Problem 1

The ionization potential tells us how much energy we need to use to remove an electron, so we know that any energy left afterwards will be the kinetic energy of the ejected electron.

So first we need to calculate the total energy we’re putting into the system; namely, we need to calculate the energy of the photon, \( E \):

\[
E = h \nu_{\text{light}} = \frac{hc}{\lambda}
\]

where

\[
\begin{align*}
h &= 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \\
\nu_{\text{light}} &= 2.99 \times 10^8 \text{ m/s} \\
\lambda &= 100 \times 10^{-9} \text{ m} \\
c &= 1.602 \times 10^{-19} \text{ J} \\
&= 1.98 \times 10^{-18} \text{ J} \\
&= 12.34 \text{ eV}
\end{align*}
\]

The ionization potential, \( V \), is 8 eV, so we subtract that amount of energy off from the energy of the photon. All the remaining energy is the kinetic energy. So the kinetic energy, \( T \), is

\[
T = E - V = 12.34 \text{ eV} - 8 \text{ eV} = 4.34 \text{ eV}
\]

Problem 2

It seemed that there was a lot of confusion on this problem as to what was going on in this problem. Perhaps many students were unfamiliar with the term “diffraction,” which you should have seen in either a physics class or in your general chemistry textbook. For a brief picture of electron diffraction, check out the website http://7.ebsd.com/ebsdbeginners2.htm.

Many students also used the equation \( E = \frac{hc}{\lambda} \). That equation is only relevant for particles moving at the speed of light (which is why \( c \), the speed of light, appears in the equation). According to currently accepted science (general relativity), electrons could never move at the speed of light.

So what’s the correct way to solve it? Well, since the de Broglie wavelength of the scattered electron has to be about the same size as the diffraction, we’ll just assume that they’re equal. Then we plug the lattice spacing in as the de Broglie wavelength for the particle we’re looking for:

\[
p = \frac{h}{\lambda}
\]

\[
\begin{align*}
\left[ p = 1.33 \times 10^{-24} \text{ kg} \cdot \text{m/s} \right] & \quad \left[ v = 1.46 \times 10^6 \text{ m/s} \right]
\end{align*}
\]

Kinetic energy, \( T \), is given by \( \frac{p^2}{2m} \), so all we have to do now is plug in the de Broglie relation (1)
for \( p \) in that equation:

\[
T = \frac{p^2}{2m} = \frac{\hbar^2}{2m \lambda^2} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2 (9.11 \times 10^{-31} \text{ kg}) (0.5 \times 10^{-9} \text{ m})^2} = 9.64 \times 10^{-19} \text{ J}
\]

That will be the kinetic energy of an electron that will diffract off of this lattice.

### Problem 3

In this problem we are asked to study some properties of a wavefunction that is a superposition of two stationary states, each of which satisfies the time-independent Schrödinger equation:

\[
\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \tag{2}
\]

It’s worth pointing out that \( \hat{H} \) hasn’t been specified in any way – it’s not the particle in a box-like Hamiltonian \( \hat{H} = \frac{\hat{p}^2}{2m} \) or any other specific Hamiltonian. Indeed, even if it had been specified, we wouldn’t have needed that information to solve the problem. All we need to know is what we’re told in (2).

The specific combination of states we’ve been asked to study is

\[
|\psi\rangle = \frac{1}{\sqrt{2}} |\psi_1\rangle + \frac{1}{\sqrt{2}} |\psi_2\rangle
\]

The meaning of this equation is a little bit subtle. As would be the case if our wavefunction were chosen to be just one from the set of \( \{|\psi_n\rangle\} \), we are describing the state of a single particle. That state is a mixture of those described by \( |\psi_1\rangle \) and \( |\psi_2\rangle \), and we’ll have more to say about what this means a little bit later.

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1In the problem statement, Prof. Miller omitted the hat on the Hamiltonian, which is a pretty typical omission after one’s been doing quantum mechanics for a while – the distinction between operators and other objects becomes pretty engrained, and the notation is no longer necessary except as a reminder. Even so, we’ll try to be scrupulous about it here.
In part a, we are asked to find \( \langle H \rangle = \langle \psi | \hat{H} | \psi \rangle \). Let's do it:\(^2\)

\[
\langle \psi | \hat{H} | \psi \rangle = \left( \frac{1}{\sqrt{2}} | \psi_1 \rangle + \frac{1}{\sqrt{2}} | \psi_2 \rangle \right) \hat{H} \left( \frac{1}{\sqrt{2}} | \psi_1 \rangle + \frac{1}{\sqrt{2}} | \psi_2 \rangle \right)
\]

\[
= \frac{1}{2} \times \left( \langle \psi_1 | \hat{H} | \psi_1 \rangle + \langle \psi_1 | \hat{H} | \psi_2 \rangle + \langle \psi_2 | \hat{H} | \psi_1 \rangle + \langle \psi_2 | \hat{H} | \psi_2 \rangle \right)
\]

