[TP] The energy required to remove a second electron from nitrogen, $N^+(g) \rightarrow N^{2+}(g) + e^-(g)$, is called the second ionization energy, I_2. Compared to the first ionization energy, I_1, the second ionization energy

82% 1. must be smaller
0% 2. must be about the same
9% 3. must be larger
0% 4. Further information required
9% 5. Not sure

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Lecture 3 CH131 Summer 1 2021

Wednesday, May 26, 2021

- Anatomy of electron clouds
- $IE_1 \rightarrow$ electron cloud expansion
- Electron affinity: $X^-(g) \rightarrow X(g) + e^-$
- Electronegativity: $EN \sim IE_1 + EA$
- Dipole moment and ionic character: $\sim \Delta EN$
- Lewis diagrams

Next lecture: Complete: Lewis diagrams; Shapes and polarity of molecules; Begin ch9.1–9.6. The gaseous state

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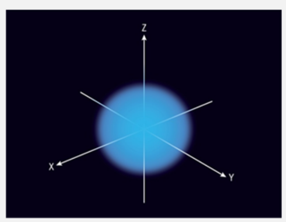
Anatomy of electron clouds

The volume of atoms is due to their electron clouds.

Studying successive ionization energies (how much energy is needed to remove an electron from the cloud) reveals the anatomy of the cloud.



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Anatomy of electron clouds

Let's do this for the nitrogen atom.

Here is the equation describing removal of one electron from a neutral N atom.

$$N(g) \rightarrow N^+(g) + e^-(g), I_1 = 2.32 \text{ aJ} = 2.32 \times 10^{-18} \text{ J}$$

I_1 is called the first ionization energy, and $1 \text{ aJ} = 1 \times 10^{-18}$ J (attojoule)

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[TP] The energy required to remove a second electron from nitrogen, $N^+(g) \rightarrow N^{2+}(g) + e^-(g)$, is called the second ionization energy, I_2. Compared to the first ionization energy, I_1, the second ionization energy

- 7% 1. must be smaller
- 0% 2. must be about the same
- 93% 3. must be larger
- 0% 4. Further information required
- 0% 5. Not sure

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Anatomy of electron clouds

The key in comparing ionization energies, the ionizations

$N(g) \rightarrow N^+(g) + e^-(g), I_1$

$N^+(g) \rightarrow N^{2+}(g) + e^-(g), I_2$

is Coulomb's law,

$E_{\text{Coulomb}} \sim \frac{Q_1 Q_2}{d}$

In words, Coulomb's law says that opposite charges attract, the more so the greater the charges, Q_1 and Q_2, and the more so the closer, d, they are.

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Structure of electron clouds

The key in comparing ionization energies, the ionizations

$N(g) \rightarrow N^+(g) + e^-(g) \quad I_1$

$N^+(g) \rightarrow N^{2+}(g) + e^-(g) \quad I_2$

The greater the product of the charges, the more energy required to separate them.

Therefore, I_2 must be larger than I_1, because

for I_2, $Q_1Q_2 = (+2)(-1) = -2$

for I_1, $Q_1Q_2 = (+1)(-1) = -1$

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[TP] For the 5th ionization energy of N atom, I_5, what are the values of the Coulomb's law charges Q_1 and Q_2?

- 0% 1. $Q_1 = +1$ and $Q_2 = -1$
- 0% 2. $Q_1 = +2$ and $Q_2 = -1$
- 7% 3. $Q_1 = +4$ and $Q_2 = -1$
- 71% 4. $Q_1 = +5$ and $Q_2 = -1$
- 7% 5. $Q_1 = +6$ and $Q_2 = -1$
- 0% 6. Something else
- 14% 7. Not sure

$Q_1 \quad Q_2$

$N \rightarrow N^+ + e^- \quad I_1$

$N^+ \rightarrow N^{2+} + e^- \quad I_2$

⋮

$N^{4+} \rightarrow N^{5+} + e^- \quad I_5$

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[TP] The energy required to remove a third electron from nitrogen, $N^{2+}(g) \rightarrow N^{3+}(g) + e^-(g)$, is called the third ionization energy, I_3. How do the first three ionization energies compare? Tell your classmates why.

