu}^{(0)} - \left( e_k \cdot R''_{\mu}^{(0)} \right) \right) (e_k \cdot e_\ell) ,
\]
(56)

and the term on the RHS, i.e.
\[
e_k \cdot l_\alpha \cdot e_\ell = \sum_{\mu=1}^{N} \sqrt{\mathcal{M}_\mu} (e_k \times X_{\mu}) \cdot \left( e_\ell \times R''_{\mu}^{(0)} \right) ,
\]
(57)

is shown in Appendix \[F\] to be symmetric, i.e.
\[
e_k \cdot l_\alpha \cdot e_\ell = e_\ell \cdot l_\alpha \cdot e_k .
\]
(58)

As shown in detail in Appendix \[F\], the commutation relations between the operators \( Q^\alpha, P_\alpha, q_{(\nu)}, p_{(\nu)}, \omega, \Omega \) accounting for internal degrees of freedom are determined using the commutation relations \[51\] and \[52\], the definitions \[53\] and \[42\], and the constraints \[45\]–\[48\].
The canonical commutation relations are given by,

\[
\begin{align*}
[ Q^\alpha, Q^\beta ] &= 0,  \\
[ Q^\alpha, e^k \cdot q_{(\nu')} ] &= 0,  \\
[ Q^\alpha, e^k \cdot \omega ] &= 0,  \\
[ e^j \cdot q_{(\nu)}, e^k \cdot q_{(\nu')} ] &= 0,  \\
[ e^j \cdot q_{(\nu)}, e^k \cdot \omega ] &= 0.
\end{align*}
\]

The other non-canonical commutation relations vanish as well, i.e.

\[
\begin{align*}
[ P_\alpha, P_\beta ] &= 0,  \\
[ Q^\alpha, e^k \cdot p_{(\nu')} ] &= 0,  \\
[ P_\alpha, e^k \cdot p_{(\nu')} ] &= 0,  \\
[ P_\alpha, e^k \cdot q_{(\nu')} ] &= 0,  \\
[ P_\alpha, e^k \cdot \omega ] &= 0,  \\
[ e^j \cdot p_{(\nu)}, e^k \cdot p_{(\nu')} ] &= 0,  \\
[ e^j \cdot p_{(\nu)}, e^k \cdot \omega ] &= 0.
\end{align*}
\]

The canonical commutation relations are given by,

\[
\begin{align*}
[ P_\alpha, Q^\beta ] &= -i\hbar \delta^\beta_\alpha \mathbb{1},  \\
[ e^j \cdot p_{(\nu)}, e^k \cdot q_{(\nu')} ] &= -i\hbar (e^j \cdot e^k) \delta_{\nu\nu'} \mathbb{1}.
\end{align*}
\]

The operator \( \Omega \) does not commute with the operators \( Q^\alpha, P_\alpha, q_{(\nu)}, p_{(\nu)} \) and \( \omega \), i.e.

\[
\begin{align*}
[ e^j \cdot \Omega, Q^\alpha ] &= \\
&= -i\hbar \sum_{\mu=1}^N \left( e^j \cdot (Q^\alpha)^{-1} \cdot (X^\alpha_{\mu} \times X^\beta_{\mu}) \cdot Q^\beta \right),  \\
[ e^j \cdot \Omega, P_\alpha ] &= \\
&= -\frac{1}{2} i\hbar \sum_{\mu=1}^N \left( e^j \cdot (Q^\alpha)^{-1} \cdot X^\alpha_{\mu}, P^\beta_{\mu} X^\beta_{\mu} \right)_\times,  \\
[ e^j \cdot \Omega, e^k \cdot q_{(\nu)} ] &= \\
&= -i\hbar \left( e^j \cdot (Q^\alpha)^{-1} \cdot e^k \right) (e_\ell \times e_k) \cdot q_{(\nu)},  \\
[ e^j \cdot \Omega, e^k \cdot p_{(\nu')} ] &= \\
&= -i\hbar \left( e^j \cdot (Q^\alpha)^{-1} \cdot e^k \right) (e_\ell \times e_k) \cdot p_{(\nu')},  \\
[ e^j \cdot \Omega, e^k \cdot \omega ] &= -i\hbar \left( e^j \cdot (Q^\alpha)^{-1} \cdot m^{(k)}(\omega) \right),
\end{align*}
\]

where we used the notation convention,

\[
[ A, B ]_\times = A \times B - B \times A.
\]

According to the commutation relations (62), the angular velocity operator \( \Omega \) does not commute with the other internal observables. Thus, it is not a suitable observable for a quantum description of molecular rotation. Therefore, we introduce the angular momentum operator \( L' \) defined as,

\[
L' = \sum_{\mu=1}^N R'_\mu \times P'_\mu + \sum_{\nu=1}^n r'_{\nu} \times p'_{\nu},
\]

and the angular momentum operator \( L \) defined as,

\[
L = \frac{1}{2} \sum_{\mu=1}^N \left[ R''_\mu, P''_\mu \right]_\times + \frac{1}{2} \sum_{\nu=1}^N \left[ r''_{\nu}, p''_{\nu} \right]_\times,
\]

where we used the notation convention (63).

As shown in Appendix C, using the definitions (40)-(44), (54)-(58) and the notation conventions (63) and,

\[
\{ A, B \}_\times = A \cdot B + B \cdot A,
\]

the orbital angular momentum (65) is recast as,

\[
L = \frac{1}{2} \left\{ (Q^\alpha), \Omega \right\}_\times + \frac{1}{2} \sum_{\mu=1}^N \left[ Q^\alpha X^\mu_{\alpha}, P^\beta_{\mu} X^\beta_{\mu} \right]_\times
\]

\[
+ \frac{1}{2} \sum_{\nu=1}^n \left[ q_{(\nu)}, p_{(\nu)} \right]_\times,
\]

which is a self-adjoint operator. Since the orbital angular momentum operator commutes with the position and momentum operators, as shown explicitly below, it is convenient to recast the angular rotation rate \( \Omega \) in terms of \( L \). In order to do so, we define the molecular orbital angular momentum \( L \), the deformation orbital angular momentum \( L' \) and the electronic orbital angular momentum \( \ell \) respectively as,

\[
L = \frac{1}{2} \left\{ (Q^\alpha), \Omega \right\}_\times,
\]

\[
L' = \frac{1}{2} \sum_{\mu=1}^N \left[ Q^\alpha X^\mu_{\alpha}, P^\beta_{\mu} X^\beta_{\mu} \right]_\times,
\]

\[
\ell = \frac{1}{2} \sum_{\nu=1}^n \left[ q_{(\nu)}, p_{(\nu)} \right]_\times.
\]

Using the definitions (68) and the fact that the inertia tensor \( I(Q^\cdot) \) commutes with the operators \( L, q_{(\nu)} \) and \( p_{(\nu)} \), the inversion of the expression (67) yields the rotation rate, i.e.

\[
\Omega = \frac{1}{2} \left\{ (Q^\cdot)^{-1}, L \right\}_\times.
\]
where
\[ \mathcal{L} = L - L' - \ell. \quad (70) \]

As shown in Appendix I, the commutation relations involving the orbital angular momentum operator \( L \) are obtained using the expression (67) and the commutation relations (59).

The orbital angular momentum operator \( L \) commutes with the configuration and momentum operators \( Q^\alpha, P_\alpha, q_{(\nu)} \) and \( p_{(\nu)} \), i.e.
\[
\begin{align*}
[ L, Q^\alpha ] &= 0, \\
[ L, P_\alpha ] &= 0, \\
[ L, e^k \cdot q_{(\nu)} ] &= 0, \\
[ L, e_k \cdot p_{(\nu)} ] &= 0.
\end{align*}
\]

The orbital angular momentum operator \( L \) does not commute with the operators \( \omega, \Omega \) and \( L \), i.e.
\[
\begin{align*}
[ L, e^j \cdot \omega ] &= -i \hbar m^{(j)} (\omega), \\
[ L, e^j \cdot \Omega ] &= i \hbar \left( e^j \cdot 1 (Q)^{-1} \cdot e^k \right) (e_k \times L), \\
[ L, e_j \cdot L ] &= i \hbar \delta_{\mu\nu} (e_j \times e_k) \cdot L.
\end{align*}
\]

The third commutation relation (72) implies that,
\[
\begin{align*}
[ L^2, e_j \cdot L ] &= 0, \\
[ e_j \cdot L, e_k \cdot L ] &= i \hbar \delta_{\mu\nu} (e_j \times e_k) \cdot L,
\end{align*}
\]
as expected. Finally, the property (34) and the commutation relation (72) imply that the canonical commutation relations for a quantum rotation are given by,
\[
[ n_{(j)} (\omega) \cdot L, e^k \cdot \omega ] = -i \hbar (e_j \cdot e_k). \quad (74)
\]

The internal spin observables are the nuclear spin operator \( S_{(\mu)} \) and the electronic spin operator \( s_{(\nu)} \) that are respectively defined as,
\[
\begin{align*}
e_j \cdot S_{(\mu)} &= (e^k \cdot R(\omega) \cdot e_j) \cdot e_k \cdot S_\mu, \\
e_j \cdot s_{(\nu)} &= (e^k \cdot R(\omega) \cdot e_j) \cdot e_k \cdot s_\nu.
\end{align*}
\]

As shown in Appendix I, the definitions (75), the commutation relations (3) and (6), and the fact that the spins commute with the molecular orientation observable \( \omega \) imply that,
\[
\begin{align*}
[ e_j \cdot S_{(\mu)}, e_k \cdot S_{(\mu)} ] &= i \hbar \delta_{\mu\nu} (e_j \times e_k) \cdot S_{(\mu)}, \\
[ e_j \cdot s_{(\nu)}, e_k \cdot s_{(\nu)} ] &= i \hbar \delta_{\mu\nu} (e_j \times e_k) \cdot s_{(\nu)}.
\end{align*}
\]

The operators \( Q^\alpha, q_{(\nu)} \) and \( \omega \) commute with the nuclear spin operators \( S_{(\mu)} \), i.e.
\[
\begin{align*}
[ S_{(\mu)}, e^j \cdot q_{(\nu)} ] &= 0, \quad (77) \\
[ S_{(\mu)}, Q^\alpha ] &= 0, \quad (78) \\
[ S_{(\mu)}, e^j \cdot \omega ] &= 0. \quad (79)
\end{align*}
\]

and also with the electronic spin operators \( s_{(\mu)} \), i.e.
\[
\begin{align*}
[ s_{(\mu)}, e^j \cdot q_{(\nu)} ] &= 0, \quad (80) \\
[ s_{(\mu)}, Q^\alpha ] &= 0, \quad (81) \\
[ s_{(\mu)}, e^j \cdot \omega ] &= 0. \quad (82)
\end{align*}
\]

Moreover, as demonstrated in the Appendix I, the operators \( P_\alpha \) and \( p_{(\nu)} \) commute with the nuclear spin operators \( S_{(\mu)} \), i.e.
\[
\begin{align*}
[ S_{(\mu)}, e_j \cdot p_{(\nu)} ] &= 0, \quad (83) \\
[ S_{(\mu)}, P_\alpha ] &= 0, \quad (84) \\
[ s_{(\mu)}, e_j \cdot p_{(\nu)} ] &= 0, \quad (85) \\
[ s_{(\mu)}, P_\alpha ] &= 0. \quad (86)
\end{align*}
\]

Finally, as shown in the Appendix I, the commutation relations between the orbital angular momentum \( L \) and the spin operators \( S_{(\mu)} \) and \( s_{(\nu)} \) are respectively given by,
\[
\begin{align*}
[ S_{(\mu)}, e_j \cdot L ] &= i \hbar (e_j \cdot S_{(\mu)}), \\
[ s_{(\nu)}, e_j \cdot L ] &= i \hbar (e_j \cdot s_{(\nu)}). \quad (87)
\end{align*}
\]

IV. DYNAMICAL DESCRIPTION OF A ROTATING AND VIBRATING MOLECULE

The observable corresponding to the kinetic energy is defined as,
\[
T = \sum_{\mu=1}^{N} \frac{P_\mu^2}{2M_\mu} \otimes I_e + \sum_{\nu=1}^{n} \frac{P_{\nu}^2}{2m} \otimes I_e, \quad (88)
\]

As shown in Appendix I, it is recast as,
\[
T = \frac{\mathcal{P}^2}{2\mathcal{M}} + \sum_{\mu=1}^{N} \frac{P_\mu'^2}{2M_\mu'} + \sum_{\nu=1}^{n} \frac{P_{\nu}''^2}{2m'} + \frac{\hbar^2}{8} \Phi_{\text{res}} (Q'), \quad (89)
\]

where \( \Phi_{\text{res}} (Q') \) is a residual operator resulting from the non-commutation of the rotation operator \( R(\omega) \) and the momentum operator \( P_\mu \) that is given by,
\[
\Phi_{\text{res}} (Q') = \text{Tr} (I_{00}) \text{Tr} \left( 1 (Q')^{-2} \right) - 2 \text{Tr} (I_{00} \cdot 1 (Q')^{-1}) \text{Tr} (1 (Q')^{-1}) + \text{Tr} \left( I_{00} \cdot 1 (Q')^{-2} - 2 \left( I_a \cdot 1 (Q')^{-1} \right)^2 \right) + 2 \text{Tr} \left( 1 (Q')^{-2} \cdot I_{03} \cdot Q^3 \right), \quad (90)
\]
and the rank-2 tensors $l_{0\alpha}$ and $l_{0\beta}^{\alpha}$ are defined respectively as,

$$l_{0\alpha} = \sum_{\mu, \nu = 1}^{N} M_{\mu \nu} R_{\mu}^{(0)} R_{\nu}^{(0)},$$  \hspace{1cm} (91)

$$l_{0\beta}^{\alpha} = \sum_{\mu, \nu = 1}^{N} R_{\mu}^{(0)} \left( \left( R_{\nu}^{(0)} \cdot X_{\mu \nu}^{(0)} \right) X_{\nu \beta}^{(0)} - \left( R_{\mu}^{(0)} \cdot X_{\nu \beta}^{(0)} \right) X_{\nu \beta}^{(0)} \right)$$ \hspace{1cm} (92)

As shown in Appendix I, using the appropriate commutation relations, the kinetic energy \(89\) is recast in terms of the internal observables as,

$$T = \frac{p^2}{2M} + \frac{1}{2} \left\{ \mathcal{L}, 1(Q^{-1}) \right\} \cdot l_{0} \cdot \left\{ 1(Q^{-1}), \mathcal{L} \right\},$$

$$+ \frac{1}{2} P_{\alpha} P_{\alpha} + \sum_{\nu = 1}^{n} \frac{p_{\nu}^2}{2m} + \frac{\hbar^2}{8} \Phi_{\text{res}} (Q^{-1}).$$ \hspace{1cm} (93)

The expression \(94\) of the kinetic energy \(T\) separates the rotational and vibrational degrees of freedom. It is a consequence of the Eckart conditions \(46\), \(47\) and \(48\) and of the physical definition \(50\) of the rotation operator $R(\omega)$. It is the quantum counterpart of the expression derived by Jellinek and Li \[20\] \[21\] and extended by Essen \[22\] in a classical framework.

