How to Calculate Huang-Rhys Factors using Gaussian

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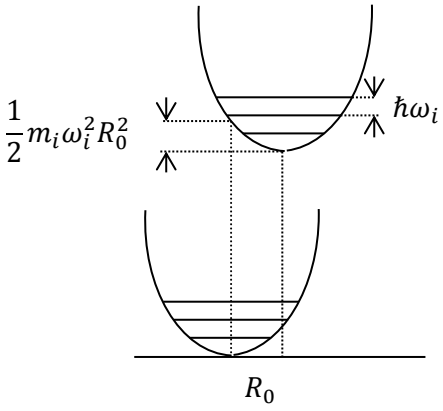
This is the theory behind the program I wrote to calculate the Huang-Rhys (HR) factors from Gaussian output. I begin by describing the general theory of the HR factor, and end with the methodology the program uses to calculate these factors.



We assume the ground and excited states have harmonic nuclear potential wells with energy defined by

$$U_i(q_i) = \frac{1}{2}m_i\omega_i^2q_i^2$$

where U_i is the potential energy of normal mode i, m_i is the reduced mass and ω_i is the frequency of the normal mode and q_i is the displacement along the normal coordinate. Hence, the frequency of the normal mode is given by the square root of the second derivative of the potential divided by the reduced mass of the mode

$$\sqrt{\frac{1}{m_i}\frac{d^2U_i(q_i)}{dq_i^2}} = \omega_i$$

Upon excitation, the equilibrium position of the harmonic well shifts by an amount $R_{i,0}$ relative to the ground state. From this shift, we calculate the dimensionless HR (S_i) factor according to

$$S_i = \frac{m_i\omega_i^2}{2\hbar\omega}R_{i,0}^2 = \frac{m_i\omega_i}{2\hbar}R_{i,0}^2$$

where the relaxation energy is given by

$$\lambda = \frac{1}{2}m_i\omega_i^2R_0^2$$

(note that the HR factor is just the relaxation energy divided by $\hbar\omega_i$)

The HR factor can be calculated using the assistance of quantum chemical software. The following algorithm was implemented to calculate these quantities. The first step for calculating the HR factors is obtaining accurate geometries for each configuration of the molecule of interest. Following Gisslen and Scholz, I use the DFT/B3LYP formalism to calculate the geometries of the ground, anion, and cation states, and TD-DFT/B3LYP for the excited state. Gisslen and Schulz recommend using constrained-DFT, with $n_{occ} = n_{virt} = 1$, for the excited states, but I have not figured out how to do this with Gaussian yet (maybe constrained DFT is implemented in Gaussian 2016?). The vibrational information of the ground state is also needed, so the vibrational frequencies of the ground state are calculated along with the geometry optimization.

Given the optimized geometries, the displacement vectors from the ground state geometry ($R_{i,0}$) in terms of each normal mode can be calculated. Starting with the Cartesian coordinates of the ground, x_g, and excited, x_e, states, the total displacement is calculated according to

$$\Delta_i = x_{e,i} - x_{g,i}$$

where the i is the atom number. We can project this displacement onto the complete set of normal modes to find the displacement in terms of the normal modes. Rather than take the normal modes straight from Gaussian, I prefer to calculate them directly from the Hessian so that I have a complete set on which to

project the displacements (it seemed that the eigenvectors in the Gaussian output were not orthogonal, and furthermore, did not make a complete set because the low frequency translation/rotation modes were not included). Gaussian provides the Hessian in Cartesian coordinates. Mathematically this is expressed as

$$H = \begin{bmatrix} \frac{d^2U}{dx_1^2} & \frac{d^2U}{dx_1 dx_2} & \cdots & \frac{d^2U}{dx_1 dx_N} \\ \frac{d^2U}{dx_1 dx_2} & \frac{d^2U}{dx_2^2} & \cdots & \frac{d^2U}{dx_1 dx_2} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{d^2U}{dx_N dx_1} & \frac{d^2U}{dx_N dx_2} & \cdots & \frac{d^2U}{dx_N^2} \end{bmatrix}$$

