Chem221a : Solution Set 10

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December 12, 2007

Problem 1

First let's work on writing out the Hamiltonian in a useful form. Defining $k = \frac{e^2}{4\pi\epsilon_0}$, we know our Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - k\frac{2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - k\frac{2}{r_2} + \frac{k}{r_{12}} \tag{1}$$

By adding and subtracting terms of the form $k\frac{Z'}{r}$, we obtain

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\nabla_1^2 - k\frac{Z'}{r_1} + k\frac{Z'-2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - k\frac{Z'}{r_2} + k\frac{Z'-2}{r_2} + \frac{k}{r_{12}} && (2)\\ &= H_{Z',1} + H_{Z',2} + k\left(\frac{Z'-2}{r_1} + \frac{Z'-2}{r_2} + \frac{1}{r_{12}}\right) && (3)\end{aligned}$$

where $H_{Z',n}$ is the Hamiltonian for the hydrogenic ion with electron n and nuclear charge of Z'. Fortunately, we just happen to have chosen our trial wavefunction to be the product of the two hydrogenic wavefunction of nuclear charge Z'. So $|\psi_{\text{trial}}\rangle = |\psi_{Z',1}\rangle\,|\psi_{Z',2}\rangle$.

We want to calculate the energy as a function of the parameter Z'. So we plug the Hamiltonian into our trial wavefunction:

$$\begin{aligned} E(Z') &= \langle\psi_{\text{trial}}|H|\psi_{\text{trial}}\rangle \,/\, \langle\psi_{\text{trial}}|\psi_{\text{trial}}\rangle && (4)\\ &= \left\langle\psi_{Z',1}\middle|\left\langle\psi_{Z',2}\middle|H_{Z',1} + H_{Z',2} + k\left(\frac{Z'-2}{r_1} + \frac{Z'-2}{r_2} + \frac{1}{r_{12}}\right)\middle|\psi_{Z',2}\right\rangle\middle|\psi_{Z',1}\right\rangle && (5)\\ &= \langle\psi_{Z',1}|H_{Z',1}|\psi_{Z',1}\rangle + \langle\psi_{Z',2}|H_{Z',2}|\psi_{Z',2}\rangle + k(Z'-2)\left\langle\psi_{Z',1}\middle|\frac{1}{r_1}\middle|\psi_{Z',1}\right\rangle \\ &\quad + k(Z'-2)\left\langle\psi_{Z',2}\middle|\frac{1}{r_2}\middle|\psi_{Z',2}\right\rangle + k\left\langle\psi_{Z',1}\psi_{Z',2}\middle|\frac{1}{r_{12}}\middle|\psi_{Z',1}\psi_{Z',2}\right\rangle && (6)\end{aligned}$$

We've been able to simplify this far by seeing that some of the terms only depend on one of the electron coordinates (so the other part of the trial wavefunction, being normalized, doesn't contribute). Since the wavefunctions for each electron have the same term, the two integrals $\left\langle\psi_{Z'}\middle|\frac{1}{r}\middle|\psi_{Z'}\right\rangle$ are the same, regardless of the subscripts 1 and 2. So we can combine them. We can also now use the fact that our wavefunctions are eigenfunctions for the one-electron hydrogenic Hamiltonians $H_{Z'}$, which will also be equal to one another. So our energy function is now

$$E(Z') = 2E_{Z'} + 2k(Z'-2)\left\langle\psi_{Z'}\middle|\frac{1}{r}\middle|\psi_{Z'}\right\rangle + k\left\langle\psi_{Z',1}\psi_{Z',2}\middle|\frac{1}{r_{12}}\middle|\psi_{Z',1}\psi_{Z',2}\right\rangle \tag{7}$$

So let's calculate each of these things.

