

Experiment 446.3**DIPOLE MOMENTS****Theory**

A molecule has an electric dipole moment if it has a net separation of centers of positive and negative charge. If the separation of charge is characteristic of the molecule without the application of an electric field, it is said to have a *permanent electric dipole moment*. Molecules with no net separation of charge outside a field may also have, through interaction with the field, an *induced electric dipole moment* that exists only when the molecule is in the field.

Permanent dipole moments are fixed relative to molecular axes. A permanent electric dipole may be modeled as two charges, $-Q$ and $+Q$, of equal magnitude and opposite sign, separated by a distance given by the vector \mathbf{r} . If the vector \mathbf{r} points from the negative to the positive charge, the electric dipole is

$$\mathbf{d} = Q\mathbf{r}. \quad (3.1)$$

In real molecules, charges are distributed (as shown for electrons by a plot of the square of the electronic wave function.), and the dipole moment results from the fact that the distributions of positive and negative charge are not commensurate. The dipole moment of such a molecule is determined by integration over the charge distributions.

In the SI system of units, the appropriate unit of dipole moment is the coulomb-m. This is much too large a unit to be useful, so one typically finds molecular dipole moments reported in *debyes*.¹ [$1 \text{ D} = 1 \times 10^{-18} \text{ statcoulomb-cm}$]² In SI units, the debye is 3.33564×10^{-30} coulomb-meter. In what follows, I shall use the centimeter-gram-second (cgs) set of units, where the unit of charge is the statcoulomb.

When an electric field is applied, a dipole has an energy of interaction, U , with the electric field, \mathbf{E} , that depends on the orientation, θ , of the dipole relative to the electric field.

$$U = -\mathbf{d} \cdot \mathbf{E} = -|\mathbf{d}||\mathbf{E}| \cos \theta. \quad (3.2)$$

For N molecules, each of which has a permanent dipole, \mathbf{d} , exposed to an electric field, at equilibrium there is a tendency for the dipoles, on average, to be oriented along the field. This situation is described by the *molar electric polarization*, \mathbf{P} , the total electric dipole moment per mole. If L is Avogadro's number, the total equilibrium polarization is

$$\mathbf{P} = L\bar{\mathbf{d}} \quad (3.3)$$

where $\bar{\mathbf{d}}$ is the average molecular dipole moment.

¹ The naming of this unit honors the great Dutch scientist, Peter J. W. Debye, who did pioneering work on the electrical properties of solutions, among his many contributions to science.

² The statcoulomb is the unit of charge in the cgs system of units. $1 \text{ statcoulomb} = 3.3356 \times 10^{-10} \text{ coulomb}$.

The molar electric polarization contains two contributions, one due to permanent electric dipoles, \mathbf{P}_p , and a second, \mathbf{P}_i , due to induced electric dipoles caused by distortion of the electric cloud and of the nuclear framework:

$$\mathbf{P} = \mathbf{P}_p + \mathbf{P}_i \quad (3.4)$$

To determine any one of these quantities, the other two must be measured or estimated.

The molar polarization can be determined from the dielectric constant, κ , of a material through the use of the *Clausius-Mosotti equation*:

$$P = \frac{\kappa - 1}{\kappa + 2} \left(\frac{M}{\rho} \right), \quad (3.5)$$

where M is the molar mass and ρ is the mass density of the dielectric material. The dielectric constant is unitless, and so the molar polarization has units of cm^3/mol .

Measurement of Dielectric Constants

In this experiment, we focus on determining the contribution of permanent dipoles to the polarization (and, from it, the average dipole moment of a molecule) through a measurement of the polarizations of solutions containing the molecules in a nonpolar solvent. To do so, one must generate a known electric field [equation (3.6)] to produce a polarization, and determine the polarization.

