COMPUTATIONAL MATERIALS SCIENCE

Fundamentals of Quantum theory applied to materials science:-

Quantum theory is the backbone of materials science. It is the quantum mechanical principles that tell us the behavior of fundamental constituents of matter. No wonder Materials science has its roots in quantum mechanics. The various fundamental quantum mechanical principles employed to compute the properties of materials are:-

***Adiabatic or Born-Oppenheimer approximation*:-**

Matter is nothing but an entity that comprises of many electrons and ions. Its very nature creates complexity when one tries to describe the system with a simple analytical mindset. The complexity arises in its modeling as there are many electrons whose dynamics have to be considered first. In addition to this ion dynamics has to be taken into account. Furthermore one has to keep at the back of his mind that these electrons and ions are not separate or independent by themselves rather they form a system whose very behavior is dependent on the interactions between these electrons and ions.

The total Hamiltonian H is given by

$$H = \sum_{i=1}^{N} \frac{P_I^2}{2M} + \sum_{j=1}^{n} \frac{p_j^2}{2m} + \sum_{i>j} \frac{e^2}{\left|r_i - r_j\right|} + \sum_{I>J} \frac{Z_I Z_J e^2}{\left|R_I - R_J\right|} - \sum_{I,J} \frac{Z_I e^2}{\left|R_I - r_J\right|}$$

The Schrödinger eqn. is given by

$$H\,\Phi(x,R) = E\,\Phi(x,R)$$

The first step towards the reduction of this complexity is the Bohn-Oppenheimer approximation. Since the dynamics of electrons (that are lighter) occurs at a time scale much faster than the heavier ions, it is reasonable to assume that the electrons are in the ground state irrespective of the instantaneous configuration of the ions. Essentially the electron and the nuclei motions are decoupled. It's because of this BO approximation the nuclei are treated as point charges of zero volume. "Adiabatic" refers to the fact that the system comprising of nuclei & electrons is similar to the thermo dynamical concept of quasi-steady state in an adiabatic process.

In mathematical terms this means we write overall wavefunction as product of nuclei wavefunction and electronic wavefunction,

$$\Phi(x,R) = \Psi(x,R)\,\chi(R)$$

$$x = \{r, w\}$$

Where r is spatial coordinate and w is the spin coordinate.

The decoupled Schrödinger equations become

$$\left[K.E_e + V_{ee}(r) + V_{eI}(r,R)\right]\psi_n(x,R) = \varepsilon_n(R)\psi_n(x,R)$$

$$\left[K.E_I + V_I(R) + \varepsilon(R)\right]\chi_n(R,t) = i\hbar\partial/\partial t(\chi(R,t))$$

Assuming that we can treat ion dynamics without quantum-relativistic effects

$$\left[K.E_I + V_I(R) + \varepsilon(R)\right]\chi_n(R) = E\chi(R)$$

The above approximation fails only when small atoms like hydrogen are involved. In that case the Fermi-Dirac time dependent equation must be solved.

In the adiabatic approximation we assume that ions move on the potential energy surface of only the electronic ground state. In other words the total electronic ground state energy is function of nuclear coordinates.
The motion of nuclei can also be well described by classical mechanics.
We thus get Newton's equations

$$\frac{\partial^2 P_I}{\partial t^2} = -\nabla_I E_o(R)$$

$$E_o(R) = \varepsilon_0(R) + V_{II}(R)$$

Now to determine the forces acting on the nuclei, an important theorem is then applied:
The ***Hellmann-Feynman Theorem***:

$$\begin{aligned}\nabla_I \varepsilon_o(R) &= \frac{\partial}{\partial R_I}\langle\psi_0|H_e|\psi_0\rangle \\ &= \langle\nabla_I\psi_0|H_e|\psi_0\rangle + \langle\psi_0|\nabla_I H_e|\psi_0\rangle + \langle\psi_0|H_e|\nabla_I\psi_0\rangle \\ &= \langle\psi_0|\nabla_I H_e|\psi_0\rangle\end{aligned}$$

The first and third term vanish because of the variational property of the ground state.
The gradient of total ground state energy gives the force acting.
The BO approximation rarely breaks down except in some cases where coupling of the electron and nuclei dynamics becomes crucial and this may not yield accurate results. (For e.g. in electronic transport, superconductivity, etc).

The BO approximation leads to separate Hamiltonians for nuclei and electrons.
Hamiltonian of ion is thus given by:-

$$H_{\text{ion}} = \sum_{I=1}^{N}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \vec{R}_I^2}\right) + \frac{1}{2}\sum_{\substack{I,J=1\\ I\neq J}} V_{\text{ion-ion}}(|\vec{R}_I - \vec{R}_J|) + E_{\text{tot}}(\{\vec{R}_I\})$$

The effective potential comprises of ion-ion interaction and the electronic total energy as a function of the ionic coordinates. And there is also the kinetic energy term. Now BO approximation leads to independent solving of Schrödinger equation for nuclei as well as many-electron system.

Obtaining the many-electron wavefunction:-

In the adiabatic approximation the Hamiltonian of many- electron system comprises of kinetic energy of say n electrons, their interaction with nuclei represented by means of columbic interaction potential of N nuclei whose position are described in terms of nuclear coordinates. There is this electron-electron-electron interaction potential term also.
Hamiltonian of electrons got by BO approximation:

$$H_{\text{elec}} = \sum_{i=1}^{n}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \vec{r}_i^2} + \sum_{I=1}^{N} V_{\text{el-ion}}(\vec{r}_i, \vec{R}_I)\right] + \frac{1}{2}\sum_{i}^{n}\sum_{j\neq i}^{N}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}.$$

This is now a quantum many-electron system whose wavefunction is what we need to obtain by solving the eigenvalue problem

$$H_{elec}\Psi_e = \varepsilon\ \Psi_e$$

Where, Ψ_e is the overall wavefunction of the many-electron system.
ε is the total electronic energy

Now our aim is to get the overall wavefunction. Desired wavefunction Ψe is the one which minimizes the Rayleigh coefficient,

$$Q_e = <\Psi_e \mid H_{elec} \mid \Psi_e> / <\Psi_e \mid \Psi_e>$$

This is called as variational principle. It implies that Q_e is an upper bound to the true energy E_e and is as close to the true energy depending on how good is the approximated wavefunction. As such one can't guess the Ψe as computationally it is impossible to minimize Q_e . However there are ways to solve this problem.

