Critical Points and Catastrophes of Molecular Electrostatic potential

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Certificate of Examination

This is to certify that the dissertation titled **Critical Points and Catastrophes of Molecular Electrostatic potential** submitted by **Ms. Ashima (Reg. No. MS13062)** for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Declaration

The work presented in this dissertation has been carried out by me with Dr. P. Balanarayan and Professor Kapil Hari Paranjape at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. P. Balanarayan

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Ashima

"Your availability is more important than your ability.Work for a cause,not for applause"

Baba Hardev Singh Ji.

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Dedicated to my family.

Abstract

The present work deals with the construction of an approach to find critical points of a 3-D scalar field(Molecular Electrotatic Potential). This approach gives an insight to the zero flux surfaces which help us visualize critical points using Euler Characterstic. Along with the marching cubes, some catastrophe theory on some reaction pathways of molecules has also been performed as the transition state has been compared to reactant or product.

Chapter 1

Introduction

Over the past few decades, studies on critical points of scalar fields have been happening in applied mathematics research in chemistry,physics.These critical points are of great importance to the chemists for identifying the geometry and reactivity of the molecule.There have been various approaches to find out all the critical points of special scalar fields that are most commonly used such as Molecular Electrostatic Potential and electron density of molecules.[1].The algorithms so far that have been published deal with the topography of the molecules and people have investigated on classification of their critical points.

1.1 Critical Points

A critical point is a point at which all the first order partial derivative of a function or gradient of a field vanish,viz

$$\vec{\nabla}_i f(x_1, x_2, ..., x_n) = 0 \qquad \forall i = 1, 2, ..., n$$

OR

$$\frac{\partial f}{\partial x_i} = 0 \qquad \forall i = 1, 2, ..., n$$

1.1.1 Nature/Type of Characterization of a critical Point

- **Isolated Critical Points** A Critical point which have a neighbourhood such that there is no critical point in that neighbourhood.
- **Hessian Matrix**A matrix whose elements are defined by second order partial derivatives of the function.

$$H_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

- If none of the eigenvalues of the Hessian Matrix atthe critical point is zero,then the critical point is said to be *non-degenerate.*
- A critical point for which atleast one of the eigenvalues of the Hessian matrix is zero,is called a *degenerate* one.
- *Rank(R)*Number of non-zero eigenvalues at the Critical Point.
- *Signature(S)*Number of positive eigenvalues at the Critical Point-Number of negative eigenvalues at the Critical Point.

In case of 3-Dimension,
(3,+3) - minimum
(3,-3) - maximum
(3,+1) - minimum in atleast one direction
(3,-1) - maximum in atleast one direction

1.2 Manifolds

A manifold M is a *topological space* on which every point p has a neighbourhood U which is homeomorphic to $\mathbb{R}^n$. Thus dimension of M is equal to n. A more formal mathematical definition of a manifold will be given as follows
A topological manifold of dimension n has the following properties:

- M is a Hausdorff space i.e. For any pair of points p, q $\in$ M , we have p $\in$U and q$\in$V where U,V are disjoint open subsets such that U, V $\subset$ M .

- M is second countable: M has a countable local basis of its topology.
- M is locally Euclidean of dimension n: Every point p ∈ M has a neighbourhood that is topologically equivalent to an open subset of $\mathbb{R}^n$.

The locally Euclidean property is to find the following for each p∈M,

- an open set U ⊂ M which contains p ;
- an open set $\tilde{U}$ of $\mathbb{R}^n$ and
- a homeomorphism $\theta : U \to \tilde{U}$ (i.e, a bijective continuous map with continuous inverse).

Let M be a topological n-manifold,Then we define a **coordinate chart** on M as a pair (U,θ),U is an open subset ⊂ M and $\theta : U \to \tilde{U}$is a homeomorphism from U to an open subset $\tilde{U} = \theta(U) \subset \mathbb{R}^n$ An **atlas** for M is a collection of charts whose domain covers M.It is said to be a **smooth atlas** if any two charts in the atlas A are smoothly compatible with each other. i.e. transition maps $\theta\ o\ \phi^{-1}$ are smooth.

A manifold M with a smooth atlas A is **smooth manifold(M,A).**

1.2.1 Examples

- $\mathbb{R}^n$ is a smooth manifold of dimension n.
- **Sphere**$\mathbb{S}^n$ denote the unit n-sphere,that is the set of unit length vectors in $\mathbb{R}^{n+1}$.

  $\mathbb{S}^n = \{x \in \mathbb{R}^n \mid |x| = 1\}$.

  *Justification:*It is Hausdorff space as well as second countable since it is a subspace of $\mathbb{R}^n$. For it to be locally Euclidean, for each i=1,...,n+1, take V_i^+ as subset of $\mathbb{S}^n$ such that the ith coordinate is positive: V_i^+=$\{(x_1, ..., x_{n+1}) \in \mathbb{S}^n \| x_i \geq 0\}$. In a similar manner,$V_i^-$ is the set where $x_i \leq$0.For all such i, define maps $\psi_{\pm i} : V_{\pm i} \to \mathbb{R}^n$ by

$\psi_{\pm i}(x_1, ..., x_{n+1}) = (x_1, ..., \hat{x}_i, ..., x_{n+1})$,here the hat over x_i denotes that x_i is removed. Each $\psi_{\pm i}$ is a continuous map by evidence, because it is the restriction to $\mathbb{S}^n$ of a linear map on $\mathbb{R}^{n+1}$. It is a homeomorphism to the image, which is the unit ball $\mathbb{B}^n \subset \mathbb{R}^n$, as it(ψ) has a continuous inverse given by
$\phi_{\pm i}(u_1, ..., u_n) = (u_1, ..., u_{i-1}, \sqrt{1-|u|^2}, u_i, ..., u_n)$

As every point on $\mathbb{S}^{n+1}$ belongs to the domain of one of the above mentioned 2n+2 charts,$\mathbb{S}^{n+1}$ is locally Euclidean (dimension n) and hence it is a topological n-manifold.

1.3 Simplicial Complex And Triangulations

Simplices. A d-simplex σ is the convex hull of a set S of d + 1 independent points $x_0, ..., x_d$ in Euclidean space $\mathbb{R}^k$ (where $k \geq d$).S spans the simplex σ. A face of simplex σ is the one which is spanned by a subset S' of S.
If ι is a face of σ we denote it as $\tau < \sigma$. A face is said to be proper if ; $\phi \neq S' \neq S$.We define,the dimension of the face as $|S'|$ - 1.
A vertex is a 0-dimensional face,an edge is a 1-dimensional face. An orientation of σ is defined by the ordering of its 0-dimensional faces i.e. vertices, denoted by $<x_0, ..., x_k>$.

Simplicial complexes. A finite set of simplices in some Euclidean space $\mathbb{R}^m$ is called as simplicial complex K , such that
(1) if ι is a face of σ where σ is a simplex of K, then ι is considered as a simplex of K, and
(2) if σ and ι are two simplices of given simplicial complex K, then $\sigma \cap \iota$ i.e. their intersection is either empty or a common face of σ and ι.
The dimension of the simplicial complex K is defined to be the maximum of the dimensions of its simplices.

The **underlying space of K** $|K|$,is defined as the union of all simplices of K, provided with a subspace topology of $\mathbb{R}^m$.

The *i-skeleton* of K,which is denoted by K^i, is considered to be the union of all simplices of K of maximum dimension i. A sub-complex L of simplicial complex K is a subset of K which is a simplicial complex.

A **triangulation** of a topological space T is denoted by a pair (K,ϕ), where K is a simplicial complex and ϕ is a homeomorphism mapping from the underlying space $|K|$ to T.
The Euler characteristic of a simplicial k-complex K χ(K) is defined as the number $\sum_{i=0}^{k}(-1)^i x_i$, where x_i denotes the the number of i-simplices of K. Some of the examples of simplicial complexes are listed here:
(i). Any graph is taken as a 1-dimensional simplicial complex (imagine a graph as immersed in $\mathbb{R}^3$. A complete graph with m vertices is known as 1-skeleton of an (m-1)-simplex.

1.3.1 Chain spaces and Euler Characterstic

Consider a finite simplicial complex K.The formal sum of the form $\sum_j x_j\sigma_j$ over the oriented k-simplices x_j in K is called as a simplicial k-chain,where coefficients x_j are in the field of rational numbers $\mathbb{Q}$.
The set consisting of all simplicial k-chains form a vector space $C_k(K,\mathbb{Q})$, ans is known as the vector space of simplicial k-chains of K.

The dimension of this vector space is equal to the number of k-simplices of K.

Thus, the **Euler characteristic** of a d-dimensional simplicial complex K can be interpreted in form of an alternating sum of dimensions of the spaces of k-chains as

$$\chi(K) = \sum_{i=0}^{d} dim(C_k(K,\mathbb{Q}))$$

Moving further we define **boundary operator** $\partial_k\sigma : C_k(K,\mathbb{Q}) \to C_{k-1}(K,\mathbb{Q})$ as For a single k-simplex,$\sigma =< v_{i_0}....v_{i_k} >, k > 0$, let $\partial_k\sigma = \sum_{j=0}^{d}(-1)^j < v_{i_0}....\hat{v}_{i_h}...v_{i_k} >$,

and then ∂_k is linearly extended, viz., $\partial_k \sum_j x_j \sigma_j = \sum_j x_j \partial_k \sigma_j$.
For consistency we state $C_{-1}(K, \mathbb{Q}) = 0$, and entitle $\partial_0 : C_k(K, \mathbb{Q}) \to C_{k-1}(K, \mathbb{Q})$ as the zero-map.
The boundary operator is observed as a linear map between vector spaces. It is easy to clarify that it confirms the relation $\partial_k \partial_{k+1} = 0$.

The vector space $Z_k(K, \mathbb{Q}) = \ker(\partial_k)$ is known as the vector space of simplicial k-cycles.
The vector space $B_K(K, \mathbb{Q}) = \mathrm{im}(\partial_{k+1})$ is known to be the vector space of simplicial k-boundaries.
As the boundary of a boundary is 0, $B_k(K, \mathbb{Q})$ is a subspace of $C_k(K, \mathbb{Q})$. The quotient vector space denoted by $H_k(K, \mathbb{Q}) = Z_K(K, \mathbb{Q})/B_K(K, \mathbb{Q})$ is called the k-th homology vector space of K.

The k-th **Betti number** of a simplicial complex K, marked as $\beta_k(K, \mathbb{Q})$, is defined as the dimension of $H_k(K, \mathbb{Q})$. In particular:

$$\beta_k(K, \mathbb{Q}) = dim Z_k(K, \mathbb{Q}) - dim b_k(K, \mathbb{Q}).$$

Theorem 1.1. *Betti numbers are homotopy invariants: if K and L are simplicial complexes with underlying spaces which are homotopy equivalent, then the i-th homology vector spaces of K and L are isomorphic. In fact, $\beta_i(K, \mathbb{Q}) = \beta_i(L, \mathbb{Q})$, for all i.[2]*

Theorem 1.2. *Let K be a d-dimensional simplicial complex. Then*

$$\chi(K) = \sum_{j=0}^{d} (-1)^j \beta_j(K, \mathbb{Q})$$

Proof.[2] Rewriting $\chi(K) = \sum_{i=0}^{d} (-1)^i dim C_k(K, \mathbb{Q})$. Since $H_i(K, \mathbb{Q}) = \frac{kernel(\partial_i)}{Image(\partial_i)}$. and $\beta_i(K, \mathbb{Q}) = dim H_i(K, \mathbb{Q})$
$= dim kernel(\partial_i) - dim Image(\partial_i)$
$= dim C_k(K, \mathbb{Q}) - dim Image(\partial_i) - dim Image(\partial_{i+1})$.

