Name: ________________________ **Student Number:** ___________________

CHM 2311
Final Exam
April 29 2009
Professor Darrin Richeson

There are 15 pages in this exam (including supporting materials and tables). Please count the pages to make sure none are missing.

You may *carefully remove* the last three pages of the exam and use them for scratch work.

Please write legibly and show your work to receive credit for your answers.
Partial marks ***may in some cases*** be awarded for partially correct work.

Question	Mark	Question	Mark
1	**/5**	**8**	**/4**
2	**/ 9**	**9**	**/13**
3	**/ 7**	**10**	**/16**
4	**/ 16**	**11**	**/5**
5	**/ 10**	**12**	**/12**
6	**/9**		
7	**/4**		
		Total	**/110**

Good luck and have a great summer!

1. (**5 points**) A hydrogen orbital has the following ***complete*** wave function (both angular and radial portions of the wave function are included and the angular part is written in Cartesian coordinate form):

$$\psi(r,\theta,\varphi) = R(r)\{Y(\theta,\varphi)\} = \frac{1}{81\sqrt{15}}\left(\frac{2Z}{a_o}\right)^{3/2}(\rho)^2 e^{-\rho/3}\left\{1/4\sqrt{\frac{15}{\pi}}\frac{x^2-y^2}{r^2}\right\}$$

where $\rho = \dfrac{Zr}{a_o}$ and Z = 1 for a hydrogen atom

$a_o = 52.9$ pm

a. For this orbital, determine the distance from the nucleus in picometers at which **all *radial*** nodes occur.

The radial component becomes zero (has a node) when $\rho^2 = 0$ or
$\rho = 0 = Zr/a_o$
*This is only true at the r = 0 – the nucleus **no radial nodes***

b. Determine the quantum numbers n and l for this orbital. ***Clearly*** show the process by which you determined these values. Identify the orbital (1s, 2s, $2p_x$, etc...).

*In part (a) we determined that there are **no radial node**s.*

The number of angular nodes can be determined from the angular part of the wavefunction. From the equation, $\psi = 0$ for x^2-y^2 = 0 (and all values for z). Rearranging gives a node for x = y and for x = -y
There are 2 angular nodes. This corresponds to l = 2 or a d orbital.

The equation for the number of radial nodes is given by n-l-1 = number of radial nodes. Since n-l-1= 0 then n = 2+1 = 3

Therefore this is a 3d orbital and specifically the $3d_{x2-y2}$ orbital.

2. **(9 points)** a. Calculate Z_{eff} for a 2p electron on each of the following species. O^{2-}, F^-, Na^+, Mg^{2+}.

Each of these ions has the same electronic configuration:

$$(1s^2)\ (2s^2, 2p^6)$$

This means that they all have the same s value

$$s = (2 \times 0.85) + (7 \times 0.35) = 4.15$$

$$Z_{eff} = Z_{actual} - s$$

Ion	*Z*	Z_{eff}
O^{2-}	*8*	*3.85*
F^-	*9*	*4.85*
Na^+	*11*	*6.85*
Mg^{2+}	*12*	*7.85*

Match the ion with the radii in the following table.

Crystal (Ionic) Radius	Ion
119pm	
86pm	
116pm	
126pm	

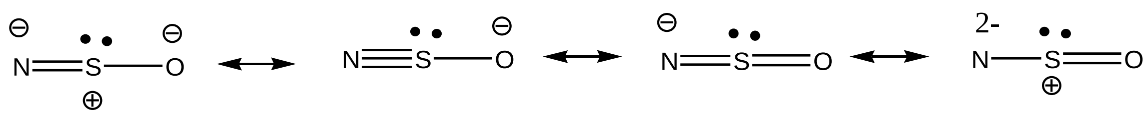
Calculate the Z_{eff} for a 4d electron of antimony (symbol Sb)

(1s2) (2s2, 2p6) (3s2, 3p6) (3d10) (4s2, 4p6) (4d10) (5s2, 5p3)

$Z_{eff} = Z - s = 51 - 9x0.35 + 36x1 = 51 - 39.15 = 11.85$

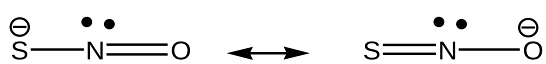
3. **(7 points)** There are potentially three isomers for the anion NSO^-. The two known species are NSO^- and SNO^-. The isomer SON^- is unknown.
Suggest reasonable resonance structures for each of these three isomers.

