

## Green's function application to chemical perturbation studies

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**Abstract.** The Green's function and partitioning techniques developed by De Wames and Wolfram for isotopic perturbation in molecules have been extended to chemical perturbation in some simple molecules of the linear  $XY_2$  type. The force field changes consequent on chemical perturbation are calculated. The results clearly show the successful extension of the above technique to such studies in these molecules.

**Keywords.** Green's function; chemical perturbation.

### 1. Introduction

De Wames and Wolfram (1964) demonstrated the applicability of Green's function and partitioning techniques in calculating the vibrational frequencies of simple molecules involved in isotopic perturbation. The Green's function refers to the inverse of the secular equation in cartesian coordinates. An example for isotopic perturbation is given by  $H_2O-D_2O$ , where the hydrogen atoms are replaced by deuterium atoms. Here  $D_2O$  is the isotopically perturbed system and by generating the Green's function for the system  $H_2O$ , the vibrational frequencies of the perturbed system can be calculated from a knowledge of the unperturbed frequencies. As against this, an example for chemical perturbation will be  $CO_2-CS_2$ , where the Oxygen atoms are replaced by sulphur atoms. De Wames and Wolfram (1966) also attempted a qualitative extension of this technique to the calculation of the force constant changes consequent on chemical perturbation but with limited success. Here we apply to the above formalism to calculate the changes in all the force constants of the system, accompanying a chemical perturbation.

### 2. Theory

De Wames and Wolfram (1964) obtained the following secular determinantal equation from first principles.

$$| G(\omega^2) \{ \epsilon\omega^2 - \Delta D \} + I | = 0, \quad (1)$$

which takes into account the mass and force field changes consequent on a chemical perturbation. Here,

$$G(\omega^2) = (\omega^2 - D)^{-1} \quad (2)$$

where  $\omega$  is the frequency of the perturbed system, and

$$D = M^{-1/2} F M^{-1/2} \quad (3)$$

with  $F$  being the force constant matrix in cartesian coordinates and  $M$  being a diagonal matrix containing the various masses of the system as its elements.  $\Delta D$  is the change in the force constant matrix due to perturbation  $\epsilon = (m^p - m)/m$ , where  $m^p$  is the perturbed atomic mass and  $m$  the unperturbed mass,  $I$  is a unit matrix of appropriate order. The Green's function  $G(\omega^2)$  can be constructed in the usual way. A chemical perturbation is different from an isotopic perturbation in a number of ways. The mass, geometry and the force field change because of chemical perturbation, whereas, only mass changes for isotopic perturbations. Equation(1) can also be used to calculate the force field changes for electronic perturbation for which  ${}^2\pi_g\text{BO}^2 - {}^2\pi_u\text{BO}_2$  can be cited as an example.

### 3. Calculation procedure

By making use of (1) the force field changes  $\Delta D$  were calculated in the case of  $XY_2$  linear molecules involved in two different types of chemical perturbations  $XY_2 - ZY_2$  and  $XY_2 - XZ_2$  knowing the perturbed and unperturbed frequencies. The frequencies for the various systems used in the calculations are given in table 1.

Since the system is centro-symmetric the  $\Delta D$  matrix will have many identical elements for both the above cases. The form of  $\Delta D$  is shown in table 2.

The force constant matrix  $F$  in cartesian coordinates, can be expressed in terms of the force constant matrix in valence coordinates,  $f$  as

$$F = \tilde{X} f X, \quad (4)$$

Table 1. Vibrational frequencies of molecules.

