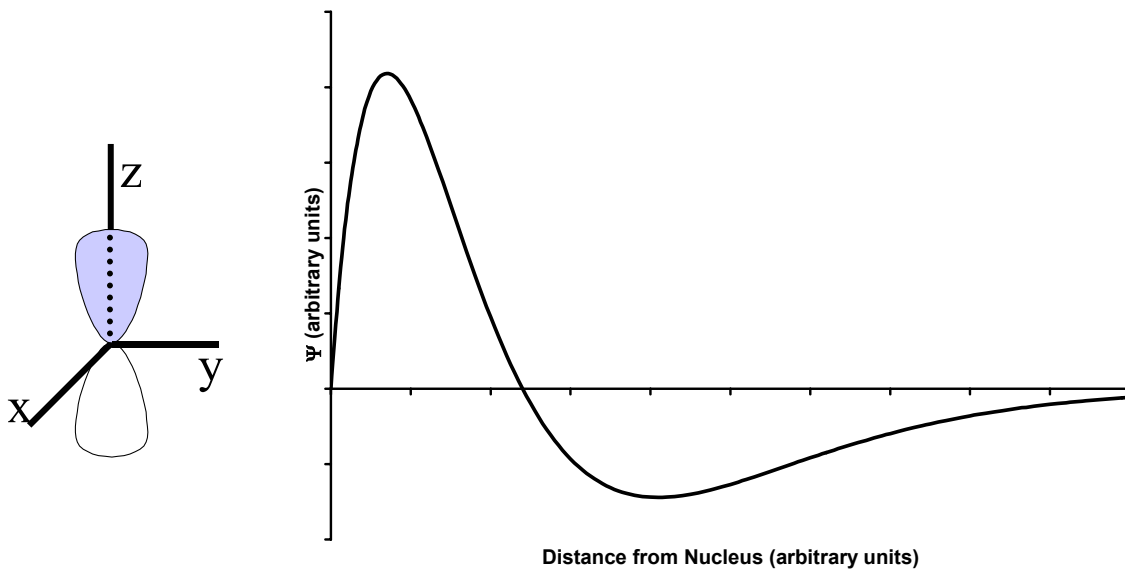


CHEM 121
Supplemental Questions for the
Electronic Structure of the Hydrogen and Multi-Electron Atoms

1. Fill in the blanks.

n	ℓ	m_ℓ	Orbital Name(s)
2	1	0, ± 1	2p
1	0	0	1s
5	2	0, ± 1 , ± 2	5d
4	3	0, ± 1, ± 2, ± 3	4f

2. The radial and angular wavefunctions for a certain orbital are given below. What orbital is it (give both the letter and number designation)?



This is a p orbital, so $\ell = 1$. The number of radial nodes is given by $n - \ell - 1$, so $n - 1 - 1 = 1$, and thus $n = 3$. The p orbital is oriented along the z axis, so this is the $3p_z$ orbital.

3. Consider a $d_{x^2-y^2}$ orbital. Will there be any points on the x axis where the probability of finding an electron is zero? Explain.

A $d_{x^2-y^2}$ orbital is oriented such that its lobes are aligned along the x and y axes with angular nodes at 45° angles to the axes running through the nucleus. There will, thus, be no probability of finding the electron at $x = 0$. There may be additional places on the x-axis where there is no probability of finding an electron, depending on the value of the principal quantum number, n . The number of radial nodes is equal to $n - \ell - 1$ (where $\ell = 2$ for a $d_{x^2-y^2}$ orbital), and for all $n > 3$ there will be at least one radial node. That is, if the principal quantum number is greater than 3, there will be $n - 3$ places where there is no probability of finding the electron on the x axis.

4. The nucleus of a hydrogen atom is located at the origin (0, 0, 0).

a. If the probability of finding the 2s electron at some distance, d , from the nucleus is 0.01. Is the probability of finding the electron at $y = d$ greater than, less than, or equal to 0.01? Why?

The probability of finding a 2s electron at $y = d$ is the same as at $x = d$, because s orbitals are spherically symmetric.

