Chapt 11 summary
More about activation energies

Chapter 11 has three topics

- Qualitative effects of the Polanyi equation: Hammett equation, etc
- Using the methods quantitatively
- Introduction to quantum methods - useful when the methods fail.

Qualitative effects of the Polayni's model:

Polayni's equation is:

$$\boxed{E_a = E_a^o + \gamma_P \Delta H_r}$$

(10.14)

Note that from arhenius' law equation

$$k = k_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

rearranging

$$\ln(k) = \frac{E_a}{kT} = \frac{E_a^0}{kT} + \gamma_p \frac{\Delta H_r}{kT}$$

Hammett rewrote the result as

$$\ln(k) = \frac{E_a}{kT} = \frac{E_a^0}{kT} + \gamma_p \frac{\Delta G_r}{kT}$$

note

$$\mathrm{Ln}[K_{ac}] = -\frac{\Delta G_{ac}}{k_B T}$$

Therefore:

$$\ln(k) = \frac{E_a^0}{kT} + \gamma_p \ln(K)$$

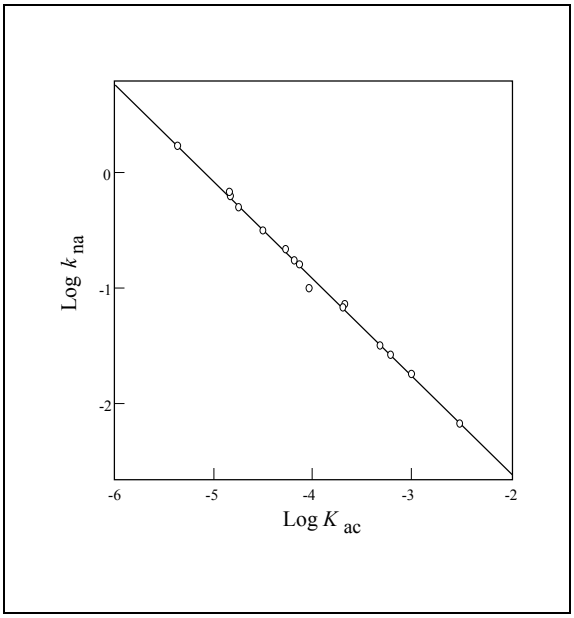


Figure 11.1. The rate constant for the acid catalyzed dissociation of nitramide, k_{na}, as a function of the dissociation constant for the acid K_{ac}. Data from Brønsted and Pederson[1924].

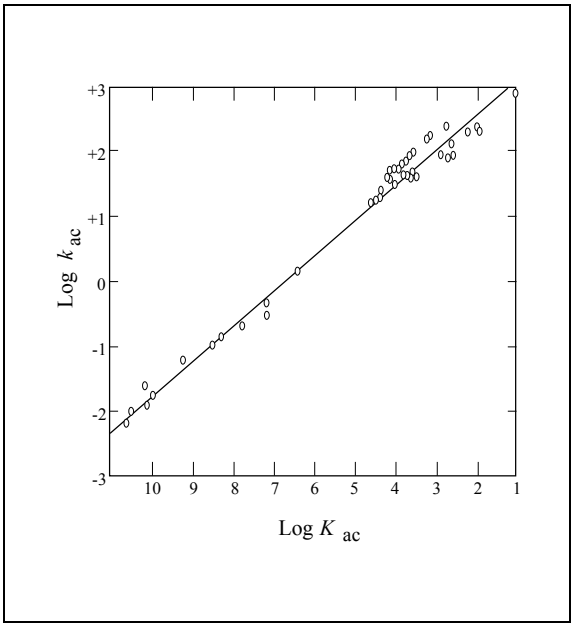


Figure 11.2. A plot of the rate constant of the acid catalyzed dehydration of $CH_3CH(OH)_2$ in acetone. Replot of the data of Bell and Higginson[1949].

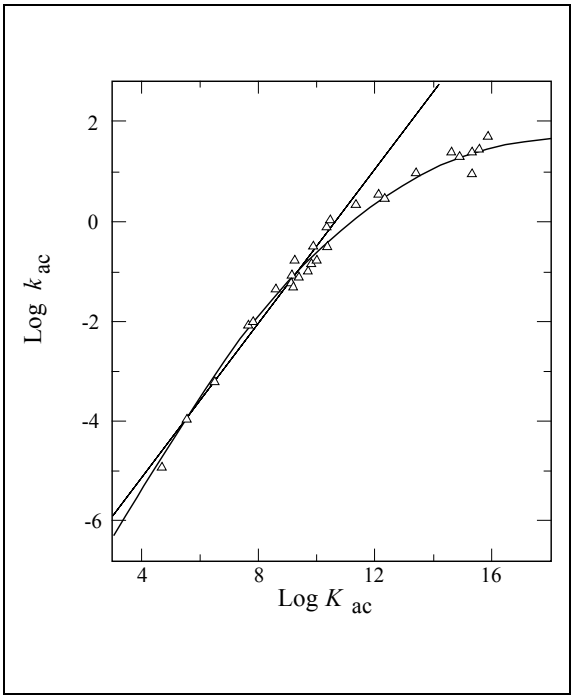


Figure 11.3 A Brønsted plot of the base catalyzed enolization of $NO_2(C_6H_4)O(CH_2)_2COCH_3$. Data from Hupe and Wu[1977]. The solid line is a fit of the data by the Marcus equation.

