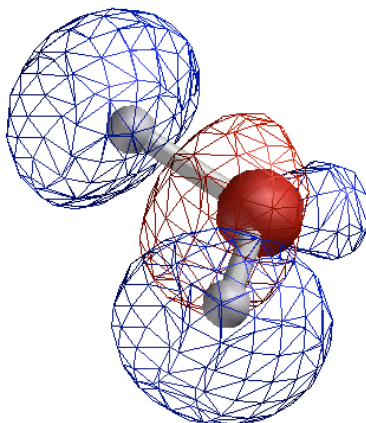


Lecture 31, April 12, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 275-281.)

Solved Homework

An extra electron would be expected to localize in the lowest-energy unoccupied molecular orbital (LUMO). In water, that is orbital 6. The appearance of orbital 6 is



This orbital is antibonding between oxygen and the two hydrogen atoms, so filling it would be expected to lengthen the O–H bonds. A good way to think about the quantum mechanical rationale behind the lengthening of the bonds is that this decreases the curvature of the orbital wave function associated with the nodes (by moving the nodes further from one another) and thereby lowers the kinetic energy.

The same argument (the decrease in kinetic energy associated with moving the nodes further from one another) suggests that one would expect the bond angle at oxygen to open up to be wider.

The geometry of the water radical anion (from an independent computation) has bond lengths of 1.274 Å and an HOH angle of 135.4 deg. This agrees with our analysis based on the LUMO.

Other Computed Properties—Partial Atomic Charges

An enormous amount of chemical reactivity can ultimately be rationalized by a rather simple observation: positively charged things like to associate with negatively charged things and vice versa, but charges of like sign repel one another. This simple precept explains most acid/base reactions, bimolecular nucleophilic substitution (as we'll see in more detail below), ester hydrolysis, and many other reactions at a mechanistic level. As such, a key property about which chemists like to think is the so-called partial charge associated with an atom. Thus, for example, in formaldehyde, $\text{H}_2\text{C}=\text{O}$, we know that the $\text{C}=\text{O}$ double bond is polarized in a way that makes the oxygen end more negative and the carbon end more positive, and that's why nucleophilic reagents add to the carbon atom of carbonyl groups. In principle, we might try to quantify that polarization by assigning partial charges to each atom (typically being fractional in magnitude, e.g., +0.25 for C and -0.25 for O, ignoring the H atoms for the moment). Part of the driving force for this conceit is that it allows one to conveniently ignore the wave character of the electrons and deal only with the pleasantly more particulate atoms, these atoms reflecting electronic distribution by the degree to which they carry positive or negative charge.

From quantum mechanics, at least as associated with Hartree-Fock calculations, we have a natural way to come up with quantitative charges on atoms because we have occupied orbitals that are made up of basis functions on different atoms. So, if basis functions on oxygen are used more than basis functions on carbon for the occupied orbitals, we'd see more charge on the oxygen than the carbon. Let's look at this in a bit more detail.

Dividing the electrons up and assigning them to specific atoms is called "population analysis". One of the first such schemes for such a partitioning was proposed by R. S. Mulliken in 1955, and this method of population analysis now bears his name. Conceptually, it is very simple, with the electrons being divided up amongst the atoms according to the degree to which different AO basis functions contribute to the overall wave function. Note that in restricted Hartree-Fock theory we may compute the total number of electrons N as

$$N = 2 \sum_j^{\text{occupied}} \int \psi_j^*(\mathbf{r}_j) \psi_j(\mathbf{r}_j) d\mathbf{r}_j \quad (31-1)$$

since each normalized, occupied molecular orbital ψ contains two electrons. If we now replace each ψ by its linear expansion in AO basis function we have

$$\begin{aligned}
N &= 2 \sum_j^{\text{occupied}} \int \left(\sum_r c_{jr} \varphi_r(\mathbf{r}_j) \right) \left(\sum_s c_{js} \varphi_s(\mathbf{r}_j) \right) d\mathbf{r}_j \\
&= 2 \sum_j^{\text{occupied}} \sum_{r,s} \int c_{jr} \varphi_r(\mathbf{r}_j) c_{js} \varphi_s(\mathbf{r}_j) d\mathbf{r}_j \\
&= 2 \sum_j^{\text{occupied}} \left(\sum_r c_{jr}^2 + \sum_{r \neq s} c_{jr} c_{js} S_{rs} \right)
\end{aligned} \tag{31-2}$$

