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Many-body Hamiltonians in implicitly defined frames

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Abstract
We study the quantization of three-dimensional many-body systems in rotating coordinate frames defined implicitly by frame conditions. We carry out the elimination of orientational degrees of freedom in general, giving the Hamiltonian for the N-particle system in a broad class of body frames in terms of frame conditions and internal coordinates. We obtain several forms for the kinetic-energy operator and compare them to related expressions in the literature.

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1. Introduction

The problem of separating the dynamics of quantum many-body systems into collective rotations and internal motions leads to their quantization in rotating frames. We refer to a rotating frame as a body frame when the components of the total angular-momentum operator in a space-fixed frame and in the rotating frame satisfy the same commutator algebra as in the rigid body problem. In the latter case, the body frame is essentially unique, up to time-independent rotations and symmetry transformations of the rigid body. For a general N-particle system there is a large freedom to choose a body frame. It is thus of interest to study the quantization of many-body systems in a class of body frames as wide as possible.

In this paper, we study the quantization of three-dimensional many-body systems in rotating coordinate frames defined in implicit form by frame, or gauge, conditions. We carry out the elimination of orientational degrees of freedom in general, giving the Hamiltonian for the N-particle system in a broad class of body frames in terms of frame conditions and internal coordinates. We obtain several forms for the kinetic-energy operator and compare them to related expressions in the literature, showing how the coefficient functions are fixed by the frame convention, through frame conditions, and internal coordinates. In the case of linear frames and body-frame coordinates, our results reduce to those previously obtained in [1].

The generic Hamiltonians discussed here can be applied to specific physical systems by choosing internal coordinates appropriate to the system under consideration. Those physical problems include, for instance, the determination of molecular rotation–vibration energy levels and their wavefunctions [2], and scattering problems in molecular, atomic and nuclear physics. There is a vast body of literature on the quantization of many-body systems which we do not try to summarize here. Broad reviews relevant to the point of view adopted in this paper are given in [3, 4].

The outline of the paper is the following. In the next section, we discuss several technical issues related to body frames and the frame conditions defining them that are needed in order to obtain the Hamiltonian and quantum inner product for a many-body system. Those include the form of admissible frame conditions and their reparametrizations, the body-frame angular momentum and internal coordinates. In section 3, we derive the body-frame kinetic-energy operator in standard order in terms of internal coordinates and frame conditions. The form of wavefunctions referred to the body frame and their inner product is discussed in section 4, where we also give the representations of the total angular momentum and kinetic-energy operators both as irreducible matrices and in rigid-rotator form. In section 5, we give two alternate forms for the Hamiltonian and discuss their equivalence with the standard-ordered form given in section 3. Also, we make contact with the gauge-field formalism of [3] by locally expressing gauge fields in terms of frame conditions. Examples with $N = 3$ and 4 are briefly examined in sections 6 and 7 as verifications of the formalism of the previous sections, and the results compared with those from the molecular literature. In section 8, we give some final remarks.

2. Preliminaries

We consider rotating frames whose definition depends only on the coordinates of the particles and not on their velocities, nor on the angular velocity of the frame itself. Those frames can always be defined implicitly by imposing conditions on the position vectors of the particles. Most of the body frames commonly used in the literature belong to this class, as illustrated in sections 6 and 7 with two familiar examples. Another well-known example is the Eckart frame [5, 6]. We do not impose any restriction on the form of frame conditions, provided they fix the frame uniquely. The particular case of frame conditions depending linearly on the particle coordinates was considered in [1] from the point of view of gauge invariance.

2.1. Frame conditions and their reparametrizations

The frame conditions defining the body frame must fix its 6 degrees of freedom. The translational degrees of freedom are fixed by choosing the centre-of-mass frame. Thus, the frame conditions take the form[1],

$$\boldsymbol{\mathcal{C}}(\{\boldsymbol{r}\}) \equiv \sum_{\alpha=1}^{N} m_\alpha \boldsymbol{r}_\alpha = 0, \qquad \mathcal{G}_a(\{\boldsymbol{r}\}) = 0, \quad a = 1, 2, 3, \tag{1}$$

where $\mathcal{G}_a$ are three conditions fixing the orientational degrees of freedom. We denote by $\{\boldsymbol{r}\} = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N\}$ a generic configuration[2] of the N-particle system. Since lab-frame configurations are not restricted, any $\{\boldsymbol{r}\}$ can be a lab-frame configuration. Those configurations satisfying

[1] The letters a, b, c, d are used for non-tensorial indices, as in $\mathcal{G}_a$. Summation over those indices and their ranges of variation are always explicitly indicated. We only use the summation convention for tensor indices, denoted by Latin letters $i, j, k, l, \ldots$, which always run from 1 to 3. Greek indices number particles.

[2] A configuration of the system is actually $\{\boldsymbol{r}, \dot{\boldsymbol{r}}\}$. We refer to $\{\boldsymbol{r}\}$ as a configuration here for convenience.

the frame conditions are denoted by $\{\boldsymbol{R}\}$. Thus, $\boldsymbol{\mathcal{C}}(\{\boldsymbol{R}\}) \equiv 0 \equiv \mathcal{G}_a(\{\boldsymbol{R}\})$ and such a set $\{\boldsymbol{R}\}$ of N position vectors can be a body-frame configuration. We also introduce the following notation:

$$\frac{\partial \mathcal{G}_a}{\partial \boldsymbol{R}_\alpha} \equiv \frac{\partial \mathcal{G}_a}{\partial \boldsymbol{r}_\alpha}(\{\boldsymbol{R}\}), \qquad \mathcal{Q}_{ai}(\{\boldsymbol{R}\}) \equiv \sum_{\alpha=1}^{N} \frac{\partial \mathcal{G}_a}{\partial R_{\alpha j}} \varepsilon_{jik} R_{\alpha k},$$
$$\mathcal{R}^2_{ab}(\{\boldsymbol{R}\}) \equiv \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial \mathcal{G}_a}{\partial R_{\alpha l}} \frac{\partial \mathcal{G}_b}{\partial R_{\alpha l}} \tag{2}$$

which will be used throughout the paper.

In order for the conditions $\mathcal{G}_a = 0$ to fix the orientational freedom they must not be rotation invariant. Thus, they must satisfy the admissibility condition,

$$\det(\mathcal{Q}_{ai}(\{\boldsymbol{R}\})) \neq 0 \qquad \text{for} \quad \mathcal{G}_a(\{\boldsymbol{R}\}) = 0, \tag{3}$$

except maybe at singular configurations. We also assume that, except for singular configurations, the relation $\det\left(\mathcal{R}^2_{ab}(\{\boldsymbol{R}\})\right) \neq 0$ for $\mathcal{G}_a(\{\boldsymbol{R}\}) = 0$ is fulfilled so that the frame manifold possesses a tangent space at $\{\boldsymbol{R}\}$. Typically, $\{\boldsymbol{R}_\alpha = 0\}$ is a singular configuration. Furthermore, for the two sets of conditions in (1) to be compatible the rotational conditions $\mathcal{G}_a$ must be translation invariant, $\mathcal{G}_a(\{\boldsymbol{r}_\alpha + \boldsymbol{v}\}) = \mathcal{G}_a(\{\boldsymbol{r}_\alpha\})$, for any $\boldsymbol{v}$. This is satisfied by all usual frame conditions (see, e.g., [1, 5]). In what follows, however, it will be enough to assume only the weaker form

$$\sum_{\alpha=1}^{N} \frac{\partial \mathcal{G}_a}{\partial R_{\alpha j}} = 0. \tag{4}$$

The condition $\boldsymbol{\mathcal{C}} = 0$, on the other hand, is clearly rotation invariant.

The frame conditions are obviously not unique. Consider the class of reparametrizations,

$$\mathcal{G}'_a(\{\boldsymbol{r}\}) = \sum_{b=1}^{3} \mathcal{P}_{ab}(\{\boldsymbol{r}\}) \mathcal{G}_b(\{\boldsymbol{r}\}), \tag{5}$$

where $\mathcal{P}_{ab}(\{\boldsymbol{r}\})$ is non-singular on the frame manifold,

$$\det(\mathcal{P}_{ab}(\{\boldsymbol{R}\})) \neq 0 \qquad \text{for} \quad \mathcal{G}_c(\{\boldsymbol{R}\}) = 0. \tag{6}$$

The frame conditions $\mathcal{G}'_a$ define the same frame as $\mathcal{G}_a$ and we have

$$\mathcal{R}'^2_{cd} = \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial \mathcal{G}'_c}{R_{\alpha j}} \frac{\partial \mathcal{G}'_d}{R_{\alpha j}} = \sum_{c_1, d_1=0}^{3} \mathcal{P}_{cc_1} \mathcal{P}_{dd_1} \mathcal{R}^2_{c_1 d_1}, \qquad \mathcal{Q}'_{ai} = \sum_{b=1}^{3} \mathcal{P}_{ab} \mathcal{Q}_{bi}. \tag{7}$$

Note that the reparametrization (5) is not necessarily linear in the frame conditions, since the coefficients $\mathcal{P}_{ab}$ can depend on $\mathcal{G}_a$. For instance $\mathcal{P}_{ab} = \mathcal{R}^{-2}_{ab}$ satisfies (6) by assumption and leads to $\mathcal{G}'_a$ orthonormal on the frame manifold, i.e., $\mathcal{R}'^2_{ab} = \delta_{ab}$. Thus, we could assume without loss of generality that frame conditions are orthonormal in this sense. We shall not do so, however, because orthonormalizing a set of frame conditions can be inconvenient in practice.

Another important example is furnished by the reparametrization

$$\mathcal{F}_i(\{\boldsymbol{r}\}) = \sum_{b=1}^{3} \mathcal{Q}^{-1}_{ib}(\{\boldsymbol{r}\}) \mathcal{G}_b(\{\boldsymbol{r}\}). \tag{8}$$

From (3) we see that (6) is satisfied. Clearly, $\mathcal{F}_i$ depend nonlinearly on the $\mathcal{G}_a$. If $\mathcal{G}'_a$ are any frame conditions equivalent to the $\mathcal{G}_a$ then, in a neighbourhood of the frame manifold $\mathcal{G}_a = 0$, they can be related by a reparametrization of the form (5). Using (7) and (8) we see that the frame conditions $\mathcal{F}_i$ are invariant under reparametrizations of $\mathcal{G}_a$,

$$\mathcal{F}'_i(\{\boldsymbol{r}\}) \equiv \sum_{b=1}^{3} \mathcal{Q}'^{-1}_{ib}(\{\boldsymbol{r}\})\mathcal{G}'_b(\{\boldsymbol{r}\}) = \sum_{c=1}^{3} \mathcal{Q}^{-1}_{ic}(\{\boldsymbol{r}\})\mathcal{G}_c(\{\boldsymbol{r}\}) = \mathcal{F}_i(\{\boldsymbol{r}\}). \tag{9}$$

Other reparametrization-invariant quantities involving the frame conditions $\mathcal{G}_a$ can be expressed most economically in terms of $\mathcal{F}_i$ and their derivatives

$$\mathcal{F}_{i\alpha j} \equiv \frac{\partial \mathcal{F}_i}{\partial R_{\alpha j}} = \sum_{a=1}^{3} \mathcal{Q}^{-1}_{ia} \frac{\partial \mathcal{G}_a}{\partial R_{\alpha j}}. \tag{10}$$

These quantities play an important role in what follows since, as shown below, the frame conditions $\mathcal{G}_a$ enter the Hamiltonian only through $\mathcal{F}_i$ and their derivatives. This ensures that $\mathcal{H}$ is reparametrization invariant, as all observables should be.