The application of a voltage across a capacitor, which in its simplest form consists of two conducting plates of area A separated by a space l , produces an electric field that is determined by the *capacitance*, C , the voltage, and the *dielectric constant*, κ , of the material filling the capacitor. One may show that the capacitance is

$$C = \kappa \epsilon_0 \frac{A}{l}, \quad (3.6)$$

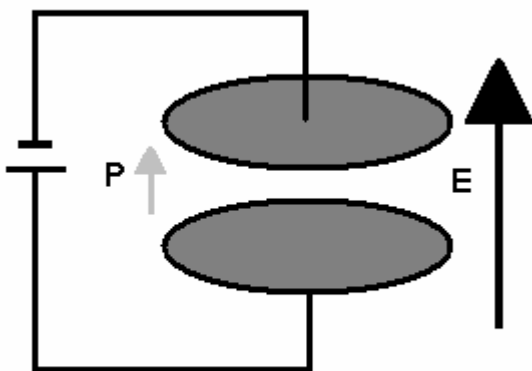


Figure 3.1. The field in a parallel-plate capacitor.

where ϵ_0 is the *permittivity of free space*.³ The SI unit of capacitance is the *farad*, but in many circuits, the practical unit is much smaller, so one often sees capacitances described in *microfarads* or *picofarads*. Equation (3.6) implies that, for a given configuration of electrodes, the capacitance and the dielectric constant of the material in the capacitor are directly related. Hence, a measurement of capacitance may be viewed as a measurement of the dielectric constant of the material between the plates. For two materials **measured in the same circuit**, the following equation holds:

$$\frac{C_1}{C_2} = \frac{\kappa_1}{\kappa_2}. \quad (3.7)$$

We shall use this relationship to make measurements and to calibrate the meter. The dielectric constants of several organic materials are given in Table 3.1.

³ The permittivity of free space is $8.854187817... \times 10^{-12} \text{ F m}^{-1}$.

Table 3.1. Dielectric Constants of Some Pure Organic Liquids at 20°C

Substance	κ	Substance	κ
CCl ₄	2.238	CHCl ₃	4.806
C ₆ H ₁₄	1.890	C ₆ H ₁₂ (Cyclohexane)	2.023
C ₄ H ₁₀ O (Diethylether)	4.335	C ₆ H ₇ N	6.89

Source: R. C. Weast and M. J. Astle (eds.), *CRC Handbook of Chemistry and Physics*, 63rd Edition, CRC Press, Inc., Boca Raton, FL, 1982.

The Contribution of Induced Dipoles

To determine the contribution of permanent dipoles, one must estimate the contribution from induced dipoles. This can be done by noting that, at the high frequencies of visible light, the permanent dipoles make essentially no contribution to the polarization. A measure of the dielectric constant for these conditions allows one to estimate the contribution of induced dipoles. What is usually reported for optical systems is the refractive index, n . The dielectric constant at these high frequencies is related to the refractive index by the simple formula:

$$\kappa = n^2. \quad (3.8)$$

Hence, use of the Clausius-Mosotti equation provides an estimate of this contribution:

$$P_i = \left(\frac{M_2}{\rho_2} \right) \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right), \quad (3.9)$$

where the molar mass, density, and refractive index of the solute (component 2) are indicated with subscripts.

Dielectric Properties of Dilute Solutions

Strictly speaking, the above discussion applies only to gases where the molecules are not interacting. A solution presents a complication to the analysis of dielectric properties, since each component contributes to the properties. If the dielectric material is a solution, then the dielectric constant depends on concentration. In a dilute binary solution, one assumes the properties of the solution are sums of the properties of the components, in proportion to mole fraction of each component. Thus, the effective molar polarization of a binary solution may be expressed in terms of the molar polarizations of the two components:

$$P = X_1 P_1 + X_2 P_2. \quad (3.10)$$

If component 1 is the solvent, then P_1 is its molar polarization and X_2 is the solute mole fraction, with the solute molar polarization of P_2 .

If the components of the mixtures do not interact, the molar polarizations would be constants. However, these quantities also depend on concentration. In dilute solution, one may assume that the molar polarization of the solvent is constant and equal to the molar polarization of the pure solvent, P_1^0 .

$$P = X_1 P_1^0 + X_2 P_2, \quad (3.11)$$

where the superscript ⁰ indicates the property of the pure component. The molar polarization of a nonpolar pure solvent (component 1) can be found from its dielectric constant:

$$P_1^0 = \left(\frac{\kappa_1^0 - 1}{\kappa_1^0 + 2} \right) \left(\frac{3M_1}{\rho_1^0} \right). \quad (3.12)$$

