



**Computational Chemistry Workshops**  
**West Ridge Research Building-UAF Campus**  
**9:00am-4:00pm, Room 009**

**Electronic Structure - July 19-21, 2016**  
**Molecular Dynamics - July 26-28, 2016**

**Interpreting the Results of MO Calculations**

## Total Energy

The total energy of a molecule is minus the energy that it takes to separate all particles (electrons and nuclei) in the molecule and put them in infinite distance of each other. Thus, the total energy is a very large number. It is measured in Hartree units (also called atomic units) which is abbreviated with the symbol  $E_h$ . It is very useful to remember conversion factors for more chemically relevant units of energy:

$$1 E_h = 27.2107 \text{ eV} = 627.51 \text{ kcal/mol} = 2625.5 \text{ kJ/mol} = 219474.2 \text{ cm}^{-1} \quad (1)$$

The majority of the quantum chemical literature still reports energy differences in kcal/mol ( $1 \text{ eV} = 23.06 \text{ kcal/mol}$ ;  $1 \text{ kcal/mol} = 4.184 \text{ kJ/mol}$ ). The spectroscopic literature is dominated by the units of  $\text{cm}^{-1}$  ( $1 \text{ eV} = 8065.73 \text{ cm}^{-1}$ ). It is a very good idea to familiarize yourself with several units of energy.

The nonrelativistic total energy of the CO molecule is approximately  $113 E_h$ , or  $\sim 71000 \text{ kcal/mol}$ . Chemically relevant energy differences are on the order of  $1 \text{ kJ/mol}$  which places the tremendous task of quantum chemistry into perspective. In quantum chemistry, there is the challenge of having to compute small differences between large numbers and do this with high accuracy. Fortunately, it is not necessary to compute the total energy of molecules to an accuracy of  $1 \text{ kJ/mol}$ . If this were the case, quantum chemistry would be a very frustrating research field. Only in recent years it is possible to reach such a high absolute accuracy and this is only possible for very small molecules.

In chemistry, energy differences are usually measured, and upon taking these differences, most of the errors that are made in computing the total energies will cancel. In fact, most of the total energy comes from the very strong interaction of the core level electrons with the nuclei, and such core electrons do not contribute appreciably to the chemical behaviour of atoms in molecules. Still, the basic problem of quantum chemistry is one of reaching sufficiently high accuracy to cope with energy differences that are quite small on the molecular scale, but that are dominant for the chemical behaviour of a molecule. It is relatively easy, for example, to recover  $\sim 99\%$  of the total energy, and the Hartree-Fock method is good enough to do that. Yet, the remaining error is huge on the chemical scale.

## Orbital Energies

In Hartree-Fock theory, each canonical molecular orbital is associated with a unique molecular orbital (MO) energy. Unlike the total energy, these orbital energies do not have an absolute meaning since they have been introduced into the theory only in order to satisfy the orthonormality constraint between different molecular orbitals. Fortunately, the orbital energies of the occupied orbitals can be given an approximate interpretation from Koopman's theorem. Thus, the orbital energy of a given canonical MO is approximately equal to minus the energy that it takes to remove an electron from this orbital, and is approximately equal to the first or a higher ionization potential.

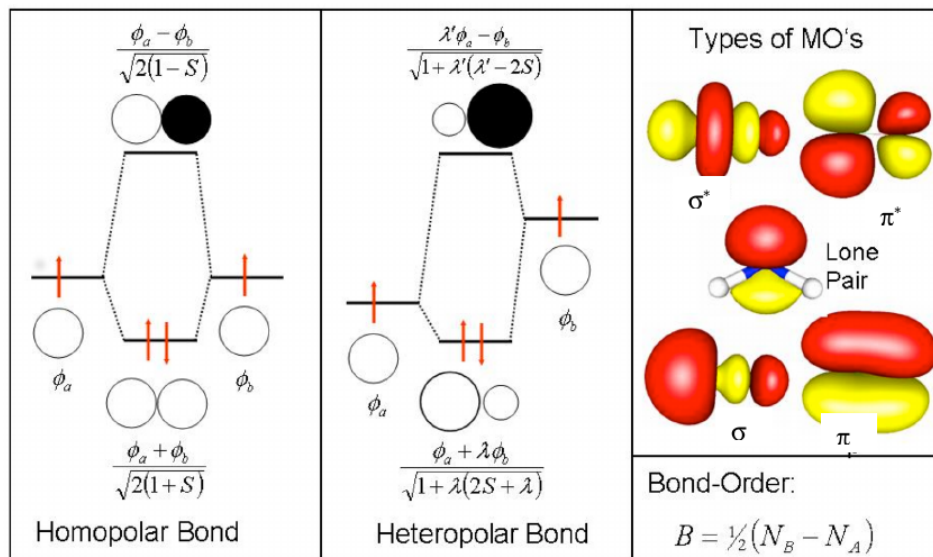
Koopman's Theorem makes the important prediction that minus the orbital energy of the

HOMO (the highest occupied MO) is approximately equal to the ionization potential of the molecule. Furthermore, by plotting the orbital energies as vertical bars on graph that has orbital energy on the  $x$ -axis, one should obtain a good idea where to expect peaks in the photoelectron spectrum of the molecule. This is a rather nice connection between MO calculations and spectroscopy and therefore the canonical orbitals are also called spectroscopist's orbitals. Upon comparing calculation and experiment, important deviations are usually discovered, and it is worthwhile to think about the origin of such discrepancies.

