



CHM 2045 SECOND PROBLEM SET



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QUESTIONS ON THE PROPERTIES OF LIGHT

- What are the wavelengths, in meters, associated with radiation of the following frequencies?
a) $5.09 \times 10^{14} \text{ s}^{-1}$ b) $8.6 \times 10^{12} \text{ s}^{-1}$ c) $2.0 \times 10^9 \text{ s}^{-1}$
- Give the frequency and energy (per photon) associated with radiation of the following wavelengths.
a) 1.8 cm b) 480 Å ($1 \text{ Å} = 1 \times 10^{-10} \text{ m}$) c) 305 nm
- Give the frequency and wavelength (in meters) of radiation with the following photon energies.
a) $6.95 \times 10^{-20} \text{ J}$ b) $5.96 \times 10^{-26} \text{ J}$ c) $2.00 \times 10^{-15} \text{ J}$
- Restate each of the following in the new units indicated and tell in which region of the spectrum it lies:

See handout at the end of this problem set for spectral regions.

Example: $5.00 \times 10^{15} \text{ s}^{-1}$ to J. First, J is an energy unit and s^{-1} is a unit of frequency, ν .

Therefore, since $E = h \cdot \nu$, then, $(6.6262 \times 10^{-34} \text{ J} \cdot \text{s}) \times (5.00 \times 10^{15} \text{ s}^{-1}) = 3.31 \times 10^{-18} \text{ J}$.

- 150 pm to cm^{-1}
 - 4000 cm^{-1} to J
 - $1.50 \times 10^{15} \text{ s}^{-1}$ to nm
 - 10 cm to J
 - $1.0 \times 10^{-18} \text{ J}$ to s^{-1}
 - $1.20 \times 10^{14} \text{ s}^{-1}$ to cm^{-1}
- If each atom in one mole of atoms emits a photon of wavelength 650 nm, how much energy is lost? Express the answer in J/mol. As a reference point, burning gaseous CH_4 to form liquid water and gaseous CO_2 produces 890 kJ/mol of heat.
 - Compare the energy of an x-ray photon ($\lambda = 0.15 \text{ nm}$) with that of a microwave photon ($\lambda = 1.0 \text{ mm}$).
 - If the human eye receives a $1.59 \times 10^{-17} \text{ J}$ signal from photons whose wavelength is 500 nm, how many photons have hit the eye?
 - Chlorophyll absorbs blue light, $\lambda = 460 \text{ nm}$, and emits red light, $\lambda = 660 \text{ nm}$. Calculate the net energy change in chlorophyll when a single photon of 460 nm is absorbed and one of 660 nm is emitted.
 - The lowest-frequency light that will produce the photoelectric effect on a material is called the threshold frequency.
 - If the threshold frequency for Pt is $1.3 \times 10^{15} \text{ s}^{-1}$, what is the energy of a quantum of this radiation?
 - Will platinum display the photoelectric effect when exposed to ultraviolet light ($\lambda \sim 100 \text{ nm}$)? infrared light ($\lambda \sim 1.00 \times 10^{-3} \text{ cm}$)?
 - What would happen in both cases if the original intensities of the UV and IR light were doubled?
 - What would happen if the wavelength of UV light used was decreased.

10. Cesium metal requires radiation with a minimum threshold frequency of $4.60 \times 10^{14} \text{ s}^{-1}$ before it can emit an electron from its surface via the photoelectric effect. If cesium is irradiated with light whose wavelength is 540 nm, what is the kinetic energy of the emitted electron?
11. Indicate whether energy is emitted or absorbed when the following electron transitions occur in hydrogen:
- a. $n = 2$ to $n = 1$ b. $n = 2$ to $n = 4$ c. ionization of an e^- in the $n = 2$ state.
12. a) using the Bohr equation, calculate the energy of the photon emitted for each of the following electronic transitions;
- i) $n = 4$ to $n = 3$ ii) $n = 3$ to $n = 2$ iii) $n = 2$ to $n = 1$
- Take note of the magnitude of the energy differences between adjacent levels as n increases.
- b) Calculate the wavelength of each of the photons above and classify each with respect to the region of the spectrum.
13. a) Calculate the energy required to ionize a hydrogen atom in the ground state,
 I.e., $\text{H (g)} + \text{energy(photon)} \longrightarrow \text{H}^+ \text{ (g)} + e^-$
- b) The Li^{+2} ion has only one electron. Would you expect the ionization energy for Li^{+2} to be larger or smaller than that for the H atom? Explain.
14. According to de Broglie, matter in motion has an associated wave character which is dependent on the mass and velocity.
- (Note: $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$, therefore $h = 6.6262 \times 10^{-34} \text{ kg}\cdot\text{m}^2/\text{s}$)
- a) What is the wavelength associated with a grain of sand that has a mass of 0.0000100 g and is moving at a speed of 10.0 m/s?
- b) What is the wavelength associated with an electron ($9.11 \times 10^{-28} \text{ g}$) traveling at one tenth of the velocity of light?
15. Describe briefly the several differences between the orbits of the Bohr atom and the orbitals of the wave mechanical atom. Are there any similarities?

