Introduction to potential energy surfaces and graphical interpretation

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Introduction into PES and graphical representation

1 Potential Energy Surfaces

Information about the Potential Energy Surface (PES) has improved enormously in recent years, both from the analysis of experimental data and from ab initio calculations. However it is still a major task to gather available information to construct a functional representation which can be used for dynamical calculations. In general, different experiments experience different parts of the surface and highly accurate calculations are expensive to perform. Therefore, it is only by using chemical judgement that one can combine information from different sources to produce a satisfactory function for the whole surface. Moreover, there is often a conflict between the accuracy with which a function represents a surface and the simplicity of the function; the more mathematically elaborate is the function, the more demanding will be the dynamical calculations in which this function appear.

Chemistry is a dynamical process with interactions between molecules and atoms dependent on the forces between the atoms: $F_r = \frac{-dV(r)}{dr}$.

To understand the dynamics of an chemical system we need to understand all the forces operating within the system, hence we need to know $V(r)$. In a multi-dimensional system $V(r)$ is known as the potential energy surface.

The potential energy surface is typically defined within the Born Oppenheimer approximation: electrons are much lighter than nuclei, thus they move much faster and adjust adiabatically to any change in nuclear configuration. This means that a separate PES is defined for each possible electronic state. Generally, the dynamics are studied on the ground electronic state surface. Unless stated otherwise the discussion here is for the ground electronic state surface. (This is also known as the electronic adiabatic approximation).

Degrees of freedom:

An N atom system is uniquely defined by $3N$ coordinates x, y, z for each atom. However, we are not worried about overall translation of the system (3 coordinates) or overall rotation (3 coordinates). Therefore, a PES is a function of $3N$-6 (nonlinear system) or $3N$-5 (linear system) coordinates

$N = 2$: potential curve

$N = 3$: potential energy hypersurface

Note - the zero of energy is arbitrary for a PES. It describes interaction energies and not absolute energies. It is common to define the zero of energy to be reactants.

Diatomic potential energy curves

To understand what a potential energy surface is, it is useful to start with something we have all seen - the potential energy curve for a diatom:

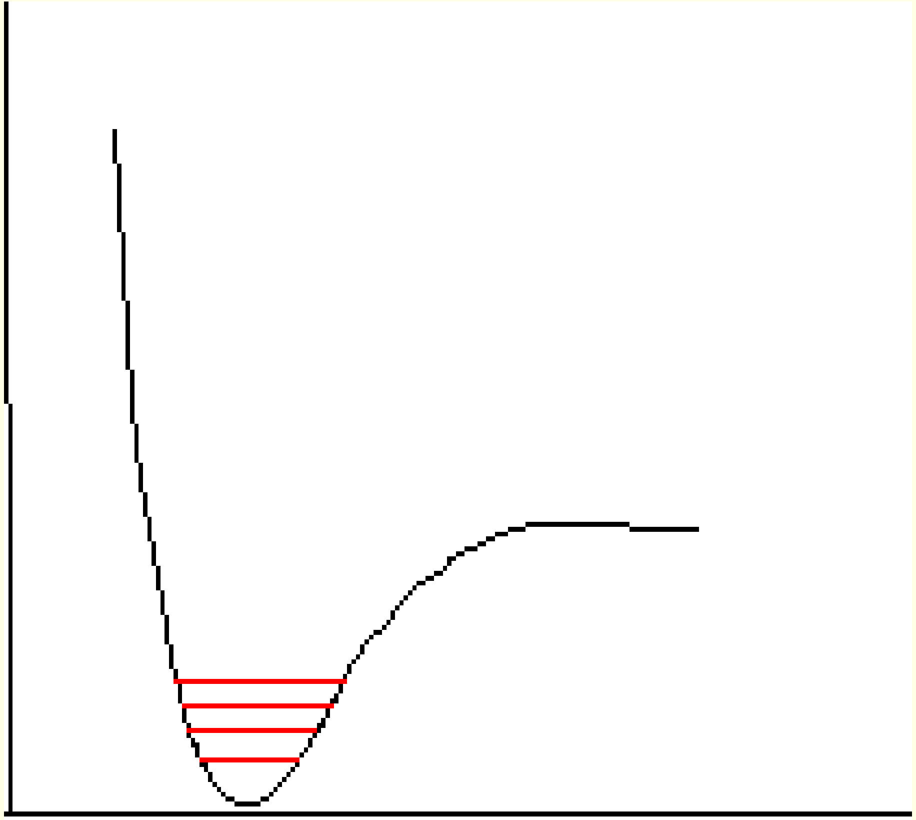

Figure 1: This is Energy vs. r(AB) (distance between A and B). Where are r_e (equilibrium bond length), D_0 (dissociation energy from the ground state) and D_e (classical dissociation energy) on this figure?

A. Examples of empirical intermolecular potentials

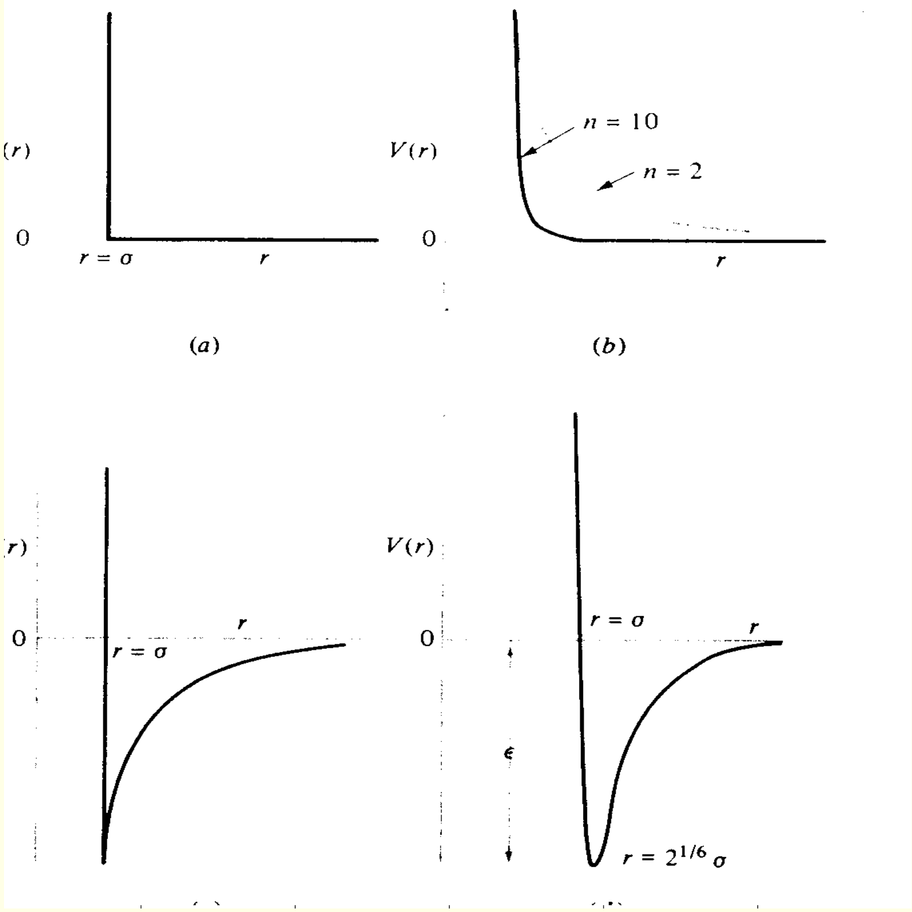

Figure 2:

Hard sphere (Fig. 2.a):

$V(r) = \infty, \qquad r < \sigma$
$V(r) = 0, \qquad r > \sigma$

This model treats atoms as rigid, impenetrable spheres. It accounts for short range repulsive forces but not long range attraction.

