

Chemistry 120A Midterm 1

Useful formulas

Schrödinger's time-dependent equation with solution $\Psi(x, t)$ formed from the normalized stationary state wave-functions, $\phi_n(x)$, for the n th energy level:

$$i\hbar \partial\Psi(x, t)/\partial t = H\Psi(x, t),$$
$$\Psi(x, t) = \sum_n a_n \phi_n(x) e^{-iE_n t/\hbar}$$
$$H\phi_n(x) = E_n\phi_n(x).$$

The constants a_n are specified by the wave-function in which your system is prepared before measurement, i.e., $a_n = \langle \phi_n | \Psi(x, 0) \rangle$. Expectation values are obtained from the wave-function by:

$$\langle \hat{G} \rangle = \int dx \Psi^*(x, t) \hat{G} \Psi(x, t),$$

where \hat{G} is the operator for the observable G , and $\Psi^*(x, t)$ stands for the complex conjugate of $\Psi(x, t)$. In one-dimension, the momentum operator and Hamiltonian are:

$$p = (-i\hbar) d/dx$$
$$H = p^2/2m + V(x) = -(\hbar^2/2m) d^2/dx^2 + V(x)$$

Properly normalized eigenstates of the momentum operator will be specified where necessary.

1. (40 pts) A particle of mass m is confined to a box between $x=0$ and $x=a$ where there is no potential energy. The stationary state wave functions are $\phi_n(x) = (\sqrt{2/a})\sin(k_n x)$ with the quantized energy eigenvalues $E_n = \hbar^2 k_n^2 / 2m$, where $k_n = n\pi/a$, with $n = 1, 2, 3, \dots$. Within this spatial region, the normalized eigenstates of the momentum operator are $e^{ik_n x} / \sqrt{a}$ where $k_n = \pm n\pi/a$.

Consider that the particle in the box is prepared in the following properly normalized, non-stationary state:

$$\Psi(x, 0) = (\sqrt{2/3})(\phi_1(x)) - (\sqrt{1/3})(\phi_2(x))$$

- A measurement of the energy is made. What is the probability that E_1 would be measured? And E_2 ?
- Find the expectation (average) value of energy.
- What are the possible momenta that you would measure at $t=0$? With what probabilities?
- Write out the time evolution of the non-stationary state wave function given above. With what frequency would the probability density oscillate in position? Please state your answer in terms of \hbar , m , π , and a .

Solution

The system begins in a superposition of the $n=1$ and $n=2$ particle-in-a-box states such that:

$$\Psi(x, 0) = \sqrt{\frac{2}{3}}\phi_1(x) - \sqrt{\frac{1}{3}}\phi_2(x)$$

- A measurement of the energy is made. The probability that E_1 is measured is given by

$$|c_1|^2 = |\langle \phi_1 | \Psi \rangle|^2 = \frac{2}{3}.$$

Similarly, the probability that E_2 is measured is given by

$$|c_2|^2 = |\langle \phi_2 | \Psi \rangle|^2 = \frac{1}{3}.$$

- The expectation value of the energy is given by

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= \sum_n |c_n|^2 E_n \\ &= |c_1|^2 E_1 + |c_2|^2 E_2 \\ &= \frac{2}{3} \frac{\hbar^2 \pi^2}{2ma^2} + \frac{1}{3} \frac{4\hbar^2 \pi^2}{2ma^2} \\ &= \frac{\hbar^2 \pi^2}{ma^2} \end{aligned}$$

- To find the possible momenta, we write the wave function as a superposition of (normalized) momentum eigenstates:

$$\begin{aligned}
\Psi(x, 0) &= \sqrt{\frac{2}{3}}\phi_1(x) - \sqrt{\frac{1}{3}}\phi_2(x) \\
&= \sqrt{\frac{2}{3}}\sqrt{\frac{2}{a}}\sin(k_1x) - \sqrt{\frac{1}{3}}\sqrt{\frac{2}{a}}\sin(k_2x) \\
&= \sqrt{\frac{4}{3}}\frac{1}{2i}\left(\frac{\exp(ik_1x)}{\sqrt{a}} - \frac{\exp(-ik_1x)}{\sqrt{a}}\right) - \sqrt{\frac{2}{3}}\frac{1}{2i}\left(\frac{\exp(ik_2x)}{\sqrt{a}} - \frac{\exp(-ik_2x)}{\sqrt{a}}\right)
\end{aligned}$$