Within this approximation, one may determine the solute molar polarization at each concentration from the molar polarization of the solution:

$$P_2 = \frac{(P - X_1 P_1^0)}{X_2} \quad (3.13)$$

For an ideal solution, one expects P_2 to be independent of concentration, *i.e.* it is a quality only of the molecular structure.⁴ However, it is generally not constant for a real solution. The limiting molar polarization at infinite dilution is a convenient parameter to determine in this case:

$$P_2^0 = \lim_{X_2 \rightarrow 0} P_2. \quad (3.14)$$

One may determine this quantity by a method suggested by Hedestrand.⁵ To do so, one determines the concentration dependences of the dielectric constant of a material and the density of the material:

$$\kappa = \kappa_1^0 + a X_2 \quad (3.15)$$

$$\rho = \rho_1^0 + b X_2 \quad (3.16)$$

from data collected on various solutions.⁶ Using parameters of these equations, one calculates the limiting molar polarization at infinite dilution from the following equation:

$$P_2^0 = \frac{3a}{(\kappa_1^0 + 2)^2} \left(\frac{M_1}{\rho_1^0} \right) + \left(\frac{\kappa_1^0 - 1}{\kappa_1^0 + 2} \right) \left(\frac{M_2}{\rho_1^0} - \frac{M_1 b}{(\rho_1^0)^2} \right) \quad (3.17)$$

The polarization at this limit contains contributions from the permanent dipoles and from induced dipoles. However, one may estimate the contribution of the induced dipoles from the Clausius-Mosotti equation, if the refractive index determined at high frequencies is known. This contribution may be subtracted to give the contribution at infinite dilution of just the permanent dipoles:

$$P_{2,p}^0 = P_2^0 - P_i \quad (3.18)$$

The Average Dipole Moment

The molar polarization is related to the average dipole moment of the molecule, d . The average dipole moment is found from the thermal average over orientations, using the energy of equation (3.2) in the Boltzmann factor. Upon doing the integration, one obtains an equation to determine the dipole moment of the molecule, when using cgs units:

$$d = \sqrt{\frac{9kT}{4\pi L}} P_{2,p}^0, \quad (3.19)$$

where d is the molecular dipole moment and k is Boltzmann's constant. One expresses the value of the molecular dipole moment in debyes.

⁴ For nonideal solutions, P_2 depends on concentration, usually increasing as the concentration decreases due to strong solute-solvent interactions.

⁵ G. Hedestrand, *Z. phys. Chem.* **1929**, 2, 428.

⁶ For this experiment, you determine the variation of the dielectric constant from laboratory data, but the dependence of density on concentration is determined from literature values.

Operation of the Dipole Meter

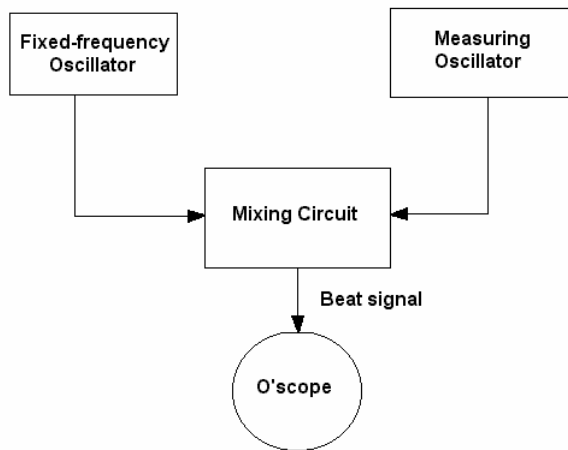


Figure 3.2. Schematic diagram of the dipole meter.

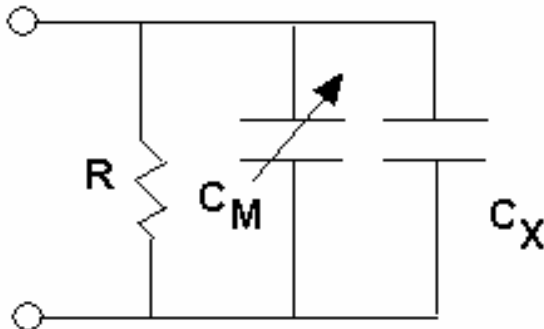


Figure 3.3. Circuit of a simple oscillator.