The previous analysis can be extended to a more general class of reparametrizations of the frame conditions $\mathcal{G}'_a = \mathcal{P}_a[\{\mathcal{G}_b\}]$, involving arbitrary functionals $\mathcal{P}_a$ of $\mathcal{G}_b$ which are not singular at $\mathcal{G}_b = 0$. Clearly, only the behaviour of the new frame conditions $\mathcal{G}'_a$ in a small neighbourhood of the frame manifold $\mathcal{G}_a = 0$ is relevant. In such a neighbourhood we can expand $\mathcal{P}_a$ about $\mathcal{G}_a = 0$, thus obtaining a reparametrization of the form (5).

2.2. Body-frame transformation and angular momentum

The transformation relating a configuration $\{\boldsymbol{r}\}$ of the system in the laboratory frame to the corresponding configuration $\{\boldsymbol{R}\}$ in the body frame defined by the conditions (1) is

$$\boldsymbol{R}_\alpha = \boldsymbol{U}(\boldsymbol{r}_\alpha - \boldsymbol{r}_{\mathrm{cm}}) \tag{11}$$

with $\boldsymbol{r}_{\mathrm{cm}}$ the centre-of-mass position in the lab frame and $\boldsymbol{U} = \boldsymbol{U}(\{\theta_a\})$ an orthogonal matrix parametrized by three angular variables $\{\theta_a\}_{a=1}^{3}$. Although our approach and results do not depend on any specific parametrization of the rotation group, some parametrization-dependent quantities such as the momenta p_{θ_a} conjugate to θ_a are physically meaningful and play an important role in some intermediate calculations. All the information we will need about the parametrization of $\boldsymbol{U}$ is encoded in the matrices $\boldsymbol{\Lambda}$ and $\boldsymbol{\lambda}$ defined by

$$\frac{\partial \boldsymbol{U}}{\partial \theta_a}\boldsymbol{U}^\dagger = \Lambda_{ai}\boldsymbol{T}_i, \qquad \boldsymbol{U}^\dagger \frac{\partial \boldsymbol{U}}{\partial \theta_a} = \lambda_{ai}\boldsymbol{T}_i, \qquad a = 1, 2, 3, \tag{12}$$

where $\boldsymbol{U}^\dagger$ is the transpose of $\boldsymbol{U}$ and $\boldsymbol{T}_j$ are the standard generators of the $so(3)$ algebra, $(\boldsymbol{T}_j)_{ik} = \varepsilon_{ijk}$. The three matrices $\partial \boldsymbol{U}/\partial\theta_a \boldsymbol{U}^\dagger$, $a = 1, 2, 3$, must be a basis of $so(3)$ for all values of $\{\theta_b\}$ if the parametrization is to be well defined. Thus, the matrix Λ_{ai} is invertible and, analogously, so is λ_{ai}. From the unimodularity of $\boldsymbol{U}$ it follows that $\boldsymbol{U}^\dagger \boldsymbol{T}_i \boldsymbol{U} = U_{ij}\boldsymbol{T}_j$ and then, from (12), $\lambda_{aj} = \Lambda_{ai}U_{ij}$.

The frame conditions (1) determine the time dependence of $\{\theta_a\}$ so that, given a trajectory $\{\boldsymbol{r}_\alpha(t)\}$ of the system in the lab frame, we have $\mathcal{G}_a(\{\boldsymbol{R}_\alpha(t)\}) = \mathcal{G}_a(\{\boldsymbol{U}(\{\theta_a(t)\})(\boldsymbol{r}_\alpha(t) - \boldsymbol{r}_{\mathrm{cm}})\}) = 0$ for all t. From (11) we then have, with M the total mass of the system,

$$\frac{\partial R_{\beta i}}{\partial r_{\alpha j}} = \left(\delta_{\alpha\beta} - \frac{m_\alpha}{M}\right) U_{ij} + \frac{\partial U_{ik}}{\partial r_{\alpha j}} U_{lk} R_{\beta l}. \tag{13}$$

Substituting (13) into the relation $\partial\mathcal{G}_a/\partial R_{\alpha j} = 0$, and using the definition (2) for $\mathcal{Q}$ and the antisymmetry of $(\partial U_{ik}/\partial r_{\alpha j} U_{lk})$ in i and l, we obtain the relation

$$\frac{\partial U_{ik}}{\partial r_{\alpha j}} U_{lk} = \sum_{a=1}^{3} \varepsilon_{ilm} \mathcal{Q}^{-1}_{ma} \frac{\partial \mathcal{G}_a}{\partial R_{\alpha n}} U_{nj} = \varepsilon_{ilm}\mathcal{F}_{m\alpha n} U_{nj}, \tag{14}$$

which expresses $\partial \boldsymbol{U}/\partial r_{\alpha j}\boldsymbol{U}^\dagger$ in terms of $\{\boldsymbol{R}_\gamma\}$ and $\{\theta_b\}$. This expression characterizes the dependence of $\boldsymbol{U}$ on $\{\boldsymbol{r}_\alpha\}$, and will be important below, especially in the discussion of angular momentum. Some further consequences of (14) are discussed in appendix A. Together, (13) and (14) lead to

$$\frac{\partial R_{\beta i}}{\partial r_{\alpha j}} = \left(\delta_{\alpha\beta} - \frac{m_\alpha}{M}\right) U_{ij} + \varepsilon_{ikl}\mathcal{F}_{l\alpha m}U_{mj}R_{\beta k}, \tag{15}$$

which will also be useful below.

From (11) and $\partial R_{\alpha i}/\partial\theta_a = 0$, we get

$$\frac{\partial r_{\alpha i}}{\partial \theta_a} = \frac{\partial U_{ki}}{\partial \theta_a} U_{kj}(r_{\alpha j} - r_{\mathrm{cm}\,j}). \tag{16}$$

We assume that interactions among particles do not depend on their velocities. Classically, the momenta p_{θ_a} conjugate to θ_a is then $p_{\theta_a} = \partial\mathcal{L}/\partial\dot\theta_a = \sum_{\alpha=1}^{N}(\partial r_{\alpha i}/\partial\theta_a)(\partial\mathcal{L}/\partial\dot r_{\alpha i})$ where $\mathcal{L}$ is the classical Lagrangian in the lab frame. Thus, taking (12) and (16) into account, we have

$$p_{\theta_a} = -\lambda_{ai}(l_i - l_{\mathrm{cm}i}) = -\Lambda_{aj}L_j \qquad \text{with} \quad \boldsymbol{l}_{\mathrm{cm}} \equiv M\boldsymbol{r}_{\mathrm{cm}} \wedge \dot{\boldsymbol{r}}_{\mathrm{cm}}, \quad \boldsymbol{L} = \boldsymbol{U}(\boldsymbol{l} - \boldsymbol{l}_{\mathrm{cm}}). \tag{17}$$

$\boldsymbol{l}_{\mathrm{cm}}$ is the centre-of-mass angular momentum in the lab frame and $\boldsymbol{L}$ the total angular momentum about the centre of mass in the moving frame.

In the lab frame, the angular-momentum operator $\boldsymbol{l}$ satisfies the usual commutator algebra. Using (14), the definition (2) of $\mathcal{Q}$, and the unimodularity of $\boldsymbol{U}$, we obtain

$$[l_i, U_{jk}] = \sum_{\alpha=1}^{N} \varepsilon_{ilm} r_{\alpha l} \frac{1}{\mathrm{i}} \frac{\partial U_{jk}}{\partial r_{\alpha m}} = i\varepsilon_{ikn}U_{jn}. \tag{18}$$

Using (18) and the definition (17) of $\boldsymbol{L}$, its commutators can now be computed

$$[L_i, U_{jk}] = -\mathrm{i}\varepsilon_{ijn}U_{nk}, \qquad [l_i, L_j] = 0, \qquad [L_i, L_j] = -\mathrm{i}\varepsilon_{ijk}L_k. \tag{19}$$

The commutators among components of $\boldsymbol{l}$ and $\boldsymbol{L}$ are the same as those for a rigid body, with $\boldsymbol{l}$ the angular momentum in the laboratory and $\boldsymbol{L}$ in the body frame. We also note that $[l_i, R_{\alpha j}] = 0 = [L_i, R_{\alpha j}]$ as expected, since in the body-frame rotations act only on the angles $\{\theta_a\}$.

2.3. Internal coordinates

In order to describe the dynamics, we introduce a set of $3N-6$ internal coordinates $\{t_a\}_{a=1}^{3N-6}$ defined locally as independent rotation- and translation-invariant functions of configuration space $t_a = t_a(\{\boldsymbol{r}\})$. Some consequences of the Euclidean invariance of t_a which will be used below are $t_a(\{\boldsymbol{r}\}) = t_a(\{\boldsymbol{R}\})$ and, introducing notation analogous to the first of (2),

$$\frac{\partial t_a}{\partial \boldsymbol{R}_\alpha} \equiv \frac{\partial t_a}{\partial \boldsymbol{r}_\alpha}(\{\boldsymbol{R}\}) = \boldsymbol{U}\frac{\partial t_a}{\partial \boldsymbol{r}_\alpha}(\{\boldsymbol{r}\}), \qquad \frac{\partial^2 t_a}{\partial R_{\alpha j}\partial R_{\alpha j}} \equiv \frac{\partial^2 t_a}{\partial r_{\alpha j}\partial r_{\alpha j}}(\{\boldsymbol{R}\}) = \frac{\partial^2 t_a}{\partial r_{\alpha j}\partial r_{\alpha j}}(\{\boldsymbol{r}\}) \tag{20}$$

which can be derived using (11) and (14). The body frame, specified by the frame conditions (1), fixes relations of the form $\boldsymbol{R}_\alpha = \boldsymbol{R}_\alpha(\{t_a\})$ such that the conditions (1) are satisfied identically when evaluated on $\boldsymbol{R}_\alpha(\{t_a\})$. Thus, the functions $\boldsymbol{R}_\alpha(\{t_a\})$ are a parametric solution to the conditions (1). Through the relation inverse to (11), $\boldsymbol{r}_\alpha = \boldsymbol{U}^\dagger(\{\theta_a\})\boldsymbol{R}_\alpha(\{t_b\}) + \boldsymbol{r}_{\mathrm{cm}}$, the internal coordinates $\{t_b\}$ together with the orientational and translational ones, $\{\theta_a\}$ and $\boldsymbol{r}_{\mathrm{cm}}$ resp., give a set of $3N$ local coordinates in configurations space.

