Molecular Modelling and Simulation

Quiz-1

(1) Explain conjugate gradient minimization method [4 marks]

Ans- In Conjugate gradients, The gradient s at each point are orthogonal but the directions are Conjugate. A set of Conjugate directions has the property that for a quadratic function of M variables, the minimum will be reached in M steps. The Conjugate gradients method moves in a direction V_k from point x_k where V_k is computed from the gradient at the point and the previous direction vector V_{k-1}.

$$V_k = -g_k + \gamma_k V_{k-1}$$

↳ Scalar Constant, $\gamma_k = \dfrac{g_k \cdot g_k}{g_{k-1} \cdot g_{k-1}}$

In the Conjugate gradient method all of the directions and gradients satisfy the following relationships:

$$g_i \cdot g_j = 0$$

$$V_i \cdot V_{ij}'' \cdot V_j = 0$$

$$g_i \cdot V_j = 0$$

5.4.4 Conjugate Gradients Minimisation

The conjugate gradients method produces a set of directions which does not show the oscillatory behaviour of the steepest descents method in narrow valleys. In the steepest descents method both the gradients and the direction of successive steps are orthogonal.

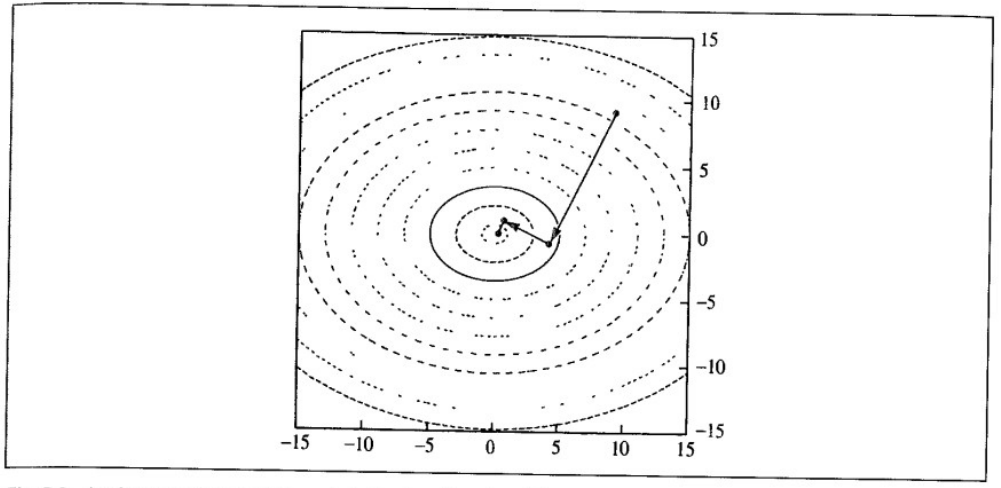


Fig 5 9. Application of steepest descents to the function $x^2 + 2y^2$.

In conjugate gradients, the gradients at each point are orthogonal but the directions are *conjugate* (indeed, the method is more properly called the conjugate directions method). A set of conjugate directions has the property that for a quadratic function of M variables, the minimum will be reached in M steps The conjugate gradients method moves in a direction $\mathbf{v}_k$ from point $\mathbf{x}_k$ where $\mathbf{v}_k$ is computed from the gradient at the point and the previous direction vector $\mathbf{v}_{k-1}$:

$$\mathbf{v}_k = -\mathbf{g}_k + \gamma_k \mathbf{v}_{k-1} \tag{5.6}$$

γ_k is a scalar constant given by

$$\gamma_k = \frac{\mathbf{g}_k \cdot \mathbf{g}_k}{\mathbf{g}_{k-1} \cdot \mathbf{g}_{k-1}} \tag{5 7}$$