There are 18 electrons in this anion.
The following are reasonable Lewis structures for the NSO^- ion:



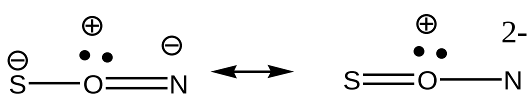
Other Lewis structures can be drawn with more bonds on O or S, but this creates unlikely positive formal charges on oxygen, the most electronegative of the three atoms. The second structure shown (triple bond between N and S) should be most correct, as it not only involves the lowest formal charges, but has the negative formal charge on the most electronegative atom (O).

For the SNO^- ion:



The most correct Lewis structure should be the second one (S-N double bond). Again, the negative formal charge is on the O-atom for this structure. Other structures can be drawn, but again, positive formal charges on O or structures which break the octet rule would be obtained.

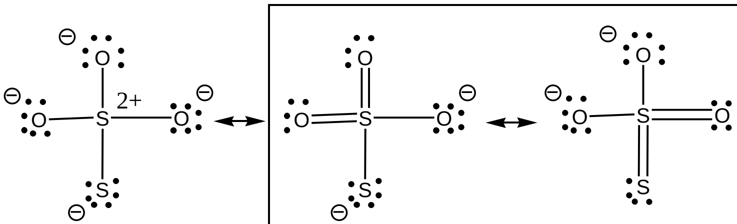
For the SON^- ion, both reasonable resonance structures have positive formal charges on O.



4. **(16 points)** Draw the most stable Lewis structure and all ***significant*** resonance contributors for each of the molecules below. In your final answer, show all bonded pairs of electrons as lines between the bonded atoms and show all non-bonded electrons as dots. Indicate any ***non-zero formal charges*** on every element where they occur.

a. SSO_3^{2-} (thiosulfate)

Final Answer: ***(32 electrons)***



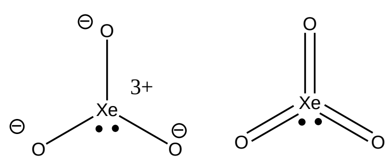
Geometry: ___tetrahedral________

Shape: ___tetrahedral________

Hybridization of S: _____sp^3__

b. XeO_3

Final Answer: ***(26 electrons)***



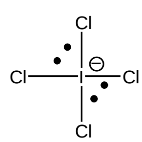
Geometry: ___tetrahedral

Shape: ____pyramidal_

Hybridization of I: ___sp^3____

c. ICl_4^-

Final Answer: ***(36 electrons)***



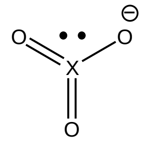
Geometry: __octahedral_

Shape: ____square planar_______

Hybridization of Se: __d^{2}sp^3__

5. (**10 points**) The series of halate anions IO_3^-, BrO_3^-, and ClO_3^- is known.

This part is not necessary – 26 electrons



Predict a trend in bond angles for these species. Explain.

_____________<____________<____________

$IO_3^- < BrO_3^- < ClO_3^-$

The larger the central atom allows for closer approach of the bonding pairs = smaller angle (could also mention the decreasing relative role of s orbital in bonding down the group)

Predict a trend in bond lengths for these species. Explain.

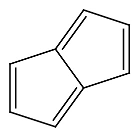
_____________<____________<____________

$ClO_3^- < BrO_3^- < IO_3^-$

As the radius increases the bond length increases – $R_I > R_{Br} > R_{Cl}$

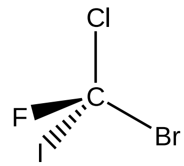
6. **(9 points)** Determine the point group for each of the following molecules.

A.

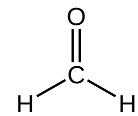


(planar)

B.

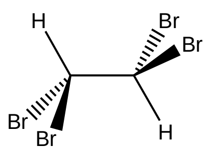


C.



Point Group: A.___D_{2h}___ B. ___C_1_____ C.___C_{2v}_____

D.

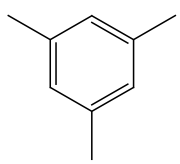


E. SbF_5

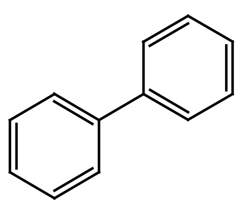
F. d_{xz} orbital

Point Group: D.___C_{2h}___ E. ____D_{3h}____ F. ____D2h_____

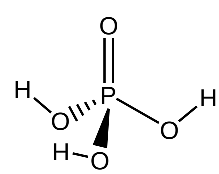
G.



