First-Principle Calculation of Reduced Masses in Vibrational Analysis Using Generalized Internal Coordinates: Some Crucial Aspects and Examples[†]

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In this paper we present and analyze the most essential aspects of reduced masses along generalized internal coordinates. The definition of reduced masses in the internal coordinate formalism is established through the Wilson *G*-matrix concept and includes sophisticated relations between internal and Cartesian coordinates. Moreover, reduced masses in internal coordinates are, in general, no longer constant but coordinate-dependent. Based on the approach presented earlier [Stare, J.; Balint-Kurti, G. G. *J. Phys. Chem. A* **2003**, *107*, 7204−7214] and on our experience with reduced masses discussed in this paper, we have developed a robust program for the calculation of Wilson *G*-matrix elements and their functional coordinate dependence. The approach is based on the first principles and can be used in virtually any (internal) coordinate set. Since the program allows for projection of any kind of nuclear motion on the selected internal coordinates, the method is particularly suitable for ab initio or DFT potential energy functions calculated by partial geometry optimization. Moreover, reduced masses obtained by this program can be used as a decision tool for selecting the most appropriate internal coordinates for the considered vibrational problem and for the inclusion or omission of the kinetic coupling terms in the vibrational Hamiltonian.

1. INTRODUCTION

Vibrational analysis is a valuable computational tool that can greatly assist the assignment of vibrational spectra of a wide variety of molecular systems and improve the understanding of the structural and functional properties of matter. Owing to the fact that the underlying physics allows for very simple yet reliable mathematical formulation that can be easily implemented in program codes and run even on the most primitive computers, classical normal-mode (harmonic) vibrational analysis, as outlined by perhaps the most prominent author in this field, Wilson,[1] has been used along with experimental methods for decades. Harmonic vibrational analysis is one of the most used methods even with sophisticated quantum-mechanical computational program packages, among the rest because it provides the most straightforward verification for the consistency of a geometry optimization.

Despite its general usefulness, harmonic vibrational analysis has its own well-defined limits. Obviously the fundamental assumption—that the potential energy surface can be simplified to a quadratic function—is not valid in a number of cases. This is particularly pronounced in systems that feature double-well potentials separated by a low barrier, among which hydrogen bonds (H-bonds) are probably the most well-known example. Another feature that is not accounted for in the classical harmonic analysis is the fact that the motion of some light nuclei (hydrogen in the first place) is essentially quantum in its nature; this effect is particularly significant for potentials that considerably deviate from the harmonic form. In such cases, harmonic analysis is usually insufficient, and its results typically feature large offsets from experimental vibrational frequencies. Evidently, an upgrade in the computational approach is required to overcome these problems; perhaps the most general solution is the quantum treatment of selected vibrational modes of the system which is based on the solving of the vibrational Schrödinger equation. There exist a variety of corresponding computational strategies,[2−8] and all share the problem of considerable complexity and high costs—namely, a large number of evaluations of the potential energy is required; this number increases exponentially with the number of considered vibrational degrees of freedom. Moreover, when coordinates other than Cartesian or normal are used, the kinetic part of the vibrational Hamiltonian becomes quite complicated (*see below*). It is for these reasons that the quantum treatment of fully coupled anharmonic vibrations is extremely difficult, and its application is limited to only a few degrees of freedom.

When potential energy function deviates considerably from the harmonic form and when high-amplitude atomic motion is involved (e.g., a proton in a double well potential with low barrier), it is convenient to formulate and solve the vibrational problem in *internal* rather than in Cartesian or normal coordinates; thus, coordinates such as bond distances, valence angles, torsions, etc., are often used for the computational treatment of anharmonic vibrations.[7,9−12] The main feature of an internal coordinate set is that its origin is fixed to some internal parameter of the system so that internal coordinates are invariant under translation or rotation of the system. Clearly, possible choices of internal coordinates are well beyond the simple bond distances or angles, although these are most likely to be used. The advantage of a concept of internal coordinates is that they can depict the system from a chemically relevant point of view, but, on the other hand,

there is an inconvenient drawback concerning the formulation of masses. Namely, transformation of equations of motion from Cartesian to internal coordinates introduces the concept of reduced masses which assume a very sophisticated form and are difficult to determine. The kinetic energy formulation in internal coordinates can include (i) mixed second derivatives (kinetic coupling terms) and (ii) coordinate-dependent reduced masses. The formulation of reduced masses in a generalized internal coordinate set requires the first derivatives of all internal coordinates with respect to all the Cartesian coordinates of the system to be computed, as reflected in the Wilson G-matrix whose elements have the meaning of reciprocal reduced masses (*see section 2 for details*).

Despite the fact that the exact formulation for reduced masses in internal coordinates has been known for decades, a notable lack of published experience in this field has been observed. Among numerous studies dedicated to anharmonic vibrational problems in internal coordinates, only a few have included the first-principle approach for the determination of reduced masses and their coordinate dependence;[7,10,12,13] rather than that, simplified or intuitively determined forms of reduced masses have been used, with their coordinate dependence and kinetic coupling often neglected. Another difficulty often met in advanced vibrational analysis is that reduced masses along some nonbonded internal coordinates, such as the O···O distance in an O−H···O H-bond, are difficult even for intuitive estimation. The main motivation for our work was to fill this gap and provide a robust computational approach that allows for the calculation of reduced masses in a generalized internal coordinate set. In our earlier work we addressed this problem and demonstrated the significance of reduced masses in vibrational analysis;[7] however, we found that the complexity of the concept requires a more detailed presentation and analysis of various aspects, among the rest individual atomic contributions to reduced masses, isotope effects, and, particularly, the role of reduced masses in various strategies of calculating the potential energy surface.

In this paper we provide a detailed analysis and examples of all the relevant aspects of the first-principle determination of reduced masses in a generalized internal coordinate formalism, together with the corresponding computer program. The core part of the approach is taken from our earlier work.[7] The approach is based on the exact definition of the elements of Wilson G-matrix and its inverse; it has been also inspired by the work of Alexandrov et al.[10] Partial derivatives of Cartesian coordinates with respect to internal ones are obtained by interpolation of coordinates of the considered geometries, with translational and rotational components of atomic motion previously removed from the system by enforcing the Eckart conditions to all the structures considered.[14] The input to the program are Cartesian coordinates of several geometries of the system together with, for each geometry, the corresponding values of the considered internal coordinates. The output consists of the elements of the G-matrix in the given set of internal coordinates for each of the structures given in the input. The program can treat large sets of input geometries and is intended to be used along with pointwise multidimensional potential energy surface scans, although standalone application is also possible. Special attention has been paid to relaxed potential

energy surface scans where partial geometry optimization is performed at each point of the scan. We show that relaxed scan can have a dramatic impact to reduced masses, as additional nuclear motion that results from optimization is coupled to the selected vibratonal coordinates. Consequently, the resulting anharmonic frequencies can be considerably affected, and caution is needed when setting up the potential energy surface scan. In that sense, we show that reduced masses can be used as valuable decision tools for determining the strategy of the treatment of molecular vibrations beyond the harmonic approximation. The Fortran program code is available from the author upon request.

