

Solutions to Lectures on Quantum Mechanics

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Chapter 1 Problem Set Solutions

1. Consider a non-relativistic particle of mass M in one dimension, confined in a potential that vanishes for $-a \leq x \leq a$, and becomes infinite at $x = \pm a$, so that the wave function must vanish at $x = \pm a$.
 - Find the energy values of states with definite energy, and the corresponding normalized wave functions.
 - Suppose that the particle is placed in a state with a wave function proportional to $a^2 - x^2$. If the energy of the particle is measured, what is the probability that the particle will be found in the state of lowest energy?

The states of definite energy are those which are solutions of the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x).$$

The potential for the infinite square well is given by

$$V(x) = \begin{cases} 0 & \text{for } |x| < a \\ \infty & \text{for } |x| \geq a. \end{cases}$$

This potential requires that the wave function vanishes outside the well

$$\psi(x) = 0 \quad \text{for } |x| \geq a,$$

while inside the well the Schrödinger equation becomes

$$\frac{d^2}{dx^2} \psi(x) = -\frac{2ME}{\hbar^2} \psi(x) \quad \text{for } |x| < a.$$

The solution of this differential equation takes the form

$$\psi(x) = A \sin(kx) + B \cos(kx),$$

where we have defined

$$k \equiv \frac{\sqrt{2ME}}{\hbar}.$$

Continuity of the wave function requires that we impose the boundary conditions

$$\psi(x = \pm a) = 0,$$

and so

$$\begin{aligned} 0 &= A \sin(ka) + B \cos(ka), \\ 0 &= -A \sin(ka) + B \cos(ka). \end{aligned}$$

Adding these two equations gives

$$0 = 2B \cos(ka),$$

which requires that

$$B = 0 \text{ or } k = \frac{n\pi}{2a} \text{ where } n = 2, 4, 6, \dots,$$

and subtracting the equations gives

$$0 = 2A \sin(ka),$$

which requires that

$$A = 0 \text{ or } k = \frac{n\pi}{2a} \text{ where } n = 1, 3, 5, \dots$$

In either case, the energy levels are given by

$$E_n = \frac{\hbar^2 k^2}{2M} = \frac{n^2 \hbar^2 \pi^2}{8Ma}.$$

Next, we need to normalize the wave functions in the sense of Eq. (1.5.4), such that

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1.$$

For n odd, we have

$$\int_{-a}^a \left| B \cos\left(\frac{n\pi x}{2a}\right) \right|^2 dx = |B|^2 \int_{-a}^a \cos^2\left(\frac{n\pi x}{2a}\right) dx = |B|^2 a = 1,$$

which requires that

$$B = \frac{1}{\sqrt{a}},$$

where we have fixed the arbitrary complex phase for convenience. For n even, the normalization condition takes the form

$$\int_{-a}^a \left| A \sin\left(\frac{n\pi x}{2a}\right) \right|^2 dx = |A|^2 \int_{-a}^a \sin^2\left(\frac{n\pi x}{2a}\right) dx = |A|^2 a = 1,$$

which requires that

$$A = \frac{1}{\sqrt{a}},$$

where we have again fixed the arbitrary complex phase for convenience. Summarizing our results, the normalized wave functions of states with definite energy are

$$\psi_n(x) = \begin{cases} \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) & \text{for } |x| < a \text{ and } n = 1, 3, 5, \dots \\ \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) & \text{for } |x| < a \text{ and } n = 2, 4, 6, \dots \\ 0 & \text{for } |x| \geq a \end{cases}$$

and the energy levels are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{8Ma}.$$

Since these states are normalized and the energy level is determined by n , the argument below Eq. (1.4.26) proves that the states of definite energy are orthonormal

$$\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = \delta_{mn}.$$

Let us define a state which vanishes for $|x| \geq a$, while for $|x| < a$ it is given by

$$\Phi(x, t = 0) = C (a^2 - x^2).$$

We must normalize this state in order to determine C .

