A perspective on nonresonant and resonant electronic response theory for time-dependent molecular properties

Dalton2015

**DALTON INPUT
.RUN RESPONSE
**WAVE FUNCTION
.DFT
 B3LYP
**RESPONSE
*LINEAR
 .DIPLEN
 .SINGLE RESIDUE
 .ROOTS
 10
*END OF INPUT

Gaussian09

#p TD=(nstates=10) B3LYP

ethylene

0 1
C 0.6680 0.0000 0.0000
C -0.6680 0.0000 0.0000
H 1.2437 0.9222 0.0000
H -1.2437 0.9222 0.0000
H 1.2437 -0.9222 0.0000
H -1.2437 -0.9222 0.0000

End of input

\[ \pi \rightarrow \pi^* \]

\[ \lambda = 168 \text{ nm} \]

\[ f = 0.33 \]
In a simplistic and generalized view of spectroscopy, the observable is the number of detected particles (e.g. photons or electrons) per unit time in a narrow energy interval and into a small solid angle.

The observable is recorded under certain conditions regarding parameters such as temperature, pressure, concentration, and there exist a model (or connection) from which one can deduce molecular properties from the set of measured data.

Under typical circumstances in molecular spectroscopies, these connections can be viewed upon as measures of changes in an observable due to the presence of electromagnetic fields with origins attributed to external sources.

Compared to atomic fields, the electric fields of conventional lasers are relatively weak. A laser delivering pulses of 10 ns duration and 1 mJ in energy and with a spot size of 100 µm produces an intensity of about 0.3 GW/cm². This intensity corresponds to an electric field amplitude of some $F_\omega = 5 \times 10^{-5}$ a.u., which is several orders of magnitude smaller than the internal electric fields that bind electrons in atomic and molecular systems.
Reasons to employ Perturbation Theory

Why do we not simply determine time propagate the Schrödinger equation in a direct and nonperturbational manner?

- The response functions defined in perturbation theory provide the natural meeting point between experiment and theory with a distinct separation of one-, two-, three-photon, etc., optical processes.
- It is a numerically elaborate process to separate out nonlinearities from dominant lower-order components in the polarization.
- Only a small number of states \( n \approx 10^1 - 10^2 \) can be included in nonperturbational approaches.
- Calculation of vibrational contributions can hardly be made practical in a nonperturbational approach.
Response Theory and Perturbation Theory

Response theory may be thought of as a reformulation of standard time-dependent perturbation theory into a form suitable for approximate state theory. Virtually all spectroscopic properties are encompassed by the theory.

Possible perturbations are:

- time-independent or time-dependent
- electric or magnetic
- internal or external
- geometric distortions
Selection of molecular properties

**Electric**
- Polarizability
- Hyperpolarizabilities

**Magnetic**
- Magnetizability

**Electric–Magnetic**
- Optical rotation
- Circular dichroism
- Faraday rotation
- Magnetic circular dichroism

**Electric–Geometric**
- IR intensities
- Raman intensities
- Vibrational polarizabilities
- ZPVA polarizabilities

**Internal fields**
- $g$-tensor
- Fine-structure
- Spin-spin coupling
- Shieldings
Motivation for derivation of exact state response functions

- First and foremost, it reveals the dependence of molecular response properties on intrinsic properties of the system, such as excitation energies and transition moments, and it thereby connects different spectroscopies.
- It offers the possibility of constructing few-states-models upon which one can base rational molecular design.
- It provides explicit formulas for response functions in the configuration interaction (CI) approximation.
- It reveals general properties and symmetries of response functions that are also valid in approximate state theories.
- It suggests the identification of excited state properties from a study of poles and residues of ground state response functions, e.g., excitation energies are identified as poles of linear response functions.
- The formulations of quantum mechanics and perturbation theory that are suitable for approximate state theories are best illustrated in exact state theory.
A few words about QM operators

An operator in quantum mechanics maps one wave function into another:

\[ \hat{\Omega} \psi(x) = \psi'(x). \]

An eigenfunction of an operator fulfills:

\[ \hat{\Omega} \psi_\omega(x) = \omega \psi_\omega(x). \]

A function of an operator is defined by its Taylor series:

\[ f(\hat{\Omega}) = \sum_n a_n \hat{\Omega}^n \]

and we thus have

\[ f(\hat{\Omega}) \psi_\omega(x) = f(\omega) \psi_\omega(x). \]
A few words about wave functions

A state vector $|\psi\rangle$ in Hilbert space represents the state of a QM system. The inner product between two state vectors is given by:

$$\langle \psi | \psi' \rangle = \int \psi^*(x) \psi'(x) dx.$$ 

The projection of a state vector onto the coordinate basis is given by the wave function according to:

$$\psi(x) = \langle x | \psi \rangle = \int \langle x | x' \rangle \langle x' | \psi \rangle dx' = \int \delta(x - x') \psi(x') dx'.$$

The square modulus of the wave function gives the probability density:

$$\rho(x) = \langle x | \psi \rangle \langle \psi | x \rangle = \psi^*(x) \psi(x).$$

Using Dirac’s bra–ket notation, an eigenvalue equation takes the form:

$$\hat{\Omega} |\psi_\omega\rangle = \omega |\psi_\omega\rangle.$$
A few words about the Schrödinger equation

The Schrödinger equation reads as:

\[ i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H}(t)\psi(t). \]

The time-independent Schrödinger equation reads as:

\[ \hat{H}_0 \psi_n(x) = E_n \psi_n(x), \]

\[ \psi(t) = \psi_n(x)e^{-iE_n t/\hbar}. \]

The wave function \( \psi(t) \) is always time-dependent, but for a stationary state \( \langle \hat{p} \rangle = 0 \) and the density \( \rho(t) \) is time-independent.
Displaced harmonic oscillator: \( \psi(0) = \psi_0(x - x_0) \)
Time-evolution for conservative systems; $\hat{H}(t) = \hat{H}_0$

The evolution of the wave function from some initial time $t_0$ to time $t$ is given by

$$\psi(t) = \hat{U}(t, t_0)\psi(t_0),$$

where

$$\hat{U}(t, t_0) = e^{-i\hat{H}_0(t-t_0)/\hbar}.$$ 

The operator $\hat{U}(t, t_0)$ is referred to as the time evolution operator, or time propagator.

Alternatively, the time-dependent wave function can be written in terms of the eigenfunctions of the Hamiltonian:

$$\psi(t) = \sum_n c_n(0)\psi_n(x)e^{-iE_n(t-t_0)/\hbar}$$

Note:

For cases when the Hamiltonian is time-dependent, a time propagator cannot be constructed in such a simple manner.
Molecular properties from the “exact” wave function

We will now study a simple system for which we, for an arbitrary external electric field turned on at \( t = 0 \), will have access to the exact time-dependent wave function that solves the Schrödinger equation.