In this experiment, you determine the capacitance with a dipole meter. The circuit of the dipole meter, shown schematically in Figure 3.2, consists of two oscillators. The first is a measuring oscillator and the second is a fixed-frequency oscillator. An oscillator is a circuit containing at least one capacitor and a resistor or inductor, as in Figure 3.3. When subject to a dc voltage, an oscillator responds by producing an oscillating voltage at a frequency determined by the values of the capacitance, resistance, and inductance. A measurement of the frequency of such an oscillator is a measurement of the capacitance if the resistance (and/or inductance) is fixed.

In this meter, the frequency of one oscillator is determined by comparing it to another fixed oscillator in a mixing circuit, which gives an oscillating signal on an oscilloscope at the **difference of the two frequencies**. By setting the conditions in the measuring oscillator by varying the capacitance, one can accurately adjust it to have exactly the same frequency as the fixed-frequency oscillator, resulting in a zero beat frequency. This is an extremely accurate way of determining capacitance, since one can determine the frequency very precisely by the beat method. (NOTE: There are controls on the instrument to adjust both the brightness and the focus of the oscilloscope display.) The condition of exact frequency match is found when the display on the oscilloscope seems to be a straight line that stands still. (NOTE: This straight-line condition also occurs when the system is very far from the

match condition, so you must vary the capacitor until you see the Lissajous pattern that indicates you are getting close to the resonance condition, and then set it for the exact match.)

When the range switch of the dipole meter is in the position KORR, the measuring oscillator is set to have a very well known capacitance, C_p , and the cell is not a part of the circuit. The capacitance of the fixed-frequency oscillator can be adjusted with the correction knob (KORR) to match this specific condition. This is a way of maintaining calibration. **Before and during each measurement, this check must be performed to ensure that the fixed-frequency oscillator is constant, as it tends to drift a bit.**

In the measuring state, the range switch is set at D1, which is appropriate for liquids. The capacitance of the measuring oscillator is actually two capacitors in parallel (Figure 3.3), one being the cell into which the dielectric is put, C_X , and the other being a variable capacitor, C_M , which you can change in very finely divided steps with a knob on the dipole meter. The scale on C_M goes from 0 to 4500. This is not directly in units of capacitance; it is just a scale to indicate changes in the capacitor; to make it useful one must calibrate the instrument with known materials.

Since C_M is in parallel with the capacitance of the cell and the sum of the two must be a constant at the matching condition, a recording of C_M is an indirect measure of the capacitance, C_X , of the cell.

The instrument must be calibrated before use. This is done by a measurement of at least two fluids of known, but different, dielectric constant. At Delaware, we use diethyl ether and cyclohexane to give a two-point calibration curve. The scale for C_M is linear. One may use the following equation (in terms of dielectric constant):

$$\kappa = A + B*(SR) \quad (3.20)$$

to calibrate the meter from the known dielectric constants of two fluids to obtain A and B.

IMPORTANT: In past years, we have had a lot of trouble with the instrument because of buildup of insoluble deposits. We found this was a result of deposition during the evaporation step. When we were taking the air reading we needed to evaporate all the remaining solvent in the cell. For this reason, we no longer take an air reading.

1. Always leave the cell filled with cyclohexane and do not dry it.
2. All glassware used in this experiment is to be washed with cyclohexane (C_6H_{12}) and dried completely in the oven before use. Any adsorbed water (This is Delaware!) will really affect readings.
3. Be sure the instrument is turned on BEFORE you turn on the thermostat, and be sure you turn off the thermostat BEFORE you turn off the instrument. (Your instructor will have already done this.)
4. The dipole meter's operation will be explained by the instructor. **DO NOT ATTEMPT TO OPERATE THE DIPOLE METER WITHOUT HAVING HAD AN EXPLANATION OF ITS OPERATION FROM THE INSTRUCTOR.**

Filling the Cell and Making a Reading

1. Submerge the bottom of the cell's glass tube in 15 to 20 mL of the sample solution in a small beaker.
2. **Carefully (!)** put the green thumb pipetter over the end of the upper glass tube and slowly draw the liquid from the beaker into the cell until it is visible in the upper glass tube. Close the stopcocks and remove the aspiration device. Be sure there are no bubbles in the sample region.
3. Allow the sample to sit for a minute or two and drain the cell.
4. Repeat steps 2 and 3, so the cell is rinsed twice with the solution to be measured.
5. Fill the cell a third time and allow the solution to equilibrate for five to ten minutes.
6. Take a reading with the dipole meter as described above, making sure the oscillator is stable.