Usually, internal coordinates are given as $3N-6$ independent functions $\{t_a\}$ of as many independent Euclidean invariants chosen out of the set of all dot and triple products among $\{\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta\}_{\alpha,\beta=1}^{N}$. One way of introducing local coordinates in configuration space is to start with a parametric solution $\{\boldsymbol{R}(\{Q\})\}$ to the frame conditions, where $\{Q\} = \{Q_a\}_{a=1}^{3N-6}$ is a set of independent parameters. These parametric relations can be inverted to give $3N-6$ local coordinates $Q_a(\{\boldsymbol{R}\})$ on the body frame. Such 'inverse' is clearly not unique, however, since at each point $\{\boldsymbol{R}\}$ in the body frame the functions

$$Q'_a(\{\boldsymbol{r}\}) = Q_a(\{\boldsymbol{r}\}) + \sum_{b=1}^{3} \lambda_{ab}(\{\boldsymbol{r}\})\mathcal{G}_b(\{\boldsymbol{r}\}) + \boldsymbol{\lambda}_a(\{\boldsymbol{r}\}) \cdot \mathcal{C}(\{\boldsymbol{r}\}),$$

with λ_{ab} and $\boldsymbol{\lambda}_a$ arbitrary coefficient functions, take on the same values as $Q_a(\{\boldsymbol{r}\})$. That ambiguity can be fixed by imposing additional conditions such as $\sum_{\alpha=1}^{3} \partial Q_a/\partial \boldsymbol{R}_\alpha = 0$ and either

$$\sum_{\alpha=1}^{3} \frac{1}{m_\alpha} \frac{\partial \mathcal{G}_a}{\partial \boldsymbol{R}_\alpha} \frac{\partial Q_b}{\partial \boldsymbol{R}_\alpha} = 0, \qquad 1 \leqslant a \leqslant 3, \quad 1 \leqslant b \leqslant 3N-6 \tag{21a}$$

or

$$\sum_{\alpha=1}^{3} \boldsymbol{R}_\alpha \wedge \frac{\partial Q_b}{\partial \boldsymbol{R}_\alpha} = 0, \qquad 1 \leqslant b \leqslant 3N-6. \tag{21b}$$

The first set of conditions fixes the ambiguity because $\det(\mathcal{R}^2(\{\boldsymbol{R}\})) \neq 0$, and the second because $\det(\mathcal{Q}_{ai}(\{\boldsymbol{R}\})) \neq 0$, by assumption. Once the ambiguity has been fixed, to each configuration $\{\boldsymbol{R}\}$ in the body frame there corresponds one and (except at singular points) only one set of parameters $Q_a(\{\boldsymbol{R}\})$. We call those parameters body-frame coordinates. Rotation- and translation-invariant coordinates in configuration space can be obtained locally by extending the body-frame coordinates by rotation and translation, $t_a(\{\boldsymbol{r}\}) = Q_a(\{\boldsymbol{R}(\{\boldsymbol{r}\})\})$, with $\boldsymbol{R}_\alpha(\{\boldsymbol{r}\})$ given by (11). These t_a are invariant under Euclidean motions because $\{\boldsymbol{R}(\{\boldsymbol{r}\})\}$ are.

The body-frame coordinates Q_a, considered as local functions of configuration space $Q_a(\{\boldsymbol{r}\})$ are not, in general, rotation or translation invariant. For instance, when the frame conditions are linear the $Q_a(\{\boldsymbol{r}\})$ can be chosen to be linear functions of $\{\boldsymbol{r}\}$, therefore not rotation invariant, as in the case of normal coordinates in the Eckart frame. A simple example is given in section 6.1. The derivation of the Hamiltonian operator and Hilbert-space inner product in terms of linear body-frame coordinates and their conjugate momenta has been discussed in detail in [1, 7]. In this paper, we confine ourselves to a dynamical description in terms of Euclidean-invariant internal coordinates $\{t_a\}$.

2.4. Hamiltonian operator in configuration space

The kinetic-energy operator in the lab frame is given by the familiar expression

$$\mathcal{K} = -\frac{1}{2} \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial^2}{\partial r_{\alpha j} \partial r_{\alpha j}}. \tag{22}$$

In this equation and in what follows we use units such that $\hbar = 1$ unless otherwise stated. In terms of mass-weighted position vectors $\boldsymbol{r}'_\alpha = \sqrt{m_\alpha}\boldsymbol{r}_\alpha$, $\mathcal{K}$ takes the form of $(-1/2$ times) a Laplacian operator in Cartesian coordinates in $3N$-dimensional space. Given a set $\{q\} = \{q_1, \ldots, q_{3N}\}$ of curvilinear coordinates in configuration space we can write $\mathcal{K}$ as a Laplacian in either one of two commonly used forms. Application of the chain rule to (22) leads to the standard ordering, with all derivative operators to the right of coefficient functions,

$$\begin{aligned} \mathcal{K} &= -\frac{1}{2}\sum_{a,b=1}^{3N} k_{ab}^{-1}\frac{\partial}{\partial q_a}\frac{\partial}{\partial q_b} - \frac{1}{2}\sum_{b=1}^{3N} k_b\frac{\partial}{\partial q_b}, & k_{ab}^{-1} &= \sum_{\alpha=1}^{N}\frac{1}{m_\alpha}\frac{\partial q_a}{\partial r_{\alpha j}}\frac{\partial q_b}{\partial r_{\alpha j}}, \\ k_{ab} &= \sum_{\alpha=1}^{N} m_\alpha \frac{\partial r_{\alpha j}}{\partial q_a}\frac{\partial r_{\alpha j}}{\partial q_b}, & k_b &= \sum_{\alpha=1}^{N}\frac{1}{m_\alpha}\frac{\partial^2 q_b}{\partial r_{\alpha j}\partial r_{\alpha j}}. \end{aligned} \tag{23}$$

This form for the kinetic energy has been widely used in molecular physics and leads to expressions which are usually simpler than in Weyl ordering. An equivalent expression is

$$\mathcal{K} = -\frac{1}{2J}\sum_{a,b=1}^{3N}\frac{\partial}{\partial q_a}k_{ab}^{-1}J\frac{\partial}{\partial q_b}, \qquad J = \det(k_{ab})^{1/2}. \tag{24}$$

Despite their equivalence, (23) and (24) lead to considerably different forms for the kinetic-energy operator for many-body systems, especially after the momenta conjugate to orientational variables are eliminated in favour of the total angular momentum. Those forms, and the relations among them, are discussed below in sections 3 and 5.

3. Hamiltonian operator in standard ordering

The kinetic energy can be expressed in terms of internal coordinates within a given frame convention (1) by taking $\{q\}$ in (23) to be the union of the set $\{t_a\}_{a=1}^{3N-6}$ with the orientational coordinates $\{\theta_b\}_{b=1}^{3}$ and the lab-frame centre-of-mass vector $\boldsymbol{r}_{\rm cm}$. The kinetic-energy term depending on $\boldsymbol{r}_{\rm cm}$ trivially decouples from the other degrees of freedom so we simply ignore it in what follows. We introduce the notation $p_a = -\mathrm{i}\partial/\partial t_a$ $(a = 1,\ldots,3N-6)$, $p_{\theta_b} = -\mathrm{i}\partial/\partial\theta_b$ $(b = 1, 2, 3)$ and $\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_{\theta 1} + \mathcal{K}_{\theta 2}$, where $\mathcal{K}_0$, the vibrational kinetic energy, does not contain p_{θ_a}, $\mathcal{K}_{\theta 1}$ contains the term quadratic in p_{θ_a} and those terms linear in p_{θ_a} whose coefficients involve only first derivatives of θ_a with respect to $\{\boldsymbol{r}\}$ and $\mathcal{K}_{\theta 2}$ gathers the remaining terms linear in p_{θ_a}, with coefficients given by second derivatives of θ_a.

An expression for $\mathcal{K}_0$ can be immediately obtained from (23) as

$$\begin{aligned} \mathcal{K}_0 &= \frac{1}{2}\sum_{a,b=1}^{3N-6} g_{ab}p_a p_b + \frac{1}{2\mathrm{i}}\sum_{b=1}^{3N-6} g_b p_b, \\ g_{ab} &= \sum_{\alpha=1}^{N}\frac{1}{m_\alpha}\frac{\partial t_a}{\partial R_{\alpha j}}\frac{\partial t_b}{\partial R_{\alpha j}}, \qquad g_b = \sum_{\alpha=1}^{N}\frac{1}{m_\alpha}\frac{\partial^2 t_b}{\partial R_{\alpha j}\partial R_{\alpha j}}, \end{aligned} \tag{25}$$

where use was made of (20). Note that g_{ab} and g_b depend only on $\{t_a\}$.

In order to obtain $\mathcal{K}_{\theta 1}$ we need to specify the dependence of the orientational coordinates $\{\theta_a\}$ on the lab-frame coordinates $\{\boldsymbol{r}\}$. Using (12), we have

$$\frac{\partial U_{ik}}{\partial r_{\alpha j}}U_{lk} = \sum_{b=1}^{3}\frac{\partial\theta_b}{\partial r_{\alpha j}}\Lambda_{bm}\varepsilon_{iml}. \tag{26}$$

Equating the rhs of (26) to that of (14), we obtain the dependence of θ_a on lab-frame coordinates in terms of the frame conditions (1)

$$\frac{\partial\theta_a}{\partial r_{\alpha j}} = -\Lambda_{ma}^{-1}\mathcal{F}_{m\alpha i}U_{ij}, \qquad a = 1, 2, 3. \tag{27}$$

This expression is independent of the frame-condition parametrization, as it should be. From (27) and (20), the corresponding blocks in the matrix k^{-1}_{ab} defined in (23) are

$$
\begin{aligned}
k^{-1}_{a\theta_b} &= \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial t_a}{\partial r_{\alpha j}} \frac{\partial \theta_b}{\partial r_{\alpha j}} = -\sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \mathcal{F}_{m\alpha j} \frac{\partial t_a}{\partial R_{\alpha j}} \Lambda^{-1}_{mb} \\
k^{-1}_{\theta_a\theta_b} &= \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial \theta_a}{\partial r_{\alpha j}} \frac{\partial \theta_b}{\partial r_{\alpha j}} = \mathcal{N}^{-1}_{mn} \Lambda^{-1}_{ma} \Lambda^{-1}_{nb}, \\
\mathcal{N}^{-1}_{ij} &= \sum_{c,d=1}^{3} \mathcal{R}^2_{cd} \mathcal{Q}^{-1}_{ic} \mathcal{Q}^{-1}_{jd} = \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \mathcal{F}_{i\alpha k} \mathcal{F}_{j\alpha k}.
\end{aligned}
\tag{28}
$$

The remaining block $k^{-1}_{\theta_a b}$ is obtained from $k^{-1}_{a\theta_b}$ by symmetry. The coefficients (28) fix the form of $\mathcal{K}_{\theta 1}$. Furthermore, we can eliminate p_{θ_a} in favour of the body-frame angular momentum $\boldsymbol{L}$ with the aid of (17). Taking account of the ordering of operators we get

$$
\begin{aligned}
\mathcal{K}_{\theta 1} &= \sum_{a=1}^{3N-6} \mathcal{D}_{ak} p_a L_k + \frac{1}{2} \mathcal{N}^{-1}_{ij} L_i L_j + \mathcal{N}^{-1}_{ij} \sum_{a,b=1}^{3} \Lambda^{-1}_{ia} \frac{\partial \Lambda^{-1}_{jb}}{\partial \theta_a} \frac{\partial}{\partial \theta_b}, \\
\mathcal{D}_{ak} &= \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \mathcal{F}_{k\alpha l} \frac{\partial t_a}{\partial R_{\alpha l}}.
\end{aligned}
\tag{29}
$$

The coefficients of the first two terms in $\mathcal{K}_{\theta 1}$ depend only on $\{t_a\}$. There is still dependence on $\{\theta_b\}$ in the last term, which will cancel against an analogous term in $\mathcal{K}_{\theta 2}$. We turn to the latter next.