From the last line of eq. 31-2, we see that we may divide the total number of electrons up into two sums, one including only squares of single AO basis functions, the other including products of two different AO basis functions. Clearly, electrons associated with only a single basis function (i.e., terms in the first sum in parentheses on the r.h.s. of the last line of eq. 31-2) should be thought of as belonging entirely to the atom on which that basis function resides. As for the second term, which represents the electrons “shared” between basis functions, Mulliken suggested that one might as well divide these up evenly between the two atoms on which basis functions r and s reside. If we follow this prescription and furthermore divide the basis functions up over atoms k so as to compute the atomic population N_k , eq. 31-2 becomes

$$N_k = 2 \sum_j^{\text{occupied}} \left(\sum_{r \in k} c_{jr}^2 + \sum_{r,s \in k, r \neq s} c_{jr} c_{js} S_{rs} + \sum_{r \in k, s \notin k} c_{jr} c_{js} S_{rs} \right) \tag{31-3}$$

Note from the definition of the density matrix (eq. 29-3) that this can also be written

$$N_k = \sum_{r \in k} P_{rr} + \sum_{r,s \in k, r \neq s} P_{rs} S_{rs} + \sum_{r \in k, s \notin k} P_{rs} S_{rs} \tag{31-4}$$

Now, let's recall the density and overlap matrices for water. The overlap matrix we've already seen.

$$\mathbf{S} = \begin{bmatrix} 1.000 & & & & & & \\ 0.237 & 1.000 & & & & & \\ 0.000 & 0.000 & 1.000 & & & & \\ 0.000 & 0.000 & 0.000 & 1.000 & & & \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 & & \\ 0.055 & 0.479 & 0.000 & 0.313 & -0.242 & 1.000 & \\ 0.055 & 0.479 & 0.000 & -0.313 & -0.242 & 0.256 & 1.000 \end{bmatrix} \tag{31-5}$$

The *final* density matrix is

$$\mathbf{P} = \begin{bmatrix} 2.106 & & & & & & & \\ -0.445 & 1.964 & & & & & & \\ 0.000 & 0.000 & 2.000 & & & & & \\ 0.000 & 0.000 & 0.000 & 0.736 & & & & \\ -0.105 & 0.619 & 0.000 & 0.000 & 1.246 & & & \\ -0.015 & -0.032 & 0.000 & 0.539 & -0.470 & 0.597 & & \\ -0.015 & -0.032 & 0.000 & -0.539 & -0.470 & -0.193 & 0.597 & \end{bmatrix} \quad (31-6)$$

Let's compute the partial atomic charge for hydrogen atom a. The only basis function entirely on H_a is #6, so P_{66} contributes 0.597 electrons as belonging to H_a . There is only one basis function on H_a , so we don't need to worry about the second summation in eq. 31-4. As for the last term, we need $P_{61}S_{61} + P_{62}S_{62} + P_{63}S_{63} + P_{64}S_{64} + P_{65}S_{65} + P_{67}S_{67} = -0.015 \cdot 0.055 + -0.032 \cdot 0.479 + 0 \cdot 0 + 0.539 \cdot 0.313 + -0.470 \cdot -0.242 + -0.193 \cdot 0.256 = 0.217$. Thus, the total number of electrons on H_a is $0.597 + 0.217$ or 0.814. We compute partial atomic charge q as

$$q_k = Z_k - N_k \quad (31-7)$$

For H, $Z = 1$, so the partial atomic charge is $1 - 0.814 = 0.186$. By symmetry it is clear that this will also be the charge on H_b , and, since the water molecule has a net charge of zero, it must be the case that the partial atomic charge on O is equal to the opposite of the sum of the charges on the H atoms, or -0.372 . These charges are qualitatively as we expect them to be: oxygen is partially negative and the hydrogen atoms are partially positive. Mulliken population analysis is very simple and continues to be used extensively for assessing molecular polarity in quantum calculations.

