Intensities and rates in the spectral domain without eigenvectors.

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The Matrix Fluctuation Dissipation to calculate spectral intensities from energy level fluctuations.
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Abstract

A computational prediction of spectrum for polyatomic molecules typically requires the need to diagonalize an $N^2$ matrix, a computationally demanding effort at large values of $N$. Although matrix diagonalization techniques, such as the Lanczos diagonalization, are accurate, it is computationally cumbersome for molecules of even moderate size. The technique discussed in this paper allows for calculating peaks, peak widths, and other spectral features with relatively small computational effort. Matrix fluctuation dissipation theorem is a technique that allows one to calculate the eigenvalues (spectral amplitude) with superficial knowledge of the eigenfunctions. These eigenfunctions correspond to states that are formed due to anharmonic coupling between bright states and dark states of the molecule.

Introduction

Spectroscopy is of great interest to the physics, chemistry, and biology community. Many spectroscopic techniques provide insight on quantum properties of systems ranging from materials to biomolecules. Much of spectroscopy involves the excitation and emission of electrons to and from energy levels, such as from electronic or vibrational states, corresponding to intramolecular interactions. Intuitively, if an electron is moved into an excited state, one would expect to see an indefinitely thin peak corresponding to the specific frequency of the excitation and/or emission. A typical spectrum typically is, nevertheless, a broad distribution of intensities. This broadening of the spectral intensities related to leaking of population density from an excited energy states to states in the neighboring vicinity during vibrational spectroscopy is called *Intramolecular Vibrational Relaxation*.

Intramolecular Vibrational Relaxation (IVR)

In polyatomic molecules, short LASER pulses can populate vibrational states of higher energy. This population can redistribute itself to other energy levels of similar energy, in the vicinity of the initial state, without any external influence of the surrounding or molecular collisions called *Intramolecular Vibrational Relaxation*. IVR is the fundamental process by which the vibrational relaxation of an activated intermediate leads to stabilization of the product so it does not go back to the reactant state, thus playing an important role in many chemical and biochemical reaction rates, from unimolecular decomposition and isomerization to protein folding, to explaining data in molecular *fluorescence spectra*. It is hence important, in the field of chemistry, to have a detailed knowledge of this process.

To obtain a general estimation of the frequency corresponding to peaks within the spectral domain, one can base calculations from the harmonic oscillator model as energy states. The energy of these states can be calculated using the Harmonic Hamiltonian. This would result in indefinitely thin peaks corresponding to individual energy states of the molecule; peak broadening, therefore, can be explained by basing calculations from an anharmonic oscillator model. Here we define the terms *dark states* and *bright states* for use in the future in terms of the harmonic model.

**Dark and Bright States**

To enumerate the process underlying IVR we first describe the nature of vibrational states in

*Figure 1: The Harmonic Model vs. Anharmonic Potential (Morse Potential in this case)*
polyatomic molecules. The vibrations in polyatomic molecules can be described by oscillations of nuclei of the equilibrium configuration in a Harmonic Potential also called the Normal Modes. Under this assumption each atom in the molecule moves with the same frequency and phase for a given Normal Mode and hence the Hamiltonian of the molecule under the harmonic potential consist of a potential energy and kinetic energy both of which are square terms.

The Hamiltonian with the explicit treatment of states as in the framework of a Harmonic Model is the called the Zero Order Hamiltonian. These eigenstates, $|i\rangle$, are the normal modes of vibration of the polyatomic molecule. Among the states $|i\rangle$, one state, $|0\rangle$, carries all of the oscillator strength or population. This is called the Zero Order Bright State (ZOBS). Only a few states are bright states due to severe selection rules (Frank-Condon etc.). As one goes from lower to higher energy the density of energy levels increases exponentially; there are hence a large number of energy levels in the vicinity of the Bright States that are isoenergetic but are sparsely populated as compared to the Bright States. These states are then called the Zero Order Dark States (ZODS). These bright and dark states, $|i\rangle$ are eigenstates of the zero order Hamiltonian $H^0$ with energy $E^0_i$.

