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REGULAR ARTICLE

Rotational symmetry of the molecular potential energy in the Cartesian coordinates

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Abstract We consider the molecular Born-Oppenheimer potential energy as a function of atomic Cartesian coordinates and discuss the non-stationary Hessian properties arising due to rotational symmetry. A connection with the extended Hessian theory is included. New applications of Cartesian representation for examining and correcting raw numerical Hessian data and a simple formulation of harmonic vibrational analysis of partially optimized systems are proposed. Exemplary calculations for the porphyrin molecule with an internal proton transfer are reported. We also develop the normal transformation method to incorporate the rotational symmetry into the approximate analytical potentials, which are parametrized in the Cartesian coordinates. The transformation converts the coordinates from the space fixed frame to the frame which translates and rotates with the molecule and is determined by the Eckart conditions. New simple analytical formulas for the first and second derivatives of the transformed potential are derived. This fast method can be used to calculate the potential and its derivatives in the simulations of chemical reaction dynamics in the space fixed Cartesian frame without the need to constrain the molecular rotation or to define the local non-redundant internal coordinates.

Keywords Potential energy surface · Hessian · Rotations · Cartesian coordinates

1 Introduction

In the dynamics of chemical reactions, one often approximates the Born-Oppenheimer potential energy by an analytical function of the atomic coordinates. Such approximations allow for fast computing of the atomic forces in the classical dynamics, as well as of the higher derivatives which are useful e.g., in semi-classical Gaussian wave packets dynamics [1, 2]. Analytical potentials are in practice necessary for modeling the full quantum dynamics of the nuclei, for instance the proton transfer quantum dynamics [3], and for the mixed dynamical models with quantum description of the proton(s) and classical description of other nuclei, see e.g. [4, 5]. In the mixed models one needs an efficient method for "on the fly" computation of the whole potential energy surface for protons at instantaneous positions of the classical nuclei. To describe the evolution of the protonic quantum wave function, one may also need to localize the minima on the instantaneous protonic potential energy surface, and to determine the corresponding local normal modes, what makes the analytical second derivatives important. One of the analytical approximations of the potential, which can be used for the above purposes, is the modified Shepard interpolation, see e.g. [6–9]. It is based on the local Taylor expansions of the exact potential with respect to the atomic coordinates, and the expansions are centered in the stationary and non-stationary configurations which sample the dynamically accessible space. The values and derivatives of the exact potential in the expansion centers can be obtained from the high level ab initio or density functional electronic calculations. The expansions are usually limited to the local harmonic approximation (LHA) because only the first and second analytical derivatives are available from the high level calculations. A similar parameterization

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strategy based on LHAs can be implemented in the approximate valence bond potential (AVB, see e.g. [10]) and the AVB/LHA approach is currently being developed by the author and coworkers for intramolecular proton transfer. The motivation for the current study arose from the need for some auxiliary parameterization tools.

The simplest representation for the local Taylor expansion of the potential are the Cartesian coordinates, especially in case of large number of atoms. Unfortunately, a model potential expressed with the Cartesian LHA or the Shepard interpolation of several Cartesian LHAs is not invariant under molecular rotations, what should be the case for an isolated molecule. The problem is due to the fact that rotations of a molecule with fixed internal configuration and fixed center of mass yield a compact hypersurface in the multidimensional space of the atomic Cartesian coordinates, while the Cartesian LHA is constant on a hyperplane which represents local directions of infinitesimal rotations. The problem can be avoided by using the internal coordinates but then the computational simplicity is lost and some other limitations appear. For instance, when using the conventional Z-matrix representation one has to ensure the local, complete and non-redundant set of valence coordinates for a particular molecular topology, and to deal with complicated analytical derivatives, including the singularity problems. Furthermore sometimes it is difficult to define non-reduntant valence coordinates consistently with the molecular point symmetries. Other local, non-redundant, internal coordinates that avoid the symmetry problem can be constructed based on the reciprocal inter-atomic distances [8, 9]. Their additional advantage is a correct qualitative behavior of LHA both at small and large inter-atomic separations what allows to describe molecular association and dissociation [6, 9]. Unfortunately, inter-atomic distances are not complete coordinates for planar molecular geometries [9]. It follows that the Cartesian coordinates remain an interesting option for the bound systems with internal reactions, especially when planar geometries are involved, as in case of the aromatic molecules with internal proton transfer. In order to extend the validity of LHA one may also use special curvilinear valence coordinates [11] for selected reactive degrees of freedom (e.g. for the mobile protons) and retain the simple Cartesian representation for the rest of the molecule.

When parameterizing the potential in Cartesian coordinates one needs special tools for reproducing the molecular rotational symmetry. This symmetry is reflected in particular in the gradient and Hessian properties which can be accounted for even in the simplest LHA. It is a common approach to project out the spurious translational and rotational components from the Hessian in the stationary geometries. In this study, we extend this approach to the non-stationary case, allowing for correcting of raw numerical data which can be used in non-stationary LHA parameterization, and for normal mode analysis of partially optimized system. We also consider a method for ensuring rotational invariance of the potential described with an arbitrary analytic function of Cartesian coordinates. One of so-far proposed approaches to this problem was a generalization of the modified Shepard interpolation based on the invariant integral over molecular orientations [7]. Analytical derivatives of such potential were derived but are computationally very expensive. A rotation invariant potential can be also obtained in a simple way by transforming the molecule to a definite position and orientation prior to calculating the analytical function in the Cartesian coordinates. The orientation can be defined based on three atoms of the molecule [12, 13]. In this study, we consider a more general transformation, which both conserves the molecular point symmetries and provides inexpensive analytical first and second derivatives in Cartesian coordinates, which are simpler than those resulting from transforming from internal to Cartesian coordinates. Our approach can be applied to construct the total potential energy of an isolated molecule, as well as the intramolecular contribution to the total potential energy of a molecule in solution. The approximate potential can be combined with the classical, semi-classical, or mixed quantum-classical equations of motion for the atomic nuclei in the space fixed Cartesian frame, without the need of separating out the molecular rotations and translations.

2 Gradient and Hessian properties in Cartesian coordinates

Let $V(\mathbf{r})$ be the Born-Oppenheimer potential energy of an isolated molecule, where $\mathbf{r}$ is the $3N$-dimensional column vector of mass scaled Cartesian coordinates of N atomic nuclei. We use auxiliary notation $\mathbf{r} = \{\sqrt{m_i}\mathbf{R}_i\}_{i=1}^{N}$, where $\mathbf{R}_i$ are Cartesian vectors and m_i are atomic masses. Mass-scaling is irrelevant for the properties of the potential itself but it is included to simplify the further vibrational analysis. The translational and rotational symmetry can be expressed with the equation [14],

$$V(\mathbf{r}_{\mathrm{tr}}(\mathbf{r})) = V(\mathbf{r}), \qquad (1)$$

where $\mathbf{r} \rightarrow \mathbf{r}_{\mathrm{tr}}$ represents a molecular rotation or translation. In the latter case, we set $\mathbf{r}_{\mathrm{tr}}(\mathbf{r}) = \mathbf{r} + \mathbf{t}(\boldsymbol{\Lambda})$, where $\mathbf{t}(\boldsymbol{\Lambda}) = \{\sqrt{m_i}\boldsymbol{\Lambda}\}_{i=1}^{N}$ and $\boldsymbol{\Lambda}$ is a Cartesian vector.

