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Cartesian formulation of the mobile block Hessian approach to vibrational analysis in partially optimized systems

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Partial optimization is a useful technique to reduce the computational load in simulations of extended systems. In such nonequilibrium structures, the accurate calculation of localized vibrational modes can be troublesome, since the standard normal mode analysis becomes inappropriate. In a previous paper [A. Ghysels *et al.*, J. Chem. Phys. **126**, 224102 (2007)], the mobile block Hessian (MBH) approach was presented to deal with the vibrational analysis in partially optimized systems. In the MBH model, the nonoptimized regions of the system are represented by one or several blocks, which can move as rigid bodies with respect to the atoms of the optimized region. In this way unphysical imaginary frequencies are avoided and the translational/rotational invariance of the potential energy surface is fully respected. In this paper we focus on issues concerning the practical numerical implementation of the MBH model. The MBH normal mode equations are worked out for several coordinate choices. The introduction of a consistent group-theoretical notation facilitates the treatment of both the case of a single block and the case of multiple blocks. Special attention is paid to the formulation in terms of Cartesian variables, in order to provide a link with the standard output of common molecular modeling programs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2789429]

I. INTRODUCTION

Partial optimization is of interest to model extended molecular systems where a full optimization is still computationally too expensive. Examples include polymer chains,[1] supramolecular assemblies, systems embedded in a solvent or (macro)molecules adsorbed within porous materials,[2] etc. The reference point is obtained by optimizing the geometry with respect to a subset of internal coordinates, keeping the remainder fixed during the optimization. The fixed internal coordinates, e.g., correspond to the fixed geometry of a part of the molecule, which is not expected to influence the more interesting region—the active site—of the molecule, and may even be calculated at a lower level of theory.

After partial optimization, the system is still in a global nonequilibrium state, and severe difficulties arise when normal mode analysis is applied in a standard fashion.[3–6] Several approaches have been developed for the determination of normal modes in such partially optimized geometries. As a general rule, one should restrict the normal mode analysis to the degrees of freedom that have been optimized, since the dynamical system corresponding to the subset of optimized internal coordinates is in equilibrium.

A method based on a subblock of the Cartesian Hessian was first introduced by Head and co-workers[7,8] and further developed by Li and Jensen.[9] Within this methodology, hereafter referred to as the partial Hessian vibrational analysis (PHVA), the normal modes are calculated for the system with the fixed atoms frozen at their reference positions as if they were given an infinite mass, and only the relaxed atoms can participate in the vibrations. An improved version of the PHVA was investigated by Head[10–12] but this method requires the knowledge of an additional off-diagonal block of the Hessian.

Recently, we presented the mobile block Hessian approach[13] (MBH) which has an equal computational load compared to the plain PHVA. In the MBH method, the group of fixed atoms is considered as a rigid block, which is allowed to participate in the small amplitude vibrations with the restriction that the internal geometry of the block remains unchanged. As a result, the unphysical effects related with nonequilibrium structures are avoided. The extension was made to the multiple MBH where several rigid blocks are introduced in the vibrational analysis. In Ref. 13, the MBH method was analyzed in a few test applications on small molecules, for which comparison with an exact treatment is feasible. The results indicated that the MBH approach is capable of reproducing localized modes, but also gives consistently better results for the low frequency modes with respect to the PHVA method. Also, the derived thermodynamical quantities such as entropy and free enthalpy are better reproduced when calculated with MBH frequencies instead of PHVA frequencies.

An important issue is the implementation in existing *ab initio* and molecular mechanics programs. In Ref. 13, the MBH equations are formulated in a set of internal coordinates. However, some standard packages only give the full Hessian in Cartesian coordinates as output, and the transformation between differents sets of coordinates can be cumbersome. It is therefore of interest to analyze the derivation of the MBH normal mode equations in both internal and Carte-

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sian coordinates, and to provide explicit formulae for the case where only Cartesian Hessian elements are available after the partial optimization. The introduction of some group-theoretical aspects will result, at the end of the discussion, in a rather simple calculation scheme for the MBH approach.

Apart from the physical content of the method, the computational cost of its implementation is of great importance. Partial optimization reduces the computational cost in finding the (approximate) reference geometry. It is then desirable that the subsequent frequency analysis is less time consuming as well, by a reduction in the required number of second derivatives. In this respect the PHVA is highly economical, as it only needs a simple submatrix of the Cartesian Hessian. The MBH as formulated in Ref. 13 needs an equivalent number of second derivatives, but requires a submatrix of the Hessian in internal coordinates when multiple blocks are involved. Special attention will therefore be paid to the required number of second derivatives in internal as well as in Cartesian coordinates.

The paper is organized as follows. In Sec. II we start with the introduction of some group-theoretical concepts which will be used extensively throughout the paper. Section III treats the MBH model with one single block. The formulation in internal coordinates is revised and it is shown that it is always possible to express the MBH equations using only the derivatives with respect to the Cartesian coordinates of the relaxed atoms. The same analysis is applied in Sec. IV to the multiple MBH model with an arbitrary number of blocks. In Sec. V the practical calculation scheme is summarized. Finally, in Sec. VI, we discuss the computational profit of the MBH approach compared to a full Cartesian Hessian calculation.

II. SOME GROUP-THEORETICAL CONCEPTS

Consider a molecule with N masses m_A, $A=1,\ldots,N$. The positions are described by Cartesian coordinates $\mathbf{r}_A \equiv \{r_{A\mu}\}_{\mu=x,y,z}$, with respect to a space-fixed frame. The energy of the system reads

$$E = \frac{1}{2}\sum_{A\mu} m_A \dot{r}_{A\mu}^2 + V(\{\mathbf{r}_A\}), \tag{1}$$

where $\dot{r}_{A\mu}$ is a time derivative and V is the potential energy.

In the MBH approach, one can select parts of the molecule (blocks) of which the internal geometry is kept fixed, but which can move as rigid bodies (i.e., rotate and translate). The analysis of MBH in Cartesian coordinates is greatly facilitated by introducing some (elementary) group-theoretical concepts, which will be used extensively in the following sections. We first consider the relevant transformation group in three-dimensional space that leaves the potential energy invariant. This six-parameter group consists of combinations of translations and rotations, taking coordinates $\mathbf{r}$ to their translated/rotated positions $\mathbf{r}'$,

$$r_\mu \to r'_\mu = g_\mu(\mathbf{r},p). \tag{2}$$

Here, p stands for the six parameters p_α, $\alpha=1,\ldots,6$. The composition of two transformations can be written as

$$\mathbf{g}(\mathbf{g}(\mathbf{r},p),p') = \mathbf{g}(\mathbf{r},\Phi(p,p')), \tag{3}$$

where $\Phi(p,p')$ are the parameters of the composition (i.e., the group multiplication law).

