Calculating High-Pressure Vibrational Frequencies Analytically with the Extended Hydrostatic Compression Force Field Approach

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We report the implementation of the analytical Hessian for the mechanochemical eXtended Hydrostatic Compression Force Field (X-HCFF) method in the Q-Chem program package. To verify the implementation, the analytical Hessian was compared with finite difference calculations. Additionally, we calculated the pressure dependency of all IR and Raman active vibrational modes of the Buckminsterfullerene and compared the results with experimental and theoretical data. Our implementation paves the way for analyses of geometric points on a pressure-deformed potential energy surface and provides a straightforward model to calculate the vibrational properties of molecules under high pressure.

I. INTRODUCTION

The invention of the diamond anvil cell (DAC) by Weir, Lippincott, Van Velkenburg, and Bunting in 1959¹ marked the beginning of a new era in high-pressure chemistry. Static pressure in the magnitude of multiple GPa became attainable while simultaneously allowing in situ spectroscopic characterization.¹,² The following advancements enabled enormous progress in high pressure chemistry research³–⁶ in various fields such as biochemistry,⁷,⁸ materials science⁹–¹¹ and organic synthesis,¹²,¹³ which also raised the need for computational methods that describe molecular changes induced by pressure.¹⁴ One of the oldest theoretical approaches for this purpose is to manipulate the box parameters in calculations with periodic boundary conditions (PBC).¹⁵–¹⁷ Another route of access to pressure is to quantify it as the negative partial derivative of the electronic energy with respect to the volume of a molecule’s cavity. This approach is utilized in the eXtreme Pressure Polarizable Continuum Model (XP-PCM) by shrinking the molecule-shaped cavity while simulating the Pauli repulsion of the electron density with the surrounding medium.¹⁸–²² Since the implementation of a second derivative,²³ the XP-PCM has been applied in a considerable amount of vibrational spectra calculations,²⁴–²⁷ Quantum mechanochemical approaches,²⁸ by contrast, add an external potential to the Born-Oppenheimer potential energy surface of a single molecule.²⁹–³⁴ Among these the Generalized Force Modified Potential Energy Surface (G-FMPES) model,³² and the eXtended Hydrostatic Compression Force Field (X-HCFF),³⁴ method as well as its predecessor³³ use an approach in which the added external force is spatially varying. The G-FMPES approach was used for the simulation of organic reactions under pressure;³⁵,³⁶ the HCFF approach was applied to model a pressure-induced spin crossover³³ and the X-HCFF model successfully predicted structural properties under high-pressure³⁷ and was utilized in a study on mechanophores.³⁸ One great advantage of the X-HCFF method is the user’s ability to define a pressure a priori, as the required external potential is obtained via the classical definition of pressure acting on the Van der Waals (VdW) surface of the molecule.

In this article, we present the formulation of the analytical Hessian of the X-HCFF model. This implementation allows computationally efficient calculations for the characterization of geometric critical points on the pressure-deformed potential energy surface (PES) and the calculation of high-pressure vibrational spectra. The former is particularly interesting because of the changes in the curvature of the PES, which can lead to the merging of a transition state (TS) with an energy minimum, as indicated by Subramanian, Mathew, and Leiding.³² We previously presented such a possible trapping of a TS in a [2,3]-sigmatropic rearrangement by application of pressure,³⁹ motivating the implementation work presented in this paper.

The structure of this paper is as follows: In section II A we give an overview of the X-HCFF model; in section II B we outline the deduction of its analytical second derivative; section III discloses the computational methods and parameters used in all calculations; in section IV A we report the results of testing the implementation against finite differences and in section IV B as a first application we present the pressure dependencies of IR and Raman active vibrational frequencies in the fullerene C₆₀ within the range of pressures between 0 and 18 GPa and compare them with experimental and theoretical data.

