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Construction of Darboux coordinates and Poincaré–Birkhoff normal forms in noncanonical Hamiltonian systems

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HIGHLIGHTS

- An extension of Ref. [15] to the case of *noncanonical* coordinates.
- Detailed description of normal form expansions in variational approaches to quantum systems.
- The method allows to apply transition state theory directly to quantum wave packets.
- The crucial mathematical steps are presented in five central theorems.
- A complete numerical example including script code is presented in the appendix.

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ABSTRACT

We demonstrate a general method to construct Darboux coordinates via normal form expansions in noncanonical Hamiltonian system obtained from e.g. a variational approach to quantum systems. The procedure serves as a tool to naturally extract canonical coordinates out of the variational parameters and at the same time to transform the energy functional into its Poincaré–Birkhoff normal form. The method is general in the sense that it is applicable for arbitrary degrees of freedom, in arbitrary orders of the local expansion, and it is independent of the precise form of the Hamilton operator. The method presented allows for the general and systematic investigation of quantum systems in the vicinity of fixed points, which e.g. correspond to ground, excited or transition states. Moreover, it directly allows to calculate classical and quantum reaction rates by applying transition state theory.

1. Introduction

It is at the core of physical sciences to describe and investigate the dynamics of systems. Depending on their nature, these can either be described by the Schrödinger equation in case of quantum mechanical systems, or e.g. in terms of Hamiltonian mechanics in case of a classical system. In both cases, a canonical structure of the dynamical equations [1,2] is inherent which is expressed in the existence of conjugate pairs of field operators $\hat{\psi}$, $\hat{\psi}^\dagger$ with infinite degrees of freedom or conjugate coordinates $\boldsymbol{q}$, $\boldsymbol{p}$ with a finite number of degrees of freedom. Both approaches serve as powerful frameworks to investigate a huge amount of different physical problems. In addition to the global dynamics of a physical system which can be determined by solving the corresponding equations of motion, its fixed points play a crucial role in many investigations: For example, fixed points which correspond to a (local) minimum of the Hamiltonian form (metastable) ground states of the system. Moreover, fixed points which are related to saddle points of the Hamiltonian are unstable, excited states. A special class of such unstable fixed points are rank-1 saddle points which possess exactly one unstable direction. These points are of special interest in dynamical systems, because they form bottlenecks in the underlying phase space which separate different regions therein. Considering a dynamical system, the transition from one to the other subregion of phase space is then mediated by the saddle point. Therefore, the latter determines the reaction dynamics between the different subregions which is the basic statement of transition state theory [3–19].

Beyond the fixed points of the system's dynamical equations themselves, their local properties are of high interest in many applications. For example, the local properties of a minimum of the Hamiltonian determine the physics of the system for small excitations from the

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ground state. Moreover, the local properties in the vicinity of a rank-1 saddle point or transition state determine the reaction dynamics and rates of the system.

For a detailed analysis of the local fixed point properties of a canonical Hamiltonian system a standard and powerful tool is its normal form expansion [15,20,21]. Especially in the field of reaction dynamics, the normal form Hamiltonian in the vicinity of rank-1 saddle points is important, because it provides a way of defining a normally hyperbolic invariant manifold [15,18,21–34] with which a nonrecrossing dividing surface between reactants and products in multi-degree-of-freedom systems can be constructed.

In Ref. [15], Waalkens et al. describe this procedure in detail, of which our work will be a natural extension to *noncanonical* coordinates. We therefore give a brief overview of the method in the following: If the Hamiltonian H is given in terms of a set of canonical coordinates $\boldsymbol{q}, \boldsymbol{p}$ then its normal form can be constructed via the following expansion,

$$\tilde{H}(\boldsymbol{q}, \boldsymbol{p}) = \sum_{j=0}^{\infty} \frac{1}{j!} \mathrm{ad}_W^j H(\boldsymbol{q}, \boldsymbol{p}). \tag{1}$$

Here, W is an appropriate generating function and $\mathrm{ad}_W H = \{W, H\}$ is the adjoint operator that equals the definition of the Poisson bracket. Usually, the normal form Hamiltonian is required up to a certain polynomial order within a local expansion at a fixed point. Consequently, it is appropriate to regard, in general, expansions of all quantities occurring in Eq. (1), i.e. the original Hamiltonian, the transformed one, and the generating function. This procedure has the advantage that the transformation in Eq. (1) can be applied order by order. Waalkens et al. [15] describe in detail how these single steps are performed and how exactly the generating function W needs to be constructed through a homological equation in order to obtain the Poincaré–Birkhoff normal form of the Hamilton function (we refer the reader to this reference for more details). The final result is then, by construction, a Hamiltonian $H(\boldsymbol{J})$ which depends on the actions coordinates $\boldsymbol{J}$ all being constants of motion up to the respective order of the expansions.