QUESTIONS ON ELECTRON CONFIGURATIONS

16. Each electron in an atom may be characterized by a set of four quantum numbers. For each of the following parts, tell how many different sets of quantum numbers are possible such that each set contains all of the values listed:
- a) $n = 4, \ell = 0$ b) $n = 4, \ell = 1$ c) $n = 4, \ell = 2$
- d) $n = 4, \ell = 3$ e) $n = 4, \ell = 3, m_\ell = 0$

17. Which of the following sets of quantum numbers is not allowable? Why not?

- | | | |
|-----------------------------------|-----------------------------------|----------------------------------|
| a) $n = 2, \ell = 1, m_\ell = 0$ | b) $n = 2, \ell = -1$ | c) $n = 3, \ell = 0, m_\ell = 0$ |
| d) $n = 3, \ell = 1, m_\ell = -1$ | e) $n = 2, \ell = 0, m_\ell = -1$ | f) $n = 3, \ell = 3, m_\ell = 2$ |

18. What type of electron orbital (i.e., s, p, d, or f) is designated by:

- | | | |
|-----------------------------------|----------------------------------|----------------------------------|
| a) $n = 2, \ell = 1, m_\ell = -1$ | b) $n = 4, \ell = 0, m_\ell = 0$ | c) $n = 5, \ell = 2, m_\ell = 0$ |
|-----------------------------------|----------------------------------|----------------------------------|

19. What are the n and ℓ quantum number designations for the subshells 3s, 4p, and 5d?

20. What is the Pauli Exclusion Principle?

21. Write down the aufbau order as developed in class for the first seven levels.

22. What is Hund's Rule of maximum multiplicity?

23. How many orbitals constitute each of the sublevels, s, p, d, and f, respectively? Use \uparrow or \downarrow designations to distinguish between $+\frac{1}{2}$ and $-\frac{1}{2}$ spins on electrons, respectively, and write the correct box diagram electron configurations for:

- | | |
|--|--|
| a) 2, 4 and 5 electrons in a p sublevel; | b) 2, 5 and 7 electrons in a d sublevel; |
| c) 6, 7, and 8 electrons in an f sublevel. | |

Comment on the relative degree of magnetic character of each of the configurations.

24. Five electrons in an atom have the quantum numbers given below. Arrange these electrons in order of increasing energy. If any two have the same energy, so indicate.

- | | |
|--|---|
| a) $n = 4, \ell = 0, m_\ell = 0, s = +\frac{1}{2}$ | b) $n = 3, \ell = 1, m_\ell = -1, s = -\frac{1}{2}$ |
| c) $n = 3, \ell = 2, m_\ell = 0, s = +\frac{1}{2}$ | d) $n = 3, \ell = 2, m_\ell = -2, s = -\frac{1}{2}$ |
| e) $n = 3, \ell = 0, m_\ell = 0, s = -\frac{1}{2}$ | |

25. Write the notations for the ground state electronic configuration of the following atoms, and state whether each atom is paramagnetic or diamagnetic. Diagram the valence electron configurations.

- | | | | |
|-------|-------|------|-------|
| a) C | b) Cl | c) K | d) Al |
| e) Sr | f) Sn | g) V | h) Zn |

26. Consider the electron configurations for Mo and Au. Might you expect these configurations to differ from a standard aufbau order? Why?

