# Problem Set 6 Solutions

**Daily problem for 25 Oct** On last week's homework, you proved (presumably) that in quantum mechanics one can find the average force from the average gradient of the potential:

$$\langle F_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle \tag{1}$$

Use this result to verify that the average force on a particle in a simple harmonic oscillator potential $(V = \frac{1}{2}m\omega^2 x^2)$ is zero. You may restrict your solution to the ground state, whose wave function you can find readily in your text.

**Solution:** First we need to find $\partial V / \partial x$. Easy enough.

$$\frac{\partial V}{\partial x} = \frac{\partial}{\partial x}\frac{1}{2}m\omega^2 x^2 = m\omega^2 x \tag{2}$$

The average vale of force is then

$$\langle F_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle = \int\limits_{-\infty}^{\infty} -\frac{\partial V}{\partial x}|\psi|^2 \, dx \tag{3}$$

We know the ground state of the simple harmonic oscillator has a wavefunction of the form $Ae^{-x^2/a^2}$ (the constants will not matter). Thus,

$$\langle F_x \rangle = \int\limits_{-\infty}^{\infty} -\frac{\partial V}{\partial x}|\psi|^2 \, dx = -\int\limits_{-\infty}^{\infty} m\omega^2 x A e^{-2x^2/a^2} \, dx = 0 \tag{4}$$

This is an odd function, and by inspection it integrates to zero. In fact, this is a general result - the square of any wave function is going to be an even function, and so long as the potential is also an even function, its derivative is an odd function and the result will be zero. This is just a mathematical expression of the fact that a particle will sit at equilibrium with zero net force at the center of an attractive potential.

**Daily problem for 28 Oct (a)** How many different sets of quantum numbers $(n, l, m_l, m_s)$ are possible for an electron on the $4f$ level? **(b)** Suppose a certain atom has three electrons in the $4f$ level. What is the maximum possible value of the total $m_s$ of the three electrons? **(c)** What is the maximum possible total $m_l$ of three $4f$ electrons? **(d)** Suppose an atom has ten electrons in the $4f$ level. What is the maximum possible value of the total $m_s$ of the ten $4f$ electrons? **(e)** What is the maximum possible total $m_l$ of ten $4f$ electrons?

**The remaining problems are due 30 Oct 2013**

**1.** *Variational Principle I.* The energy of a system with wave function $\psi$ is given by

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} \tag{5}$$

where $H$ is the energy operator. The variational principle is a method by which we guess a trial form for the wave function $\psi$, with adjustable parameters, and minimize the resulting energy with respect to the adjustable parameters. This essentially chooses a "best fit" wave function based on our guess. Since the energy of the system with the correct wave function will always be minimum, our guess will always lead to an energy which is slightly too high, but the variational principle allows us to get as close as possible to the correct energy with our trial wave function.

Use the variational principle to estimate the ground state energy for the anharmonic oscillator,

$$H = \frac{p^2}{2m} + \lambda x^4 \qquad \text{i.e., } H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \lambda x^4 \psi \tag{6}$$

Compare your result with the exact result

$$E_o = 1.060\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \tag{7}$$

Note that this is a one-dimensional problem, so take $dV = dx$. The wavefunction for the *harmonic* oscillator ground state might not be a bad choice, $\psi = e^{-cx^2}$, though many other choices are possible.

***Solution:*** The easiest thing to do is see how bad the normal harmonic oscillator solution is, so we will take $\psi = e^{-cx^2}$. First we need to find $H\psi$.

$$H\psi = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \lambda x^4 \psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{-cx^2} + \lambda x^4 e^{-cx^2} \tag{8}$$

$$= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left(-2cxe^{-cx^2}\right) + \lambda x^4 e^{-cx^2} = -\frac{\hbar^2}{2m}\left(2ce^{-cx^2}\right)\left(2cx^2 - 1\right) + \lambda x^4 e^{-cx^2} \tag{9}$$