The Hamiltonian \(9\) is expressed in terms of the kinetic energy as,

$$H = T + V_{N-N}(Q^+) + V_{r-e}(q_{(\nu)}) + V_{N-e}(Q^+, q_{(\nu)})$$

$$+ V_{N}^{SO}(Q^+, P, L, S_{(\nu)}) + V_{ae}^{SO}(q_{(\nu)}, p_{(\nu)}, s_{(\nu)})$$

$$+ V_{N-e}^{SO}(Q^+, P, L, S_{(\nu)}, q_{(\nu)}, p_{(\nu)}, s_{(\nu)})$$ \hspace{1cm} (95)

Taking into account the fact that the norm is invariant under rotation and using the definitions \(10\), \(13\) and \(40\), the nuclear, electronic and interaction Coulomb potentials are recast in terms of the internal observables respectively as,

$$V_{N-N}(Q^+)$$

$$= \frac{e^2}{8\pi \varepsilon_0} \sum_{\mu, \nu = 1}^{N} \left\| \left( R_{\mu}^{(0)} - R_{\nu}^{(0)} \right) 1 + Q^\alpha (Y_{\mu \alpha} - Y_{\nu \alpha}) \right\|,$$

$$V_{r-e}(q_{(\nu)}) = \frac{e^2}{8\pi \varepsilon_0} \sum_{\mu, \nu = 1}^{n} \left\| \bar{q}_{(\mu)} - \bar{q}_{(\nu)} \right\|,$$

$$V_{N-e}(Q^+, q_{(\nu)})$$

$$= -\frac{e^2}{4\pi \varepsilon_0} \sum_{\mu, \nu = 1}^{N} \sum_{\mu, \nu = 1}^{n} \left\| R_{\mu}^{(0)} \right\| + Q^\alpha Y_{\mu \alpha} - \bar{q}_{(\nu)} \right\|,$$

where the orthogonal basis vector $Y_{\mu \alpha}$ is related to the orthonormal basis vector $X_{\mu \alpha}$ by,

$$X_{\mu \alpha} = \sqrt{M_{\mu}} Y_{\mu \alpha},$$ \hspace{1cm} (97)

and the operator $\bar{q}_{(\nu)} = r_{(\nu)}^\mu$ is a function of the operators $q_{(\nu)}$ according to the relation \(41\).

The potential energy operator associated to the spin-orbit coupling between the nuclei is given by,

$$V_{N}^{SO}(Q^+, P, L, S_{(\nu)}) = -\sum_{\mu = 1}^{N} \gamma_{\mu} S_{(\mu)} \cdot B_{(\mu)}^{N}(Q^+, P, L),$$ \hspace{1cm} (98)

where $\gamma_{\mu} > 0$ is the gyromagnetic ratio of the nucleus $\mu$ and $B_{(\mu)}^{N}(Q^+, P, L)$ is a pseudo-vectorial operator corresponding to the internal magnetic field exerted on the nucleus $\mu$ and generated by the relative motion of the other nuclei. Similarly, the potential energy operator associated to the spin-orbit coupling between the electrons yields,

$$V_{e}^{SO}(q_{(\nu)}, p_{(\nu)}, s_{(\nu)}) = -\sum_{\nu = 1}^{n} \gamma_{e} s_{(\nu)} \cdot B_{(\nu)}^{e}(q_{(\nu)}, p_{(\nu)}),$$ \hspace{1cm} (99)

where $\gamma_{e} < 0$ is the gyromagnetic ratio of the electron and $B_{(\nu)}^{e}(q_{(\nu)}, p_{(\nu)})$ is a pseudo-vectorial operator corresponding to the internal magnetic field exerted on the electron $\nu$ and generated by the relative motion of the other electrons. Finally, the potential energy operator associated to the spin-orbit coupling between the nuclei and the electrons is given by,

$$V_{N-e}^{SO}(Q^+, P, L, S_{(\nu)}, q_{(\nu)}, p_{(\nu)}, s_{(\nu)})$$

$$= -\sum_{\nu = 1}^{n} \gamma_{e} s_{(\nu)} \cdot B_{(\nu)}^{e-N}(Q^+, P, L)$$

$$- \sum_{\mu = 1}^{N} \gamma_{\mu} S_{(\mu)} \cdot B_{(\mu)}^{N-e}(q_{(\nu)}, p_{(\nu)}),$$ \hspace{1cm} (100)

where $B_{(\nu)}^{e-N}(Q^+, P, L)$ is a pseudo-vectorial operator corresponding to the internal magnetic field exerted on the electron $\nu$ and generated by the relative motion of the nuclei and $B_{(\mu)}^{N-e}(q_{(\nu)}, p_{(\nu)})$ is a pseudo-vectorial operator corresponding to the internal magnetic field exerted on the nucleus $\mu$ and generated by the relative motion of the electrons.

V. MOLECULAR GROUND STATE AND VIBRATIONAL MODES

A molecular system is described by bound states defined in the neighbourhood of the ground state in the Hilbert space \(1\). For such states, the vibrational degrees of freedom are sufficiently small to allow a series expansion in terms of the deformation operators $Q^\alpha$ \(1\).
To second-order, the series expansion of the Coulomb potentials read,
\[
V_{N-N} (Q') = V_{N-N} (0) 1 + V_{N-N} (0) Q^a
\]
\[+ \frac{1}{2} V_{N-N} (\alpha\beta) Q^a Q^\beta + O (Q^3) , \tag{101}
\]
\[
V_{N-e} (Q', q_{(i)}) = V_{N-e} (0) (q_{(i)}) 1 + V_{N-e} (\alpha) (q_{(i)}) Q^a
\]
\[+ \frac{1}{2} V_{N-e} (\alpha\beta) (q_{(i)}) Q^a Q^\beta + O (Q^3) . \tag{102}
\]

To establish the molecular equilibrium conditions defining the ground state, we neglect the contributions due to the spin-orbit couplings. Moreover, the contribution due to the residual term \( \Phi_{\text{res}} (Q') \) in the kinetic energy operator \( (94) \) is proportional to \( h^2 \) and can be neglected also. Furthermore, the effects of the deformation modes \( Q^a \) on the molecular inertia tensor \( I (Q') \) are second-order contributions that we neglect as well. Thus, to zeroth-order in \( Q^a \) the inertia tensor \( I (Q') \) reduces,
\[
I (Q') = I_0 + O (Q^3) . \tag{103}
\]

Using the definitions \( (96) \) and \( (100) \), and the relation \( (103) \), the rotational part of the Hamiltonian \( H \) in equation \( (94) \) is explicitly recast to zeroth-order in \( Q^a \) as,
\[
\frac{1}{8} \left\{ \mathcal{L}, I (Q')^{-1} \right\} , L_0 \cdot \left\{ I (Q')^{-1}, \mathcal{L} \right\} , \tag{104}
\]
\[
= \frac{1}{2} L \cdot L_0^{-1} \cdot L_0 + \frac{1}{2} L \cdot L_0^{-1} \cdot L - L \cdot L_0^{-1} \cdot L + O (Q^3) .
\]

According to the relations \( (93), (95), (101), (102) \) and \( (103) \), the Hamiltonian \( H \) is expanded in terms of the deformation operators \( Q^a \) as,
\[
H = H_{(0)} + H_{(\alpha)} Q^a + \frac{1}{2} H_{(\alpha\beta)} Q^a Q^\beta + O (Q^3) , \tag{105}
\]
where
\[
H_{(0)} = \frac{p^2}{2m} + \frac{1}{2} p_a p^a + \frac{1}{2} L \cdot L_0^{-1} \cdot L + V_{N-N} (0) 1 ,
\]
\[+ \sum_{\nu=1}^{n} \frac{p_{(\nu)}^2}{2m} + \frac{1}{2} L \cdot L_0^{-1} \cdot L + V_{N-e} (q_{(i)}) , \tag{106}
\]
\[
H_{(\alpha)} = V_{N-N} (\alpha) + V_{N-e} (\alpha) (q_{(i)}) ,
\]
\[
H_{(\alpha\beta)} = V_{N-N} (\alpha\beta) + V_{N-e} (\alpha\beta) (q_{(i)}) .
\]

In order to ensure that the molecular dynamics occurs in the neighbourhood the equilibrium ground state, we vary the energy \( E = \langle H \rangle \) of the system with respect to the deformation modes \( Q^a \), where the brackets denote the expectation value taken on the Hilbert space \( \mathcal{H} \) of the molecular system. At equilibrium, the density matrix commutes with the Hamiltonian \( \hat{H} \). We assume that this is also the case in the neighbourhood of the equilibrium state. Thus, to first-order, the variation of the energy yields the equilibrium condition, i.e.
\[
V_{N-N} (\alpha) + \langle V_{N-e} (\alpha) (q_{(i)}) \rangle = 0 , \tag{107}
\]

which defines the ground state of the molecular system. Using the definitions \( (96) \), the series expansions \( (101) \) and \( (102) \), and the fact that molecular vibration modes \( X_{\mu\alpha} \) are linearly independent, the condition \( (107) \) implies that,
\[
\frac{\varepsilon^2}{4\pi\varepsilon_0} \sum_{\nu=1}^{N} Z_\nu \frac{R_{\nu}^{(0)} - R_{\nu}^{(0)}}{\| R_{\nu}^{(0)} - R_{\nu}^{(0)} \|^3} - \frac{\varepsilon^2}{4\pi\varepsilon_0} \sum_{\nu=1}^{n} \langle R_{\nu}^{(0)} \cdot 1 - q_{(\nu)} \rangle = 0 . \tag{108}
\]

The first term in the condition \( (108) \) represents the classical Coulomb force exerted by the nuclei on the nucleus \( \mu \). The second term in the condition \( (108) \) represents the expectation value of the quantum Coulomb force exerted by the electrons on the nucleus \( \mu \). The equilibrium condition \( (108) \) implies that the resulting force exerted on the nucleus \( \mu \) vanishes at the equilibrium.

The 3\(N-6\) equilibrium conditions \( (108) \) imposed all the vibrations modes \( X_{\mu\alpha} \), the 3 conditions \( (109) \) imposed on the origin of the coordinate system and the 3 conditions \( (19) \) imposed on the orientation of the coordinate system fully determine the 3\(N\) degrees of freedom corresponding to the positions of the nuclei.

The molecular deformation modes \( X_{\mu\alpha} \) and \( X_{\nu\beta} \) are orthogonal if \( \alpha \neq \beta \) according to the condition \( (15) \). Moreover, to second-order with respect to the deformation \( Q^a \), the deformation modes are decoupled. Thus, the variation of the energy \( E = \langle H \rangle \) with respect to the deformation \( Q^a \) yields,
\[
V_{N-N} (\alpha\beta) + \langle V_{N-e} (\alpha\beta) (q_{(i)}) \rangle = 0 , \quad \forall \alpha \neq \beta . \tag{109}
\]

As shown in Appendix \( K \) the diagonal components, i.e. \( \alpha = \beta \), of the Hessian matrix of the Hamiltonian \( (95) \) yield the square of the angular frequency of the molecular vibration eigenmodes, i.e.
\[
\omega_{\alpha}^2 = V_{N-N} (\alpha\alpha) + \langle V_{N-e} (\alpha\alpha) (q_{(i)}) \rangle > 0 , \tag{110}
\]

which ensures that \( \omega_{\alpha} > 0 \) in the neighbourhood of the molecular ground state.

VI. CONCLUSION

A rigorous quantum treatment of a molecular system includes kinetic couplings between nuclei and electrons and leads to quantum deviations in the commutation relations between the position and momentum operators.
These deviations are proportional to ratio of the electron mass to the molecular mass and to the ratio of a specific nuclear mass to the molecular mass. Thus, these deviations are larger for smaller molecules.

In this quantum description, the vibrational and rotational degrees of freedom are treated in a genuine quantum framework. Since quantum nonlocality forbids the existence of a center of mass frame and a molecular rest frame, we defined “relative” position and momentum observables, which are the quantum equivalent of the relative position and momentum variables expressed with respect to the centre of mass frame in a classical framework. In order to define “rest” position and momentum observables expressed with respect to a rotating molecule we defined a molecular rotation operator that is function of a molecular orientation operator. Then, we defined internal observables that account for the quantum degrees of freedom of the molecular system. These observables are the deformation and orientation operators of the molecule as well as a the position and the momentum operators of the electrons.