The operator $\mathcal{K}_{\theta 2}$ is linear in p_{θ_a}, with coefficients k_{θ_a} given by (23) with q_b substituted by θ_a. The second derivative of θ_a is obtained by differentiating both sides of (27) with respect to $r_{\alpha j}$. Using

$$
\frac{\partial \Lambda^{-1}_{ma}}{\partial r_{\alpha j}} = \sum_{d=1}^{3} \frac{\partial \theta_d}{\partial r_{\alpha j}} \frac{\partial \Lambda^{-1}_{ma}}{\partial \theta_d}
$$

with $\partial \theta_d / \partial r_{\alpha j}$ given by (27), and the expression for $\partial U_{ij} / \partial r_{\alpha j}$ from (14), we get

$$
\begin{aligned}
k_{\theta_a} &= \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial^2 \theta_a}{\partial r_{\alpha j} \partial r_{\alpha j}} = \sum_{d=1}^{3} \mathcal{N}^{-1}_{lm} \Lambda^{-1}_{ld} \frac{\partial \Lambda^{-1}_{ma}}{\partial \theta_d} + \Lambda^{-1}_{la} \mathcal{B}_l \\
\mathcal{B}_l &= -\sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \frac{\partial \mathcal{F}_{l\alpha i}}{\partial r_{\alpha j}} U_{ij} - \varepsilon_{inm} \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \mathcal{F}_{l\alpha i} \mathcal{F}_{m\alpha n}.
\end{aligned}
\tag{30}
$$

Since $\mathcal{F}_{r\alpha i}$ by its definition (10) depends on $\{t_a\}$ only, using the rotation invariance of t_a we can write

$$
\mathcal{B}_l = -\sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \left(\frac{\partial \mathcal{F}_{l\alpha i}}{\partial R_{\alpha i}} + \varepsilon_{inm} \mathcal{F}_{m\alpha n} \mathcal{F}_{l\alpha i} \right), \tag{31a}
$$

with

$$
\frac{\partial \mathcal{F}_{l\alpha i}}{\partial R_{\alpha i}} \equiv \frac{\partial \mathcal{F}_{l\alpha i}}{\partial r_{\alpha i}}(\{\boldsymbol{R}\}) = \sum_{a=1}^{3N-6} \frac{\partial \mathcal{F}_{l\alpha i}}{\partial t_a} \frac{\partial t_a}{\partial R_{\alpha i}}. \tag{31b}
$$

(In appendix A, we rewrite (31b) in a completely different way in terms of $\boldsymbol{U}$.) Therefore,

$$\mathcal{K}_{\theta 2} = -\frac{1}{2}\sum_{a=1}^{3} k_{\theta_a}\frac{\partial}{\partial\theta_a} = -\frac{1}{2}\sum_{a=1}^{3}\mathcal{N}_{lm}^{-1}\Lambda_{ld}^{-1}\frac{\partial\Lambda_{ma}^{-1}}{\partial\theta_d}\frac{\partial}{\partial\theta_a} + \frac{\mathrm{i}}{2}\mathcal{B}_k L_k. \tag{32}$$

Thus, $\mathcal{K}_0$, $\mathcal{K}_{\theta 1}$ and $\mathcal{K}_{\theta 2}$ add up to the total kinetic-energy operator

$$\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_1 + \mathcal{K}_2, \qquad \mathcal{K}_1 = \sum_{a=1}^{3N-6}\mathcal{D}_{ak}p_a L_k + \frac{\mathrm{i}}{2}\mathcal{B}_k L_k, \qquad \mathcal{K}_2 = \frac{1}{2}\mathcal{N}_{ij}^{-1}L_i L_j, \tag{33}$$

where $\mathcal{K}_0$ is given in (25), $\mathcal{D}_{ak}$ and $\mathcal{B}_k$ are given in (29) and (31a) respectively, and $\mathcal{N}_{ij}^{-1}$ in (28). The notation used in (33) is such that $\mathcal{K}_n, n = 0, 1, 2$, depends on the nth power of the body-frame angular momentum. The coefficient functions in $\mathcal{K}$ depend on $\{t_a\}$ only, as expected by rotation invariance. Clearly, $\mathcal{K}$ is invariant under frame-condition reparametrizations and independent of the parametrization of the rotation group used to define the orientational variables $\{\theta_a\}$. The second term in $\mathcal{K}_1$ is purely quantum mechanical, since $\mathcal{B}_k \propto \hbar$ as can easily be checked by dimensional analysis. The origin of this term lies in the operator ordering, in the same way as other orderings (such as e.g., Weyl ordering) give rise to quantum potentials [1]. The form of $\mathcal{B}_k$ is further simplified by the fact that the first term in the parentheses in (31a) vanishes for the most usual choices of frame such as the N-body Eckart frame, and also in the examples in sections 6 and 7 below.

4. Inner product. Matrix and rigid-rotator Hamiltonians

Due to translation invariance the lab-frame wavefunction can be factored as $\Psi_{(0)}(\{\boldsymbol{r}\}) = \psi_{(0)}(\{\boldsymbol{r}_\alpha - \boldsymbol{r}_{\mathrm{cm}}\})\exp(\mathrm{i}\boldsymbol{k}_{\mathrm{cm}}\cdot\boldsymbol{r}_{\mathrm{cm}})$, with the subindex (0) indicating lab frame. Starting with the canonical inner product in the lab frame and changing variables to $\{t_a\}$, $\{\theta_b\}$, $\boldsymbol{r}_{\mathrm{cm}}$, we get

$$\langle\widetilde{\Psi}|\Psi\rangle = \int\prod_{a=1}^{3N-6}\mathrm{d}t_a\prod_{b=1}^{3}\mathrm{d}\theta_b\mathcal{J}\widetilde{\psi}^*_{(0)}(\{\boldsymbol{U}^\dagger\boldsymbol{R}_\alpha\})\psi_{(0)}(\{\boldsymbol{U}^\dagger\boldsymbol{R}_\alpha\}). \tag{34}$$

Here we already integrated over $\boldsymbol{r}_{\mathrm{cm}}$, obtaining a momentum-conservation δ function which we omit. The Jacobian $\mathcal{J}$ can be expressed in terms of internal coordinates by means of the relation

$$\mathcal{J} = \left|\det\left(\frac{\partial q_a}{\partial r_{\alpha j}}\right)^{-1}\right| = \left|\det\left(\frac{\partial q_a}{\partial R_{\alpha j}}\right)^{-1}\right| = |\Lambda|\widetilde{\mathcal{J}}, \tag{35}$$

where $|\Lambda| = \det(\Lambda_{ai})$, with Λ_{ai} defined in (14), and $\partial q_a/\partial R_{\alpha j} = U_{kj}\partial q_a/\partial r_{\alpha k}$ and we used (27). $1/\widetilde{\mathcal{J}}$ in (35) is the absolute value of the determinant of the $3N\times 3N$ matrix

$$\begin{pmatrix} \partial t_1/\partial R_{1X} & \partial t_1/\partial R_{1Y} & \ldots & \partial t_1/\partial R_{NZ} \\ \vdots & \vdots & & \vdots \\ \partial t_{3N-6}/\partial R_{1X} & \partial t_{3N-6}/\partial R_{1Y} & \ldots & \partial t_{3N-6}/\partial R_{NZ} \\ -\mathcal{F}_{11X} & -\mathcal{F}_{11Y} & \ldots & -\mathcal{F}_{1NZ} \\ \vdots & \vdots & & \vdots \\ -\mathcal{F}_{31X} & -\mathcal{F}_{31Y} & \ldots & -\mathcal{F}_{3NZ} \\ \partial r_{\mathrm{cm}X}/\partial r_{1X} & \partial r_{\mathrm{cm}X}/\partial r_{1Y} & \ldots & \partial r_{\mathrm{cm}X}/\partial r_{NZ} \\ \vdots & \vdots & & \vdots \\ \partial r_{\mathrm{cm}Z}/\partial r_{1X} & \partial r_{\mathrm{cm}Z}/\partial r_{1Y} & \ldots & \partial r_{\mathrm{cm}Z}/\partial r_{NZ} \end{pmatrix}. \tag{36}$$

The minus signs in the three middle rows are of course unimportant in (35). Note that the quantities $\mathcal{F}_{i\alpha j}$ are completely determined by the frame conditions and are usually much simpler in form than gradients of Euler angles. The Jacobian J as given in (24), which is proportional to $\mathcal{J}$, can be computed with the derivatives (27) in terms of the matrix g_{ab} from (25). The procedure in this case is closely analogous to the case of linear frame conditions discussed in [1]. We will not dwell on that calculation, whose result and its derivation have been considered in [3]. With our notation, we have

$$J = \prod_{\alpha=1}^{N} m_\alpha^{3/2} \mathcal{J} = M^{3/2} |\Lambda| \frac{|\boldsymbol{M}|^{1/2}}{|g|^{1/2}}, \tag{37}$$

where $M = \sum_\alpha m_\alpha$, $\boldsymbol{M}$ is the body-frame inertia tensor and $|\boldsymbol{M}|$ its determinant and $|g| = \det g_{ab}$ with g_{ab} from (25). Below we denote $\mathrm{d}V_\theta = \prod_{b=1}^{3} \mathrm{d}\theta_b |\Lambda|$ the invariant measure on SO(3), with total volume $V_\theta = 8\pi^2$.

Since $\mathcal{K}$ commutes with $(\boldsymbol{l} - \boldsymbol{l}_{\mathrm{cm}})^2 = \boldsymbol{L}^2$ and $(l_z - l_{\mathrm{cm}\,z})$, we can choose $\psi_{(0)} = \psi_{(0)\ell m}(\{\boldsymbol{r}_\alpha - \boldsymbol{r}_{\mathrm{cm}}\})$ to be an eigenfunction of those operators. The body-frame wavefunctions are then

$$\psi_{\ell m}(\{\boldsymbol{R}\}, \{\theta_a\}) = \psi_{(0)\ell m}(\{\boldsymbol{U}^\dagger(\{\theta_a\})\boldsymbol{R}\}) = \sqrt{2\ell+1} \sum_{s=-\ell}^{\ell} \psi_{(0)\ell s}(\{\boldsymbol{R}\}) D^{\ell *}_{ms}(\{\theta_a\}) \tag{38a}$$

with

$$D^{\ell *}_{m'm}(\{\theta_a\}) = \int \mathrm{d}^2\widehat{\boldsymbol{e}}\, Y^*_{lm'}(\widehat{\boldsymbol{e}}) Y_{lm}(\boldsymbol{U}(\{\theta_a\})\widehat{\boldsymbol{e}}) \tag{38b}$$

where $\widehat{\boldsymbol{e}}$ is a unit vector varying over the unit sphere and $D^{\ell}_{m'm}(\{\theta_a\})$ is the irreducible matrix representing the rotation $\boldsymbol{U}(\{\theta_a\})$. In terms of the wavefunctions (38), we have

$$\langle \widetilde{\Psi}_{\ell m} | \Psi_{\ell m'} \rangle = \delta_{mm'} V_\theta \sum_{n=-\ell}^{\ell} \int \prod_{a=1}^{3N-6} \mathrm{d}t_a \widetilde{\mathcal{J}} \widetilde{\psi}^*_{(0)_{\ell n}}(\{\boldsymbol{R}\}) \psi_{(0)_{\ell n}}(\{\boldsymbol{R}\}). \tag{39}$$

The action of the lab-frame angular momentum on the body-frame wavefunctions (38) is given by

$$l_i \psi_{\ell m}(\{\boldsymbol{R}\}, \{\theta_a\}) = -\sqrt{2\ell+1} \sum_{s,q=-\ell}^{\ell} \psi_{(0)\ell s}(\{\boldsymbol{R}\}) \left(\mathcal{L}^{(\ell)}_i\right)_{qm} D^{\ell *}_{qs}(\{\theta_a\}), \tag{40}$$

where $\mathcal{L}^{(\ell)}_i$ is the standard angular-momentum Hermitian matrix in the representation of irreducible tensors of order ℓ [8]

$$\left(\mathcal{L}^{(\ell)}_i\right)_{km} = \int \mathrm{d}^2\widehat{\boldsymbol{e}}\, Y^*_{lk}(\widehat{\boldsymbol{e}}) \varepsilon_{ipq} e_p \frac{1}{\mathrm{i}} \frac{\partial}{\partial e_q} Y_{lm}(\widehat{\boldsymbol{e}}) = \sum_{a=1}^{3} \left(\lambda^{-1}_{ia}(\{\alpha_a\}) \frac{1}{\mathrm{i}} \frac{\partial}{\partial \alpha_a} \right)_{\alpha_a=0} D^{\ell}_{km}(\{\alpha_a\}). \tag{41}$$