Next, we multiply by $\psi$ again to get $\psi H\psi$, and integrate that over all space. Multiplying by $\psi$ just makes the exponents all $-2cx^2$.

$$\int \psi H\psi \, dV = \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m}\left(2ce^{-2cx^2}\right)\left(2cx^2 - 1\right) + \lambda x^4 e^{-2cx^2} \, dx \tag{10}$$

$$= \int_{-\infty}^{\infty} e^{-2cx^2}\left(\lambda x^4 - \frac{2\hbar^2 c^2}{m}x^2 + \frac{\hbar^2 c}{m}\right) \tag{11}$$

All the integrals are known (you can ask Wolfram):

$$\int \psi H \psi \, dV = \lambda \frac{3}{16} \sqrt{\frac{\pi}{2c^5}} - \frac{2\hbar^2 c^2}{m} \frac{1}{4} \sqrt{\frac{\pi}{2c^3}} + \frac{\hbar^2 c}{m} \sqrt{\frac{\pi}{2c}} = \frac{3\lambda}{16} \sqrt{\frac{\pi}{2c^5}} + \frac{\hbar^2}{2m} \sqrt{\frac{\pi c}{2}} \tag{12}$$

$$= \sqrt{\frac{\pi}{2c}} \left( \frac{3\lambda}{16} \frac{1}{c^2} + \frac{\hbar^2}{2m} c \right) \tag{13}$$

The denominator in the variational expression is simpler:

$$\int_{-\infty}^{\infty} \psi^2 \, dx = \int_{-\infty}^{\infty} e^{-2cx^2} \, dx = \sqrt{\frac{\pi}{2c}} \tag{14}$$

Our energy expression is thus

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} = \frac{3\lambda}{16c^2} + \frac{\hbar^2 c}{2m} \tag{15}$$

To minimize the energy with this wavefunction, we require $dE/dc = 0$.

$$\frac{dE}{dc} = -\frac{6\lambda}{16c^3} + \frac{\hbar^2}{2m} = 0 \tag{16}$$

$$\implies \quad c = \sqrt[3]{\frac{3\lambda m}{4\hbar^2}} \tag{17}$$

Now we plug that back in our expression for $E$ to find the minimum energy and simplify.

$$E_{\min} = \frac{3\lambda}{16c^2} + \frac{\hbar^2 c}{2m} = \frac{3\lambda}{16} \left( \frac{4\hbar^2}{3\lambda m} \right)^{2/3} + \frac{\hbar^2}{2m} \left( \frac{3\lambda m}{4\hbar^2} \right)^{1/3} \tag{18}$$

$$= \frac{3}{16} \lambda^{1/3} \left( \frac{\hbar^2}{2m} \right)^{2/3} \left( \frac{8}{3} \right)^{2/3} + \frac{1}{2} \lambda^{1/3} \left( \frac{\hbar^2}{2m} \right)^{2/3} 3^{1/3} = \left( \frac{3\sqrt[3]{3}}{4} \right) \lambda^{1/3} \left( \frac{\hbar^2}{2m} \right)^{2/3} \tag{19}$$

$$\approx 1.082 \lambda^{1/3} \left( \frac{\hbar^2}{2m} \right)^{2/3} \tag{20}$$

This differs from the exact result by only $\sim 2\%$. Not bad!

**2.** *Variational Principle II.* Repeat the problem above with a different trial wave function. You know physically a trial function must be peaked around $x = 0$ and must be normalizable (i.e., $\int_{-\infty}^{\infty} \psi^2 \, dx$ is finite). Such functions would include $e^{-c|x|}$ or $1/(c+x^2)$, for instance. Choose wisely, and the mathematics will be far simpler.