By exact, we mean "for all practical purposes exact" and limited only by the numerical representation on the computer, but this aspect is a side-issue to the present discussion.

\[
i\hbar \frac{\dot{\psi}}{\dot{t}} = \hat{H} \psi
\]

This toolbox will let us explore the different formulations of the theory of molecular properties without relying on perturbation theory.
Two-level atom in static electric field (conservative system)

In the electric dipole approximation, the Hamiltonian of the system will equal

\[ \hat{H} = \hat{H}_0 - \hat{\mu} F^0 \]

where \( \hat{H}_0 \) is the Hamiltonian of the isolated atom, \( \hat{\mu} \) is the electric dipole operator, and \( F^0 \) is the amplitude of the external static electric field.

\[
\begin{align*}
\Delta E &= E_b - E_a \\
E_b &\quad \psi_b \\
E_a &\quad \psi_a
\end{align*}
\]

\[
\hat{H}_0 = \begin{bmatrix}
E_a & 0 \\
0 & E_b
\end{bmatrix}
\]

\[
\hat{\mu} = \begin{bmatrix}
0 & \mu_{ab} \\
\mu_{ba} & 0
\end{bmatrix}
\]
The energies of the ground and excited states are given as the eigenvalues of the Hamiltonian:

$$\det \left( \hat{H} - \hbar \omega \hat{I} \right) = 0$$

The two eigenvalues become

$$\hbar \omega = \frac{E_a + E_b}{2} \pm \sqrt{\frac{(E_b - E_a)^2}{4} + (\mu_{ab} F^0)^2}$$

from which, for small fields, the electric-field dependent energies are found to be

$$E'_a(F^0) = E_a - \frac{(\mu_{ab} F^0)^2}{\Delta E} + \frac{(\mu_{ab} F^0)^4}{(\Delta E)^3} + \cdots$$

$$E'_b(F^0) = E_b + \frac{(\mu_{ab} F^0)^2}{\Delta E} - \frac{(\mu_{ab} F^0)^4}{(\Delta E)^3} + \cdots$$
From these energy expansions we readily determine the electric polarization properties by taking the field derivatives of the energy in the limit of zero field strength. For the ground state, we get

\[ \mu_a = - \frac{\partial E'_a}{\partial F^0} \bigg|_{F^0=0} = 0 \]

\[ \alpha_a = - \frac{\partial^2 E'_a}{\partial (F^0)^2} \bigg|_{F^0=0} = 2 \frac{(\mu_{ab})^2}{\Delta E} \]

\[ \beta_a = - \frac{\partial^3 E'_a}{\partial (F^0)^3} \bigg|_{F^0=0} = 0 \]

\[ \gamma_a = - \frac{\partial^4 E'_a}{\partial (F^0)^4} \bigg|_{F^0=0} = -24 \frac{(\mu_{ab})^4}{(\Delta E)^3} \]

where we have introduced the electric dipole moment (\( \mu \)), polarizability (\( \alpha \)), first-order hyperpolarizability (\( \beta \)), and second-order hyperpolarizability (\( \gamma \)).
Induced polarization
The permanent dipole moment of the atom is zero, but, in the presence of the external field, there will appear an *induced* polarization.

Polarizability
With $\Delta E = 0.5\ E_h$ and $\mu_{ab} = 1.0$ a.u., the static ground state polarizability $\alpha_a$ is equal to 4.0 a.u., and, with $F^0 = 5 \times 10^{-5}$ a.u., the induced dipole moment amounts to $\mu'_a = 2.0 \times 10^{-4}$ a.u. (nonlinear terms are ignored).

Charge dislocation
The static electric field (with the strength of a conventional laser field) is effectively capable of causing a displacement of an elementary charge in this system by a distance of $2.0 \times 10^{-4}$ a.u.
Two-level atom in optical field (nonconservative system)

In the electric dipole approximation, the Hamiltonian of the system will equal

\[ \hat{H}(t) = \hat{H}_0 - \hat{\mu} F(t) \]

where \( \hat{H}_0 \) is the Hamiltonian of the isolated atom, \( \hat{\mu} \) is the electric dipole operator, and \( F(t) \) is the external electric field.

\[ \Delta E = E_b - E_a \]

\[ \hat{H}_0 = \begin{bmatrix} E_a & 0 \\ 0 & E_b \end{bmatrix} \]

\[ \hat{\mu} = \begin{bmatrix} 0 & \mu_{ab} \\ \mu_{ba} & 0 \end{bmatrix} \]
Non-stationary states in laser fields

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse energy</td>
<td>1 mJ</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>10 ns</td>
</tr>
<tr>
<td>Spot size</td>
<td>100 µm</td>
</tr>
<tr>
<td>Intensity</td>
<td>0.3 GW/cm²</td>
</tr>
<tr>
<td>Electric field</td>
<td>$4.6 \times 10^{-5}$ a.u.</td>
</tr>
</tbody>
</table>

$\Delta E = 0.5$ a.u.
$\mu_{ab} = 1.0$ a.u.

$\psi(0) = \psi_a$

$i \dot{\psi}(t) = H \psi(t)$

$H = H_0 - \mu F(t)$
Nonconservative system: Study of Induced Dipole Moment

By $\psi(t)$ we will denote the time-dependent wave function that is a solution to the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H} \psi(t).$$

We will assume that a nonresonant ($\omega = 0.1$ a.u.) external perturbation is slowly switched on ($a = 1/100$ a.u.) in accordance with

$$F(t) = F^\omega \sin \omega t \times \text{erf}(at).$$
**Initial Condition**

The initial condition for our system is that it resides in the ground state prior to exposure of the perturbation and with a phase that is zero at $t = 0$, i.e.

$$
\psi(t) = \psi_a e^{-iE_a t/\hbar} \quad \text{for } t \leq 0
$$

**Infinitesimal Time Propagation**

With a time step $\Delta t$ that is small, we can consider the external field to be constant between $t_0$ and $t_0 + \Delta t$ and thereby get

$$
\psi(t_0 + \Delta t) = \hat{U}(t_0, t_0 + \Delta t)\psi(t_0)
$$

where the time-evolution propagator equals

$$
\hat{U}(t_0, t_0 + \Delta t) = e^{-i\hat{H}(t_0)\Delta t/\hbar}
$$
Time Propagation

Repeated application of $\hat{U}$ enables us to determine the wave function in the region $t > 0$, and, given the time-dependent wave function, the dipole moment is obtained as the expectation value of the electric dipole operator according to

$$\mu(t) = \langle \psi(t) | \hat{\mu} | \psi(t) \rangle$$

Initialization

\begin{verbatim}
psi[:,0]=[1, 0]
H=array([[Ea, 0],
          [0, Eb]])
mu=array([[0, muab],
          [muba, 0]])
F=Fw*sin(w*t)*erf
\end{verbatim}

for k in range(1,n):
    psi[:,k]=dot(expm(-1j*(H-mu*F[k-1])*delta),psi[:,k-1])
P[k]=dot(conj(psi[:,k]),dot(mu,psi[:,k]))
Populations of States

As a measure of the effect of the perturbation on the system, we may study the population in the ground and excited states which we denote by $\rho_a(t)$ and $\rho_b(t)$, respectively. The populations are given by the projections of the wave function on the eigenfunctions of $\hat{H}_0$ according to

$$\rho_a(t) = |\langle \psi_a | \psi(t) \rangle|^2 \quad \rho_b(t) = |\langle \psi_b | \psi(t) \rangle|^2$$

**Program code**

```python
popa=conj(psi[0,:])*psi[0,:]
popb=conj(psi[1,:])*psi[1,:]
```
The figure shows three graphs against time (0 to 500) with different scales:

1. $\mu(t)$ with a range of $10^{-4}$ to $10^{-1}$.
2. $\rho_b(t)$ with a range of $10^{-8}$ to $10^{-5}$.
3. $F(t)$ also with a range of $10^{-5}$ to $10^{-2}$.

The time scale on the right indicates 10 fs.
Induced Dipole Moment

Molecular properties are defined by an expansion of the induced dipole moment in orders the time-dependent electric field

\[
\mu(t) = \alpha F(t) + \frac{1}{6} \gamma F^3(t) + \cdots
\]

Polarizability

The linear polarizability can be read off directly as the ratio of the amplitudes of the polarization and the electric field

\[
\alpha = \frac{\max[\mu(t)]}{F \omega} \approx 4.17 \text{ a.u.}
\]

Dispersion

The dependency of the molecular property (in this case the polarizability) to the frequency of the perturbation is referred to as the \textit{dispersion} of the property.
Dispersion and Rayleigh scattering: practical example

A clear cloudless day-time sky is blue because molecules in the air scatter blue light from the sun more than they scatter red light. When we look towards the sun at sunset, we see red and orange colours because the blue light has been scattered out and away from the line of sight.