The paper is organized in the following way. In section 2 the formalism of the quantum kinetic vibrational operator and of the reduced masses in generalized internal coordinates, as reflected in the Podolsky Hamiltonian and Wilson G-matrix, is summarized. Decoupling of translational and rotational modes from vibrational ones via the Eckart frame is discussed, and its implementation in the approach is presented. The problem with determination of G-matrix elements, originating in nonunique transformation of internal coordinates to Cartesians, is discussed together with a consistent strategy of overcoming it. Section 3 includes various test examples regarding the most critical aspects of reduced masses, while concluding remarks are given in section 4.

2. THEORY

Kinetic Energy in Generalized Internal Coordinates and Wilson G-Matrix. The nuclear quantum kinetic energy operator in the Cartesian coordinate set ($\hat{T}_x$) can be written as

$$\hat{T}_x \equiv -\frac{\hbar^2}{2} \sum_{i=1}^{3N} \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2} \tag{1}$$

where m_i are atomic masses, and x_i are Cartesian coordinates (the number of atoms in the system is N). If a transformation between the Cartesian and generalized internal coordinate set is performed ($\{x_i\} \rightarrow \{q_i\}$), the kinetic operator ($\hat{T}_q$), according to Podolsky,[15] takes on the form

$$\hat{T}_q \equiv -\frac{\hbar^2}{2} \sum_{r=1}^{M} \sum_{s=1}^{M} \left[g^{1/4} \frac{\partial}{\partial q_r} \left[g^{-1/2} \cdot G^{rs} \frac{\partial}{\partial q_s} [g^{1/4}] \right] \right] \tag{2}$$

with q_r and q_s being internal coordinates, G^{rs} are the elements of the Wilson G-matrix,[1] and g is its determinant. M denotes the number of considered vibrational degrees of freedom which is equal to the size of the G-matrix; for a complete description of a nonlinear system, $M = 3N - 6$, but any noncomplete subset ($M < 3N - 6$) may also be used.

The G-matrix elements are defined as

$$G^{rs} \equiv \sum_{i=1}^{3N} \frac{1}{m_i} \frac{\partial q_r}{\partial x_i} \frac{\partial q_s}{\partial x_i} \tag{3}$$

and include partial derivatives of internal coordinates with respect to Cartesians, a consequence of the transformation between coordinate sets. Obviously, G-matrix is symmetric, $G^{rs} = G^{sr}$. It can be seen from the above formulation that

G-matrix elements may be regarded as "projection-weighted" inverses of atomic masses with the projection of Cartesian to internal coordinates being sought. Because kinetic energy operator includes double derivatives, each element of the *G*-matrix corresponds to a pair of internal coordinates (q_r and q_s) with respect to which the differentiation is performed. While diagonal elements of the matrix have the meaning of reciprocal masses along the respective internal coordinates, the off-diagonals correspond to pairwise kinetic couplings between them. In general, the derivatives $\partial q_r/\partial x_i$ are not constant but rather coordinate dependent. Consider, for example, a valence angle bending coordinate of an O−H group bound, say, to a carbon atom. A small variation of the bending angle C−O−H will result in a certain Cartesian displacement of the hydrogen atom. Since the O−H bond acts as a bending "arm", the Cartesian displacement (δx_i) per unit of change in the angle (δq_r) will be larger at large O−H distances, and the corresponding contribution $\partial q_r/\partial x_i$ to the *G*-matrix will decrease. As a result, the reduced mass pertaining to the O−H bending coordinate will be a significant function of the O−H stretching coordinate.[7]

Although both G^{rs} and g are, in general, functions of coordinates q_i, the coordinate dependence of the determinant g is in most cases small and can be neglected.[16] Thus g may be regarded as being constant, and the kinetic Hamiltonian takes on a simplified form

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\frac{\partial}{\partial q_r}\left[G^{rs}\frac{\partial}{\partial q_s}\right] \qquad (4)$$

The simplification that leads to this form is widely acceptable. Further simplifications are possible in some cases— one can either find the coordinate dependence of G^{rs} to be negligible, or neglect the coupling mixed derivative terms, or even both.[7] Eventually, in the normal coordinate formalism, all normal coordinates are expressed as linear functions of Cartesian coordnates, hence all derivatives $\partial q_r/\partial x_i$ of eq 3 (with q_r being normal coordinates) are constants, resulting in constant values of G^{rs}. Moreover, it can be shown that normal coordinates are free of kinetic coupling since all the off-diagonal elements of the *G*-matrix are equal to zero; therefore, for normal coordinates, the most simplified version of the kinetic operator can be used:

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}G^{rr}\frac{\partial^2}{\partial q_r^{\,2}} \qquad (5)$$

Note that the expression for $\hat{T}_q$ in eq 5 is exact in any set of normal coordinates but is not generally acceptable for internal coordinates because of the variable *G*-matrix elements and its nonzero off-diagonals. The computational approach for the calculation of *G*-matrix elements, proposed in this paper, is compliant with any form of $\hat{T}_q$ (eqs 2, 4, or 5 or any other simplified version), no matter what the level of simplification.

Removal of Translation and Rotation. Virtually all studies of molecular vibrations beyond the harmonic approximation are based on pointwise potential energy surface scans. Since not only potential energy but also geometry of the system can be extracted from each point of the scan, this is a good starting point for the evaluation of reduced masses. Namely, from a set of different geometries, deriva-

tives of the type $\partial q_r/\partial x_i$ can be evaluated and elements of the *G*-matrix can be computed by using eq 3. However, Cartesian coordinates of geometries acquired from the scan can include some unknown translational and rotational contribution that affects the derivatives. Therefore, in order to deal with pure vibrational motion, translational and rotational components need to be removed from Cartesian coordinates. This can be effectively achieved by displacing and rotating all the considered structures in such a way that for each of the structures the Eckart conditions[14] are satisfied relative to a reference structure:

$$\sum_{\alpha=1}^{N} m_\alpha(\mathbf{d}_\alpha \cdot \mathbf{r}_\alpha^0) = 0 \qquad (6)$$

$$\sum_{\alpha=1}^{N} m_\alpha(\mathbf{d}_\alpha \times \mathbf{r}_\alpha^0) = 0 \qquad (7)$$

In the above equations, $\mathbf{r}_\alpha^0$ denotes the position vector of the αth atom in the reference structure, and $\mathbf{d}_\alpha$ is the displacement vector of the same atom from its position in the reference structure. Note that the choice of the reference structure is arbitrary. The first equation represents translational invariance and can be satisfied simply by setting the origin of the coordinate system to the center of mass. The second condition represents rotational invariance and can be met by rotating the system around the origin; we have used numerical techniques to determine the parameters of rotation needed to satisfy the condition, although analytical solution also exists.[17] While numerical solution is satisfactory for the scope of our work, analytical solution is essential, for example, in symplectic molecular dynamics algorithms[18−21] to preserve the stability of the simulation.

