

Chapter 5

The reaction plane approach

5.1 Reaction coordinates

5.1.1 Overview

Chapter 3 and Chapter 4 were concerned with methods to describe tunneling processes by means of classical trajectories. Classical trajectories (also those of the TU theory) are obtained by ordinary differential equations (ODE) with respect to time. The solution of these ODE requires only the knowledge of the PES at a certain position. Moreover, the individual trajectories are independent of each other facilitating a parallelization of corresponding computer codes. These features allow for the combination with *on-the-fly* quantum chemistry calculations (see, for instance, Ref. [103]).

In this Chapter the reduction of complexity of the underlying PES of the tunneling reaction is discussed making a quantum mechanical (as opposed to semiclassical) treatment possible. Reduction of complexity means to select relevant DOF. The reaction path concept of chemistry is the most prominent example for such a reduction [67]. A full-dimensional reaction path Hamiltonian was derived by Miller *et al.* [111, 142]. This Hamiltonian relies on curvilinear coordinates (s, \mathbf{q}) , where s is the intrinsic reaction coordinate and \mathbf{q} are the orthogonal DOF. For small reaction path curvature an adiabatic approximation is reasonable and corner cutting, a multidimensional effect, can be treated by introduction of an effective mass [cf. Eq. (3.10)]. If the reaction path curvature is too large then the reaction swath has to be taken into account (cf. Section 3.1.3). Moreover, the orthogonal DOF \mathbf{q} may become non-unique for distances away from the reaction path that are larger than the radius of curvature. Yet the path concept may be reasonable for the semiclassical description of tunneling by resorting to the least action principle of classical mechanics (keywords: LSLA, instanton theory, GT paths; cf. Sec. 3.1.2 and Sec. 3.1.3).

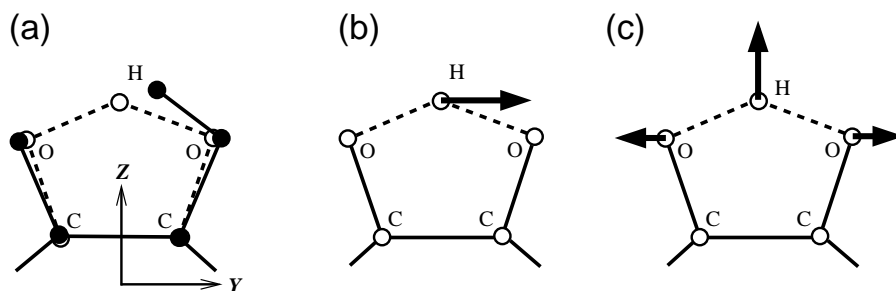


Figure 5.1: The OCCO-H fragment of tropolone [TRN(OH)]. (a) Overlay of minimum \mathbf{X}_R (filled circles) and saddle point \mathbf{X}_{TS} (open circles) geometry. Coordinate origin is the center of mass. (b) Atom displacement corresponding to direction \mathbf{w}_1 (anti-symmetric). The displacement of the remaining atoms is small. (c) *Ditto* for direction \mathbf{w}_2 (symmetric). The results were obtained by Gaussian 03 [152] with the DFT(B3LYP) method and the 6-31+G(d) basis set.

A large reaction path curvature indicates large couplings among the reactive and orthogonal DOF. Thus, a reliable quantum mechanical treatment requires the explicit consideration of more than one DOF. In the reaction surface Hamiltonian approach (and variations thereof), instead of the intrinsic reaction coordinate, few internal coordinates (i.e., bond lengths and angles) serve as relevant DOF [143, 144]. For fixed relevant DOF, the remaining DOF are optimized such as to minimize the energy. For instance, the approach was applied to malonaldehyde [145, 146, 147], tropolone [148], and the formic acid dimer [119, 120] with up to three internal DOF.

The kinetic energy operator of the forementioned approaches has a rather complicated form making a numerical treatment difficult. A simple structure of the kinetic energy operator is obtained by adopting a formulation based on Cartesian coordinates (cf. Section 2.2.1), e.g., the *Cartesian reaction surface* (CRS) Hamiltonian by Ruf and Miller [42]. The CRS Hamiltonian relies on the selection of few *atomic* Cartesian coordinates that perform large amplitude displacements upon reaction. For instance, in tropolone [cf. Reaction (R1) in the Introduction] the planar (y, z) coordinates of the reacting hydrogen are a reasonable choice. The remaining Cartesian DOF are considered to perform only small amplitude displacements and the full PES is approximated by a second order Taylor expansion with respect to the small amplitude DOF. A number of successful applications document that the method is reasonable [149, 150]. However, there may be significant couplings between small amplitude coordinates and large amplitude coordinates and a complete separation between these two does not necessarily yield the most compact representation of the PES. For tropolone, the situation is illustrated in Fig. 5.1.

Panel (a) shows an overlay of the minimum geometry (C_s symmetry) and saddle point geometry (C_{2v} symmetry). A significant motion of the heavy atoms upon approaching the saddle point geometry is visible; especially the oxygen-oxygen distance is shortened. The chemical bonding has significantly changed between the two considered geometries, i.e., the PES seen by the two oxygens differs also quite strongly. Thus, the conventional choice of the (y, z) coordinates leads to a strong coupling of large amplitude (H-atom) and small amplitude coordinates.