Note: Ψe should satisfy Pauli's exclusion principle. In mathematical terms it should have the anti-symmetry property,

$$\Psi e\ (x1, x2, x3, \ldots, xn) = -\ \Psi e\ (x2, x1, \ldots, xn)$$

Same is true for all pairs (xi, xj). Note x = {r, w},
Where r is spatial coordinate and w is the spin coordinate.

Once the wavefunction is got the properties can be estimated. Estimation of properties like total energy, molecular structure, heats of formation, band structure etc shall be explained later. Also certain specific examples will be taken to demonstrate this.
Some of the ways to tackle this quantum many body problem:

Quantum mechanical methods that are used for studying the molecular properties can be broadly classified into two categories.

- ✓ Ab-intio methods
- ✓ Semi-empirical methods

Ab-intio technique:
In this method there is no compromise made on theoretical quantum mechanical framework that is used to describe the molecular systems exactly. There is no compromise made in calculating the integrals that crop up in course of the detailed computations.
These are the various ab-intio techniques in use:

- Hartree Fock or MO theory
- Configuration interaction (CI) method
- Perturbation theory (PT)

- Density Functional Theory (DFT)

These ab-initio techniques use the correlation functionals (this shall be explained later) so that the calculated structure and energies agree well with the experiment. However, these ab-intio techniques are computationally demanding.

Semi-empirical technique:

In this method the complex integrals are not evaluated, instead these are approximated with values fitted by comparing with experiments. These lie midway between ab-intio and Molecular mechanics methods. The latter is completely empirical whereas the former is completely non-empirical. These semi-empirical methods depend on parameters derived from experimental fitting for their accuracy. Nevertheless one advantage is that these are computationally very cheap. So these are most suitable for large systems. Empirical Tight Binding is one such technique which describes the band structure of Si well.

The idea is to emulate to the maximum possible extent, the energies and forces described by the ab-intio techniques. First conjectures is made for any functional, say potential field, using free parameters and then these parameters are fitted or optimized to match the exact energies and forces determined either from experiment or validated ab-intio techniques.

The very nature of empiricism is that it can't be generalized. So if an empirical fit is made for potential for a particular system, then the parameters will work only in similar systems. That is to say that reliability of these methods is not guaranteed.

Reducing the many-electron Hamiltonian:

We are now faced with the Herculean task of solving many-electron system. Let's see how this is solved.

Hartree-Fock Theory:-

The idea is decompose the overall wavefunction as an antisymmetrized product of one-electron wavefunctions. The way to go about doing it is to apply variational principle to the expectation value of the Hamiltonian which is nothing but the total energy of the system.

In the resulting equations we observe instead of electron-electron interaction potentials, interaction of an electron with the average electrostatic field created by charge distribution of all other electrons. Also there is this exchange potential term which comes into picture because of Pauli's exclusion principle. This exchange potential keeps two electrons with identical spins ($S_j = S_i$) away from each other. This is ideally represented by the Kroenecker delta function which takes the value 1 if $S_j = S_i$ and 0 when $S_j \neq S_i$. There are techniques that take into account the short-distance coulomb interactions also (Hartee-Fock Configuration-Interaction or HF-CI schemes). But we shall not delve into those for time being.

The Schrödinger equation of n one-electron wavefunctions looks something like this:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \vec{r}^2} + V_{\text{el-ion}} + \quad e^2 \sum_j \int \frac{\left|\psi_j(\vec{r}\,')\right|^2}{\left|\vec{r}-\vec{r}\,'\right|} \mathrm{d}\vec{r}\,' \right] \psi_i(\vec{r}) - \sum_j \delta_{s_i s_j} \int \frac{\psi_j^*(\vec{r}\,')\psi_i(\vec{r}\,')}{\left|\vec{r}-\vec{r}\,'\right|} \mathrm{d}\vec{r}\,' \; \psi_j(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \qquad (3)$$

Where i, j run from 1 to n.

What we have actually done is that we have decomposed the complex many electron system (or state) to one electron states and thereby described the many electron quantities like total energy with contributions from single electron states. In fact this decomposition is central to both the Hatree-Fock and DFT schemes. Only that wave function formulation differs.

Self Consistent Field Procedure [2, 7]*:*

Deriving HF:
Putting the trial wavefunction –slater determinant for the overall wavefunction in the eigen equation to minimize the total energy by variational principle leads to set of equations given below:
$E_{HF} = \Sigma < \Psi \mid h \mid \Psi > + (1/2) * \Sigma (<ij|ij> - <ij|ji>)$
The variational energy is called the Hartree Fock energy.
h = one- electron core Hamiltonian
<ij|kl> = electron repulsion integral.
Now, the one-electron spin-orbitals are written as linear combination of atomic orbitals

$\Psi_i = \Sigma (C_{vi} . \varphi_v)$ where φ_v are the basis functions, and the coefficients C_{vi} are obtained by optimizing E_{HF}
This leads to set of non-linear equations,

$$\sum_{\nu} \left[h_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left(\langle \mu\sigma | \nu\lambda \rangle - \langle \mu\sigma | \lambda\nu \rangle \right) \right] C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

Where $P_{\mu\nu} = \sum_{i \varepsilon OCC} C_{\nu i}{}^{*} C_{\mu_i}$

To solve the non-linear system iteration is done as follows.
1) First C_{vi} is guessed. The calculated $P_{\mu v}$ is combined with two-electron integrals and added to $h_{\mu v}$. Left hand side of the equation is now fully known.
2) After $S_{\mu v}$ is taken into account ε_i & C_{vi} are calculated.
3) The choice of what orbitals are occupied is made and new $P_{\mu v}$ is recalculated.
4) This is continued till the changes in ε_i and C_{vi} are less than some convergence criteria.