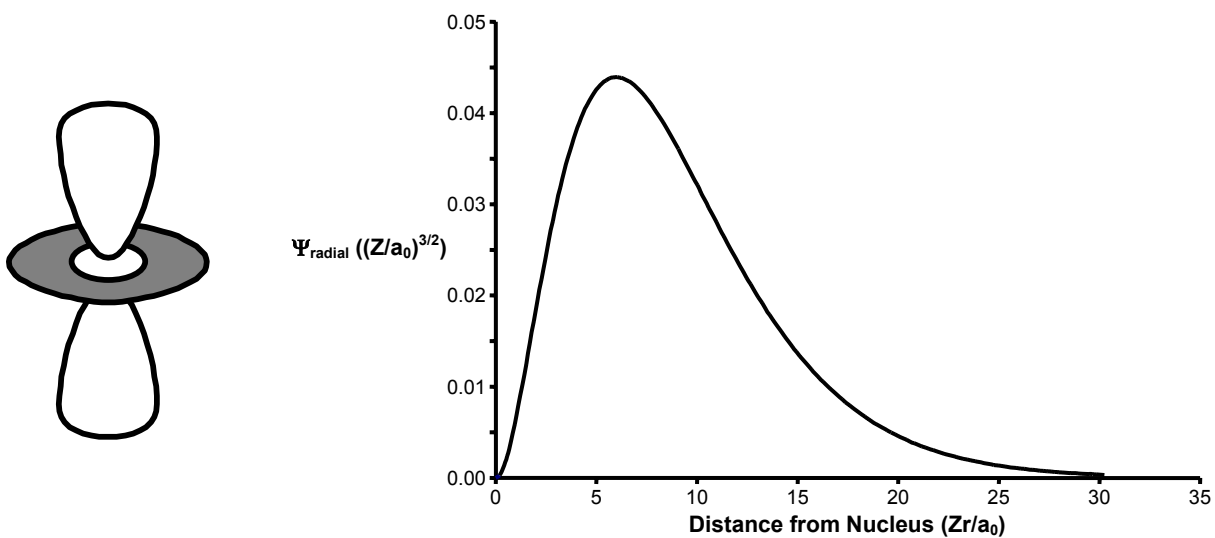
b. Is there anywhere along the x axis (is there any value of d) where the probability of finding a 2s electron is zero? Explain.

Yes, there will be a point on the x-axis where the probability of finding an electron in a 2s orbital is zero. The 2s orbital has one radial node, and at that point the probability of finding the electron is zero.

c. The probability of finding a $2p_x$ electron on the x-axis at distance d is 0.001. Is the probability of finding this electron on the y axis at distance d greater than, less than or equal to 0.001? Why?

The probability of finding an electron in a $2p_x$ orbital at any point on the y-axis is zero because this is the position of the angular node for this orbital.

5. The next questions refer to the pictures below.



a. The picture shown above left is the **angular** portion of the wavefunction and the picture shown above right is the **radial** portion of the wavefunction for a(n) d_{z^2} orbital.

b. The value of ℓ for the orbital shown above is **2**.

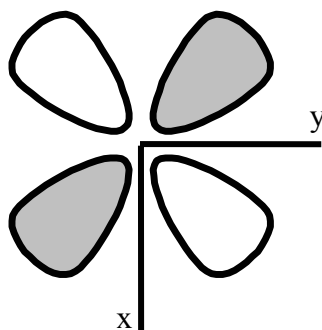
c. The principal quantum number for this orbital is **3**.

d. The number of angular nodes in this orbital is **2**.

e. The number of radial nodes in this orbital is **0**.

f. The possible value(s) of m_s is/are **$\pm 1/2$** .