where the coordinate index runs from $i = 1, N$ where N is the number of atoms. The potential is a function of all of the coordinates

$$U = \frac{1}{2}\sum_{i,j}^{N} \sqrt{m_i}\omega_i x_i \sqrt{m_j}\omega_j x_j$$

We need to transform the basis from cartesian coordinates, to normal coordinates q_j. This is done by diagonalizing the mass weighted Hessian. The coordinates are mass weighted by multiplying by the square root of the mass. This is a simple change of variable operation

$$\zeta_i = \sqrt{m_i} x_i$$
$$d\zeta_i = \sqrt{m_i} dx_i$$

so that

$$U = \frac{1}{2}\sum_{i}^{N} \omega_i^2 \zeta_i^2$$

I show that the second derivative of this potential gives the same result as the case in Cartesian coordinates

$$\sum_{i,j} \frac{dU}{dx_i dx_j} = \frac{1}{2}\sum_{i,j}\sum_{k,l}^{N} \frac{d}{dx_i dx_j}\sqrt{m_k}\omega_k x_k \sqrt{m_l}\omega_l x_l = \frac{1}{2}\sum_{i,j}\sqrt{m_i}\omega_i\sqrt{m_l}\omega_l \delta_{i,k}\delta_{j,l}$$
$$= \frac{1}{2}\sum_{i,j}\sqrt{m_i m_j}\omega_i\omega_j =$$
$$= \sum_{i,j}\sqrt{m_i m_j}\frac{dU}{d\zeta_i d\zeta_j} = \frac{1}{2}\sum_{i,j}\sum_{k,l}^{N}\sqrt{m_i m_j}\frac{d}{d\zeta_i d\zeta_j}\omega_k\omega_l\zeta_k\zeta_l = \frac{1}{2}\sum_{i,j}\sqrt{m_i m_j}\omega_i\omega_j$$

By taking the second derivative of just the mass weighted coordinates, we can derive the normal modes

$$\sum_{i,j} \frac{dU}{d\zeta_i d\zeta_j} = \frac{1}{2} \sum_{i,j} \omega_i \omega_j$$

$$H_{MWC} = \sum_{i,j} \frac{H_{i,j}}{\sqrt{m_i m_j}} = \begin{bmatrix} \frac{d^2U}{d\zeta_1^2} & \frac{d^2U}{d\zeta_1 d\zeta_2} & \cdots & \frac{d^2U}{d\zeta_1 d\zeta_N} \\ \frac{d^2U}{d\zeta_1 d\zeta_2} & \frac{d^2U}{d\zeta_2^2} & \cdots & \frac{d^2U}{d\zeta_1 d\zeta_2} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{d^2U}{d\zeta_N d\zeta_1} & \frac{d^2U}{dx_N dx_2} & \cdots & \frac{d^2U}{d\zeta_N^2} \end{bmatrix}$$

Diagonalizing the mass weighted hessian gives the normal modes in mass weighted coordinates along with the vibrational frequencies. Let L_{MWC} be the matrix that diagonalizes H_{MWC}, then

$$L_{MWC}^{\dagger} H_{MWC} L_{MWC} = \Omega^2$$

where Ω^2 is the diagonal matrix containing the squared frequencies of the mass weighted normal modes. In terms of the normal modes, the potential is diagonal and given by

$$U = \frac{1}{2} \sum_i \omega_i^2 q_i^2$$

where ω_i are the vibrational frequencies of normal mode i and q_i is the normal coordinate. The normal coordinates are given in mass weighted coordinates by the columns of L_{MWC}

$$q_i = \sum_j L_{MWC,j,i} = \sum_j c_{j,i} \frac{dU}{d\zeta_i d\zeta_j} = \sum_j c_{j,i} \frac{dU}{\sqrt{m_i m_j} dx_i dx_j}$$

