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Novel equations to predict vibrational spectroscopic and electrodynamics properties of molecules

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Abstract

Mathematical relations linking electric and magnetic field-dependent physical properties of molecules have been unveiled. These relations are analogous to Maxwell relations in thermodynamics and are derived from mixed third-order partial derivatives of every alternative Legendre representation of the energy of molecules with respect to the electric or magnetic field and normal coordinates. Some of these novel physical relationships have practical applications in the low computational cost calculation of parameters commonly used in vibrational spectroscopy like the Stark and Zeeman Tuning Rates. Furthermore, other equalities have shown connections and alternative ways of computing physical properties used in electrodynamics as permanent dipolar moments and polarizabilities.

1. Introduction

In thermodynamics\[1\], the relation that gives the internal energy \( U \) as a function of the extensive parameters like entropy \( S \), volume \( V \), and number of particles \( N \) is known as the fundamental relation of a thermodynamical system (equation (1)). If the fundamental equation of a system is known, every thermodynamical attribute is completely and precisely determined. The derivative of the internal energy as a function of the extensive parameters gives rise to the intensive parameters, which are important physical properties such as the temperature \( T \), pressure \( P \) and electrochemical potential \( \mu \). Therefore, the differential equation of the fundamental relation of the internal energy is expressed as a function of the intensive parameters and the differentials of the extensive parameters (equation (2)).

\[
\frac{dU}{dS} \frac{dS}{dV} - \frac{dV}{dN} \frac{dN}{dT} = T \frac{dU}{dT} - P \frac{dV}{dP} + \mu \frac{dN}{d\mu}
\]

A mathematical formalism known as Legendre transformations \[1\] is used in thermodynamics to obtain other fundamental equations from the fundamental relation of the internal energy. In such reformulations, the intensive parameters replace extensive parameters as mathematically independent variables. All these fundamental equations are known as thermodynamic potentials. Gibbs free energy \( G \), Enthalpy \( H \), Helmholtz free energy \( F \) and Grand Canonical potential \( C \) are some of the most commonly used thermodynamic potentials and their corresponding differential equations (3).

\[
\begin{align*}
F(T, V, N) &\iff dF = -SdT - PdV + \mu dN \\
H(S, P, N) &\iff dH = TdS + VdP + \mu dN \\
G(T, P, N) &\iff dG = -SdT + VdP + \mu dN \\
C(T, V, \mu) &\iff dC = -SdT - PdV - Nd\mu
\end{align*}
\]

A formal aspect of thermodynamics is the set of Maxwell relations \[1\]. These relations arise from the equality of the mixed partial second derivatives of the fundamental relation expressed in any of the various possible alternative representations. One example of a Maxwell relation is shown in equation (4).
\[ \frac{\partial^2 U}{\partial s \partial V} - \frac{\partial^2 U}{\partial V \partial s} = -\left( \frac{\partial P}{\partial s} \right)_{V,N} = \left( \frac{\partial T}{\partial V} \right)_{S,N} \]  

(4)

The second derivatives of fundamental equations are also descriptive of material properties of direct physical interest like the coefficient of thermal expansion (\( \alpha \)), the isothermal or adiabatic compressibility (\( \kappa \)), and the molar heat capacity at constant volume or pressure [1]. Using Jacobian operations and Maxwell relations, the isothermal compressibility (\( \kappa_T \)) can be related to adiabatic compressibility (\( \kappa_S \)), and the heat capacity at constant volume (\( c_V \)) to the heat capacity at constant pressure (\( c_P \)) (equation (5)) [1]. An analogous mathematical approach used in thermodynamics to develop equation (5) will be used later on.

\[ c_P = c_V + \frac{TV\alpha^2}{NKT} \]

\[ \kappa_T = \kappa_S + \frac{TV\alpha^2}{Ncp} \]  

(5)

In this work, all these equivalent mathematical relations will be derived for a molecular system where the fundamental equation is the potential energy of the molecule and the independent variables are the nuclear normal coordinates and the elements of an external uniform electric (or magnetic) field vector. Similar equalities are formulated from mixed third-order partial derivatives of the energy and other Legendre representations. The obtained relations carry practical uses in alternative and faster ways of computing properties used in vibrational spectroscopy and electrodynamics such as the Stark and Zeeman Tuning Rates, permanent dipolar moments and polarizabilities. In most cases, these parameters can be obtained by means of these novel relations without the application of an external electric or magnetic field during their computation, thus reducing the cost of the calculation. Furthermore, relations obtained by Jacobian operations show other connections between these electrodynamics parameters.

The vibrational Stark effect [3–11] is the shifting of vibrational frequencies due to the presence of an external electric field. These frequencies can be measured using Infrared or Raman Spectroscopy [12, 13]. The dependence of the wavenumber (\( \nu \)) of a particular mode \( m \) with an electric field strength (\( F \)) can be described using a Taylor expansion as:

\[ \nu_m(F \rightarrow 0) = \nu_m(F = 0) + \left( \frac{\partial \nu_m}{\partial F} \right)_{F=0} F + \frac{1}{2!} \left( \frac{\partial^2 \nu_m}{\partial F^2} \right)_{F=0} F^2 + \ldots \]  

(6)

The vibrational Zeeman effect [14] is the same phenomenon caused by an external magnetic field. The Stark Tuning Rate [15–17] (STR) and the Zeeman Tuning rate [18] (ZTR) are defined as the derivative of the frequency with respect to the electric field (\( F \)) or magnetic field (\( B \)) at the limit of zero field. These parameters are broadly used for estimating the electric or magnetic field magnitude experimentally by monitoring the shift in the frequency of molecular probes. It is a common practice to calculate theoretically the STR and ZTR due to the experimental difficulties in measuring them.

In this paper, a theoretical development of these new relationships is presented alongside some particular practical applications. Subsequently, as a proof of concept, the Stark Tuning Rate is numerically computed employing one of these novel equations for different chemical compounds typically used as molecular probes. Moreover, for the purpose of comparison, the STR is also calculated in a traditional manner with the computational approach normally adopted in the literature.

2. Theoretical development

2.1. Mixed second and third-order partial derivative equalities

The potential energy (\( E \)) of a molecular system with fixed nuclear positions is a function of all atom coordinates. When a molecule is under the presence of an external uniform electric field (\( EF \)), the energy also depends on the vector element values of this new variable (\( F, F_x, F_y, F_z \)). For convenience, the normal coordinates of a molecule calculated in the absence electric field (\( Q_1, \ldots, Q_n \)) where \( n \) is the total number of normal modes) are used instead of nuclear Cartesian coordinates [12, 13]. Therefore, the potential energy of a molecule under the effect of an EF can be expressed as a function of the vector elements of the EF and the normal coordinates of the molecule as shown in equation (7).

\[ E(F_x, F_y, F_z, Q_1, \ldots, Q_n) \]  

(7)
The total differential of $E$ is given by:

$$
dE = \left(\frac{\partial E}{\partial F_i}\right)_{F_2, F_3, Q_1, \ldots, Q_n} dF_i + \left(\frac{\partial E}{\partial F_j}\right)_{F_2, F_3, Q_1, \ldots, Q_n} dF_j + \left(\frac{\partial E}{\partial Q_1}\right)_{F_2, F_3, Q_2, \ldots, Q_n} dQ_1 + \ldots + \left(\frac{\partial E}{\partial Q_n}\right)_{F_2, F_3, Q_1, \ldots, Q_{n-1}} dQ_n
$$

It can be noticed that the first derivative of the energy with respect to the EF vector elements yields the vector elements of the electric dipolar moment ($\mu_x$, $\mu_y$, $\mu_z$) as [13]:

$$
\mu_x = -\left(\frac{\partial E}{\partial F_i}\right)_{F_2, F_3, Q_1, \ldots, Q_n}, \quad \mu_y = -\left(\frac{\partial E}{\partial F_j}\right)_{F_2, F_3, Q_1, \ldots, Q_n}, \quad \mu_z = -\left(\frac{\partial E}{\partial Q_1}\right)_{F_2, F_3, Q_1, \ldots, Q_n}
$$

