

Appendix C

Vibrational Hamiltonian in internal coordinates

C.1 General remarks

There exist two procedures for formulation of the quantum mechanical Hamilton operator in arbitrary nuclear coordinates [163, 164]. The first one is to:

- Write the quantum mechanical Hamiltonian for the system in Cartesian coordinates (The application of the correspondence principle, i.e. replacing the classical momenta by the corresponding operators, is implicit, since this procedure is straightforward for Cartesian coordinates).
- Change to the desired coordinates in this quantum Hamiltonian, using the chain rule to calculate the derivatives [this method was used to obtain the equation (4.15)].

Alternatively, one can

- Write the classical Hamiltonian in Cartesian coordinates.

- In the classical expression, change to the desired coordinates.
- Apply the correspondence principle by replacing the generalized coordinates and momenta by their operators.

Taken as it is, the second procedure might lead to incorrect results, unless the classical expression for the Hamiltonian is written in a certain form suggested by Podolsky [147](this is also known as *Podolsky trick*). With this correction, both procedures, in principle, should lead to identical quantum Hamilton operators.

C.2 Derivation of the Hamiltonian

Let us consider the derivation of the Hamilton operator along the lines of the second procedure described above, including the Podolsky trick. It is known from the literature [111, 164, 165], that in this case the Hamilton operator has the following form:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} \frac{\partial}{\partial q_j} G_{jk} \frac{\partial}{\partial q_k} + V'(\mathbf{q}) + V(\mathbf{q}). \quad (\text{C.1})$$

Here $\mathbf{q} = (q_i), i = 1, 3N - 6$ are the internal molecular coordinates (the molecule is assumed to be nonlinear, hence there are $3N-6$ of them), G is an instantaneous function of molecular geometry (for the derivation of G -matrix elements see, for example [41]), $V(\mathbf{q})$ is the molecular potential energy function, and $V'(\mathbf{q})$ is a ‘purely quantum-mechanical’ mass-dependent contribution to the potential energy, sometimes referred to as the Watson term [111, 166]. The Watson term is given by the formula

$$V'(\mathbf{q}) = \frac{\hbar^2}{8} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} \frac{\partial G_{jk}}{\partial q_j} \frac{\partial \ln g}{\partial q_k} + \frac{\hbar^2}{32} \sum_{j=1}^{3N-6} \sum_{k=1}^{3N-6} G_{jk} \frac{\partial \ln g}{\partial q_j} \frac{\partial \ln g}{\partial q_k}, \quad (\text{C.2})$$

where $g = |\mathbf{I}|/|\mathbf{G}|$ [111] and \mathbf{I} is the 3×3 simultaneous inertial tensor [41].

For an asymmetric triatomic ABC molecule, the G matrix elements are given below. For the sake of consistency, the notation is that used throughout this paper,

describing the 3-D model of the HONO₂ molecule.

$$G = \begin{pmatrix} \frac{1}{\mu_1} & -\frac{\cos \alpha}{m_2} & \frac{\sin \alpha}{m_2 r_2} \\ -\frac{\cos \alpha}{m_2} & \frac{1}{\mu_2} & \frac{\sin \alpha}{m_2 r_1} \\ \frac{\sin \alpha}{m_2 r_2} & \frac{\sin \alpha}{m_2 r_1} & \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2}\right) + \frac{2 \cos \alpha}{m_2 r_1 r_2} \end{pmatrix}. \quad (\text{C.3})$$

Substituting this G-matrix in the equation (C.1) yields for the 'kinetical' (i.e. containing operators of the momentum) part of the Hamiltonian

$$\begin{aligned} \hat{T} = & -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} - \frac{\hbar^2 \cos \alpha}{m_2} \frac{\partial^2}{\partial r_1 \partial r_2} \\ & + \frac{\hbar^2 \cos \alpha}{2m_2} \left(\frac{1}{r_2} \frac{\partial}{\partial r_1} + \frac{1}{r_1} \frac{\partial}{\partial r_2} \right) \\ & - \left(\frac{\hbar^2}{2\mu_1 r_1^2} + \frac{\hbar^2}{2\mu_2 r_2^2} - \frac{\hbar^2 \cos \alpha}{m_2 r_1 r_2} \right) \frac{\partial^2}{\partial \alpha^2} - \frac{\hbar^2 \sin \alpha}{2m_2 r_1 r_2} \frac{\partial}{\partial \alpha} \\ & + \frac{\hbar^2 \sin \alpha}{m_2} \left(\frac{1}{r_2} \frac{\partial}{\partial r_1} + \frac{1}{r_1} \frac{\partial}{\partial r_2} \right) \frac{\partial}{\partial \alpha}. \end{aligned} \quad (\text{C.4})$$