Molecule	Electronic states	Frequencies*		
		$\omega_1$	$\omega_2$	$\omega_3$
C <sub>3</sub>	${}^1\Sigma_g^+$	1230.0 (H)	63.0 (H)	2040.0 (H)
	${}^1\pi_u$	1085.0 (H)	307.0 (H)	—
	${}^2\pi_g$	1070.0 (H)	464.0 (H)	1322.0 (H)
BO <sub>2</sub>	${}^2\pi_u$	994.0 (H)	502.0 (H)	2357.0 (H)
	${}^2\pi_g$	1280.0 (H)	—	1469.0 (H)
CO <sub>2</sub> <sup>+</sup>	${}^2\pi_u$	1131.0 (H)	—	2731.0 (H)
	${}^3\Sigma_g^-$	1197.0 (H) (M)	423.0 (H) (M)	1475.0 (H)(M)
CN <sub>2</sub>	${}^3\pi_u$	1192.0 (H) (M)	510.0 (H) (M)	1533.0 (H) (M)
	${}^1\Sigma_g^+$	363.0 (H) (M)	75.0 (H) (M)	413.0 (H) (M)
HgCl <sub>2</sub>	${}^1\pi_u^+$	289.0 (H) (M)	60.0 (H) (M)	263.0 (H) (M)
	—	221.0 (G)	53.0 (G)	295.0 (G)
HgBr <sub>2</sub>	—	185.0 (G)	20.0 (G)	224.0 (G)
CO <sub>2</sub>	${}^1\Sigma_g^+$	1354.9 (H)	673.0 (H)	2396.49 (H)

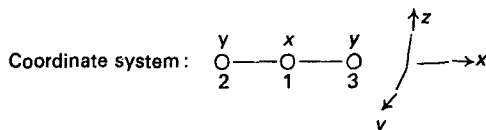
(\*) Frequencies are given in the units of  $\text{cm}^{-1}$

(H) Herzberg (1966); (M) Milligan and Jacox (1966)

(G) Gedanken *et al* (1969)

Table 2.  $\Delta D$  Matrix.

$\Delta D_{11}$	0	0	$\Delta D_{14}$	0	0	$\Delta D_{17}$	0	0
0	$\Delta D_{22}$	0	0	$\Delta D_{25}$	0	0	$\Delta D_{28}$	0
0	0	$\Delta D_{33}$	0	0	$\Delta D_{36}$	0	0	$\Delta D_{39}$
$\Delta D_{41}$	0	0	$\Delta D_{44}$	0	0	$\Delta D_{47}$	0	0
0	$\Delta D_{52}$	0	0	$\Delta D_{55}$	0	0	$\Delta D_{58}$	0
0	0	$D_{63}$	0	0	$\Delta D_{66}$	0	0	$\Delta D_{69}$
$\Delta D_{71}$	0	0	$\Delta D_{74}$	0	0	$\Delta D_{77}$	0	0
0	$\Delta D_{82}$	0	0	$\Delta D_{85}$	0	0	$\Delta D_{88}$	0
0	0	$\Delta D_{93}$	0	0	$\Delta D_{96}$	0	0	$\Delta D_{99}$



where  $X$  relates the internal and the cartesian coordinates. Using the above equation various  $\Delta D$  elements can be ultimately expressed in terms of three basic parameters  $\Delta f_d$ ,  $\Delta f_{dd}$  and  $\Delta f_a$ . Here  $\Delta f_d$  represents the change in the stretching force constant  $\Delta f_{dd}$  change in the stretch-stretch interaction constant and  $\Delta f_a$  change in the bending constant. The Green's function matrix  $G(\omega^2)$  was generated such that it took into account both the force field and the mass changes.

### 3.1. $XY_2 - ZY_2$ perturbation

The following equations were obtained for the force constant changes in the case of  $XY_2 - ZY_2$  perturbation.

$$\Delta(f_d + f_{dd})(G_{44} - G_{47}) = m_y \quad (5)$$

$$\begin{aligned} \Delta(f_d - f_{dd}) [m_x \epsilon \omega^2 \{2G_{14}^2 - G_{11}(G_{44} + G_{47})\} + 4G_{14}(m_x m_y)^{1/2} \\ - m_x(G_{44} + G_{47}) - 2m_y G_{11}] = -m_x m_y (1 + G_{11} \epsilon \omega^2) \end{aligned} \quad (6)$$

$$\begin{aligned} 2\Delta f_a \{m_x \epsilon \omega^2 [2G_{25}^2 - G_{22}(G_{55} + G_{58})] + 4G_{25}(m_x m_y)^{1/2} - m_x(G_{55} + G_{58}) \\ - 2m_y G_{22}\} = -m_x m_y (1 + G_{22} \epsilon \omega^2) \end{aligned} \quad (7)$$