Source: http://math.ucr.edu/home/baez/physics/General/BlueSky/blue_sky.html
Where are the nonlinearities?

\[ \mu(t) = \alpha F(t) + \frac{1}{6} \gamma F^3(t) + \cdots \]

There are three ways to enhance nonlinear responses:

- Design system with large \( \gamma \)-value
- Increase the electric field strength
- Tune the frequency to multi-photon resonances
Nonlinear responses

\[ \mu(t) = \alpha(-\omega; \omega)F^\omega \sin(\omega t) + \frac{1}{6} \gamma(-3\omega; \omega, \omega, \omega)F^\omega F^\omega F^\omega \sin(3\omega t) + \ldots \]

Let us choose: \( F^\omega = 0.02 \) a.u. and \( \omega = 0.166 \) a.u.:
Nonlinear responses: practical example

A robust fiber-coupled PPLN frequency-conversion waveguide device is suitable for use with fiber-based frequency combs and spectroscopy. The device shown is designed to accept a supercontinuum light source in the 2000 nm region and outputs a frequency-doubled signal centered at 1064 nm.

Source: http://www.laserfocusworld.com/
Nonconservative system: expectation value summary

- The energy of the system is not well defined as energy transfer occurs between field and system.
- The dipole moment and other observables (expectation values) are well defined and time-dependent.
- Molecular properties (response functions) are defined as expansion coefficients of the observable in terms of field strengths.
- The overall phase of the wave function is of no concern.
- Linear response functions are directly identified as ratios of induced dipole moments and field strengths (in the small field limit).
- Nonlinear response functions can be obtained in the same manner but the procedure is hampered by numerical issues.
- This time-resolved procedure is applicable to real systems but limited by the need to maintain low matrix ranks.
Nonconservative system: Study of quasi-energy

We write the wave function $\psi(t)$ as the product of two
time-dependent functions in the following manner

$$\psi(t) = e^{-i\phi(t)}\bar{\psi}(t)$$

This division is made unique by requiring that $\phi(t)$ is a real
function (a phase) and that the phase of the projection of $\bar{\psi}(t)$
onto $\psi_a$ is zero.
In absence of the external field, the wave function become equal to

$$\psi(t) = \psi_a e^{-iE_at/\hbar}$$

and the two requirements on $\phi(t)$ and $\bar{\psi}(t)$ lead to the division

$$\bar{\psi}(t) = \psi_a \quad \phi(t) = E_a t/\hbar$$

This is the reason why $\bar{\psi}(t)$ is referred to as the phase isolated
wave function.
Equation of motion for phase-isolated wave function

We substitute the product function into the Schrödinger equation to arrive at

\[
\left( \hat{H} - i \hbar \frac{\partial}{\partial t} \right) \bar{\psi}(t) = Q(t) \bar{\psi}(t)
\]

where \( Q(t) \), which is known as the time-dependent quasi-energy, has been introduced for the time derivative of the phase function, i.e.,

\[ Q(t) = \hbar \dot{\phi}(t) \]

It is clear that, given \( Q(t) \), the phase function \( \phi(t) \) is obtained by time integration according to

\[ \phi(t) = \int_{t}^{t'} Q(t') \, dt' \]
We obtain two coupled differential equations

\[ Q(t) = \langle \bar{\psi} | \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) | \bar{\psi} \rangle \]

and

\[ \langle \bar{\psi}_\perp | \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) | \bar{\psi} \rangle = 0. \]

As orthogonal complement vector, we may choose

\[ \bar{\psi}_\perp(t) = \psi_b - b^*(t) \psi_a, \]

and, we arrive at

\[ \hbar \dot{b}(t) = -i\Delta E b(t) + i \mu_{ab} F(t) \left[ 1 - b^2(t) \right]. \]
Variations of the wave function

The square norm of the wave function is a functional

\[ N[\psi] = \int \psi^* \psi \, d\tau = \langle \psi | \psi \rangle \]

The first variation of \( N \) is

\[
\delta N = \left. \frac{d}{d\varepsilon} N[\psi + \varepsilon \delta \psi] \right|_{\varepsilon=0} = \left. \frac{d}{d\varepsilon} \int (\psi + \varepsilon \delta \psi)^* (\psi + \varepsilon \delta \psi) \, d\tau \right|_{\varepsilon=0} \\
= \int (\delta \psi^* \psi + \psi^* \delta \psi) \, d\tau = \langle \delta \psi | \psi \rangle + \langle \psi | \delta \psi \rangle
\]

Since \( \delta N \) must be zero, we have that variations in the wave function must fulfill

\[
\delta \psi(t) = \delta \psi_\perp + \delta \psi_\parallel; \quad \delta \psi_\parallel = i\epsilon(t)\psi; \quad \epsilon(t) \in \mathcal{R}
\]
Allowed variations in phase isolated wave functions

Since $\bar{\psi}$ and $\psi$ differ by a mere overall phase factor, we have

$$N[\bar{\psi}] = \langle \bar{\psi} | \bar{\psi} \rangle = \langle \psi | \psi \rangle = 1$$

and, since,

$$\frac{dN}{dF\omega} = \langle \frac{d\bar{\psi}}{dF\omega} | \bar{\psi} \rangle + \langle \bar{\psi} | \frac{d\bar{\psi}}{dF\omega} \rangle = 0$$

we conclude that

$$\delta \bar{\psi}(t) = \frac{d\bar{\psi}}{dF\omega}$$

is an allowed variation.
First variation of the energy

The energy associated with a time-independent wave function is a functional

$$E[\psi] = \int \psi^* \hat{H} \psi \, d\tau = \langle \psi | \hat{H} | \psi \rangle$$

At points $\psi = \psi_n$ with $\hat{H} \psi_n = E_n \psi_n$, the first variation of $E$ is

$$\delta E = \frac{d}{d\varepsilon} E[\psi_n + \varepsilon \delta \psi] \bigg|_{\varepsilon=0} = \frac{d}{d\varepsilon} \int (\psi_n + \varepsilon \delta \psi)^* \hat{H} (\psi_n + \varepsilon \delta \psi) \, d\tau \bigg|_{\varepsilon=0}$$

$$= E_n \int (\delta \psi^* \psi_n + \psi_n^* \delta \psi) \, d\tau = E_n \delta N = 0$$

As a consequence for a system in a static field $F^0$, we get

$$\frac{dE}{dF^0} = \langle \psi_n | \frac{\partial \hat{H}}{\partial F^0} | \psi_n \rangle + \delta E = -\langle \psi_n | \hat{\mu} | \psi_n \rangle$$

which is known as the Hellmann–Feynman theorem.
First variation of the quasi-energy

The quasi-energy

\[ Q(t) = \langle \bar{\psi} \mid \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) \mid \bar{\psi} \rangle \]

is a functional that depends on \( \bar{\psi} \).

For allowed variations in \( \bar{\psi} \), it is readily shown that

\[ \delta Q(t) + i\hbar \frac{\partial}{\partial t} \langle \bar{\psi} \mid \delta \bar{\psi} \rangle = 0 \]

which may be used as the starting point for the formulation of a time-dependent variational principle.
Time-dependent Hellmann–Feynman theorem

We consider as an allowed variation

$$\delta \bar{\psi}(t) = \frac{d \bar{\psi}(t)}{d F^\omega}$$

As a consequence, we get

$$\frac{d Q(t)}{d F^\omega} = \langle \bar{\psi} | \frac{\partial \hat{H}}{\partial F^\omega} | \bar{\psi} \rangle + \delta Q(t) = \langle \bar{\psi} | \frac{\partial \hat{H}}{\partial F^\omega} | \bar{\psi} \rangle - i \hbar \frac{\partial}{\partial t} \langle \bar{\psi} | \frac{d \bar{\psi}}{d F^\omega} \rangle$$

which is known as the time-dependent Hellmann–Feynman theorem.