Point centers of attraction or repulsion (Fig. 2.b): $V(r) = Cr^{-n}$, if C is large (positive) and $n > 10$ this is nearly the hard sphere model

$C > 0$: repulsion of ions of like charge (n=2 ??)

$C < 0$: attraction

Sutherland model (combine each of proceeding) (Fig. 2.c):

$V(r) = \infty, \qquad r < \sigma$
$V(r) = -Cr^{-n}, \qquad r > \sigma$

This model includes both attractive and repulsive forces. The minimum will be at $r = \sigma$. It is good for ion-ion interactions when n = 2.

Lennard-Jones (6-12)(Fig. 2.d):

$V(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$

The parameters in this equation have the following physical interpretations:

$-\epsilon$: = depth of well, $\qquad r_e = 2^{\frac{1}{6}}\sigma$

σ = value of r at which $V = 0$

The first term (12th) is the attractive part and the second (6th) is the repulsion. This model is good for interactions between uncharged molecules. It is reasonably simple and realistic.

$V(r) = Cr^n$ - **behaviour:**

r^{-1}: charge - charge
r^{-2}: charge - dipole
r^{-3}: charge - quadrupole or dipole - dipole
r^{-4}: dipole - quadrupole
r^{-5}: quadrupol - quadrupole
r^{-6}: induced dipole - induced dipole
r^{-8}: induced dipole - induced quadrupole
r^{-10}: induced quadrupole - induced quadrupole

B. Examples of Molecular Bonding Potentials

When atoms in a molecule form a chemical bond we have to take into account the chemical nature of the species. The attractive interactions will become much stronger when the atoms become a few angstroms apart. In the case of a diatomic the only bonding interaction is a bond stretch. A very good model for this is the Morse potential.

Morse potential (handling 2-body interaction)

$V(r) = D[e^{-2\beta\rho} - 2e^{-\beta\rho}]$

where:

$\rho = r - r_e$

$D =$ dissociation energy (from bottom of well)

$\beta =$ Morse parameter - can be determined from spectroscopic measurements

$$\beta = \omega\sqrt{\mu/D}$$

Vibrational frequencies computed using this potential agree will with experimental observations of the same vibrational levels

The Morse potential is good in the vicinity of r_e (poor quartic force constants).

Rydberg potential

$$V(r) = -D[1 + \beta(r - r_e)]e^{-\gamma(r-r_e)}$$

Murrell et al.

$$V(r) = -D[1 + a_1(r - r_e) + a_2(r - r_e)^2 + a_3(r - r_e)^3]e^{-\gamma(r-r_e)}$$

where:

$\beta, a_1, a_2, a_2, \gamma$ are adjustable parameters general functional forms: see later chapters

Polyatomic potential energy surfaces

We can now expand upon what we learned from diatomics to polyatomic systems. All that really changes is the number of degrees of freedom. But it becomes increasingly more important as the size of the system grows to use chemical intuition as a guide when representing chemical interactions with mathematical formulas.

Instead of a simple one dimensional curve we now have a multi-dimensional hypersurface. For a linear 3 atom system the surface is in 3 dimensions and we can draw it. Usually the surface is drawn as a contour diagram.

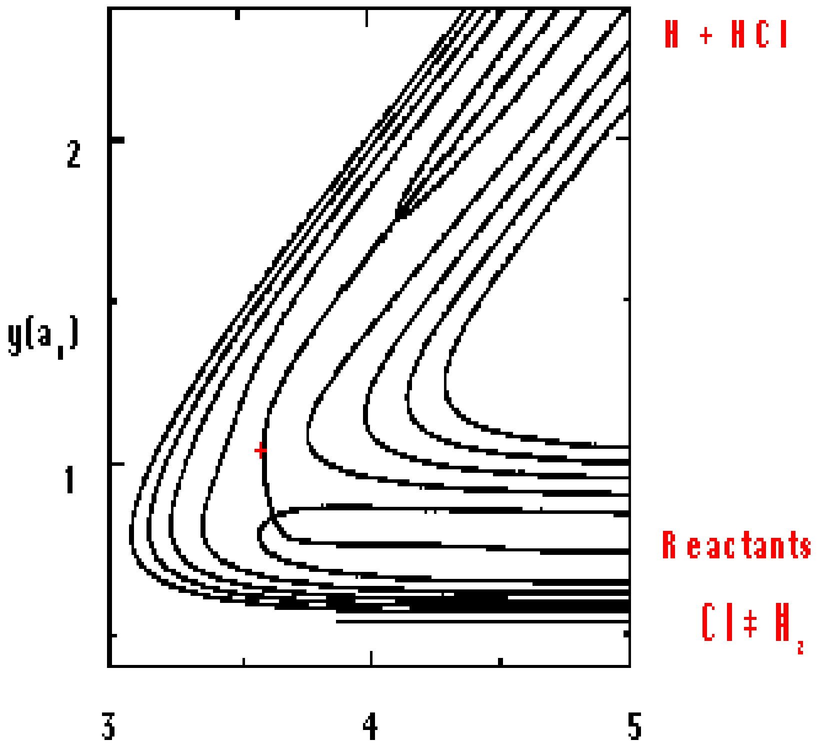

Figure 3: The collinear PES is useful to show characteristics and regions that are crucial to surfaces of many dimensions.

It is important to recognize the following:

- saddle point (transition state)
- reactants ($H2 + Cl$)
- products ($H + HCl$)
- minimum energy reaction path
- reaction coordinate (s) (-: reactants, $+$: products)

The saddle point is located at the '$+$' in the figure at approx. (3.6, 1.1). The reactants and products are labeled. The minimum energy reaction path or MEP is defined as the path of steepest descents from the saddle point to the reactants and products. The coordinate used to define the location along this path is the reaction coordinate (s). The reaction coordinate is defined to be zero at the saddle point and $-$ at reactants and $+$ at products.

One can take the minimum energy path and plot it separately as a function of the reaction coordinate to obtain the potential energy profile. This representation of the potential energy of a chemical system is very useful for understanding and analyzing the dynamics.