Other Computed Properties—Multipole Moments

In cartesian coordinates, the expectation values of multipole moment operators are computed as

$$\langle \mathbf{x}^k \mathbf{y}^l \mathbf{z}^m \rangle = \sum_i^{\text{atoms}} Z_i x_i^k y_i^l z_i^m - \int \Psi^*(\mathbf{r}) \left(\sum_j^{\text{electrons}} x_j^k y_j^l z_j^m \right) \Psi(\mathbf{r}) d\mathbf{r} \quad (31-8)$$

where the sum of k , l , and m determines the type of moment ($0 =$ monopole, $1 =$ dipole, $2 =$ quadrupole, etc.), Z_i is the nuclear charge on atom i , and the integration variable \mathbf{r} contains the x , y , and z coordinates of all of the electrons j . When Ψ is expressed as a single Slater determinant, we may write

$$\langle \mathbf{x}^k \mathbf{y}^l \mathbf{z}^m \rangle = \sum_i^{\text{atoms}} Z_i x_i^k y_i^l z_i^m - \sum_j^{\text{electrons}} \int \psi_j^*(\mathbf{r}_j) (x_j^k y_j^l z_j^m) \psi_j(\mathbf{r}_j) d\mathbf{r}_j \quad (31-9)$$

where ψ_j and \mathbf{r}_j are the molecular orbital occupied by electron j and its cartesian coordinate system, respectively.

The simplest moment to evaluate is the monopole moment, which has only the component $k=l=m=0$, so that the operator becomes $\mathbf{1}$ and, independent of coordinate system, we have

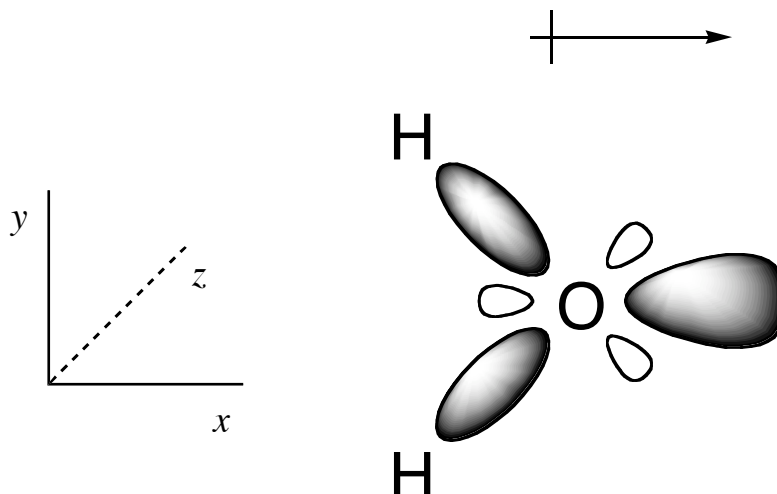
$$\begin{aligned} \langle \mathbf{1} \rangle &= \sum_i^{\text{atoms}} Z_i - \sum_j^{\text{electrons}} \int \psi_j^*(\mathbf{r}_j) \psi_j(\mathbf{r}_j) d\mathbf{r}_j \\ &= \sum_i^{\text{atoms}} Z_i - N \end{aligned} \quad (31-10)$$

where N is the total number of electrons (the simplification of the second term on the r.h.s. follows from the normalization of the MOs). The monopole moment is thus the difference between the sum of the nuclear charges and the number of electrons, i.e., it is simply the molecular charge.