The precise parameterization of the group is arbitrary, but it is convenient to take $p_\alpha=0$ as the identity (no translation or rotation). As an example, one can take

$$\mathbf{g}(\mathbf{r},p) = \sum_\mu p_\mu \mathbf{e}_\mu + \hat{R}_x(p_4)\hat{R}_y(p_5)\hat{R}_z(p_6)\mathbf{r}, \tag{4}$$

where $\mathbf{e}_\mu$, for $\mu=x,y,z$, are unit vectors along the x,y,z directions, and $\hat{R}_\mu(\phi)$ is a rotation around the μ axis over an angle ϕ, e.g., $\mathbf{r}'=\hat{R}_z(\phi)\mathbf{r}$ has components

$$x' = x\cos\phi - y\sin\phi; \quad y' = x\sin\phi + y\cos\phi; \quad z' = z. \tag{5}$$

The invariance properties of the potential energy surface are now simply expressed as

$$V(\{\mathbf{r}_A\}) = V(\{\mathbf{g}(\mathbf{r}_A,p)\}). \tag{6}$$

Taking the first- and second-order derivatives of Eq. (6) at a reference point $\{\mathbf{r}_A^0\}$ and at the identity ($p=0$), one finds

$$\frac{\partial}{\partial p_\alpha} \to 0 = \sum_{A\mu} G_{A\mu} D_{A\mu}^{(\alpha)}, \tag{7}$$

$$\frac{\partial^2}{\partial p_\alpha \partial p_{\alpha'}} \to 0 = \sum_{A\mu,A'\mu'} H_{A\mu,A'\mu'} D_{A\mu}^{(\alpha)} D_{A'\mu'}^{(\alpha')} + \sum_{A\mu} G_{A\mu} C_{A\mu}^{(\alpha\alpha')}, \tag{8}$$

$$\frac{\partial^2}{\partial p_\alpha \partial r_{A\mu}} \to 0 = \sum_{A'\mu'} H_{A\mu,A'\mu'} D_{A'\mu'}^{(\alpha)} + \sum_{\mu'} G_{A\mu'} \left(\frac{\partial D_{A\mu'}^{(\alpha)}}{\partial r_{A\mu}^0} \right), \tag{9}$$

in terms of the Cartesian gradient $G_{A\mu}=(\partial V/\partial r_{A\mu})_0$ and Hessian matrix $H_{A\mu,A'\mu'}=(\partial^2 V/\partial r_{A\mu}\partial r_{A'\mu'})_0$ at the reference point. The vectors $D^{(\alpha)}$ and $C^{(\alpha\alpha')}$ have components

$$D_{A\mu}^{(\alpha)} = \frac{\partial g_\mu}{\partial p_\alpha}(\mathbf{r}_A^0,0), \tag{10}$$

$$C_{A\mu}^{(\alpha\alpha')} = \frac{\partial^2 g_\mu}{\partial p_\alpha \partial p_{\alpha'}}(\mathbf{r}_A^0,0), \tag{11}$$

and are listed in Table I for the parameterization defined in Eq. (4).

Equation (9) implies that at an equilibrium point (where $G=0$) the $D^{(\alpha)}$ are six zero eigenvectors of the Hessian. At a nonequilibrium point, this is no longer the case, except when $(\partial D_{A\mu'}^{(\alpha)}/\partial r_{A\mu}^0)=0$. This is indeed the case for the translational subgroup (see Table I). So when the gradient is nonzero, the full Cartesian Hessian still has three zero eigenvectors from the translational invariance, but in general no zero eigenvectors related to the rotational invariance of V.

TABLE I. Derivatives of the transformation g for the parametrization defined in Eq. (4). The Levi-Civita symbol $\epsilon_{\lambda\mu\nu}$ equals 1 (−1) if $\lambda_{\mu\nu}$ is a cyclic (anticyclic) permutation of xyz and zero otherwise.

α	$D^{(\alpha)}_{A\mu}$	α	$\frac{\partial D^{(\alpha)}_{A\mu}}{\partial r^0_{A\nu}}$	α	α'	$C^{(\alpha\alpha')}_{A\mu}$
1	$\delta_{\mu x}$	1	0	1	1–6	0
2	$\delta_{\mu y}$	2	0	2	1–6	0
3	$\delta_{\mu z}$	3	0	3	1–6	0
4	$\Sigma_\lambda \epsilon_{\lambda\mu x} r^0_{A\lambda}$	4	$\epsilon_{\nu\mu x}$	4	4	$\delta_{\mu x} r^0_{Ax} - r^0_{A\mu}$
5	$\Sigma_\lambda \epsilon_{\lambda\mu y} r^0_{A\lambda}$	5	$\epsilon_{\nu\mu y}$		5	$\delta_{\mu y} r^0_{Ax}$
6	$\Sigma_\lambda \epsilon_{\lambda\mu z} r^0_{A\lambda}$	6	$\epsilon_{\nu\mu z}$		6	$\delta_{\mu z} r^0_{Ax}$
				5	5	$\delta_{\mu y} r^0_{Ay} - r^0_{A\mu}$
					6	$\delta_{\mu z} r^0_{Ay}$
				6	6	$\delta_{\mu z} r^0_{Az} - r^0_{A\mu}$

III. MOBILE BLOCK HESSIAN: CASE OF A SINGLE BLOCK

A. Blocks with fixed geometry

For simplicity, we first consider the case where one MBH block is considered, consisting of N_F atoms which will be labeled $\{F\}$. The internal geometry of the block has been fixed (e.g., using a lower-level theoretical method) and is described by the configuration $\{\mathbf{r}^0_F\}$. Keeping the latter fixed, one can optimize the positions of the remaining $N_E=N-N_F$ atoms, which will be labeled $\{E\}$. This requires a partial optimization,

$$\frac{\partial V}{\partial r_{E\nu}}(\{\mathbf{r}^0_F\},\{\mathbf{r}_{E'}\}) = 0, \quad \forall\, E\nu. \tag{12}$$

The solution $\{\mathbf{r}^0_E\}$ determines the total reference structure of the system $\{\mathbf{r}^0_A\}=\{\mathbf{r}^0_F,\mathbf{r}^0_E\}$.

