5. Theoretical Model for Molecular Vibronics

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Potential Energy Surface

When we treat molecules by quantum mechanics, the nuclei are often assumed to be fixed due to their large mass.

This allows us to solve the Schrödinger for only electrons, under the electrostatic field created by nuclei (Born-Oppenheimer approximation)

The calculation yields multiple energy eigenvalues, each of which is a function of nuclear coordinates.

Collecting these eigenvalues for different molecular geometry leads to the concept of (adiabatic) potential energy surface (PES).

Transition between different PESs are called non-adiabatic transition.

Potential Energy Surface

The structure of a molecule can be represented by a vector

$$\vec{R} = \sum_{j=1}^{3N_{\text{atom}}} R_j \mathbf{e}_j,$$

where $\{\mathbf{e}_j\}$ are the unit vectors along the generalized nuclear coordinates $\{r_j\}$ and $\{R_j\}$ are the corresponding displacements.

If we express an adiabatic PES by $V(\vec{R})$, its gradient vector $\mathbf{g}$ becomes zero at the PES minimum $\vec{R}_0$,

$$\mathbf{g}(\vec{R}_0) = \nabla V(\vec{R}_0) = \sum_{j=1}^{3N_{\text{atom}}} \frac{\partial V(\vec{R})}{\partial r_j}\bigg|_{\vec{R}=\vec{R}_0} \mathbf{e}_j = 0.$$

Normal Modes

The Hessian matrix $\mathbf{H}$ of a PES is composed of its second derivatives, so that

$$H_{jk}(\vec{R}_0) = \frac{\partial^2 V(\vec{R})}{\partial r_j \partial r_k}\bigg|_{\vec{R}=\vec{R}_0}.$$

Diagonalization of $\mathbf{H}$ leads to the eigenvalues $\{\lambda_n\}$ and (normalized) eigenvectors $\{\mathbf{x}_n\}$.

By recalling that the PES for an 1-dimensional harmonic oscillator is $V(R) = m\omega^2 R^2/2$, we can model the molecular PES as

$$V(x_1,\, x_2,\, \cdots,\, x_n) = \sum_{n=1}^{3N_{\mathrm{atom}}} \frac{\lambda_n x_n^2}{2},$$

where x_n is the coordinate along $\mathbf{x}_n$.

Normal Modes

In short, the diagonalization of the Hessian matrix lets us approximate the PES in terms of independent harmonic oscillators.

Of the $3N_{\mathrm{atom}}$ coordinates along the eigenvector directions, 6 are translational and rotational coordinates which does not change energy

These coordinates correspond to zero eigenvalues, and therefore can be easily excluded from our consideration

The remaining $3N_{\mathrm{atom}} - 6$ coordinates are called normal modes, and can be routinely obtained by quantum chemistry calculations

Note that the normal modes are generally different for different adiabatic PESs.

Harmonic Approximation of PES

The harmonic oscillator-based description of PES is appropriate when the molecule does not undergo any drastic structural fluctuations.

This is satisfied when the molecule does not undergo bond dissociation, have freely rotating dihedrals, etc.

As a result, the harmonic description becomes less appropriate as we move up to electronic excited states.

However, for a few biological chromophore molecules, this description often remains accurate for chemically relevant electronic states.

Vibrational Hamiltonian

Based on our observation, we can write the nuclear Hamiltonian as

$$H_{\text{vib}} = \sum_j \left(\frac{p_j^2}{2\mu_j} + \frac{\mu_j \omega_j^2 x_j^2}{2} \right).$$

We switch to the corresponding mass-weighted coordinate, by applying substitutions $p_j' = p_j/\sqrt{\mu_j}$ and $x_j' = \sqrt{\mu_j} x_j$. The result is

$$H_{\text{vib}} = \sum_j \left(\frac{p_j'^2}{2} + \frac{\omega_j^2 x_j'^2}{2} \right).$$

The corresponding quantum mechanical Hamiltonian operator is

$$\hat{H}_{\text{vib}} = \sum_j \left(\frac{\hat{p}_j'^2}{2} + \frac{\omega_j^2 \hat{x}_j'^2}{2} \right).$$

Vibrational Hamiltonian

Note that the mass-weighted operators still satisfy the commutation relation $[\hat{x}'_j, \hat{p}'_j] = i\hbar$.