Now, $\sum_{i=0}^{d}(-1)^i(dimImage(\partial_i) + dimImage(\partial_{i+1})) = 0$.

Hence,

$$\chi(K) = \sum_{i=0}^{d}(-1)^i\beta_i(K, \mathbb{Q})$$

If T is a topological space with a simplicial complex K triangulating it, then we define $\chi(K) = \chi(K, \mathbb{Q})$ It is following from the above theorems that the Euler characteristic does not depend on the specific choice of the triangulation K.

Remark

- Betti numbers depend on field of scalars.
- Euler characteristic is independent of the coefficient field.

1.4 Morse Theory

Morse theory studies the relationship between a scalar function and the topology of its domain.

1.4.1 Morse Function

A smooth scalar function is called a Morse Function if all of its critical points are non-degenerate.

1.4.2 Degree of Instability/Index.:

It is the number of negative eigenvalues of the Hessian Matrix at the critical points.
at minima-0
at maxima-1

Lemma 1.3. *(Morse Lemma)Morse Function has quadratic behaviour in the neighbourhood of its critical points.[3]*

OR

Let p be a critical point of a Morse Function f defined on a Manifold M.Then,we can choose appropriate local coordinates $(x_1, x_2, ..., x_n)$ *in neighbourhood of p with p as the origin in such a way that the function f expressed in terms of the local coordinates has the following standard form:*

$$f(x) = f(p) - x_1^2 - x_2^2 - .... - x_\lambda^2 + x_{\lambda+1}^2 + ... + x_n^2$$

OR

In other words,every non-degenerate critical point is isolated.

Proof: We firstly show that if such an expression for f exists,then λ must be the index of f at p.For any coordinate system $(\mathrm{z}^1, z^2, ..., z^n)$, if

$$f)q) = f(p) = (z^1(q))^2 - .... - (z^\lambda(q))^2 + (z^{\lambda+1}(q))^2 + ... + (z^n(q))^2$$

then we have

$$\frac{\partial^2 f}{\partial z^i \partial z^j}(p) = \left\{ \begin{array}{ll} -2, & i = j \leq \lambda \\ 2, & i = j > \lambda \\ 0, & \text{otherwise} \end{array} \right\}$$

which shows that the matrix representing f_{**} with respect to the basis

$$\frac{\partial}{\partial x^1}|_p, ..., \frac{\partial}{\partial x^n}|_p i$$

$$\begin{bmatrix} -2 & & & & & \\ & \ddots & & & & \\ & & -2 & & & \\ & & & 2 & & \\ & & & & \ddots & \\ & & & & & 2 \end{bmatrix}$$

So there is subspace of TM_p of dimension λ,here f_{**} is negative definite, and a subspace V of dimension n-λ,here f_{**} is positive definite.If there would have been a subspace of TM_p of dimension greater than λ where f_{**} were negative definite then this subspace would have intersected V,which is definitely not possible.Therefore λ has to be the index of f_{**}.

We now show that a suitable coordinate system $(y^1, ..., y^n)$ exists.Obviously we can assume that p is the origin of $\mathbb{R}^n$ and that f(p)=f(0).We can write,

$$f(x_1, ..., x_n) = \sum_{j=1}^{n} x_j g_j(x_1, ..., x_n)$$

for $(x_1, ..., x_n)$ in some neighbourhood of 0.Since 0 is taken to be a critical point.

$$g_j(0) = \frac{\partial f}{\partial x^j}(0) = 0.$$

Therefore,again we can express g in terms of x_i's as

$$g(x_1, ..., x_n) = \sum_{i=1}^{n} x_j h_{ij}(x_1, ..., x_n)$$

for some smooth functions h_ij.It follows that

$$f(x_1, ..., x_n) = \sum_{i,j=1}^{n} x_i x_j h_{ij}(x_1, ..., x_n)$$

We can suppose that h_{ij}=h_{ji},because we can write $\hat{h}_{ij}$=$\frac{1}{2}$(h_{ij}+h_{ji}),and then we have $\hat{h}_{ij} = \hat{h}_{ji}$ and f= $\sum x_i x_j \hat{h}_{ij}$. Although the matrix $(\hat{h}_{ij}(0))$is equal to $\frac{1}{2}\frac{\partial^2 f}{\partial x^i \partial x^j}(0)$, that is why it is non-singular.

There is a non-singular transformation of the coordinate functions which gives us the desired formulation for f,in a very smaller neighbourhood of 0.To see this we just consider the usual diagonalization proof for quadratic forms.The main step can be explained as.

Assume by induction that there exists coordinates $u_1, ..., u_n$ in a neighbourhood U_1

of 0 so that

$$f = \pm(u_1)^2 \pm ..... \pm (u_{r-1})^2 + \sum_{i,j \geq r} u_i u_j H_{ij}(u_1, ..., u_n)$$

throughout U_1 where these matrices $(H_{ij}(u_1, ..., u_n))$ are symmetric.After linear transformation in the last n-r+1 coordinates we may assume that $H_{rr} \neq 0$.Let $g(u_1, .., u_n)$ denote the square root of $|H_{rr}(u_1, ..., u_n|$. This will be a smooth ,non-zero function of $u_1, ..., u_n$ throughout some small neighbourhood $U_2 \subset U_1$ of 0.Now introduction new coordinates $v_1, ..., v_n$ by
$v_i = u_i$ for $i \neq r$

$$v_r(u_1, ..., u_n) = g(u_1, ..., u_n)[u_r + \sum_{i>r} \frac{u_i H_{ir}(u_1, ..., u_n)}{H_r(u_1, ..., u_n)}.$$

It infers from the inverse function theorem that $v_1, ..., v_n$ will act as coordinate functions within some sufficiently small neighbourhood U_3 of 0. It is easily seen that f can be written as

$$f = \sum_{i \leq r} \pm(v_i)^2 + \sum_{i,j>r} v_i v_j H'_{ij}(v_1, ..., v_n)$$

throughout U_3.Hence proving the induction and lemma.

1.4.3 Morse Number

The k-th Morse number of a Morse function f, denoted by k(f), is the number of critical points of f of index k.We denote it by μ_k.

1.4.4 Morse Inequalities

Let f be a Morse function on a m-dimensional compact and smooth submanifold of $\mathbb{R}^n$. The k-th Morse number of f is dominating over the k-th Betti number of M,for each k, $0 \leq k \leq m$:[4] $\mu_k(f) \geq \beta_k(M, \mathbb{Q})$

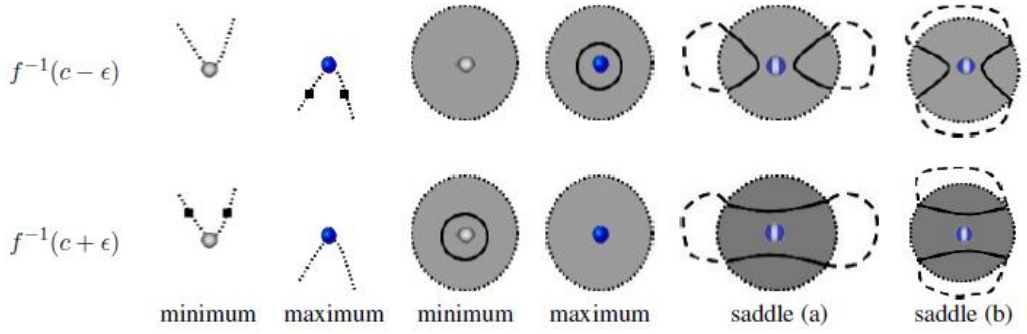

Figure 1.4: The level set of a Morse function gains a component after passing a minimum and loses a component after passing a maximum. In 2D functions, the isocontour either gains or loses a component when it passes a saddle point.

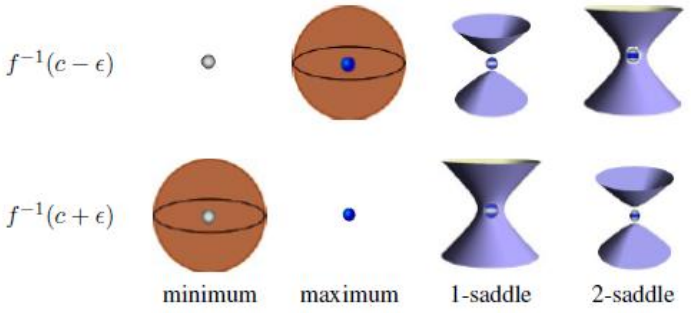

Figure 1.5: Upon passing a critical value, the isosurface topology changes either in the number of components or in the number of holes.

FIGURE 1.1: How the Isosurface Changes when it passes through a Critical Point?[1]

$$n_{-3} \geq 1,$$

$$n_{-3} - n_{-1} \leq 1,$$

$$n_{-3} - n_{-1} + n_{+1} \geq 1,$$

$$n_{+3} \geq 0$$

$$n_{+3} - n_{+1} \leq 0,$$

$$n_{+3} - n{+}1 + n_{-1} \geq 0$$

Similarly,one can prove that the Morse numbers of f are linked to the Betti numbers and the Euler characteristic of M by the given expression as follows:

$$\sum_{i=0}^{d}(-1)^i\mu_i(f) = \chi(K) = \sum_{i=0}^{d}(-1)^i\beta_i(M,\mathbb{Q})$$

1.5 Surfaces and Orientability of Surfaces

Definition A subset M$\neq \phi \subset \mathbb{R}^3$ is said to be a regular surface if for every point p $\in$ M there is a neighbourhood U $\subset \mathbb{R}^3$, an open subset V $\subset \mathbb{R}^2$ and a diferentiable map,ϕ : V $\rightarrow$ U $\cap$M $\subset \mathbb{R}^3$ with the following conditions:
(1) ϕ : V $\rightarrow \phi(V)\cap$M is a homeomorphism.
(2) For every q $\in$ V, the differential Dϕ(q) : $\mathbb{R}^2 \rightarrow \mathbb{R}^3$ is injective.
Orientability of surfaces A regular surface M is said to be orientable if it is feasible to cover it with an atlas A, so that

$$\forall i; j \in I; \forall p \in U_i \cap U_j : det(\phi_j \circ \phi_j^{-1})(\phi_i(p)) > 0.$$

Gauss Map Suppose (M,n) be an oriented surface in $\mathbb{R}^3$ and (θ;V) a local chart for M with a basis (θ_u, θ_v) for T_pM, with (u, v) coordinates in V. The Gauss map is the map:

$$n : M \rightarrow \mathbb{S}^2 \subset \mathbb{R}^3$$

$$p \rightarrow n(p) = \frac{\phi_u \times \phi_v(p)}{|||\phi_u \times \phi_v|||}$$

The Gauss map is a differentiable map.
Gauss Bonnet Formula Gaussian Curvature The Gaussian curvature of a regular surface M at any point p $\in$ M is defined as

$$K(p) = det(Dn(p))$$

here Dn(p) is the differential of the Gauss map(n) at p.[5] The **Gauss Bonnet Formula** introduced to the nineteenth century which is applied to a compact surface M

whose Euler characteristic χ(M) is given by:

$$\int_M K.dA = 2\chi(M)$$

.