***Solution:*** Same drill, different function. How do we pick an appropriate function? What properties should your wave function have for the ground state? We can come up with a few rules by

looking at the potential and thinking about the generic properties of wavefunctions. First, for the lowest energy state the function should be even and peaked near $x=0$, just like it is for the simple harmonic oscillator. Second, it should be normalizable (i.e., the integral of the function squared over all space should be finite). Third, for the variational integral to converge, the square of the wavefunction must decay faster than $x^4$, since we have to integrate $|\psi|^2 x^4$ over all space and come up with a finite answer.

This is already pretty restrictive, when you get down to it. For instance, $1/(x^2 + a^2)$ will not work, since when squared and multiplied by $x^4$, its integral will not converge. You'll run in to weirder problems trying things like $e^{-x^4}$, pushing the analogy with the harmonic oscillator. Just to cut to the chase, one thing that does work is $1/(x^2 + a)^2$. (It is not even that messy if you let Wolfram do the heavy lifting.) This isn't the only possibility, certainly. You might just try two Gaussians with two adjustable parameters, or possibly $e^{-a|x|}$. We'll try $\psi = 1/(x^2 + a^2)^2$. First, we need the second derivative.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^4} \tag{21}$$

With that, we can find $H\psi$

$$H\psi = -\frac{\hbar^2}{2m} \frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^4} + \lambda x^4 \frac{1}{\left(a^2 + x^2\right)^2} \tag{22}$$

Now, $\psi H \psi$ just means multiplying through by $\psi$ again:

$$\psi H\psi = -\frac{\hbar^2}{2m} \frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^6} + \lambda x^4 \frac{1}{\left(a^2 + x^2\right)^4} \tag{23}$$

With Wolfram's help, we can integrate it over all space[i]

$$\int \psi H\psi \, dV = \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m} \frac{4\left(5x^2 - a^2\right)}{\left(a^2 + x^2\right)^6} + \lambda \frac{x^4}{\left(a^2 + x^2\right)^4} \, dx$$

$$= -\frac{2\hbar^2}{m}\left(\frac{35\pi}{256a^9} - \frac{63\pi a^2}{256a^{11}}\right) + \lambda \frac{\pi}{16a^3} = \frac{-\hbar^2}{128ma^9}\left(35\pi - 63\pi\right) + \frac{\pi\lambda}{16a^3}$$

$$= \frac{7\pi\hbar^2}{32ma^9} + \frac{\pi\lambda}{16a^3} = \frac{\pi}{16a^3}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) \tag{24}$$

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[i]Note that you can tell Wolfram to include limits to the integral, which simplifies things a lot. Compare typing in `integral of x^2/(a =^2+x^2)^6 from -infinity to infinity` to `integral of x^2/(a^2+x^2)^6`. Nice, right?

Now we need the denominator in our variational expression, the normalization condition:

$$\int |\psi|^2 \, dV = \int_{-\infty}^{\infty} \frac{1}{(x^2+a)^4} \, dx = \frac{5\pi}{16a^7} \tag{25}$$

Combining and factoring a bit,

$$E[\psi] = \frac{\int \psi^* H \psi \, dV}{\int |\psi|^2 \, dV} = \frac{\pi}{16a^3}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) \cdot \frac{16a^7}{5\pi} = \frac{a^4}{5}\left(\lambda + \frac{7\hbar^2}{2ma^6}\right) = \frac{1}{5}a^4\lambda + \frac{7\hbar^2}{10ma^2} \tag{26}$$

To minimize the energy with this wavefunction, we require $dE/da = 0$.