In a rigorous quantum description of a molecule, the molecular orientation and rotation are described by operators of the electrons.

The rigorous quantum description of the dynamics of a rotating and vibrating molecule presented in this publication, is a prelude to the study of quantum dissipation at the molecular level. In order to describe molecular dissipation, the quantum statistical framework provided by the quantum master equations needs to be introduced. In such a framework, where certain internal observables are treated as a statistical bath that is weakly coupled and weakly correlated to the other internal observables representing the system of interest. The quantum master equations of the molecular system are expected to lead to dissipative couplings between the rotational, vibrational and magnetic quantum modes and to describe molecular dissipative phenomena such as molecular magnetism.

Appendix A: Killing form of the rotation algebra

In this appendix, we determine the explicit expression of the Killing form \( n_{(j)}(\omega) \cdot n_{(l)}(\omega) \) of the rotation algebra.

The rotation group action \( \Phi_{res}(Q \cdot) \) implies that,

\[
\text{Tr} \left( \left( e_j \cdot G^T \right) \left( e_k \cdot G \right) \right) = e_i \cdot \left( \left( e_j \cdot G^T \right) \left( e_k \cdot G \right) \right) e_i \nonumber = -e_i \cdot (e_j \cdot G) \left( (e_k \cdot G) e_i \right) = -e_i \cdot (e_j \times (e_k \times e_i)) \nonumber = (e_j \cdot e_k) \cdot (e_i \cdot e_j) - (e_j \cdot e_i) \left( e_k \cdot e_i \right) = 2 \left( e_j \cdot e_k \right) .
\]

(A1)

Thus, using the identity \( (A1) \) and the definitions \( (A2) \) and \( (A3) \), the Killing form is expressed as,

\[
n_{(j)}(\omega) \cdot n_{(l)}(\omega) = \frac{1}{2} \text{Tr} \left( \left( n_{(j)}(\omega) \cdot G^T \right) \cdot \left( n_{(l)}(\omega) \cdot G \right) \right) = \frac{1}{2} \text{Tr} \left( (e_j \cdot \partial_\omega) R(\omega)^{-1} \cdot (e_l \cdot \partial_\omega) R(\omega) \right) .
\]

Moreover, the rotation group action \( (A1) \) implies that \( \forall x \in \mathbb{R}^3 \),

\[
(\omega \cdot G)^2 x = \omega \times (\omega \times x) = -\omega^2 x + \omega (\omega \cdot x) \nonumber = -\omega^2 (1 - P_\omega) x .
\]

(A3)

where the self-adjoint projection operator \( P_\omega \) satisfies the following identity \( \forall n \in \mathbb{N}^* \),

\[
P_\omega^2 = P_\omega \Rightarrow (1 - P_\omega)^n = 1 - P_\omega .
\]

(A4)

The projection operator \( (A4) \) is orthogonal to the rotation group action \( (A1) \), i.e.

\[
P_\omega \cdot (\omega \cdot G) x = P_\omega \cdot (\omega \times x) = \frac{\omega}{||\omega||^2} (\omega \cdot (\omega \times x)) = 0 .
\]

(A5)

Using the properties \( (A3) \), \( (A4) \) and \( (A5) \), the rotation operator \( (A6) \) is recast as,

\[
R(\omega) = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n \omega^{2n}}{(2n)!} (1 - P_\omega) \nonumber \nonumber + \frac{1}{\omega} \sum_{n=0}^{\infty} \frac{(-1)^n \omega^{2n+1}}{(2n+1)!} (\omega \cdot G) .
\]

(A6)

The definition \( (A6) \) of the trace properties

\[
\text{Tr} \left( P_\omega \right) = 1 ,
\]

\[
\text{Tr} \left( \omega \cdot G \right) = 0 ,
\]

\[
\text{Tr} \left( P_\omega \cdot P_\omega \right) = \frac{(\omega' \cdot \omega)^2}{\omega'^2 \omega^2} ,
\]

(A7)

\[
\text{Tr} \left( (\omega' \cdot G) (\omega \cdot G) \right) = -2 \omega' \cdot \omega ,
\]

\[
\text{Tr} \left( P_{\omega'} \cdot (\omega \cdot G) \right) = 0 ,
\]

\[
\text{Tr} \left( (\omega' \cdot G) (\omega \cdot G) \right) = -2 \omega' \cdot \omega ,
\]

\[
\text{Tr} \left( P_{\omega'} \cdot (\omega \cdot G) \right) = 0 ,
\]
and trigonometric identities imply that,

\[
\text{Tr} \left( R (\omega')^{-1} \cdot R (\omega) \right) = 4 \left( \frac{\omega' \cdot \omega}{2} + \frac{\omega' \cdot \omega}{2} \cdot \sin \frac{\omega' \cdot \omega}{2} \cdot \sin \frac{\omega' \cdot \omega}{2} \right)^2 - 1.
\]

The relations \([A2]\) and \([A8]\) with the help of trigonometric identities then imply in turn that,

\[
n_{(j)} (\omega) \cdot n_{(\ell)} (\omega) = \frac{1}{2} \left( e_j \cdot \partial_\omega \right) n_{(\ell)} (\omega) \cdot \left( e_\ell \cdot \partial_\omega \right) \text{Tr} \left( R (\omega')^{-1} \cdot R (\omega) \right) \delta_\omega \omega = 2 \left( e_j \cdot \partial_\omega \right) n_{(\ell)} (\omega) \cdot \left( e_\ell \cdot \partial_\omega \right) \left( \frac{\cos \frac{\omega' \cdot \omega}{2} \cos \frac{\omega' \cdot \omega}{2} + \omega' \cdot \omega \cdot \sin \frac{\omega' \cdot \omega}{2} \cdot \sin \frac{\omega' \cdot \omega}{2} }{2} \right)^2 \delta_\omega \omega = e_j \cdot \left( \frac{\omega \cdot \omega}{\| \omega \|^2} + \left( \frac{2}{\| \omega \|^2} \right) \left( 1 - \frac{\omega \cdot \omega}{\| \omega \|^2} \right) \right) \cdot e_\ell.
\]

Finally, the bilinear form \([A9]\) correspond to the Killing form \([35]\) that is expressed in components as

\[
e_j \cdot K (\omega) \cdot e_\ell \equiv n_{(j)} (\omega) \cdot n_{(\ell)} (\omega) = e_j \cdot \left( P_\omega + A (1 - P_\omega) \right) \cdot e_\ell.
\]

The components of the symmetric rank-2 tensor \(K (\omega)^{-1}\) are given by

\[
e^j \cdot K (\omega)^{-1} \cdot e^\ell = e^j \cdot \left( P_\omega + A (1 - P_\omega) \right) \cdot e^\ell.
\]

The expressions \([A10]\) and \([A11]\) imply that,

\[
K (\omega) \cdot \omega = \omega,
K (\omega)^{-1} \cdot \omega = \omega.
\]

The operator \(m^{(j)} (\omega)\) is defined as the dual of the operator \(n_{(\ell)} (\omega)\), i.e.

\[
m^{(j)} (\omega) \equiv \left( e^j \cdot K (\omega)^{-1} \cdot e^\ell \right) n_{(\ell)} (\omega).
\]

The expressions \([A10]\) and \([A13]\) yield the duality condition \([34]\), i.e.

\[
m^{(j)} (\omega) \cdot n_{(\ell)} (\omega) = \left( e^j \cdot K (\omega)^{-1} \cdot e^k \right) n_{(k)} (\omega) \cdot n_{(\ell)} (\omega) = \left( e^j \cdot K (\omega)^{-1} \cdot e^k \right) \left( e_k \cdot K (\omega) \cdot e_\ell \right) = e^j \cdot e_\ell.
\]

The definitions \([28]\) and \([33]\) imply that

\[
\left( e^j \cdot \omega \right) n_{(j)} (\omega) \cdot \mathbf{G} = \left( e^j \cdot \omega \right) R (\omega)^{-1} \cdot \left( e_j \cdot \partial_\omega \right) \text{Tr} (\omega) = R (\omega)^{-1} \cdot \left( \omega \cdot \partial_\omega \right) R (\omega) = R (\omega)^{-1} \cdot \left( \omega \cdot \mathbf{G} \right) \cdot R (\omega) = \omega \cdot \mathbf{G}.
\]

which yields the identity,

\[
\left( e^j \cdot \omega \right) n_{(j)} (\omega) = \omega.
\]

Moreover, the Killing form \([A10]\) and the identity \([A16]\) then imply that,

\[
\omega \cdot n_{(\ell)} (\omega) = \left( e^j \cdot \omega \right) n_{(j)} (\omega) \cdot n_{(\ell)} (\omega) = \left( e^j \cdot \omega \right) \left( e_j \cdot K (\omega) \cdot e_\ell \right) = \omega \cdot e_\ell.
\]

Using the definition \([A13]\), the first property \([A12]\) yields,

\[
\left( e_j \cdot \omega \right) m^{(j)} (\omega) = \left( e_j \cdot \omega \right) \left( e^j \cdot K (\omega)^{-1} \cdot e^\ell \right) n_{(\ell)} (\omega) = \left( e^j \cdot \omega \right)n_{(\ell)} (\omega) = \omega.
\]

Moreover, the identity \([A18]\) and the Killing form \([A10]\) then imply that,

\[
\omega \cdot m^{(j)} (\omega) = \omega \cdot \left( e^j \cdot K (\omega)^{-1} \cdot e^\ell \right) n_{(\ell)} (\omega) = \left( e^j \cdot K (\omega)^{-1} \cdot e^\ell \right) \left( \omega \cdot e_\ell \right) = e^j \cdot \omega.
\]

Appendix B: Commutation relations of the momentum and orientation operators

In this appendix, we determine the commutations relations of the momentum operators \(P_{\mu}''\) and \(p_{\mu}'\) with the orientation \(\omega\).

In order to determine these relations, we use the Baker-Campbell-Hausdorff formulas, i.e.

\[
e^X Y e^{-X} = \sum_{k=0}^{\infty} \frac{1}{k!} \left[ X, Y \right]_k,
\]

\[
e^{-X} Y e^X = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \left[ X, Y \right]_k,
\]

where

\[
[ X, Y ]_k = [ [ X, [ X, Y ] ] ]_{k-1},
\]

[ X, Y ]_0 = Y.

According to the properties \([28]\), \([30]\) and the formulas \([B1]\),

\[
[ e_\ell \cdot P_\nu', R (\omega) ] = R (\omega) \cdot \left[ \exp \left( -\omega \cdot \mathbf{G} \right) (e_\ell \cdot P_\nu') \exp (\omega \cdot \mathbf{G}) - e_\ell \cdot P_\nu' \right) = R (\omega) \cdot \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \left[ \omega \cdot \mathbf{G}, e_\ell \cdot P_\nu' \right]_k
\]

\[
= R (\omega) \cdot \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \left[ \omega \cdot \mathbf{G}, e_\ell \cdot P_\nu' \right]_{k-1}
\]

where the \(k = 0\) term cancels out on the third line and the orientation operator is a function of the rest positions of
the nuclei $R_i(0)$ and the deformation operators $R'_\mu$. Using the relation,
\[
\left[ e_j \cdot \partial, \omega \cdot G \right] x = (e_j \cdot \partial) (\omega \times x) - \omega \times (e_j \cdot \partial) x = (e_j \cdot \partial) \omega \times x = e_j \times x = (e_j \cdot G) x,
\]
the Baker-Campbell-Hausdorff formula (B1) and the group identity (33), the commutator (B3) is recast as,
\[
\left[ e_\ell \cdot P'_\nu, R(\omega) \right] = -R(\omega) \cdot \left[ e_\ell \cdot P'_\nu, e^j \cdot \omega \right] = \frac{1}{\ell} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} e_\ell \cdot n j (\omega) \cdot G.
\]
Performing a similar calculation using the properties (30) and (33) yields,
\[
\left[ e_\ell \cdot P'_\nu, R(\omega) \right] = -\frac{1}{\ell} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} e_\ell \cdot n j (\omega) \cdot G \cdot R(\omega)^{-1}.
\]

The condition (50) implies that,
\[
\left[ e_\ell \cdot P'_\nu, \sum_{\mu=1}^{N} M_\mu \left( R(\omega) \cdot R_i^\mu(0) \right) \times R'_\mu \right] = 0,
\]
which is expanded as,
\[
\sum_{\mu=1}^{N} M_\mu \left( \left[ e_\ell \cdot P'_\nu, R(\omega) \right] \right) \times R'_\mu + \sum_{\mu=1}^{N} M_\mu \left( R(\omega) \cdot R_i^\mu(0) \right) \times \left[ e_\ell \cdot P'_\nu, R'_\mu \right] = 0.
\]

The commutator (B5) and the rotation group action (31) imply that,
\[
\sum_{\mu=1}^{N} M_\mu \left( \left[ e_\ell \cdot P'_\nu, R(\omega) \right] \right) \times R'_\mu = \left[ e_\ell \cdot P'_\nu, e^j \cdot \omega \right] \times R'_\mu = \left[ e_\ell \cdot P'_\nu, e^j \cdot \omega \right] \times \left( \delta_{\nu \mu} - \frac{M_\nu}{M} \right) e_\ell
\]
\[
= -i \hbar \sum_{\mu=1}^{N} M_\mu \left( R(\omega) \cdot R_i^\mu(0) \right) \times \left( \delta_{\nu \mu} - \frac{M_\nu}{M} \right) e_\ell
\]
\[
= -i \hbar M_\nu \left( R(\omega) \cdot R_i^\mu(0) \right) \times e_\ell.
\]

