

# Computational Chemistry I

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Text book Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

## Chapter 4. Electronic properties (Cramer: chapter 9)

We have now some kind of wave functions and total energy of our system. What can we learn from them? As said in the first chapter the atomic total energy is very useful for many chemical properties. In this chapter we focus on the electronic properties which can be computer from the wave functions. One of the simplest quantities is the electron density

$$\rho(r) = \int \int \Psi^*(r, r_2 \dots, r_N) \Psi(r, r_2 \dots, r_N) dr_2 \dots dr_N$$

Note that the integral is over the coordinated  $r_2 \dots r_N$ . In the case of HF and DFT the  $\rho(r) = \sum_n |\varphi_n(r)|^2$ . Very often the dipole and higher moments of the molecule are interesting. The most general moment is

$$\langle x^n y^m z^k \rangle = \sum_{i \text{ atoms}} Z_i x_i^n y_i^m z_i^k + \sum_{j \text{ elec}} \int \Psi^*(r_1, r_2 \dots, r_N) x_j^n y_j^m z_j^k \Psi(r_1, r_2 \dots, r_N) dr_1 \dots dr_N$$

Again form DFT and HF

$$\langle x^n y^m z^k \rangle = \sum_{i \text{ atoms}} Z_i x_i^n y_i^m z_i^k + \sum_{n, j \text{ elec}} \int \varphi_n(r) x_j^n y_j^m z_j^k \varphi_n(r) dr$$

The dipole moment is  $\langle \mu \rangle = \langle r \rangle$  or  $\langle \mu \rangle = \sqrt{\langle x \rangle^2 + \langle y \rangle^2 + \langle z \rangle^2}$ . On average the DFT models will produce good dipole moments. The higher moments are also easy to compute but one need to remember that they depend on the origin of the coordinate system. This is typically the centre of mass of the molecule.

A good database for comparing the experimental and computer data can be found from:

<http://cccbdb.nist.gov/compdipole2x.asp>

Remember that the dipole moment can be computed for an arbitrary molecular geometry. This is useful if we are interested to IR vibrational intensities. The IR intensity will depend on the *change* of the dipole moment in the molecular vibration. Thus the difference in dipole moment can be computed with

$\Delta\mu = \mu(R_0) - \mu(R_0 + \delta V_i)$  where  $V_i$  is the atomic displacement of the  $i$ :th vibrational mode.

### Total electrostatic potential

One quantity that can be computed is the total electrostatic potential

$$V_{el}(r) = \sum_I \frac{Z_I}{|r - R_I|} - \int \frac{\rho(r_1)}{|r - r_1|} dr_1$$

The electrostatic potential is useful for analyzing the charge distribution of the molecules.

### Point charges

In chemistry it would be interesting to know the charge of each atom. Even this sounds simple it is not. The true quantity is the electron density and there is no unique (correct) way to determine the atomic charge.

One type of charge definition is based on the basis functions,  $\varphi_n(r) = \sum_m c_{n,m} \xi_m(r)$  now we can assign the basis functions to each atom. We use notation  $m(I)$  meaning that functions  $m$  are centered to atom  $I$ . Now the total amount of electrons is  $N$

$$N = \sum_{n \text{ elec}} \int |\varphi_n(r)|^2 d^3r = \sum_{n \text{ elec}} \sum_{m,l} \int c_{n,m} c_{n,l} \xi_m(r) \xi_l(r) d^3r$$

$$N = \sum_{n \text{ elec}} \left( \sum_I c_{n,m(I)}^2 + \sum_{J \neq I} S_{m(I),l(J)} c_{n,m(I)} c_{n,l(J)} \right)$$

The term in parenthesis for each atom I can be interpreted as an atomic charge. This is so called Mulliken charge. It is very easy to compute since all needed information in the quantum chemical calculations. Unfortunately it has strong basis function dependence (meaning that different basis function will give very different charges). Also the overlap contribution is odd.