The matrix $\lambda^{-1}_{ia}(\{\alpha_a\})$ in (41) is as defined in (12). Analogously, the body-frame angular-momentum operator acts as

$$L_i \psi_{\ell m}(\{\boldsymbol{R}\}, \{\theta_a\}) = -\sqrt{2\ell+1} \sum_{s,q=-\ell}^{\ell} \psi_{(0)\ell s}(\{\boldsymbol{R}\}) \left(\mathcal{L}^{(\ell)}_i\right)_{sq} D^{\ell *}_{mq}(\{\theta_a\}). \tag{42}$$

Thus, we can represent $\mathcal{K}$ by means of its matrix elements between angular-momentum eigenfunctions in terms of the matrices $\mathcal{L}^{(\ell)}_i$. We need to consider only matrix elements between wavefunctions with different 'radial' quantum numbers, but the same angular dependence, so that

$$\frac{1}{V_\theta}\int \mathrm{d}V_\theta \widetilde{\psi}^*_{lm}(\{\boldsymbol{R}\},\{\theta_a\})\mathcal{K}\psi_{lm}(\{\boldsymbol{R}\},\{\theta_b\}) = \sum_{p,q=-\ell}^{\ell} \widetilde{\psi}^*_{(0)lp}(\{\boldsymbol{R}\})\widehat{\mathcal{K}}_{pq}\psi_{(0)lq}(\{\boldsymbol{R}\})$$
$$\widehat{\mathcal{K}}_{pq} \equiv \mathcal{K}_0\delta_{pq} - \sum_{a=1}^{3N-6}\mathcal{D}_{ak}p_a\big(\mathcal{L}^{(\ell)}_k\big)_{qp} - \frac{\mathrm{i}}{2}\mathcal{B}_k\big(\mathcal{L}^{(\ell)}_k\big)_{qp} + \frac{1}{2}\mathcal{N}^{-1}_{ij}\big(\mathcal{L}^{(\ell)}_i\big)_{qr}\big(\mathcal{L}^{(\ell)}_j\big)_{rp}. \tag{43}$$

In this equation, the operator $\mathcal{K}_0$ and the coefficient functions $\mathcal{D}_{ak}$, $\mathcal{B}_k$ and $\mathcal{N}^{-1}_{ij}$ are as in (33).

Instead of the body-frame wavefunctions (38), we can introduce the alternative basis

$$\phi_\ell(\{\boldsymbol{R}\},\widehat{\boldsymbol{e}}) = \sum_{m=-\ell}^{\ell}\psi_{(0)lm}(\{\boldsymbol{R}\})Y^*_{lm}(\widehat{\boldsymbol{e}}). \tag{44}$$

These wavefunctions, not eigenfunctions of l_z, depend on a unit vector $\widehat{\boldsymbol{e}}$ representing a fictitious rigid rotator of total angular momentum ℓ. In terms of ϕ_ℓ, we have

$$\frac{1}{V_\theta}\int \mathrm{d}V_\theta \widetilde{\psi}^*_{lr}(\{\boldsymbol{R}\},\{\theta_a\})L_p\psi_{ls}(\{\boldsymbol{R}\},\{\theta_b\}) = \delta_{rs}\int \mathrm{d}^2\widehat{\boldsymbol{e}}\widetilde{\phi}^*_\ell(\{\boldsymbol{R}\},\widehat{\boldsymbol{e}})S_p\phi^*_\ell(\{\boldsymbol{R}\},\widehat{\boldsymbol{e}}), \tag{45a}$$

$$S_p = \frac{1}{\mathrm{i}}\varepsilon_{pqr}e_q\frac{\partial}{\partial e_r}. \tag{45b}$$

The factor δ_{rs} on the rhs of (45a) is due to the fact that L_p commutes with l_z (see (19)). Expression (45b) for S_p is not affected by the constraint $\widehat{\boldsymbol{e}}\cdot\widehat{\boldsymbol{e}} = 1$, that is, the derivatives can be computed without taking that constraint into account, as can be easily checked. Alternatively, the operator S_p can be expressed in terms of the spherical angles θ, ϕ of $\widehat{\boldsymbol{e}}$ and derivatives with respect to them. Therefore, from (33) and (45a), we have

$$\frac{1}{V_\theta}\int \mathrm{d}V_\theta \widetilde{\psi}^*_{lm}(\{\boldsymbol{R}\},\{\theta_a\})\mathcal{K}\psi_{lm}(\{\boldsymbol{R}\},\{\theta_b\}) = \int \mathrm{d}^2\widehat{\boldsymbol{e}}\widetilde{\phi}^*_l(\{\boldsymbol{R}\},\widehat{\boldsymbol{e}})\widehat{\mathcal{K}}\phi_l(\{\boldsymbol{R}\},\widehat{\boldsymbol{e}}) \tag{46}$$

with $\widehat{\mathcal{K}}$ having the same form as $\mathcal{K}$ in (33), but with the angular momentum $\boldsymbol{L}$ replaced by $\boldsymbol{S}$ as given by (45b). Actually, the product L_iL_j in (33) is mapped into S_jS_i, but that product is contracted with $\mathcal{N}^{-1}_{ij}$ which is symmetric. This rigid-rotator formalism, based on the wavefunctions (44) and the Hamiltonian (46), is a useful alternative to the matrix formalism based on (38), (41) and (43). It appears naturally in the gauge-invariant approach of [1].

5. Other forms for the Hamiltonian

Other forms for the many-body Hamiltonian in a body-fixed frame, based on expression (24) for the Laplacian, have been given in the literature (see, e.g., [9, 3] and references therein). In this section, we discuss the derivation of the kinetic-energy operator in the form (24) from the point of view of frame conditions and establish relations among these results and those of section 3. Our notation follows that of [3].

In order to express the kinetic energy in the form (24), it is convenient to write the matrix k^{-1}_{ab} in a form different from that used in section 3. Defining

$$h_{ab} = \sum_{\alpha=1}^{N} m_\alpha\frac{\partial R_{\alpha i}}{\partial t_a}\frac{\partial R_{\alpha i}}{\partial t_b} \tag{47}$$

and using the chain rule, we get

$$\frac{\partial t_a}{\partial r_{\alpha i}} = \sum_{b=1}^{3N-6}\sum_{\beta=1}^{N} m_\beta h^{-1}_{ab}\frac{\partial R_{\alpha j}}{\partial t_b}\frac{\partial R_{\alpha j}}{\partial r_{\alpha i}}. \tag{48}$$

Substituting (48) into the definition (25) of g_{ab}, and using the derivatives (15), we get

$$g_{ab} = h^{-1}_{ab} + \sum_{c,d=1}^{3N-6} h^{-1}_{ac} h^{-1}_{bd} a_{ci} a_{dj} \mathcal{N}^{-1}_{ij} \tag{49}$$

with $\mathcal{N}^{-1}_{ij}$ defined in (28) and

$$\boldsymbol{a}_d = \sum_{\beta=1}^{N} m_\beta \boldsymbol{R}_\beta \wedge \frac{\partial \boldsymbol{R}_\beta}{\partial t_a}. \tag{50}$$

Several relations between g_{ab} and h_{ab}, and between $\boldsymbol{M}$ and $\boldsymbol{\mathcal{N}}$, analogous to (49) are summarized in appendix B. Equation (49) fixes the form of k^{-1}_{ab} in (24) for $1 \leqslant a, b \leqslant 3N-6$.

Similarly, we can obtain a compact expression for the off-diagonal blocks of k^{-1}_{ab}. Using (48) and (15) together with the frame conditions $\mathcal{G}_a$ and their translation invariance, we obtain

$$k^{-1}_{a\theta_b} = \sum_{c=1}^{3N-6} h^{-1}_{ac} a_{cj} \mathcal{N}^{-1}_{jk} \Lambda^{-1}_{kb}, \tag{51}$$

to be compared with the corresponding expression in (28). The block $k^{-1}_{\theta_a\theta_b}$ is as given in (28). As in section 3, we omit here for brevity the terms involving the centre-of-mass degrees of freedom, which are dynamically trivial. With these expressions for k^{-1}_{ab} we can compute its determinant $1/J^2$, by factoring the matrix appropriately. We again omit the details [3, 1] and state the result

$$J = M^{3/2} |\Lambda| |\mathcal{N}|^{1/2} |h|^{1/2}, \tag{52}$$

with $|h| = \det(h_{ab})$ and $|\mathcal{N}| = \det(\mathcal{N})$. Comparing (52) with (37) yields $|\boldsymbol{M}|/|g| = |h||\mathcal{N}|$ [3].

The matrix k^{-1}_{ab} and J are all we need in order to obtain the kinetic-energy operator $\mathcal{K}$ from (24). We can, however, eliminate all dependence on orientational degrees of freedom by means of the well-known relations (see [1] and references therein)

$$L_i = \mathrm{i} \sum_{a=1}^{3} \Lambda^{-1}_{ia} \frac{\partial}{\partial \theta_a} = \frac{\mathrm{i}}{|\Lambda|} \sum_{b=1}^{3} \frac{\partial}{\partial \theta_b} \Lambda^{-1}_{ib} |\Lambda|. \tag{53}$$

With this, we finally get

$$\mathcal{K} = \frac{1}{2|\mathcal{N}|^{1/2}|h|^{1/2}} \sum_{a,b=1}^{3N-6} p_a h^{-1}_{ab} |h|^{1/2} |\mathcal{N}|^{1/2} p_b + \frac{1}{2|\mathcal{N}|^{1/2}|h|^{1/2}} \times \left(L_i - \sum_{b,b'=1}^{3N-6} p_b h^{-1}_{bb'} a_{b'i} \right) |\mathcal{N}|^{1/2} |h|^{1/2} \mathcal{N}^{-1}_{ij} \left(L_j - \sum_{d,d'=1}^{3N-6} h^{-1}_{dd'} a_{d'j} p_d \right). \tag{54}$$

Note the ordering of operators in (54). $\mathcal{K}$ can be Weyl ordered most easily after performing a transformation of the form $J\mathcal{K}\,1/J$, leading to a quantum potential term. Weyl ordering is considered in detail in the case of linear frame conditions in [1], and the same procedure can be applied to the case of general frame conditions discussed in this paper. The expression for the quantum potential, however, seems to us to be too complicated to be useful in practice so we omit the results. Other orderings are of course possible, although with similar caveats about the associated quantum potentials. That is an advantage, from our point of view, of the standard ordering given in section 3.

We can rewrite $\mathcal{K}$ as given by (54) in terms of g_{ab} and $\boldsymbol{M}^{-1}$, instead of h^{-1}_{ab} and $\boldsymbol{\mathcal{N}}^{-1}$, by using relations (49), (37) and (52) and (B.4) to find

$$\mathcal{K} = \frac{1}{2} M^{-1}_{ij} L_i L_j + \frac{1}{2} \frac{|g|^{1/2}}{|M|^{1/2}} \sum_{a,b=1}^{3N-6} (p_a - A_{ai} L_i) \frac{|M|^{1/2}}{|g|^{1/2}} g_{ab} (p_b - A_{bj} L_j). \tag{55}$$

Here, we defined [3]

$$\boldsymbol{A}_a = \boldsymbol{M}^{-1} \boldsymbol{a}_a, \qquad 1 \leqslant a \leqslant 3N - 6. \tag{56}$$

In the form (55) all dependence of $\mathcal{K}$ on frame conditions is implicit in the relations $\boldsymbol{R}_\alpha = \boldsymbol{R}_\alpha(\{t_a\})$, which enters $\mathcal{K}$ through g_{ab} and $\boldsymbol{A}_a$ and also through $\boldsymbol{M}^{-1}$ when expressed in terms of internal coordinates. It is interesting to point out that for the most commonly used frames the 3×3 matrix $\mathcal{Q}_{ai}$ defined in (2) is much simpler to invert than $\boldsymbol{M}$, and that is the only matrix inversion needed to obtain $\mathcal{K}$ as given in (33).