First, we just change e^2 into $Z'e^2$ in the hydrogen solution to get the hydrogenic solution (remember not to forget how e^2 is involved in the definition of a_0!). That gives us

$$E_{Z'} = -\frac{{Z'}^2 k}{2a_0} \tag{8}$$

That was easy enough. Now let's do the one-electron integrals. The angular integrals immediately gives us 4π (note that the function in the problem is normalized over *all space*, not just over $r \in \mathbb{R}_+$).

$$\begin{aligned}
\left\langle \psi_{Z'} \left| \frac{1}{r} \right| \psi_{Z'} \right\rangle &= 4\pi \int_{\mathbb{R}_+} \mathrm{d}r\, r^2 \left(\frac{1}{\sqrt{\pi}} \left(\frac{Z'}{a_0}\right)^{3/2} e^{-Z'r/a_0} \right) \frac{1}{r} \left(\frac{1}{\sqrt{\pi}} \left(\frac{Z'}{a_0}\right)^{3/2} e^{-Z'r/a_0} \right) &(9)\\
&= 4 \left(\frac{Z'}{a_0}\right)^3 \int_{\mathbb{R}_+} \mathrm{d}r\, r e^{-2Z'r/a_0} &(10)\\
&= 4 \left(\frac{Z'}{a_0}\right)^3 \left(\frac{a_0}{2Z'}\right)^2 &(11)\\
&= \frac{Z'}{a_0} &(12)
\end{aligned}$$

where the integration can be done by parts or by looking it up in a table (or by using a CAS).

The last integral is not so fun. The first trick is to get the term $\frac{1}{r_{12}}$ into a useful form. There are several approaches; I'm going to use one which may not be the fastest, but requires the least typing on my part (because I can steal it wholesale from other sources).

I'll just jump to the useful form we'll have:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \tag{13}$$

If you want to see how to get this, there's a (half) derivation by those geniuses at hyperblazer.net — http://www.hyperblazer.net/teaching/MS07x31_details.pdf for the explanation.

From there, it is just a matter of doing the integral. I'm going to switch notation, so Z' becomes Z. Also, "the book" will refer to McQuarrie and Simon's PChem book. Not that I'm copying and pasting from the solution to M&S 7-31 that I wrote last fall when I was a GSI for 120a. Not at all.

As the problem suggests, we'll just do the integral from 7.50:

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \iint \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \psi_{1s}^*(\mathbf{r}_1) \psi_{1s}^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2)$$

Plugging in $1/r_{12}$ from the problem we obtain:

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \iint \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \psi_{1s}^*(\mathbf{r}_1) \psi_{1s}^*(\mathbf{r}_2) \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2)$$

Now, we know that the wavefunction $\psi_{1s}(\mathbf{r}_i) = R_{10}(r_i) Y_0^0(\theta_i, \phi_i)$, and that the volume element $\mathrm{d}\mathbf{r}_i = \mathrm{d}r_i\, r_i^2 \mathrm{d}\theta\, \sin(\theta) \mathrm{d}\phi$. To simplify our notation, use the shorthand $\Omega_i \equiv (\theta_i, \phi_i)$ and $\mathrm{d}\Omega_i \equiv$

$\mathrm{d}\theta_i\,\sin(\theta_i)\mathrm{d}\phi_i\,.$

$$
\begin{aligned}
E^{(1)} = \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} \\
\times \int \mathrm{d}\Omega_1\, \underbrace{{Y_0^0}^*(\Omega_1)}_{\psi^*_{1\mathrm{s}}(\mathbf{r}_1)}\underbrace{Y_0^0(\Omega_1)}_{\psi_{1\mathrm{s}}(\mathbf{r}_1)}\underbrace{Y_l^m(\Omega_1)}_{1/r_{12}}\int \mathrm{d}\Omega_2\, \underbrace{{Y_0^0}^*(\Omega_2)}_{\psi^*_{1\mathrm{s}}(\mathbf{r}_2)}\underbrace{Y_0^0(\Omega_2)}_{\psi_{1\mathrm{s}}(\mathbf{r}_2)}\underbrace{Y_l^{m*}(\Omega_2)}_{1/r_{12}}
\end{aligned}
$$

where the underbraces show you where each term came from. Now we're going to take advantage of the fact that we know what Y_0^0 is. In fact, since Y_0^0 is constant (as is ${Y_0^0}^*$), we're going to take one of them out of each integral. We'll also take the angular dependence off of the one outside the integral.

$$
\begin{aligned}
E^{(1)} = \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} \\
\times \left(Y_0^0\int \mathrm{d}\Omega_1\, {Y_0^0}^*(\Omega_1)Y_l^m(\Omega_1)\right)\left({Y_0^0}^*\int \mathrm{d}\Omega_2\, Y_l^{m*}(\Omega_2)Y_0^0(\Omega_2)\right)
\end{aligned}
$$

