

Key for Unit I Exam

On the following pages are six problems that explore how an atom's properties depend upon its electronic structure, and the experimental data that informs our model of an atom's electronic structure. Read each problem carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer a problem, then move on to another; working on a new problem may suggest an approach to the one that is more troublesome. If a problem requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation and that work is relevant to the question.

Problem	Points	Maximum	Problem	Points	Maximum
1	14.0 (82.4%)	17	4	11.4 (76.2%)	15
2	6.9 (86.4%)	8	5	13.7 (85.6%)	16
3	13.4 (83.7%)	16	6	23.0 (82.3%)	28
			Total	81.7	100

high score	scores 100–90	scores 89–80	scores ≤ 79
98	6	7	9

Constants, equations, and Slater's rules are on a supplemental handout. A periodic table also is available.

Problem 1. For each of the following prompts, provide a **single** example of an element that fulfills the stated condition. If no element meets the condition, then write **NONE**. Limit your elements to those in the first four rows of the periodic table (H through Kr). **Do not use any element more than once!**

Note: all acceptable elements listed below with explanation (which were not required for answers)

- has no unpaired electrons

He \rightarrow Kr, Be \rightarrow Ca, and Zn (all have filled s , p , or d orbitals)

- whose core electron configuration is expressed as [Ne]

Na \rightarrow Ar (for third row, the electron configuration for Ne is equivalent to the core)

- has exactly six electrons in a d -orbital

Fe (only d^6 element in first four rows)

- is deflected by a magnetic field

all but He \rightarrow Kr, Be \rightarrow Ca, and Zn (need at least one unpaired electron to be deflected by magnetic field)

- has exactly two unpaired valence-shell electrons

C \rightarrow Ge, O \rightarrow Se, Ti, and Ni (valence shell must include p^2 , p^4 , d^2 or d^8)

- is in the same period as bromine

K \rightarrow Kr (same period means same row)

- has three peaks in its photoelectron spectrum

B \rightarrow Ne (must have $1s$, $2s$, and $2p$ electrons)

- has a valence shell that contains only p electrons

None (all valence shells begin with ns)

- is in the same group as Mg but with a larger radius

Ca (same group means same column, size increases down a group)

- forms an ion with a charge of +2 that has the same electron configuration as a noble gas

Be, Mg, and Ca (all have valence shell of ns^2 and loss of two electrons leaves a noble gas electron configuration)

- has exactly three core electrons

None (smallest possible core is $1s^2$ with two electrons and next smallest core is $1s^22s^22p^6$, which has 10 electrons)

- has an electron with $n = 4$ and $l = 1$

Ga \rightarrow Kr ($n = 4$ and $l = 1$ means a $4p$ electron)

- has the largest first ionization energy

He (IE increases across a row and up a group, which means the element in the upper right corner has greatest IE)

- has a Z of 15

P (Z is atomic number)

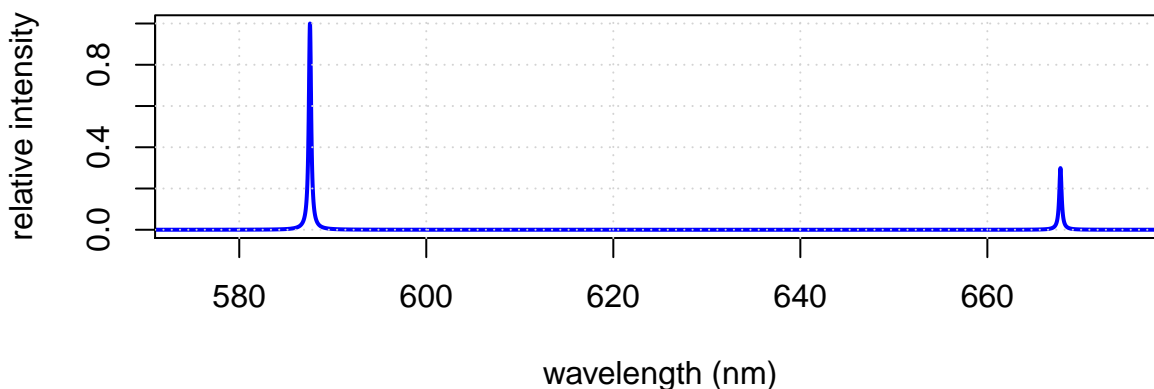
Problem 2. Consider the following five sets of quantum numbers for electrons a–e. For each prompt below the table, identify the appropriate electron(s) by their letters and explain your reasoning in one sentence. You will use each electron just once.

electron	n	l	m_l	m_s	$n + l$
a	2	0	0	$+1/2$	2
b	3	2	0	$+1/2$	5
c	2	1	-1	$+1/2$	3
d	3	2	+1	$-1/2$	5
e	3	3	+2	$+1/2$	—

Assuming that all five electrons are from the same atom and, therefore, have the same Z , which ...