Expanding (1) into Taylor series with respect to $\mathbf{\Lambda}$, and separating out the term of the first order, we derive

$$\mathbf{g}(\mathbf{r})^{\mathrm{T}}\mathbf{t}(\mathbf{\Lambda}) = 0. \tag{2}$$

Here $\mathbf{g}(\mathbf{r})^{\mathrm{T}} = \partial V/\partial \mathbf{r}$ is the gradient vector in a transposed (row) form. Differentiating the earlier equation with respect to $\mathbf{r}$ we further obtain

$$\hat{\mathbf{h}}(\mathbf{r})\mathbf{t}(\mathbf{\Lambda}) = 0, \tag{3}$$

where $\hat{\mathbf{h}}(\mathbf{r}) = \partial \mathbf{g}/\partial \mathbf{r}$ is the Hessian matrix. Consider now that $\mathbf{r} \to \mathbf{r}_{\mathrm{tr}}$ is a rotation, which can be also parameterized with a vector $\mathbf{\Lambda}$ whose modulus and orientation represent the clockwise rotation angle and the rotation axis, respectively. For convenience we assume that the rotation axis passes through the molecule's center of mass. The rotation can be expanded into the Taylor series with respect to $\mathbf{\Lambda}$,

$$\mathbf{r}_{\mathrm{tr}}(\mathbf{r}) = \mathbf{r} + \hat{\mathbf{u}}(\mathbf{\Lambda})\mathbf{r}' + O(\mathbf{\Lambda}^2), \tag{4}$$

where $\mathbf{r}' = \{\sqrt{m_i}\mathbf{R}'_i\}_{i=1}^{N}$ denotes coordinates relative to the molecular center of mass,

$$\mathbf{R}'_i = \mathbf{R}_i - \frac{1}{M}\sum_{j=1}^{N}\mathbf{R}_j, \quad M = \sum_{i=1}^{N} m_i, \tag{5}$$

and $\hat{\mathbf{u}}(\mathbf{\Lambda})\mathbf{r}' = \{\mathbf{\Lambda} \times \sqrt{m_i}\mathbf{R}'_i\}_{i=1}^{N}$ describes the linear component of the rotation (i.e., direction vector of the infinitesimal rotation). Substituting (4) in (1) and repeating the procedure as in case of (2) we derive,

$$\mathbf{g}(\mathbf{r})^{\mathrm{T}}\hat{\mathbf{u}}(\mathbf{\Lambda})\mathbf{r} = 0. \tag{6}$$

In the last equation we omitted, based on (2), the translation to the center of mass. Differentiating (6) with respect to $\mathbf{r}$ and taking into account that $\hat{\mathbf{u}} = -\hat{\mathbf{u}}^{\mathrm{T}}$ we obtain,

$$\hat{\mathbf{h}}(\mathbf{r})\hat{\mathbf{u}}(\mathbf{\Lambda})\mathbf{r} = \hat{\mathbf{u}}(\mathbf{\Lambda})\mathbf{g}(\mathbf{r}). \tag{7}$$

A particular form of this equation in case of planar molecule and in-plane rotation was discussed in [15]. Equations equivalent to (2–3) and (6–7) were also obtained in a more general group theoretical formulation [16].

The earlier results can be formulated in the orthonormal basis of translation and rotation vectors. Following a conventional procedure (see e.g. [17]), we determine Cartesian unit vectors, $\mathbf{\Lambda}_k(\mathbf{r})$, which describe principal axes of molecular inertia tensor, and the corresponding moments of inertia, I_k $(k = 1, 2, 3)$

$$\sum_{i=1}^{N} m_i\left[R_i'^2\mathbf{\Lambda}_k - \mathbf{R}'_i(\mathbf{R}_i'^{\mathrm{T}}\mathbf{\Lambda}_k)\right] = I_k\mathbf{\Lambda}_k. \tag{8}$$

In the case of degenerated moments, $I_k = I_l$, we additionally apply the orthogonality condition, $\mathbf{\Lambda}_k^{\mathrm{T}}\mathbf{\Lambda}_l = \delta_{kl}$. It is hereafter assumed that $N > 2$ and that the molecule is non-linear what ensures that all three I_k moments are non-zero. The corresponding orthonormal translation and rotation vectors are $(k = 1, 2, 3)$,

$$\mathbf{t}_k(\mathbf{r}) = \frac{\mathbf{t}(\mathbf{\Lambda}_k)}{\sqrt{M}}, \quad \mathbf{e}_k(\mathbf{r}) = \frac{\hat{\mathbf{u}}(\mathbf{\Lambda}_k)\mathbf{r}'}{\sqrt{I_k}}. \tag{9}$$

One also defines the vibrational projection matrix $\hat{\mathbf{p}}$,

$$\hat{\mathbf{p}}(\mathbf{r}) = \hat{\imath} - \sum_{k=1}^{3}(\mathbf{e}_k\mathbf{e}_k^{\mathrm{T}} + \mathbf{t}_k\mathbf{t}_k^{\mathrm{T}}), \tag{10}$$

where $\hat{\imath}$ denotes the $3N$-dimensional identity matrix. Notice that in case of linear molecules one could define the projection matrix with three translational and two rotational vectors, however, a general expression is missing which could encompass both linear and non-linear cases. The projection in the form $\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}}$ is commonly applied in quantum chemistry to the Hessians in the stationary configurations. We extend this approach to the non-stationary case and combine Eqs. (2–3), (6) and (7) together to the following form,

$$\mathbf{g} = \hat{\mathbf{p}}\mathbf{g}, \tag{11}$$

$$\hat{\mathbf{h}} = \hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}} + \delta\hat{\mathbf{h}}_{\mathrm{g}}, \tag{12}$$

where we denoted the gradient-dependent Hessian component,

$$\delta\hat{\mathbf{h}}_{\mathrm{g}} = \sum_{k=1}^{3}(\mathbf{f}_k\mathbf{e}_k^{\mathrm{T}} + \mathbf{e}_k\mathbf{f}_k^{\mathrm{T}}) - \sum_{k,l=1}^{3}\mathbf{e}_k(\mathbf{e}_k^{\mathrm{T}}\mathbf{f}_l)\mathbf{e}_l^{\mathrm{T}}, \tag{13}$$

and an auxiliary vector $(k = 1, 2, 3)$,

$$\mathbf{f}_k = \frac{\hat{\mathbf{u}}(\mathbf{\Lambda}_k)\mathbf{g}}{\sqrt{I_k}}. \tag{14}$$

Equations (11–14) describe the rotational and translational symmetry of the potential derivatives in Cartesian coordinates in the general case of non-stationary geometry. It can be deduced from (12) that in contrast to the projected Hessian, $\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}}$, the full non-stationary Hessian, $\hat{\mathbf{h}}$, may have up to three non-zero rotational eigenvalues [15, 18]. For a simple algebraic description of this phenomenon in a diatomic molecule the reader may see e.g. [22]. Furthermore, the $\mathbf{f}_k$ vectors may have both the rotational and the vibrational components, ($\mathbf{e}_l^{\mathrm{T}}\mathbf{f}_k$ and $\hat{\mathbf{p}}\mathbf{f}_k$, respectively, where k, $l = 1, 2, 3$), what destroys the separation into the pure vibrational and rotational eigenvectors in non-stationary geometries.

The Cartesian Hessian can be also considered as a special case of a more general Riemannian representation. Let $\mathbf{r} = \mathbf{r}(q)$, where $q = \{q^i\}_{i=1}^{3N}$ are locally complete generalized coordinates, for instance the internal and external (rotation and translation) coordinates. Given the potential function, $U(q) = V(\mathbf{r}(q))$, one defines the covariant second derivatives, also refered to as the extended Hessian [19, 20] or simply the Hessian [21, 22] ($i, j, k \leq 3N$),

