10.1) 
\[ E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{sec})(3 \times 10^8 \text{ m/s})}{6.80 \times 10^{-7} \text{ m}} = 2.92 \times 10^{-19} \text{ J/photons} \]
\[ = (2.92 \times 10^{-19} \text{ J/photons})(1 \text{ eV/1.602} \times 10^{-19} \text{ J}) = 1.82 \text{ eV/photons} \]

One einstein corresponds to 1 mole of photons...so the energy per einstein is 
\( 2.92 \times 10^{-19} \, \text{J/photons} \times 6.02 \times 10^{23} \, \text{photons/einstein} = 175.8 \times 10^3 \, \text{J/einstein} = 175.7 \, \text{kJ/einstein} \)

b) Number of Einsteins = \( \frac{485 \, \text{kJ}}{175.7 \, \text{kJ/einstein}} = 2.76 \, \text{einstens} \)

Quantum Yield = \( \frac{\text{number of molecules reacted}}{\text{number of photons absorbed}} \approx \frac{2.76}{8} \) to \( \frac{2.76}{9} \)

Additional Problems:

1) In the text, the probability that an electron occurs between a distance \( r_1 \) and \( r_2 \) from the nucleus is 
\[ P_{n,0} (r_1, r_2) = \frac{\int_{r_1}^{r_2} \psi_{n,0}^2 \, dr}{4\pi} \]

Note this expression is only valid for an “s” orbital \((l=0)\), because the integration over the angles \( \theta \) and \( \phi \) yield simply a factor of \( 4\pi \).

a) Calculate the probability that in a hydrogen atom a 2s electron occurs between 1 and three 3 Bohr radii of the nucleus.

Solution:

\[ P_{2,0} = 4\pi \int_{a_0}^{3a_0} dr r^2 \cdot R_{2,0}^2 = 4\pi \int_{a_0}^{3a_0} dr \cdot r^2 \left( \frac{1}{4\sqrt{2}\pi} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \right)^2 \]
\[ = \frac{1}{8a_0^3} \int_{a_0}^{3a_0} dr \cdot \left( 4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2} \right) e^{-r/a_0} \]
\[
= \frac{1}{8a_0^3} \left\{ \int_0^{3a_0} dr \cdot 4r^2 e^{-r/a_0} - \int_0^{3a_0} dr \frac{4r^3}{a_0} e^{-r/a_0} + \int_0^{3a_0} dr \frac{r^4}{a_0^2} e^{-r/a_0} \right\}
\]

Make the substitution \( \rho = r/a_0 \), \( a_0 d\rho = dr \) and obtain...

\[
\frac{1}{8} \left\{ \int_1^{3} \rho \cdot 4\rho^2 e^{-\rho} - \int_1^{3} \rho 4\rho^3 e^{-\rho} + \int_1^{3} \rho \rho^4 e^{-\rho} \right\}
\]

Now proceed exactly as in Example 9.5 pg 514 of the text. Use the standard integrals

\[
\int x^2 e^{ax} \, dx = e^{ax} \left[ \frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3} \right]
\]

\[
\int x^3 e^{ax} \, dx = e^{ax} \left[ \frac{x^3}{a} - \frac{3x^2}{a^2} + \frac{6x}{a^3} - \frac{6}{a^4} \right]
\]

\[
\int x^n e^{ax} \, dx = \frac{x^n e^{ax}}{a} - \frac{n}{a} \int x^{n-1} e^{ax} \, dx
\]

Substitute these forms into the equation and evaluate the results between \( \rho=1 \) and \( \rho=3 \).

You can do this numerically by plotting the function in the integrand (I left out the constants because I am going to calculate a percentage at the end...)

I summed up the probability column between 1 and three Bohr orbits and divided it by the area under the curve between 0 and 20 Bohr orbits. Numerically the probability is about 4%.

b) Calculate the most probable value of the distance \( r \) for a 2s electron and a 2p electron. Hint: maximize the probability by settings its first derivative w.r.t. \( r \) to zero and solving for the resulting \( r \). Confirm these values by plotting the radial wave functions for the 2s and 2p electrons.
\begin{align*}
P_{1,0} &= 4a_0^3 r^2 e^{-2r/a_0} \
\Rightarrow \frac{dP}{dr} &= 0 = 4a_0^3 \left(2r - 2 \frac{r^2}{a_0}\right) e^{-2r/a_0} \
\therefore r &= a_0 \\
P_{2,p} &= \frac{1}{8a_0^3} r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} \times \text{angular terms} \\
\frac{dP_{2,p}}{dr} &= 0 = \frac{1}{24a_0^5} \left(4r^3 - r^4\right) e^{-r/a_0} \\
\therefore r &= 4a_0 \\
\end{align*}