## Qualitative Shapes of Molecular Orbitals

Unlike the total Hartree-Fock  $N$ -electron wavefunction and its associated charge density, molecular orbitals themselves do not have a rigorous physical meaning. The orbitals are introduced into the theory as an auxiliary construct. Yet, in Hartree-Fock theory, each orbital describes the motion of one electron and the square of the orbital describes its probability distribution.

Recall that the canonical orbitals transform under the irreducible representations of the point group to which the molecule belongs. Also recall that the total symmetry of the state under investigation can be deduced from the symmetries of the singly occupied orbitals in a given electronic configuration. Each completely filled subshell is totally symmetric. Thus, closed shell molecules have a totally symmetric ground state. The basic types of molecular orbitals and the principle of their formation from fragment orbitals are shown in [Figure 1](#):



**Figure 1:** Basic Types of Molecular Orbitals.

In the left panel the formation of a homopolar bond is exemplified when two isoenergetic, singly occupied fragment orbitals form a standard two-electron bond. The lower component is bonding and features constructive overlap of the fragment orbitals. The higher MO is antibonding and more destabilized than the lower one is stabilized. The formation of a heteropolar bond is shown in the middle panel. Here two orbitals of different energy interact.

The initially higher-lying orbital is destabilized and becomes antibonding. The larger the energy gap and the smaller the orbital interaction, the more the orbital retains its initial character. Likewise, the lower energy component becomes bonding but also retains the character of the originally lower-lying fragment orbital,  $\phi_b$ .

The polarity of the bond depends on the energy gap between the two initial fragment orbitals and their mutual interaction which may be taken to be proportional to the fragment orbital overlap. The right panel shows some typical members of fragment orbitals, including a  $\sigma^*$  antibonding MO which is usually very high in energy, a  $\pi^*$ -orbital, a lone-pair orbital, as well as  $\sigma$ -bonding and  $\pi$ -bonding orbitals. The bond order of A-B bond is defined as one-half the number of electrons in the bonding orbitals minus the number of electrons in the antibonding orbitals. The bond order is indicative of but not directly proportional to the bond dissociation energy which, of course, depends on many factors.

## Total Charge Density, Dipole Moments and Population Analysis

In Hartree-Fock and DFT theory, the total electron density is given as a sum of contributions of the individual orbitals that make up the single Hartree-Fock or Kohn-Sham determinant. For a closed-shell system this is:

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\psi_i(\mathbf{r})|^2 \quad (2)$$

Where the factor of 2 arises because each MO is doubly occupied. From the total charge density, one can compute the various moments of the charge distribution. The most important is, of course, the dipole moment, an observable which is related to the polarity of the molecule. It is computed from the charge density, the nuclear positions ( $\mathbf{R}_A$ ), and nuclear charges ( $Z_A$ ), as follows:

$$\mu_{\text{dipole}} = \sum_{A=1}^M Z_A \mathbf{R}_A - \int \rho(\mathbf{r}) \mathbf{r} d\mathbf{r} \quad (3)$$

where the minus sign arises from the negative charge on the electrons. The dipole moment is given in atomic units. In order to convert to the more convention unit (Debye), one has to multiply the computed dipole moment given in a.u. by 2.541798. The dipole moment is a vector that points from the center of negative charge of the molecule to the center of positive charge.

An important concept of chemistry is that of a partial charge of an atom in a molecule. Unlike the dipole moment the partial charges are not observables. Unfortunately, it seems to be impossible to arrive at a unique decomposition of the total electron density, which is a continuous function of space, into parts that belong to individual atoms. Many different attempts have been made to arrive at an approximate decomposition and these procedures are collectively referred to as population analysis. None of these schemes can claim any rigorous physical reality. Yet, if viewed with appropriate caution, partial charge can tell much

about the *trends* of the charge distribution in a series of related molecules. Consequently, almost all quantum chemical programs print one or the other form of population analysis in their output files. For example, ORCA prints by default, the Mulliken analysis, the Löwdin analysis, and the Mayer analysis.

The origin of Mulliken population analysis is reviewed briefly below. The Mulliken population analysis is, despite all its known considerable weaknesses, is standard output in most quantum chemical programs. It partitions the total density using the assignment of basis functions to given atoms in the molecules and the basis function overlap. Mulliken proposed to divide the second term equally between each pair of atoms involved and define the number of electrons,  $N_A$ , on center  $A$  as:

$$N_A = \sum_{\mu}^A \sum_{\nu}^A P_{\mu\nu}^{AA} S_{\mu\nu}^{AA} + \sum_{B \neq A}^A \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu}^{AB} S_{\mu\nu}^{AB} \quad (4)$$

where the overlap integral is defined as  $S_{\mu\nu} = \int \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) d\mathbf{r}$  and  $P_{\mu\nu}$  are elements of the density matrix,  $\mathbf{P}$ .

The charge,  $Q_A$ , on atom  $A$ , in a molecule is

$$Q_A = Z_A - N_A \quad (5)$$

where  $Z_A$  is the core charge of atom  $A$ .