$$H^0|i\rangle = E^0_i|i\rangle$$

However, these zero order states $|i\rangle$ are not the eigenstates of the overall Hamiltonian of the molecule, $H$. Had the real vibrational spectrum followed a purely harmonic behavior, they would resemble a $\delta$ function centered at the ZOBS which is not the case. It should be noted that the density of states – which consists of both bright states and dark states – drastically increases as one moves higher to a higher energy state. Due to this at higher energies, coupling between several normal modes has to be assumed thus creating anharmonicity. These new states $|n\rangle$, resulting from the superposition of the zero order states $|i\rangle$, are the eigenstates of the Hamiltonian $H$ with perturbations of cubic and higher orders to account for coupling. The Hamiltonian $H$, hence, accounts for the anharmonic coupling between the bright and the dark states with energy eigenvalues $E_n$.

$$H|n\rangle = E_n|n\rangle$$

![Diagram](image.png)

Figure 2: Mixing of the bright state and the dark states to give new states $|n\rangle$. $V$ is the perturbation on the zero order Hamiltonian to yield $H$. 
During IVR, the ZOBS is coupled to the manifold of ZODSs thus distributing the population to a broader distribution accounting for how actual spectral intensities, the center of the peak still lying at the ZOBS.

This anharmoniscity allows for inter-state coupling between the bright state and the dark state, forming new states. This is due to the overlap between the bright state and the dark state. This leads to a high density of accessible states, which results in the broadening of peaks in the spectral domain. In order to evaluate the frequency associated with these peaks, corrections must be made in the Hamiltonian to account for the effects of coupling between the bright state and the dark state. This correction is highly analogous to a first-order perturbation.

**Current Theories vs. Matrix Fluctuation Dissipation**

In order to computationally predict the spectral intensities for a polyatomic molecule it is only intuitive to calculate the eigenstates and eigenvalues of the overall hamiltonian matrix, $H$. Generally, the method of computing the energy for eigenstates, or peaks on a spectrum, is by using Lanczos diagonalization. This becomes an inefficient method when the amount of states becomes high because an $N \times N$ ($N^2$) matrix must be calculated, where $N$ may reach numbers of magnitudes of $10^6$ or higher.

But noted that an $N$ line spectrum contains only $2N$ pieces of information, the $N$ eigenvalues $E_n$ and the intensities $C_{nm} = |\langle n | 0 \rangle|^2$, one might question whether it is important to calculate the $N^2$ eigenstates of $H$. The computationally intensive calculation of $N^2$ is both time consuming and requires a large amount of memory space even on a dedicated workstation. The number of eigenstates would also increase exponentially as the complexity of the systems in question increases. One must hence find ways in which these calculations can be performed in a more efficient way for complex molecules like proteins etc.
Figure 4: A typical Vibrational Spectra

Because this method of computation may become computationally inefficient, a new method of calculating the peaks for systems with over $10^6$ eigenstates is introduced to calculate the eigenvalues of such states in a practical fashion. This method is entitled the “matrix fluctuation-dissipation” theorem (MFD).

In this paper it has been shown that using the Matrix Fluctuation Dissipation Theorem does not require explicit knowledge of all the eigenstates, but only two calculations of the eigenvalues are sufficient.

A time dependent IVR calculation is also possible, as will be shown mathematically later in this paper, via the equation:

$$P_1(t) = |\langle i(0)|i(t) \rangle|^2 = \sum_{n,n'} |C_{ni}|^2 |C_{n'l}|^2 e^{-i(E_n-E_{n'})t/h}$$

A Short Note on the Fluctuation-Dissipation Theorem

The fluctuation dissipation theorem (FDT) is a tool to characterize non-equilibrium thermodynamic systems where small fluctuations at equilibrium lead to an irreversible dissipation of energy as heat. When the particles in a system are said to be in a random motion a number of effects are generated. Random collisions on a particle generate a driving force that sets of a random motion. On application of an external driving force, such as a field, the particles would still continue to perform random motion through random collisions but would then set off a systematic response to the external field which can be experimentally measured.

Random collisions in the neighborhood of an observed particle, therefore, lead to:

- A random force for it to maintain its irregular random motion.
- A systematic drag or resistance for a forced motion that is due to a large number of collisions.