Now to show why we only took one of the Y_0^0 factors out. We know that the spherical harmonics are orthonormal. That means that $\int \mathrm{d}\Omega\, Y_l^{m*}(\Omega)Y_{l'}^{m'}(\Omega) = \delta_{l,l'}\delta_{m,m'}$. (Take a look at Drew's Delta Functions paper in the Extra Study Aids section if you don't remember how the Kronecker delta works.) Basically, this means that the whole thing will be zero unless $l = l'$ and $m = m'$. This restriction allows us to "pick out" values from the sums (specifically, we pick out the values where $l = 0$ and $m = 0$.

$$
\begin{aligned}
E^{(1)} &= \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} \\
&\quad\times Y_0^0\delta_{0,l}\delta_{0,m}{Y_0^0}^*\delta_{0,l}\delta_{0,m} \\
&= \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y_0^0{Y_0^0}^*\delta_{0,l}
\end{aligned}
$$

Now we'll use the fact that $Y_0^0 = \frac{1}{\sqrt{4\pi}}$.

$$
\begin{aligned}
&= \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\sum_{l=0}^{\infty}\frac{1}{2l+1}\frac{r_<^l}{r_>^{l+1}}\delta_{0,l} \\
&= \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\frac{1}{(2)(0)+1}\frac{r_<^0}{r_>^{0+1}} \\
&= \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}r_1\, {r_1}^2 R^*_{10}(r_1)R_{10}(r_1)\int \mathrm{d}r_2\, {r_2}^2 R^*_{10}(r_2)R_{10}(r_2)\frac{1}{r_>}
\end{aligned}
$$

The last thing we have to do is plug in for $R_{10}(r_i)$. The problem set gives us $\psi_{1\mathrm{s}}(\mathbf{r}_i) = \sqrt{\frac{Z^3}{{a_0}^3\pi}}e^{-Zr_i/a_0}$. As we pointed out earlier, $\psi_{1\mathrm{s}}(\mathbf{r}_i) = R_{10}(r_i)Y_0^0(\theta_i,\phi_i)$, which means that $R_{10}(r_i) = \psi_{1\mathrm{s}}(\mathbf{r}_i)/Y_0^0(\theta_i,\phi_i)$.

We also mentioned earlier that $Y_0^0 = \frac{1}{\sqrt{4\pi}}$. This gives us:

$$R_{10} = \sqrt{\frac{4Z^3}{{a_0}^3}} e^{-Zr_i/a_0}$$

Plugging that into our expression for $E^{(1)}$, we find

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{{a_0}^6} \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0} \int \mathrm{d}r_2\, r_2^2 \frac{e^{-2Zr_2/a_0}}{r_>}$$

which is the equation at the bottom of page 271. One thing that should be made clear before we proceed is that $r_>$ is *not* a constant. When $r_1 < r_2$, $r_> = r_2$. When $r_2 < r_1$, $r_> = r_1$. This means that the two integrals are actually *nested*, not multiplying each other.

So to get to the first equation on page 272, we'll split the integral r_2 into two integrals — one that goes from 0 to r_1, and one that goes from r_1 to ∞. So we have:

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{{a_0}^6} \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0} \left(\int_0^{r_1} \mathrm{d}r_2\, r_2^2 \frac{e^{-2Zr_2/a_0}}{r_>} + \int_{r_1}^{\infty} \mathrm{d}r_2\, r_2^2 \frac{e^{-2Zr_2/a_0}}{r_>} \right)$$

In the first integral in the sum, r_2 is always less than r_1, which means that $r_> = r_1$. In the second integral in the sum, r_2 is always greater than r_1. This means that $r_> = r_2$. So plugging in the appropriate values for $r_>$ in each case, we obtain

$$\begin{aligned} E^{(1)} &= \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{{a_0}^6} \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0} \left(\int_0^{r_1} \mathrm{d}r_2\, r_2^2 \frac{e^{-2Zr_2/a_0}}{r_1} + \int_{r_1}^{\infty} \mathrm{d}r_2\, r_2^2 \frac{e^{-2Zr_2/a_0}}{r_2} \right) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{{a_0}^6} \left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0} \int_0^{r_1} \mathrm{d}r_2\, r_2^2 e^{-2Zr_2/a_0} + \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0} \int_{r_1}^{\infty} \mathrm{d}r_2\, r_2 e^{-2Zr_2/a_0} \right) \end{aligned}$$