1.6 Poincaré Hopf Theorem

Let v be a vector field on M without boundary, which also just possess isolated zeros. Then,the the theorem states that the sum of the indices of the zeros of the vector field is equal to the Euler characteristic of the manifold.[6] For a 3 dimensional Manifold,the relation is as follows:

$$n_{+3} - n{+}1 + n_{-1} - n_{-3} = \chi$$

Proof: We have shown that the sum of the indices of a vector field is not a variable, because it is exactly equal to the degree of the Gauss map, which tells that it is sufficent to find only one example of a vector field and calculate its index. Using Morse theory, we got that there exists a vector field, such that for this vector field, we get the sum of the indices at the zero to be equal to the Euler characteristic. Hence the theorem is true for manifolds with boundary with non-degenerate zeros only. Let us consider, we have a vector field v which is defined on an open set V $\subset \mathbb{R}^k$ with a degenerate zero z. Take $\delta > 0$ be very small such that z is the only zero lying in a ball of radius 2δ. Suppose g : U $\rightarrow$ [0, 1] be a smooth function with the condition that f (x) = 1 inside ball of radius δ around z, and 0 outside the ball of radius 2δ. Let the vector field $\hat{v}$(x) = v(x)-f(x)y, y is a regular value of the vector field v (whose existence is assured by Sards theorem). In reality, observe that $||v(x)||$ is greater than $\epsilon > 0$ for all x outside the ball of radius δ and inside the ball of radius 2δ. Thus we can choose y so small such that $||y|| < \delta$, so that all of the zeros of the new vector field are inside of the ball of radius ϵ. Now, if we consider any zero of the new vector field,we observe that since f(x) is constant inside the ball of radius ϵ, that d$\hat{v}$(z') = v(z') $\neq$ 0. Thus this is a nondegenerate vector field. Doing this for every zero, we thereby obtain a non-degenerate vector field. Now, we must show that the index of the vector

field is not changed. Especially, say $i_{v,z}$ be the index of a zero of the original vector field. Looking into, by the definition of the index,v(x) the index is equal to the degree of the map $\frac{v(x)}{||v(x)||}$ around $\partial B_{2\epsilon}$ (z). We prove that,$\sum_{z'} i_{\hat{v},z'}$ is the sum of the indices of $\hat{v}$ at the zeros z' in the ball of radius 2δ, then $i_{v,z} = \sum_{z'\hat{v},z'}$. Consider $\delta' > 0$ be very small such that there are no zeros outside of a ball of radius δ' around each zero z'. Omitting these balls, we take the degrees of the maps at each of the boundary components. This must be zero, as it is oriented as the boundary and it extends to a smooth vector field. The degree on the outer component is clearly i z , because v = $\hat{v}$ on this component. Using an similar argument as above, on the other components we have the degree is -$\sum_{z'} i_{\hat{v},z'}$. Hence $i_{v,z} - \sum_{z'} i_{\hat{v},z'}$=0 and the required result is proved.

1.7 Plan of the Thesis

We have looked at the definitions and basic theorems related to manifolds and scalar fields.Now we plan to implement them in constructing our algorithm to find critical points of a 3D Scalar field.As discussed in the previous section the Euler Characteristic of a smooth manifold is an intrinsic property which can be calculated by knowing number of asymptotic negative regions and number of asymptotic positive regions and vice-versa.The goal of this work is to create an general approach for finding critical points of any 3D function and provide an interesting algorithm for the same.The plan of the work is therefore given as follows:

- Visualize and classify critical points for Molecular Electrostatic potential of some molecules using any visualization software and deriving Poincaré Hopf relation verifying Euler Characteristic.
- Generating and Triangulating Zero Flux Surfaces by applying gradient separating criteria to Marching Cubes Algorithm.
- Reduction of dimensions approach to approximate a separatix and hence the critical points.

- Categorizing Catastrophes of Reaction Pathways(Molecular Electrostatic Potential of Water) using Catastrophe theory.

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Chapter 2

Zero Flux Surfaces and Optimization of Critical Points

The critical points of MESP of molecules have been visualized using a visualization software.[1] have computed the topography using various relation such as Poincaré Hopf relation and Morse inequalities.The Zero flux surfaces of MESP of molecules have been a subject in characterizing a molecule's topography. These Surfaces separate the minima and maxima regions of the scalar field involved.The surfaces contain the separatix which contains all the critical points of the scalar field. An algorithm has been developed to generate the zero flux surfaces of any general 3D Scalar Field or any general 3D function using a well known algorithm Marching Cubes(refer to Appendix A). Then these surfaces are used to locate critical points by using Newton Raphson optimization to find a minimum.The guess points for the critical point optimization are figured by the criteria of zero magnitude of the gradient near the critical points. In this chapter, analysis has been done to arrive at a similar result by localizing the critical points of MESP of some molecules.

2.1 Visualization

In order to verify Poincaré hopf relation, molecules were visualized in Gabedit(a software) and critical points were found along with the function(MESP) value at that points.Then were characterized on the basis of effect of varying the function(MESP) value slightly to a nearby value.According to the Morse Theory discussed in previous chapter,if the isosurface at that isovalue of the critical points shrinks or contracts on decresing or increasing the isovalue then it will be either a **(3,+1) and (3,-1)** critical point.[2] The Euler charactestic for MESP of some molecules have been calculated using Poincaré Hopf Relation i.e. $n_{+3} - n + 1 + n_{-1} - n_{-3} = \chi$ and tabulated in Tables below.

TABLE 2.1: Critical points of Water

Location	Number	Type	Isovalue
OH BOND	2	(3,-1)	1.15
Lone pair	2	(3,+3)	-0.080978
on C2 b/w lp	1	(3,+1)	-0.07947
On nucleus	3	(3,-3)	-1.0 x e^{10}

$$\chi = 2 - 1 + 2 - 3 = 0$$

TABLE 2.2: Critical points of Carbon Monoxide

Location	Number	Type	Isovalue
CO BOND	1	(3,-1)	-1.6
LP(CO)	1	(3,+3)	-0.02529
LP(O)	1	(3,+3)	-0.016
On nucleus	2	(3,-3)	-198.6

$$\chi = 2 - 0 + 1 - 2 = 1$$

TABLE 2.3: Critical points of Acetylene

Location	Number	Type	Isovalue
CC BOND	1	(3,-1)	-1.39
CH bond	1	(3,-1)	0.925
ring $\perp$ C-∞	infinite	(2,-)	-0.0345
On nucleus	3	(3,-3)	372.83

$$\chi = 0 - 0 + 1 - 2 = -1$$

TABLE 2.4: Critical points of Benzene

Location	Number	Type	Isovalue
CC BOND	6	(3,-1)	0.845
CH BOND	6	(3,-1)	0.81
middle	1	(3,+1)	0.13
On C6 axis	2	(3,-1)	-0.02385
ring	12	(3,+3)	-0.024332
ring	12	(3,+1)	-0.024295
On nucleus	12	(3,-3)	364.48 x e^{10}

$$\chi = 12 - 13 + 14 - 12 = 1$$

2.2 Generating Zero Flux Surfaces

A Zero Flux Surface is defined by the condition $\nabla\vec{V}.\vec{ds} = 0$, where V is the scalar Field,$\nabla\vec{V}$ is the gradient on the scalar field and dS is the normal to the required surface.Thus the zero flux surface [3] comprise of all the points of scalar field on which the gradient to the scalar field is perpendicular to the that point of scalar field.We have produced this surface by simply computing gradient to the scalar field at each point and its angle with surface in all three directions/axis.Then,applying **Marching Cubes Algorithm** to the angle and at isovalue=$\pi/2$, the isosurface is the zero flux surface. We have generated zero flux surfaces for electrostatic potential for some molecules i.e. acetylene,water,benzene,carbon monoxide,carbon dioxide,hydrogen flouride molecule. Here are the plots of zero flux surfaces.

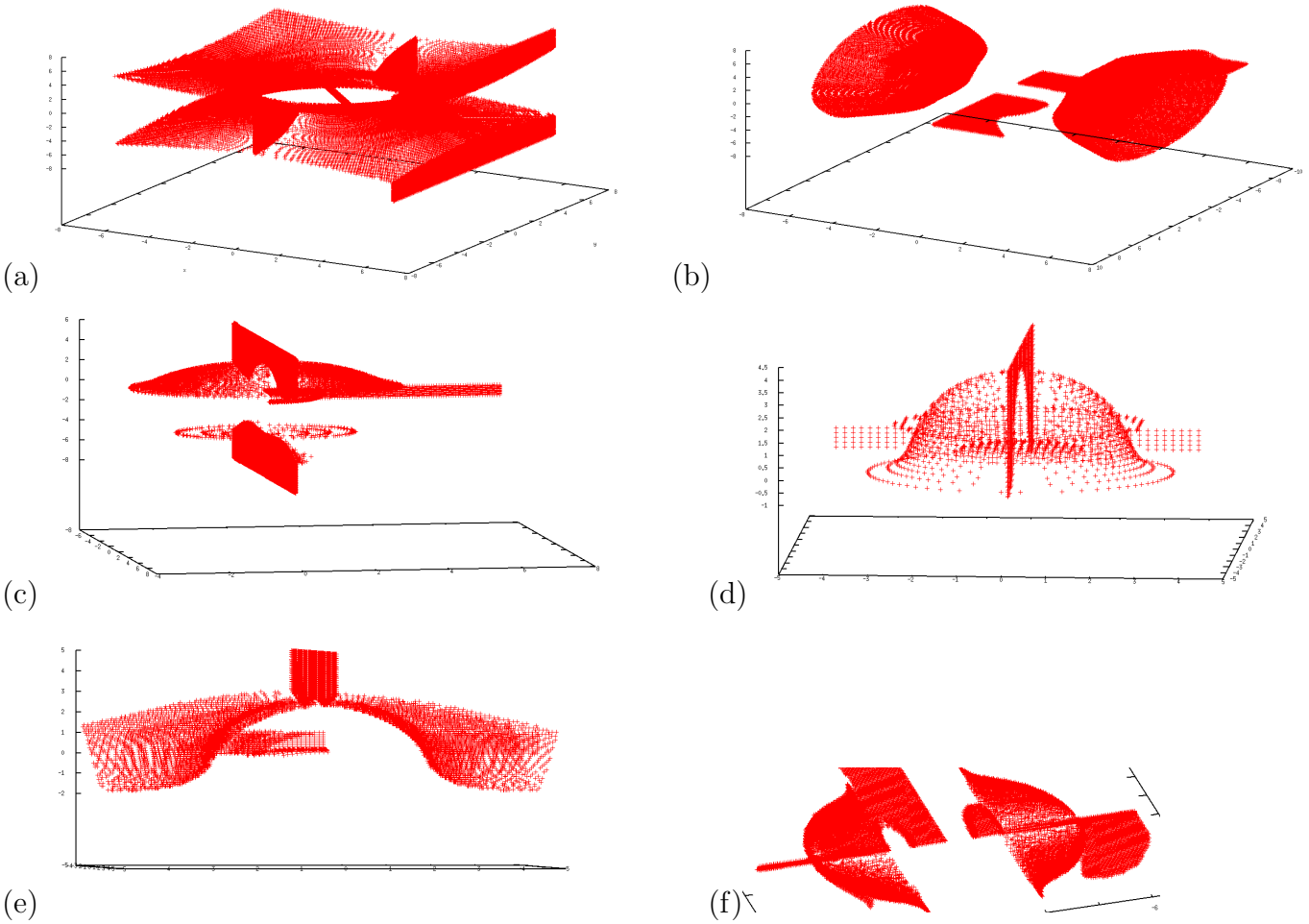

FIGURE 2.1: Zero Flux Surfaces

(a)Acetylene,(b)Benzene,(c)Carbon mono-oxide,(d)Hydrogen Flouride,(e)Water,(e)Carbondioxide