$$H_{ij} = (U)_{ij} - \Gamma^{k}_{ij}(U)_{k}. \tag{15}$$

Here the abbreviation $(\cdot)_i = \partial(\cdot)/\partial q^i$ and the Einstein summation are used. Other denotations are: the Christoffel symbol of the second kind, $\Gamma^k_{ij} = G^{nk}[(G_{ni})_j + (G_{nj})_i - (G_{ij})_n]/2$, the metric tensor, $G_{nk} = (\mathbf{r})^{\mathrm{T}}_n(\mathbf{r})_k$, the inverse tensor, G^{nk}. Applying the chain rule for U derivatives, and taking into account a property $(\mathbf{r})_{ij} = (\mathbf{r})_k\Gamma^k{}_{ij}$, one can transform (15) into a simple relation which links the Riemannian and Cartesian Hessians, $H_{ij} = (\mathbf{r})^T_i\hat{\mathbf{h}}(\mathbf{r})_j$. When using the Riemannian representation one can determine the set of $3N$ frequencies, ν, and generalized normal mode vectors, ν, from the equation $H_{ij}\nu^j{}_k = \nu^2{}_k G_{ij}\nu^j{}_k$, see e.g. [19]. It can be checked that the same frequencies result from the Cartesian normal mode equation, $\hat{\mathbf{h}}\mathbf{v}_k = \nu^2_k\mathbf{v}_k$, and that $\mathbf{v}_k = (\mathbf{r})_i\nu^i_k$. The above considerations are valid for arbitrary complete coordinates q, and they confirm that the extended Hessian's spectrum is coordinate-independent [21, 22]. The $\mathbf{r}(q)$ transformation can be defined in a particular way so that $\hat{\mathbf{p}}(\mathbf{r})_i = (\mathbf{r})_i$ for internal coordinates ($i \leq 3N - 6$) and $\hat{\mathbf{p}}(\mathbf{r})_i = 0$ for external coordinates ($i = 3N - 5,\ldots,3N$), see e.g. [24]. In this case, the Cartesian projected Hessian, $\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}}$, corresponds to the internal block of H, whereas the component $\delta\hat{\mathbf{h}}_g$ corresponds to the rotational and rotational-internal elements of H. The extended Hessian can be used for coordinate-invariant analysis of the potential surface in non-stationary geometries including quantum zero-point correction [20], the steepest descent path [21] and the instantaneous normal mode analysis of liquid dynamics [22, 23]. The above problems can be considered either in the full space of internal and external coordinates or in the internal subspace, which is equivalent with using $\hat{\mathbf{h}}$ or $\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}}$, respectively.

3 Applications in the non-stationary Hessian analysis

The preceding section described the case of ideal potential, where the Hessian's rotational components are due to a non-zero gradient. However, the raw gradient and Hessian data generated by computer programs for quantum chemistry may include also spurious translational and rotational components which are due to numerical errors. Given the raw Hessian, $\hat{\mathbf{h}}_{\mathrm{r}}$, one can eliminate its components of the latter type and derive the symmetry-corrected Hessian in the general case of non-stationary geometry

$$\hat{\mathbf{h}}_{\mathrm{g}} = \hat{\mathbf{p}}\hat{\mathbf{h}}_{\mathrm{r}}\hat{\mathbf{p}} + \delta\hat{\mathbf{h}}_{\mathrm{g}}, \tag{16}$$

where $\delta\hat{\mathbf{h}}_{\mathrm{g}}$ is calculated from (13–14) using the symmetry-corrected gradient, $\hat{\mathbf{p}}\mathbf{g}_{\mathrm{r}}$. The corrected Hessian can be used for analyzing of the quantum potential surface, as well as for parameterizing the approximate analytical potentials as discussed in the next section. The earlier formula is a generalization of the projected Hessian, $\hat{\mathbf{h}}_{\mathrm{p}} = \hat{\mathbf{p}}\hat{\mathbf{h}}_{\mathrm{r}}\hat{\mathbf{p}}$, which is used in the standard vibrational analysis in the stationary geometries. In the standard analysis, one often performs a preliminary calculation to check whether the rotational and translational frequencies of the raw Hessian are close to zero, what indicates that stationary geometry was sufficiently optimized [25]. This test can be extended by analyzing also the $\hat{\mathbf{h}}_{\mathrm{g}}$ matrix, which reveals the rotational components due to the incomplete optimization but excludes the components caused by numerical errors. If the rotational frequency magnitudes of $\hat{\mathbf{h}}_{\mathrm{g}}$ are as large as those of $\hat{\mathbf{h}}_{\mathrm{r}}$, then the vibrational analysis can be improved by more accurate geometry optimization. The above approach can be also applied to Hessians obtained from molecular mechanics or coarse-grained potentials for molecular clusters and macromolecules.

Another potential application of Eq. (12) is the normal mode analysis of partially optimized systems. Consider a non-optimized system with all fixed atoms apart from those in a small subsystem. The subsystem can be optimized and be subject of the vibrational analysis. For simplicity we assume that atoms in the optimized part are labelled with $i \leq n$ ($n < N$). The normal mode analysis can be performed in the $3n$-dimensional configuration subspace of the optimized subsystem what is equivalent to analyzing the following $3N$-dimensional Hessian,

$$\hat{\mathbf{h}}_0 = \begin{bmatrix} \{h_{ij}\}^{3n}_{i,j=1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix}. \tag{17}$$

The zero elements can be interpreted as resulting from infinite atomic masses in the non-optimized part of the molecule. In the partial Hessian vibrational analysis (PHVA) the projected matrix, $\hat{\mathbf{h}}_{\mathrm{P}} = \hat{\mathbf{p}}\hat{\mathbf{h}}_0\hat{\mathbf{p}}$, is further derived in order to exclude the contributions of the overall rotations and translations from the partial modes and from related quantities, such as vibrational enthalpy and entropy [26]. The use of the projection operator is not quite consistent with the assumption of infinite atomic masses in the non-optimized part of the system. This problem is avoided in the mobile block Hessian (MBH) approach where the non-optimized part is treated as a rigid body composed of atoms with finite masses and moving with respect to the optimized part [16, 27]. The approach was first formulated in the internal coordinates, and later in the Cartesian representation based on the group theoretical concepts [16]. Another and simpler formulation in the Cartesian representation is presented below. Let $\delta\mathbf{r}$ denote a small time-dependent deformation from the fixed configuration $\mathbf{r}$. The Lagrangian in the LHA is,

$$L(\delta\mathbf{r},\delta\dot{\mathbf{r}}) = \frac{1}{2}|\delta\dot{\mathbf{r}}|^2 - \left[V(\mathbf{r}) + \mathbf{g}^{\mathrm{T}}\delta\mathbf{r} + \frac{1}{2}\delta\mathbf{r}^{\mathrm{T}}\hat{\mathbf{h}}\delta\mathbf{r}\right]. \tag{18}$$

We introduce the generalized rectilinear coordinates, $q = \{q^i\}_{i=1}^{3n}$, which describe deformations in the optimized part excluding the contributions from the molecular rotations and translations,

$$\delta\mathbf{r}(q) = \hat{\mathbf{p}}\mathbf{n}_i q^i. \tag{19}$$

Here $\mathbf{n}_i$ denotes a constant $3N$-dimensional vector with all coordinates equal to 0, except for the ith coordinate which is equal to 1, and hereafter we use the Einstein summation in the range 1,...,$3n$. From the partial optimization it follows that $\mathbf{g}^{\mathrm{T}}\delta\mathbf{r}$ (q) = 0. Substituting (19) to (18) we derive,

$$L(q,\dot{q}) = \frac{1}{2}p_{ij}\dot{q}^i\dot{q}^j - V - \frac{1}{2}H_{ij}q^iq^j, \tag{20}$$

where $p_{ij} = \mathbf{n}_i^{\mathrm{T}}\hat{\mathbf{p}}\mathbf{n}_j$ are the elements of the projection matrix, which here plays the role of the constant metric tensor, and $H_{ij} = \mathbf{n}_i^{\mathrm{T}}(\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}})\mathbf{n}_j$ are the elements of the partial Hessian $(i, j \le 3n)$. Based on Eq. (12) we substitute $\hat{\mathbf{p}}\hat{\mathbf{h}}\hat{\mathbf{p}} = \hat{\mathbf{h}} - \delta\hat{\mathbf{h}}_{\mathrm{g}}$, and by taking into account that $\mathbf{n}_i^{\mathrm{T}}\mathbf{f}_k = 0$ $(i \le 3n$, $k \le 3)$, we obtain a practical formula $(i, j \le 3n)$,

$$H_{ij} = h_{ij} + \sum_{k,l=1}^{3} e_{ki}e_{lj}(\mathbf{e}_k^{\mathrm{T}}\mathbf{f}_l), \tag{21}$$

where e_{ki} denote elements of the $\mathbf{e}_k$ vectors. From (20) we derive the normal mode equation for the vibrational frequencies, ν, and generalized normal mode vectors, v $(i$, j, $k \le 3n)$,

$$H_{ij}v_k^j = \nu_k^2 p_{ij}v_k^j. \tag{22}$$

The solution is obtained in the transformed representation $\tilde{H}_{ij}\tilde{v}_k^j = \nu_k^2\tilde{v}_k^j$, where $\tilde{H} = p^{-\frac{1}{2}}Hp^{-\frac{1}{2}}$, and $\tilde{v} = p^{\frac{1}{2}}v$. The corresponding $3N$-dimensional normal mode vectors are $\mathbf{v}_k = \hat{\mathbf{p}}\mathbf{n}_i v_k^i$ $(k \le 3n)$. The results are equivalent to those arising from the earlier formulations of the MBH method. Notice that the present approach can be also applied to the optimized fragments in macromolecules without the need to determine and diagonalize the full multi-dimensional Hessian. The methods discussed in this section can be also applied to the protonic energy surface at instantaneous non-stationary positions of heavy atoms in the molecule, as presented further in this study.