Although, not completely intuitive the random forces can then, through experimental calculations, be correlated with the systematic resistance caused by friction. One could, hence, in effect calculate the systematic response of a system in question to any external disturbance, this phenomena is manifested in the Fluctuation Dissipation Theorem.
Henceforth, it is clear that the systematic response of a system to any external disturbance, measure during any experiment is the dissipation, while fluctuations are intrinsic perturbations in the system due to random forces like collisions.

The Fluctuation Dissipation Theorem can then:

1. Relate the response to an external disturbance to the intrinsic fluctuations in absence of all external perturbations through a general function where:
   a. The response is characterized by a response function.
   b. The fluctuation is a correlation function of physical properties of the system in thermal equilibrium.
2. Determine the characteristics of the internal fluctuations or the correlation function through an experimental measurement of response in the presence of an external field,
3. Calculate the response through a time correlation of internal fluctuations at thermal equilibrium in the absence of perturbing forces.

Let a dynamical system be characterized by the Hamiltonian \( H_0(x) \) and observable ‘\( x(t) \)’. The switching on of an external field causes the Hamiltonian to alter to \( H \). Given the scalar field \( f(t) \):

\[
H = H_0(x) + x(t)f(t)
\]

\[H'_t = x(t)f(t)\]

Then according to FDT the linear response due to the external field is given by an autocorrelation function \( A \) and the perturbation \( f(t) \):

\[
\langle x(t) \rangle = \langle x \rangle_0 - \beta f_0 A(t)
\]

Later we show the correlation between the FDT and calculation of spectral intensities by the method derived in the paper, and hence call the procedure Matrix Fluctuation-Dissipation Theorem for later references.

**The Hamiltonian:**

In reference to the text above, the overall Hamiltonian \( H \) of a polyatomic molecule can be represented as:

\[
H = H_0 + V
\]

Where, \( V \) is higher order perturbations on the zero order Hamiltonian \( H_0 \) to account for the anharmonic terms due to mixing and superposition of bright states and dark states. The \( H \) is partitioned such that the term \( V \) is comprised of coupling Hamiltonians, one of which \( H^{(1)} \) is the coupling of the bright state to dark states and the other \( H^{(1)'} \) is the coupling of a dark state to other dark states. These Hamiltonians are scaled by factors \( \lambda \) and \( \lambda' \) that are independent of each other.

\[
H = H_0 + \lambda_i H_i^{(1)} + \lambda'_i H_i^{(1)'}
\]

It is intuitively clear that as \( \lambda \) and \( \lambda' \) increases from 0 to 1, the spectral intensities diffuse from the single bright state into other states thus giving rise to the fragmented true spectrum.

**The Matrix Fluctuation-Dissipation Theorem:**
Considering the Matrix treated of the fluctuation-dissipation theorem we represent the Hamiltonian as a Matrix consisting of:

1. Diagonal elements representing the Zero - Order Hamiltonian or the normal modes. \( E_0^{(0)} \) is the zero order bright state. The rest of the states on the diagonal are then dark states.

2. Section \( H^{(1)} \) representing the coupling effects of dark states with respect to the bright state, and

3. Section \( H^{(1)' } \) representing the coupling effects of bright states with respect to the dark state.

As stated above for the ease of comprehension and evaluation, the bright state and dark state coupling effects were explicitly considered to be independent of one another. These two latter fractions may be calculated by superficially knowing the eigenfunction, \( |n> \). This will be explained in the following derivation of the complete Hamiltonian, which is a linear function containing the zero-order Hamiltonian and the coupling effects from the bright state and the dark state.

If the Hamiltonian \( H \) has matrix elements \( H_{jk} \) in an arbitrary basis \( \{|j>\} \) and both the eigenbasis \( \{|i>\} \) of the zero order Hamiltonian \( H_0 \) and \( \{|n>\} \) of the overall Hamiltonian \( H \) are in the basis set \( \{|j>\} \), it can be said that:

\[
\langle j|H|k \rangle = H_{jk}
\]

\[
\sum_{j,k} |j> \langle j|H|k \rangle \langle k| = H - (i)
\]

One of the states \( |0> \) is the bright state and the row and column corresponding/coupled to this \( |0> \) state then is the Hamiltonian \( H^{(1)} \). From equation (i) we have by replacing \( |k> \) by \( |0> \)

\[
\sum_{j} |j> \langle j|H|0 \rangle \langle 0| = H^{(1)}
\]