Swapping the Role of Variables—the Inverse of the *G*-Matrix. Having set all the considered structures into the Eckart frame, it is possible to evaluate the derivatives $\partial q_r/\partial x_i$ and to determine the *G*-matrix elements according to eq 3. However, such a formulation does not account for the coupling between Cartesian and internal coordinates that originates from the removal of translational and rotational components from the atomic motion, as reflected in the Eckart conditions. Namely, in the formulation of derivatives in eq 3, Cartesian coordinates are independent variables, while internal coordinates are dependent variables. Since translation and rotation of the system, as governed by Eckart conditions, only affect Cartesian coordinates but not internal ones, there would be no variations in the internal coordinates due to the constraints of the Eckart frame, and the resulting derivatives $\partial q_r/\partial x_i$ would all be equal to zero except for the case when the Cartesian coordinate x_i is explicitly included in the definition of the internal coordinate q_r. The result of such a treatment would be that, for example, the reduced mass associated with the O···O motion in H-bonds of the O−H···O type would have been equal to 8 amu, regardless of the chemical composition of the system; the same number would have been obtained for a free diatomic oxygen molecule (O_2) (in other words, the corresponding *G*-matrix element would have assumed the value of 0.125 amu^{-1}). The constraints of the Eckart frame effectively make no sense in eq 3. An appropriate solution is to exchange the role of dependent and independent variables and, rather than G^{rs},

calculate the elements of the inverse of the *G*-matrix (G_{rs}), deifned as

$$G_{rs} \equiv \sum_{i=1}^{3N} m_i \frac{\partial x_i}{\partial q_r} \frac{\partial x_i}{\partial q_s} \qquad (8)$$

Elements of the *G*-matrix are then obtained by inverting the matrix of G_{rs}.[7]

Clearly, variation in the independent variable q_r would affect *all* Cartesian coordinates x_i through Eckart conditions, leading to (generally) nonzero derivatives $\partial x_i/\partial q_r$. In this sense, our approach differs from some previously published analytical formulations of *G*-matrix elements[13] in that contributions of *all* atoms are considered rather than only of those atoms that constitute the particular internal coordinates q_r and q_s pertaining to the G^{rs} element. Additionally, while those formulations are based on complete sets of predefined types of internal coordinates, our approach also works with incomplete internal coordinate subsets, making it ideal for the application to relaxed potential energy scans where the residual nuclear motion invoked by partial geometry optimization is reflected in the reduced masses.

The formal link between elements of the inverse-*G* (eq 8) and physical masses can best be seen from the classical expression for kinetic energy (*T*) of a polyatomic system in generalized internal coordinates. Starting from its well-known Cartesian analogue

$$T = \sum_{i=1}^{3N} m_i \dot{x}_i^2 \qquad (9)$$

where $\dot{x}_i = dx_i/dt$ corresponds to velocity along x_i, one can switch to internal coordinates ($\{x_i\} \rightarrow \{q_i\}$) by applying the fundamental transformation formula

$$dx_i = \sum_{r=1}^{M} \frac{\partial x_i}{\partial q_r} dq_r \qquad (10)$$

This results in the following expression for Cartesian velocities ($\dot{x}$) based on velocities along internal coordinates ($\dot{q}$):

$$\dot{x}_i = \sum_{r=1}^{M} \frac{\partial x_i}{\partial q_r} \dot{q}_r \qquad (11)$$

Substituting this expression into eq 9 yields

$$T = \sum_{r=1}^{M} \sum_{s=1}^{M} \left[\sum_{i=1}^{3N} m_i \frac{\partial x_i}{\partial q_r} \frac{\partial x_i}{\partial q_s} \right] \dot{q}_r \dot{q}_s$$

$$= \sum_{r=1}^{M} \sum_{s=1}^{M} G_{rs} \dot{q}_r \dot{q}_s \qquad (12)$$

Clearly, on the basis of analogy between terms in eqs 9 and 12, it can be seen that on transformation from Cartesian to internal coordinates physical masses are replaced by elements of the inverse-*G* and off-diagonal terms are introduced.

Outline of the Program. Direct application of eq 8 is in general possible for any single structure of the system, even if there is no information about other structures acquired from the scan or, ultimately, without any scan being carried out.
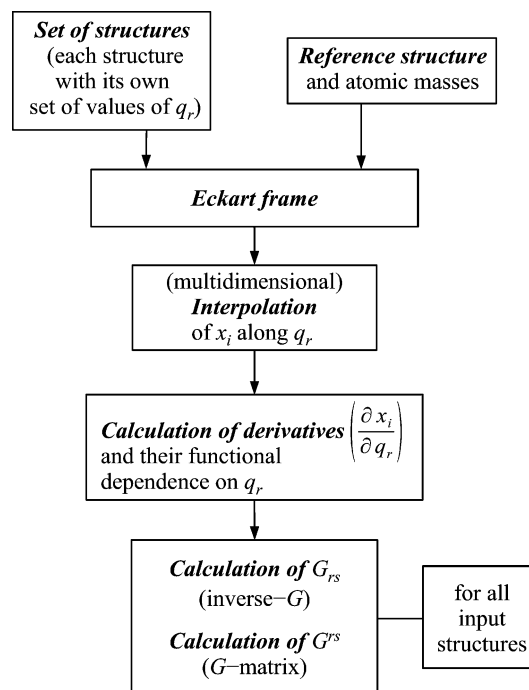

Figure 1. The program flowchart.

In practice however, there is a drawback that the variation of the internal coordinate q_r cannot be performed in a unique way. For that sake it is very useful to have a set of structures (e.g., acquired from a potential energy surface scan), because their Cartesian coordinates can be interpolated along the internal ones so that the derivatives in eq 8 can be estimated without the need to perform disputable variations in internal coodinates. In our program code, we have used the simple one-dimensional cubic spline scheme[22] for interpolating x_i along q_r; this scheme allows for analytic determination of the derivatives $\partial x_i/\partial q_r$. For calculation of the reduced mass along a single internal coordinate q the procedure is the following:

(1) Set all the structures into the Eckart frame.

(2) Perform cubic spline interpolation of all Cartesian coordinates along q.

(3) Calculate $\partial x_i/\partial q$ for the selected value of q and for all x_i and use eq 8 to determine the reduced mass.

Note that the reduced mass can be evaluated for any value of q. Typically, one may want to determine reduced masses for values of q that correspond to the input geometries. Extension to multidimensional determinantion of reduced masses, i.e., when several internal coordinates are taken into account, is also straightforward:

(1) Set all the structures into the Eckart frame.