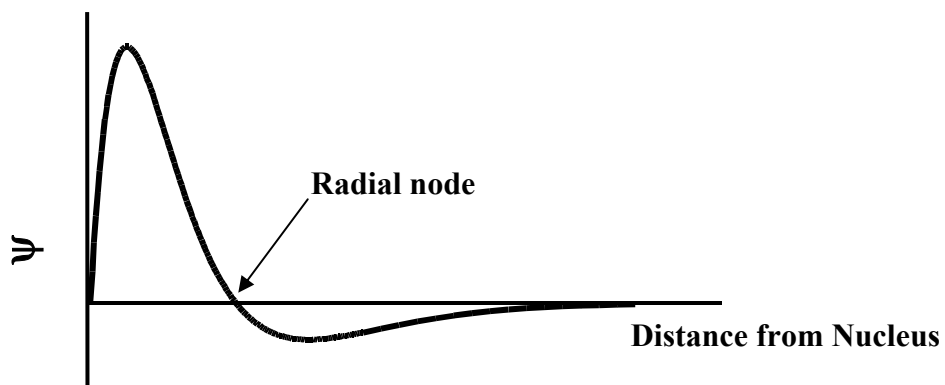
6. Consider a hydrogen orbital whose angular wavefunction is shown below. In this picture we are looking down the z axis (it is coming directly up out of the page at you).



a. The possible ℓ value(s) that this orbital can have is/are **2**

b. Number of angular nodes in this wavefunction **2**

c. The radial part of this wavefunction is shown below. Indicate the position of all radial nodes.



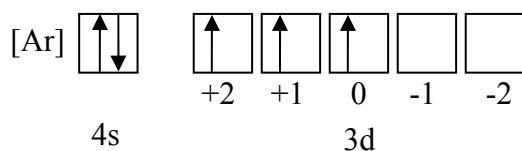
d. What is the name of this orbital?

This is the $4d_{xy}$ orbital.

7. Name all orbitals that can possibly exist with $n = 3$. How many electrons can be placed in the M shell?

The ℓ values that can exist with $n = 3$ are 0, 1 and 2. For $\ell = 0$ $m_\ell = 0$ (the 3s orbital), while there are three values of m_ℓ for $\ell = 1$ ($3p_x, 3p_y, 3p_z$) and there are five values of m_ℓ when $\ell = 2$ ($3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{z^2}, 3d_{x^2-y^2}$). There are a total of nine orbitals with $n = 3$. And since each orbital can hold two electrons, the maximum number of electrons that can be placed in the M ($n = 3$) shell is 18.

8. The electronic configuration of an element is given below.



a. The electronic configuration in spectroscopic notation is $[\text{Ar}] 4s^2 3d^3$.

b. The element is **vanadium**.

c. The element is located in group **5** and period **4**.

d. It belongs to the grouping of elements known as the **transition metals**.

e. Is the element diamagnetic or paramagnetic? **paramagnetic**

f. Write a complete set of quantum numbers for the five electrons shown.

$$n = 4, \ell = 0, m_\ell = 0, m_s = +1/2$$

$$n = 4, \ell = 0, m_\ell = 0, m_s = -1/2$$

$$n = 3, \ell = 2, m_\ell = +2, m_s = +1/2$$

$$n = 3, \ell = 2, m_\ell = +1, m_s = +1/2$$

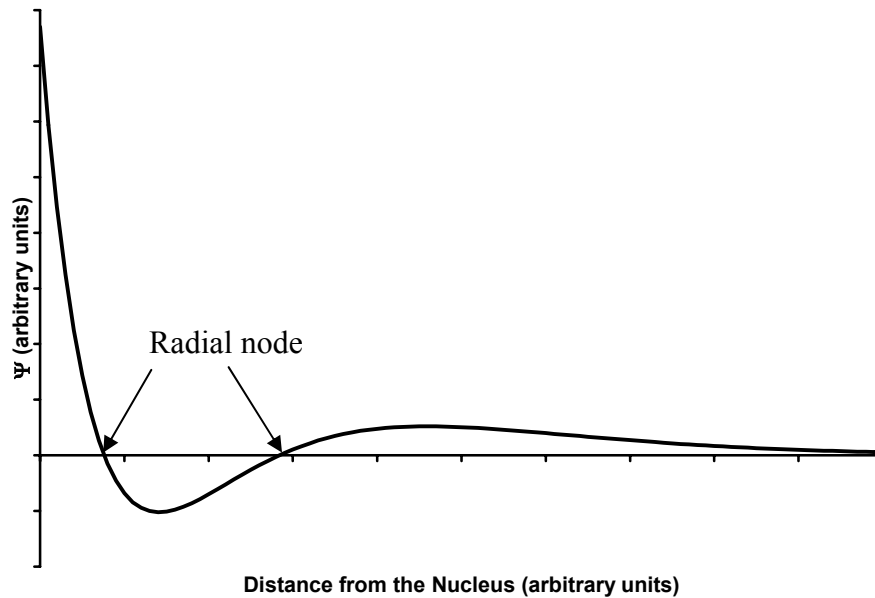
$$n = 3, \ell = 2, m_\ell = 0, m_s = +1/2$$