2.3 Optimization

The quadratic approximation method [4]to find a minimum of any function of one variable which produces a sequence of second degree Lagrange polynomials and we use them to approximate where the minimum is situated.It was understood that near the minimum,the shape of the objective function y=f(x) is approximated by the shape of the quadratics.The resulting sequence of minimums of the quadratics generated a sequence which converges to the minimum of the objective function y=f(x).This process id extended to functions of n independent variables f($\vec{X}$)=f($x_1, ..., x_n$) by Newton's

search method[4].Starting at an initial point . A sequence of second-degree polynomials in n variables is build recursively.Following the conditions that objective function is well-behaved and the initial guess point is near the actual minimum point,the sequence of minimums of the quadratics converge to the minimum of the objective function. Both the first- and second-order partial derivatives of the objective function are used by this process. As we see that only the first partial derivatives are used by the gradient method .This is expected that Newton's method will be more efficient than the gradient method.

2.3.1 Taylor Expansion

Suppose that f($\vec{X}$)=f(x,y,z) is a 3D function, $\vec{X}$=(x,y,z), and up to the order two its partial derivatives exists.On the basis of series and matrices,the quadrartic approximation to f(x,y,z) can be written in two ways,respectfully.Consider that the point of expansion is $\vec{P}$=(p,q,r) and using the symbol as $\Delta\vec{P} = (\Delta p, \Delta q, \Delta r)$ and ,then $\vec{X} = \vec{P} + \Delta\vec{P}$

Using series notation ,the Taylor polynomial is given by

$$f(p+\Delta p, q+\Delta q, r+\Delta r) = f(p,q,r) + f_x(p,q,r)\Delta p + f_y(p,q,r)\Delta q + f_z(p,q,r)\Delta r +$$

$$\frac{1}{2!}(f_{xx}(p,q,r)\Delta p^2 + f_{yy}(p,q,r)\Delta q^2 + f_{zz}(p,q,r)\Delta r^2 + 2(f_{xy}\Delta p\Delta q + f_{yz}\Delta q\Delta r + f_{xz}\Delta p\Delta r)$$

using vector and matrix notation it can be expressed as

$$f(p+\Delta p, q+\Delta q, r+\Delta r) = f(p,q,r) + \begin{bmatrix} f_x(p,q,r) & f_y(p,q,r) & f_z(p,q,r) \end{bmatrix} \begin{bmatrix} \Delta p \\ \Delta q \\ \Delta r \end{bmatrix} +$$

$$\frac{1}{2!} \begin{bmatrix} \Delta p & \Delta q & \Delta r \end{bmatrix} \cdot \begin{bmatrix} f_{xx}(p,q,r) & f_{xy}(p,q,r) & f_{xz}(p,q,r) \\ f_{xy}(p,q,r) & f_{yy}(p,q,r) & f_{yz}(p,q,r) \\ f_{xz}(p,q,r) & f_{yz}(p,q,r) & f_{zz}(p,q,r) \end{bmatrix} \begin{bmatrix} \Delta p \\ \Delta q \\ \Delta r \end{bmatrix}$$

The latter can be re-expressed in the form

$$f(p+\Delta p, q+\Delta q, r+\Delta r) = f(p,q,r)+\nabla f(p,q,r)\begin{bmatrix}\Delta p\\ \Delta q\\ \Delta r\end{bmatrix}+\begin{bmatrix}\Delta p & \Delta q & \Delta r\end{bmatrix}.H(p,q,r)\begin{bmatrix}\Delta p\\ \Delta q\\ \Delta r\end{bmatrix}$$

Using vector notations $\vec{P}, \Delta\vec{P}$, and $\vec{X} = \vec{P} + \Delta\vec{P}$ it seems

$$f\vec{(}X) = f(\vec{P}) + \nabla f(\vec{P}).\Delta\vec{P} + \frac{1}{2!}\vec{P}.H(\vec{P}).\Delta\vec{P}^T$$

2.3.2 Newton's Method to find a Minimum

We move towards minimizing the function f($\vec{X}$) of n variables, where we know $\vec{X}$=($x_1, ..., x_n$) and the partial derivatives of f($\vec{X}$). Consider the existence of first and second partial derivatives of w = f($\vec{X}$) =f($x_1, ..., x_n$) and their continuity in a region containing the point P_0 , minimum is at the point $\vec{P}$. The quadratic polynomial approximation to f($\vec{X}$) is

$$Q(\vec{X}) = f(\vec{P_0}) + \nabla f(\vec{P_0}).\Delta\vec{P_0} + \frac{1}{2!}\vec{P_0}.H(\vec{P_0}).\Delta\vec{P_0}^T$$

A minimum of Q($\vec{X}$) will occur when Δ Q($\vec{X}$)=0
Using the symbols $\vec{P_0} = (p_0, q_0, r_0)$ and $\Delta P_0 = \vec{X} - P_0 = (x - p_0, y - q_0, z - r_0)$ and the symmetry of H($\vec{P_0}$), we express

$$Q(x,y,z) = f(p_0,q_0,r_0) + \begin{bmatrix}f_x(p_0,q_0,r_0) & f_y(p_0,q_0,r_0) & f_z(p_0,q_0,r_0)\end{bmatrix}\cdot\begin{bmatrix}x-p_0\\ y-p_0\\ z-p_0\end{bmatrix}+$$

$$\begin{bmatrix}x-p_0 & y-p_0 & z-p_0\end{bmatrix}\cdot\begin{bmatrix}f_{xx}(p_0,q_0,r_0) & f_{xy}(p_0,q_0,r_0) & f_{xz}(p_0,q_0,r_0)\\ f_{xy}(p_0,q_0,r_0) & f_{yy}(p_0,q_0,r_0) & f_{yz}(p_0,q_0,r_0)\\ f_{xz}(p_0,q_0,r_0) & f_{yz}(p_0,q_0,r_0) & f_{zz}(p_0,q_0,r_0)\end{bmatrix}\begin{bmatrix}x-p_0\\ y-q_0\\ z-r_0\end{bmatrix}$$

Thus the formulation for Δ Q$(\vec{X})$=0 can be expressed as

$$\nabla f\vec{P_0} + (\vec{X} - \vec{P_0}).H(\vec{P_0}) = \vec{0}$$

Let $\vec{P_0}$ is very close to the point $\vec{P}$ (where a minimum of f is supposed to occur),thus H($\vec{P_0}$) has inverse,the above mentioned equation can be solved for $\vec{X}$, and we get

$$\vec{X} = \vec{P_0} - \nabla f(\vec{P_0})(H(\vec{P_0}))^{-1}$$

This value of $\vec{X}$ is used as the next approximation to $\vec{P}$ and is the first step in Newton's method for finding a minimum.

$$\vec{P_1} = \vec{P_0} - \nabla f(\vec{P_0})(H(\vec{P_0}))^{-1}$$

The initial points are the guess points to the critical points computed by magnitude being very close to 0. Here are plots of the some critical points of MESP calculated using this method.

