Problem 1. A particle is initially in the the ground state of an infinite one-dimensional potential box with walls at $x = 0$ and $x = L$. During the time interval $0 \leq t \leq \infty$, the particle is subject to a perturbation $V(t) = x^2 e^{-t/\tau}$, where τ is a time constant. Calculate, to first order in perturbation theory, the probability of finding the particle in its first excited state as a result of this perturbation.

Solution. The wave functions and energy eigenstates for a particle in an infinite one-dimensional box are given by Eq. (A.2.4) in Sakurai:

$$\psi_E(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \qquad E = \frac{\hbar^2 n^2 \pi^2}{2mL^2},$$

where $n = 1, 2, 3, \ldots$ Equation (5.6.19) gives the general expression for the transition probability from state i to state n, which is

$$P(i \to n) = \left|c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots\right|^2.$$

We are looking for the first order contribution, $c_n^{(1)}(t)$, which may be found using Eq. (5.6.17):

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} \langle n|V_I(t')|t\rangle \, dt' = -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'} V_{ni}(t') \, dt' \,, \tag{1}$$

where

$$e^{i(E_n - E_i)t/\hbar} = e^{i\omega_{ni}t}$$

from Eq. (5.6.18).

Let ψ_n denote the wavefunctions corresponding to the eigenstates of H_0. We are interested in the transition probability from $i = 1$ to $n = 2$, so the relevant wavefunctions are

$$\psi_1(t) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), \qquad \psi_2(t) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right),$$

and the corresponding energies are

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2}, \qquad E_2 = \frac{2\hbar^2\pi^2}{mL^2}.$$

The relevant matrix element of $V(t)$ is

$$\begin{aligned}
\langle 2|V(t)|1\rangle &= \int_0^\infty \int_0^\infty \langle \psi_2|x'\rangle \langle x'|V|x''\rangle \langle x''|\psi_1\rangle \, dx' \, dx'' \\
&= \frac{2}{L} e^{-t/\tau} \int_0^L \int_0^L \sin\left(\frac{2\pi x'}{L}\right) x'^2 \delta(x' - x'') \sin\left(\frac{\pi x''}{L}\right) dx' \, dx'' \\
&= \frac{2}{L} e^{-t/\tau} \int_0^L \sin\left(\frac{2\pi x'}{L}\right) x'^2 \sin\left(\frac{\pi x'}{L}\right) dx' = \frac{4}{L} e^{-t/\tau} \int_0^L x'^2 \sin^2\left(\frac{\pi x'}{L}\right) \cos\left(\frac{\pi x'}{L}\right) dx' \,.
\end{aligned}$$

Let $u = \pi x'/L$. Then

$$\begin{aligned}
\langle 2|V(t)|1\rangle &= \frac{4L^2}{\pi^3} e^{-t/\tau} \int_0^\pi u^2 \sin^2 u \cos u \, du = \frac{4L^2}{\pi^3} e^{-t/\tau} \int_0^\pi u^2 (\cos u - \cos^3 u) \, du \\
&= \frac{4L^2}{\pi^3} e^{-t/\tau} \int_0^\pi u^2 \left(\cos u - \frac{3}{4}\cos u - \frac{1}{4}\cos 3u\right) du = \frac{L^2}{\pi^3} e^{-t/\tau} \int_0^\pi u^2 (\cos u - \cos 3u) \, du \,.
\end{aligned}$$

For the first integral, we integrate by parts twice:

$$\int_0^\pi u^2 \cos u \, du = \Big[u^2 \sin u\Big]_0^\pi - 2\int_0^\pi u \sin u \, du = 2\Big[u \cos u\Big]_0^\pi + 2\int_0^\pi \cos u \, du = -2\pi + 2\Big[\sin u\Big]_0^\pi = -2\pi.$$

For the second, let $v = 3u$. Then we again integrate by parts twice:

$$\int_0^{\pi} u^2 \cos 3u \, du = \frac{1}{27}\int_0^{3\pi} v^2 \cos v \, dv = \frac{1}{27}\Big[v^2 \sin v\Big]_0^{3\pi} - \frac{2}{27}\int_0^{3\pi} v \sin v \, dv = \frac{2}{27}\Big[v \cos v\Big]_0^{3\pi} + \frac{2}{27}\int_0^{3\pi} \cos v \, dv$$
$$= -\frac{2\pi}{9} + \frac{2}{27}\Big[\sin v\Big]_0^{3\pi} = -\frac{2\pi}{9}.$$