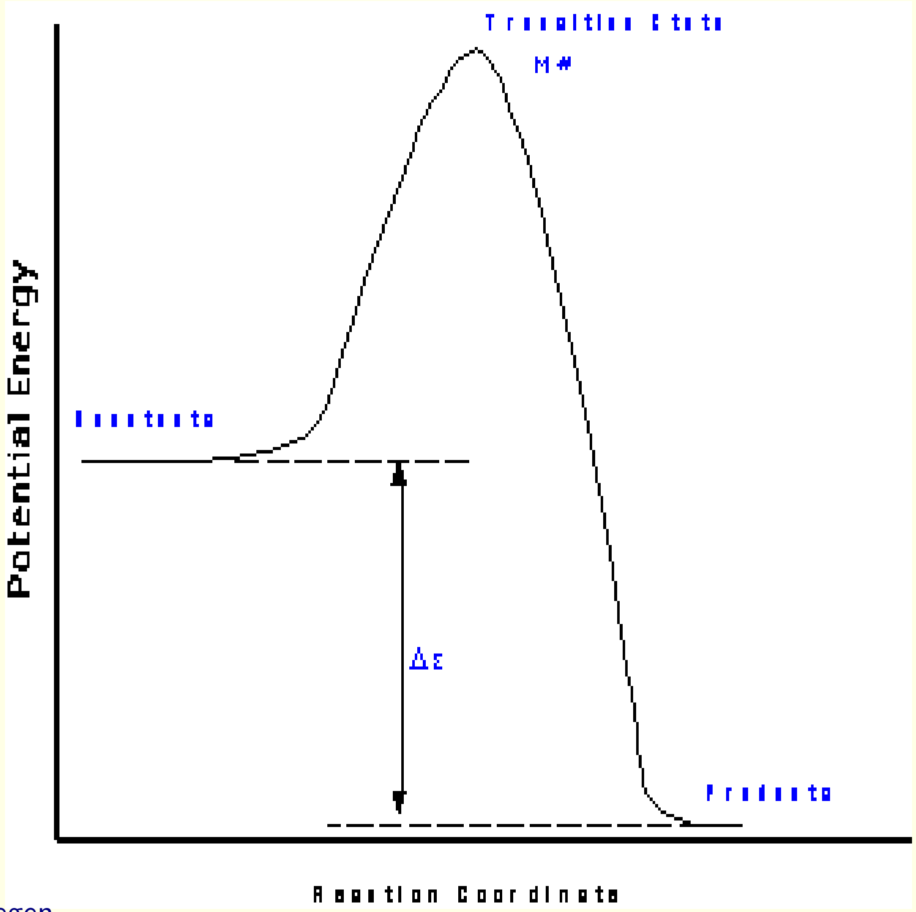

Figure 4:

Determination of potential energy surfaces

A. Ab initio potential energy surfaces

Potential energy surfaces may be determined by ab initio electronic structure calculations. In this method one performs a large number of electronic structure calculations (which may be very expensive) and then fits the results using a least squares procedure. The reliability of the PES depends on the basis set completeness and how well electron correlation is accounted for. Drawbacks to this method are:

- For large systems, the size and the number of calculations necessary to characterize the entire surface is too expensive, especially when more than the reactant, product, and saddle point regions are important for the dynamics of the system.

- To be sure that ab initio calculations are performed for the most important geometries may require an iterative process in which some type of dynamics calculation is done on a preliminary surface, and the results are analyzed for their sensitivity to various PES regions to determine where further calculations are most important to refine the surface.
- It is difficult to obtain a good fit when using general least squares fitting of ab initio results unless physically motivated functional forms are used.

Examples:

– F + H_2 → HF + H:Polyani and Schreiber, Chem. Phys. Lett. 29, 319 (1974)

– H + H_2 → H_2 + H: Truhlar and Horowitz, J. Chem. Phys. 68, 2457 (1978)

Their general strategy was to fit a subset of data then add terms as needed. They made sure that the new terms vanished for the original subset of geometries. They used two sets of terms:

a) linear geometries were modeled with London equations

b) bend potential was modeled using 5 potential functions which vanished at linear geometries.

– O + H_2 → OH + H: Schinke and Lester, J. Chem. Phys. 70, 4893 (1979)

This surface is a 56 parameter least squares fit to a sum of Morse functions and a three-body term that consists mainly of a polynomial of up to sixth order in all three variables multiplied by a hyperbolic tangent switching function to attenuate the potential.

– O + H_2 → OH + H: Schatz et al., J. Chem. Phys. 74, 4984 (1981)

Rotated Morse oscillator spline function – ab initio calculations were done with the fitting function in mind. Thus, the geometries for which ab initio calculations were performed were chosen in a systematic way to aid in the fitting process.

– Cl + HCl → HCl + Cl: Garrett et. al., J. Chem. Phys. 78, 4400 (1983)

Rotated Morse oscillator spline fit for collinear geometries plus analytic bend potential. Additional calculations and the final fit were carried out after dynamical calculations on a preliminary fit gave an indication of which regions of the surface were critical.

– He + H_2^+: Sathymurthy et. al., J. Chem. Phys. 63, 464 (1975); 64, 4606 (1976)

1D, 2D, 3D spline fits to ab initio data. The resulting surface has spurious structure outside the regions where ab initio values had been calculated, including a barrier in the entrance channel which is higher than the saddle point. This is an illustration of the problem from doing potential fitting independent of any dynamics.

B. Analytic potential energy surfaces

Use available experimental and ab initio information to calibrate functional forms based on simple valence theory or bond functions. A successful strategy for designing a polyatomic PES is to use a standard formulation as a starting point and then either add additional terms or add more flexibility to the adjustable parameters to remedy deficiencies or to improve selected areas of the surface.

The major difficulty in this approach is that it is time consuming for systems larger than 3 atoms. (For a 5 atom problem it can take ?? years to generate an accurate surface.)

In general for a reaction of the type, **A + BC** → **AB + C** , a PES will have the form:

$$V(R_A + R_{BC}) = V_A(R_A) f_1(R_{BC}) + V(R_{BC}) f_2(R_A)$$

f_1 and f_2 are switching functions: $(0 \rightarrow 1)$

Thus, a potential function is a mediator between reactants and products

One standard function of this type is the London-Erying-Polanyi-Sato (LEPS) surface:

$$V(R_{BC}) = Q_{BC} \pm J_{BC}$$

where:

Q_{BC}: coulomb contribution and J_{BC}: exchange contribution

$(+)$ singlet electronic state

(-) triplet electronic state

if 3 atoms are in close proximity

$$V(R_1, R_2, R_3) = \sum_{i=1}^{3} Q_i(R_i) - \frac{1}{2}\sqrt{\sum_{i<j=1}^{3} (J_i(R_i) - J_j(R_j))^2}$$

This is the London equation. The full LEPS formulation adds adjustable parameters to this equation (Sato parameters).

Examples:

– Diatomics-in-Molecules (DIM): Ellison, J. Amer. Chem. Soc. 85, 3540 (1963)

The potential of a polyatomic molecule is written in terms of information about its diatomic and atomic fragments.

– DIM-3C: Last and Baer, J. Chem. Phys. 75, 288 (1981)

A three center energy term was added to the standard DIM theory to give realistically high exchange barriers for the reactions H + XD → HX + D, where X is a halogen.

– DIM+ for SiH2: Viswanathan et. al., J. Phys. Chem. 89, 1428 (1985)

Adjustable parameters and extra an bending term to account for the fact that the H-Si-H angle is influenced by the nonbonded electrons on silicon (which were omitted), were added to DIM formulation. This is a promising starting point for polyatomic systems.

– London-Eyring-Polanyi-Sato (LEPS)

A special way to parameterize DIM theory. These equations contain "Sato parameters" which can be adjusted to give a desired surface feature:
a) saddle point height
b) calculated rate constant
c) calculated energy of activation
d) calculated product vibrational distribution

A standard LEPS potential can be made more flexible by making the Sato parameter a function of any of the bond length, bond angle, or reaction path variables, and through the addition of ”three-center type” energy terms. This is a good starting place for polyatomic systems but can be complicated since localized changes are not easy to design.

– Hyperbolic Map Function (HMF)

A product of a Morse function and another function F that can be altered from system to system to better match available experimental and theoretical information. In the Morse function the depth parameter (D_M) and range parameter (b_M) are Eckart functions of the distance along a reaction path, and F is a function of the A-B-C angle. A further development of this function leads to the rotated-Morse-curve (RMC) method.

– Murrell's Method

Murrell et. al.; Molecular Potential Energy Surfaces Wiley, New York (1984)

Murrell has devised a systematic strategy for the design on potential energy surfaces. Total potential = sum of the potentials of the dissociation fragments. This method gives the correct dissociation limits (by definition), and, with the use of switching functions to turn on the necessary terms in the interaction regions, flexibility is available to adjust to other available information. Special caution is required to avoid spurious wells and oscillations in this approach.

