UNIVERSITY OF ALABAMA Department of Physics and Astronomy PH 253-002 Spring 2019

Homework 4 Solutions

1. Can you see me now? Using the Bohr model for the hydrogen atom, which possible emitted or absorbed wavelengths fall in the visible region of the spectrum (380-770 nm)? Include transitions that involve the "level" $n = \infty$, e.g., an electron absorbing a photon and subsequently escaping the proton to a state with E = 0.

Solution: You can quickly verify that for transitions starting and ending on n = 1, possible wavelengths range from 121.5 nm to 91.2 nm, well into the ultraviolet. Similarly, for n = 3, you can verify that all transitions give wavelengths in the infrared, greater than 800 nm. Only transitions involving n = 2 and a higher level give visible wavelengths, the so-called *Balmer series*, and the transitions have visible wavelengths when the higher level is $n' = \{3, 4, \ldots, 9\}$. For n' = 10 and beyond, the wavelengths are shorter than 380 nm in the ultraviolet.

2. Spatial distribution of probability for a H state. What is the probability of finding an n=3, l=2 electron between $5a_o$ and $6a_o$? Hint: you need only use the radial wave function R(r), see section 7.4 in your text.

Solution: The relevant radial wave function is

$$\mathsf{R} = \frac{4}{81\sqrt{30}a_{o}^{3/2}}\frac{\mathsf{r}^{2}}{a_{o}^{2}}e^{-\mathsf{r}/3a_{o}}$$
(1)

We know then that $P(r) = |R|^2 r^2$, or

$$P(\mathbf{r}) = \frac{2^4}{9^4 \cdot 30a_0^3} \left(\frac{\mathbf{r}}{a_0}\right)^4 e^{-2\mathbf{r}/3a_0} \cdot \mathbf{r}^2 = \frac{2^4}{9^4 \cdot 30a_0} \left(\frac{\mathbf{r}}{a_0}\right)^6 e^{-2\mathbf{r}/3a_0}$$
(2)

The probability the electron is between $5a_o$ and $6a_o$ is then integrating P(r) dr from $5a_o$ and $6a_o$:

$$\mathsf{P}(\mathrm{in} \ [5\mathfrak{a}_{\mathrm{o}}, 6\mathfrak{a}_{\mathrm{o}}]) = \frac{2^4}{9^4 \cdot 30\mathfrak{a}_{\mathrm{o}}} \int_{5\mathfrak{a}_{\mathrm{o}}}^{6\mathfrak{a}_{\mathrm{o}}} \left(\frac{\mathsf{r}}{\mathfrak{a}_{\mathrm{o}}}\right)^6 e^{-2\mathsf{r}/3\mathfrak{a}_{\mathrm{o}}} \,\mathrm{dr} \tag{3}$$

It is more convenient to define a variable $\rho = r/a_o$, $d\rho = dr/a_o$. The resulting integral can be looked up or evaluated numerically.

$$\mathsf{P}(\mathrm{in} \ [5\mathfrak{a}_{\mathbf{o}}, 6\mathfrak{a}_{\mathbf{o}}]) = \frac{2^4}{9^4 \cdot 30} \int_{5}^{6} \rho^6 e^{-2\rho/3} \, \mathrm{d}\rho = \frac{2^4}{9^4 \cdot 30} \approx \frac{2^4}{9^4 \cdot 30} \cdot 707.0 \approx 0.057 \tag{4}$$

3. Angular distribution of probability for a H state. Find the directions in space where the angular probability density for the l=3, $m_l=0$ electron in hydrogen has its maxima and minima. Hint: you only need $P(\theta, \phi)$. See section 7.5 in your text.

Solution: For l = 3, $m_l = 0$, the radial wave function is

$$p(\theta) = \sqrt{\frac{7}{16\pi}} \left(5\cos^3\theta - 3\cos\theta \right) \tag{5}$$

The angular probability density is then

$$\mathsf{P}(\theta) = |\mathsf{p}(\theta)|^2 = \frac{7}{16\pi} \left(5\cos^3\theta - 3\cos\theta \right)^2 \tag{6}$$

Finding the extreme values means setting $dP/d\theta = 0$. Let $A = \frac{7}{16\pi}$ for convenience.

