Chap 4. Time-dependent Method of Fermi's Golden Rule

$$w_{km} = \frac{2\pi}{\hbar}|U_{km}|^2\delta(E_k - E_m \pm \hbar\omega)$$

Molecular systems : $|m\rangle = |i, \nu\rangle \rightarrow |k\rangle = |f, \nu'\rangle \cdots |\text{electrons, nuclei}\rangle$

$$\begin{aligned} U_{f\nu', i\nu} &= \int dR \chi_{f\nu'}(R) \underbrace{\int dr \varphi_f(r;R) U(r,R) \varphi_i(r;R)} \chi_{i\nu}(R) \\ &\equiv \langle \chi_{f\nu'}(R) | \underbrace{\tilde{U}_{fi}(R)} | \chi_{i\nu}(R) \rangle_R \end{aligned}$$

$$\tilde{U}_{fi}(R) \equiv \langle \varphi_{\varepsilon'}(r;R) | U(r,R) | \varphi_{\varepsilon}(r;R) \rangle_r$$

Suppose : we cannot specify the final nuclear quantum state ν'

(e.g., have not sufficient energy resolution, or not interested)

$$w(f \leftarrow i\nu) = \sum_{\nu'} w_{f\nu', i\nu}$$

(Note : normally, vib. rot. energy $\sim k_B T$, electronic energy $\gg k_B T$)

And : thermal average over the initial nuclear states ν

$$w(f \leftarrow i) = \sum_\nu P_{i\nu} w(f \leftarrow i\nu), \qquad P_{i\nu} = e^{-\beta E_{i\nu}}/Z_i$$

(Boltzmann distribution)

- Partition function : ($\Rightarrow$ normalization $\sum_\nu P_{i\nu} = 1$)

$$Z_i = \sum_\nu e^{-\beta E_{i\nu}} = \sum_\nu \langle \nu | e^{-\beta H_i} | \nu \rangle = \mathrm{Tr}_{(\mathrm{nuc})}[e^{-\beta H_i}]$$

[BO approx. $H_e(r;R)\varphi_i(r;R) = W_i(R)\varphi_i(r:R)$
$H_i \chi_{i\nu}(R) = E_{i\nu}\chi_{i\nu}(R)$, where $\underline{H_i \equiv T_N + W_i(R)}$]

- Density operator for nuclear states on adiabatic potential $W_i(R)$

$$\rho_i \equiv e^{-\beta H_i}/Z_i, \quad Z_i = \mathrm{Tr}_{(\mathrm{nuc})}[e^{-\beta H_i}]$$

- Thermal average (on $W_i(R)$) of a quantity $A(R)$

$$\begin{aligned} \langle A \rangle &= \sum_\nu P_{i\nu} \langle \nu | A | \nu \rangle = \sum_\nu \frac{e^{-\beta E_{i\nu}}}{Z_i} \langle \nu | A | \nu \rangle = \sum_\nu \langle \nu | \frac{e^{-\beta H_i}}{Z_i} A | \nu \rangle \\ &= \mathrm{Tr}_{(\mathrm{nuc})}[\rho_i A] \end{aligned}$$

• **Time-dependent form** (Kubo-Toyozawa)

Using : $\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}dt$, (and hence $\delta(\hbar\omega) = \frac{1}{\hbar}\delta(\omega)$)

$$
\begin{aligned}
w(f \leftarrow i\nu) \quad &= \frac{2\pi}{\hbar}\sum_{\nu'} |U_{f\nu',i\nu}|^2 \delta(E_{f\nu'} - E_{i\nu} \pm \hbar\omega) \\
&= \frac{1}{\hbar^2}\sum_{\nu'} |\langle\nu'|\tilde{U}_{fi}|\nu\rangle|^2 \int_{-\infty}^{\infty} dte^{-iE_{f\nu'}t/\hbar} e^{+iE_{i\nu}t/\hbar} e^{\mp i\omega t} \\
&= \frac{1}{\hbar^2}\sum_{\nu'} \int_{-\infty}^{\infty} dt\langle\nu|\tilde{U}^*_{fi}e^{-iH_f t/\hbar}|\nu'\rangle\langle\nu'|\tilde{U}_{fi}e^{iH_i t/\hbar}|\nu\rangle e^{\mp i\omega t} \\
&= \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\langle\nu|\underbrace{\tilde{U}^*_{fi}e^{-iH_f t/\hbar}\tilde{U}_{fi}e^{iH_i t/\hbar}}_{\equiv A \quad \text{(for brevity)}}|\nu\rangle e^{\mp i\omega t}
\end{aligned}
$$

$$
\boxed{w(f \leftarrow i) = \sum_{\nu} P_{i\nu} w(f \leftarrow i\nu) = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\mathrm{Tr}_{(\mathrm{nuc})}[\rho_i A]e^{\mp i\omega t}}
$$