$$\int_{-a}^a |C (a^2 - x^2)|^2 dx = |C|^2 \left[\frac{x^5}{5} - \frac{2a^2 x^3}{3} + a^4 x \right]_{-a}^a = \frac{16a^5}{15} |C|^2 = 1,$$

and so we find (after fixing an arbitrary phase)

$$C = \sqrt{\frac{15}{16a^5}},$$

which then gives

$$\Phi(x, t = 0) = \sqrt{\frac{15}{16a^5}} (a^2 - x^2).$$

Since the states of definite energy that we found above form a complete orthonormal set on the interval $-a < x < a$, we can express Φ in terms of those states

$$\Phi(x, t = 0) = \sum_n c_n \psi_n(x),$$

and the probability of measuring the state Φ to have energy E_m , following Eq. (1.5.18), is given by

$$P(\Phi(x, t = 0) \rightarrow \psi_m(x)) = |c_m|^2 = \left| \int_{-a}^a \psi_m^*(x) \Phi(x, t = 0) dx \right|^2.$$

For the state of lowest energy this gives

$$\begin{aligned}
 c_1 &= \int_{-a}^a \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right) \sqrt{\frac{15}{16a^5}} (a^2 - x^2) dx \\
 &= \sqrt{\frac{15}{16}} \frac{1}{a^3} \left[\frac{2a^3}{\pi} \sin\left(\frac{\pi x}{2a}\right) - \frac{8xa^2}{\pi^2} \cos\left(\frac{\pi x}{2a}\right) - \frac{\frac{\pi^2 x^2}{4a^2} - 2}{\frac{\pi^3}{8a^3}} \sin\left(\frac{\pi x}{2a}\right) \right]_{-a}^a \\
 &= \sqrt{\frac{15}{16}} \frac{1}{a^3} \left[\frac{4a^3}{\pi} - \frac{4a^3}{\pi} + \frac{32a^3}{\pi^3} \right] \\
 &= \frac{8\sqrt{15}}{\pi^3},
 \end{aligned}$$

and so the probability of finding Φ in the lowest energy state is

$$P(\Phi(x, t = 0) \rightarrow \psi_1(x)) = |c_1|^2 = \frac{960}{\pi^6} \approx 0.9986.$$

2. Consider a non-relativistic particle of mass M in three dimensions, described by a Hamiltonian

$$H = \frac{\mathbf{P}^2}{2M} + \frac{M\omega_0^2}{2} \mathbf{X}^2.$$

- Find the energy values of states with definite energy, and the number of states for each energy.
- Find the rate at which a state of next-to-lowest energy decays by photon emission into the state of lowest energy.

Hint: You can express the Hamiltonian as a sum of three Hamiltonians for one-dimensional oscillators, and use the results given in Section 1.4 for the energy levels and x -matrix elements for one-dimensional oscillators.

First, we will rewrite the Hamiltonian in components

$$\begin{aligned}
 H &= \frac{\mathbf{p}^2}{2M} + \frac{M\omega_0^2}{2} \mathbf{x}^2 \\
 &= \left(\frac{p_1^2}{2M} + \frac{M\omega_0^2}{2} x_1^2 \right) + \left(\frac{p_2^2}{2M} + \frac{M\omega_0^2}{2} x_2^2 \right) + \left(\frac{p_3^2}{2M} + \frac{M\omega_0^2}{2} x_3^2 \right) \\
 &= H_1 + H_2 + H_3,
 \end{aligned}$$

where H_1 , H_2 , and H_3 are the one-dimensional harmonic oscillator Hamiltonians for x_1 , x_2 , and x_3 , respectively. Now, we will assume a separable solution of the form

$$\psi(\mathbf{x}) = \psi_1(x_1)\psi_2(x_2)\psi_3(x_3),$$

where

$$\begin{aligned}
 H_1 \psi_1(x_1) &= E_{n_1} \psi_1(x_1) \\
 H_2 \psi_2(x_2) &= E_{n_2} \psi_2(x_2) \\
 H_3 \psi_3(x_3) &= E_{n_3} \psi_3(x_3) \\
 H_1 \psi_2(x_2) &= 0 \\
 H_1 \psi_3(x_3) &= 0 \\
 &\vdots
 \end{aligned}$$

and the E_n are given by the energies of the one-dimensional harmonic oscillator, Eq. (1.4.15)