The cross terms between pairs of basis functions centered on different atoms is the overlap charge and is used to define the Mulliken overlap population analysis,  $B_{AB}$ :

$$B_{AB} = 2 \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu}^{AB} S_{\mu\nu}^{AB} \quad (6)$$

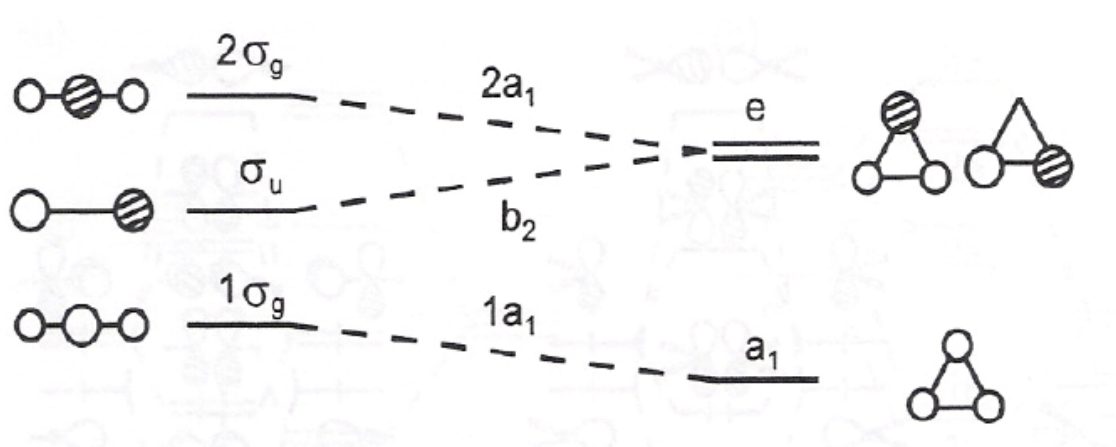
It is important to observe the results of the population analysis schemes and try to determine whether the observed trends compare well with chemical intuition. In addition to the problems with population analysis schemes mentioned above, be aware that they are sensitive to the basis set used, and do not converge to a well-defined basis set limit. Therefore, when comparing population analysis results for different molecules, make sure that the calculation are performed with identical basis sets. Do not compare absolute populations between different basis sets.

## Walsh Diagrams

Walsh diagrams are the graphical representation of the MO energies which depend upon the change of a geometrical parameter, most commonly a bond angle.

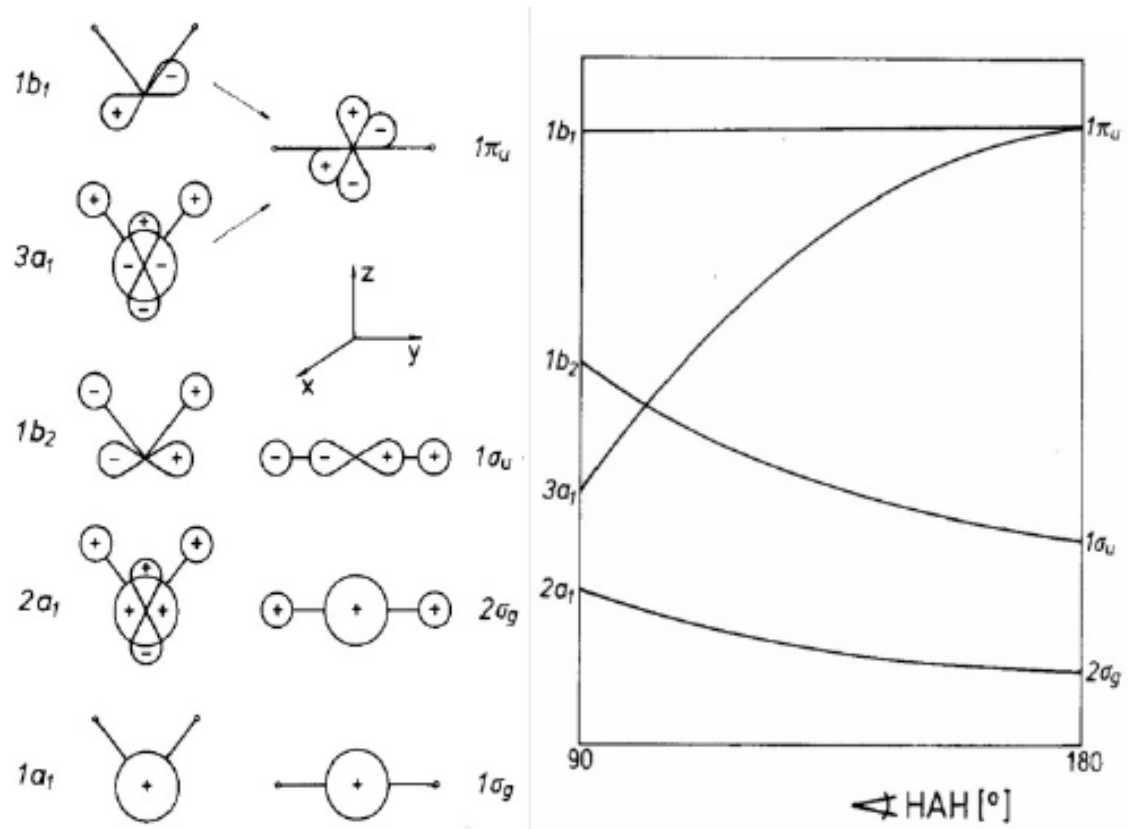
The variations of the orbital energies with geometry obtained from walsh diagrams can be used to obtain important, general insights about the geometric structures of molecules. In fact, many areas of chemistry have profited from performing such qualitative calculations.

For example, consider the case of the  $\text{H}_3$  molecule in linear and triangular geometries as shown in [Figure 2](#). It is observed that upon bending, the energy of the nonbonding  $\sigma_u$  orbital correlates with a  $b_2$  orbital in  $C_{2v}$  symmetry, strongly increases in energy, and finally correlates with one component of the antibonding  $e$ -orbital in the final  $D_{3h}$  structure. Since there are three electrons to be placed into the three MOs, it is predicted that  $\text{H}_3$  should be linear with configuration  $(1\sigma_g)^2(1\sigma_u)^1$  while  $\text{H}_3^+$  should be bent with an  $(a_1)^2$  configuration, since the  $a_1$  orbital is stabilized upon bending.