Application - 1 : Vibration / rotation spectra [SR 9.6, 9.7]

In the same electronic state : $H_f = H_i = H$

$$\Rightarrow \tilde{U}_{fi} = \tilde{U}_{ii} \propto \mu \text{ (dipole moment)}$$

Vibration / rotation spectra (absorption)

$$\sigma(\omega) \propto \int_{-\infty}^{\infty} dt \mathrm{Tr}_{(\mathrm{nuc})}[\rho\mu^* \underbrace{e^{-iHt/\hbar}\mu e^{+iHt/\hbar}}_{\mu(-t)\ \text{(Heisenberg rep.)}}]e^{i\omega t}$$

$$= \int_{-\infty}^{\infty} dt \langle \mu^*(0)\mu(-t)\rangle e^{i\omega t}$$

- Vib-rot spectra $\Leftrightarrow$ TCF of vib-rot (thermal) motion

Application - 2 : Electronic spectra, Nonadiabatic transitions

1. Gaussian Wavepacket method
2. Cumulant Expansion method

- **Gaussian Wavepacket** [SR 9.4, 7.3.2]

$$\chi_{p_t,q_t}(q,t) = \exp[\frac{i}{\hbar}\alpha_t(q-q_t)^2 + \frac{i}{\hbar}p_t(q-q_t) + \frac{i}{\hbar}\gamma_t]$$

- $q_t = \langle q \rangle, \;\; p_t = \langle p \rangle$: average position and momenta

  follow classical eq of motion : $\dot{x}_t = \partial H/\partial p_t, \;\; \dot{p}_t = -\partial H/\partial x_t$
- α_t, γ_t : width and phase (time dependent)

  $\dot{\alpha}_t = -(2/m)\alpha_t^2 - V_{xx}/2, \;\; \dot{\gamma}_t = i\hbar\alpha_t/m + p_t\dot{x}_t - E$
- Exact on quadratic potentials

  $V(x) = V_0 + V_x(x - x_t) + \frac{1}{2}V_{xx}(x - x_t)^2$

$$\text{Using : } \mathrm{Tr}_{(\mathrm{nuc})}[A] \rightarrow \frac{1}{h^n} \int dq_0^n dp_0^n \langle \chi_{p_0,q_0} | A | \chi_{p_0,q_0} \rangle$$

$$w(f \leftarrow i) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} C(t) e^{\mp i\omega t} dt$$

$$C(t) \propto \int dq_0^n dp_0^n \langle \chi_{p_0,q_0} | \rho_i \tilde{U}_{fi}^* e^{-iH_f t/\hbar} \tilde{U}_{fi} e^{iH_i t/\hbar} | \chi_{p_0,q_0} \rangle$$

$$= \frac{1}{Z} \int dq_0^n dp_0^n \langle \Phi_i(t - i\beta\hbar) | \Phi_f(t) \rangle$$

$$|\Phi_i(t - i\beta\hbar)\rangle = \tilde{U}_{fi} e^{-iH_i(t - i\beta\hbar)/\hbar} |\chi_{p_0,q_0}\rangle$$

$$|\Phi_f(t)\rangle = e^{-iH_f t/\hbar} \tilde{U}_{fi} |\chi_{p_0,q_0}\rangle$$

1. Propagate wavepackets $|\chi_{p_0,q_0}\rangle$ on H_i and H_f
2. Calculate the overlap $\langle \Phi_i | \Phi_f \rangle$
3. Fourier transform

Cumulant expansion method

- **Condon Approximation :**

Neglect $\mathbf{R}$ dependence of $\tilde{U}_{fi}(\mathbf{R})$

or take 0th term of : $\tilde{U}_{fi}(\mathbf{R}) = \tilde{U}_{fi}(\mathbf{R}_0) + \left(\frac{\partial \tilde{U}_{fi}}{\partial \mathbf{R}}\right)_{\mathbf{R}_0} (\mathbf{R} - \mathbf{R}_0) + \cdots$

