

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:

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

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

$$P(i \rightarrow n) = |c_n^{(1)}(t) + c_n^{(2)}(t) + \dots|^2.$$

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

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

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

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

and the corresponding energies are

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

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:

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

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

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

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 (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

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

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

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

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:

$$\bar{H} = \frac{\langle \tilde{0} | H | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}, \quad (2)$$

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

For this problem, the numerator of (2) is

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

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,

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

where we have used

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

For the second integral, we also have

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

For the third integral,

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

For the fourth integral, we also have

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

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

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

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

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

where we have used $r_a, r_b > 0$ and our assumption that $r_a > r_b$. Picking up from (3), we now have

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

Putting this all together,

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

For the denominator of (2),

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

Finally,

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

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 (4), 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 (4),

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

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?

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 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.