100% 1. $I_1 < I_2 < I_3$
0% 2. $I_1 < I_3 < I_2$
0% 3. $I_3 < I_2 < I_1$
0% 4. Not sure

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Successive ionization energies

TABLE 3.1

Successive Ionization Energies of the Elements Hydrogen through Argon (in eV Atom^{-1})

Z	Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
1	H	13.60									
2	He	24.59	54.42								
3	Li	5.39	75.64	122.45							
4	Be	9.32	18.21	153.89	217.71						
5	B	8.30	25.15	37.93	259.37	340.22					
6	C	11.26	24.38	47.89	64.49	392.08	489.99				
7	N	14.53	29.60	47.45	77.47	97.89	552.06	667.03			
8	O	13.62	35.12	54.93	77.41	113.90	138.12	739.32	871.39		
9	F	17.42	34.97	62.71	87.14	114.24	157.16	185.18	953.89	1103.08	
10	Ne	21.56	40.96	63.45	97.11	126.21	157.93	207.27	239.09	1195.79	1362.16
11	Na	5.14	47.29	71.64	98.91	138.39	172.15	208.47	264.18	299.87	1465.10
12	Mg	7.65	15.04	80.14	109.24	141.26	186.50	224.94	265.90	327.94	367.53
13	Al	5.99	18.83	28.45	119.99	153.71	190.47	241.43	284.59	330.21	398.57
14	Si	8.15	16.35	33.49	45.14	166.77	205.05	246.52	303.17	351.10	401.43
15	P	10.49	19.73	30.18	51.37	65.02	220.43	263.22	309.41	371.73	424.50
16	S	10.36	23.33	34.83	47.30	72.68	88.05	280.93	328.23	379.10	447.10
17	Cl	12.97	23.81	39.61	53.46	67.8	97.03	114.19	348.28	400.03	455.62
18	Ar	15.76	27.63	40.74	59.81	75.02	91.01	124.32	143.46	422.43	478.68
19	K	4.34	31.63	45.72	60.91	82.66	100.0	117.56	154.86	175.82	503.44
20	Ca	6.11	11.87	50.91	67.10	84.41	108.78	127.7	147.24	188.54	211.27
21	Sc	6.54	12.80	24.76	73.47	91.66	111.1	138.0	158.7	180.02	225.32

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Plot log(IE_n) versus n for Mg

You will need the final two ionization energies, IE_{11} and IE_{12}.

https://en.wikipedia.org/wiki/Ionization_energies_of_the_elements_(data_page)

IE_{11} = 1762 eV

IE_{12} = 1962 eV

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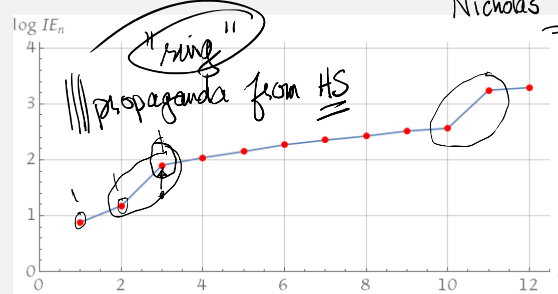
Plot log(IE_n) versus n for Mg

$E_{coulomb} \sim \frac{Q_1 Q_2}{d}$

Physically (in terms of Coulomb's law), what accounts for the discontinuity between n = 2 and n = 3?

Nicholas discontinuity



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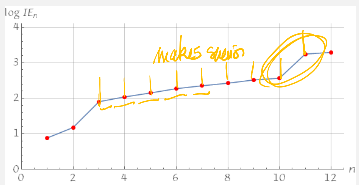
Successive IE_n → electron cloud contraction

$IE_2 > IE_1$: $Mg^{2+} > Mg^{+}$ increase in residual ion charge
$IE_3 \gg IE_2$: $Mg^{3+} \gg Mg^{2+}$ large contraction of electron cloud
$IE_{10} > IE_9 > \cdots > IE_3$: increase in residual ion charge
$IE_{11} \gg IE_{10}$: $Mg^{11+} \gg Mg^{10+}$ large contraction of electron cloud
$IE_{12} > IE_{11}$: $Mg^{12+} > Mg^{11+}$ integer increase in residual ion charge



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Structure of electron clouds

Evidence of charge cloud contraction is seen in every element other than H and He. For example,

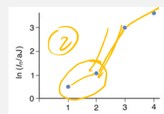

Figure 4.4 The logarithms of the four successive ionization energies (ln I_n/aJ) of a beryllium atom versus the number of electrons removed (n). This graph suggests that the electrons in a beryllium atom are arranged in two shells: an inner shell consisting of two electrons and an outer shell consisting of two electrons.