$\Rightarrow$

$$w(f \leftarrow i) = \frac{1}{\hbar^2} |\tilde{U}_{fi}(\mathbf{R}_0)|^2 \int_{-\infty}^{\infty} dt \langle \underbrace{e^{-iH_f t/\hbar} e^{+iH_i t/\hbar}} \rangle_i e^{\mp i\omega t}$$

(Time ordered exponential) $\quad \exp_{(-)}[\frac{i}{\hbar} \int_0^t d\tau \Delta V_i(\tau)]$

$$\Delta V \equiv H_f - H_i, \;\; \Delta V_i(t) \equiv e^{-iH_i t/\hbar} \Delta V e^{+iH_i t/\hbar}$$

• Time ordered exponential

$$(f(t) \equiv) \qquad e^{-iH_f t/\hbar} e^{+iH_i t/\hbar} = \exp_{(-)}[\frac{i}{\hbar}\int_0^t d\tau \Delta V_i(\tau)]$$

Note : Since $[H_i, H_f] \neq 0$, $e^{-iH_f t/\hbar} e^{iH_i t/\hbar} \neq e^{-i(H_f - H_i)t/\hbar}$

$$\frac{\partial f}{\partial t} = \frac{i}{\hbar} e^{-iH_f t/\hbar}(H_f - H_i) e^{+iH_i t/\hbar}$$

$$= \frac{i}{\hbar} e^{-iH_f t/\hbar} e^{+iH_i t/\hbar} e^{-iH_i t/\hbar}(H_f - H_i) e^{+iH_i t/\hbar}$$

$$= \frac{i}{\hbar} f(t) \Delta V_i(t)$$

Integrate : $f(t) = f(0) + \frac{i}{\hbar}\int_0^t d\tau f(\tau)\Delta V_i(\tau)$

Sequential expansion $(f(0) = 1)$:

$$f(t) = 1 + \frac{i}{\hbar}\int_0^t d\tau \Delta V_i(\tau) + (\frac{i}{\hbar})^2 \int_0^t d\tau \int_0^\tau d\tau' \Delta V_i(\tau')\Delta V_i(\tau) + \cdots$$

$$\equiv \exp_{(-)}[\frac{i}{\hbar}\int_0^t d\tau \Delta V_i(\tau)] \qquad (\Leftarrow \text{Definition})$$

• **Note** :

The original formula was

$$\begin{aligned} w(f \leftarrow i) &= \sum_{\nu} \sum_{\nu'} P_{i\nu} w(f\nu' \leftarrow i\nu) \\ &= \frac{2\pi}{\hbar} \sum_{\nu} \sum_{\nu'} P_{i\nu} |\langle f\nu' | \tilde{U}_{fi} | i\nu \rangle|^2 \delta(E_{f\nu'} - E_{i\nu} \pm \hbar\omega) \end{aligned}$$

Condon Approx.

$$w(f \leftarrow i) \simeq \frac{2\pi}{\hbar} |\tilde{U}_{fi}(\mathbf{R}_0)|^2 \sum_{\nu} \sum_{\nu'} P_{i\nu} |\langle f\nu' | i\nu \rangle|^2 \delta(E_{f\nu'} - E_{i\nu} \pm \hbar\omega)$$

We will obtain $w(f \leftarrow i)$ in p.7 from the Fourier transform of this.

• If we correctly evaluate $w(f \leftarrow i)$ in p.7, it takes into account of the (thermal average of) the Franck-Condon overlap $|\langle f\nu' | i\nu \rangle|^2$

⇒ Quantum effects of the nuclear motion (e.g., tunneling) are accounted

- **Cumulant expansion**

"average of exponential" → "exponential of averages"

$$\langle e^{i\lambda x} \rangle = e^{i\lambda \langle x \rangle_c + \frac{1}{2}(i\lambda)^2 \langle x^2 \rangle_c + \cdots}$$

[Expand both sides and compare (in order of λ) to find

Cumulant average : $\langle x \rangle_c = \langle x \rangle$

$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2$ (= variance)

$\langle x^3 \rangle_c = \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3$]

Advantages :

- Average of oscillatory function $\langle e^{i\lambda x} \rangle$
  → average first, then place on exponent $e^{i\lambda \langle x \rangle_c} + \cdots$