For the dipole moment, there are three possible components: x , y , or z depending on which of k , l , or m is one (with the others set equal to zero). These are written μ_x , μ_y , and μ_z . Experimentally, however, one rarely measures the separate components of the dipole moment, but rather the total magnitude, μ , which can be determined as

$$\langle \mu \rangle = \sqrt{\langle \mu_x \rangle^2 + \langle \mu_y \rangle^2 + \langle \mu_z \rangle^2} \quad (31-11)$$

The dipole moment measures the degree to which positive and negative charges are differentially distributed relative to one another, i.e., the overall molecular polarity. Thus, for instance, if the electronic wave function has a large amplitude at some positive x value while the nuclear charge is concentrated at some negative x value, inspection of eq. 31-8 indicates that the dipole moment in the x direction will be negative. If they are both concentrated at the same position and the total electronic charge is equal to the total nuclear charge, the first and second terms on the r.h.s. of eq. 31-8 cancel, and the dipole moment is zero. The figure below illustrates these concepts for the case of the water molecule.



The nuclear charges of the water molecule, here lying flat in the xy plane, are entirely at the nuclear positions. The electrons of the hydrogen atoms, however, are pulled to the positive x direction relative to the H nuclei by bonding interactions with the more electronegative O atom (the polarization is exaggerated here by depicting the σ orbitals with surfaces that fail to encompass the nuclear positions). In addition, the oxygen atom contributes two electrons into its in-plane lone pair, the orbital for which is localized at large, positive values of x , while only contributing a single electron each to the σ orbitals, resulting in another net polarization of negative charge in the positive x direction. The sum of these and other effects is such that water has a dipole moment of 1.8 D in the direction indicated (parallel with the x axis by symmetry). Note that the out-of-plane p orbital may be thought of as “canceling” two protons in the oxygen nucleus when the dipole moment is computed, since it is circularly symmetric about the nucleus when projected into the xy plane (since it is also symmetric above and below the xy plane, as are all other orbitals, there is no z component to the dipole moment). Note that any movement of the origin will change the coordinates of all charges by the same amount; since the total amount of positive charge is equal to the total amount of negative charge in water, the dipole moment is unaffected by such an origin change, but this would not be true for a charged species.

Our computed dipole moment for water at the HF/STO-3G level (from evaluation of eq. 31-9, which we will leave to the digital computer) was 1.74 D, in outstanding agreement with the experimental moment of 1.8 D!

Electrical moments are useful because at long distances from a molecule the total electronic distribution can be increasingly well represented as a truncated multipole expansion, and thus molecular interactions can be approximated as multipole-multipole interactions (charge-charge, charge-dipole, dipole-dipole, etc.), which are computationally particularly simple to evaluate. At short distances, however, the multipole expansion may be very slowly convergent, and the multipole approximation has less utility.

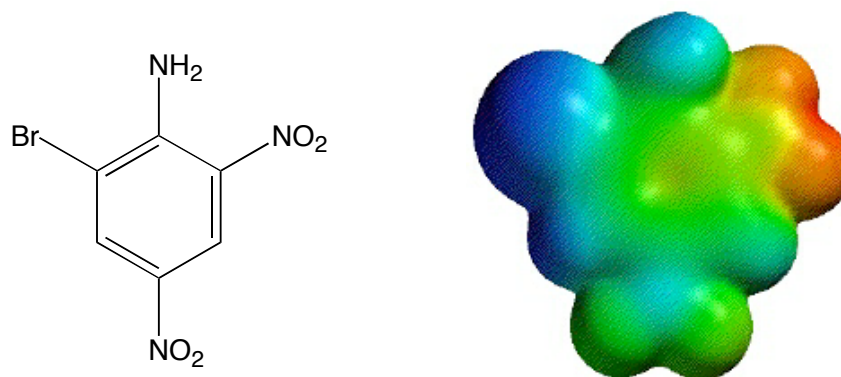
Other Computed Properties—Molecular Electrostatic Potential