4 Cartesian potential invariant under rotations

The Born-Oppenheimer potential energy of an isolated molecule can be approximated in a limited domain in the configuration space with an expression,

$$V_{\mathrm{inv}}(\mathbf{r}) = V_{\mathrm{c}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r})), \tag{23}$$

where $V_{\mathrm{c}}(\mathbf{r})$ is an analytical function of atomic Cartesian coordinates, and $\mathbf{r}_{\mathrm{n}}(\mathbf{r})$ is hereafter called the normal transformation which includes translation and rotation of the molecule to a definite position and orientation,

$$\mathbf{r}_{\mathrm{n}}(\mathbf{r}) = \hat{\mathbf{w}}(\mathbf{r}')\mathbf{r}' = \{\sqrt{m_i}\hat{\mathbf{W}}(\mathbf{r}')\mathbf{R}_i'\}_{i=1}^{N}. \tag{24}$$

Here the prime sign denotes a translation according to Eq. (5) and $\hat{\mathbf{W}}(\mathbf{r})$ is a three-dimensional orthogonal matrix which describes a finite rotation of vectors in the Cartesian frame. The function $\hat{\mathbf{W}}(\mathbf{r})$ is designed to make the normal transformation to be invariant under the rotation of $\mathbf{r}$. In one of the approaches the $\mathbf{r}_{\mathrm{n}}(\mathbf{r})$ transformation yields a definite relative orientation of selected three atoms in the molecule [12] but this choice is not convenient for calculating the Cartesian derivatives and may violate the symmetry of the potential energy surface around a configuration with a point symmetry. Another solution is to set the principal axes of the molecular tensor of inertia in directions of the reference Cartesian system. The corresponding rotation matrix has a simple $(\boldsymbol{\Lambda}_1, \boldsymbol{\Lambda}_2, \boldsymbol{\Lambda}_3)$ form, however, this method is problematic when molecular inertia tensor has degenerated eigenvalues and indefinite principal axes. In order to obtain an unambiguous and continuous transformation we chose the rotation matrix $\hat{\mathbf{W}}(\mathbf{r})$, which minimizes the configuration distance $\delta^2 = |\mathbf{r}_{\mathrm{n}}(\mathbf{r}) - \mathbf{r}_0|^2$,where $\mathbf{r}_0$ is a fixed reference configuration such that $\mathbf{r}_0^{\prime} = \mathbf{r}_0$. Minimizing δ^2 with respect to elements of the rotation matrix under the orthogonality constraint, $\hat{\mathbf{W}}^{-1} = \hat{\mathbf{W}}^{\mathrm{T}}$, yields the following equation [7],

$$\left(\hat{\mathbf{S}}\hat{\mathbf{S}}^{\mathrm{T}}\right)^{\frac{1}{2}}\hat{\mathbf{W}} = \hat{\mathbf{S}}, \tag{25}$$

where $\hat{\mathbf{S}}$ denotes an auxiliary matrix,

$$\hat{\mathbf{S}} = \sum_{i=1}^{N} m_i\mathbf{R}_{0i}\mathbf{R}_i^{\mathrm{T}}, \tag{26}$$

and $\mathbf{R}_{0i}$ are atomic Cartesian vectors in configuration $\mathbf{r}_0$. The square root in (25) is calculated by taking the positive roots of all eigenvalues of the $\hat{\mathbf{S}}\hat{\mathbf{S}}^{\mathrm{T}}$ matrix what corresponds to the proper rotation [7]. Notice that in case of planar configurations one eigenvalue is zero. In practice it is convenient to determine the $\hat{\mathbf{W}}(\mathbf{r})$ elements from two equations, which result from the projection of Eq. (25) on the directions of the two eigenvectors of $\hat{\mathbf{S}}\hat{\mathbf{S}}^{\mathrm{T}}$ corresponding to highest eigenvalues, and from the third equation representing the orthogonality condition. This method provides numerically smooth results for both planar and non-planar configurations.

By definition $\hat{\mathbf{W}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r}))$ is the identity matrix, and in this case Eq. (25) reads $\hat{\mathbf{S}} = \hat{\mathbf{S}}^{\mathrm{T}}$ what is equivalent to,

$$\sum_{i=1}^{N} m_i \mathbf{R}_{0i} \times (\mathbf{R}_{\mathrm{n}i} - \mathbf{R}_{0i}) = 0, \tag{27}$$

where $\mathbf{R}_{\mathrm{n}i}$ are atomic Cartesian vectors in configuration $\mathbf{r}_{\mathrm{n}}(\mathbf{r})$. Equation (27) together with $(\mathbf{r} - \mathbf{r}_0)' = 0$ are known as the Eckart conditions [14, 28]. The $\mathbf{r}_{\mathrm{n}}(\mathbf{r})$ vector represents the mass-scaled atomic Cartesian coordinates in a molecule-fixed frame, which is determined by the molecular normal axes [14], and hence we use the name of the normal transformation. Calculating and rearranging scalar triple products of Eq. (27) with vectors $\boldsymbol{\Lambda}_k(\mathbf{r}_0)$, we get an equivalent equation ($k = 1, 2, 3$),

$$\mathbf{e}_k(\mathbf{r}_0)^{\mathrm{T}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r}) - \mathbf{r}_0) = 0, \tag{28}$$

which is essential for obtaining analytical derivatives of the normal transformation. The latter are described with a matrix, $\hat{\mathbf{a}} = \partial \mathbf{r}_{\mathrm{n}}/\partial \mathbf{r}$ matrix, and a tensor of rank 3, $\hat{\mathbf{b}} = \partial \hat{\mathbf{a}}/\partial \mathbf{r}$, which are calculated in the Appendix. Derivatives of the invariant potential can be calculated using the chain rule,

$$\mathbf{g}_{\mathrm{inv}} = \hat{\mathbf{a}}^{\mathrm{T}} \mathbf{g}_{\mathrm{c}}, \tag{29a}$$

$$\hat{\mathbf{h}}_{\mathrm{inv}} = \hat{\mathbf{a}}^{\mathrm{T}} \hat{\mathbf{h}}_{\mathrm{c}} \hat{\mathbf{a}} + \hat{\mathbf{b}}^{\mathrm{T}} \mathbf{g}_{\mathrm{c}}, \tag{29b}$$

