Molecular Dipole Moments

The dipole moment of a molecule is defined in terms of the molecules response to an applied electric field. Consider a molecule in a constant electric field of strength F. The molecular energy is a function of the electric field and may be expanded in powers of the field.

$$E(F)=E^0+\left(\partial E/\partial F\right)_0 F+\left(\partial^2 E\big/\partial F^2\right)_0 F^2\big/2+\left(\partial^3 E\big/\partial F^3\right)_0 F^3\big/3!+\ldots$$

E^0 is the energy in the absence of the field, while the first derivative of the energy with respect to the field, evaluated at zero field is the negative of the dipole moment in the direction of the field, $\mu_{F.}$ The higher derivatives define various polarizabilities that we will consider in detail latter. So

$$\mu_F=-\left(\partial E/\partial F\right)_0$$ dipole moment along F

$$\alpha_{FF}=-\left(\partial^2 E\big/\partial F^2\right)_0$$ Dipole polarizability

$$\beta_{FFF}=-\left(\partial^3 E\big/\partial F^3\right)_0$$ First hyperpolarizability

$$\gamma_{FFFF}=-\left(\partial^4 E\big/\partial F^4\right)_0$$ Second hyperpolarizability

Accordingly one may write

$$E(F)=E^0-\mu_F F-\alpha_{FF}F^2/2-\beta_{FFF}F^3/6-\gamma_{FFFF}F^4/24\ldots$$

One makes the connection with Quantum Mechanics by noting that the Hamiltonian for a molecule in the presence of a constant electric field along the z direction is

$$\hat{H}(F)=\hat{H}^0-F\hat{\mu}_z$$

where the dipole moment operator is defined as

$$\hat{\mu}_z=\sum_{i=1}^{particles} z_i q_i=-\sum_{i=1}^{electrons} z_i+\sum_{k=1}^{nuclei} Z_k z_k=\hat{\mu}_z^{electrons}+\hat{\mu}_z^{nuclei}$$

where the sum is over all charged particles in the molecule (electrons for which q_i =-1 and & nuclei for which q_i =Z_i, the atomic number). The eigenvalue problem to be solved is

$$\hat{H}(F)\psi(F) = E(F)\psi(F)$$

Where we suppress all electron and nuclear coordinates. Accordingly the energy in the field is

$$E(F) = \left\langle \psi(F) \middle| \hat{H}(F) \middle| \psi(F) \right\rangle$$

The wavefunction $\psi(F)$ may be expanded in powers of the electric field

$$\psi(F) = \psi(0) + \left(\partial\psi/\partial F\right)_0 F + \left(\partial^2\psi/\partial F^2\right)_0 F^2/2 + \ldots$$

$$\psi(F) = \psi^0 + \psi^{(1)}F + \psi^{(2)}F^2 + \ldots$$

and therefore the energy in the field may be written as

$$E(F) = \left\langle \psi^0 + \psi^1 F + \psi^2 F^2 \ldots \middle| \hat{H}^0 - F\hat{\mu}_z \middle| \psi^0 + \psi^1 F + \psi^2 F^2 \ldots \right\rangle$$

Expanding *E(F)* and keeping terms up those linear in *F* results in

$$E(F) = E^0 + 2F\left\langle \psi^{(1)} \middle| \hat{H}^0 \middle| \psi^0 \right\rangle - F\left\langle \psi^0 \middle| \hat{\mu}_z \middle| \psi^0 \right\rangle + O(F^2)$$

Since ψ^0 is an eigenfunction of $\hat{H}$ with eigenvalue E^0 we can write

$$\left\langle \psi^{(1)} \middle| \hat{H}^0 \middle| \psi^0 \right\rangle = E^0\left\langle \psi^{(1)} \middle| \psi^0 \right\rangle$$

and since the first order correction $\psi^{(1)}$ is orthogonal to ψ^0 (perturbation theory) one writes

$$E(F) = E^0 - F\left\langle \psi^0 \middle| \hat{\mu}_z \middle| \psi^0 \right\rangle + O(F^2)$$

From the definition of the dipole moment given above we see that

$$\mu_z = \left\langle \psi^0 \middle| \hat{\mu}_z \middle| \psi^0 \right\rangle = \left\langle \psi^0 \middle| \hat{\mu}_z^{electrons} \middle| \psi^0 \right\rangle + \mu_z^{nuclei}$$

One can show, in general that

$$\left\langle \psi^0 \middle| \hat{\mu}_z^{electrons} \middle| \psi^0 \right\rangle = -\int z\rho(\vec{r})dV$$

where $\rho(\vec{r})$ is the number electron density. The dipole moment is then calculated from

$$\mu_z = -\int z\rho(\vec{r})dV + \sum_{k=1}^{nuclei} z_k Z_k$$

and consists of an electronic and a nuclear contribution. One easily generalizes this formula to an arbitrary component, μ_a where $\alpha = x, y, z$

$$\mu_\alpha = -\int r_\alpha \rho(\vec{r})dV + \sum_{k=1}^{nuclei} r_{\alpha k} Z_k$$

Some observations on dipole moments

Dipole moments have the dimensions of charge times length and the traditional units of the dipole moment are Debyes, (D) defined as 10^{-18} esu (or electrostatic) units where an esu unit is a statcoulomb cm. These units are not SI units and the conversion factor is 1D= 3.333 10^{-30} C m (Coulomb meters). The above equations are written in atomic units (au) and 1au = 2.541765 D

Only netural molecules have a unique dipole moment. This is easily seen from the dipole moment formulae given above.

$$\mu_z = -\int z\rho(\vec{r})dV + \sum_{k=1}^{nuclei} z_k Z_k$$

The coordinates z and zk are relative to some origin in the molecule. If we translate the origin to the point $z = a$ and recomputed the dipole moment we have

$$\mu_z = -\int (z-a)\rho(\vec{r})dV + \sum_{k=1}^{nuclei} (z_k - a) Z_k$$

where the molecular density $\rho(\vec{r})$ remains unchanged in the translated coordinate system because it depends only on the coordinate of the point r relative to the molecular frame. From this expression we have

$$\mu_z(a) = -\int z\rho(\vec{r})dV + \sum_{k=1}^{nuclei} z_k Z_k + a\left(\int \rho(\vec{r})dV - \sum_{k=1}^{nuclei} Z_k\right) = \mu_z + a\left(N_{electrons} - \sum_{k=1}^{nuclei} Z_k\right)$$

If $\mu_z(a) = \mu_z$ then the number of electrons must equal the sum of the nuclear atomic numbers or the molecule must be neutral.

A dipole moment does not have a unique algebraic sign as it depends on the coordinate system. This is because the dipole operator is a linear function of the cartesian coordinate, x, y, or z and when one changes the orientation of the molecule in the coordinate system one changes its sign. For example consider the HF molecule. If one orients HF with the F atom at the origin and the H atom in the +z direction the dipole moment is +1.826 D. However if one keeps the F atom at the origin and places the H atom in the -z direction the dipole moment is -1.826 D.

The above demonstration of the equivalence between calculating the dipole moment from the energy (by adding an electric field (F) to the Hamiltonian, calculating the energy as a function of F and then numerically differentiating it) and calculating it as an expectation value was seen to depend on the wavefunction being an eigenfunction of $\hat{H}$. One can show that the equivalence obtains under significantly weaker conditions. In particular SCF and MCSCF wavefunctions where the orbitals are optimized with respect to all variational parameters will give the same dipole moment when calculated with either method. CI wave functions however will give different results when calculated as an expectation value or an energy derivative, and the energy derivative is preferred.