Before projecting the vibronic displacement onto the normal modes, we need to convert it from Cartesian coordinates to mass weighted coordinates so that the units are the same as the eigenvectors. Hence, we take

$$\Delta_i = x_{e,i} - x_{g,i}$$

$$\sqrt{m_i}\Delta_i = \sqrt{m_i} x_{e,i} - \sqrt{m_i} x_{g,i}$$

$$\sqrt{m_i}\Delta_i = \zeta_{e,i} - \zeta_{g,i}$$

Now, we can project the mass weighted displacement onto the normal coordinates

$$R_{0,i} = q_i \sum_j \sqrt{m_j}\Delta_j$$

Finally, we can calculate the huang rhys factor after converting $R_{0,i}$ from mass weighted coordinates to normal coordinates by dividing by the square root of the reduced mass of the normal mode.

The next pages define a mathematical framework the method described above:

Let there be N atoms in the molecule. Each atom has three Cartesian coordinates, which will be symbolized by $\chi_{a\in[1,2\ldots N],c\in[x,y,z]}$ where the subscript a denotes the atom and c denotes the coordinate. We define our basis as

$$|\boldsymbol{\mathcal{X}}\rangle = \left[\frac{d}{d\chi_{1,x}}, \frac{d}{d\chi_{1,y}}, \frac{d}{d\chi_{1,z}}, \frac{d}{d\chi_{2,x}}, \ldots, \frac{d}{d\chi_{N,z}}\right]$$

The Hessian is given by

$$\boldsymbol{H} = \langle \boldsymbol{\mathcal{X}}|\boldsymbol{U}|\boldsymbol{\mathcal{X}}\rangle = \begin{bmatrix} \frac{d^2U}{d\chi_{1,x}^2} & \frac{d^2U}{d\chi_{1,x}d\chi_{1,y}} & \cdots & \frac{d^2U}{d\chi_{1,z}d\chi_{N,z}} \\ \frac{d^2U}{d\chi_{1,x}d\chi_{1,y}} & \frac{d^2U}{d\chi_{1,y}^2} & \cdots & \frac{d^2U}{d\chi_{1,y}d\chi_{N,z}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{d^2U}{d\chi_{1,z}d\chi_{N,z}} & \frac{d^2U}{d\chi_{1,y}d\chi_{N,z}} & \cdots & \frac{d^2U}{d\chi_{N,z}^2} \end{bmatrix}$$

Where $U = \frac{1}{2}\sum_{(a,c),(b,d)} \sqrt{m_a}\omega_{a,c}\chi_{a,c}\sqrt{m_b}\omega_{b,d}\chi_{b,d}$ defines the nuclear potential well. Define the mass weighted coordinates as

$$\zeta_{a,c} = \sqrt{m_a}\chi_{a,c}$$
$$d\zeta_{a,c} = \sqrt{m_a}d\chi_{a,c}$$

The elements of the mass weighted hessian are given by

$$\boldsymbol{W}_{(a,c),(b,d)} = \frac{\boldsymbol{H}_{(a,c),(b,d)}}{\sqrt{m_a m_b}}$$

$$\boldsymbol{W} = \langle \boldsymbol{\mathcal{Z}}|\boldsymbol{U}|\boldsymbol{\mathcal{Z}}\rangle = \begin{bmatrix} \frac{d^2U}{d\zeta_{1,x}^2} & \frac{d^2U}{d\zeta_{1,x}d\zeta_{1,y}} & \cdots & \frac{d^2U}{d\zeta_{1,z}d\zeta_{N,z}} \\ \frac{d^2U}{d\zeta_{1,x}d\zeta_{1,y}} & \frac{d^2U}{d\zeta_{1,y}^2} & \cdots & \frac{d^2U}{d\zeta_{1,y}d\zeta_{N,z}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{d^2U}{d\zeta_{1,z}d\zeta_{N,z}} & \frac{d^2U}{d\zeta_{1,y}d\zeta_{N,z}} & \cdots & \frac{d^2U}{d\zeta_{N,z}^2} \end{bmatrix}$$

