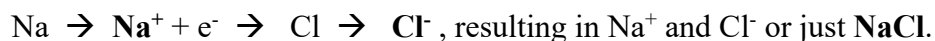


**Exam instructions:** This is the final question 3 of 3 for your “take-home” exam. During this exam, you may use your textbook, lab notebook, class notes, and/or any other documents you prepared. ***This question is due by 5 pm TODAY...please take a picture/scan and email them to me.***

***I agree to follow the guidelines listed above and state that I have neither given nor received any unauthorized aid on this exam.***

\_\_\_\_\_ (signature)

The concept of **bond length** is introduced early in the chemistry curriculum and is seemingly a very basic concept. **Ionic bonding** is introduced early in the curriculum since the idea of forming charged atoms, ie **cations** and **anion**, that are electrostatically attracted makes sense.

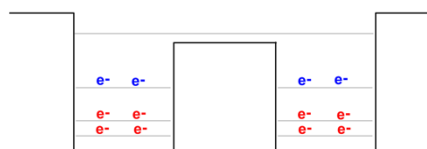


Once the concept of ionic bonding is introduced as the **transfer** of electrons from one atom to another, **covalent bonding** can be introduced as a variant of ionic bond, where electrons are not fully transferred but are instead **shared**. I would like to review/reframe this covalent bonding concept in terms of the chapter 5, “particle in a box” model; this model clearly demonstrates the concept of bonding, bond length, but not bonds.

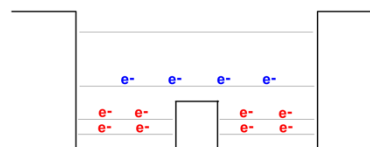
**Stage 1:** two sets of trapped electrons (*atom-like*) that have no interactions,



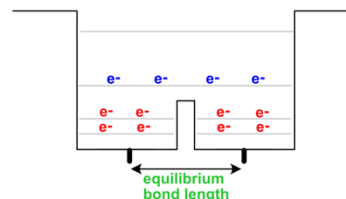
**Stage 2:** two sets of trapped electrons start to interact. At this stage, we can now define two different types of electrons based on behavior: 1) **core e<sup>-</sup>** (red) are deep in the box/well, and 2) **valance e<sup>-</sup>** (blue) are in the higher energy level.



**Stage 3:** two sets of valance e<sup>-</sup> are interacting, although the core e<sup>-</sup> retain full association with the original box/well.



**Stage 4:** two sets of trapped electrons establish an equilibrium distance as a result of the valance e<sup>-</sup> interactions. The concept of equilibrium bond length is established, hence a there must be something called a “bond.”



Chapter 8 introduces the concepts of vibrational and rotational spectroscopy. As shown in Figure 8.3, our discussion moves from the details of a quantum mechanical system to thinking about (ie. modeling) the two “*particle in a box*” (2-PIB) model (above) as a “*ball and spring*” model. The difference in these models is that the 2-PIB model is a static model (*fixed-in-time*) and the ball and spring model is a dynamic model (*moving-in-time*). Note that when modeling vibrational motion, as opposed to translational motion, we don’t use the PIB model but more of a “*particle in a well*” model, also referred to as the harmonic oscillator.

New concepts that arise in the ball in spring model is **reduced mass**. Please calculate the reduced mass (in kg) of  $^1\text{H}^{19}\text{F}$ ? **Show your work.**

As you learned from our gas-phase IR lab experience with HCl, the vibrational spectrum is quite complex due to the rotational hyperfine. I have always wanted to purchase some HF so that we could do the similar experiment, *I just have not allocated time to do it!* You will notice, in table 8.2, that if we did collect some gas-phase IR data for HF, then the forbidden transition (derived from data analysis),  $\tilde{\nu}$  is  $4138\text{ cm}^{-1}$ . Using this  $\tilde{\nu}$  value calculate the force constant ( $k$ ) of the H – F “spring”/bond: **Show all work**

Further analysis of the gas-phase IR data (ie. assigning *m-values* to *transition frequencies*, and making a graph of *m-value vs. frequency*) lead to the determination of the rotational constant *B*, which in turn then lead to the determination of the equilibrium bond length (*r*<sub>0</sub>). Table 8.3 gives rotational constants [*B*<sub>H<sup>19</sup>F</sub> = 20.9557 cm<sup>-1</sup>]; show below the calculation of the equilibrium bond length for H<sup>19</sup>F based on the *B*<sub>H<sup>19</sup>F</sub>:

Also tabulated in Table 8.3 are the determined ionization energies ( $D_0$ ) for various diatomic systems. Considering that the  $D_0$  value is directly proportional to the depth of the vibrational “well”, the higher the  $D_0$  value, the stronger the bond.

Q: what does the  $D_0$  value mean to me?

A: A version of the following table is found in most general chemistry books...PLEASE NOTE: The analysis of the gas-phase IR does not only determine the force constant ( $k$ ), “fictitious” equilibrium bond length ( $r_0$ ), and the rotational constant,  $B$ , but also the bond strength... $D_0$ ...when in units of kJ/mol is also referred to as the **bond energy**...check this...

$D_0$  for HF in Table 8.3 = 570 kJ/mol ~ Bond energy in table below = 565 kJ/mol

Now the similar gas-phase IR experiment that can determine the bond energy for C-C or C-H are not as simple as  $^1\text{H}-^{35}\text{Cl}$  or  $^1\text{H}-^{19}\text{F}$ , but it can be done...welcome to graduate school in Chemical Physics!

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)											
Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
<b>Single Bonds</b>											
H—H	432	74	N—H	391	101	Si—H	323	148	S—H	347	134
H—F	565	92	N—N	160	146	Si—Si	226	234	S—S	266	204
H—Cl	427	127	N—P	209	177	Si—O	368	161	S—F	327	158
H—Br	363	141	N—O	201	144	Si—S	226	210	S—Cl	271	201
H—I	295	161	N—F	272	139	Si—F	565	156	S—Br	218	225
			N—Cl	200	191	Si—Cl	381	204	S—I	~170	234
C—H	413	109	N—Br	243	214	Si—Br	310	216	F—F	159	143
C—C	347	154	N—I	159	222	Si—I	234	240	F—Cl	193	166
C—Si	301	186	O—H	467	96	P—H	320	142	F—Br	212	178
C—N	305	147	O—P	351	160	P—Si	213	227	F—I	263	187
C—O	358	143	O—O	204	148	P—P	200	221	Cl—Cl	243	199
C—P	264	187	O—S	265	151	P—F	490	156	Cl—Br	215	214
C—S	259	181	O—F	190	142	P—Cl	331	204	Cl—I	208	243
C—F	453	133	O—Cl	203	164	P—Br	272	222	Br—Br	193	228
C—Cl	339	177	O—Br	234	172	P—I	184	246	Br—I	175	248
C—Br	276	194	O—I	234	194				I—I	151	266
C—I	216	213									
<b>Multiple Bonds</b>											
C=C	614	134	N=N	418	122	C≡C	839	121	N≡N	945	110
C=N	615	127	N=O	607	120	C≡N	891	115	N≡O	1020	106
C=O	745	123	O <sub>2</sub>	498	121	C=O	1070	113			
	(799 in CO <sub>2</sub> )										

To finish this question, please send me a scan/picture of your Hamiltonian/Wavefunction/Energy table I handed out in class. I will post a picture of this on the website in case you have misplaced this document.

END of Question 3.