(2) Choose an "active" internal coordinate q_r.

(3) Perform one-dimensional cubic spline interpolation of all Cartesian coordinates along q_r for all possible combinations of constant values of other internal coordinates that appear in the data set and calculate $\partial x_i/\partial q_r$ at all the corresponding points.

(4) Repeat (2) and (3) for all internal coordinates q_r.

(5) Using eq 8, calculate all the elements of the inverse of the Wilson *G* for all the geometries in the data set. Perform matrix inversion to obtain the corresponding *G*-matrices for all given structures.
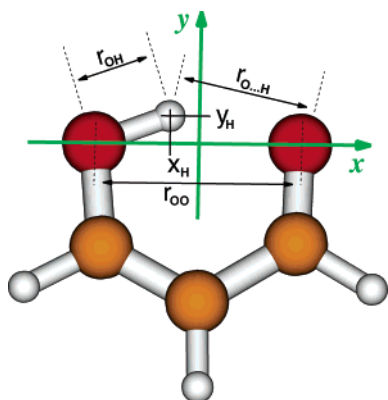
Figure 2. Structure and selected internal coordinates of malonaldehyde (MALD).

A flowchart describing the course of our program is displayed in Figure 1. The above procedure offers an instant insight into the functional dependence of the *G*-matrix elements on the considered internal coordinates. Together with the magnitude of the off-diagonal terms (G^{rs} with $r \neq s$, which may be negligible in many cases), this represents a valuable decision tool for the level of simplification of the model Hamiltonian in the further treatment.[7]

3. TEST APPLICATIONS

Methods and Models. Our model system on which the presented approach was tested was malonaldehyde (3-hydroxypropenal, see Figure 2), which has been known for years as a benchmark system for a short intramolecular H-bond. Malonaldehyde (abbreviation MALD) features an anharmonic double well potential with energetically equivalent minima separated by a low barrier. With a large body of various experimental data available in the gas phase, MALD proved to be a rewarding system for extensive computational studies. Because of its small size, MALD has been for a long time at the focal point of computational research of short H-bonds; a number of studies included advanced anharmonic treatment of the proton motion.[23-26] As such, MALD is a reasonable choice for the demonstration of the proposed program package. Moreover, MALD offers a convenient insight into the issue of selecting an appropriate strategy for a consistent treatment of anharmonic vibrations of its O–H···O moiety.

In this section, the following three aspects of reduced masses along selected internal coordinates associated with the H-bond of MALD are presented and discussed. First, the isotope effect on the reduced mass for a simple O–H stretching motion is taken into account. Next, the somewhat intriguing issue of choosing between single point and relaxed potential energy surface scan is considered by using the aspect of reduced masses. In both cases, one-dimensional vibrational models are sufficient for the demonstration. Finally, extension to multidimensional vibrational problems is discussed by using a simple two-dimensional model.

It should be noted that the term "reduced mass" for a single internal coordinate denotes the corresponding G_{11} element (eq 8); by "inverse reduced mass" is then meant the G^{11} term (eq 3); since the size of the *G*-matrix is 1, these values are mutually reciprocal. For multidimensional vibrational models it is the inversion of the entire *G*-matrix, rather than its

individual components, that converts between "reduced masses" and "inverse reduced masses" (G_{ij} and G^{ij} are in general not reciprocal to one another).

All potential energy calculations in this section were carried out at the common quantum-mechanical B3LYP/6-31+G(d,p) level of theory (isolated molecule model) using the *Gaussian 03* program package.[28] Note that, since the focal point of this paper is in the demonstration of the concept of reduced mass in advanced vibrational analysis rather than in providing very accurate multidimensional quantum vibrational models, the models demonstrated in this paper probably do not represent the most advanced treatments of the underlying vibrational problems of MALD. We demonstrate, however, that the concept of reduced masses presented here can serve as an important guideline for the design of novel, improved computational strategies. The reader is also referred to ref 7 for other examples that demonstrate the significance of the variable reduced masses and off-diagonal *G*-matrix elements for quantum-mechanical modeling of selected vibrations in short hydrogen bonds.

Single Internal Coordinate and Isotope Effect. In the first stage, the B3LYP/6-31+G(d,p) equilibrium geometry of MALD was taken, and the hydrogen atom was pointwise displaced along the O–H bond from r_{OH} = 0.8 to 1.8 Å in 0.1 Å steps such that the remainder of the molecule was kept frozen in the optimized conformation. The so obtained 11 structures, each pertaining to a different value of r_{OH}, have been subjected to determination of the reduced mass along r_{OH}. The isotope effect was modeled by setting the hydrogen mass (m_H) to 1, 3, 10, and 100 amu, respectively. While the values of 1 and 3 amu correspond to real isotopes, the higher masses were used solely to demonstrate the impact of atomic contributions to the profile of the reduced mass. Figure 3 shows the overlaid Eckart frame structures of MALD for different values of m_H and the resulting profile of G_{11} and some of its individual atomic components. For m_H = 1 amu, atoms other than the H-bonded hydrogen seem to be virtually at rest and not affected by its displacements. This is due to the fact that hydrogen is very light comparing to the rest of the molecule, and its displacements do not significanlty alter the center of mass or rotational axes. With increasing m_H, the center of mass and rotational axes become more affected, and the structures exhibit larger offsets from one another when Eckart conditions are enforced. Ultimately, at m_H = 100 amu, the "displaced" proton seems to be nearly at rest, while the surrounding atoms are heavily smeared.