All geometries \mathbf{X} (mass-weighted) of the molecule span a N -dimensional vector space (cf. Section 2.2.1), where N is the total number of DOF (i.e., $N = 45$ in tropolone). Thus, instead of Cartesian coordinates of individual atoms one may alternatively choose any orthonormal set of N -dimensional vectors to describe large amplitude coordinates of the molecular geometry. Moreover, for a symmetric double well system the displacement vector $\mathbf{X}_R - \mathbf{X}_{TS}$ can be partitioned into the two symmetry components, where the normalized vectors are denoted \mathbf{w}_1 and \mathbf{w}_2 for the anti-symmetric and symmetric component, respectively. These vectors were already defined in Section 3.3.2. The atom displacements corresponding to these vectors are shown in panel (b) and (c) of Fig. 5.1. Coordinate w_1 [panel (b)] is similar to the y coordinate, while coordinate w_2 [panel (c)] describes a concerted motion of the hydrogen together with the oxygens. This coordinate describes a collective motion of atoms. The two coordinates span a plane that was called *reaction plane* by Yagi *et al.* [43]. The reaction plane is subject of the following Section.

5.1.2 The Reaction Plane

The reaction plane coordinates were introduced by Takada and Nakamura [75] in order to derive a simple SMC PES fit. The method was applied to carboxylic acid dimers in Section 3.3.2. Yagi *et al.* [43] used the reaction plane as a guide for the relevant region of configuration space in their full-dimensional treatment of malonaldehyde. Moreover, the concept was implicitly used by other authors as well [151]. The aim of this Chapter is to derive a Cartesian Hamiltonian, where the reaction plane coordinates are the large amplitude coordinates while the remaining DOF are considered to perform small amplitude displacements with respect to the reaction plane. To this end, in Section 5.2, a reformulation [V]¹ of the CRS framework of Ruf and Miller [42] is given. The present Section addresses the relevance of the reaction plane for a chemical reaction.

For the definition of the reaction plane directions, \mathbf{w}_1 and \mathbf{w}_2 , the recipe of Ref. [75] is used (cf. Section 3.3.2). Thus, the distance between \mathbf{X}_R and \mathbf{X}_L is

¹Paper (V) of the publication list

minimal with respect to rotation of the right minimum geometry and vice-versa. The same applies for \mathbf{X}_C and \mathbf{X}_{TS} . The two directions \mathbf{w}_1 and \mathbf{w}_2 defined in Eq. (3.22) and (3.23), respectively, are orthogonal, $\mathbf{w}_1 \cdot \mathbf{w}_2 = 0$, because they transform according to different irreducible representations. There seems to be no proof that the minimum criterion is equivalent to the requirement that \mathbf{X}_R and \mathbf{X}_L are connected by a rotation free path. Moreover, the minimum criterion only applies to the planar case. In the non-planar case, the minimization procedure would involve the three Euler angles, but only one angle can be fixed. In order to keep the reaction plane unique, the definition can be based on the IRP, because it is a rotation free path connecting the two minima and the saddle point. Thus, for given \mathbf{X}_{TS} it is in principle possible to obtain the left and right minimum via solution of Eq. (2.49).

For the planar case, the minimum criterion implies that \mathbf{w}_1 is *exactly* orthogonal with respect to infinitesimal rotations of \mathbf{X}_R , \mathbf{X}_L , and \mathbf{X}_C [V]. Likewise, for \mathbf{w}_2 with respect to \mathbf{X}_C and \mathbf{X}_{TS} . This can be shown as follows [V]: Let $\mathbf{R}(\alpha)$ be the rotation matrix with rotational axis perpendicular to the molecular plane. The corresponding infinitesimal rotation matrix $\delta\mathbf{R} = \delta\mathbf{R}(\alpha)$ is defined as the linear term of the Taylor series expansion,

$$\mathbf{R}(\alpha) = \mathbf{I} + \left. \frac{\partial \mathbf{R}(\alpha)}{\partial \alpha} \right|_{\alpha=0} \alpha + \dots = \mathbf{I} + \delta\mathbf{R} \alpha + \dots \quad (5.1)$$

Let ε be a small angle. Then, because the distance $|\mathbf{X}_R - \mathbf{X}_L|$ is minimal with respect to rotations generated by $\delta\mathbf{R} \mathbf{X}_R$, it follows,

$$\begin{aligned} \frac{\partial}{\partial \varepsilon} (\mathbf{X}_R + \varepsilon \delta\mathbf{R} \mathbf{X}_R - \mathbf{X}_L)^2 \Big|_{\varepsilon=0} \\ = 2 (\mathbf{X}_R - \mathbf{X}_L) \delta\mathbf{R} \mathbf{X}_R = 0 \end{aligned} \quad (5.2)$$

i.e., the direction \mathbf{w}_1 is orthogonal to an infinitesimal rotation of \mathbf{X}_R . The same holds for \mathbf{X}_L and \mathbf{X}_C . Concerning direction \mathbf{w}_2 , one can repeat the line of arguments also for the geometries \mathbf{X}_C and \mathbf{X}_{TS} .

The generator of the infinitesimal rotation, $\delta\mathbf{R} \mathbf{X}$, is a function of the geometry \mathbf{X} . Thus, local rotational invariance as considered above does not guarantee global rotational invariance of the reaction plane. However, for large enough molecules the total change of the generator for displaced geometries is rather small, because a significant change is mostly confined to the reacting atom(s). On the opposite, the reaction plane is obviously inappropriate for molecules with only few atoms.