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_0,$$

where $n = 0, 1, 2, \dots$. We therefore find for the three-dimensional harmonic oscillator

$$\begin{aligned}
 H \psi(\mathbf{x}) &= E_N \psi(\mathbf{x}) \\
 &= H_1 \psi_1(x_1) \psi_2(x_2) \psi_3(x_3) + \psi_1(x_1) H_2 \psi_2(x_2) \psi_3(x_3) \\
 &\quad + \psi_1(x_1) \psi_2(x_2) H_3 \psi_3(x_3) \\
 &= E_{n_1} \psi_1(x_1) \psi_2(x_2) \psi_3(x_3) + \psi_1(x_1) E_{n_2} \psi_2(x_2) \psi_3(x_3) \\
 &\quad + \psi_1(x_1) \psi_2(x_2) E_{n_3} \psi_3(x_3),
 \end{aligned}$$

and so

$$E_N = E_{n_1} + E_{n_2} + E_{n_3} = \left(n_1 + n_2 + n_3 + \frac{3}{2}\right) \hbar \omega_0,$$

where n_1, n_2 , and n_3 are each non-negative integers. If we define

$$N = n_1 + n_2 + n_3,$$

then the energy levels for states of definite energy are

$$E_N = \left(N + \frac{3}{2}\right) \hbar \omega_0,$$

where $N = 0, 1, 2, \dots$

Now we must count the number of states with each energy. For a definite value of N , the integer n_1 can take values $0, 1, \dots, N$, then n_2 will take values $0, 1, \dots, N - n_1$ (which represents $N - n_1 + 1$ possibilities), and n_3 is fixed to be $N - n_1 - n_2$. Then for each energy E_N there is a degeneracy

$$g_N = \sum_{n_1=0}^N (N - n_1 + 1) = N(N+1) - \frac{1}{2}N(N+1) + N + 1 = \frac{1}{2}(N+1)(N+2).$$

The rate of spontaneous emission of photons carrying energy $\hbar\omega_{nm} = E_m - E_n$ is given by Eq. (1.4.5) to be

$$A_m^n = \frac{4e^2\omega_{nm}^3}{3c^3\hbar} |[\mathbf{x}]_{nm}|^2.$$

In three dimensions, we have $E_1 = \frac{5}{2}\hbar\omega_0$ and $E_0 = \frac{3}{2}\hbar\omega_0$, so $\omega_{01} = \omega_0$. The relevant matrix elements for the one-dimensional harmonic oscillator are given by Eq. (1.4.15) to be

$$[x]_{n+1,n}^* = [x]_{n,n+1} = e^{-i\omega_0 t} \sqrt{\frac{(n+1)\hbar}{2m_e\omega_0}}.$$

Since the wave function for the three-dimensional harmonic oscillator is just a product of three one-dimensional harmonic oscillator wave functions, we can also take these matrix elements to represent the matrix elements of a single spatial component x_1 , x_2 , or x_3

$$[x_i]_{mn} = [x]_{mn}.$$

The first excited state has n_1 , n_2 , or n_3 equal to 1 with the others equal to zero, and so the rate of spontaneous emission from the first excited state to the ground state for the three-dimensional harmonic oscillator is given by

$$A_1^0 = \frac{4e^2\omega_{01}^3}{3c^3\hbar} \left(\frac{\hbar}{2m_e\omega_0} \right) = \frac{2e^2\omega_0^2}{3c^3m_e}.$$

3. Suppose the photon had three polarization states rather than two. What difference would that make in the relations between Einstein's A and B coefficients?

For black-body radiation in a cubical box with side L , the frequency of a normal mode is given by Eq. (1.1.2) as $\nu = |\mathbf{n}|c/L$. The number of normal modes $N(\nu)d\nu$ in a range of frequencies between ν and $\nu + d\nu$ is three times the volume of a spherical shell in frequency space (the factor of three here comes from the assumed three polarization states of the photon)

$$N(\nu)d\nu = 3 \times 4\pi |\mathbf{n}|^2 d|\mathbf{n}| = 12\pi \left(\frac{L}{c} \right)^3 \nu^2 d\nu.$$

Assuming that the energies of the light quanta are integer multiples of $h\nu$, the mean energy is

$$\bar{E} = \frac{\sum_n \exp\left(\frac{-nh\nu}{k_B T}\right) nh\nu}{\sum_n \exp\left(\frac{-nh\nu}{k_B T}\right)} = \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}.$$