Really useful in organic chemistry and electrochemistry

Electrochemistry first

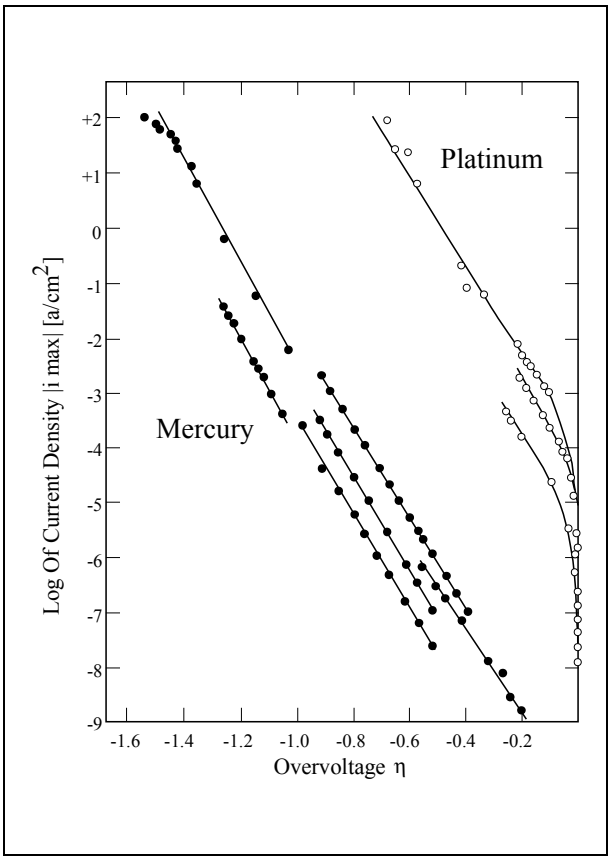


Figure 11.4. The current produced during the electrolysis of water as a function of the applied potential over mercury and platinum electrodes. The various lines are data taken at different conditions. Data from Vetter[1967].

Butler-Volmer equation

$$i_{net} = i_0 \exp\left[-\frac{n_e \mathcal{F} \gamma_a}{k_B T} \eta_v \right] - i_0 \exp\left[-\frac{n_e \mathcal{F} \gamma_c}{k_B T} \eta_v \right] \quad (11.15)$$

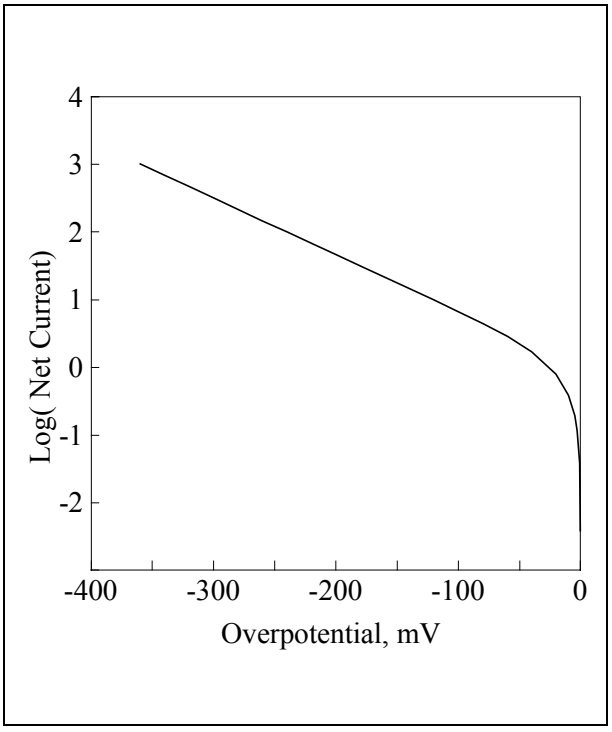
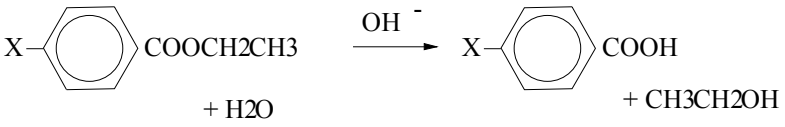


Figure 11.5. A plot of the current predicted by the Butler-Volmer equation as a function of the applied potential.

Applications of the polanyi relationships in organic chemistry:

Idea: use Polanyi relationship to see how rates change when substituents change.



(11.17)

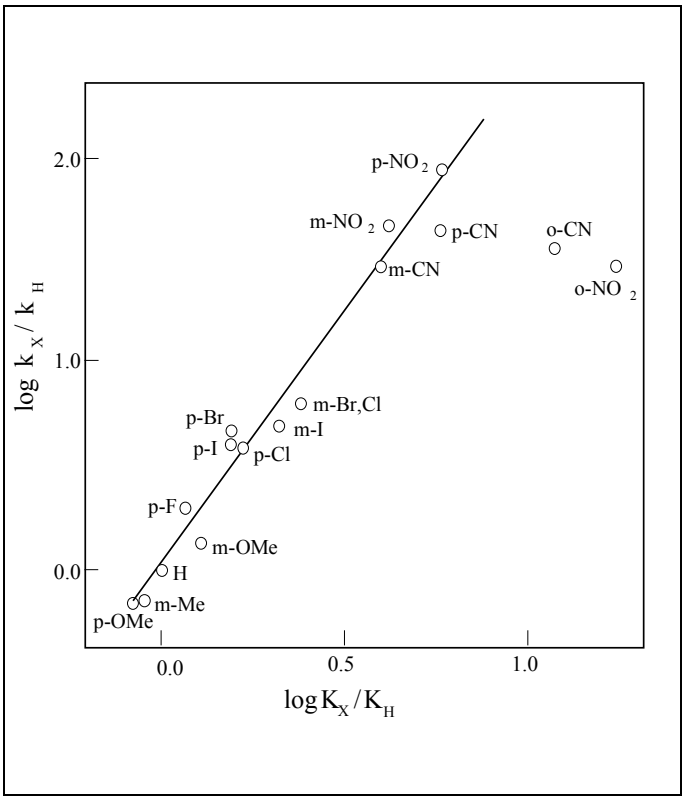


Figure 11.6. A plot of the rate constant for the hydrolysis of a series of substituted ethyl benzoates versus the dissociation constant of the corresponding benzoic acid. Data of Ingold et al.[1936] and Evans et al.[1937].