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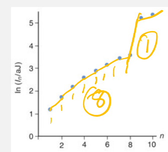

Figure 4.5 The logarithms of the ten successive ionization energies (ln I_n/aJ) of a neon atom versus the number of electrons removed (n). This graph suggests that the electrons in a neon atom are arranged in two shells: an inner shell consisting of two electrons and an outer shell consisting of eight electrons.

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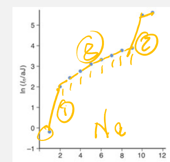

Figure 4.6 The logarithms of the 11 successive ionization energies (ln I_n/aJ) of a sodium atom versus the number of electrons removed (n).

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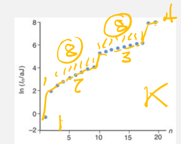

Figure 4.7 The logarithms of the 19 successive ionization energies (ln I_n/aJ) of a potassium atom versus the number of electrons removed (n).

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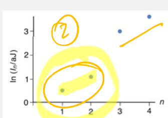
Structure of electron clouds

The "easier to remove" electrons are called valence electrons. The remaining "harder to remove" electrons are called core electrons.



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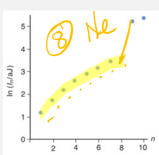

Figure 4.5 The logarithms of the ten successive ionization energies (ln I_n/aJ) of a neon atom versus the number of electrons removed (n). This graph suggests that the electrons in a neon atom are arranged in two shells: an inner shell consisting of two electrons and an outer shell consisting of eight electrons.

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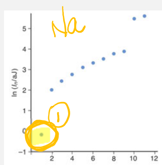

Figure 4.6 The logarithms of the 11 successive ionization energies (ln I_n/aJ) of a sodium atom versus the number of electrons removed (n).

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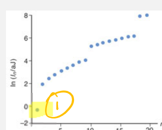

Figure 4.7 The logarithms of the 19 successive ionization energies (ln I_n/aJ) of a potassium atom versus the number of electrons removed (n).

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Structure of electron clouds

The "easy-to-remove" part of electron clouds account for the periodicity of atom properties.

The Lewis electron-dot formula summarizes the number of easily removed (valence) electrons until the much smaller cloud of inner-core electrons remains.

TABLE 4.2 A simple representation of the first 18 elements, indicating their noble-gas-like inner core and their outer electrons

Symbol	Inner-core representation	Lewis electron-dot formula
H	H	H·
He	[He]	He:
Li	[He]·	Li·
Be	[He]:	Be:
B	[Ḣe]:	Ḃ:
C	·[Ḣe]:	·Ċ:
N	·[Ḣe]:	·Ṅ:
O	·[He]·	·O·
F	:[He]:	:F:
Ne	[Ne]	:Ne:
Na	[Ne]·	Na·
Mg	[Ne]:	Mg:
Al	[Ṅe]:	Ȧl:
Si	·[Ṅe]:	·Ṡi:
P	·[Ne]·	·P·
S	·[Ne]·	·S·
Cl	:[Ne]:	:Cl:
Ar	[Ar]	:Ar:
K	[Ar]·	K·
Ca	[Ar]:	Ca:

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IE_1 → electron cloud expansion

Elements in successive rows of the same column of the periodic table contain the same number of valence electrons but increasing numbers of core electrons.

This means the valence portion of the electron clouds of successive elements in the same column is larger and so farther from the nucleus.

This in turn means it is increasingly easier to remove valence electrons going down a column of the periodic table.

Ionization energies decrease due to this expansion of the valence region of the electron cloud.