This is, of course, the first equation on page 272. To get to our next milestone, the second equation on page 272, we start doing some integrals. First note that the integrals are still nested: the bounds of the inner integral (over r_2) depend on the variable of integration of the outer integral (over r_1). So we'll have to solve the integrals over r_2 first. All of these integrals can be done exactly using integration by parts, and if trapped with these integrals on a desert island, you should be able to solve them that way. That said, I'm not on a desert island, so I have the options of looking them up in a table of integrals or using a computer algebra program such as Mathematica (expensive) or Maxima (free).

According to Maxima,

$$\int_0^{r_1} \mathrm{d}r_2\, r_2^2 e^{-2Zr_2/a_0} = \frac{1}{4Z^3} \left({a_0}^3 - \left(2a_0 r_1^2 Z^2 + 2{a_0}^2 r_1 Z + {a_0}^3 \right) e^{-2Zr_1/a_0} \right)$$

and

$$\int_{r_1}^{\infty} \mathrm{d}r_2\, r_2 e^{-2Zr_2/a_0} = \frac{1}{4Z^2} \left(2a_0 r_1 Z + {a_0}^2 \right) e^{-2Zr_1/a_0}$$

Plugging those into our expression above, we find

$$
\begin{aligned}
E^{(1)} &= \frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{{a_0}^6}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0}\frac{1}{4Z^3}\left({a_0}^3 - \left(2a_0 r_1^2 Z^2 + 2{a_0}^2 r_1 Z + {a_0}^3\right)e^{-2Zr_1/a_0}\right)\right.\\
&\qquad\left. + \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0}\frac{1}{4Z^2}\left(2a_0 r_1 Z + {a_0}^2\right)e^{-2Zr_1/a_0}\right)\\
&= \frac{e^2}{4\pi\epsilon_0}\frac{16Z^6}{{a_0}^6}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0}\frac{{a_0}^3}{4Z^3}\left(1 - \left(\frac{2r_1^2 Z^2}{{a_0}^2} + \frac{2r_1 Z}{a_0} + 1\right)e^{-2Zr_1/a_0}\right)\right.\\
&\qquad\left. + \int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0}\frac{{a_0}^3}{4Z^3}\frac{Z}{a_0}\left(\frac{2r_1 Z}{a_0} + 1\right)e^{-2Zr_1/a_0}\right)\\
&= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0}\left(1 - \left(\frac{2r_1^2 Z^2}{{a_0}^2} + \frac{2r_1 Z}{a_0} + 1\right)e^{-2Zr_1/a_0}\right)\right.\\
&\qquad\left. + \frac{Z}{a_0}\int \mathrm{d}r_1\, r_1^2 e^{-2Zr_1/a_0}\left(\frac{2r_1 Z}{a_0} + 1\right)e^{-2Zr_1/a_0}\right)
\end{aligned}
$$

This is equivalent to the second equation on page 272 of the book. Now we're going to organize our terms by the whether the integral includes e^{-2Zr_1/a_0} or e^{-4Zr_1/a_0} in order to obtain the third equation.

$$
\begin{aligned}
E^{(1)} &= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, e^{-2Zr_1/a_0}\left(r_1 - \left(\frac{2r_1^3 Z^3}{{a_0}^2} + \frac{2r_1^2 Z}{a_0} + r_1\right)e^{-2Zr_1/a_0}\right)\right.\\
&\qquad\left. + \int \mathrm{d}r_1\, e^{-4Zr_1/a_0}\left(\frac{2Z^2 r_1^3}{{a_0}^2}\frac{Zr^2}{a_0}\right)\right)\\
&= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0} + \int \mathrm{d}r_1\, e^{-4Zr_1/a_0}\right.\\
&\qquad\left. \times\left(\left(\frac{-2r_1^3 Z^2}{{a_0}^2} + \frac{-2r_1^2 Z}{a_0} - r_1\right) + \left(\frac{2r_1^3 Z}{{a_0}^2} + \frac{Zr_1^2}{a_0}\right)\right)\right)\\
&= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0} + \int \mathrm{d}r_1\, e^{-4Zr_1/a_0}\left(\frac{-r_1^2 Z}{a_0} - r_1\right)\right)\\
&= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0} - \int \mathrm{d}r_1\, e^{-4Zr_1/a_0}\frac{Z^3}{{a_0}^3}\left(\frac{r_1^2 {a_0}^2}{Z^2} + \frac{r_1 {a_0}^3}{Z^3}\right)\right)
\end{aligned}
$$