II. THEORY

In this section, we review the basic aspects of the X-HCFF model and introduce the deduction of the model’s analytical second derivatives.
A. An overview of the X-HCFF method

The extended hydrostatic compression force field method, in short X-HCFF, simulates molecules under hydrostatic pressure by adding an external force to the nuclear gradient of an electronic structure geometry optimization. The interaction with the compressing medium is modeled as forces acting on the molecule’s VdW surface, and these forces are then projected on the appropriate atom. The VdW cavity is formed by superimposing spheres centered at the atoms, with their radii corresponding to those presented by A. Bondi, and its surface is discretized using a Lebedev grid algorithm. The individual forces acting on each tessera \( t \) are calculated according to the classical definition of pressure, \( P = \frac{F}{A} \), and are multiplied with the tessera’s surface unit normal \( n_{t,i} \):

\[
f_{i,t} = -P \cdot A_i \cdot n_{t,i} \tag{1}
\]

where \( n_{t,i} \) is defined as \( \frac{\left( x_i - r_i \right)}{|x_i - r_i|} \) with \( x_i \) being the atom’s cartesian coordinate vector and \( r_i \) the respective tessellation point’s coordinate vector, \( P \) is the user-defined pressure, and \( A_i \) is the area of the tessera. The force \( f_i \) that is applied to a molecule’s atom \( i \) is calculated as the sum over all forces \( f_{i,t} \) acting on tesserae \( t \) attributed to the atom \( i \):

\[
f_i = \sum_{t}^{N_{\text{Tess}(i)}} f_{i,t} \tag{2}
\]

These forces are added to the nuclear gradient during geometry optimizations, and the surface tessellation is recalculated for every optimization step. The X-HCFF model is agnostic towards the underlying electronic structure method, so both wavefunction-based methods and Density Functional Theory (DFT)\(^{42,43} \) can be applied. To ensure no translations and rotations are added due to unequally distributed tessellation points, the correctional term given in Eq. 3 is subtracted from every atom’s force vector. It deducts the mean of the non-zero total gradient. Here \( N \) denotes the number of atoms and \( n_t \) is defined with the Cartesian coordinate vector of the atom to which tessellation point \( t \) belongs.

\[
f_{\text{corr}} = -P \cdot \frac{1}{N} \sum_{t}^{N_{\text{Tess}}} A_t \cdot n_t \tag{3}
\]

Besides the pressure, two other parameters are defined by the user. These are the scaling factor for the VdW radii and the number of tessellation points used for each atom. Altogether, the computational overhead of the X-HCFF method is negligible, and the computational cost is dictated by the underlying electronic structure calculations.

B. Deduction of the analytical second derivative

When an external force \( f_{\text{ext}} \) acts on a molecule, its potential energy surface changes. This force-deformed potential energy functional \( V_{\text{def}}(R) \) can be denoted as the sum of the zero-force potential energy \( V_{\text{BO}}(R) \), based on the Born-Oppenheimer approximation, and the applied external potential energy \( V_{\text{ext}}(R) \).

\[
V_{\text{def}}(R) = V_{\text{BO}}(R) + V_{\text{ext}}(R) \tag{4}
\]

Eq. 4 is the basis of the G-FMPES approach, and since the X-HCFF method is closely related, the deduction of the analytical second derivative is quite similar. The second derivative of the potential energy, i.e. the Hessian \( \mathbf{H}_{\text{def}} \) of a force-deformed PES is denoted by:

\[
\mathbf{H}_{\text{def}}(R) = \mathbf{J} \{ \nabla V_{\text{def}}(R) \} \tag{5}
\]

where \( \mathbf{J} \) is the Jacobian matrix and \( \nabla \) is the gradient operator, both with respect to Cartesian coordinates of atomic nuclei. Because both the Jacobian and the gradient operator obey the distributive law, Eq. 5 can be rewritten as:

\[
\mathbf{H}_{\text{def}}(R) = \mathbf{J} \{ \nabla V_{\text{BO}}(R) + \nabla V_{\text{ext}}(R) \} = \mathbf{H}_{\text{BO}}(R) + \mathbf{J} \{ \nabla V_{\text{ext}}(R) \} \tag{6}
\]

With the gradient of a potential energy function \( \nabla V \) equalling a negative force vector \( f \), this yields the Hessian of the externally applied potential, \( \mathbf{H}_{\text{ext}} \), as the Jacobian matrix of the external force vector.