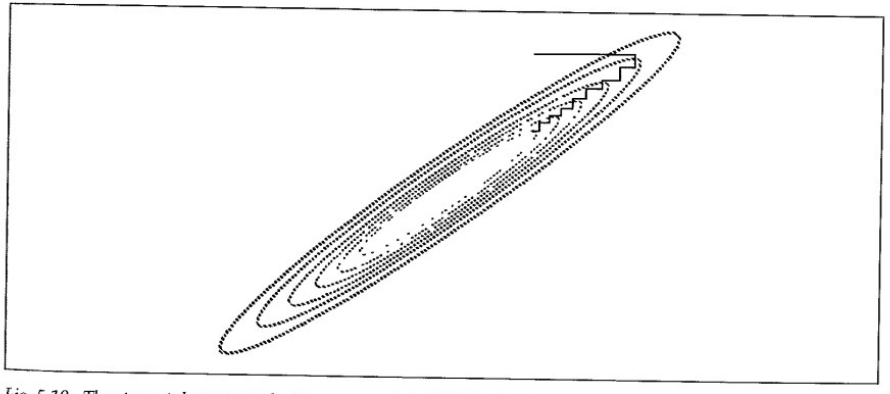


Fig 5 10 The steepest descents method can give undesirable behaviour in a long narrow valley

In the conjugate gradients method all of the directions and gradients satisfy the following relationships:

$$\mathbf{g}_i \cdot \mathbf{g}_j = 0 \tag{5.8}$$

$$\mathbf{v}_i \cdot \mathscr{V}''_{ij} \cdot \mathbf{v}_j = 0 \tag{5 9}$$

$$\mathbf{g}_i \cdot \mathbf{v}_j = 0 \tag{5 10}$$

Ref-Molecular modelling by Andrew Leach

The conjugate gradients method deals with our simple quadratic function $f(x, y) = x^2 + 2y^2$ as follows. From the initial point $(9, 9)$ we move to the same point as in steepest descents, $(4,-1)$. To find the direction of the next move, we first determine the negative gradient at the current point. This is the vector $(-8, 4)$. This is then combined with the vector corresponding to minus the gradient at the initial point, $(-18,-36)$ multiplied by γ:

$$\mathbf{v}_k = \begin{pmatrix} -8 \\ 4 \end{pmatrix} + \frac{(-8)^2 + (4)^2}{(-18)^2 + (-36)^2} \begin{pmatrix} -18 \\ -36 \end{pmatrix} = \begin{pmatrix} -80/9 \\ +20/9 \end{pmatrix} \tag{5.11}$$

To locate the second point we therefore need to perform a line search along the line with gradient $-1/4$ that passes through the point $(4,-1)$. The minimum along this line is at the origin, at the true minimum of the function. The conjugate gradients method thus locates the exact minimum of the function exactly in just two moves, as illustrated in Figure 5.11.

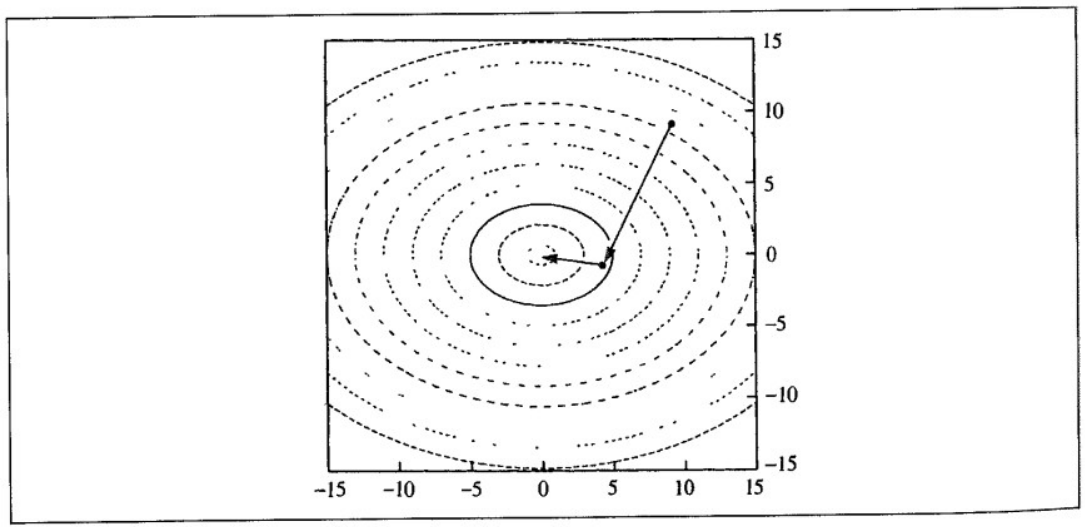
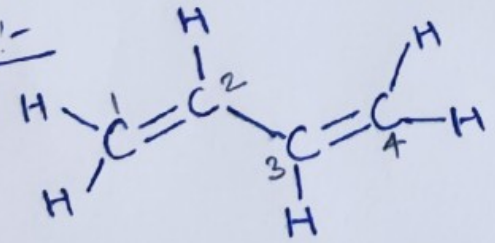