**Figure 2:** Walsh Diagram for the Distortion of  $\text{H}_3$ .

The Walsh diagram for the bending mode of an  $\text{AH}_2$  molecule is shown in [Figure 3](#). The energy of the lowest valence MOs decrease upon bending as three-center bonding between  $s$ -AOs becomes more favourable in the bent form. The  $1\sigma_u$  MO is strongly bonding in the linear case, but upon reducing the angle, the  $1b_2$  MO becomes only weakly bonding. The reason is that, in the linear case, the  $2p_y$  AO can interact more strongly with the AOs of the H atoms. The  $1\pi_u$  MO separates into the  $1b_1$  and  $2a_1$  orbitals. The energy of the  $1b_1$  MO remains essentially constant, while the  $2a_1$  orbital decreases in energy upon bending. The overlap of the  $2p_z$  AO from A with  $1s$  AOs from the H atoms is zero in the linear case, but results in three-center bonding by reducing the angle.

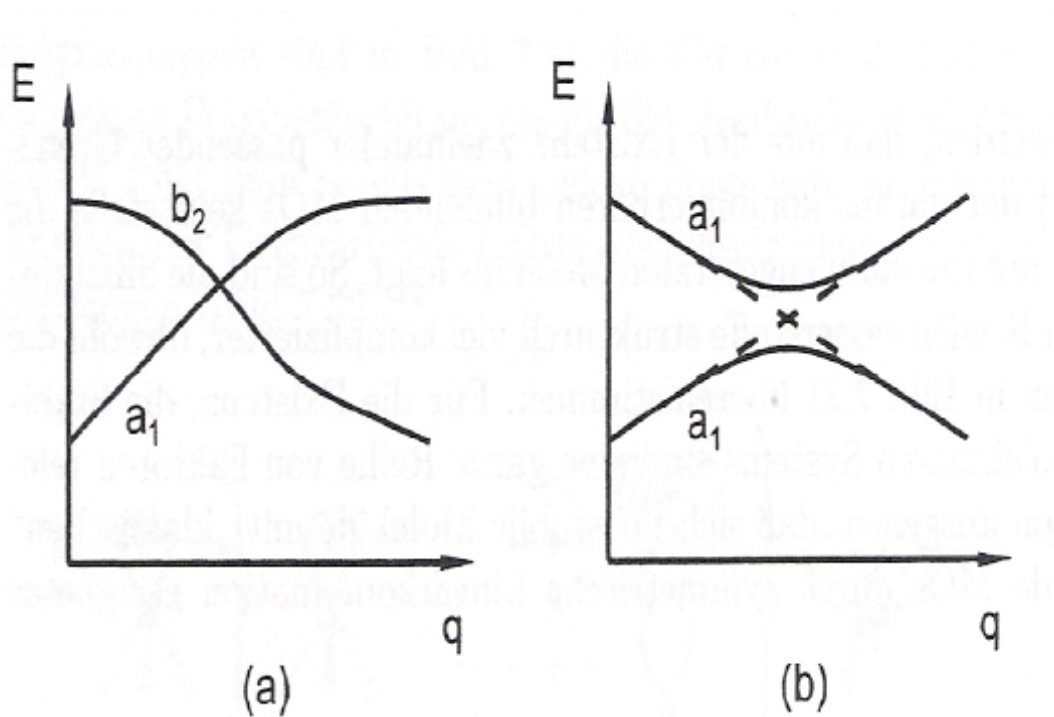


**Figure 3:** Walsh Diagram for an  $AH_2$  Molecule.

## The Non-Crossing Rule

The variation of a geometrical degree of freedom may cause a crossing of different MO energy levels. In general, such a crossing is allowed if the two MOs transform under different irreducible representations and is avoided otherwise which is called the *non-crossing rule* as shown in [Figure 4](#).

The non-crossing rule is particularly important for the interpretation of photochemical reactions. The occurrence of a HOMO-LUMO crossing, both of the same symmetry, implies that the reaction is symmetry forbidden, because of non-conservation of orbital symmetry for these occupied MOs. Therefore, a high activation energy for the reaction is expected.



**Figure 4:** Crossing and Avoided Crossing of Two Energy Levels.



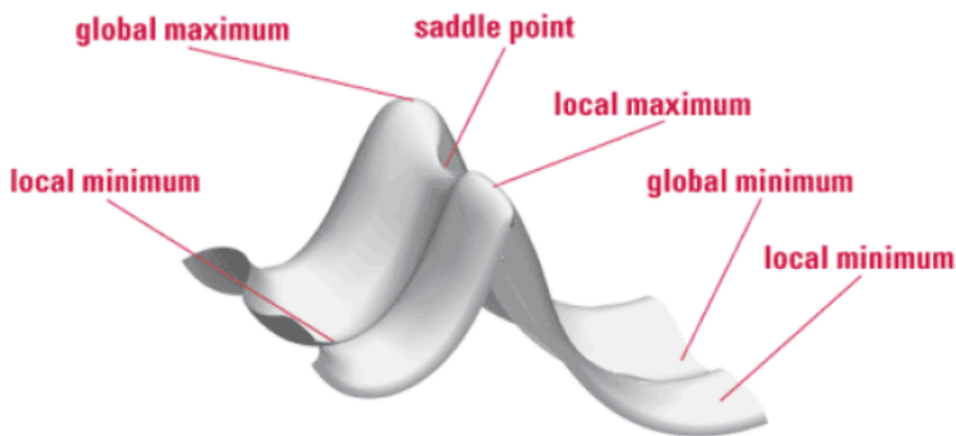
# Geometry Optimization

One of the salient capabilities of computational chemistry calculations is an ability to locate the most stable arrangement of the atoms in molecules under study. In the case of a diatomic molecule, geometry optimization is employed to search for the suitable interatomic distance between two atoms, which gives rise to the lowest energy among all possible interatomic distances.

