Programming Project 2: Harmonic Vibrational Frequencies

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Summer 2012

1 Introduction

This is the second programming project at the Center for Computational Quantum Chemistry. In this program, you will use several PSI4 output files to determine molecular vibrational frequencies and spectroscopic intensities. All matrices are provided in the cartesian coordinate framework. Again, ethylene in the provided test case. This program should be completed in C or C++ along with certain PSI4 libraries.

Good luck!

2 Procedure

1. **Read in the molecular geometry from file11.dat.**

   File11.dat is an output file generated by `PSI4`. The first line is a title specifying the calculation that was run, including the basis set. The next line contains the number of atoms, N, and the calculated SCF energy. The next N lines contain the atomic charge and the molecular Cartesian coordinates:

$$
\begin{matrix}
Z_1 & x_1 & y_1 & z_1 \\
Z_2 & x_2 & y_2 & z_2 \\
\vdots & \vdots & \vdots & \vdots \\
Z_n & x_n & y_n & z_n
\end{matrix}
\tag{1}
$$

   The final N lines contain the derivative of the energy with respect to each Cartesian coordinate, and are not required for this project. All units are bohr.

2. **Read in the Hessian matrix (H) from file15.dat.**

   The Hessian matrix contains the second-order partial derivatives of the energy with respect to nuclear coordinates. It is a $3N$ by $3N$ matrix symbolically filled as follows. The label x_1 refers to the x coordinate of atom 1, y_1 refers to the y coordinate of atom 1, and so forth.

$$
\begin{bmatrix}
\dfrac{\partial^2 E}{\partial^2 x_1} & \dfrac{\partial^2 E}{\partial x_1 \partial y_1} & \dfrac{\partial^2 E}{\partial x_1 \partial z_1} & \dfrac{\partial^2 E}{\partial x_1 \partial x_2} & \dfrac{\partial^2 E}{\partial x_1 \partial y_2} & \cdots & \dfrac{\partial^2 E}{\partial x_1 \partial z_n} \\[2ex]
\dfrac{\partial^2 E}{\partial y_1 \partial x_1} & \dfrac{\partial^2 E}{\partial^2 y_1} & \dfrac{\partial^2 E}{\partial y_1 \partial z_1} & \dfrac{\partial^2 E}{\partial y_1 \partial x_2} & \dfrac{\partial^2 E}{\partial y_1 \partial y_2} & \cdots & \dfrac{\partial^2 E}{\partial y_1 \partial z_n} \\[2ex]
\dfrac{\partial^2 E}{\partial z_1 \partial x_1} & \dfrac{\partial^2 E}{\partial z_1 \partial y_1} & \dfrac{\partial^2 E}{\partial^2 z_1} & \dfrac{\partial^2 E}{\partial z_1 \partial x_2} & \dfrac{\partial^2 E}{\partial z_1 \partial y_2} & \cdots & \dfrac{\partial^2 E}{\partial z_1 \partial z_n} \\[2ex]
\dfrac{\partial^2 E}{\partial x_2 \partial x_1} & \dfrac{\partial^2 E}{\partial x_2 \partial y_1} & \dfrac{\partial^2 E}{\partial x_2 \partial z_1} & \dfrac{\partial^2 E}{\partial^2 x_2} & \dfrac{\partial^2 E}{\partial x_2 \partial y_2} & \cdots & \dfrac{\partial^2 E}{\partial x_2 \partial z_n} \\[2ex]
\vdots & \vdots & \vdots & \vdots & \vdots & & \vdots \\[2ex]
\dfrac{\partial^2 E}{\partial z_n \partial x_1} & \dfrac{\partial^2 E}{\partial z_n \partial y_1} & \dfrac{\partial^2 E}{\partial z_n \partial z_1} & \dfrac{\partial^2 E}{\partial z_n \partial x_2} & \dfrac{\partial^2 E}{\partial z_n \partial y_2} & \cdots & \dfrac{\partial^2 E}{\partial^2 z_n}
\end{bmatrix}
\tag{2}
$$