Density Functional theory (DFT) [1]***:-***

This is another conventional ab-intio approach to solve many-electron Schrödinger equation. This is more so applied for large systems for which well-defined measurable quantities like electron density makes more sense from computational viewpoint.
The same one-electron picture is invoked by decomposing the Hamiltonian but the exchange and correlation potentials are got differently. The description is based on electron density which is very well defined for large system.
All the ground state properties of many-electron system are expressed as functions of ground state electron density n(r).
This is based on the famous Hohenberg-Kohn-Sham Theorem which states that
1) Ground state energy of a many body system can be described by a unique function of particle (electron) density.
2) This function has its minimum relative to variations of the electron density at the equilibrium density

Total energy of system is written as:

$$E[n] = T[n] + V_{ne}[n] + V_{ee}[n];$$
$$\mathrm{Vne}[n] = \int (v_{ne}(r) \,.\, n(r)\,.dr)$$

T[n] is the kinetic energy of electrons and $V_{ne}[n]$ is the coulomb energy of charge density n(r) in the external potential $v_{ne}(r)$ and the third term is the electron-electron interactions.
The variational principle is applied to E[n] with respect to n.
Thus solving many-electron problem for total energy just boils down to optimizing the total energy with respect to electron density of the system. In other words we search for n(r).
This leads to the Kohn-Sham [2] equations.

The Kohn-Sham equations are:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\vec{r}^{\,2}} + V_{\mathrm{el-ion}} + e^2\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\mathrm{d}\vec{r}\,' + V_{\mathrm{xc}}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i^n \left|\psi_i(\vec{r})\right|^2, \quad V_{\mathrm{xc}}(\vec{r}) = \frac{\delta E_{\mathrm{xc}}[n(\vec{r})]}{\delta n(\vec{r})}$$

All that has been done till this point is that we have looked at solving the many-electron system from the electron density perspective. We have not yet determined the forms of the exchange-correlation functional that have cropped up in the Kohn-Sham equations. In fact the form of these functionals is unknown. Now that we have the equations in terms of electron density which is realizable for large systems, we look for methods or further approximations that circumvent the problem of unknown correlation functionals. First step in this light is the local density approximation.

Local Density approximation:

From the DFT theory we see that the exact form for the exchange-correlation function is not known. One way to resolve this would be relate it to the local density. In other words The exchange correlation of single electron at position r is related to the exchange-correlation energy of a single electron in a homogenous electron gas having density say no equal to the local density n(r). In mathematical terms the E_{xc} (n) is given by [3]

$$E_{xc}(n) = \int e_{xc}(n(r), r)dr$$

The function inside the integration depends only on the local density n(r). The simplest version of LDA is the X_a method [4] which uses

$$E_{xc}(n) = -\frac{9}{8}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \alpha \int n(r)^{4/3} dr$$

Where α is an adjustable parameter.

Electron Density Functionals for Correlation energy [7]:

The major problem that we have in the calculations is that the form of Exc is not known. So there have been different methods that give different forms of Exc in terms of the local density. One such is the Generalized Gradient Approximations (GGA) technique. The gradient corrected functionals not only depend on the local density but also on its gradient and laplacian as well. Its common knowledge that if a function is not known but its dependency on particular variable is known, the function is approximated by the Taylor's series expansion. The form is

$$E_{xc}(n) = \int e_{xc}(n(r), \nabla n(r), \nabla^2 n(r), r)dr$$

Several such forms have been published.

Now that one-electron eigenvalue problem has been set up, next step is to get the one-electron wavefunction. First step in guessing a wavefunction is to expand it in terms of some set of basis function.

Basis Functions [7]:

Just like we did for Hydrogen, we expand the one-electron wave functions in terms of basis functions. Many different forms are available. These are used depending on the specific calculations that we do. For e.g. for ab-initio calculations in fullerenes the nuclei centered Cartesian Gaussian-type functions (CGTFs) are used,

$$\phi_v(r) = (x - X_I)^{l_x}(y - Y_I)^{l_y}(z - Z_I)^{l_z} \exp\left[-\varsigma(r - R_I)^2\right]$$

The individual basis wave functions are called primitives whereas the combined form got by means of multiplication with fixed coefficients is called contraction.

As we all know in NLP (non-linear optimization) the more the number of basis functions that one uses the better the accuracy. Same is the case with one-electron wave-functions.

As we increase the domain of the basis-set, we have the advantage of increased variational freedom. This implies higher accuracy.
But this of course increases the computational effort. So a balance needs to be maintained. Choice of basis sets depends on accuracy required and the available computational efficiency.
Various basis sets have been used can be broadly classified as:

- Linear Combination of Atomic Orbitals (LCAOs)
- Linearized Augmented Plane Waves (LAPWs)
- Plane Waves (PWs) in combination with pseudopotentials (PWPP)
- Linearized muffin tin orbitals(LMTO)
- Projector augmented waves(PAW)

LCAO [9]:
As the name suggests, the one-electron wave functions are approximated as a linear combination of atomic orbitals. And the atomic orbitals are expressed as product of the radial orbitals (which are either Slater-Type Orbitals or GTO- Gaussian Type Orbitals) and angular momentum eigenfunctions. In mathematical terms,
$\phi_{\mu k}(r) = u_{nl}(r)Y_{lm_l}(r)$

The radial orbitals are actually slater orbitals that decay exponentially with increasing distance from the nuclei. Nevertheless, these radial orbitals are approximated as GTOs comprising of primitives only for the sake of numerical accuracy and computational ease as the GTOs have good analytical properties.
The GTOs can further be classified as:

- ✓ Minimal basis sets: This is the smallest of basis sets consisting of GTOs.
  It is represented by STO-XG where X is an integer denoting the number of GTOs comprising the basis function. The available minimal sets are: STO-2G, STO-3G STO-6G
  There are two additions to the minimal basis sets:
  - *Polarization Functions*: These are additional unoccupied atomic orbitals added to the original set. For instance, a p orbital is added to minimal set comprising of s orbitals or a d orbital is added to minimal set comprising of s & p orbitals and so on. E.g. STO-3G*. These give the additional needed flexibility to the basis set. Notation (p,d). These functions are useful for describing the band structures wherein information of unoccupied orbitals becomes crucial in determination of band gap. Polarization functions are important for polar molecules as they allow for non-uniform displacement of charge around nucleus.
  - *Diffuse functions*: These are additional functions in the minimal set that are used to represent the part of orbital that is away from the nuclei. In other words it accurately describes the “tail-part” of the atomic orbital. Useful for describing the barely bound electrons in anions.