## Potential Energy Surface (PES)

The way in which the energy of a polyatomic molecule varies with coordinates is usually referred to as the potential energy surface (PES), sometimes called the hyper-surface. Except for the very simplest systems, the PES is a complicated, multi-dimensional function of all degrees of freedom of the molecule. For a non-linear molecule with  $N$  atoms, the energy is thus a function of  $3N - 6$  internal coordinates. It is, therefore, impossible to visualize the entire energy surface except for some simple cases where the energy is a function of just one or two coordinates.

For a typical PES depicted in Figure 5, each point corresponds to the specific arrangement of the  $N$  atoms in the molecule, and each point represents a particular molecular structure, with the height of the surface at that point corresponding to the energy of that structure.



**Figure 5:** Schematic PES Adapted from Exploring Chemistry with Electronic Structure Methods, Second Edition.

There are three minima on the PES shown in Figure 5:

- Minima that are at the bottom of a valley on the PES, and, any movement away from such a point gives a configuration with a higher energy. A minimum can be either a *local minimum* or a *global minimum* which is the lowest energy on the entire PES.

Minima occur at equilibrium structures for a molecular system, with each specific minimum corresponding to a different conformation or structural isomer, in the case of

a single molecule, or reactant and product molecules, in the case of a multi-component system.

- A point which is a maximum in one direction, but a minimum in all other directions, is called a *saddle point*, or more precisely, a first-order saddle point.

A saddle point corresponds to a *transition structure* connecting the two equilibrium structures, or to a reactant and product.

## Searching for Minima

A geometry optimization usually attempts to locate a minimum on the PES, thus predicting equilibrium structures of molecular system. Optimizations can also locate transition states which may be desired or undesired. At both minima and saddle points, the first derivative of the energy (gradient) with respect to every internal degree of freedom is zero. Since the gradient is the negative of the force, it means that at such points the forces are zero as well. Points at which the gradient of the energy vanishes are called *stationary points*, and may represent true minima or saddle points.

The energy,  $E$ , of a molecular system obtained under the Born-Oppenheimer approximation is a parametric function of the nuclear coordinates, denoted by  $\mathbf{R}$ . The energy can be expanded in a Taylor series about the  $k^{\text{th}}$  iteration point of the geometry optimization,  $\mathbf{R}^k$ , as follows:

$$E(\mathbf{R}) = E(\mathbf{R}^k) + (\mathbf{R} - \mathbf{R}^k) \mathbf{f} + \frac{1}{2}(\mathbf{R} - \mathbf{R}^k)^T \mathbf{H} (\mathbf{R} - \mathbf{R}^k) + \dots \quad (7)$$

where  $\mathbf{R}_0$  are the equilibrium coordinates, and the gradient is defined as

$$f_i(\mathbf{R}) = \left. \frac{\partial E(\mathbf{R})}{\partial R_i} \right|_{\mathbf{R}=\mathbf{R}^k} \quad (8)$$

The Hessian or force constant matrix is given as

$$H_{ij} = \left. \frac{\partial^2 E(\mathbf{R})}{\partial R_i \partial R_j} \right|_{\mathbf{R}=\mathbf{R}^k} \quad (9)$$

An energy function of a molecule as a function of  $\mathbf{R}$  is hardly quadratic and the Taylor series expansion, known as the harmonic approximation, can be considered as only an approximation. Close to a minimum, it is supposed that a quadratic form is adequate for the description of the PES. For a stationary point,  $\bar{\mathbf{R}}$ , it is required by definition that the gradient at  $\bar{\mathbf{R}}$ ,  $\mathbf{f}(\bar{\mathbf{R}}) = 0$ . In order to determine whether or not a stationary point is a local minimum and not a saddle point, the following condition must be met:

$$\eta_i(\bar{\mathbf{R}}) > 0 \quad (10)$$

where  $\eta_i(\bar{\mathbf{R}})$  is the  $i^{\text{th}}$  eigenvalue of the Hessian matrix after the translations and rotations have been projected out. This corresponds to the condition that there is no imaginary frequency from a frequency calculation, and is, consequently, either a local or global minimum.

For a first-order saddle point, the following conditions are necessary:

- $\mathbf{f}(\bar{\mathbf{R}}) = 0$
- $\eta_i(\bar{\mathbf{R}}) < 0$  for one specific coordinate, i.e. the internal reaction coordinate.
- $\eta_i(\bar{\mathbf{R}}) > 0$  for all other coordinates within the molecule.

Exactly one imaginary frequency is indicative of a first-order saddle point. In a similar manner, higher order saddle points can be defined according to the number of imaginary frequencies and may be important for conical intersections.

Note that geometry optimization searches only for stationary points, and it is not known for sure whether or not the structures are located at a local minimum or a saddle point. In order to determine which is correct with certainty, it is necessary to perform a frequency calculation on the optimized structure.

## Optimization Techniques

There are a number of numerical methods, including Newton-Raphson and quasi-Newton algorithms, for finding stationary point of a function of many variables. Close to a stationary point, a Taylor series expansion of the energy of the molecule under study is valid:

$$E_{\text{quadratic}}(\mathbf{R}) = E(\bar{\mathbf{R}}) + (\mathbf{R} - \bar{\mathbf{R}}) \mathbf{f} + \frac{1}{2}(\mathbf{R} - \bar{\mathbf{R}})^T \mathbf{H} (\mathbf{R} - \bar{\mathbf{R}}) + \dots \quad (11)$$

If  $\mathbf{R}$  is close enough to  $\mathbf{f}(\bar{\mathbf{R}})$ , the structure of the molecule is considered to be in the quadratic regime, and it is reasonable to replace the exact surface  $E(\mathbf{R})$  with the quadratic model surface,  $E_{\text{quadratic}}(\mathbf{R})$ . It is now straightforward to minimize the energy of this model surface. If the geometry optimization process takes the molecular system close to the quadratic regime, optimization will be quadratically convergent. The system will be brought to the desired stationary point in a few iterations.