This first step has only involved pulling out the constants and evaluating a typical binomial product. Now we use (2) and pull out the (constant) energies to obtain

\[
\langle \psi | \hat{H} | \psi \rangle = \frac{1}{2} \times (E_1 | \psi_1 \rangle + E_2 | \psi_2 \rangle + E_1 | \psi_2 \rangle + E_2 | \psi_1 \rangle)
\]

We saw in class that the eigenfunctions of a Hermitian operator are orthogonal to each other, and we can assume that our stationary states are normalized. In other words, we can use the relationship \( \langle \psi_m | \psi_n \rangle = \delta_{mn} \) to get the answer:

\[
\langle \psi | \hat{H} | \psi \rangle = \frac{1}{2} \times (E_1 + 0 + 0 + E_2)
\]

\[
= \frac{1}{2} E_1 + \frac{1}{2} E_2
\]

That takes care of part a. Now we are asked (part b) to find the “uncertainty” in the energy, \( \Delta E = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} \)

We already know \( \langle H \rangle \) from part a, so we only need to find \( \langle H^2 \rangle = \langle \psi | \hat{H}^2 | \psi \rangle \). The procedure here is exactly the same as for part a, so here it is:

\[
\langle \psi | \hat{H}^2 | \psi \rangle = \left( \frac{1}{\sqrt{2}} | \psi_1 \rangle + \frac{1}{\sqrt{2}} | \psi_2 \rangle \right) \hat{H}^2 \left( \frac{1}{\sqrt{2}} | \psi_1 \rangle + \frac{1}{\sqrt{2}} | \psi_2 \rangle \right)
\]

\[
= \frac{1}{2} \times \left( \langle \psi_1 | \hat{H}^2 | \psi_1 \rangle + \langle \psi_1 | \hat{H}^2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}^2 | \psi_1 \rangle + \langle \psi_2 | \hat{H}^2 | \psi_2 \rangle \right)
\]

\[
= \frac{1}{2} \times (E_1^2 \langle \psi_1 | \psi_1 \rangle + E_2^2 \langle \psi_1 | \psi_2 \rangle + E_1^2 \langle \psi_2 | \psi_1 \rangle + E_2^2 \langle \psi_2 | \psi_2 \rangle)
\]

\[
= \frac{1}{2} \times (E_1^2 + 0 + 0 + E_2^2)
\]

\[
= \frac{1}{2} E_1^2 + \frac{1}{2} E_2^2
\]

\(^2\)This may be done either in Dirac notation or using functions. We noticed while grading, though, that some of you were using mixed notations, where functions, bras, kets, and integrals might appear in the same expression. It’s possible to get away with this sometimes, but, in general, it will lead you astray. For a given problem (or, at least, part thereof), you should choose a notational scheme and stick with it. For the purposes of this one, we’ve chosen to use Dirac notation.
We can plug this result directly into (4) and do a little arithmetic:

\[
\sqrt{\langle H^2 \rangle - \langle H \rangle^2} = \sqrt{\frac{1}{2} E_1^2 + \frac{1}{2} E_2^2 - \left( \frac{1}{2} E_1 + \frac{1}{2} E_2 \right)^2}
\]

\[
= \sqrt{\frac{1}{2} E_1^2 + \frac{1}{2} E_2^2 - \left( \frac{1}{4} E_1^2 + \frac{1}{4} E_1 E_2 + \frac{1}{4} E_2^2 \right)}
\]

\[
= \sqrt{\frac{1}{4} E_1^2 - \frac{1}{4} E_1 E_2 + \frac{1}{4} E_2^2}
\]

\[
= \frac{1}{2} \sqrt{(E_2 - E_1)^2}
\]

Finally, we recall that the square root of a number squared is going to give its absolute value, and we see that

\[
\Delta E = \frac{1}{2} |E_2 - E_1|
\]  

which is what we were asked to show in part b.