Where the basis is now in mass weighted coordinates

$$|\mathcal{Z}\rangle = \left[\frac{d}{\sqrt{m_1}d\chi_{1,x}}, \frac{d}{\sqrt{m_1}d\chi_{1,y}}, \frac{d}{\sqrt{m_1}d\chi_{1,z}}, \frac{d}{\sqrt{m_2}d\chi_{2,x}}, \cdots, \frac{d}{\sqrt{m_N}d\chi_{N,z}}\right]$$
$$= \left[\frac{d}{d\zeta_{1,x}}, \frac{d}{d\zeta_{1,y}}, \frac{d}{d\zeta_{1,z}}, \frac{d}{d\zeta_{2,x}}, \cdots, \frac{d}{d\zeta_{N,z}}\right]$$

Let $\mathcal{L}$ be the matrix that diagonalizes W, then

$$\Omega^2 = \mathcal{L}^\dagger W \mathcal{L}$$

Where $\boldsymbol{\Omega}^2$ are the vibrational frequencies squared, as

$$\boldsymbol{W} = \frac{1}{2}\sum_{(e,g),(f,h)} \frac{d}{\sqrt{m_e}d\chi_{e,g}} \frac{d}{\sqrt{m_f}d\chi_{f,h}} \sum_{(a,c),(b,d)} \sqrt{m_a}\omega_{a,c}\chi_{a,c}\sqrt{m_b}\omega_{b,d}\chi_{b,d}$$

$$\boldsymbol{W} = \frac{1}{2}\sum_{(a,c),(b,d)} \frac{d}{\sqrt{m_a}d\chi_{a,c}} \frac{d}{\sqrt{m_b}d\chi_{b,d}} \sqrt{m_a}\omega_{a,c}\chi_{a,c}\sqrt{m_b}\omega_{b,d}\chi_{b,d}$$

$$\boldsymbol{W} = \frac{1}{2}\sum_{(a,c),(b,d)} \omega_{a,c}\omega_{b,d}$$

So

$$\boldsymbol{\mathcal{L}^\dagger W \mathcal{L}} = \sum_i \Omega_i^2$$

The normal coordinates corresponding to the normal frequencies are given by

$$\boldsymbol{\mathcal{L}_i} = \sum_{a,c} \gamma_{a,c}^i \frac{d}{d\zeta_{a,c}}$$

where $\gamma_{a,c}^i$ is the coefficient of the change in the mass weighted coordinate $\zeta_{a,c}$ for the i^{th} normal mode. These form a complete set. We project the mass weighted geometrical displacements

$$\boldsymbol{\Gamma} = \sum_{\mathrm{a,c}} \Gamma_{ac}^{eg}\zeta_{a,c}$$

where $\Gamma_{ac}^{eg} = \left(\zeta_{a,c}^e - \zeta_{a,c}^g\right) = \sqrt{m_a}\left(\chi_{a,c}^e - \chi_{a,c}^g\right)$ is the coefficient defining the magnitude of the displacement in mass weighted coordinates, onto these normal modes to find the displacement along each normal coordinate

$$\boldsymbol{Q_0 = L\Gamma}$$

$$= \sum_{i} \sum_{a,c} \gamma_{a,c}^{i} \frac{d}{d\zeta_{a,c}} \Gamma_{ac}^{eg} \zeta_{a,c}$$
$$= \sum_{i} \sum_{a,c} \gamma_{a,c}^{i} \Gamma_{ac}^{eg}$$

The Huang-Rhys factor is calculated directly by

$$\boldsymbol{S = \frac{\Omega Q_0^2}{2\hbar}}$$

As in Cartesian coordinates, the Huang Rhys factors is

$$S = \frac{m\omega^2 R_0^2}{2\hbar\omega} = \frac{m\omega R_0^2}{2\hbar}$$

But our $Q_0 = \sqrt{m}R_0$ is mass weighted so that

$$S = \frac{\omega Q_0^2}{2\hbar}$$