Fig 5 11· Application of conjugate gradients method to the function $x^2 + 2y^2$.

(2) (a) Model Butadiene using variational method using the approximations used in Huckel Molecular Orbital method and calculate the energies of the four molecular orbitals. (b) Calculate the stabilization energy due to π-conjugation in butadiene. [1+4+1 = 6 marks]

Ans:-



Here is four π-electrons.

Approximate π-electronic wave function

$$\phi_a = C_1 X_1 + C_2 X_2 + C_3 X_3 + C_4 X_4$$

Butadiene (1,3-Butadiene)

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

→ The diagonal H's in Secular determinant

Quiz - 1

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* Coloumb integral → Represent the Energy of an electron in the $2p_z$ orbital on the i^{th} C-atom.

H_{ij} $(i=j)$ are represented by 'α'.

Ex- H_{11}, H_{22} --- H_{nn} etc. [$\alpha = 0\ KJ\ mol^{-1}$]

* Resonance or Exchange integral - The off diagonal H's in Secular determinant.

H_{ij} $(i \neq j)$ Ex- $H_{12}, H_{13}, H_{21}, H_{32}$ ----

↳ Represents the interaction of electrons in the $2p_z$ orbitals on the i^{th} & j^{th} ~~Coloumn~~ C-atoms.

$$H_{ij} = \begin{cases} \beta, & \text{if } i \& j \text{ are connected} \\ 0, & \text{if } i \& j \text{ are not connected.} \end{cases} \quad [\beta = -75\ KJ\ mol^{-1}]$$

* Overlap integral (S_{ij}) -

$$S_{ij} = \begin{cases} 1, & \text{if } i=j \rightarrow \text{Diagonal}, S=1, S_{11}, S_{22} --- \\ 0 & \text{if } i \neq j \rightarrow \text{Off Diagonal}, S=0, S_{12}, S_{21} --- \end{cases}$$

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

Dividing the ~~above~~ above determinant by β, we get

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha-E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha-E}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha-E}{\beta} \end{vmatrix} = 0$$

Let $\frac{\alpha-E}{\beta} = x$

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$x\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1\begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} + 0\begin{vmatrix} 1 & x & 0 \\ 0 & 1 & 1 \\ 0 & 0 & x \end{vmatrix} - 0\begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 0 & 0 & 1 \end{vmatrix} = 0$$