The first line of file15.dat contains the number of atoms, N, and six times that number, $6N$. The next $3N^2$ lines each contain 3 partial derivatives as follows:

$$
\begin{array}{ccc}
\dfrac{\partial^2 E}{\partial^2 x_1} & \dfrac{\partial^2 E}{\partial x_1 \partial y_1} & \dfrac{\partial^2 E}{\partial x_1 \partial z_1} \\[2ex]
\dfrac{\partial^2 E}{\partial x_1 \partial x_2} & \dfrac{\partial^2 E}{\partial x_1 \partial y_2} & \dfrac{\partial^2 E}{\partial x_1 \partial z_2} \\[1ex]
\vdots & \vdots & \vdots \\[1ex]
\dfrac{\partial^2 E}{\partial x_1 \partial x_n} & \dfrac{\partial^2 E}{\partial x_1 \partial y_n} & \dfrac{\partial^2 E}{\partial x_1 \partial z_n} \\[2ex]
\dfrac{\partial^2 E}{\partial y_1 \partial x_1} & \dfrac{\partial^2 E}{\partial^2 y_1} & \dfrac{\partial^2 E}{\partial y_1 \partial z_1} \\[1ex]
\vdots & \vdots & \vdots \\[1ex]
\dfrac{\partial^2 E}{\partial z_n \partial x_n} & \dfrac{\partial^2 E}{\partial z_n \partial y_n} & \dfrac{\partial^2 E}{\partial^2 z_n}
\end{array}
\tag{3}
$$

You will read in the values in the order of file15.dat, but you should store them analagously to the example Hessian. The units are hartree/bohr^2.

3. **Read in the dipole moment derivative matrix, D, from file17.dat.**
   File17.dat contains the first partial derivatives of the Cartesian dipole moments (μ_x, μ_y, μ_z) with respect to nuclear coordinates. μ_x is the partial derivative of the energy (E) with respect to an applied electric field (E_x). Mathematically, this is $\mu_x = \partial E / \partial E_x$. Thus, the x dipole derivative with respect to nuclear coordinate z_1 is $\partial \mu_x / \partial z_1 = \partial^2 E / \partial E_x \partial z_1$. The dipole derivative matrix, $\mathbf{D}$, is a 3 by $3N$ matrix symbolically filled as follows:

$$
\begin{bmatrix}
\dfrac{\partial \mu_x}{\partial x_1} & \dfrac{\partial \mu_x}{\partial y_1} & \dfrac{\partial \mu_x}{\partial z_1} & \dfrac{\partial \mu_x}{\partial x_2} & \dfrac{\partial \mu_x}{\partial y_2} & \cdots & \dfrac{\partial \mu_x}{\partial z_n} \\[2ex]
\dfrac{\partial \mu_y}{\partial x_1} & \dfrac{\partial \mu_y}{\partial y_1} & \dfrac{\partial \mu_y}{\partial z_1} & \dfrac{\partial \mu_y}{\partial x_2} & \dfrac{\partial \mu_y}{\partial y_2} & \cdots & \dfrac{\partial \mu_y}{\partial z_n} \\[2ex]
\dfrac{\partial \mu_z}{\partial x_1} & \dfrac{\partial \mu_z}{\partial y_1} & \dfrac{\partial \mu_z}{\partial z_1} & \dfrac{\partial \mu_z}{\partial x_2} & \dfrac{\partial \mu_z}{\partial y_2} & \cdots & \dfrac{\partial \mu_z}{\partial z_n}
\end{bmatrix}
\tag{4}
$$

The first line of file17.dat contains the number of atoms, N, and three times that number, $3N$. The next $3N$ lines each contain 3 partial derivatives as follows:

$$
\begin{array}{ccc}
\dfrac{\partial \mu_x}{\partial x_1} & \dfrac{\partial \mu_x}{\partial y_1} & \dfrac{\partial \mu_x}{\partial z_1} \\[2ex]
\dfrac{\partial \mu_x}{\partial x_2} & \dfrac{\partial \mu_x}{\partial y_2} & \dfrac{\partial \mu_x}{\partial z_2} \\[2ex]
\vdots & \vdots & \vdots \\[2ex]
\dfrac{\partial \mu_x}{\partial x_n} & \dfrac{\partial \mu_x}{\partial y_n} & \dfrac{\partial \mu_x}{\partial z_n} \\[2ex]
\dfrac{\partial \mu_y}{\partial x_1} & \dfrac{\partial \mu_y}{\partial y_1} & \dfrac{\partial \mu_y}{\partial z_1} \\[2ex]
\vdots & \vdots & \vdots \\[2ex]
\dfrac{\partial \mu_z}{\partial x_n} & \dfrac{\partial \mu_z}{\partial y_n} & \dfrac{\partial \mu_z}{\partial z_n}
\end{array}
\tag{5}
$$

The values will be read in according to file17.dat, but should be stored in your program as in (4). The units are Debye/Å.