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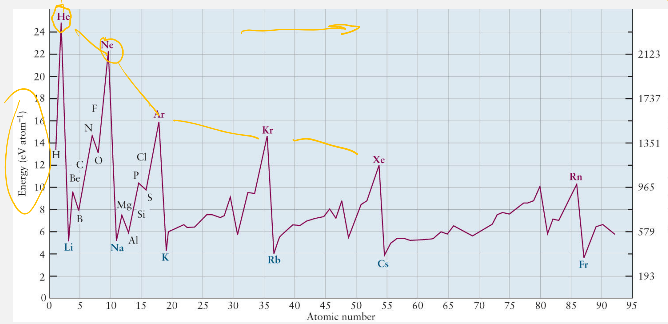
IE_1 → electron cloud expansion



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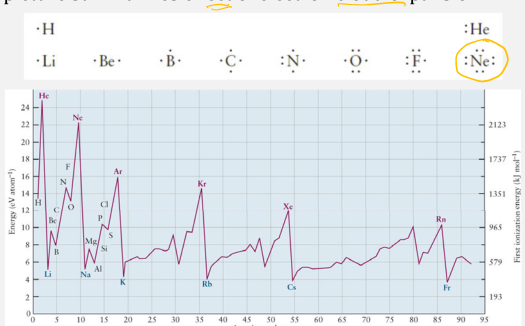
IE_1 → electron cloud expansion

Lewis dot picture summarizes effect of electron cloud expansion.



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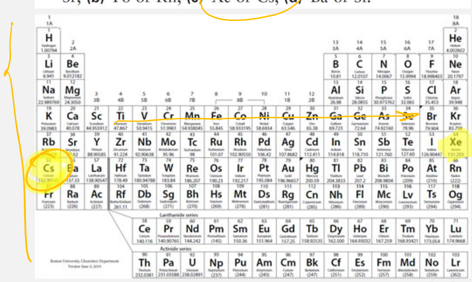
Problem 3.9

9. For each of the following pairs of atoms, state which you expect to have the higher first ionization energy: **(a)** Rb or Sr; **(b)** Po or Rn; **(c)** Xe or Cs; **(d)** Ba or Sr.



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[TP] Which is the correct order of first ionization energy of the atoms barium, beryllium, chlorine, and iodine.

0%	1.	Ba < Be < Cl < I
0%	2.	I < Cl < Be < Ba
0%	3.	I < Ba < Cl < Be
0%	4.	Be < Cl < Ba < I
93%	5.	Ba < I < Cl < Be
0%	6.	Ba < Be < I < Cl
0%	7.	Something else
7%	8.	Not sure

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IE_1 of barium, beryllium, chlorine, and iodine

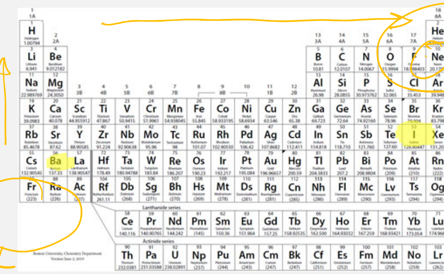
Ba < Be < I < Cl

Ba = 502.9 kJ/mol

Be = 899.5 kJ/mol

Cl = 1251.2 kJ/mol

I = 1008.5 kJ/mol



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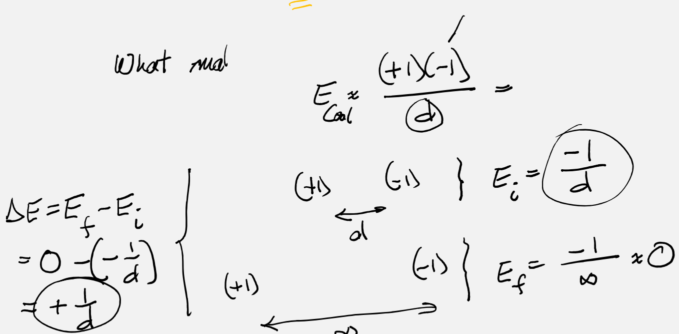
Electron affinity, EA: $X^-(g) \rightarrow X(g) + e^-$



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Electron affinity, EA: $X^-(g) \rightarrow X(g) + e^-$

TABLE 3.2

Electron Affinity of Selected Atoms (in kJ mol^{-1})

H 73							He *
Li 60	Be *	B 27	C 122	N *	O 141	F 328	Ne *
Na 53	Mg *	Al 42	Si 134	P 72	S 200	Cl 349	Ar *
K 48	Ca 2	Ga 41	Ge 119	As 79	Se 195	Br 325	Kr *
Rb 47	Sr 5	In 29	Sn 107	Sb 101	Te 190	I 295	Xe *
Cs 46	Ba 14	Tl 19	Pb 35	Bi 91	Po 183	At 270	Rn *

*No stable anion A^- exists for this element in the gas phase.

