Theory, Modeling & Computation in Chemistry: Its Scope and Role in Frontier Areas of Research in Chemistry- Part 1

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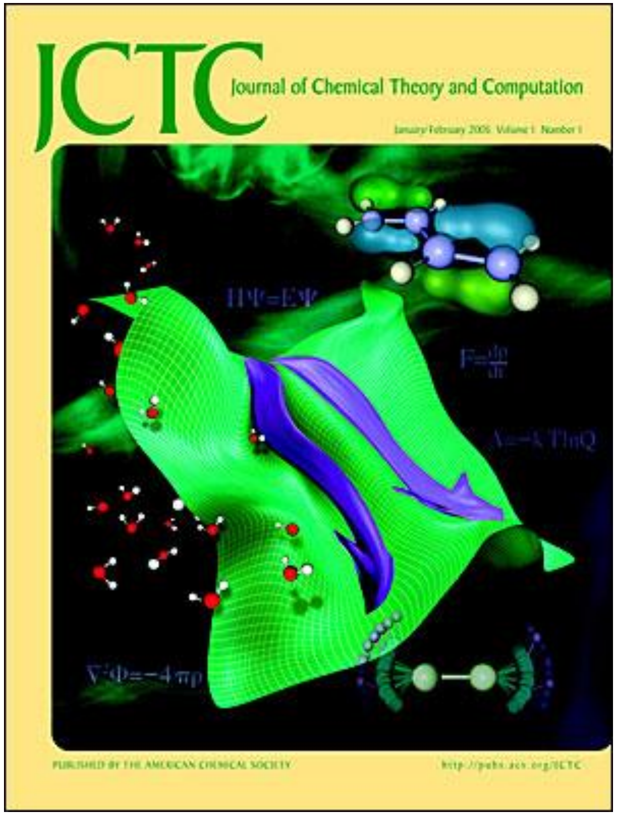
PLAN

- What is Theoretical & Computational Chemistry ?
- What can it do ?
- Theory, Modeling, Computation & Simulation ?
- General Overview of Methodology / Strategy used at different length & time scales.
- Typical Illustrative Examples .

FAQs:

- Is it important ?
- Is it relatively more difficult / more easy ?
- Is it relatively more useful / less useful ?
- Reliability of predictions ?
- What is the scope for a career in Theoretical / Computational Chemistry (General & in DAE) ?



American Chemical Society has launched
a new journal
Journal of Chemical Theory and Computation
devoted fully to theoretical & computational
chemistry, which clearly reflects that
this area of research is considered as a
separate and important frontier.

Theoretical & Computational Chemistry
is now a separate credit course in US Univ.

The *JCTC* cover design is a combination of ideas from Editor William L. Jorgensen. It depicts the four fundamental equations of computational chemistry, from top, clockwise: the Schrödinger equation, Newton's equation of motion, the relationship between Helmholtz free energy and the partition function and the Poisson's equation.

Theoretical & Computational Chemistry: *Its Scope and Role in Frontier Areas of Research in Chemistry*

- Theoretical Chemistry is an integral component of research in frontier areas of chemistry.
- It is a separate branch of chemistry adding to the list of physical, inorganic, organic, analytical, bio-chemistry, etc
- It has interface with other areas such as materials science, condensed matter physics, chemical engineering & biological science: Computational Fluid Dynamics (CFD), Computational Materials Science (CMS).
- It is a major contributor to the frontier areas of inter-disciplinary research.
- Availability of powerful computational resources has contributed significantly to the growth of this field.

Primary Goal

- Provide an understanding & rationalisation of physicochemical phenomena observed in laboratory experiments or in nature

- Arrive at new predictions hitherto unexplored.

- Simulation of complex systems not accessible experimentally.

- Intellectual pursuit & creation of knowledge.

- Short listing of molecular candidates for experimentation

:Strategy:

•Develop concepts and build models to explain observed facts.

