

Chem 6 Sample Exam 2 Brief Answers

1a. Two possible approaches here to find the energy difference and hence the frequency. Either find the energy of both states and subtract, or use one of the formulas that includes the subtraction for you.

$$\Delta E = h\nu$$

The energy of the $n = 253$ and $n = 252$ states is given by

$$E_n = -2.18 \times 10^{-18} \text{ J} (Z^2/n^2) \text{ where } Z = 1 \text{ for the hydrogen atom}$$

$$E_{253} = -2.18 \times 10^{-18} \text{ J} (1^2/253^2) = -3.406 \times 10^{-23} \text{ J}$$

$$E_{252} = -2.18 \times 10^{-18} \text{ J} (1^2/252^2) = -3.433 \times 10^{-23} \text{ J}$$

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{252} - E_{253} = -2.7 \times 10^{-25} \text{ J} \text{ (a negative number, so energy is emitted)}$$

$$h\nu = \Delta E \text{ so } \nu = |\Delta E|/h = 2.7 \times 10^{-25} \text{ J} / 6.626 \times 10^{-34} \text{ Js} = \mathbf{4.1 \times 10^8 \text{ s}^{-1}} \text{ or } 410 \text{ MHz}$$

(radiofrequency)

your final numerical result may be somewhat different, depending on how you rounded off the numbers above

$$\text{Or, } \nu = 3.29 \times 10^{15} \text{ s}^{-1} Z^2 (1/n_f^2 - 1/n_i^2).$$

$$\text{Plug in } Z = 1, n_f = 252, n_i = 253, \text{ to get } \mathbf{\nu = 4.1 \times 10^8 \text{ s}^{-1}}$$

1b. The Bohr radius is given by $r = a_0 n^2 / Z$ Å where $a_0 = 0.529 \text{ Å} = 0.529 \times 10^{-10} \text{ m}$

Plug in $n = 253$ and $Z = 1$ to get

$$r = 0.529 \times 10^{-10} \text{ m} (253)^2$$

$= \mathbf{3.39 \times 10^{-6} \text{ m}}$ x 1000mm/m = $3.39 \times 10^{-3} \text{ mm}$. That seems a bit small to see unless you've got really good vision. But still, mighty big for an atom!

2. $E_n = n^2 h^2 / 8mL^2$

Plug in $n=1$ and 2 , plus all the constants

$$E_1 = (6.626 \times 10^{-34} \text{ Js})^2 (1)^2 / 8(9.11 \times 10^{-31} \text{ kg})(1.34 \times 10^{-10} \text{ m})^2$$

$$= 3.35 \times 10^{-18} \text{ J}$$

$$E_2 = \text{same thing, but multiplied by } 2^2 \text{ instead of } 1^2, \text{ so it's } 1.34 \times 10^{-17} \text{ J}$$

The energy difference is $\Delta E = |E_2 - E_1| = 1.01 \times 10^{-17} \text{ J}$

$$E = h\nu = hc/\lambda \text{ so } \lambda = hc/E = (6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s}) / 1.01 \times 10^{-17} \text{ J}$$

$$= 1.97 \times 10^{-8} \text{ m} \times 10^9 \text{ nm/m} = \mathbf{\sim 20 \text{ nm}}$$

You could also do this by using the formula for the energy difference between states of quantum numbers n and $n+1$:

$$\Delta E = (2n+1)h^2/8mL^2, \text{ plugging in } n=1 \text{ to get the separation between } E_1 \text{ and } E_2.$$

3. Zero-point energy is defined as the minimum energy of the system. So for the H atom it's the energy of the ground state, where $n = 1$, given by

$$E_n = -2.18 \times 10^{-18} \text{ JZ}^2/n^2$$

Plug in $n=1$ and $Z=1$ for hydrogen to get $-2.18 \times 10^{-18} \text{ J}$.

For the particle in a box, energy is

$$E_n = n^2 h^2 / 8mL^2$$

The minimum is in the ground state at $n = 1$; plug in the mass of the electron and set the energy equal to the magnitude of the ZPE above:

$$E_1 = 1^2 h^2 / 8mL^2 = |E_{\text{atom}}| = 2.18 \times 10^{-18} \text{ J}$$

Set up to solve for L , then plug in the numbers as follows

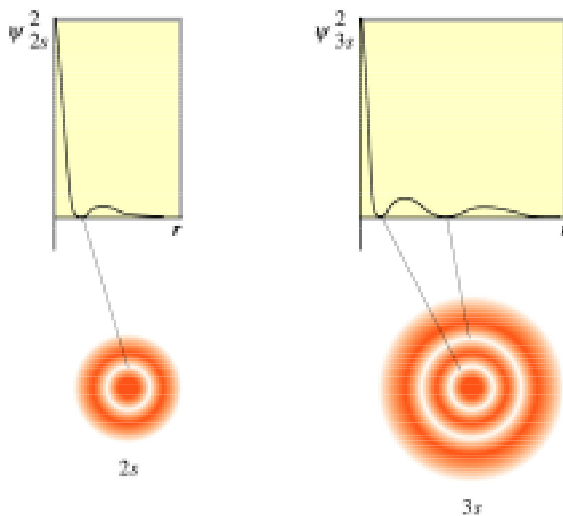
$$[n^2 h^2 / 8mE_{\text{atom}}]^{1/2} = L$$