The resulting reduced mass, calculated along the r_{OH} coordinate and displayed in Figure 3 and Table 1, is constant within the displayed precission for m_H = 1 amu; at higher hydrogen masses, a slight coordinate dependence arises which becomes significant at m_H = 100 amu. For m_H = 1, 3, and 10 amu, the major contribution to the reduced mass originates from the displaced hydrogen; relative contributions of other nuclei, particularly O(2), O(6), and C(3), increase with the increasing m_H at the expense of the contribution of H(1). At m_H = 100 amu, the hydrogen contributes less to the overall reduced mass than O(2) for most of the values of r_{OH}. The notable dependence of the reduced mass on r_{OH} can be explained through the fact that the "motion" of individual atoms is essentially nonlinear. Although this may naively not be expected—the hydrogen motion is parallel to the O–H line—the Eckart frame constraints that remove
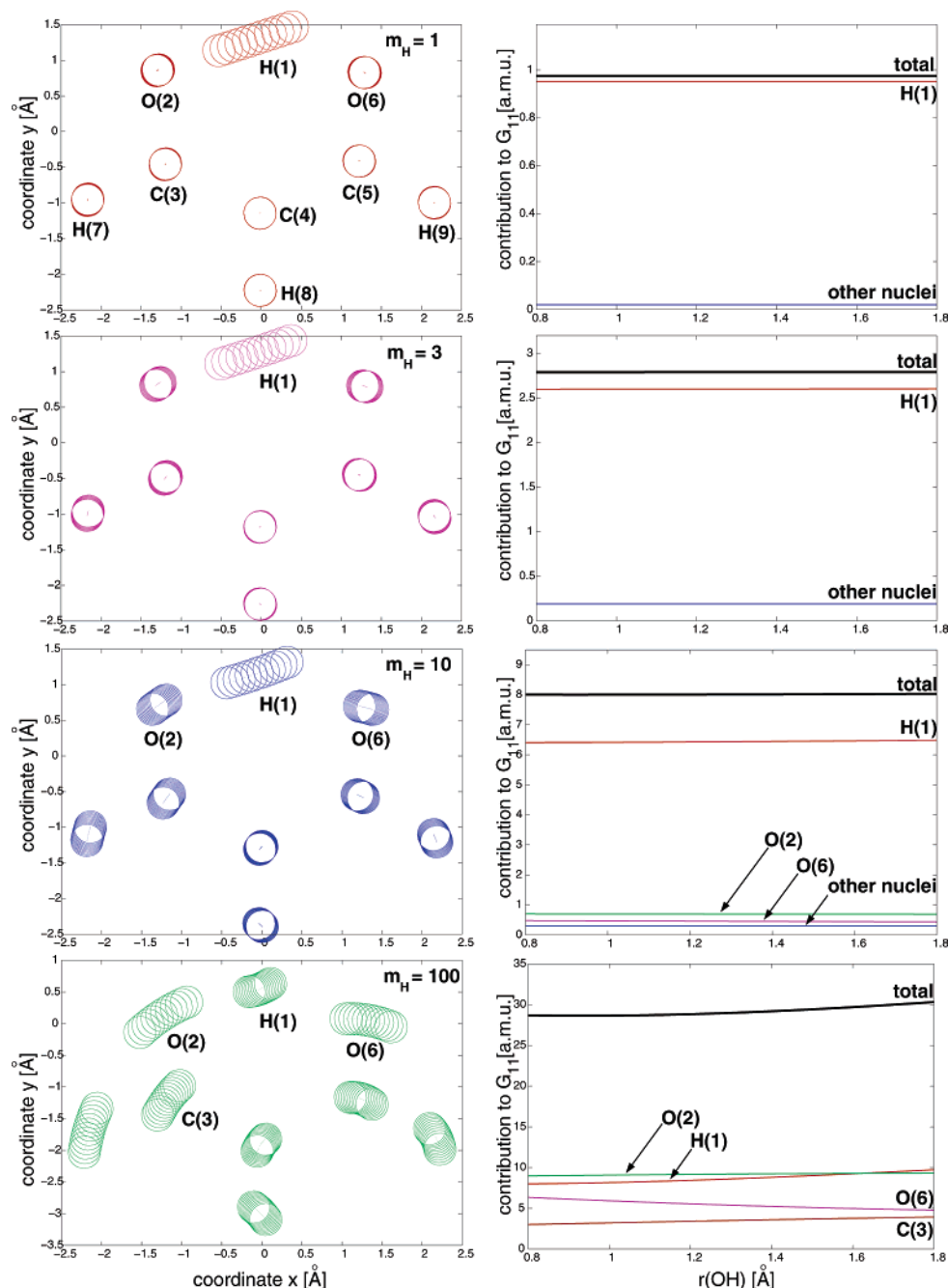
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Figure 3. Left column: overlaid Eckart frame structures of malonaldehyde with different atomic mass of the displaced proton (m_H, in amu). Atoms are represented as dotted circles. Note that these overlays were obtained from a unique set of Cartesian coordinates of 11 structures corresponding to values of r_{OH} from 0.8 to 1.8 Å. Right column: the corresponding profiles of the reduced mass together with selected individual atomic contributions.

rotational components from the atomic motion render the atomic trajectories to be off straight lines.

Worthy of noting is that the simplified but quite often used two-body approach (Figure 4) for the determination of reduced masses yields values that can be sometimes quite different from ones obtained from first principles according to the strategy described above. Namely, the formula for the reduced mass (μ)

$$\mu = \frac{m_H M}{m_H + M} \tag{13}$$

corresponding to a "diatomic" oscillator with two particles (masses m_H and M; in the case of MALD $M = 71$ amu) is

essentially oversimplified since it disregards the distribution of atoms in the structure. The simplification that treats several atoms as a single particle does not correctly account for the position of the center of mass and the principal rotational axes; therefore, a "diatomic" model cannot correctly absorb the Eckart conditions. This results in erratic estimates of the derivatives in eq 8. Although eq 13 can sometimes yield acceptable estimates for reduced masses, its general application is discouraged; in addition, no coordinate dependence of reduced masses can be deduced by using it. Note that two-particle systems represent an exception to the general rule that the reduced masses along internal coordinates are coordinate-dependent. Namely, it can be shown analytically that all the $\partial x_i / \partial q_r$ derivatives are constants for any diatomic

Table 1. Profile of Reduced Mass (in amu) along the r_{OH} Internal Coordinate in Malonaldehyde as a Function of r_{OH}, for Different Masses of the Displaced Hydrogen (m_H, in amu)[a]

r_{OH}	$m_H = 1$	$m_H = 3$	$m_H = 10$	$m_H = 100$
0.8	0.9757	2.7913	8.0057	28.6874
0.9	0.9757	2.7913	8.0051	28.6425
1.0	0.9757	2.7913	8.0054	28.6545
1.1	0.9757	2.7914	8.0065	28.7188
1.2	0.9757	2.7915	8.0085	28.8324
1.3	0.9756	2.7916	8.0112	28.9914
1.4	0.9757	2.7917	8.0147	29.1920
1.5	0.9757	2.7919	8.0189	29.4298
1.6	0.9757	2.7921	8.0238	29.7005
1.7	0.9757	2.7923	8.0295	30.0003
1.8	0.9757	2.7927	8.0358	30.3228
diatomic	0.9861	2.8784	8.7654	41.5205

[a] Note that only the hydrogen atom has been displaced while the other nuclei were kept fixed in their equilibrium positions. Reduced masses (constant) calculated with the diatomic model (eq 13) are also listed. The corresponding Eckart frame structures are displayed in Figure 3.
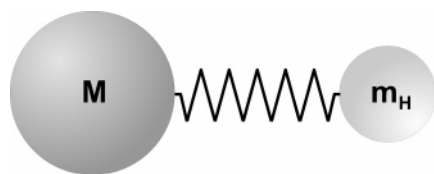
Figure 4. A simple two-body model for the calculation of reduced mass according to eq 13.

system, even after Eckart conditions have been enforced; thus, for all diatomics, the reduced masses are *always* constant, making diatomic models generally inappropriate for the treatment of vibrations of realistic systems.