Note in the 2 probability the angular terms are constants when we differentiate with respect to \(r\). They just divide out when we equal the derivative to zero…

You can check these results using the graphs in Tinoco or in any standard Pchem text. In fact, the relevant plots for the 2p orbitals are in the Honors Chem text…Oxtoby, Gills, and Nachtrieb…Principles of Modern Chemistry (4\text{th} \text{ed})…pg 558.

c) The probability that in hydrogen an electron is in the angular range \(\phi_1\) to \(\phi_2\) and \(\theta_1\) to \(\theta_2\) is given by

\[
P = \int_0^{\theta_1} \int_{\phi_1}^{\phi_2} \frac{\partial}{\partial \theta} \left[ d\phi \int_{\phi}^{\phi} Y_{l,m}(\theta, \phi) \right] \left[ d\theta \int_{\theta}^{\theta} \right] \left(3 \cos^2 \theta - 1\right)
\]

where \(Y_{l,m}\) is the angular wave function. Calculate the probability that a electron is in the \(dz^2\) orbital between \(\theta = 54^\circ\) and \(125^\circ\). Confirm this result graphically.

The angular wavefunction for the relevant \(dz^2\) orbital can be found in the lecture notes.

This wave function is proportional to

\[
P = \frac{2\pi}{16\pi} \left(3 \cos^2 \theta - 1\right)
\]

\[
P = \int_0^{\theta=125^\circ} \int_{\phi=54^\circ}^{\phi=125^\circ} \left(3 \cos^2 \theta - 1\right)^2 \sin \theta d\theta = 0.384
\]

2) The “del-squared” operator has the form

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]

and if a wave function is a function of \(x, y,\) and \(z\),

\[
\nabla^2 \psi(x, y, z) = \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2}.
\]

In spherical coordinate the “del-squared” operator has the form

\[
\nabla^2 \psi(r, \theta, \phi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right)
\]

\[
+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2}
\]

a) Write the Hamiltonian for an electron in hydrogen in spherical coordinates.
\[ \hat{H} = -\frac{\hbar^2}{8\pi^2m} \left( \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \right) - \frac{e^2}{4\pi\varepsilon_0 r} \]

b) According to the variational principle of quantum mechanics for an approximate wave function \( \psi' \), the energy defined as
\[
E' = \frac{\int \psi' \hat{H} \psi' d\tau}{\int \psi' \psi' d\tau}
\]
will be greater than the true energy \( E \), i.e. \( E' \geq E \). Note
\[
d\tau = dx \cdot dy \cdot dz = r^2dr \cdot \sin\theta d\theta \cdot d\phi.
\]
Accordingly, as the approximate wave function approaches its true value, the variational energy \( E' \) approaches its true value, i.e. as \( \psi' \to \psi \), \( E' \to E \). See text problem 9.6.

Assume the 1s wave function has the approximate form \( \psi'_{1s} = e^{-cr} \) where \( c \) is a constant. Use the variational principle to determine the constant \( c \) and the corresponding energy. Compare these results to the exact expressions for the 1s wave function and energy obtained by solving Schroedinger’s equation. Hint: Minimize \( E' \) w.r.t. \( c \). Solve the resulting equation for \( c \).

\[
\psi'_{1s} \hat{H} \psi' = -\frac{\hbar^2}{8\pi^2m} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \psi'_{1s} \right) \right] - \frac{e^2}{4\pi\varepsilon_0 r} \psi'_{1s}
\]

\[
= -\frac{\hbar^2}{8\pi^2m} \left[ \frac{1}{r^2} \left( 2r \frac{d}{dr} \psi'_{1s} + r^2 \frac{d^2}{dr^2} \psi'_{1s} \right) \right] - \frac{e^2}{4\pi\varepsilon_0 r} \psi'_{1s}
\]

\[
= -\frac{\hbar^2}{8\pi^2m} \left[ \frac{1}{r^2} \left( 2r \frac{d e^{-cr}}{dr} + r^2 \frac{d^2 e^{-cr}}{dr^2} \right) \right] - \frac{e^2}{4\pi\varepsilon_0 r} e^{-2cr}
\]