Obviously, the total system is not in equilibrium since $G_{E\mu}=(\partial V/\partial r_{E\mu})_0=0$, but the gradients $G_{F\mu}\neq 0$ are in general nonzero. However, the MBH system with fixed internal geometry of the block has a reduced number, $3N_E+6$, of degrees of freedom (6 coming from translation/rotation of the rigid-body motion of the block, and $3N_E$ of the remaining atoms $\{E\}$). The reduced MBH system is in an equilibrium state, and normal mode analysis can be applied without problems. In particular, the symmetry of the potential surface will give rise to six normal modes at zero energy, corresponding to global translations and rotations.

B. MBH normal modes in internal coordinates

In Ref. 13, the MBH normal mode equations were derived using internal coordinates, as this is the most transparent. The choice of $3N-6$ internal coordinates $\{\theta_I\}$ is not completely arbitrary: in the present case of a single MBH block, one should arrange that $3N_F-6$ of the internal coordinates $\{\theta_{I_F}\}$ describe the internal geometry of the atoms F in the block. The remaining $3N_E$ internal coordinates will be labeled $\{\theta_{I_E}\}$. Such an arrangement is always possible, e.g., using Z matrix internal coordinates with the atoms of the block numbered consecutively, as indicated in Fig. 1.

The fixed geometry of the block determines $\{\theta^0_{I_F}\}$. If the potential energy in internal coordinates is given by $W(\{\theta_I\})$, finding the MBH equilibrium geometry now requires a partial optimization,

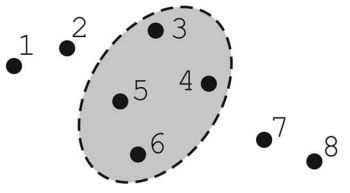
$$\frac{\partial W}{\partial \theta_{J_E}}(\{\theta^0_{I_F}\},\{\theta_{I_E}\}) = 0, \quad \forall\, \theta_{J_E}, \tag{13}$$

and the solution $\{\theta^0_{I_E}\}$ determines the total reference structure $\{\theta^0_I\}=\{\theta^0_{I_F},\theta^0_{I_E}\}$.

With a body frame whose origin is at the center of mass $\mathbf{r}_{\text{c.m.}}$, the energy of Eq. (1) can be rewritten in terms of the internal coordinates $\{\theta_I\}$, the three components of $\mathbf{r}_{\text{c.m.}}$, and three angles specifying the orientation of the body frame, as

$$E = \frac{1}{2}\mathcal{M}\dot{\mathbf{r}}^2_{\text{c.m.}} + \frac{1}{2}\omega\cdot\bar{\bar{\mathbf{I}}}\cdot\omega + \omega\cdot\sum_I \mathbf{A}_I\dot{\theta}_I + \frac{1}{2}\sum_{IJ} B_{IJ}\dot{\theta}_I\dot{\theta}_J + W(\{\theta_I\}). \tag{14}$$

Here $\mathcal{M}$ is the total mass and ω the angular velocity vector of the body frame. The inertial tensor $\bar{\bar{\mathbf{I}}}$, the Coriolis coupling $\mathbf{A}_I$ between the body-frame rotation and internal velocity $\dot{\theta}_I$, and the B_{IJ} matrix are all functions of the internal coordinates.



atom	coordinates		
1			
2	r_{12}		
3	r_{23}	a_{123}	
4	$\mathbf{r_{34}}$	a_{234}	d_{1234}
5	$\mathbf{r_{45}}$	$\mathbf{a_{345}}$	d_{2345}
6	$\mathbf{r_{56}}$	$\mathbf{a_{456}}$	$\mathbf{d_{3456}}$
7	r_{67}	a_{567}	d_{4567}
8	r_{78}	a_{678}	d_{5678}

FIG. 1. System of eight atoms with a single block. In the Z-matrix construction of internal coordinates, the atoms of the block (3–6) should be numbered consecutively. Notation r is used for distances between atoms, a for angles, and d for dihedral angles. The Z coordinates indicated in boldface describe the internal geometry of the block and are kept fixed during the vibrational analysis.

Normal mode equations are generally obtained by expanding the energy in Eq. (1) up to quadratic terms in the displacements $\Delta_I = \theta_I - \theta_I^0$ and the velocities $\dot{\Delta}_I$, ω, and $\dot{\mathbf{r}}_{\mathrm{c.m.}}$. In the MBH approach, the block is allowed to move as a rigid body during the small amplitude motion, with fixed geometry. This can now be simply expressed by setting the displacements $\Delta_{I_F}=0$ and velocities $\dot{\Delta}_{I_F}=0$. The quadratic expansion of the MBH potential energy, e.g., becomes

$$W(\{\theta_I\}) \approx V_0 + \frac{1}{2}\sum_{I_E J_E}\left(\frac{\partial^2 W}{\partial \Delta_{I_E}\partial \Delta_{J_E}}\right)_0 \Delta_{I_E}\Delta_{J_E}$$

$$= V_0 + \frac{1}{2}\sum_{I_E J_E} H^{(ii)}_{I_E J_E}\Delta_{I_E}\Delta_{J_E}. \tag{15}$$

The corresponding MBH normal mode equations are just the standard ones in internal coordinates, but with the columns and rows corresponding to the fixed θ_{I_F} omitted from the Hessian and mass matrix,

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & H^{(ii)} \end{pmatrix}\begin{pmatrix} v^{(c)} \\ v^{(r)} \\ v^{(i)} \end{pmatrix} = \omega^2 \begin{pmatrix} M^{(cc)} & 0 & 0 \\ 0 & M^{(rr)} & M^{(ri)} \\ 0 & (M^{(ri)})^T & M^{(ii)} \end{pmatrix} \times \begin{pmatrix} v^{(c)} \\ v^{(r)} \\ v^{(i)} \end{pmatrix}, \tag{16}$$

where $v^{(c)}$, $v^{(r)}$, and $v^{(i)}$ have dimensions 3, 3, and $3N_E$, respectively, and the mass matrix entries read $M^{(cc)}_{\mu\nu}=\mathcal{M}\delta_{\mu\nu}$, $M^{(rr)}_{\mu\nu}=I_{\mu\nu}(\{\theta_I^0\})$, $M^{(ri)}_{\mu I_E}=A_{\mu I_E}(\{\theta_I^0\})$, and $M^{(ii)}_{I_E J_E}=B_{I_E J_E}(\{\theta_I^0\})$. The MBH eigenvalue problem of dimension $3N_E+6$ still has six zero eigenvalues corresponding to overall translation and rotation. These can be decoupled in the usual way[14–16] by a congruent transformation, $\tilde{v}^{(c)}=v^{(c)}$, $\tilde{v}^{(i)}=v^{(i)}$, $\tilde{v}^{(r)}=v^{(r)}+(M^{(rr)})^{-1}M^{(ri)}v^{(i)}$, yielding the final $3N_E$-dimensional normal mode equation,

$$H^{(ii)}\tilde{v}^{(i)} = \omega^2[M^{(ii)} - (M^{(ri)})^T(M^{(rr)})^{-1}M^{(ri)}]\tilde{v}^{(i)}. \tag{17}$$