where $\mathbf{g}_{\mathrm{c}}^{\mathrm{T}} = \partial V_{\mathrm{c}}(\mathbf{r})/\partial \mathbf{r}$ and $\hat{\mathbf{h}}_{\mathrm{c}} = \partial \mathbf{g}_{\mathrm{c}}(\mathbf{r})/\partial \mathbf{r}$. The matrix transposition in (29a) is consistent with the expression for elements of the $\mathbf{g}_{\mathrm{inv}}$ vector, $\partial V_{\mathrm{inv}}/\partial r_i = (\partial \mathbf{r}_{\mathrm{n}}/\partial r_i)^{\mathrm{T}} \mathbf{g}_{\mathrm{c}}$, where r_i ($i = 1,\ldots,3N$) are elements of $\mathbf{r}$. Calculating the derivatives of the invariant potential can be simplified based on a property which can be derived from considering the molecular translation and rotation in the space fixed Cartesian frame, $\mathbf{r} \to \mathbf{r}' \to \mathbf{r}_{\mathrm{n}}(\mathbf{r}) = \hat{\mathbf{w}}\mathbf{r}'$. During this transformation the atomic force vectors related with a rotation invariant potential should behave like $\mathbf{g}_{\mathrm{inv}}(\mathbf{r}) = \mathbf{g}_{\mathrm{inv}}(\mathbf{r}') \to \mathbf{g}_{\mathrm{inv}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r})) = \hat{\mathbf{w}}\mathbf{g}_{\mathrm{inv}}(\mathbf{r})$. This reasoning can be also used for the Hessian eigenvectors, and we derive that,

$$\mathbf{g}_{\mathrm{inv}}(\mathbf{r}) = \hat{\mathbf{w}}^{\mathrm{T}} \mathbf{g}_{\mathrm{inv}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r})), \tag{30a}$$

$$\hat{\mathbf{h}}_{\mathrm{inv}}(\mathbf{r}) = \hat{\mathbf{w}}^{\mathrm{T}} \hat{\mathbf{h}}_{\mathrm{inv}}(\mathbf{r}_{\mathrm{n}}(\mathbf{r}))\hat{\mathbf{w}}, \tag{30b}$$

where $\hat{\mathbf{w}}^{\mathrm{T}} = \hat{\mathbf{w}}^{-1}$ is the inverse rotation. It follows that it is sufficient to determine quantities $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}^{\mathrm{T}}\mathbf{g}_{\mathrm{c}}$ in the configuration $\mathbf{r}_{\mathrm{n}}(\mathbf{r})$, what is shown in the Appendix. with the final results given in Eqs. (42–43). The corresponding form of (29b) in a configuration such that $\mathbf{r}_{\mathrm{n}}(\mathbf{r}) = \mathbf{r}$ is,

$$\hat{\mathbf{h}}_{\mathrm{inv}} = \hat{\mathbf{a}}^{\mathrm{T}}(\hat{\mathbf{h}}_{\mathrm{c}} - \delta\hat{\mathbf{h}}_{\mathrm{g}})\hat{\mathbf{a}} + \delta\hat{\mathbf{h}}_{\mathrm{g}}, \tag{31}$$

where $\delta\hat{\mathbf{h}}_{\mathrm{g}}$ is the gradient-dependent Hessian component (13–14) corresponding to the gradient $\mathbf{g}_{\mathrm{inv}}$. Expressions (29a), (31) and (30a, 30b) are used to compute the analytical gradient and Hessian of the invariant potential $V_{\mathrm{inv}}(\mathbf{r})$ at arbitrary configuration $\mathbf{r}$. In a configuration such that $\mathbf{r}_{\mathrm{n}}(\mathbf{r}) = \mathbf{r}$ an additional relation, $\mathbf{a}^{\mathrm{T}}\hat{\mathbf{p}} = \hat{\mathbf{p}}$ can be derived from (42). One can further show that if $\mathbf{g}_{\mathrm{c}}$ and $\hat{\mathbf{h}}_{\mathrm{c}}$ have correct rotational symmetry then the Eqs. (29a) and (31) yield $\mathbf{g}_{\mathrm{inv}} = \mathbf{g}_{\mathrm{c}}$ and $\hat{\mathbf{h}}_{\mathrm{inv}} = \hat{\mathbf{h}}_{\mathrm{c}}$, respectively, what implies that the normal transformation does not disturb the Hessian and gradient parameterization in the LHA.

According to the discussion following Eq. (41) in the Appendix, the normal transformation is differentiable if the rotation vectors $\mathbf{e}_k\,(\mathbf{r})$ are linearly dependent on the vectors $\mathbf{e}_k(\mathbf{r}_0)$ ($k = 1, 2, 3$). This condition is satisfied for geometries $\mathbf{r}$ which are close to the reference geometry $\mathbf{r}_0$, what makes the current approach useful for describing vibrations and intramolecular chemical reactions which do not deform substantially the overall molecular shape corresponding to $\mathbf{r}_0$ (see the example in the next section). In general, it is convenient to select $\mathbf{r}_0$ with the highest point group symmetry that can be assumed by the molecule. If the system includes two or more protons which may exchange the positions during dynamics, one can set the same $\mathbf{R}_0$ location for protons, so as the normal transformation is invariant under the exchange. If the dynamics involves excessive changes of molecular conformation, one may use the normal transformation with multiple local reference configurations. Such approach can be consistently implemented in the modified Shepard interpolation and other methods which are also based on combining the multiple local approximations of the potential.

5 Examples

The methods derived in this study were tested on an isolated porphyrin molecule in the ground electronic state. Porphyrin serves as a prototype for a family of molecules which play an important role in many biological processes, including the tautomerization, and are subject of intense studies, for review see e.g. [29]. The Gaussian program [30] was used to obtain stationary configurations and analytical derivatives with the B3LYP/6-31G(d,p) method and with standard setup of other parameters for electronic calculations. Porphyrin has two mobile protons which can move between four nitrogen atoms. The global minimum of the potential is in the *trans* (t) configuration with protons bound to α and γ, or equivalently β and δ nitrogen atoms, see Fig. 1. The potential has also local minima in the *cis* (c) configuration, with protons located in neighbour sites (α and β or β and γ etc), and the transitions states, *tc* and *tt*, corresponding to single and double proton transfers from t to c and from t to t states, respectively. All these states have planar geometry. In Table 1, we reported the residual gradients and the rotation frequency magnitudes in the stationary configurations including various approximations of t obtained with coarse, tight or very tight (vtight) optimizations. Notice that the rotation frequencies of the raw

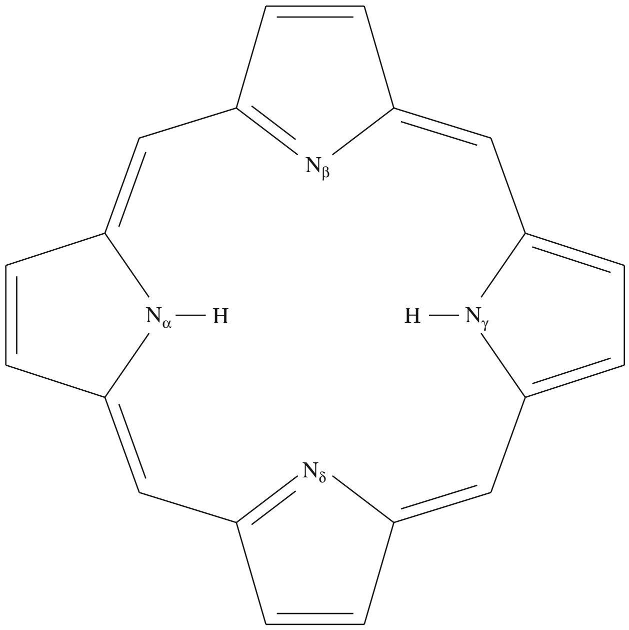

Fig. 1 Porphyrin in one of the equivalent trans (*t*) configurations

Hessian (ν_r^{rot}) are due to the numerical errors in the electronic calculations as well as due to the non-zero residual gradient. The numerical factor is dominant and is responsible for the rotational frequencies of magnitude 5–10 cm^{-1} at all tested optimization levels. In contrast, the frequencies of the corrected Hessian (ν_g^{rot}) are due to the gradient only and are less than 1 cm^{-1} for all tightly optimized configurations. The translation frequencies are negligible (below 0.05 cm^{-1}) in all cases. We also calculated the optimization-dependent vibrational frequency errors from the projected Hessians in approximate *t* configurations using as a reference the vtight spectrum. The results are presented in Table 1 and show that the vibrational spectrum has already converged at tight optimization. Similar results were also obtained for the finite difference Hessian at tight *t* optimization, $\nu_r^{rot} = 5.5$ cm^{-1} and $\Delta\nu_p^{vib} = 0.4$ cm^{-1}.

