Molecular quantum dynamics: Solutions 9

Exercise 9a: Collisional line broadening

We have to verify that the Fourier transform of the correlation function

$$C(t) = C(0)e^{-\Gamma|t|} \tag{1}$$

has a Lorentzian shape.
We will directly evaluate $\sigma(\omega)$ given in the question:

$$\begin{aligned}\sigma(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} C(t)e^{i\omega t}dt \\ &= \frac{1}{2\pi}C(0)\int_{-\infty}^{\infty} e^{-\Gamma|t|+i\omega t}dt \\ &= \frac{C(0)}{2\pi}\left(\int_{-\infty}^{0} e^{\Gamma t+i\omega t}dt + \int_{0}^{\infty} e^{-\Gamma t+i\omega t}dt\right),\end{aligned} \tag{2}$$

where we have used

$$|t| = \begin{cases} t, & t > 0, \\ -t, & t < 0. \end{cases} \tag{3}$$

We obtain

$$\sigma(\omega) = \frac{C(0)}{2\pi}\left[\int_{0}^{\infty} e^{-(\Gamma+i\omega)\tau}d\tau + \int_{0}^{\infty} e^{-(\Gamma-i\omega)t}dt\right], \tag{4}$$

by making a change of variable:

$$t \to -\tau \tag{5}$$

in the first term.
We then carry out the integration:

$$\begin{aligned}\sigma(\omega) &= \frac{C(0)}{2\pi}\left[\frac{e^{-(\Gamma+i\omega)\tau}}{-(\Gamma+i\omega)}\Big|_0^\infty + \frac{e^{-(\Gamma-i\omega)t}}{-(\Gamma-i\omega)}\Big|_0^\infty\right] \\ &= \frac{C(0)}{2\pi}\left(\frac{1}{\Gamma+i\omega} + \frac{1}{\Gamma-i\omega}\right) \\ &= \frac{C(0)}{2\pi}\left[\frac{\Gamma-i\omega+\Gamma+i\omega}{(\Gamma+i\omega)(\Gamma-i\omega)}\right] \\ &= \frac{C(0)}{2\pi}\cdot\frac{2\Gamma}{\Gamma^2+\omega^2} \\ &= \frac{C(0)}{\pi}\cdot\frac{\Gamma}{\Gamma^2+\omega^2}.\end{aligned} \tag{6}$$

Exercise 9b: Properties of the Fourier transform and convolution

a) We will use the following from the lecture:

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \tag{7}$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(k) e^{ikx} dk \tag{8}$$

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dk. \tag{9}$$

We can obtain the left hand side of the equation by making substitutions for $\tilde{f}(k)$ and $\tilde{g}(k)$ [see Eq. (7)] on the right hand side:

$$\begin{aligned}
\int_{-\infty}^{\infty} \tilde{f}(k)\tilde{g}(k) e^{ikx} dk &\overset{(7)}{=} \int_{-\infty}^{\infty} dk \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx' f(x') e^{-ikx'} \right] \left[\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx'' g(x'') e^{-ikx''} \right] e^{ikx} \\
&= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{2\pi} f(x') g(x'') e^{ik[x-(x'+x'')]} dk dx' dx'' \\
&\overset{(9)}{=} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{2\pi}{2\pi} \delta\big(x - (x' + x'')\big) f(x') g(x'') dx' dx'' \\
&= \int_{-\infty}^{\infty} f(x') g(x - x') dx'.
\end{aligned} \tag{10}$$

b) As defined in the lecture,

$$(f * g)(x) = \int_{-\infty}^{\infty} f(x') g(x - x') dx'. \tag{11}$$

If $g(x) = \delta(x)$ then

$$(f * g)(x) = (f * \delta)(x) = \int_{-\infty}^{\infty} f(x') \delta(x - x') dx' = f(x) \quad \forall x. \tag{12}$$