2 Graphical Representations of the PES

The first analysis of a PES and qualitative reasoning about its reactivity can be carried out on appropriate graphical representations. For atom diatom systems the PES is a function of three variables. The most commonly used variables are the three internuclear distances (r(AB), r(BC) and r(AC)), two internuclear distances and the included angle (eg. r(AB), r(BC) and Φ_B). More recently, hyperspherical coordinates (ρ, θ, and χ)[1] and bond order variables (eg. n(AB), n(AC) and n(BC), or n(AB), n(BC) and Φ_b[2] have been used. Two dimensional graphical representations can be obtained by:

a) constraining two variables or
b) constraining one variable and plotting contour maps of the PES.

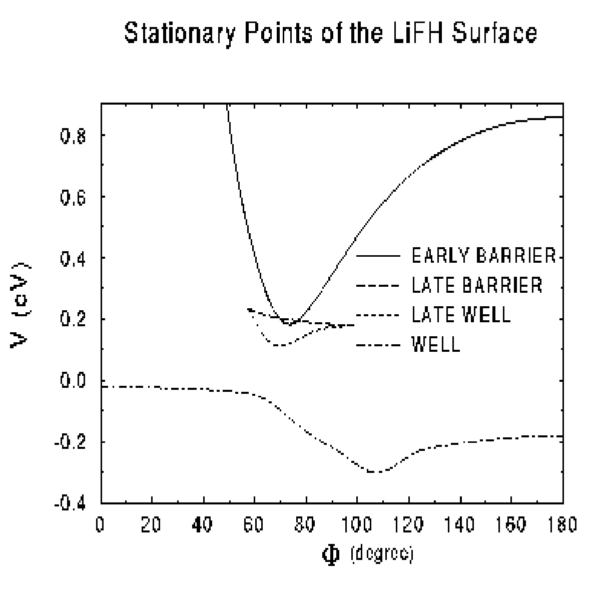

Figure 5:

As an example of representations of type a) we show in Fig. 5 the variation with ϕ_F of the height of the barriers to reaction and of the depth of the intermediate wells for the Li + FH reaction.

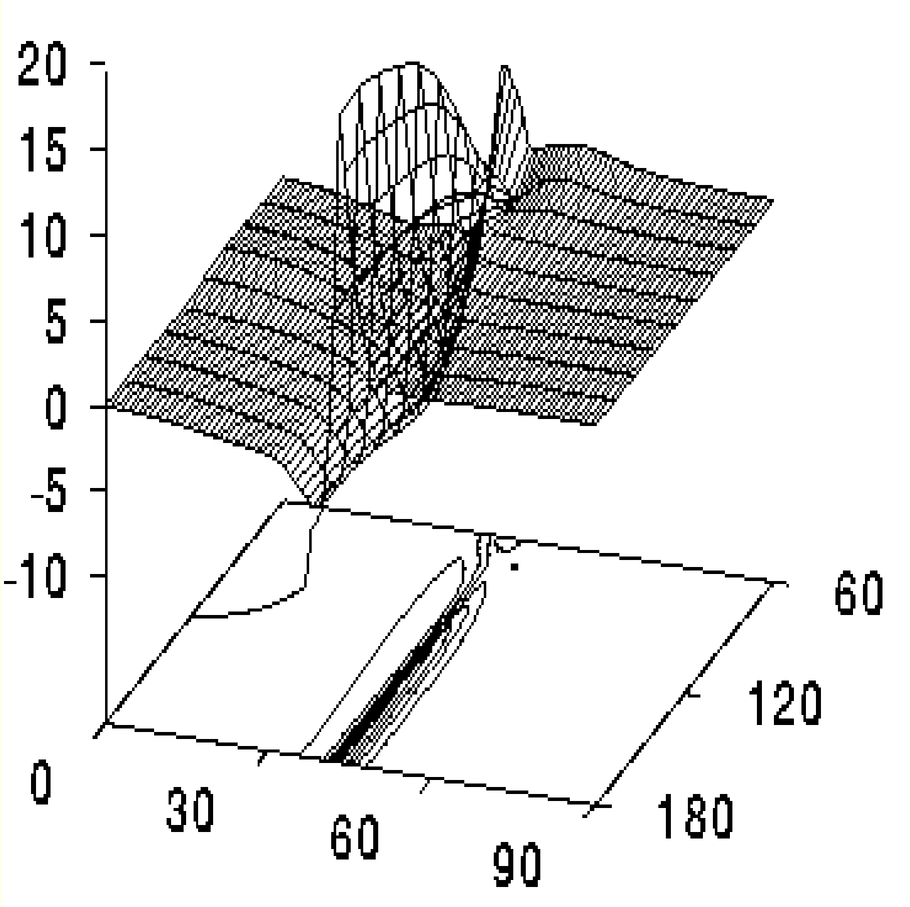

Figure 6:

Another example of representations of type a) is the fixed Φ minimum energy path (MEP) of the PES. In this case, however, it is possible to group together several fixed angle MEPs and plot them as a function of Φ (see an example for LiFH in Fig. 6).

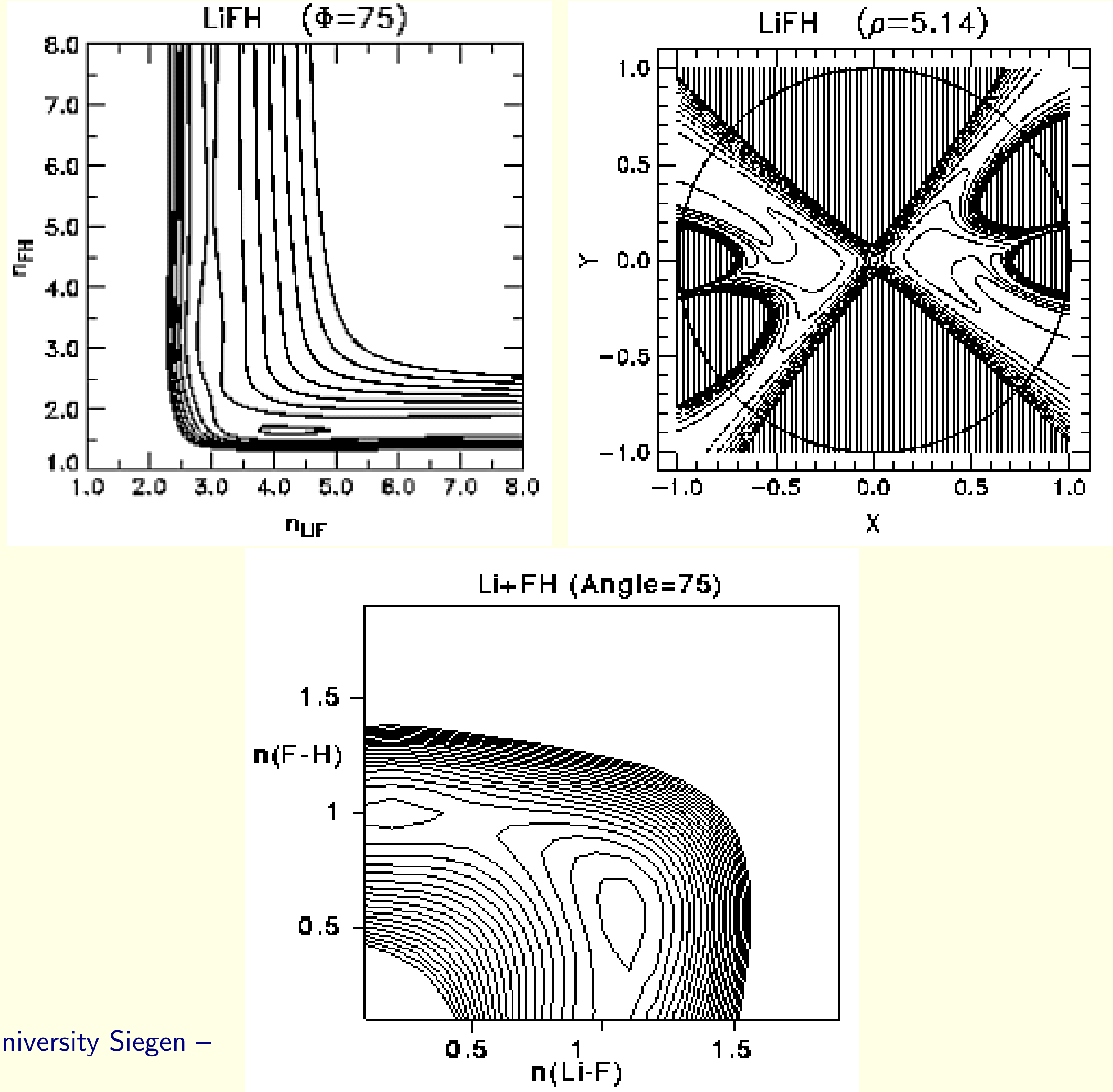
LiFH (Φ=75)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
n_{FH}
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
n_{LiF}
LiFH (ρ=5.14)
1.0
0.5
0.0
−0.5
−1.0
Y
−1.0
−0.5
0.0
0.5
1.0
X
Li+FH (Angle=75)
1.5
n(F-H)
1
0.5
0.5
1
1.5
n(Li-F)