Now we are left with the conundrum of part c: why are our results from parts a and b intuitively reasonable? The short version of the answer is that, since our stationary states are equally mixed, their energies will be as well. The uncertainty in energy is essentially a standard deviation from the expected value, and its magnitude should therefore be proportional to the energy difference between the two states. The constant comes out to \(\frac{1}{2}\) because \(E_1\) and \(E_2\) are spaced equally from \(\langle H \rangle\). This sounds much simpler than it really is, though, and it’s hard to understand the uncertainty result in particular without thinking a little more carefully.

With that said, let’s go back to the beginning, except now we have some more general superposition of states,  

\[\psi(x) = c_1 \psi_1(x) + c_2 \psi_2(x)\]  

We can multiply each side of the equation by its complex conjugate to get

\[|\psi(x)|^2 = [c_1^* \psi_1^*(x) + c_2^* \psi_2^*(x)] \times [c_1 \psi_1(x) + c_2 \psi_2(x)]\]

\[= |c_1|^2 \times |\psi_1(x)|^2 + |c_2|^2 \times |\psi_2(x)|^2 + \text{two cross terms}\]

Remember that \(|\psi(x)|^2\) is a probability distribution, \(P(x)\), so we can rewrite our expression as

\[P(x) = |c_1|^2 \times P_1(x) + |c_2|^2 \times P_2(x) + \text{two cross terms}\]

If we integrate this expression over all space, each of the probability distributions will give us 1, and the cross terms will go away. That would leave us with the identity

\[1 = |c_1|^2 + |c_2|^2\]

\[\text{3 I’m going to use functions here instead of Dirac notation. It’s crucial to the argument that we decouple integration and multiplying by } \psi^*(x).\]
This expression can be fulfilled by all kinds of combinations of $c_1$ and $c_2$, for example,

$$(c_1, c_2) = (0, 1) \text{ or } \left( \frac{1}{\sqrt{3}}, \sqrt{\frac{2}{3}} \right) \text{ or } \left( \frac{i}{\sqrt{8}}, -i \sqrt{\frac{7}{8}} \right) \text{ or } \ldots$$

The particular choice that was made in this problem was $\left( \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)$, and, within a sign or some complex multiplier, it’s the only choice that corresponds to an equal mixture of the two states.

This conclusion doesn’t take us much farther than what we stated in the first part of our answer, though – it confirms the idea that equal mixing is an important feature of this particular superposition. The key to moving beyond this superficial understanding is to reexamine (8). On the left side of the equation we have the total probability for finding the particle somewhere in space, which is equal to 1, as we would hope. On the right side we have two constants. We have to conclude, therefore, that these represent contributions to the total probability from different “events” – in this case, different ways of observing the particle. Specifically, referring back to (7) would indicate that we have $|c_1|^2$ chance of observing the particle in a spot consistent with $P_1(x)$ and $|c_2|^2$ chance of observing it in a spot consistent with $P_2(x)$.

Following similar work and recalling (2), we can write down

$$\psi(x)^* \hat{H} \psi(x) = |c_1|^2 \times E_1 \times P_1(x) + |c_2|^2 \times E_2 \times P_2(x) + \text{two cross terms}$$

Recalling that the cross terms will disappear on integration, we can now interpret this expression to mean that we have $|c_1|^2$ chance of measuring an energy consistent with $P_1(x)$ and $|c_2|^2$ chance of measuring an energy consistent with $P_2(x)$.

It might help to think about that statement more concretely: we can prepare $N$ systems, where $N$ is very large, such that they are described by (6). We can measure the energy for each one. In doing so, we will measure the energy to be $E_1$ for some of the systems and $E_2$ for the others. In the specific case given in this problem, $E_1$ and $E_2$ will each be measured for exactly $|c_1|^2 = |c_2|^2 = \frac{1}{2}$ of the systems (at least in the limit that $N \to \infty$). If we index our experiments using $j$ (such that the value of $E$ measured in experiment $j$ is $E_j$) and average our experimental findings, we’ll get

$$\langle H \rangle = \frac{1}{N} \sum_{j=1}^{N} E_j = \frac{1}{N} \times \left( \frac{N}{2} E_1 + \frac{N}{2} E_2 \right) = \frac{1}{2} E_1 + \frac{1}{2} E_2$$

which is just what we say when we solved part a and got (3). In other words, the expectation value is an average in quantum mechanics to the extent that it describes the expected outcome of a large series of experiments on a set of identical systems. Equally importantly, the expectation value is not in general going to be a value that can be observed when actually performing a measurement on a system – that will only be the case when the system in question is a “pure state” rather than a superposition of states. Figure 1 is meant to highlight this.