Because the Hamiltonian is Hermitian we can further expand as follows:

\[
\sum_{j \neq 0} |j> \langle j|H|0 \rangle \langle 0| + \sum_{j \neq 0} |0> \langle 0|H|j \rangle \langle j| = H^{(1)} - (ii)
\]

From the properties of the identity matrix we know that:

\[
I = \sum_{j} |j> \langle j|
\]

\[
I = \sum_{j \neq 0} |j> \langle j| + |0> \langle 0| - (iii)
\]

\[
If: |0> \langle 0| = P
\]
Where, $P$ is the projection operator on the bright state $|0\rangle$, then equation (iii) can be written as:

$$I = \sum_{j \neq 0} |j\rangle\langle j| + P - (iv)$$

$$I - P = \sum_{j \neq 0} |j\rangle\langle j| - (v)$$

Using equations (iv) and (v) we can then evaluate (ii) to be:

$$PH(I - P) + (I - P)HP = PH + HP - 2PHP = H^{(1)} - (vi)$$

For the eigenstates $|n\rangle$ of the overall Hamiltonian $H$:

$$\langle n|H^{(1)}|n\rangle = \langle n|PH + HP - 2PHP|n\rangle$$

$$\langle n|H^{(1)}|n\rangle = \langle n|PH|n\rangle + \langle n|HP|n\rangle - 2\langle n|PHP|n\rangle - (vii)$$

Inserting value of $P$ from above:

$$\langle n|H^{(1)}|n\rangle = \langle n|0\rangle\langle 0|H|n\rangle + \langle n|H|0\rangle\langle 0|n\rangle - 2\langle n|0\rangle\langle 0|H|0\rangle\langle 0|n\rangle - (viii)$$

Since $|n\rangle$ is an eigenstate of $H$ we have:

$$\langle 0|H|n\rangle = \langle n|H|0\rangle = E_n - (ix)$$

$$\langle 0|H|0\rangle = E_0^{(0)} - (x)$$

Substitution from equations (ix) and (x) into (viii),

$$\langle n|H^{(1)}|n\rangle = E_n \langle n|0\rangle\langle 0|n\rangle + E_n \langle n|0\rangle\langle 0|n\rangle - 2E_0^{(0)} \langle n|0\rangle\langle 0|0\rangle\langle 0|0\rangle - (xi)$$

For normalized basis states:

$$\langle j|j\rangle = 1$$

$$\langle n|H^{(1)}|n\rangle = 2E_n \langle n|0\rangle\langle 0|n\rangle - 2E_0^{(0)} \langle n|0\rangle\langle 0|n\rangle - (xi)$$

$$\langle n|H^{(1)}|n\rangle = 2(E_n - E_0^{(0)})\langle n|0\rangle^2 - (xii)$$

Using the Hellmann-Feynman theorem in order to obtain a new expression for the Hamiltonian on $|n\rangle$. The only requirement for this theorem is that the function must be an eigenfunction of the Hamiltonian. This new representation, which represents the spectral intensity, can be seen as follows:

$$\langle n|H^{(1)}|n\rangle = \langle n|H^{(1)}|n\rangle + 0 - (xiii)$$

Since $\langle n|n\rangle$ is a constant with value 1 for normalized basis states we get:

$$E_n \frac{d\langle n|n\rangle}{d\lambda} = 0 - (xiv)$$

Substitution of equation (xiv) into equation (xiii):
Now the energy level fluctuations, in equation (xx) and the spectral intensity, $|\langle n|0\rangle|^2$, equation (xii) can be related by the following equation:

$$|\langle n|0\rangle|^2 = \frac{1}{2(E_n - E_0^{(0)})} \frac{dE_n(\lambda, \lambda')}{d\lambda} - (xxi)$$

Equation (xxi) relates the fluctuation $dE/d\lambda$ due to coupling in the ground state bright state $|0\rangle$ and an eigenstate $|n\rangle$. Any arbitrary eigenstate $|n\rangle$ can be used to measure the relative broadening and intensity due to this coupling. This expression is evaluated for different magnitudes of coupling, represented by $\lambda$ and $\lambda'$. When the coupling effect is at its maximum, $\lambda=1$ and $\lambda'=1$. When the coupling effects do not have any contribution, $\lambda=0$ and $\lambda'=0$. Using central differencing one can also extrapolate further that:

$$\lambda = \frac{E_n(1 + \Delta, \lambda' = 1) - E_n(1 - \Delta, \lambda' = 1)}{2\Delta} - (xxi)$$