Single Point vs Relaxed Scan: Impact to Reduced Masses and Frequencies. In a similar way as described in the previous paragraph, two distinct one-dimensional potential energy scans were performed on MALD. The selected internal coordinate was the longitudinal projection (x_H) of the proton position on the O···O line; the origin of this internal coordinate system was set to the midpoint between the oxygens (see Figure 2). Such a choice of the internal coordinate is essential for obtaining a symmetric one-dimensional proton potential. In both cases the proton ($m_H = 1$ amu) was pointwise displaced in 0.1 Å steps with x_H assuming values from -1.2 to $+1.2$ Å. While for each distinct proton position the rest of the molecule has been in one case frozen in its equilibrium geometry ("single point scan"), it has been optimized in the other case ("relaxed scan"). Both potentials are shown in the top row of Figure 5. While the relaxed potential is obviously symmetric, the second minimum of the single point potential is about 8 kcal/mol higher than the global one. It is also notable that the relaxed potential is much flatter, and its barrier is several times lower than with the single point potential. The second row in Figure 5 shows the overlaid Eckart frame structures acquired along the potential energy scan. While with the single point scan (rightmost diagram) virtually only the proton is moving, the case with the relaxed scan (leftmost diagram) is quite different—a notable motion of the other nuclei is observed, particularly both oxygen atoms feature large displacements. This "motion" results from the partial geometry optimization, when the atoms are allowed to follow the proton along the minimum energy path. The resulting profiles of the reduced

mass and individual atomic contributions are displayed in the third row. As expected with the relaxed scan (leftmost figure), heavy atoms, particularly O(2) and O(6), have a dramatic impact on the profile of the reduced mass along x_H. When the proton moves from one side of the H-bond (where the global energy minimum is) to its center (the transition state between the two minima), the O···O distance is significantly reduced, which is a well-known effect. This yields significant contributions of oxygen atoms to the respective $\partial x_i / \partial q_r$ terms in eq 8 and, along with contributions of other heavy atoms, dramatically increases the reduced mass. When reaching the transition state at the midpoint of the H-bond ($x_H = 0$), the O···O shortening (as well as the motion of other nuclei) is halted, resulting in the minimum in the reduced mass profile which is close to unity. Due to the symmetry of the system, there is a mirror plane at $x_H = 0$ both in the relaxed potential energy function as well as in the reduced mass profile. As opposed to the relaxed scan, the reduced mass along the single point scan is a constant of 0.977 amu (rightmost figure in the third row of Figure 5).

For both potentials the vibrational Schrödinger equation has been solved,[7] and one may easily guess that their corresponding anharmonic vibrational levels and transition frequencies should be quite different from one another. We demonstrate the significance of the reduced mass profile to the solution by using with the relaxed potential both the (physically correct) variable profile of the reduced mass as well as the (intuitively sought but physically incorrect) constant value of 0.977 amu acquired from the single point scan. For the single point potential the Schrödinger equation was solved solely with the constant reduced mass of 0.977 amu which is physically correct in that case. Each of these three strategies is represented by a corresponding column in Figure 5. The resulting fundamental anharmonic frequency acquired from a single point scan is 2179 cm^{-1}, and the 0 → 2 transition is at 2797 cm^{-1}. For the relaxed scan one obtains a value of 282 cm^{-1} if the variable profile of the reduced mass is used, and 723 cm^{-1} if the reduced mass is a constant of 0.977 amu. Note that in both cases the ground vibrational level features a tunneling splitting of 2.6 (not shown) and 93 cm^{-1}, respectively, for the variable and constant reduced mass profile. Diversity of the displayed frequencies demonstrates a large effect of the computational strategy to the results. Eventually, the value of 282 cm^{-1}, obtained with the relaxed scan and variable reduced mass, matches exceptionally well with the experimental experimental heavy atom (O···O) stretching frequency,[23] although it has been obtained by using the protonic stretching coordinate x_H as a control variable. Given the simplicity of the model, this match is probably due to a fortunate cancellation of errors, but the model is undoubtedly physically consistent and reliable; at least it can be claimed that it qualitatively reproduces the position of the observed band in the spectrum. On the other hand, the single point scan yields a value of 2179 cm^{-1}, which is much closer to the actual O—H stretching frequency[23] (located at around 2850 cm^{-1}), although it is clearly too low (the experimental value is quite reasonably reproduced by the calculated 0 → 2 overtone). It should be noted that the "middle" strategy of Figure 5 (relaxed potential combined with a constant reduced mass) is not consistent with the physical behavior of the system; this is supported by the fact that the calculated
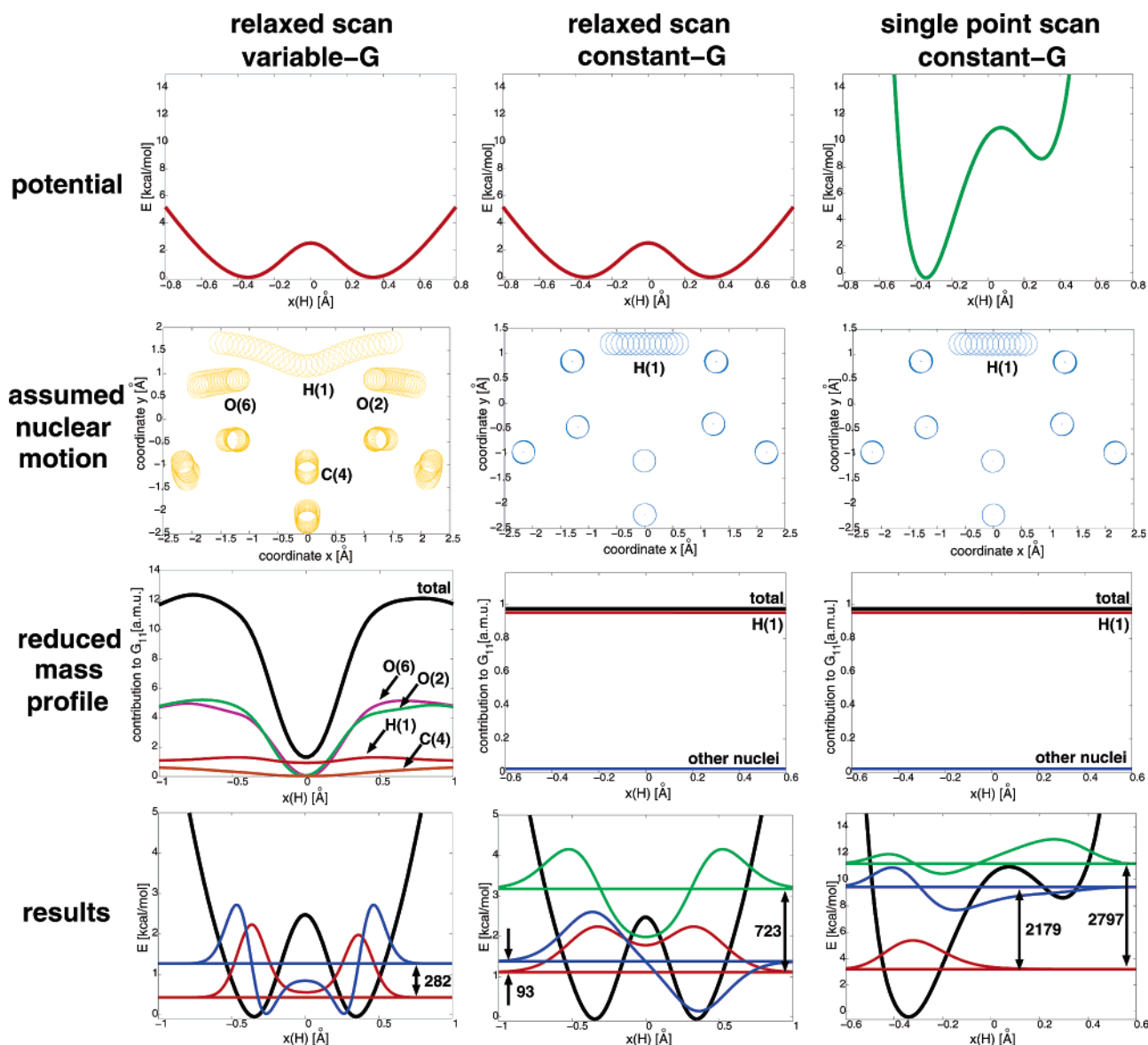
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Figure 5. Potential energy function (first row), overlaid Eckart frame structures characteristic of the assumed nuclear motion (second row), reduced mass profile (third row), and the resulting anharmonic vibrational levels and wavefunctions together with transition frequencies in cm^{-1} (fourth row), for three distinct strategies for the calculation of the potential energy and the reduced mass of protonic motion along x_H in malonaldehyde.

