Problem Set 4

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1. If an ionic molecule results from the transfer of exactly one electron from one atom to the other, it should have a dipole moment $p = eR_0$, where R_0 is the bond length. Predict the dipole moments of KCl, LiF, NaBr, and NaCl in coulomb meters. The observed values are, respectively, $3.42 \times 10^{-29}, 2.11 \times 10^{-29}, 3.04 \times 10^{-29}$, and 3.00×10^{-29} C$\cdot m$; ; express these as percentages of your predicted values.

> **Solution:** KCl: $0.27e = 4.32 \times 10^{-29}, 79.2\%$
> LiF: $0.16e = 2.56 \times 10^{-29}, 82.4\%$
> NaBr: $0.25e = 4.00 \times 10^{-29}, 76.0\%$
> NaCl: $0.24e = 3.84 \times 10^{-29}, 78.1\%$

2. If a diatomic molecule is ionically bonded by the complete transfer of one electron, its dipole moment should be $p = eR_0$. Given the data in the table that follows, discuss the extent to which the molecules concerned are ionically bonded.

> **Solution:** NaF: $2.72 \times 10^{-29} \div (0.193 \times 10^{-9}e) = 88.1\%$
> HF: $6.07 \times 10^{-30} \div (0.0917 \times 10^{-9}e) = 41.4\%$
> CO: $3.66 \times 10^{-31} \div (0.113 \times 10^{-9}e) = 2.02\%$

3. As a simple classical model of the covalent bond, suppose that an H_2 molecule is arranged symmetrically. Write down the total potential energy U of the four charges and, treating the protons as fixed, find the value of the electrons' separation s for which U is a minimum. Show that the minimum value is $U_{\min} \approx 4.2\frac{ke^2}{R_0}$.

> **Solution:** Using superpostion, we get
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> $$U = \frac{ke^2}{R_0} + 4 \times \frac{ke^2}{\sqrt{R_0^2 + s^2}/2} + \frac{ke^2}{s} = ke^2\left(\frac{1}{R_0} - \frac{8}{\sqrt{R_0^2 + s^2}} + \frac{1}{s}\right)$$
>
> Differentiating and setting to 0,
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> $$s = \frac{R_0}{\sqrt{3}}$$
>
> Which gives
>
> $$U \approx -4.2\frac{ke^2}{R_0}$$

4. (a) Octane, C_8H_{18} is called a straight chain hydrocarbon because its carbon atoms are arranged in a straight line. Draw a picture of the octane molecule showing all bonds.

(b) Do the same for the straight-chain propane, C_3H_8.

Solution: No u

5. Make a sketch of ethane C_2H_6.

Solution: ”

6. Make a sketch of acetylene C_2H_2.

Solution: ”

7. (a) Assuming that the following pairs of elements combine covalently, predict the formulas of the resulting molecules.
   (b) Use the observed dipole moments and bondlengths to confirm that these molecules are predominantly covalent.

Solution: FCl: $3.0 \times 10^{-30} \div (0.16 \times 10^{-9} e) = 11.7\%$ ionic
BrCl: $1.9 \times 10^{-30} \div (0.21 \times 10^{-9} e) = 5.65\%$ ionic
ICl: $4.1 \times 10^{-30} \div (0.23 \times 10^{-9} e) = 11.1\%$ ionic

8. (a) What should be the valence of Be in its ground state ($1s^2 2s^2$)?
   (b) The $2s$ and $2p$ levels are close together, and when another atom is nearby, it is often energetically favorable to promote one of the $2s$ electrons to a 2p state, so that a bond can form. What is the valence of Be in the configuration.
   (c) Predict the chemical formulas for the compounds of Be with fluorine, with oxygen, and with nitrogen.

Solution: 2, 3, BeF_2, BeO, Be_3N_2.

9. Consider the H_2^+ wavefunctions $\psi_\pm$. In that discussion we did not worry about normalization, but $\psi_\pm$ should strictly have been defined as $\psi_+ = B(\psi_1 + \psi_2)$ and $\psi_- = C(\psi_1 - \psi_2)$, where B and C are normalization constants needed to ensure that $\int |\psi|^2 dV = 1$.
   (a) If ψ_1 and ψ_2 do not overlap, show that $B = C = \frac{1}{\sqrt{2}}$.
   (b) If ψ_1 and ψ_2 overlap a little, argue that B is a little less than $\frac{1}{\sqrt{2}}$ and hence that at the midpoint between the two protons, $|\psi_+|^2$ is just a little less than $2|\psi_1|^2$. This proves our claim that ψ_+ concentrates the probability density between the two protons.
   (c) Argue similarly that C must be a little larger than $\frac{1}{\sqrt{2}}$.

Solution: If they do not overlap, $\psi_1\psi_2 = 0$. Normalising,

$$\int_{-\infty}^{\infty} B^2(\psi_1^2 + \psi_2^2 + 2\psi_1\psi_2)dx = 1$$
$$B^2\left(\int_{-\infty} \psi_1^2 dx + \int_{-\infty}^{\infty} \psi_2^2 dx\right) = 1$$
$$2B^2 = 1$$
$$B = \frac{1}{\sqrt{2}}$$

Similarly we get the same result for C. Note that there is a hidden term

$$2\int_{-\infty}^{\infty} \psi_1\psi_2 dx$$

added in the first case and subtracted in the second. Therefore, if the wavefunctions overlap a little, the term becomes slightly positive. Then

$$(2+\epsilon)B^2 = 1$$

which makes B slightly less. Similarly, it would make C slightly larger. Then at the midpoint,

$$|\psi_+|^2 \approx 4B^2|\psi_1|^2$$

Where $4B^2$ is slightly less than 2.

10. The water molecule is partially ionic, in that an electron is partially transferred from each hydrogen to the oxygen, where q denotes the magnitude of each of the two charges transferred.
    (a) Write down the electric dipole moment p of the H_2O molecule in terms of the charge q, the H-O bond length d, and the angle θ.
    (b) The measured values are $p = 6.46 \times 10^{-30}\text{C m}, d = 0.0956\text{nm}$ and $\theta = 104.5°$. Find the magnitude q of the charge transferred and express it as a fraction of the electron charge e.

Solution:

$$p = 2qd\cos\frac{\theta}{2}$$

Rearranging, we get

$$q = \frac{p}{2d\cos\frac{\theta}{2}} = 5.52 \times 10^{-20} = 0.345e$$

11. Prove that the angle between any two bonds in a molecule like CH_4 is $109.5°$.

Solution: Consider a cube. Starting from any vertex, one can construct a tetrahedron by drawing diagonals joining opposite vetices on every face. Then the centre of the tetrahedron is obviously the centre of the cube. Letting cube length be a, bond length is $\frac{\sqrt{3}}{2}a$, and the line joining any two bonds has a length of $\sqrt{2}a$. Using the law of cosines,

$$\begin{aligned} 2a^2 &= \frac{3}{4}a^2 + \frac{3}{4}a^2 - 2 \times \frac{3}{4}a^2 \cos\theta \\ \cos\theta &= -\frac{1}{3} \\ \theta &= 109.5^\circ \end{aligned}$$

Where we take the smaller θ.