$$\ln\left(\frac{k_X}{k_H}\right)=\square\gamma_H\ln\left(\frac{K_X}{K_H}\right)=\square\gamma_H\sigma\square_1^o \quad (11.19)$$

$$\sigma\ {}_1^o=\ln\left(\frac{K_X}{K_H}\right) \quad (11.20)$$

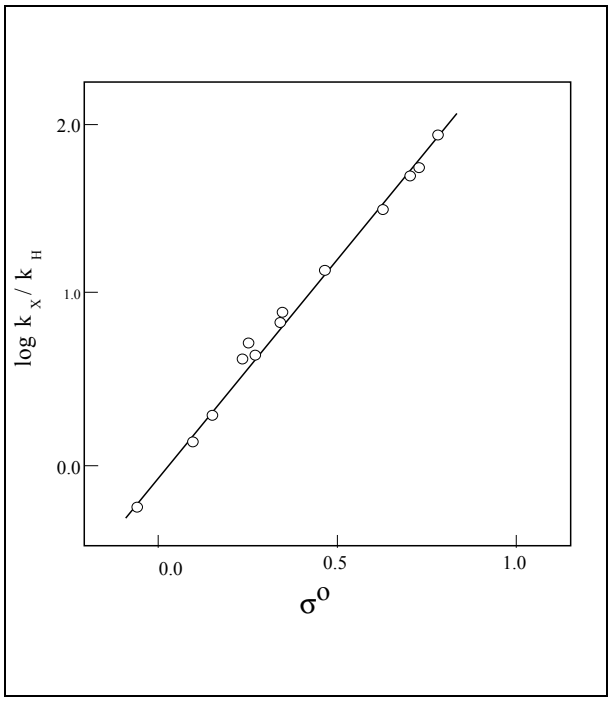
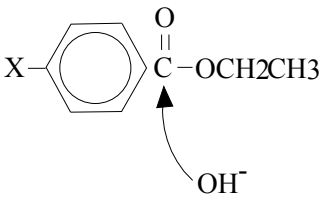
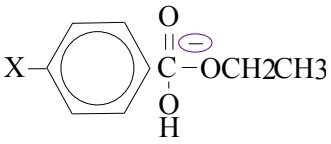


Figure 11.7 A replot of the meta and para data from Figure 11 using the modified values of σ^o from the tabulation of Exner[1978].

Only works for negatively charged transition states



(11.26)



(11.27)

(11.28)

Another negatively charged transition state

(11.29)

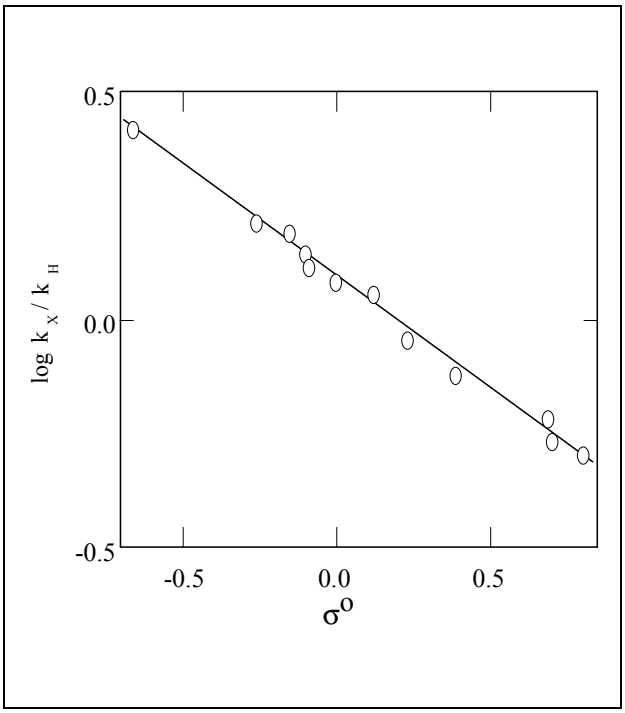


Figure 11.8 A plot of the log of the rate constant for the reaction of a series of substituted benzenesulfinic acids with hydrogen peroxide against σ^o values determined for substituted benzoic acids. Data of Lindberg[1966].