7. Repeat this procedure several times to get sufficient numbers of points to give some idea of the statistical error. (Scale readings of ± 10 are not uncommon over a period of weeks since controlling the moisture in solvents is difficult.)
8. If you feel it is appropriate, drain and refill the cell and repeat the measurement. It is important that you are sure that the data you get are representative of the solution.

Procedure

The object is to measure the dielectric constants of various solutions of substituted benzenes in cyclohexane. The instrument must have been turned on for **at least an hour** before any significant measurements are made. The internal parts must warm up and come to equilibrium before you use it, and this takes time. The cell must be thermostatted at the temperature of measurement. Trying to rush to make measurements gives meaningless results. Take time to do things right.

a. Calibration Measurements

To calibrate the instrument, use diethyl ether as one calibration point and pure cyclohexane, the solvent for your subsequent experiments, as the other. All measurements are to be performed at 20°C (or room temperature) using scale D1. On this scale, one should be able to balance the dipole meter for cyclohexane, diethyl ether, and the solutions of chlorobenzenes in cyclohexane. If the room temperature is not 20°C (or if you choose to examine the temperature variation of the dipole moment), you must use appropriate values to calibrate the instrument. (Look these up in the literature.)

First, measure diethyl ether using the seven-step procedure above. After you have obtained three consecutive measurements on diethyl ether that agree, the cell should be washed free of ether by rinsing several times with 2-propanol (isopropyl alcohol) and dried. Diethyl ether has a boiling point near room temperature. If you see bubbles in the liquid, it is probable that the ether is boiling, which will give an incorrect measurement of the capacitance. Let it sit for a while until this has settled down. Since this is a calibration measurement, a mistake at this point will cause all of the subsequent values to be in error.

One can determine when the cell is free of ether by making a dipole measurement on cyclohexane. After the cell has been thoroughly cleaned, measure cyclohexane. Repeat this measurement until a constant measurement is achieved for cyclohexane. If it is not, clean the cell again. Once you have achieved three consecutive, consistent readings, you may presume that the cell is clean. By this procedure, you have also made repeated measurements of the dielectric constant of cyclohexane!

b. Measurements on Solutions

After calibration by the procedure described above, a series of solutions (described below) is to be measured following the seven-step procedure. Because you are only measuring solutions of two solutes, you have sufficient time to do this accurately and to repeat any measurements that seem to be out of line.

Prepare 50 mL each of solutions containing **approximately**⁷ 1, 2, 3 and 4 mole % solute by pipetting, respectively, into a 50-mL volumetric flask approximately 2, 5, 7 or 10 mL of a

⁷ 'Approximately' means that you are not likely to have concentrations that are exactly these. Just be sure you know exactly what the concentrations are and that they cover a range of a few percent. The more data points you get the

stock solution of the solute in cyclohexane.⁸ You are provided 2-mL and 5-mL pipettes for this purpose. After pipetting the appropriate amount of stock solution, fill the volumetric flask to the mark with cyclohexane; mix thoroughly. These are the solutions used for measurements; be sure they are made carefully, as the accuracy of knowing these concentrations affects your results and your grade. You may wish to make a few more solutions to get more accurate results.

Make measurements first on the solution of lowest concentration, and then subsequently on solutions of higher concentration. With 50 mL of each solution, you should be able to obtain at least four readings for each solution, of which the first will probably be unacceptable because of poor rinsing.

If your experiments run over to a second lab period, you must repeat the pure cyclohexane run and adjust your results for the shift between periods; that is, you must recalibrate.

IMPORTANT: At the end of the laboratory period, wash the cell twice with pure cyclohexane to make sure all the solute residues have been removed.