In addition, the first derivative of the energy with respect to the normal mode coordinates produces the normal forces ($f_1, \ldots, f_n$) as [13]:

$$
f_1 = -\left(\frac{\partial E}{\partial Q_1}\right)_{F_2, F_3, Q_2, \ldots, Q_n}, \ldots, f_n = -\left(\frac{\partial E}{\partial Q_n}\right)_{F_2, F_3, Q_1, \ldots, Q_{n-1}}
$$

Now, equation (8) can be summarised as:

$$
dE = -\mu_x dF_x - \mu_y dF_y - \mu_z dF_z - f_1 dQ_1 - \ldots - f_n dQ_n
$$

The second derivatives of the energy yield other known parameters such as the polarizability tensor elements ($\alpha_{ij}$, where $i, j, k = x, y, z$) and the normal force constants ($\lambda_m$ where $1 \leq m \leq n$) [12, 13]:

$$
\alpha_{ij} = -\left(\frac{\partial^2 E}{\partial F_i \partial F_j}\right)_{F_2, Q_p}, \quad (\forall k = i, j \land \forall p)
$$

$$
\lambda_m = \left(\frac{\partial^2 E}{\partial Q_m \partial Q_m}\right)_{F_2, Q_p}, \quad (\forall i \land \forall p = m)
$$

A Legendre transformation [1] can be applied to the energy to define other fundamental expressions of the energy, so-called energy potentials, depending on $f_1, \ldots, f_n$ and $\mu_x, \mu_y, \mu_z$ in addition to $Q_1, \ldots, Q_n$ and $F_2, F_3, F_z$ [13]:

$$
R(F_x, F_y, F_z, f_1, \ldots, f_n)
$$

$$
T(\mu_x, \mu_y, \mu_z, Q_1, \ldots, Q_n)
$$

$$
Y(\mu_x, \mu_y, \mu_z, f_1, \ldots, f_n)
$$

The Legendre transformation implies that:

$$
\mu_i = -\left(\frac{\partial R}{\partial F_i}\right)_{F_j, F_p} = -\left(\frac{\partial E}{\partial F_i}\right)_{F_j, Q_p}, \quad \forall j \neq i \land \forall p
$$

$$
f_m = -\left(\frac{\partial T}{\partial Q_m}\right)_{\mu_i, Q_p} = -\left(\frac{\partial E}{\partial Q_m}\right)_{F_j, Q_p}, \quad \forall j \land \forall p = m
$$

$$
F_i = \left(\frac{\partial T}{\partial \mu_i}\right)_{\mu_j, Q_p} = \left(\frac{\partial Y}{\partial \mu_i}\right)_{\mu_j, F_p}, \quad \forall j \neq i \land \forall p
$$

$$
Q_m = \left(\frac{\partial R}{\partial f_m}\right)_{F_j, f_p} = \left(\frac{\partial Y}{\partial f_m}\right)_{\mu_i, f_p}, \quad \forall j \land \forall p = m
$$

where $i, j, k = x, y, z$ and $1 \leq m, p \leq n$, and that:

$$
R = E + \sum_{m=1}^{n} f_m Q_m
$$

$$
T = E + \mu_x F_x + \mu_y F_y + \mu_z F_z
$$

Note that the Legendre transformation is only valid when the second derivative of the energy is non-zero. Due to this fact some of the next relationships are not valid in the inflexion points of the potential energy surface [1].
\[
Y = E + \sum_{m=1}^{n} f_m Q_m + \mu_x F_x + \mu_y F_y + \mu_z F_z
\]

(23)

When the molecular geometry is optimised, the forces are zero, then \( R \) equals \( E \). When the electric field is absent, \( T \) equals \( E \). If both conditions are satisfied, \( Y \) equals \( E \). Thus, the same applies to the total differentials of such energy potentials.

The differentials of the new fundamental expressions of the energy (\( R \), \( T \) and \( Y \)) can be obtained similarly to the one for \( E \):

\[
dR = -\mu_x dF_x - \mu_y dF_y - \mu_z dF_z + Q_\ell d\ell + \ldots + Q_n d\ell_n
\]

(24)

\[
dT = F_x d\mu_x + F_y d\mu_y + F_z d\mu_z - F_\ell d\ell - \ldots - F_n d\ell_n
\]

(25)

\[
dY = F_x d\mu_x + F_y d\mu_y + F_z d\mu_z + Q_\ell d\ell + \ldots + Q_n d\ell_n
\]

(26)

Based on the symmetry of partial derivatives, the equality of mixed second-order partial derivatives of \( E \), \( T \), and \( Y \) produces the relations shown in section A.1. From all equations only the following two will be used in further derivations.

\[
\frac{\partial^2 R}{\partial f_m^2} \frac{\partial f_m}{\partial F_i} = \frac{\partial^2 R}{\partial F_i^2} \frac{\partial f_m}{\partial f_m^2} \implies -\frac{\partial \mu_i}{\partial f_m} F_{f_f f_f(j \wedge p \neq m)} = \frac{\partial Q_m}{\partial F_i} F_{f_f f_f(j \wedge i \wedge p)}
\]

(27)

\[
\frac{\partial^2 T}{\partial Q_m \partial \mu_i} = \frac{\partial^2 T}{\partial \mu_i \partial Q_m} \implies \frac{\partial F_i}{\partial Q_m} F_{Q Q Q(j \wedge i \wedge p \neq m)} = \frac{\partial f_m}{\partial \mu_i} F_{\mu Q Q(j \neq i \wedge \neq p)}
\]

(28)

Analogously, the equality of the mixed third-order partial derivatives [19] of \( E \), \( R \), \( T \), and \( Y \) provides the useful relations in section A.2 from which just the following two will be utilised later:

\[
\frac{\partial^3 E}{\partial Q_m^2 \partial F_i} = \frac{\partial^3 E}{\partial F_i^2 \partial Q_m} \implies -\frac{\partial \mu_i}{\partial Q_m} F_{Q Q Q(j \wedge i \wedge p \neq m)} = \frac{\partial Q_m}{\partial F_i} F_{Q Q Q(j \neq i \wedge \neq p)}
\]

(29)

\[
\frac{\partial^3 R}{\partial f_m^3} \frac{\partial f_m}{\partial F_i} = \frac{\partial^3 R}{\partial F_i^3} \frac{\partial f_m}{\partial f_m^3} \implies -\frac{\partial \mu_i}{\partial f_m} F_{f_f f_f(j \wedge i \wedge p \neq m)} = \frac{\partial^2 Q_m}{\partial F_i \partial f_m} F_{f_f f_f(j \neq i \wedge \neq p)}
\]

(30)

The second and third derivatives of \( E \) and \( T \) in sections A.1 and A.2 are defined as restrained since the molecular normal coordinates are constant during derivation, while the derivatives of \( R \) and \( Y \) are defined as unrestrained since the nuclear coordinates are variable and the forces are constant. In the following text, an underscore will denote unrestrained parameters.

Exact equivalent equations relating the magnetic field (\( B \)), the magnetic dipole moment (\( \mu \)) and the magnetic polarizability (\( \sigma \)) instead of their electric counterparts are obtained for the case of vibrational Zeeman effects (equations not shown).

2.2. Vibrational Stark effect

The vibrational Stark effect provides to experimentalists the possibility of determining the local electric field of molecules at diverse environments by measuring the shift of their vibrational frequencies. As shown in equation (6), knowing in advance the lower order derivatives of the Taylor expansion provides the necessary information for precisely calculating the magnitude of such field. The first-order Stark Tuning Rate (STR or \( \sigma \)) is defined as the derivative of the wavenumber\(^2\) of a particular mode \( \ell \) (\( \ell_m \)) with respect to the electric field at \( F = 0 \) [3]. The second derivative is known as second-order Stark Tuning Rate.

2.2.1. Restrained first-order Stark Tuning Rate

The restrained Stark Tuning Rate (\( rSTR \) or \( \sigma \)) has been previously used by Brewer et al [5]. The \( rSTR \) is defined as the first derivative of the wavenumber with respect to the field holding \( Q \) constant (the nuclear configuration coordinates are constant):

\[
\sigma = \frac{\partial \nu_m}{\partial F_i} F_{F F Q \ldots Q}
\]

(31)

A shortcut relation to determine the \( rSTR \) avoiding the application of an electric field using the mixed third-order derivative relation is stated in equation (29). Based on this equation, the derivative of the normal force

\[^2\text{It can also be the frequency } \nu, \nu = \frac{\ell}{T}.\]
constant \( \lambda_m \) with respect to the electric field at \( F_i \) (right term) at fixed nuclear positions (\( Q_p \) constants, \( \forall p \)) can be determined as the second derivative of the electrical dipolar moment over the \( i \) axis with respect to the normal coordinate \( m \).