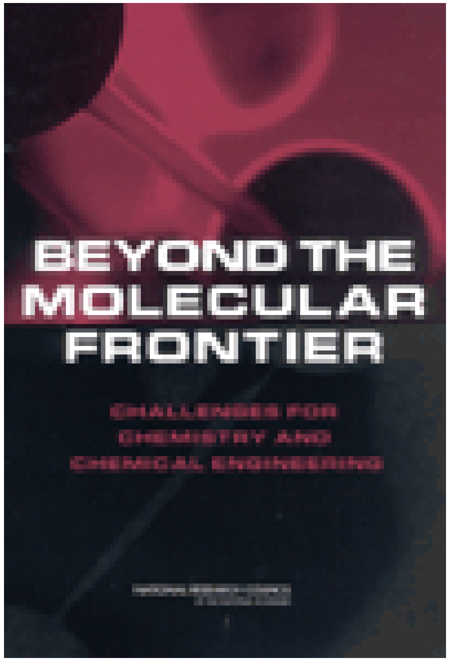
•Do calculations within appropriate theoretical framework.

•Perform computer simulation using suitable force field

•Formulation of new theoretical tools, modeling strategies and simulation techniques forms an integral part of research in theoretical Chemistry: *Analogy with development of new experimental techniques.*

•Device experiments to establish reliability of theoretical predictions.

• Theory, Modeling & Computation to understand rich diversity in the physical world.



Beyond the Molecular Frontier: Challenges for Chemistry and Chemical Engineering

Committee on Challenges for the Chemical Sciences in the 21st Century, National Research Council

ISBN: 0-309-08477-6, 240 pages, 6 x 9, paperback (2003)

CHEMICAL THEORY & COMPUTER MODELING: FROM COMPUTATIONAL CHEMISTRY TO PROCESS SYSTEMS ENGINEERING: *Goals, Progress to Date, Challenges and Opportunities for the Future, Why all this Is Important:*

Chapter 6 deals with **computation and theory, from the most fundamental aspects to the role that this subject plays in manufacturing**.

Computer revolution has made it possible to approach a number of important goals:

•Predicting properties of unknown substances & pathways of chemical & physical processes, & designing optimal processes for manufacturing useful substances.

•One can expect to be able to create and manufacture new substances with drastic reduction of development times, thus bypassing substantial amounts of empirical experimental work and optimally meeting our needs in areas like medicine and advanced materials.

•This area of research has tremendous promise and importance and should be pursued vigorously.

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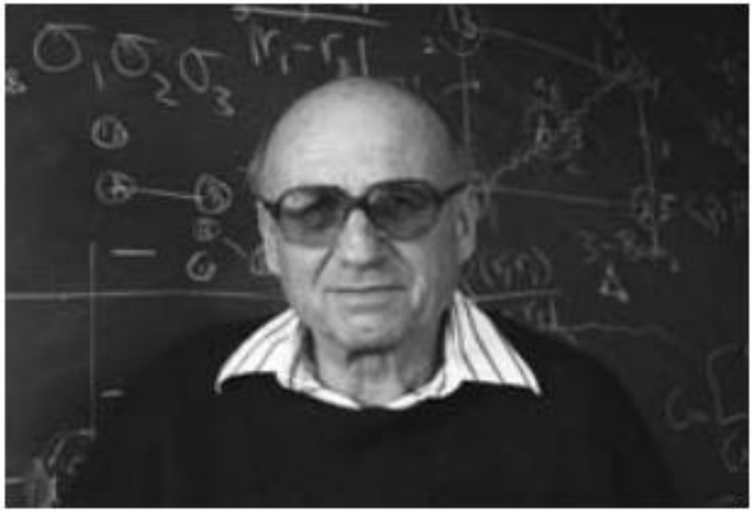
:Nobel Prize in Chemistry 1998:

The Royal Swedish Academy of Sciences has awarded
The 1998 Nobel Prize in Chemistry in the area of quantum chemistry to

Walter Kohn, University of California at Santa Barbara, USA and
John A. Pople, Northwestern Univ., Evanston, Ill., USA (British citizen).

Citation:
"to Walter Kohn for his development of the **density-functional theory** and to John Pople for his development of **computational methods in quantum chemistry**."



