Solved Homework

We are asked to give the minimum energy required for the ionization reaction

$$Be^{3+} \rightarrow Be^{4+} + e^-$$

Since Be is atomic number $Z = 4$, this corresponds to ionization of the electron from a one-electron atom. One-electron atoms are the systems that we know how to deal with exactly based on our work of last lecture.

Note that the reason the poorly worded problem presumably says the "minimum energy" is that it has in mind the energy required to just separate the electron from the nucleus and leave both particles at rest (this defines the system's zero of energy). You could, however, provide *more* energy, so that not only would the particles be infinitely separated, but they'd have some kinetic energy too, instead of being at rest. However, the problem is poorly worded because the correct answer is that the minimum energy is ε, where ε is a positive number arbitrarily close to zero. How can this be? Well, what if the electronic wave function corresponds to principle quantum number $n = 10^9$? The binding energy in that case is incredibly small (ε), and it's easy to remove the electron.

To clean up the wording, one need only specify that Be^{3+} is in its *ground state*. In that case, we know that the binding energy of the electron to the nucleus is

$$E_{n=1}\left(Be^{3+}\right) = -\frac{Z_{Be}^2 e^4 \mu_{Be}}{32\pi^2 \varepsilon_0^2 (1)^2 \hbar^2}$$

Now, we could go look up all the necessary constants and plug them in, and that would give a very nice answer. A quicker approach, however, is to use the datum provided that $E_{n=1}(H) = -13.6$ eV. Then we can consider

$$\frac{E_{n=1}\left(\mathrm{Be}^{3+}\right)}{E_{n=1}(\mathrm{H})} = \frac{\left[-\dfrac{Z_{\mathrm{Be}}^2 e^4 \mu_{\mathrm{Be}}}{32\pi^2 \varepsilon_0^2 (1)^2 \hbar^2}\right]}{\left[-\dfrac{Z_{\mathrm{H}}^2 e^4 \mu_{\mathrm{H}}}{32\pi^2 \varepsilon_0^2 (1)^2 \hbar^2}\right]}$$

$$= \frac{16\mu_{\mathrm{Be}}}{\mu_{\mathrm{H}}}$$

$$= 16\frac{\dfrac{m_{\mathrm{Be}} m_e}{m_{\mathrm{Be}} + m_e}}{\dfrac{m_{\mathrm{H}} m_e}{m_{\mathrm{H}} + m_e}} \approx 16\frac{\dfrac{m_{\mathrm{Be}} m_e}{m_{\mathrm{Be}}}}{\dfrac{m_{\mathrm{H}} m_e}{m_{\mathrm{H}}}} = 16$$

Thus, the final ionization potential for Be should be 16 times the ionization potential for H, or −217.6 eV.

Hydrogenic Orbitals

Last lecture, we went through a fairly complicated process to derive the quantum restrictions on the energy levels of one-electron atoms, but we did not take the final step of putting our final quantum numbers back into our various differential equations to pull out the eigenfunctions themselves.

If one attempts to do this in a completely general way (i.e., for arbitrary quantum numbers n and l) one can write a general wave function in terms of what are called the associated Laguerre polynomials. This general form, however, is not terribly informative, and it is more useful to simply consider some of the specific functions associated with smaller quantum numbers. For example, what if we pick the principle quantum number $n = 1$? From our previous work, and in particular eq. 14-30, this requires that l and m both be zero, and $\beta = n = 1$.

The requirement that l be zero means that the spherical harmonic for this hydrogenic wave function will have to be $Y_{0,0}$. From the table that is part of Lecture 12, we see

$$Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \tag{15-1}$$

which is pleasantly simple.

As for the radial function, since $m = 0$, the only term in $\Sigma(\rho)$ that is non-zero is the zeroth order term a_0. This means, based on our earlier work

$$\Sigma(\rho) = a_0$$

$$S(\rho) = \rho^0 a_0 = a_0 \qquad (15\text{-}2)$$

$$P(\rho) = a_0 e^{-\rho/2}$$

Recall that ρ was defined as the dimensionless quantity $2\alpha r$. If we plug back in all of the constants we get

$$\begin{aligned}
\alpha &= \sqrt{-\frac{2\mu E}{\hbar^2}} \\
&= \sqrt{\frac{2\mu^2 Z^2 e^4}{32\pi^2 \varepsilon_0^2 n^2 \hbar^4}} \qquad (15\text{-}3) \\
&= \frac{\mu Z e^2}{4\pi\varepsilon_0 n \hbar^2}
\end{aligned}$$

So, the full wave function becomes

$$\begin{aligned}
\Psi_{100}(r,\theta,\phi) &= P_1(\rho) Y_{0,0}(\theta,\phi) \\
&= \sqrt{\frac{1}{4\pi}} a_0 e^{-\mu Z e^2 r / 4\pi\varepsilon_0 n \hbar^2} \qquad (15\text{-}4)
\end{aligned}$$

To solve for a_0, we simply have to normalize Ψ_{100}, where the subscripts on the wave function specify the principle quantum number n, the azimuthal quantum number l, and the z component of the angular momentum quantum number m_l, respectively.