$$\frac{dE}{da} = \frac{4}{5}a^3\lambda - \frac{7\hbar^2}{5ma^3} \tag{27}$$

$$\implies \quad a = \sqrt[6]{\frac{7\hbar^2}{4m\lambda}} \tag{28}$$

Inserting this into our energy expression, we have the minimum energy

$$E_{\min} = \frac{1}{5}a^4\lambda + \frac{7\hbar^2}{10ma^2} = \frac{\lambda}{5}\left(\frac{7\hbar^2}{4m\lambda}\right)^{2/3} + \frac{7\hbar^2}{10m}\left(\frac{4m\lambda}{7\hbar^2}\right)^{1/3} \tag{29}$$

$$= \lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}\left[\frac{1}{5}\left(\frac{7}{2}\right)^{2/3} + \frac{7}{10}\left(\frac{16}{7}\right)^{1/3}\right] = \lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3}\left[\frac{3}{5}\left(\frac{7}{2}\right)^{2/3}\right] \tag{30}$$

$$\approx 1.38\lambda^{1/3}\left(\frac{\hbar^2}{2m}\right)^{2/3} \tag{31}$$

This trial wave function is off by about 30%, not nearly as good as just using the harmonic oscillator solution as our guess.

**3.** The two figures below show small sections of two different possible surfaces of a NaCl surface. In the left arrangement, the NaCl(100) surface, charges of $+e$ and $-e$ are arranged on a square lattice as shown. In the right arrangement, the NaCl(110) surface, the same charges are arranged in a rectangular lattice. **(a)** What is the potential energy of each arrangement (symbolic answer)? **(b)** Which is more stable?
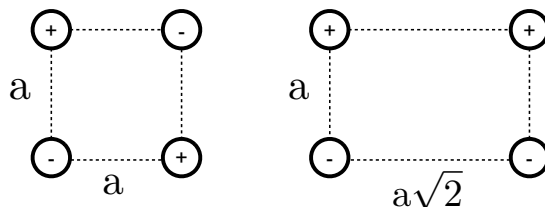
*Solution:* We need only add up the potential energies of all possible pairs of charges. In each case we have four charges, so there must be $\binom{4}{2} = 6$ combinations. Let the upper left charge be $q_1$, and number the charges in a clockwise fashion. The combinations are thus

$$q_1q_2, q_1q_3, q_1q_4 \tag{32}$$

$$q_2q_3q_2q_4 \tag{33}$$

$$q_3q_4 \tag{34}$$

For either arrangement,t he energy is then

$$U = \frac{k_e q_1 q_2}{r_{12}} + \frac{k_e q_1 q_3}{r_{13}} + \frac{k_e q_1 q_4}{r_{14}} + \frac{k_e q_2 q_3}{r_{23}} + \frac{k_e q_2 q_4}{r_{24}} + \frac{k_e q_3 q_4}{r_{34}} \tag{35}$$

For the first arrangement, NaCl(100), we need only plug in the distances and charges:

$$U_{100} = \frac{-k_e e^2}{a} + \frac{k_e e^2}{a\sqrt{2}} + \frac{-k_e e^2}{a} + \frac{-k_e e^2}{a} + \frac{k_e e^2}{a\sqrt{2}} + \frac{-k_e e^2}{a} = \frac{ke^2}{a}\left(-4 + \sqrt{2}\right) \approx -2.58\frac{ke^2}{a} \tag{36}$$

For the second arrangement, NaCl(110), we have:

$$U_{110} = \frac{k_e e^2}{a\sqrt{2}} + \frac{-k_e e^2}{a\sqrt{3}} + \frac{-k_e e^2}{a} + \frac{-k_e e^2}{a} + \frac{-k_e e^2}{a\sqrt{3}} + \frac{k_e e^2}{a\sqrt{2}} = \frac{ke^2}{a}\left(-2 + \sqrt{2} - \frac{2}{\sqrt{3}}\right) \approx -1.74\frac{ke^2}{a} \tag{37}$$

Since $U_{100} < U_{110}$, the (100) surface is more stable, in agreement with experiments.