- ... electron has an impossible set of quantum numbers?
- electron e: if $n = 3$, then maximum value for l is $3 - 1 = 2$
- ... electron has the greatest ionization energy?
- electron a: from Madelung's rule, the smaller $n + l$ the greater the electron's energy (note that values for $n + l$ are added to the table above; a value for the final electron is not included as it does not have a valid set of quantum numbers)
- ... electron is in a p orbital?
- electron c: the quantum number l gives the type of orbital with $l = 1$ being a p -orbital
- ... two electrons have identical energies
- electrons d and b: from Madelung's rule, electrons with same n and l will have the same energy

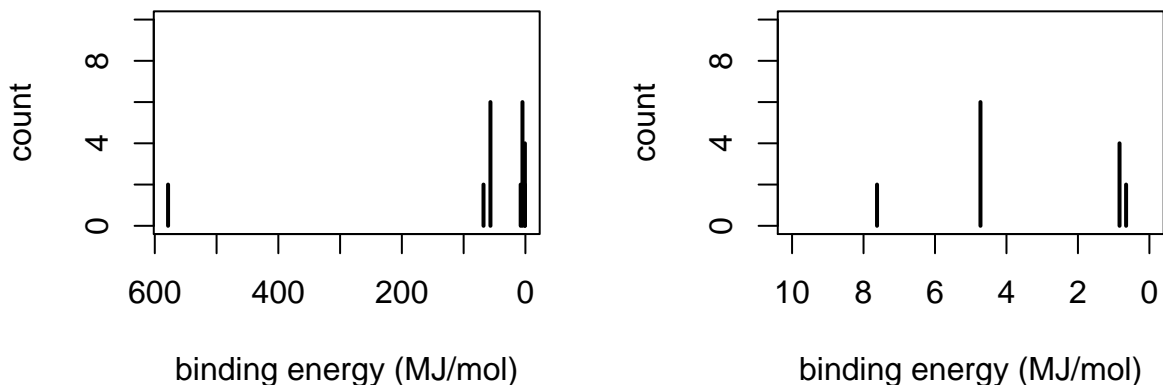
Problem 3. Shown below is part of the atomic emission spectrum for helium, showing emission intensity as a function of wavelength. There are two peaks in this region of the spectrum, one at a wavelength of 588 nm and one at 668 nm. Select the peak whose photons have the smallest energy and report that energy in Joules. In one sentence, explain why you selected this peak.



- We know that energy is inversely proportional to wavelength, so the longer the wavelength the smaller then energy; thus, the peak at 668 nm has the smaller energy. Note that it also is the least intense peak, but intensity is not a measure of energy.

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ m/s})}{668 \times 10^{-9} \text{ m}} = 2.97 \times 10^{-18} \text{ J}$$

Problem 4. The figures below show two views for the photoelectron spectrum of the element X . The view on the left shows the full spectrum and the view on the right shows only those peaks with binding energies less than 10 MJ/mol.



Identify the element X and explain your reasoning in 2–3 sentence.

- There are 24 total electrons shown in these two spectra, which means the element is chromium, Cr. There are three groups of peaks in the spectrum on the left; the spectrum on the right shows the right-most cluster of these peaks.

Selecting the appropriate spectrum, draw a circle around the peak(s) in the spectrum that corresponds to X 's valence electron(s). In one sentence, explain the reason for your choice.

- The valence electrons are the two lowest energy peaks in the spectrum on the right as they have the smallest ionization energies.

What are the quantum numbers n and l for the peak with a binding energy of approximately 8 MJ/mol? In one sentence, explain the reason for your choice.

- These are $3s$ electrons; thus, $n = 3$ and $l = 0$

Problem 5. The first ionization energies, IE_1 , for fluorine and chlorine are 1650 kJ/mol and 1250 kJ/mol, respectively. Using Slater's rules, calculate Z_{eff} for a valence electron in each element. Are your results for Z_{eff} consistent with the relative first ionization energies of the two elements? Defend your conclusion in 2–3 sentences. If your results for Z_{eff} are not consistent with their relative ionization energies, then offer a reason that can account for their relative ionization energies.