27. Complete the following electron configurations for the elements using part (a) as an example:

- | | | | |
|--------------------|----------------------------------|--------------------|---|
| a) Na ($Z = 11$) | $1s^2 2s^2 2p^6 3s^1$ | d) Zr ($Z = 40$) | $[\text{Kr}] 5s^2 4d^{(?)}$ |
| b) | $1s^2 2s^2 2p^6 3s^2 3p^3$ | e) | $[\text{Kr}] 5s^{(?) 4d^{(?) 5p^5}$ |
| c) | $[\text{Kr}] 5s^2 4d^{(?) 5p^4}$ | f) Bi ($z = 83$) | $[\text{Xe}] 6s^{(?) 4f^{(?) 5d^{(?) 6p^{(?)}}$ |

28. Identify the atoms that have the following ground state electronic configurations.
- a) $[\text{Ne}]3s^23p^3$ b) $[\text{Ar}]4s^23d^{10}4p^4$ c) $[\text{Ar}]4s^13d^5$
 d) $[\text{Kr}]5s^24d^2$ e) $[\text{Xe}]6s^1$ f) $[\text{Xe}]6s^24f^{14}5d^{10}6p^6$
29. Identify the groups that have the following electronic structures in their valence shells (n represents the principal quantum number).
- a) ns^2 b) ns^2np^2 c) ns^2np^6 d) $ns^2(n-1)d^2$ e) $ns^2(n-1)d^5$
30. The electron configurations described in the text are all for normal atoms in their ground states. An atom may absorb a quantum of energy and promote one or more electrons to a higher energy level; it becomes an "excited" atom. The following configurations represent excited states. Explain why.
- a) $1s^22s^12p^1$ b) $[\text{Ne}]3s^23p^23d^2$ c) $[\text{Ar}]4s^13d^{10}4p^3$

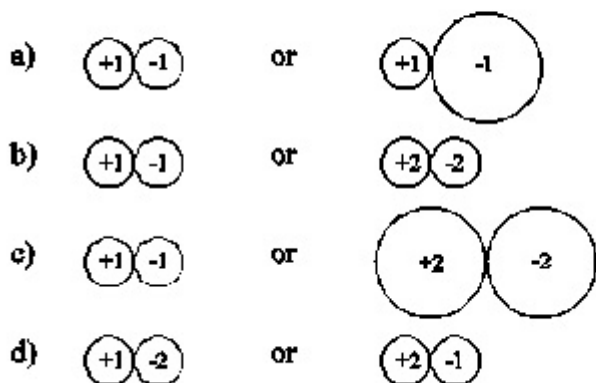
QUESTIONS ABOUT PERIODIC TRENDS

31. Predict which member of each of the following pairs has the larger atomic (covalent) radius.
- a) Sr or Sb b) Cl or I c) P or Ge d) Si or Se
32. Arrange the following series in order of decreasing atomic radii (largest one first):
- a) Ar, H, Ba, Te, Au, Ag b) K, Ca, Rb, Ti, Br, Cl
33. Why is the second ionization energy of an element always larger than the first ionization energy?
34. Although the first ionization energy of Na is smaller than for Mg, the second ionization energy of Na is much greater than for Mg. Why is this so?
35. How do the first ionization energies of metals compare to those of nonmetals?
36. Which member of each of the following pairs has the higher first ionization energy?
- a) Ar or K b) S or As c) Cs or Ba
 d) Cl or I e) S or P f) Sr or Sn
37. Arrange the following atoms in terms of:
- a) increasing first ionization energies: O, Rb, Br, Ca, Sc, Se, F, Cs, He
 b) decreasing metallic character: I, O, Cs, K, Te, F, Ca, Al
38. Explain the following trends on the basis of electron configuration:
- a) The electron affinity of S is -200 kJ/mol and of Cl is -348 kJ/mol
 b) The electron affinity of Si is -120 kJ/mol and of P is -74 kJ/mol
 c) The electron affinity of Li is -60 kJ/mol and of Be is +240 kJ/mol
39. List the following elements in order of increasing favorability of ΔH_{EA} : Ba, Cl, Cs, F, P, Si

40. Without looking at the table of electronegativities (refer to a periodic table instead), arrange the members of each of the following sets in order of increasing electronegativity:
- a) C, N, O b) Cu, Fe, K c) Br, Cl, F d) C, Si, N e) B, Cs, Ga
41. Of all the elements in the third period (Na through Ar):
- a) Which has the largest atomic radius? b) Which has the highest first ionization energy?
- c) Which is the most reactive metal? d) Which is the most reactive nonmetal?
- e) Which is the least reactive?