From now on, we will drop prime (′) from the operators.

If we represent the harmonic oscillators with ladder operators, the Hamiltonian becomes

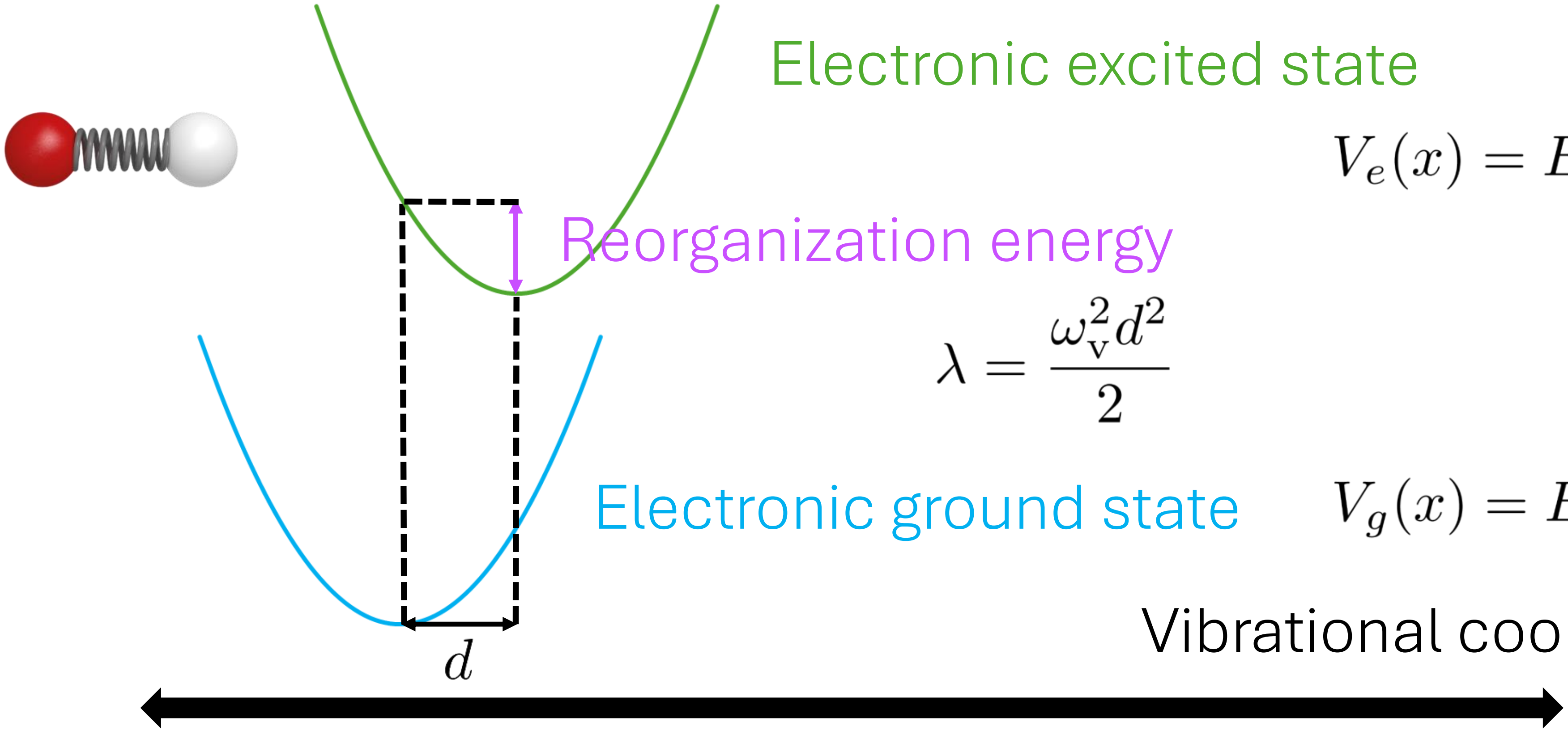
$$\hat{H}_{\mathrm{vib}} = \sum_j \hbar\omega_j \left(\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2} \right),$$

where

$$\hat{a}_j = \sqrt{\frac{\omega_j}{2\hbar}}\hat{x}_j + \frac{i}{\sqrt{2\hbar\omega_j}}\hat{p}_j, \quad \hat{a}_j^\dagger = \sqrt{\frac{\omega_j}{2\hbar}}\hat{x}_j - \frac{i}{\sqrt{2\hbar\omega_j}}\hat{p}_j.$$