Figure 7:

As an example of plots of type b) we give in Fig. 7 the isoenergetic contours of the Li + FH PES relevant to the definition of the transition state. In the left panel we give the Φ_F=75^o contours of the Li + FH PES as a function of r_{LiF} and r_{FH}. In the right panel the same plot is given as a function of the BO variables n(LiF) and n(FH). In the central panel isoenergetic contours at fixed hyperradius (ρ=5.14 bohr) are plotted as a function of Θ and χ. Pseudo three dimensional representations of these plots can be given by assuming the energy axes as the third axis.

2.a Analytical representations of the PES

There have been considerable advances in recent years in developing analytical functions for the potential energy surfaces of small molecules. The concept of the potential energy surface for molecules is defined by the Born-Oppenheimer approximation for the separation of electronic and nuclear motion. The molecular potential energy surface is the potential energy that determines the motion of the nuclei. In the Born-Oppenheimer approximation the electrons adjust their positions instantaneously to follow any movement of the nuclei, so that the potential energy surface can equally be thought of as the potential for the movement of atoms within a molecule or atoms in collision with one another. This type of motion is called adiabatic. The dynamical properties of the system are associated with characteristics of the motion of it representative point on a single potential energy surface.

2.b Bond Order Fit

Frequently potential energy surfaces are given the following functional representations:

a) LEPS[3] (and its variants)
b) MBE[4] (and its variants)
c) DIM[5] (and its variants)

One often uses the functional representations based on bond order variables. The BO variable of the i-th diatom as is defined as

$$n_i = \exp\left(-b_i(r_i - r_{0i})\right), \quad V(n) = D(1-n)^2$$

(where i is either AB, BC or AC diatom, b_i is the parameter related to its force constants and r_i is the internuclear distance whose equilibrium value is r_{oi}). The conceptual strength of the BO coordinates lies in the fact that they incorporate the basic ingredients of the chemical interaction. The Bond Order space, in fact, is distorted in a way that makes the description of both the break-up and the formation of chemical bonds easier to represent analytically. To this end polynomials in the BO variables (BO) and polynomials in the product of the BO variables [2] and related internuclear distances (RBO)[6], rotating BO models (ROBO), and their generalizations making use of a linear combination of possible ROBO models (LAGROBO)[7] can be adopted.

References:

1. R.T Pack and G.A. Parker, J. Chem. Phys., 87, 3888 (1987).
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4. J.N. Murrell, S. Carter, S.C. Farentas, P. Huxley and A.J.C. Varandas, Molecular Potential Energy Functions, J. Whiley and Sons, Chichester 1984.
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6. M. Dini, Tesi di Laurea, Perugia (1986); A. Lagana‘, M. Dini, E. Garcia, J.M. Alvarino and M. Paniagua, J. Phys. Chem., 95, 8389 (1991).
7. E. Garcia and A. Lagana‘, J. Chem. Phys., 103, 5410 (1995).

Acknowledgement:

Large parts of this introduction are based on the work of A. Lagana and coworkers (Perugia, Italy). Some of the pictures are taken from the web and need improvement. The basic part of the introduction is based on the textbooks of Weston and Schwarz, and Johnston on "Chemical Kinetics".

Appendix: selected pictures from my german course on "Theoretical Chemistry".

Discussion of PES

First approximation: independent solution of the electronic and nuclear motion (BO approximation)

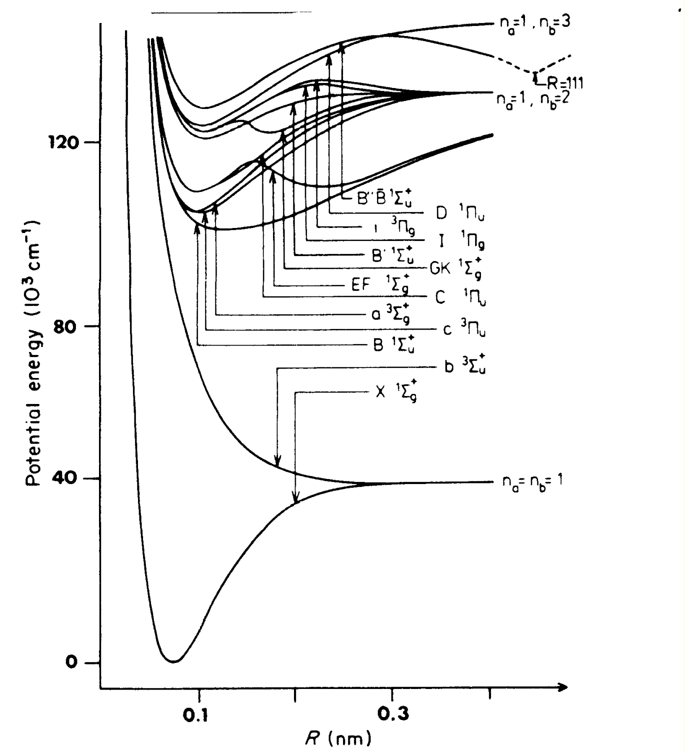


Figure 8: BO potential energy curves of several electronic states of H_2.