Prior to carrying out that normalization, however, it is time to do something to simplify our lives from here on out. It is time to introduce a new system of units, called "atomic units" (a.u.) In atomic units, the magnitude of various quantities is defined to be 1, so that we need not write them! For instance, h-bar is defined to be one atomic unit of action. The dielectric permittivity of the vacuum is defined to be one. The charge on the electron is defined to be one. The mass of the electron (which is very close to μ) is defined to be one. In atomic units, eq. 15-4 simplifies to

$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{1}{4\pi}} a_0 e^{-Zr/n} \qquad (15\text{-}5)$$

which certainly will involve less bookkeeping when we work with it! Of course, if you want to convert from atomic units to other units, you'll have to make use of the proper conversion factors, but those are easy to look up. A handy table is provided on the next page.

Useful Quantities in Atomic and Other Units

Physical quantity (unit name)	Symbol	Value in a.u.	Value in SI units	Value(s) in other units
Angular momentum	$\hbar$	1.	1.055×10^{-34} J s	2.521×10^{-35} cal s
Mass	m_e	1.	9.109×10^{-31} kg	
Charge	e	1.	1.602×10^{-19} C	1.519×10^{-14} statC
Vacuum permittivity	$4\pi\varepsilon_0$	1.	1.113×10^{-10} C^2 J^{-1} m^{-1}	2.660×10^{-21} C^2 cal^{-1} Å^{-1}
Length (bohr)	a_0	1.	5.292×10^{-11} m	0.529 Å
				52.9 pm
Energy (hartree)	E_{h}	1.	4.360×10^{-18} J	627.51 kcal mol^{-1}
				2.626×10^3 kJ mol^{-1}
				27.211 eV
				2.195×10^5 cm^{-1}
Electric dipole moment	ea_0	1.	8.478×10^{-30} C m	2.542 D
Electric polarizability	$e^2 a_0{}^2 E_{\mathrm{h}}{}^{-1}$	1.	1.649×10^{-41} C^2 m^2 J^{-1}	
Planck's constant	h	2π	6.626×10^{-34} J s	
Speed of light	c	1.370×10^2	2.998×10^8 m s^{-1}	
Bohr magneton	μ_{B}	0.5	9.274×10^{-24} J T^{-1}	
Nuclear magneton	μ_{N}	2.723×10^{-4}	5.051×10^{-27} J T^{-1}	

Note that by adopting a.u. for our unit system in eq. 15-5, it becomes implicit that we measure r in the atomic unit of distance, the bohr, which is 0.529 Å. An example of how quickly a.u. simplify expressions is that the energy of the hydrogenic atom (eq. 14-34) is given in these units as $E_n = -Z^2/2n^2$. So, a ground state ($n = 1$) hydrogen atom has energy $-0.5\ E_h$.

So, now if we want to normalize Ψ_{100}, we must solve

$$1 = \langle \Psi_{100}(r,\theta,\phi) | \Psi_{100}(r,\theta,\phi) \rangle$$

$$= \frac{a_0^2}{4\pi} \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-Zr/n} e^{-Zr/n} r^2 dr \sin\theta d\theta d\phi$$

$$= \frac{a_0^2}{2} \int_0^\infty \int_0^\pi e^{-2Zr/n} r^2 dr \sin\theta d\theta \qquad (15\text{-}6)$$

$$= a_0^2 \int_0^\infty r^2 e^{-2Zr/n} dr$$

$$= a_0^2 \frac{n^3}{4Z^3}$$

or

$$a_0 = 2\left(\frac{Z}{n}\right)^{3/2} \qquad (15\text{-}7)$$

If we use this in eq. 15-5 (now explicitly taking $n = 1$; we've carried it as a variable up until now because that will help to explain later results) we have

$$\Psi_{100}(r,\theta,\phi) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Zr} \qquad (15\text{-}8)$$

This is really a rather simple form.