The equation (32) [12] relates \( \bar{\rho}_m \) with \( \lambda_m \):

\[
\bar{\rho}_m = \frac{\sqrt{\lambda_m}}{2\pi e}
\]  

(32)

To obtain the \( r\text{STR} \), equations (32) and (31) can be used to express \( \sigma \) as a function of the normal force constant:

\[
\sigma = \frac{1}{4\pi \sqrt{\lambda_m}} \left( \frac{\partial \lambda_m}{\partial F_i} \right)_{F_i Q_j Q_k \ldots Q_u} \]  

(33)

Subsequently, by performing a replacement using equation (29), the desired relation (equation (34)) is derived.

\[
\sigma = \frac{1}{4\pi \sqrt{\lambda_m}} \left( \frac{\partial^2 \mu_i}{\partial Q_m^2} \right)_{F_i Q_j(\forall j \neq i \land \forall p \neq m)} \]  

(34)

Equation (34) shows how \( r\text{STR} \) can be computed alternatively to equation (31). Starting from an optimised molecular geometry in vacuum, a frequency analysis can be performed to obtain all normal force constants, thus, their vibrational frequencies. For a selected frequency, the corresponding normal coordinate is obtained. A normal coordinate is a displacement vector for all atoms in the Cartesian space. This vector is used to displace the coordinates of each atom by multiplying the vector by small displacement values and adding this values to the relaxed structure. For each distorted geometry, an electrical dipolar moment is calculated. Finally, the coordinates of each atom by multiplying the vector by small displacement values and adding this values to the normal coordinate is a displacement vector for all atom in the Cartesian space. This vector is used to displace the molecular geometry in vacuum, a frequency analysis can be performed to obtain all normal force constants, together with the desired relation (equation (34))

2.2.2. Unrestrained first-order Stark Tuning Rate

The unrestrained equation (35) implies that all the normal mode forces are constants3.

\[
\bar{\sigma} = \frac{\partial \lambda_m}{\partial F_i} \left( F_j F_k Q_j Q_k \ldots Q_u \right)_{F_i(\forall j \neq i \land \forall p \neq m)} \]  

(35)

In the particular case when all forces are zero (\( f_p = 0, \ \forall p \)), the molecular geometry is in a minimum (relaxed state) or maximum (transition state) of energy. Combining the equation (32) together with the \( \bar{\sigma} \) equation, it leads to equation (36).

\[
\bar{\sigma} = \frac{1}{4\pi \sqrt{\lambda_m}} \left( \frac{\partial \lambda_m}{\partial F_i} \right)_{F_j F_k Q_j Q_k \ldots Q_u} \]  

(36)

From the mixed third-order partial derivative relations, an equality for the derivative in equation (36) can be obtained.

By using the demonstration in section A.3 (equation (83)), it can be proven that equation (13) is equivalent to equation (37).

\[
\lambda_m = -\left( \frac{\partial f_p}{\partial Q_m} \right)_{F_i Q_j} = -\left( \frac{\partial f_p}{\partial Q_m} \right)_{F_i Q_j} (\forall i \land \forall p \neq m) \]  

(37)

3 The upperscore denotes that it is an unrestrained derivative.
Based on equation (30) and replacing by the inverse of equation (37) to obtain:

\[
\left( \frac{\partial^2 \psi_j}{\partial F_m^2} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} = - \lambda_m^2 \left( \frac{\partial \lambda_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} \]

(38)

and finally:

\[
\left( \frac{\partial \lambda_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} = - \lambda_m^2 \left( \frac{\partial^2 \mu_j}{\partial F_j^2} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(39)

The combination of equations (36) and (39) yields the final relation for the alternative calculation of the unrestrained first-order Stark Tuning Rate (\(\sigma\)):

\[
\sigma = - \lambda_m^2 \frac{\partial^2 \mu_j}{\partial F_j^2} \left( \frac{\partial Q_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(40)

It is demonstrated in section A.4 of the appendix (equation (86)) that equation (40) is equivalent to equation (41):

\[
\sigma = - \lambda_m^2 \frac{\partial^2 \mu_j}{\partial F_j^2} \left( \frac{\partial Q_m}{\partial F_j} \right)_{F_{i,Q}, (\forall j \neq i \text{ and } p=m)}
\]

(41)

2.2.3. Connection between restrained and unrestrained first-order Stark Tuning Rates

Presently, it is feasible to relate the restrained Stark Tuning Rate (\(\sigma\)) with the unrestrained Stark Tuning Rate (\(\tilde{\sigma}\)) using equation (98) in section A.6 where \(l = f\text{ or } Q\), indistinctly:

\[
\left( \frac{\partial Q_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} = \sum_{m=1}^{n} \left( \frac{\partial \psi_j}{\partial Q_m} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} \cdot \left( \frac{\partial Q_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(42)

Now replacing equation (42) by equations (35) and (31) leads to equation (43):

\[
\sigma = \tilde{\sigma} - \sum_{m=1}^{n} \left( \frac{\partial \psi_j}{\partial Q_m} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} \cdot \left( \frac{\partial Q_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(43)

For the case \(l = f\), the last derivative in equation (43) can be replaced by equation (27) and then using equation (88) it is proven that the equation (44) is valid for \(l = f\text{ or } Q\), indistinctly:

\[
\sigma = \tilde{\sigma} + \sum_{m=1}^{n} \left( \frac{\partial \psi_j}{\partial Q_m} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} \cdot \left( \frac{\partial \mu_j}{\partial F_m} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(44)

2.2.4. Unrestrained second-order Stark Tuning Rate

There is also a relation that links the second-order Stark Tuning Rate [20] with the polarizability. The second derivative of equation (32) with respect to the electric field provides under unrestrained configuration (constant forces) the following:

\[
\left( \frac{\partial^2 \psi_j}{\partial F_j^2} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} = \frac{1}{4\pi \epsilon_0} \lambda_m \left( \frac{\partial^2 \lambda_m}{\partial F_j^2} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)} - \frac{1}{2} \lambda_m \left( \frac{\partial \lambda_m}{\partial F_j} \right)_{F_{i,j}, (\forall j \neq i \text{ and } p=m)}
\]

(45)
The second derivative of $\lambda_m$ is obtained by taking the derivative of equation (39):

$$\left(\frac{\partial^2 \lambda_m}{\partial F_j \partial F_l}\right)_{F_{0j},(\forall k \neq j \land \forall p)} = \left(-\lambda_m^2 \left(\frac{\partial F_l}{\partial \mu_i}\right)\right)_{F_{0j},(\forall k \neq j \land \forall p)}$$

$$=-2\lambda_m \left(\frac{\partial \lambda_m}{\partial F_l}\right)_{F_{0j},(\forall k \neq j \land \forall p)} \left(\frac{\partial^2 \mu_i}{\partial F_m^2}\right)_{F_{0j},(\forall k \neq j \land \forall p)} = \lambda_m^2 \left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m^2}\right)_{F_{0j},(\forall k \neq j \land \forall p)} \right)$$

(46)

where:

$$\left(\frac{\partial^3 \mu_i}{\partial F_j \partial F_m^2}\right)_{F_{0j},(\forall k \neq j \land \forall p)} = \left(\frac{\partial^3 \phi_{ij}}{\partial F_j \partial F_m^2}\right)_{F_{0j},(\forall k \neq j \land \forall p)} \right)$$

(47)

Using equation (46) in conjunction with equations (47) and (39) affords:

$$\left(\frac{\partial^2 \lambda_m}{\partial F_j \partial F_l}\right)_{F_{0j},(\forall k \neq j \land \forall p)} = -2\lambda_m^3 \left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m}\right)^2_{F_{0j},(\forall k \neq j \land \forall p)} = \lambda_m^2 \left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m^2}\right)_{F_{0j},(\forall k \neq j \land \forall p)} \right)$$

(48)

Replacing in equation (45) using equations (48) and (39) yields:

$$\left(\frac{\partial \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},(\forall k \neq j \land \forall p)} = -\frac{\lambda_m}{2\pi c} \frac{2\lambda_m}{\mu_i^2} \left(\frac{\partial F_j}{\partial \mu_i}\right)_{F_{0j},Q_p} + \lambda_m \left(\frac{\partial F_j}{\partial \mu_i}\right)_{F_{0j},Q_p} \right)$$

(49)

With relation (49) it is possible to calculate the unrestrained second coefficient of the Taylor expansion in equation (6) by determining the normal force constant as well as the second derivative of the permanent dipolar moment and the polarizability with respect to the normal force.