Does not work as well for a negatively charged transition state

$$(XAr)_3C\text{-}Cl \rightleftharpoons (XAr)_3C^+ + Cl^- \quad \textbf{(11.30)}$$

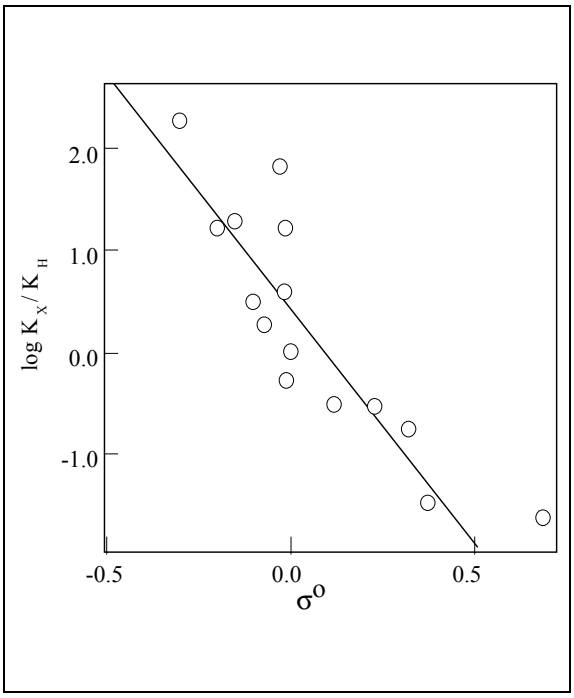


Figure11.9. A Hammett plot of the equilibrium constant for the ionization of $(XAr)_3C\text{-}Cl$ in liquid SO_2. The data is replotted from data in Isaacs [1987].

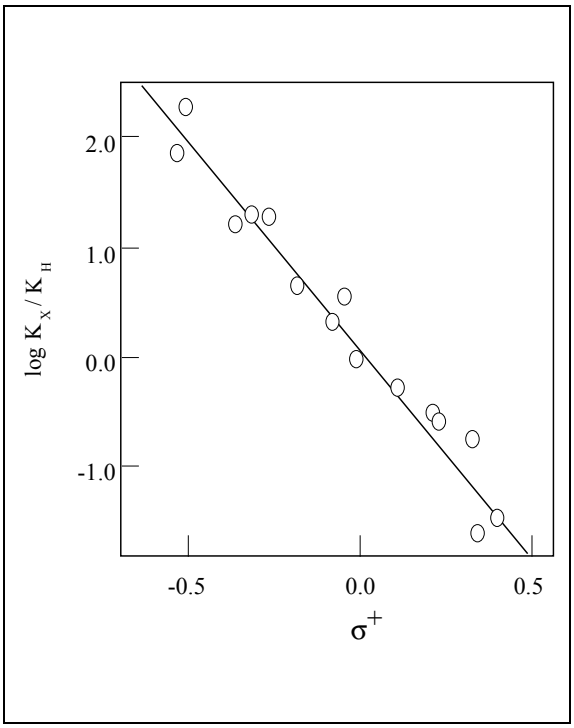


Figure 11.10 A replot of the data from Figure 11. on the σ^+ scale.

Polanyi can also be used quantitatively:

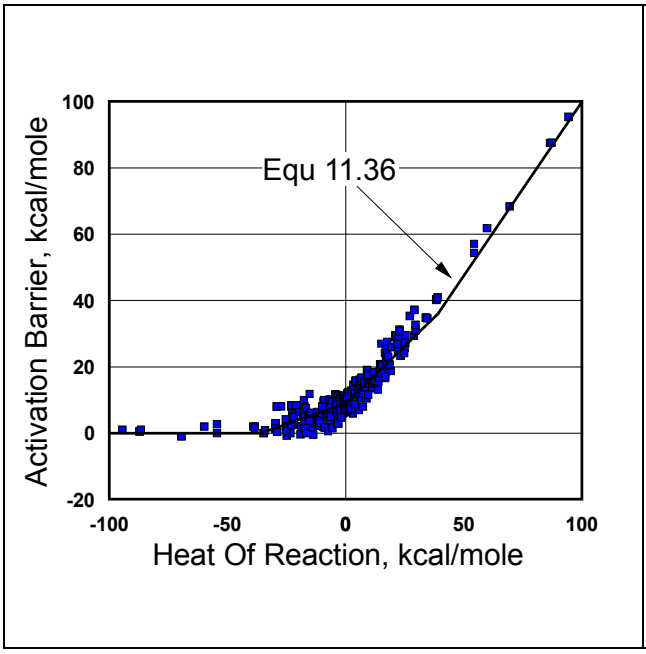


Figure 11.13 A comparison of the activation energies of 482 hydrogen transfer reactions to those predicted by equation (11.36).

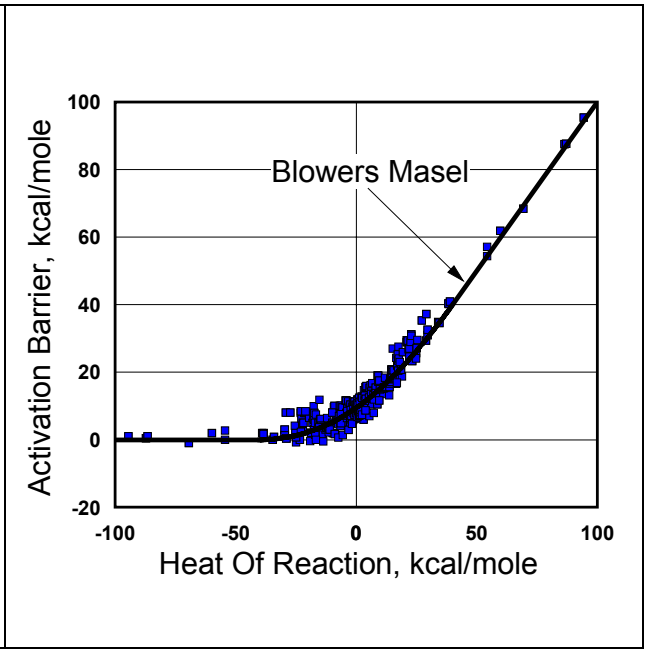


Figure 11.14 A comparison of the activation energies of 482 hydrogen transfer reactions to those predicted by the Blowers-Masel approximation with E_a^0 =9.5 kcal/mole and w_O= 105 kcal/mole.