Displaced Harmonic Oscillator PES

Individual electronic PESs have different energy minima, which is illustrated by the figure below:



Electronic excited state

$$V_e(x) = E_e + \frac{\omega_\mathrm{v}^2 (x-d)^2}{2}$$

Reorganization energy

$$\lambda = \frac{\omega_\mathrm{v}^2 d^2}{2}$$

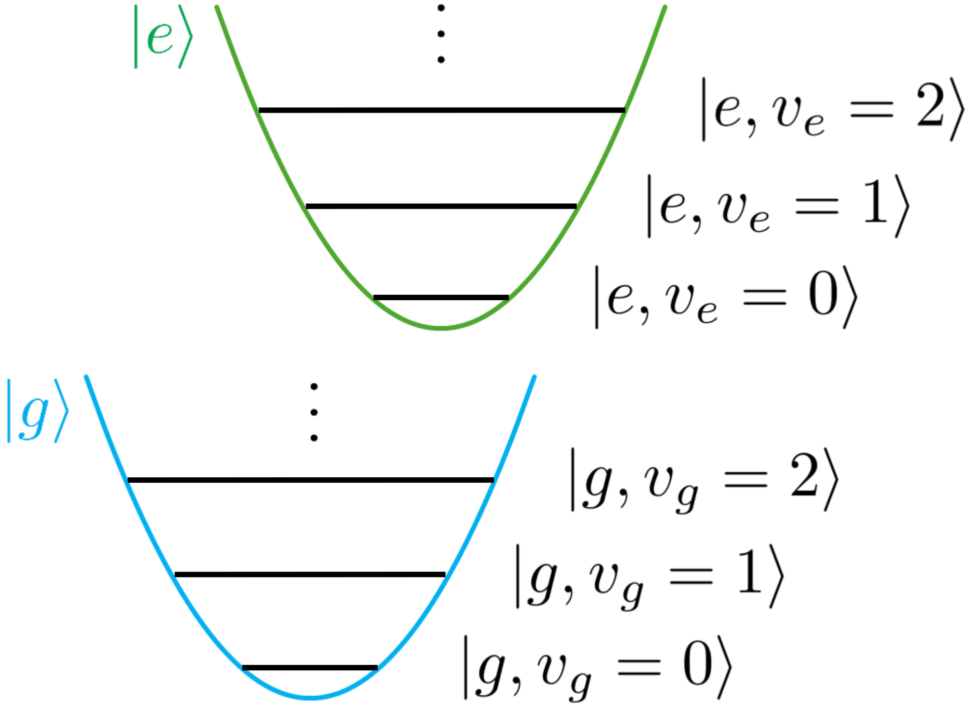
Electronic ground state

$$V_g(x) = E_g + \frac{\omega_\mathrm{v}^2 x^2}{2}$$

Vibrational coordinate

Displaced Harmonic Oscillator PES

We denote the electronic ground and excited states as $|g\rangle$ and $|e\rangle$, which is connected to its own harmonic PES.



$$E = E_e + \hbar\omega_{\mathrm{v}}\left(v_e + \frac{1}{2}\right)$$

$$E = E_g + \hbar\omega_{\mathrm{v}}\left(v_g + \frac{1}{2}\right)$$

Displaced Harmonic Oscillator PES

For a single vibrational coordinate, the electron-nuclear Hamiltonian is written as

$$\hat{H} = \begin{pmatrix} E_g + \hat{h}_g & \vec{\mathcal{E}}(t)\cdot\vec{\mu} \\ \vec{\mathcal{E}}(t)\cdot\vec{\mu} & E_e + \hat{h}_e \end{pmatrix},$$

$$\hat{h}_g = \frac{\hat{p}^2}{2} + \frac{\omega_{\mathrm{v}}^2 \hat{x}^2}{2}, \qquad \hat{h}_e = \frac{\hat{p}^2}{2} + \frac{\omega_{\mathrm{v}}^2 (\hat{x} - d)^2}{2}.$$

We have assumed that the transition dipole moment is independent on the molecular geometry (Condon approximation).