This is the third equation on page 272. From here, it's just a matter of doing the integrals. These are again the sort of integrals you could solve using integration by parts if you're stuck doing integrals in a prison and they refuse to give you a table of integrals. But since I'm not in prison (yet) I'll use

Maxima again.

$$
\begin{aligned}
E^{(1)} &= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\int \mathrm{d}r_1\, r_1 e^{-2Zr_1/a_0} - \frac{Z}{a_0}\int \mathrm{d}r_1\, r_1^2 e^{-4Zr_1/a_0} - \int \mathrm{d}r_1\, r_1 e^{-4Zr_1/a_0}\right) \\
&= \frac{e^2}{4\pi\epsilon_0}\frac{4Z^3}{{a_0}^3}\left(\frac{{a_0}^2}{4Z^2} - \frac{Z}{a_0}\frac{{a_0}^3}{32Z^3} - \frac{{a_0}^2}{16Z^2}\right) \\
&= \frac{e^2}{4\pi\epsilon_0}\frac{Z}{a_0}\left(1 - \frac{1}{8} - \frac{1}{4}\right) \\
&= \frac{5}{8}Z\frac{e^2}{4\pi\epsilon_0 a_0}
\end{aligned}
$$

And that's the answer!

And with that answer, which I was obviously excited to obtain, we can now plug everything back into equation (7) (and go back to having numbered equations, and go back to Z'):

$$
\begin{aligned}
E(Z') &= 2\left(-\frac{Z'^2 k}{2a_0}\right) + 2k(Z'-2)\frac{Z'}{a_0} + k\frac{5}{8}\frac{Z'}{a_0} && (14) \\
&= \frac{k}{a_0}\left(-Z'^2 + 2Z'^2 - 4Z' + \frac{5}{8}Z'\right) && (15) \\
&= \frac{k}{a_0}\left(Z'^2 - \frac{27}{8}Z'\right) && (16)
\end{aligned}
$$

Once you have the energy as a function of your parameter (as we do above) the variational principle is very easy. We just take the derivative, find the point where it has a minimum, and plug that value back into the energy function:

$$
\begin{aligned}
0 &= E'(Z') && (17) \\
&= \frac{k}{a_0}\left(2Z' - \frac{27}{8}\right) && (18) \\
Z' &= \frac{27}{16} = 1.6875 && (19)
\end{aligned}
$$

There's only one extremum, so it darn well better be a minimum: by inspection, we can tell that the second derivative is positive (everywhere) so any extremum must be a minimum.

Now we plug that value of Z' into the function $E(Z')$:

$$E\left(\frac{27}{16}\right) = \frac{k}{a_0}\left(\left(\frac{27}{16}\right)^2 - \frac{27}{8}\frac{27}{16}\right) \tag{20}$$
$$= \frac{k}{a_0}\left(\left(\frac{27}{16}\right)^2 - 2\left(\frac{27}{16}\right)^2\right) \tag{21}$$
$$= -\frac{k}{a_0}\left(\frac{27}{16}\right)^2 \tag{22}$$
$$= -\frac{k}{2a_0}2\left(\frac{27}{16}\right)^2 \tag{23}$$
$$= (-13.6\text{ eV})2\left(\frac{27}{16}\right)^2 \tag{24}$$
$$= 77.4\text{ eV} \tag{25}$$

where we have used the fact that $\frac{k}{2a_0}$ is the ionization energy of hydrogen, approximately 13.6 eV.