To first order in the field strength $F^\omega$, the last term vanishes in our simple example and we get

$$\frac{d Q(t)}{d F^\omega} = \langle \bar{\psi} | \frac{\partial \hat{H}}{\partial F^\omega} | \bar{\psi} \rangle = - \langle \bar{\psi} | \hat{\mu} | \bar{\psi} \rangle \sin \omega t \times \text{erf}(at)$$
\[ \alpha = - \frac{\min \left[ \frac{dQ(t)}{dF^\omega} \right]}{F^\omega} \approx 4.17 \text{ a.u.} \]
Time-averaged quasi-energy

Since

\[ \frac{1}{T} \int_0^T \dot{f}(t) dt = 0 \]

for any periodic function \( f(t) \) with period time \( T \), we have, for

\[ Q_T = \frac{1}{T} \int_t^{t+T} Q(t') dt' \]

that the time-dependent variational principle reduces to

\[ \delta Q_T = 0 \]

The time-dependent Hellmann–Feynman theorem assumes the form

\[ \frac{dQ_T}{dF_\omega} = \frac{1}{T} \int_t^{t+T} \langle \overline{\psi}(t') | \frac{\partial \hat{H}}{\partial F_\omega} | \overline{\psi}(t') \rangle dt' \]
Nonconservative system: quasi-energy summary

- Based on the overall phase factor of the wave function we define a quantity known as the quasi-energy
- This quasi-energy is not an observable
- The formulation of a time-dependent Hellmann–Feynman theorem allows us to identify molecular properties (response functions) as the expansion coefficients of the time-averaged quasi-energy
- The quasi-energy technique becomes similar to energy derivative techniques in the time-independent case
- The quasi-energy approach allows for a common formulation of response theory for variational and nonvariational wave function models
Molecular properties from perturbation theory expansions of the wave function

—expansions are made in the basis of the exact eigenstates of the zeroth-order Hamiltonian—
The response theory cookbook recipe

1. Find an efficient parameterization of wave function
   - redundancy
   - state vector normalization
   - phase isolation and secular divergencies

2. Choose an appropriate equations-of-motion
   - based on Schrödinger equation
   - equivalent in exact state theory
   - important in approximate state theory

3. Apply perturbation theory
   - not much to say, mostly boring work...

4. Form a quantity of interest, $Q(t)$ or $\mu(t)$, and identify response functions
Parametrization by projections

\[ \psi(t) = \sum_n c_n(t) \psi_n; \quad c_n(t) = \langle n | \psi(t) \rangle \]

requires that

\[ \sum_n |c_n(t)|^2 = 1. \]
Parametrization by rotations

\[
|\psi(t)\rangle = e^{-i\hat{P}(t)}|0\rangle; \quad \hat{P}(t) = \sum_{n>0} \left[ P_n(t)|n\rangle\langle 0| + P_n^*(t)|0\rangle\langle n| \right]
\]

\[
e^{-i\hat{P}(t)}|0\rangle = |0\rangle \cos \alpha - i \sum_{n>0} P_n|n\rangle \frac{\sin \alpha}{\alpha}; \quad \alpha = \sqrt{\sum_{n>0} |P_n|^2}.
\]
The Hamiltonian and the Generator-of-Rotations for a three-states system equal

\[
\hat{H} = \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix} \quad \hat{P} = \begin{pmatrix} 0 & P_1^* & P_2^* \\ P_1 & 0 & 0 \\ P_2 & 0 & 0 \end{pmatrix}
\]

and the energy as a function of transition state amplitudes is

\[
E(P_1, P_2) = \langle 0 | e^{i\hat{P}} \hat{H} e^{-i\hat{P}} | 0 \rangle.
\]
Electronic Hessian

\[ E(P_1, P_2) = \langle 0|\hat{H}|0\rangle + i\langle 0|[\hat{P}, \hat{H}]|0\rangle - \frac{1}{2}\langle 0|[\hat{P}, [\hat{P}, \hat{H}]]|0\rangle + \ldots, \]

which gives an expression for the second-order derivatives of the energy (or Hessian) with respect to the transition state amplitudes that equals

\[
\left. \frac{\partial^2 E}{\partial P_n \partial P_m} \right|_{P=0} = -\frac{1}{2} \left( \langle 0| \left[ |n\rangle\langle 0|, [m\rangle\langle 0|, \hat{H} \right] |0\rangle \\
+ \langle 0| \left[ |m\rangle\langle 0|, [n\rangle\langle 0|, \hat{H} \right] |0\rangle \right) \\
= 0,
\]

\[
\left. \frac{\partial^2 E}{\partial P_n \partial P_m^*} \right|_{P=0} = -\frac{1}{2} \left( \langle 0| \left[ |n\rangle\langle 0|, [0\rangle\langle m|, \hat{H} \right] |0\rangle \\
+ \langle 0| \left[ |0\rangle\langle m|, [n\rangle\langle 0|, \hat{H} \right] |0\rangle \right) \\
= (E_n - E_0) \delta_{nm}.
\]
Choice of Equation of Motion

- **Rayleigh–Schrödinger**
  \[ i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H} \psi(t); \quad \psi(t) = \sum_n c_n(t) \psi_n \]

- **Ehrenfest theorem**
  \[ \frac{\partial}{\partial t} \langle \bar{\psi}(t)|\hat{\Omega}|\bar{\psi}(t) \rangle = \frac{1}{i\hbar} \langle \bar{\psi}(t)|[\hat{\Omega}, \hat{H}]|\bar{\psi}(t) \rangle \]

- **Quasi-energy**
  \[ Q(t) = \langle \bar{\psi} | \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) | \bar{\psi} \rangle \]

- **Liouville equation**
  \[ \frac{\partial}{\partial t} \rho_{mn} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]_{mn} - \gamma_{mn} (\rho_{mn} - \rho_{mn}^{eq}) \]
Perturbation Theory

—the not quite so fun part—
Hamiltonian and initial conditions

The Hamiltonian can be divided:

\[ \hat{H} = \hat{H}_0 + \hat{V}(t); \quad \hat{V}(t) = \sum_\omega \hat{V}_\omega F_\omega e^{-i\omega t} e^{\epsilon t}. \]

The solutions to the eigenvalue problem of \( \hat{H}_0 \) are known:

\[ \hat{H}_0 |n\rangle = E_n |n\rangle, \]

where \( |n\rangle \) are the exact eigenstates and \( E_n \) the respective energies. Before being exposed to the perturbation, we assume the molecule to be in a reference state \( |0\rangle \) — in most cases the molecular ground state — which corresponds to \( P_n(\neg \infty) = 0 \) for all \( n > 0 \).
Ehrenfest theorem

The time-evolution of an observable (expectation value) is determined from the Ehrenfest theorem. For a general time-independent operator $\hat{\Omega}$, we have

$$\frac{\partial}{\partial t} \langle \psi(t) | \hat{\Omega} | \psi(t) \rangle = \langle \psi(t) | \hat{\Omega} | \frac{\partial}{\partial t} \psi(t) \rangle + \langle \frac{\partial}{\partial t} \psi(t) | \hat{\Omega} | \psi(t) \rangle = \frac{1}{i \hbar} \langle \psi(t) | [\hat{\Omega}, \hat{H}] | \psi(t) \rangle.$$  

Example: For a conservative system, the application of the above equation for $\hat{\Omega} = \hat{H}_0$ gives the result:

$$\frac{\partial}{\partial t} \langle \psi(t) | \hat{H}_0 | \psi(t) \rangle = 0,$$

which shows that the energy is conserved.
Response Functions from the Polarization

The time-evolution of $P_n(t)$ is determined from the Ehrenfest theorem applied to $\hat{\Omega} = |0\rangle \langle n|$: 

$$\frac{\partial}{\partial t} \langle \bar{\psi}(t)|\hat{\Omega}|\psi(t)\rangle = \frac{1}{i\hbar} \langle \bar{\psi}(t)|[\hat{\Omega}, \hat{H}_0 + \hat{V}(t)]|\psi(t)\rangle.$$ 