Then the energy density in radiation between ν and $\nu + d\nu$ is given by

$$\rho(\nu) d\nu = \frac{\bar{E} N(\nu) d\nu}{L^3} = \frac{12\pi h}{c^3} \frac{\nu^3 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}.$$

Now assume that we have black-body radiation in equilibrium with atoms at a temperature T . The transition rate for atoms to go from state m to state n must equal the rate for the transition from state n to state m , so

$$N_m [A_m^n + B_m^n \rho(\nu_{nm}, T)] = N_n B_n^m \rho(\nu_{nm}, T).$$

Using the Boltzmann distribution for the atoms gives

$$\frac{N_m}{N_n} = \exp\left(-\frac{(E_m - E_n)}{k_B T}\right) = \exp\left(\frac{-h\nu_{nm}}{k_B T}\right).$$

We can then rearrange the condition of equilibrium to give

$$A_m^n = \frac{12\pi h}{c^3} \frac{\nu^3 d\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \left[\exp\left(\frac{-h\nu_{nm}}{k_B T}\right) B_n^m - B_m^n \right].$$

Requiring that the Einstein coefficients A and B are temperature independent then gives

$$B_m^n = B_n^m,$$

and

$$A_m^n = \left(\frac{12\pi h \nu_{nm}^3}{c^3} \right) B_m^n.$$

This conclusion gives a value for A which is larger than the usual expression Eq. (1.2.16) by a factor of 3/2.

4. Show that the solution $\psi(\mathbf{x}, t)$ of the time-dependent Schrödinger equation for a particle in a real potential has the property that $\partial|\psi|^2/\partial t$ is the divergence of a three-vector.

We wish to calculate

$$\frac{\partial}{\partial t} |\psi(x, t)|^2,$$

for some $\psi(x, t)$ which is a solution of the time-dependent Schrödinger equation, which reads

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \frac{-\hbar^2}{2M} \nabla^2 \psi(x, t) + V(x, t) \psi(x, t).$$

Taking the complex conjugate of the Schrödinger equation gives

$$-i\hbar \frac{\partial}{\partial t} \psi^*(x, t) = \frac{-\hbar^2}{2M} \nabla^2 \psi^*(x, t) + V(x, t) \psi^*(x, t).$$

Recall that $|\psi(x, t)|^2$ can be rewritten as $\psi(x, t)\psi^*(x, t)$, and so we have

$$\frac{\partial}{\partial t}|\psi(x, t)|^2 = \psi^*(x, t)\frac{\partial}{\partial t}\psi(x, t) + \psi(x, t)\frac{\partial}{\partial t}\psi^*(x, t).$$

Using the Schrödinger equation to replace the time derivatives (now dropping space and time arguments), this becomes

$$\begin{aligned}\frac{\partial}{\partial t}|\psi|^2 &= \psi^* \left(\frac{i\hbar}{2M} \nabla^2 \psi - \frac{i}{\hbar} V \psi \right) + \psi \left(\frac{-i\hbar}{2M} \nabla^2 \psi^* + \frac{i}{\hbar} V \psi^* \right) \\ &= \frac{i\hbar}{2M} \psi^* \nabla^2 \psi - \frac{i\hbar}{2M} \psi \nabla^2 \psi^* - \frac{i}{\hbar} V |\psi|^2 + \frac{i}{\hbar} V |\psi|^2 \\ &= \frac{i\hbar}{2M} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) \\ &= \frac{i\hbar}{2M} \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*).\end{aligned}$$

We see that we can identify a three-vector

$$\mathbf{j} \equiv \frac{-i\hbar}{2M} (\psi^* \nabla \psi - \psi \nabla \psi^*),$$

such that

$$\frac{\partial}{\partial t}|\psi|^2 = -\nabla \cdot \mathbf{j}.$$

Notice that this is a continuity equation which implies that probability is conserved in quantum mechanics. The time rate of change of probability density $|\psi|^2$ in some infinitesimal volume is equal to the rate at which the probability current $\mathbf{j}$ flows into the same infinitesimal volume.