A better way to compute the basis function based charge is to use a method proposed by Löwdin where an orthonormal basis is used.

$$\vartheta_n(r) = \sum_m S_{nm}^{-1/2} \xi_m(r)$$

Now

$$\varphi_n(r) = \sum_m a_{n,m} \vartheta_m(r) = \sum_{nm} c_{n,m} S_{nm}^{1/2} \vartheta_m(r)$$

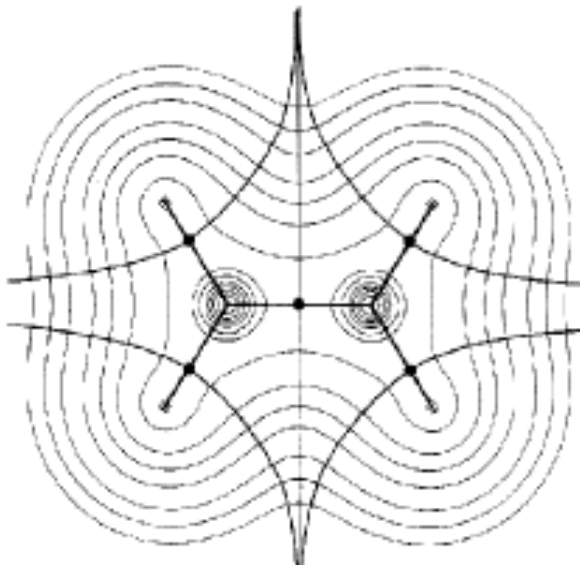
The Löwdin charges are much better than the Mulliken ones. Similar but even more realistic method is the Natural Population Analysis (NPA).

### Bader and similar charges

A completely different approach to determine the charge is the Bader method. In the Bader method the space is divided to parts and each atom has a relevant volume  $\Omega_I$ . The charge is defined as a simple integral

$$q_I = Z_I + \int_{\Omega_I} \rho(r) dr$$

Unfortunately the integration areas are complex. Bader have one definition of the integration volumes but other volumes, like Voronoy cells, can be used. The Bader analysis is usually done with separate program.



The charges can also be determined from the electrostatic potential. We can find the atomic charges that reproduced best the total el. potential.

$$V_{el}(r) = \sum_I \frac{Z_I}{|r - R_I|} - \int \frac{\rho(r_1)}{|r - r_1|} dr_1 = \sum_I \frac{q_I}{|r - R_I|}$$

These EPS charges are very useful for empirical modelling.

Polarization

If any molecule is in external electric field (or next to other molecules) its charge distribution will change. We can define polarization as

$$\alpha_{ij} = \frac{\partial \mu_i}{\partial E_j}$$

Where  $\mu$  is the dipole moment and  $E$  is the electric field. The polarization is useful to understand the "rigidity" of the electrons and also the Raman intensities are based on the change of polarization in the vibrational mode. (In Orca the Raman analysis require numerical frequency calculation, NumFreq.)

The polarization can be significant. In the case of water, in gas phase the dipole moment is 1.85 D and in liquid water around 3.0 D. The increase is due to the polarization.

The polarization can be computed with elprop keyword.

Also the higher order polarization terms can be defined

$$\mu = \mu_0 + E_i \frac{\partial \mu}{\partial E_i} + \frac{1}{2} E_i E_j \frac{\partial^2 \mu}{\partial E_i \partial E_j} = E_i \alpha_i + \frac{1}{2} E_i E_j \beta_{ij} + \dots$$

Here  $\beta$  is hyperpolarization. (Orca do not calculate hyperpolarization.)

## Vibrations

As mentioned in the first chapter the molecular vibrations can be calculated from the second derivative,

$$A_{IJ} = \frac{\partial^2 E_{tot}^{el}}{\partial R_I \partial R_J}$$

Often the second derivative can be computed analytically, but with more complex methods numerical second derivative has to be used. Once the  $A$  has been computed it can be used to solve the vibrational eigenvalues and -vectors.

$$\left( -\sum_i \frac{1}{2m_i} \frac{d^2}{dX_i^2} + \sum_{ij} X_i A X_j \right) \Phi(X) = E \Phi(X)$$

One need to choose mass weighted coordinates  $Q_i = \sqrt{m_i} X_i$  and  $B_{ij} = \sqrt{m_i m_j} A_{ij}$

$$\left( -\sum_i \frac{1}{2} \frac{d^2}{dQ_i^2} + \sum_{ij} Q_i B Q_j \right) \Phi(Q) = E \Phi(Q)$$

The vibrational modes ( $Q_i$ ) are eigenvectors of the matrix B.