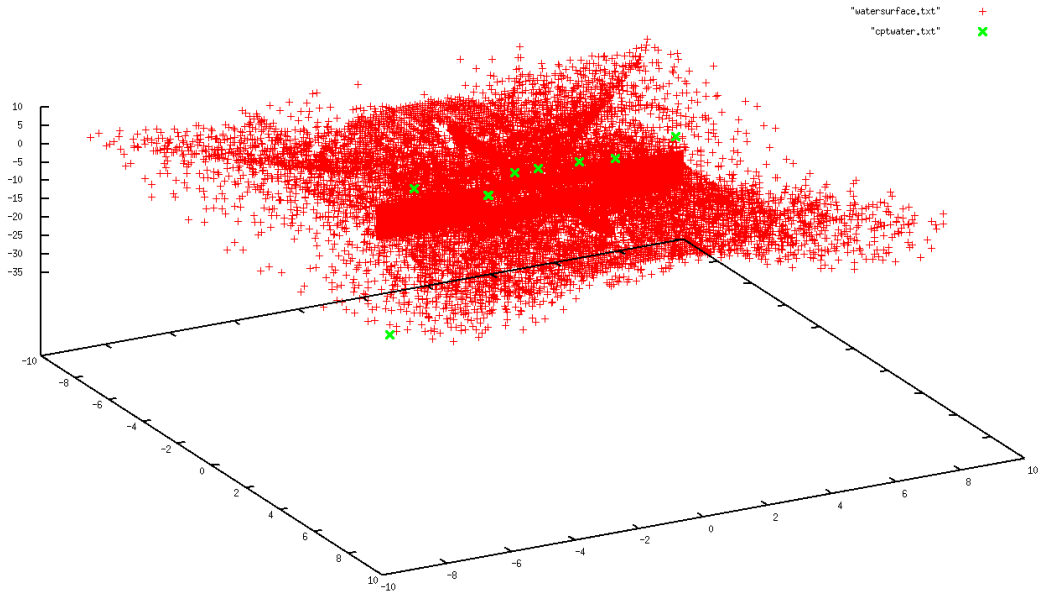

FIGURE 2.2: Critical points of Water

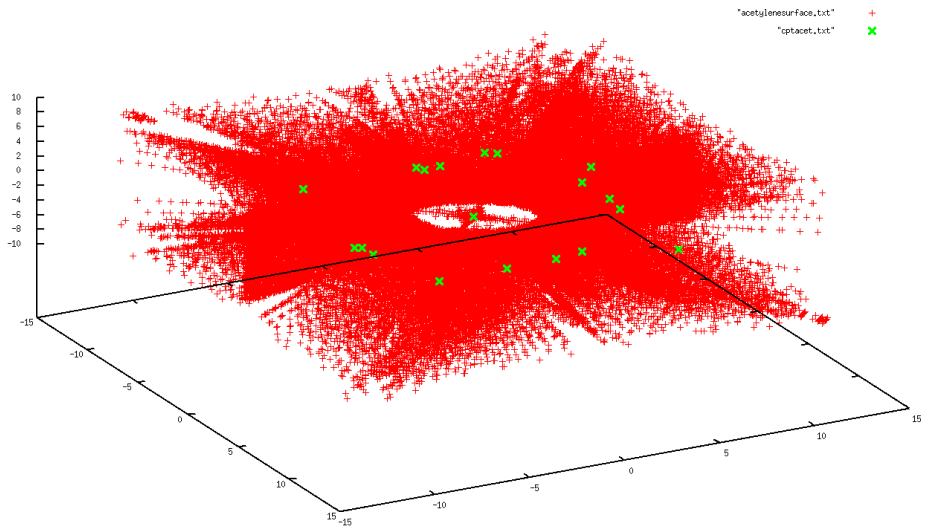

FIGURE 2.3: Critical points of Acetylene

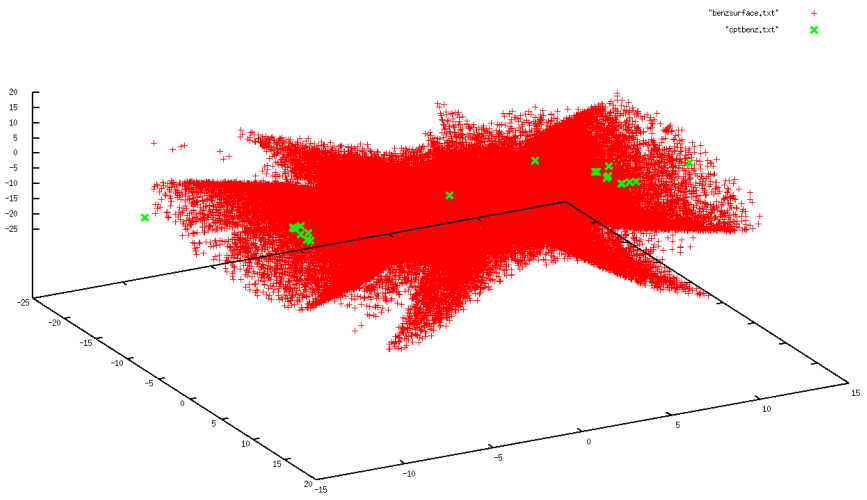

FIGURE 2.4: Critical points of Benzene

These results conclude this chapter and in next chapter we introduce catastophe theory.

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Chapter 3

Introduction to Catastrophe Theory

Catastrophe Theory[1] is a study of sudden changes that occur when control variables of a system are perturbed to a small extent.Then the behaviour of the change in the system is measured in terms of the various types of catastrophes.In chemistry,we consider the reactions as systems and observe the behaviour of the reaction and categorize based on the polynomial form of the behavioural function.Hence, on the basis of number of catastrophes involved in the reaction pathway,we conclude that the number of catastrophes between two steps is inversely proportional to the similarity of the extremes of that step.

3.1 Definition

3.1.1 System

The system to be analyzed consists of control parameters and variables of the function(f) governing the system which can be changed to observe the discontinuous behaviour of the equilibrium state of the system.

Equilibrium State

Let $f_{(x,y)}(z)$ be a family of smooth function/potential of the system,where (x, y) can be considered as control parameters and z is the variable of function f.

The **surface of equilibria**:

$$M_f = \{(x, y, z) \mid f\prime(x, y)(z) = 0\}$$

Catastrophe

The set of catastrophes:

$$C_f = \{(x, y, z) \mid f\prime_{(x,y)}(z) = 0, f\prime\prime_{(x,y)}(z) = 0\}$$

Its projection over the plane xy defines the **bifurcation set**:

$$B_f = \{(x, y) \in \mathbb{R}^2 \mid (x, y, z) \in C_f for some z\}$$

The projection $\chi_f : C_f \to B_f$ is called **catastrophe germ**.

3.1.2 Germ Theory

Two smooth functions f, g : $\mathbb{R}^n \to \mathbb{R}$ defined the same germ if they agree over some neighbourhood of the origin.

Equivalence of Germs

Two germs f, g are equivalent if there exists $\phi \in \mathcal{G}(n)$ such that g = f $\circ\phi$, we denote it as g $\sim$ f.

The set of all the germs over R n with the usual addition and multiplication forms a ring denoted $\mathcal{E}(n)$.

The elements of the subring

$$\mathcal{M}(n) = \{g \in \mathcal{E}(n) \mid g(0) = 0\}$$

have no inverse, and they form an ideal.

$\mathcal{M}(n)$ is the sole **maximal ideal** of the ring $\mathcal{E}(n)$, hence $\mathcal{E}(n)$ is a local ring.

Codimension of Germs

$\mathcal{M}$(n) k = $\mathcal{M}$(n)... $^{k-times}$ ... $\mathcal{M}$(n).

We define the **Jacobs ideal of a germ** f as the ideal:

$$\Delta(f) = \left\{ g_1 \frac{\partial f}{\partial x_1} + ... + g_n \frac{\partial f}{\partial x_n} \mid g_i \in \mathcal{E}(n) \right\}$$

Remark If f ϵ $\mathcal{M}$(n)^2 $\Rightarrow$ Δ(f) $\subset$ $\mathcal{M}$(n).

We call **codimension** of a germ f ϵ $\mathcal{M}$(n)^2 as:

$$codim(f) = dim(\mathcal{M}(n) \Big/ \Delta(f)) \epsilon \mathbb{N} \cup \{\infty\}$$

Unfolding of a germ

Let f ϵ $\mathcal{M}$(n)^2 be a germ, another germ F $\in$ $\mathcal{M}$(n + r) is a **r-unfolding** of f if f(x)=F(x,0).

The **universal unfoldings** are the universal objects in the category of unfoldings.

3.1.3 Canonical form of Catastrophe

[2] Let $\mathcal{F}$: $\mathbb{R}^n$ $\mathbb{R}^r$ $\rightarrow$ $\mathbb{R}$ be a smooth function $\mathcal{F}$(z,p).Let (z_0, p_0) such that z_0 is a critical point of $\mathcal{F}$ (,p_0): $\frac{\partial f}{\partial z_1}$=0 ..... $\frac{\partial f}{\partial z_n}$=0

We move to the origin: $\mathcal{F}$(z,p) $\equiv$ $\mathcal{F}$(z+z_0,p+p_0)-$\mathcal{F}$(z_0,p_0).$\mathcal{F}$ satisfies $\mathcal{F}$(,0) has 0 as a critical point a$\mathcal{F}$ F(0,0)=0.

$\mathcal{F}$(z,p) is a unfolding of f(z) $\equiv$ $\mathcal{F}$(z,0). We assume that it is a universal unfolding (and r = codim(f)). f(0) = 0 and 0 is a critical point of f , then f$\in$ $\mathcal{M}$(n)^2.

If 0 is a **non degenerate** critical point, them by Morse lemma there exists $\phi \in \mathcal{G}$(n) such that:

$$f(\phi(z)) = -z_1^2 - .... - z_k^2 + z_{k+1}^2 + ... + z_n^2$$

where k = morse index(f). In a neighbourhood of the origin there are no more critical points of f.Besides codim(f) = 0.

Let us now assume that 0 is a **degenerated** critical point of f and codim(f) $\leq$ 5,

then there exists $\phi \in \mathcal{G}$(n) such that:

$$f(\phi(z)) = -z_1^2 - .... - z_k^2 + z_{k+1}^2 + ... + z_n^2 + Q$$

where k = morse index(f)$\leq$ rg(f) $\in$ {n-2,n-1} and Q is a polynomial of (n-rg(f)) $\in$ {1,2} variables. Q is one and only one of the 11 possible polynomials (we will see them later) and satisfies codim(Q) = codim(f).

Once we have the unique Q we build a canonical universal unfolding $\bar{Q}$ of Q, with r = codim(f) parameters. Hence $\bar{F} \equiv$ q + $\bar{Q}$ is a universal unfolding of q + Q = f $\circ\phi$. On the other hand $\mathcal{F}$ is a universal unfolding of f , then $\mathcal{F}\circ$ ($\phi \times \mathrm{Id}_{\mathbb{R}^r}$) is a universal unfolding of f $\circ\phi$ = q + Q with r parameters.

So we have F and F $\circ$ ($\phi \times \mathrm{Id}_r$) universal unfoldings of f with the same number of parameters, they are this isomorphic. Furthermore, their catastrophe germ $\chi_{\mathcal{F}} \sim \chi_F$ are equivalent.

The catastrophe germs are called **elementary catastrophes**.

Theorem 3.1. *Rene Thom's Theorem Any smooth function f : $\mathbb{R}^n \to \mathbb{R}$, having a critical point at the origin, and having codimension $\leq$ 5 , is right equivalent (up to sign) to one of the following:*

TABLE 3.1: Thom's Classification of Catastrophes

Name	r=codim(f)	f	unfolding
(Morse)	0	x^2	x^2
Fold	1	x^3	x^3+ax
Cusp	2	x^4	x^4+ax^2+bx
Swallowtail	3	x^5	x^5+ax^3+bx^2+cx
Butterfly	4	x^6	x^6+ax^4+bx^3+cx^2+dx
Hyperbolic Umbilic	3	x^3+y^3	x^3+y^3+axy+bx+cy
Elliptic Umbilic	3	x^3-3xy^2	x^3-3xy^2+a(x^2+y^2)+bx+cy
Parabolic Umbilic	4	x^2y+y^4	x^2y+y^2+ax^2+by^2+cx+dy
Symbolic Umbilic	5	x^3y+y^4	x^3y+y^4+axy^2+bxy+cy^2+dx+ey
Second Elliptic Umbilic	5	x^2y-y^5	x^2y-y^5+ax^2+by^2+bx+cy^3+dx+ey
Second Hyperbolic Umbilic	5	x^2y+y^5	x^2y+y^5+ax^2+by^2+bx+cy^3+dx+ey

Here a,b,c,d,e are the control parameters of the system.

*Remark:*The Morse function x^2 is not a catastrophe function.The other are *Thom's elementary catastrophes.*

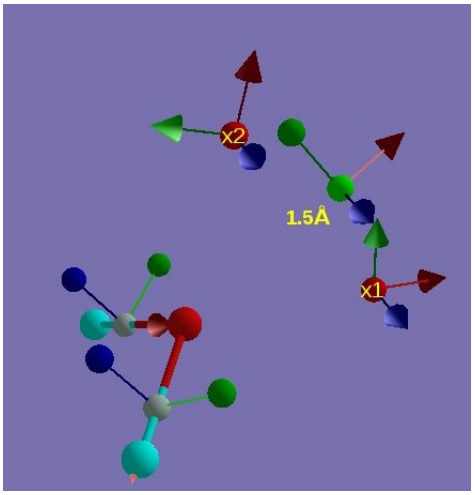
Here,we take Water as a system with MESP of water governing the changes in the system.We know that water in its equilibirium state have parameter bond angle(HOH)=104.5°.

When we increase this angle from 90° to 180° making it linear,we observe the changes in the MESP(its isosurfaces and critical points at different stages).We observe catastrophes at steps in-between and categorize them.[3]

- At lowest angle i.e. 90°, it is seen that there are two minima(3,+3) points at lone pairs on **O**xygen and a (3,+1) saddle indexed +1 connecting the two minimas.There are two (3,-1) 2-saddles at OH Bond.AS we increase the angle,the distance between the two minima decrease and they come closer and at angle 126°,the three critical points(including two minima's and one 1-saddle) merge to give a single minima,which denotes a catastrophe at this step.On observing the behaviour of the curve(going from two minima and 1-saddle to a single minima) we conclude that it is a **cusp** because the function is an even function.