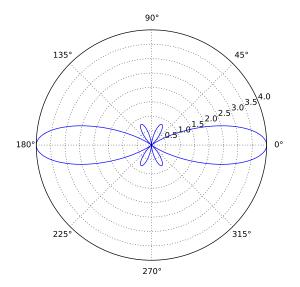
$$\frac{\mathrm{dP}}{\mathrm{d\theta}} = 2\mathrm{A}\left(5\cos^3\theta - 3\cos\theta\right)\left(-15\sin\theta\cos^2\theta + 3\sin\theta\right) = 0\tag{7}$$

$$0 = 6A(\sin\theta)(\cos\theta)(5\cos^2\theta - 3)(1 - 5\cos^2\theta)$$
(8)

Any of the four factors in parentheses above can separately be zero. For each, we will need to do a second derivative test or make a plot to see whether we have found maxima or minima, the results of which are summarized below for $0 \le \theta \le 90$.

condition	θ	max or min?
$\begin{aligned} \sin \theta &= 0\\ \cos \theta &= 0\\ 5\cos^2 \theta &= 3\\ 5\cos^2 \theta &= 1 \end{aligned}$	0 90 39 63	max min min max

Here's what a cross-section of the orbital looks like.



4. Most probable radius for a H state. Find the most probable radius of an electron in the 3p state. Note

$$R_{3p}(r) = \frac{8}{9\sqrt{2} (3a_o)^{3/2}} \left(\frac{r}{a_o} - \frac{r^2}{6a_o^2}\right) e^{-r/3a_o}$$
(9)

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_ee^2} = 0.529 \times 10^{-10} \text{ m}$ is the Bohr radius.

Solution: First, define a new variable $\rho = r/a_o$, and let $A = \frac{8}{9\sqrt{2}(3a_o)^{3/2}}$ for convenience. We have then

$$R = A \left(\rho - \rho^2 / 6 \right) e^{-\rho / 3}$$
(10)

$$|\mathbf{R}|^2 = \mathbf{A}^2 \left(\rho - \rho^2 / 6\right)^2 e^{-2\rho / 3} \tag{11}$$

The probability density is $\mathsf{P}(\mathsf{r})=4\pi r^2|\mathsf{R}|^2,$ or

$$P(\mathbf{r}) = 4\pi r^2 A^2 \left(\rho - \rho^2/6\right)^2 e^{-2\rho/3} = 4\pi a_o^2 A^2 \rho^2 \left(\rho - \rho^2/6\right)^2 e^{-2\rho/3}$$
(12)

Overall constants are not terribly important here, so let $B=4\pi a_o^2 A^2,$ so

$$P(r) = B\rho^2 \left(\rho - \rho^2/6\right)^2 e^{-2\rho/3}$$
(13)

The most probable radius is when dP/dr = 0, so we grind through it.

$$\frac{dP}{dr} = B\left(-\frac{2}{3}\right)e^{-2\rho/3}\rho^2\left(\rho - \rho^2/6\right)^2 + 2Be^{-2\rho/3}\rho\left(\rho - \rho^2/6\right)^2$$
(14)

+
$$B\rho^2 e^{-2\rho/3} \rho^2 \cdot 2(\rho - \rho^2/6)(1 - \rho/3) = 0$$
 (15)

Factor out ρ^2 and $(\rho - \rho^2/6)$, meaning $\rho = \{0, 6\}$ are extreme values. Perform the requisite cancellations and simplify.

$$0 = -\frac{2}{3} \left(\rho - \rho^2 / 6\right) + 2 \left(1 - \rho / 6\right) + 2 \left(1 - \rho / 3\right)$$
(16)

$$0 = -\frac{2}{3}\rho + \frac{1}{9}\rho^2 + 2 - \rho/3 + 2 - 2\rho/3$$
(17)

$$0 = \frac{\rho^2}{9} - \frac{5}{3}\rho + 4 = 0 \tag{18}$$

$$0 = \rho^2 - 15\rho + 36 = (\rho - 12)(\rho - 3)$$
(19)

Thus, the other extreme values are 12 and 3, meaning the whole set is $\rho = \{0, 3, 6, 12\}$. A quick plot or substitution verifies that P is maximal for $\rho = 12$, or $r = 12a_o$.