$$= [1^2 (6.626 \times 10^{-34} \text{ Js})^2 / 8(9.11 \times 10^{-31} \text{ kg})(2.18 \times 10^{-18} \text{ J})]^{1/2}$$

$$= 1.66 \times 10^{-10} \text{ m} \times 10^{10} \text{ \AA/m} = 1.66 \text{ \AA} \text{ or } 0.166 \text{ nm}$$

4a. These spherical shells are **nodes**, regions of space where the value of the wavefunction is zero; this means Ψ^2 is zero and the probability of finding the particle there is zero.

(b) See the picture. For the 2s orbital there is one such node, with 2 for the 3s. Note that Ψ^2 becomes small, *but not zero!*, at large r .



(c) To find the r values, set Ψ equal to zero and solve for σ (since this is equal to Zr/a_0 , you will get r).

For 2s, Ψ is zero at $\sigma = 2$; since $Z = 1$ for the H atom, then $r = 2a_0 = \mathbf{1.06\text{\AA}}$

For 3s, Ψ is zero when the function $27 - 18\sigma + 2\sigma^2 = 0$

Solve this with the quadratic formula from the equation sheet. First divide through by two to get $27/2 - 9\sigma + \sigma^2 = 0$

Then solve for σ :

$$\sigma = [-b \pm (b^2 - 4ac)^{1/2}] / 2a = [9 \pm (81 - 54)^{1/2}] / 2 = \mathbf{1.90 \text{ or } 7.10 \text{ (2 nodes)}}$$

convert this to r -values:

$\sigma = Zr/a_0$, but $Z = 1$ for the H atom, so $r = \sigma a_0$. There are 2 solutions (nodes):

$$\mathbf{r = 1.9a_0 = 1.9(0.529\text{\AA}) = 1\text{\AA}}$$

$$\mathbf{r = 7.1a_0 = 7.1(0.529\text{\AA}) = 3.76\text{\AA}}$$

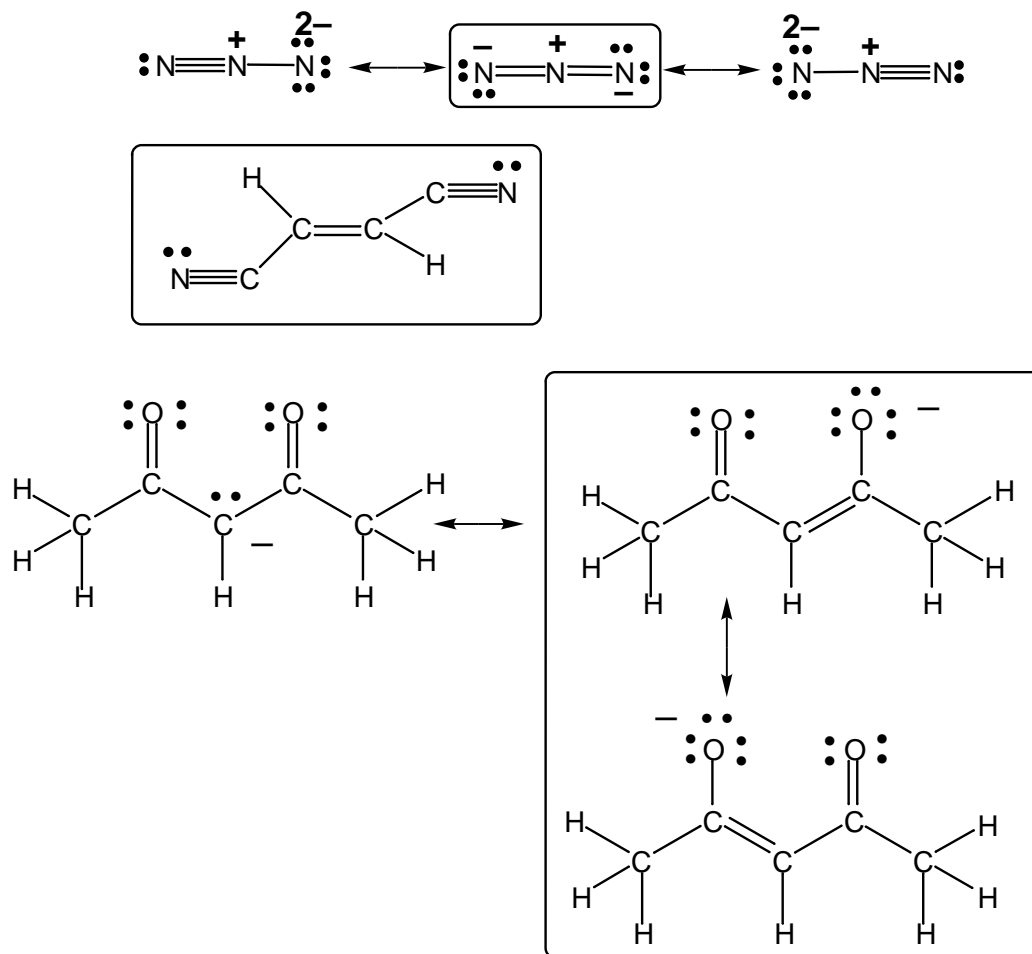
5.(a) As you go down the column, the valence electrons are **farther from the nucleus** (as n increases and the orbitals have greater radial extent), so they have **reduced Coulombic attraction** to the nucleus and are easier to ionize.