The measurable momenta are the eigenvalues of $\hat{p} = -i\hbar\frac{d}{dx}$ associated with each of these eigenstates, i.e.

$$p = \frac{\hbar\pi}{a}, -\frac{\hbar\pi}{a}, \frac{2\hbar\pi}{a}, -\frac{2\hbar\pi}{a}$$

And the corresponding probabilities are just the squared magnitudes of the coefficients, i.e.

$$\begin{aligned}
\Pr(p = \frac{\hbar\pi}{a}) &= \left|\sqrt{\frac{4}{3}}\frac{1}{2i}\right|^2 = \frac{1}{3} \\
\Pr(p = -\frac{\hbar\pi}{a}) &= \left|-\sqrt{\frac{4}{3}}\frac{1}{2i}\right|^2 = \frac{1}{3} \\
\Pr(p = \frac{2\hbar\pi}{a}) &= \left|\sqrt{\frac{2}{3}}\frac{1}{2i}\right|^2 = \frac{1}{6} \\
\Pr(p = -\frac{2\hbar\pi}{a}) &= \left|-\sqrt{\frac{2}{3}}\frac{1}{2i}\right|^2 = \frac{1}{6}
\end{aligned}$$

(d) Expressed in the basis of energy eigenstates, the time evolution of the wave function is given by

$$\begin{aligned}
\Psi(x, t) &= \sqrt{\frac{2}{3}}\phi_1(x)\exp\left(-\frac{iE_1t}{\hbar}\right) - \sqrt{\frac{1}{3}}\phi_2(x)\exp\left(-\frac{iE_2t}{\hbar}\right) \\
&= \sqrt{\frac{2}{3}}\phi_1(x)\exp\left(-\frac{i\hbar\pi^2t}{2ma^2}\right) - \sqrt{\frac{1}{3}}\phi_2(x)\exp\left(-\frac{2i\hbar\pi^2t}{ma^2}\right)
\end{aligned}$$

The probability density is then

$$\begin{aligned}
|\Psi(x, t)|^2 &= \Psi^*(x, t)\Psi(x, t) \\
&= \frac{2}{3}\phi_1^2(x) + \frac{1}{3}\phi_2^2(x) - \frac{2\sqrt{2}}{3}\phi_1(x)\phi_2(x)\cos\left(\frac{E_2 - E_1}{\hbar}t\right)
\end{aligned}$$