g. This element forms several cations, but not the 6+ cation. Explain why.

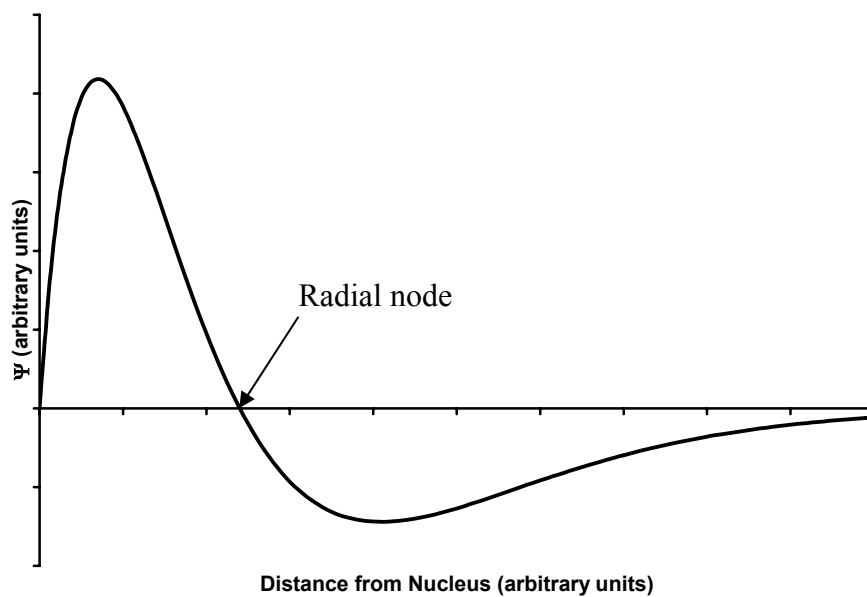
Removing the sixth electron breaks the particularly stable noble gas configuration. This requires a lot of energy, which is not usually available. So, the 6+ does not exist under normal circumstances.

9a. In the space provided, draw the radial wavefunction for a 3s and for a 3p orbital. Be sure to label which graph is which, label the axes, and indicate all radial nodes.

3s Orbital



3p Orbital



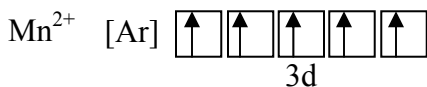
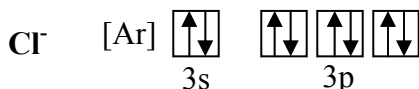
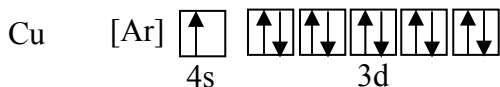
c. In the H atom are the 3s and 3p orbitals degenerate? Explain.

Yes the 3s and 3p orbitals are degenerate in the H atom. There is only one electron, so there is no shielding, electron-electron repulsion, or exchange effects. In the absence of these effects the only thing that determines the energy of the electron is its interaction with the nucleus.

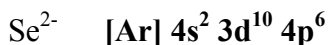
d. In the P atom are the 3s and 3p orbitals degenerate? Explain.

