Electronic supplementary information

to

A general formulation of the quasiclassical trajectory method for reduced-dimensionality calculations

Tibor Nagy[1], Anna Vikár[1], György Lendvay[1,2]**

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar tudósok körútja 2., H-1117 Budapest, Hungary

[2]Department of General and Inorganic Chemistry, University of Pannonia, Egyetem u. 10, H-8800 Veszprém, Hungary

Partially analytical derivation of matrix $\mathbf{G}_{\mathrm{y,vib}}$

To speed up the evaluation of the derivative of matrix $\mathbf{G}_{\mathrm{y,vib}}(\mathbf{y}) = \mathbf{M}_{\mathrm{y,vib}}^{-1}(\mathbf{y})$, the following analytical formulae can be used based on the relationships $\mathbf{M}_{\mathrm{y,vib}}(\mathbf{y}) = \mathbf{C}^{\mathrm{T}}(\mathbf{y})\mathbf{M}_{\mathrm{vib}}(\mathbf{x}(\mathbf{y}))\mathbf{C}(\mathbf{y})$, $\mathbf{M}_{\mathrm{vib}}(\mathbf{x}(\mathbf{y})) = \mathbf{M}^{1/2}\mathbf{P}_{\mathrm{vib}}(\mathbf{x}(\mathbf{y}))\mathbf{M}^{1/2}$ and $\mathbf{P}_{\mathrm{vib}}\big(\mathbf{x}(\mathbf{y})\big) = \mathbf{E} - \mathbf{P}_{\mathrm{trans}} - \mathbf{P}_{\mathrm{rot}}(\mathbf{x}(\mathbf{y}))$ (see also Eqs. (24) and Eqs. (22) and (13)), where $\mathbf{y} = (y_1, \dots, y_n)^{\mathrm{T}}$ are the non-constrained set of independent internal coordinates and $\mathbf{x} = \left(x_{1x}, x_{1y}, x_{1z}, \dots, x_{Nz}\right)^{\mathrm{T}}$ are the Cartesian coordinates in the body-fixed frame.

$$\frac{\partial \mathbf{G}_{\mathrm{y,vib}}(\mathbf{y})}{\partial y_i} = -\mathbf{G}_{\mathrm{y,vib}}(\mathbf{y})\frac{\partial \mathbf{M}_{\mathrm{y,vib}}(\mathbf{y})}{\partial y_i}\mathbf{G}_{\mathrm{y,vib}}(\mathbf{y}) \tag{S1}$$

$$\begin{aligned}\frac{\partial \mathbf{M}_{\mathrm{y,vib}}(\mathbf{y})}{\partial y_i} = &\left(\mathbf{C}^{\mathrm{T}}(\mathbf{y})\mathbf{M}_{\mathrm{vib}}\big(\mathbf{x}(\mathbf{y})\big)\frac{\partial \mathbf{C}(\mathbf{y})}{\partial y_i} + \text{its tranpose}\right)\\ &+\mathbf{C}^{\mathrm{T}}(\mathbf{y})\mathbf{M}^{1/2}\frac{\partial \mathbf{P}_{\mathrm{vib}}(\mathbf{x}(\mathbf{y}))}{\partial y_i}\mathbf{M}^{1/2}\mathbf{C}(\mathbf{y}),\end{aligned} \tag{S2}$$

$$\frac{\mathrm{d}\mathbf{P}_{\mathrm{vib}}(\mathbf{x}(\mathbf{y}))}{\mathrm{d}\mathbf{y}} = -\frac{\mathrm{d}\mathbf{P}_{\mathrm{rot}}(\mathbf{x}(\mathbf{y}))}{\mathrm{d}\mathbf{y}}. \tag{S3}$$

Matrices $\mathbf{G}_{\mathrm{y,vib}}(\mathbf{y})$, $\mathbf{M}_{\mathrm{y,vib}}(\mathbf{y})$ and $\mathbf{P}_{\mathrm{rot}}\big(\mathbf{x}(\mathbf{y})\big)$are symmetric, thus their partial derivatives are also symmetric (in the row and column variables), which can also be exploited during the evaluation of Eqs. (S1-S3). When the square root and products of matrix $\mathbf{M}$ are evaluated, its diagonal structure should be exploited to avoid unnecessary multiplications with zero.

Method of Lagrange multipliers for holonomic and scleronomic constraints

The Lagrange's multipliers method offers an easy means to determine constraint forces originating from geometric (holonomic and scleronomic) constraints. Good descriptions for the determination of Lagrange multipliers in practice can be found in Refs. 1–4. For completeness, the equations are repeated here for immediate availability for the readers.