Expansion is made with 

$$e^{i\hat{P}(t)\hat{\Omega}}e^{-i\hat{P}(t)} = \hat{\Omega} + i[\hat{P}, \hat{\Omega}] - \frac{1}{2}[\hat{P}, [\hat{P}, \hat{\Omega}]] - \frac{i}{6}[\hat{P}, [\hat{P}, [\hat{P}, \hat{\Omega}]]] + \ldots,$$

and 

$$\langle 0|[\hat{P}, \hat{\Omega}]|0\rangle = -P_n,$$
$$\langle 0|[\hat{P}, [\hat{P}, \hat{\Omega}]]|0\rangle = 0,$$
$$\langle 0|[\hat{P}, [\hat{P}, [\hat{P}, \hat{\Omega}]]]|0\rangle = -4P_n \sum_{m>0} |P_m|^2.$$

as well as 

$$[\hat{\Omega}, \hat{H}_0] = \hbar \omega_n \hat{\Omega}.$$
Perturbation expansion

With

\[ P_n(t) = P_n^{(1)} + P_n^{(2)} + P_n^{(3)} + \cdots , \]

the first-order equation reads

\[ \frac{\partial}{\partial t} \langle 0 | [\hat{P}^{(1)}, \hat{\Omega}] | 0 \rangle = \frac{1}{i\hbar} \langle 0 | [\hat{P}^{(1)}, [\hat{\Omega}, \hat{H}_0]] | 0 \rangle - \frac{1}{\hbar} \langle 0 | [\hat{\Omega}, \hat{V}(t)] | 0 \rangle. \]

or, equivalently,

\[ \frac{\partial}{\partial t} P_n^{(1)} = -i\omega_n P_n^{(1)} + \frac{1}{\hbar} \langle n | \hat{V}(t) | 0 \rangle, \]

which, by direct time-integration, yields

\[ P_n^{(1)} = e^{-i\omega_n t} \int_t^1 \frac{1}{\hbar} \langle n | \hat{V}(t') | 0 \rangle e^{i\omega_n t'} dt' \]

\[ = \frac{1}{i\hbar} \sum_\omega \langle n | \hat{V} \omega | 0 \rangle F_\omega e^{-i\omega t} \frac{e^{i\omega t}}{\omega_n - \omega}. \]
Linear response function

The response functions of the observable $\hat{\Omega}$ are defined by:

$$
\langle \bar{\psi}(t) | \hat{\Omega} | \bar{\psi}(t) \rangle = \langle 0 | \hat{\Omega} | 0 \rangle + \sum_{\omega_1} \langle \langle \hat{\Omega}; \hat{V}_{\omega_1} \rangle \rangle F_{\omega_1} e^{-i\omega_1 t}
$$

$$
+ \frac{1}{2} \sum_{\omega_1 \omega_2} \langle \langle \hat{\Omega}; \hat{V}_{\omega_1}, \hat{V}_{\omega_2} \rangle \rangle F_{\omega_1} F_{\omega_2} e^{-i(\omega_1 + \omega_2) t} + \ldots
$$

We identify:

$$
i \langle 0 | [\hat{P}^{(1)}, \hat{\Omega}] | 0 \rangle = \sum_{\omega} \langle \langle \hat{\Omega}; \hat{V}_{\omega} \rangle \rangle F_{\omega} e^{-i\omega t}
$$

or, equivalently,

$$
\langle \langle \hat{\Omega}; \hat{V}_{\omega} \rangle \rangle = -\frac{1}{\hbar} \sum_{n > 0} \left[ \frac{\langle 0 | \hat{\Omega} | n \rangle \langle n | \hat{V}_{\omega} | 0 \rangle}{\omega n_0 - \omega} + \frac{\langle 0 | \hat{V}_{\omega} | n \rangle \langle n | \hat{\Omega} | 0 \rangle}{\omega n_0 + \omega} \right].
$$
Two-level atom: response function value

Observable: $\hat{\Omega} = \hat{\mu}$
Perturbation: $\hat{V}_\omega = -\hat{\mu}$

$\Delta E = E_b - E_a$ \hspace{1cm} $\Delta E = 0.5 \text{ a.u.}$
$E_b \quad \psi_b$ \hspace{1cm} $\mu_{ab} = 1.0 \text{ a.u.}$
$E_a \quad \psi_a$ \hspace{1cm} $\hbar \omega = 0.1 \text{ a.u.}$

$\alpha(\omega) = \frac{|\mu_{ab}|^2}{\Delta E - \hbar \omega} + \frac{|\mu_{ab}|^2}{\Delta E + \hbar \omega} = 4.16666...$
Secular divergencies

The Rayleigh–Schrödinger expression for the linear response function is:

\[
\langle\langle \hat{\Omega}; \hat{V}_\omega \rangle\rangle = -\frac{1}{\hbar} \sum_n \left[ \frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}_\omega|0\rangle}{\omega_{n0} - \omega} + \frac{\langle 0|\hat{V}_\omega|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega} \right]
\]

This response function is not convergent as \( \omega \to 0 \), and the sum-over-states expression in this form cannot be used in the static limit.

Response functions free of secular divergencies are obtained with derivations based on phase-isolated wave functions.
Overall permutation symmetry

The linear response can be compactly written as

\[
\langle\langle \hat{\Omega}; \hat{V}^{\omega_1} \rangle\rangle = \sum_{\mathcal{P}_{-\sigma,1}} \sum_{n>0} \frac{\langle 0 | \hat{\Omega} | n \rangle \langle n | \hat{V}^{\omega_1} | 0 \rangle}{\omega_{n0} - \omega_{\sigma}}
\]

where \( \omega_\sigma = \omega_1 \) is the sum of optical frequencies and \( \mathcal{P}_{-\sigma,1} \) permutes pairs of operators and frequencies: \((-\omega_\sigma, \hat{\Omega})\) and \((\omega_1, \hat{V}^{\omega_1})\).

Poles and residues

A residue analysis provides a means to obtain excited state properties from the ground state response function. The poles equal excitation energies and the residues are given by

\[
\lim_{\omega_1 \to -\omega_{f0}} (\omega_{f0} - \omega_1) \langle\langle \hat{\Omega}; \hat{V}^{\omega_1} \rangle\rangle = \langle 0 | \hat{\Omega} | f \rangle \langle f | \hat{V}^{\omega_1} | 0 \rangle
\]
First-order nonlinear response functions

The first-order nonlinear response function comprises six terms:

\[
\langle \langle \hat{\Omega}; \hat{V}_{\omega_1}, \hat{V}_{\omega_2} \rangle \rangle = \frac{1}{\hbar^2} \sum P_{1,2} \sum_{n,k>0} \times \\
\left[ \frac{\langle 0|\hat{\Omega}|n\rangle \langle n|\hat{V}_{\omega_1}|k\rangle \langle k|\hat{V}_{\omega_2}|0\rangle}{[\omega_{n0} - (\omega_1 + \omega_2)][\omega_{k0} - \omega_2]} + \frac{\langle 0|\hat{V}_{\omega_2}|n\rangle \langle n|\hat{V}_{\omega_1}|k\rangle \langle k|\hat{\Omega}|0\rangle}{[\omega_{n0} + \omega_2][\omega_{k0} + (\omega_1 + \omega_2)]} + \frac{\langle 0|\hat{V}_{\omega_1}|n\rangle \langle n|\hat{\Omega}|k\rangle \langle k|\hat{V}_{\omega_2}|0\rangle}{[\omega_{n0} + \omega_1][\omega_{k0} - \omega_2]} \right]
\]

where the overbar denotes a fluctuation operator in accordance with \( \overline{\hat{\Omega}} = \hat{\Omega} - \langle 0|\hat{\Omega}|0\rangle \).
Overall permutation symmetry

The nonlinear response can be compactly written as

\[
\langle \langle \hat{\Omega}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle \rangle = \frac{1}{\hbar^2} \sum \mathcal{P}_{-\sigma,1,2} \times \sum_{n,k>0} \frac{\langle 0 | \hat{\Omega} | n \rangle \langle n | \hat{V}^{\omega_1} | k \rangle \langle k | \hat{V}^{\omega_2} | 0 \rangle}{[\omega_{n0} - \omega_{\sigma}][\omega_{k0} - \omega_{2}]}
\]

where \( \omega_{\sigma} = \omega_1 + \omega_2 \) is the sum of optical frequencies.