Comparing the expressions (54) and (55) with (33), we can obtain relations among their coefficients. The equivalence of the purely vibrational terms in (33) and (54) is immediate once we take into account (B.6) and the equivalence between the two standard forms for the Laplacian (23) and (24). Similarly, the terms quadratic in $\boldsymbol{L}$ in (33) and (54) are obviously equal and equivalent to that in (55) by (B.4). Note that $\mathcal{N}^{-1}_{ij}$, which is usually defined [3] as in (B.2) or (B.4), can be compactly expressed in terms of frame conditions by our definition (28).

Equating the terms linear in $\boldsymbol{L}$ in (33), (54) and (55), we get the relations

$$\mathcal{D}_{dq} = -M^{-1}_{qr} \sum_{d'=1}^{3N-6} g_{dd'} a_{d'r} = -\mathcal{N}^{-1}_{qr} \sum_{d'=1}^{3N-6} h^{-1}_{dd'} a_{d'r} \tag{57a}$$

$$\frac{\mathrm{i}}{2} \mathcal{B}_q = \frac{1}{2} \frac{|g|^{1/2}}{|M|^{1/2}} \sum_{d=1}^{3N-6} \left(p_d \frac{|M|^{1/2}}{|g|^{1/2}} \mathcal{D}_{dq} \right) = \frac{1}{2|\mathcal{N}|^{1/2}|h|^{1/2}} \sum_{d=1}^{3N-6} (p_d |\mathcal{N}|^{1/2} |h|^{1/2} \mathcal{D}_{dq}) \tag{57b}$$

with $\mathcal{D}_{dq}$ and $\mathcal{B}_q$ defined in (29) and (30), respectively. These relations can be proved directly, providing a consistency check on our results. An important consequence of (57a) is that it allows us to write $\boldsymbol{A}_a$, at least locally, in terms of frame conditions,

$$A_{bi} = -\sum_{c=1}^{3N-6} g^{-1}_{bc} \mathcal{D}_{ci} \qquad \text{or} \qquad a_{bi} = -\mathcal{N}_{ik} \sum_{c=1}^{3N-6} h_{bc} \mathcal{D}_{ci}, \qquad a = 1, \ldots, 3N - 6, \tag{58}$$

with $\mathcal{D}_{ci}$ given by (29). Note that these relations cannot be obtained from (49) or the equalities in appendix B, which always involve $\boldsymbol{a}_a$ or $\boldsymbol{A}_a$ quadratically. Through (58) we can write any expression involving the gauge fields $\boldsymbol{A}_a$ [3] in terms of internal coordinates and frame conditions.

6. The case $N = 3$

We consider here the case $N = 3$ both as an example and a verification of the foregoing, obtaining the Hamiltonian in two different body frames, one defined by linear conditions and the other by quadratic ones. We choose internal coordinates $t_1 \equiv \rho_1, t_2 \equiv \rho_2$ and $t_3 \equiv \theta$ which are standard in molecular physics,

$$\rho_1 = |\boldsymbol{r}_1 - \boldsymbol{r}_3|, \qquad \rho_2 = |\boldsymbol{r}_2 - \boldsymbol{r}_3|, \qquad \cos\theta = \frac{1}{\rho_1 \rho_2} (\boldsymbol{r}_1 - \boldsymbol{r}_3) \cdot (\boldsymbol{r}_2 - \boldsymbol{r}_3), \tag{59}$$

with conjugate momenta denoted by $p_a, a = 1, 2, 3$. We also define the reduced masses $1/m_{13} = 1/m_1 + 1/m_3$ and analogously m_{23}.

6.1. Linear frame conditions

A linear body frame with origin at the centre of mass can be defined by choosing the Y axis orthogonal to the plane of the system, $\widehat{\boldsymbol{Y}} \propto (\boldsymbol{r}_2 - \boldsymbol{r}_3) \wedge (\boldsymbol{r}_1 - \boldsymbol{r}_3)$, the Z axis along $\boldsymbol{r}_1 - \boldsymbol{r}_3$, and $\widehat{\boldsymbol{X}} = \widehat{\boldsymbol{Y}} \wedge \widehat{\boldsymbol{Z}}$. The frame conditions are then

$$\boldsymbol{\mathcal{C}} \equiv \sum_{\alpha=1}^{N} \frac{m_\alpha}{M} \boldsymbol{r}_\alpha = 0, \qquad \mathcal{G}_1 \equiv r_{1x} - r_{3x} = 0, \quad \mathcal{G}_2 \equiv r_{1y} - \mathcal{C}_y = 0, \quad \mathcal{G}_3 \equiv r_{2y} - \mathcal{C}_y = 0. \tag{60}$$

Note that $\mathcal{G}_a$ are written so they are explicitly translation invariant. From (25) and (59), we get

$$\begin{aligned}
g_{11} &= \frac{1}{m_{13}}, & g_{12} &= \frac{\cos\theta}{m_3}, & g_{13} &= -\frac{\sin\theta}{m_3 \rho_2} \\
g_{22} &= \frac{1}{m_{23}}, & g_{23} &= -\frac{\sin\theta}{m_3 \rho_1}, & g_{33} &= \frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} - \frac{2\cos\theta}{m_3\rho_1\rho_2} \\
g_1 &= \frac{2}{m_{13}\rho_1}, & g_2 &= \frac{2}{m_{23}\rho_2}, & g_3 &= \cot\theta \left(\frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} \right) - \frac{2}{m_3\rho_1\rho_2 \sin\theta},
\end{aligned} \tag{61}$$

and the Jacobian entering the inner product (39) is found to be $\widetilde{\mathcal{J}} = \rho_1^2 \rho_2^2 \sin\theta$. The coefficients (61) fix the form of $\mathcal{K}_0$ as given in (23). With the frame conditions (60) and the internal coordinates (59), from (10) we obtain

$$\begin{aligned}
\boldsymbol{\mathcal{F}}_{11} &= -\frac{1}{\rho_1}\widehat{\boldsymbol{Y}}, & \boldsymbol{\mathcal{F}}_{12} &= 0, & \boldsymbol{\mathcal{F}}_{13} &= \frac{1}{\rho_1}\widehat{\boldsymbol{Y}}, \\
\boldsymbol{\mathcal{F}}_{21} &= \frac{1}{\rho_1}\widehat{\boldsymbol{X}}, & \boldsymbol{\mathcal{F}}_{22} &= 0, & \boldsymbol{\mathcal{F}}_{23} &= -\frac{1}{\rho_1}\widehat{\boldsymbol{X}}, \\
\boldsymbol{\mathcal{F}}_{31} &= -\frac{\cot\theta}{\rho_1}\widehat{\boldsymbol{Y}}, & \boldsymbol{\mathcal{F}}_{32} &= \frac{1}{\rho_2 \sin\theta}\widehat{\boldsymbol{Y}}, & \boldsymbol{\mathcal{F}}_{33} &= -\frac{\rho_1 - \rho_2\cos\theta}{\rho_1\rho_2\sin\theta}\widehat{\boldsymbol{Y}},
\end{aligned} \tag{62}$$

with the notation $\boldsymbol{\mathcal{F}}_{a\alpha} \equiv (\mathcal{F}_{a\alpha 1}, \mathcal{F}_{a\alpha 2}, \mathcal{F}_{a\alpha 3})$. We omit the details of the calculation of $\mathcal{N}_{ij}^{-1}$, $\mathcal{D}_{ak}$ and $\mathcal{B}_l$ (see (28), (29) and (30), respectively). Rather, we give the result for $\mathcal{K}$, from which those coefficients can be read off. The kinetic-energy operator for this system is given by (33) as $\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_1 + \mathcal{K}_2$, with $\mathcal{K}_0$ resulting from (61) and with

$$\begin{aligned}
\mathcal{K}_1 &= -\frac{\sin\theta}{m_3\rho_1} p_2 L_Y + \left(\frac{1}{m_{13}\rho_1^2} - \frac{\cos\theta}{m_3\rho_1\rho_2} \right) p_3 L_Y + \frac{\mathrm{i}}{2\sin\theta} \left(\frac{1}{m_3\rho_1\rho_2} - \frac{\cos\theta}{m_{13}\rho_1^2} \right) L_Y \\
\mathcal{K}_2 &= \frac{1}{2m_{13}\rho_1^2} L_X^2 + \frac{1}{2} \left(\frac{1}{m_3\rho_1\rho_2\sin\theta} - \frac{1}{m_{13}\rho_1^2 \tan\theta} \right) \{L_X, L_Z\} + \frac{1}{2m_{13}\rho_1^2} L_Y^2 \\
&\quad + \frac{1}{2} \left(\left(\frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} \right) \frac{1}{\sin^2\theta} - \frac{1}{m_{13}\rho_1^2} - \frac{2\cos\theta}{m_3\rho_1\rho_2\sin^2\theta} \right) L_Z^2 .
\end{aligned} \tag{63}$$

These results agree exactly with those of [2] once we take into account that the kinetic operator defined there is $\rho_1\rho_2\mathcal{K}1/(\rho_1\rho_2)$ in our notation.

In this example, since the frame conditions are linear, we can choose a set of linear body-frame coordinates satisfying (21*a*). We set $Q_1 = R_{1Z} - R_{3Z}$, $Q_2 = R_{2Z} - R_{3Z}$, $Q_3 = R_{2X} - R_{3X}$. These coordinates Q_a can be extended to all of configuration space by linearity, yielding a set of non-rotation-invariant coordinates $Q_1(\{\boldsymbol{r}\}) = r_{1z} - r_{3z}$, etc. In order to extend them to rotation-invariant internal coordinates, we express them in terms of scalar products of body-frame position vectors. Such procedure leads to a set of coordinates equivalent to (59), which with the same notation are written as ρ_1, $\rho_2 \cos\theta$, $\rho_2 \sin\theta$.

6.2. *Quadratic frame conditions*

Another frame for the three-body system used in the molecular-physics literature is defined as a modification of the previous one, choosing the Z axis to bisect the angle θ between $\boldsymbol{r}_1 - \boldsymbol{r}_3$ and $\boldsymbol{r}_2 - \boldsymbol{r}_3$. The frame conditions are as in (60), except that $\mathcal{G}_1$ now takes the form

$$\mathcal{G}_1(\{\boldsymbol{r}\}) \equiv (r_{1x} - r_{3x})(r_{2z} - r_{3z}) + (r_{1z} - r_{3z})(r_{2x} - r_{3x}) = 0. \tag{64}$$

This frame differs from the body-frame of section 6.1 by a time-dependent rotation in an angle $\theta/2$ around the $\widehat{\boldsymbol{Y}}$ axis. Since internal coordinates are rotation invariant, g_{ab} and g_b, and therefore also $\mathcal{K}_0$, are as in (61). The Jacobian $\widetilde{\mathcal{J}}$ also remains the same as above.