Concerning the non-planar case, with the reaction plane defined by the IRP geometries, there seems to be no argument that would support strict rotational invariance of the reaction plane with respect to particular geometries. If the reaction

plane is orthogonal to infinitesimal rotations or not in the non-planar case depends on the system at hand.

It was shown that the least action principle applied to the GT paths (cf. Section 3.1.3) yields reasonable semiclassical tunneling splittings for molecules like malonaldehyde [108, 114], tropolone [114], and various carboxylic acid dimers [126]. Direction \mathbf{w}_1 is essentially the straight line part of the family of GT paths. Based on these observations, the physical relevance of the reaction plane can be established, when it is possible to show that the IRP (the other extremum of the family of GT paths) lies approximately in the reaction plane. To be specific, consider the projection of the IRP onto the reaction plane,

$$\bar{\mathbf{X}}(s) = [(\mathbf{X}(s) - \mathbf{X}_{TS}) \cdot \mathbf{w}_1] \mathbf{w}_1 + [(\mathbf{X}(s) - \mathbf{X}_{TS}) \cdot \mathbf{w}_2] \mathbf{w}_2 + \mathbf{X}_{TS}. \quad (5.3)$$

The difference between the IRP and its projection can be expressed by the root mean squared (RMS) atomic displacement,

$$\sigma(s) = \frac{1}{\sqrt{N_{\text{at}}}} \sqrt{(\mathbf{x}(s) - \bar{\mathbf{x}}(s))^2}, \quad (5.4)$$

where lower case letters refer to non-mass weighted coordinates. The smaller $\sigma(s)$ the closer is the IRP to the reaction plane. Of course, this property will depend upon the molecule at hand. In anticipation of the following Chapter, the issue is demonstrated for the case of tropolone [TRN(OH)].

The present quantum chemical calculations were performed using the Gaussian03 software package [152]. The level of theory was DFT/B3LYP/6-31+G(d). Single point energies, gradients, and Hessians for a total of 330 ab initio points (using symmetry relations) were calculated on a grid around the projected IRP (with $0.1 a_0 \text{ amu}^{1/2}$ as typical displacement of individual points). Given the ab initio points the potential energy U , and the first and second derivatives can easily be interpolated (and extrapolated) by a modified Shepard scheme [153]. The details are summarized in Appendix C.

Fig. 5.2 shows a contour plot of the potential along the reaction plane together with the projection of the IRP $\bar{\mathbf{X}}(s)$. The potential energy along the IRP for the protonated [TRN(OH)] and deuterated [TRN(OD)] species, respectively, is shown in Fig 5.3a. The difference between the IRP and its projection is shown in Fig. 5.3b in terms of $\sigma(s)$, the RMS atom displacement [cf. Eq. (5.4)]. The solid and dashed curves were calculated within the Shepard interpolated potential $U(\mathbf{X})$ by direct solution of the ordinary differential equation (2.49). A fifth-order Runge-Kutta integrator was used and the calculation was started at the transition state plus a small displacement in direction of the normal mode with imaginary frequency. The displacement was $0.005 a_0 \text{ amu}^{1/2}$. The filled squares and circles were obtained using the Gonzalez-Schlegel method [154] (implemented in

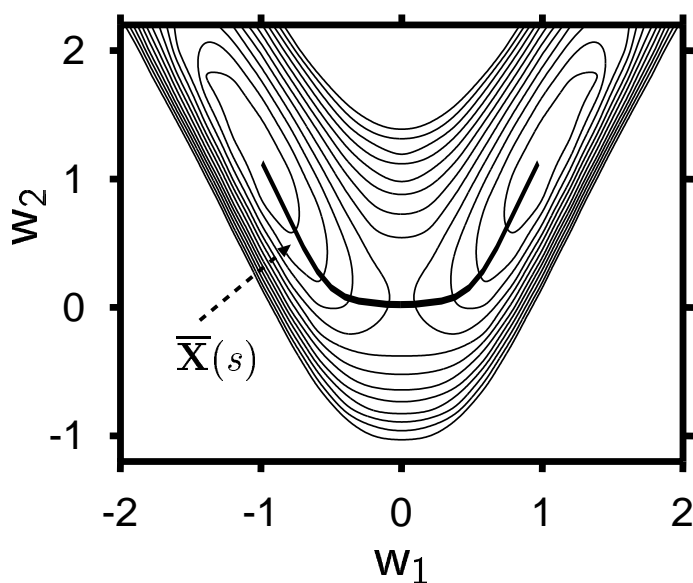


Figure 5.2: Tropolone [TRN(OH)]: Contour plot of the potential cut along the reaction plane spanned by w_1 and w_2 (in $a_0 amu^{1/2}$). The contour line spacing is $500 cm^{-1}$ and the maximum contour line is at $6000 cm^{-1}$. The thick black line is the projection of the IRP onto the reaction plane $\bar{X}(s)$ [cf. Eq. (5.3)], and the barrier is $2161 cm^{-1}$ [B3LYP/6-31+G(d)].