A (truncated) multipole expansion is a computationally convenient single-center formalism that allows one to quantitatively compute the degree to which a positive or negative test charge is attracted to or repelled by the molecule that is being represented by the multipole expansion. This quantity, the molecular electrostatic potential (MEP), can be computed *exactly* for any position \mathbf{r} as

$$V_{\text{MEP}}(\mathbf{r}) = \sum_k^{\text{nuclei}} \frac{Z_k}{|\mathbf{r} - \mathbf{r}_k|} - \int \Psi^*(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \Psi(\mathbf{r}') d\mathbf{r}' \quad (31-12)$$

Note that this assumes no polarization of the molecule in response to the test charge. The MEP is an observable, although in practice it is rather difficult to design appropriate experiments to measure it.

The MEP is particularly useful when visualized on surfaces or in regions of space, since it provides information about local polarity. Typically, after having chosen some sort of region to be visualized, a color-coding convention is chosen to depict the MEP. For instance, the most negative potential is assigned to be red, the most positive potential is assigned to be blue, and the color spectrum is mapped to all other values by linear interpolation. If this is done on the molecular van der Waals surface, one can immediately discern regions of local negative and positive potential, which may be informative for purposes of predicting chemical reactivity. The below figure provides a particular example.



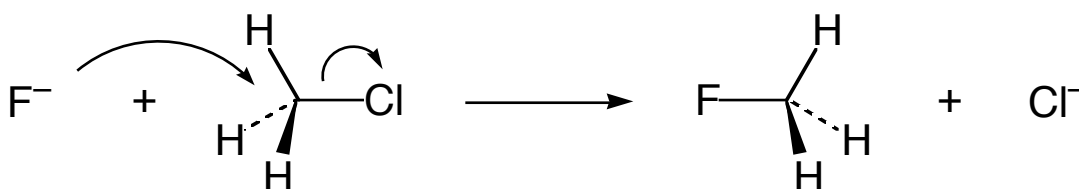
Above is the MEP of the radical anion produced by one-electron reduction of the dinitroaromatic shown at left (an environmental contaminant from the dying of cloth). The spectrum is mapped so that red corresponds to maximum negative charge density and deep blue to minimum. This depiction indicates that the buildup of negative charge density is larger on the nitro group *ortho* to the amino group than on that *para* to NH₂. Such polarization is consistent with the observed reactivity of the molecule under reducing conditions, where protonation of the more negative nitro group in water leads to

its ultimate reduction to an amino group but the *para* nitro group is not reduced. Quantum mechanics explains this selectivity.

Other Computed Properties—Frontier Molecular Orbital Reactivity

A slight wrinkle on our above discussion vis a vis reactivity being explicable based on opposite-charge attraction is to consider how charge is most likely to flow from one molecule to another. If we think about this question for a moment, it should be clear that an electron is most easily removed from the highest occupied molecular orbital (HOMO) of a nucleophile and added to the LUMO of an electrophile. Thus, in addition to recognizing that positively and negatively charged regions will tend to attract one another, we should recognize that that attraction will likely follow a spatial path mapped out by the HOMO and LUMO of the reacting partners.

Perhaps the most classic example of this analysis is the backside attack involved in nucleophilic substitution of alkyl halides via the S_N2 mechanism. For example



From our analyses up to this point, and from our knowledge that halogen atoms are more electronegative than carbon, we would expect the carbon atom to bear a partial positive charge and the halogen atom a partial negative charge. This alone partly rationalizes why an incoming nucleophile like fluoride might prefer to attack the carbon atom from the back side.