- For fluorine, the electron configuration is $1s^2 2s^2 2p^5$, which we then group as $(1s^2) (2s^2 2p^5)$. This gives Z_{eff} as

$$Z_{\text{eff}} = 9 - (6)(0.35) - (2)(0.85) = 5.2$$

- > For chlorine, the electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$, which we then group as $(1s^2) (2s^2 2p^5) (3s^2 3p^5)$. This gives Z_{eff} as

$$Z_{\text{eff}} = 17 - (6)(0.35) - (8)(0.85) - (2)(1.00) = 6.1$$

These results are not consistent with the ionization energies as we $IE \propto Z_{\text{eff}}$, which would leave us to believe that chlorine should have the larger ionization energy. The difference in ionization energies is explained by recognizing that $IE \propto 1/r$ and that r is greater for $n = 3$ than for $n = 2$.

Problem 6. The table below lists several properties of the elements in the third row of the periodic table. IE stands for ionization energy and the subscript indicates the source of ionization: removal of first electron, removal of a second electron, removal of a third electron, and removal of a single $3s$ electron. AVEE is the average valence electron energy. **Choose 4 of the 5 prompts below the table** and provide a thoughtful answer in 2–4 sentences each. Be sure you clearly indicate which four prompts you wish for me to evaluate.

property	Na	Mg	Al	Si	P	S	Cl	Ar
IE_1 (kJ/mol)	496	738	578	787	1012	1000	1251	1521
IE_2 (kJ/mol)	4562	1451	1817	1577	1907	2252	2298	2666
IE_3 (kJ/mol)	6910	7733	2745	3233	2914	3357	3822	3931
IE_{3s} (kJ/mol)	496	738	1090	1460	1950	2050	2440	2820
AVEE (kJ/mol)	496	738	920	1125	1416	1350	1590	1845
radius (pm)	190	145	118	111	98	88	79	71

Explain the trend in the values for IE_{3s} as you move from Na \rightarrow Ar.

- The most important trend as we move across a row is the increase in the charge on the nucleus, Z , and the resulting effective nuclear charge, Z_{eff} as “felt” by the electron. This increase in Z_{eff} explains why the $3s$ valence electron is increasingly difficult to remove. You can discuss size as well; however, that, too, is a function of Z_{eff} .

Explain why the values for IE_1 and IE_{3s} are the same for sodium, but different for aluminum.

- For Na the valence shell is $3s^1$, which means that its IE_1 is the energy needed to remove the $1s$ electron. For Al, the valence shell is $3s^23p^1$, which means IE_1 is the energy to remove a $3p$ electron, not a $3s$ electron.

Explain why the values for IE_1 increase by approximately 200 kJ/mol per element for the elements Na \rightarrow P and for the elements S \rightarrow Ar, but are essentially identical for the elements P and S.

- The most important trend as we move across a row is the increase in the charge on the nucleus, Z , and the resulting effective nuclear charge, Z_{eff} as “felt” by the electron. This increase in Z_{eff} explains why the values for IE_1 generally increase across a row. When we move from phosphorous to sulfur, however, we also have to consider how the p orbitals are filled: for P this is $p^1p^1p^1$ and for S this is $p^2p^1p^1$. The pairing of two electrons in the same orbital means that electron-electron repulsion will make it easier to remove an electron, in this case giving an ionization for S that is not very different than that for P.

Explain why the radius increases in steps of approximately 10 pm for the elements Ar \rightarrow Al but increases by much larger steps for the elements Al \rightarrow Na.

- The most important trend as we move across a row is the increase in the charge on the nucleus, Z , and the resulting effective nuclear charge, Z_{eff} as “felt” by the electron. The increase in Z_{eff} also decreases size because it pulls electrons toward the nucleus. The relative effect—that is, the relative change in the radius—becomes smaller as the radius decreases for the same reason that it becomes increasingly more difficult to shrink a Nerf ball when we squeeze it.

Explain why IE_2 for Na is approximately $10\times$ greater than its IE_1 , but IE_2 is just $2 - 3\times$ greater than IE_1 for other elements in this period.

- For IE_2 we are interested in the second electron to be removed. For Na, which has a valence shell electron configuration of $1s^22s^22p^63s^1$, IE_1 removes the one valence electron and IE_2 is for a core electron. For the other elements in the same period as Na, both IE_1 and IE_2 are for valence electrons. It requires more energy to remove a core electron; thus, the difference in relative ionization energies.