- Partial sum to infinite order :
  even if the exponent on the right-hand-side is truncated at finite order, terms up to the infinite order in λ is partially included

- In a particular case where the variable x follows Gaussian distribution (Gaussian process), the 3rd and higher order cumulants exactly vanish

- **Cumulant expansion of time-ordered exponential**

$$\langle \exp_{(-)}[\frac{i}{\hbar}\int_0^t d\tau \Delta V(\tau)]\rangle$$
$$= \exp\left[\frac{i}{\hbar}\int_0^t d\tau \langle \Delta V(\tau)\rangle_c + \left(\frac{i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau' \langle \Delta V(\tau')\Delta V(\tau)\rangle_c + \cdots\right]$$

Expand both sides and compare order by order (up to 2nd order) :

$\Rightarrow \langle \Delta V(\tau)\rangle_c = \langle \Delta V(\tau)\rangle = \langle \Delta V(0)\rangle = \langle \Delta V\rangle$ (independent of time in steady-state)

$$\langle \Delta V(\tau')\Delta V(\tau)\rangle_c = \langle \Delta V(\tau')\Delta V(\tau)\rangle - \langle \Delta V\rangle^2 = \langle \delta\Delta V(\tau')\delta\Delta V(\tau)\rangle$$

($\delta\Delta V(t) \equiv \Delta V(t) - \langle \Delta V\rangle$)

- Line-broadening function : $g(t) \equiv \dfrac{1}{\hbar^2}\displaystyle\int_0^t d\tau \int_0^\tau d\tau' \langle \delta\Delta V(\tau')\delta\Delta V(\tau)\rangle$

- In thermal equilibrium : $\langle A(\tau')A(\tau)\rangle = \langle A(0)A(\tau' - \tau)\rangle$

(depends only on the time interval $\tau - \tau'$)

[Verify using $\langle ...\rangle = \mathrm{Tr}\{\rho ...\}$ and Heisenberg rep. of $A(t)$]

Changing integration variable $(\tau, \tau') \rightarrow (\tau', s \equiv \tau - \tau')$: Jacobian = 1

$g(t) = \frac{1}{\hbar^2} \int_0^t ds \int_0^{t-s} d\tau' \langle \delta\Delta V(0) \delta\Delta V(s) \rangle = \frac{1}{\hbar^2} \int_0^t ds (t-s) \langle \delta\Delta V(0) \delta\Delta V(s) \rangle$

Thus,

$$w(f \leftarrow i) = \frac{1}{\hbar^2} |\tilde{U}_{fi}|^2 \int_{-\infty}^{\infty} dt e^{-g_i(t)} e^{i(\langle \Delta V \rangle_i / \hbar \mp \omega) t}$$

$$g_i(t) = \frac{1}{\hbar^2} \int_0^t ds (t-s) \langle \delta\Delta V(0) \delta\Delta V(s) \rangle_i$$

(correct up to 2nd-order cumulant)

- $\langle \Delta V \rangle_i$: average over nuclear motion on potential V_i (electronic state i)
- $\langle \delta\Delta V(0) \delta\Delta V(t) \rangle_i$: TCF = thermal fluctuation of ΔV

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Time correlation functions

$C(t) = \langle \delta A(0) \delta A(t) \rangle$: fluctuation $\delta A(t) = A(t) - \langle A \rangle$

Classical : phase-space distribution function $f(\mathbf{r}, \mathbf{p})$

$$C(t) = \int d\mathbf{r} \int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) \delta A(\mathbf{r}, \mathbf{p}; 0) \delta A(\mathbf{r}, \mathbf{p}; t)$$

Statistical (ensemble) average $\Leftarrow$ distribution of the initial condition $f(\mathbf{r}, \mathbf{p})$

Quantum :

$$C(t) = \mathrm{Tr}[\rho \delta A e^{-iHt/\hbar} \delta A e^{iHt/\hbar}]$$

Thus, $C(-t) = C^*(t) \Rightarrow$ Re $C(-t) =$ Re $C(t)$ ... even,

Im $C(-t) = -$Im $C(t)$ ... odd

In classical mech. $C(t)$ is real and even (for real quantities)

$C(0) = \langle \delta A(0)^2 \rangle \geq 0$ (variance, fluctuation)

When quantity A shows stochastic random motion (eg, in solution phase), $C(t) \to 0$ as $t \to \infty$.