Quantum Calculations

With present-day computers, one may do numerical estimations of the electronic wave functions of a molecule rather easily and with quite good precision.⁹ Once known, the functions can be numerically integrated to give estimates of the values of parameters such as the dipole moment, based on that particular electronic state. Many operations can be done easily and straightforwardly with “canned” programs such as GAUSSIAN03¹⁰ or SPARTAN.

The principal problem one must understand in carrying out *ab initio* quantum calculations is that any procedure uses some approximation to the electronic wave function(s) of the molecule. The quality of the approximation determines how good calculated properties are. A commonly used method is linear combination of atomic orbitals (LCAO), in which one expresses the molecular electronic wave function (or molecular orbital [MO]) in terms of orbitals of the constituent atoms. Since the forms of atomic orbitals are not well known except for hydrogen, even the choice of functional forms of atomic orbitals is an approximation whose quality will affect the results. The set of functions used is called the **basis**. A commonly used basis is the Slater-type orbitals (STO), but other bases are sometimes used, for example Gaussian-type orbitals. These have esoteric acronyms that denote certain features of the set of orbitals, such as 3-21G or 6-31G or 6-311+G(d,p). In principle, an infinitely large set of any of these should allow one to approximate the electronic state exactly. However, that would take a great amount of time, so that calculations are always done with a truncated basis; again, the quality of the results depends on how well the truncated set approximate the real wave function.

Once chosen, the basis is used to determine the “best” electronic wave function by some criterion, often minimization of energy. A common method is the Hartree-Fock self-consistent field (HF-SCF) method, which emphasizes the average effects of interelectronic interactions,

better, so if time permits, try several intermediate concentrations as well. This is a minimum number of solutions. If you wish to get more accurate results you should make more solutions.

⁸ The stock solution you make should contain approximately 0.26 g of solute per mL of solution. Weigh this out appropriately. Take time to do this properly; it determines all of the rest of the experiments. Be sure to record the concentration of this solution, as you will need it for calculations.

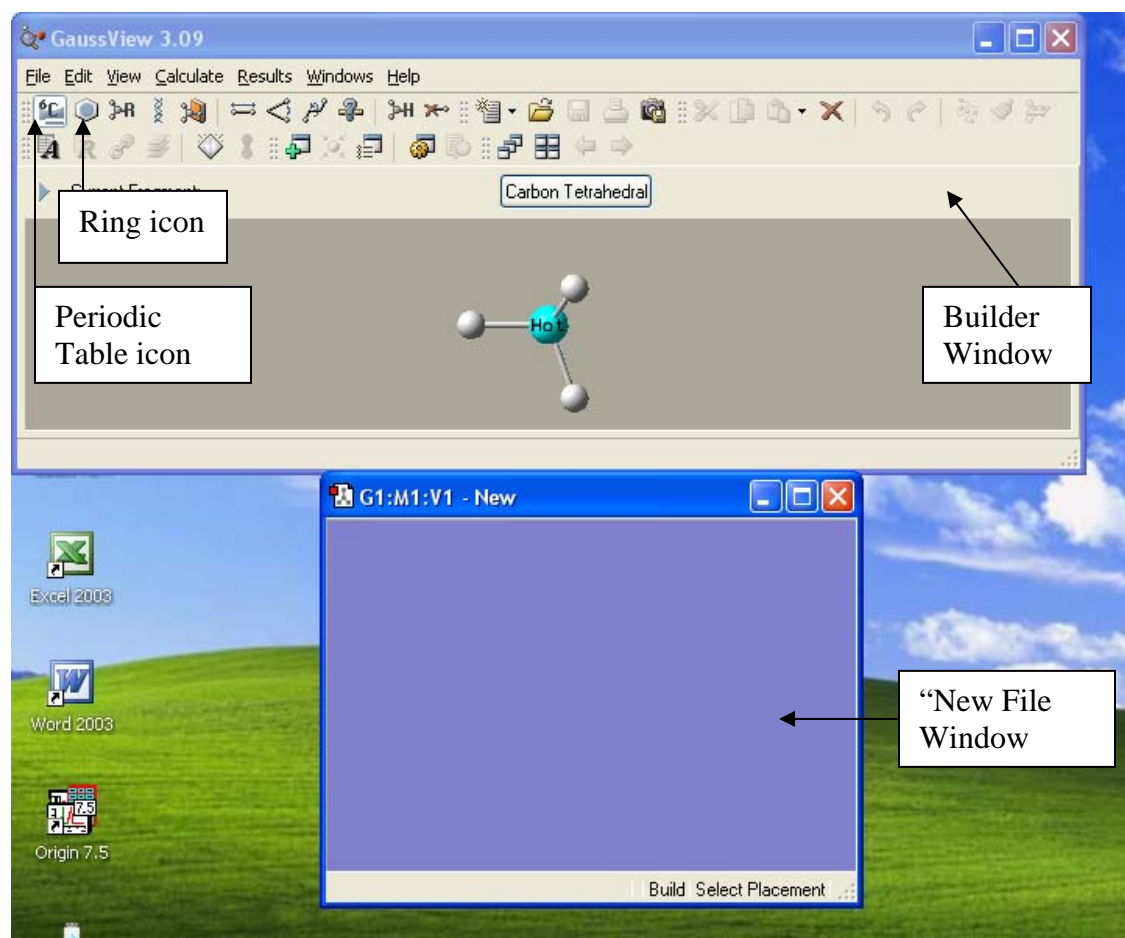
⁹ Only a few years ago, such calculations were only done by a rather small number of experts on rather large computers.