The internal motion allowed by the n unconstrained internal coordinates $(y_1, \dots, y_n)$ of the system of reactants, can be reformulated as a $3N$-dimensional motion in Cartesian coordinates in the presence of $c = f - n$ constraints, where f is the internal degrees of freedom of the unconstrained system. To derive constraint forces, we introduce function vector $\mathbf{g}(\mathbf{X}) = \big(g_1(\mathbf{X}), \dots, g_c(\mathbf{X})\big)$, whose elements are the deviations of the constrained internal coordinates $y_{n+i}(\mathbf{X})$ ($i = 1, \dots, c$) from their corresponding frozen values $y_{n+i,0}$ at a given $\mathbf{X} = \big(X_{1x}, X_{1y}, X_{1z}, \dots, X_{Nz}\big)^{\mathrm{T}}$geometry in a lab-fixed Cartesian coordinates. Setting them to zero expresses the constraints.

$$\mathbf{g}(\mathbf{X}) = \mathbf{0} \tag{S4}$$

These type of constraints are holonomic as they depend only on the position coordinates (and not on higher derivatives) and they are also scleronomic as they do not depend on time explicitly. Component i of Eq. (S4) constrains the system to the $3N - 1$ dimensional surface which fulfill $g_i(\mathbf{X}) = 0$ and thus the corresponding constraint force $\mathbf{F}_i^{\mathrm{constr}}$ for constraint i is looked for in a form perpendicular to the surface, consequently $\mathbf{F}_i^{\mathrm{constr}}$ is parallel with ∇g_i. They are added to Hamilton's equations (supplementing potential forces) for the lab-frame Cartesian momentum $\mathbf{P}_X$ with so-called $\boldsymbol{\lambda} = (\lambda_1, \dots, \lambda_c)$ Lagrange's multipliers.

$$\dot{\mathbf{P}}_X = -\nabla_X V + \mathbf{A}^{\mathrm{T}}\boldsymbol{\lambda} \tag{S5}$$

Matrix $\mathbf{A}$ denotes the derivative matrix of function $\mathbf{g}(\mathbf{X})$, whose elements are $A_{ij} = \partial g_i / \partial X_j$. To determine Lagrange's multipliers $\boldsymbol{\lambda}$, the term $\dot{\mathbf{P}}_X$ needs to be expressed from known quantities.

Swapping the sides of Eq. (S5), rearranging it and exploiting that in Cartesian coordinates $\dot{\mathbf{P}}_X = \mathbf{M}\ddot{\mathbf{X}}$ holds (where $\mathbf{M}$ is the diagonal Cartesian mass-matrix), the following is obtained.

$$\mathbf{A}^{\mathrm{T}}\boldsymbol{\lambda} = \mathbf{M}\ddot{\mathbf{X}} + \nabla_X V \tag{S6}$$

Acceleration $\ddot{\mathbf{X}}$ can be algebraically related to velocity $\dot{\mathbf{X}}$ by differentiating Eq. (S4) twice with respect to time.

$$\ddot{\mathbf{g}}(\mathbf{X}) = \dot{\mathbf{A}}\dot{\mathbf{X}} + \mathbf{A}\ddot{\mathbf{X}} = \mathbf{0} \tag{S7}$$

The time-derivative $\dot{\mathbf{A}}$ can be expressed with known quantities: the second derivative of the constraints and the velocities:

$$\dot{A}_{ij}(\mathbf{X}) = \sum_{k=1}^{3N} \frac{\partial A_{ij}}{\partial X_k}\dot{X}_k = \sum_{k=1}^{3N} \frac{\partial^2 g_i}{\partial X_j \partial X_k}\dot{X}_k. \tag{S8}$$

Multiplying Eq. (S6) with the diagonal inverse mass matrix $\mathbf{G}$ (i.e. $\mathbf{GM}$ gives unit matrix $\mathbf{E}$) and then with matrix $\mathbf{A}$ from the left, term $\mathbf{A}\ddot{\mathbf{X}}$ appears, which can be expressed with velocities (Eq. (S7)), which are known along a trajectory.

$$\underbrace{\mathbf{AGA}^{\mathrm{T}}}_{\mathrm{H}}\boldsymbol{\lambda} = \mathbf{A}\underbrace{\mathbf{GM}}_{\mathbf{E}}\ddot{\mathbf{X}} + \mathbf{AG}\nabla_X V = \underbrace{\mathbf{AG}\nabla_X V - \dot{\mathbf{A}}\dot{\mathbf{X}}}_{\mathbf{b}} \tag{S9}$$

The obtained $\mathbf{H}\boldsymbol{\lambda} = \mathbf{b}$ equation is a system of linear equations for $\boldsymbol{\lambda}$ with a symmetric positive definite (square) coefficient matrix $\mathbf{H} = \mathbf{AGA}^{\mathrm{T}}$. For such problems efficient solution can be obtained via Cholesky decomposition[5], which gives matrix $\mathbf{H}$ in the form $\mathbf{U}^{\mathrm{T}}\mathbf{U}$, where $\mathbf{U}$ is an upper triangular matrix, whose inverse can be computed much easier. After solving Eq. (S9), the Lagrange-multipliers and the constraint forces can be formally written as:

$$\boldsymbol{\lambda} = (\mathbf{AGA}^{\mathrm{T}})^{-\mathbf{1}}(\mathbf{AG}\nabla_X V - \dot{\mathbf{A}}\dot{\mathbf{X}}), \tag{S10}$$

$$\mathbf{F}^{\mathrm{constr}} = \sum_{i=1}^{c} \mathbf{F}_i^{\mathrm{constr}} = \mathbf{A}^{\mathrm{T}}\boldsymbol{\lambda} = \mathbf{A}^{\mathrm{T}}(\mathbf{AGA}^{\mathrm{T}})^{-\mathbf{1}}(\mathbf{AG}\nabla_X V - \dot{\mathbf{A}}\dot{\mathbf{X}}). \tag{S11}$$