The modified frame conditions (64) lead to

$$\begin{aligned}
\mathcal{F}_{11} &= -\frac{1}{2\rho_1 \cos\frac{\theta}{2}}\widehat{\boldsymbol{Y}}, & \mathcal{F}_{21} &= \frac{1}{2\rho_1}\cos\frac{\theta}{2}\widehat{\boldsymbol{X}} - \frac{1}{2\rho_1}\sin\frac{\theta}{2}\widehat{\boldsymbol{Z}}, & \mathcal{F}_{31} &= \frac{1}{2\rho_1 \sin\frac{\theta}{2}}\widehat{\boldsymbol{Y}} \\
\mathcal{F}_{12} &= -\frac{1}{2\rho_2 \cos\frac{\theta}{2}}\widehat{\boldsymbol{Y}}, & \mathcal{F}_{22} &= \frac{1}{2\rho_2}\cos\frac{\theta}{2}\widehat{\boldsymbol{X}} + \frac{1}{2\rho_2}\sin\frac{\theta}{2}\widehat{\boldsymbol{Z}}, & \mathcal{F}_{32} &= -\frac{1}{2\rho_2 \sin\frac{\theta}{2}}\widehat{\boldsymbol{Y}} \\
\mathcal{F}_{13} &= -\frac{\rho_1 + \rho_2}{2\rho_1\rho_2 \cos\frac{\theta}{2}}\widehat{\boldsymbol{Y}}, & \mathcal{F}_{23} &= -\frac{1}{2\rho_+}\cos\frac{\theta}{2}\widehat{\boldsymbol{X}} - \frac{1}{2\rho_-}\sin\frac{\theta}{2}\widehat{\boldsymbol{Z}}, & \mathcal{F}_{33} &= \frac{\rho_1 - \rho_2}{2\rho_1\rho_2 \sin\frac{\theta}{2}}\widehat{\boldsymbol{Y}},
\end{aligned} \tag{65}$$

where the notation is as in (62) and $1/\rho_\pm = \pm 1/\rho_1 + 1/\rho_2$. The kinetic energy is then $\mathcal{K} = \mathcal{K}_0 + \mathcal{K}_1 + \mathcal{K}_2$, with $\mathcal{K}_0$ given by (61) and with

$$\begin{aligned}
\mathcal{K}_1 &= \frac{\sin\theta}{2m_3}\left(\frac{1}{\rho_2}p_1 - \frac{1}{\rho_1}p_2\right)L_Y + \frac{1}{2}\left(\frac{1}{m_{13}\rho_1^2} - \frac{1}{m_{23}\rho_2^2}\right)\left(\frac{\cot\theta}{2\mathrm{i}} + p_3\right)L_Y \\
\mathcal{K}_2 &= \frac{1}{8\cos^2\frac{\theta}{2}}\left(\frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} + \frac{2}{m_3\rho_1\rho_2}\right)L_X^2 + \frac{1}{8}\left(\frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} + \frac{2\cos\theta}{m_3\rho_1\rho_2}\right)L_Y^2 \\
&\quad + \frac{1}{8\sin^2\frac{\theta}{2}}\left(\frac{1}{m_{13}\rho_1^2} + \frac{1}{m_{23}\rho_2^2} - \frac{2}{m_3\rho_1\rho_2}\right)L_Z^2 \\
&\quad + \frac{1}{4\sin\theta}\left(\frac{1}{m_{23}\rho_2^2} - \frac{1}{m_{13}\rho_1^2}\right)\{L_X, L_Z\}.
\end{aligned} \tag{66}$$

This expression for $\mathcal{K}$ agrees with the result given in [10], as corrected in [2], taking into account that their operator corresponds to $\rho_1\rho_2\mathcal{K}1/(\rho_1\rho_2)$ in our notation.

7. The case $N = 4$

As a further example we consider in this section a four-particle system. Our choices of frame and internal coordinates below are appropriate for a system with the topology of the formaldehyde molecule, though the results are also applicable to other systems for which those choices are not singular at the equilibrium configuration. The vibrational Hamiltonian for the formaldehyde molecule has been given, in the Born–Oppenheimer approximation, e.g., in [2] (see section 4.3 and appendix A). Other explicit results for four-body systems are given in [4] and references therein. Here we use a set of internal coordinates which, combined with the general results given above, greatly simplify calculations and lead to moderately simple results for the total Hamiltonian, including rotation and vibration–rotation terms. One drawback of our coordinate choice, however, is that it also results in a complicated expression for the inner product. This section is not meant as an exhaustive kinematic analysis of the four-body problem, but rather as an example of the results given above.

In this section, we label the particles with capital letters, $\alpha = A, \ldots, D$. In the case of the formaldehyde molecule D would refer to the carbon atom, A to the oxygen, and B and C to the hydrogen atoms. We choose a frame with origin at the centre of mass whose Z axis lies along $\boldsymbol{R}_{AD} \equiv \boldsymbol{R}_A - \boldsymbol{R}_D$ and the Y axis is defined by the condition that $\boldsymbol{R}_{CD}$ lies on the YZ coordinate plane. This choice of frame is singular when $\boldsymbol{R}_{CD}$ is parallel to $\boldsymbol{R}_{AD}$. The rotational frame conditions are

$$\mathcal{G}_1 \equiv r_{ADx} = 0, \qquad \mathcal{G}_2 \equiv r_{ADy} = 0, \qquad \mathcal{G}_3 \equiv r_{CDx} = 0. \tag{67}$$

The frame is completely determined by (67) together with the auxiliary conditions $R_{ADZ} > 0$ and $R_{CDY} > 0$ defining the direction of the axes. From (67) and (2), we get

$$\mathcal{R}^2_{ab} = \begin{pmatrix} \mu_{AD}^{-1} & 0 & \mu_D^{-1} \\ 0 & \mu_{AD}^{-1} & 0 \\ \mu_D^{-1} & 0 & \mu_{CD}^{-1} \end{pmatrix}, \qquad \mathcal{Q}_{ai} = \begin{pmatrix} 0 & R_{ADZ} & 0 \\ -R_{ADZ} & 0 & 0 \\ 0 & R_{CDZ} & -R_{CDY} \end{pmatrix}, \tag{68}$$

with $1/\mu_{AD} = 1/\mu_A + 1/\mu_D$ and similarly for the other reduced masses. The frame conditions are therefore singular when $\det(\mathcal{Q}) = -R^2_{ADZ} R_{CDY} = 0$, i.e., when $\boldsymbol{R}_{AD}$ and $\boldsymbol{R}_{CD}$ are parallel or either one vanishes. With the matrix $\mathcal{Q}$ in (68) from (10) we obtain

$$\begin{gathered} \mathcal{F}_{1A2} = -\frac{1}{R_{ADZ}}, \qquad \mathcal{F}_{1D2} = \frac{1}{R_{ADZ}}, \qquad \mathcal{F}_{2A1} = \frac{1}{R_{ADZ}}, \qquad \mathcal{F}_{2D1} = -\frac{1}{R_{ADZ}}, \\ \mathcal{F}_{3A1} = \frac{R_{CDZ}}{R_{ADZ} R_{CDY}}, \qquad \mathcal{F}_{3C1} = -\frac{1}{R_{CDY}}, \qquad \mathcal{F}_{3D1} = \frac{R_{ADZ} - R_{CDZ}}{R_{ADZ} R_{CDY}}, \end{gathered} \tag{69}$$

all other $\mathcal{F}_{i\alpha j}$ vanishing. In turn this leads to

$$\begin{gathered} \mathcal{N}^{-1}_{11} = \frac{1}{\mu_{AD} R^2_{ADZ}}, \qquad \mathcal{N}^{-1}_{23} = \frac{R_{CDZ}}{\mu_{AD} R^2_{ADZ} R_{CDY}} - \frac{1}{\mu_D R_{ADZ} R_{CDY}} = \mathcal{N}^{-1}_{32}, \\ \mathcal{N}^{-1}_{22} = \frac{1}{\mu_{AD} R^2_{ADZ}}, \qquad \mathcal{N}^{-1}_{33} = \frac{R^2_{CDZ}}{\mu_{AD} R^2_{ADZ} R^2_{CDY}} + \frac{1}{\mu_{CD} R^2_{CDY}} - 2\frac{R_{CDZ}}{\mu_D R_{ADZ} R^2_{CDY}}, \end{gathered} \tag{70}$$

and the remaining components vanishing. With $\mathcal{N}^{-1}$ from (70), the rotational kinetic energy $\mathcal{K}_2$ (33) is completely determined.

Our choice of internal coordinates is motivated by calculational simplicity. We introduce translation- and rotation-invariant internal coordinates depending polynomially on the position vectors

$$\begin{gathered} t_1 = \boldsymbol{r}^2_{AD}, \qquad t_2 = \boldsymbol{r}^2_{CD}, \qquad t_3 = \boldsymbol{r}_{CD} \cdot \boldsymbol{r}_{AD}, \\ t_4 = \boldsymbol{r}_{BD} \cdot \boldsymbol{r}_{AD}, \qquad t_5 = \boldsymbol{r}_{BD} \cdot \boldsymbol{r}_{CD}, \qquad t_6 = \boldsymbol{r}_{BD} \cdot \boldsymbol{r}_{CD} \wedge \boldsymbol{r}_{AD}. \end{gathered} \tag{71}$$

The ranges of variation for the first three coordinates are $t_{1,2} > 0$, $|t_3| < t_1^{1/2} t_2^{1/2}$, whereas the last three can take any real value. In the frame defined by conditions (67) and the associated supplementary conditions, relative particle positions are given by

$$\begin{gathered} \boldsymbol{R}_{AD} = \sqrt{t_1}\,\widehat{\boldsymbol{Z}}, \qquad \boldsymbol{R}_{CD} = \frac{\sqrt{t_1 t_2 - t_3^2}}{\sqrt{t_1}} \widehat{\boldsymbol{Y}} + \frac{t_3}{\sqrt{t_1}} \widehat{\boldsymbol{Z}}, \\ \boldsymbol{R}_{BD} = \frac{t_6}{\sqrt{t_1 t_2 - t_3^2}} \widehat{\boldsymbol{X}} + \frac{t_1 t_5 - t_3 t_4}{\sqrt{t_1}\sqrt{t_1 t_2 - t_3^2}} \widehat{\boldsymbol{Y}} + \frac{t_4}{\sqrt{t_1}} \widehat{\boldsymbol{Z}}. \end{gathered} \tag{72}$$

Particle position vectors $\boldsymbol{R}_{A,B,C,D}$ can of course be found from (72) together with the centre-of-mass condition.

The vibrational kinetic energy $\mathcal{K}_0$ in standard order is determined by the coefficients g_{ab} and g_b in (25). Due to the polynomial nature of t_a, the results for g_b are remarkably simple

$$g_1 = \frac{6}{\mu_{AD}}, \qquad g_2 = \frac{6}{\mu_{CD}}, \qquad g_3 = g_4 = g_5 = \frac{6}{\mu_D}, \qquad g_6 = 0. \tag{73}$$

The expressions for g_{ab} are unavoidably more complicated, even though their dependence on $\boldsymbol{R}_\alpha$ is polynomial. Expressing g_{ab} in terms of internal coordinates t_a we get, taking into account its symmetry,

$$\begin{aligned}
&g_{11} = \frac{4}{\mu_{AD}} t_1, \qquad g_{12} = \frac{4}{\mu_D} t_3, \qquad g_{13} = \frac{2}{\mu_{AD}} t_3 + \frac{2}{\mu_D} t_1, \qquad g_{14} = \frac{2}{\mu_{AD}} t_4 + \frac{2}{\mu_D} t_1,\\
&g_{15} = \frac{2}{\mu_D}(t_3 + t_4), \qquad g_{16} = \frac{2}{\mu_A} t_6, \qquad g_{22} = \frac{4}{\mu_{CD}} t_2, \qquad g_{23} = \frac{2}{\mu_{CD}} t_3 + \frac{2}{\mu_D} t_2,\\
&g_{24} = \frac{2}{\mu_D}(t_3 + t_5), \qquad g_{25} = \frac{2}{\mu_{CD}} t_5 + \frac{2}{\mu_D} t_2, \qquad g_{26} = \frac{2}{\mu_C} t_6,\\
&g_{33} = \frac{1}{\mu_{AD}} t_2 + \frac{1}{\mu_{CD}} t_1 + \frac{2}{\mu_D} t_3, \qquad g_{34} = \frac{1}{\mu_{AD}} t_5 + \frac{1}{\mu_D}(t_1 + t_3 + t_4),\\
&g_{35} = \frac{1}{\mu_{CD}} t_4 + \frac{1}{\mu_D}(t_2 + t_3 + t_5), \qquad g_{36} = 0, \qquad g_{44} = \frac{1}{\mu_{AD}} \boldsymbol{R}_{BD}^2 + \frac{1}{\mu_{BD}} t_1 + \frac{2}{\mu_D} t_4,\\
&g_{45} = \frac{1}{\mu_{BD}} t_3 + \frac{1}{\mu_D}\left(\boldsymbol{R}_{BD}^2 + t_4 + t_5\right), \qquad g_{46} = 0, \qquad g_{55} = \frac{1}{\mu_{BD}} t_2 + \frac{1}{\mu_{CD}} \boldsymbol{R}_{BD}^2 + \frac{2}{\mu_D} t_5,\\
&g_{56} = 0, \qquad g_{66} = \frac{1}{\mu_A}\left(\boldsymbol{R}_{BD}^2 t_2 - t_5^2\right) + \frac{1}{\mu_B}\left(t_2 t_1 - t_3^2\right) + \frac{1}{\mu_C}\left(\boldsymbol{R}_{BD}^2 t_1 - t_4^2\right).
\end{aligned} \tag{74}$$

Here we have left $\boldsymbol{R}_{BD}^2$ indicated for convenience, its expression in terms of internal coordinates is given by (72).