$$[x\{x(x^2-1)-x\}] - [1\{1(x^2-1)-1(0)+0\}] + 0 + 0 = 0$$

$$[x\{x^3-x-x\}] - [1\{x^2-1\}] = 0$$

$$[x^4 - x^2 - x^2] - [x^2-1] = 0$$

$$x^4 - x^2 - x^2 + 1 = 0$$

Let, $x^2 = y$

$$y^2 - 3y + 1 = 0$$

$$y = \frac{-(-3) \pm \sqrt{(-3)^2 - 4\times1\times1}}{2\times1}$$

$$= \frac{3 \pm \sqrt{9-4}}{2}$$

$$y = \frac{3 \pm \sqrt{5}}{2}$$

$$y = \frac{3 \pm 2.23}{2}$$

$$y = \frac{3+2.23}{2} = \frac{5.23}{2} = 2.615$$

$$y = \frac{3-2.23}{2} = \frac{0.77}{2} = 0.385$$

As, we assumed $y = x^2$

$x^2 = 2.615$

$x = \pm\sqrt{2.615}$, $\boxed{x = \pm 1.618}$

& $x^2 = 0.385$

$x = \pm\sqrt{0.385}$, $\boxed{x = \pm 0.618}$

(i) $\frac{\alpha-E}{\beta} = 1.618$

$\alpha - E = 1.618\beta$

$\boxed{E = \alpha - 1.618\beta}$

$\frac{\alpha-E}{\beta} = -1.618$

$\alpha - E = -1.618\beta$

$\boxed{E = \alpha + 1.618\beta}$

(ii) $\frac{\alpha-E}{\beta} = 0.618$, $\alpha - E = 0.618\beta$

$\boxed{E = \alpha - 0.618\beta}$

$\frac{\alpha-E}{\beta} = -0.618$, $\alpha - E = -0.618\beta$

$\boxed{E = \alpha + 0.618\beta}$

$\alpha - 1.618\beta$

$\alpha - 0.618\beta$

$\alpha + 0.618\beta$ — 1½

$\alpha + 1.618\beta$ — 1½

Therefor 4π electrons in, 1,3 butadiene, are in bonding molecular orbital

$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

$= 2\alpha + 3.236\beta + 2\alpha + 1.236\beta$

$= 4\alpha + 4.472\beta$

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(3) (a) Write the Hamiltonian of Hydrogen MOLECULE CATION (one electron removed from hydrogen molecule). (b) After Born-Oppenheimer approximation, is it possible to solve the Schrodinger equation? Explain (no derivations)

[2+2 = 4 marks]

Ans- (a) Hydrogen molecule Cation (H_2^+)

$H = T + V$

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

(b) B-O approximation assumes that the motion of atomic nuclei is much slower compared to the motion of electrons in a molecule

After B.O, Schrodinger Eq^n

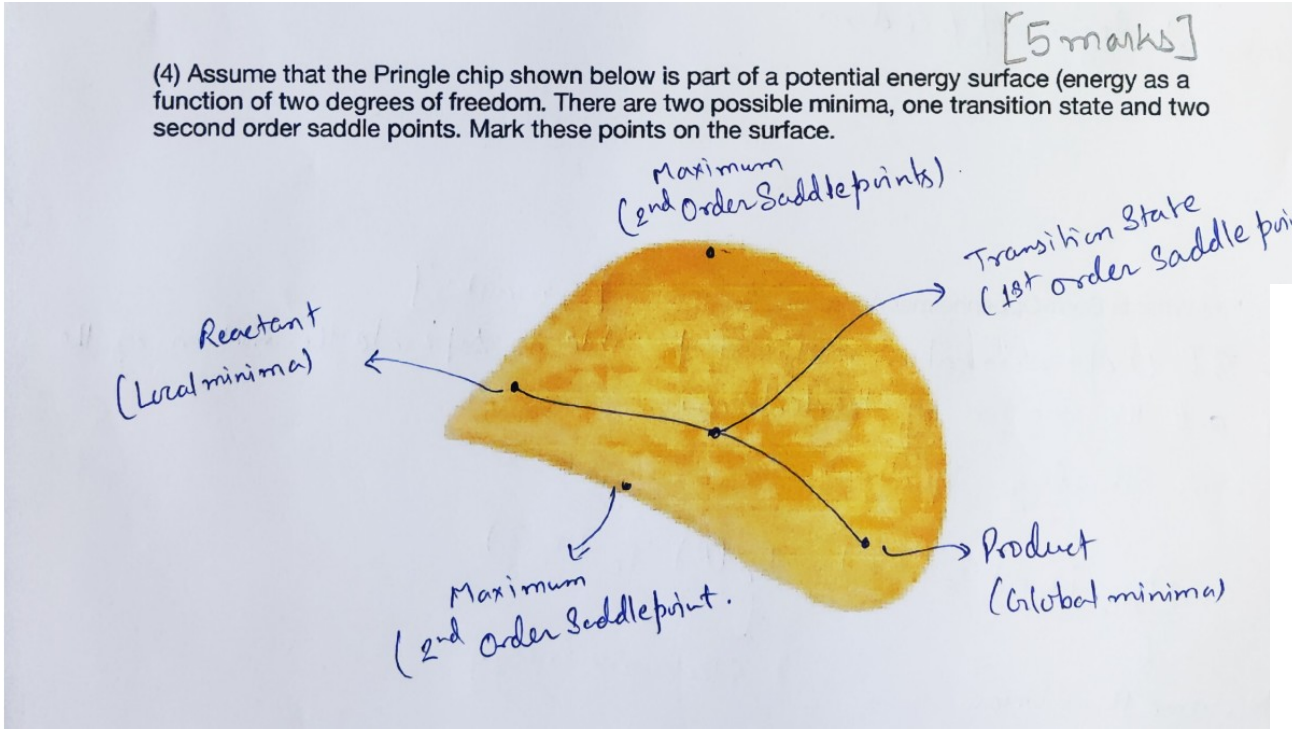
$H_{elec}(R)\,\Psi_{elec}(r;R) = E_{elec}(R)\,\Psi_{elec}(r;R)$