QUESTIONS ABOUT IONIC SUBSTANCES

42. a) Why is the radius of a positive ion smaller than the radius of its parent atom?
b) Why do negative ions have larger radii than their parent atoms?
43. How would you expect the sizes of the hydrogen ion (H^+) and the hydride ion (H^-) to compare with that of the He atom? Explain.
44. Certain elements react to form salts by forming their characteristic ions. Based on their positions in the periodic table, predict the charges for the ions expected for the following elements.
- a) Mg b) K c) Al
d) P e) I f) Te
45. Based on their positions in the periodic table and the expected charges for their respective characteristic ions predict the formulas for the salts formed by the following pairs of elements.
- a) Ca and S_8 b) Li and P_4 c) Ga and F_2
d) Mg and N_2 e) Al and O_2 f) Na and H_2
46. Write the notations for the ground state electronic configurations of the following ions:
- a) O^{-2} b) Ca^{+2} c) Co^{+3} d) Ag^+
e) I^- f) Bi^{+3} g) Sc^{+3} h) P^{-3}
47. What is unusual about NH_4^+ ? What is unusual about salts such as NH_4Cl or $(NH_4)_2SO_4$?
48. For each of the following set of ion pairs, decide which pair of ions has the higher or larger force of attraction and why?



49. How would you expect the force of attraction between positive ion A and negative ion B to be affected by the following changes?
- the charge on A is doubled
 - the charge on B is doubled
 - the charges on both A and B are doubled
 - the radii of both A and B are simultaneously doubled
50. For each of the following pairs of salts, decide which salt contains the greater cation-anion force of attraction. Explain your reasoning.
- NaF or NaCl
 - NaF or MgO
 - KCl or RbBr
51. The following species are isoelectronic with the noble gas krypton. Arrange them in order of increasing size and comment on the principles involved in doing so:
 Rb^+ , Y^{+3} , Br^- , Kr , Sr^{+2} , Se^{-2}
52. Which member of each of the following pairs would you predict to be larger?
- Br or Br^-
 - Ag or Ag^+
 - O^{-2} or F^-
 - Au^+ or Au^{+3}
 - In^{+3} or Tl^{+3}
 - In^+ or Sn^{+2}
53. Arrange the members of the following sets in order of increasing size:
- Li^+ , Rb^+ , Cs^+ , Na^+ , K^+
 - Na^+ , Mg^{+2} , Al^{+3}
 - Na^+ , Cs^+ , Be^{+2} , Al^{+3}
 - F^- , I^- , Cl^- , Br^-
 - O^{-2} , N^{-3} , F^-
 - S^{-2} , I^- , P^{-3} , O^{-2}

QUESTIONS ABOUT BONDING

54. Examine the valence electron configuration for the elements grouped at or near the left-hand side of the periodic table and comment on why metals customarily "give-up" electrons in chemical reactions.
55. Same as Q #54 but with respect to the right-hand side elements.
56. Arrange the following individual bonds in order of increasing polarity:
- H-F, H-C, H-H
 - P-S, Si-Cl, Al-Cl
 - Cl-I, P-P, C-N, O-H
57. Based on actual electronegativity differences, classify the bonds in the following as ionic, polar covalent, or nonpolar covalent. Are there any surprises based on "general trends"?
- I_2
 - LiCl
 - MgTe
 - Cl_2O
 - H_2S
 - Cs_2O
 - BCl_3
 - SO_2
 - Al_2O_3

QUESTIONS ABOUT LEWIS STRUCTURES

58. Write Lewis electron structures for the molecules **most likely** to be formed from the simple combination of nonmetals (Note: More than one atom of each element may be required):

- | | | | |
|-----------|---------|----------|----------|
| a) H, Cl | b) H, S | c) Cl, O | d) N, Br |
| e) Br, Br | f) C, S | g) P, I | h) C, F |

59. The following molecules contain one or more multiple bond(s). The sequence of bonding is indicated. Write the correct Lewis structure for each.