We can carry out similar manipulations for each additional choice of n and possible l values. Note that (a) when $n > l + 1$, we will have terms past a_0 in $\Sigma(\rho)$ that are non-zero, but by the recursion formula eq. 14-26, every one can be written in terms of a_0, whose ultimate value for the particular wave function will be determined by requiring normalization, and (b) when $l > 0$ we will have a polynomial in r up to r^l multiplying the spherical harmonic and the exponential parts in the wave function. The table below shows the final results for the various hydrogenic one-electron wave functions without going through the detailed derivation for each one.

The Hydrogenic One-Electron Wave Functions

Complex form	Real (spherical) form	Real (cartesian) form[a]	Nomenclature
$\dfrac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr}$	(same as complex)	(same as complex)	Ψ_{100}; 1s
$\dfrac{Z^{3/2}}{4\sqrt{2\pi}}(2-Zr)e^{-Zr/2}$	(same as complex)	(same as complex)	Ψ_{200}; 2s
$\dfrac{Z^{5/2}}{8\sqrt{\pi}}r\sin\theta e^{-i\phi}e^{-Zr/2}$			Ψ_{21-1}; $2p_{-1}$
	$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}r\sin\theta\sin\phi e^{-Zr/2}$	$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}ye^{-Zr/2}$	$\Psi_{21\sin\phi}$; $2p_y$
$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}r\cos\theta e^{-Zr/2}$	(same as complex)	$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}ze^{-Zr/2}$	Ψ_{210}; $2p_z$
	$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}r\sin\theta\cos\phi e^{-Zr/2}$	$\dfrac{Z^{5/2}}{4\sqrt{2\pi}}xe^{-Zr/2}$	$\Psi_{21\cos\phi}$; $2p_x$
$\dfrac{Z^{5/2}}{8\sqrt{\pi}}r\sin\theta e^{i\phi}e^{-Zr/2}$			Ψ_{211}; $2p_{-1}$
$\dfrac{Z^{3/2}}{81\sqrt{3\pi}}\left[27-18Zr+2(Zr)^2\right]e^{-Zr/3}$	(same as complex)	(same as complex)	Ψ_{300}; 3s
$\dfrac{Z^{5/2}}{81\sqrt{\pi}}\left[6-Zr\right]r\sin\theta e^{-i\phi}e^{-Zr/3}$			Ψ_{31-1}; $3p_{-1}$

$$\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)r\sin\theta\sin\phi\, e^{-Zr/3} \qquad \frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)y\, e^{-Zr/3} \qquad \Psi_{31\sin\phi};\ 3p_y$$

$$\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)r\cos\theta\, e^{-Zr/3} \qquad \text{(same as complex)} \qquad \frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)z\, e^{-Zr/3} \qquad \Psi_{310};\ 3p_z$$

$$\frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)r\sin\theta\cos\phi\, e^{-Zr/3} \qquad \frac{\sqrt{2}Z^{5/2}}{81\sqrt{\pi}}(6-Zr)x\, e^{-Zr/3} \qquad \Psi_{31\cos\phi};\ 3p_x$$

$$\frac{Z^{5/2}}{81\sqrt{\pi}}[6-Zr]r\sin\theta\, e^{i\phi}e^{-Zr/3} \qquad \Psi_{311};\ 3p_1$$

$$\frac{Z^{7/2}}{162\sqrt{\pi}}r^2\sin^2\theta\, e^{-2i\phi}e^{-Zr/3} \qquad \Psi_{32-2};\ 3d_{-2}$$

$$\frac{Z^{7/2}}{81\sqrt{2\pi}}r^2\sin^2\theta\sin 2\phi\, e^{-Zr/3} \qquad \frac{Z^{7/2}}{81\sqrt{2\pi}}xy\, e^{-Zr/3} \qquad \Psi_{31\sin 2\phi};\ 3d_{xy}$$

$$\frac{Z^{7/2}}{81\sqrt{\pi}}r^2\sin\theta\cos\theta\, e^{-i\phi}e^{-Zr/3} \qquad \Psi_{32-1};\ 3d_{-1}$$

$$\frac{\sqrt{2}Z^{7/2}}{81\sqrt{\pi}}r^2\sin\theta\cos\theta\sin\phi\, e^{-Zr/3} \qquad \frac{\sqrt{2}Z^{7/2}}{81\sqrt{\pi}}yz\, e^{-Zr/3} \qquad \Psi_{31\sin\phi};\ 3d_{yz}$$