The identities (B10), (B11) and (B12) yield,
\[
\left[ e_\ell \cdot P'_\nu, e^j \cdot \omega \right] \sum_{\mu=1}^{N} M_\mu \left( R(\omega) \cdot \left( n j (\omega) \times R_i^\mu(0) \right) \right) \times R'_\mu
\]
\[
= i \hbar M_\nu \left( R(\omega) \cdot R_i^\mu(0) \right) \times \left( \delta_{\nu \mu} - \frac{M_\nu}{M} \right) e_\ell
\]
\[
= i \hbar M_\nu \left( R(\omega) \cdot R_i^\mu(0) \right) \times \left( \delta_{\nu \mu} - \frac{M_\nu}{M} \right) e_\ell
\]
\[
= i \hbar M_\nu R_i^\mu(0) \times e_\ell.
\]
Now, by analogy with the commutation relation \[ (B5), \]
\[
[ e_\ell \cdot p'_\nu, \ R(\omega) ] = [ e_\ell \cdot p'_\nu, \ e^j \cdot \omega ] \ R(\omega) \cdot (n_{ij}) (\omega) \ G
\]
\[ (B17) \]
The condition \[ (50) \] implies that,
\[
\left[ e_\ell \cdot p'_\nu, \ \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times R'_\mu \right] = 0, \quad (B18)
\]
which is expanded as,
\[
\sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times R'_\mu
\]
\[ + \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times [ e_\ell \cdot p'_\nu, \ R'_\mu ] = 0. \quad (B19) \]
The commutator \[ (B17) \] and the rotation group action \[ (31) \] imply that,
\[
\sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times [ e_\ell \cdot p'_\nu, \ e^j \cdot \omega ]
\]
\[ = e_\ell \cdot p'_\nu, \ e^j \cdot \omega \]
\[ + \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot (n_{ij}) (\omega) \ G ) R^{(0)}_\mu \times R'_\mu \quad (B20) \]
\[ = e_\ell \cdot p'_\nu, \ e^j \cdot \omega \]
\[ - \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot (n_{ij}) (\omega) \times R^{(0)}_\mu ) \times R'_\mu, \quad (B21) \]
the commutations relations \[ (24) \] and the constraint \[ (46) \] imply that,
\[
\sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times [ e_\ell \cdot p'_\nu, \ R'_\mu ]
\]
\[ = -i \hbar \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot R^{(0)}_\mu ) \times \left( \frac{m}{\mathcal{M}} \right) e_\ell = 0. \quad (B21) \]
The identities \[ (B19), (B20) \] and \[ (B21) \] yield,
\[
[ e_\ell \cdot p'_\nu, \ e^j \cdot \omega ]
\]
\[ \cdot \sum_{\mu=1}^{N} M_\mu \ ( R(\omega) \cdot (n_{ij}) (\omega) \times R^{(0)}_\mu ) \times R'_\mu = 0. \quad (B22) \]
Finally, by analogy with the identities \[ (B13)-(B16) \], we obtain the last commutation relation \[ (60) \], i.e.,
\[
[ e_\ell \cdot p'_\nu, \ e^j \cdot \omega ] = 0. \quad (B23) \]

**Appendix C: Commutation relations of the position and momentum operators**

In this appendix, we determine the commutations relations of the momentum operator \[ P'_\mu \] with the position operators \[ R'_\mu \] and \[ r''_\nu \], and the momentum operators \[ P''_\nu \] and \[ p''_\nu \] respectively.

Using the relations \[ (25) \] and \[ (26) \], the commutation relation yields,
\[
[ e_\ell \cdot P''_\mu, \ e^k \cdot r''_\nu ]
\]
\[ = \left( R(\omega) \cdot e_\ell \right) \cdot P''_\mu, \ \left( e^k \cdot R(\omega)^{-1} \right) \cdot r''_\nu \quad (C1) \]
\[ = (e^\ell \cdot R(\omega) \cdot e_j) \left[ e_\ell \cdot P'_\mu, \ e^k \cdot R(\omega)^{-1} \cdot e_m \right] e^m \cdot r''_\nu
\]
\[ + (e^\ell \cdot R(\omega) \cdot e_j) \left( e^k \cdot R(\omega)^{-1} \cdot e_m \right) \left[ e_\ell \cdot P'_\mu, \ e^m \cdot r''_\nu \right] \]

Using the commutation relations \[ (24) \] and \[ (B9) \], the definition of the group action \[ (31) \] and the relations \[ (25) \] and \[ (26) \], the commutation relation \[ (C1) \] yields the first commutation relation \[ (52) \], i.e.,
\[
[ e_\ell \cdot P''_\mu, \ e^k \cdot r''_\nu ]
\]
\[ = \left( e^\ell \cdot R(\omega) \cdot e_j \right) \left[ e_\ell \cdot P'_\mu, \ e^k \cdot \omega \right] \]
\[ \cdot e^k \cdot (n_{ij}) (\omega) \ G \right) \left( R(\omega)^{-1} \cdot e_m \right) \left( R(\omega) r''_\nu \right)
\]
\[ + (e^\ell \cdot R(\omega) \cdot e_j) \left( e^k \cdot R(\omega)^{-1} \cdot e_m \right) \left[ e_\ell \cdot P'_\mu, \ e^m \cdot r''_\nu \right] \]
\[ = -[ e_\ell \cdot P''_\mu, \ e^s \cdot \omega ] \]}
\[ \cdot \left( n_{ij} \right) (\omega) \times r''_\nu \quad (C2) \]
\[ + i \hbar \left( e_\ell \cdot e^k \right) \left( M_\mu / \mathcal{M} \right) \]

Similarly, using the relations \[ (25) \] and \[ (26) \], the commutation relation yields,
\[
[ e_\ell \cdot P''_\mu, \ e_k \cdot p''_\nu ]
\]
\[ = \left( R(\omega) \cdot e_\ell \right) \cdot P''_\mu, \left( R(\omega) \cdot e_k \right) \cdot p''_\nu \quad (C3) \]
\[ = (e^\ell \cdot R(\omega) \cdot e_j) \left[ e_\ell \cdot P'_\mu, \ e^m \cdot R(\omega) \cdot e_k \right] e_m \cdot p''_\nu
\]
\[ + (e^\ell \cdot R(\omega) \cdot e_j) \left( e^m \cdot R(\omega) \cdot e_k \right) \left[ e_\ell \cdot P'_\mu, \ e^m \cdot e'_k \right] \]

Using the commutation relations \[ (24) \] and \[ (B9) \], the definition of the group action \[ (31) \] and the relation \[ (26) \], the commutation relation \[ (C3) \] yields the second commutation relation \[ (52) \], i.e.,
\[
[ e_\ell \cdot P''_\mu, \ e_k \cdot p''_\nu ]
\]
\[ = (e^\ell \cdot R(\omega) \cdot e_j) \left[ e_\ell \cdot P'_\mu, \ e^s \cdot \omega \right] \]
\[ \cdot e^k \cdot (n_{ij}) (\omega) \cdot G \right) \left( R(\omega)^{-1} \cdot e_m \right) \cdot p''_\nu
\]
\[ = [ e_\ell \cdot P''_\mu, \ e^s \cdot \omega ] \]}
\[ \cdot \left( n_{ij} \right) (\omega) \times p''_\nu \right). \quad (C4) \]

By analogy with the commutation relation \[ (C1) \], using the relations \[ (25) \] and \[ (26) \], the commutation relation yields,
\[
[ e_\ell \cdot P''_\mu, \ e^k \cdot R''_\nu ]
\]
\[ = (e^\ell \cdot R(\omega) \cdot e_j) \left[ e_\ell \cdot P'_\mu, \ e^k \cdot R(\omega)^{-1} \cdot e_m \right] e^m \cdot R''_\nu
\]
\[ + (e^\ell \cdot R(\omega) \cdot e_j) \left( e^k \cdot R(\omega)^{-1} \cdot e_m \right) \left[ e_\ell \cdot P'_\mu, \ e^m \cdot R''_\nu \right] \]
By analogy with the commutation relation (C2), using the commutation relations (24) and (36), the definition of the group action (31) and the relations (25) and (26) yield the third commutation relation (52), i.e.
\[
\left[ e_j \cdot P''_{\mu}, e^k \cdot R''_{\nu} \right] = -i\hbar \left( e_j \cdot e^k \right) \left( \delta_{\mu\nu} - \frac{M_\mu}{M} \right) I + \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^k \cdot (n_{(m)}(\omega)) \times R''_{\nu} \right).
\]
(C6)

Using the relation (26), the commutation relation of the momentum operators is expressed as,
\[
\left[ e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu} \right] = \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu}, e^\ell \cdot R(\omega) \cdot e_k \right)
\]
\[
- \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu}, e^\ell \cdot R(\omega) \cdot e_j \right).
\]
(C7)

According to equation (B7),
\[
\left[ e_j \cdot P''_{\mu}, e^m \cdot \omega \right] = \left[ e_j \cdot P''_{\mu}, e^m \cdot (n_{(m)}(\omega) \cdot G) \right) \cdot e_k.
\]
Introducing the rank-2 tensorial operator,
\[
A_{\mu(j)} = \left[ e_j \cdot P''_{\mu}, e^m \cdot \omega \right] (n_{(m)}(\omega) \cdot G),
\]
and the relation (C8), the commutator (C7) is recast as,
\[
\left[ e_j \cdot P''_{\mu}, e^m \cdot \omega \right] = \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot R(\omega) \cdot e_k \right)
\]
\[
- \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot R(\omega) \cdot e_j \right).
\]
(C9)

The relation (26) implies that the commutation relation (C10) reduces to,
\[
\left[ e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu} \right] = \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot A_{\mu(j)} \cdot e_k \right)
\]
\[
- \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot A_{\nu(k)} \cdot e_j \right).
\]
(C11)

Finally, using the expression (C9) of the rank-2 tensorial operator $A_{\mu(j)}$ and the definition of the rotation group action (31), the commutation relation (C11) yields the last commutation relation (52), i.e.
\[
\left[ e_j \cdot P''_{\mu}, e^k \cdot P''_{\nu} \right] = \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot A_{\mu(j)} \cdot e_k \right)
\]
\[
- \frac{1}{2} \left( e_j \cdot P''_{\mu}, e^\ell \cdot A_{\nu(k)} \cdot e_j \right).
\]
(C12)

**Appendix D: Internal observables**

In this appendix, we determine the expressions for the internal observables $Q^\alpha, P_\alpha$ and $\Omega$. The definition (40) and the constraint (45) imply that
\[
\sum_{\mu=1}^{N} \sqrt{M_\mu} (X^\alpha_{\mu} \cdot R''_{\mu}) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( X^\alpha_{\mu} \cdot R''_{\mu} \right) \frac{1}{2} + Q^\alpha
\]
\[
- \frac{1}{M} \sum_{\mu=1}^{N} \sum_{\nu'=1}^{n} \sqrt{M_\mu A_{\nu\nu'} \left( R''_{\mu} \cdot q_{(\nu')} \right)}.
\]
(D1)

Using the constraint (47), the identity (D1) yields the expression (53) for the internal observable $Q^\alpha$, i.e.
\[
Q^\alpha = \sum_{\mu=1}^{N} \sqrt{M_\mu} X^\alpha_{\mu} \cdot \left( R''_{\mu} - R''_{(0)} \right).
\]
(D2)

Similarly, the definition (43) and the constraint (45) imply that,
\[
\sum_{\mu=1}^{N} \frac{1}{\sqrt{M_\mu}} (X_{\mu\alpha} \cdot P''_{\mu}) = \frac{1}{\sqrt{M_\mu}} (X_{\mu\alpha} \cdot \left( R''_{(0)} \right)) + P_{\alpha}
\]
\[
- \frac{1}{M} \sum_{\mu=1}^{N} \sum_{\nu'=1}^{n} \sqrt{M_\mu A_{\nu\nu'} \left( X_{\mu\alpha} \cdot P_{(\nu')} \right)}.
\]
(D3)

Using the constraints (47) and (48) the identity (D3) yields the expression (55) for the internal observable $P_\alpha$, i.e.
\[
P_{\alpha} = \sum_{\mu=1}^{N} \frac{1}{\sqrt{M_\mu}} (X_{\mu\alpha} \cdot P''_{\mu})
\]
(D4)

The relation (26), the constraints (47)-48 and the definition (55) imply that,
\[
\sum_{\mu=1}^{N} R''_{\mu} \times P''_{\mu} = \sum_{\mu=1}^{N} R''_{\mu} \times \left( X_{\mu\alpha} \cdot \left( M_\mu R''_{\mu} \right) \right)
\]
\[
= (e^k \cdot \Omega) \sum_{\mu=1}^{N} M_\mu e_\ell \cdot \left( R''_{\mu} \times (e_k \times R''_{(0)}) \right) e^\ell
\]
\[
= (e^k \cdot \Omega) \sum_{\mu=1}^{N} M_\mu \left( e_\ell \times R''_{\mu} \right) \cdot (e_k \times R''_{(0)}) e^\ell
\]
\[
= (e^k \cdot \Omega) (e_\ell \cdot l_0 \cdot e_k) e^\ell,
\]
(D5)

which implies in turn that,
\[
\sum_{\mu=1}^{N} (e_k \times R''_{\mu}) \cdot P''_{\mu} = (e_k \cdot l_0 \cdot e_j) (e^j \cdot \Omega).
\]
(D6)

Using the property (56) of the inertia tensor $l_0$, the identity (D6) yields the internal observable $e^k \cdot \Omega$, i.e.
\[
e^k \cdot \Omega = \sum_{\mu=1}^{N} \left( e_k \times R''_{\mu} \right) \cdot P''_{\mu}.
\]
(D7)
Appendix E: Rotation operator

In this appendix, we show that the Eckart conditions (46) and (48), and the relations (25) and (40) imply the physical definition (50) of the rotation operator $R(\omega)$.