Likewise, an electron to be added would, **for the same reason**, have **reduced (as you go down the column) Coulombic attraction to the nucleus**, so electron affinities are expected to be less exothermic (smaller in magnitude).

(b) Going **across a row**, filling in the p -electrons, Z_{eff} **increases** since these valence electrons don't shield each other efficiently. So **the valence electrons are held more tightly/closely to the nucleus and atomic radius decreases across the row**; thus Ne is smaller than B.

(c) Br^- and Kr are **isoelectronic**, but **Kr has larger Z** , so there is greater Coulombic attraction between nucleus and electrons, so **the electrons are held tighter/closer to the nucleus**, and hence the size of the Kr atom is smaller than that of Br^- .

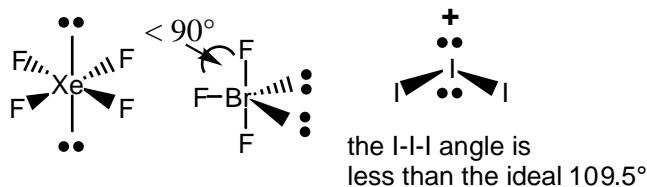
6. Here are the resonance structures.



7. (a) XeF_4 is **square planar**. It's based on 6 electron pairs around the central Xe (octahedral electron pair geometry), with the lone pairs at 180° to minimize repulsions between them. No distortions expected.

(b) BrF_3 is **T-shaped**. It's based on 5 electron pairs around the central Br (trigonal bipyramidal electron pair geometry), with the lone pairs in the equatorial position to minimize repulsions. Because the lone pairs "take more room" than bonding pairs, expect that the axial Br atoms will bend away from the lone pairs so the $\text{F}_{\text{eq}}-\text{Br}-\text{F}_{\text{ax}}$ angle is less than 90° .

(c) I_3^+ is **bent**. The I-I-I angle is less than the expected 109.5° (based on tetrahedral electron pair geometry at the central I) just as in water.



8. (a) Ni < Pd -- ionic radius. The ionic radius of Pd is larger, since **the valence electrons are in a shell with larger n (greater radial extent)**. So, on average, they are farther from the nucleus, leading to a larger ionic radius for Pd²⁺ than for Ni²⁺.

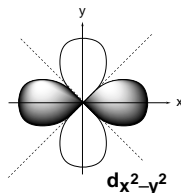
Pd = Pt -- ionic radius. why doesn't this same effect work here, so that Pt²⁺ is bigger than Pd²⁺? This is due to the **lanthanide contraction**. As you go from Pd to Pt you also fill in the lanthanide elements. **The added f electrons, because of their poor penetration to the nucleus, are not efficient in shielding the added nuclear charge that arises as you go across that row. The result is that Z_{eff} increases**, the outer shell electrons feel a greater attraction to the nucleus, and the ionic radius is decreased (in this case, so Pt²⁺ is the same size as Pd²⁺).

(b) The key idea here is **penetration** effects.

1. 3s vs 3p vs 3d. An electron in a 3s orbital has greater probability of being very close to the nucleus (penetration) than a 3p electron, which in turn has greater probability of getting close to the nucleus than a 3d electron. Since the Coulombic attraction between electron and nucleus depends on distance, closer penetration is associated with lower energy.

2. 4s vs 3d. Although an electron in a 4s orbital is on average farther from the nucleus than a 3d electron (because n is bigger and the 4s orbital has greater radial extent), again it penetrates closer (no node at the nucleus for an s-orbital), so it has lower energy.

9. (a) **4d** (b) **-2, -1, 0, 1, 2** (c) Here's a sketch of one of the simpler ones, $d_{x^2-y^2}$. For the others, see the handout from class. I have added the nodal planes here as dotted lines. You can draw similar ones readily for most of the others, but d_{z^2} has nodal surfaces instead, which are not as easy to draw.



10. (a) **ii** (b) **i and ii** (c) **ii** (d) **iv** (e) **iv** (f) see below (g) **iii**

| Statement # | True for the H atom only | True for all atoms | False for all atoms |
|-------------|--------------------------|--------------------|---------------------|
| i | x | | |
| ii | | x | |
| iii | | x | |
| iv | | | x |