$$E_a = \Delta H_r \text{ when } \Delta H_r > 36$$
$$E_a = 9\text{kcal/mole} + 0.75\Delta H_r \text{ when } 0 < \Delta H_r < 36$$
$$E_a = 9\text{kcal/mole} + 0.25\Delta H_r \text{ when } 0 > \Delta H_r > -36$$
$$E_a = 0 \text{ when } \Delta H_r < -36$$

(11.36)

Fails with quantum effects:

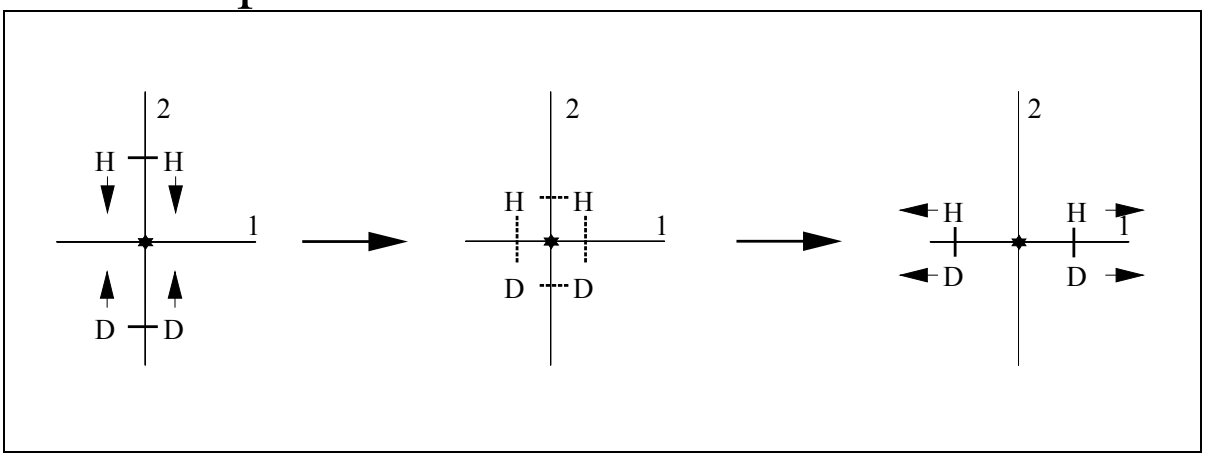


Figure 10.39 A hypothetical four-centered mechanism for H_2/D_2 exchange. The dotted lines in the figure denotes mirror planes which are preserved during the reaction (see the text). This reaction is symmetry forbidden.

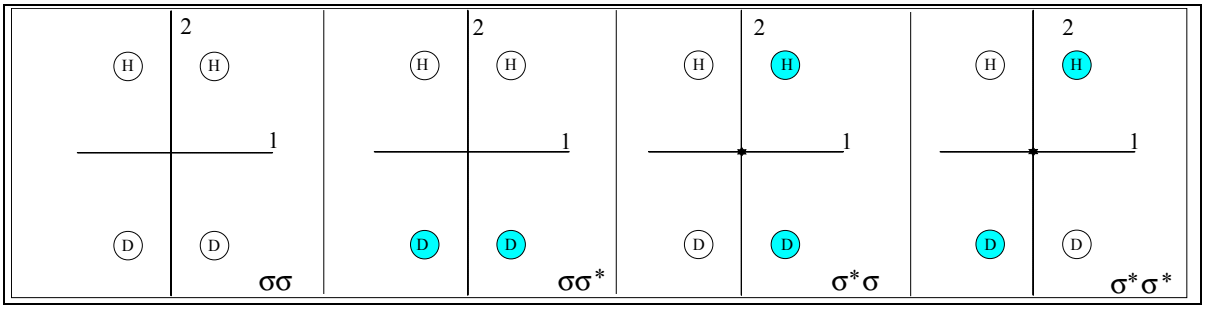


Figure 10.40 A schematic of the key molecular orbitals for the transition state of reaction (10.92). Positive atomic orbitals are depicted as open circles, negative orbitals are depicted as shaded circles.

If Reaction Quantum limited, need Quantum Mechanics to calculate rates

Idea:

Solve schroedinger equation

$$H\left(\hat{r},\hat{R}\right) \quad \Psi\left(\hat{r},\hat{R}\right) = E \quad \Psi\left(\hat{r},\hat{R}\right)$$

(11.39)

Calculate Saddle point properties

General Method:

Expand wavefunction in a basis set

$$\psi_i = \sum_j C_{i,j}\phi_j$$

(11.56)

Plug into schroedinger equation:

$$\left\langle \Psi_e^1 \middle| V_{ee} \middle| \Psi_e^1 \right\rangle = \left(\frac{1}{2}\right) \iiint \iiint \psi_{ls}^{\alpha}(\vec{r}_1)^* \psi_{ls}^{\beta}(\vec{r}_2)^* \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{ls}^{\alpha}(\vec{r}_1) \psi_{ls}^{\beta}(\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2$$

$$- \left(\frac{1}{2}\right) \iiint \iiint \psi_{ls}^{\alpha}(\vec{r}_2)^* \psi_{ls}^{\beta}(\vec{r}_1)^* \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{ls}^{\alpha}(\vec{r}_2) \psi_{ls}^{\beta}(\vec{r}_1) \, d\vec{r}_1 \, d\vec{r}_2$$

(11.55)

Minimize energy (HF limit)

Use additional expansion

$$\Psi(\hat{r}) = \sum_i \mathbb{C}_i \Psi_{HF}^i(\hat{r})$$

(11.57)

minimize again.