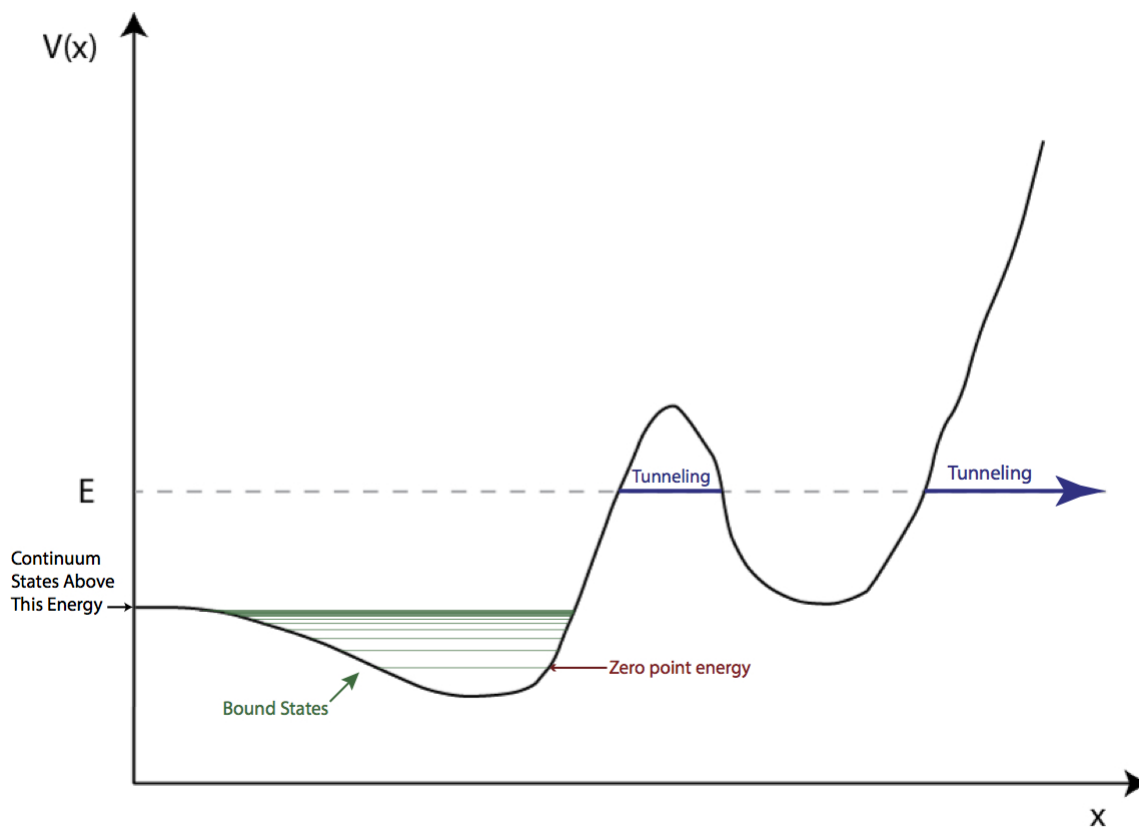
Thus, we see the probability density oscillates with frequency

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

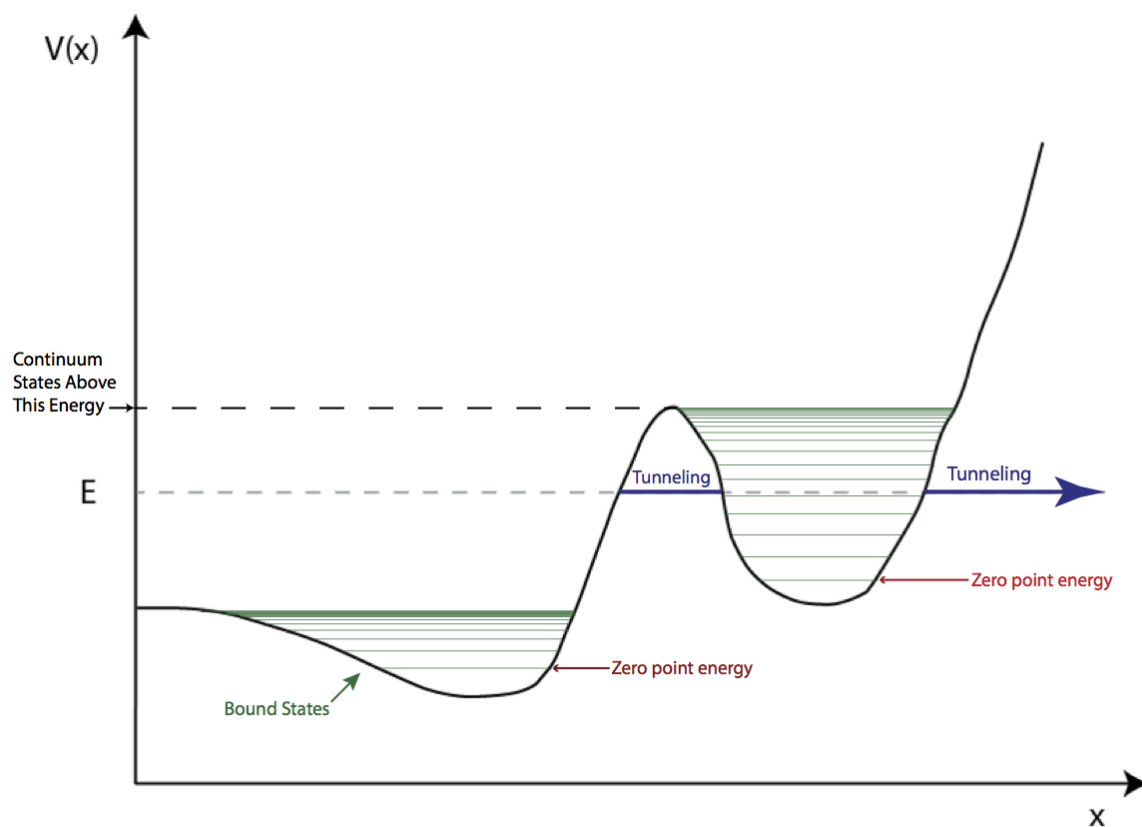
2. (20 pts) Consider a mass moving in the 1D potential, $V(x)$, shown in Figure 1, describing a particle that could exist in either of the two potential wells shown.
- Sketch the energy levels of the discrete, bound states.
 - Label the potential along the y-axis above which the states are continuous for all x .
 - Label the level that is considered the "zero point" energy level for each well.
 - For the energy, E , indicated on the graph, label the region(s) along the x -axis where you would expect quantum mechanical tunneling.