In the P atom the 3s and 3p orbitals are not degenerate. Electrons in both orbitals are shielded by the electrons with $n < 3$, and experience a charge that is somewhat less than the full nuclear charge. The electrons in the 3s orbital can penetrate the intervening electron cloud, because their wavefunction is not 0 at the nucleus. Since $\Psi \neq 0$ at the nucleus, s electrons have a probability of being found at the nucleus, they thus will experience a higher Z^* and have a lower energy than the 3p electrons which can not penetrate as well.

10a. Write the ground state electronic configuration of the following atoms and ions using the *orbital box* notation. Indicate the *diamagnetic* species.



b. Write the ground state electronic configuration of the following atoms and ions using spectroscopic notation. Indicate the *paramagnetic* species.



14a. Place the following atoms in order of increasing atomic radius. Briefly explain the rationale for your order.

B C N O F Ne

In order of increasing atomic radius: Ne, F, O, N, C, B

As one goes from left to right on the periodic table the electrons are being added to the same shell (same n), so the average distance from the nucleus for the valence electrons remains the same. The core electrons remain the same, so shielding does not change. The nuclear charge does change as one more proton is added to the nucleus, and since shielding remains the same Z^* increases. An increase in Z^* means that there will be a stronger attraction between the valence electrons and the nucleus, which results in the valence electrons being pulled closer to the nucleus, and a decrease in atomic size. This effect will be the greatest for Ne (therefore it is the smallest) and least for B (so it is the largest).

b. Place the following ions in order of increasing ionic radius. Briefly explain why you placed them in this order.

F⁻ Cl⁻ Br⁻ I⁻

In order of increasing size: F⁻, Cl⁻, Br⁻, I⁻

As we descend a group shielding increases because there are more electrons between the valence electrons and the nucleus. The orbitals are also becoming larger and more diffuse. So although the nuclear charge is increasing down a group, it is counteracted by the effect of shielding and the larger orbitals. This means that Z^* is decreasing and the outer electrons are less tightly held, which in turn leads them to be further from the nucleus (atomic/ionic radius increases).

c. Place the following ions in order of increasing ionic radius and explain why you chose this order.

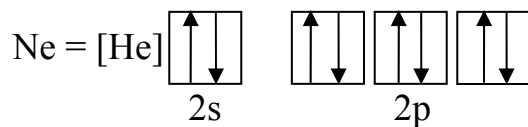
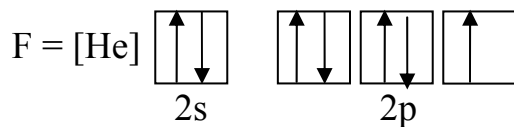
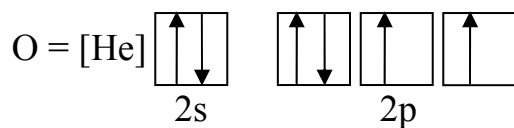
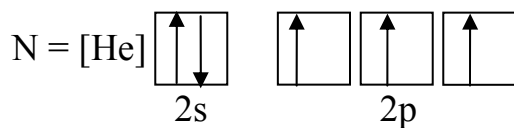
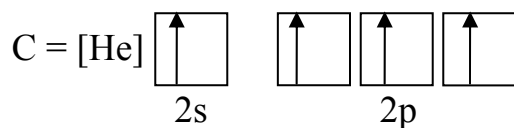
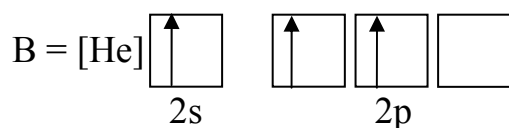
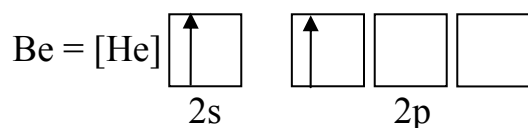
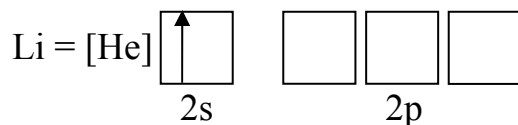
P³⁻ S²⁻ Cl⁻ K⁺ Ca²⁺

In order of increasing ionic radius: Ca²⁺, K⁺, Cl⁻, S²⁻, P³⁻

All of these ions have the same electronic configuration, but they differ in Z^* . Ca has 20 protons in the nucleus, so it has a higher nuclear charge to begin with than P which has only 15. When two electrons are removed to form Ca²⁺, the remaining electrons experience a higher Z^* , and are pulled closer to the nucleus. Three electrons must be added to P to form P³⁻, these electrons experience more electron-electron repulsion and a smaller Z^* ; so they are not pulled as closely to the nucleus.