2.2.5. Restrained second-order Stark Tuning Rate

Another relation links the restrained second-order Stark Tuning Rate [20] with the polarizability. The second derivative of equation (32) with respect to the electric field at restrained nuclear configuration provides:

$$\left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_l}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = \frac{1}{2\pi c} \left(\frac{\partial^2 \lambda_m}{\partial F_j \partial F_l}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)}$$

(50)

The second derivative of $\lambda_m$ is obtained by taking the derivative of equation (29):

$$\left(\frac{\partial \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = \left(\frac{\partial \phi_{ij}}{\partial \mu_i}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = \left(\frac{\partial \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)}$$

(51)

where:

$$\left(\frac{\partial \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = \left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = \left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)}$$

(52)

Using equation (51) in conjunction with equation (52) affords:

$$\left(\frac{\partial^2 \lambda_m}{\partial F_j \partial F_l}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)} = -\left(\frac{\partial^2 \phi_{ij}}{\partial F_j \partial F_m}\right)_{F_{0j},Q_p,(\forall k \neq j \land \forall p)}$$

(53)
equation (50) along with equations (53) and (29), yields:

$$
\left( \frac{\partial^2 \mathcal{V}_m}{\partial F_i \partial F_j} \right)_{F_i, F_j, Q} = - \frac{1}{4 \pi \varepsilon \lambda_m} \left( \frac{\partial^2 \alpha_{ij}}{\partial Q^2} \right)_{F_i, F_j, Q} + \frac{1}{2 \lambda_m} \left( \frac{\partial^2 \mu_i}{\partial Q^2} \right)_{F_i, F_j, Q} + \frac{\partial^2 \mu_j}{\partial Q^2} \right)_{F_i, F_j, Q}
$$

(54)

With relation (54) it is possible to calculate the restrained second coefficient of the Taylor expansion of equation (6) by determining the normal force constant as well as the second derivative of the permanent dipolar moment and the polarizability with respect to the normal force along the normal coordinate $m$.

### 2.3. Dipolar moments and polarizabilities

#### 2.3.1. Restrained and unrestrained dipolar moments

So far, the permanent dipolar moment was defined as the derivative of the energy with respect to the electric field at constant normal coordinates ($\mu$; equation (55)). In quantum chemistry, this restrained dipole moment $\mu$ is usually computed by applying the dipole moment operator to the wavefunction of a molecule with fixed nuclear geometry. Alternatively, an unrestrained dipole moment can also be defined ($\bar{\mu}$; equation (55)). Under this definition, when forces are constant, the nuclear configuration has no geometric restraint. At constant null forces, the system is in a relaxed state (minimum of energy) or a transition state (maximum of energy). The restrained dipole moment implies that the nuclear configuration is fixed and the electronic configuration is unrestrained. While for the unrestrained dipole moment, the nuclear and electronic configuration are unrestrained. The numerical calculation of $\bar{\mu}$ by using the equation (55) requires a geometry optimisation for each electric field value which increase the computational cost compared to $\mu$.

$$
\mu_i = - \left( \frac{\partial E}{\partial F_i} \right)_{F_i, F_j, Q_i, \ldots, Q_n}, \quad \bar{\mu}_i = - \left( \frac{\partial E}{\partial F_i} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}
$$

(55)

It is feasible to link both dipole moment definitions by combining equations (55) and (98) derived from Jacobian properties, in section A.6:

$$
\left( \frac{\partial E}{\partial Q} \right)_{F_i, F_j, Q_i, \ldots, Q_n} = \left( \frac{\partial E}{\partial F} \right)_{F_i, F_j,\bar{Q}_i, \ldots, \bar{Q}_n} - \sum_{m=1}^{n} \left( \frac{\partial E}{\partial Q_m} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n} \left( \frac{\partial Q_m}{\partial F} \right)_{F_i, F_j, Q_i, \ldots, Q_n}
$$

where $l = f$ or $Q$, indistinctly. By replacing $\left( \frac{\partial E}{\partial Q_m} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}$ for $-f_m$ and reorganising:

$$
\bar{\mu}_i = \mu_i + \sum_{m=1}^{n} f_m \left( \frac{\partial Q_m}{\partial F_i} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}
$$

(56)

For a relaxed molecular structure (at $f_m = 0$), the unrestrained and restrained dipolar moments are equal ($\mu_i = \bar{\mu}_i$). In equation (56), the derivatives $\left( \frac{\partial \mu_i}{\partial Q_m} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}$ provide information regarding the molecular geometry distortion given by an electric field. However, as it was done for the derivation of equation (44), these derivatives can be replaced by their mixed second order derivative counterparts (equation (27)) and yield the final expression:

$$
\bar{\mu}_i = \mu_i - \sum_{m=1}^{n} f_m \left( \frac{\partial \mu_i}{\partial f_m} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}
$$

(57)

With equation (57), it is possible to compute the unrestrained dipole moment when the molecular structure is away from a minimum energetic state.

#### 2.3.2. Restrained and unrestrained polarizabilities

Similarly to the permanent dipolar moment, the polarizability can be defined as restrained ($\alpha$) (equation (58)) and unrestrained ($\bar{\alpha}$) (equation (59)) where, for $\alpha$ the nuclear configuration is restrained and the electronic configuration is unrestrained, while for $\bar{\alpha}$ the nuclear and electronic configurations are unrestrained.

$$
\alpha_{ij} = - \left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right)_{F_i, F_j, Q_i, \ldots, Q_n}, \quad \bar{\alpha}_{ij} = \left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right)_{F_i, F_j, \bar{Q}_i, \ldots, \bar{Q}_n}
$$

(58)
\[ \alpha_{ij} = -\left( \frac{\partial^2 E}{\partial F_i \partial F_j} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} = \left( \frac{\partial \mu_i}{\partial F_j} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} \]  

(59)

Linking both definitions by combining the relations using equation (98) from section A.6:

\[ \left( \frac{\partial \mu_i}{\partial Q_n} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} = \sum_{m=1}^{n} \left( \frac{\partial \mu_i}{\partial Q_m} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} \frac{\partial Q_m}{\partial F_j} \]

\[ \alpha_{ij} = \bar{\alpha}_{ij} = \sum_{m=1}^{n} \left( \frac{\partial \mu_i}{\partial Q_m} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} \frac{\partial Q_m}{\partial F_j} \]

(60)

where indistinctly \( l = f \) or \( Q \).

By defining the nuclear polarizability \( \bar{\alpha} \) as shown in equation (61):

\[ \bar{\alpha}_{ij} = \frac{n}{m=1} \left( \frac{\partial \mu_i}{\partial Q_m} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} \frac{\partial Q_m}{\partial F_j} \]

(61)

and replacing the last derivative by its mixed second order derivative counterpart from equation (27) yields:

\[ \bar{\alpha}_{ij} = -\sum_{m=1}^{n} \left( \frac{\partial \mu_i}{\partial Q_m} \right)_{F_i \neq F_j, \ldots, \delta_{ij}} \frac{\partial Q_m}{\partial F_j} \frac{\partial \mu_i}{\partial F_j} \frac{\partial Q_m}{\partial F_j} \]

(62)

Rewriting equation (60) by replacing the sum in equation (61), the equation (63) is obtained.

\[ \bar{\alpha}_{ij} = \alpha_{ij} + \bar{\alpha}_{ij} \]

(63)

By renaming the term \( \alpha \) as the electronic polarizability and \( \bar{\alpha} \) as the total polarizability, the equation (63) states that the total polarizability \( \bar{\alpha} \) is equivalent to the sum of the electronic \( \alpha \) and the nuclear polarizabilities \( \bar{\alpha} \). The necessity for separation of the total polarizability in nuclear and electronic contributions has been previously discussed [21].