Gaussian 03 [152]). The results obtained within these two methods do agree for both species. (However, the Gonzalez-Schlegel method is insufficient to determine the IRP in the vicinity of the minimum, but there the Shepard interpolated PES is rather accurate.) The RMS difference vanishes by definition at the transition state and the minimum geometries. It reaches a maximum at $s = 0.74$ [0.97] of 2.3 [2.0] $\cdot 10^{-2} \text{ \AA}$ for TRN(OH) [TRN(OD)], i.e., the mean displacement is only a few per cent of a typical bond length. The mean displacement accounts for a maximum energy difference along IRP and projected IRP of about $120 cm^{-1}$ [$100 cm^{-1}$]. Thus, if some DOFs orthogonal to the reaction plane are taken into account, they may well be described in harmonic approximation for each fixed value of the reaction coordinates w_1 and w_2 . Apparently, the reaction plane is of physical relevance for TRN.

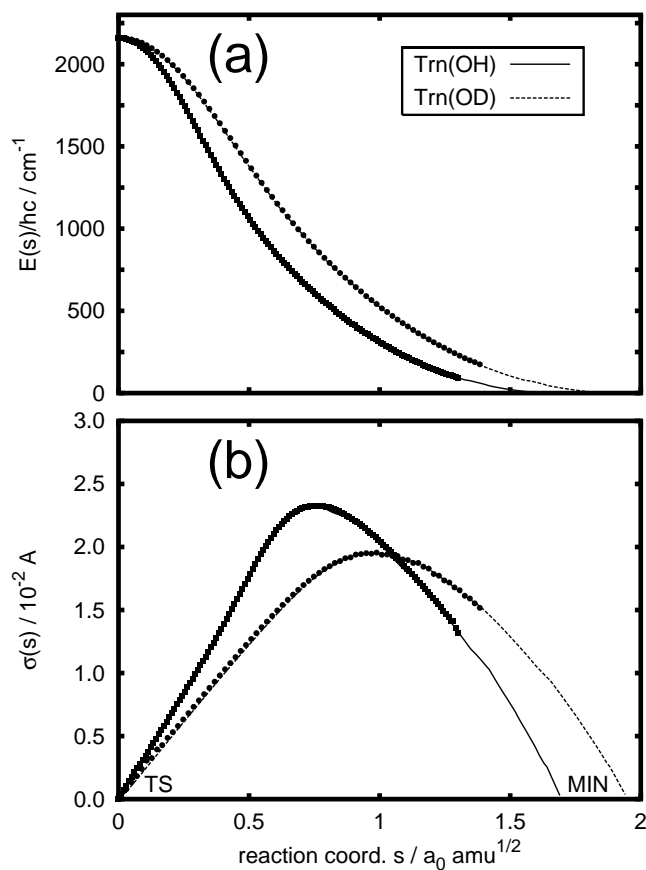


Figure 5.3: Results for isotopomers of tropolone (TRN): (a) Energy along the IRP for the protonated and deuterated species, respectively. Filled squares and dots correspond to a Gaussian 03 IRP calculation using a $0.01 a_0 \text{ amu}^{1/2}$ step size together with the *VeryTight* convergence criterion. The solid and dashed lines were obtained by solving the Eq. (2.49) for the Shepard interpolated full-dimensional potential. (b) Root mean squared atom displacements [Eq. (5.4)] of the IRP geometries $\mathbf{X}(s)$ and those geometries, that are projected onto the reaction plane spanned by the Cartesian directions \mathbf{w}_1 and \mathbf{w}_2 [legend equivalent to (a)]

5.2 The Cartesian reaction surface Hamiltonian

5.2.1 Reformulation for general Cartesian reaction coordinates

The original formulation of the CRS Hamiltonian by Ruf and Miller [42] is already general enough to include the reaction plane coordinates considered in the previous Section. Here, the CRS Hamiltonian is derived for generic reaction coordinates v_1 and v_2 with corresponding vectors \mathbf{v}_1 and \mathbf{v}_2 . There are at least two reasonable choices. First, one may choose (v_1, v_2) to equal certain *atomic* coordinates, for instance, the position (y, z) of the reactive hydrogen atom in TRN (cf. Sec. 5.1). This is identical to the choice of Ruf and Miller [42]. Second, one may choose (v_1, v_2) to equal the reaction plane coordinates (w_1, w_2) discussed in Sec. 5.1.2 [V]. Both choices are discussed below. Note, an extension to more than two reaction coordinates is easily possible. Moreover, an extension to the asymmetric case is also possible: a reaction plane can be defined by the two (non-equivalent) minima and the saddle point. An additional orthogonalization of the vectors \mathbf{w}_1 and \mathbf{w}_2 would be, however, necessary for the asymmetric case.