:Nobel Prize in Chemistry 2013:

Scientific Background on the Nobel Prize in Chemistry 2013

DEVELOPMENT OF MULTISCALE MODELS FOR COMPLEX CHEMICAL SYSTEMS

Martin Karplus, Harvard U., Cambridge, MA, USA

Michael Levitt, Stanford U., Stanford, CA, USA

and

Arieh Warshel, U. Southern Ca., Los Angeles, CA, USA

Quantum Mechanics / Molecular Mechanics (QM/MM)

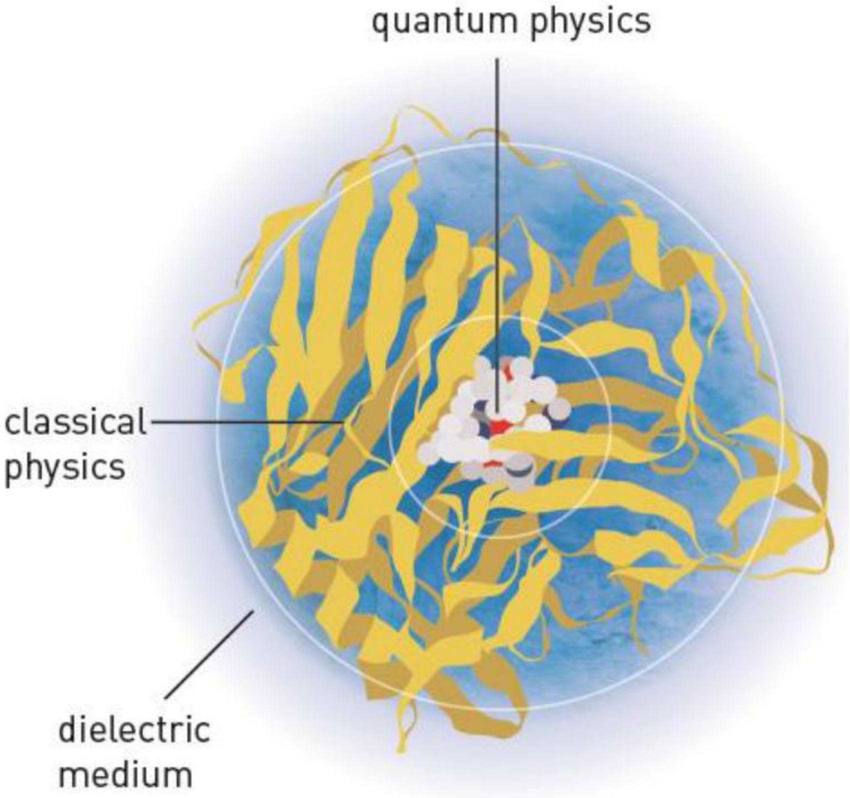
Bridging the electronic and atomistic length scales

Karplus

Levitt

Warshel

One interesting aspect of this year's chemistry Nobel laureates lies in their Israel connection. All the three scientists have become US citizens. Levitt holds American, British and Israeli citizenship and spends half of the year in Israel, where his wife and children live. Warshel, was born in Israel and holds US and Israeli citizenship. Karplus spent a semester in Weizmann Institute, Israel. According to Levitt, Israel had two profound influences on his life, the first being that he met his wife in Israel and the second being that it was Israel where he initiated his research path that ultimately led to the coveted prize. It may also be mentioned that Warshel and Levitt mark Israel's fifth and sixth winners of the chemistry Nobel Prize in a decade, joining the group of other chemistry Nobel laureate Israeli scientists, Avram Hershko and Aaron Ciechanover (2004), Ada Yonath (2006), and Daniel Shechtman (2011).