Practically use approximations:

Key Approximations

Hartree-Fock → Assume electrons move independently (no correlated motions)

All others put in some correlated motion – one electron appears, others move out of the way.

Table 11.4 Some common methods used to solve the Schroedinger equation for molecules. All the methods in this table are based on the Hartree-Fock method plus corrections.

Method	Description
HF	One electron wavefunctions, no correlation energy as described in section 11.5.2
CI	One of a number of methods where the configuration interaction is used to estimate the correlation energy as described in section 11.5.4. In the literature the CI keyword is sometimes erroneously used to denote the CIS method
GVB	A minimal CI calculation where the sum in equation 11.57 includes 2 configurations per bond. The configurations are to improve bond dissociation energies.
MCSCF, CASSCF	A CI calculation where the sum in equation 11.57 includes the all the single excitations of the "active orbitals" and ignores excitations of the "inactive" orbitals. In the limit of large number of configurations, MCSCF gives to the exact result. However, Often people only use a few configurations and still call the calcualtion MCSCF.
CIS	A CI calculation where the sum in equation 11.57 includes all the single excitations. This method tends to not be very accurate.
CID	A CI calculation where the sum in equation 11.57 includes all the double excitations.
CISD	A CI calculation where the sum in equation 11.57 includes all the single and double excitations.

CISDT	A CI calculation where the sum in equation 11.57 includes all the single double and triple excitations.
CCSD, QCISD	An improved version of a CISD calculation, where the single and double excitations are included exactly, and an approximation is used to estimate the coefficients for the higher order excitations.
CCSD(T) QCISD(T)	An improved version of a CCSD calculation, where triple excitations are included.
MP2, MP3, MP4	A calculation where Moller-Plesset perturbation theory is used to estimate the correlation energy as described in section 11.5.5. The various numbers refer to the level of perturbation theory used in the calculation.
G2, G3	A combined method where you compute the energy as a weighted sum of CCSD(T) with different basis sets, an MP4 calculation with a large basis set, plus other corrections.
G2(MP2)	A combined method where you substitute a MP2 calculation for the MP4 calculation in the G2 calculation
CBS	A different combined method, where you use a series of intermediate calculations to extrapolate the CCSD(T) results to infinite basis set size.

Density functional methods:

Table 11.5 Some common methods used to solve the Schroedinger equation for molecules. All the methods in this table are based on density functional theory (DFT). Generally, in DFT, one combines approximations for the exchange integral with approximations for the correlation function

Method	
	Exchange approximations
Slater	A simple exchange approximation where the exchange energy is approximated as being 2/3 times the integral of the electron density to the 4/3 power. This is exact for a uniform electron gas.
Becke	A modification of the Slater approximation, where corrections are included for changes in the exchange energy due to gradients in the electron density
Perdew-Wang	A modification of the Becke approximation. Perdew and Wang fit the exchange energy for an electron gas as $V_{eX}=F_1[\rho_e]+F_2\left[\frac{d\rho_e}{dx}\right]$ where V_{ex} is the exchange energy, ρ_e is the electron density, and F_1 and F_2 are functions that were fit to calculations for electron gases.
Modified Perdew Wang	Modifications of the Perdew-Wang where different functionals are used.
	Correlation Approximation
VWN	A correlation approximation due to Vosko, Wilk, and Nusair, which assumes that the correlation is only a function of the local electron density. The function is calculated assuming that you have a uniform electron gas and the given density. This method is sometimes called the local spin density method.
Becke	A modified version of the VWN approximation, where an extra correction is added to account for variations in the correlation energy due to the gradients in the electron density. The Becke gradient approximation is optimized for metals.
LYP	A different modification of the VWN approximation, where an extra correction is added to account for variations in the correlation energy due to the gradients in the electron density. The LYP gradient approximation is optimized for molecules
Perdew Wang	A modification of the Becke approximation. Perdew and Wang fit the exchange energy for an electron gas as $V_{cor}=F_3[\rho_e]+F_4\left[\frac{d\rho_e}{dx}\right]$ where V_{cor} is the exchange energy, ρ_e is the electron density, and F_3 and F_4 are functions that were fit to calculations for electron gases.
Modified Perdew Wang	There are a number of modifications of Perdew-Wang in the literature. Generally, people use different functions to tailor F_3 and F_4 for a specific application. I find it difficult to use the methods, because one never knows whether they are going to work. However, they are common in the literature.

Mixed Methods	
X-alpha	An approximation that uses the Slater approximation for the exchange integral and ignores the correlation. It is common in X-alpha to also change the coefficent in the Slater approximation from 2/3 to 0.7
LDA, LDSA	A method which used the Slater approximation for the exchange and the VWN approximation for the correlation
B3LYP	A hybrid method where the exchange energy is approximated as a weighted average of the Hartree-Fock exchange energy and the Slater-Becke exchange energy, while the correlation is calculated via the LYP approximation.
AM1, MINDO, CINDO, Huckel	These are several semiempirical methods. These methods are similar, in spirit, to the DFT methods, but one also approximates the coulomb repulsions with empirical functions

Table 11.6 The energy of the transition state of the reaction $H + H_2 \rightarrow H_2 + H$ calculated by a number of methods. All of the calculations used a 6-311G++(3df, 3pd) basis set. Results of Johnson et al Chem. Phys. Lett. **221** 100 (1994).