- Then at 144°,appearance of a critical point (3+1) on the opposite side of the minima between two H-atoms at centre indicates another catastrophe which is taken as **fold** again from the behaviour.

- Then this point disappears again as the molecule gets linear,and form a ring of degenerate minima around **O**xygen,which is **cusp** catastrophe.



Equilibirium(104.5°)

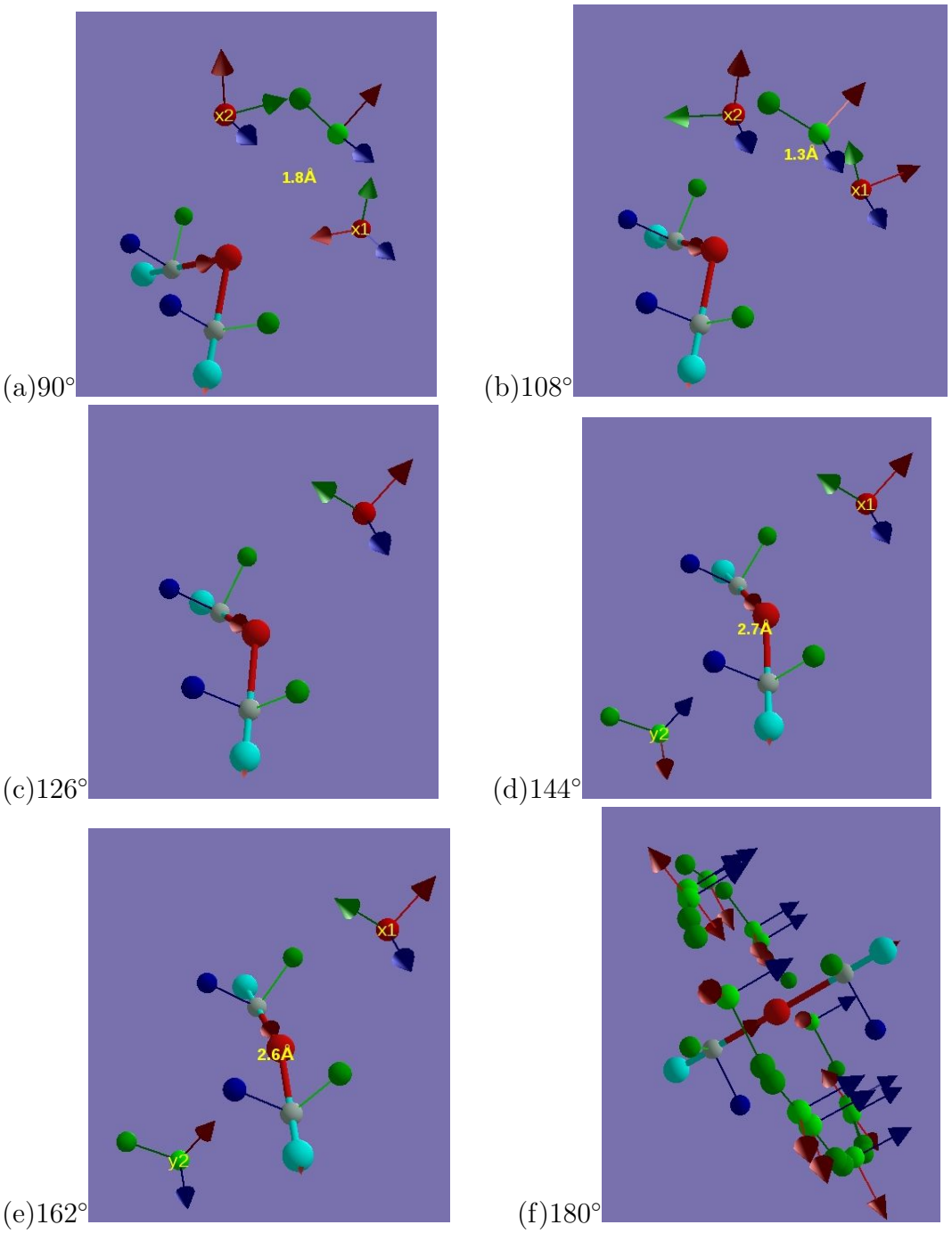


FIGURE 3.1: Characterizing Catastrophes of MESP of Water on changing bond angle

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Appendix A

Marching Cubes Algorithm

Marching Cubes was proposed by Lorensen and Cline in 1987.It generates isosurface of any given general 3D Scalar Field at a given isovalue.to the algorithm is isovalue.
Grid Vertex is categorized as

- **positive**, +, if its scalar value is greater than or equal to σ.
- **negative**, -, if its scalar value is less than σ.
- **strictly positive** if its scalar value does not equal σ.

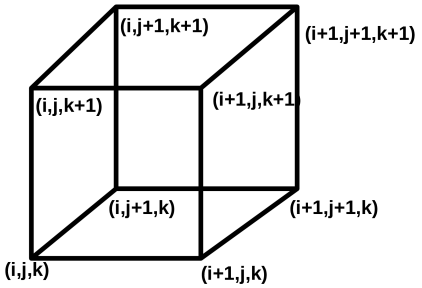
Grid Edge is catagorized as

- **positive** if both its endpoints are positive.
- **negative** if both its endpoints are negative.
- **strictly positive** if both its endpoints are strictly positive.
- **bipolar** if one endpoint is positive and one endpoint is negative

A.1 Algorithm

Create cells (cubes)

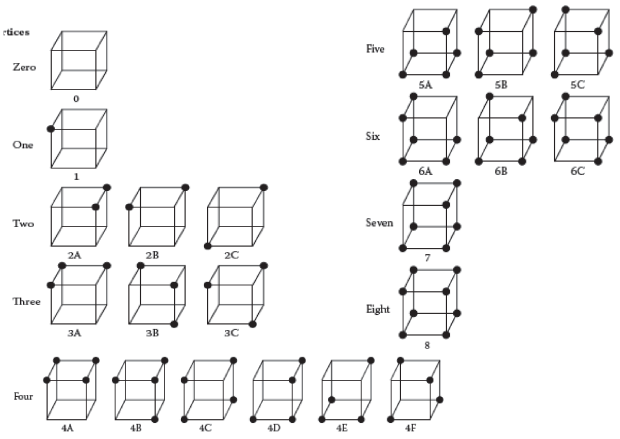
Consider a cube defined by 8 data values,4 from slice k, and another 4 from slice k+1.[1]



↓

Classify each vertex.

Grid vertices are labeled positive or negative.[2]



↓

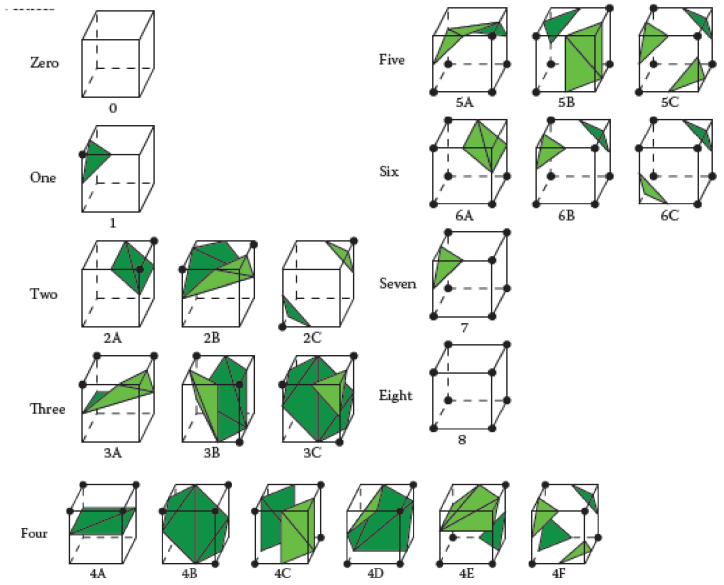
Get edge list based on look-up table

- $E_k^{+/-}$ set of edges with one positive and one negative endpoint.
- contains 256 entries,one for each configuration.

[1]Image Source:R. Wenger Isosurfaces: Geometry Topology & Algorithms Boca Raton FL USA:CRC Press 2013.

[2]Image Source:R. Wenger Isosurfaces: Geometry Topology & Algorithms Boca Raton FL USA:CRC Press 2013.

- Each entry is a list of triples of edges with one positive and one negative endpoint.
- Each triple (e_1, e_2, e_3) represents a triangle whose vertices lie on e_1, e_2, and e_3.
- The isosurface patch intersects every edge of $E_k^{+/-}$ exactly once and does not intersect any other grid cube edges.[1]



↓ Interpolate triangle vertices

Let p=(p_x, p_y, p_z) and q=(q_x, q_y, q_z) be edge endpoints

and Let r=(r_x, r_y, r_z) be the isovalued point on [p,q].[1]

$$\alpha = \frac{\sigma - \phi(p)}{\phi(q) - \phi(p)},$$

$$r_x = (1-\alpha)p_x + \alpha q_x,$$

$$r_y = (1-\alpha)p_y + \alpha q_y,$$

$$r_z = (1-\alpha)p_z + \alpha q_z,$$

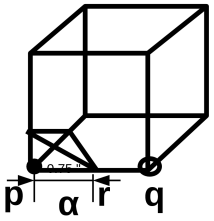
↓

Obtain polygon list and do shading in image space.

Isosurface Lookup Table

[1]Image Source:R. Wenger Isosurfaces: Geometry Topology & Algorithms Boca Raton FL USA:CRC Press 2013.

[1]Image Source:R. Wenger Isosurfaces: Geometry Topology & Algorithms Boca Raton FL USA:CRC Press 2013.



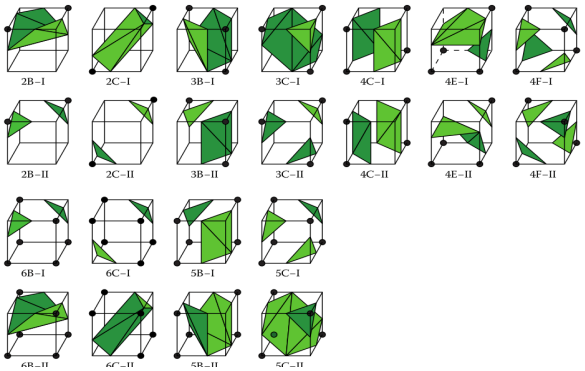
- The isosurface lookup table is constructed on the unit cube with vertices (0, 0, 0), (1, 0, 0), (0, 1, 0), . . . , (0, 1, 1), (1, 1, 1).
- construct the isosurface in grid cube (i, j, k)
- map unit cube edges to edges of cube (i, j, k).
- Each vertex v = (v_x, v_y, v_z) of the unit cube maps to v + (i, j, k) = (v_x, v_y, v_z) +(i, j, k) = $(v_x + i, v_y + j, v_z + k)$.
- Each edge e of the unit square with endpoints (v, v) maps to edge e + (i, j, k) = (v + (i, j, k), v + (i, j, k)).
- each edge triple (e_1, e_2, e_3) maps to $(e_1 + (i, j, k), e_2 + (i, j, k), e_3 + (i, j, k))$.