5. Expectation value of the radius for a H state. Using the radial wave function in the previous problem, find the expected value of the radial position $\langle r \rangle$ of an electron in the 3p state. Is this position the same you found in the previous question? Why or why not?

Solution: From the previous problem,

$$P(\mathbf{r}) = |\mathbf{R}|^2 \mathbf{r}^2 = A^2 \mathbf{r}^2 \left(\frac{\mathbf{r}}{a_0} - \frac{\mathbf{r}^2}{6a_0^2}\right) e^{-2\mathbf{r}/3a_0}$$
(20)

To find $\langle r \rangle$, we have to integrate rP(r) from 0 to ∞ . Use the same substitution $\rho = r/a_o$, $d\rho = dr/a_o$, the resulting integral is known.

$$\langle \mathbf{r} \rangle = \int_{0}^{\infty} \mathbf{r} \mathbf{P}(\mathbf{r}) \, d\mathbf{r} = \int_{0}^{\infty} \mathbf{r} \cdot \mathbf{A}^{2} \mathbf{r}^{2} \left(\frac{\mathbf{r}}{a_{o}} - \frac{\mathbf{r}^{2}}{6a_{o}^{2}} \right) e^{-2\mathbf{r}/3a_{o}} \, d\mathbf{r} \qquad \text{let } \rho = \mathbf{r}/a_{o}, \, d\rho = d\mathbf{r}/a_{o} \tag{21}$$

$$= A^{2} a_{o}^{4} \int_{0}^{\infty} \rho^{3} \left(\rho - \rho^{2}/6\right) e^{-2\rho/3} d\rho = A^{2} a_{o}^{4} \cdot \frac{54675}{64}$$
(22)

$$=\frac{64}{81\cdot 2\cdot 3^3\mathfrak{a}_o^3}\mathfrak{a}_o^4\frac{54675}{64}=\mathfrak{a}_o\frac{3^75^2}{3^43^32}=\frac{25}{2}\mathfrak{a}_o=12.5\mathfrak{a}_o$$
(23)

Nearly the same as the most probable radius, but slightly larger since the 3p radial distribution is not quite symmetric about its maximum value.

6. *Quantum numbers.* Explain why each of the following sets of quantum numbers (n, l, m_l, m_s) is not permitted for hydrogen:

$$(3,3,-1,+\frac{1}{2})$$
 $(2,1,+2,-\frac{1}{2})$ $(2,1,+1,-\frac{3}{2})$ $(3,-1,+1,+\frac{1}{2})$

Solution: First set: l must be less than n. Second set: $|m_l|$ cannot exceed l. Third set: spin cannot be $m_s = -3/2$ for an electron. Fourth set: l cannot be negative.

7. Multiplicity of atomic magnetic moments. Calculate the magnetic moments that are possible for the n=4 level of Hydrogen, making use of the quantization of angular momentum. You may neglect spin. Compare this with the Bohr prediction for n=4.

Solution: If n = 4, then we have possible values for l of $l = \{0, 1, 2, 3\}$. This gives us the magnetic moments possible:

$$\mu = -\mu_{\rm B}\sqrt{l(l+1)} \tag{24}$$

$$\mu = \{0, \sqrt{2}, \sqrt{6}, 2\sqrt{3}\}\mu_{\rm B} \tag{25}$$

By comparison, the Bohr model would predict for level n a magnetic moment of $n\mu_B$, or $4\mu_B$ in this case, since $L = n\hbar$ and $\mu = \mu_B L/\hbar$.