Table 1 Gradient norms, |**g**|, rotational frequency magnitudes, ν^{rot}, and vibrational frequency errors, $\Delta\nu^{vib}$ (in cm^{-1}), in the stationary configurations

Config.	|**g**| [au]	ν_r^{rot}	ν_g^{rot}	$\Delta\nu_p^{vib}$
c tight	7×10^{-6}	9.9	0.6	–
tc tight	8×10^{-6}	5.8	0.7	–
tt tight	1×10^{-5}	7.3	0.5	–
t coarse	2×10^{-3}	6.8	4.9	7.2
t coarse	2×10^{-4}	4.9	1.5	0.7
t tight	1×10^{-5}	4.7	0.4	0.0
t vtight[a]	2×10^{-6}	4.7	0.2	0[a]

The rotational frequencies were obtained from the $\hat{\mathbf{h}}_r$, and $\hat{\mathbf{h}}_g$ Hessians and the vibrational frequencies from the $\hat{\mathbf{h}}_p$ Hessian

[a] Reference for vibrational frequencies

Table 2 Rovibrational frequencies (ν_g), symmetry corrections ($\Delta\nu_{rg} = \nu_r - \nu_g$) and the projected vibrational frequencies (ν_p) in t' and t, as well as the approximate rovibrational frequencies derived in t' from the *t*-centered LHA (see text for details)

$\nu_g(t')$	$\Delta\nu_{rg}(t')$	$\nu_p(t')$	$\nu_p(t)$	$\nu_g^{LHA}(t')$
−104.6	0.0	−104.6	95.1	95.1
100.5	0.0	100.5	55.5	55.5
−91.0	−0.2	−69.9	133.3	−61.2
−25.2	0.2			134.7
−15.0	−5.1	23.8	98.9	7.7
26.9	2.5			99.0
18.3	0.0	18.3	66.7	66.7
35.2	0.2	0.0	0.0	13.5

The imaginary frequencies are shown as negative numbers

The exemplary non-stationary configuration, t', was constructed from *t* by moving the protons from α and γ to β and δ nitrogens. The protonic coordinates were further locally optimized at fixed locations of other atoms, so as the ring geometry could not adapt to the modified protonation state, yielding the total gradient $|\mathbf{g}| = 5 \times 10^{-2}$ au. The spectra of the $\hat{\mathbf{h}}_r$, $\hat{\mathbf{h}}_g$ and $\hat{\mathbf{h}}_p$ Hessians in the t' configuration differ only in the lowest frequency range, which is presented in Table 2. The corresponding modes of the full and projected Hessians were assigned by finding eigenvectors pairs with high overlap, $|\mathbf{v}_g^T \mathbf{v}_p|^2$. Notice that the two projected vibrational modes, −69.9 and 23.8 cm^{-1}, couple with the rotational modes and yield four rovibrational modes. In particular, the 23.8 cm^{-1} mode which represents a planar deformation promoting the proton transfer, see Fig. 2, is coupled with the rotation in the plane of the molecule and has the highest rotational symmetry correction ($\Delta\nu_{ng} = 5$ cm^{-1}). The t' configuration can be also considered as a result of the ring deformation of *t*, where the protons are bound to β and δ nitrogens. The deformation is only of about 0.1 Å in positions of nitrogens and protons, but has a considerable effect on the frequencies, compare $\nu_p(t')$ and $\nu_p(t)$ data in Table 2. On the other hand, the corresponding modes have very high overlap, $|\mathbf{v}_p^T(t')\mathbf{v}_p(t)|^2 > 0.96$, except of the two mode pairs shown first in Table 2, which are cross-coupled. We further examined to what extent the non-stationary spectrum of $\hat{\mathbf{h}}_g(t')$ can be reproduced by using a single LHA potential centered in the *t* configuration, and the normal transformation. The approximate Hessian in t' is given with Eq. (31) where $\hat{\mathbf{h}}_c(t') = \hat{\mathbf{h}}_p(t)$ and $\mathbf{g}_c(t') = \hat{\mathbf{h}}_p(t)[\mathbf{r}(t') - \mathbf{r}(t)]$, and its frequencies, $\nu_g^{LHA}(t')$, are presented in Table 2. Notice that although the qualitative scheme of rovibrational coupling in t' is reproduced by the invariant LHA, the frequencies $\nu_g(t')$ are not, what is due to high

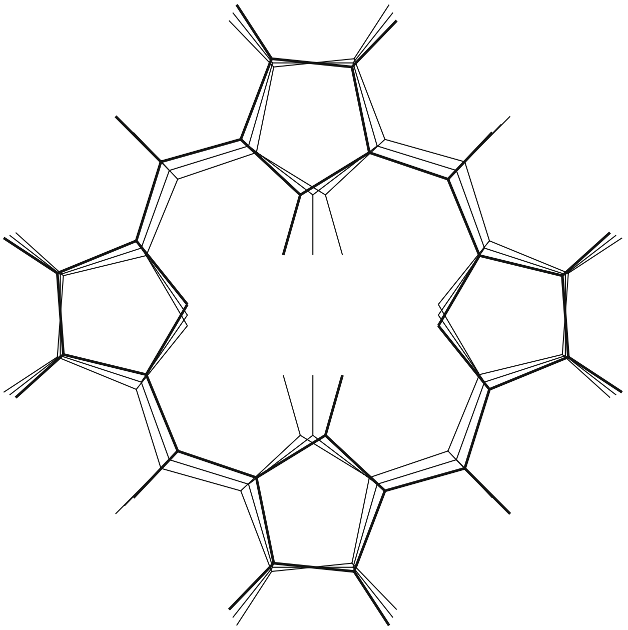

Fig. 2 The projected vibrational mode, $\nu_{\mathrm{p}} = 23.8\ \mathrm{cm}^{-1}$, promoting the proton transfer in t' configuration

Table 3 Partial protonic frequencies obtained with PHVA and MBH methods (ν_{P} and ν_{M}, respectively) and the full protonic frequencies (ν) in t' and t configurations

vm	$\nu_{\mathrm{P}}(t')$	$\nu_{\mathrm{M}}(t')$	$\nu(t')$	$\nu_{\mathrm{P}}(t)$	$\nu_{\mathrm{M}}(t)$	$\nu(t)$
o−	477	478	498	627	628	631
o+	706	710	727	754	759	748
p−	988	988	924	1,154	1,155	1,262
p+	1,073	1,080	955	1,204	1,212	1,269
s−	3,437	3,459	3,575	3,421	3,444	3,558
s+	3,510	3,510	3,631	3,479	3,479	3,601

The NH bond vibration modes (vm) are: bending out of the plane (o), bending in the plane (p), stretching (s) with symmetric (+) or antisymmetric (−) protons' motion

anharmonicity of the lower part of the spectrum. We also tested that the $\nu_{\mathrm{g}}^{\mathrm{LHA}}(t')$ frequencies are in practice insensitive (effect less than 1 cm^{-1}) on choice of the reference configuration, $\mathbf{r}_0$, including stationary states and a symmetrized D_{4h} configuration with two indistinguishable protons located in the central point.

As an example of the partial vibrational analysis, in Table 3 we presented the protonic normal mode frequencies in configurations t and t'. The full protonic mode frequencies, ν, were obtained from the full Hessians $\hat{\mathbf{h}}_{\mathrm{p}}(t)$ and $\hat{\mathbf{h}}_{\mathrm{g}}(t')$. The partial protonic modes were determined for the subspace of six protonic Cartesian coordinates using PHVA and MBH methods, and the resulting vibrational frequencies are denoted with labels P and M, respectively. Notice that M frequencies are in general higher than the P frequencies, what is in agreement with the results reported for the ethanol molecule [27], however, the maximum difference is only 22 cm^{-1} for the antisymmetric NH bond stretching. Furthermore, the plain partial Hessian (Eq. 17) yields the protonic frequencies which are intermediate between the P and M values in the same configuration. Eliminating the contribution from rotations and translations has a minor effect on the protonic partial modes in the current example due to the disproportion between the protonic and molecular mass.