Properties of Isosurface

1. It separates sample points with scalar value above isovalue from scalar points with value below isovalue.
2. It does not intersect a grid edge more than once.
3. It does not intersect grid edges with both endpoint scalar values above or both endpoint scalar values below the isovalue.
4. The isosurface is piecewise linear.
   Properties 5 and 6 apply to Marching Cubes isosurfaces whose isovalues do not equal the scalar value of any grid vertex.
5. The isosurface is a piecewise linear, orientable 2-manifold with boundary.
6. The boundary of the isosurface lies on the boundary of the grid.

Ambiguities

- 2B,2C,3B,3C,4C,4E,4F,5B,5C AND 6B are ambiguous configurations.
- If some configurations isosurface patch separates the negative vertices on the facet while an adjacent configurations isosurface patch separates the positive ones, then the isosurface edges on the common facet will not align.[1]



References [1] Wenger,. "Introduction", Isosurfaces Geometry Topology and Algorithms, 2013.

[1]Image Source:R. Wenger Isosurfaces: Geometry Topology & Algorithms Boca Raton FL USA:CRC Press 2013.

Appendix B

Algorithm to generate Zero flux Surfaces and Approximating Critical Points

```
PROGRAM CPTS

IMPLICIT NONE

INTEGER*4::I,J,K,L,N1,N2,N3,XINT,YINT,ZINT,XINT1,YINT1,ZINT1,I1
REAL*8::XMIN,DX,YMIN,DY,ZMIN,DZ,MAG,PI2,A,XX,YY,ZZ,EPS,MAGDER
REAL*8,ALLOCATABLE::F(:,:,:),FX(:,:,:),FY(:,:,:),FZ(:,:,:)
REAL*8,ALLOCATABLE::VX(:,:,:),VY(:,:,:),VZ(:,:,:)
REAL*8,ALLOCATABLE::UX(:,:,:),UY(:,:,:),UZ(:,:,:)
REAL*8,ALLOCATABLE::D1(:,:,:),D2(:,:,:),D3(:,:,:)
REAL*8,ALLOCATABLE::XTHETA(:,:,:),YTHETA(:,:,:),ZTHETA(:,:,:)
REAL*8,ALLOCATABLE::X(:),Y(:),Z(:)
REAL*8::XBACK,XFWD,YBACK,YFWD,ZBACK,ZFWD,XDER,YDER,ZDER
REAL*8::CONV,DELTA(3),H(3,3),HINV(3,3),EPS1
REAL*8::XREAL,YREAL,ZREAL,P0(3),XREAL1,YREAL1,ZREAL1,P(3)
CHARACTER(LEN=60)::A1,A2,A3,A4,A5,A6,A7,A8,A9,A10,A11,FN,SURFACE
CHARACTER(LEN=60)::A12,GUESSPOINT
```

```
          OPEN(1,FILE="INPUT.TXT")
/STEP1:Input 3d data of function.
          READ(1,*) A1
          READ(1,*) N1
          READ(1,*) A2
          READ(1,*) N2
          READ(1,*) A3
          READ(1,*) N3
          READ(1,*) A4
          READ(1,*) XMIN
          READ(1,*) A5
          READ(1,*) DX
          READ(1,*) A6
          READ(1,*) YMIN
          READ(1,*) A7
          READ(1,*) DY
          READ(1,*) A8
          READ(1,*) ZMIN
          READ(1,*) A9
          READ(1,*) DZ
          READ(1,*) A10
          READ(1,*) FN
          READ(1,*) A11
          READ(1,*) SURFACE
          READ(1,*) A12
          READ(1,*) GUESSPOINT
/STEP2:Allocating 3D Arrays of Gradients
          ALLOCATE(X(N1),Y(N2),Z(N3))
          ALLOCATE(F(N1,N2,N3))
          ALLOCATE(FX(N1,N2,N3))
```

```
          ALLOCATE(FY(N1,N2,N3))
          ALLOCATE(FZ(N1,N2,N3))
          ALLOCATE(UX(N1,N2,N3))
          ALLOCATE(UY(N1,N2,N3))
          ALLOCATE(UZ(N1,N2,N3))
          ALLOCATE(VX(N1,N2,N3))
          ALLOCATE(VY(N1,N2,N3))
          ALLOCATE(VZ(N1,N2,N3))
          ALLOCATE(D1(N1,N2,N3))
          ALLOCATE(D2(N1,N2,N3))
          ALLOCATE(D3(N1,N2,N3))
          ALLOCATE(XTHETA(N1,N2,N3))
          ALLOCATE(YTHETA(N1,N2,N3))
          ALLOCATE(ZTHETA(N1,N2,N3))

          OPEN(2,FILE=FN)
          OPEN(3,FILE=SURFACE)
          OPEN(4,FILE=GUESSPOINT)
          OPEN(5,FILE="watercpts.txt")
          OPEN(7,FILE="indexes.txt")
          OPEN(8,FILE="potential.txt")
          OPEN(9,FILE="surfacenew.txt")

/Step3:Numerically defining function on grid

          DO I=1,N1

          X(I)=XMIN+(I-1)*DX

          DO J=1,N2
```

```
          Y(J)=YMIN+(J-1)*DY

          DO K=1,N3

          Z(K)=ZMIN+(K-1)*DZ

           READ(2,*) F(I,J,K)

          ENDDO

          ENDDO

          ENDDO

/Step4:Defining unit gradients numeerically using central difference formula.

          DO I=3,N1-2

          DO J=3,N2-2

          DO K=3,N3-2

          FX(I,J,K)=(8*F(I+1,J,K)-8*F(I-1,J,K)-F(I+2,J,K)+F(I-2,J,K))/(12*DX)
          FY(I,J,K)=(8*F(I,J+1,K)-8*F(I,J-1,K)-F(I,J+2,K)+F(I,J-2,K))/(12*DY)
          FZ(I,J,K)=(8*F(I,J,K+1)-8*F(I,I,K-1)-F(I,J,K+2)+F(I,J,K-2))/(12*DZ)

          MAG=DSQRT(FX(I,J,K)**2+FY(I,J,K)**2+FZ(I,J,K)**2)

          VX(I,J,K)=DX*FX(I,J,K)/MAG
          VY(I,J,K)=DY*FY(I,J,K)/MAG
          VZ(I,J,K)=DZ*FZ(I,J,K)/MAG
```

```
          UX(I,J,K)=X(I)+VX(I,J,K)
          UY(I,J,K)=Y(J)+VY(I,J,K)
          UZ(I,J,K)=Z(K)+VZ(I,J,K)

          write(8,*) X(I),Y(J),Z(K),F(I,J,K),FX(I,J,K),FY(I,J,K),FZ(I,J,K)

          ENDDO

          ENDDO

          ENDDO

/Step5: Measuring Distance and angles between adjacent gradients

          DO I=3,N1-3

          DO J=3,N2-3

          DO K=3,N3-3

          D1(I,J,K)=DSQRT((UX(I+1,J,K)-UX(I,J,K))**2+(UY(I+1,J,K)-&
                    UY(I,J,K))**2+(UZ(I+1,J,K)-UZ(I,J,K))**2)
          D2(I,J,K)=DSQRT((UX(I,J+1,K)-UX(I,J,K))**2+(UY(I,J+1,K)-&
                    UY(I,J,K))**2+(UZ(I,J+1,K)-UZ(I,J,K))**2)
          D3(I,J,K)=DSQRT((UX(I,J,K+1)-UX(I,J,K))**2+(UY(I,J,K+1)-&
                    UY(I,J,K))**2+(UZ(I,J,K+1)-UZ(I,J,K))**2)

          XTHETA(I,J,K)=DACOS(VX(I,J,K)/DSQRT(VX(I,J,K)**2+VY(I,J,K)**2+&
                              VZ(I,J,K)**2))
          YTHETA(I,J,K)=DACOS(VY(I,J,K)/DSQRT(VX(I,J,K)**2+VY(I,J,K)**2+&
```

```
                    VZ(I,J,K)**2))
ZTHETA(I,J,K)=DACOS(VZ(I,J,K)/DSQRT(VX(I,J,K)**2+VY(I,J,K)**2+&
                    VZ(I,J,K)**2))

ENDDO

ENDDO

ENDDO

PI2=1.5707960d0

EPS=3.000000E-003

EPS1=0.100000E-004

CONV=0.0000010D0

DO I=3,N1-4

DO J=3,N2-4

DO K=3,N3-4

IF(D1(I,J,K).GE.DX.AND.XTHETA(I,J,K).LT.PI2.AND.&
   XTHETA(I+1,J,K).GT.PI2)THEN

A=(PI2-XTHETA(I,J,K))/(XTHETA(I+1,J,K)-XTHETA(I,J,K))

XX=(1-A)*X(I)+X(I+1)
YY=(1-A)*Y(J)+Y(J)
```

```
          ZZ=(1-A)*Z(K)+Z(K)

                    YBACK=(1-A)*F(I,J-1,K)+A*f(I+1,J-1,K)
                    YFWD=(1-A)*f(I,J+1,K)+A*F(I+1,J+1,K)

                    ZBACK=(1-A)*F(I,J,K-1)+A*F(I+1,J,K-1)
                    ZFWD=(1-A)*F(I,J,K+1)+a*F(I+1,J,K+1)

                    XDER=(F(I+1,J,K)-F(I,J,K))/(DX)
                    YDER=(YBACK-YFWD)/(2*DY)
                    ZDER=(ZBACK-ZFWD)/(2*DZ)

/Step6:Computing points of Zero flux Surfaces

          WRITE(3,*) XX,YY,ZZ,XDER,YDER,ZDER

          MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

          IF(MAGDER.LT.EPS)THEN

          WRITE(4,*) XX,YY,ZZ

          ENDIF

          IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN

          WRITE(9,*) XX,YY,ZZ

          ENDIF

          ENDIF
```

```
      IF(D2(I,J,K).GE.DY.AND.YTHETA(I,J,K).LT.PI2.AND.&
         YTHETA(I,J+1,K).GT.PI2)THEN

      A=(PI2-YTHETA(I,J,K))/(YTHETA(I,J+1,K)-YTHETA(I,J,K))

      XX=(1-A)*X(I)+X(I)
      YY=(1-A)*Y(J)+Y(J+1)
      ZZ=(1-A)*Z(K)+Z(K)

                XBACK=(1-A)*F(I-1,J,K)+A*F(I-1,J+1,K)
                XFWD=(1-A)*f(I+1,J,K)+A*F(I+1,J+1,K)

                ZBACK=(1-A)*F(I,J,K-1)+A*F(I,J+1,K-1)
                ZFWD=(1-A)*F(I,J,K+1)+a*F(I,J+1,K+1)

                YDER=(F(I,J+1,K)-F(I,J,K))/(DY)
                XDER=(XBACK-XFWD)/(2*DX)
                ZDER=(ZBACK-ZFWD)/(2*DZ)

!          WRITE(3,*) XX,YY,ZZ,XDER,YDER,ZDER

      MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