Now that we’ve built up this understanding, we can easily explain the result in (5) by recalling

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4In this case, we could also simply make the interpretation that we find the particle in a spot consistent with the mixed probability distribution $P(x)$, but that becomes problematic once we start measuring things.
Figure 1: The quantum mechanical probability distribution in energy for a state described by (6) with $c_1 = c_2 = \frac{1}{\sqrt{2}}$, $E_1 = 2$, and $E_2 = 4$ is compared to a normal distribution (which is roughly “classical”) with the same mean and standard deviation, as given by (3) and (5). Note how all of the probability is split equally between two distinct energies in the quantum case (shown in red). Note also that the expected value of energy and many others are never observed.

the statistical equation for the standard deviation:

$$\sigma_E = \sqrt{\frac{1}{N} \sum_{j=1}^{N} (E_j - \langle H \rangle)^2}$$

We already know that we’ll measure $E_1$ and $E_2$ half the time, and we know $\langle H \rangle$ from (3). Plugging in that information yields

\[
\sigma_E = \sqrt{\frac{1}{N} \times \frac{N}{2} \times \left[ E_1 - \left( \frac{1}{2} E_1 + \frac{1}{2} E_2 \right) \right]^2 + \frac{N}{2} \times \left[ E_2 - \left( \frac{1}{2} E_1 + \frac{1}{2} E_2 \right) \right]^2}
\]

\[
= \frac{1}{2} \times \left\{ \left[ \frac{1}{2} E_1 - \frac{1}{2} E_2 \right]^2 + \left[ \frac{1}{2} E_2 - \frac{1}{2} E_1 \right]^2 \right\}
\]

\[
= \frac{1}{2} \times \left\{ 2 \times \left[ \frac{1}{2} E_2 - \frac{1}{2} E_1 \right]^2 \right\}
\]

\[
= \sqrt{\left[ \frac{1}{2} E_2 - \frac{1}{2} E_1 \right]^2}
\]

\[
= \frac{1}{2} \times |E_2 - E_1|^2
\]

\[
= \frac{1}{2} |E_2 - E_1|
\]
which is exactly the same as (5). So $\Delta E$ describes an uncertainty in the sense of a standard deviation of a set of measurements of the energy from its expected value for a large number of systems. With that said, welcome to the weird world of quantum measurement theory in its most basic form.

**Problem 4**

For an operator $\hat{A}$ that has no explicit time dependence, the time evolution of $\langle A \rangle_t$ follows the *Heisenberg equation of motion*:

$$i\hbar \frac{d}{dt} \langle A \rangle_t = \langle \Psi(t) | [\hat{A}, \hat{H}] | \Psi(t) \rangle$$

Thus in the following two situations we would have $\frac{d}{dt} \langle A \rangle_t = 0$:

(a) **Condition on Operator**: $[\hat{A}, \hat{H}] = 0$.

(b) **Condition on State**: $| \Psi(t) \rangle$ is a *stationary state*, i.e. $| \Psi(t) \rangle = |\psi_n\rangle e^{-iE_n t/\hbar}$ where $|\psi_n\rangle$ is an energy eigenstate with energy $E_n$.

The above is all you need to receive full credit on this problem.  

**Condition on Operator**  If operator $\hat{A}$ commutes with the Hamiltonian $\hat{H}$, i.e. $[\hat{H}, \hat{A}] = 0$, then by Heisenberg equation of motion $\frac{d}{dt} \langle A \rangle_t = 0$ for any state $| \Psi(t) \rangle$. In this case $\hat{A}$ is called a *constant of motion*.

**Condition on State** If $| \Psi(t) \rangle$ is a separable solution to the Schrödinger equation, such that $
abla(x,t) = \psi(x) f(t)$ then we found by separation of variables that

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}$$

where $\psi_n(x)$ must solve the time independent Schrödinger equation

$$\hat{H} \psi_n(x) = E_n \psi_n(x)$$

i.e. $\psi_n(x)$ is an energy eigenstate with energy eigenvalue $E_n$.