The reaction coordinates are assumed to be orthogonal to the 3 infinitesimal translational vectors, and they are assumed to be orthogonal to the 3 infinitesimal rotational vectors corresponding to the saddle point geometry \mathbf{X}_{TS} (i.e., rotations and rotation-vibrational couplings are neglected). For two generic reaction coordinates there is a $(N - 2)$ -dimensional subspace of the space of all geometries \mathbf{X} , where N is the number of DOF, i.e., $N = 3 N_{\text{at}}$ for a molecule with N_{at} atoms. A basis for this subspace can be obtained, e.g., by considering a projection of the full-dimensional Hessian at the saddle point geometry onto the subspace. Let $U(\mathbf{X})$ be the full-dimensional PES, then the full-dimensional Hessian at the saddle point is given by,

$$K_{ij}^{(f)}(\mathbf{X}_{\text{TS}}) = \left. \frac{\partial^2 U}{\partial X_i \partial X_j} \right|_{\mathbf{X}_{\text{TS}}} . \quad (5.5)$$

The projector onto the subspace is given by $\mathbf{I} - \mathcal{P}$, where \mathbf{I} is the identity matrix and \mathcal{P} is the projector onto the space spanned by \mathbf{v}_1 and \mathbf{v}_2 ,

$$\mathcal{P} = \mathbf{v}_1^T \mathbf{v}_1 + \mathbf{v}_2^T \mathbf{v}_2 . \quad (5.6)$$

A diagonalization of the projected matrix,

$$(\mathbf{I} - \mathcal{P}) \mathbf{K}^{(f)}(\mathbf{X}_{\text{TS}}) (\mathbf{I} - \mathcal{P}), \quad (5.7)$$

yields N eigenvectors; the set of eigenvectors is denoted as $\{\mathbf{v}_1, \mathbf{v}_2, \mathbf{e}_1, \dots, \mathbf{e}_{N-2}\}$. There are 8 eigenvectors with vanishing eigenvalue: two

correspond to the reaction coordinate vectors \mathbf{v}_1 and \mathbf{v}_2 , the others correspond to the 3 infinitesimal translations, and to the 3 infinitesimal rotations with respect to the saddle point geometry. For convenience, the set of eigenvectors is ordered such, that the 6 translational/rotational vectors are $\mathbf{e}_{N-7}, \dots, \mathbf{e}_{N-2}$. The remaining $N - 8$ vectors \mathbf{e}_j are the normal modes of the saddle point with respect to the subspace. Coordinates corresponding to the eigenvectors \mathbf{e}_j including rotation and translation are denoted as Q_j . For system with two symmetrically equivalent minima, the eigenvectors \mathbf{e}_j and the associated coordinates Q_j are either symmetric or anti-symmetric with respect to the molecular symmetry transformation T (cf. Section 2.2.1).

Any geometry \mathbf{X} can be expanded in terms of the set of eigenvectors discussed so far,

$$\mathbf{X} = \mathbf{X}_{\text{TS}} + v_1 \mathbf{v}_1 + v_2 \mathbf{v}_2 + \sum_{j=1}^{N-2} Q_j \mathbf{e}_j, \quad (5.8)$$

where the saddle point geometry serves as reference, i.e., the coordinates $(v_1, v_2, Q_1, \dots, Q_{N-2})$ describe displacements from the saddle point geometry.

In the CRS framework small displacements $\Delta \mathbf{X} = \mathbf{X} - \mathbf{X}_0$ with respect to a so-called *reaction surface* \mathbf{X}_0 are considered,

$$\Delta \mathbf{X} = \sum_{j=1}^{N-2} (Q_j - Q_j^{(\text{ref})}) \mathbf{e}_j. \quad (5.9)$$

The displacements are orthogonal to the space spanned by \mathbf{v}_1 and \mathbf{v}_2 and the reaction surface is parameterized by the reaction coordinates, i.e., $Q_j^{(\text{ref})} = Q_j^{(\text{ref})}(v_1, v_2)$. The Taylor expansion of the PES with respect to the reaction surface reads,

$$U(\mathbf{X}) = U(\mathbf{X}_0) + \mathbf{G}^{(f)}(\mathbf{X}_0) \cdot \Delta \mathbf{X} + \frac{1}{2} \Delta \mathbf{X}^T \mathbf{K}^{(f)}(\mathbf{X}_0) \Delta \mathbf{X} + \dots, \quad (5.10)$$

where $G_i^{(f)} = \partial U / \partial X_i$ is the full dimensional gradient and the Hessian is defined according to Eq. (5.5). For small displacements of the \mathbf{Q} a truncation of the Taylor series after the harmonic term is reasonable. The truncated PES is denoted V in the following. The 3 translational DOF can be discarded without loss of generality; the 3 rotational DOF can be discarded under the assumption, that the infinitesimal rotational vectors do only slightly change on the plane spanned by the reaction coordinates. The PES is then expressed as, $V = V(v_1, v_2, Q_1, \dots, Q_{N-8})$. The potential values, gradients, and the Hessians on the reaction surface can be obtained by quantum chemistry calculations [44, 45, 46, 124, 152].

Fixed reference

The choice $Q_j^{(\text{ref})} \equiv \text{const}_j$ corresponds to a reaction surface that is independent of (v_1, v_2) and was termed the *fixed reference* case [42]. [This kind of reference has to be distinguished from the choice of \mathbf{X}_{TS} as reference in Eq. (5.8).] Formally, due to this choice, the reaction surface becomes a plane. The special case $Q_j^{(\text{ref})} \equiv 0$ is important for the formulation of the Cartesian Reaction Plane Hamiltonian; in this case, the PES reads

$$V(v_1, v_2, \mathbf{Q}) = U(v_1, v_2) - \sum_i F_i(v_1, v_2) Q_i + \frac{1}{2} \sum_{ij} K_{ij}(v_1, v_2) Q_i Q_j, \quad (5.11)$$

where $U(v_1, v_2) \equiv U(\mathbf{X}_0)$, and the force F_i acting on mode Q_i and the Hessian K_{ij} are related to the full-dimensional quantities by, respectively,

$$F_i(v_1, v_2) = -\mathbf{G}^{(\text{f})}(\mathbf{X}_0) \cdot \mathbf{e}_i, \quad (5.12)$$

$$K_{ij}(v_1, v_2) = \mathbf{e}_i^T \mathbf{K}^{(\text{f})}(\mathbf{X}_0) \mathbf{e}_j. \quad (5.13)$$