      IF(MAGDER.LT.EPS)THEN

      WRITE(4,*) XX,YY,ZZ

      ENDIF

      IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN
```

```
            WRITE(9,*) XX,YY,ZZ

            ENDIF

            ENDIF

            IF(D2(I,J,K).GE.DY.AND.YTHETA(I,J,K).GT.PI2.AND.&
               YTHETA(I,J+1,K).LT.PI2)THEN

            A=(PI2-YTHETA(I,J+1,K))/(YTHETA(I,J,K)-YTHETA(I,J+1,K))

            XX=(1-A)*X(I)+X(I)
            YY=(1-A)*Y(J+1)+Y(J)
            ZZ=(1-A)*Z(K)+Z(K)

                      XBACK=(1-A)*F(I-1,J,K)+A*F(I-1,J+1,K)
                      XFWD=(1-A)*f(I+1,J,K)+A*F(I+1,J+1,K)

                      ZBACK=(1-A)*F(I,J,K-1)+A*F(I,J+1,K-1)
                      ZFWD=(1-A)*F(I,J,K+1)+a*F(I,J+1,K+1)

                      YDER=(F(I,J+1,K)-F(I,J,K))/(DY)
                      XDER=(XBACK-XFWD)/(2*DX)
                      ZDER=(ZBACK-ZFWD)/(2*DZ)

!            WRITE(3,*) XX,YY,ZZ,XDER,YDER,ZDER

            MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

            IF(MAGDER.LT.EPS)THEN
```

```
WRITE(4,*) XX,YY,ZZ

ENDIF

IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN

WRITE(9,*) XX,YY,ZZ

ENDIF

ENDIF

IF(D3(I,J,K).GE.DX.AND.ZTHETA(I,J,K).LT.PI2.AND.&
   ZTHETA(I,J,K+1).GT.PI2)THEN

A=(PI2-ZTHETA(I,J,K))/(ZTHETA(I,J,K+1)-ZTHETA(I,J,K))

XX=(1-A)*X(I)+X(I)
YY=(1-A)*Y(J)+Y(J)
ZZ=(1-A)*Z(K)+Z(K+1)

           XBACK=(1-A)*F(I-1,J,K)+A*F(I-1,J,K+1)
           XFWD=(1-A)*f(I+1,J,K)+A*F(I+1,J,K+1)

           YBACK=(1-A)*F(I,J-1,K)+A*F(I,J-1,K+1)
           YFWD=(1-A)*F(I,J+1,K)+a*F(I,J+1,K+1)

           ZDER=(F(I,J,K+1)-F(I,J,K))/(DZ)
           XDER=(XBACK-XFWD)/(2*DX)
           YDER=(YBACK-YFWD)/(2*DY)
```

```
!           WRITE(3,*) XX,YY,ZZ,XDER,YDER,ZDER

            MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

            IF(MAGDER.LT.EPS)THEN

            WRITE(4,*) XX,YY,ZZ

            ENDIF

            IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN

            WRITE(9,*) XX,YY,ZZ

            ENDIF

            ENDIF

            IF(D3(I,J,K).GE.DX.AND.ZTHETA(I,J,K).GT.PI2.AND.&
               ZTHETA(I,J,K+1).LT.PI2)THEN

            A=(PI2-ZTHETA(I,J,K+1))/(ZTHETA(I,J,K)-ZTHETA(I,J,K+1))

            XX=(1-A)*X(I)+X(I)
            YY=(1-A)*Y(J)+Y(J)
            ZZ=(1-A)*Z(K+1)+Z(K)

                      XBACK=(1-A)*F(I-1,J,K)+A*F(I-1,J,K+1)
                      XFWD=(1-A)*f(I+1,J,K)+A*F(I+1,J,K+1)
```

```
                    YBACK=(1-A)*F(I,J-1,K)+A*F(I,J-1,K+1)
                    YFWD=(1-A)*F(I,J+1,K)+a*F(I,J+1,K+1)

                    ZDER=(F(I,J,K+1)-F(I,J,K))/(DZ)
                    XDER=(XBACK-XFWD)/(2*DX)
                    YDER=(YBACK-YFWD)/(2*DY)

!            WRITE(3,*) XX,YY,ZZ,XDER,YDER,ZDER

           MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

           IF(MAGDER.LT.EPS)THEN

           WRITE(4,*) XX,YY,ZZ

           ENDIF

           IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN

           WRITE(9,*) XX,YY,ZZ

           ENDIF

           ENDIF

           IF(D1(I,J,K).GE.DX.AND.XTHETA(I,J,K).GT.PI2.AND.&
              XTHETA(I+1,J,K).LT.PI2)THEN

           A=(PI2-XTHETA(I+1,J,K))/(XTHETA(I,J,K)-XTHETA(I+1,J,K))

           XX=(1-A)*X(I+1)+X(I)
```

```
YY=(1-A)*Y(J)+Y(J)
ZZ=(1-A)*Z(K)+Z(K)

WRITE(3,*) XX,YY,ZZ

          YBACK=(1-A)*F(I,J-1,K)+A*F(I+1,J-1,K)
          YFWD=(1-A)*F(I,J+1,K)+A*F(I+1,J+1,K)

          ZBACK=(1-A)*F(I,J,K-1)+A*F(I+1,J,K-1)
          ZFWD=(1-A)*F(I,J,K+1)+a*F(I+1,J,K+1)

          XDER=(F(I+1,J,K)-F(I,J,K))/(DX)
          YDER=(YBACK-YFWD)/(2*DY)
          ZDER=(ZBACK-ZFWD)/(2*DZ)

IF(ABS(XX*XDER+YY*YDER+ZZ*ZDER).LT.EPS1)THEN

WRITE(9,*) XX,YY,ZZ

ENDIF

MAGDER=DSQRT(XDER**2+YDER**2+ZDER**2)

IF(MAGDER.LT.EPS)THEN

WRITE(4,*) XX,YY,ZZ

XREAL=(XX-XMIN)/DX
YREAL=(YY-YMIN)/DY
ZREAL=(ZZ-ZMIN)/DZ
```

```
          XINT=INT(XREAL)+1
          YINT=INT(YREAL)+1
          ZINT=INT(ZREAL)+1

          P0(1)=X(XINT)
          P0(2)=Y(YINT)
          P0(3)=Z(ZINT)

         DO L=1,1

          XREAL1=(P0(1)-XMIN)/DX
          YREAL1=(P0(2)-YMIN)/DY
         ZREAL1=(P0(3)-ZMIN)/DZ

          XINT1=INT(XREAL1)+1
          YINT1=INT(YREAL1)+1
          ZINT1=INT(ZREAL1)+1

         WRITE(7,*) XINT1,YINT1,ZINT1


          IF(YINT1.GT.N2)THEN
          EXIT
          ENDIF

          IF(ZINT1.GT.N3)THEN
          write(*,*) "hi"
         exit
         ENDIF
/Step7 :Newton's Optimization method
          DELTA(1)=(F(XINT1+1,YINT1,ZINT1)-F(XINT1-1,YINT1,ZINT1))/(2*DX)
```

```
 DELTA(2)=(F(XINT1,YINT1+1,ZINT1)-F(XINT1,YINT1-1,ZINT1))/(2*DY)
 DELTA(3)=(F(XINT1,YINT1,ZINT1+1)-F(XINT1,YINT1,ZINT1-1))/(2*DZ)

 P0(1)=X(XINT1)
 P0(2)=Y(YINT1)
 P0(3)=Z(ZINT1)

 CALL HESSIAN(F,XINT1,YINT1,ZINT1,N1,N2,N3,H,DX,DY,DZ)
 CALL INVERSE(H,HINV,3)
 P=P0-MATMUL(DELTA,HINV)

 IF(DSQRT((P(1)-P0(1))**2+(P(2)-P0(2))**2+(P(3)-P0(3))**2)&
     .LT.CONV) EXIT

 IF((XINT1.GT.N1).or.(YINT1.GT.N2).OR.(ZINT1.GT.N3).OR.&
  (DSQRT((P(1)-P0(1))**2+(P(2)-P0(2))**2+(P(3)-P0(3))**2).LT.CONV))THEN
  WRITE(5,*) (P(I1),I1=1,3)
  exit
 ENDIF
 P0=P

ENDDO

 ENDIF

 ENDIF

 ENDDO

 ENDDO
```

```
   ENDDO

   END

   subroutine HESSIAN(f,i,j,k,n1,n2,n3,h,dx,dy,dz)

   implicit none

   integer*4:: i,j,k,n1,n2,n3
   real*8::f(n1,n2,n3),h(3,3),dx,dy,dz


   h(1,1)=(f(i+2,j,k)-2*f(i,j,k)+f(i-2,j,k))/(4*dx**2)
   h(2,2)=(f(i,j+2,k)-2*f(i,j,k)+f(i,j-2,k))/(4*dy**2)
   h(3,3)=(f(i,j,k+2)-2*f(i,j,k)+f(i,j,k-2))/(4*dz**2)
   h(1,2)=(f(i+1,j+1,k)-f(i+1,j-1,k)-f(i-1,j+1,k)+f(i-1,j-1,k))/(4*dx*dy)
   h(1,3)=(f(i+1,j,k+1)-f(i+1,j,k-1)-f(i-1,j,k+1)+f(i-1,j,k-1))/(4*dx*dz)
   h(2,3)=(f(i,j+1,k+1)-f(i,j+1,k-1)-f(i,j-1,k+1)+f(i,j-1,k-1))/(4*dz*dy)
   h(2,1)=h(1,2)
   h(3,1)=h(1,3)
   h(3,2)=h(2,3)

   end subroutine

   subroutine INVERSE(a,c,n)

   implicit none
integer n
double precision a(n,n), c(n,n)
double precision L(n,n), U(n,n), b(n), d(n), x(n)
double precision coeff
```

```
  integer i, j, k

! step 0: initialization for matrices L and U and b
! Fortran 90/95 aloows such operations on matrices
      L=0.0
      U=0.0
      b=0.0

! step 1: forward elimination
      do k=1, n-1
       do i=k+1,n
      coeff=a(i,k)/a(k,k)
      L(i,k) = coeff
      do j=k+1,n
         a(i,j) = a(i,j)-coeff*a(k,j)
      end do
      end do
      end do

! Step 2: prepare L and U matrices
! L matrix is a matrix of the elimination coefficient
! + the diagonal elements are 1.0
      do i=1,n
       L(i,i) = 1.0
      end do
! U matrix is the upper triangular part of A
      do j=1,n
      do i=1,j
      U(i,j) = a(i,j)
      end do
      end do
```

```
! Step 3: compute columns of the inverse matrix C
      do k=1,n
      b(k)=1.0
      d(1) = b(1)
! Step 3a: Solve Ld=b using the forward substitution
      do i=2,n
      d(i)=b(i)
      do j=1,i-1
      d(i) = d(i) - L(i,j)*d(j)
      end do
      end do
! Step 3b: Solve Ux=d using the back substitution
      x(n)=d(n)/U(n,n)
      do i = n-1,1,-1
      x(i) = d(i)
      do j=n,i+1,-1
      x(i)=x(i)-U(i,j)*x(j)
      end do
      x(i) = x(i)/u(i,i)
      end do
! Step 3c: fill the solutions x(n) into column k of C
      do i=1,n
      c(i,k) = x(i)
      end do
      b(k)=0.0
      end do
      end subroutine INVERSE
```