If one has access to selected Hessian matrix elements in the chosen internal coordinates, this is obviously the most straightforward way of implementing MBH. However, the Hessian is commonly given in Cartesian coordinates, and it is of interest to analyze the elements of $H^{(ii)}$ in terms of these. At first sight, one may think that *all* Cartesian Hessian elements are needed (including those involving the atoms $\{F\}$ of the fixed block) for the evaluation of $H^{(ii)}$, since a displacement Δ_{I_E} can change the position or orientation of the block with respect to a space-fixed frame. In fact, it is always possible to use the global translational/rotational invariance of the potential surface to rewrite $H^{(ii)}$ in terms of the Cartesian Hessian matrix elements of the relaxed atoms $\{E\}$.

This was already noted in Ref. 13, where a particular set of internal coordinates $\{\theta_{I_E}\}$ was used (the Cartesian coordinates of the atoms $\{E\}$ in a frame attached to the rigid block). We now show that this holds for the most general choice of internal coordinates $\{\theta_I\}$, provided that $3N_F-6$ of them determine the geometry of the block.

Suppose that for each shape $\{\theta_I\}$ one has selected a configuration $\{\mathbf{r}_A^{\mathrm{bf}}(\{\theta_I\})\}$ in coordinate space. This corresponds to the selection of a body frame.[17] Then the additional global translational/rotational coordinates can be defined as the parameters p of the symmetry transformation needed to let the actual configuration in the space-fixed frame coincides with the body-frame configuration,

$$\mathbf{r}_A = \mathbf{g}(\mathbf{r}_A^{\mathrm{bf}}(\{\theta_I\}),p), \tag{18}$$

and the potential energy becomes

$$V(\{\mathbf{r}_A\}) = V(\{\mathbf{g}(\mathbf{r}_A^{\mathrm{bf}}(\{\theta_I\}),p)\}) = V(\{\mathbf{r}_A^{\mathrm{bf}}(\{\theta_I\})\}) \equiv W(\{\theta_I\}). \tag{19}$$

When describing the reduced (MBH) system, the $\{\theta^0_{I_F}\}$ are fixed. It is then always possible to attach the body frame to the fixed MBH block. As a consequence, the body-frame coordinates of the $\{F\}$ atoms are constant,

$$\frac{\partial r^{\mathrm{bf}}_{F\mu}}{\partial \theta_{I_E}}(\{\omega^0_{I_F}\},\{\theta_{I_E}\}) = 0, \tag{20}$$

and the Hessian $H^{(ii)}$ in Eq. (15) simply becomes

$$H^{(ii)}_{I_E J_E} = \sum_{E'\mu',E''\mu''}\left(\frac{\partial^2 V}{\partial r_{E'\mu'}\partial r_{E''\mu''}}\right)_0\left(\frac{\partial r^{\mathrm{bf}}_{E'\mu'}}{\partial \theta_{I_E}}\right)_0\left(\frac{\partial r^{\mathrm{bf}}_{E''\mu''}}{\partial \theta_{J_E}}\right)_0, \tag{21}$$

where only Cartesian matrix elements involving the $\{E\}$ atoms are needed in the summation.

C. Cartesian formulation of single-block MBH using group coordinates

In the following section, we develop an alternative formulation of the MBH normal mode equations, suitable when only Cartesian (Hessian and gradient) information is available. It has the advantage that no system of internal coordinates and body frame needs to be specified. This avoids the evaluation of the body-frame coordinate derivatives in Eq. (21), and facilitates the automization of the input for the numerical code. The method was used in the practical calculations of Ref. 13, as it can be very easily extended to the case of multiple blocks (see Sec. IV).

The movement of the block as a rigid body can be described in a natural way by treating the six group parameters in Eq. (2) as dynamical variables, such that the instantaneous position of each atom F in the block is given by the result of a common translation/rotation of the reference position $\{\mathbf{r}^0_F\}$ in the block,

$$\mathbf{r}_F(t) = \mathbf{g}(\mathbf{r}^0_F, p(t)). \tag{22}$$

The velocities of the N_F atoms in the block are

$$\dot{r}_{F\mu} = \sum_\alpha \frac{\partial g_\mu}{\partial p_\alpha}(\mathbf{r}^0_F,p)\dot{p}_\alpha. \tag{23}$$

In order to link the MBH normal mode equations in Eq. (17) with the Cartesian Hessian, we will therefore choose as variables the six parameters p_α, combined with the $3N_E$ Car-

tesian coordinates $\{\mathbf{r}_E\}$ of the remaining atoms. The potential energy expressed in the new coordinates becomes

$$\tilde{V}(p,\{\mathbf{r}_E\}) = V(\{\mathbf{g}(\mathbf{r}_F^0,p)\},\{\mathbf{r}_E\}). \tag{24}$$

Obviously, the partially optimized MBH reference structure $\{\mathbf{r}_A^0\}$, determined in Sec. III A, corresponds to $p=0$ and $\{\mathbf{r}_E^0\}$ in the present coordinates. At this reference point, the first derivatives of $\tilde{V}$ vanish,

$$\tilde{G}_\alpha = \left(\frac{\partial \tilde{V}}{\partial p_\alpha}\right)_0 = \sum_{F\mu} G_{F\mu} D_{F\mu}^{(\alpha)} = 0, \tag{25}$$

$$\tilde{G}_{E\mu} = \left(\frac{\partial \tilde{V}}{\partial r_{E\mu}}\right)_0 = G_{E\mu} = 0, \tag{26}$$

as can also be seen from Eqs. (7) and (12).