Efficient form of constraints allowing simple analytic gradients and Hessians

Equations (S5) and (S8) require the evaluation of the first and second derivative of the constraints. The constraints applied in this paper can be expressed as sum of scalar (or dot) products of vectors between coordinate vectors of atoms (see Table 1.). Such constraints can describe the equality of Z_iZ_j atom-atom distances (e.g. $g_1(\mathbf{X}) = \mathbf{R}^2_{\mathrm{Z1Z2}} - \mathbf{R}^2_{\mathrm{Z2Z3}} = 0$, $g_2(\mathbf{X}) = \mathbf{R}^2_{\mathrm{Z2Z3}} - \mathbf{R}^2_{\mathrm{Z3Z1}} = 0$) and also CZ_i bond lengths (e.g. $g_3(\mathbf{X}) = \mathbf{R}^2_{\mathrm{CZ1}} - \mathbf{R}^2_{\mathrm{CZ2}} = 0$, $g_4(\mathbf{X}) = \mathbf{R}^2_{\mathrm{CZ2}} - \mathbf{R}^2_{\mathrm{CZ3}} = 0$), or that a bond length (e.g. $[g_3(\mathbf{X}) = \mathbf{R}^2_{\mathrm{CZ1}} - r^2_{\mathrm{eq}} = 0]$, $[g_4(\mathbf{X}) = \mathbf{R}^2_{\mathrm{CZ2}} - r^2_{\mathrm{eq}} = 0]$, $g_5(\mathbf{X}) = \mathbf{R}^2_{\mathrm{CZ3}} - r^2_{\mathrm{eq}} = 0$) or an angle ($g_6(\mathbf{X}) = \mathbf{R}_{\mathrm{CY}}\mathbf{R}_{\mathrm{Z2Z3}} = 0$) is constant. For example, expanding the products of constraint $g_6(\mathbf{X})$ gives:

$$g_6(\mathbf{X}) = \mathbf{R}_{\mathrm{CY}}^{\mathrm{T}}\mathbf{R}_{\mathrm{Z2Z3}} = (\mathbf{R}_{\mathrm{Y}} - \mathbf{R}_{\mathrm{C}})^{\mathrm{T}}(\mathbf{R}_{\mathrm{Z3}} - \mathbf{R}_{\mathrm{Z2}}) = \\ = \mathbf{R}_{\mathrm{Y}}^{\mathrm{T}}\mathbf{R}_{\mathrm{Z3}} - \mathbf{R}_{\mathrm{Y}}^{\mathrm{T}}\mathbf{R}_{\mathrm{Z2}} - \mathbf{R}_{\mathrm{C}}^{\mathrm{T}}\mathbf{R}_{\mathrm{Z3}} + \mathbf{R}_{\mathrm{C}}^{\mathrm{T}}\mathbf{R}_{\mathrm{Z2}}. \quad \text{(S12)}$$

This expression is built up from terms of the following type (*i.e.* for atoms i and j), for which the derivatives, that are needed for the evaluation of $\mathbf{A}$ and $\dot{\mathbf{A}}$, can be derived analytically:

$$\mathbf{R}_i^{\mathrm{T}}\mathbf{R}_j = \sum_{\alpha=1}^{\mathbf{3}} X_{i\alpha}X_{j\alpha}. \quad \text{(S13)}$$

The $k\beta$ component ($k = 1, \dots, N$ and $\beta = x, y, z$) of the gradient of a single such term can be obtained as:

$$\frac{\partial(\mathbf{R}_i^{\mathrm{T}}\mathbf{R}_j)}{\partial X_{k\beta}} = \sum_{\alpha=1}^{\mathbf{3}} \delta_{\alpha\beta}\left(\delta_{ik}X_{j\alpha} + \delta_{jk}X_{i\alpha}\right) = \delta_{ik}X_{j\beta} + \delta_{jk}X_{i\beta}. \quad \text{(S14)}$$

Similarly, the ($k\beta$, $l\gamma$) component of the Hessian ($l = 1, \dots, N$ and $\gamma = x, y, z$) of a single product term is also straightforward to derive:

$$\frac{\partial^2(\mathbf{R}_i^{\mathrm{T}}\mathbf{R}_j)}{\partial X_{k\beta}\,\partial X_{l\gamma}} = \delta_{\beta\gamma}(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}). \quad \text{(S15)}$$

This Hessian is independent of the geometry and has a very sparse structure, as only the diagonal elements (i.e. $\beta = \gamma$) of the 3x3 blocks corresponding to atoms (i, j) or (j, i) will be 1 if $i \neq j$ or 2 if $i = j$ and the rest of the elements will be zero. Consequently, the Hessian of constraints built from sum of dot products of atomic coordinate vectors need to be evaluated only once, at the beginning of the simulation.

References

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