**4.** *Energetics of diatomic systems* An approximate expression for the potential energy of two ions as a function of their separation is (treating the problem one dimensionally),

$$V = -\frac{ke^2}{x} + \frac{b}{x^9} \tag{38}$$

The first term is the usual Coulomb interaction, while the second term is introduced to account for the repulsive effect of the two ions at small distances. **(a)** What is the equilibrium spacing $x_o$? **(b)** Find $b$ as a function of the equilibrium spacing $x_o$. **(c)** For NaCl, with an equilibrium spacing of $r_o = 0.236\,\text{nm}$, calculate the frequency of small oscillations about $x = x_o$. *Hint: do a Taylor expansion of the potential energy to make it look like a harmonic oscillator for small $x = x_o$.*

*Solution:* The equilibrium spacing will be characterized by the net force between the ions being zero, or equivalently, the potential energy being zero:

$$F(r_o) = -\frac{dU}{dr}\bigg|_{r=r_o} = 0 = \frac{ke^2}{r_o^2} - \frac{9b}{r_o^{10}} \tag{39}$$

$$ke^2 r_o^8 = 9b \tag{40}$$

$$b = \frac{1}{9}ke^2 r_o^8 \tag{41}$$

Substituting this result back into our potential energy expression, we can find the potential energy at equilibrium, how much energy is gained by the system of ions condensing into a crystal. First, the potential energy as a function of spacing:

$$PE = U(r) = -\frac{ke^2}{r} + \frac{ke^2 r_o^8}{9r^9} \tag{42}$$

Evaluating at equilibrium, $r_o = 0.279\,\text{nm}$,

$$U(r_o) = -\frac{ke^2}{r_o} + \frac{ke^2}{9r_o} = -\frac{8ke^2}{9r_o} \approx -5.42\,\text{eV} \tag{43}$$

The frequency of small oscillations can be found by Taylor expanding the potential about equilibrium for small displacements from equilibrium:

$$U(r - r_o) \approx U(r_o) + U'(r_o)(r - r_o) + \frac{1}{2}U''(r_o)(r - r_o)^2 \tag{44}$$

The first term in the expansion is just the potential energy at equilibrium which we found above. The second term, linear in displacement, must vanish at equilibrium (which is exactly the condition we enforced to find $b$, after all). The third term is quadratic in displacement, just as it would be for a simple harmonic oscillator, $U = \frac{1}{2}k(r - r_o)^2$. Thus, the coefficient of the quadratic term must be $\frac{1}{2}k$, which means the frequency of small oscillations is $\omega = \sqrt{k/\mu}$, where $\mu$ is the reduced mass of the system:

$$\mu = \frac{m_{\text{Na}} m_{\text{Cl}}}{m_{\text{Na}} + m_{\text{Cl}}} \approx 13.95\,\text{u} = 2.32 \times 10^{-26}\,\text{kg} \tag{45}$$

That is, the diatomic molecule looks like two masses coupled by a spring.

$$\frac{1}{2}k = \frac{1}{2}U''(r_o) \tag{46}$$

$$k = U''(r_o) = -\frac{2ke^2}{r_o^3}\frac{90b}{r_o^{11}} = \frac{8ke^2}{r_o^3} \approx 140\,\text{N/m} \tag{47}$$

$$\omega = \sqrt{\frac{k}{\mu}} = 2\pi f \tag{48}$$

The frequency of oscillation $f$ is then

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \approx 1.24 \times 10^{13}\,\text{Hz} \approx 414\,\text{cm}^{-1} \tag{49}$$

A reliable experimental value is about $365\,\text{cm}^{-1}$, in good agreement with our simple model.[ii]

**5.** A collection of hydrogen atoms is placed in a magnetic field of $3.50\,\text{T}$. Ignoring the effects of electron spin, find the wavelengths of the three normal Zeeman components of **(a)** the $3d$ to $2p$ transition, **(b)** the $3s$ to $2p$ transition.