Global translational/rotational invariance can now be expressed by applying the same transformation P to both the block and to the atoms $\{E\}$,

$$\tilde{V}(p,\{\mathbf{r}_E\}) = \tilde{V}(\Phi(p,P),\{\mathbf{g}(\mathbf{r}_E,P)\}). \tag{27}$$

In order to calculate derivatives of Eq. (27) one needs an elementary property of the group multiplication law $\Phi(p,P)$ near the identity. Since $\Phi(p,0)=p$ and $\Phi(0,P)=P$, one has

$$\frac{\partial \Phi_\beta}{\partial p_\alpha}(0,0) = \delta_{\alpha,\beta} = \frac{\partial \Phi_\beta}{\partial P_\alpha}(0,0). \tag{28}$$

Calculating the derivatives of Eq. (27) at the reference point and at $P=0$, one now finds

$$\frac{\partial^2}{\partial P_\alpha \partial p_{\alpha'}} \to \tilde{H}_{\alpha,\alpha'} + \sum_{E\mu} \tilde{H}_{E\mu,\alpha'} D_{E\mu}^{(\alpha)} = 0, \tag{29}$$

$$\frac{\partial^2}{\partial P_\alpha \partial r_{E\mu}} \to \tilde{H}_{\alpha,E\mu} + \sum_{E'\mu'} \tilde{H}_{E\mu,E'\mu'} D_{E'\mu'}^{(\alpha)} = 0, \tag{30}$$

where we used the obvious notation

$$\tilde{H}_{\alpha,\alpha'} = \left(\frac{\partial^2 W}{\partial p_\alpha \partial p_{\alpha'}}\right)_0, \tag{31}$$

$$\tilde{H}_{\alpha,E\mu} = \left(\frac{\partial^2 W}{\partial p_\alpha \partial r_{E\mu}}\right)_0, \tag{32}$$

$$\tilde{H}_{E\mu,E'\mu'} = \left(\frac{\partial^2 W}{\partial r_{E\mu} \partial r_{E'\mu'}}\right)_0. \tag{33}$$

It is now easy to check from Eqs. (29) and (30) that the six vectors $v^{(\alpha)}$, with components

$$v_{\alpha'}^{(\alpha)} = \delta_{\alpha,\alpha'}; \quad v_{E\mu}^{(\alpha)} = D_{E\mu}^{(\alpha)}, \tag{34}$$

are eigenvectors of the Hessian $\tilde{H}$ with zero eigenvalue.

The normal mode equations in the group coordinates are of dimension $3N_E+6$ and read in standard form,

$$\tilde{H}v = \omega^2 \tilde{M} v, \tag{35}$$

with $\tilde{M}$ the corresponding mass matrix, to be derived from the kinetic energy. Expanding around the total reference structure $\{r_A^0\}$, the kinetic energy [see Eq. (23)] is

$$T = \frac{1}{2}\sum_{F\mu} m_F \left(\sum_\alpha D_{F\mu}^{(\alpha)} \dot{p}_\alpha\right)^2 + \frac{1}{2}\sum_E m_E \dot{\mathbf{r}}_E^2. \tag{36}$$

This determines the mass matrix components,

$$\tilde{M}_{\alpha,\alpha'} = \sum_{F\mu} m_F D_{F\mu}^{(\alpha)} D_{F\mu}^{(\alpha')}, \tag{37}$$

$$\tilde{M}_{\alpha,E\mu} = 0, \tag{38}$$

$$\tilde{M}_{E\mu,E'\mu'} = \delta_{E,E'}\delta_{\mu,\mu'} m_E. \tag{39}$$

Note that the mass matrix is block diagonal in the block structure induced by the present choice of the six coordinates p_α and $3N_E$ coordinates $r_{E\mu}$.

The six zero eigenvectors in Eq. (34) can now be decoupled from the intrinsic normal modes, using congruent transformations to affect a simultaneous block diagonalization of $\tilde{H}$ and $\tilde{M}$. The required transformation matrices are then given by

$$T_1 = \begin{pmatrix} 1_{6\times 6} & 0_{6\times d} \\ x & 1_{d\times d} \end{pmatrix} = (u\ w); \quad T_2 = \begin{pmatrix} 1_{6\times 6} & y \\ 0_{d\times d} & 1_{d\times d} \end{pmatrix}, \tag{40}$$

where the dimensions of the identity and zero submatrices are explicitly indicated, and with the dimension $d=3N_E$. When the first transformation matrix is determined by the submatrix $x_{E\mu,\alpha}=D_{E\mu}^{(\alpha)}$, the first six columns of T_1 become the zero eigenvectors in Eq. (34), collected in the matrix u. The transformed Hessian,

$$T_1^T \tilde{H} T_1 = \begin{pmatrix} 0_{6\times 6} & 0_{6\times d} \\ 0_{d\times 6} & \tilde{H}' \end{pmatrix}, \tag{41}$$

has zero at its first six rows and columns, while the remainder is left unchanged,

$$\tilde{H}'_{E\mu,E'\mu'} = \tilde{H}_{E\mu,E'\mu'}. \tag{42}$$

The second transformation leaves the Hessian matrix in Eq. (41) intact, and can be used to block diagonalize the mass matrix. This requires the choice

$$y_{\alpha,E\mu} = -\sum_{\alpha'} [S^{-1}]_{\alpha,\alpha'} D_{E\mu}^{(\alpha')} m_E, \tag{43}$$

or, in matrix notation,

$$y = -S^{-1} u^T \tilde{M} w. \tag{44}$$

The matrix S has components

$$S_{\alpha,\alpha'} = \sum_{A\mu} m_A D_{A\mu}^{(\alpha)} D_{A\mu}^{(\alpha')}, \tag{45}$$

and contains the information (mass and inertial tensor) for rigid-body motion of the global system in the reference configuration $\{\mathbf{r}_A^0\}$. One can now verify that the transformed

Hessian and mass matrix have a decoupled form,

$$T_2^T T_1^T \tilde{H} T_1 T_2 = \begin{pmatrix} 0_{6\times 6} & 0_{6\times d} \\ 0_{d\times 6} & \tilde{H}' \end{pmatrix},$$

$$T_2^T T_1^T \tilde{M} T_1 T_2 = \begin{pmatrix} S & 0_{6\times d} \\ 0_{d\times 6} & \tilde{M}' \end{pmatrix}, \tag{46}$$

and the final normal mode equations for the $3N_E$ intrinsic modes are

$$\tilde{H}' v' = \omega^2 \tilde{M}' v', \tag{47}$$

where the correct mass matrix is given by

$$\tilde{M}'_{E\mu,E'\mu'} = \delta_{E,E'}\delta_{\mu,\mu'} m_E - \sum_{\alpha\alpha'} m_E m_{E'} D^{(\alpha)}_{E\mu} [S^{-1}]_{\alpha,\alpha'} D^{(\alpha')}_{E'\mu'}, \tag{48}$$

or, in matrix notation,

$$\tilde{M}' = w^T \tilde{M} w - w^T \tilde{M} u S^{-1} u^T \tilde{M} w. \tag{49}$$