where 
$$G_{11} = \frac{2m_y}{d_1^2(\omega^2 - \omega_3^2)} + \frac{m_x}{d_1^2 \omega^2}; \quad (8)$$

$$G_{22} = \frac{2m_y}{d_1^2(\omega^2 - \omega_2^2)} + \frac{m_x}{d_1^2 \omega^2}; \quad (9)$$

$$G_{44} = + \frac{1}{2(\omega^2 - \omega_1^2)} + \frac{m_x}{2d_1^2(\omega^2 - \omega_3^2)} + \frac{m_y}{d_1^2 \omega^2}; \quad (10)$$

$$G_{55} = \frac{1}{2\omega^2} + \frac{m_x}{2d_1^2(\omega^2 - \omega_2^2)} + \frac{m_y}{d_1^2\omega^2}; \quad (11)$$

$$G_{14} = -\frac{(m_x m_y)^{1/2}}{d_1^2(\omega^2 - \omega_3^2)} + \frac{(m_x m_y)^{1/2}}{d_1^2\omega^2}; \quad (12)$$

$$G_{25} = -\frac{(m_x m_y)^{1/2}}{d_1^2(\omega^2 - \omega_2^2)} + \frac{(m_x m_y)^{1/2}}{d_1^2\omega^2}; \quad (13)$$

$$G_{47} = -\frac{1}{2(\omega^2 - \omega_1^2)} + \frac{m_x}{2d_1^2(\omega^2 - \omega_3^2)} + \frac{m_y}{d_1^2\omega^2}; \quad (14)$$

$$G_{58} = -\frac{1}{2\omega^2} + \frac{m_x}{2d_1^2(\omega^2 - \omega_2^2)} + \frac{m_y}{d_1^2\omega^2}; \quad (15)$$

which give the Green's function elements, where  $d_1^2 = 2m_y + m_x$ .

The individual changes  $\Delta f_a$ ,  $\Delta f_{ad}$  and  $\Delta f_\alpha$  calculated using (5)–(7) are given in table 3 for various systems along with the values calculated directly from the frequencies.

### 3.2. $XY_2$ – $XZ_2$ perturbation

The following equations were obtained for the force constant changes in the case of  $XY_2$ – $XZ_2$  perturbation.

$$\{\Delta(f_a + f_{ad}) - \epsilon\omega^2 m_y\} (G_{44} - G_{47}) = m_y \quad (16)$$

$$\begin{aligned} \Delta(f_d - f_{dd}) [2\epsilon\omega^2 m_y \{2G_{14}^2 - G_{11}(G_{44} + G_{47})\} + 4G_{14}(m_x m_y)^{1/2} \\ - m_x(G_{44} + G_{47}) - 2m_y G_{11}] = -m_x m_y \{1 + (G_{44} + G_{47})\epsilon\omega^2\} \end{aligned} \quad (17)$$

$$\begin{aligned} 2\Delta f_\alpha [2\epsilon\omega^2 m_y \{2G_{25}^2 - G_{22}(G_{55} + G_{58})\} + 4G_{25}(m_x m_y)^{1/2} \\ - m_x(G_{55} + G_{58}) - 2m_y G_{22}] = -m_x m_y \{1 + (G_{55} + G_{58})\epsilon\omega^2\}. \end{aligned} \quad (18)$$

Table 3.  $XY_2 \rightarrow ZY_2$  perturbation

Perturbation	Calculated from equations* (5)–(7)			Calculated directly*		
	$\Delta f_a$	$\Delta f_{ad}$	$\Delta f_\alpha$	$\Delta f_a$	$\Delta f_{ad}$	$\Delta f_\alpha$
${}^3\pi_g \text{BO}_2 \rightarrow \Sigma_g^+ \text{CO}_2$	8.573	-2.053	0.326	8.573	-2.058	0.326
${}^3\pi_g \text{BO}_2 \rightarrow {}^3\pi_g \text{CO}_2^+$	3.024	1.632	—	3.024	1.632	—
${}^3\pi_u^+ \text{BO}_2 \rightarrow {}^3\pi_u^+ \text{CO}_2^+$	4.358	-1.611	—	4.358	1.611	—
${}^3\pi_u \text{BO}_2 \rightarrow \Sigma_g^+ \text{CO}_2$	4.776	3.224	0.283	4.776	3.224	0.283

\*Change in the force constants are given in the units of m.dy/Å

The individual changes from the above equations along with the directly calculated values are given in table 4.