With special regard to reactive systems, this normal form is of particular advantage, because – if J_1 corresponds to the reaction channel of the system, i.e. the unstable direction of a rank-1 saddle point – then a local, recrossing-free dividing surface is defined by $J_1 = 0$, The directional flux through the dividing surface at fixed energy E is then given by

$$f(E) = (2\pi)^{d-1}\, \mathcal{V}(E), \tag{2}$$

where $\mathcal{V}(E)$ is the volume of actions $(J_2, \ldots, J_d)$ enclosed by the contour $H(0, J_2, \ldots, J_d) = E$ and the thermal reaction rate Γ at temperature $\beta = 1/k_{\mathrm{B}}T$ is obtained from the Boltzmann average of Eq. (2) which yields (cf. Ref. [35])

$$\Gamma = \frac{1}{2\pi\beta} \frac{\int \mathrm{d}J_2 \ldots \mathrm{d}J_d \, \exp\big(-\beta H(0, J_2, \ldots, J_d)\big)}{\int \mathrm{d}J_1' \ldots \mathrm{d}J_d' \, \exp\big(-\beta H'(J_1', \ldots, J_d')\big)}. \tag{3}$$

Here, H is the normal form at the transition state and H' that at the metastable ground state. In this context of reaction dynamics the importance of the knowledge of a normal form Hamiltonian and, in order to be able to actually calculate reaction rates, an explicit construction scheme of the local action variables become obvious. We note that the work of Waalkens et al. [15] goes even beyond this by also introducing how quantum reaction rates can be calculated within a formally equivalent procedure that merely requires a redefinition of the adjoint operator.

It is the purpose of this paper to extend the scheme of Waalkens et al. [15] to the more general field of *noncanonical* Hamiltonian systems, as e.g. quantum mechanical wave packets whose dynamics is governed by the Schrödinger equation (see below). Therefore, we will describe in the following a quantum system within a variational approach, determine the respective dynamical equations by applying a time-dependent variational principle [36,37], and show that it defines a general, *noncanonical* Hamiltonian system (see below for a precise definition). In such quantum systems, fixed points of the dynamical equations and their local properties have the same meaning for the quantum reaction dynamics as they have in classical systems. For a detailed analysis of the local properties, it is, therefore, desirable to obtain an analogue of the classical normal form also for the quantum system. However, the usual treatment (1) cannot be applied, because neither a classical Hamilton function $H(\boldsymbol{q}, \boldsymbol{p})$ in canonical coordinates nor such coordinates themselves are known.

Here, we present a method by which both the transformation of the variational approach as a noncanonical Hamiltonian system into its Poincaré–Birkhoff normal form and simultaneously the construction of canonical coordinates is obtained. The result of the transformations is, by construction, a set of canonical normal form coordinates. In the latter, the energy functional of the system will serve as a classical Hamilton function which has the advantageous property that it is directly formulated in action variables. If truncated at a certain order, the constructed Hamiltonian will serve as an approximation to the true quantum system which directly allows for the application of transition state theory and the evaluation of quantum reaction rates via Eqs. (2) and (3). In technical terms, the crucial difference between our procedure in noncanonical coordinates and the usual treatment in canonical ones is that we treat the dynamical equations as well as the energy functional separately. From the mathematical point of view, this brings with it that the generating function of the transformation and the corresponding operators require a different definition than in Eq. (1).

Our paper is organized as follows: In Section 2 we introduce a variational approach to quantum systems which defines a noncanonical Hamiltonian system for the variational parameters. Furthermore, we discuss its formal relation to classical canonical mechanics and some important fixed point properties of the linearized dynamical equations. In Section 3, the method to construct local canonical coordinates in the vicinity of the fixed point is introduced. Therefore, a symplectic basis formed by appropriately normalized eigenvectors of the linearized dynamical equations is used and higher-order terms of the expansions are treated via normal form transformations. As a key feature – and in contrast to the usual transformation (1) of canonical Hamiltonians – this procedure treats the dynamical equations and the energy functional separately. Moreover, the normal form expansions are carried out in two steps: First, its polynomial structure is generated using the nonresonant terms of the corresponding generating function (see below for the latters' definition). Second, the remaining resonant coefficients of the generating function which are free parameters are chosen in such a way that the dynamical equations as well as the energy functional in normal form coordinates fulfil canonical equations, i.e. the normal form coordinates are canonical ones by construction. We have written the paper such that the essential steps that go beyond the work in Refs. [15,20] are presented in the Theorems 1–5 presented in Section 3. In the Appendix, we provide in addition both a numerical example of the presented procedure and an exemplary MATHEMATICA script code, in which the reader is welcome to execute the respective steps while reading the paper.