Flexible reference

With a *flexible reference*, $Q_j^{(\text{ref})} = Q_j^{(\text{ref})}(v_1, v_2)$, \mathbf{X}_0 describes a generally non-planar surface. This facilitates the selection of the region of the configuration space that is relevant for the reaction. Inserting Eq. (5.9) into Eq. (5.10), and multiplying terms out, yields the PES of the CRS Hamiltonian with respect to the flexible reference,

$$V(v_1, v_2, \mathbf{Q}) = \tilde{U}(v_1, v_2) - \sum_i \tilde{F}_i(v_1, v_2) Q_i + \frac{1}{2} \sum_{ij} K_{ij}(v_1, v_2) Q_i Q_j, \quad (5.14)$$

with abbreviations,

$$\tilde{U} = U + \sum_j F_j Q_j^{(\text{ref})} + \frac{1}{2} \sum_{ij} K_{ij} Q_i^{(\text{ref})} Q_j^{(\text{ref})}, \quad (5.15)$$

$$\tilde{F}_i = F_i + \sum_j K_{ij} Q_j^{(\text{ref})}, \quad (5.16)$$

where all quantities are considered to be (v_1, v_2) -dependent and evaluated with respect to \mathbf{X}_0 .

5.2.2 Selection of relevant modes

The PES of the CRS Hamiltonian of the previous Section and the exact PES agree only up to second order terms with respect to \mathbf{Q} , but the CRS Hamiltonian is full-dimensional. Thus, for any numerical treatment, it is necessary to select certain

modes out of the set $\{Q_j\}$ that are especially important and to introduce a further approximation for the remaining modes. The selection procedure depends on the choice that was made for the reaction coordinates. The goal is to formulate a reduced dimensional CRS Hamiltonian ($\hbar = 1$),

$$\hat{H}_{\text{CRS}} = -\frac{1}{2} \frac{\partial^2}{\partial v_1^2} - \frac{1}{2} \frac{\partial^2}{\partial v_2^2} - \sum_{k=1}^n \frac{1}{2} \frac{\partial^2}{\partial q_k^2} + V(v_1, v_2, \mathbf{q}), \quad (5.17)$$

where $\mathbf{q} = (q_1, \dots, q_n)$ is a set of relevant coordinates.

The choice of \mathbf{Q} -modes is formally arbitrary, i.e., one may switch to another -equivalent- set of modes by a linear transformation,

$$\mathbf{Q}' = \mathbf{A} \mathbf{Q}, \quad (5.18)$$

where \mathbf{A} is an orthogonal transformation matrix that does not mix modes with unequal symmetry. It is assumed in the following, that the vector \mathbf{Q}' can be expressed as,

$$\mathbf{Q}' = \begin{pmatrix} \mathbf{q} \\ \mathbf{S} \end{pmatrix}, \quad (5.19)$$

where the vector \mathbf{q} accounts for the set of relevant modes and the vector $\mathbf{S} = (S_1, \dots, S_{n'})$ with $N = n + n' + 8$ accounts for the set of irrelevant modes. The set of reaction coordinates plus the relevant modes, $\{v_1, v_2, q_1, \dots, q_n\}$, is called *model coordinates*; the irrelevant modes are denoted as *spectator modes*. Moreover, to simplify the notation, the prime ($'$) is dropped.

Generic reaction coordinates

Generic reaction coordinates include atomic reaction coordinates as discussed in Section 5.2.1. Therefore, one may, for instance, identify (v_1, v_2) with the planar position of the reactive hydrogen atom of TRN or similar molecules. For generic reaction coordinates the choice of a flexible reference is preferred. Thus, the starting Equation is Eq. (5.14). A reformulation of this Equation is necessary. Let $\mathbf{Q}^{(0)} = \mathbf{Q}^{(0)}(v_1, v_2)$ be such that $V(v_1, v_2, \mathbf{Q}^{(0)})$ is minimal among all \mathbf{Q} for any fixed value of the reaction coordinates, i.e., $\mathbf{Q}^{(0)}$ satisfies,

$$\tilde{F}_i = \sum_j K_{ij} Q_j^{(0)}. \quad (5.20)$$

With this definition the linear and harmonic term of the PES can be joined in a displaced harmonic term,

$$\begin{aligned} V(v_1, v_2, \mathbf{Q}) &= \tilde{U}(v_1, v_2) - E^Q(v_1, v_2) \\ &+ \frac{1}{2} \sum_{i,j} K_{ij}(x, y) (Q_i - Q_i^{(0)})(Q_j - Q_j^{(0)}), \end{aligned} \quad (5.21)$$

where the so-called *reorganization energy*,

$$E^Q(v_1, v_2) = \frac{1}{2} \sum_{i,j} K_{ij}(v_1, v_2) Q_i^{(0)} Q_j^{(0)}, \quad (5.22)$$

is introduced.