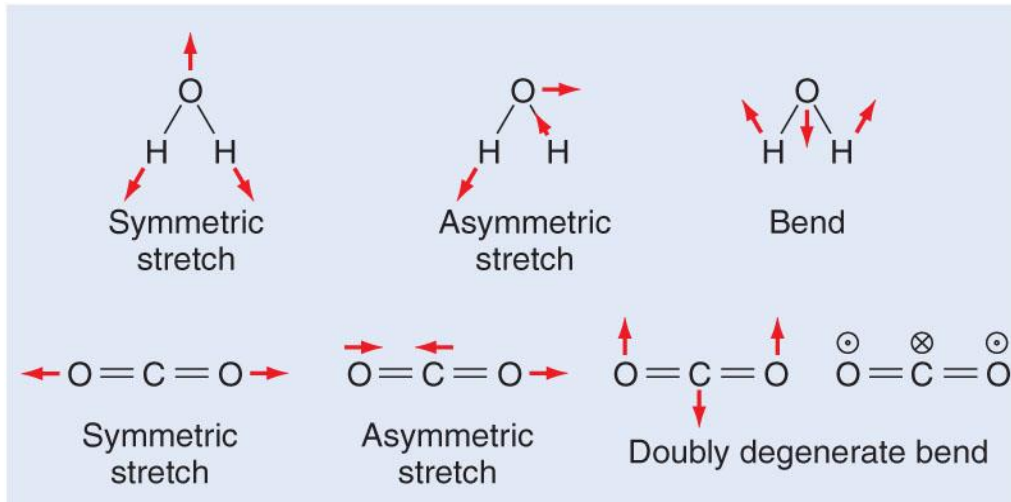
In classical mechanics the vibrational problem is easy. We can construct system of atoms connected with harmonic springs. We can take a water molecule as an example. It has 3 vibrational modes and we can build the molecules with two OH bonds (with force constant  $k_1$ ) and one H-O-H bending bond (with force constant  $k_2$ ). This sounds reasonable but in reality stretching one OH bond has small effect to the other OH bond (coupling constant  $k_{11}$ ). We can write a matrix equation of

$$M \ddot{x} = \begin{pmatrix} b_1 & b_{11} & b_{12} \\ b_{11} & b_1 & b_{12} \\ b_{12} & b_{11} & b_2 \end{pmatrix} x$$

Where the b's are the proper force constants in some coordinate system. M is a matrix containing the molecular masses (it depend on the coordinate system). Note usually this coordinate system is cartesian. We can diagonalize the B matrix and we find a new orthogonal coordinate systems  $\xi = \xi(x)$

$$\tilde{M} \ddot{\xi} = \begin{pmatrix} \kappa_1 & 0 & 0 \\ 0 & \kappa_2 & 0 \\ 0 & 0 & \kappa_3 \end{pmatrix} \xi$$

We know how the vibrational coordinate system depend of the old coordinates (x) and the values  $\kappa$  are the vibrational eigenvalues. Also  $\tilde{M}$  is diagonal but it depend on the atoms masses and the coordinate transform.



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## IR intensities

First, we need a term that describe the interaction of light and the molecule. The light is described with an time dependent electric field  $E(t) = E_0 \sin(\omega t)$ . In the first approximation the electric field is coupled to the **dipole moment,  $\mu(t)$** , of the molecule (there are higher order term like the quadrupole moment but we ignore them here.) So the coupling term is (both  $\mu$  and  $E$  are vectors)

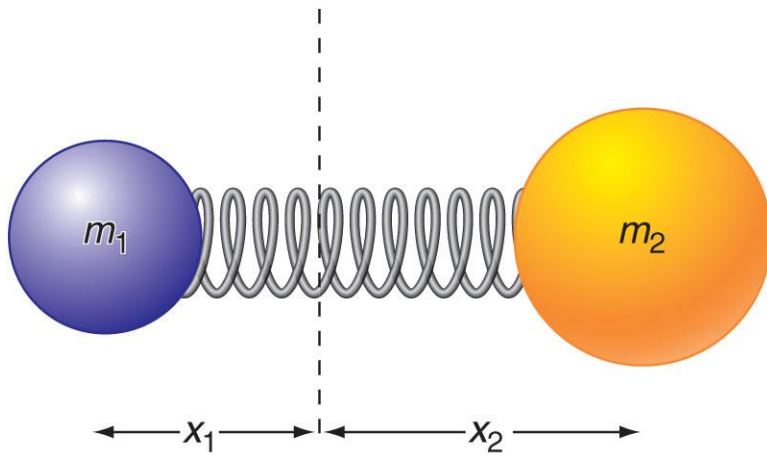
$$H(t) = -\mu(t) \cdot E(t)$$

The main result is the transition dipole rule:

$$\mu_{nm} = \int \varphi_n^*(x) \hat{\mu} \varphi_m(x) dx \quad (2.1)$$

In this equation the  $\varphi_n$  is the wave functions of the starting state and  $\varphi_m$  is the wave functions of the end state. Now we can compute any transition probability when the wave functions are known. (Even a good approximation of the wf will do.)

Let us apply this to a harmonic oscillator. The wave function is  $H_n(x) \exp(-\alpha x^2/2)$  but now we need to think carefully what the  $x$  means. It is the oscillation coordinate. In the case of two atom molecule it is the distance between the atoms.