In the absence of the external electromagnetic field,

$$\hat{H}\left|g, v_g\right\rangle = \left[E_g + \hbar\omega_{\mathrm{v}}\left(v_g + \frac{1}{2}\right)\right]\left|g, v_g\right\rangle, \quad \hat{H}\left|e, v_e\right\rangle = \left[E_e + \hbar\omega_{\mathrm{v}}\left(v_e + \frac{1}{2}\right)\right]\left|e, v_e\right\rangle.$$

The Franck-Condon Factor

The vibrational eigenstates for the ground and excited electronic states are not orthonormal due to the displacement between PESs:

$$\langle e, v_e | g, v_g \rangle = C_{v_e, v_g}(d) \neq \delta_{v_e v_g}.$$

The overlap $C_{v_g v_e}(d)$ are called the Franck-Condon (F-C) factor.

As usual, it can be evaluated by casting the overlap in the positional space in terms of wavefunctions.

For $v_g = v_e = 0$, we have

$$C_{0,0}(d) = \sqrt{\frac{\omega_{\mathrm{v}}}{\pi\hbar}} \int_{-\infty}^{\infty} \exp\left(-\frac{\omega_{\mathrm{v}}(x-d)^2}{2\hbar}\right) \exp\left(-\frac{\omega_{\mathrm{v}} x^2}{2\hbar}\right) dx = \exp\left(-\frac{\omega_{\mathrm{v}} d^2}{4\hbar}\right).$$

The Franck-Condon Factor

We now define $s = \omega_{\mathrm{v}} d^2/2\hbar$, which represents the average number of vibrational quanta gained upon excitation from the ground state.

$$C_{0,0}(s) = \exp(-s/2).$$

The parameter s is often called Huang-Rhys factor.

For the F-C factors for higher-lying eigenstates, we can use the recurrence relations (Manneback, C. *Physica* **1951**, *17*, 1001-1010)

$$C_{v_e+1,v_g} = \sqrt{\frac{v_g}{v_e+1}} C_{v_e,v_g-1} - \sqrt{\frac{s}{v_e+1}} C_{v_e,v_g},$$

$$C_{v_e,v_g+1} = \sqrt{\frac{v_e}{v_g+1}} C_{v_e-1,v_g} - \sqrt{\frac{s}{v_g+1}} C_{v_e,v_g}.$$

Vibrational Progression

In Chapter 3, the absorption and fluorescence only occurred at

$$\hbar\omega_0 = E_e - E_g.$$

However, the presence of vibrational modes makes the absorption and fluorescence spectrum is no longer monochromatic.

If we consider the absorption from the ground vibrational eigenstate of the ground electronic state, the absorption occurs at the frequency

$$\begin{aligned}\hbar\omega &= E_e + \hbar\omega_{\mathrm{v}}\left(v_e + \frac{1}{2}\right) - \left(E_g + \frac{\hbar\omega_{\mathrm{v}}}{2}\right) \\ &= \hbar\omega_0 + v_e\hbar\omega_{\mathrm{v}},\end{aligned}$$

with the scaled transition dipole moments $\vec{\mu}' = C_{v_e,0}\vec{\mu}$.

Vibrational Progression

Therefore, the absorption spectrum follows (Fermi's golden rule)

$$I_A(\omega) \propto \sum_{j=0}^{\infty} |C_{j,0}|^2 \delta(\omega - \omega_0 - j\omega_{\mathrm{v}}).$$

Following the same argument for the fluorescence spectrum leads to

$$I_F(\omega) \propto \sum_{j=0}^{\infty} |C_{0,j}|^2 \delta(\omega - \omega_0 + j\omega_{\mathrm{v}}).$$

The F-C factors satisfy the property $C_{j,k} = (-1)^{j+k} C_{k,j}$.

Therefore, the absorption and fluorescence spectra for displaced harmonic PES form mirror images with respect to $\omega = \omega_0$.