8. Transitions in a magnetic field. Transitions occur in an atom between l=2 and l=1 states in a magnetic field of 3.5000 T, obeying the selection rules $\Delta m_l = 0, \pm 1$. If the wavelength before the field was turned on was 543.00 nm, determine the wavelengths that are observed. You may find the following relationship useful:

$$\left|\Delta\lambda\right| = \left|\frac{d\lambda}{dE}\right|\Delta E = \frac{hc}{E^2}\Delta E = \frac{\lambda^2}{hc}\Delta E \tag{26}$$

Recall that the Zeeman effect changes the energy of a single-electron atom in a magnetic field by

$$\Delta \mathsf{E} = \mathfrak{m}_{\mathfrak{l}} \left(\frac{e\hbar}{2\mathfrak{m}_{e}} \right) \mathsf{B} \qquad \text{with} \qquad \mathfrak{m}_{\mathfrak{l}} = -\mathfrak{l}, -(\mathfrak{l}-1), \dots, 0, \dots, \mathfrak{l}-1, \mathfrak{l}$$
(27)

For convenience, note that $e\hbar/2m_e = \mu_B \approx 57.9 \,\mu\,eV/T$, and neglect the existence of spin.

Solution: In a magnetic field B, the energy levels for a given l state will split according to their value of m_1 . If the original energy of the level is E_1 , then the original level will be split symmetrically into 2l + 1 sub-levels, with adjacent levels shifted by $\mu_B B$:

$$\mathsf{E}_{\mathsf{l},\mathsf{m}_{\mathsf{l}}} = \mathsf{E}_{\mathsf{l}} + \mathsf{m}_{\mathsf{l}} \mathsf{\mu}_{\mathsf{B}} \mathsf{B} \tag{28}$$

This is shown schematically below for l=2 and l=1 levels. The l=2 level has possible \mathfrak{m}_l values of $\mathfrak{m}_l = \{-2, -1, 0, 1, 2\}$, and thus in a magnetic field B what was a single level is now 5 individual levels. For l=1, we have \mathfrak{m}_l values of only $\mathfrak{m}_l = \{-1, 0, 1\}$, and the original level becomes a triplet upon applying a magnetic field.

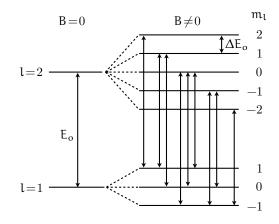


Figure 1: Allowed transitions from l=2 to l=1 with a magnetic field applied.

Before calculating anything, we can apply the dipole selection rules, which states that \mathfrak{m}_{l} can change by only $0, \pm 1$. This means that, for example, from the l=2, $\mathfrak{m}_{l}=1$ level an electron may "jump" to the any of the l=1, $\mathfrak{m}_{l}=\{2,1,0\}$ levels. On the other hand, from l=2, $\mathfrak{m}_{l}=2$ level

an electron may only jump to the l=1, $m_l=1$ level. Following these rules, we see from the figure above that there are only 9 possible transitions allowed. Further, noting that the levels are equally spaced, we have in fact only three different transition energies.

The spacing between the levels ΔE_o is the Zeeman energy given above, $\Delta E_o = \mu_B B$. From our schematic above, it is clear that the only possible transition energies in a magnetic field are the original transition energy (no change in m_l), or the original transition energy plus or minus ΔE_o (m_l changes by ± 1). The original transition energy E_o is readily found from the given wavelength $\lambda = 543.00 \,\mathrm{nm}$:

$$\mathsf{E}_{\mathbf{o}} = \frac{\mathsf{hc}}{\lambda} \approx 2.28 \,\mathrm{eV} \tag{29}$$

Thus, the new transition energies must be

$$\mathsf{E}_{o} \longmapsto \{\mathsf{E}_{o} - \Delta \mathsf{E}_{o}, \mathsf{E}_{o}, \mathsf{E}_{o} + \Delta \mathsf{E}_{o}\} = \{\mathsf{E}_{o} - \mu_{B}B, \mathsf{E}_{o}, \mathsf{E}_{o} + \mu_{B}B\}$$
(30)