Problem 2

First, we need to justify that the sudden approximation is valid. I'll do that in a very handwaving way: as shown on p. 477 of Shankar, the ratio of the timescale of the beta particle (relativistic electron) escape to the timescale of motion by the captured electron is on the order of $Z\alpha$, where α is the fine structure constant, approximately 1/137. Since Z is of order 1, $Z\alpha$ remains small (less than, say 0.1). So the sudden approximation is acceptable.[1]

The probability amplitude of being in the ground (1s) state of the helium ion in the sudden approximation is given simply by the overlap:

$$\mathit{Amplitude}(1s,\ {}^3\mathrm{He}^+) = \left\langle 1s,\ {}^3\mathrm{He}^+ \middle| 1s,\ {}^3\mathrm{H}\right\rangle \tag{26}$$
$$= \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta\, \sin(\theta) Y_0^{0*}(\theta,\phi) Y_0^0(\theta,\phi) \int_{\mathbb{R}_+} \mathrm{d}r\, r^2 R_{10}^{{}^3\mathrm{He}^+ *}(r) R_{10}^{{}^3\mathrm{H}}(r) \tag{27}$$
$$= \int_{\mathbb{R}_+} \mathrm{d}r\, r^2 \left(2\left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0}\right)\left(2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\right) \tag{28}$$
$$= 4\frac{2\sqrt{2}}{{a_0}^3}\int_{\mathbb{R}_+} \mathrm{d}r\, r^2 e^{-3r/a_0} \tag{29}$$
$$= \frac{8\sqrt{2}}{{a_0}^3}\left(\frac{2!\ {a_0}^3}{3^3}\right) \tag{30}$$
$$= \frac{16\sqrt{2}}{27} \tag{31}$$

[1] This is a horribly hand-waving approximation of a justification. But it'll do for now.

The integral over r can be calculated by integration by parts, or by finding the following (usually after some massaging of gamma functions) in a table of integrals:

$$\int_{\mathbb{R}_+} \mathrm{d}t\, t^n e^{-\alpha t} = \frac{n!}{\alpha^{n+1}} \tag{32}$$

The overlap $\left\langle n = 16, l = 3, m = 0;\ {}^3\mathrm{He}^+ \middle| 1s;\ {}^3\mathrm{H} \right\rangle$ is zero because we can split of an angular overlap $\left\langle Y_3^0 \middle| Y_0^0 \right\rangle$ and the orthogonality of spherical harmonics means that this is zero.

Problem 3

The first order transition will be:

$$\begin{aligned}
Prob_{2p\leftarrow 1s} &= \left| -\frac{i}{\hbar} \int_{\mathbb{R}_+} \mathrm{d}t\ \langle 2p|H(t)|1s\rangle\, e^{i\omega_{21}t} \right|^2 && (33)\\
&= \left| \frac{1}{\hbar} \int_{\mathbb{R}_+} \mathrm{d}t\ \left\langle 2p \middle| E_0 q z e^{-(t/\tau)^2} \cos(\omega t) \middle| 1s \right\rangle e^{i\omega_{21}t} \right|^2 && (34)\\
&= \left| \frac{1}{\hbar} \int_{\mathbb{R}_+} \mathrm{d}t\, E_0 q e^{-(t/\tau)^2} \cos(\omega t) e^{i\omega_{21}t}\, \langle 2p|r\cos(\theta)|1s\rangle \right|^2 && (35)\\
&= \left| \frac{E_0 q}{\hbar} \langle 2p|r\cos(\theta)|1s\rangle \int_{\mathbb{R}_+} \mathrm{d}t\, e^{-(t/\tau)^2 + i\omega_{21}t} \cos(\omega t) \right|^2 && (36)\\
&= \left| \frac{E_0 q}{\hbar} \langle 2p|r\cos(\theta)|1s\rangle \int_{\mathbb{R}_+} \mathrm{d}t\, e^{-(t/\tau)^2 + i\omega_{21}t} \frac{1}{2} \left(e^{i\omega t} + e^{-i\omega t}\right) \right|^2 && (37)\\
&= \left| \frac{E_0 q}{2\hbar} \langle 2p|r\cos(\theta)|1s\rangle \int_{\mathbb{R}_+} \mathrm{d}t\ \left(e^{-(t/\tau)^2 + i(\omega_{21}+\omega)t} + e^{-(t/\tau)^2 + i(\omega_{21}-\omega)t} \right) \right|^2 && (38)\\
&= \left| \frac{E_0 q}{2\hbar} \langle 2p|r\cos(\theta)|1s\rangle\, \tau\sqrt{\pi} \left(e^{-\tau^2(\omega_{21}+\omega)} + e^{-\tau^2(\omega_{21}-\omega)} \right) \right|^2 && (39)
\end{aligned}$$

