Appendix A

Mathematics of classical mechanics

A.1 Canonical transformations

Classical mechanics can be expressed by Hamilton's integral principle [51, 64]. Consider a N-dimensional system described by the *Lagrangian* $\mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)$. The Lagrangian is defined by the difference of kinetic energy T and potential energy V, $\mathcal{L} = T - V$. Any continuos vector function $\mathbf{q}(t)$ is called a *path*. The classical trajectories are those special kinds of paths that are extrema of the functional,

$$S[\mathbf{q}(t)] = \int_{t_1}^{t_2} \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t)dt. \tag{A.1}$$

A path is extremal if the variation δ among all paths $\mathbf{q}(t)$ from $\mathbf{q}(t_1)$ to $\mathbf{q}(t_2)$ with boundary conditions $\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0$ vanishes,

$$\delta S[\mathbf{q}(t)] = 0. \tag{A.2}$$

The Lagrangian and the Hamiltonian are connected by a Legendre transformation,

$$H(\mathbf{p}, \mathbf{q}, t) = \dot{\mathbf{q}} \cdot \mathbf{p} - \mathcal{L}(\mathbf{q}, \dot{\mathbf{q}}, t), \tag{A.3}$$

where the momentum $\mathbf{p} = \partial\mathcal{L}/\partial\dot{\mathbf{q}}$ is *canonical conjugated* to the position $\mathbf{q}$. Note, momenta and positions are *generalized*. For each generalized position q_j, there is a conjugated momentum p_j. For instance, a system with rotational symmetry may be conveniently expressed by using cylinder coordinates. Then, the angular momentum L is the generalized momentum canonical conjugated to the angle θ, a generalized position.

Hamilton's principle can be recast into the form [51],

$$\delta \int_{t_1}^{t_2} \left[\dot{\mathbf{q}} \cdot \mathbf{p} - H(\mathbf{p}, \mathbf{q}, t)\right] dt = 0. \tag{A.4}$$

Here, the positions $\mathbf{q}$ *and* momenta $\mathbf{p}$ are independent variables and the variations is performed with respect to both. This leads to the well-known Hamilton's equation of motion,

$$\dot{p}_j = -\frac{H}{\partial q_j}, \quad \dot{q}_j = \frac{H}{\partial p_j}, \quad j = 1, \ldots, N. \tag{A.5}$$

Consider an arbitrary transformation from the old variables $(\mathbf{p}, \mathbf{q})$ to new variables $(\mathbf{P}, \mathbf{Q})$,

$$\mathbf{P} = \mathbf{P}(\mathbf{p}, \mathbf{q}), \tag{A.6}$$

$$\mathbf{Q} = \mathbf{Q}(\mathbf{p}, \mathbf{q}), \tag{A.7}$$

where the new variables are expressed as functions of the old variables. Confi guration space coordinate transformations are only a special kind of such transformations. For instance, in Appendix B transformations are discussed, that mix momentum and position. The transformation is *canonical* if there is a new Hamiltonian $\tilde{H}(\mathbf{P}, \mathbf{Q}, t)$ and Hamilton's principle is satisfi ed in the new variables,

$$\delta \int_{t_1}^{t_2} \left[\dot{\mathbf{Q}} \cdot \mathbf{P} - \tilde{H}(\mathbf{P}, \mathbf{Q}, t)\right] dt = 0. \tag{A.8}$$

The simultaneous satisfaction of Equation (A.4) and (A.8) is only possible, if the integrands differ only by the total differential dF/dt of a function F [51]. This function is called the *generator* of the canonical transformation. Assuming, that F is a function of the old and new positions and the time, $F = F_1(\mathbf{q}, \mathbf{Q}, t)$, it follows,

$$\dot{\mathbf{q}} \cdot \mathbf{p} - H(\mathbf{p}, \mathbf{q}, t) = \dot{\mathbf{Q}} \cdot \mathbf{P} - \tilde{H}(\mathbf{P}, \mathbf{Q}, t) + \frac{dF(\mathbf{q}, \mathbf{Q})}{dt}. \tag{A.9}$$