H.



I.



Point Group: A.___D_{3h}___ B. ___D2h______ C.___C_{3v}_____

7. **(4 points; ½ point per blank)** In the questions below you will determine the irreducible representations for specific orbitals on a central atom of a molecule in a given point group. You may use the back of one of the exam pages for your scratch work. It is ***not necessary to determine the symmetry labels.***

a. A d_{z^2} orbital on the central atom of a molecule in the D_3 point group

D_3	E	$2C_3$	$3C_2$		
	1	***1***	***1***		d_{z^2}

b. A p_z orbital on the central atom of a molecule in the D_{3h} point group

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
	1	***1***	***-1***	***-1***	-1	*1*	p_z

8. **(4points; ½ point per blank)** Given the symmetry labels for the following irreducible representations, fill in the missing characters:

C_{3v}	E	$2C_3$	$3\sigma_v$
A_2	***1***	***1***	***-1***

C_{2v}	E	C_2	σ_v (xz)	σ_v' (yz)	
B_2	***1***	***-1***	***-1***	***1***	d_{yz}

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
A_{2g}	1	***1***	***-1***	***1***	1	-1

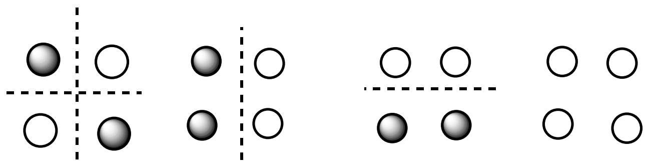
9. **(13 points)** We discussed the bonding in a planar AH_4 species. In this problem we will extend these ideas to include d orbitals on the central A atom.

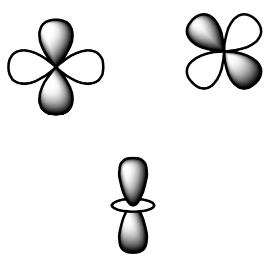
(i) What are the group orbitals for planar AH_4? (provide simple drawings)

(ii) Consider all of the d orbitals on the the central atom. Clearly indicate the group orbitals that have appropriate symmetry to interact with the d orbitals on A?

(iii) What is the maximum number of bonds that could be made for this hypothetical AH_4 molecule?

Group Orbitals





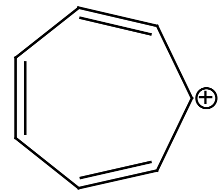
No intereactions with xz or yz

Two possible interactions z^2 and 4th orbital, x^2-y^2 and the 1st **OR** xy and 1st orbital (depends on orientation of x and y axes)

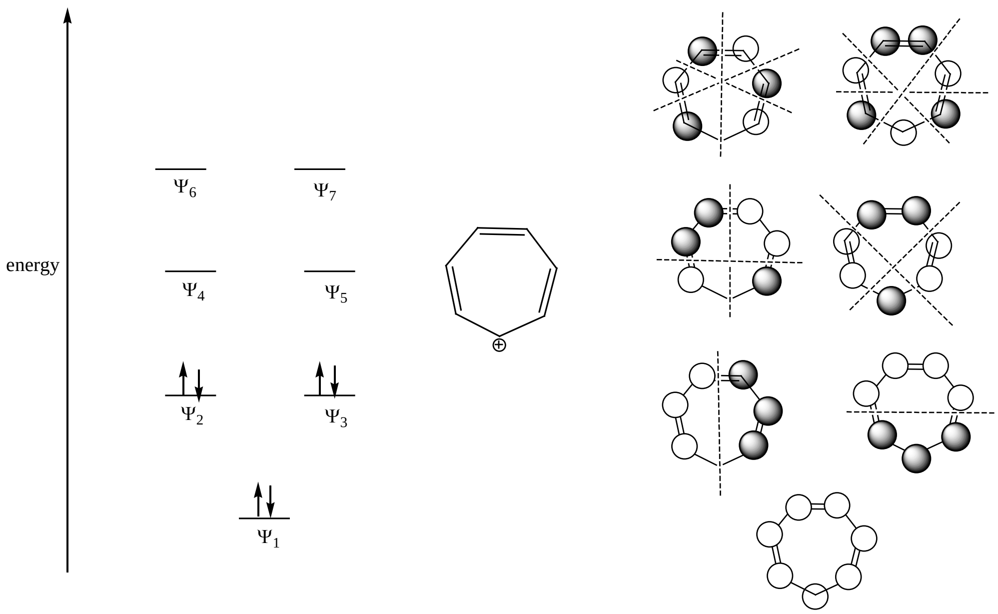
As a result two bonds can form.