For real surfaces which are not quadratic, convergences will be considerably slower. In general, convergence slows down substantially, if the present point,  $\mathbf{R}$ , is far from the stationary point. Using an appropriate optimization technique and a reasonably starting point for the initial geometry, convergence can usually be achieved in 10-40 iterations, depending on the size and nature of the molecule. In general, floppy molecules are much more difficult to optimize because low energy rotations around single bonds may lead to very large geometry changes along very soft vibrational modes. All optimization techniques have difficulty with these situations, and it is important to guide the calculation to the desired minimum and to carefully monitor the progress of a geometry optimization.

# Computational Thermochemistry

Within the framework of computational thermochemistry, methods of statistical thermodynamics are applied, in order to derive thermochemical reaction quantities and energies of chemical bonds, which are important properties for the experimental chemist. It will become evident that frequency analysis is an essential tool of computational thermochemistry.

## Basics of Statistical Thermodynamics

The link between microscopic molecular quantities and macroscopic observables of a chemical system is provided by the partition function,  $q$ , of the system which is based on the Boltzmann distribution over the available microstates as shown in [Equation 12](#)

$$q = \sum_{j=0}^N \omega_j e^{-\frac{\varepsilon_j}{k_B T}} \quad (12)$$

Here  $N$  denotes the total number of accessible states,  $\varepsilon_j$ , the energy of the  $j^{\text{th}}$  state,  $k_B$  the Boltzmann constant, and  $T$ , the temperature in Kelvin. The term  $k_B T$  can be interpreted as the available thermal energy. The factor,  $\omega_j$ , is given by the degeneracy of the  $j^{\text{th}}$  state and equals one if the corresponding state is not degenerate.

Consider a homogenous chemical system consisting of molecules, e.g. a monomolecular gas. From the macroscopic perspective, the components of the system include molecules and energy states,  $\varepsilon_j$ , which depend on the arrangement of the components and the corresponding energies. The corresponding **microcanonical** partition function,  $q$  shown in ??, treats the single molecule as a sum configurations, along with the corresponding molecular energy states. As an initial approximation, the total energy of a molecule can be split up into contributions from each of the degrees of freedom, a direct result of the Born-Oppenheimer approximation:

$$\varepsilon = \varepsilon^{\text{trans}} + \varepsilon^{\text{rot}} + \varepsilon^{\text{vib}} + \varepsilon^{\text{el}} \quad (13)$$

Thus, the molecular partition can be factorized according to:

$$q = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{el}} \quad (14)$$

With this result, the calculation of the molecular partition function is now feasible by employing quantum chemical solutions of various models, such as the particle in a box or harmonic oscillator with appropriate degrees of freedom, which can then be used to calculate the molecular partition function. For example, the application of the harmonic oscillator energy eigenvalues to the vibrational partition function of a diatomic molecule yields the expression:

$$q_{\text{vib}} = \frac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}} \quad (15)$$

Thus, the normal mode frequencies of the system are the only variables needed to compute the vibrational partition function. Similar expressions for partition functions can also be derived which depend on the degrees of freedom and molecular quantities, such as the moment of inertia and volume determined from the ideal gas law.

The electronic partition function includes a summation over quantum states of the system which are obtained by solving the electronic Schrödinger equation:

$$q_{\text{el}} = \sum_{j=0}^N \omega_j e^{-\frac{\epsilon_j^{\text{el}}}{k_B T}} \quad (16)$$

In most cases, excited electronic states cannot be populated by the available thermal energy, and are left out of the summation. A further simplification is implemented by setting the zero of energy to the electronic energy ground state, which leads to the reduction of the degeneracy factor to  $\omega_1$  for electronic partition function.

## Thermochemical Quantities

The partition function contains all necessary information for the determination of the thermochemical quantities of the system. For example, the internal thermal energy,  $E$  can be obtained from the partition function by using the following equation:

$$E = N_A k_B T^2 \left( \frac{\partial \ln q_{\text{tot}}}{\partial T} \right)_V \quad (17)$$

which equals the internal energy,  $E$  of the system, if the volume,  $V$ , remains constant and the internal energy at 0 K is zero. Since the internal energy is a basic quantity in equilibrium thermodynamics, expressions for all other thermochemical state functions can be derived on the basis of the partition function.

After the partition function for the system is calculated, it can be used to determine thermochemical quantities such as the internal energy. Since partition function factorization is the basis of these calculations, it is common to distinguish between the contributions from the different molecular degrees of freedom to the quantity under investigation. For calculating the energy  $E$ , the corresponding partition function,  $q$  becomes:

$$q_{\text{tot}} = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{el}} \quad (18)$$

Other thermochemical quantities, similar to [Equation 17](#), can be derived in an analogous manner by starting with the classical expression and substituting a known function by its derived from Statistical Mechanics. For example, in case of enthalpy,  $H$ , the following additive equation can be used:

$$H_{\text{tot}} = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + H_{\text{el}} \quad (19)$$