[
- $\delta A(0)$ and $\delta A(t)$ at large t (long time interval) lose mutual correlation, such that both $\delta A(0)\delta A(t) > 0$ and < 0 realize randomly.
- In other words, at long time interval, $\delta A(0)$ and $\delta A(t)$ become "statistically independent", as described by $C(t) \to \langle \delta A(0) \rangle \langle \delta A(t) \rangle = 0 \times 0 = 0$.
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- **Ergodic hypothesis**

Statistical (ensemble) average = average over the time

$$C(t) = \langle \delta A(0)\delta A(t) \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt_0 \delta A(t_0) \delta A(t_0 + t)$$

TCF and spectral line shape

Vib. / rot. spectra : $\sigma(\omega) \propto \int_{-\infty}^{\infty} \langle \mu(t)\mu(0) \rangle e^{i\omega t} dt = \int_{-\infty}^{\infty} C(t) e^{i\omega t} dt$

- **Exponential TCF**

$$C(t) = C(0)e^{-\gamma|t|} \Rightarrow \sigma(\omega) \propto C(0)\frac{2\gamma}{\gamma^2 + \omega^2} \quad \text{(Lorentzian line shape)}$$

- **Gaussian TCF**

$$C(t) = C(0)e^{-\lambda^2 t^2} \Rightarrow \sigma(\omega) \propto C(0)e^{-\omega^2/4\lambda^2} \quad \text{(Gaussian line shape)}$$

- **Damped-oscillating TCF**

(1) $C(t) = C(0)e^{-\gamma|t|} \cdot e^{i\omega_0 t} \Rightarrow \sigma(\omega) \propto \dfrac{2\gamma}{\gamma^2 + (\omega - \omega_0)^2}$

(2) $C(t) = C(0)e^{-\lambda^2 t^2} \cdot e^{i\omega_0 t} \Rightarrow \sigma(\omega) \propto e^{-(\omega - \omega_0)^2/4\lambda^2}$

(Note : oscillatory factor $e^{i\omega_0 t}$ just introduces peak shift)

[Verify by yourself (just elementary integrations!)]

- **<u>Example of Gaussian TCF</u>**

Consider : **dilute solution of dipolar molecules**

Short-time motion $\simeq$ nearly free rotation (with angular velocity Ω)

("inertial motion")

Dipole correlation : $\mu(0)\mu(t) = |\mu|^2 \cos \Omega t$

Kinetic energy of rotation $= I\Omega^2/2$ (I = inertial moment)

$\Rightarrow$ Thermal population of Ω : $P(\Omega)d\Omega \propto e^{-E/k_BT} d\Omega = e^{-I\Omega^2/2k_BT} d\Omega$

(Normalization : $\int_0^\infty P(\Omega)d\Omega = 1 \Rightarrow$ prefactor $2(I/2\pi k_BT)^{1/2}$)

Hence,

$$\langle \mu(0)\mu(t) \rangle = \int_0^\infty P(\Omega)|\mu|^2 \cos \Omega t d\Omega = |\mu|^2 e^{-k_BTt^2/2I}$$

(Gaussian TCF)

• Example of Exponential TCF

Langevin equation (Brownian motion model)

$$m\dot{v} = -m\gamma v + R(t)$$

$(R(t)$: random force, γ : friction coefficient)

$v(0)\times$ and statistical average

$$\langle v(0)\dot{v}(t)\rangle = -\gamma\langle v(0)v(t)\rangle + \frac{1}{m}\langle v(0)R(t)\rangle$$

Define $C(t) \equiv \langle v(0)v(t)\rangle$, and assume $\langle v(0)R(t)\rangle = 0$

(no correlation between $v(0)$ and the random force)

$$\frac{d}{dt}C(t) = -\gamma C(t) \Rightarrow C(t) = C(0)e^{-\gamma t}$$

• <u>Example : Brownian oscillator model</u>

Harmonic oscillator + friction + random force

$$m\ddot{x} = -m\omega_0^2 x - m\gamma\dot{x} + R(t)$$

$$\langle x(0)\ddot{x}(t)\rangle = -\omega_0^2\langle x(0)x(t)\rangle - \gamma\langle x(0)\dot{x}(t)\rangle + \frac{1}{m}\langle x(0)R(t)\rangle$$

$$\ddot{C}(t) + \gamma\dot{C}(t) + \omega_0^2 C(t) = 0$$

$$\Rightarrow C(t) = C(0)(\cos\omega_1 t + \frac{\gamma}{2\omega_1}\sin\omega_1 t)e^{-\gamma t/2}$$

