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 $0 \le t \le \infty$, 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 $n = 1, 2, 3, \dots$ 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

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

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:

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

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 (**??**), we may now find the first-order coefficient. First note that

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

Then

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

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.

Solution. The general expression for the variational energy $\bar{H}$ is (5.4.1) in Sakurai:

$$\bar{H} = \frac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}, \tag{2}$$

where $|\tilde{0}\rangle$ is our trial ket.

For this problem, the numerator of (**??**) is

$$\begin{aligned}\langle\tilde{0}|H|\tilde{0}\rangle = \langle\Psi|H|\Psi\rangle &= \iint \langle\Psi|\mathbf{x}_a,\mathbf{x}_b\rangle \langle\mathbf{x}_a,\mathbf{x}_b|H|\mathbf{x}'_a,\mathbf{x}'_b\rangle \langle\mathbf{x}'_a,\mathbf{x}'_b|\Psi\rangle \\ &= \iint\iint \Psi(\mathbf{x}_a,\mathbf{x}_b) \langle\mathbf{x}_a,\mathbf{x}_b|H|\mathbf{x}'_a,\mathbf{x}'_b\rangle \Psi(\mathbf{x}'_a,\mathbf{x}'_b)\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b\,,\end{aligned}$$

where

$$H = \frac{\mathbf{p}_a^2}{2m} + \frac{\mathbf{p}_b^2}{2m} - \frac{Z\alpha\hbar c}{|\mathbf{x}_a|} - \frac{Z\alpha\hbar c}{|\mathbf{x}_b|} + \frac{\alpha\hbar c}{|\mathbf{x}_a - \mathbf{x}_b|},$$

so we have five integrals. For the first,

$$\begin{aligned}&\frac{A^2}{32\pi^2 m}\iint\iint e^{-B(r_a+r_b)} \langle\mathbf{x}_a,\mathbf{x}_b|\mathbf{p}_a^2|\mathbf{x}'_a,\mathbf{x}'_b\rangle^2 e^{-B(r'_a+r'_b)}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b \\ &\quad= \frac{A^2}{32\pi^2 m}\iint\iint e^{-B(r_a+r_b)}\Big(i^2\hbar^2\delta(\mathbf{x}_a-\mathbf{x}'_a)\delta(\mathbf{x}_b-\mathbf{x}'_b)\nabla^2_{a'}\Big)e^{-B(r'_a+r'_b)}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b \\ &\quad= -\frac{A^2\hbar^2}{2m}\iint e^{-B(r_a+r_b)}\left(\frac{\partial^2}{\partial r_a^2}e^{-B(r_a+r_b)}\right) r_a^2 r_b^2\, dr_a\, dr_b = -\frac{A^2B^2\hbar^2}{2m}\int_0^\infty r_a^2 e^{-2Br_a}\, dr_a \int_0^\infty r_b^2 e^{-2Br_b}\, dr_b \\ &\quad= -\frac{A^2\hbar^2}{32B^4 m},\end{aligned}$$

where we have used

$$\begin{aligned}\int_0^\infty r^2 e^{-2Br}\, dr &= \left[-\frac{r^2e^{-2Br}}{2B}\right]_0^\infty + \frac{1}{B}\int_0^\infty re^{-2Br}\, dr = \frac{1}{B}\left[-\frac{re^{-2Br}}{2B}\right]_0^\infty + \frac{1}{2B^2}\int_0^\infty e^{-2Br}\, dr = \frac{1}{2B^2}\left[-\frac{e^{-2Br}}{2B}\right]_0^\infty \\ &= \frac{1}{4B^3}.\end{aligned}$$

For the second integral, we also have

$$\frac{A^2}{16\pi^2}\frac{1}{2m}\iint\iint e^{-B(r_a+r_b)} \langle\mathbf{x}_a,\mathbf{x}_b|\mathbf{p}_b^2|\mathbf{x}'_a,\mathbf{x}'_b\rangle^2 e^{-B(r'_a+r'_b)}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b = -\frac{A^2\hbar^2}{32B^4 m}.$$

For the third integral,

$$\begin{aligned}&-\frac{Z\alpha\hbar c}{16\pi^2}\iint\iint e^{-B(r_a+r_b)} \langle\mathbf{x}_a,\mathbf{x}_b|\frac{1}{|\mathbf{x}_a|}|\mathbf{x}'_a,\mathbf{x}'_b\rangle e^{-B(r'_a+r'_b)}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b \\ &\quad= -\frac{Z\alpha\hbar c}{16\pi^2}\iint\iint e^{-B(r_a+r_b)}\left(\delta(\mathbf{x}_a-\mathbf{x}'_a)\delta(\mathbf{x}_b-\mathbf{x}'_b)\frac{1}{|\mathbf{x}_a|}\right) e^{-B(r'_a+r'_b)}\, dr_a\, dr_b\, dr'_a\, dr'_b \\ &\quad= -A^2 Z\alpha\hbar c\iint \frac{e^{-2B(r_a+r_b)}}{r_a} r_a^2 r_b^2\, dr_a\, dr_b = -A^2Z\alpha\hbar c\int_0^\infty r_a e^{-2Br_a}\, dr_a \int_0^\infty r_b^2 e^{-2Br_b}\, dr_b \\ &\quad= -\frac{A^2 Z\alpha\hbar c}{16B^5}.\end{aligned}$$