Most common quantum chemical program packages use the ideal gas law and models of the *rigid rotor* and *harmonic oscillator* as the basis for the calculation of the partition function. Carrying out the differentiations according to the statistical expressions yield enthalpy contributions of  $H_{\text{trans}} = H_{\text{rot}} = \frac{3}{2}RT$  (*Equipartition Theorem*) for the rotational and translational degrees of freedom, whereas the vibrational component is given by

$$H_{\text{vib}} = N_A k_B \sum_{i=1}^{3N-6(7)} \left( \frac{h\nu_i}{2k_B} + \frac{h\nu_i}{k_B} \cdot \frac{1}{e^{\frac{h\nu_i}{k_B T}} - 1} \right) \quad (20)$$

The summation is carried out over all vibrational degrees of freedom, which in the case of a non-linear molecule, equals  $3N - 6$ . If the structure under investigation is a transition state, i.e. a maximum on the potential energy surface along one direction, the corresponding vibrational degree of freedom is imaginary and left out in the summation, thus reducing the number of vibrational degrees of freedom to  $3N - 7$ . The first term of the vibrational enthalpy is a sum of temperature-independent terms ( $h\nu_i/2k_B$ ), which is referred to as the zero point energy (ZPE), whereas the second term depends on the temperature, and accounts for the energy molecules which are not in the vibrational ground state. If the electronic ground state is not degenerate,  $H^{\text{el}}$  and  $S^{\text{el}}$  reduce to zero, and reaction enthalpies are directly given by the difference of the electronic energies of the reactants.

The following table summarizes the most common thermochemical functions and their expression in terms of the partition function.

Thermodynamic Quantity	Equation
Entropy, $S$	$S = N_A k_B T \left( \frac{\partial \ln q}{\partial T} \right)_V + N_A k_B \ln q$
Enthalpy, $H$	$H = N_A k_B T^2 \left( \frac{\partial \ln q}{\partial T} \right)_V + N_A k_B T V \left( \frac{\partial \ln q}{\partial V} \right)_T$
Free Energy, $G$	$G = N_A k_B T V \left( \frac{\partial \ln q}{\partial T} \right)_V - N_A k_B T \ln q$

**Table 1:** Thermodynamic Quantities in Terms of Partition Functions

The entropic contributions can be partitioned into individual component contributions as shown in [Table 2](#).

Entropy Component
$S_{\text{trans}} = \frac{5}{2} N_A k_B + N_A k_B \cdot \ln \left( \frac{V}{N_A} \cdot \left( \frac{2\pi M k_B T}{h^2} \right)^{\frac{3}{2}} \right)$
$S_{\text{rot}} = \frac{1}{2} N_A k_B \left( 3 + \ln \left( \frac{\sqrt{\pi}}{\sigma} \cdot \sqrt{I_1 I_2 I_3} \cdot \left( \frac{8\pi^2 k_B T}{h^2} \right)^{\frac{3}{2}} \right) \right)$
$S_{\text{vib}} = N_A k_B \sum_{i=1}^{3N-6(7)} \left( \frac{h\nu_i}{k_B T} \cdot \frac{1}{e^{\frac{h\nu_i}{k_B T}} - 1} - \ln \left( 1 - e^{-\frac{h\nu_i}{k_B T}} \right) \right)$

**Table 2:** Individual Entropic Contributions to the Total Entropy

Here  $V$  and  $M$  denote the volume of the system, according to the ideal gas law, and the molecular mass, respectively. For a molecule which belongs to a point group with rotational

symmetry operations, the symmetry number,  $\sigma$ , is determined by the order of the rotational subgroup and the number of rotational operations needed to take the molecule to the starting structure. The principle moments of inertia,  $I_1, I_2, I_3$  are the eigenvalues of the diagonalized moment of inertia matrix, which are included in the output of the frequency calculation, as well as the vibrational frequencies,  $\nu_i$ . Knowledge of these basic thermochemical quantities allows the calculation of the free energy,  $G = H - TS$ . As mentioned above, the output of a frequency calculation contains information about the partition function as well as most thermochemical quantities.

## Transition State Theory

From a microscopic point of view, one is interested in understanding the value of the kinetic reaction rate constant,  $k$ , from first principles. Phenomenologically, one already knows that  $k$  is temperature dependent and obeys the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}} \quad (21)$$

where  $A$  is a pre-exponential factor,  $R$  the gas constant,  $T$  the temperature, and  $E_a$  is a key quantity, called the activation energy. The larger the value of  $E_a$ , the slower the reaction.

More detailed insight into reaction rates can be obtained from the *transition state theory* of Eyring. In this case, one assumes that two reactants,  $A$  and  $B$ , pass through a special geometrical arrangement,  $(AB)^\ddagger$ -the *transition state*, before decaying to the products  $C$  and  $D$  according to the equation



The assumption of a pseudo-steady state concentration for  $(AB)^\ddagger$ , leads to the rate constant for bimolecular decay is given by:

$$k = K^* k^* \quad (23)$$

where  $K^*$  (equilibrium constant for transition state) =  $\frac{k_1}{k_{-1}}$ .

From Quantum Mechanics,

$$k^* = \kappa \frac{k_B T}{h} \quad (24)$$

where  $k_B = 1.38 \times 10^{-38}$  J/K is the Boltzmann constant,  $h$  Planck's constant, and  $\kappa$  is a transmission coefficient, which is usually close to unity. The equilibrium constant,  $K^*$ , is related to the free energy of the transition state relative to the reactant energies is by:

$$K^* = e^{-\frac{\Delta G^\ddagger}{RT}} \quad (25)$$

and

$$k = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (26)$$

Where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the enthalpy and entropy of the transition state. Thus, one identifies the parameters of the Arrhenius equation with:

$$A = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}}, \quad E_a = \Delta H^\ddagger \quad (27)$$

$\Delta H^\ddagger$  can be calculated, but  $\Delta S^\ddagger$  is slightly more difficult to obtain.