The total (unrestrained) polarizability can be computed numerically by means of its definition (equation (59)) or by computing the electronic and nuclear polarizability terms and equation (63). The electronic polarizability is a well-known property usually computed by default in several quantum chemistry programs [22–24]. The nuclear polarizability can be determined either by using the equation (62) or by using in conjunction equations (61) and (56). In this way, the determination of the nuclear polarizability term at null electric field can be done avoiding the application of an electric field.

2.4. Vibrational Zeeman effect

The vibrational Zeeman effect [14] is the shifting of vibrational frequencies due to the presence of an external magnetic field \( B \). Analogously to the STR, the first and second derivatives of the wavenumber with respect to the magnetic field yield the first- and second-order Zeeman Tuning Rates [18] (ZTR), respectively. The exact equivalent equations found above can be obtained relating the magnetic field \( B \), the magnetic dipole moment \( \mu_i \) and the magnetic polarizability \( \bar{\alpha} \) instead of their electric counterparts:

Restrained Zeeman Tuning Rate:

\[ \left( \frac{\partial \nu_m}{\partial B_i} \right)_{B_j Q_j \forall j \neq i \land \forall p} = -\frac{1}{4\pi c \sqrt{\lambda_m}} \left( \frac{\partial^2 \mu_i}{\partial F_j^2} \right)_{B_j Q_j \forall j \neq i \land \forall p} \]

(64)

Unrestrained Zeeman Tuning Rate:

\[ \left( \frac{\partial \nu_m}{\partial B_i} \right)_{B_j Q_j \forall j \neq i \land \forall p} = -\frac{\lambda_m^2}{4\pi c} \left( \frac{\partial^2 \mu_i}{\partial F_j^2} \right)_{B_j Q_j \forall j \neq i \land \forall p} \]

(65)

Restrained and Unrestrained Zeeman Tuning Rate relation:

\[ \left( \frac{\partial \nu_m}{\partial B_i} \right)_{B_j Q_j \forall j \neq i \land \forall p} = \left( \frac{\partial \nu_m}{\partial B_i} \right)_{B_j Q_j \forall j \neq i \land \forall p} + \sum_{m=1}^{n} \left( \frac{\partial \nu_m}{\partial B_i} \right)_{B_j Q_j \forall j \neq i \land \forall p} \left( \frac{\partial \mu_i}{\partial Q_m} \right)_{B_j Q_j \forall j \neq i \land \forall p} \]

(66)
3.1.1. Traditional method for computing uSTR

Using the selected normal mode vector computed at $F = 0$, the structure of all molecules were displaced along these vectors by the following module values: $\pm 0.1, \pm 0.05, \pm 0.002, \pm 0.001, \pm 0.0001, \pm 0.00005, \pm 0.000005, 0.0 \text{ au}$. Single point calculations were performed for all the displaced geometries. Energies and dipolar moments were extracted from the output files. The dipolar moment was obtained by applying the dipolar moment operator to the wavefunction. Forces for the selected mode were numerically computed according to equation (10) by fitting an 8th degree polynomial to the total energy versus displaced distance and extrapolating the data by taking a derivative of this polynomial. The component of the dipolar moment along the direction of the electric field was computed for each single point calculation. From the obtained dipolar moment component versus the computed forces, uSTR was numerically computed by fitting an 8th degree polynomial, while the second derivative was computed from this polynomial and the value extrapolated at 0.0 au of displacement according to equation (41).

4 Gaussian Keywords used: ‘Opt = VeryTight Int = UltraFine’.

3. Proof of concept

As a proof of principle, in this section, the unrestrained Stark Tuning Rate (uSTR) was numerically computed for a set of small molecules in two ways as a matter of comparing the traditional method and the proposed method in this paper. The traditional way uses the equation by definition (equation (35)) and the newly developed method uses the singular equation (41).

3.1. Methods

Quantum calculations were performed using methodologies based on Density Functional Theory (DFT). The hybrid three parameters exchange functional from Becke combined with the correlation functional from Lee, Yang and Parr (B3LYP) was chosen to compute the electric field effects on the wavenumber modes [25–27]. All calculations were performed with Gaussian 03 [24] using the basis set TZV. The molecules selected for this study are commonly used molecular probes: CO, NO, HCN, water, methane and 4-Chloro-Benzonitrile. For the HCN and 4-Chloro-Benzonitrile, the STR was computed for the vibrational mode corresponding to C-N vibration. For water, the vibrational mode of 1567 cm$^{-1}$ was selected. For methane, the vibrational mode with highest vibrational frequency was chosen. The electric field vector was pointed in the direction of the vibration of the selected mode. A geometry optimisation was performed for all structures in vacuum with an extremely tight converge criteria. A frequency analysis for all optimised structures in vacuum was performed to obtain the normal mode vectors for all the molecules. Unrestrained first-order Stark Tuning Rate was then computed using the traditional method and the novel method presented in this work.

Restrained second-order Zeeman Tuning Rate:

$$\frac{\partial^2 \nu_m}{\partial B_i \partial B_j} = \frac{\lambda_m}{4 \pi c} \left(2 \lambda_m \left(\frac{\partial^2 \mu_i}{\partial f_m^2} \right)_{B_i, Q_p} + \frac{\lambda_m}{2} \left(\frac{\partial^2 \mu_j}{\partial f_m^2} \right)_{B_i, Q_p} + \left(\frac{\partial^2 \alpha_{ij}}{\partial f_m^2} \right)_{B_i, Q_p}\right) \tag{67}$$

Unrestrained second-order Zeeman Tuning Rate:

$$\frac{\partial^2 \nu_m}{\partial B_i \partial B_j} = -\frac{1}{4 \pi c} \left(\frac{\partial^2 \alpha_{ij}}{\partial Q_m^2} \right)_{B_i, Q_p} + \frac{1}{2 \lambda_m} \left(\frac{\partial^2 \mu_i}{\partial Q_m^2} \right)_{B_i, Q_p} + \left(\frac{\partial^2 \mu_j}{\partial Q_m^2} \right)_{B_i, Q_p} \tag{68}$$
3.2. Results
The obtained $u$STR values from both methods were compared for precision and computational cost. Table 1 shows that the values of the computed $u$STR are close and well within the numerical error.

The percentage differences in the $u$STR for the standard and the new method seem to be higher in polar molecules ($\text{H}_2\text{O}$, HCN and 4-Chloro-Benzonitrile) and with greater number of atoms. One possible explanation is that at higher number of atoms the numerical errors in the determination of the derivatives increase. The results from the traditional method cannot be considered as exact, neither from the new method. Nevertheless, the standard method may be prompt to higher numerical errors due to the application of the electric field and optimisation, the molecular geometry changes, allowing the molecule to slightly rotate. This difference could be reduced if the electric field vector was applied in the direction of the net dipolar moment. This may explain the reason for a higher difference in polar molecules considering that the higher the dipolar moment is, the greater the rotation. The frequency analysis could be also another source of imprecision. However, the relation found in this paper that connects both methods are mathematically equivalent and further analysis should be done to identify the source of inaccuracy in each method and to determine which method is more precise. The new method may yield more accurate $u$STR values as it does not require the application of an electric field and requires just a one time frequency analysis computation. This reduces the mentioned sources of error.

A comparison of the computation time is shown in Table 2. It can be seen that for bimolecular species the time spent for computing STR using the standard method is about 1.5 times longer than using the new method. For three-atom molecules, the ratio almost doubles and for molecules of more than 5 atoms it is $\sim$3 fold. It is expected that the ratio would increase for higher number of atoms. The numerical computation time for the new method can be considerably reduced by using less number of points. In this example, to obtain a precise $u$STR value with the new method, more than enough number of points were used (27). However, this number can be reduced at least by 2 or more to yield a faster calculation. The main goal of this section is to show that the applicability of equation (41) and it is not focused specifically on the timing performance.