The expression (40) of the rest momentum $R'_\mu$ in terms of the equilibrium position $R^{(0)}_\mu$ and the rest observables $Q^\alpha$ and $q_{(\nu')}$ implies that,

$$
\sum_{\mu=1}^{N} M_\mu R^{(0)}_\mu \times R'_\mu = \sum_{\mu=1}^{N} M_\mu \left( R^{(0)}_\mu \times R^{(0)}_\mu \right) \mathbb{I} + Q^\alpha \left( \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( R^{(0)}_\mu \times X_{\mu\alpha} \right) \right) - \left( \sum_{\mu=1}^{N} M_\mu R^{(0)}_\mu \right) \times \left( \sum_{\nu'=1}^{N} A_{\nu''} q_{(\nu')} \right).
$$

Using the Eckart conditions (46) and (48), the RHS of the relation (E1) vanishes, i.e.

$$
\sum_{\mu=1}^{N} M_\mu R^{(0)}_\mu \times R''_\mu = 0 \quad \text{(E2)}
$$

Finally, using the relation (25) the condition (E2) is recast as,

$$
\sum_{\mu=1}^{N} M_\mu R^{(0)}_\mu \times \left( R(\omega)^{-1} \cdot R'_\mu \right) = 0 \quad \text{(E3)}
$$

which is equivalent to the condition

$$
\sum_{\mu=1}^{N} M_\mu \left( R(\omega) \cdot R^{(0)}_\mu \right) \times R'_\mu = 0 \quad \text{(E4)}
$$

The condition (E3) is the physical definition (50) of the rotation operator $R(\omega)$.

Appendix F: Commutation relations of the internal observables

In this appendix, we determine the commutation relations between the internal observables $Q^\alpha$, $P_\alpha$, $q_{(\nu')}$, $p_{(\nu')}$, $\omega$ and $\Omega$.

Using the definition (B23) of the operator $P_\alpha$, the constraint (48) and the identity (B16) imply that,

$$
\left[ P_\alpha, \ e^{j} \cdot \omega \right] = i \hbar \sum_{\nu=1}^{16} \sqrt{M_\nu} \left( R^{(0)}_\nu \times X_{\nu\alpha} \right) = 0 \quad \text{(F1)}
$$

which yields the fifth commutation relation (60), i.e.

$$
\left[ P_\alpha, \ e^{j} \cdot \omega \right] = 0 \quad \text{(F2)}
$$

Moreover, the definition (44) and the commutation relation (B23) imply that,

$$
\left[ e^{k} \cdot p_{(\nu')}, \ e^{j} \cdot \omega \right] = 0 \quad \text{(F3)}
$$

Using the expression (D7) for the operator $e^{k} \cdot \Omega$, the constraint (46) and the diagonality condition (56), the identity (B16) is recast as,

$$
\left[ e^{k} \cdot \Omega, \ e^{j} \cdot \omega \right] \sum_{\mu=1}^{N} M_\mu \left( n_{(j)}(\omega) \times R^{(0)}_\mu \right) \times R''_\mu = i \hbar \sum_{\nu=1}^{N} M_\nu \left( e_{k} \times R^{(0)}_\nu \right) \times \left( e_{k} \cdot l_{0} \cdot e_{k} \right)
$$

$$
= i \hbar \left( \frac{e_{k} \cdot l_{0} \cdot e_{k}}{e_{k} \cdot l_{0} \cdot e_{k}} \right) e^{k} = i \hbar e^{k} \quad \text{(F4)}
$$

The condition (48) implies that,

$$
\sum_{\mu=1}^{N} \sqrt{M_\mu} e_{k} \cdot \left( e_{\ell} \times \left( R^{(0)}_\mu \times X_{\mu\alpha} \right) \right) = 0 \quad \text{(F5)}
$$

which is recast as,

$$
\sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) \quad \text{(F6)}
$$

Using the identity (F6), the expression (57) yields the property (58), i.e.

$$
e_{k} \cdot l_{\alpha} \cdot e_{\ell} = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \times R^{(0)}_\mu \right) \cdot \left( e_{\ell} \times X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot R^{(0)}_\mu \right) \left( e_{\ell} \cdot X_{\mu\alpha} \right) = \sum_{\mu=1}^{N} \sqrt{M_\mu} \left( e_{k} \cdot l_{0} \cdot e_{k} \right) = e_{k} \cdot l_{\alpha} \cdot e_{k} \quad \text{(F7)}
$$
which shows that the tensors $I_\alpha$ and $I (Q \cdot 1)$ are symmetric. Using the relation (404), the constraint (46), and the properties (48), (64), and (66), we obtain,

\[
\sum_{\mu=1}^{N} M_\mu \left( \left( n_{(j)} (\omega) \times R^{(0)}_\mu \right) \times R''_\mu \right) \cdot e_\ell \\
= - \sum_{\mu=1}^{N} M_\mu \left( n_{(j)} (\omega) \times R^{(0)}_\mu \right) \cdot (e_\ell \times R'_\mu) \\
= - e^k \cdot n_{(j)} (\omega) \sum_{\mu=1}^{N} M_\mu \left( e_k \times R^{(0)}_\mu \right) \left( e_k \times R^{(0)}_\mu \right) \\
= - e^k \cdot n_{(j)} (\omega) \sqrt{M_\mu} \left( e_k \times R^{(0)}_\mu \right) (e_k \times Q^\alpha X_{\mu\alpha}) \\
= - \left( e^k \cdot n_{(j)} (\omega) \right) \cdot (1 (Q \cdot 1)) \cdot e_\ell.
\]

Using the identity (F8), the identity (F4) is recast as,

\[
\left[ e^k \cdot \Omega, e^j \cdot \omega \right] n_{(j)} (\omega) \cdot 1 (Q \cdot 1) \cdot e_\ell = - i h \left( e^k \cdot e_\ell \right).
\]

Using the property (A14), which implies that,

\[
(n_{(j)} (\omega) \cdot 1 (Q \cdot 1))^{-1} = 1 (Q \cdot 1) \cdot m^{(j)} (\omega),
\]

the identity (F9) yields the fifth commutation relation (52), i.e.

\[
\left[ e^k \cdot \Omega, e^j \cdot \omega \right] = - i h \left( e^k \cdot 1 (Q \cdot 1) \cdot m^{(j)} (\omega) \right) .
\]

The relation (43), the commutation relations (B23) and (F2) imply that,

\[
\left[ e_\ell \cdot P''_\mu, e^j \cdot \omega \right] = \left[ e^k \cdot \Omega, e^j \cdot \omega \right] \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e_\ell \\
= \left[ e^k \cdot \Omega, e^j \cdot \omega \right] \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e_\ell \\
= - i h \left( e^k \cdot 1 (Q \cdot 1) \cdot m^{(j)} (\omega) \right) \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e_\ell
\]

Now, we establish a useful commutation relation for the dynamics. The identities (A14), (B3) and (F12) imply that,

\[
\left[ e_\ell \cdot P''_\mu, \ R (\omega) \cdot 1 \right] \ R (\omega) \\
= - \left[ e_\ell \cdot P''_\mu, e^j \cdot \omega \right] n_{(j)} (\omega) \cdot G \\
= i h \left( e^k \cdot 1 (Q \cdot 1) \cdot m^{(j)} (\omega) \right) \\
\cdot \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e_\ell \left( n_{(j)} (\omega) \cdot G \right) \\
= i h \left( e^k \cdot 1 (Q \cdot 1) \cdot e^j \right) \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e_\ell \left( e_\ell \cdot G \right)
\]

The orthogonality condition (30) and the commutation relation (F13) imply that,

\[
\left[ e^\ell \cdot P''_\mu, e^k \cdot R (\omega) \cdot e_\ell \right] \left( e^m \cdot R (\omega) \cdot e_k \right) \\
= \left[ e_\ell \cdot P''_\mu, e^k \cdot R (\omega) \cdot e_\ell \right] \left( e^m \cdot R (\omega) \cdot e_k \right) \\
= i h \left( e^k \cdot 1 (Q \cdot 1) \cdot e^j \right) \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot (e_\ell \cdot e^m) \\
= - i h \left( e^k \cdot 1 (Q \cdot 1) \cdot e^j \right) \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \cdot e^m
\]

The definitions (42) and (52), the commutation relation (51) and the condition (47) yield the commutation relations (59), i.e.

\[
\left[ Q^\alpha, Q^\beta \right] = 0, \\
\left[ e^j \cdot q_{(\nu)}, e^k \cdot q_{(\nu')} \right] = 0, \\
\left[ e_\ell \cdot p_{(\nu)}, e_k \cdot p_{(\nu')} \right] = 0, \\
\left[ e^j \cdot Q^\beta \right] = 0, \\
\left[ e_\ell \cdot Q^\beta \right]
\]

\[
= i h \sum_{\nu'=1}^{n} \sum_{\mu=1}^{m} \frac{M_\mu \cdot M_{\nu'}}{m} \ A_{\nu'\nu}^{-1} \left( e_\ell \cdot X_{\nu \mu} \right) \ 1 = 0,
\]

\[
\left[ e_\ell \cdot p_{(\nu)}, e^k \cdot q_{(\nu')} \right] \\
= - i h \sum_{\nu',\nu'=1}^{m} \ A_{\nu'\nu}^{-1} \left( \delta_{\nu'\nu} - \frac{1}{m} \right) A_{\nu'\nu}^{-1} \left( e_\ell \cdot e^k \right) 1.
\]

The definitions (46) and (42) yield the relation,

\[
\sum_{\nu',\nu'=1}^{m} \ A_{\nu'\nu}^{-1} \left( \delta_{\nu'\nu} - \frac{1}{m} \right) A_{\nu'\nu}^{-1} \\
= \sum_{\nu,\nu'=1}^{m} \left( \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{ \frac{M_\mu}{M} - 1 } \right) \right) \left( \delta_{\nu\nu'} - \frac{1}{m} \right) \\
= \left( \frac{1}{n} - \frac{1}{M} \right) \left( 2 \left( \sqrt{ \frac{M_\mu}{M} - 1 } \right) + \left( \sqrt{ \frac{M_\mu}{M} - 1 } \right)^2 \right) \\
- \frac{m}{M} + \delta_{\nu\nu'} = \delta_{\nu\nu'},
\]

which implies that the last commutation relation (F15) yields the second canonical commutation relation (61), i.e.

\[
\left[ e_\ell \cdot p_{(\nu)}, e^k \cdot q_{(\nu')} \right] = - i h \left( e_\ell \cdot e^k \right) \delta_{\nu\nu'} .
\]

The definitions (41) and (44), the constraint (47), and the commutation relations (F2) and (F12) yield the fourth
The definitions (44) and (D4) and the commutation relations (C4) and (F11) yield the third commutation relation (60), i.e.

\[ [P_\alpha, e^k \cdot q_{(\nu')} ] = - \sum_{\nu = 1}^{n} \frac{1}{\sqrt{M_\mu}} \left[ X_{\mu \alpha} \cdot P''_{\mu}, e^s \cdot \omega \right] \sum_{\nu = 1}^{n} A_{\nu \nu}^{-1} e^k \cdot (n_{(s)}(\omega) \times r''_{\nu}) + i\hbar \sum_{\mu = 1}^{N} \sqrt{M_\mu} A_{\nu \nu}^{-1} (X_{\mu \alpha} \cdot e^k) 1 = - [P_\alpha, e^s \cdot \omega \sum_{\nu = 1}^{n} A_{\nu \nu}^{-1} e^k \cdot (n_{(s)}(\omega) \times r''_{\nu}) = 0. \]

The definition (D2) and (D4), the constraint (47) and the commutation relation (60) yield the first canonical commutation relation (61), i.e.

\[ [P_\alpha, Q^3 ] = - \sum_{\mu = 1}^{N} \frac{1}{\sqrt{M_\mu}} \left[ X_{\mu \alpha} \cdot P''_{\mu}, e^s \cdot \omega \right] \sum_{\nu = 1}^{n} A_{\nu \nu}^{-1} e^k \cdot (n_{(s)}(\omega) \times p''_{\nu}) - i\hbar \sum_{\mu = 1}^{N} \sqrt{M_\mu} (X_{\mu \alpha} \cdot X_{\mu \alpha}^3) \left( \delta_{\mu \nu} - \frac{M_\mu}{M} \right) 1 = - i\hbar \delta^3_\alpha. \]

Similarly, the definition (44), the properties (A14) and (D7), and the commutation relations (C4) and (F11) yield the fourth commutation relation (62), i.e.

\[ [e^k \cdot \Omega, e^j \cdot p_{(\nu')} ] = - \left[ \sum_{\mu = 1}^{N} \frac{e_k \times R^{(0)}_{\mu} \cdot P''_{\mu}, e^s \cdot \omega }{e_k \cdot l_0 \cdot e_k} \right] e^j \cdot (n_{(s)}(\omega) \times p''_{\nu}) + i\hbar \sum_{\mu = 1}^{N} \left( \frac{e_k \times (M_\mu R^{(0)}_{\mu})}{\mathcal{M} (e_k \cdot l_0 \cdot e_k)} \right) \left( e^j \sum_{\nu = 1}^{n} A_{\nu \nu}^{-1} 1 \right) = \left[ e^k \cdot \Omega, e^s \cdot \omega \right] n_{(s)}(\omega) \cdot \left( e^j \times p_{(\nu')} \right) = - i\hbar \left( e^k \cdot 1 (Q^{-1} \cdot m(s))(\omega) \right) \left( n_{(s)}(\omega) \cdot \left( e^j \times p_{(\nu')} \right) \right) = - i\hbar \left( e^k \cdot 1 (Q^{-1} \cdot e^j) \left( e_k \times e_j \right) \cdot p_{(\nu')} \right). \]
yield the first commutation relation (62), i.e.

\[
\left[ e^k \cdot \Omega, \Omega^\alpha \right] = -\sum_{\mu=1}^N \frac{1}{\sqrt{M_\mu} \cdot \sqrt{M_\nu}} \left[ X_{\mu\alpha} \cdot P_\mu'' \cdot X_{\nu\beta} \cdot P_\nu'' \right] - \frac{1}{2} \sum_{\mu=1}^N \frac{1}{\sqrt{M_\mu}} \left\{ e_{\nu}', \cdot \Omega', \cdot P_\mu'' \cdot e_{\mu}', \cdot \Omega'' \right\} = 0.
\]

The definition (D4), and the commutation relations (C12) and (F2) yield the first commutation relation (60), i.e.

\[
\left[ e^k \cdot \Omega, \cdot P_\alpha \right] = \frac{1}{2} \sum_{\mu=1}^N \frac{1}{\sqrt{M_\mu}} \left\{ e_{\mu}', \cdot P_\mu'', \cdot e_{\alpha}', \cdot e^k \cdot \Omega'' \right\} \cdot \left( n_{(m)} (\Omega) \times \cdot X_{\nu\alpha} \right) = 0.
\]

Appendix G: Orbital angular momentum

In this appendix, we establish an explicit expression of the orbital angular momentum in terms of the internal observables.