DFT Methods		
Exchange Approximation	Correlation Approximation	Transition State Engery, kcal/mole
Slater	VWN	-2.81
Slater	LYP	-3.45
Slater	Perdew-Wang	-3.58
Becke	VWN	+3.65
Becke	LYP	+2.86
Becke	Perdew-Wang	+2.84
Perdew-Wang	VWN	+2.75
Perdew-Wang	LYP	+1.98
Perdew-Wang	Perdew-Wang	+1.95
Non-DFT Methods		
MP2		+13.21
CCSD (T)		+9.91
G-2		+9.8
Experiment		+9.7

Table 11.7 Some of the basis sets commonly used for ab initio calculations.

STO-3G, 3-21G, 3-21++G, 3-21G*, 3-21++G*, 3-21GSP, 4-31G, 4-22GSP, 6-31G, 6-31++G, 6-31G*, 6-31G**, 6-31+G*, 6-31++G*, 6-31++G**, 6-31G(3df,3pd), 6-311G, 6-311G*, 6-311G**, 6-311+G*, 6-311++G**, 6-311++G(2d,2p), 6-311G(2df,2pd), 6-311++G(3df,3pd), MINI, MIDI, SVP, SVP + Diffuse, DZ, DZP, DZP + Diffuse, TZ, cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, cc-pV6Z, pV6Z, cc-pVDZ(seg-opt), cc-pCVDZ, cc-pCVTZ, cc-pCVQZ, cc-pCV5Z, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, aug-cc-pV5Z, aug-cc-pV6Z, aug-cc-pCVDZ, aug-cc-pCVTZ, aug-cc-pCVQZ, aug-cc-pCV5Z, LANL2DZ ECP, SBKJC VDZ ECP, CRENBL ECP, CRENBS ECP, DZVP, DZVP2, TZVP

11.A Sample AbInitio Calculations

Calculate the equilibrium geometry of ethane at the MP2/6-31+G(d) level.

Solution:

I decided to solve this problem using GAUSSIAN98. GAUSSIAN calculations are simple. You specify 1) the geometry of the molecule and 2) the computational method. The GAUSSIAN98 program does the rest.

Table 12.A.1 shows my input file. The first line tells the computer that I want to use MP2/6-31+G(d) to solve the problem. I added an opt keyword to say that I want to optimize the geometry. I also added a test keyword. This prevents huge output files from being stored on disk.

Table 11.A.1 The input file needed to calculate the equilibrium geometry of ethane using GAUSSIAN 98

```
#MP2/6-31+G(d) opt test

Ethane molecule

0  1
C
C 1 RCC
H 1 RCH 2 ACH
H 1 RCH 2 ACH 3 DHH
H 1 RCH 2 ACH 4 DHH
H 2 RCH 1 ACH 3 DCT
H 2 RCH 1 ACH 6 DHH
H 2 RCH 1 ACH 7 DHH

RCC 1.87
RCH 1.09
ACH 111.
DHH 120.
DCT 60.
```

The second line is blank by convention while the third line lists the name of the job, in this case "ethane molecule"

The fourth line is again blank.

The fifth line contains two numbers, the charge and spin multiplicity of the molecule. The charge is the charge on the molecule. A neutral molecule will have a charge of zero. A ion with a +1 charge will have a charge of +1.

The spin multiplicity is the degeneracy of the electronic configuration. Recall that each electron has a spin of + ½ (up) or (- ½) down. It is useful to define a quantity “net spin” by

$$\text{Net spin} = \sum_{\text{all electrons}} (\text{spin of each electron})$$

If all of the electrons are paired into bonds, the net spin will be zero. If there is one unpaired electron the net spin will be 0.5. If there are two unpaired electrons there are two possibilities: if both

electrons have the same spin the net spin will be ½ + ½ = 1. If both electrons have the opposite spin the net spin will be ½ - ½ = D.

The spin multiplicity is defined by

$$\text{spin multiplicity} = 2(\text{net spin}) + 1$$

The ground states of most stable molecules have a multiplicity of 1 because all of the electrons are paired up into bonds. Radicals, on the other hand usually have a multiplicity of 2 because there is always a net spin a di-radical or an oxygen atom can have a multiplicity of 3.

Physically, the spin multiplicity is the degenerating of the spin state. A stable molecule will only have one spin state. A radical has two spin states, one with spin up one with spin down.

For our case, the charge is zero because we are choosing a neutral molecule. The multiplicity is

one because we are looking at the ground state of a neutral molecule.

Next comes the geometric description. There are two ways to enter geometries in GAUSSIAN. Either one can either list the X,Y and Z coordinates for each atom or one can list the bond lengths and bond angles. I choose the later.

Note people call the list of bond lengths and bond angles the "Z-matrix"

I create Z matrixes, by first listing all of the atoms and then adding coordinates. There are two carbons and 6 hydrogens in ethane so I made a list of 8 atoms. Two Carbons and six hydrogens. The first atom is atom 1, the second is atom 2 etc. as shown in Figure 11.A.1.