Solution

We accepted two different solutions for this problem. The correct solution is given immediately below. Notice that the second (higher energy) well has no bound states. This is due to quantum tunneling. Imagine a state (any state) prepared in the second well. That state will eventually tunnel through the barrier to the left out into the continuum, and thus there are no states that remain localized indefinitely within that second well.



This is the other solution we accepted: bound states in both wells, with a corresponding zero point energy in each well, and continuum states at all x at energies above the barrier between the two wells.



3. (36 pts) This problem concerns the one-dimensional harmonic oscillator. The potential energy function of the harmonic oscillator is $V(x) = \kappa x^2/2$, where κ is the force constant. The eigen-values in this case are $E_n = (n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \dots$, where $\omega = \sqrt{\kappa/m}$. The normalized wave-function for the lowest energy state is a gaussian:

$$\phi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

where $\alpha = \sqrt{\kappa m/\hbar^2}$.

Useful integrals are:

$$\int_{-\infty}^{\infty} dx \exp(-\alpha x^2) = \sqrt{\pi/\alpha}, \quad \int_0^{\infty} dx x \exp(-\alpha x^2) = 1/2\alpha,$$

$$\int_{-\infty}^{\infty} dx x^2 \exp(-\alpha x^2) = \sqrt{\pi/4\alpha^3}$$

Consider that the particle in the harmonic oscillator is prepared in the properly normalized, $n=0$ stationary state:

$$\Psi(x, 0) = \phi_0(x)$$

- Find the expectation (average) value of position. Classically, would you expect any forces to act on the particle at this position?
- The spring then is suddenly loosened, such that the new spring constant is $\kappa/4$ and the new α is $\alpha/2$. If a measurement of energy is made afterwards, what is the probability that the particle will be found in the ground state ($n=0$) of the new spring?
- Imagine instead that for the particle initially in the $n=0$ stationary state the spring constant is suddenly completely loosened ($\kappa = 0$). What is the expectation (average) value of the energy you would measure afterwards?

Solution

The system begins in the $n=0$ energy eigenstate of the harmonic oscillator, such that

$$\Psi(x, 0) = \phi_0(x)$$

- The expectation value of position is given by

$$\langle \Psi | \hat{x} | \Psi \rangle = \int_{-\infty}^{\infty} dx \phi_0^*(x) x \phi_0(x)$$

We know $\phi_0(x) = \phi_0^*(x)$ is a Gaussian in x and is hence an even function. Thus, the integrand above is overall odd (since x is an odd function), and hence we have $\langle x \rangle = 0$. This corresponds to the center of the well. Classically, there are no forces acting on the particle at this position.