## Approximate Distribution of Conformations

Briefly, the total energy of a molecule consists, to a good approximation, of additive contributions from its electronic energy, nuclear repulsion, the translational energy, the rotational energy, and vibrational energy. The vibrational energy contribution may be divided into a component corresponding to the zero-point energy,  $E_{\text{zpe}}$ , which is the sum of the energies of all  $\nu = 0$  vibrational levels and a thermal correction ( $E_{\text{vib}^*}$ ), derived from a Boltzmann-population for the higher vibrational levels of the system.

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}^*} + E_{\text{zpe}} \quad (28)$$

Contributions from translational, rotational and excited vibrational states are frequently negligible in comparison to the energies of different isomers, but the zero-point correction, where  $\nu_k$  is the  $k^{\text{th}}$  vibrational frequency of the molecule,

$$E_{\text{zpe}} = \sum_{k=1}^{3N-6} h\nu_k \quad (29)$$

may be important.

After determining several stationary points and their character on the potential energy surface which correspond to different conformers or electronic states, it may be of interest to determine the population of these states at a specified temperature. In this situation, Boltzmann statistics can be employed. In Boltzmann statistics the fractional population of the  $i^{\text{th}}$  state is given by:

$$\frac{N_i}{N} = \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_j e^{-\frac{\epsilon_j}{kT}}} \quad (30)$$

where  $N_i$  is the number of molecules in the  $i^{\text{th}}$  energy level,  $\epsilon_i$ ,  $N$ , the total number molecules,  $k$  is the Boltzmann constant, and  $T$  the temperature in Kelvin where the sum includes all energy states.



A word of caution: to find a transition state with quantum chemical programs is not an easy task. Since a calculation has no way to guess a transition state from a stable structure, it is important to guide the calculation to the desired transition state by providing structures that are close to the final TS. However, this means necessarily, that the outcome of the calculations depends on skill to guess a reasonable TS. There is no guarantee that the calculation, based on the initial guess, will lead to a TS with the lowest energy. If the calculation does not find a desired TS, it may be necessary to start over and provide a better starting structure. In calculating chemical reactions, chemical intuition, experience and luck are crucial for success.

## Kinetic Isotope Effects

There are two origins of the kinetic isotope effect.

1. quantum mechanical tunnelling through the reaction potential energy barrier, is usually only important at very low temperatures and for reactions involving very light atoms. It may be estimated from the change in the transmission coefficient caused by the change in the imaginary frequency that leads to the transition state (See Wigner's expression above.).
2. more importantly, however, kinetic isotope effects are also caused by differences in the activation energy for reactions involving different isotopes, since the reactants and the transition state have different zero-point vibrational energies.

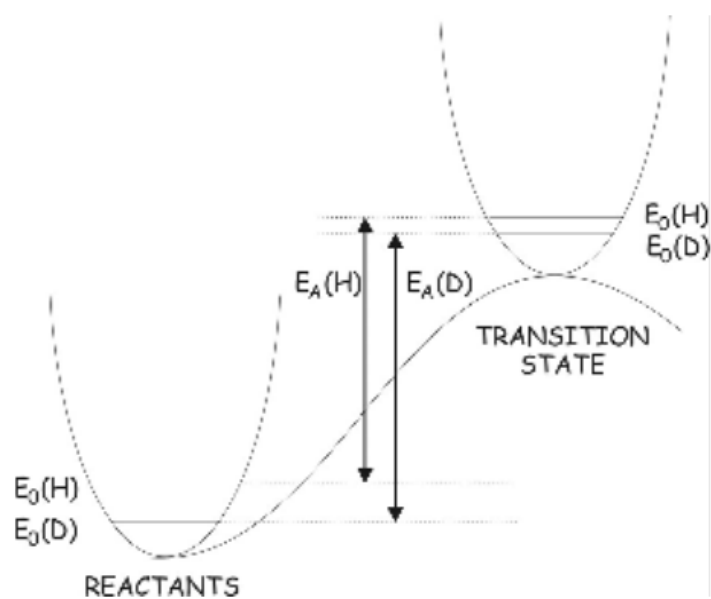
The effect on the activation barrier for a reaction involving, involving both H and D atoms, is shown in [Figure 6](#) below:

The net effect is that the activation energy is *higher* for the heavier isotope, and, therefore the reaction will be slower. The maximum isotope effect is obtained when the bond involving the isotope is completely broken in the transition state, and the difference in activation energies becomes simply the difference in zero point energies of the stretching frequencies for the bond being broken. From transition state theory, one readily deduces:

$$\frac{k_H}{k_D} = e^{-\frac{\Delta H^\ddagger(H) - \Delta H^\ddagger(D)}{k_B T}} \quad (31)$$

where H and D indicate the two isotopes hydrogen and deuterium, and is the most frequently studied isotope effect.

The difference,  $\Delta H^\ddagger(H) - \Delta H^\ddagger(D)$ , is almost entirely determined by the differential contributions to the ZPE,  $\Delta H_{\text{vib}}^\ddagger$ . In some reactions, it is mainly the zero point energy difference between isotopically substituted reactant species and the transition state which governs the kinetic isotope effect. In this case, the activation energy is larger for the lighter isotope and an inverse isotope effect is observed, in which the heavier isotope containing reactant undergoes faster reaction.



**Figure 6:** Energetic quantities in the calculation of chemical reactions of qualitative potential energy surfaces. The reaction path is plotted on the  $x$ -axis, while the the total energy is is given on the  $y$ -axis