4. Discussion and conclusions
The intention of this work is to present the developed relations from sections A.1 and A.2, their uses to obtain physically meaningful relations uncovered in sections 2.2, 2.3 and 2.4, and finally showing a simple application example with the unrestrained Stark Tuning Rate in section 3. According to the traditional way of computing the $u$STR, the geometry of several structures at diverse electric field strengths ought to be optimised prior to the

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Table 1. Unrestrained STR values (in au) computed using new and traditional methods and the Percentage Difference (PD).

| Compound          | STR standard | STR new  | PD (%) |
|-------------------|--------------|----------|--------|
| CO                | $-1.344 \times 10^{-5}$ | $-1.345 \times 10^{-5}$ | 0.074  |
| NO                | $-9.930 \times 10^{-6}$  | $-9.939 \times 10^{-6}$  | 0.091  |
| H$_2$O            | $2.758 \times 10^{-5}$  | $2.832 \times 10^{-5}$  | 2.648  |
| HCN               | $-1.541 \times 10^{-5}$ | $-1.434 \times 10^{-5}$ | 7.193  |
| CH$_4$            | $1.410 \times 10^{-6}$  | $1.437 \times 10^{-6}$  | 1.897  |
| 4-Chloro-Benzonitrile | $1.361 \times 10^{-5}$  | $1.166 \times 10^{-5}$  | 15.433 |

Table 2. Comparison of the computation time in seconds.

| Compound          | Standard method | New method | Time ratio |
|-------------------|-----------------|------------|------------|
| CO                | 308.9           | 195.5      | 1.58       |
| NO                | 405.2           | 264.1      | 1.53       |
| H$_2$O            | 337.1           | 173.4      | 1.94       |
| HCN               | 416.5           | 221.3      | 1.88       |
| CH$_4$            | 844.1           | 277.6      | 3.04       |
| 4-Chloro-Benzonitrile | 30838.5      | 10275.5    | 3.00       |

---

5 Relative Difference $= 200 \times |(STR1 - STR2)/(STR1 + STR2)|$. 

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frequency analysis yielding the wavenumber. This procedure is computationally very expensive and is increasingly hindered by the number of atoms in the molecule. The relation obtained in equation (41) significantly reduces the computation time of the uSTR and may increase the precision in the calculation of its value. Additionally, the application of an electric field is not required to compute the unrestricted and restricted STRs. Incorporation of this method for computing the restrained and unrestrained first order and second order uSTR in traditional quantum computing packages is encouraged. With little extra computational cost, all these extra parameters can be obtained after the frequency analysis calculation. A more focused study to optimise the performance (speed and precision) of the implementation of the new STR method should be done. The study should determine and compare the speed and precision of this method with the traditional one with more diverse molecules.

The novel mathematical relationships developed here can be used as shortcut equations to compute restrained/unrestrained first/second-order Stark Tuning Rate (STR) and Zeeman Tuning Rate (ZTR). Furthermore, an equation that connects the uSTR and rSTR has been found, in addition to other important electric or magnetic field-dependent properties of molecules relevant for vibrational spectroscopy. For electrodynamics, novel definitions for unrestrained dipolar moment and nuclear polarizability were introduced and an important relation between electronic, nuclear and total polarizabilities was developed. These relationships are obtained from mixed third order partial derivatives of the Legendre transformation of the energy which depend on the normal coordinates and the external uniform electric or magnetic field vector. A direct application of these relationships is the faster and efficient computation of the STR and ZTR. Additionally, this work can be a starting point for future theoretical developments in this field. Whether this novel framework will prove to be useful for other practical applications is yet to be discovered.

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Appendix

A.1. Mixed second-order partial derivatives of E, R, T and Y

Based on the symmetry of second derivatives, the equality of mixed second partial derivatives of E, R, T, and Y produce the following relations:

$$\frac{\partial^2 E}{\partial Q_m \partial F_i} = \frac{\partial^2 E}{\partial F_i \partial Q_m} \Rightarrow \frac{\partial \mu_i}{\partial Q_m} F_{jQ_k(\nu j \land \nu p = m)} = \left(\frac{\partial F_m}{\partial F_i} F_{jQ_k(\nu j \land \nu p = m)} \right)$$

(69)

$$\frac{\partial^2 R}{\partial f_m \partial F_i} = \frac{\partial^2 R}{\partial F_i \partial f_m} \Rightarrow \frac{\partial \mu_i}{\partial f_j} F_{jQ_k(\nu j \land \nu p = m)} = \left(\frac{\partial Q_m}{\partial F_i} F_{jQ_k(\nu j \land \nu p = m)} \right)$$

(70)

$$\frac{\partial^2 T}{\partial Q_m \partial \mu_j} = \frac{\partial^2 T}{\partial \mu_j \partial Q_m} \Rightarrow \left(\frac{\partial F_{jQ_k(\nu j \land \nu p = m)}}{\partial Q_m} \right) = \left(\frac{\partial f_m}{\partial \mu_j} F_{jQ_k(\nu j \land \nu p = m)} \right)$$

(71)

$$\frac{\partial^2 Y}{\partial f_m \partial \mu_j} = \frac{\partial^2 Y}{\partial \mu_j \partial f_m} \Rightarrow \left(\frac{\partial F_{jQ_k(\nu j \land \nu p = m)}}{\partial \mu_j} \right) = \left(\frac{\partial Q_m}{\partial f_m} F_{jQ_k(\nu j \land \nu p = m)} \right)$$

(72)

A.2. Mixed third-order partial derivatives of E, R, T and Y

Analogously, the equality of the mixed third-order partial derivatives [19] of E, R, T, and Y provides the following useful relations.\(^6\),\(^7\)

$$\frac{\partial^3 E}{\partial Q_m \partial F_j \partial F_i} = \frac{\partial^3 E}{\partial F_j \partial F_i \partial Q_m} \Rightarrow \left(\frac{\partial \alpha_{ji}}{\partial Q_m} \right) F_{kQ_p(\nu k \land \nu p = m)} = \left(\frac{\partial^2 f_m}{\partial F_j \partial F_i} F_{kQ_p(\nu k \land \nu p = m)} \right)$$

(73)

\(^6\) Based on the mixed second partial derivative equality, note that \(\alpha_{ji} = \alpha_{ij}\)

\(^7\) Note that \(\frac{\partial^2 E}{\partial Q_m \partial Q_p \partial \nu m} = 0\) (which are the non-diagonal elements of the diagonalized Hessian) [12, 13]
\[
\frac{\partial^2 E}{\partial Q_m^2} = \frac{\partial^2 E}{\partial F_i \partial \Omega_m^2} \quad \Rightarrow \quad - \left( \frac{\partial^2 \mu_i}{\partial Q_m^2} \right)_{F_i, Q_j (\forall p \neq m)} = \frac{\partial \lambda_m}{\partial F_i} \frac{\partial F_i}{\partial Q_j (\forall p = m)} 
\]  
(74)

\[
\frac{\partial^3 R}{\partial f_m \partial F_i \partial \lambda_i} = \frac{\partial^3 R}{\partial F_i \partial \Omega_m \partial \Omega_m} \quad \Rightarrow \quad - \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{F_i, Q_j (\forall p \neq m)} = \left( \frac{\partial Q_m}{\partial F_i} \right)_{F_i, Q_j (\forall p \neq m)} \frac{\partial F_i}{\partial Q_j (\forall p = m)} 
\]  
(75)

\[
\frac{\partial^3 R}{\partial f_m \partial F_i \partial \Omega_m} = \frac{\partial^3 R}{\partial F_i \partial \Omega_m \partial \Omega_m} \quad \Rightarrow \quad - \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{F_i, Q_j (\forall p \neq m)} = \left( \frac{\partial^2 Q_m}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_i, Q_j (\forall p \neq m)} \frac{\partial F_i}{\partial Q_j (\forall p = m)} 
\]  
(76)

\[
\frac{\partial^3 T}{\partial Q_m \partial \mu_j \partial \mu_i} = \frac{\partial^3 T}{\partial \mu_j \partial \mu_i \partial \Omega_m} \quad \Rightarrow \quad \left( \frac{\partial^2 F_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_j, Q_k (\forall p \neq m)} = \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_j, Q_k (\forall p \neq m)} \frac{\partial F_i}{\partial \Omega_m (\forall p = m)} 
\]  
(77)