The vibrational–rotational coupling term $\mathcal{K}_1$ is given in (33) in terms of the coefficients $\mathcal{D}_{ak}$ and $\mathcal{B}_k$ (see (29) and (31*a*)). The expression for $\mathcal{D}_{ak}$ can be written most compactly in terms of position vectors. Its non-vanishing components are

$$\begin{aligned}
&\mathcal{D}_{21} = -\frac{2}{\mu_D} \frac{R_{CDY}}{R_{ADZ}}, \qquad \mathcal{D}_{31} = -\frac{1}{\mu_{AD}} R_{CDY}, \qquad \mathcal{D}_{41} = -\frac{1}{\mu_{AD}} \frac{R_{BDY}}{R_{ADZ}},\\
&\mathcal{D}_{42} = \frac{1}{\mu_{AD}} \frac{R_{BDX}}{R_{ADZ}}, \qquad \mathcal{D}_{43} = \frac{1}{\mu_{AD}} \frac{R_{BDX} R_{CDZ}}{R_{ADZ} R_{CDY}} - \frac{1}{\mu_D} \frac{R_{BDX}}{R_{CDY}},\\
&\mathcal{D}_{51} = -\frac{1}{\mu_D} \frac{R_{CDY} + R_{BDY}}{R_{ADZ}}, \qquad \mathcal{D}_{52} = \frac{1}{\mu_D} \frac{R_{BDX}}{R_{ADZ}},\\
&\mathcal{D}_{53} = \frac{1}{\mu_D} \frac{R_{BDX} R_{CDZ}}{R_{ADZ} R_{CDY}} - \frac{1}{\mu_{CD}} \frac{R_{BDX}}{R_{CDY}}, \qquad \mathcal{D}_{61} = \frac{1}{\mu_A} \frac{R_{BDX} R_{CDZ}}{R_{ADZ}},\\
&\mathcal{D}_{62} = \frac{1}{\mu_A R_{ADZ}} (\boldsymbol{R}_{BD} \wedge \boldsymbol{R}_{CD})_X, \qquad \mathcal{D}_{63} = \frac{R_{CDZ}}{R_{CDY}} \mathcal{D}_{62} + \frac{1}{\mu_C} \frac{R_{ADZ} R_{BDY}}{R_{CDY}}.
\end{aligned} \tag{75}$$

The coefficients $\mathcal{B}_k$, on the other hand, acquire a very simple form because the first term in (31*a*) vanishes, leaving only the contribution from the second term,

$$\mathcal{B}_1 = \frac{1}{R_{ADZ}^2 R_{CDY}} \left(-\frac{1}{\mu_{AD}} R_{CDZ} + \frac{1}{\mu_D} R_{ADZ} \right) = \frac{1}{\sqrt{t_1 t_2 - t_3^2}} \left(-\frac{1}{\mu_{AD}} \frac{t_3}{t_1} + \frac{1}{\mu_D} \right), \qquad (76)$$

and $\mathcal{B}_2 = 0 = \mathcal{B}_3$.

Finally, the Jacobian $\widetilde{\mathcal{J}}$ in the inner product (39) can be computed to give

$$\frac{1}{\widetilde{\mathcal{J}}} = 4(\boldsymbol{R}_{AD} \wedge \boldsymbol{R}_{CD})^2 + 4\frac{\mu_B}{M}(\boldsymbol{R}_{AD} \wedge \boldsymbol{R}_{CD}) \cdot (\boldsymbol{R}_{AD} \wedge \boldsymbol{R}_{BD} + \boldsymbol{R}_{BD} \wedge \boldsymbol{R}_{CD} + \boldsymbol{R}_{CD} \wedge \boldsymbol{R}_{AD}). \qquad (77)$$

$\widetilde{\mathcal{J}}$ is singular at $\boldsymbol{R}_{AD} \wedge \boldsymbol{R}_{CD} = 0$, as expected from our choice of frame and internal coordinates. This singularity, together with the somewhat involved integration limits resulting from (71), makes the expression for the inner product computationally cumbersome. For systems whose equilibrium configuration is far from the singularity, however, the contribution from that region should be strongly suppressed by the wavefunctions in (39).

8. Final remarks

In this paper, we derived the body-frame Hamiltonian for a system of N particles in terms of frame conditions and internal coordinates. Obtaining the Hamiltonian in terms of frame conditions instead of Euler angles and the inertia tensor and their derivatives leads arguably to computational simplifications. All frames used in applications are defined by polynomial conditions, usually of first or second degree. The coefficients $\mathcal{N}$, $\mathcal{D}$ and $\mathcal{B}$ in the kinetic-energy operator (33), given by algebraic expressions in terms of first derivatives of those frame conditions, can be efficiently evaluated with symbolic computer algorithms or, depending on N and the internal coordinates t_a being used, even by hand. In particular, there is no need to invert the inertia tensor, or to compute its determinant or that of the vibrational kinetic tensor g_{ab} (25). Similarly, neither those determinants nor derivatives of Euler angles are required for the computation of the volume element in the quantum inner product as given by (35) and (36), and the derivatives of internal coordinates involved in (36) are evaluated only at the frame manifold. These computational simplifications become more relevant for larger values of N. Furthermore, given a set of internal coordinates $\{t_a\}$, it is straightforward to compute the Hamiltonian in different frames by changing the conditions $\mathcal{G}_a$, as illustrated in the examples of section 6.

The Hamiltonian is given in standard order in (33) and in the alternate forms (54) and (55). Comparing those three forms leads to some useful relations among their coefficients, in particular the expression (50) for the gauge field $\boldsymbol{A}_a$ in terms of frame conditions. One advantage of the standard-order form (33) is that it is known to be equivalent to a path-integral formulation in phase space with post-point discretization, whereas for the undefined orderings of (54) and (55) the path-integral equivalents are in principle not known and have to be constructed. In section 4, in connection with the quantum inner product in the body-frame, we discuss two equivalent representations for the angular-momentum operators and the kinetic energy. Namely, as irreducible matrices acting on ℓ-component wavefunctions, (43), and as differential operators acting on rigid-rotator wavefunctions, (46). The rigid-rotator representation, which can be a convenient alternative to the matricial one for some computations, appears naturally in the gauge-invariant approach of [1].

In section 2, we discuss frame conditions from the point of view of their admissibility and reparametrizations. Not discussed in this paper is the problem of frame singularities. From (3), we see that the singular points on the frame manifold are determined by the equations $\det(\mathcal{Q}_{ai}(\{\boldsymbol{R}\})) = 0 = \mathcal{G}_a(\{\boldsymbol{R}\})$, which are polynomial in $\boldsymbol{R}$ for polynomial $\mathcal{G}_a$. Such algebraic formulation of the problem might be useful in the study of frame singularities for larger values of N.

Applications of the approach presented here to the analysis of systems with $N > 3$ are currently in progress and will be discussed elsewhere.

Appendix A. Remarks on the body-frame transformation

Equation (14) for $\partial \boldsymbol{U}/\partial \boldsymbol{r}_\alpha$ gives a relation between the dependence of $\boldsymbol{U}(\{\theta_b\})$ on $\boldsymbol{r}_\alpha$ and the frame conditions $\mathcal{G}_a$. Note that on the rhs of (14) the dependences on $\{t_a\}$ and $\{\theta_b\}$ are completely factorized, with $\mathcal{F}_{m\alpha n}$ depending only on $\{t_a\}$. We can rewrite (14) as

$$\mathcal{F}_{i\alpha j} = \frac{1}{2}\varepsilon_{ikl}\frac{\partial U_{km}}{\partial r_{\alpha n}} U_{lm} U_{jn}. \tag{A.1}$$

Differentiating both sides of (A.1) and using (20) and (31b), we obtain

$$\frac{\partial \mathcal{F}_{i\alpha j}}{\partial R_{\alpha j}} = \frac{1}{2}\varepsilon_{ikl}\frac{\partial^2 U_{kn}}{\partial r_{\alpha m}\partial r_{\alpha m}} U_{ln}. \tag{A.2}$$

Note that the lhs of (A.1) and (A.2) depend only on $\{t_a\}$. The lhs of (A.2) appears in the coefficient $\mathcal{B}_l$ defined by (31a).

Appendix B. Some useful identities

In this appendix, we gather some useful relations analogous to (49) [3]. The last of these, (B.7), is a closure relation which must hold on the frame manifold (1), except at singular points.

$$g^{-1}_{ab} = h_{ab} - a_{ai}a_{bj}M^{-1}_{ij} \tag{B.1}$$

$$\mathcal{N}_{ij} = M_{ij} - \sum_{c,d=1}^{3N-6} h^{-1}_{cd} a_{ci} a_{dj} \tag{B.2}$$

$$\sum_{b=1}^{3N-6} g_{ab} a_{bi} = M_{ij}\mathcal{N}^{-1}_{jk} \sum_{b=1}^{3N-6} h^{-1}_{ab} a_{bk} \tag{B.3}$$

$$\mathcal{N}^{-1}_{ij} = M^{-1}_{ij} + \sum_{a,b=1}^{3N-6} A_{ai} g_{ab} A_{bj} \tag{B.4}$$

$$h^{-1}_{ab} = g_{ab} - \sum_{c,d=1}^{3N-6} g_{ac} A_{ci} \mathcal{N}_{ij} A_{dj} g_{db} \tag{B.5}$$

$$\frac{\det(\boldsymbol{M})}{\det(g_{ab})} = \det(h_{ab})\det(\mathcal{N}) \tag{B.6}$$

$$m_\gamma \delta_{\gamma\beta}\delta_{jk} = \sum_{a,b=1}^{3} \mathcal{R}^{-2}_{ab}\frac{\partial \mathcal{G}_a}{\partial \mathcal{R}_{\gamma k}}\frac{\partial \mathcal{G}_b}{\partial \mathcal{R}_{\beta j}} + \sum_{c,d=1}^{3N-6} m_\gamma \frac{\partial R_{\gamma k}}{\partial t_c} h^{-1}_{cd} m_\beta \frac{\partial R_{\beta j}}{\partial t_d} + \delta_{jk}\frac{m_\gamma m_\beta}{M}. \tag{B.7}$$

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