In analogy to Eq. (5.19), the vector $\mathbf{Q}^{(0)}$ can be divided according to

$$\mathbf{Q}^{(0)} = \begin{pmatrix} \mathbf{q}^{(0)} \\ \mathbf{S}^{(0)} \end{pmatrix}. \quad (5.23)$$

Formally, the coupling between model coordinates and spectator modes is assumed to be negligible. Then, the number of actual DOF of the PES can be reduced by setting,

$$\mathbf{S} \equiv \mathbf{S}^{(0)}(v_1, v_2). \quad (5.24)$$

This choice is preferred among all other possible choices, because even when there is a small coupling that is not strictly negligible, the energetics of the reduced dimensional PES is still equivalent to the full-dimensional one, i.e., the barrier height is the same. The reduced-dimensional PES reads,

$$\begin{aligned} V(v_1, v_2, \mathbf{q}) &= V_{\text{eff}}(v_1, v_2) - E^S(v_1, v_2) - E^{Sq}(v_1, v_2) \\ &- \sum_i F_i^q(v_1, v_2) q_i + \frac{1}{2} \sum_{i,j} K_{ij}^q(v_1, v_2) q_i q_j, \end{aligned} \quad (5.25)$$

with abbreviations,

$$E^S = \frac{1}{2} \sum_{i,j} K_{ij}^S S_i^{(0)} S_j^{(0)}, \quad (5.26)$$

$$E^{Sq} = \sum_{ij} K_{ij}^{Sq} S_i^{(0)} q_j^{(0)}, \quad (5.27)$$

$$F_i^q = \sum_j K_{ij}^q q_j^{(0)}, \quad (5.28)$$

$$V_{\text{eff}} = \tilde{U} + \frac{1}{2} \sum_i \hbar \omega_i^S. \quad (5.29)$$

The superscript ‘S’ (‘q’) for K_{ij}^S (K_{ij}^q) means to keep only that rows and columns of K_{ij} that correspond to spectator modes S_j (relevant modes q_j). Likewise, the superscript ‘Sq’ means to keep only that rows of matrix K_{ij} that correspond to spectator modes S_j and that columns that correspond to modes q_j . The reorganization energy consists of a direct term Eq. (5.26), corresponding to the reorganization of the spectator modes, and a cross-term Eq. (5.27) corresponding to the coupling of spectator modes and relevant modes.

The second term on the r.h.s. of Eq. (5.29) corresponds to the zero-point energy (ZPE) of the spectator modes. It is computed by diagonalizing \mathbf{K}^S for

each value of (v_1, v_2) yielding a set of n' frequency functions $\omega_i^S = \omega_i^S(v_1, v_2)$. The inclusion of this term into the reduced-dimensional PES is motivated by the adiabatic approximation; the change of frequencies of many modes may lead to a contribution to the potential, that would have been neglected otherwise.

Reaction plane coordinates

The minima and the transition state geometries are points on the reaction plane. Therefore, the choice of a fixed reference, $\mathbf{Q}^{\text{ref}} \equiv 0$, is reasonable. This implies, $\mathbf{X}_0(w_1, w_2) = \mathbf{X}_{\text{TS}} + w_1 \mathbf{w}_1 + w_2 \mathbf{w}_2$. Let \mathcal{Q} denote the projection operator onto the n -dimensional subspace spanned by the relevant modes \mathbf{q} . Diagonalization of the matrix,

$$(\mathbf{I} - \mathcal{P} - \mathcal{Q}) \mathbf{K}^{(f)}|_{\mathbf{x}_0} (\mathbf{I} - \mathcal{P} - \mathcal{Q}), \quad (5.30)$$

for each fixed value of (w_1, w_2) yields n' non-vanishing eigenvalues $\omega_k^2(w_1, w_2)$ for the spectator modes as a function of the reaction plane coordinates. The PES in terms of the model coordinates is given by Eq. (5.11) with $\mathbf{S} \equiv 0$ plus an intuitive ZPE term (see above),

$$\begin{aligned} V(w_1, w_2, \mathbf{q}) = & U(w_1, w_2) - \sum_i^n F_i(w_1, w_2) q_i \\ & + \frac{1}{2} \sum_{ij}^n K_{ij}(w_1, w_2) q_i q_j + \frac{1}{2} \sum_i^{n'} \hbar \omega_i(w_1, w_2). \end{aligned} \quad (5.31)$$

For all three extremal points of the reduced PES, $\mathbf{q} = 0$ holds. Furthermore, neglecting the ZPE term, the energetics of the reduced PES, e.g., the barrier height, is identical to the full PES *by definition* of the reaction plane. This is a very important feature of the present formulation, which distinguishes it from the choice of atomic reaction coordinates according to Ref. [42], because one does not need to include relaxed spectator modes in order to yield the same PES energetics as in the full dimensional case (see, for instance, Ref. [150]).

The dipole function of the reduced model can be approximately expressed in a similar manner. For numerical convenience, only the first derivative with respect to the reaction plane is employed while the dipole function is treated numerically exact on the reaction plane. The approximation reads

$$\mu_\alpha(w_1, w_2, \mathbf{q}) = \mu_\alpha^{(\text{full})}(w_1, w_2, \mathbf{q})|_{\mathbf{q}=0} + \sum_k \left. \frac{\partial \mu_\alpha^{(\text{full})}}{\partial q_k} \right|_{\mathbf{q}=0} q_k, \quad (5.32)$$

where $\mu_\alpha^{(\text{full})}$ is the full-dimensional dipole function and $\alpha = X, Y, Z$ is the Cartesian component of the dipole vector.