Evaluating the total differential,

$$\frac{dF_1(\mathbf{q}, \mathbf{Q})}{dt} = \sum_j \frac{\partial F}{\partial q_j}\dot{q}_j + \sum_j \frac{\partial F}{\partial Q_j}\dot{Q}_j + \frac{\partial F_1}{\partial t}, \tag{A.10}$$

and collecting terms yields the transformation equations,

$$p_j = \frac{\partial F_1(\mathbf{q}, \mathbf{Q}, t)}{\partial q_j}, \tag{A.11}$$

$$P_j = -\frac{\partial F_1(\mathbf{q}, \mathbf{Q}, t)}{\partial Q_j}, \tag{A.12}$$

$$\tilde{H} = H + \frac{\partial F_1(\mathbf{q}, \mathbf{Q}, t)}{\partial t}. \tag{A.13}$$

By inverting the N Eqs. (A.11) with respect to the Q_j and inserting the result in the N Eqs. (A.12) the transformation Eqs. (A.6-A.7) is rediscovered. Moreover, the new Hamiltonian $\tilde{H}$ is given by Eq. (A.13). Therefore, these $2 \cdot N + 1$ equations are the reason why F_1 is called the generator of the canonical transformation, because the canonical transformation is uniquely characterized by this function. There are more types of generator functions, all dependent on exactly N old and N new variables. They are related to the present F by corresponding Legendre transformations. For instance, the generator $F_2(\mathbf{q}, \mathbf{P}, t)$ that depends on the old positions and new momenta is given by,

$$F_2(\mathbf{q}, \mathbf{P}, t) = F_1(\mathbf{q}, \mathbf{Q}) + \mathbf{P} \cdot \mathbf{Q}, \tag{A.14}$$

where Eqs. (A.12) must be inverted with respect to the Q_j and inserted in the right-hand side of Eq. (A.14). The transformation equations in this case read,

$$p_j = \frac{\partial F_2(\mathbf{q}, \mathbf{P}, t)}{\partial q_j}, \tag{A.15}$$

$$Q_j = \frac{\partial F_2(\mathbf{q}, \mathbf{P}, t)}{\partial P_j}, \tag{A.16}$$

$$\tilde{H} = H + \frac{\partial F_2(\mathbf{q}, \mathbf{P}, t)}{\partial t}. \tag{A.17}$$

The remaining generator functions and transformation equations are given in a similar way. However, in this work only the present generator functions are of certain importance.

The F_1-type generator function $S_{\mathrm{cl}}(\mathbf{q}, \mathbf{q}_0; t)$ of the *dynamical transformation* is given by [51],

$$S_{\mathrm{cl}}(\mathbf{q}, \mathbf{q}_0; t) \equiv S[\mathbf{q}_{\mathrm{cl}}(t)], \tag{A.18}$$

where the functional S is defi nes in Eq. (A.1) and $\mathbf{q}_{\mathrm{cl}}(t)$ is a classical trajectory that evolves from $\mathbf{q}_0$ to $\mathbf{q}$ in time t. One can show that derivative with respect to $\mathbf{q}$, $\mathbf{q}_0$, and t yields, respectively, the fi nal momentum $\mathbf{p}$, the initial momentum (times -1) $-\mathbf{p}_0$, and the energy (times -1) $-E$ [51].

There is another important class of canonical transformations that lead to the notion of *integrability*. Consider a time-independent canonical transformation, characterized by a F_2-type generator function $S(\mathbf{q}, \mathbf{P})$, where the new momenta $\mathbf{P}$ are constant. Hamilton's equation of motion with respect to the new set of coordinates $(\mathbf{P}, \mathbf{Q})$ reads,

$$\dot{P}_j = -\frac{\partial \tilde{H}}{\partial Q_j} = 0, \tag{A.19}$$

$$\dot{Q}_j = \frac{\partial \tilde{H}}{\partial P_j}. \tag{A.20}$$

That is, the new Hamiltonian $\tilde{H} = \tilde{H}(\mathbf{P})$ is a function of the constant momenta alone. If each DOF corresponds to a vibration then the submanifold corresponding to fixed $\mathbf{P}$ is an invariant torus. Thus, one can choose the N actions I_j associated to the N irreducible curves $\mathcal{C}_j$, i.e., $\mathbf{P} = \mathbf{I}$. The generalized positions become angles, $\mathbf{Q} = \boldsymbol{\varphi}$, and the integration of Eq. (A.20) yields,

$$\varphi_j = \omega_j(\mathbf{I})\, t + \varphi_j^{(0)}, \tag{A.21}$$

where $\varphi_j^{(0)}$ are integration constants and,

$$\omega_j(\mathbf{I}) = \frac{\partial \tilde{H}}{\partial I_j}, \tag{A.22}$$

are the N fundamental frequencies as a function of the actions $\mathbf{I}$. A system for which a canonical transformation like the present one exists are called *integrable*. Equation A.21 is equivalent to the time evolution of the phases of a set of N uncoupled harmonic oscillators, i.e., an integrable system is equivalent to a system of harmonic oscillators.