frequency of 732 cm^{-1} does not even qualitatively fit to any plausible range characteristic of the H-bond vibrations.

Since the relaxed scan involves considerable motion of heavy atoms, the frequency of the heavy atom mode is reasonably reproduced, but frequencies of predominantly protonic modes, including the tunneling splitting, are not. The calculated splitting of 2.6 cm^{-1} is most probably an artifact of the model and has no clear significance; as such it should not be compared to the observed[27] value of 21.6 cm^{-1} (the reason why the calculated value is so low lies in the high mass applied). Note that, in order to correctly account for the hydrogen tunneling splitting, one should construct another model that would include at least a symmetric potential that is based on predominantly protonic motion.

It is thus evident that, despite obvious drawbacks in the given case, single point scans are much more appropriate than relaxed scans for calculations of high-frequency bands, as has been previously observed.[29] On the other hand, relaxed

scans associated with the proton motion in H-bonds seem to be the method of choice for the modeling of low-frequency modes. A qualitative comparison of the three strategies depicted in Figure 5 reveals that the switching from single point to relaxed scan (without altering the reduced mass which is assumed to be constant) results in an about 3-fold decrease in the frequency (from 2179 to 723 cm^{-1}). When the reduced mass is switched from constant to variable with the relaxed potential, the frequency is further decreased by a factor of about 2.5 (from 723 to 282 cm^{-1}). Thus both contributions to the frequency lowering (flatter potential and increased reduced mass) are of a comparable magnitude.

Two-Dimensional Models and Off-Diagonal Elements. The one-dimensional representation of the proton motion as described above with the single point potential energy scan along x_H is quite a raw simplification. The assumed trajectory of the hydrogen atom is linear and parallel to the O···O line, which is likely not to be quite realistic. The $0 \rightarrow 1$ transition frequency of 2179 cm^{-1}, obtained for this model, is obviously
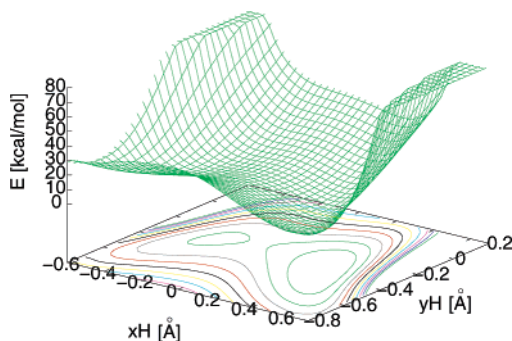
Figure 6. Two-dimensional single point potential of malonaldehyde calculated at the B3LYP/6-31+G(d,p) level of theory. The spacing of contours is 5 kcal/mol.
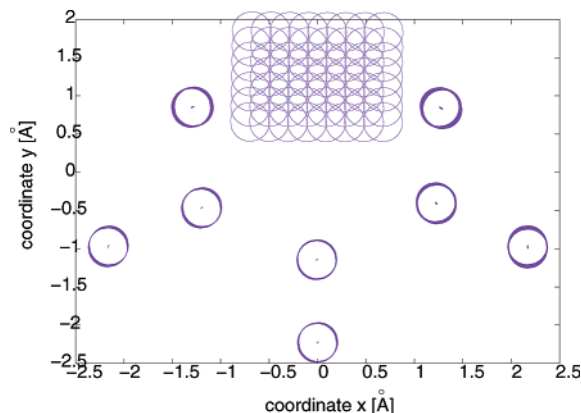

Figure 7. Overlaid Eckart frame structures of malonaldehyde corresponding to the potential energy scan along internal coordinates x_H and y_H (see Figure 2).

too low. If the O−H bond distance is used instead, the frequency acquired from the single point potential increases to 2620 cm^{-1}, which is much closer to the experimentally determined peak of the O−H stretching band of MALD, yet still too low. Evidently, the choice of a coordinate in which the vibrational problem is formulated is of high importance for the quality of the results. On the other hand, both mentioned models are one-dimensional; thus among the 21 internal degrees of freedom of MALD there are 20 internal modes that are not accounted for in the model, although it is very likely that at least some of these modes are significantly coupled to the stretching motion of hydrogen. It is therefore desirable to consider possible extensions that would improve the quality of the model. Starting from the x_H coordinate that mimics the longitudinal motion of the proton in the H-bond of MALD, inclusion of another independent variable y_H as the second dimension looks like a plausible upgrade of the model. In such a way both the

longitudinal and in-plane transversal component of the protonic motion are included.