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Problem 3.23a

$IE_1(\text{K}) = 4.34$ eV/atom
$IE_1(\text{Cl}) = 12.97$ eV/atom
$EA(\text{K}) = 48$ kJ/mol
$EA(\text{Cl}) = 349$ kJ/mol

23. Use the data in Figure 3.7 and Table 3.2 to calculate the energy changes (ΔE) for the following pairs of reactions:
(a) $K(g) + Cl(g) \longrightarrow K^+(g) + Cl^-(g)$
$K(g) + Cl(g) \longrightarrow K^-(g) + Cl^+(g)$
(b) $Na(g) + Cl(g) \longrightarrow Na^+(g) + Cl^-(g)$
$Na(g) + Cl(g) \longrightarrow Na^-(g) + Cl^+(g)$
Explain why K^+Cl^- and Na^+Cl^- form in preference to K^-Cl^+ and Na^-Cl^+.

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Electronegativity: $EN \sim IE_1 + EA$

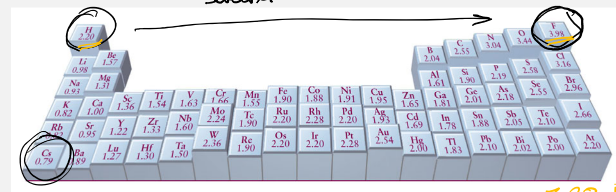

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Fig. 3-10, p. 90

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Dipole moment and ionic character: ~ ΔEN

μ = charge × separation

Dipole moment of charges e^+ and e^- separated by 0.2082×10^{-10} m is defined as one Debye,

$1\ \text{D} = 3.336 \times 10^{-30}$ C m

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Dipole moment

Typically, only a fraction, δ, of an electron charge is displaced

$\pm q = \pm\delta\ |e|$

Where δ is the fractional ionic character.

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Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D.

Calculate dipole moment, assuming displacement of one full unit of charge, |e| .

Answer: $1.602 \times 10^{-19}\text{C} \times 0.917 \times 10^{-10}\text{m} \times \frac{\text{D}}{3.336\times10^{-30}\text{C m}} = 4.40\ \text{D}$

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Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D.

Calculate what fraction of an electron charge is displaced, that is, the fractional ionic character of HF.

Answer: $\delta = \frac{1.82\ \text{D}}{4.40\ \text{D}} = 0.41$

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Ionic character

The internuclear distance of HF is $R_e = 0.917 \times 10^{-10}$ m and its dipole moment is 1.82 D. The fractional ionic character of HF is 0.41.

Percent ionic character is $\delta \times 100\ \% = 41\ \%$

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Ionic character

If the ionic character were 100 %, the molecule would be

$$H^{1.0+}F^{1.0-} \text{ with } \mu = \mu_{max} = e^- \times R_e \times \frac{\text{D}}{3.336\times10^{-30}\text{C m}} = 4.40\ \text{D}$$

with one full unit of electron charge transferred.

Since the ionic character is 41 %, the molecule actually is

$$H^{0.41+}F^{0.41-} \text{ with } \mu = \mu_{observed} = 0.41e^- \times R_e \times \frac{\text{D}}{3.336\times10^{-30}\text{C m}} = 1.82\ \text{D}$$

That is, only 0.41 of an electron charge is transferred. So the fractional charge transferred is $\delta = 0.41$.