However, if we consider that the alkyl halide is accepting a transfer of an electron across its framework to the chloride ion, we would expect that electron to move into the LUMO of the alkyl halide. That LUMO is depicted on the next page from a Hartree-Fock calculation with a somewhat better basis set than STO-3G. Note that the LUMO has extensive amplitude *behind* the methyl group (in the backside attack region) so this trajectory is dictated in part by frontier orbital considerations. (Note also that the orbital is formally a σ^* orbital between C and Cl, which is why the C–Cl bond breaks when it becomes populated.)

Such analysis is often helpful in understanding the reactivity of π systems, too. Thus, substituted aromatic rings have π -type HOMOs and LUMOs that have larger amplitudes at some atoms than others, and their regioselective reactivity is dictated by these amplitudes and the nature of the other reagent—either electrophile or nucleophile.

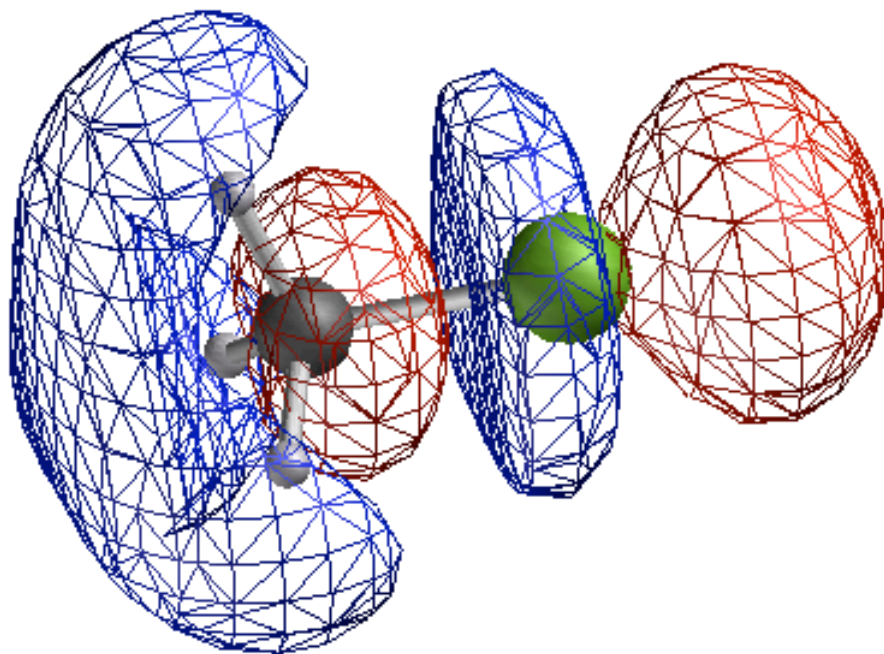


Figure. The lowest unoccupied molecular orbital (LUMO) of chloromethane.

Homework

To be solved in class:

In eq. 31-9, the nuclei contribute to multipole moments in a classical way: they are point charges multiplied by their cartesian coordinates. The total multipole moment then considers the electrons' "positions" which, because electrons are quantum mechanically "smeared out", requires integration. What if we were simply to replace the full nuclear charges in eq. 31-9 with the partial atomic charges from Mulliken analysis and ignore the electronic term—what is the dipole moment in that case? (Hint: the atomic unit of dipole moment is electron charge bohr. So, you already have charges in atomic units, but you'll need to convert the cartesian coordinates of the atoms in water given in Lecture 29 to bohr. You'll also need to convert your atomic units dipole moment to the more standard

units of "debye" (D). You'll find the relevant conversion factors in the notes to Lecture 15.)

To be turned in for possible grading Apr. 14:

Instead of thinking about the electrons that belong to a single atom, it is sometimes interesting to ask about the electrons belonging to each basis function. It should be reasonably clear from inspection of eq. 31-4 that the population of an AO basis function r , as opposed to an atom, is

$$N_r = P_{rr} + \sum_{s \neq r} P_{rs} S_{rs}$$

where r and s are AO basis functions. Compute the population of each basis function for water using the \mathbf{P} and \mathbf{S} matrices given above. What chemical interpretation(s) can be associated with your computed values?