$\Delta$ is usually in the range $10^{-2}$ to $10^{-6}$ depending on the accuracy of the diagonalization technique employed. Further on the time dependence of the decay of population density from a bright state into the dark manifold is given by:

$$P(t) = |\langle 0|0(t)\rangle|^2 = \sum_{n,n'} |C_{ni}|^2 |C_{n'i}|^2 e^{-i(E_n - E_{n'})t/h}$$

The effect of small external perturbations ($\Delta$) can be easily seen on the spectral intensity using equation (xxi) thus allowing for a sensitivity analysis of spectral features:

$$\frac{\partial}{\partial \Delta} |\langle n|0\rangle|^2 = \frac{1}{2(E_n - E_0^{(0)})^2} \left( \frac{\partial^2 E_n}{\partial \Delta^2} - \frac{1}{E_n - E_0^{(0)}} \left( \frac{\partial E_n}{\partial \Delta} \right)^2 \right)$$

It is clear that the second derivative can be evaluated by central differencing at the cost of another set of eigenvalues such that:

$$y'' = \frac{y_+ - 2y_0 + y_-}{4\Delta^2}$$
Finally although equation (xxi) was derived only for discrete levels it can extended for a continuum:

\[ \langle | \langle E | 0 \rangle \rangle^2 = \frac{1}{2} \frac{\partial \ln [E - E_0^0]}{\partial \lambda} \]

It is now apparent that “dissipation” corresponds to the change in spectral intensities or broadening of a predicted sharp line spectrum due to energy crossing between a bright state and a new eigenstate, due to coupling with a dark state. This line broadening is in the above terms a systematic response to the external force of excitation caused by a LASER pulse. It also begins to become apparent that the term “fluctuation” is derived from the fact that there is a large probability overlap for transition states in a highly dense area of eigenstates with similar energies, and thus peak broadening occurs in the spectral domain. Spectral intensities can then be calculated from energy level fluctuations \( dE/d\lambda \) which is in agreement with the fluctuation-dissipation theorem.

**Applications**

Because the fluctuation dissipation theorem enables for simplification of computationally demanding work, we can apply the theorem to simplify problems and gain a closer approximation to true values, if coupling effects contribute to the desired calculations. An example of this would be in density-functional theory (DFT), as described by Furche et al. DFT is a technique that is used to measure the electronic states of complex polyatomic systems; however, this technique can only lead to an approximation of the energy for the calculated state. By using the fluctuation-dissipation theorem in DFT, we can in theory obtain a closer exactness corresponding of the eigenvalue corresponding to the state of interest. Furche et al. describes his efforts to be relatively disappointing due to the failure of accuracy with respect to using DFT alone; however, there is still much appeal in coupling these two techniques because of the theoretical aspect of obtaining accurate results.

The electronic-vibrational relaxation frequencies associated with certain molecules are relatively distinct for a particular molecule. However, the electronic-vibrational frequency associated with the relaxation can shift due to impurities within the molecule of interest. This is described in the work by Shugard et al. Impurities inside a solid matrix or solution influence the energy of the system, which includes the corresponding relaxation frequencies of the molecule of interest. The effect of the impurity on the molecule can be treated as a perturbation in that it contributes a weak or strong coupling contribution.
References

Intensities and rates in the spectral domain without eigenvectors
Martin Gruebele

Matrix Fluctuation-Dissipation Theorem: Application to Quantum Relaxation Phenomena
The Journal of Physical Chemistry (1996)
Martin Gruebele

Vibrationally Mediated Photodissociation
Salmon Zamik Rosenwaks
RCS Publishing

Fluctuation-dissipation theorem density-functional theory
The Journal of Chemical Physics 122 (2005)
Filipp Furche, Troy Van Voorhis

Stochastic classical trajectory approach to relaxation phenomena. I. Vibrational relaxation of impurity molecules in solid matrices
The Journal of Chemical Physics 69 (1978)
Mary Shugard, John C. Tully, and Abraham Nitzan

www.wikipedia.org