\[
\mathbf{H}_{\text{ext}}(R) = -\mathbf{J} \{ f_{\text{ext}}(R) \} \tag{7}
\]

Accordingly, the Hessian \( \mathbf{H}_{\text{def}} \) for atoms \( i \) and \( j \) of the PES with an external force \( f_i \) applied via the X-HCFF method is defined by:

\[
\mathbf{H}_{\text{def}}(R)_{ij} = \frac{\partial^2 V_{\text{def}}}{\partial x_i \partial x_j} = \frac{\partial^2 V_{\text{BO}}}{\partial x_i \partial x_j} + \frac{\partial f_i}{\partial x_j} \tag{8}
\]

in which \( x_i \) and \( x_j \) denote the Cartesian coordinate vectors of atoms \( i \) and \( j \), respectively. Therefore, Eq. 8 corresponds to a \((3 \times 3)\) submatrix of the Hessian. The expression for the force vector with the inclusion of the correctional term is given by subtracting Eq. 3 from Eq. 1:

\[
f_i = P \left( -\sum_{t}^{N_{\text{Tess}(i)}} A_t n_{t,i} + \frac{1}{N} \sum_{t}^{N_{\text{Tess}}} A_t n_t \right) \tag{9}
\]

Note that the first sum is solely over all tessellation points \( N_{\text{Tess}(i)} \) associated with atom \( i \), while the second sum includes the tessellation points \( N_{\text{Tess}} \) of all atoms. The general form of the partial differential \( \frac{\partial f_i}{\partial x_j} \) is:

\[
\frac{\partial f_i}{\partial x_j} = P \left( -\sum_{t}^{N_{\text{Tess}(i)}} n_{t,i} \frac{\partial A_t}{\partial x_j} + A_t \frac{\partial n_{t,i}}{\partial x_j} \right) + \frac{1}{N} \sum_{t}^{N_{\text{Tess}}} \left( n_t \frac{\partial A_t}{\partial x_j} + A_t \frac{\partial n_t}{\partial x_j} \right) \tag{10}
\]

The second term of each sum in Eq.(10), containing the differential of the tessellation points’ surface normal vector \( \frac{\partial n_t}{\partial x_j} \), becomes null because the movement of atom \( j \) induces the
same movement for its tessellation point \( t \). Consequently, the expression for a \((3 \times 3)\) submatrix of the analytical X-HCFF-Hessian \( H_{\text{ext}}(\mathbf{R}) \) reduces to:

\[
H_{\text{ext}}(\mathbf{R})_{ij} = P \left( - \sum_{\tau} n_{\tau} \frac{\partial A_{\tau}}{\partial x_j} + \frac{1}{N} \sum_{\tau} n_{\tau} \frac{\partial A_{\tau}}{\partial x_j} \right) \tag{11}
\]

This leaves only the gradient of the tessellation areas to be evaluated. For this, the area derivatives by Lange and Herbert are used,\(^{41,44}\) which are based upon a switching function by York and Karplus.\(^{45}\) The switching function handles the disappearance or emergence of tessellation points on the VdW surface induced by the movement of nuclei. As a result, the derivative of the tessellation areas with respect to the nuclei coordinates is not strictly continuous, and Schwarz’s theorem regarding the symmetry of second derivatives does not apply to the X-HCFF Hessian. Therefore the resulting Hessian of the X-HCFF model is symmetrized before its addition to the force-free Hessian of the SCF energy.

### III. COMPUTATIONAL DETAILS

The analytical second derivatives were verified by comparing against finite differences of the analytical gradients (cf. section IV A). The corresponding test calculations were carried out at the HF\(^{46-48}\)/cc-pVDZ\(^{49}\) level of theory and with an applied pressure of 100 GPa, a scaling factor of 1.0 and a varying number of tessellation points. As a measurement of deviation from the reference Hessian, we chose the Frobenius norm of the absolute difference matrix. The Frobenius norm is a matrix norm based on the Euclidean norm of a vector and defined for any real or complex \((m \times n)\) matrix as

\[
||A||_F := \sqrt{\sum_{i,j} |a_{ij}|^2}, \quad \text{where } a_{ij} \text{ are single matrix elements.}
\]