To a very good approximation, we can drop the first term. This is because when $\omega_{21} \approx \omega$, the first term's exponent becomes $-2\tau\omega$, whereas the term in the second term's exponent becomes 0. When exponentiated, this makes the second term much larger than the first term, so we can ignore the first term. That gives us

$$Prob_{2p\leftarrow 1s} = \left| \frac{E_0 q}{2\hbar} \langle 2p|r\cos(\theta)|1s\rangle\, \tau\sqrt{\pi} e^{-\tau^2(\omega_{21}-\omega)} \right|^2 \tag{40}$$

Now let's calculate that matrix element.

$$\langle 2p|r\cos(\theta)|1s\rangle = \left\langle R_{21} Y_1^m \middle| r\sqrt{\frac{4\pi}{3}} Y_1^0 \middle| R_{10} Y_0^0 \right\rangle \tag{41}$$

Recalling that $Y_0^0 = 1/\sqrt{4\pi}$, a constant, we can take it out of the angular integral and invoke the orthogonality of the spherical harmonics to require that the bra be $\left\langle R_{21} Y_1^0 \right|$. With the angular integral done, we have:

$$\langle 2p | r\cos(\theta) | 1s \rangle = \left\langle R_{21} \middle| r \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}} \middle| R_{10} \right\rangle \tag{42}$$

$$= \int_{\mathbb{R}_+} \mathrm{d}r\, r^2 R_{21}{}^*(r) r \frac{1}{\sqrt{3}} R_{10}(r) \tag{43}$$

$$= \frac{1}{\sqrt{3}} \int_{\mathbb{R}_+} \mathrm{d}r\, r^3 \left(\frac{1}{\sqrt{24 a_0{}^5}} r e^{-r/2a_0} \right) \left(\frac{2}{\sqrt{a_0{}^3}} e^{-r/a_0} \right) \tag{44}$$

$$= \sqrt{\frac{4}{72 a_0{}^8}} \int_{\mathbb{R}_+} \mathrm{d}r\, r^4 e^{-3/2a_0} \tag{45}$$

Now we use equation (32) from problem 2 (or do some messy integration by parts, but if I do that, you won't get to see this solution set before the exam):

$$\langle 2p | r\cos(\theta) | 1s \rangle = \frac{1}{3\sqrt{2} a_0{}^4} \frac{4!}{(3/2a_0)^5} \tag{46}$$

$$= \frac{2^3 \cdot 3 \cdot 2^5 a_0}{3^6 \sqrt{2}} \tag{47}$$

$$= \frac{2^7 \sqrt{2} a_0}{3^5} \tag{48}$$

Now we plug this back into our expression (40).

$$Prob_{2p \leftarrow 1s} = \left| \frac{E_0 q}{2\hbar} \frac{2^7 \sqrt{2} a_0}{3^5} \tau \sqrt{\pi} e^{-\tau^2(\omega_{21} - \omega)} \right|^2 \tag{49}$$

$$= \left| \frac{E_0\, q\, 2^{13/2} a_0 \sqrt{\pi}}{3^5 \hbar} \tau e^{-\tau^2(\omega_{21} - \omega)} \right|^2 \tag{50}$$

$$= \frac{E_0{}^2 q^2 a_0{}^2}{\hbar^2} \frac{2^{13}\pi}{3^{10}} \tau^2 e^{-2\tau^2(\omega_{21} - \omega)} \tag{51}$$

That's the transition probability. Now, if ω is exactly resonant, then the exponent becomes zero (because $\omega = \omega_{21}$) and therefore the system scales quadratically with the timescale of the pulse.

From an intuitive level, this makes sense. We would certainly expect that a longer pulse gives more probability of a transition! We also note that the probability scales in time the same way it scales in intensity: if we increase E_0, we also see quadratic scaling in the transition probability. This seems reasonable to me!