- We now suddenly loosen the spring such that our new spring constant is $\frac{1}{4}$ its original value. We'll make the approximation that the process is diabatic, so that although the Hamiltonian has changed, the wave function has not. The probability that the spring will be found in the $n=0$ state of the new Hamiltonian (harmonic oscillator with $\alpha = \frac{\alpha}{2}$, for which we will denote the eigenstates φ_n) is then simply

$$\begin{aligned}
|\langle \varphi_0 | \Psi \rangle|^2 &= |\langle \varphi_0 | \phi_0 \rangle|^2 \\
&= \left| \int_{-\infty}^{\infty} dx \varphi_0^*(x) \phi_0(x) \right|^2 \\
&= \left| \int_{-\infty}^{\infty} dx \sqrt{\frac{\alpha}{\sqrt{2\pi}}} \exp\left(-\frac{\alpha x^2}{4}\right) \exp\left(-\frac{\alpha x^2}{2}\right) \right|^2 \\
&= \frac{\alpha}{\sqrt{2\pi}} \left| \int_{-\infty}^{\infty} dx \exp\left(-\frac{3\alpha x^2}{4}\right) \right|^2 \\
&= \frac{\alpha}{\sqrt{2\pi}} \left| \sqrt{\frac{4\pi}{3\alpha}} \right|^2 \\
&= \frac{2\sqrt{2}}{3}
\end{aligned}$$

(c) Instead of loosening the spring constant to $\frac{1}{4}$ its initial value, as in (b), let's consider completely loosening it, such that $\kappa=0$. Again, we employ the sudden approximation (the implication being that the loosening of the spring does not change the wave function). Our new Hamiltonian is just the free particle Hamiltonian, $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$, and so we can calculate the average energy as:

$$\begin{aligned}
\langle E \rangle &= \langle \Psi | \hat{H} | \Psi \rangle \\
&= \langle \phi_0 | \hat{H} | \phi_0 \rangle \\
&= \int_{-\infty}^{\infty} dx \phi_0^*(x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \phi_0(x) \\
&= -\frac{\hbar^2 \sqrt{\alpha}}{2m \sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp\left(-\frac{\alpha x^2}{2}\right) \frac{d^2}{dx^2} \left[\exp\left(-\frac{\alpha x^2}{2}\right) \right] \\
&= -\frac{\hbar^2 \sqrt{\alpha}}{2m \sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp\left(-\frac{\alpha x^2}{2}\right) \frac{d}{dx} \left[-\alpha x \exp\left(-\frac{\alpha x^2}{2}\right) \right] \\
&= -\frac{\hbar^2 \sqrt{\alpha}}{2m \sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp\left(-\frac{\alpha x^2}{2}\right) \left[\alpha^2 x^2 \exp\left(-\frac{\alpha x^2}{2}\right) - \alpha \exp\left(-\frac{\alpha x^2}{2}\right) \right] \\
&= -\frac{\hbar^2 \sqrt{\alpha^5}}{2m \sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-\alpha x^2) x^2 + \frac{\hbar^2 \sqrt{\alpha^3}}{2m \sqrt{\pi}} \int_{-\infty}^{\infty} dx \exp(-\alpha x^2) \\
&= -\frac{\hbar^2 \sqrt{\alpha^5}}{2m \sqrt{\pi}} \sqrt{\frac{\pi}{4\alpha^3}} + \frac{\hbar^2 \sqrt{\alpha^3}}{2m \sqrt{\pi}} \sqrt{\frac{\pi}{\alpha}} \\
&= \frac{\hbar^2 \alpha}{4m}
\end{aligned}$$

Commentary: we know $\alpha = \sqrt{\frac{\kappa m}{\hbar^2}}$ and $\omega = \sqrt{\frac{\kappa}{m}}$, so we can rewrite our answer as

$$\langle E \rangle = \frac{1}{4} \hbar \omega$$

This is precisely half the ground-state energy of the 1D harmonic oscillator, i.e. $\langle E \rangle = \frac{1}{2} E_0$. Now let's think about what we actually calculated here: we've calculated what amounts to the average kinetic energy for a harmonic oscillator in its ground state, and we've calculated a value that is half of the total energy (implying the other half is potential energy). This makes intuitive sense, and in CHEM120B

you'll learn about something in statistical mechanics called the equipartition theorem, which basically states that for systems in thermal equilibrium, any degree of freedom that contributes quadratically to the energy contributes the same average energy, $\frac{1}{2}k_B T$. For the harmonic oscillator, the kinetic energy is quadratic in velocity, and the potential is quadratic in position, so we have equal contributions to the average energy for each. That's exactly what we're seeing here!