Split valence basis sets:

Whenever there is a change in the environment the orbitals should change shape and have different properties to result in correct computations. Like if add an extra electron to a p orbital what one should observe is the contraction of the p orbital. But these features are not there in the GTOs. So to incorporate an alteration in the orbitals to respond to changing molecular environment we have this split valence basis set. The ideas is split the AOs into inner compact core orbital and an outer diffuse valence orbital. The coefficient of these two orbitals are varied to respond to the changing molecular environment.

e.g. 3-21G = 3 core GTOs + 2 inner valence GTOs + 1 outer valence GTO.

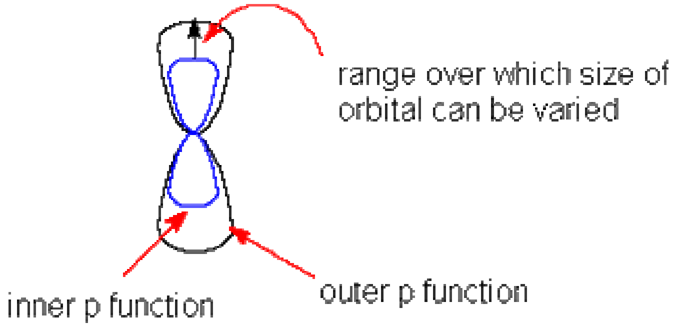

Fig 1. Split valence P orbital. The variation of p orbital with incoming extra electron [13].

Choice of basis sets: For any successful ab-initio computation it is essential that the basis set is properly chosen. It is common knowledge that an extended basis set with as many additional functions like polarization functions, diffuse functions would lead to more accuracy. However, it is imperative that a compromise be made in these issues as computational cost is the most important criterion. Apart from this, sometimes for specific situations only particular basis sets yield better results. This evident as in case of bond length calculations wherein use of STO-3G basis set gives erroneous results when size of basis set is increased. Also in HF calculations of Bond angles the type of basis set used doesn't matter at all. And so on.

It is to be noted that LCAO procedure was developed for finite systems like molecules, clusters with finite number of atoms. However for large systems also LCAO can be used. The idea here is to represent the large system as combination of identical computational units or supercells and applying the LCAO to one particular unit. Also the explicit interaction of all the supercells has to be kept in mind and has to appear as boundary conditions in the computations. This is also called as embedding technique.

LAPW METHOD--SALIENT FEATURES:

- This basis set is constructed for solutions that are rapidly varying and atomic-like (like isolated-atom solutions) near the atoms but more smoothly varying and not atomic-like throughout the rest of the cell.
- The space is partitioned into: 1. Spheres around each atom,
  2. Interstitial region
- Within the spheres expansion of wavefunction in terms of atomic-like orbitals
- In the interstitial region expansion in terms of plane waves where solutions are not atom like.

- The atomic-like nature leads to efficient representation whereas plane wave nature leads to highly accurate solutions for any atomic arrangement.

PWPP[9]:

Plane wave pseudo potential method uses plane waves basis set in conjunction with the pseudo potential approximation. This is an approximation based on the fact that the core electrons are seldom affected by the external environment of an atom. The idea is that the core electron wavefunctions are very costly from computational viewpoint. The same is true with the strong nuclear potential. The core electrons are localized in the vicinity of the nucleus so the valence electron wavefunction oscillates in order to maintain the orthogonality with the core electron wavefunction. The representation of these oscillations is computationally costly. Moreover, the valence electrons are only weakly bound to the nucleus, so it is better if the strong nuclear coulomb potential is replaced by a pseudo potential that is weaker and the valence electron wavefunction is replaced by a pseudo-wavefunction that doesn't have any radial nodes and behaves more like a plane wave.

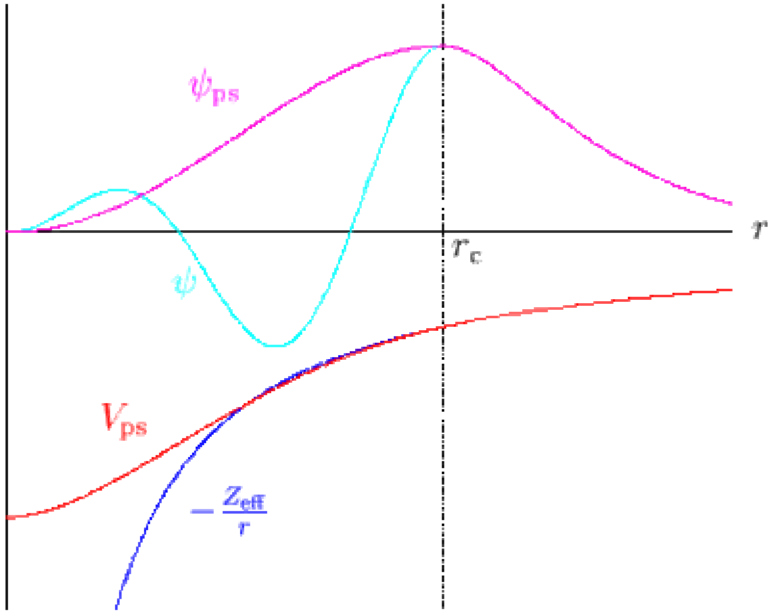

Fig 2. Schematic diagram of the relationship between all-electron and pseudo- potentials and wave-functions [14]

Solving Eigenvalue problem Diagonalization

The eigenvalues and eigenfunctions need to be calculated by solving the set of n equations. By choice of any proper basis set, we have at hand a matrix equation to solve. Solving procedure for matrix equation requires diagonalization of matrix which is computation intensive. Say for N basis functions used, O (N^3) computations are required. Car-Parinello technique requires about O (N log N) computations for N basis functions. Ab-initio is order O (N^4) method as N^4 four-centre electrons need to be evaluated. LDA and ETB are O (N^3) methods. Thus, there is presently a quest for methods that scale linearly with the size of the system.

Order N techniques [9, 11]:

The salient features of this methodology are explained below:

- Write all the quantities like energies, forces in terms of the density matrix whose off diagonal terms decay exponentially. Thus the matrix becomes essentially a diagonal matrix.

This is highly mathematical and we have not attempted here to give any further details.