$$\frac{Z^{7/2}}{81\sqrt{6\pi}}r^2\left(3\cos^2\theta-1\right)e^{-Zr/3} \qquad \text{(same as complex)} \qquad \frac{Z^{7/2}}{81\sqrt{6\pi}}\left(3z^2-r^2\right)e^{-Zr/3} \qquad \Psi_{320};\ 3d_0;\ 3d_{z^2}$$

$$\frac{\sqrt{2}Z^{7/2}}{81\sqrt{\pi}}r^2\sin\theta\cos\theta\cos\phi\, e^{-Zr/3} \qquad \frac{\sqrt{2}Z^{7/2}}{81\sqrt{\pi}}xz\, e^{-Zr/3} \qquad \Psi_{31\cos\phi};\ 3d_{xz}$$

$$\frac{Z^{7/2}}{81\sqrt{\pi}} r^2 \sin\theta \cos\theta e^{i\phi} e^{-Zr/3} \qquad\qquad \Psi_{321};\ 3d_1$$

$$\frac{Z^{7/2}}{81\sqrt{2\pi}} r^2 \sin^2\theta \cos 2\phi e^{-Zr/3} \qquad \frac{Z^{7/2}}{162\sqrt{2\pi}}\left(x^2 - y^2\right)e^{-Zr/3} \qquad \Psi_{31\cos2\phi};\ 3d_{x^2-y^2}$$

$$\frac{Z^{7/2}}{162\sqrt{\pi}} r^2 \sin^2\theta e^{2i\phi} e^{-Zr/3} \qquad\qquad \Psi_{322};\ 3d_2$$

[a] The radial variable r is still used in these expressions to avoid the tedium of replacing it with $(x^2 + y^2 + z^2)^{1/2}$ throughout.

There are many qualitative features to notice about these wave functions, some of which are familiar to even beginning students of chemistry, and some of which are only clear with our quantum mechanics background upon which now to draw. Let's focus on the most important:

1.   s orbitals are radially symmetric, p orbitals are axially symmetric, d orbitals have alternating four-fold symmetry, etc.

2.   The exponential radial decay of a hydrogenic wave function depends inversely on the principle quantum number.

3.   The orbital energy for a given atom having atomic number Z depends only on the principle quantum number n (see eq. 13-34). Thus, all wave functions having the same principle quantum number are degenerate in energy *irrespective of whether they are s, p, or d*, etc. Each principle quantum level has a total degeneracy of n^2. (Count up the first few if you don't see this).

4.   Because of the incorporation of the spherical harmonics in the wave functions, we may use either complex or real forms. The complex forms are eigenfunctions of L_z, while the real ones generally are not. Most people are used to the depictions of the real ones.

5.   Every wave function has $n - 1$ nodes where n is the principle quantum number. There are $n - l - 1$ spherical nodes in the *radial* direction, and the remainder of the nodes, if there are any, are associated with spherical harmonic nodal planes that include the nucleus (i.e., the origin of the spherical polar coordinate system).

6.   With increasing atomic number Z, the wave functions decay more quickly with r and have larger amplitude near the nucleus to ensure normalization.

7.   s wave functions have non-zero amplitude at the nucleus. Indeed, the s wave functions have cusps (maxima at which they are *not* differentiable) at the nucleus. All other wave functions are zero at the nucleus.

8.   Hydrogenic wave functions have non-zero values *everywhere* except at nodal positions. What is usually *illustrated*, though, is a surface of *constant probability density* (e.g., $|\Psi|^2 = 0.0001$ a.u., where the atomic unit of probability density is $bohr^{-3}$).

Homework

To be solved in class:

For a hydrogenic atom in a.u., $\langle H \rangle = -Z^2/2n^2$ and $\langle r^{-1} \rangle = -Z/n^2$. What is the value of $\langle -\nabla^2/2 \rangle$? It may not look like it, but this problem is very easy and should not require the solution of any integrals. Hint: What *is* the Hamiltonian for the hydrogenic atom?

To be turned in for possible grading Feb. 25:

If you were to measure the distance of a 2s electron from the nucleus in a He^+ atom, what would be the average value, in Å, that you would obtain after a very, very large number of measurements? (Hint: if you've no idea where to start on this problem, think about what operator gives the distance of the electron from the nucleus.) (Caveat: be very careful about using proper limits and volume elements in any integrals you might try to solve—perhaps with the help of an integral table…) Will the value for Li^{2+} be the same, or different? Why?