We still need to express $\tilde{H}$ in terms of Cartesian quantities. A direct evaluation starting from Eq. (24) yields

$$\tilde{H}_{\alpha,\alpha'} = \sum_{F\mu,F'\mu'} H_{F\mu,F'\mu'} D^{(\alpha)}_{F\mu} D^{(\alpha')}_{F'\mu'} + \sum_{F\mu} G_{F\mu} C^{(\alpha\alpha')}_{F\mu}, \tag{50}$$

$$\tilde{H}_{\alpha,E\mu} = \sum_{F'\mu'} H_{E\mu,F'\mu'} D^{(\alpha)}_{F'\mu'}, \tag{51}$$

$$\tilde{H}_{E\mu,E'\mu'} = H_{E\mu,E'\mu'}. \tag{52}$$

In agreement with the discussion in Sec. III B, it is clear that only the Cartesian Hessian matrix elements of the $\{E\}$ atoms are needed for the normal mode equations in Eq. (47). In fact, for a single MBH block, one can even show that the other Hessian elements $\tilde{H}_{\alpha,E\mu}$ and $\tilde{H}_{\alpha,\alpha'}$ can be rewritten solely in terms of the $H_{E\mu,E'\mu'}$. This is indeed the case, since Eqs. (8) and (9) imply that zero is obtained when the summations over the $\{F\}$ atoms in Eqs. (50) and (51) are extended over *all* atoms $\{A\}$. As a consequence,

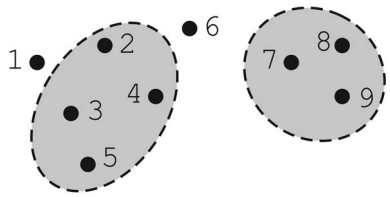
$$\tilde{H}_{\alpha,\alpha'} = \sum_{E\mu,E'\mu'} H_{E\mu,E'\mu'} D^{(\alpha)}_{E\mu} D^{(\alpha')}_{E'\mu'}, \tag{53}$$

$$\tilde{H}_{\alpha,E\mu} = -\sum_{E'\mu'} H_{E\mu,E'\mu'} D^{(\alpha)}_{E'\mu'}. \tag{54}$$

IV. MOBILE BLOCK HESSIAN: CASE OF MULTIPLE BLOCKS

A. Blocks with fixed geometry in internal coordinates

We now discuss the extension to the case where multiple blocks with fixed geometry are present, each of which can move as a rigid body. The blocks will be labeled $b = 1, \ldots, K$, where block b contains N_{F_b} atoms labeled $\{F_b\}$. As before, the remaining N_E atoms (which can move freely) are labeled $\{E\}$, and $N_E + \Sigma_b N_{F_b} = N$, where N is the total number of atoms in the molecule.



atom	coordinates
1	
2	r_{12}
3	$\mathbf{r_{23}}$ a_{123}
4	$\mathbf{r_{34}}$ $\mathbf{a_{234}}$ d_{1234}
5	$\mathbf{r_{45}}$ $\mathbf{a_{345}}$ $\mathbf{d_{2345}}$
6	r_{56} a_{456} d_{3456}
7	r_{67} a_{567} d_{4567}
8	$\mathbf{r_{78}}$ a_{678} d_{5678}
9	$\mathbf{r_{89}}$ $\mathbf{a_{789}}$ d_{6789}

FIG. 2. System of nine atoms with two MBH blocks. In the Z-matrix construction, the atoms of each block (2–5 and 7–9) should be numbered consecutively. The Z coordinates in boldface are kept fixed during the vibrational analysis.

Again, the most transparent derivation of the MBH approach proceeds through the introduction of $3N-6$ internal coordinates $\{\theta_I\}$. One now should take care that the internal geometry of the atoms in each block b is described by $3N_{F_b}-6$ internal coordinates $\{\theta_{I_{F_b}}\}$. The fixed geometry of the blocks is known beforehand, and given by $\{\theta^0_{I_{F_b}}\}$. The remaining $3N_E+6(K-1)$ coordinates $\{\theta_{I_E}\}$ are determined by partial optimization of the potential energy $W(\{\theta_I\})$:

$$\frac{\partial W}{\partial \theta_{J_E}}(\{\theta^0_{I_{F_b}}\},\{\theta_{I_E}\}) = 0, \quad \forall\ \theta_{J_E}, \tag{55}$$

and the solution $\{\theta^0_{I_E}\}$ determines the total reference structure $\{\theta^0_I\} = \{\theta^0_{I_{F_b}}, \theta^0_{I_E}\}$.

We emphasize that a suitable set of internal coordinates can always be constructed. In the Z-matrix formalism, e.g., one should only take care that the numbering of the atoms occurs consecutively in each block, as indicated in the example of Fig. 2.

The same reasoning as in Sec. III B leads to the conclusion that the normal mode equations of the multiple-block MBH system are identical to the single-block equations in Eq. (16) or (17), except that now the rows and columns corresponding to all the fixed $\{\theta_{I_{F_b}}\}$ should be omitted from the Hessian and mass matrix.

If one has access to the selected Hessian matrix elements $(\partial^2 W/\partial\theta_{I_E}\partial\theta_{I_{E'}})_0$ in internal coordinates, this is the most economical method (in terms of Hessian elements evaluations). If only Cartesian Hessian matrix elements are available, we will show that it is possible to generalize the description of Sec. III C in terms of group coordinates, thereby avoiding the construction of internal coordinates altogether.

B. Cartesian formulation of multiple-block MBH using group coordinates

The Cartesian formulation for one single block can easily be extended to multiple blocks in a straightforward way. Most of the expressions (22)–(54) remain unaffected apart from an additional index b running over the various blocks.

The potential energy $\tilde{V}$ now becomes a function of the $6K$ block parameters $\{p_b\}$, combined with the Cartesian co-

ordinates $\{\mathbf{r}_E\}$ of the remaining atoms. For completeness, we mention that one can make a distinction between a "normal" block and a block of collinear atoms, where the latter only requires five group parameters instead of six. For the sake of brevity, this distinction is not made here. Moreover, the final normal mode equations apply also in the presence of a "collinear block," except that one additional zero eigenvalue appears corresponding to rotation over the symmetry axis of the block.