4. **Read in the polarizability derivative matrix, P, from file18.dat.**

File18.dat is an file containing the partial derivatives of the polarizability with respect to nuclear coordinates. The `xy` polarizability tensor is a 3 by 3 matrix, α.

$$
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\tag{6}
$$

α_{xy} is the second-order partial derivative of the energy (E) with respect to applied electric fields (E_x, E_y). Mathematically, this is $\alpha_{xy} = \partial^2 E/\partial E_x \partial E_y$. Thus, the `xy` polarizability derivative with respect to nuclear coordinate z_1 is $\partial \alpha_{xy}/\partial z_1 = \partial^3 E/\partial E_x \partial E_y \partial z_1$.

The polarizability derivative matrix, $\mathbf{P}$, is a 6 by $3N$ matrix symbolically filled as follows:

$$
\begin{bmatrix}
\dfrac{\partial \alpha_{xx}}{\partial x_1} & \dfrac{\partial \alpha_{xx}}{\partial y_1} & \dfrac{\partial \alpha_{xx}}{\partial z_1} & \dfrac{\partial \alpha_{xx}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{xx}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{xy}}{\partial x_1} & \dfrac{\partial \alpha_{xy}}{\partial y_1} & \dfrac{\partial \alpha_{xy}}{\partial z_1} & \dfrac{\partial \alpha_{xy}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{xy}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{yy}}{\partial x_1} & \dfrac{\partial \alpha_{yy}}{\partial y_1} & \dfrac{\partial \alpha_{yy}}{\partial z_1} & \dfrac{\partial \alpha_{yy}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{yy}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{zx}}{\partial x_1} & \dfrac{\partial \alpha_{zx}}{\partial y_1} & \dfrac{\partial \alpha_{zx}}{\partial z_1} & \dfrac{\partial \alpha_{zx}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{zx}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{zy}}{\partial x_1} & \dfrac{\partial \alpha_{zy}}{\partial y_1} & \dfrac{\partial \alpha_{zy}}{\partial z_1} & \dfrac{\partial \alpha_{zy}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{zy}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{zz}}{\partial x_1} & \dfrac{\partial \alpha_{zz}}{\partial y_1} & \dfrac{\partial \alpha_{zz}}{\partial z_1} & \dfrac{\partial \alpha_{zz}}{\partial x_2} & \cdots & \dfrac{\partial \alpha_{zz}}{\partial z_n}
\end{bmatrix}
\tag{7}
$$

The first line of file18.dat contains the number of atoms, N, and three times that number, $3N$. The next $6N$ lines each contain 3 partial derivatives:

$$
\begin{array}{ccc}
\dfrac{\partial \alpha_{xx}}{\partial x_1} & \dfrac{\partial \alpha_{xx}}{\partial y_1} & \dfrac{\partial \alpha_{xx}}{\partial z_1} \\[1ex]
\vdots & \vdots & \vdots \\[1ex]
\dfrac{\partial \alpha_{xx}}{\partial x_n} & \dfrac{\partial \alpha_{xx}}{\partial y_n} & \dfrac{\partial \alpha_{xx}}{\partial z_n} \\[2ex]
\dfrac{\partial \alpha_{xy}}{\partial x_1} & \dfrac{\partial \alpha_{xy}}{\partial y_1} & \dfrac{\partial \alpha_{xy}}{\partial z_1} \\[1ex]
\vdots & \vdots & \vdots \\[1ex]
\dfrac{\partial \alpha_{zz}}{\partial x_n} & \dfrac{\partial \alpha_{zz}}{\partial y_n} & \dfrac{\partial \alpha_{zz}}{\partial z_n}
\end{array}
\tag{8}
$$

The values will be read in according to file18.dat, but should be stored in your program following the polarizability derivative matrix example. The units are Å.