\[
\frac{\partial^3 Y}{\partial f_m \partial F_i \partial \mu_i} = \frac{\partial^3 Y}{\partial F_i \partial \Omega_m \partial \Omega_m} \quad \Rightarrow \quad \left( \frac{\partial^2 F_i}{\partial \Omega_m \partial \Omega_m} \right)_{F_i, Q_j (\forall p \neq m)} = \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{F_i, Q_j (\forall p \neq m)} \frac{\partial F_i}{\partial \Omega_m (\forall p = m)} 
\]  
(78)

\[
\frac{\partial^3 Y}{\partial f_m \partial \mu_i \partial \mu_i} = \frac{\partial^3 Y}{\partial \mu_i \partial \mu_i \partial \Omega_m} \quad \Rightarrow \quad \left( \frac{\partial^2 F_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_i, Q_k (\forall p \neq m)} = \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_i, Q_k (\forall p \neq m)} \frac{\partial F_i}{\partial \Omega_m (\forall p = m)} 
\]  
(79)

\[
\frac{\partial^3 Y}{\partial \mu_i \partial \mu_i \partial \Omega_m} = \frac{\partial^3 Y}{\partial \mu_i \partial \mu_i \partial \Omega_m} \quad \Rightarrow \quad \left( \frac{\partial^2 F_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_i, Q_k (\forall p \neq m)} = \left( \frac{\partial^2 \mu_i}{\partial \Omega_m \partial \Omega_m} \right)_{\mu_i, Q_k (\forall p \neq m)} \frac{\partial F_i}{\partial \Omega_m (\forall p = m)} 
\]  
(80)

### A.3. Specific demonstration 1 (normal force constant equality)

The normal force constant is defined as the second derivative of the energy with respect to a normal coordinate while the rest of the normal coordinates and all the elements of the electric field vector are kept constant. Considering a system with \(n\) normal vibrational modes:

\[
\lambda_i = \left( \frac{\partial^2 E}{\partial Q_i^2} \right)_{F_i, F_j, F_k, \ldots, Q_0} = \left( \frac{\partial F_i}{\partial Q_i} \right)_{F_i, F_j, F_k, \ldots, Q_0} 
\]  
(81)

Additionally, another normal force constant can be defined this time while holding constant the rest of the normal forces instead of the normal coordinates.

\[
\lambda_{i1} = \left( \frac{\partial^2 E}{\partial Q_i^2} \right)_{\mu_i, F_j, F_k, \ldots, Q_0} = \left( \frac{\partial F_i}{\partial Q_i} \right)_{\mu_i, F_j, F_k, \ldots, Q_0} 
\]  
(82)

The equality of both normal force constants is proven based on Jacobian properties [1] as shown in section A.5:

\[
\lambda_i = \lambda_{i1} \quad \Rightarrow \quad \left( \frac{\partial F_i}{\partial Q_i} \right)_{\mu_i, F_j, F_k, \ldots, Q_0} = \left( \frac{\partial F_i}{\partial Q_i} \right)_{F_i, F_j, F_k, \ldots, Q_0} 
\]  
(83)

### A.4. Specific demonstration 2

Using general demonstration A (section A.5), the following equalities are proven:

\[
\gamma_i = \left( \frac{\partial^2 \mu_i}{\partial F_i \partial Q_j (\forall p \neq m)} \right)_{F_j, Q_k (\forall p \neq m)} = \left( \frac{\partial \mu_i}{\partial F_j} \right)_{F_i, Q_j (\forall p \neq m)} 
\]  
(84)

\[
\left( \frac{\partial \gamma_i}{\partial F_i} \right)_{F_j, Q_k (\forall p \neq m)} = \left( \frac{\partial \gamma_i}{\partial F_i} \right)_{F_j, Q_k (\forall p \neq m)} 
\]  
(85)

Replacing \(\gamma_i\) in equation (85) by using equation (84) leads to:

\[
\left( \frac{\partial^2 \mu_i}{\partial f_m \partial f_m} \right)_{F_i, Q_j (\forall p \neq m)} = \left( \frac{\partial^2 \mu_i}{\partial f_m \partial f_m} \right)_{F_i, Q_j (\forall p \neq m)} 
\]  
(86)
A.5. General demonstration A

It will be demonstrated that the following relations are valid for any variable \( x \) for a system with \( n \) normal modes where \( f \) is the normal force and \( Q \) is the normal coordinate:

\[
\frac{\partial x}{\partial Q_i} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} = \left( \frac{\partial x}{\partial f_j} \right) f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} = \left( \frac{\partial x}{\partial f_j} \right) f_{j, \ldots, f_{j, n}, \ldots, f_{n}} \tag{87}
\]

\[
\left( \frac{\partial x}{\partial f_j} \right) f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} = \left( \frac{\partial x}{\partial f_j} \right) f_{j, \ldots, f_{j, n}, \ldots, f_{n}} \tag{88}
\]

\[
\left( \frac{\partial Q_i}{\partial x} \right) Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} = \left( \frac{\partial Q_i}{\partial f_j} \right) f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} = \left( \frac{\partial Q_i}{\partial f_j} \right) f_{j, \ldots, f_{j, n}, \ldots, f_{n}} \tag{89}
\]

\[
\left( \frac{\partial f_j}{\partial x} \right) f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} = \left( \frac{\partial f_j}{\partial f_j} \right) f_{j, \ldots, f_{j, n}, \ldots, f_{n}} \tag{90}
\]

The following is the demonstration of equation (87). This demonstration can be extended for equations (88), (89) and (90).

The derivative of the left term of equation (87) can be rewritten using Jacobian’s notation as shown in equation (91).

\[
\left( \frac{\partial x}{\partial Q_1} \right) Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} = \frac{\partial (x, Q_0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n)}{\partial (Q_0, Q_1, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n)} \tag{91}
\]

The first variable to change, in this case \( Q_2 \), should be in the second position. The first step is to multiply equation (91) by a unity Jacobian which is constructed by using the denominator of equation (91) with the first variable to change replaced:

\[
\frac{\partial x}{\partial Q_2} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} = \frac{\partial (x, Q_0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n)}{\partial (Q_0, Q_1, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n)} \cdot \frac{\partial (Q_2, f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}})}{\partial (Q_2, f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}})} \tag{92}
\]

Developing both obtained Jacobians:

\[
\frac{\partial (Q_0, f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}})}{\partial (Q_0, Q_1, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n)} = \frac{\partial (f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}})}{\partial (Q_1, Q_2, \ldots, Q_n)} = \left( \frac{\partial f_j}{\partial Q_1} \right) Q_{0, \ldots, Q_n} \tag{93}
\]

\[
\begin{vmatrix}
\frac{\partial x}{\partial Q_2} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} & \frac{\partial x}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial x}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial x}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\frac{\partial Q_0}{\partial Q_2} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} & \frac{\partial Q_0}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_0}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_0}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
\frac{\partial Q_{n-1}}{\partial Q_2} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} & \frac{\partial Q_{n-1}}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_{n-1}}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_{n-1}}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\frac{\partial Q_n}{\partial Q_2} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} & \frac{\partial Q_n}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_n}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_n}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}
\end{vmatrix}
= \det
\begin{vmatrix}
\frac{\partial x}{\partial Q_2} & \frac{\partial x}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial x}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial x}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\frac{\partial Q_0}{\partial Q_2} & \frac{\partial Q_0}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_0}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_0}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
\frac{\partial Q_{n-1}}{\partial Q_2} & \frac{\partial Q_{n-1}}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_{n-1}}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_{n-1}}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n} \\
\frac{\partial Q_n}{\partial Q_2} & \frac{\partial Q_n}{\partial f_j} f_{j, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \cdots & \frac{\partial Q_n}{\partial Q_{n-1}} f_{n-1, Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}} & \frac{\partial Q_n}{\partial Q_n} Q_{0, \ldots, Q_{n-1}, Q_{n}, \ldots, Q_n}
\end{vmatrix}
\]
Since the set of normal coordinates and normal forces are orthonormal and independent variable sets:

\[
\begin{vmatrix}
\frac{\partial x}{\partial Q_1} & \frac{\partial x}{\partial Q_2} & \cdots & \frac{\partial x}{\partial Q_n} \\
\frac{\partial x}{\partial Q_n} & \frac{\partial x}{\partial Q_1} & \cdots & \frac{\partial x}{\partial Q_{n-1}} \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & 1
\end{vmatrix}
= \det \begin{vmatrix}
0 & \ldots & 0 & 0 \\
\frac{\partial Q_1}{\partial f_1} & \frac{\partial Q_2}{\partial f_1} & \cdots & \frac{\partial Q_n}{\partial f_1} \\
\frac{\partial Q_1}{\partial f_2} & \frac{\partial Q_2}{\partial f_2} & \cdots & \frac{\partial Q_n}{\partial f_2} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial Q_1}{\partial f_n} & \frac{\partial Q_2}{\partial f_n} & \cdots & \frac{\partial Q_n}{\partial f_n}
\end{vmatrix}_{Q_0,\ldots,Q_n}
\]  