¹⁰ John Pople was awarded the 1998 Nobel Prize in Chemistry principally for the development of GAUSSIAN.

rather than instantaneous interactions. This iterative method finds the parameters of the expansion of the molecular orbital in the chosen basis that minimizes the variational energy integral. Conveniently, computer programs like GAUSSIAN do all of the work if one describes the desired basis and situation appropriately, returning useable information on the state in the form of parameters.

Another method is called density functional theory, which is based on an idealized problem of a electron gas of uniform density. This may be used as the basis to solve the exact problem, which includes correlation effects. Density functional theory is particularly attractive because it takes less computational time to solve a problem than other models that include correlation.

GAUSSIAN03 has a graphical interface called GaussView, which makes calculations easy to set up, execute and analyze. To use the program, start the PC in the laboratory. On the desktop, you should see icons for GAUSSIAN03 and GaussView. Click on its icon to start GaussView. This will show you the main window of GaussView and open another window for the new file. You are ready to create your molecule in the file.



1. Click on the ring icon in the toolbar of the main window, the **Builder** Window. A variety of ring structures will appear.

2. Click on the benzene ring to put it into the **Current Fragment** display. Now click in the window of the “New” file. You should see a benzene ring appear.¹¹
3. Now, in the **GaussView** window, click on the Periodic Table icon (a button with a carbon atom; sometimes you have to click it twice). Click on the chlorine atom in the Periodic Table. Now click on one of the hydrogen atoms of the benzene ring in the “New” file. This should cause it to change into a chlorine atom. (which is green!)
4. Click on the appropriate other hydrogen atom to create either **o**-dichlorobenzene or **m**-dichlorobenzene. You have now created a structure on which GAUSSIAN can operate.
5. Go to the **Calculate** menu and select **Gaussian**. On the Job Type tab, set this to **Optimization**. Under the **Method** tab, the method should be “Ground State Hartree-Fock Default Spin” and the basis set should be 6-31G(d) basis set. Leave the charge at 0 and spin at “Singlet.” Click the **Title** tab and write a title for your job in the space. Click the **Link 0** tab and be sure that it has the following three lines:

```
%chk=  
%mem=6MW  
%nproc=1
```