Molecular Dynamics:

Apart from determining the ground energy and excited states of many electron system, it is necessary to determine the equilibrium structure, the dynamic and thermodynamic properties of many-electron systems. Molecular dynamics methods that have been developed for this purpose are:

Car-Parinello, Hellman-Feynmann Tight Binding molecular dynamics [10]:

For a given set up comprising of nuclei positions { R_I }, the force acting on an atom situated at R_I, given by Hellmann-Feynman theorem,

$$\vec{F}_I(\{\vec{R}_I\}) = -\left\langle \Phi_0 \left| \frac{\partial H}{\partial \vec{R}_I} \right| \Phi_0 \right\rangle.$$

Where $|\Phi_0\rangle$ is the ground state wavefunction. This theorem helps us calculate $\{F_I\}$ which can then be used to calculate the dynamics using the Newton's equation of motion. This is also used to find the optimized geometry.

Dynamics represented as:

$$M_I \ddot{\vec{R}}_I(t) = \vec{F}_I(\{\vec{R}_I(t)\}),$$

Note: The classical equations of motion are not valid for light atoms like Hydrogen. (Valid only for heavier atoms)

The total energy is clearly a function of nuclei positions and in course of dynamics of nuclei, their positions get changed. So one is faced with the problem of recalculating the total energy ever time the nuclei positions are changed.

However, this problem was solved by Car-Parinello who coupled the two phenomena in the following fashion.The dynamics of nuclei given by,

$$M_I \ddot{\vec{R}}_I(t) = -\frac{\partial E(\{\vec{R}_I\}, \{\psi_i\})}{\partial \vec{R}_I(t)}$$

And dynamics of electronic orbitals given by,

$$m_e \ddot{\psi}_i(t) = -\frac{\partial E(\{\vec{R}_I\}, \{\psi_i\})}{\partial \psi_i^*(t)} + \sum_{i,j} \Lambda_{ij}(\langle \psi_j | \psi_i \rangle - \delta_{ji})$$

Where the Lagrange multipliers Λ_{ij} are used to ensure conservation of orthonormality of the $\{\psi_i\}$ during the dynamical simulation.

Empirical Tight Binding method [9]:

This is one of the simplest explicit electronic structure calculation methodologies. In this the one-electron wavefunction is written as a linear combination of atomic orbitals. The basis functions need to orthonormal. This leads to simplification.

$\Psi_i = \Sigma (A_{ui} . \varphi_u)$, where u is the orbital index, summation is over dimension of basis set. The potential energy or the interaction term in the one-electron Hamiltonian encompasses on the nearest neighbors (NNs) and has only pair potentials. The sum of eigenvalues of the occupied orbitals (those are the only ones considered in this anyway) gives only the (attractive) electronic contribution to the total energy. To get the total energy of the system which includes both the nuclei and the electrons a repulsive interaction is added. This is usually done by fitting procedure. This falls under the semi empirical category. This methodology works better for covalently bonded materials like amorphous Si etc. The forces acting on the nuclei are calculated as discussed in the preceding section.

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Simulation Packages Available [11]***:***

Crystal, Gaussian, CASTEP & VASP, Fluer code, SIESTA etc

DETERMING PROPERTIES:

1. How to determine molecular structure? (Potential Energy Surface) [8]***:***

The central idea here is that the total energy of the system can be expressed as a function of nuclear coordinates. And that we can get equilibrium nuclear distances by optimizing the total energy with respect to the nuclear coordinates (i.e. total energy minimized wrt nuclear coordinates).

It is to be noted that it is because of Born-Oppenheimer approximation that we are able to express the total energy as function of nuclear-coordinates.

Just like any other generalized procedure, the potential energy is plotted vs. nuclear coordinates and point at which it attains the minimum gives the equilibrium structure. Such a surface formed by plotting Potential energy vs. nuclear coordinates is known as potential energy hyper surface (PES).

Standard mathematical optimization techniques like Newton-Raphson can be employed to get the stationary points. In mathematical terms,

Minimization of E_{total} with respect to set of nuclear coordinates $\{R_I\}$,

$$\frac{\partial E_{total}}{\partial R_I} = 0$$

However stationary point has to be characterized as minimum before proceeding any further. For this, second differential i.e. Hessian matrix in this case (as more than one variable involved) is used. Mathematically it is expressed as:

$$\frac{\partial^2 E_{total}}{\partial^2 R_I} > 0 \quad \text{for all nuclear coordinates implies local minimum}$$

$$\frac{\partial^2 E_{total}}{\partial^2 R_I} < 0 \quad \text{for at least one nuclear coordinate implies local saddle point.}$$

From the aforementioned expression we observe that Hessian can have either no negative eigenvalue or can have nonzero negative eigenvalues. Former case represents minimum and corresponds to the equilibrium structure. Transition state is represented by first order saddle point. The nth order saddle point means a maximum which has no meaning chemically. This is clearly shown in the diagram. The number of negative eigenvalues of the Hessian matrix is also called Hessian index.

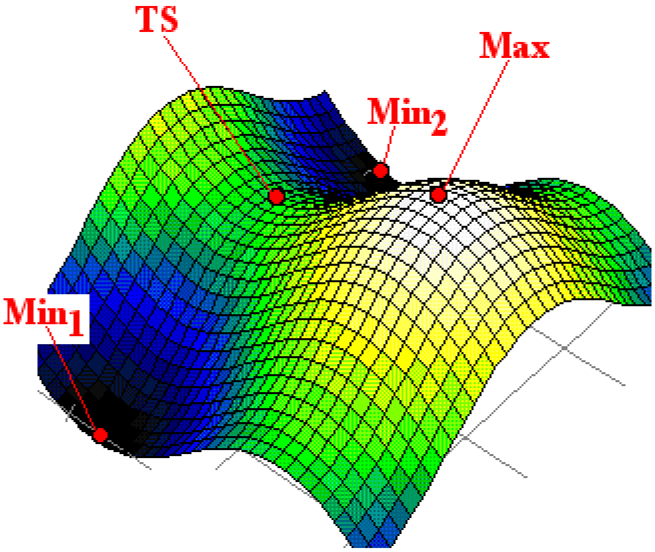

Fig 3. Min1→before reaction, Min2→after reaction, TS→Transition state. Determination of reaction paths will be explained later as a case study [15].

2. Calculating Ionization Potentials and Electron Affinities (EA) [7]*:*

- ✓ Negative of the orbital energies of the occupied spin orbitals (wavefunctions depending on the spin coordinate as well) gives the Ionization Potentials
- ✓ Negative of the orbital energies of the unoccupied or virtual spin orbitals gives the Electron Affinities.
- ✓ This is called as ***Koopman's theorem***.