The corresponding part of the kinetic energy operator given by equation (4.15) (which was derived according to the first procedure described here) is identical to this expression. The only difference lies in the potential-like Watson term, which we shall now define according to the second procedure.

In order to derive the Watson term V' , we have to obtain the determinant of the instantaneous inertial tensor I . In terms of bond distances and angles, the nonzero components of this tensor for a planar asymmetric triatomic molecule are [166]

$$\begin{aligned} I_{xx} &= (u_1 + u_3 - 2u_{13} \cos \alpha)/m, \\ I_{yy} &= (u_1 \cos^2(\alpha - \epsilon) + u_3 \cos^2 \epsilon + 2u_{13} \cos \epsilon \cos(\alpha + \epsilon))/m, \\ I_{zz} &= (u_1 \sin^2(\alpha + \epsilon) + u_3 \sin^2 \epsilon + 2u_{13} \sin \epsilon \sin(\alpha + \epsilon))/m, \\ I_{yz} &= (u_1 \sin 2(\alpha + \epsilon) - u_3 \sin 2\epsilon - 2u_{13} \sin(\alpha + 2\epsilon))/2m. \end{aligned} \quad (\text{C.5})$$

Here an angle ϵ between r_1 bond and the z-axis was introduced, which for the adopted reference configuration of the molecule is given by

$$\epsilon = \frac{\pi - \alpha}{2} + \frac{u_1 - u_3}{\sqrt{(u_1 + u_3)^2 - 4u_{13}^2}} \arctan \left(\sqrt{\frac{u_1 + u_3 - 2u_{13}}{u_1 + u_3 + 2u_{13}}} \tan \frac{\pi - \alpha}{2} \right), \quad (\text{C.6})$$

where $u_1 = m_1(m_2 + m_3)r_1^2$, $u_3 = m_3(m_2 + m_1)r_2^2$, $u_{13} = m_1m_2r_1r_2$. The instantaneous inertial tensor has the form

$$\mathbf{I} = \begin{pmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & I_{yz} \\ 0 & I_{yz} & I_{zz} \end{pmatrix}. \quad (\text{C.7})$$

The evaluation of the determinants of \mathbf{I} and \mathbf{G} matrices gives the following result for the factor g , appearing in equation (C.2):

$$g = \frac{m_2^6 r_1^4 r_2^4 \mu_1^3 \mu_2^3 \sin^2 \alpha}{(m_2^2 - \mu_1 \mu_2)^3}. \quad (\text{C.8})$$

Substituting this in (C.2) gives us

$$V'(r_1, r_2, \alpha) = \frac{\cos^3 \alpha}{4m_2 r_1 r_2 \sin^2 \alpha} - \frac{1}{8} \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) (1 + \csc^2 \alpha). \quad (\text{C.9})$$

The Hamilton operator defined by equations (C.1) and (C.9) is well-known [111–113, 115]. However, in these approaches V' has a singularity at $\alpha = \pi$, which is not present in the kinetic energy operator derived “quantum mechanically” (equation (4.15)). The origin of the differences lies in the inherently classical procedure used to obtain the Watson term given by the equation (C.9). In the case of a linear molecule ($\alpha = \pi$), the I_{zz} component of the \mathbf{I} tensor vanishes (equation C.7), in which case the determinant of \mathbf{I} is zero, and the logarithmic derivatives in (C.2) yield infinities. This is the origin of singularities in equation (C.9).

To circumvent the problem of singularities in the Hamilton operator, one may subject the Hamilton operator to a similarity transformation [112, 113]. A more consistent approach requires certain rearrangement of the classical Hamiltonian, as an extension of the Podolsky trick, which in general should lead to a non-singular Hamilton operator [166].