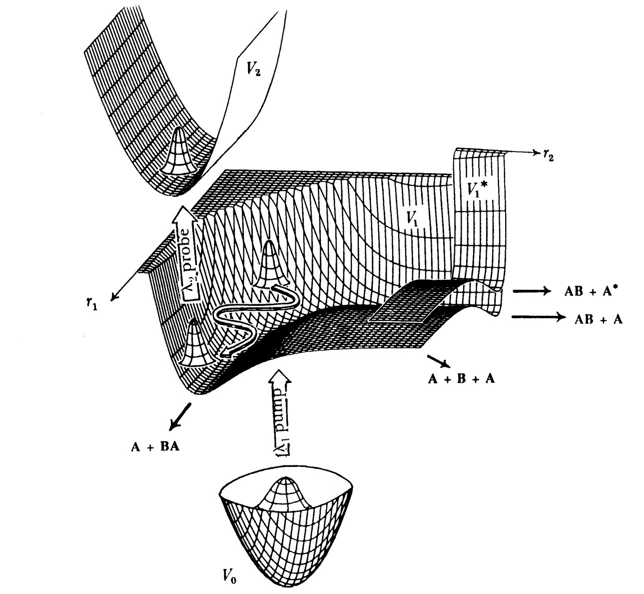


Figure 9: Wave packet motion on several PESs of HgI_2.

Interrel

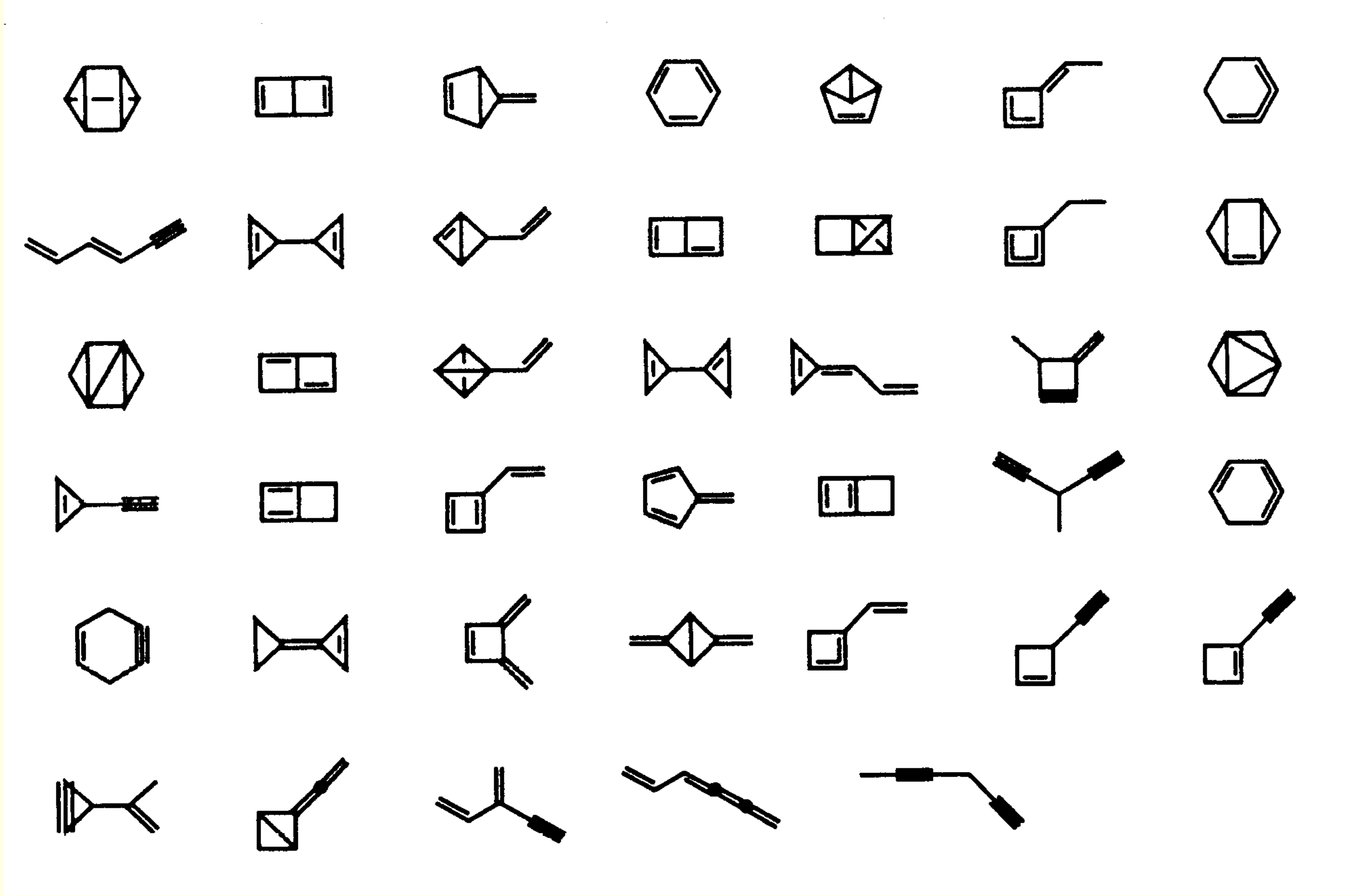


Figure 10: Configurations (minima ??) of C_6H_6 belonging to one BO-PES.