The global translational/rotational invariance of $\tilde{V}$ is expressed by applying the same transformation P to all the blocks and the atoms $\{E\}$,

$$\tilde{V}(\{p_b\},\{\mathbf{r}_E\}) = \tilde{V}(\{\Phi(p_b,P)\},\{\mathbf{g}(\mathbf{r}_E,P)\}). \tag{56}$$

The ensuing consequences for the Hessian are readily derived by calculating the derivatives of Eq. (56) at the reference point and at $P=0$:

$$\frac{\partial^2}{\partial P_\alpha \partial p_{b'\alpha'}} \rightarrow \sum_b \tilde{H}_{b\alpha,b'\alpha'} + \sum_{E\mu} \tilde{H}_{E\mu,b'\alpha'} D^{(\alpha)}_{E\mu} = 0, \tag{57}$$

$$\frac{\partial^2}{\partial P_\alpha \partial r_{E\mu}} \rightarrow \sum_b \tilde{H}_{b\alpha,E\mu} + \sum_{E'\mu'} \tilde{H}_{E\mu,E'\mu'} D^{(\alpha)}_{E'\mu'} = 0, \tag{58}$$

using obvious notations for $\tilde{H}_{b\alpha,b'\alpha'}$, $\tilde{H}_{b\alpha,E\mu}$, and $\tilde{H}_{E\mu,E'\mu'}$ similar to those of Eqs. (31)–(33).

We see that the extension to multiple blocks is very straightforward: an extra index b indicates the block under consideration. In the kinetic energy expression [see Eq. (36)], an obvious summation over the multiple blocks b is introduced. It determines the mass matrix elements $\tilde{M}_{b\alpha,E\mu}$, $\tilde{M}_{E\mu,E'\mu'}$, and $\tilde{M}_{b\alpha,b'\alpha'}$. The first two are similar to Eqs. (38) and (39), while the last one is diagonal in the block index b,

$$\tilde{M}_{b\alpha,b'\alpha'} = \delta_{b,b'} \sum_{F_b\mu} m_{F_b} D^{(\alpha)}_{F_b\mu} D^{(\alpha')}_{F_b\mu}. \tag{59}$$

The normal mode equations are formally identical to Eq. (35), and are of dimension $6K+3N_E$. Inspection of Eqs. (57) and (58) indicates the form of the six eigenvectors $v^{(\alpha)}$ with zero eigenvalue, which express the translational/rotational invariance, as in Eq. (34). Elimination of these six zero modes $v^{(\alpha)}$ proceeds in much the same way as in the case of a single block. We (arbitrarily) select one of the blocks, B, and label this as the first block. The required transformation matrices T_1 and T_2 are then again given by Eq. (40) with the dimension $d=6(K-1)+3N_E$. The submatrix x in the first transformation has dimension $d\times 6$ and must be such that the first six columns of T_1 are the eigenvectors with zero eigenvalues. This requires $x_{b'\alpha',B\alpha}=\delta_{\alpha,\alpha'}$ for $b'=2,\ldots,K$ (or equivalently $b'\neq B$) and $x_{E\mu,B\alpha}=D^{(\alpha)}_{E\mu}$. The transformed Hessian $T_1^T\tilde{H}T_1$ now has zero at its first six rows and columns, while the remainder is left unchanged. The second transformation T_2 leaves $T_1^T\tilde{H}T_1$ intact. Block diagonalization of the mass matrix is obtained with the choice

$$y_{B\alpha,b'\alpha'} = -\sum_{\alpha''} [S^{-1}]_{\alpha,\alpha''} \sum_{F_{b'}\mu} D^{(\alpha)}_{F_{b'}\mu} D^{(\alpha')}_{F_{b'}\mu} m_{F_{b'}}$$

$$\text{for } b' \neq B, \tag{60}$$

$$y_{B\alpha,E\mu} = -\sum_{\alpha'} [S^{-1}]_{\alpha,\alpha'} D^{(\alpha')}_{E\mu} m_E, \tag{61}$$

or in matrix notation $y=-S^{-1}u^T\tilde{M}w$, where the 6×6 matrix S is given by Eq. (45). One can now verify that the transformed Hessian and mass matrix have the same decoupled form as in Eq. (46). The final normal mode equations for the d intrinsic modes are again formally identical to Eq. (47). The correct mass matrix is given by $(b,b'\neq B)$

$$\tilde{M}'_{b\alpha,b'\alpha'} = \tilde{M}_{b\alpha,b'\alpha'} - \sum_{\beta\beta'} [S^{-1}]_{\beta,\beta'} \tilde{M}_{b\alpha,b\beta} \tilde{M}_{b'\alpha',b'\beta'}, \tag{62}$$

$$\tilde{M}'_{b\alpha,E\mu} = 0, \tag{63}$$

$$\tilde{M}'_{E\mu,E'\mu'} = \delta_{E,E'}\delta_{\mu,\mu'} m_E - \sum_{\alpha\alpha'} m_E m_{E'} D^{(\alpha)}_{E\mu} [S^{-1}]_{\alpha,\alpha'} D^{(\alpha')}_{E'\mu'}. \tag{64}$$

In matrix notation, these expressions equal Eq. (49).

Note that the reduced Hessian $\tilde{H}'$ in the intrinsic normal mode equations has identical components as $\tilde{H}$, but the subspace involving the block B has been eliminated. It is again straightforward to express $\tilde{H}$ in terms of Cartesian quantities, with $\tilde{H}_{b\alpha,E'\mu'}$ and $\tilde{H}_{E\mu,E'\mu'}$ as in Eqs. (51) and (52), and

$$\tilde{H}_{b\alpha,b'\alpha'} = \sum_{F_b\mu,F'_{b'}\mu'} H_{F_b\mu,F'_{b'}\mu'} D^{(\alpha)}_{F_b\mu} D^{(\alpha')}_{F'_{b'}\mu'} + \delta_{b,b'} \sum_{F_b\mu} G_{F_b\mu} C^{(\alpha\alpha')}_{F_b\mu}. \tag{65}$$

It is now clear that, in order to evaluate the reduced Hessian $\tilde{H}'$, one only needs the Cartesian Hessian and gradient involving the blocks $b\neq B$, as well as the atoms $\{E\}$. In practice, it is therefore advantageous to pick the largest block, as the block B that is eliminated.