Second-order residue

A residue analysis provides a means to obtain excited state properties from the ground state response function:

\[
\lim_{\omega_1 \to -\omega_{f0}} (\omega_{f0} + \omega_1) \left[ \lim_{\omega_2 \to \omega_{g0}} (\omega_{g0} - \omega_2) \langle \langle \hat{\Omega}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle \rangle \right] = \langle 0 | \hat{V}^{\omega_1} | f \rangle \langle f | \hat{\Omega} | g \rangle \langle g | \hat{V}^{\omega_2} | 0 \rangle.
\]
Excited state properties with Dalton2015

Transition Moments

**DALTON INPUT
.RUN RESPONSE
**WAVE FUNCTION
.DFT
   B3LYP
**RESPONSE
*LINEAR
.DIPLEN
.SINGLE RESIDUE
.ROOTS
  10
*END OF INPUT

Excited State Dipole Moment

**DALTON INPUT
.RUN RESPONSE
**WAVE FUNCTION
.DFT
   B3LYP
**RESPONSE
*PROPAVE
.ZDIPLEN
*QUADRATIC
.DIPLEN
.DOUBLE RESIDUE
.ROOTS
  10
*END OF INPUT
Response Functions from the Quasi-Energy

\[
\frac{dQ(t)}{dF_\omega} = \langle \bar{\psi} | \frac{\partial \hat{H}}{\partial F_\omega} | \bar{\psi} \rangle + \delta Q(t) = \langle \bar{\psi} | \frac{\partial \hat{H}}{\partial F_\omega} | \bar{\psi} \rangle - i\hbar \frac{\partial}{\partial t} \langle \bar{\psi} | \frac{d\bar{\psi}}{dF_\omega} \rangle,
\]

Since

\[
\frac{1}{T} \int_0^T \dot{f}(t) dt = 0
\]

for any periodic function \( f(t) \) with period time \( T \), we have, for

\[
Q_T = \frac{1}{T} \int_t^{t+T} Q(t') \, dt',
\]

that the time-dependent variational principle reduces to

\[
\delta Q_T = 0.
\]

and the time-dependent Hellmann–Feynman theorem assumes the form

\[
\frac{dQ_T}{dF_\omega} = \frac{1}{T} \int_t^{t+T} \langle \bar{\psi}(t') | \frac{\partial \hat{H}}{\partial F_\omega} | \bar{\psi}(t') \rangle \, dt'.
\]
Field amplitude expansion of $Q_T$

After time averaging, only the non-oscillating component in $Q(t)$ survives, and $Q_T$ is thus the zero-frequency Fourier amplitude of the quasi-energy. The function $Q_T$ is expanded in the amplitudes according to

$$Q_T(F^\omega) = E_0 + \sum_{\omega_a} \left. \frac{dQ_T}{dF^\omega_a} \right|_{F^\omega=0} F^\omega_a + \frac{1}{2} \sum_{\omega_a \omega_b} \left. \frac{d^2 Q_T}{dF^\omega_a dF^\omega_b} \right|_{F^\omega=0} F^\omega_a F^\omega_b \ldots$$

The expansion coefficients in this expansion of $Q_T$ can be identified as corresponding to molecular properties due to the time-dependent Hellmann–Feynman theorem

$$\frac{dQ_T}{dF^\omega} = \frac{1}{T} \int_t^{t+T} \langle \bar{\psi}(t') | \frac{\partial \hat{H}}{\partial F^\omega} | \bar{\psi}(t') \rangle \, dt'$$
Variational principle for quasi-energy

Variational principle:
\[ \delta Q_T = 0. \]

We understand \( Q_T \) as a function:
\[ Q_T(P_n^{(1)}(\omega_a), [P_n^{(1)}(-\omega_a)]^*, P_n^{(2)}(\omega_a, \omega_b), [P_n^{(2)}(-\omega_a, -\omega_b)]^*, ..., F^{\omega_a}, F^{\omega_b}, ...). \]

Due to the variational principle, we have vanishing derivative w.r.t. the Fourier amplitudes:
\[ \frac{\partial Q_T}{\partial P_n^{(1)}} = 0; \quad \frac{\partial Q_T}{\partial [P_n^{(1)}]^*} = 0; \quad \frac{\partial Q_T}{\partial P_n^{(2)}} = 0; \quad \frac{\partial Q_T}{\partial [P_n^{(2)}]^*} = 0; \quad \cdots. \]
The first-order response in parameters is obtained from:

\[
\frac{d}{dF_a} \frac{\partial Q}{\partial P_n} \bigg|_{F^0} = \frac{\partial^2 Q}{\partial F_a \partial P_n} \bigg|_{F^0} + \sum_m \left[ \frac{\partial^2 Q}{\partial P_m} \frac{\partial P_m}{\partial F_a} + \frac{\partial^2 Q}{\partial P_m} \frac{\partial P_m^*}{\partial F_a} \right] \bigg|_{F^0} = 0,
\]

\[
\frac{d}{dF_a} \frac{\partial Q}{\partial P_m^*} \bigg|_{F^0} = \frac{\partial^2 Q}{\partial F_a \partial P_m^*} \bigg|_{F^0} + \sum_m \left[ \frac{\partial^2 Q}{\partial P_m^*} \frac{\partial P_m}{\partial F_a} + \frac{\partial^2 Q}{\partial P_m^*} \frac{\partial P_m^*}{\partial F_a} \right] \bigg|_{F^0} = 0,
\]

or, with a short-hand notation,

\[
P^a = - \left[ Q_T^{2;0} \right]^{-1} Q_T^{1;a}
\]

\[
\begin{pmatrix}
\frac{\partial P_m^*}{\partial F_a} \bigg|_{F^0} \\
\frac{\partial P_m}{\partial F_a} \bigg|_{F^0}
\end{pmatrix} = - \begin{pmatrix}
\frac{\partial^2 Q}{\partial P_m \partial P_m^*} \bigg|_{F^0} \\
\frac{\partial^2 Q}{\partial P_m^* \partial P_m} \bigg|_{F^0}
\end{pmatrix}^{-1} \begin{pmatrix}
\frac{\partial^2 Q}{\partial F_a \partial P_m} \bigg|_{F^0} \\
\frac{\partial^2 Q}{\partial F_a \partial P_m^*} \bigg|_{F^0}
\end{pmatrix}
\]
The first and second-order derivative become:

\[
\frac{dQ_T}{dF^{\omega_a}} \bigg|_{F^{\omega}=0} = Q_T^{0;\text{a}} + Q_T^{1;0} P^a = Q_T^{0;\text{a}}
\]

\[
\frac{d^2 Q_T}{dF^{\omega_a} dF^{\omega_b}} \bigg|_{F^{\omega}=0} = Q_T^{0;ab} + Q_T^{1;a} P^b = Q_T^{1;a} P^b
\]

We here used the variational principle (which leads to \(Q_T^{1;0} = 0\)) and the fact that there is no second-order field dependence in the Hamiltonian (which leads to \(Q_T^{0;ab} = 0\)).