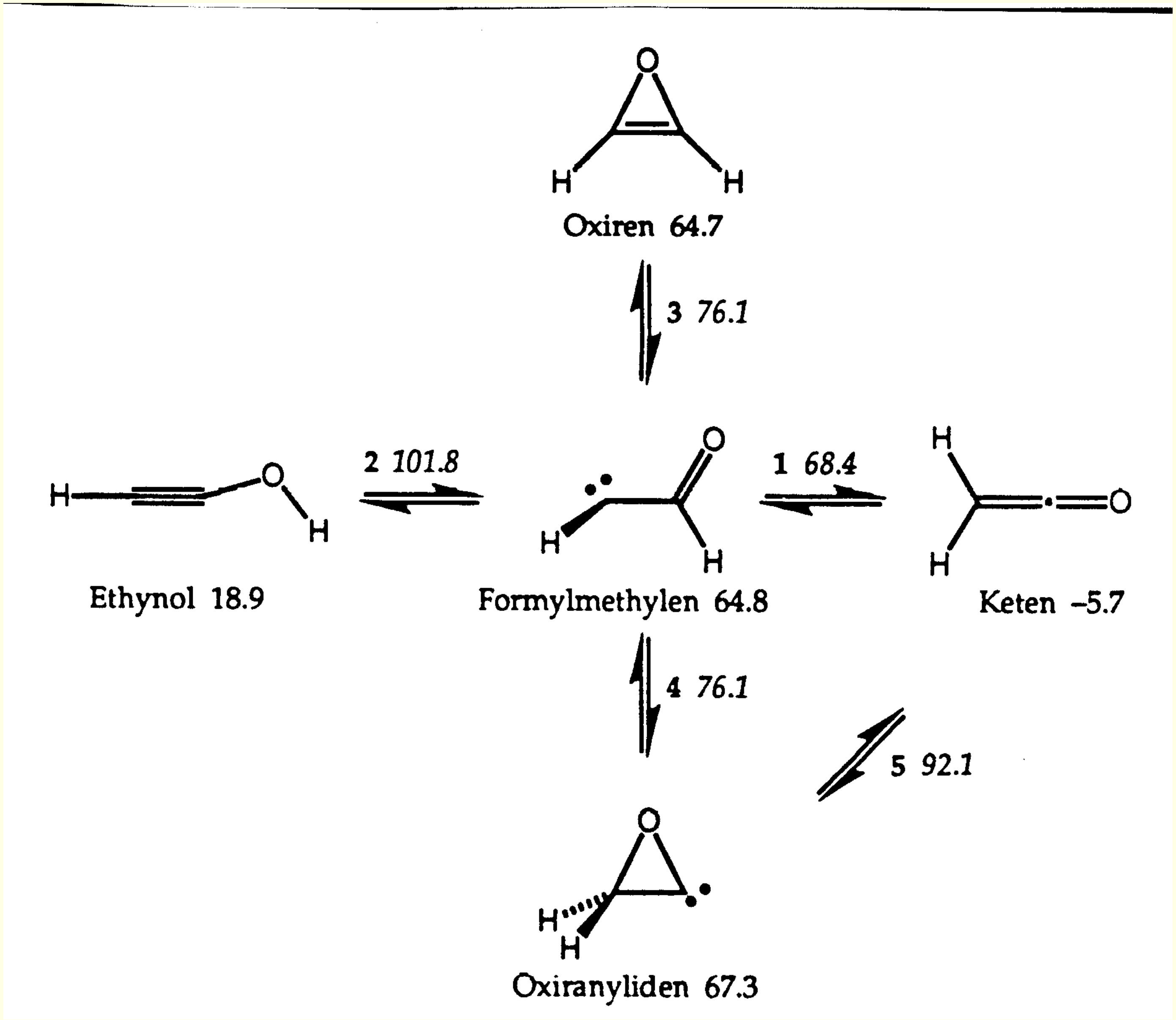


Figure 11: Configurations (minima ??) of C_2H_2O belonging to one BO-PES

Conical intersections: based on the work of M. Robb

What is a Conical Intersection?

Ref: "Modelling Photochemical Reactivity of Organic Systems: A new Challenge to Computational Chemistry" F.Bernardi, M. Olivucci, M. A. Robb (Is. J. Chem. 33, 256-276 1993)

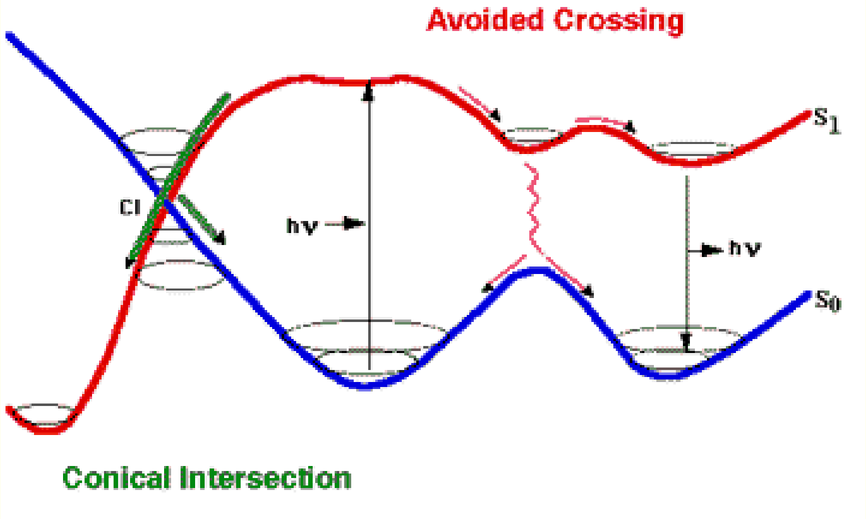
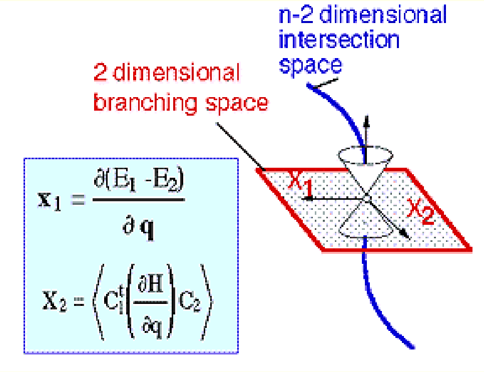


Figure 12:

While a thermal reaction starts and ends on the ground state of the reacting system, a photochemical reaction involves a stage where the system evolves on one or more excited states. The photochemical process starts via a photoexcitation of the reactant molecule, which then begins to relax on the excited state potential energy surface. Ultimately, the photoexcited system will decay back to the ground state. The different excited state relaxation mechanisms are shown in the diagram above.

In a polyatomic molecule the non-crossing rule, which is valid for diatomics, fails and two electronic states of the same symmetry are allowed to cross at a Conical Intersection. Radiationless decay from the upper to the lower intersecting state occurs within a vibrational period when the system travels in the vicinity of such intersection points. The crossing region of two potential energy surfaces is defined by the following statement: Two surfaces, even with the same symmetry, may intersect in an n-2 dimensional hyperline (the surface-crossing) as the energy is plotted against the n nuclear coordinates.

Conical intersections may provide a common decay mechanism from the lowest excited states of polyatomic systems.


n-2 dimensional intersection space
2 dimensional branching space
$\mathbf{x}_1 = \frac{\partial(E_1 - E_2)}{\partial \mathbf{q}}$
$X_2 = \left\langle C_1^t \left(\frac{\partial H}{\partial q} \right) C_2 \right\rangle$
X_1
X_2

At a conical intersection one can distinguish two directions, X1 and X2 such that if one were to plot the energy in the subspace (the branching space) of these two geometric variables (combinations of the bond lengths, angles etc), the potential energy would have the form of a double cone in the region of the degeneracy. The remaining n-2 directions define the crossing surface (the intersection space) over which the energies of ground and excited states are equal. A movement in the plane (X1, X2) from a point on the intersection will result in the degeneracy being lifted. The two vectors X1 and X2 correspond to the gradient difference vector and non-adiabatic coupling vector respectively.

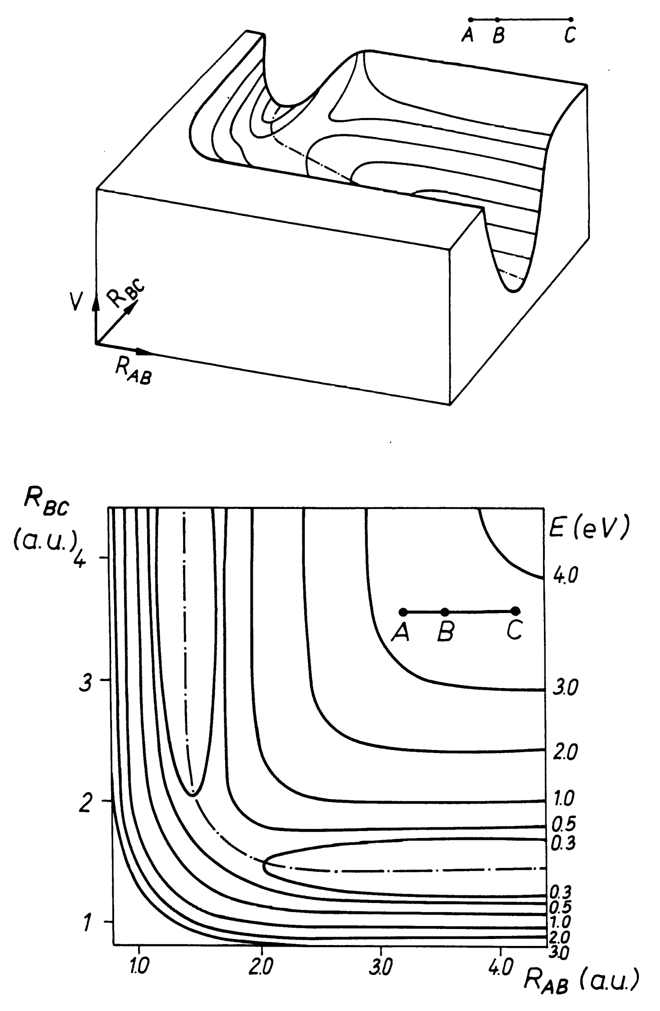


Figure 13: 3D potential energy surface.

