Quantum Dynamics, NWI-SM295, exercises week 1

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Question 1: Time propagator

1a. Show that

$$\lim_{n\to\infty}(1+\frac{x}{n})^n = \sum_{k=0}^{\infty}\frac{1}{k!}x^k. \tag{1}$$

Hint: use

$$(a+b)^n = \sum_{k=0}^{n}\begin{pmatrix} n \\ k \end{pmatrix} a^{n-k}b^k, \tag{2}$$

with binomial coefficients

$$\begin{pmatrix} n \\ k \end{pmatrix} \equiv \frac{n!}{(n-k)!\,k!}. \tag{3}$$

Answer:

$$\left(1+\frac{x}{n}\right)^2 = \sum_{k=0}^{n}\begin{pmatrix} n \\ k \end{pmatrix}\left(\frac{x}{n}\right)^k \tag{4}$$

$$= \sum_{k=0}^{n}\frac{n!}{(n-k)!\,k!}\left(\frac{x}{n}\right)^k \tag{5}$$

$$\equiv \sum_{k=0}^{n} c_k^{(n)} x^k \tag{6}$$

so

$$c_k^{(n)} = \frac{n!}{(n-k)!\,k!}\frac{1}{n^k} \tag{7}$$

$$= \frac{n(n-1)(n-2)\ldots(n-k+1)}{n^k}\frac{1}{k!} \tag{8}$$

$$= \frac{n}{n}\frac{n-1}{n}\frac{n-2}{n}\ldots\frac{n-k+1}{n}\frac{1}{k!} \tag{9}$$

Since for any fixed k we have

$$\lim_{n\to\infty}\frac{n-k+1}{n} = 1, \tag{10}$$

we find

$$\lim_{n\to\infty} c_k^{(n)} = \frac{1}{k!}. \tag{11}$$

Question 2: Autocorrelation function and spectrum

Let $\{\phi_1, \phi_2, \ldots, \phi_N\}$ be solutions of the time-independent Schrödinger equation

$$\hat{H}\phi_i = \epsilon_i\phi_i, \quad i = 1, \ldots, N.$$

with Hamiltonian $\hat{H}$ and eigenvalues ϵ_i. Assume that the eigenfunctions are orthonormal $\langle\phi_i|\phi_j\rangle = \delta_{ij}$.

The time-dependent Schrödinger equation is given by

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

The solution can be expanded in the solutions of the time-independent Schrödinger equation

$$\Psi(t) = \sum_{i=1}^{N} c_i(t)\phi_i$$

2a. Find the expansion coefficients $c_i(t)$ for given initial state $\Psi(0) = \Theta$.

Answer: *At $t = 0$ the wave function is given by*

$$\Psi(0) = \Theta = \sum_{j=1}^{N} c_j(0)\phi_j. \tag{12}$$

The coefficients $c_i(0)$ can be found by projecting with $\langle\phi_i|$

$$\langle\phi_i|\Theta\rangle = \sum_{j=1}^{N} c_j(0)\langle\phi_i|\phi_j\rangle \tag{13}$$

$$= \sum_{j=1}^{N} c_j(0)\delta_{i,j} = c_i(0), \tag{14}$$

so

$$c_i(0) = \langle\phi_i|\Theta\rangle. \tag{15}$$

The time-dependent expansion coefficients are (see lecture notes)

$$c_i(t) = e^{-\frac{i}{\hbar}\epsilon_i t} c_i(0) = e^{-\frac{i}{\hbar}\epsilon_i t}\langle\phi_i|\Theta\rangle. \tag{16}$$

2b. Find an expression for the autocorrelation function

$$P(t) = \langle\Psi(t)|\Psi(0)\rangle.$$

Answer: *The time-dependent wave function is*

$$|\Psi(t)\rangle = \sum_{i=1}^{N} |\phi_i\rangle e^{-\frac{i}{\hbar}\epsilon_i t}\langle\phi_i|\Theta\rangle \tag{17}$$

For the autocorrelation function we get

$$P(t) = \langle\Psi(t)|\Theta\rangle = \langle\Theta|\Psi(t)\rangle^* = \sum_{i=1}^{N} |\langle\phi_i|\Theta\rangle|^2 e^{\frac{i}{\hbar}\epsilon_i t}. \tag{18}$$

The Fourier transform is given by

$$F(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt. \tag{19}$$

2c. Compute the Fourier transform of the autocorrelation function $P(t)$. Hint:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ixt}dt = \delta(x). \tag{20}$$

The delta function $\delta(x)$ has the property

$$\int_{-\infty}^{\infty} f(x)\delta(x-y)dx = f(y) \tag{21}$$

for any reasonably smooth function f.