15. In the currently accepted model of the multi-electron atom, the 2s and 2p orbitals are not degenerate. This model was developed by examining spectroscopic and magnetic data for the elements. One option that was considered, but discarded, was that the 2s and 2p orbitals are degenerate.

a. Assuming that the 2s and 2p orbitals are degenerate, and that Hund's rules and the Pauli exclusion principal still hold, write the electronic configuration, in orbital box notation, for the elements Li, Be, B, C, N, O, F and Ne. You will need to label each set of boxes with the appropriate element symbol.



b. To have the 2s and 2p orbitals be degenerate in this alternative model, what do we have to assume about them that is different than in the accepted model? Why?

For the 2s and 2p orbitals to be degenerate we must assume that they are able to equally penetrate the shielding 1s electrons. The energy difference between s and p orbitals arises from a difference in penetration, which in turn leads to a higher Z^* for the s electrons over the p electrons and a stabilization of the s orbital relative to the p orbital. If the s and p orbitals are to have the same energy, the effect that causes them to have different energy must be made to be the same for both.

c. Which of the elements in this model would be paramagnetic, and which are diamagnetic?

In this model all of the elements shown, except Ne, would be paramagnetic. Ne would be the only diamagnetic second period element.

d. For which elements does this model predict the correct electronic configuration?

This model predicts the correct electronic configuration for Li, N, O, F and Ne.

e. What does this model predict as the trend in the atomic radius across the period? Why?

The prediction is that the atomic radius should decrease across the period. Shielding is not changing as electrons are added to the $n = 2$ shell, but the nuclear charge increases as additional protons are added to the nucleus. This means that Z^* increases and the valence electrons (in the $n = 2$ shell) are pulled more strongly toward the nucleus. Because the electrons are pulled more strongly toward the nucleus, the size of the atom decreases.

f. Why was this model, where the 2s and 2p orbitals are degenerate, discarded?

The model was discarded because it does not explain the experimental results. For example, Be is predicted to be paramagnetic, but it is not. This model also does not predict the correct electronic configurations for B and C.

16. The general rule for removing electrons to form ions is to take the electrons out in the order p, s, d. But, in the atom the s orbitals are lower in energy and further out than the d orbitals (consider the fourth period, 4s fills before 3d). Is there a contradiction here? What has to change between the atom and the ion for the general rule to work?

There is no contradiction. The rule only predicts what the ground state for the ion is; it does not tell us how we got to that electronic configuration.

In the atoms the s orbital is lower in energy than the d orbitals, but in the ions the d orbitals must have lower energy. Otherwise, the rule would be different (i. e., the electrons would be removed in the reverse order in which they are “placed” into the atom by the Aufbau Principle, that is p, d, s).

17. The initial step in the formation of O₃ from O₂ in the stratosphere is the absorption of light by O₂, which causes it to split into O atoms. The balanced chemical equation for this process is: O₂ (g) → 2 O (g). If ΔH_f⁰ for O (g) is +249.17 kJ/mole, what wavelength of light, in nm, must be absorbed by O₂ to make this reaction occur? You are given that h = 6.6262 x 10⁻³⁴ J·s.