3. Calculating the heats of formation [7]*:*

- ✓ Since the exchange-correlation energies are only approximately calculated, the heats of formation can't be calculated accurately with ab-intiio methods.
- ✓ Atom and group equivalent technique needs to be employed which reduces error drastically.
- ✓ Sets of group equivalents are available in literature for converting the HF energies into heats of formation.
- ✓ Thus, this is basically a semi-empirical technique wherein difference in actual energy and HF energy is fitted and same is used for other systems having same kind of groups of atoms.
- ✓ For e.g. consider hydrocarbon C_nH_m:

$$\Delta H_f = E_{HF} - m\, E_{=CH-} - (n-m)\, E_{=C<}$$

Where $E_{=CH-}$, $E_{=C<}$ are equivalents for the =CH- and =C< respectively.

CASE STUDIES

Heterogeneous Catalysis: Catalytic oxidation of CO on Pt surface[5, 6].

The transition metals can catalyze the oxidation of CO into CO_2. For this reason car exhaust catalytic converters have been using transition metals like Pt, Pd, and Rh supported on metal oxides. Though much research has been done from a technological viewpoint still these catalytic reactions are widely studied. For understanding this reaction or for that matter any catalytic reaction it is necessary that two things are known:

- ✓ Transition state
- ✓ Reaction barrier to achieve the transition state

Understanding of catalytic reactions helps us in design of newer, better catalysts.
We will now take up the case of CO oxidation on Pt (111) surface.

Methodology:

Density functional theory is employed which is basic framework for calculating the energies of the atoms comprising the periodic system. Plane wave basis set is used. This describes a periodic system in very efficient fashion. It is the valence electrons that take part in a reaction. So part of wavefunction that is away from nuclei is imperative.
As one would expect for such cases pseudo potentials works well for this kind of system.
LDA and GGA techniques are employed to get the form of exchange-correlation potentials.
Our periodic system consists of three layers of Pt atoms with each layer comprising of 4 Pt atoms, a Carbon atom and two O atoms. The CO-O co adsorption is such that the O atoms are adsorbed onto the hollow sites of the structure. Periodic system here refers to that part of the system that is representative of the system as a whole and which can generate the whole system by mere repetition. The periodic system is shown below:

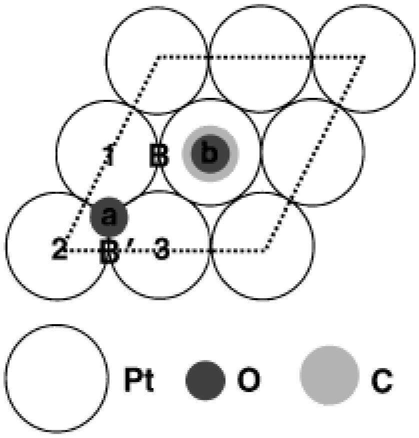

Fig. 4. The geometry of the CO/*p* (2X2)-O/Pt (111) configuration. The unit cell in the surface plane is indicated with dotted lines [5].

The reaction path way (low-energy one) is found by constrained minimization technique: This is a general technique employed to get mechanism for organic reactions.

Constrained minimization: It is assumed here at this point that the concept of PES is understood.

Steps are:

- Keep the C-O bond distance constant and minimize the total energy with respect to other degrees of freedom (i.e. all other nuclear coordinates)
- Now the total energy is plotted as function of C-O bond distance.
- Transition state occurs when the Hessian of the total energy has one negative value. In other words for the transition state the total energy is the maximum so look out for a maximum in the graph. This gives the transition state. It is to be noted here that the transition energy is maximum only with respect to the C-O bond distance but minimum for other nuclear coordinates.

Hence the reaction path way is obtained. Some snapshots for the reaction pathway:

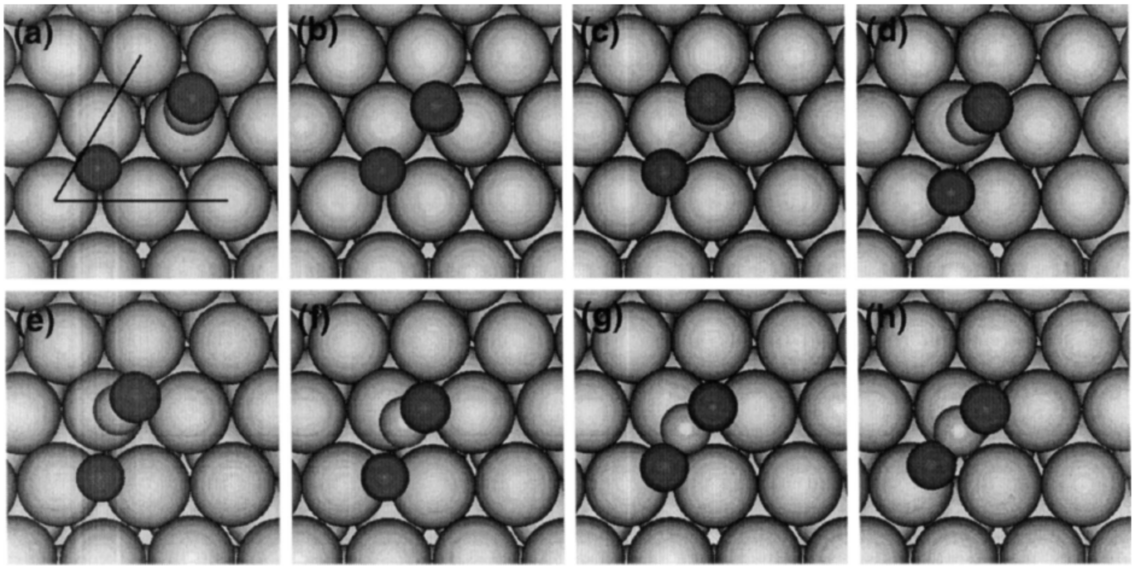

Fig. 5. Snapshots of the reaction pathway from the initial state [top left, (a)] to the final state [bottom right, (h)]. The lattice vectors are indicated in (a). For clarity, the periodic images of the molecules are not shown, and the view is slightly tilted from the vertical. The Pt atoms are the largest spheres, the O atoms are the darkest spheres, and the small grey spheres are the C atoms. The transition state is (e). In (h), the molecular geometry of the CO2 molecule is bond lengths C-O (a) - 1.29 Å and C-O (b) - 1.21 Å and bond angle 131. The gas-phase molecule is linear with a bond length of 1.16 Å [5].