That is, the original transition energy plus two new ones. We can easily convert these two new energies into two new wavelengths by the energy-wavelength relationship $E = hc/\lambda$. However, this does require some numerical precision (i.e., carrying at least 7-8 digits in your calculations, and knowing the requisite constants to commensurate precision), and it is somewhat easier to simply calculate the change in energy by itself. Since we know the energy changes by $\pm \Delta E_o$, using the formula given we have

$$\left|\Delta\lambda\right| = \frac{\lambda^2 \Delta E_o}{hc} = \frac{\lambda^2 \mu_B B}{hc} \approx 0.0482 \,\mathrm{nm} \tag{31}$$

The shift in energy of ΔE_o implies a shift in wavelength of $\Delta \lambda \approx 0.0482 \,\mathrm{nm}$, meaning the new transitions must be at the original wavelength λ plus or minus $\Delta \lambda$:

$$\lambda \longmapsto \{\lambda - \Delta\lambda, \lambda, \lambda + \Delta\lambda\} = \{542.95, 543.00, 543.05\} \text{ nm}$$
(32)

9. Gaussian Wave Packets and minimum uncertainty. A particle of mass m is in the state

$$\psi(\mathbf{x}, \mathbf{t}) = \mathbf{A} e^{-\mathfrak{a}\left[\left(\mathfrak{m} \mathbf{x}^2/\hbar\right) + \mathfrak{i} \mathbf{t}\right]}$$
(33)

where $\{A, a\} \in \mathbb{R}$ and $\{A, a\} > 0$. (a) Find A. (b) For what potential energy function V(x) does ψ satisfy the Schrödinger equation? (c) Calculate the expected values of x, x^2 , p, and p^2 . (d) Find Δx and Δp . Is their product consistent with the uncertainty principle?

Solution: In order to find A, we have to normalize. First, since we have a complex wavefunction, let's make sure we get the square right. We will assume A is a positive real constant for convenience.ⁱ

ⁱIf A were complex, we could always absorb the imaginary part into the exponential, which would make it an

$$|\psi|^{2} = \psi^{*}\psi = \left(Ae^{-\alpha\left[\left(mx^{2}/\hbar\right)-it\right]}\right)\left(Ae^{-\alpha\left[\left(mx^{2}/\hbar\right)+it\right]}\right) = A^{2}e^{-2\alpha mx^{2}/\hbar}$$
(34)

You didn't forget to do the complex conjugate, right? Now we can normalize, remembering that

$$1 = \int_{-\infty}^{\infty} |\psi|^2 dx = \int_{-\infty}^{\infty} A^2 e^{-2a\mathfrak{m}x^2/\hbar} dx = A^2 \sqrt{\frac{\pi\hbar}{2a\mathfrak{m}}}$$
(35)

$$\implies \qquad A = \sqrt[4]{\frac{2\mathfrak{a}\mathfrak{m}}{\pi\hbar}} \tag{36}$$

What potential energy function gives this wave function? The function in question is a gaussian, and if you read the book carefully you should have seen it already. Let's not spoil the function. If we know the wave function, and plug it into the time-dependent Schrödinger's equation, the only unknown should be the potential, so we should be able to solve for it. First, we will need various derivatives of ψ .ⁱⁱ Conveniently, for each of the derivatives you can factor out ψ to simplify things.

$$\frac{\partial \psi}{\partial x} = -\frac{2am}{\hbar} x \psi \tag{37}$$

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2am}{\hbar}\psi + \frac{4a^2m^2}{\hbar^2}x^2\psi = -\frac{2am}{\hbar}\left(1 - \frac{2am}{\hbar}x^2\right)\psi \tag{38}$$

$$\frac{\partial \psi}{\partial t} = -ia\psi \tag{39}$$

Substituting into the time-dependent Schrödinger equation, and solving for the $V\psi$ term:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \tag{40}$$

$$V\psi = i\hbar \frac{\partial \psi}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$
(41)

$$V\psi = a\hbar\psi - \frac{\hbar^2}{2m}\frac{2am}{\hbar}\left(1 - \frac{2am}{\hbar}x^2\right)\psi$$
(42)