- | | | |
|---------------|-----------------|------------|
| a) H, N, N, H | b) S, C, S | c) C, O |
| d) S, C, O | e) Cl, C, C, Cl | f) H, C, N |

60. Write ALL acceptable Lewis structures for each of the following molecules or polyatomic ions. Include formal charges where required. (Note: these are CHM 1025 structures!)

- | | | | | |
|-----------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|-----------------------------------|
| a) NO | b) NO_2^+ | c) CO_2 | d) C_6H_{14} | e) NF_2^+ |
| f) COCl_2 | g) NH_2^- | h) PH_3 | i) C_3H_4 | j) $^*\text{H}_2\text{CO}_3$ |
| k) PF_4^+ | l) $^*\text{HNO}_2$ | m) $^*\text{HOCl}$ | n) CH_2O | o) C_2H_4 |
| p) $\text{C}_2\text{H}_3\text{F}$ | q) $\text{C}_2\text{H}_2\text{F}_2$ | r) $\text{C}_2\text{H}_5\text{F}$ | s) $\text{C}_2\text{H}_4\text{F}_2$ | t) $\text{C}_2\text{H}_6\text{O}$ |

* H's are attached to O

61. Write acceptable Lewis structures for each of the following molecules or polyatomic ions. Include formal charges where required and indicate if resonance is possible.

- | | | | | |
|-------------------------|--------------------|-----------------------|------------------------------|-----------------------|
| a) SO_2 | b) NO_2^- | c) CO_3^{2-} | d) $^*\text{H}_2\text{SO}_4$ | e) PO_4^{3-} |
| f) PF_5 | g) IF_3 | h) IF_2^- | i) PF_6^- | j) XeO_4 |
| k) $^{**}\text{XeOF}_4$ | l) IF_4^- | m) XeF_4 | | |

* H's are attached to O

** Xe is the central atom

QUESTIONS ABOUT GEOMETRY AND VSEPR

See handout at the end of this problem set for VSEPR summary.

62. i) For each of the species listed in problem 60, predict the geometry based on VSEPR theory and state whether the species is expected to be polar, non-polar or whether the idea doesn't apply.
- ii) For each of the species listed in problem 61, predict the geometry based on VSEPR theory and state the expected hybridization of the central atom.
- iii) Based on your predicted VSEPR geometries in problems 61, which are expected to be polar?

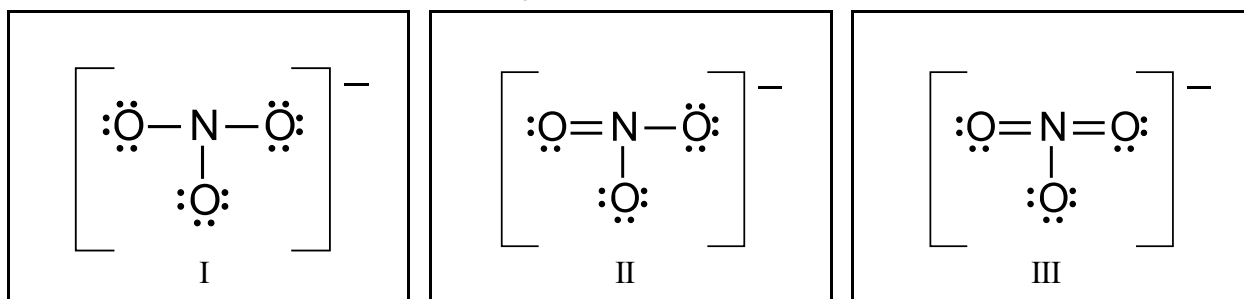
63. Each of the following molecules only contain one covalent bond. Therefore, the individual bond polarity is indicative of net molecular polarity. List the following molecules in order of increasing molecular polarity: I-Cl, Br-Cl, Cl-Cl, Br-F, Cl-F