We get an expression for the linear response function that reads as

\[
\langle \langle \hat{V}^{\omega_a}, \hat{V}^{\omega_b} \rangle \rangle = -[Q_T^{1;a}]^\dagger \left[ Q_T^{2;0} \right]^{-1} Q_T^{1;b}.
\]
\[ Q(t) = \langle \tilde{\psi} | \hat{H}_0 + \hat{V}(t) - i\hbar \frac{\partial}{\partial t} | \tilde{\psi} \rangle \]
\[ = \langle 0 | \hat{Q} | 0 \rangle + i\langle 0 | [\hat{P}(t), \hat{Q}] | 0 \rangle - \frac{1}{2} \langle 0 | [\hat{P}(t), [\hat{P}(t), \hat{Q}]] | 0 \rangle + \ldots, \]

\[ Q_{T}^{1:b} = i \left[ -\langle 0 | \hat{V}_{\omega b} | n \rangle \right] \delta_{\omega_a + \omega_b}; \quad Q_{T}^{2:0} = \left( E^{[2]} - \hbar \omega_a S^{[2]} \right) \delta_{\omega_a + \omega_b}, \]

\[ E^{[2]} = \begin{pmatrix} \hbar \omega_{n0} \delta_{nm} & 0 \\ 0 & \hbar \omega_{n0} \delta_{nm} \end{pmatrix} \delta_{\omega_a + \omega_b}; \quad S^{[2]} = \begin{pmatrix} \delta_{nm} & 0 \\ 0 & -\delta_{nm} \end{pmatrix} \delta_{\omega_a + \omega_b}. \]

\[ \langle \langle \hat{V}_{\omega a}; \hat{V}_{\omega b} \rangle \rangle = -\frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle 0 | \hat{V}_{\omega a} | n \rangle \langle n | \hat{V}_{\omega b} | 0 \rangle}{\omega_{n0} - \omega_b} + \frac{\langle 0 | \hat{V}_{\omega b} | n \rangle \langle n | \hat{V}_{\omega a} | 0 \rangle}{\omega_{n0} - \omega_a} \right] \delta_{\omega_a + \omega_b}. \]
Summary: perturbation theory expansions

- Response functions identified from perturbation theory expansions equal sum-over-states expressions.
- In exact state theory, response function expressions are identical regardless of whether an Ehrenfest or quasi-energy approach is taken.
- An understanding is provided as to how response properties depend on excitation energies and transition moments, which allows for rational material design.
- With use of phase isolated wave functions, response functions are free of secular divergencies.
- From residue analyses of ground state response functions we are able to identify excited state properties.
- A typical calculation of an excitation energy is made by finding a pole of the linear response function (polarizability) rather than an eigenvalue of the molecular Hamiltonian.
Resonant fields

\[ b \]
\[ \Delta E = 0.5 \text{ a.u.} \]
\[ \mu_{ab} = 1.0 \text{ a.u.} \]
\[ a \]
\[ \psi(0) = \psi_a \]

\[ F(t) = F^\omega \sin(\omega t) \]

\[ i \dot{\psi}(t) = H \psi(t) \]
\[ H = H_0 - \mu F(t) \]

What happens if \( \hbar \omega = \Delta E \)?
Resonances of the linear response function

\[ \alpha(\omega) = \frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle 0|\hat{\mu}|n\rangle \langle n|\hat{\mu}|0\rangle}{\omega_{n0} - \omega} + \frac{\langle 0|\hat{\mu}|n\rangle \langle n|\hat{\mu}|0\rangle}{\omega_{n0} + \omega} \right] \]
\[ \rho_B(t) = \frac{1}{\hbar^2} |\langle f| \hat{V}^\omega |0\rangle F^\omega| \] \[ \times t^2 \]
Rabi Oscillations
Relaxation
Density matrix formalism

The density operator is defined as

\[ \hat{\rho} = \sum_s p(s) |\psi_s(t)\rangle \langle \psi_s(t)|, \]

where the sum denoted a classical ensemble average. If all systems in the ensemble are identical then the summation contains a single term with unit probability.

With wave function expansions in the form of projections onto the eigenstates

\[ |\psi_s(t)\rangle = \sum_n c^s_n(t) |n\rangle, \]

the matrix elements of the density operator becomes equal to

\[ \rho_{mn} = \sum_s p(s) c^s_m c^n_{s*}. \]
Coherence

An ensemble of systems with equal state populations, but for which the phases of the wave function components varies in an incoherent manner, will have vanishing elements $\rho_{mn}$ ($m \neq n$):

$$\rho = \frac{1}{2} \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

An ensemble that can be described by a single wave function, on the other hand, is fully coherent and is said to be in pure state:

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left( e^{i\phi_a} |\psi_a\rangle + e^{i\phi_b} |\psi_b\rangle \right)$$

with a density matrix:

$$\rho = \frac{1}{2} \times \begin{pmatrix} 1 & e^{i(\phi_a-\phi_b)} \\ e^{i(\phi_b-\phi_a)} & 1 \end{pmatrix}.$$
Time evolution and the Liouville equation

Let us consider a pure state situation. Then

\[ \frac{\partial}{\partial t} \hat{\rho} = |\frac{\partial}{\partial t} \psi \rangle \langle \psi | + |\psi \rangle \langle \frac{\partial}{\partial t} \psi | \]

\[ = \frac{1}{i\hbar} [H, \hat{\rho}], \]

which is known as the Liouville equation. For all intents and purposes, this equation provides an identical description of the QM system as if one chooses to work with the Schrödinger equation and a wave function approach.

The difference lies in the possibility to modify the Liouville equation as to treat effects of spontaneous and collision-induced relaxation and heat bath interactions.
Liouville equation with relaxation

\[
\frac{\partial}{\partial t} \rho_{mn} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]_{mn} - \gamma_{mn}(\rho_{mn} - \rho_{mn}^{\text{eq}})
\]

The diagonal elements of the damping parameter matrix will govern the spontaneous population decays:

\[
\tau_n = 1/\gamma_{nn}; \quad \Gamma_n = \gamma_{nn}, \quad n \neq 0; \quad \Gamma_0 = 0
\]

we can, for a pure state, draw a conclusion that the off-diagonal elements of the density matrix will depend on time according to

\[
|\rho_{mn}(t)| = |c_m(t)c_n^*(t)| = |c_m(0)c_n^*(0)|e^{-(\Gamma_m + \Gamma_n)t/2},
\]

and we must therefore have

\[
\gamma_{mn} = (\Gamma_m + \Gamma_n)/2.
\]
Time propagation of density matrix

\[ \frac{\partial}{\partial t} \rho_{mn} = \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]_{mn} - \gamma_{mn}(\rho_{mn} - \rho_{mn}^{eq}) \]

Initialization

\[
H = \begin{bmatrix}
Ea & 0 \\
0 & Eb
\end{bmatrix}
\]

\[
u = \begin{bmatrix}
0 & \mu_{ab} \\
\mu_{ba} & 0
\end{bmatrix}
\]

\[F = Fw \sin(w \cdot t) \cdot \text{erf}\]

\[
rho_{eq} = \begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\]

\[
rho[:, :, 0] = \begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\]

Time Propagation

for \( k \) in range(1, n):

\[
rho[:, :, k] = rho[:, :, k-1] - \delta \cdot 1.0j \cdot (\dot{\rho} - \rho^{eq})
\]

\[
P[k] = \text{dot(rho[:, :, k], mu).trace()}
\]

\[
popa = rho[0, 0, :]
\]

\[
popb = rho[1, 1, :]
\]
\[
\rho(0) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}; \quad \rho_{eq} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \quad \gamma = \Gamma \times \begin{pmatrix} 1 & 1/2 \\ 1/2 & 1 \end{pmatrix}
\]
Induced polarization in two-level atom (resonant field, relaxation)

\[ \Gamma = 0.025 \text{ a.u.} \]
\[ \alpha = i \frac{\max[\mu(t)]}{F \omega} \approx 80i \text{ a.u.} \]
Density matrix from perturbation theory

\[ \rho_{mn}(t) = \rho_{mn}^{(0)} + \rho_{mn}^{(1)} + \rho_{mn}^{(2)} + \ldots \]

with

\[ \rho_{mn}^{(0)} = \delta_{m0}\delta_{n0} \]

leads to

\[ \rho_{mn}^{(N)} = e^{-(i\omega_{mn}+\gamma_{mn})t} \int_{-\infty}^{t} \frac{1}{i\hbar} [\hat{V}, \hat{\rho}^{(N-1)}]_{mn} e^{(i\omega_{mn}+\gamma_{mn})t'} dt'. \]