Now every term still has a ψ left, so we can cancel all of those.

$$V = a\hbar - a\hbar + 2a^2mx^2 \implies V = 2ma^2x^2$$
(43)

The potential that produces this wavefunction is a quadratic one, i.e., the simple harmonic oscillator potential. Knowing this, we can make the usual identification that $V = \frac{1}{2}kx^2$, from which we would deduce $k=4ma^2$ and $\omega = \sqrt{k/m} = 2a$ for the given state of the oscillator.

offset in the t term. That amounts to a choice of when to zero your clock, which we can always do, so we lose nothing by making the assumption that A is real.

 $^{^{}ii} {\rm Remember},$ if you are not familiar with partial derivatives, just read $^{\circ} \partial \psi / \partial t$ as $^{\circ} d \psi / d t.$

How about the expectation values? You can quickly convince yourself that $\langle x \rangle = 0$, since $x |\psi|^2$ is an odd function of x. You could also just asset this to be true - since the potential is symmetric, the expected position should be in the center, at x=0.

$$\langle \mathbf{x} \rangle = \int_{-\infty}^{\infty} \mathbf{x} |\psi|^2 \, \mathrm{d}\mathbf{x} = \int_{-\infty}^{\infty} \mathbf{x} A^2 e^{-2\alpha \mathfrak{m} \mathbf{x}^2/\hbar} \, \mathrm{d}\mathbf{x} = 0 \tag{44}$$

The same will hold for $\langle p \rangle$, though again you could assert that the particle must spend as much time going one way as the other in a symmetric potential.

$$\langle \mathbf{p} \rangle = \int_{-\infty}^{\infty} \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x} \, d\mathbf{x} = \int_{-\infty}^{\infty} A e^{-\alpha [(\mathbf{m} \mathbf{x}^2/\hbar) - i\mathbf{t}]} \frac{\hbar}{i} \left(-\frac{2a\mathbf{m}}{\hbar} \mathbf{x} A e^{-\alpha [(\mathbf{m} \mathbf{x}^2/\hbar) + i\mathbf{t}]} \right) d\mathbf{x} \tag{45}$$

$$= 2iamA^2 \int_{-\infty}^{\infty} xe^{-2amx^2/\hbar} dx = 0$$
(46)

There is no really clever way to do the other two by inspection, just grind it out.

$$\langle \mathbf{x}^2 \rangle = \int_{-\infty}^{\infty} \mathbf{x}^2 |\psi|^2 \, \mathrm{d}\mathbf{x} = \int_{-\infty}^{\infty} \mathbf{x}^2 \mathbf{A}^2 e^{-2\mathfrak{a}\mathbf{m}\mathbf{x}^2/\hbar} \, \mathrm{d}\mathbf{x} = \mathbf{A}^2 \frac{\sqrt{\pi}}{2} \left(\frac{\hbar}{2\mathfrak{a}\mathbf{m}}\right)^{3/2} = \frac{\hbar}{4\mathfrak{a}\mathbf{m}} \tag{47}$$

The momentum operator is $(\hbar/i)(d/dx)$, you can either square that or use 2m times kinetic energy. Either way, it is $-\hbar^2(d^2/dx^2)$.

$$\langle \mathbf{p}^2 \rangle = \int_{-\infty}^{\infty} \psi^* \left(-\hbar^2 \right) \frac{\partial^2 \psi}{\partial x^2} \, \mathrm{d}\mathbf{x} = A^2 \hbar^2 \int_{-\infty}^{\infty} |\psi|^2 \frac{2am}{\hbar} \left(1 - \frac{2am}{\hbar} x^2 \right) \, \mathrm{d}\mathbf{x} \tag{48}$$

$$\langle \mathbf{p}^2 \rangle = 2\mathfrak{a}\mathfrak{m}\hbar \int_{-\infty}^{\infty} A^2 |\psi|^2 \, \mathrm{d}x - 4\mathfrak{a}^2 \mathfrak{m}^2 \int_{-\infty}^{\infty} A^2 x^2 |\psi|^2 \tag{49}$$