64. Indicate which of the following molecules would be expected to have a net dipole moment:

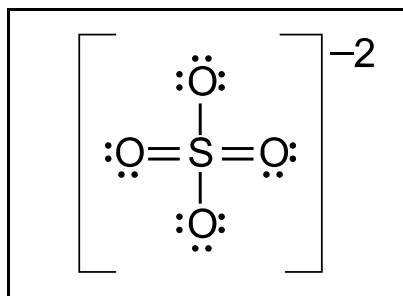
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|-------------------------|-------------------------|-------------------|--------------------|
| a) H_2O | b) F_2O | c) CO_2 | d) OCS |
| e) BCl_3 | f) PCl_3 | g) CCl_4 | h) HCCl_3 |
| i) SF_6 | j) XeF_4 | | |

65. a) How would you expect the C-O bond distance in CO_3^{2-} to compare with that in CO_2 ?
- b) In the gaseous state, HNO_3 molecules have two nitrogen-to-oxygen bond distances of 121 pm and one of 140 pm. Draw a plausible Lewis structure(s) to represent this fact.
- c) The C-F bond length in trifluoromethyl cation, CF_3^+ , is 127 pm, much less than the "normal" C-F single bond length of 138 pm in CF_4 . Explain these observations in terms of resonance theory.

66. Critique the following structures for NO_3^- (ie. Which is best and why?)

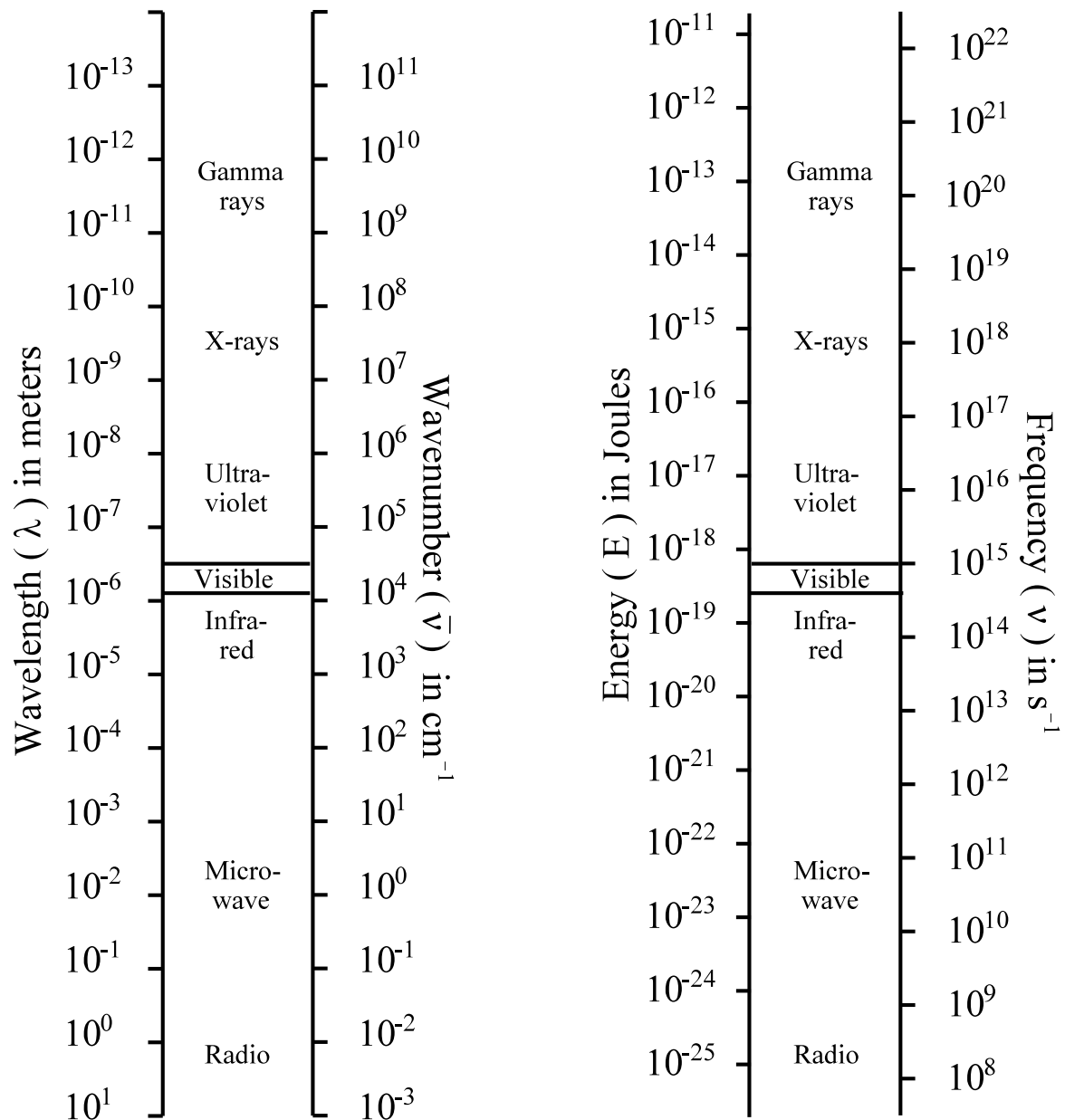


67. Below is an acceptable Lewis Structure for SO_4^{2-} .



- Label each bond as either σ or π and indicate what orbitals are overlapping to form that bond.
- Are other resonance structures possible, if so draw them, if not explain why not?

THE ELECTROMAGNETIC SPECTRUM



Basic Laws of Radiation

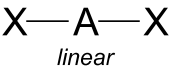
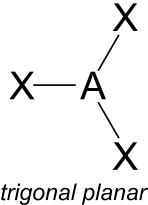
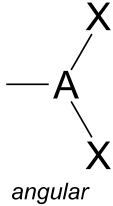
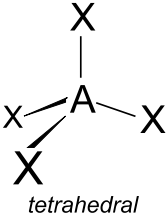
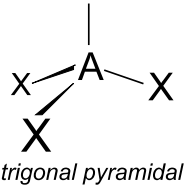
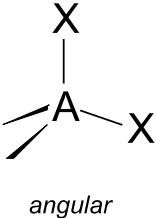
$$E = h \cdot \nu$$

$$c = \lambda \cdot \nu$$

$$\bar{\nu} = 1/\lambda$$

Valence Shell Electron Pair Repulsion Theory

*Molecular geometry as a function of geometrical distribution