Problem 4

We'll change x to z to use our normal z-polarized light reference. The main thing to calculate is the matrix element, so let's foccus on that to start:

$$\langle N,p,m|z|1s\rangle = \langle N,p,m|r\cos(\theta)|1s\rangle \tag{52}$$

$$= \left\langle N,p,m\middle| r\sqrt{\frac{4\pi}{3}}Y_1^0 \middle| 1s\right\rangle \tag{53}$$

Remembering that the angular part of the $1s$ state is Y_0^0, which is just a constant, we find that the angular integral requires that $\langle N,p,m|$ be $\langle N,p,0|$ (due to orthogonality of spherical harmonics) and that the constant $Y_0^0 = 1/\sqrt{4\pi}$ is all that is left. That gives us:

$$\langle N,p,0|z|1s\rangle = \int_{\mathbb{R}_+} \mathrm{d}r\, r^2 \frac{1}{\sqrt{4\pi}} r\sqrt{\frac{4\pi}{3}} R_{N1}{}^*(r) R_{10}(r) \tag{54}$$

$$= \frac{1}{\sqrt{3}}\int_{\mathbb{R}_+} \mathrm{d}r\, r^3 R_{N1}{}^*(r) R_{10}(r) \tag{55}$$

In problem 3, we solved this integral for $N = 2$ and found that it gave us

$$\langle 2p, m=0|z|1s\rangle = \frac{a_0}{\sqrt{2}}\frac{2^8}{3^5} \tag{56}$$

Now we'll solve the integral for the case $N = 3$:

$$\langle 3,p,0|z|1s\rangle = \frac{1}{\sqrt{3}}\int_{\mathbb{R}_+} \mathrm{d}r\, r^3 R_{31}{}^*(r) R_{10}(r) \tag{57}$$

$$= \frac{1}{\sqrt{3}}\int_{\mathbb{R}_+} \mathrm{d}r\, r^3 \left(\frac{8}{27\sqrt{6a_0{}^3}}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\right)\left(\frac{2}{\sqrt{a_0{}^3}}\right)e^{-r/a_0} \tag{58}$$

$$= \left(\frac{2}{3a_0}\right)^4 \frac{1}{\sqrt{2}}\int_{\mathbb{R}_+} \mathrm{d}r\, r^4 \left(1 - \frac{r}{6a_0}\right) e^{-4/3a_0} \tag{59}$$

$$= \left(\frac{2}{3a_0}\right)^4 \frac{1}{\sqrt{2}}\left(\int_{\mathbb{R}_+} \mathrm{d}r\, r^4 e^{-4/3a_0} - \frac{1}{6a_0}\int_{\mathbb{R}_+} \mathrm{d}r\, r^5 e^{-4/3a_0}\right) \tag{60}$$

From here, we invoke that useful integral formula given in problem 2 (geez, I hope you people didn't do all of this by parts):

$$\langle 3, p, 0|z|1s\rangle = \left(\frac{2}{3a_0}\right)^4 \frac{1}{\sqrt{2}} \left(\frac{4!}{(4/3a_0)^5} - \frac{1}{6a_0}\frac{5!}{(4/3a_0)^6}\right) \tag{61}$$

$$= \left(\frac{2}{3a_0}\right)^4 \frac{1}{\sqrt{2}} \left(\left(1 - \frac{5}{6a_0}\frac{3a_0}{4}\right)\left(\frac{3a_0}{4}\right)^5 4!\right) \tag{62}$$

$$= \left(\frac{2}{3a_0}\right)^4 \frac{24}{\sqrt{2}}\frac{3}{8}\left(\frac{3a_0}{4}\right)^5 \tag{63}$$

$$= \frac{a_0}{\sqrt{2}}\frac{2^4 \cdot 3^2 \cdot 3^5}{3^4 \cdot 2^{10}} \tag{64}$$

$$= \frac{a_0}{\sqrt{2}} \cdot \frac{27}{64} \tag{65}$$

We get the oscillator strengths by plugging this into the formula from the problem set. Note that this formula has a dependence on the energy spacing, which we can get from the fact that $E_n = \frac{1}{n^2}$ for the hydrogen atom.