A.2 The method of characteristics

The *method of characteristics* is a well known means to construct a submanifold of phase space on which an action function $S(\mathbf{q})$ is (piecewise) defined [52, 53]. Consider an initial manifold Λ^{N-1} of dimension $N-1$ that is a submanifold of the full $2N$-dimensional phase space with the property that for each $(\mathbf{p}, \mathbf{q}) \in \Lambda^{N-1}$ there is a function $\mathbf{p} = \mathbf{p}(\mathbf{q})$ such that the energy E is fixed, $H(\mathbf{p}(\mathbf{q}), \mathbf{q}) = E$, and such that,

$$\oint_p \mathbf{p}(\mathbf{q}) d\mathbf{q} = 0, \tag{A.23}$$

for any closed path p in the projection of Λ^{N-1} onto configuration space. [For instance, in a two-dimensional system, the projection of Λ^1 onto configuration space is a line and one may choose $\mathbf{p}(\mathbf{q})$ perpendicular to that line with magnitude determined by the energy constraint.] Any $(\mathbf{p}, \mathbf{q}) \in \Lambda^{N-1}$ can be regarded as the initial condition of a classical trajectory. Propagating all points of the initial manifold by a time step t leads to a new manifold Λ_t^{N-1}. Maslov and Fedoriuk [52] showed, that for this new manifold Eq. (A.23) holds, too. Moreover, these authors showed that for the joint N-dimensional manifold for the time interval $0 \leq t \leq T$,

$$\Lambda^N = \cup_{0 \leq t \leq T} \Lambda_t^{N-1}, \tag{A.24}$$

a similar property holds, where there are certain branches $\mathbf{p}^{(r)}(\mathbf{q})$ corresponding to the different projections onto configuration space and for each branch Eq. (A.23) holds. This implies, that there exists a function $S^{(r)}(\mathbf{q})$ for each branch with $\mathbf{p}^{(r)} = \boldsymbol{\nabla} S^{(r)}(\mathbf{q})$. A submanifold of phase space with these properties is called

Lagrange manifold. Thus, the invariant tori discussed in Section 2.1.1 are special types of Lagrange manifolds.

A.3 Derivation of the Hydroperoxyl-Lagrangian

The Lagrangian of the hydroperoxyl anion HO_2^- reads

$$\mathcal{L} = \frac{1}{2} m_O \left(\dot{\mathbf{r}}_1^2 + \dot{\mathbf{r}}_2^2 \right) + \frac{1}{2} m_H \dot{\mathbf{r}}_3^2 - V(r_1, r_2, r_3), \tag{A.25}$$

where m_O and m_H is the mass of an oxygen and hydrogen atom, respectively, and $M = m_H + 2m_O$ is the total mass. Inserting Eqs. (3.26-3.28) yields

$$\begin{aligned} \mathcal{L} = & \frac{1}{2}(2m_O) \left(\dot{\mathbf{R}}^2 + \dot{\mathbf{r}}^2 \right) \\ + & \frac{1}{2} m_H \left(\dot{\mathbf{R}}^2 + \dot{\mathbf{s}}^2 + 2\dot{\mathbf{R}} \cdot \dot{\mathbf{s}} \right) \\ - & V(\mathbf{r}, \mathbf{s}). \end{aligned} \tag{A.26}$$

The PES V only depends on the vectors $\mathbf{r}$ and $\mathbf{s}$. Equation (3.29) holds if the center of mass is assumed (without restriction) to be fi xed at the origin. This implies

$$\begin{aligned} \mathcal{L} = & \frac{1}{2}(2m_O) \left(\frac{m_H^2}{M^2} \dot{\mathbf{s}}^2 + \dot{\mathbf{r}}^2 \right) \\ + & \frac{1}{2} m_H \left(\frac{m_H^2}{M^2} + 1 - 2\frac{m_H}{M} \right) \dot{\mathbf{s}}^2 \\ - & V(\mathbf{r}, \mathbf{s}). \end{aligned} \tag{A.27}$$

And after rearanging terms one arives at Eq. (3.30).