In this case $| \Psi_n(t) \rangle$ is called a *stationary state*, because the expectation value of any observable $\hat{A}$ (which has no explicit time-dependence) on a stationary state is independent of time. There are two ways to show why this is true,

(a) By substituting $| \Psi_n(t) \rangle$ into $\langle A \rangle_t = \langle \Psi_n(t) | \hat{A} | \Psi_n(t) \rangle$ and seeing that the time-dependent phase

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5 Refer to your lecture notes on 9/18/2006.
6 Refer to Exam 1 review notes, Section 4.4.
factor $e^{-iE_nt/\hbar}$ cancels.

$$\langle \Psi_n(t)|\hat{A}|\Psi_n(t)\rangle = \int_{-\infty}^{+\infty} dx \psi_n^*(x,t)\hat{A}\psi_n(x,t)$$
$$= \int_{-\infty}^{+\infty} dx \psi_n^*(x)e^{+iE_nt/\hbar}\hat{A}\psi_n(x)e^{-iE_nt/\hbar}$$
$$= e^{+iE_nt/\hbar} e^{-iE_nt/\hbar} \int_{-\infty}^{+\infty} dx \psi_n^*(x)\hat{A}\psi_n(x)$$
$$= \int_{-\infty}^{+\infty} dx \psi_n^*(x)\hat{A}\psi_n(x)$$
$$= \langle \psi_n|\hat{A}|\psi_n \rangle$$

which is independent of time. In the above manipulation, I was able to move the time-dependent factor $e^{+iE_nt/\hbar}$ out of the integral because the integral is over space $x$, and because the operator $\hat{A}$ only acts on space.

(b) Using Heisenberg Equation of motion. The time evolution of expectation of $A$ on the state $|\Psi_n(t)\rangle$ is given by

$$i\hbar \frac{d}{dt} \langle A \rangle = (\langle \Psi_n(t)|[\hat{A},\hat{H}]|\Psi_n(t)\rangle)$$
$$= \langle \psi_n|e^{+iE_nt/\hbar}[\hat{A},\hat{H}]e^{-iE_nt/\hbar}|\psi_n \rangle$$
$$= \langle \psi_n|\hat{A}\hat{H}|\psi_n \rangle - \langle \psi_n|\hat{H}\hat{A}|\psi_n \rangle$$
$$= \langle \psi_n|\hat{A}\hat{H}|\psi_n \rangle - \langle \psi_n|E_n \hat{A}|\psi_n \rangle$$
$$= E_n \left\{ \langle \psi_n|\hat{A}|\psi_n \rangle - \langle \psi_n|\hat{A}|\psi_n \rangle \right\}$$
$$= 0$$

Thus $\langle A \rangle$ is independent of time. Again, I was able to pull the time-dependent factors out of the integral because the integral is over space, and operator $[\hat{A},\hat{H}]$ only acts on space. I also applied the fact that $|\psi_n \rangle$ is an eigenstate of $\hat{H}$ with real eigenvalue $E_n$, such that

$$\hat{H}\psi_n(x) = E_n\psi_n(x)$$

Note that for a stationary state, we require $\psi_n(x)$ to be an eigenstate of the Hamiltonian $\hat{H}$, we do not require it to be an eigenstate of $\hat{A}$. In fact eigenstates of $\hat{A}$ will not be stationary (have time-independent expectation values $\langle A \rangle_t$) unless $\hat{A}$ and $\hat{H}$ commute, in which case $\hat{A}$ is a constant of motion for any wavefunction.
Problem 5

First, recall the solutions to the Schrödinger equation for the 1-D particle in a box of length $a$. Starting with the Schrödinger equation in 1 dimension ($x$), we have:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E\psi(x) \quad (9)$$

Taking the derivatives and rearranging we have

$$\psi'' = -\frac{2m}{\hbar^2} [E - V(x)] \psi \quad (10)$$

Typically we say that inside the box $V = 0$ and outside the box $V = \infty$. However, we are free to define the potential in the box as finite $V_0$. If we do that and apply the usual boundary conditions for the problem, we get inside the box

$$\psi(x) = \sqrt{\frac{2}{a}} \sin(kx) \quad k = \sqrt{\frac{2m}{\hbar^2} (E - V_0)} = \frac{n\pi}{a} \quad (11)$$

where $n$ is an integer. If $n = 0$ the wavefunction itself is zero for all $x$, which means we are no longer talking about a particle (or at most we are talking about a particle which can never be measured anywhere). Negative values of $n$ do not change the probability distribution, so these are not different quantum states. Therefore the allowed values of $n$ are which will provide us with a complete set of quantum states are the positive integers. The energies associated with these quantum numbers can be found by inverting (11).