Reduced normal modes

In this Section generic reaction coordinates (including atomic and reaction plane coordinates) are considered. The model coordinates - except v_1 and v_2 - are arbitrary in the sense, that any linear combination of them will yield exactly the same results. There are three sets of coordinates, however, that are unique, these are - as in the full-dimensional system - the normal modes of the reduced $n + 2$ -dimensional system at the two symmetrically related minima and at the transition state. These normal modes are called *reduced* normal modes. By neglecting changes of the ZPE, which are small, one can compute, e.g., the reduced normal modes of the right minimum geometry by diagonalizing the Hessian

$$\mathcal{R} \mathbf{K}^{(f)}(\mathbf{X}_R) \mathcal{R}, \quad (5.33)$$

where \mathcal{R} is the projector onto the space span by the model coordinates $(v_1, v_2, q_1, \dots, q_n)$. The corresponding $n + 2$ reduced normal modes are denoted $\mathcal{Y}_k^{(n+2)D}$ with $k = 1, \dots, n + 2$ in the following. Recall that the vectors \mathbf{v}_1 and \mathbf{v}_2 are both N dimensional. Likewise, the vectors \mathbf{e}_j are N dimensional according to their definition by diagonalization of Expr. (5.7). Thus, the $(n + 2)$ -dimensional model coordinates define a $(n + 2)$ -dimensional subspace that is embedded in the full N dimensional space. This subspace is denoted the *reduced space*.

While for setting up the Hamiltonian it is most convenient to use model coordinates, all physically relevant quantities should be related to the unique reduced normal modes. Additionally, to analyze the connection of the reduced dimensional model with the full-dimensional system, one has to investigate overlaps of reduced normal modes with full normal modes. Full normal modes that correspond to the right minimum geometry are given by the diagonalization of the Hessian $\mathbf{K}(\mathbf{X}_R)$; these modes are denoted $\mathcal{Y}_j^{(f)}$. The task of computing overlaps between reduced and full normal modes can be achieved by defining a $N \times (n + 2)$ -matrix \mathbf{B} that transforms from the reduced space $(v_1, v_2, q_1, \dots, q_n)$ back into the full N dimensional Cartesian space:

$$\mathbf{B} = (\mathbf{v}_1 \ \mathbf{v}_2 \ \mathbf{q}_1 \ \dots \ \mathbf{q}_n), \quad (5.34)$$

where the vectors \mathbf{v}_1 , etc., i.e., those vectors that span the so-called reduced space, constitute the columns of the matrix. This matrix always exists by definition and the property,

$$\mathbf{B}^T \mathbf{B} = \mathbf{1}, \quad (5.35)$$

holds because the constituting vectors are orthonormal by definition.

There is overwhelming evidence, that molecular spectra may (at least partly) be understood in terms of harmonic transition frequencies corresponding to normal modes [19]. Thus, a reduced model should be characterized by overlaps with

certain full normal modes being close to one. Let $\mathcal{Y}_j^{(f)}$ with $j = 1, \dots, N - 6$ be the full normal modes corresponding to the right configuration \mathbf{X}_R , and let \mathcal{Y}_k be the reduced normal modes corresponding to the right minimum configuration $(v_1^{(min)}, v_2^{(min)}, \mathbf{q} = \mathbf{0})$. Then the projection of reduced normal mode k onto full normal mode j is given by:

$$p_{jk} = \left(\mathcal{Y}_j^{(f)} \right)^T \mathbf{B} \mathcal{Y}_k. \quad (5.36)$$

A practical method to achieve the goal of a large overlap is discussed in the following Chapter.

5.3 Summary

The CRS-Hamiltonian of Ruf and Miller [42] was generalized to account for generic reaction coordinates. In particular, two choices were discussed: (i) atomic reaction coordinates (as in Ref. [42]) and (ii) reaction plane coordinates. A reduced Hamiltonian according to choice (i) requires the inclusion of relaxed spectator modes in order to maintain the PES energetics. In contrast, the minima and the saddle point are points on the reaction plane. Thus, the PES energetics is correctly reproduced by any Hamiltonian based on choice (ii), no matter what approximation is applied for the treatment of the spectator modes.

The reaction plane coordinates were first introduced by Takada and Nakamura [75]. Yagi *et al.* [43] used the reaction plane as a starting manifold for the generation of points for a full-dimensional treatment of malonaldehyde. In their approach, the whole PES is approximated by a modified Shepard scheme (that was also used in the present work). The main advantage of the present method is, however, the fact that the PES can be written as a sum of products of function of the reaction coordinates (w_1, w_2) times the remaining coordinates \mathbf{q} . This makes an efficient application of the MCTDH approach possible [25] (cf. Sec. 2.3.1).

The reaction plane coordinates were also used by other authors. For instance, Hayashi and Mukamel [151] constructed a PES for malonaldehyde by using Taylor expansions at the two minima and the saddle point including partial derivatives of order three and higher, which are numerically demanding to obtain on an *ab-initio* level. In contrast, the present approach only relies on at most second order derivatives and treats the PES on the reaction plane numerically exact.