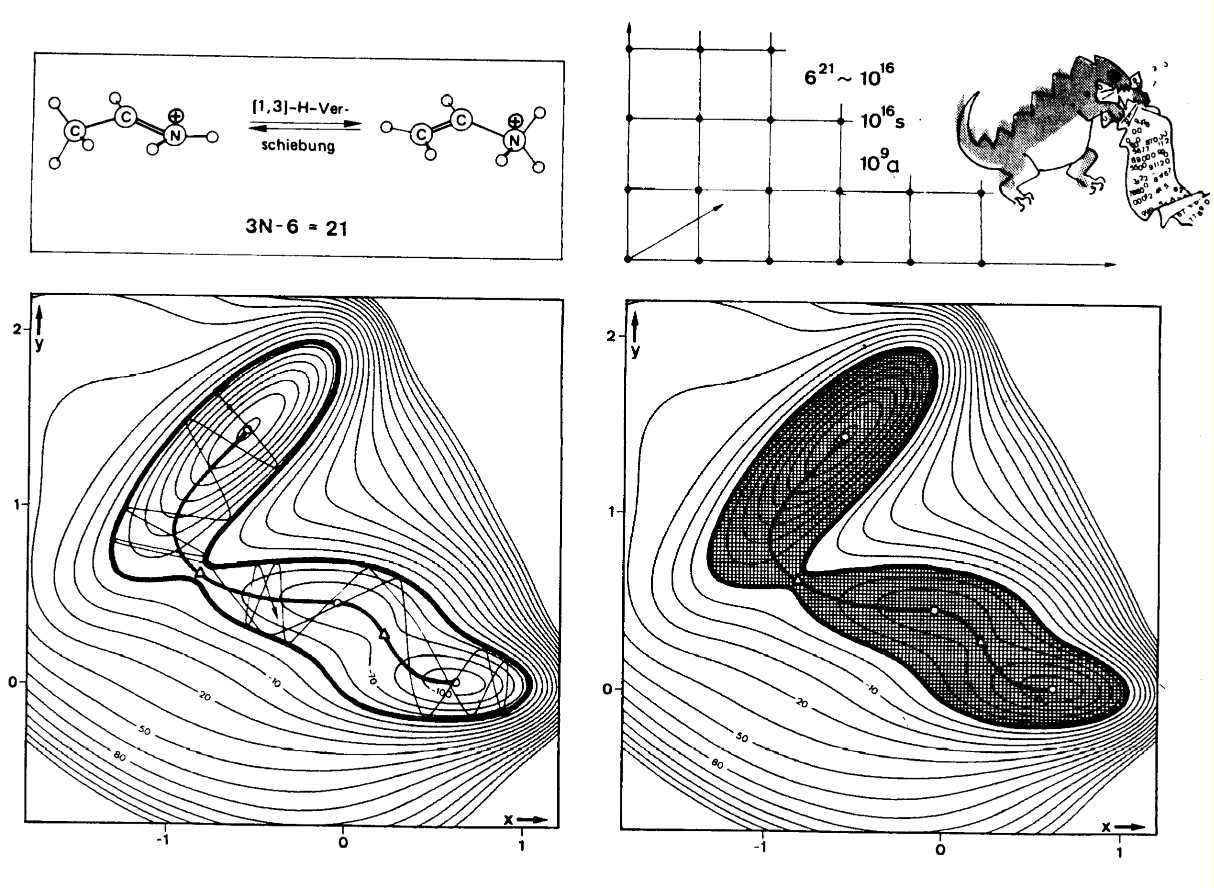


Figure 14: Problem of findind the reaction path.

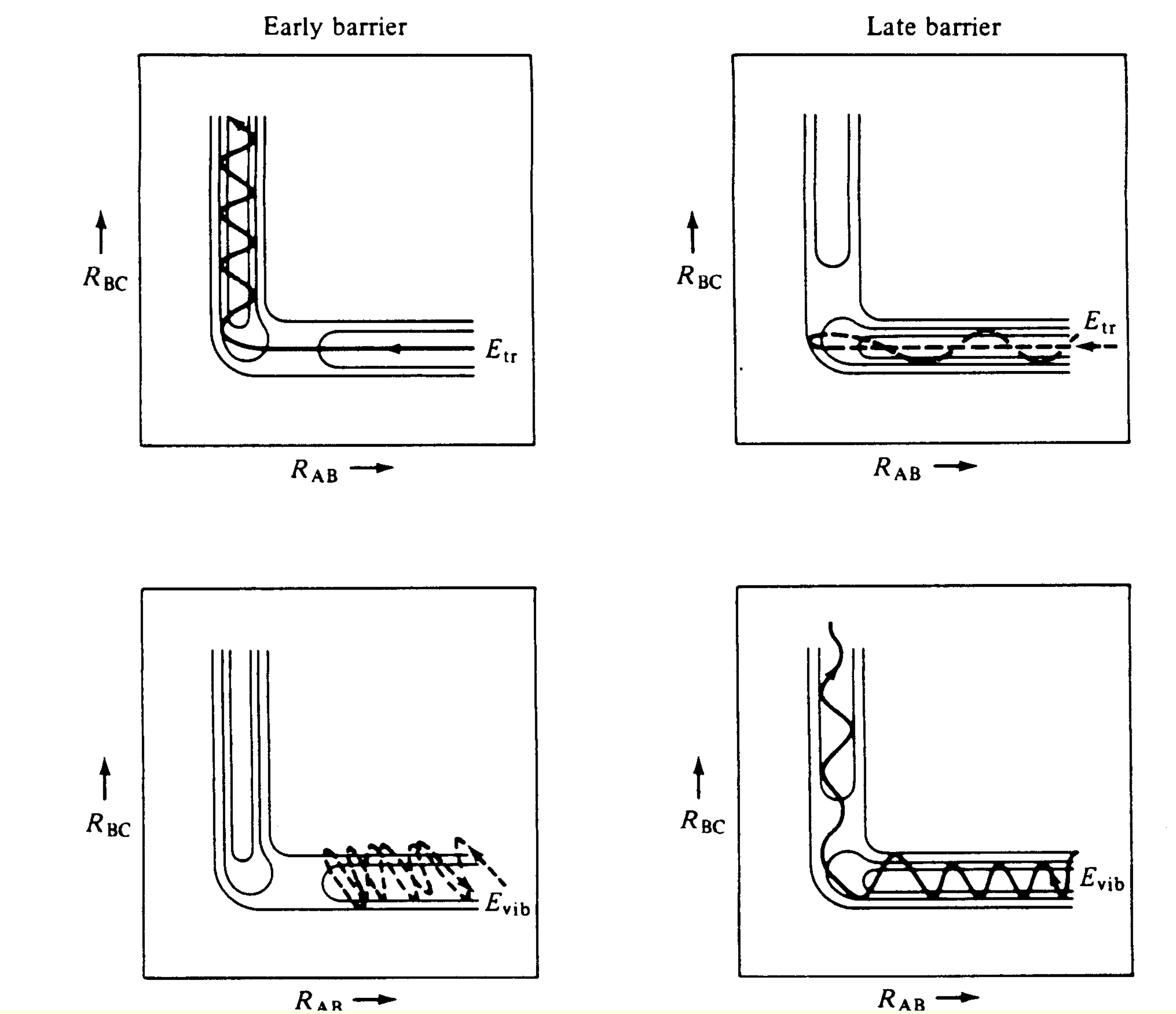


Figure 15: Polanyi rules