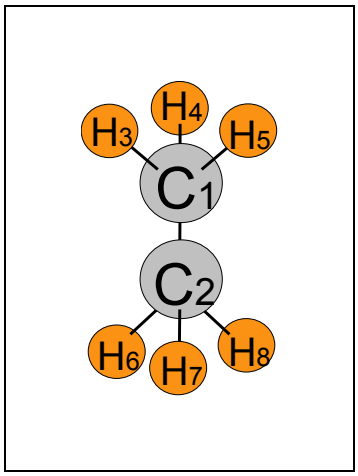


Figure 11.A.1 A diagram of ethane. The numbers represent the order of the atoms in the z-matrix

Then I need to put in bond lengths. To simplify things I called defined

RCC = the carbon-carbon bond length
RCH = the carbon-hydrogen bond length
ACH = the CH bond angle
DCH = the rotation angle between one hydrogen atom and the adjacent carbon atom

DCT = the rotation of the methyl group on one side of the molecule relative to the carbon atom on the other side of the molecule.

Now lets focus on the input file.

The first line puts the first atom at the origin.
The second line puts atom 2 a distance RCC away from atom one.
The third line puts atom 3 a distance RCH from atom 1 and an angle of ACH from atom 2.
The fourth line puts atom 4 at a distance of RCH from atom 1 and at an angle of ACH from atom 2 and rotated by DCH from atom 3.
The fifth line puts atom 5 at a distance of RCH from atom 1 and at an angle of ACH from atom 2 and rotated by DCH from atom 4.
The sixth line puts atom 6 at a distance of RCH from atom 2 and at an angle of ACH from atom 1 and rotated by DCT from atom 3.
The seventh line puts atom 7 at a distance of RCH from atom 2 and at an angle of ACH from atom 1 and rotated by DCH from atom 6.

The eighth line puts atom 8 at a distance of RCH from atom 2 and at an angle of ACH from atom 1 and rotated by DCH from atom 7.

The remaining lines in the input file give initial guesses for the input variables. For example I guessed RCC=1.87 Å, RCH=1.09 Å, ACH=111 degrees, DCH = 120 degrees clockwise and DCT=60 degrees. Most of the numbers come from typical bond lengths and bond angles from the CRC. I deliberately picked too long of a bond length for the carbon-carbon bond, because I wanted to show that GAUSSIAN calculates the correct bond length if I guess a bad one.

I ran GAUSSIAN with the input file in Table 11.A.1. Table 11.A.2 shows part of the output from the run. The GAUSSIAN job actually produces 1100 lines of output. These are the last 29 lines. From the output RCC = 1.528Å, RCH = 1.094Å, ACH = 111.1, DHH = 120., DCT = 60. Notice that GAUSSIAN optimized the structure. The carbon-carbon bond length was reduced from 1.87 Å to 1.5277 Å. All of the other variables were changed by a smaller amount. The run took about 90 seconds on the NCSA computer, which is typical for a molecule this size.

Table 11.A.2 Part of the output from GAUSSIAN for the input shown
Final structure in terms of initial Z-matrix: C C,1,RCC H,1,RCH,2,ACH H,1,RCH,2,ACH,3,DHH,0 H,1,RCH,2,ACH,4,DHH,0 H,2,RCH,1,ACH,3,DCT,0

H,2,RCH,1,ACH,6,DHH,0
H,2,RCH,1,ACH,7,DHH,0
Variables:
RCC=1.52770877
RCH=1.09407761
ACH=111.11640213
DHH=120.
DCT=60.

1\1\ NATIONAL CENTER FOR SUPERCOMPUTING APPLICATIONS-BILLIE\FOpt\RMP2-FC\6-31+G(d)\C2H6\RMASEL\30-Jun-1999\0\\#MP2/6-31+G(D) OPT TEST\\Ethane molecule\\0,1\C,0.,0.,-.7638543853\C,0.,0.,0.7638543853\H,1.0206107823,0.,-1.1580110214\H,-0.5103053912,-0.8838748649,-1.1580110214\H,-0.5103053912,0.8838748649,-1.1580110214\H,0.5103053912, 0.8838748649, 1.1580110214\H, -.0206107823, 0.,

1.1580110214 \H,0.5103053912, -0.8838748649, 1.1580110214\\Version=HP-PARisc-HPUX-G98RevA.6\HF=-79.2291737\MP2=-79.497602\RMSD=3.599e-09\RMSF=1.313e-04\Dipole=0.,0.,0.\PG=D03D [C3(C1.C1),3SGD(H2)]\\@

LOVE IS BLIND, THAT'S WHY ALL THE WORLD LOVES A LOUVER.
Job cpu time: 0 days 0 hours 1 minutes 34.6 seconds.
File lengths (MBytes): RWF= 14 Int= 0 D2E= 0 Chk= 6 Scr= 1
Normal termination of Gaussian 98.

Example 11.B. Energy calculations

Use the results in table 11.A.2 to estimate the total energy and the correlation energy of ethane.

Solution:

GAUSSIAN lists the energies in the output block at the end of the program. The HF= is the hartree fock energy in hartrees, MP2= is the MP2 energy in hartrees, where 1 hartree = 627.5095 kcal/mole.

From the output MP2=-79.497602 hartrees. Therefore the total energy is given by

Total energy =-79.497602 hartrees ×627.5095 (kcal/mole/hartree)= -49885.5 kcal/mole.

Again from the output HF=-79.2291737

HF=-79.2291737 hartrees ×627.5095 (kcal/mole/hartree)= -49717.05 kcal/mole

The correlation energy is the difference between the HF and MP2 energy

Correlation energy = HF-MP2 = -49885.5- (-49717.05)= -168.45 kcal/mole.

The correlation energy is only 168.45/49885.5= 0.3% of the total energy. However, the correlation energy is still -168 kcal/mole so it cannot be ignored.