\[
= -\frac{\hbar^2}{8\pi^2m} \left[ \left( -\frac{2c}{r} e^{-cr} + c^2 e^{-2cr} \right) \right] - \frac{e^2}{4\pi\varepsilon_0 r} e^{-2cr}
\]

\[
\int_0^\infty \psi'_{1s} \hat{H} \psi' d\tau = 4\pi \int_0^\infty \psi'_{1s} \hat{H} r^2 d\tau = 4\pi \int_0^\infty \left[ -\frac{\hbar^2}{8\pi^2m} \left[ \frac{2c}{r} e^{-2cr} + c^2 e^{-2cr} \right] - \frac{e^2}{4\pi\varepsilon_0 r} e^{-2cr} \right] r^2 d\tau
\]

\[
= 4\pi \int_0^\infty \left[ \frac{\hbar^2}{8\pi^2mc} - \frac{e^2}{16\pi\varepsilon_0 c^2} \right] d\tau
\]

\[
\int_0^\infty r^2 e^{-2cr} d\tau = \frac{\pi}{c^3}
\]

\[
\langle E \rangle = \frac{\int \psi'_{1s} \hat{H} \psi' d\tau}{\int \psi'_{1s} \psi' d\tau} = \frac{4\pi c^3}{\pi} \left( \frac{\hbar^2}{32\pi^2mc} - \frac{e^2}{16\pi\varepsilon_0 c^2} \right) = \frac{\hbar^2 c^2}{8\pi^2m} - \frac{e^2}{4\pi\varepsilon_0}.
\]
Then \[ \frac{d\langle E \rangle}{dc} = \frac{d}{dc} \left( \frac{\hbar^2 c^2}{8\pi^2 m} - \frac{e^2 c}{4\pi\varepsilon_0} \right) = \frac{\hbar^2 c}{8\pi^2 m} - \frac{e^2}{4\pi\varepsilon_0} = 0 \Rightarrow c = \frac{4\pi\varepsilon_0 m e^2}{\varepsilon_0 h^2} = \frac{\pi m e^2}{h^2} = \frac{1}{a_o} \]

Finally…use this value of \(c\)

\[ \langle E \rangle = \frac{\hbar^2 c^2}{8\pi^2 m} - \frac{e^2 c}{4\pi\varepsilon_0} = \frac{\hbar^2}{8\pi^2 m} \left( \frac{\pi m e^2}{\varepsilon_0 h^2} \right)^2 - \frac{e^2}{4\pi\varepsilon_0} \left( \frac{\pi m e^2}{\varepsilon_0 h^2} \right) = -\frac{2m e^4 \pi^2}{h^2 (4\pi\varepsilon_0)^2} \]

…which is identical to the result obtained from Schrödinger’s equation...

\[ c) \text{ Repeat the calculation in part b assuming } \psi'_{1s} = e^{-r}. \text{ From this example, what can you conclude about the accuracy of the energy obtained by the variational method? Does it depend strongly upon your guess for the form of the approximate wave function?} \]

Summary: By the same procedure as in part b we find that \[ \langle E \rangle = \frac{3h^2}{8\pi^2 m} - \frac{2e^2 \sqrt{2}}{\sqrt{\pi}} \sqrt{c} \]

\[ \frac{d\langle E \rangle}{dc} = 0 = \frac{3h^2}{8\pi^2 m} - \frac{e^2 \sqrt{2}}{\sqrt{\pi}} c^{-1/2}. \text{ Then } c = \frac{8}{9\pi a_o^2} \]

\[ \langle E \rangle = \frac{3h^2}{8\pi^2 m} c - \frac{2e^2 \sqrt{2}}{\sqrt{\pi}} \sqrt{c} = \left( \frac{3h^2}{\pi^2 m} \right) \left( \frac{1}{9\pi a_o^2} \right) - 2e^2 \sqrt{\frac{16}{9\pi^2 ma_o^2}} \]

\[ = \frac{h^2}{3\pi^2 ma_o^2} - 2e^2 \sqrt{\frac{16}{9\pi^2 ma_o^2}} \]

Now \(a_o = \left( \frac{\hbar}{2\pi} \right)^2 \frac{4\pi\varepsilon_0}{me^2} = 0.53 \times 10^{-8}\text{ cm}\). Substitution of \(a_o\) into the energy equation shows that it differs little in magnitude from the exact value. Therefore the initial form for the wave function need not be too close to the true value to produce an accurate energy.