A single point scan along x_H and y_H of MALD has been performed in a similar way as described with the one-dimensional model. The hydrogen atom has been displaced by changing x_H from −0.7 to +0.7 Å in 0.1 Å steps and y_H from −1.0 to +0.3 Å in steps of the same size. The asymmetric double-well potential is displayed in Figure 6. From the overlaid Eckart frame structures displayed in Figure 7 the G-matrix element profiles along x_H and y_H were determined. As seen from Figure 8, both G^{11} (inverse reduced mass along x_H) and G^{22} (inverse reduced mass along y_H) are both close to unity and exhibit only slight and virtually linear dependence on x_H and y_H. The coupling term G^{12} is very small and changes practically linearly from −0.01 to +0.01 amu in the considered region of x_H and y_H. It is thus reasonable that G^{11} and G^{22} can be taken as constants, while the coupling term can be neglected. Indeed, the inclusion or omission of the functional dependence and the coupling term in the vibrational Hamiltonian affects the calculated anharmonic vibrational levels by less than 1 cm^{-1}. Figure 9 displays the two lowest excited vibrational states at 2318 and 2845 cm^{-1} that correspond to the O−H stretching motion; these two states are obviously very similar to their one-dimensional analogues located at 2179 and 2797 cm^{-1}, respectively, and displayed in Figure 5. Addition of the coordinate y_H to the vibrational problem increases the lower frequency by 139 cm^{-1}, while the higher one is increased by 48 cm^{-1}, thus at least the fundamental O−H stretching frequency is brought closer to the experimental value of about 2850 cm^{-1}—most probably because of the more realistic description of the protonic motion. It should be noted, however, that a two-dimensional model still lacks much of the coupling effects involved in the proton motion; thus, an upgrade to three or four dimensions is essential for further improvements of the computational approach. For instance, Došlić and Kühn used a four-dimensional model Hamiltonian, based on O−H stretching, in-plane and out-of-plane O−H bending, and the heavy atom O···O stretching normal coordinates,[26] while Babić, Bosanac, and Došlić utilized x_H, y_H, and r_{OO} coordinates for the formulation of the vibrational problem.[25]

The coupling term, as reflected in the magnitude of G^{12}, proved to be negligible in the present case. This is due to the fact that the coordinates x_H and y_H are orthogonal to one another in the internal coordinate space. Small nonzero values of G^{12} emerge due to the enforcement of Eckart conditions that includes small rotation. In contrast to the present case, internal coordinates that are approximately parallel to one
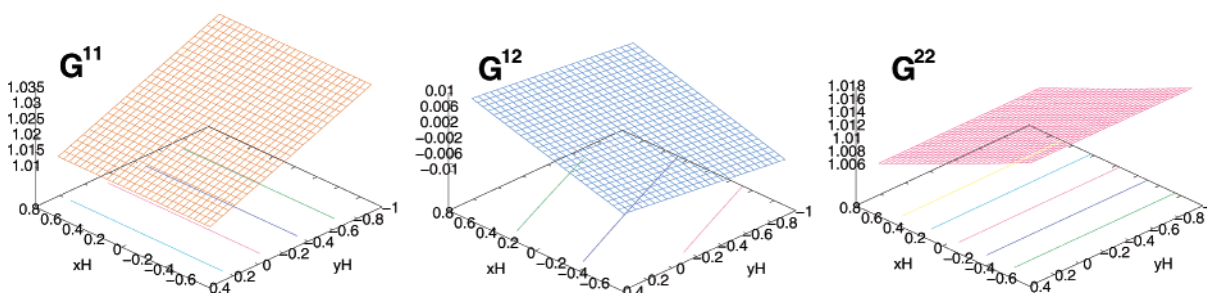

Figure 8. Profiles of the G-matrix elements (in amu^{-1}) of malonaldehyde along the x_H and y_H internal coordinates (see Figure 2).

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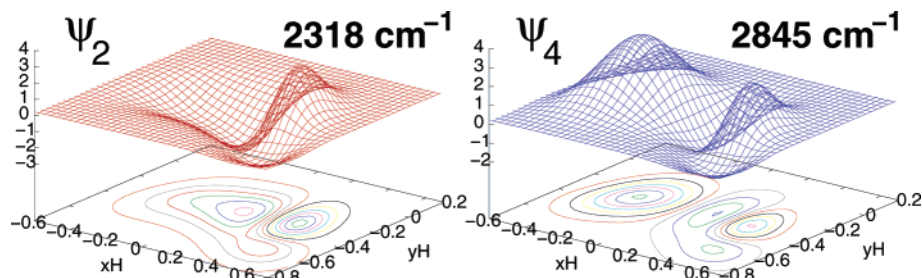*J. Chem. Inf. Model., Vol. 47, No. 3, 2007* **849**

Figure 9. Vibrational wavefunctions and excitation frequencies of the two lowest excited states corresponding to O−H stretching in malonaldehyde, calculated from the two-dimensional potential along x_H and y_H.

another exhibit a significant kinetic coupling reflected in nonzero G^{12}, especially when the atomic masses involved are alike. In such cases, the model Hamiltonian needs to account for this coupling in order to provide meaningful results.[7]

4. CONCLUSIONS

We have analyzed the most important aspects of reduced masses by using the robust first-principle method for the calculation of the coordinate-dependent G-matrix elements.[7] The presented first-principle concept of reduced masses is essential for advanced vibrational analysis in generalized internal coordinates. Test calculations have shown that the method is reliable and ready to be implemented in program codes for quantum treatment of selected molecular vibrations that possess notable degree of anharmonicity. The method is tuned for application along with potential energy surface scans. The corresponding program proved to correctly predict the G-matrix elements for a variety of molecular systems and internal coordinates as well as for various strategies of the calculation of potential energy surface. The program is particularly useful for the determintaion of reduced masses along nonbonded internal coordinates such as the O···O distance in an O−H···O hydrogen bond, for which even an intuitive estimate is not trivial. While the program has been used to date mostly in up to four-dimensional internal coordinate sets, application to larger dimensionalities is fully enabled.

One may expect that, since G-matrix elements have the meaning of reciprocal reduced masses, they can be trivially estimated by intuition or by using simplified formulas. We demonstrate that this is rarely the case and that one needs to take caution for their proper determination. In particular, when a potential energy surface scan is performed with partial geometry optimization, the residual motion of the relaxing heavy atoms may contribute to a notable increase in the reduced mass and thus to considerable frequency lowering, especially when the selected internal coordinates involve the motion of light nuclei. We have shown that the strategy based on relaxed potential energy surface scan, controlled by the position of a proton in a hydrogen bond, esentially leads to the modeling of a heavy atom mode rather than of the proton stretching mode. Since the impact of the chosen strategy to the calculated frequencies can be easily estimated in advance by monitoring the magnitude of the reduced masses, reduced masses can serve as a valuable decision tool for the selection of appropriate coordinates in which the vibrational problem should be formulated and solved. Moreover, the magnitude of the coupling (off-

diagonal) terms of the G-matrix can be used to select the level of simplification that can be applied to the model vibrational Hamiltonian.

Summarizing that, we conclude that reduced masses beyond the established and oversimplified forms represent a challenging and useful concept that is far beyond simple curiosity.

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