According to the first and last relations (24), the commutation relations between the operators \( e^k \cdot R'_\mu \) and \( e_k \cdot \cdot P''_\mu \) and the operators \( e^k \cdot \cdot P''_\mu \) and \( e^k \cdot \cdot P''_\mu \) are symmetric with respect to the permutation of the basis vectors \( e^k \) and \( e_k \), which implies that the vector product of these operators satisfies the identities,

\[
R'_\mu \times P''_\mu = -P'_\mu \times R'_\mu,
\]

\[
r''_\mu \times p''_\mu = -p''_\mu \times r''_\mu.
\]

Thus, using the relation (G1) the angular momentum (64) is recast as,

\[
L' = \frac{1}{2} \sum_{\mu=1}^N \left[ R'_\mu \cdot P''_\mu \right] + \frac{1}{2} \sum_{\nu=1}^n \left[ r''_\nu \cdot p''_\nu \right] \times. \quad (G2)
\]

The angular momentum \( L \) is a pseudo-vectorial operator that is related to the angular momentum \( L' \) by,

\[
e_{\nu} \cdot L = \frac{1}{2} \left( R(\omega) \cdot e_\ell \right) \cdot L' + L' \cdot \left( R(\omega) \cdot e_\ell \right). \quad (G3)
Using the relation (G3) and the definition (G2) of the orbital angular momentum \( L' \) yields the expression (65) for the orbital angular momentum \( L \), i.e.

\[
L = \frac{1}{2} \sum_{\mu=1}^{N} \left( [R_\mu'', P_\mu''] \times + \frac{1}{2} \sum_{\nu=1}^{N} [r_\nu'', p_\nu'] \times \right. \tag{G4}
\]

Using the relations (40)-(44) the expression (G4) is recast as,

\[
L = \frac{1}{2} \sum_{\mu=1}^{N} \left( \left( P_\mu^{(0)} \Omega + \frac{1}{\sqrt{M_\mu}} Q_\mu X_{\mu\alpha} - \frac{m}{M} \sum_{\nu', \nu=1}^{n} A_{\nu\nu'} q_{(\nu')} \Omega \right) \times \Omega \times \left( M_\mu R_\mu^{(0)} + \sqrt{M_\mu} P_\mu X_{\mu\beta} - \frac{M_\mu}{M} \sum_{\nu', \nu=1}^{n} A_{\nu\nu'} p_{(\nu')} \right) - \left( \left( M_\mu R_\mu^{(0)} + \sqrt{M_\mu} P_\mu X_{\mu\beta} - \frac{M_\mu}{M} \sum_{\nu', \nu=1}^{n} A_{\nu\nu'} p_{(\nu')} \right) \times \left( P_\mu^{(0)} \Omega + \frac{1}{\sqrt{M_\mu}} Q_\mu X_{\mu\alpha} - \frac{m}{M} \sum_{\nu', \nu=1}^{n} A_{\nu\nu'} q_{(\nu')} \Omega \right) \right) \right.
\]

Applying the relations (56)-(57) and the proper-

Using the definitions (16) and (42) yield the identity

\[
\sum_{\nu, \nu'=1}^{n} A_{\nu\nu'} \left( \delta_{\nu\nu'} + \frac{m}{M} \right) A_{\nu\nu'} = \sum_{\nu, \nu'=1}^{n} \left( \delta_{\nu\nu'} + \frac{1}{n} \left( \sqrt{\frac{M}{M}} - 1 \right) \right) \left( \delta_{\nu\nu'} + \frac{m}{M} \right) = \left( \frac{1}{n} + \frac{m}{M} \right) \left( 2 \left( \sqrt{\frac{M}{M}} - 1 \right) + \left( \sqrt{\frac{M}{M}} - 1 \right)^2 \right) + \frac{m}{M} = \delta_{\nu\nu'}. \tag{G7}
\]

Appendix H: Commutation relations of orbital angular momentum and the internal observables

In this appendix, we determine explicitly the commutation relations between the orbital angular momentum \( L \) and the internal observables \( Q^\alpha, P_\beta, q_{(\nu)}, p_{(\nu)} \), \( \omega \) and \( \Omega \).

Since the operator \( \Omega \) commutes with the operators \( Q^\alpha, P_\beta, q_{(\nu)}, p_{(\nu)} \), the commutation relations (59)-(67) and the expression (G8) yield the first commutation relation (72), i.e.

\[
[ L, e^\ell \cdot \omega ] = \frac{1}{2} \left\{ 1(Q^\ell) \cdot e_k, \left[ e^k \cdot \Omega, e^\ell \cdot \omega \right] \right\} = \frac{1}{2} \left\{ 1(Q^\ell) \cdot e_k, -i \hbar \left( e^k \cdot 1(Q^\ell)^{-1} \cdot m^{(t)}(\omega) \right) \right\} = -i \hbar m^{(t)}(\omega). \tag{H1}
\]

The commutation relation (H1) and the property (A14) yield the canonical commutation relation in rotation (A14), i.e.

\[
[ n_{(k)}(\omega) \cdot L, e^\ell \cdot \omega ] = -i \hbar (e_k \cdot e^\ell), \tag{H2}
\]

which means that \( n_{(k)}(\omega) \cdot L \) and \( e^\ell \cdot \omega \) are canonically conjugated operators.

Since the operator \( Q^\alpha \) commutes with the operators \( Q^\beta, q_{(\nu)}, p_{(\nu)} \), the commutation relations (59)-(67) and (G8) yield the canonical commutation relation in rotation (A14), i.e.

\[
[ Q^\alpha, n_{(k)}(\omega) \cdot L, e^\ell \cdot \omega ] = -i \hbar (e_k \cdot e^\ell), \tag{H2}
\]

which means that \( Q^\alpha \cdot n_{(k)}(\omega) \cdot L \) and \( e^\ell \cdot \omega \) are canonically conjugated operators.
and the expression (G8) yield the first commutation relation (71), i.e.

\[
[L, Q^\alpha] = \frac{1}{2} \left\{ 1(Q^\cdot) \cdot e_k, \left[ e^k \cdot \Omega, Q^\alpha \right] \right\} + \frac{1}{2} \sum_{\mu=1}^{N} \left( X_{\gamma \mu} \times X_{\mu}^\beta \right) \left\{ Q^\gamma, \left[ P_{\beta}, Q^\alpha \right] \right\} \tag{H3}
\]

\[
= \frac{1}{2} \left\{ 1(Q^\cdot), -i\hbar \left[ 1(Q^\cdot)^{-1}, \sum_{\mu=1}^{N} (X_{\mu}^\alpha \times X_{\mu}^\beta) \right] Q^\beta \right\} - i\hbar \sum_{\mu=1}^{N} (X_{\mu}^\alpha \times X_{\mu}^\beta) \right\} \tag{H4}
\]

The commutation relation (H4) implies that,

\[
[L, P_{\alpha}] = 0. \tag{H8}
\]

Now, the definition (54) implies that,

\[
[1(Q^\cdot), P_{\beta}] = 1, \quad [Q^\beta, P_{\beta}] = i\hbar P_{\beta}. \tag{H7}
\]

The commutation relation (B7) applies for the operator \( L \) as well as for the operator \( P_{\nu}^\prime \). The commutation relations (B7) and (H1) and the property (A14) imply that,

\[
R(\omega)^{-1} [L, R(\omega)] = [L, e^j \cdot \omega] n_{(j)}(\omega) \cdot G = -i\hbar \left( m^{(j)} (\omega) \cdot n_{(j)}(\omega) \right) G = -i\hbar G. \tag{H9}
\]

The commutation relation (H9) implies that,

\[
[e_j \cdot L, R(\omega)] = -i\hbar R(\omega) (e_j \cdot G). \tag{H10}
\]

Now, the commutation relations (32) and (H10) imply that,

\[
[ [ e_j \cdot L, e_k \cdot L ], R(\omega) ] = [ e_j \cdot L, [ e_k \cdot L, R(\omega) ] ] - [ e_k \cdot L, [ e_j \cdot L, R(\omega) ] ]
\]

\[
= -i\hbar \left( e_k \cdot G \right) [ e_j \cdot L, R(\omega) ] - [ e_j \cdot L, R(\omega) ] \left( e_k \cdot G \right)
\]

\[
= \hbar^2 R(\omega) \left( e_j \cdot G, e_k \cdot G \right) \tag{H11}
\]

identifying the terms on the LHS of the commutation relation (H11) yields the second commutation relation (72), i.e.

\[
[e_j \cdot L, e_k \cdot L] = i\hbar (e_j \times e_k) \cdot L. \tag{H12}
\]
which is recast as,

\[
[ L, e_k \cdot L ] = i\hbar ( e_k \times L ). \tag{H13}
\]

Since the operator \( L \) commutes with the operators \( Q^\alpha, P_\alpha, q^\alpha, p_\alpha \), the commutation relations \([H3],[H5]\) and \([H8]\), and the expression \([G8]\) imply that

\[
[ L, e_k \cdot L ] = \frac{1}{2} \left\{ 1 (Q^\alpha), e_k \cdot L \right\} = \frac{1}{2} \left\{ 1 (Q^\alpha) \cdot e_\ell, e^\ell \cdot e_k \cdot L \right\} = \frac{1}{2} \left\{ 1 (Q^\alpha) \cdot e_\ell, [ e_\ell \cdot \Omega, e_k \cdot L ] \right\}.
\]

The commutation relation \([H15]\) implies that

\[
[ L, e_k \cdot L ] = \frac{1}{2} \left\{ 1 (Q^\alpha) \cdot e_\ell, [ e_\ell \cdot \Omega, e_k \cdot L ] \right\}.
\]

The commutation relations \([H13]\) and \([H16]-[H17]\) imply that,

\[
[ e_k \cdot L, e^\ell \cdot \Omega ] = - \left( e^\ell \cdot 1 (Q^\alpha)^{-1} \cdot e^\ell \right) (e_j \cdot (e_k \times L))
\]

which yields the second commutation relation \([H2]\), i.e.

\[
[ L, e^\ell \cdot \Omega ] = i\hbar \left( e^\ell \cdot 1 (Q^\alpha)^{-1} \cdot e^\ell \right) (e_j \times L).
\tag{H19}
\]

\section*{Appendix I: Commutation relations of spin and the internal observables}

In this appendix, we determine explicitly the commutation relations between the nuclear spin \( S_{(\mu)} \), the electronic spin \( s_{(\mu)} \) and the internal observables \( F_\alpha, p_\alpha \) and \( L \).