$$(\omega_1^2 \equiv \omega_0^2 - \gamma^2/4\ )$$

$$\begin{cases} \text{(i)} & \omega_0^2 > \gamma^2/4 & : C(t) = \text{damped oscillation} \\ \text{(ii)} & \omega_0^2 = \gamma^2/4 & : C(t) = C(0)(1+\gamma t/2)e^{-\gamma t/2} \\ \text{(iii)} & \omega_0^2 < \gamma^2/4 & : \omega_1 = \text{imaginary} \Rightarrow C(t) = \text{double exponential} \end{cases}$$

[(i) = “under-damped”, (ii, iii) = “over-damped”]

Motional narrowing

(Back to page 14)

$$w(f \leftarrow i) = \frac{1}{\hbar^2}|\tilde{U}_{fi}(\mathbf{R}_0)|^2 \int_{-\infty}^{\infty} e^{-g_i(t)} e^{i(\langle \Delta V \rangle_i/\hbar \mp \omega)t} dt$$

$$g_i(t) = \frac{1}{\hbar^2} \int_0^t d\tau (t-\tau) \langle \delta\Delta V(0) \delta\Delta V(\tau) \rangle_i$$

Assume : Exponential TCF

$$\langle \delta\Delta V(0) \delta\Delta V(\tau) \rangle = D^2 e^{-|t|/\tau_c}$$

- $D^2 = \langle \delta\Delta V(0)^2 \rangle$ ... amplitude of fluctuation
- τ_c ... correlation time

$$\Rightarrow g(t) = \frac{1}{\hbar^2}(D\tau_c)^2 (e^{-|t|/\tau_c} + \frac{|t|}{\tau_c} - 1)$$

1. **Large τ_c case** (long correlation time / slow modulation)

$g(t) \simeq D^2 t^2 / 2\hbar^2$ (short-time expansion in t)

$$\Rightarrow w(f \leftarrow i) = \frac{1}{\hbar^2} |\tilde{U}|^2 \int_{-\infty}^{\infty} e^{-D^2 t^2 / 2\hbar^2} e^{i(\langle \Delta V \rangle_i / \hbar \mp \omega) t} dt$$

$$= \frac{2\sqrt{\pi} |\tilde{U}|^2}{\hbar D} \exp[-\frac{\hbar^2 (\omega \mp \langle \Delta V \rangle_i)^2}{2D^2}] \quad \text{(\textbf{Gaussian line shape})}$$

2. **Short τ_c case** (short correlation time / fast modulation)

$e^{-|t|/\tau_c} + |t|/\tau_c - 1 \simeq |t|/\tau_c$ (long time approximation in t)

$$\Rightarrow w(f \leftarrow i) = \frac{1}{\hbar^2} |\tilde{U}|^2 \int_{-\infty}^{\infty} e^{-D^2 \tau_c |t| / \hbar^2} e^{i(\langle \Delta V \rangle_i / \hbar \mp \omega) t} dt$$

$$= \frac{|\tilde{U}|^2}{\hbar^2} \frac{2\gamma}{\gamma^2 + (\omega \mp \langle \Delta V \rangle_i)^2} \quad \text{(\textbf{Lorentzian line shape})}$$

Width $\propto \gamma \propto \tau_c$ ($\gamma \equiv D^2 \tau_c / \hbar^2$)

- **"motional narrowing"** :

  shorter τ_c (faster fluctuation modulation) $\Rightarrow$ narrower spectra

in general :

$$\begin{cases} \text{near spectral } \textbf{peak} & \sim \text{large } t & \Rightarrow \textbf{Lorentzian shape} \\ \text{near spectral } \textbf{tail} & \sim \text{small } t & \Rightarrow \textbf{Gaussian shape} \end{cases}$$

$$\boxed{\text{Overall shape} \Leftarrow \text{parameter } D\tau_c/\hbar <> 0}$$

- **Physical interpretation**
  - Large τ_c = slow modulation (of the nuclear configuration)

    $\Rightarrow$ ΔV is fixed during the photo absorption/emission

    $\Rightarrow$ distribution of ΔV is directly reflected in the spectral shape
  - Small τ_c = fast modulation

    $\Rightarrow$ fluctuation of ΔV is averaged out in the observation time scale

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