For the fourth integral, we also have

$$-\frac{Z\alpha\hbar c}{16\pi^2}\iint\iint e^{-B(r_a+r_b)} \langle\mathbf{x}_a,\mathbf{x}_b|\frac{1}{|\mathbf{x}_b|}|\mathbf{x}'_a,\mathbf{x}'_b\rangle e^{-B(r'_a+r'_b)}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}'_a\, d^3\mathbf{x}'_b = -\frac{A^2 Z\alpha\hbar c}{16B^5}.$$

For the fifth integral, we will orient our coordinate system such that $\mathbf{x}_b$ points in the z direction and stipulate that $r_a > r_b$. Then

$$\frac{1}{|\mathbf{x}_a - \mathbf{x}_b|} = \frac{1}{\sqrt{\mathbf{x}_a^2 - 2\mathbf{x}_a \cdot \mathbf{x}_b + \mathbf{x}_b^2}} = \frac{1}{\sqrt{r_a^2 - 2r_a r_b \cos\theta_a + r_b^2}},$$

and so

$$\begin{aligned}
&\frac{\alpha\hbar c}{16\pi^2} \iint\iint e^{-B(r_a+r_b)} \left\langle \mathbf{x}_a, \mathbf{x}_b \right| \frac{1}{|\mathbf{x}_a - \mathbf{x}_b|} \left| \mathbf{x}_a', \mathbf{x}_b' \right\rangle e^{-B(r_a'+r_b')}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}_a'\, d^3\mathbf{x}_b' \\
&\quad = \frac{A^2\alpha\hbar c}{16\pi^2} \iint\iint e^{-B(r_a+r_b)} \left(\delta(\mathbf{x}_a - \mathbf{x}_a')\delta(\mathbf{x}_b - \mathbf{x}_b') \frac{1}{|\mathbf{x}_a - \mathbf{x}_b|} \right) e^{-B(r_a'+r_b')}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}_a'\, d^3\mathbf{x}_b' \\
&\quad = \frac{A^2\alpha\hbar c}{2} \int_0^\infty \int_{-1}^1 \int_0^\infty \frac{e^{-2B(r_a+r_b)}}{\sqrt{r_a^2 - 2r_a r_b \cos\theta_a + r_b^2}} r_a^2 r_b^2\, dr_a\, d(\cos\theta_a)\, dr_b \\
&\quad = \frac{A^2\alpha\hbar c}{2} \int_0^\infty \int_0^\infty r_a^2 r_b^2 e^{-2B(r_a+r_b)} \int_{-1}^1 \frac{d(\cos\theta_a)}{\sqrt{r_a^2 - 2r_a r_b \cos\theta_a + r_b^2}}\, dr_a\, dr_b\,.
\end{aligned} \tag{3}$$

For the innermost integral, let $u = r_a^2 - 2r_a r_b \cos\theta_a + r_b^2$. Then

$$d(\cos\theta_a) = -\frac{du}{2r_a r_b},$$

and we are integrating from $r_a^2 + 2r_a r_b + r_b^2 = (r_a + r_b)^2$ to $r_a^2 - 2r_a r_b + r_b^2 = (r_a - r_b)^2$. So the innermost integral becomes

$$\begin{aligned}
\int_{-1}^1 \frac{d(\cos\theta_a)}{\sqrt{r_a^2 - 2r_a r_b \cos\theta_a + r_b^2}} &= \frac{1}{2r_a r_b} \int_{(r_a-r_b)^2}^{(r_a+r_b)^2} \frac{du}{\sqrt{u}} = \frac{1}{2r_a r_b} \Big[2\sqrt{u} \Big]_{(r_a-r_b)^2}^{(r_a+r_b)^2} = \frac{|r_a + r_b| - |r_a - r_b|}{r_a r_b} \\
&= \frac{r_a + r_b - r_a + r_b}{r_a r_b} = \frac{2}{r_a},
\end{aligned}$$

where we have used $r_a, r_b > 0$ and our assumption that $r_a > r_b$. Picking up from (**??**), we now have

$$\begin{aligned}
&\frac{A^2\alpha\hbar c}{16\pi^2} \iint\iint e^{-B(r_a+r_b)} \left\langle \mathbf{x}_a, \mathbf{x}_b \right| \frac{1}{|\mathbf{x}_a - \mathbf{x}_b|} \left| \mathbf{x}_a', \mathbf{x}_b' \right\rangle e^{-B(r_a'+r_b')}\, d^3\mathbf{x}_a\, d^3\mathbf{x}_b\, d^3\mathbf{x}_a'\, d^3\mathbf{x}_b' \\
&\quad = A^2\alpha\hbar c \int_0^\infty r_a e^{-2Br_a}\, dr_a \int_0^\infty r_b^2 e^{-2Br_b}\, dr_b = \frac{A^2\alpha\hbar c}{16B^5}.
\end{aligned}$$