The definitions \([H5]\) and the commutation relations \([H1]\) and \([H3]\) imply that

\[
\begin{align*}
[ e_1 \cdot S_{(\mu)}, e_j \cdot S_{(\nu)} ] &= (e^k \cdot R (\omega) \cdot e_j) (e^\ell \cdot R (\omega) \cdot e_1) \left[ e_k \cdot S_{(\mu)}, e_\ell \cdot S_{(\nu)} \right] \\
&= i\hbar \delta_{\mu \nu} \left( e^k \cdot R (\omega) \cdot e_1 \right) \left( e^\ell \cdot R (\omega) \cdot e_j \right) \cdot (e_k \times e_\ell) \cdot e^m \left( e_m \cdot S_{(\mu)} \right)
\end{align*}
\]

The triple product \((e_k \times e_\ell) \cdot e^m\) is invariant under rotation, which implies that,

\[
\begin{align*}
&\left( e^k \cdot R (\omega) \cdot e_1 \right) \left( e^\ell \cdot R (\omega) \cdot e_j \right) (e_k \times e_\ell) \cdot e^m \\\n&\quad = (e_i \times e_j) \cdot e^m \left( e^m \cdot R (\omega) \cdot e_n \right)
\end{align*}
\tag{I3}
\]

Using the vectorial identity \([A13]\) and the definitions \([H5]\), the commutation relations \([I1]\) and \([I2]\) yield the commutation relations \([H6]\), i.e.

\[
\begin{align*}
[ e_i \cdot S_{(\mu)}, e_j \cdot S_{(\nu)} ] &= i\hbar \delta_{\mu \nu} \left( e_i \times e_j \right) \cdot e^m \left( e^m \cdot R (\omega) \cdot e_n \right) \left( e_m \cdot S_{(\mu)} \right) \\
&= i\hbar \delta_{\mu \nu} \left( e_i \times e_j \right) \cdot S_{(\mu)} \\
[ e_i \cdot s_{(\mu)}, e_j \cdot s_{(\nu)} ] &= i\hbar \delta_{\mu \nu} \left( e_i \times e_j \right) \cdot e^m \left( e^m \cdot R (\omega) \cdot e_n \right) \left( e_m \cdot s_{(\mu)} \right)
\end{align*}
\]

Using the group action \([A1]\), the identity \([A14]\), the definitions \([H5]\), the commutation relation \([H7]\) where \( e^j \cdot P_{(\nu)} \) is replaced by \( e^j \cdot L \) and the commutation relation \([H1]\), we compute the commutation relations,

\[
\begin{align*}
[ e_j \cdot L, S_{(\mu)} ] &= \left[ e_j \cdot L, e^k \cdot R (\omega) \right] (e_k \cdot S_{(\mu)}) \\
&= \left[ e_j \cdot L, e^\ell \cdot \omega \right] \left( n_i (\omega, G) S_{(\mu)} \right) \\
&= -i\hbar \left( e_j \cdot m_i (\omega) \right) \left( n_i (\omega, G) S_{(\mu)} \right) \\
&= -i\hbar \left( e_j \cdot G \right) S_{(\mu)} = -i\hbar \left( e_j \times S_{(\mu)} \right) \\
[ e_j \cdot L, s_{(\mu)} ] &= \left[ e_j \cdot L, e^k \cdot R (\omega) \right] (e_k \cdot s_{(\mu)}) \\
&= \left[ e_j \cdot L, e^\ell \cdot \omega \right] \left( n_i (\omega, G) s_{(\mu)} \right) \\
&= -i\hbar \left( e_j \cdot m_i (\omega) \right) \left( n_i (\omega, G) s_{(\mu)} \right) \\
&= -i\hbar \left( e_j \cdot G \right) s_{(\mu)} = -i\hbar \left( e_j \times s_{(\mu)} \right)
\end{align*}
\]

Using the definitions \([H5]\) and \([H4]\), the commutation relations \([H7]\) and \([H2]\), we compute the commutation
relations,

\[
\begin{align*}
\left[ P_\alpha, S_{(\mu)} \right] &= \sum_{\nu=1}^{N} \frac{1}{\sqrt{M_\nu}} \left( e^j \cdot X_{\alpha \nu} \right) \left[ e_j \cdot P''_\nu, e^k \cdot R(\omega) \right] (e_k \cdot S_\mu) \\
&= \sum_{\nu=1}^{N} \frac{1}{\sqrt{M_\nu}} \left( e^j \cdot X_{\alpha \nu} \right) \left[ e_j \cdot P''_\nu, e^\ell \cdot \omega \right] (J8) \\
&= \left[ P_\alpha, e^\ell \cdot \omega \right] \left( n_{(\ell)}(\omega) \cdot G \right) S_{(\mu)} = 0
\end{align*}
\]

Using the definitions (75), the commutation relations (18) and (23), we compute the commutation relations,

\[
\begin{align*}
\left[ e_j \cdot p_{(\nu)}, S_{(\mu)} \right] &= \left[ e_j \cdot p_{(\nu)}, e^k \cdot R(\omega) \right] (e_k \cdot S_\mu) \left\langle n_{(\ell)}(\omega) \cdot G \right\rangle S_{(\mu)} = 0 \\
&= \left[ e_j \cdot p_{(\nu)}, e^\ell \cdot \omega \right] \left\langle n_{(\ell)}(\omega) \cdot G \right\rangle S_{(\mu)} = 0 (J9)
\end{align*}
\]

\[
\begin{align*}
\left[ e_j \cdot p_{(\nu)}, \mu \left( n_{(\ell)}(\omega) \cdot G \right) \right] &= \left[ e_j \cdot p_{(\nu)}, e^k \cdot R(\omega) \right] (e_k \cdot S_\mu) \left\langle n_{(\ell)}(\omega) \cdot G \right\rangle S_{(\mu)} = 0 \\
&= \left[ e_j \cdot p_{(\nu)}, e^\ell \cdot \omega \right] \left\langle n_{(\ell)}(\omega) \cdot G \right\rangle S_{(\mu)} = 0 (J11)
\end{align*}
\]

**Appendix J: Kinetic energy operator**

In this appendix, we determine the expression of the kinetic energy operator \( T \) in terms of the internal observables.

Using the relation (17) and the definition (20), the expression (88) of the kinetic energy operator \( T \) is recast as,

\[
T = \sum_{\mu=1}^{N} \frac{1}{2M_\mu} \left( P''_\mu + \frac{M_\mu}{M} \mathcal{P} \right)^2 + \sum_{\nu=1}^{n} \frac{1}{2m} \left( p''_\nu + \frac{m}{M} \mathcal{P} \right)^2
\]

\[
= \left( \sum_{\mu=1}^{N} M_\mu + \sum_{\nu=1}^{n} m \right) \mathcal{P}^2 + \sum_{\mu=1}^{N} \frac{P''_\mu}{2M_\mu} + \sum_{\nu=1}^{n} \frac{p''_\nu}{2m} + \frac{\hbar^2}{2m} \Phi_{res}(Q^*) \quad (J1)
\]

Using the relations (16)-(17) and (22), the kinetic energy operator (J1) reduces to,

\[
T = \frac{\mathcal{P}^2}{2M} + \sum_{\mu=1}^{N} \frac{P''_\mu}{2M_\mu} + \sum_{\nu=1}^{n} \frac{p''_\nu}{2m} \quad (J2)
\]

Using the relation (26), the first term on the RHS of the expression (J2) is recast as,

\[
\sum_{\mu=1}^{N} \frac{P''_\mu}{2M_\mu} = \sum_{\mu=1}^{N} \frac{P''_\mu}{2M_\mu} + \sum_{\mu=1}^{N} \frac{\hbar^2}{8M_\mu} A_\mu(Q^*)^2
\]

\[
- \sum_{\mu=1}^{N} \frac{i\hbar}{4M_\mu} \left[ e_\ell \cdot P''_\mu, e^j \cdot A_\mu(Q^*) \right] \quad (J3)
\]

where the operator \( A_\mu(Q^*) \) is defined as,

\[
- i\hbar \left( e^k \cdot A_\mu(Q^*) \right) \left\langle n_{(\ell)}(\omega) \cdot G \right\rangle
\]

\[
\left[ e_\ell \cdot P''_\mu, e^j \cdot R(\omega) \right] (J4)
\]

Using the commutation relation (F14), the operator \( A_\mu(Q^*) \) is recast as,

\[
A_\mu(Q^*) = \left( e^j \cdot 1 \cdot (Q^*)^{-1} \cdot e^k \right) \left( e_j \times \left( e_k \times \left( M_\mu R^{(0)}_\mu \right) \right) \right)
\]

\[
= \left( e^j \cdot 1 \cdot (Q^*)^{-1} \cdot e^k \right) \left( M_\mu \left( e_j \cdot R^{(0)}_\mu \right) e_k - \left( e_j \cdot e_k \right) M_\mu R^{(0)}_\mu \right)
\]

\[
= M_\mu \left( R^{(0)}_\mu \cdot 1 \cdot (Q^*)^{-1} \right) - M_\mu R^{(0)}_\mu \text{Tr}(1 \cdot (Q^*)^{-1}) \quad (J5)
\]

Using the definitions (80) and (20), the third term on the RHS of the relation (J2) is recast as,

\[
\sum_{\nu=1}^{n} \frac{p''_\nu}{2m} = \sum_{\nu=1}^{n} \frac{p''_\nu}{2m} \quad (J6)
\]

The identities (J3) and (J6) imply that the kinetic energy (J7) is recast as,

\[
T = \frac{\mathcal{P}^2}{2M} + \sum_{\mu=1}^{N} \frac{P''_\mu}{2M_\mu} + \sum_{\nu=1}^{n} \frac{p''_\nu}{2m} + \frac{\hbar^2}{8} \Phi_{res}(Q^*) \quad (J7)
\]
Now, we determine the expression of the residual terms in the expression which implies that,

\[ \sum_{\mu=1}^{N} R^{(0)}_{\mu} \times A_{\mu}(Q') \]

\[ = \sum_{\mu=1}^{N} R^{(0)}_{\mu} \times \left( M_{\mu} \left( R^{(0)}_{\mu} \cdot 1(Q')^{-1} \right) \right) \]

\[ = \left( e^m \cdot 1(Q')^{-1} \cdot \ell_{00} \cdot e^{\ell} \right) \]

\[ \cdot \sum_{\mu=1}^{N} \left( e_{\ell} \cdot R^{(0)}_{\mu} \right) \left( e_{\ell} \cdot R^{(0)}_{\mu} \right) \left( e^{\ell} \times e_m \right) \]

\[ \text{Using the definition } \text{[J9]} \text{, equation } \text{[J14]} \text{ is recast as,} \]

\[ \sum_{\mu=1}^{N} R^{(0)}_{\mu} \times A_{\mu}(Q') \]

\[ = \sum_{\mu=1}^{N} R^{(0)}_{\mu} \times \left( M_{\mu} \left( R^{(0)}_{\mu} \cdot 1(Q')^{-1} \right) \right) \]

\[ = \left( e^m \cdot 1(Q')^{-1} \cdot \ell_{00} \cdot e^{\ell} \right) \]

\[ \cdot \sum_{\mu=1}^{N} \left( e_{\ell} \cdot R^{(0)}_{\mu} \right) \left( e_{\ell} \cdot R^{(0)}_{\mu} \right) \left( e^{\ell} \times e_m \right) \]

which implies in turn that the first term in the commutation relation \text{[J13]} becomes

\[ - \frac{2i}{\hbar} \left[ e_k \cdot \Omega, e_k \cdot \left( \sum_{\mu=1}^{N} R^{(0)}_{\mu} \times A_{\mu}(Q') \right) \right] \]

\[ = - \frac{2i}{\hbar} \left( e^m \cdot 1(Q')^{-1} \cdot \ell_{00} \cdot e^{\ell} \right) e_k \cdot \left( e_{\ell} \times e_m \right) \]

\[ \text{The definition } \text{[J5]} \text{ and the first commutation relation } \text{[J2]} \text{ and imply that,} \]

\[ \left[ e^k \cdot \Omega, 1(Q')^{-1} \right] = I_{\alpha} \left[ e^k \cdot \Omega, Q^{\alpha} \right] \]

\[ = -i\hbar I_{\alpha} \left( e^k \cdot 1(Q')^{-1} \right. \cdot \sum_{\mu=1}^{N} \left( X^{\alpha}_{\mu} \times X_{\mu\beta} \right) Q^{\beta} \]

\[ \text{which implies that,} \]

\[ \left[ e^k \cdot \Omega, 1(Q')^{-1} \right] \]

\[ = -1(Q')^{-1} \cdot \left[ e^k \cdot \Omega, 1(Q') \right] \cdot 1(Q')^{-1} \]

\[ = i\hbar \left( 1(Q')^{-1} \cdot I_{\alpha} \cdot 1(Q')^{-1} \right) \]

\[ \cdot \left( e^k \cdot 1(Q')^{-1} \cdot \sum_{\mu=1}^{N} \left( X^{\alpha}_{\mu} \times X_{\mu\beta} \right) Q^{\beta} \right) \]

\[ \text{Using the commutation relation } \text{[J18]} \text{ and the definition } \text{[J9]}, \text{ the commutation relation } \text{[J16]} \text{ can be recast} \]
Similarly, using the definition $J5$, the second term in the commutation relation $J19$ is recast as

$$- \frac{2i}{\hbar} \left[ P_{\alpha}, \sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left( X_{\mu}^{\alpha} \cdot A_{\mu} (Q') \right) \right]$$

$$= - \frac{2i}{\hbar} \left[ P_{\alpha}, \left( \epsilon^\ell \cdot (1-Q')^{-1} \cdot \epsilon^\ell \right) \right]$$

$$\sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left( X_{\mu}^{\alpha} \cdot (e_j \times (e_\ell \times R_{\mu}^{(0)})) \right).$$

The definition $J57$ implies that,

$$\sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left( X_{\mu}^{\alpha} \cdot (e_j \times (e_\ell \times R_{\mu}^{(0)})) \right)$$

$$= \sum_{\mu=1}^{N} \sqrt{M_{\mu}} \left( e_j \times X_{\mu}^{\alpha} \cdot (e_\ell \times R_{\mu}^{(0)}) \right)$$

$$= - i\hbar \left( \epsilon^\ell \cdot (1-Q')^{-1} \cdot \epsilon^\ell \right).$$

Using the relation $J21$, the commutation relation $J20$ is recast as

$$- \frac{2i}{\hbar} \left[ P_{\alpha}, \sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left( X_{\mu}^{\alpha} \cdot A_{\mu} (Q') \right) \right]$$

$$= \frac{2i}{\hbar} \left( \epsilon^\ell \cdot \epsilon^\ell \right) \left[ P_{\alpha}, \epsilon^\ell \cdot (1-Q')^{-1} \cdot \epsilon^\ell \right].$$