Answer:

$$F(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} P(t)e^{-i\omega t}dt \tag{22}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} \sum_{i=1}^{N} |\langle\phi_i|\Theta\rangle|^2 e^{i(\omega_i-\omega)t}, \tag{23}$$

where we defined $\omega_i \equiv \epsilon_i/\hbar$. *Using Eq. (20) and* $\delta(x) = \delta(-x)$, *we find for the "stick" spectrum*

$$F(\omega) = \sum_{i=1}^{N} |\langle\phi_i|\Theta\rangle|^2 \delta(\omega - \omega_i). \tag{24}$$

With a properly chosen $\Psi(0)$, the Fourier transform of the autocorrelation corresponds to a stick spectrum. The spectrum calculated in this way has infinitely sharp peaks. A more realistic spectrum is obtain by introducing the effect of a finite lifetime:

$$\widetilde{P}(t) = P(t)e^{-\Gamma|t|}$$

2d. Compute the Fourier transform of $\widetilde{P}(t)$ and show that a Lorentzian line shape arises, with width Γ.

Answer:

$$F(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} P(t)e^{-\Gamma|t|}e^{-i\omega t}dt \tag{25}$$

$$= \frac{1}{2\pi}\sum_{i=1}^{N} |\langle\phi_i|\Theta\rangle|^2 \int_{-\infty}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma|t|}dt. \tag{26}$$

We can split the integral for $t < 0$ *and* $t \geq 0$,

$$\int_{-\infty}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma|t|}dt = \int_{0}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma t}dt + \int_{-\infty}^{0} e^{i(\omega_i-\omega)t}e^{\Gamma t}dt, \tag{27}$$

and we can rewrite the second term as

$$\int_{-\infty}^{0} e^{i(\omega_i-\omega)t}e^{\Gamma t}dt = \int_{0}^{\infty} e^{-i(\omega_i-\omega)t}e^{-\Gamma t}dt. \tag{28}$$

Note that this integral is the complex conjugate of the first term on the right-hand-side in Eq. (27). For a complex number z *we have* $z + z^* = 2\Re(z)$ *(i.e., two times the real part of* z*), so*

$$\int_{-\infty}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma|t|}dt = 2\Re\left(\int_{0}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma t}dt\right). \tag{29}$$

This integral is easy, for $\alpha = -\Gamma + i(\omega_i - \omega)$ *we have*

$$\int_{0}^{\infty} e^{\alpha t}dt = \frac{1}{\alpha}e^{\alpha t}|_0^{\infty} = \frac{1}{\alpha}(e^{\alpha\infty} - e^0) = -\frac{1}{\alpha} = -\frac{\alpha^*}{|\alpha|^2}. \tag{30}$$

so

$$\int_{-\infty}^{\infty} e^{i(\omega_i-\omega)t}e^{-\Gamma|t|}dt = -2\Re\left(\frac{\alpha^*}{|\alpha|^2}\right) = -2\frac{\Re(\alpha)}{|\alpha|^2} = 2\frac{\Gamma}{\Gamma^2 + (\omega-\omega_i)^2} \tag{31}$$

Substituting this into Eq. (26) gives

$$F(\omega) = \sum_{i=1}^{N} |\langle\phi_i|\Theta\rangle|^2 \frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + (\omega-\omega_i)^2}. \tag{32}$$

The function

$$L(\omega) = \frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + (\omega - \omega_i)^2} \tag{33}$$

is called a Lorentzian. Its maximum value occurs at $\omega = \omega_i$ *and for* $\omega = \omega_i \pm \Gamma$ *it has half the maximum value*

$$L(\omega_i \pm \Gamma) = \frac{1}{\pi}\frac{\Gamma}{\Gamma^2 + \Gamma^2} = \frac{1}{2}L(\omega_i). \tag{34}$$

The integral of a Lorentzian is one, so for $\Gamma \to 0$*, it approaches a delta function.*