Putting this all together,

$$\left\langle \tilde{0} \middle| H \middle| \tilde{0} \right\rangle = \frac{A^2\alpha\hbar c}{16B^5} - \frac{A^2 B\hbar^2/m}{16B^5} - \frac{2A^2 Z\alpha\hbar c}{16B^5} = \frac{1}{16B^5}\left((1-2Z)A^2\alpha\hbar c - \frac{A^2 B\hbar^2}{m} \right).$$

For the denominator of (**??**),

$$\begin{aligned}
\left\langle \tilde{0} \middle| \tilde{0} \right\rangle &= \frac{1}{16\pi^2} \iint \left\langle \Psi \middle| \mathbf{x}_a, \mathbf{x}_b \right\rangle \left\langle \mathbf{x}_a, \mathbf{x}_b \middle| \Psi \right\rangle d^3\mathbf{x}_a\, d^3\mathbf{x}_b = \iint e^{-B(r_a+r_b)} e^{-B(r_a+r_b)} r_a^2 r_b^2\, dr_a\, dr_b \\
&= \int_0^\infty r_a^2 e^{-2Br_a}\, dr_a \int_0^\infty r_b^2 e^{-2Br_b}\, dr_b = \frac{1}{16B^6}.
\end{aligned}$$

Finally,

$$\bar{H} = A^2 B(1-2Z)\alpha\hbar c - \frac{A^2 B^2 \hbar^2}{m}. \tag{4}$$

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

Solution. By (5.4.9) in Sakurai, we can minimize $\bar{H}$ by setting to zero its derivative with respect to B. From (**??**), we have

$$\frac{\partial \bar{H}}{\partial B} = A^2(1-2Z)\alpha\hbar c - 2\frac{A^2 B\hbar^2}{m} = 0$$

which implies

$$(1-2Z)\alpha c = 2\frac{B\hbar}{m} \implies B = \frac{1-2Z}{2\hbar}\alpha cm.$$

Substituting this back into (**??**),

$$\bar{H} = A^2\frac{1-2Z}{2\hbar}\alpha cm(1-2Z)\alpha\hbar c - \frac{A^2\hbar^2}{m}\left(\frac{1-2Z}{2\hbar}\alpha cm\right)^2 = \frac{A^2\alpha^2c^2m}{4}(1-2Z)^2.$$

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?

Solution. The Hamiltonian is separable; that is, we may write $H_0 = H_x + H_y$ where

$$H_x = \frac{p_x^2}{2m} + m\omega^2\frac{x^2}{2}, \qquad H_y = \frac{p_y^2}{2m} + m\omega^2\frac{y^2}{2},$$

which are both one-dimensional oscillators. Thus, the energy of each is given by (A.4.4) in Sakurai:

$$E = \hbar\omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2, \dots$$

So the total energy for H_0 is

$$E_0 = E_x + E_y = \hbar\omega(n_x + n_y + 1), \qquad n_x, n_y = 0, 1, 2, \dots$$

For the first excited level, we may have $(n_x, n_y) = (0, 1)$ or $(1, 0)$. So there are *two* single-particle states. Do we need to consider spin?

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

Solution. For two electrons, the Hamiltonian is

$$H_0 = \frac{p_{x_1}^{\ 2} + p_{y_1}^{\ 2}}{2m} + \frac{p_{x_2}^{\ 2} + p_{y_2}^{\ 2}}{2m} + m\omega^2 \frac{x_1^2 + y_1^2}{2} + m\omega^2 \frac{x_2^2 + y_2^2}{2}.$$

From (6.3.2) in Sakurai, the Hamiltonian commutes with $\mathbf{S}_{\text{tot}}^2$—that is, $[\mathbf{S}_{\text{tot}}^2, H_0] = 0$—so the eigenfunctions ψ of H_0 are also eigenfunctions of $\mathbf{S}_{\text{tot}}^2$. This also means the eigenfunctions are separable, and so they can be written as is (6.6.3):

$$\psi = \phi(\mathbf{x}_1, \mathbf{x}_2)\chi.$$

Here, ϕ is given by (6.3.14), where $\mathbf{x}_i = (x_i, y_i)$.

$$\chi(m_{s1}, m_{s2}) = \begin{cases} \chi_{++} & \text{triplet (symmetrical),} \\ \dfrac{\chi_{+-} + \chi_{-+}}{\sqrt{2}} & \text{triplet (symmetrical),} \\ \chi_{--} & \text{triplet (symmetrical),} \\ \dfrac{\chi_{+-} - \chi_{-+}}{\sqrt{2}} & \text{singlet (antisymmetrical).} \end{cases}$$

For two fermions, we need the overall wavefunction to be antisymmetric. For the ground state we need $n_{x1} = n_{y_1} = n_{x2} = n_{y_2} = 0$

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 component 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.