Vibrational Progression

In reality, the shape of the spectrum is further complicated by
- presence of multiple vibrational modes
- thermal averages over Boltzmann distribution

Nevertheless, if all vibrational modes follow displaced harmonic oscillator model, it is possible to calculate the exact spectrum by using the line shape function.

For further information, refer to:
- Mukamel, S. Principles of Nonlinear Optical Spectroscopy
- Kim, C. W.; Franco, I. *J. Chem. Phys.* **2021**, *154*, 084109

Anharmonicity or Duschinsky rotation complicates the situation.

Multiple Vibrational Modes

We can approximate the molecular vibrational modes as independent harmonic oscillators and write the Hamiltonian as

$$\hat{H} = \left[E_g + \sum_j \left(\frac{\hat{p}_j^2}{2} + \frac{\omega_j^2 \hat{x}_j^2}{2}\right)\right] |g\rangle \langle g| \\ + \left[E_e + \sum_j \left(\frac{\hat{p}_j^2}{2} + \frac{\omega_j^2 (\hat{x}_j - d_j)^2}{2}\right)\right] |e\rangle \langle e| \\ + [\vec{\mathcal{E}}(t) \cdot \vec{\mu}]\Bigg(|g\rangle \langle e| + |e\rangle \langle g| \Bigg),$$

where $\hat{p}_j$, $\hat{x}_j$, ω_j, and d_j are operators and quantities for the j-th mode.

The Spectral Density

Each characteristic (angular) frequency ω_j corresponds to its own displacement d_j. We define a function in the frequency domain

$$J(\omega) = \sum_j \frac{\omega_j^3 d_j^2}{2} \delta(\omega - \omega_j),$$

which is called spectral density and quantifies the frequency-dependence of the electron-vibrational (vibronic) interaction.

The spectral density and the total reorganization energy Λ is related by

$$\Lambda = \sum_j \lambda_j = \sum_j \frac{\omega_j^2 d_j^2}{2} = \int_0^\infty \frac{J(\omega)}{\omega} d\omega.$$

The Spectral Density

In terms of the ladder operator,

$$
\begin{aligned}
\hat{H} = & \left[E_g + \sum_j \left\{ \hbar\omega_j \left(\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2} \right) \right\} \right] |g\rangle \langle g| \\
& + \left[E_e + \sum_j \hbar\omega_j \left(\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2} \right) + \hbar\gamma_j (\hat{a}_j^\dagger + \hat{a}_j) + \frac{\hbar\gamma_j^2}{\omega_j} \right\} \Bigg] |e\rangle \langle e| \\
& + [\vec{\mathcal{E}}(t) \cdot \vec{\mu}] \Bigg(|g\rangle \langle e| + |e\rangle \langle g| \Bigg),
\end{aligned}
$$

where the coupling constant γ_j follows the relations

$$
\gamma_j = \sqrt{\frac{\omega_j^3 d_j^2}{2\hbar}}, \qquad J(\omega) = \sum_j \hbar\gamma_j^2 \delta(\omega - \omega_j).
$$

Condensed Phase

In the condensed phase, the electronic excitation leads not only to the relaxation of intra-molecular vibrational modes, but also re-orientation of the surrounding solvent molecules.

These behavior occur much more slowly compared to the vibration, and leads to a continuous band at low-frequency region of $J(\omega)$.

Also, the molecular vibration modes are not perfectly harmonic, and behaves much more closer to damped harmonic oscillators.

As a result, the vibrational peaks in $J(\omega)$ are not perfect delta functions, but exhibit finite widths.

Analytical Models of Spectral Density

The relaxation of the solvent is often modeled by Drude-Lorentz spectral density,

$$J_{\mathrm{DL}}(\omega) = \frac{2\Lambda}{\pi} \frac{\omega_{\mathrm{c}}\omega}{\omega^2 + \omega_{\mathrm{c}}^2},$$

which corresponds to monotonous, exponential relaxation with the cutoff frequency ω_{c}.

On the other hand, the molecular vibration is modeled by Brownian oscillator,

$$J_{\mathrm{BO}}(\omega) = \frac{2\Lambda\omega_{\mathrm{c}}}{\pi} \frac{2\omega_0^2\omega}{(\omega^2 - \omega_0^2)^2 + 4\omega_{\mathrm{c}}^2\omega^2}.$$

Realistic Models of Spectral Density

The spectral density of the realistic molecular systems can be extracted by both experimental or computational methods.