To put the newly implemented Hessian into use, we performed a series of DFT\(^{42,43}\) calculations to determine the pressure dependency of vibrational frequencies of fullerene \( C_{60} \) (cf. section IV B). The geometry optimization and frequency calculations were carried out in a locally modified Q-Chem 6.0 program package\(^{50}\) using the B3LYP hybrid functional,\(^{51-54}\) the 6-31G(d) basis set\(^{55}\) and applying a uniform scaling factor on all vibrational frequencies, as has been reported to be the best compromise between accuracy and computational cost when calculating frequencies.\(^{24,56-58}\) The optimal frequency scaling factor of 0.978 was determined via a least squares method with frequency values assigned by Schettino \textit{et al.}\(^{56}\) as reference. For the X-HCFF model, 302 tessellation points and a VdW-scaling of 1.0 were used in all calculations, and pressures in the range of 0 to 18 GPa were applied. The pressure-dependent frequency shifts \( dv/dp \) were calculated by linear regression of the scaled \( v(p) \) values. Analytical calculations of high-pressure vibrational spectra using the X-HCFF Hessian presented here will be publicly available with the Q-Chem 6.1.1 update.

![FIG. 1. The Frobenius norm of the difference matrix between the analytical and numerical Hessian (HF/cc-pVDZ, 100 GPa, scaling factor 1.0).](image)

### IV. RESULTS AND DISCUSSION

In this section we will first present the results of the comparison of the fully analytical implementation with finite differences of analytical gradients and in the following subsection report the pressure coefficient \( dv/dp \) for the 14 IR and Raman active modes of fullerene \( C_{60} \) computed with the X-HCFF model. The pressure coefficient is also compared to existing experimental and theoretical data.

#### A. Code Verification

To verify the implementation of the analytical Hessian of the X-HCFF method we performed multiple test calculations on a set of eleven small to medium-sized molecules. We report the Frobenius norm \( ||H_{\text{diff}}||_F \) of the difference matrix between the analytical and semi-numerical Hessian for each of these molecules as a measure of congruence between these Hessian matrices (see Figure 1).

As can be seen in Figure 1, the yielded matrix norm is always well below \( 10^{-5} \), and no substantial increase with increasing number of atoms can be observed in cases with up to 302 tessellation points per atom, which validates the symbolic calculation of the second derivative. The slight increase in the matrix norm with a higher number of tessellation points can be attributed to the overlapping regions of the VdW spheres, where some of the tessellation points are discarded if they are located within the volume enclosed by the VdW spheres. Due to the displacement of atoms during the finite difference procedure, the overlapping area changes, and with it the number of discarded tessellae might adjust, especially if the tessellae are small in size.
B. Pressure Dependencies of IR and Raman Active Vibrational Modes in C$_{60}$

We calculated the pressure dependency ($dv/dp$) of the IR and Raman active modes of the icosahedral fullerene C$_{60}$ by applying hydrostatic pressure with the X-HCFF method (Figure 2). The results are compared with available experimental measurements$^{59,60}$ and XP-PCM calculations. For all determined values of $dv/dp$ the coefficient of determination $R^2$ is above 0.95, which confirms the linear trend. Figure 2 shows the results including plots for the H$_g$(5) and H$_g$(6) modes, for which no experimental data is available. In general, the obtained data are in good agreement with experimental and other theoretical results as presented in Table I, especially taking into account the significant deviations between the different sets of experimental data along with the calculated XP-PCM results. The experimentally observed hardening of most vibrational modes induced by pressure as well as the different degrees of stiffening are reproduced accurately by X-HCFF. The most notable differences are for those modes (H$_g$(3) and T$_{1u}$(1)) that exhibit a softening with increasing pressure in experimental measurements, while no negative pressure coefficient has been computed by any of the theoretical approaches. Pagliai, Cardini, and Cammi$^{24}$ presented their vibrational pressure coefficients divided into relaxation and curvature contributions and showed that those modes with a negative experimental frequency shift have a strong negative relaxation contribution. Although the total pressure coefficient still amounts to a positive sign in these cases, the computed values are rather small. The pressure coefficients computed with the X-HCFF model for these modes are also below 1 cm$^{-1}$ GPa$^{-1}$. Additionally, it is worth mentioning that those frequency modes T$_{1u}$(1) and H$_g$(3) have a very high portion of radial atomic motions. Some publications that are based on experimental measurements$^{59,62,63}$ ascribe the detected softening of modes with increased pressure to intermolecular interactions. This could be an explanation for the discrepancy with the theoretical results, as both X-HCFF and XP-PCM are single-molecule methods and do not explicitly include intermolecular effects.