### 3.3. Electronic perturbation

For electronic perturbation we obtained the following equations.

$$\Delta(f_d + f_{dd})(G_{44} - G_{47}) = m_y; \quad (19)$$

$$\Delta(f_d - f_{dd}) [4G_{14}(m_x m_y)^{1/2} - m_x(G_{44} + G_{47}) - 2m_y G_{11}] = -m_x m_y; \quad (20)$$

$$2\Delta f_a [4G_{25}(m_x m_y)^{1/2} - m_x(G_{58} + G_{46}) - 2m_y G_{22}] = -m_x m_y. \quad (21)$$

Table 5 shows the results obtained from the above analysis.

Table 4.  $XY_2 \rightarrow XZ_2$  perturbation.

Perturbation	Calculated from equations* (16) - (18)			Calculated directly*		
	$\Delta f_d$	$\Delta f_{dd}$	$\Delta f_a$	$\Delta f_d$	$\Delta f_{dd}$	$\Delta f_a$
$CN_2 \rightarrow CS_2$	4.704	-2.589	1.924	4.704	-2.589	1.924
$CO_2 \rightarrow CS_2$	-2.736	-0.632	-0.168	-2.736	-0.632	-0.168
$C_3 \rightarrow CS_2$	3.049	0.189	0.412	3.049	0.189	0.409
$C_3 \rightarrow CO_2$	5.786	0.822	0.579	5.787	0.823	0.578
$^1\Sigma_g^+ C_3 \rightarrow ^3\Sigma_g^- CN_2$	-1.655	2.778	0.217	-1.655	2.778	0.217
$CN_2 \rightarrow CO_2$	7.441	-1.956	0.361	7.441	-1.956	0.361
$^1\Sigma_g^+ HgCl_2 \rightarrow HgBr_2$	-0.402	-0.051	—	-0.402	-0.051	—
$^1\Sigma_u^+ HgCl_2 \rightarrow HgBr_2$	0.055	-0.191	—	0.055	-0.191	—

\*Change in the force constants are given in the units of m. dy/Å

Table 5. Electronic perturbation.

Perturbation	Calculated from equations* (19) - (21).			Calculated directly*		
	$\Delta f_d$	$\Delta f_{dd}$	$\Delta f_a$	$\Delta f_d$	$\Delta f_{dd}$	$\Delta f_a$
$^2\pi_g BO_3 \rightarrow ^2\pi_u BO_2$	3.797	-5.277	0.043	3.797	-5.277	0.043
$^1\Sigma_g^+ C_3 \rightarrow ^1\pi_u C_3$	—	—	0.106	—	—	0.106
$^2\pi_g CO_2^+ \rightarrow ^2\pi_u CO_2^+$	5.131	-8.521	—	5.131	-8.521	—
$^3\Sigma_g^- CN_2 \rightarrow ^3\pi_u CN_2$	0.167	-0.265	0.100	0.167	-0.265	0.100
$^1\Sigma_g^+ HgCl_2 \rightarrow ^1\Sigma_u^+ HgCl_2$	-1.287	0.279	-0.015	-1.287	0.279	-0.015

\*Change in the force constants are given in the units of m. dy/Å.

#### **4. Conclusions**

The results obtained clearly demonstrate the successful application of the Green's function technique for calculating the force field changes resulting from chemical and electronic perturbations in molecules. As the systems investigated are fairly simple and of high symmetry the results obtained are very good. Work is in progress to extend the above analysis to more complicated systems with lower symmetry to examine the power of the above approach.

#### **References**

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