Reaction Pathway:

1. The C-O molecule moves towards the bridge site B.
2. The O atom on Pt (1) (see fig1), actually O is at a hollow site, moves towards bridge site B'.
3. The CO molecule breaks from B and moves to Pt (1). Simultaneously the O atom breaks from Pt (1) and goes into bridge site B'. This is the transition state.
4. Then the CO molecule and the O atom come together to form the bond, thereby forming nascent CO_2

Viewing electron densities:

In this context it is worthwhile to reiterate the fact that density functional theory is employed here, which gives spatial distribution of electron densities. The electron density contours parallel to the surface looks something like this:

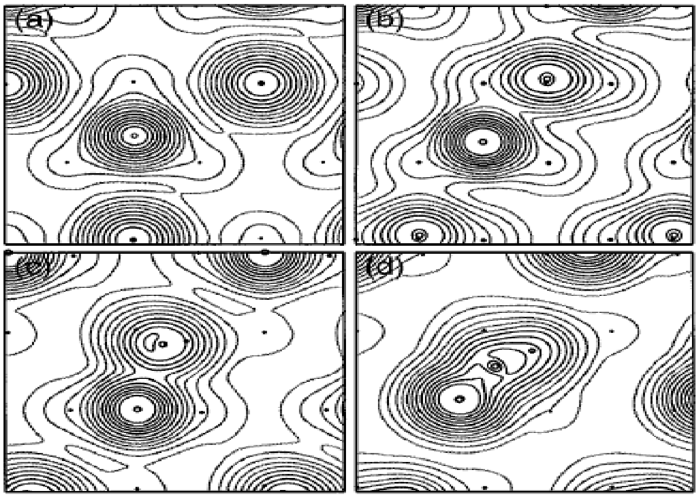

Fig. 6. Electron density contours parallel to the surface. The plane of the contours is chosen as midway between the *z* components of the C atom and O (a). The contours are logarithmically spaced. Black contours denote the highest electron density (*H)* [5].

Notes:

1. Chemical bonding is represented by increased electron density between two atoms.
2. Electron density spreads towards Pt (1) as CO moves to B.
3. Three-fold symmetry of electron density around O lost as CO comes to B.
4. In TS, O-Pt (1) bond breaks while bonding is still there with other two, Pt (2), Pt (3).
5. Finally nascent CO_2 formed. Therefore increased ρ between CO molecule and O atom.

Reaction Barrier:

- C-O bond distance in the transition state = 2.1 A > 1.16 A (C-O bond-length). So the repulsion between chemisorbed C-O and chemisorbed O is not the reason for reaction barrier.
- Calculating the chemisorption energies of O on Pt without CO
    - O in hollow site more stable than in bridge site.
- The diffusion of CO from top site to bridge site hindered by the movement of O from hollow site to opposite bridge site. This is shown in the energy barrier for diffusion of CO with and without O.
- Reaction barrier is due to the competition between CO and O in forming the surface bonds and more so because of the O-Pt bond. The Breakage of the O-Pt bonds decides the reaction barrier as this is the one which delays CO_2 formation.
- ***Conclusion:*** Reaction barrier lower if O-metal bond is weaker!!!

Design of environment responsive Nanoporous System [12]:

"Smart" nanoporous systems have been designed using molecular simulations. These systems can open or close depending on the environmental conditions like pH, temperature, solute concentration etc. This is advantageous as we can selectively trap large molecules and allow the smaller ones to diffuse through the pores. This has variety of application like filtration, size-sorting of biomolecules and chemical separation.
The idea is to make use of rod – globule transitions of polymer comb molecules. Polymer comb molecules consist of densely grafted side chains extending from a polymer backbone. Polymer molecules having a flexible backbone undergo a complete axial contraction of the side chain, when placed in a poor solvent; this is called as Globular state. On the other hand, in a good solvent these form a fully stretched cylindrical brush. Thus a nanoporous system can be proposed by grafting these comb-molecules in a nanopore slit.

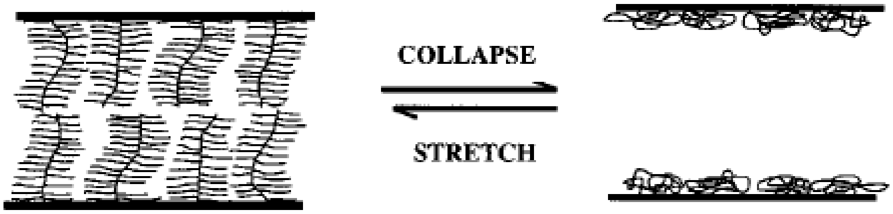

Fig. 7. Illustration of the proposed nanoporous system [12].

When the pore is open diffusional resistance is low and vice-versa.
Performance parameters of such a system:

- ✓ Response time
- ✓ Volume difference between globular state and extended state.
- ✓ Range of stimuli over which chains respond
- ✓ Efficiency of nanoporous system with respect to diffusion of species.

Methodology employed:
A bead-spring molecular model is used to explore the feasibility of proposed nanoporous system by calculating its performance parameters. Mass of each bead used is 14 amu. Lennard-Jones potential is employed to describe non-bonding interactions between beads except for the nearest neighbors. The molecular dynamics is carried with constant energy of the system and with time steps of 5fs for about 10^5-10^6 runs. In order to study contraction we define radius of gyration for the polymer consisting of N monomers as,

$$\langle R^2{}_g \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle (R_i - R_{\mathrm{COM}})^2 \rangle$$

Where R_i is the coordinate of monomer *i,* R_{COM} is the coordinate of center of mass of the molecule.