(note 1st term is normalization condition and integral is 1, 2nd is $\langle x^2\rangle$ we already found)

$$\langle \mathbf{p}^2 \rangle = 2\mathbf{a}\mathbf{m}\mathbf{h} - 4\mathbf{a}^2\mathbf{m}^2\frac{\mathbf{h}}{4\mathbf{a}\mathbf{m}} = \mathbf{a}\mathbf{m}\mathbf{h} \tag{50}$$

The uncertainties are then

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{\hbar}{4am} - 0} = \sqrt{\frac{\hbar}{4am}}$$
(51)

$$\Delta \mathbf{p} = \sqrt{\langle \mathbf{p}^2 \rangle - \langle \mathbf{p} \rangle^2} = \sqrt{a\mathfrak{m}\hbar - 0} = \sqrt{a\mathfrak{m}\hbar}$$
(52)

$$\Delta \mathbf{x} \Delta \mathbf{p} = \frac{\hbar}{2} \tag{53}$$

In fact, gaussian wave functions satisfy the *minimum* uncertainty principle allowed.

10. Is zero energy still a free choice? Suppose you add a constant V_o to the potential energy (by "constant" we mean independent of both x and t). In classical mechanics, this doesn't change anything, but what about quantum mechanics? (a) Show that the wave function picks up a time-dependent phase factor: exp($-iV_ot/\hbar$). (b) What effect does this have on the expectation value of a dynamical variable like x or p?

Solution: Suppose originally ψ solves the Schrödinger equation without V_o :

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \tag{54}$$

We want to find ψ_o such that

$$i\hbar \frac{\partial \psi_o}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_o}{\partial x^2} + (V + V_o) \psi$$
(55)

Our claim is that

$$\psi_{\rm o} = \psi e^{-iV_{\rm o}t/\hbar} \tag{56}$$

Taking the derivative of the above,

$$i\hbar \frac{\partial \psi_{o}}{\partial t} = i\hbar \frac{\partial \psi}{\partial t} e^{iV_{o}t/\hbar} + i\hbar \left(\frac{-iV_{o}}{\hbar}\right) \psi e^{-iV_{o}t/\hbar}$$
(57)

We know what $i\hbar \frac{\partial \psi}{\partial t}$ is from Eq. 55. Using that and the definition of ψ_0 ,

$$i\hbar\frac{\partial\psi_{o}}{\partial t} = \left(-\frac{\hbar^{2}}{2m}\frac{\partial^{2}\psi}{\partial x^{2}} + V\psi\right)e^{-iV_{o}t/\hbar} + i\hbar\left(\frac{-iV_{o}}{\hbar}\right)\psi e^{-iV_{o}t/\hbar}$$
(58)

Since ψ_o and ψ have the same dependence on x, their spatial derivatives only differ by the same factor $e^{iV_o t/\hbar}$ that ψ_o and ψ do:

$$\frac{\partial^2 \psi_o}{\partial x^2} = \frac{\partial^2 \psi}{\partial x^2} e^{-iV_o t/\hbar}$$
(59)

Substituting this,

$$i\hbar \frac{\partial \psi_o}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_o}{\partial x^2} + V \psi e^{-iV_o t/\hbar} + V_o \psi e^{-iV_o t/\hbar}$$
(60)

But since we claim $\psi_o = \psi e^{-iV_o t/\hbar}$,

$$i\hbar \frac{\partial \psi_o}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_o}{\partial x^2} + (V + V_o) \psi_o \tag{61}$$

Thus, shifting the overall potential energy by a constant amount V_o just adds a phase factor $e^{-iV_ot/\hbar}$ to the wavefunction. This has no effect on the expectation values dynamical variables like x and p - since neither the x nor p operator involves the time variable, the phase factor will

always cancel out when we take complex conjugates and calculate the expectation values. The overall phase of the wave function will cancel out whenever you calculate a measurable quantity.