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

$$E_{l,m_l} = E_l + m_l \mu_B B \tag{50}$$

This is shown schematically below for $l = 2$ and $l = 1$ levels. The $3d$ ($l = 2$) level has possible $m_l$ values of $m_l = \{-2, -1, 0, 1, 2\}$, and thus in a magnetic field $B$ what was a single level is now 5 individual levels. For the $2p$ ($l = 1$) level, we have $m_l$ values of only $m_l = \{-1, 0, 1\}$, and the original level becomes a triplet upon applying a magnetic field.
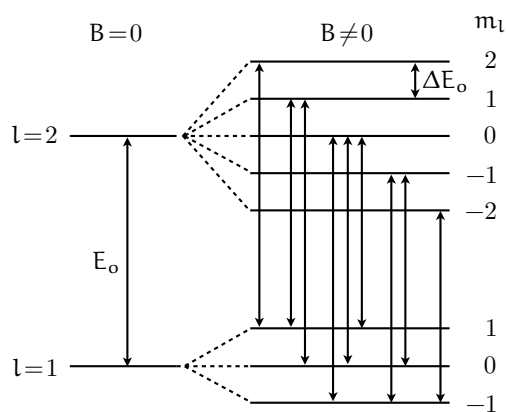


**Figure 1:** *Allowed transitions from $l = 2$ to $l = 1$ with a magnetic field applied.*

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

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[ii]See http://scitation.aip.org/content/aip/journal/jpcrd/36/2/10.1063/1.2436891.

The spacing between the levels $\Delta E$ is the Zeeman energy given above, $\Delta E = \mu_B B$. 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 $\Delta E$ ($m_l$ changes by $\pm 1$). The original transition energy $E$ and the corresponding wavelength $\lambda$ is readily found from our knowledge of the hydrogen atom

$$E = E_3 - E_2 = -13.6\,\text{eV}\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.89\,\text{eV} \qquad \Longrightarrow \qquad \lambda = \frac{hc}{E} = 656\,\text{nm} \tag{51}$$

(In the calculation of $\lambda$ we useThus, the new transition energies must be

$$E \longmapsto \{E - \Delta E, E, E + \Delta E\} = \{E - \mu_B B, E, E + \mu_B B\} \tag{52}$$

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. You can do this with propagation of uncertainty, if you aren't familiar with it we will just quote the result:

$$|\Delta\lambda| = \left|\frac{d\lambda}{dE}\right|\Delta E = \frac{hc}{E^2}\Delta E = \frac{\lambda^2}{hc}\Delta E \tag{53}$$

Since we know the energy changes by $\Delta E$ and the base energy is $E$,

$$|\Delta\lambda| = \frac{\lambda^2 \Delta E_o}{hc} = \frac{\lambda^2 \mu_B B}{hc} \approx 0.07\,\text{nm} \tag{54}$$

The shift in energy of $\Delta E_o$ implies a shift in wavelength of $\Delta\lambda \approx 0.070\,\text{nm}$, meaning the new transitions must be at the original wavelength $\lambda = 656\,\text{nm}$ plus or minus $\Delta\lambda = 0.07\,\text{nm}$.

**6.** Consider a hydrogen atom and a singly-ionized helium atom (i.e., Bohr-like). Which atom has the lower ground state energy, and how big is the difference? Justify your answer with an explicit calculation, even if it is just an order-of-magnitude estimate.

***Solution:*** For a hydrogen-like system (i.e., nucleus plus one electron) with $Z$ protons in the nucleus, the net attractive energy of the proton and electron will scale as $Z$. That's one reason already that the helium atom will be more stable, the electron is simply more attracted to the nucleus. A second factor of $Z$ comes in through the quantization of angular momentum, but the conclusion does not change. If you work out the Bohr model energy levels from the start with a nuclear

charge of $+Ze$ rather than just $+e$, you'll find the energies scale as $Z^2$.[iii] The higher $Z$ is, the more negative the electron energies are, and the more stable the atom.

We can estimate the difference as being a factor of $Z^2_{\text{He}} = 4$ compared to the hydrogen ground state energy, or $-13.6\,\text{eV} \cdot 3 \approx 54.4\,\text{eV}$, which is a very good estimate.

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[iii]See http://en.wikipedia.org/wiki/Bohr_model#Electron_energy_levels