of valence-shell electron pairs and number of lone pairs*

| Number of electron pair directions | Geometrical distribution of electron pairs | Number of lone pairs | VSEPR notation | Ideal Molecular geometry | Bond Angles | Hybrid- ization | Examples |
|--|--|----------------------------|--------------------------------|--|----------------|--------------------|------------------------------------|
| 2 | linear | 0 | AX ₂ |  linear | 180° | sp | BeCl ₂ , HCN |
| 3 | trigonal planar | 0 | AX ₃ |  trigonal planar | 120° | sp ² | BF ₃ |
| | trigonal planar | 1 | AX ₂ E |  angular | 120° | sp ² | SnCl ₂ , O ₃ |
| 4 | tetrahedral | 0 | AX ₄ |  tetrahedral | 109.5° | sp ³ | CH ₄ |
| | tetrahedral | 1 | AX ₃ E |  trigonal pyramidal | 109.5° | sp ³ | NH ₃ |
| | tetrahedral | 2 | AX ₂ E ₂ |  angular | 109.5° | sp ³ | H ₂ O |

| Number of electron pair directions | Geometrical distribution of electron pairs | Number of lone pairs | VSEPR notation | Ideal Molecular geometry | Bond Angles | Hybridization | Examples |
|------------------------------------|--|----------------------|--------------------------------|--------------------------|-------------|--------------------------------|------------------|
| 5 | trigonal bipyramidal | 0 | AX ₅ | trigonal bipyramidal | 120° & 90° | sp ³ d | PF ₅ |
| | trigonal bipyramidal | 1 | AX ₄ E | seesaw | 120° & 90° | sp ³ d | SF ₄ |
| | trigonal bipyramidal | 2 | AX ₃ E ₂ | tee-shaped | 90° | sp ³ d | BrF ₃ |
| | trigonal bipyramidal | 3 | AX ₂ E ₃ | linear | 180° | sp ³ d | XeF ₂ |
| 6 | octahedral | 0 | AX ₆ | octahedral | 90° | sp ³ d ² | SF ₆ |
| | octahedral | 1 | AX ₅ E | square pyramidal | 90° | sp ³ d ² | BrF ₅ |
| | octahedral | 2 | AX ₄ E ₂ | square planar | 90° | sp ³ d ² | XeF ₄ |