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Also  $\mu = \mu_x$ , here  $\mu_x$  is x component of the dipole moment, we can choose coordinates such that the dipole vector is in x direction.

Now the dipole moment is

$$\mu(t) = \mu_0 + \frac{\partial \mu}{\partial x} x$$

The  $\mu_0$  is the dipole moment at equilibrium distance and the derivative tells the *change* of dipole moment in the vibration. When this is inserted to (2.1) we get

$$\mu_{nm} = \int \varphi_n^*(x) \mu_0 \varphi_m(x) dx + (d\mu/dx) \int \varphi_n^*(x) x \varphi_m(x) dx + \dots$$

The first term is 0 when  $n \neq m$  because the wave functions are orthogonal. The case where  $n=m$  is not interesting since nothing happens. The next term is the key term. It shows that the intensity will depend on the **change of dipole moment in the vibration.**

### Raman intensities

The electric field is time dependent  $E(t) = E_0 \sin 2\pi\nu t$ . This external electric field will pull the electrons and ions on different directions and the dipole moment of the molecule will



change:  $\mu(t) = \mu_0 + \alpha \cdot E(t)$  here the  $\alpha$  is the polarization of the molecule. Now also this change of the dipole moment with respect of the vibration can be measured.

$$\alpha(t) = \alpha_0 + \frac{\partial \alpha}{\partial x} x$$

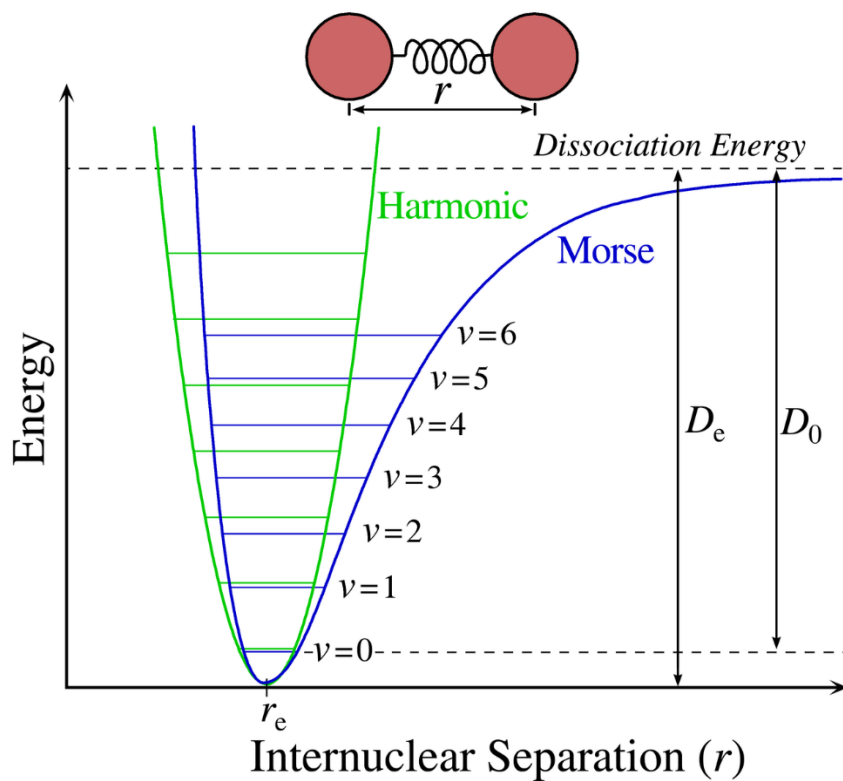
$$\mu_{nm} = \dots + E(d\alpha / dx) \int \varphi_n^*(x) x \varphi_m(x) dx + \dots$$

### Anharmonic effects

The anharmonic potential can be taken into account by fitting the scanned potential to the Morse potential

$$V(r) = D_e[(1 - \exp(-a(r - r_0)))^2 - 1] = D_e[\exp(-2a(r - r_0)) - 2\exp(-a(r - r_0))]$$

Where D is the dissociation energy.



The energies of the Morse potential are

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) - \frac{[\hbar\omega \left(n + \frac{1}{2}\right)]^2}{4D} = \hbar\omega \left(n + \frac{1}{2}\right) - \hbar\omega\chi \left(n + \frac{1}{2}\right)^2$$

The Morse potential fit can be done to all of the vibrational modes.

Orca will have an automatic methods for harmonic analysis, VPT2. So it should be used for anharmonic analysis for larger molecule than dimers. (see the manual).