(94)

Using equations (93) and (94) in equation (92) leads to:

\[
\left( \frac{\partial x}{\partial Q_0} \right)_{Q_0,\ldots,Q_n} = \left( \frac{\partial x}{\partial Q_0} \right)_{f_1,Q_0,\ldots,Q_{i-1},Q_{i+1},\ldots,Q_n} \cdot \left( \frac{\partial Q_i}{\partial f_i} \right)_{Q_0,\ldots,Q_n} = \left( \frac{\partial x}{\partial Q_i} \right)_{Q_0,\ldots,Q_n}
\]  

(95)

Therefore replacing a constant Q by f yields an equivalent derivative:

\[
\left( \frac{\partial x}{\partial Q_0} \right)_{Q_0,\ldots,Q_{i-1},Q_{i+1},\ldots,Q_n} = \left( \frac{\partial x}{\partial Q_i} \right)_{f_1,Q_0,\ldots,Q_{i-1},Q_{i+1},\ldots,Q_n}
\]  

(96)

This is also valid for the inverse replacement (f by Q).

Afterward, repeating the procedure from equations (92) to (95) for the rest of the variables (Q_2, \ldots, Q_{i-1}, Q_{i+1}, \ldots, Q_n) the final expression is obtained:

\[
\left( \frac{\partial x}{\partial Q_0} \right)_{Q_0,\ldots,Q_{i-1},Q_{i+1},\ldots,Q_n} = \left( \frac{\partial x}{\partial Q_i} \right)_{f_1,\ldots,f_i,\ldots,f_n}
\]  

(97)

A.6. General demonstration B

The validity of the following relations will be demonstrated for any variables x and y for a system with n normal modes where f is the normal force, Q is the normal coordinate and l = f or Q indistinctly (as it is shown in General Demonstration A):

\[
\left( \frac{\partial x}{\partial y} \right)_{Q_0,\ldots,Q_n} = \left( \frac{\partial x}{\partial y} \right)_{f_1,\ldots,f_n} - \sum_{i=1}^{n} \left( \frac{\partial x}{\partial Q_i} \right)_{f_1,\ldots,f_i,\ldots,f_n} \cdot \left( \frac{\partial Q_i}{\partial y} \right)_{Q_0,\ldots,Q_n}
\]  

(98)

\[
\left( \frac{\partial x}{\partial y} \right)_{f_1,\ldots,f_n} = \left( \frac{\partial x}{\partial y} \right)_{Q_0,\ldots,Q_n} - \sum_{i=1}^{n} \left( \frac{\partial x}{\partial f_i} \right)_{f_1,\ldots,f_i,\ldots,f_n} \cdot \left( \frac{\partial f_i}{\partial y} \right)_{Q_0,\ldots,Q_n}
\]  

(99)

The following is the demonstration for equation (98). This demonstration can be also extended to equation (99).

The first derivative of equation (98) can be rewritten using Jacobian’s notation as shown in equation (100). The first variable to exchange, in this case Q_l, should be in the second position.

\[
\left( \frac{\partial x}{\partial y} \right)_{Q_0,\ldots,Q_n} = \frac{\partial (x, Q_1,\ldots,Q_n)}{\partial (y, Q_1,\ldots,Q_n)}
\]  

(100)

The first step is to multiply equation (100) by a unity Jacobian which is constructed by using the right term denominator of equation (100) and replacing the first variable to exchange:

\[
\left( \frac{\partial x}{\partial y} \right)_{Q_0,\ldots,Q_n} = \left( \frac{\partial (x, Q_1,\ldots,Q_n)}{\partial (y, f_1, Q_2,\ldots,Q_n)} \right) \cdot \left( \frac{\partial (y, f_1, Q_2,\ldots,Q_n)}{\partial (y, Q_1,\ldots,Q_n)} \right)
\]  

(101)
Developing both obtained Jacobians:

\[
\frac{\partial(y, f_1, Q_2, \ldots, Q_n)}{\partial(y, Q_1, Q_2, \ldots, Q_n)} = \frac{\partial(f_1, y, Q_2, \ldots, Q_n)}{\partial(Q_1, y, Q_2, \ldots, Q_n)} = \left( \frac{\partial f_1}{\partial Q_1} \right)_{y, Q_2, \ldots, Q_n}
\]

(102)

Afterward

\[
\frac{\partial(x, Q_1, \ldots, Q_n)}{\partial(y, f_1, Q_2, \ldots, Q_n)} \equiv \begin{vmatrix}
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\end{vmatrix} = \text{det}
\]

Since the set of normal coordinates and normal forces are orthonormal variable sets:

\[
= \begin{vmatrix}
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\end{vmatrix} = \text{det}
\]

and the determinant of this \((n + 1) \times (n + 1)\) block matrix is:

\[
\begin{vmatrix}
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial x}{\partial y} & \frac{\partial Q_1}{\partial y} & \cdots & \frac{\partial Q_n}{\partial y} \\
\end{vmatrix} = \left( \frac{\partial x}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n} \cdot \left( \frac{\partial Q_1}{\partial y} \right)_{y, Q_2, \ldots, Q_n} - \left( \frac{\partial Q_1}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n} \cdot \left( \frac{\partial x}{\partial y} \right)_{y, Q_2, \ldots, Q_n}
\]

(103)

Using equations (102) and (103) in equation (101) yields:

\[
\begin{align*}
\frac{\partial x}{\partial y}_{Q_1, Q_2, \ldots, Q_n} & = \frac{\partial x}{\partial y}_{f_1, Q_2, \ldots, Q_n} - \left( \frac{\partial Q_1}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n} \cdot \left( \frac{\partial f_1}{\partial Q_1} \right)_{y, Q_2, \ldots, Q_n} \\
\frac{\partial x}{\partial y}_{Q_1, Q_2, \ldots, Q_n} & = \frac{\partial x}{\partial y}_{f_1, Q_2, \ldots, Q_n} - \left( \frac{\partial Q_1}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n} \cdot \left( \frac{\partial f_1}{\partial Q_1} \right)_{y, Q_2, \ldots, Q_n}
\end{align*}
\]

(104)

As shown in General Demonstration A (section A.5), for terms \(\left( \frac{\partial Q_i}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n}\) and \(\left( \frac{\partial Q_i}{\partial y} \right)_{y, Q_2, \ldots, Q_n}\), any \(Q_i\) held constant in those derivatives could be replaced by \(f_1\) and also the opposite replacement (except for \(f_1\) in \(\left( \frac{\partial Q_i}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n}\)). Therefore, \(I\) can be used as a notation for any \(f_i\) or \(Q\) in these cases.

\[
\begin{align*}
\frac{\partial x}{\partial y}_{Q_1, Q_2, \ldots, Q_n} & = \frac{\partial x}{\partial y}_{f_1, Q_2, \ldots, Q_n} - \left( \frac{\partial Q_1}{\partial y} \right)_{y, l_1, \ldots, l_n} \cdot \left( \frac{\partial Q_1}{\partial y} \right)_{f_1, l_1, \ldots, l_n}
\end{align*}
\]

(105)

Afterwards, repeating the procedure in \(\left( \frac{\partial x}{\partial y} \right)_{f_1, Q_2, \ldots, Q_n}\) from equations (101) to (104) until the rest of the variables \(Q_2, \ldots, Q_n\) are replaced leads to equation (98).

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