Determine ΔH⁰ for the reaction: O₂ (g) → 2 O (g)

$$\Delta H^0 = 2 \Delta H_f^0 (O, g) - 2 \Delta H_f^0 (O_2, g)$$

$$\Delta H^0 = 2 (+249.17 \text{ kJ/mole}) - (0)$$

$$\Delta H^0 = +498.34 \text{ kJ}$$

Write the wavelength of light in terms of its energy.

$$\text{Start with } \Delta E = h\nu \text{ and } \lambda \cdot \nu = c$$

$$\text{Substituting, and rearranging, gives } \lambda = \frac{h \cdot c}{\Delta E}$$

ΔH⁰ for the reaction must equal the energy of the light used. ΔH⁰ is written per mole of O₂ that reacts, but the expression for λ is for one photon. Therefore, we must convert ΔH⁰ in kJ/mole to E in J/photon using Avogadro's number.

$$\lambda = \frac{h \cdot c}{E} = \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s})(2.99792458 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{\left(498.34 \times 10^3 \frac{\text{J}}{\text{mole}}\right) \left(\frac{1 \text{ mole}}{6.0221367 \times 10^{23} \text{ photon}}\right)} = 2.4004_{48} \times 10^{-7} \text{ m}$$

Convert to nm

$$\lambda = 2.4004_{48} \times 10^{-7} \text{ m} \left(\frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}}\right) = 240.04 \text{ nm}$$

Light with a wavelength of 240.04 nm is required.

18. Mercury emits light at 253.65 nm. What energy, in eV, does this correspond to? Given that h = 6.6262 x 10⁻³⁴ J·s, 1 eV = 1.6022 x 10⁻¹⁹ J, c = 2.9978 x 10⁸ m·s⁻¹.

Start with the equations ΔE = h·ν and λ·ν = c and rearrange to get ΔE = $\frac{hc}{\lambda}$.

Substitute and solve for E then convert to eV.

$$\Delta E = \frac{(6.6262 \times 10^{-34} \text{ J} \cdot \text{s})(2.9978 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{253.65 \times 10^{-9} \text{ m}}$$

$$\Delta E = 7.8313 \times 10^{-19} \text{ J} \left(\frac{1 \text{ eV}}{1.6022 \times 10^{-19} \text{ J}}\right) = 4.8878 \text{ eV}$$

The energy of this light is 4.8878 eV.

19a. An atom in its ground state absorbs light with a wavelength of 341.2 nm, what is the energy of this transition in eV?

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979248 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{341.2 \times 10^{-9} \text{ m}} = 5.821_{95} \times 10^{-19} \text{ J}$$

$$\Delta E = 5.821_{95} \times 10^{-19} \text{ J} \left(\frac{1 \text{ eV}}{1.60218 \times 10^{-19} \text{ J}} \right) = 3.634 \text{ eV}$$

The energy of this transition is 3.634 eV.

b. If the atom in part a returns to its ground state and emits light, what will be the wavelength of this photon?

This emission is between the same two states in part a, so the wavelength is the same, 341.2 nm.

20. CO₂ absorbs light in the infrared portion of the spectrum at 1388.2 cm⁻¹. What is the wavelength of this light in nm? Given: 1 cm⁻¹ = 1.9864 × 10⁻²³ J, h = 6.62608 × 10⁻³⁴ J·s and c = 2.99792 × 10⁸ m·s⁻¹.

Convert energy in cm⁻¹ to J.

$$1388.2 \text{ cm}^{-1} \left(\frac{1.9864 \times 10^{-23} \text{ J}}{1 \text{ cm}^{-1}} \right) = 2.7575 \times 10^{-20} \text{ J}$$

Use Planck's equation to find ν from energy.

$$\Delta E = h\nu = 2.7575 \times 10^{-20} \text{ J} = (6.62608 \times 10^{-34} \text{ J} \cdot \text{s})\nu$$

$$\nu = 4.1616 \times 10^{13} \text{ s}^{-1}$$

$$\lambda\nu = c$$

$$\lambda = \frac{2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{4.1616 \times 10^{13} \text{ s}^{-1}} = 7.2037 \times 10^{-6} \text{ m}$$

$$\lambda = 7.2037 \times 10^{-6} \text{ m} \left(\frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} \right) = 7203.7 \text{ nm}$$

The wavelength is 7203.7 nm.