To get interactions with 2nd and 3rd orbitals would use the px and py. The 4th can also interact with an s orbtal.

10. a. **(15 points)** In the space below, draw a π-MO diagram for the cycloheptatrienyl cation. Your diagram should include the following:



- i. Sketches of all of the bonding and antibonding π-orbitals
- ii. Relative energy levels of all orbitals indicated by appropriate placement of orbitals on the vertial energy axis.
- iii. Electrons in the appropriate molecular orbitals



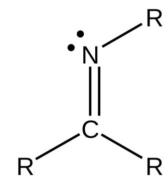
Could also do this from the linear arrangement and then cyclize – see my notes

b. **(2 points)** Does the Hückel rule predict that the cycloheptatrienyl cation will be aromatic or antiaromatic? Is your MO diagram consistent with this prediction? Explain.

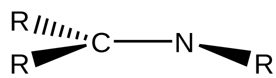
There are 6π electrons which is 4n+2 π electrons (n = 1): Huckel's rule predicts aromaticity

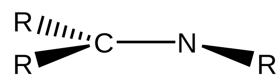
As shown in the MO diagram above, the highest-occupied orbital of the cycloheptatrienyl cation would be bonding and stabilized. This indicates the delocalization in the ring results in stabilization, which is consistent with the prediction of Huckel's rule

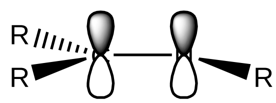
11. The molecule shown to the right belongs to a class called “imines”. (R represents a substituent group whose identity is not important for this problem.) All of the atoms of the imine are in the same plane. Even though you might not know anything about imines, you should be able to apply the orbital concepts to explain some reactivity.

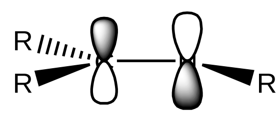


a. **(2 points)** A nucleophile is a chemical reagent that reacts with a site of positive charge on another molecule. Such a reaction can be viewed as the nucleophile donating a pair of electrons. To evaluate attack of the imine π-system by a nucleophile, we need to identify the HOMO and LUMO orbitals of the imine. On the skeletons below, sketch these “frontier orbitals” and label them as HOMO and LUMO respectively.









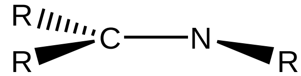
HOMO pi

Lumo pi star

b. **(1 point)** Circle the orbital above whose interaction with the nucleophile is most important to the success of this reaction.

HOMO localized on N and LUMO localized on C

c. **(2 points)** Will the nucleophile be more likely to attack at the C or the N atom? Use an arrow to show the preferred ***angle of approach*** of the nucleophile on the skeleton below and explain the rational behind your prediction.

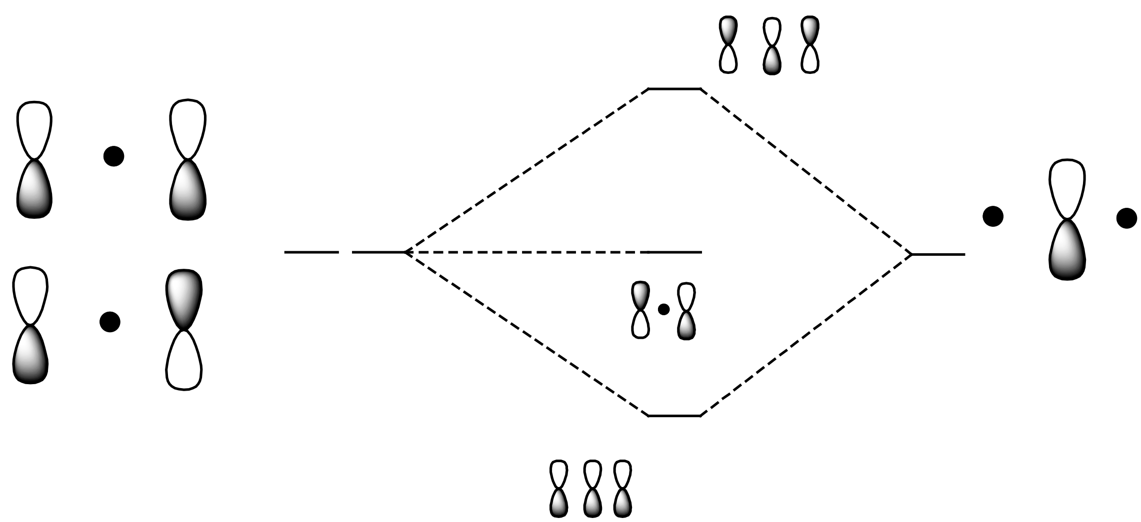


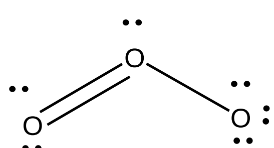
Attack at C.