Discussion of Results:

Snapshots of molecular dynamic simulations:

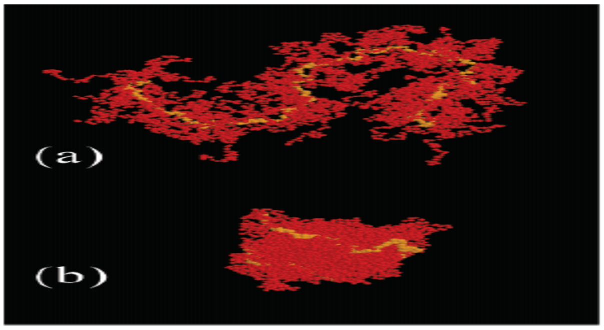

Fig. 8. Snapshots from molecular dynamics simulations of (a) stretched, and (b) collapsed comb polymer. Color code: side-chain (red), backbone (yellow) [12].

The variation of radius of gyration with temperature looks something like this:

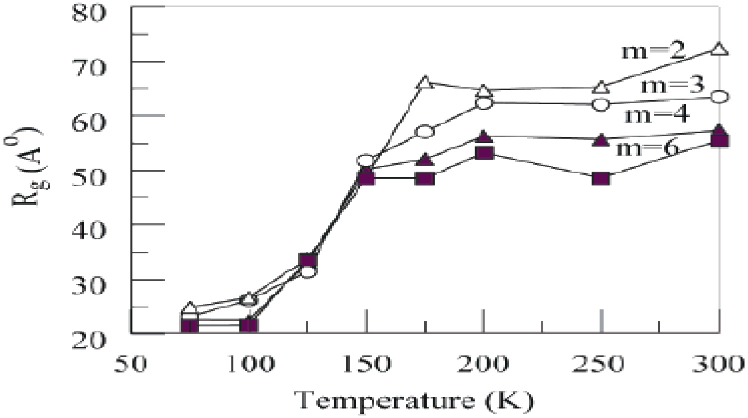

Fig. 9. Radius of gyration of the whole molecule as a function of temperature for side chain grafting distances *m)* 2, 3, 4, and 6 [12].

Clearly increase in temperature favors closing of the nanopore. Higher value of R_g implies the system is in stretched state and the pore is closed.

To characterize the time-scale of collapse transition the polymer molecules are rapidly quenched using a Nose thermostat (from 300k to 100k). Variation of R_g with time is got.

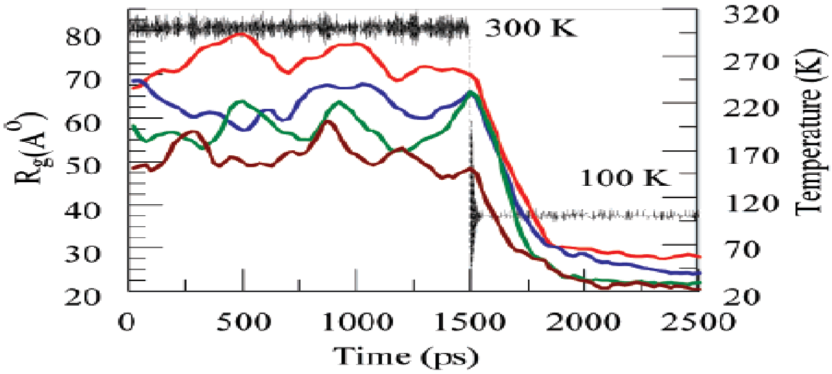

Fig. 10. Plot of *Rg* vs. time for a comb polymer with *N*=200, *n*= 40 and *m*= 2 (red), 3 (blue), 4 (green), and 6 (brown). The isolated molecules were quenched from a temperature T = 300 K to 100 K. Temperature of the system as a function of time is shown in black for reference [12].

We can observe from the graph that the response time is about 1500ps.

Characterizing the opening and closing of proposed system:

We plot the density of monomers belonging to the comb-molecules as a function of distance from the grafting surface. In good solvent conditions, the solvent molecules wet the grafted layer and as a result the comb molecules stretch and fill the entire volume. In poor solvent conditions, the interaction among the monomers of the comb polymer is preferred over interactions with the solvent molecules hence contraction occurs.

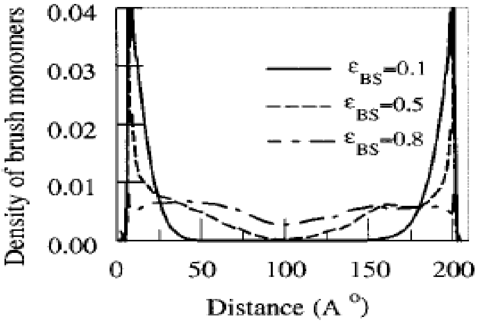

Fig. 11. Density profiles of brush monomers across the pore [12].

Snapshot for better visualization:

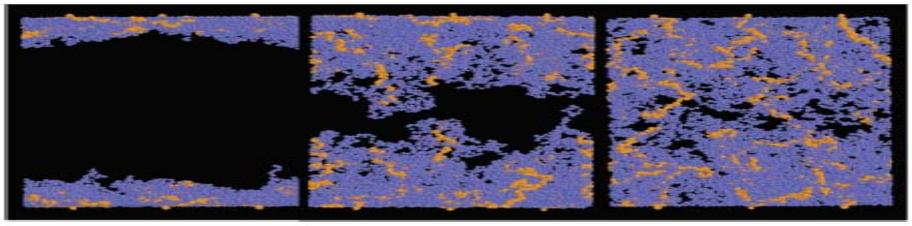

Fig. 12. Snapshots from MD simulations of the nanoporous system Solvent molecules are not shown for better visualization of the brush structure. Color code: side chains (blue) and main chain (yellow) [12].

Inferences:

Simulations reveal that indeed the nanoporous system responds to environmental characteristics. Closing of pore can be used to inhibit the diffusion process. Increase in temperature results in closing of the pore and vice-versa. Response time calculations were also done. It was about 1500ps which is good enough for process control.

C*onclusions*:

Computational materials science has added a new dimension to our basic understanding of nature itself. Since macroscopic properties are mapped to the atomic structure, effecting desired properties by changing the atomic structure becomes a possibility. In other words one can "*engineer*" the materials to get desired properties. Many of the experiments like visualizing the nanoporous systems are not possible in a laboratory whereas a computer experiment is possible. Thus computational materials science helps us in performing those studies that are not viable in a conventional laboratory. For instance the reaction pathway study of oxidation of CO on Pt was first done computationally. Only after a year was it experimentally verified using STM. Thus computational materials science is a new age tool to study materials properties.

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