Then our matrix element is

$$\langle 2|V(t)|1\rangle = -\frac{L^2}{\pi^2}e^{-t/\tau}\frac{16\pi}{9} = -\frac{16L^2}{9\pi^2}e^{-t/\tau}.$$

Returning to (1), we may now find the first-order coefficient. First note that

$$E_2 - E_1 = \frac{3\hbar^2\pi^3}{2mL^2}.$$

Then

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} e^{i(E_2-E_1)t'/\hbar} V_{21}(t')\, dt' = \frac{i}{\hbar}\frac{16L^2}{9\pi^2}\int_0^{\infty}\exp\left(i\frac{3\hbar\pi^2}{2mL^2}t'\right)e^{-t'/\tau}\, dt'$$
$$= \frac{i}{\hbar}\frac{16L^2}{9\pi^2}\int_0^{\infty}\exp\left[\left(i\frac{3\hbar\pi^2}{2mL^2} - \frac{1}{\tau}\right)t'\right] dt' = \frac{i}{\hbar}\frac{16L^2}{9\pi^2}\left[\frac{2mL^2\tau}{i3\hbar\pi^2\tau - 2mL^2}\exp\left(\frac{i3\hbar\pi^2\tau - 2mL^2}{2mL^2\tau}t'\right)\right]_0^{\infty}$$
$$= \frac{i}{\hbar}\frac{32}{9\pi^2}\frac{mL^4\tau}{i3\hbar\pi^2\tau - 2mL^2},$$

so the transition probability is

$$|c_n^{(1)}(t)|^2 = \left(\frac{i}{\hbar}\frac{32}{9\pi^2}\frac{mL^4\tau}{i3\hbar\pi^2\tau - 2mL^2}\right)\left(\frac{i}{\hbar}\frac{32}{9\pi^2}\frac{mL^4\tau}{i3\hbar\pi^2\tau + 2mL^2}\right) = \frac{1024}{81\hbar^2}\frac{L^8\tau^2}{9\hbar^2\pi^4\tau^2 + 4m^2L^4}.$$

Problem 2. Consider a system of two electrons, which is described by the Hamiltonian

$$H = H_a + H_b + V, \qquad H_i = \frac{\mathbf{p}_i^2}{2m} - \frac{Z\alpha\hbar c}{r_i}, \qquad V = \frac{\alpha\hbar c}{r_{ab}}.$$

Here, we label two electrons by $i = a, b$; $r_i = |\mathbf{x}_i|$ and $r_{ab} = |\mathbf{x}_a - \mathbf{x}_b|$ where $\mathbf{x}_i$ is the spatial coordinate for electron i; and Z and α are constants. To find an approximate ground state of H, let us try a variational wave function

$$\Psi(\mathbf{x}_a, \mathbf{x}_b) = \frac{A}{4\pi}e^{-B(r_a+r_b)},$$

where A is a normalization constant and B is your variational parameter.

2.1 Compute the variational energy for the given variational parameter B.

2.2 By minimizing the variational energy, find the optimal value of B.

Problem 3. Consider a two-dimensional harmonic oscillator described by the Hamiltonian

$$H_0 = \frac{p_x^2 + p_y^2}{2m} + m\omega^2\frac{x^2 + y^2}{2}.$$

3.1 How many single-particle states are there for the first excited level?

3.2 Write down the many-body ground state for two electrons (with spin). What is the eigenvalue of $(\mathbf{S}_1+\mathbf{S}_2)^2$ for this state? Here $\mathbf{S}_i$ are the spin operators of the electrons.

3.3 Write down all the first excited many-body states of two electrons (with spin). Choose them to be eigenstates of the total spin operator, and compute their eigenvalues of $(\mathbf{S}_1 + \mathbf{S}_2)^2$ and $S_1^z + S_2^z$ (where S_i^z is the z componenet of the spin operator $\mathbf{S}_i$).

I consulted Sakurai's *Modern Quantum Mechanics*, Shankar's *Principles of Quantum Mechanics*, and Wolfram MathWorld while writing up these solutions.