12. **(12 points)** In this problem you will prepare a molecular orbital diagram for the **<u>π system only</u>** for the molecule ozone (O_3). Explain clearly the steps that you use to reach your final answer. You should clearly indicate the nature of all of the π interactions in your MO energy level diagram, indicate the number of electrons involved in the π system and provide the **overall** bond order for ozone?

Analogue of allyl anion.
18 electrons or 9 pairs
2 pairs for sigma bonds
2 lone paris on the outer O = 4 pairs
1 lone pair on the central O = 1 pair
7 pairs are used for the non-π bonding leaving 2 pairs for π

Group (outer)



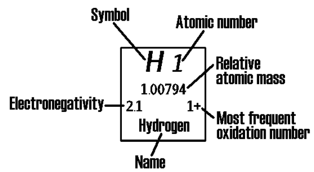


Element	Orbital Potential Energy (eV)						
	1s	2s	2p	3s	3p	4s	4p
H	-13.6						
He	-24.5						
Li		-5.5					
Be		-9.3					
B		-14.0	-8.3				
C		-19.5	-10.7				
N		-25.5	-13.1				
O		-32.4	-15.9				
F		-46.4	-18.7				
Ne		-48.5	-21.6				
Na				-5.2			
Mg				-7.7			
Al				-11.3	-6		
Si				-15.0	-7.8		
P				-18.7	-10.0		
S				-20.7	-12.0		
Cl				-25.3	-13.7		
Ar				-29.3	-15.9		
K						-4.3	
Ca						-6.1	
Zn						-9.4	
Ga						-12.6	-6
Ge						-15.6	-7.6
As						-17.6	-9.1
Se						-20.8	-11.0
Br						-24.1	-12.5
Kr						-27.5	-14.3