Experimental methods:

- Fluorescence line narrowing
- Raman spectroscopy

Computational methods:

- Molecular dynamics

Once constructed, the $J(\omega)$ can be used as it is, or represented as a sum of multiple analytical functions such as Drude-Lorentz and Brownian oscillator.

Absorption and Fluorescence Spectra of Molecules

We have learned that the absorption and fluorescence spectra in the presence of a single vibrational mode is

$$I_A(\omega) \propto \sum_{j=0}^{\infty} |C_{j,0}|^2 \delta(\omega - \omega_0 - j\omega_{\mathrm{v}}),$$

$$I_F(\omega) \propto \sum_{j=0}^{\infty} |C_{0,j}|^2 \delta(\omega - \omega_0 + j\omega_{\mathrm{v}}).$$

To generalize this to multiple modes, we start from the fundamental transition

$$I(\omega) \propto f_0(\omega) = \delta(\omega - \omega_0),$$

which is the monochromatic spectrum without any vibronic coupling.

Absorption and Fluorescence Spectra of Molecules

The next step is to define the phonon sideband for absorption and fluorescence as

$$g_{A,k}(\omega) = \sum_{j=0}^{\infty} |C_{j,0}|^2 \delta(\omega - \omega_k), \qquad g_{F,k}(\omega) = \sum_{j=0}^{\infty} |C_{0,j}|^2 \delta(\omega + \omega_k),$$

where the subscript k distinguishes different vibrational modes.

Then the effect of the first vibrational mode on the spectra can be expressed by convolution integral:

$$f_{A,1}(\omega) = \int_{-\infty}^{\infty} f_0(\omega') g_{A,1}(\omega - \omega')\, d\omega', \quad f_{F,1}(\omega) = \int_{-\infty}^{\infty} f_0(\omega') g_{F,1}(\omega - \omega')\, d\omega'.$$

Absorption and Fluorescence Spectra of Molecules

The effect of subsequent additions of the vibrational modes are expressed by recursion relations,

$$f_{A,k}(\omega) = \int_{-\infty}^{\infty} f_{A,k-1}(\omega')g_{A,k}(\omega - \omega')\,d\omega',$$

$$f_{F,k}(\omega) = \int_{-\infty}^{\infty} f_{F,k-1}(\omega')g_{F,k}(\omega - \omega')\,d\omega'.$$

In nonzero temperatures, the phonon sidebands are generalized as

$$\tilde{g}_{A,k}(\omega,\beta) = \sum_{j=0}^{\infty} \tilde{C}_j(\beta)\delta(\omega - \omega_k), \qquad \tilde{g}_{F,k}(\omega,\beta) = \sum_{j=0}^{\infty} \tilde{C}_j(\beta)\delta(\omega + \omega_k).$$

Still, this scheme is not efficient for realistic systems which involves near-infinite number of modes.

Absorption and Fluorescence Spectra of Molecules

For general systems with arbitrary number of harmonic vibrational modes, we first calculate the line-broadening function from $J(\omega)$,

$$g(t) = \frac{1}{\hbar} \int_0^\infty J(\omega) \left[\coth\left(\frac{\beta \hbar \omega}{2} \right) \frac{1 - \cos(\omega t)}{\omega^2} + i \, \frac{\sin(\omega t) - \omega t}{\omega^2} \right] d\omega .$$

Then, we calculate the two time profiles ($\Delta_{eg} = E_e - E_g$)

$$\mathcal{A}(t) = \exp\left[-\frac{it(\Delta_{eg} + \Lambda)}{\hbar} - g(t) \right], \quad \mathcal{F}(t) = \exp\left[-\frac{it(\Delta_{eg} - \Lambda)}{\hbar} - g^*(t) \right],$$

which can in turn be converted to the spectra by Fourier transform:

$$I_A(\omega) \propto \int_{-\infty}^{\infty} \mathcal{A}(t) e^{-i\omega t} \, dt, \qquad I_F(\omega) \propto \int_{-\infty}^{\infty} \mathcal{F}(t) e^{-i\omega t} \, dt.$$