From

\[ \langle \hat{\Omega} \rangle^{(1)} = \text{Tr}(\hat{\rho}^{(1)}\hat{\Omega}) \]

we identify the linear response function as

\[ \langle \langle \hat{\Omega}; \hat{V}^{\omega} \rangle \rangle = -\frac{1}{\hbar} \sum_n \left[ \frac{\langle 0|\hat{\Omega}|n\rangle\langle n|\hat{V}^{\omega}|0\rangle}{\omega_{n0} - \omega - i\gamma_{n0}} + \frac{\langle 0|\hat{V}^{\omega}|n\rangle\langle n|\hat{\Omega}|0\rangle}{\omega_{n0} + \omega + i\gamma_{n0}} \right]. \]
Two-level atom: response function value

Observable: \( \hat{\Omega} = \hat{\mu} \)

Perturbation: \( \hat{V}_\omega = -\hat{\mu} \)

\[ \Delta E = E_b - E_a \quad \Delta E = 0.5 \text{ a.u.} \]

\[ E_b \quad \psi_b \quad \mu_{ab} = 1.0 \text{ a.u.} \]

\[ E_a \quad \psi_a \quad \hbar\omega = 0.5 \text{ a.u.} \]

\[ \hbar\gamma = 0.0125 \text{ a.u.} \]

\[ \alpha(\omega) = \frac{|\mu_{ab}|^2}{\Delta E - \hbar\omega - i\hbar\gamma} + \frac{|\mu_{ab}|^2}{\Delta E + \hbar\omega + i\hbar\gamma} \approx \frac{|\mu_{ab}|^2}{-i\hbar\gamma} = 80i \]
Complex Polarizability

\[ \alpha(-\omega;\omega) \]

![Graph of complex polarizability with FWHM = \(\Gamma\).](image)

**Real part**

**Imag part**

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \]

\[ \omega \]

FWHM = \(\Gamma\)
\[
\langle \langle \hat{A}; \hat{V} \rangle \rangle_z = -\frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle 0 | \hat{A} | n \rangle \langle n | \hat{V} | 0 \rangle}{\omega_n - z - i\gamma_n} + \frac{\langle 0 | \hat{V} | n \rangle \langle n | \hat{A} | 0 \rangle}{\omega_n + z + i\gamma_n} \right]
\]

- Linear response function is convergent for all real frequencies (but will be complex).
- No poles in the upper half plane in required for causal propagators.
Relaxation in wave function theory

\[ \hat{H}_0 = \begin{pmatrix} E_0 & 0 & \cdots & 0 \\ 0 & E_1 + i\Gamma_1/2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_n + i\Gamma_n/2 \end{pmatrix} \]

- Requires a resolution of all states
- Non-Hermitian Hamiltonian is not norm conserving
Apply the Ehrenfest theorem to $\hat{\Omega} = |n\rangle \langle m|$: 

$$\frac{\partial}{\partial t} \langle m | \psi(t) \rangle \langle \psi(t) | n \rangle = \frac{1}{i\hbar} \left[ \langle m | \hat{H} | \psi(t) \rangle \langle \psi(t) | n \rangle - \langle m | \psi(t) \rangle \langle \psi(t) | \hat{H} | n \rangle \right].$$

The above equation is thus a mere repetition of the Liouville equation for density matrix element $\rho_{mn}$, and a suitable equation-of-motion with relaxation in wave function theory is:

$$\frac{\partial}{\partial t} \langle \psi | \hat{\Omega}_{nm} | \psi \rangle = \frac{1}{i\hbar} \langle \psi | [\hat{\Omega}_{nm}, \hat{H}] | \psi \rangle - \gamma_{mn} \left[ \langle \psi | \hat{\Omega}_{nm} | \psi \rangle - \langle \psi^{eq} | \hat{\Omega}_{nm} | \psi^{eq} \rangle \right].$$
Linear response functions

Molecular spectroscopies are interpreted as responses to electromagnetic fields or geometric perturbations. The linear responses of a molecular property to a perturbation are given by

$$\langle\langle \hat{A}; \hat{V} \rangle\rangle_\omega = -\frac{1}{\hbar} \sum_{n>0} \left[ \frac{\langle 0 | \hat{A} | n \rangle \langle n | \hat{V} | 0 \rangle}{\omega_n - \omega - i\gamma_{n0}} + \frac{\langle 0 | \hat{V} | n \rangle \langle n | \hat{A} | 0 \rangle}{\omega_n + \omega + i\gamma_{n0}} \right]$$

**Spectroscopies and linear response functions**

- Polarizability: $\langle\langle \hat{\mu}; \hat{\mu} \rangle\rangle_\omega$
- Magnetizability: $\langle\langle \hat{m}; \hat{m} \rangle\rangle_0$
- Optical rotation: $\langle\langle \hat{\mu}; \hat{m} \rangle\rangle_\omega$
- Electronic circular dichroism: $\langle\langle \hat{\mu}; \hat{m} \rangle\rangle_{\omega_f}$
- IR intensities: $\langle\langle \hat{\mu}; \partial \hat{H}_0 / \partial R \rangle\rangle_\omega$
- NMR parameters: ...


Nonlinear response functions

The nonlinear responses of a molecular property to a perturbation are given by

\[
\langle\langle \hat{A}; \hat{V}, \hat{V} \rangle\rangle_{\omega_1, \omega_2} = \frac{1}{\hbar^2} \sum_{P_{1,2}} \sum_{n,k>0} \left[ \frac{\langle 0|\hat{A}|n \rangle \langle n|\hat{V}_{\omega_1}|k \rangle \langle k|\hat{V}_{\omega_2}|0 \rangle}{[\omega_k - \omega_2 - i\gamma_{k0}][\omega_n - (\omega_1 + \omega_2) - i\gamma_{n0}]} + \frac{\langle 0|\hat{V}_{\omega_2}|k \rangle \langle k|\hat{V}_{\omega_1}|n \rangle \langle n|\hat{A}|0 \rangle}{[\omega_k + \omega_2 + i\gamma_{k0}][\omega_n + (\omega_1 + \omega_2) + i\gamma_{n0}]} \right] + \frac{\langle 0|\hat{V}_{\omega_1}|n \rangle \langle n|\hat{A}|k \rangle \langle k|\hat{V}_{\omega_2}|0 \rangle}{[\omega_n + \omega_1 + i\gamma_{n0}][\omega_k - \omega_2 - i\gamma_{k0}]} \]
Summary

- Molecular properties are defined by expansions of energy, quasi-energy, polarization, magnetization, etc. in orders of field amplitudes.
- The diagonal elements of the electronic Hessian contains excitation energies.
- Use of explicitly unitary parameterizations embeds the requirement of conserving the norm of the wave function.
- Use of phase-isolated wave functions in expansions yields response functions that are free of secular divergencies.
- The first variation in the time-averaged quasi-energy is zero, in accordance with the first variation of the energy in the time-independent case.
- The time-dependent Hellmann–Feynman theorem connects the quasi-energy with molecular properties.
- Nonresonant response functions are overall symmetric.
- Poles and residues of response functions are connected to excited state properties.
- With spontaneous relaxation, excited state populations may remain small under resonance conditions. The corresponding response functions become complex.