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	*i*	σ(xy)	σ(xz)	σ(yz)	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z, xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y, xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x, yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
A_1	1	1	1	1	1	z, x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z
B_1	1	-1	1	1	-1	x^2-y^2
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	(x,y) (R_x, R_y) (xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	*i*	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H 1 1.00794 2.1 1+ Hydrogen																	He 2 4.002602 - - Helium
2	Li 3 6.941 1.0 1+ Lithium	Be 4 9.012182 1.5 2+ Beryllium											B 5 10.811 2.0 3+ Boron	C 6 12.011 2.5 4+,4- Carbon	N 7 14.00674 3.0 3+,3- Nitrogen	O 8 15.9994 3.5 2- Oxygen	F 9 18.9984032 4.0 1- Fluorine	Ne 10 20.1797 - - Neon
3	Na 11 22.989768 0.9 1+ Sodium	Mg 12 24.3050 1.2 2+ Magnesium											Al 13 26.981539 1.5 3+ Aluminum	Si 14 28.0855 1.8 4+ Silicon	P 15 30.973762 2.1 5+ Phosphorus	S 16 32.066 1.8 4+ Sulfur	Cl 17 35.4527 3.0 1- Chlorine	Ar 18 39.948 - - Argon
4	K 19 39.0983 0.8 1+ Potassium	Ca 20 40.078 1.0 2+ Calcium	Sc 21 44.955910 1.3 3+ Scandium	Ti 22 47.88 1.5 4+ Titanium	V 23 50.9415 1.6 5+ Vanadium	Cr 24 51.9961 1.6 3+ Chromium	Mn 25 54.93805 1.5 2+ Manganese	Fe 26 55.847 1.8 3+ Iron	Co 27 58.9332 1.8 2+ Cobalt	Ni 28 58.6934 1.8 2+ Nickel	Cu 29 63.546 1.9 2+ Copper	Zn 30 65.39 1.6 2+ Zinc	Ga 31 69.723 1.6 3+ Gallium	Ge 32 72.61 1.6 4+ Germanium	As 33 74.92159 2.0 3+,3- Arsenic	Se 34 78.96 2.4 4+ Selenium	Br 35 79.904 2.8 1- Bromine	Kr 36 83.80 - - Krypton
5	Rb 37 85.4678 0.8 1+ Rubidium	Sr 38 87.62 1.0 2+ Strontium	Y 39 88.90585 1.3 3+ Yttrium	Zr 40 91.224 1.4 4+ Zirconium	Nb 41 92.90638 1.6 5+ Niobium	Mo 42 95.94 1.8 6+ Molybdenum	Tc 43 98.9063 1.9 7+ Technetium	Ru 44 101.57 2.2 3+,4+ Ruthenium	Rh 45 102.9055 2.2 3+ Rhodium	Pd 46 106.42 2.2 2+ Palladium	Ag 47 107.8682 1.9 1+ Silver	Cd 48 112.411 1.7 2+ Cadmium	In 49 114.82 1.7 3+ Indium	Sn 50 118.71 1.8 4+ Tin	Sb 51 121.757 1.9 3+,3- Antimony	Te 52 127.60 2.1 4+ Tellurium	I 53 126.90447 2.5 1- Iodine	Xe 54 131.29 - - Xenon
6	Cs 55 132.90543 0.7 1+ Cesium	Ba 56 137.327 0.9 2+ Barium	La 57 138.9055 1.1 3+ Lanthanum	Hf 72 178.49 1.3 4+ Hafnium	Ta 73 180.9479 1.5 5+ Tantalum	W 74 183.85 1.7 6+ Tungsten	Re 75 186.207 1.9 7+ Rhenium	Os 76 190.2 2.2 4+ Osmium	Ir 77 192.22 2.2 4+ Iridium	Pt 78 195.08 2.2 4+ Platinum	Au 79 196.96654 2.4 3+ Gold	Hg 80 200.59 1.9 2+ Mercury	Tl 81 204.3833 1.8 1+ Thallium	Pb 82 207.2 1.8 2+ Lead	Bi 83 208.98037 1.9 3+ Bismuth	Po 84 208.9824 2.0 2+ Polonium	At 85 209.9871 2.2 1- Astatine	Rn 86 222.0176 - - Radon
7	Fr 87 223.0197 0.7 1+ Francium	Ra 88 226.0254 0.9 2+ Radium	Ac 89 227.0278 1.1 3+ Actinium	Rf 104 261.11 - - Rutherfordium	Db 105 262.11 - - Dubnium	Sg 106 263.12 - - Seaborgium	Bh 107 262.12 - - Bohrium	Hs 108 264 - - Hassium	Mt 109 266.1378 - - Meitnerium	Uun 110 269 - - Ununnilium	Uuu 111 272 - - Unununium	Uu 112 277 - - Ununbium		Uuq 114 289 - - Ununquadium		Uuh 116 289 - - Ununhexium		Uuo 118 293 - - Ununoctium

6	Ce 58 140.115 1.1 3+ Cerium	Pr 59 140.90765 1.1 3+ Praseodymium	Nd 60 144.24 1.1 3+ Neodymium	Pm 61 144.9127 1.1 3+ Promethium	Sm 62 150.36 1.2 3+ Samarium	Eu 63 151.965 1.2 3+ Europium	Gd 64 157.25 1.2 3+ Gadolinium	Tb 65 168.92534 1.2 3+ Terbium	Dy 66 162.50 1.2 3+ Dysposium	Ho 67 164.93032 1.2 3+ Holmium	Er 68 167.26 1.2 3+ Erbium	Tm 69 168.93421 1.2 3+ Thulium	Yb 70 173.04 1.1 3+ Ytterbium	Lu 71 174.967 1.2 3+ Lutetium
7	Th 90 232.0381 1.3 4+ Thorium	Pa 91 231.03588 1.5 5+ Protactinium	U 92 238.0289 1.4 6+ Uranium	Np 93 237.082 1.3 5+ Neptunium	Pu 94 244.0642 1.3 4+ Plutonium	Am 95 243.0614 1.3 3+ Americium	Cm 96 247 1.3 3+ Curium	Bk 97 247.0703 1.3 3+ Berkelium	Cf 98 251.0796 1.3 3+ Californium	Es 99 252.03 1.3 - Einsteinium	Fm 100 257.0951 1.3 - Fermium	Md 101 258.01 1.3 - Mendelevium	No 102 259.1009 1.3 - Nobelium	Lr 103 260.1053 - - Lawrencium

Under normal conditions, bold symbols correspond to solid state, bold italic correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.