6 Summary

The molecular Hessian in the mass scaled atomic Cartesian coordinates can be expressed as the sum of the projected vibrational Hessian and of the gradient dependent component, which follows from the molecular rotational symmetry (12–14). The gradient-dependent component is responsible for additional pseudo-frequencies and mixing of the rotational and vibrational normal modes in the non-stationary configurations. The non-stationary normal modes can be equivalently determined from the known theory of the extended Hessian in the generalized coordinates (15). The Cartesian Hessian expression (12) can be used to correct the raw Hessian data resulting from the quantum chemistry or molecular mechanics calculations in the non-stationary configurations, as well as to qualify the spurious rotational components in the stationary configurations. Exemplary results for porphyrin presented in Table 1 show that tightening the optimization cannot reduce the rotational frequencies beyond a limit related with the numerical accuracy of electronic calculations. Table 2 shows to what extent one can correct the non-stationary Hessian, and that ensuring the rotational invariance of the Cartesian LHA does not help to reproduce anharmonic effects which are observed in the lower part of the spectrum. This shall not prevent one from using possibly precise Hessian data for parameterizing LHAs, because the anharmonicity can be reproduced by interpolating nearby LHAs, adding higher order expansion terms or introducing curvilinear coordinates.

The expression (12) was also used in a simple formulation of the partial normal mode analysis in the Cartesian representation. The method can be applied to determine harmonic normal modes of an optimized molecular fragment excluding the contributions from the molecular rotations and translations. The method requires calculating the subblock of the projection matrix (10) and of the mass-scaled Hessian matrix, eliminating the gradient-dependent component (21) and solving the generalized normal mode equation (22), and yields results equivalent to the mobile block Hessian approach [16, 27]. Table 3 shows to what extent the protonic frequencies in porphyrin depend on separation of protons and heavy atoms, optimization of the skeleton, and exclusion of the rotations. These results indicate possible inaccuracy of molecular dynamics simulations with separation into the quantum and classical descriptions for the protons and heavy atoms, respectively.

The normal transformation method was developed for computing the analytical potential energy in the atomic Cartesian coordinates preserving the molecular rotational symmetry. The method is based on molecular reorientation which maximizes the geometry overlap with a reference configuration [7] what appears equivalent to satisfying the Eckart conditions. Given an instantaneous molecular configuration in the space fixed frame one derives an auxiliary rotation matrix from (25, 26) and applies (24) to transform the molecule to a definite position and orientation in which the analytical potential (23) is calculated. The method can be applied with the potentials of arbitrary analytical form and allows for molecular dynamics computations in the space fixed Cartesian frame without constraining the molecular rotations but avoiding the internal coordinates. Novel and simple formulas for the analytical Cartesian derivatives of the transformed potential were provided. To obtain the gradient in the space fixed frame one determines the auxiliary rotation vectors (41) and the projection-like matrix (42) and applies transformations (29a) and (30a) to the gradient of the analytical potential. To obtain the second derivatives one determines the gradient-dependent Hessian component (13) and applies transformations (31) and (30b). The normal transformation is currently being implemented to the approximate valence bond method for the molecular classical and quantum dynamics of proton transfer reactions in the porphyrin molecule and its derivatives.

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Appendix: Analytical derivatives of the normal transformation

For simplicity we consider a configuration $\mathbf{r}$ which is in the normal position and orientation, i.e., $\mathbf{r}_\mathrm{n}(\mathbf{r}) = \mathbf{r}$. We define two auxiliary configurations. $\mathbf{r}_1 = \mathbf{r} + \lambda\mathbf{x}$, and $\mathbf{r}_2 = \mathbf{r}_1 + \lambda'\mathbf{x}'$, where λ and λ' are independent smallness parameters, and $\mathbf{x}$ and $\mathbf{x}'$ are arbitrary vectors in the configuration space. Notice that in the present context the prime symbol does not denote the center of mass translation. Since $\mathbf{r}_\mathrm{n}(\mathbf{r})$ is smooth, we can use the Taylor expansion,

$$\mathbf{r}_\mathrm{n}(\mathbf{r}_1) = \mathbf{r} + \lambda\hat{\mathbf{a}}\mathbf{x} + O_2, \tag{32a}$$

$$\mathbf{r}_\mathrm{n}(\mathbf{r}_2) = \mathbf{r}_\mathrm{n}(\mathbf{r}_1) + \lambda'\hat{\mathbf{a}}\mathbf{x}' + \lambda\lambda'(\hat{\mathbf{b}}\mathbf{x})\mathbf{x}' + O_2. \tag{32b}$$

Symbol O_2 denotes any terms which are of at least second order in λ or λ'. To determine the inner products of $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ with the $\mathbf{x}^{(\prime)}$ vectors, we first notice that $\mathbf{r}_\mathrm{n}(\mathbf{r})$ is invariant under rotations and translations of $\mathbf{r}$. Substituting $\mathbf{x}' = \mathbf{t}_k(\mathbf{r})$ and $\mathbf{r}_\mathrm{n}(\mathbf{r}_2) = \mathbf{r}_\mathrm{n}(\mathbf{r}_1)$ in (32b) and separating terms of different orders in λ's we obtain $\hat{\mathbf{a}}\mathbf{t}_k = 0$ and $\hat{\mathbf{b}}\mathbf{t}_k = 0$ $(k = 1,\ 2,\ 3)$. Next, assume that $\mathbf{r}_2 = \mathbf{r}_1 + \lambda'\mathbf{x}'$ is a rotation of $\mathbf{r}_1$ by the angle λ' around the axis $\boldsymbol{\Lambda}_k = \boldsymbol{\Lambda}_k(\mathbf{r})$ $(k = 1,\ 2,\ 3)$, what corresponds to $\mathbf{x}' = \hat{\mathbf{u}}(\boldsymbol{\Lambda}_k)\mathbf{r}_1 + O(\Lambda')$. Substituting the earlier expression to (32b) and separating the terms of different orders we derive $\hat{\mathbf{a}}\mathbf{e}_k = 0, \hat{\mathbf{b}}\mathbf{e}_k = -\hat{\mathbf{a}}\hat{\mathbf{u}}_k$ $(k = 1,\ 2,\ 3)$, where $\mathbf{e}_k = \mathbf{e}_k(\mathbf{r})$ and $\hat{\mathbf{u}}_k = \hat{\mathbf{u}}(\boldsymbol{\Lambda}_k)/\sqrt{I_k}$. The results obtained so far can be combined together as follows,

$$\hat{\mathbf{a}}\mathbf{x} = \hat{\mathbf{a}}\hat{\mathbf{p}}\mathbf{x} \tag{33a}$$

$$(\hat{\mathbf{b}}\mathbf{x})\mathbf{x}' = (\hat{\mathbf{b}}\hat{\mathbf{p}}\mathbf{x})\hat{\mathbf{p}}\mathbf{x}' - \sum_{k=1}^{3}\hat{\mathbf{a}}\hat{\mathbf{u}}_k\left[\mathbf{x}(\mathbf{e}_k^\mathrm{T}\mathbf{x}') + \mathbf{x}'(\mathbf{e}_k^\mathrm{T}\mathbf{x})\right], \tag{33b}$$

where $\mathbf{x}$ and $\mathbf{x}'$ are arbitrary vectors. To determine the inner products of $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ with the vibrational components, $\hat{\mathbf{p}}\mathbf{x}^{(\prime)}$, we consider the case $\mathbf{r}_2 = \mathbf{r} + \delta\mathbf{r}$, where $\delta\mathbf{r} = \lambda\hat{\mathbf{p}}\mathbf{x} + \lambda'\hat{\mathbf{p}}\mathbf{x}'$. The $\mathbf{r}_2$ conformation is now in the normal position but not necessarily in the normal orientation. The latter, $\mathbf{r}_\mathrm{s}(\mathbf{r}_2)$, is obtained by some rotation of $\mathbf{r}_2$ around the molecular center of mass. The rotation axis and angle is described with a direction and norm, respectively, of a Cartesian vector $\boldsymbol{\Lambda}(\delta\mathbf{r})$, and $\mathbf{r}_\mathrm{n}(\mathbf{r}_2)$ can be expanded into the Taylor series,

$$\mathbf{r}_\mathrm{n}(\mathbf{r}_2) = \mathbf{r}_2 + \hat{\mathbf{u}}(\boldsymbol{\Lambda})\mathbf{r}_2 + \frac{1}{2}\hat{\mathbf{u}}(\boldsymbol{\Lambda})^2\mathbf{r}_2 + O(\boldsymbol{\Lambda}^3). \tag{34}$$