V. CONCLUSION AND OUTLOOK

We implemented an analytical Hessian for the mecanochemical X-HCFF model in a development version of the Q-Chem program package, which will be publicly available with the release of Q-Chem 6.1.1. Overall, the agreement of the pressure-related frequency shifts in C$_{60}$ computed via X-HCFF with both experimental and computed values is satisfactory. Its results align well with the more sophisticated XP-PCM approach and for modes characterized predominantly by a tangential atomic motion, the sign and value of the pressure coefficient agree qualitatively with experimental measurements. The discrepancy for modes with a mostly radial atomic motion might be solved by including intermolecular interactions in the model. The work on an implementation of X-HCFF that takes intermolecular interactions in molecular clusters into account has begun in our group. In sum, our results prove the X-HCFF method with its newly added analytical Hessian to be an apt and quick tool to simulate molecules and their vibrational properties under hydrostatic pressure.

SUPPLEMENTARY MATERIAL

See the supplementary material for tables of unscaled computed $v$(p) values; the initial geometry for C$_{60}$; and geometries of all molecules used for testing.

### Table I. Experimental and theoretical data for the initial pressure slopes of frequencies of the IR or Raman active modes in C$_{60}$. Experimental data were taken from Meletov et al.$^{59}$ and Klug et al.$^{60}$ The theoretical data were taken from Pagliai et al.$^{24}$

<table>
<thead>
<tr>
<th>Mode</th>
<th>assign.</th>
<th>X-HCFF$^{a}$</th>
<th>XP-PCM$^{a,24}$</th>
<th>ref. 59</th>
<th>ref. 60</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_u$(1)</td>
<td>496</td>
<td>1.21</td>
<td>1.54</td>
<td>0.5</td>
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<tr>
<td>A$_u$(2)</td>
<td>1468</td>
<td>4.12</td>
<td>2.6</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>H$_e$(1)</td>
<td>264</td>
<td>0.27</td>
<td>1.17</td>
<td>3.3</td>
<td></td>
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<tr>
<td>H$_e$(2)</td>
<td>430</td>
<td>0.39</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>H$_e$(3)</td>
<td>709</td>
<td>0.98</td>
<td>0.43</td>
<td>-0.8</td>
<td></td>
</tr>
<tr>
<td>H$_e$(4)</td>
<td>773</td>
<td>1.75</td>
<td>1.12</td>
<td>0.1</td>
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</tr>
<tr>
<td>H$_e$(7)</td>
<td>1425</td>
<td>3.84</td>
<td>2.38</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>H$_e$(8)</td>
<td>1567</td>
<td>3.28</td>
<td>1.96</td>
<td>4.8</td>
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<tr>
<td>T$_{1u}$(1)</td>
<td>525</td>
<td>0.64</td>
<td>0.29</td>
<td>-0.5</td>
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<tr>
<td>T$_{1u}$(2)</td>
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<td>1.43</td>
<td>1.28</td>
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<td>1.6</td>
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<td>T$_{1u}$(3)</td>
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<td>2.79</td>
<td>1.57</td>
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<tr>
<td>T$_{1u}$(4)</td>
<td>1433</td>
<td>3.77</td>
<td>2.39</td>
<td>4.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^{a}$Theoretical calculations.
ACKNOWLEDGMENTS

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CONFLICT OF INTEREST STATEMENT

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

All further data that support the findings of this study are available from the corresponding author upon reasonable request.