6. Click the **Submit** tab. The program asks you to save an input file. Use a name like **ODCB** or **MDCB**. (The program should save this to the Desktop, but you may have to change the folder if it wants to save it elsewhere. The program should give it the proper extension.)
7. The calculation starts, using the Hartree-Fock approximation. GAUSSIAN will put up a window, telling you the calculation is over. (The calculation may take several minutes so be patient.) When asked if you want to close the Gaussian Window, click Yes.
8. You can look at the output with GaussView. The program automatically asks if you want to view the file, so just click Yes. The output file type (*.out or *.log) should be requested; you should see a file with the same name as you used above. Choose it and open it.
9. You may just look at the **SUMMARY** results, under the **Results** menu, to find the dipole moment, and its unit is the debye. You will also see the energy. The quantity called **E(RHF)** is the calculated energy of the molecule, in atomic units, a. u. or hartrees.¹²
10. Repeat the calculation for the other isomer.
11. After you complete the Hartree-Fock calculations, repeat the procedure with a density functional calculation. The following parameters have to be set on the tabs: Job Type **Optimization**; Method **Ground State DFT Default Spin B3LYP**; Basis Set **6-31G(d)**; Charge **0**; Spin **Singlet**; Title whatever you wish to name the file; **Link 0** as above.
12. Submit the job as you did above. This time, the calculation may take a bit longer, but Gaussian will send a message when your job is finished.
13. Delete all files you created before you leave the computer.

¹¹ GAUSSIAN always gives a species with saturated valences from the **Element** command. If you had picked carbon, you would have received CH₄ in the window. You can add other atoms using other commands in **Builder**, but that is something to explore later.

¹² 1 hartree = 627.51 kcal/mol.

Calculations

1. At 20°C the density of cyclohexane is 0.7785 gm/cm³.¹³ Using this information and other information, determine an equation for the density as a function of solute mole fraction, X_2 , for each dichlorobenzene dissolved in cyclohexane. Are there any assumptions that you have to make in doing this?
2. From your measurements, give an equation for the calibration line, equation (3.20). Be sure to indicate uncertainty in the parameters that specify the line.
3. Calculate the dielectric constant, κ , of each solution, using your calibration line and the measurements you made on the solutions. Each value should have its associated error reported.
4. For each set of solutions, plot the experimental dielectric constant as a function of solute mole fraction, X_2 , and determine the best-fit parameters for a straight line according to equation (3.15). Again, be sure to include estimates of uncertainty.
5. Calculate P_2^0 , the molar polarization at infinite dilution of the solute evaluated at low frequency for each solute.
6. Estimate the high-frequency contribution to P_2^0 from the high-frequency refractive index for both dichlorobenzenes.
7. With the results of questions 5 and 6, estimate the contribution from permanent dipoles, $P_{2,p}^0$, for each dichlorobenzene.
8. Determine the permanent dipole moments (in units of debyes) of **o**-dichlorobenzene and **m**-dichlorobenzene from the results, including an estimate of uncertainty.
9. Using GAUSSIAN03, calculate the dipole moments of **o**-dichlorobenzene and **m**-dichlorobenzene and report these values with the two different methods.

Table 3.2. Solute Parameters from the Literature

	o -dichlorobenzene	m -dichlorobenzene
n	1.5515	1.5459
$ \mathbf{d} $	2.50 D	1.72 D
ρ	1.3048 g cm ⁻³	1.2884 g cm ⁻³

From R. C. Weast and M. J. Astle (eds.), *CRC Handbook of Chemistry and Physics*, 63rd Edition, CRC Press, Inc., Boca Raton, FL, 1982.

Discussion Questions

1. Explain the origin of the unit called the debye. Why is the value so small in SI units or cgs units?
2. The dipole moment of monochlorobenzene is reported to be 1.55 D. From this value, use vector addition of carbon-chlorine bond moments to predict the values and orientations in the molecular frame of the dipole moments of **o**-dichlorobenzene and **m**-dichlorobenzene. Assume only the carbon-chlorine bonds contribute to the dipole moment. Indicate where the dipole moment vectors point relative to the molecular structures in a figure.

¹³ The density of cyclohexane at other temperatures is found from the equation:

$$\rho = [0.7785 - 9.4 \times 10^{-4}(t - 20)] \text{ gm/cm}^3, \text{ where the temperature, } t, \text{ is on the Celsius scale.}$$

3. Compare the experimentally measured dipole moments with the simple bond-additivity theory in question 2, with the results of the GAUSSIAN03 calculations, and with literature values.
4. What discrepancies do you note among the experiment and the calculations?
5. Explain why the two calculations of the dipole moment give such different results. [Note: You may have to read about the principles of computational chemistry in a book such as Engel and Reid, *Physical Chemistry*, in particular Chapter 26 to address this question.]