The $\boldsymbol{\Lambda}$ vector can be represented as a linear combination of the $\boldsymbol{\Lambda}_k(\mathbf{r})$ vectors defined in (8), and, consequently, we apply a linear combination for the $\hat{\mathbf{u}}$ matrix,

$$\hat{\mathbf{u}}(\boldsymbol{\Lambda}(\delta\mathbf{r})) = \sum_{k=1}^{3} c_k(\delta\mathbf{r})\hat{\mathbf{u}}_k, \tag{35}$$

where $\hat{\mathbf{u}}_k = \hat{\mathbf{u}}(\boldsymbol{\Lambda}_k)/\sqrt{I_k}$ and $c_k(\delta\mathbf{r}) = \sqrt{I_k}\boldsymbol{\Lambda}_k^\mathrm{T}\boldsymbol{\Lambda}(\delta\mathbf{r})(k = 1,\ 2,\ 3)$. Substituting the earlier expression for $\delta\mathbf{r}$ in $c_k(\delta\mathbf{r})$, we further introduce the expansion with respect to parameters $\lambda^{(\prime)}$ $(k = 1, 2, 3)$,

$$c_k(\delta\mathbf{r}) = \alpha_k\lambda + \alpha_k'\lambda' + \beta_k\lambda\lambda' + O_2, \tag{36}$$

where α_k, α_k' and β_k are some unknown coefficients. We dropped the zero-order term in (36) taking into account that $\hat{\mathbf{u}}(\boldsymbol{\Lambda}(\delta\mathbf{r}))$ should be zero for $\delta\mathbf{r} = 0$. We substitute Eqs. (35–36) to (34) and obtain an expansion of $\mathbf{r}_\mathrm{n}(\mathbf{r}_2)$ with respect to $\lambda^{(\prime)}$ parameters. Notice that an equivalent expansion should obtained by replacing $\mathbf{x}^{(\prime)}$ with $\hat{\mathbf{p}}\mathbf{x}^{(\prime)}$ in (32a, 32b). By comparing the corresponding terms, proportional to $\lambda^{(\prime)}$ or $\lambda\lambda'$, from the two expansions we obtain,

$$\hat{\mathbf{a}}\hat{\mathbf{p}}\mathbf{x}^{(\prime)} = \hat{\mathbf{p}}\mathbf{x}^{(\prime)} + \sum_{k=1}^{3} \mathbf{e}_k \alpha_k^{(\prime)}, \tag{37}$$

or

$$(\hat{\mathbf{b}}\hat{\mathbf{p}}\mathbf{x})\hat{\mathbf{p}}\mathbf{x}' = \gamma + \sum_{k=1}^{3} \mathbf{e}_k \beta_k, \tag{38}$$

respectively. Here we use the auxiliary denotation,

$$\gamma = \sum_{k=1}^{3} \hat{\mathbf{u}}_k \hat{\mathbf{p}}(\alpha_k \mathbf{x}' + \alpha_k' \mathbf{x}), + \frac{1}{2} \sum_{k,l=1}^{3} (\alpha_k \alpha_l' + \alpha_k' \alpha_l) \hat{\mathbf{u}}_l \mathbf{e}_k. \tag{39}$$

In order to determine the coefficients $\alpha_k^{(\prime)}$ and β_k we make use of the Eckart condition (28), which can be presented in the form,

$$\mathbf{e}_k(\mathbf{r}_0)^{\mathrm{T}}[\mathbf{r}_{\mathrm{n}}(\mathbf{r}_2) - \mathbf{r}_{\mathrm{n}}(\mathbf{r}_1)] = 0. \tag{40}$$

Substituting (32a–32b) into the earlier equation and separating the terms of different orders in λ's we get $\mathbf{e}_k(\mathbf{r}_0)^{\mathrm{T}}\hat{\mathbf{a}}\mathbf{x}^{(\prime)} = 0$ and $\mathbf{e}_k(\mathbf{r}_0)^{\mathrm{T}}(\hat{\mathbf{b}}\mathbf{x})\mathbf{x}' = 0$ $(k = 1, 2, 3)$, for arbitrary vectors $\mathbf{x}^{(\prime)}$. Applying these conditions to (37–38) we derive a system of linear equations for $\alpha_k^{(\prime)}$ and β_k $(k = 1, 2, 3)$. The solution can be represented as $\alpha_k^{(\prime)} = -\boldsymbol{\varepsilon}_k^{\mathrm{T}}\mathbf{v}^{(\prime)}$ and $\beta_k = -\boldsymbol{\varepsilon}_k^{\mathrm{T}}\gamma$, where

$$\boldsymbol{\varepsilon}_k = \sum_{l=1}^{3} E_{kl}\mathbf{e}_l(\mathbf{r}_0), \tag{41}$$

are auxiliary vectors, and E_{kl} are coefficients defined with the condition $\boldsymbol{\varepsilon}_k^{\mathrm{T}}\mathbf{e}_n = \delta_{kn}$ $(k, n = 1, 2, 3)$. Notice that the last condition can be fulfilled only if the $\mathbf{e}_k^{\mathrm{T}}\mathbf{e}_l(\mathbf{r}_0)$ matrix is invertible, what imposes some limitations on the allowed $\mathbf{r}$ configurations at given reference configuration, $\mathbf{r}_0$. Substituting the earlier expressions for $\alpha_k^{(\prime)}$ and β_k to (37–39) and further substituting (37–39) to (33a–33b) we obtain complete expressions for $\hat{\mathbf{a}}\mathbf{x}$ and $(\hat{\mathbf{b}}\mathbf{x})\mathbf{x}'$. These expressions are further differentiated with respect to $\mathbf{x}$ and $\mathbf{x}'$ yielding the target quantities $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$. Due to limitations in the notation it is more convenient to derive the expression for the symmetric matrix $\hat{\mathbf{b}}^{\mathrm{T}}\mathbf{g}_{\mathrm{c}} = \mathbf{g}_{\mathrm{c}}^{\mathrm{T}}\hat{\mathbf{b}}$ instead of the bare $\hat{\mathbf{b}}$ tensor. The results, upon some algebraic simpliciations, can be presented as,

$$\hat{\mathbf{a}} = \hat{\imath} - \sum_{k=1}^{3} \mathbf{e}_k \boldsymbol{\varepsilon}_k^{\mathrm{T}} - \sum_{k=1}^{3} \mathbf{t}_k \mathbf{t}_k^{\mathrm{T}}, \tag{42}$$

and

$$\mathbf{g}_{\mathrm{c}}^{\mathrm{T}}\hat{\mathbf{b}} = \delta\hat{\mathbf{h}}_{\mathrm{g}} - \hat{\mathbf{a}}^{\mathrm{T}}\delta\hat{\mathbf{h}}_{\mathrm{g}}\hat{\mathbf{a}}, \tag{43}$$

where $\delta\hat{\mathbf{h}}_{\mathrm{g}}$ is the gradient-dependent Hessian component (13–14) evaluated for the gradient $\mathbf{g}_{\mathrm{inv}} = \hat{\mathbf{a}}^{\mathrm{T}}\mathbf{g}_{\mathrm{c}}$.

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