5. **Form the mass-weighted Hessian matrix, $\mathbf{H_{mw}}$.**
   This can be done in one of two ways:
   1. The matrix can be scaled element by element:

   $$\mathbf{H_{mw}}[i][j] = \frac{\mathbf{H}[i][j]}{\sqrt{M_i M_j}} \tag{9}$$

   2. It can be formulated as a matrix multiply by a diagonal $3N$ by $3N$ mass matrix $\mathbf{M}$:

   $$\begin{bmatrix} \frac{1}{\sqrt{M_1}} & 0 & 0 & 0 & \dots \\ 0 & \frac{1}{\sqrt{M_1}} & 0 & 0 & \dots \\ 0 & 0 & \frac{1}{\sqrt{M_1}} & 0 & \dots \\ 0 & 0 & 0 & \frac{1}{\sqrt{M_2}} & \dots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \tag{10}$$

   $$\mathbf{H_{mw}} = \mathbf{M^T H M} \tag{11}$$

6. **Diagonalize the mass-weighted Hessian.**

   $$\mathbf{V^{-1} H_{mw} V} = \mathbf{\Lambda} \tag{12}$$

   $\mathbf{V}$ is the eigenvector matrix and $\mathbf{\Lambda}$ is the eigenvalue matrix. The eigenvalues (λ_i) appear on the diagonals of $\mathbf{\Lambda}$.

7. **Determine the harmonic vibrational frequencies, ω_i.**

   $$\omega_i = constant \times \sqrt{\lambda_i} \tag{13}$$

   The C in the above equation is a conversion factor. Frequencies should be reported in MHz and cm^{-1}. Many helpful physical constants are included in PSI4 in `physconst.h`.

8. **Mass-weight the eigenvector matrix, V, to form T.**

   $\mathbf{T}$ is the normal-coordinate transformation matrix, which can be used to transform matrices from cartesian coordinates to normal coordinates.

   $$\mathbf{T} = \mathbf{MV} \tag{14}$$

9. **Transform the dipole derivative matrix, D, to the normal coordinate system.**

$$\frac{\partial \mu_x}{\partial Q} = \frac{\partial \mu_x}{\partial X}\frac{\partial X}{\partial Q} \rightarrow \mathbf{D\,T} \tag{15}$$

X refers to cartesian coordinates and Q refers to normal coordinates.

10. **Compute the infrared intensities ($\mathbf{I}_i$) for each vibrational mode.**

IR intensities should be computed in *a)* Debye^2/(amu·Å^2), *b)* km/mol, and *c)* L/(cm^2·mol).

$$I_i = constant \times \sum_{n=1}^{3}\left(\frac{\partial \mu_i}{\partial Q_n}\right)^2 \tag{16}$$

The summation over **n** means to sum the **x**, **y**, and **z** components.

Hint: $\ell n(10)$ is involved in the conversion factor for part c).

11. **Transform the polarizability derivative matrix, P, to the normal coordinate system.**

$$\frac{\partial \alpha_{xy}}{\partial Q} = \frac{\partial \alpha_{xy}}{\partial X}\frac{\partial X}{\partial Q} \rightarrow \mathbf{P\,T} \tag{17}$$

12. **Compute the Raman scattering activity ($\mathbf{I}_i$) for each vibrational mode.**

$$I_i = 45\alpha_i^2 + 7\gamma_i^2 \tag{18}$$

where

$$\alpha_i = \frac{\alpha_{i,xx} + \alpha_{i,yy} + \alpha_{i,zz}}{3} \tag{19}$$

$$\gamma_i^2 = \frac{(\alpha_{i,xx} - \alpha_{i,yy})^2 + (\alpha_{i,yy} - \alpha_{i,zz})^2 + (\alpha_{i,zz} - \alpha_{i,xx})^2 + 6(\alpha_{i,xy}^2 + \alpha_{i,xz}^2 + \alpha_{i,yz}^2)}{2} \tag{20}$$

13. **Compute the Raman depolarization ratio (ρ_i) for each vibrational mode.**

$$\rho_i = \frac{3\gamma_i^2}{45\alpha_i^2 + 4\gamma_i^2} \tag{21}$$

3 Sample Output

Sample output is provided in the sample.out file. Please note that double-precision arithmetic and different conversion factors may result in slightly different answers.

4 References

E.B. Wilson, Jr., J.C. Decius, and P.C. Cross, "**Molecular Vibrations**", McGraw-Hill, 1955.

W.B. Person and G. Zerbi editors, "**Vibrational ntensities in Infrared and Raman Spectroscopy**", Elsevier, Amsterdam, 1982.

B.S. Galabov and T. Dudev, "**Vibrational Intensities**", Elsevier, Amsterdam, 1996.