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} + V_0 \quad (12)$$

Great, you already knew that. If we instead were to do a 2-D box with a nonzero potential in the bottom, the Schrödinger equation would have kinetic energy terms in the $x$ and $y$ directions as well as the potential energy term:

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + V_0 \right] \psi(x, y) = E\psi(x, y) \quad (13)$$

This problem is easily solved if we guess that $\psi(x, y)$ can be written as a product of a function of $x$ and a function of $y$, just like we did in solving the time dependent Schrödinger equation. Doing this we come up with the energy eigenstates given in the problem statement:

$$E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{n_x}{a_x} \right)^2 + \left( \frac{n_y}{a_y} \right)^2 \right] + V_0 \quad (14)$$

which is a sum of the energies of 2, 1-D particle in a box problems. The wavefunction will be a product of 2, 1-D wavefunctions, which is why we have the condition that neither of the quantum numbers can be zero for the particle to exist.

Now the solutions to the questions are relatively simple. For (a) we want the ground state of the square box. This box has a constant potential $V_0$ everywhere in the box, and we have just argued
that in the lowest energy state $n_x = n_y = 1$. Both sides of this box are length $a$. Therefore:

$$E_{1,1} = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{1}{a} \right)^2 + \left( \frac{1}{a} \right)^2 \right] + V_0$$

$$= \frac{\hbar^2 \pi^2}{ma^2} + V_0 \quad (15)$$

Part (b) asks for the ground state energy in the long skinny box. In this box the potential energy is everywhere 0. The quantum numbers are still both 1, but the box has dimensions $b$ and $L$.

$$E_{1,1} = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{1}{b} \right)^2 + \left( \frac{1}{L} \right)^2 \right]$$

$$(16)$$

Now as is noted in the problem, because the square box has greater potential energy then the skinny box classically a particle in the square would always have enough energy to get into the skinny box. However in quantum mechanics we have this "zero point" energy business. For a small enough long skinny box the zero point energy will be squeezed above that of the square box. In part (c) we are supposed to figure out what width $b$ would make the ground state energy in the long box higher then that in the square. The problem is simplified by letting the length of the box go to $\infty$. First we find the ground state energy in the long box when $L \rightarrow \infty$.

$$\lim_{L \to \infty} E_{1,1} = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{1}{b} \right)^2 + \left( \frac{1}{\infty} \right)^2 \right] = \frac{\hbar^2 \pi^2}{2mb^2} \quad (17)$$

Now we want to find the values of $b$ that make the ground state energy in the long box larger then the ground state energy of the square. Setting (17) $> (15)$ we have

$$\frac{\hbar^2 \pi^2}{2mb^2} > \frac{\hbar^2 \pi^2}{ma^2} + V_0 \quad (18)$$

$$\frac{1}{b^2} > \frac{2}{a^2} + \frac{2m}{\hbar^2 \pi^2} V_0 \quad (19)$$

$$b^2 < \left( \frac{2}{a^2} + \frac{2mV_0}{\hbar^2 \pi^2} \right)^{-1} \quad (20)$$

$$b < \left( \frac{2}{a^2} + \frac{2mV_0}{\hbar^2 \pi^2} \right)^{-\frac{1}{2}} \quad (21)$$

This is a find answer to the question. Combining the fractions yields

$$b < \left( \frac{2\hbar^2 \pi^2 + 2mV_0a^2}{a^2 \hbar^2 \pi^2} \right)^{-\frac{1}{2}} \quad (22)$$

$$b < \left( \frac{2\hbar^2 \pi^2 + 2mV_0a^2}{a^2 \hbar^2 \pi^2} \right)^{-\frac{1}{2}} \quad (23)$$

$$b < \frac{\sqrt{a^2 \hbar^2 \pi^2}}{2\hbar^2 \pi^2 + 2mV_0a^2} \quad (24)$$
Many people wanted to use numeric values for $\hbar$ and $m$. It’s not wrong to do this, but it’s also not necessary. Also, note that nowhere in the problem statement does it state we’re talking about an electron, so using the mass of an electron isn’t really correct for this problem. Also note that the problem didn’t state you needed to derive the energy eigenvalues, just to use them. It therefore was not necessary to solve the Schrödinger equation for this problem. Finally, as a few people noticed you have $\hbar$ and $\pi$ right next to each other in the answer, so if you want you can cancel them, $\hbar \pi = \hbar / 2$. But since this is quantum mechanics people traditionally leave $\hbar$ as is.