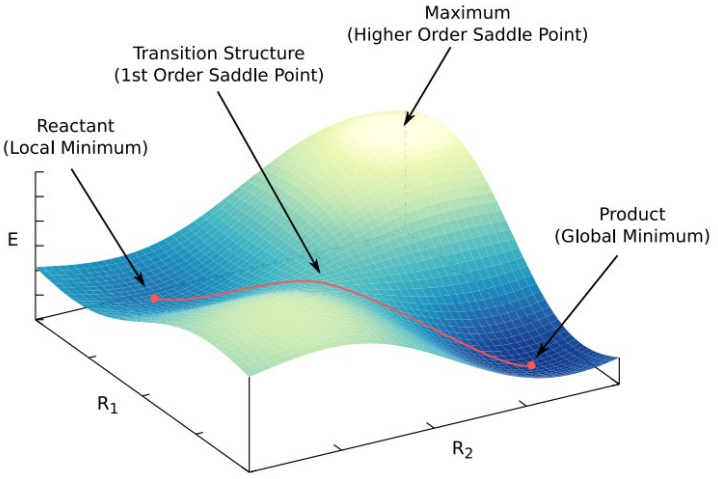
The nuclear motion equations arise from solving the electronic Schrodinger Equation for a set of fixed nuclear Coordinates.

After BO approximation, it is possible to solve the S.Eq^n for the electronic motion, treating the nuclear motion as parameters.

[5 marks]

(4) Assume that the Pringle chip shown below is part of a potential energy surface (energy as a function of two degrees of freedom. There are two possible minima, one transition state and two second order saddle points. Mark these points on the surface.





Ref-Combining Machine Learning and Computational Chemistry for Predictive Insights Into Chemical Systems

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[4 marks]

(5) Typically, there are '3N–6' degrees of freedom along which the potential energy of a N-atom molecule changes. Explain the basis.

Ans – 3N-6 → No. of Vibrational degree of freedom (Non-linear molecule)
↳ No. of atoms in the molecule.

Basis for the rule are.

① Degree of freedom for a molecule. – Total degree of freedom for a molecule are determined by its translational, rotational, and Vibrational motions.

② Vibrational Degree of freedom – Each atom in a molecule can move along three spatial dimensions (x, y, z). For N atoms in a molecule, there are a total 3N spatial Coordinates.

③ Constraints – 3N Coordinates represents independent Vibrational modes.

④ Constraints for Non-linear molecules – Three translational and three rotational degree of freedom. These Constraints reduce the number of independent vibrational degree of freedom.

(6) What is Born-Oppenheimer Approximation. [2marks]

Ans – B.O approximation makes it possible to seperate the motion of the nuclei and the motion of the electrons.

* Electronic Schrodinger Equation.

$$\hat{H}_{elec}(r,R)\,\psi_e(r,R) = E_e(R)\,\psi_e(r,R)$$

$\hat{H}_{elec}$ → Electronic Hamiltonian

$E_e(R)$ → Electronic Energy

r → Electronic Coordinates

R → Nuclear Coordinates.