As a final remark, we note that it is possible to rewrite the Cartesian gradient term in Eq. (65) in favor of Cartesian Hessian elements. Using the expressions for the zero eigenvectors of $\tilde{H}$, one finds

$$\sum_{F_b\mu} G_{F_b\mu} C^{(\alpha\alpha')}_{F_b\mu} = -\sum_{b'} \sum_{F_b\mu,F'_{b'}\mu'} H_{F_b\mu,F'_{b'}\mu'} D^{(\alpha)}_{F_b\mu} D^{(\alpha')}_{F'_{b'}\mu'} - \frac{1}{2} \sum_{F_b\mu} \sum_{E\nu} H_{F_b\mu,E\nu} \left(D^{(\alpha)}_{F_b\mu} D^{(\alpha')}_{E\nu} + D^{(\alpha')}_{F_b\mu} D^{(\alpha)}_{E\nu} \right), \tag{66}$$

where the right-hand side has been symmetrized in α and α', to reduce numerical errors. In practice, it is more convenient to use Eq. (65) since Eq. (66) requires *all* Cartesian Hessian elements, and the previous computational advantage of eliminating the elements of a selected block is lost.

V. PRACTICAL PROCEDURE FOR IMPLEMENTING MBH

For clarity, we summarize here the practical procedure for the MBH scheme for partially optimized systems. The example of Fig. 2 will be used to illustrate the procedure.

(1) *Block selection*. Choose blocks and number the atoms of the blocks consecutively. In Fig. 2, two blocks are defined: atoms 2–5 and atoms 7–9.

(2) *Partial optimization*. Optimize the system while keeping the internal geometry of the blocks fixed. In Fig. 2, the internal coordinates in boldface are kept fixed during the optimization [this option is, e.g., provided in the modeling package GAUSSIAN03 (Ref. 18)]. Note that one can as well keep the atoms of block 1 at their absolute positions, while internal coordinates should be fixed for the other blocks. This is equivalent, as we are interested in the partially optimized *internal* geometry and not the absolute space frame coordinates. In Fig. 2, for instance, the positions $\mathbf{r}_2-\mathbf{r}_5$ and the internal coordinates r_{78}, r_{89}, a_{789} of the second block can be held constant.

(3) *Calculation of second derivatives*. The second derivatives at the partially optimized (reference) structure should be calculated at the same level of theory as used in the partial optimization procedure.

- If the Hessian in internal coordinates is available, construct $H^{(ii)}$ of Eq. (16) by omitting the rows and columns of the Hessian corresponding to fixed internal coordinates. The MBH normal modes follow from solving Eq. (17). Note that it is of computational profit to calculate, if possible, only the Hessian elements corresponding to the $\{\theta_{I_E}\}$ coordinates.
- If only the Cartesian Hessian (and gradient) is available, first calculate the coefficients $D_{A\mu}^{(\alpha)}$ and $C_{A\mu}^{(\alpha\alpha')}$ using Table I. Construct $\tilde{M}$ using Eqs. (38), (39), and (59). Construct $\tilde{H}$ using Eqs. (51), (52), and (65). The MBH normal modes follow from solving Eq. (35). Note that one can obtain a reduction in the number of required Cartesian Hessian matrix elements by considering the submatrix $\tilde{H}'$ of $\tilde{H}$, in which the six rows/columns involving one block B are omitted. The reduction is considerable if the block B is large. The corresponding mass matrix $\tilde{M}'$ is given by Eqs. (62)–(64). The MBH normal modes then follow from solving Eq. (47).
- If it is possible to calculate second derivatives in arbitrary coordinates (e.g., using finite difference approximation), one may choose the set $\{p_b,\mathbf{r}_E\}$ that includes the group parameters for the blocks, and calculate $\tilde{H}$ or $\tilde{H}'$ directly.

VI. CONCLUSION

Partially optimized systems require an adapted vibrational analysis, since the standard normal mode analysis applied to nonoptimized structures yields unphysical results. Therefore, the MBH approach was developed, which introduces rigid blocks in the vibrational analysis. This paper concentrates on the formulation of the MBH model in three sets of coordinates: internal coordinates, Cartesian coordinates, and a set including group parameters. A practical calculation scheme for all cases was summarized in the previous section, to allow a simple implementation in existing simulation packages.

Concerning the computational cost of the MBH model, the first reduction in computer time is, of course, the partial optimization instead of an expensive full optimization. For a system with N atoms, treated in terms of K blocks and N_E freely moving atoms, only $d=6(K-1)+3N_E$ coordinates have to be optimized. When one has the freedom to choose which Hessian elements are calculated in the frequency analysis, the MBH approach is able to reduce the number of Hessian elements significantly as well.

In internal coordinates, one needs the second derivatives with respect to d coordinates $\{\theta_{I_E}\}$ only, where usually $d \ll 3N$, or the MBH approach is much less expensive than the full Hessian calculation.

A very natural description of the fixed block dynamics was obtained by introducing group parameters for the six translational/rotational degrees of freedom of each block. This also avoids the explicit construction of internal coordinates. The complete set of $d+6$ coordinates $\{p_b,\mathbf{r}_E\}$ consists of the group parameters $\{p_b\}$ and the Cartesian coordinates $\{\mathbf{r}_E\}$ of the relaxed atoms. Since the translational/rotational invariance is fully respected, six modes with zero eigenfrequency are found which can be decoupled easily from the intrinsic modes. These symmetries also allow to eliminate the group parameters of one arbitrary block B. As a result, the normal mode equations now require the second derivatives with respect to d variables $\{p_b,r_E\}|_{b\neq B}$.

The formulation of the MBH approach in Cartesian coordinates is of great practical importance. The implementation is perfectly possible but, at first sight, the computational profit of the MBH method is lost, since all Cartesian Hessian elements seem to be needed. Nevertheless, even in Cartesian coordinates, a certain computer time reduction can be realized. Using symmetry arguments, it is possible to eliminate the Cartesian components related to the atoms of one arbitrary block B. By choosing this block B to be the biggest one, the largest reduction in computer time is obtained: only second derivatives with respect to $3N-3N_{F_B}$ variables $\{r_{A\mu}\}|_{A\notin B}$ are required. Note that in the case of a single block ($K=1$), this implies that the MBH equations are constructed uniquely with Cartesian Hessian elements of the free atoms, and are computationally equally demanding as the PHVA method.

We remark that the MBH model aims at describing selected modes of interest, for which one assumes that they do not involve changes in the geometry of the fixed blocks. What still missing is the coupling between the normal modes of interest and those that were eliminated by fixing the block geometry. An interesting extension in the future would be to estimate this coupling in perturbation theory, using methods similar to the ones described in Refs. 10–12.

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