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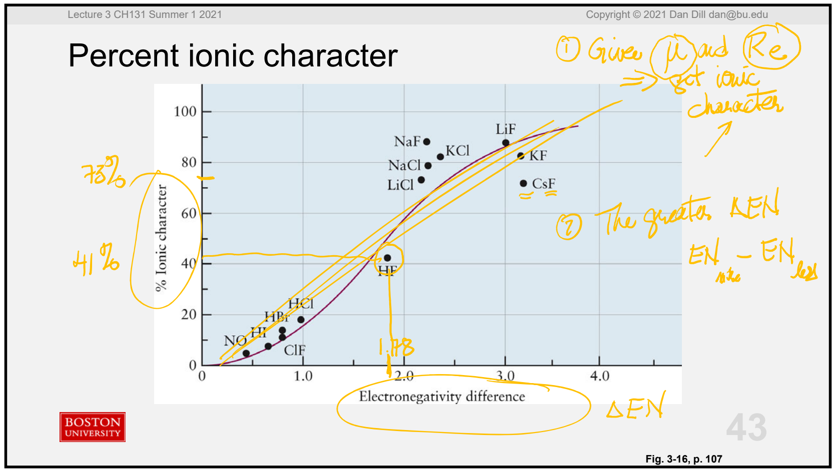
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Percent ionic character
① Given μ and Re ⇒ get ionic character
② The greater ΔEN
EN_more − EN_less
78%
41%
% Ionic character
100
80
60
40
20
0
NaF
KCl
NaCl
LiCl
LiF
KF
CsF
HF
HCl
HBr
HI
NO
ClF
1.78
0
1.0
2.0
3.0
4.0
Electronegativity difference
ΔEN
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Fig. 3-16, p. 107

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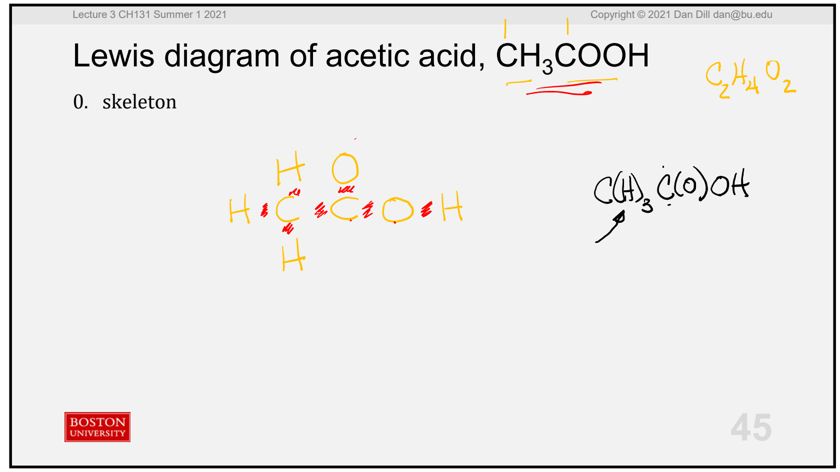
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Lewis diagram of acetic acid, CH3COOH
C2H4O2
0. skeleton
C(H)3C(O)OH
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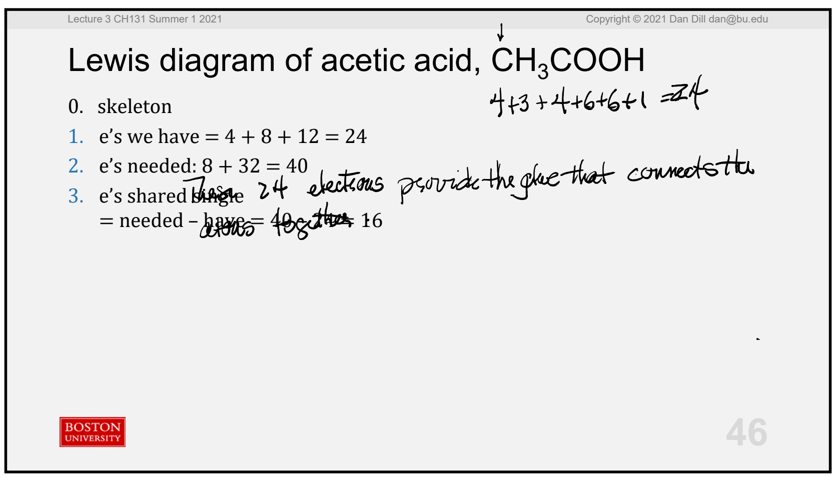
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Lewis diagram of acetic acid, CH3COOH
4+3+4+6+6+1 = 24
0. skeleton
1. e's we have = 4 + 8 + 12 = 24
2. e's needed: 8 + 32 = 40
3. e's shared single
= needed – have = 40 – 24 = 16
These 24 electrons provide the glue that connects the atoms together
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