Using the definition $J53$ and the canonical commutation relation $J02$, we commute the commutation relation on the RHS of the expression $J8$, i.e.

$$\left[ P_{\alpha}, \epsilon^\ell \cdot (1-Q')^{-1} \cdot \epsilon^\ell \right]$$

$$= i\hbar \left( \epsilon^\ell \cdot (1-Q')^{-1} \cdot \epsilon^\ell \right).$$

Using the commutation relation $J23$ and the fact that the tensor $I_{\alpha}$ is symmetric, the commutation relation $J23$ is recast as,

$$- \frac{2i}{\hbar} \left[ P_{\alpha}, \sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left( X_{\mu}^{\alpha} \cdot A_{\mu} (Q') \right) \right]$$

$$= - 2 \epsilon^\ell \cdot \left[ I_{\alpha} \cdot I_{\alpha} \cdot (Q')^{-1} \cdot \epsilon^\ell \right]$$

$$= - 2 \text{Tr} \left[ (I_{\alpha} \cdot I_{\alpha} \cdot (Q')^{-1}) \right] .$$

The commutation relations $J13$, $J19$ and $J24$ imply that the first term of the operator $J8$ is recast as,

$$- \frac{2i}{\hbar} \sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} \left[ P_{\alpha}, A_{\mu} (Q') \right]$$

$$= 2 \text{Tr} \left[ (I_{\alpha} \cdot I_{\alpha} \cdot (Q')^{-1}) \right] .$$

Using the definitions $J91$ and $J5$, the last term of the expression $J8$ is recast as,

$$\sum_{\mu=1}^{N} \frac{1}{\sqrt{M_{\mu}}} A_{\mu} (Q')^{2}$$

$$= \sum_{\mu=1}^{N} M_{\mu} \left( (R_{\mu}^{(0)} \cdot (Q')^{-1} - R_{\mu}^{(0)} \text{Tr} ((Q')^{-1})) \right)^{2}$$

$$= \text{Tr} \left( I_{00} \cdot (Q')^{-2} \right) - 2 \text{Tr} \left( I_{00} \cdot (Q')^{-1} \right) \text{Tr} \left( (Q')^{-1} \right)$$

$$+ \text{Tr} \left( I_{00} \right) \text{Tr} \left( (Q')^{-2} \right).$$

The relations $J25$ and $J26$ imply that the expression $J8$ yields the residual operator $J90$, i.e.

$$\Phi_{\text{res}} (Q') = \text{Tr} \left( I_{00} \right) \text{Tr} \left( (Q')^{-2} \right)$$

$$- 2 \text{Tr} \left( I_{00} \cdot (Q')^{-1} \right) \text{Tr} \left( (Q')^{-1} \right)$$

$$+ \text{Tr} \left( I_{00} \cdot (Q')^{-2} - 2 (I_{\alpha} \cdot (Q')^{-1})^{2} \right) .$$

**Appendix K: Vibrational modes**

In this appendix, we determine the expression of the angular frequency of the vibrational modes and show that it is positively defined.

Using the expression $J90$ of the Coulomb potential between the nuclei, we deduce the zeroth, first and second
order terms of the series expansion (101), i.e.

\[ V_{N-N}^{e-(0)}(q_{\mu}) = -\frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} Z_{\mu} Z_{\nu}, \]

\[ V_{N-N}^{e-(\alpha)}(q_{\mu}) = -\frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \sum_{\nu' \neq \mu}^{n} Z_{\mu} Z_{\nu}, \]

\[ V_{N-N}^{e-(\alpha\beta)}(q_{\mu}) = -\frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \sum_{\nu' \neq \mu}^{n} Z_{\mu} Z_{\nu}, \]

\[ + 3 \frac{\Delta Y_{\mu\nu} \cdot \Delta R_{\mu\nu}^{(0)}}{||\Delta R_{\mu\nu}^{(0)}||^3} \left( \Delta R_{\mu\nu}^{(0)} \cdot \Delta Y_{\mu\nu} \right), \tag{K1} \]

where \( \Delta R_{\mu\nu}^{(0)} = R_{\mu}^{(0)} - R_{\nu}^{(0)} \) and \( \Delta Y_{\mu\nu\alpha} = Y_{\mu\nu\alpha} - Y_{\nu\mu\alpha} \).

Similarly, using the expressions (96) of the Coulomb potential between the nuclei and the electrons, we deduce the expressions for the zeroth, first and second-order terms of the series expansion (102), i.e.

\[ V_{N-N}^{e-(0)}(q_{\mu}) = -\frac{e^2}{4\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \sum_{\mu' \neq \mu}^{n} Z_{\mu} Z_{\nu}, \]

\[ V_{N-N}^{e-(\alpha)}(q_{\mu}) = -\frac{e^2}{4\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \sum_{\nu' \neq \mu}^{n} Z_{\mu} Z_{\nu}, \]

\[ V_{N-N}^{e-(\alpha\beta)}(q_{\mu}) = -\frac{e^2}{4\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \sum_{\nu' \neq \mu}^{n} Z_{\mu} Z_{\nu}, \]

\[ + 3 \frac{Y_{\mu\nu} \cdot \Delta Q_{\mu\nu}^{(0)}}{||\Delta Q_{\mu\nu}^{(0)}||^3} \left( \Delta Q_{\mu\nu}^{(0)} \cdot Y_{\mu\nu} \right), \tag{K2} \]

where \( \Delta Q_{\mu\nu}^{(0)} = Q_{\mu}^{(0)} - Q_{\nu}^{(0)} \).

We define three symmetric and trace-free tensors, i.e.

\[ B_{\mu\nu} = \frac{e^2 Z_{\mu} Z_{\nu}}{4\pi \varepsilon_0} \left( -\frac{1}{||\Delta R_{\mu\nu}^{(0)}||^3} + 3 \frac{\Delta R_{\mu\nu}^{(0)} \cdot \Delta R_{\mu\nu}^{(0)}}{||\Delta R_{\mu\nu}^{(0)}||^3} \right), \]

\[ A_{\mu} = \frac{e^2 Z_{\mu}}{4\pi \varepsilon_0} \sum_{\nu=1}^{N} Z_{\nu} \left( -\frac{1}{||\Delta R_{\mu\nu}^{(0)}||^3} + 3 \frac{\Delta R_{\mu\nu}^{(0)} \cdot \Delta R_{\mu\nu}^{(0)}}{||\Delta R_{\mu\nu}^{(0)}||^3} \right), \]

\[ E_{\mu} = -\frac{e^2 Z_{\mu}}{4\pi \varepsilon_0} \left( \sum_{\nu=1}^{n} \left( -\frac{1}{||\Delta Q_{\mu\nu}^{(0)}||^3} + 3 \frac{\Delta Q_{\mu\nu}^{(0)} \cdot \Delta Q_{\mu\nu}^{(0)}}{||\Delta Q_{\mu\nu}^{(0)}||^3} \right) \right), \tag{K3} \]

where

\[ B_{\mu\nu} = B_{\nu\mu}, \]

\[ A_{\mu} = \sum_{\nu=1}^{N} B_{\mu\nu} - \sum_{\nu=1}^{N} B_{\nu\mu} (1 - \delta_{\mu\nu}). \tag{K4} \]

Using the definitions (96) and (K3), the second-order term of the Coulomb potential

\[ V_{N-N}^{(\alpha\beta)} \] is expressed as,

\[ V_{N-N}^{(\alpha\beta)} = \frac{e^2}{8\pi \varepsilon_0} \sum_{\mu,\nu=1}^{N} \frac{\Delta Y_{\mu\nu\alpha} \cdot \Delta R_{\mu\nu}^{(0)}}{||\Delta R_{\mu\nu}^{(0)}||^3} \left( \Delta R_{\mu\nu}^{(0)} \cdot \Delta Y_{\mu\nu} \right), \]

\[ \sum_{\mu,\nu=1}^{N} \frac{Y_{\mu\nu\alpha} \cdot A_{\mu} \delta_{\mu\nu} \cdot Y_{\nu\beta}}{||\Delta R_{\mu\nu}^{(0)}||^3} \left( \Delta R_{\mu\nu}^{(0)} \cdot Y_{\nu\beta} \right). \tag{K5} \]

Similarly, using the definitions (96) and (K3), the second-order term of the Coulomb potential \( V_{N-e(\alpha\beta)} \) is expressed as,

\[ V_{N-e(\alpha\beta)} = \sum_{\mu,\nu=1}^{N} Y_{\mu\alpha} \cdot E_{\mu} \delta_{\mu\nu} \cdot Y_{\nu\beta}. \tag{K6} \]

According to the expressions (K5) and (K6) of the second-order Coulomb potentials, the condition (109) is recast in terms of the tensors (K3) as,

\[ \sum_{\mu=1}^{N} Y_{\mu\alpha} \sum_{\nu=1}^{N} \left( (A_{\mu} + E_{\mu}) \delta_{\mu\nu} - B_{\mu\nu} (1 - \delta_{\mu\nu}) \right) \cdot Y_{\nu\beta} = 0. \tag{K7} \]

To simplify the notation, we define a symmetric and trace-free tensor \( D_{\mu\nu} \) that is a linear combination of the tensors \( A_{\mu}, B_{\mu\nu} \) and \( E_{\mu} \), i.e.

\[ D_{\mu\nu} = (A_{\mu} + E_{\mu}) \delta_{\mu\nu} - B_{\mu\nu} (1 - \delta_{\mu\nu}). \tag{K8} \]

which implies that the relation (K7) is recast as,

\[ \sum_{\mu=1}^{N} Y_{\mu\alpha} \cdot \left( \sum_{\nu=1}^{N} D_{\mu\nu} \cdot Y_{\nu\beta} \right) = 0, \tag{K9} \]

where \( \alpha \neq \beta \). The conditions (45), (47) and (48) imply that the condition (K9) is satisfied provided all the vibration modes \( Y_{\nu\beta} \) satisfy the condition,

\[ \sum_{\nu=1}^{N} D_{\mu\nu} Y_{\nu\beta} = c_{\beta} \sqrt{M_{\mu}} X_{\mu\beta} + M_{\mu} a_{\beta} + M_{\mu} \left( b_{\beta} \times R_{\mu}^{(0)} \right), \tag{K10} \]

where \( c_{\beta} \) is a scalar parameter, \( a_{\beta} \) and \( b_{\beta} \) are vectorial parameters.

Using the definition (K8), the conditions (46), (47) and (K4) and taking the sum over all the nuclei in the relation (K10) yields,

\[ \sum_{\mu=1}^{N} D_{\mu\nu} \cdot Y_{\nu\beta} = \sum_{\mu=1}^{N} E_{\mu} \cdot Y_{\mu\beta} = \sum_{\mu=1}^{N} M_{\mu} a_{\beta}. \tag{K11} \]

The definition (17) and the relation (K11) yield,

\[ a_{\beta} = \frac{1}{M} \sum_{\nu=1}^{N} E_{\nu} \cdot Y_{\nu\beta}. \tag{K12} \]
Using the conditions (K10) and (K17) and taking the sum over all the nuclei in the relation (K10) after multiplying by \( b_\beta \times R^{(0)}_\mu \) yields,

\[
\sum_{\mu, \nu=1}^N \left( b_\beta \times R^{(0)}_\mu \right) \cdot D_{\mu\nu} \cdot Y_{\nu\beta} = \sum_{\mu=1}^N M_\mu \left( b_\beta \times R^{(0)}_\mu \right) \cdot \left( b_\beta \times R^{(0)}_\mu \right)
\]  \tag{K13}

The definitions (55) implies that the relation (K13) reduces to,

\[
\sum_{\mu, \nu=1}^N \left( e_j \times R^{(0)}_\mu \right) \cdot D_{\mu\nu} \cdot Y_{\nu\beta} = e_j \cdot l_0 \cdot b_\beta \ , \tag{K14}
\]

which is recast as,

\[
b_\beta = (l_0^{-1} \cdot e^j) \sum_{\rho, \nu=1}^N \left( e_j \times R^{(0)}_\rho \right) \cdot D_{\rho\nu} \cdot Y_{\nu\beta} \ . \tag{K15}
\]

Substituting the relations (K12), (K8) and (K15) into the condition (K10) yields the eigenvalue equation,

\[
\sum_{\nu=1}^N \left( D_{\mu\nu} - \frac{M_\mu}{M} E_\nu - M_\mu \left( e_k \times R^{(0)}_\mu \right) \sum_{\rho, \nu=1}^N \left( e_k \cdot l_0^{-1} \cdot e^j \right) \cdot \left( e_j \times R^{(0)}_\rho \right) \cdot D_{\rho\nu} \right) \cdot Y_{\nu\beta} = c_\beta \sqrt{M_\mu} X_{\mu\beta} \ . \tag{K16}
\]

Using the conditions (45), (46) and (47) and taking the sum over all the nuclei in the relation (K16) after multiplying by \( Y_{\mu\beta} \) yields,

\[
\sum_{\mu=1}^N Y_{\mu\beta} \cdot \left( \sum_{\nu=1}^N D_{\mu\nu} \cdot Y_{\nu\beta} \right) = c_\beta \ . \tag{K17}
\]

At equilibrium, the energy of the stable molecular system is minimal. Thus, in the neighbourhood of the equilibrium, the relation (K17) is a positive definite quadratic form. Identifying the relations (109) and (K9) and comparing them to the relation (K17), we conclude that, i.e.

\[
\omega^2 = V_{N-\beta}(\beta) + \left\langle V_{N-\epsilon(\beta)}(q_{\epsilon}) \right\rangle \ , \tag{K18}
\]

where \( \omega^2 = c_\beta > 0 \) is identified physically as the square of the angular frequency of the vibration eigenmodes.