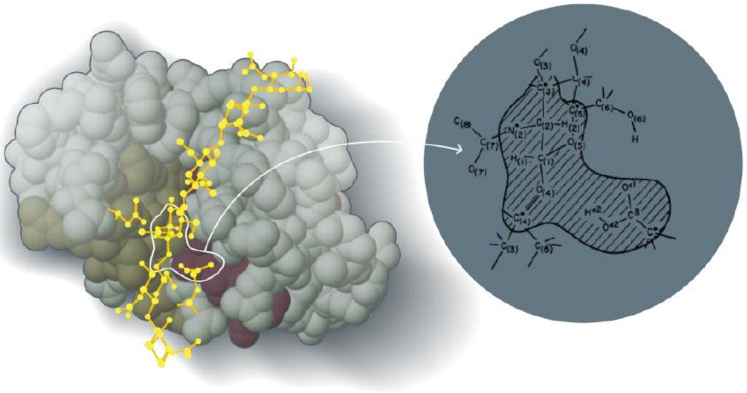
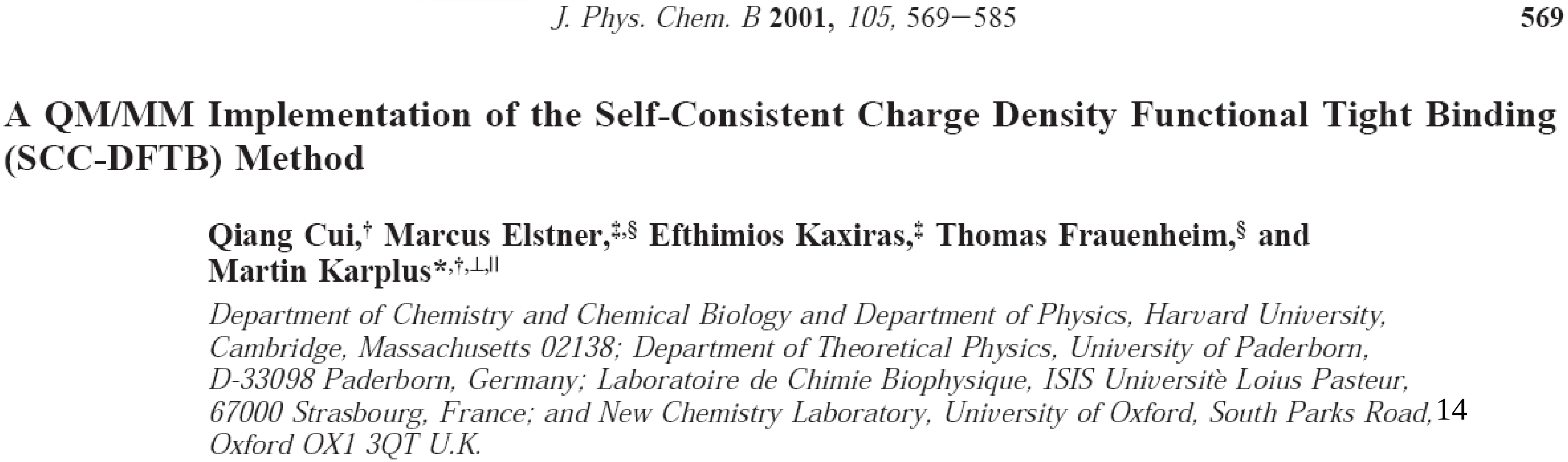


Figure 3. To understand how lysozyme cleaves a glycoside chain, it is necessary to model only the relevant parts of the system using quantum chemistry, while most of the surrounding may be treated using molecular mechanics or a continuum model. The figure is adapted from[16]



J. Phys. Chem. B **2001,** *105,* 569−585 **569**

A QM/MM Implementation of the Self-Consistent Charge Density Functional Tight Binding (SCC-DFTB) Method

Qiang Cui,[†] Marcus Elstner,[‡,§] Efthimios Kaxiras,[‡] Thomas Frauenheim,[§] and Martin Karplus*[,†,⊥,||]

Department of Chemistry and Chemical Biology and Department of Physics, Harvard University, Cambridge, Massachusetts 02138; Department of Theoretical Physics, University of Paderborn, D-33098 Paderborn, Germany; Laboratoire de Chimie Biophysique, ISIS Universitè Loius Pasteur, 67000 Strasbourg, France; and New Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QT U.K.

What do we do ?

MOLECULES TO MATERIALS: MULTI-SCALE MODELING & SIMULATION

Interdisciplinary Basic Research at the Interface between Chemistry, Physics, Materials Science, Chemical Engineering & Biology

Materials Related:
Nanomaterials

Energy Related:
Hydrogen energy

Waste-Management related:
Ligand Design

Basic Research:
Electronic Structure/ Molecules
Dynamics in Condensed Phase
Soft Matter under Confinement

Experiment-Driven Theoretical Studies

Biology-Inspired Theoretical Studies

Curiousity-Driven Investigations

Theory & Computation

- Development of new Theoretical Formalisms & Modeling/ Simulation Strategies

- Nonequilibrium thermodynamics at short length & time scales
- Coarse-Graining procedure for simulation

Class. & Quant Mech, Stat Mech: MC, MD, CPMD, MCT, DFT, PFM, ……

:Computational Science:

- Application of computational and numerical techniques to solve large and complex problems.

- Allows us to do things that were previously too difficult to do due to the complexity of the mathematics, the large number of calculations involved, or a combination of the two.

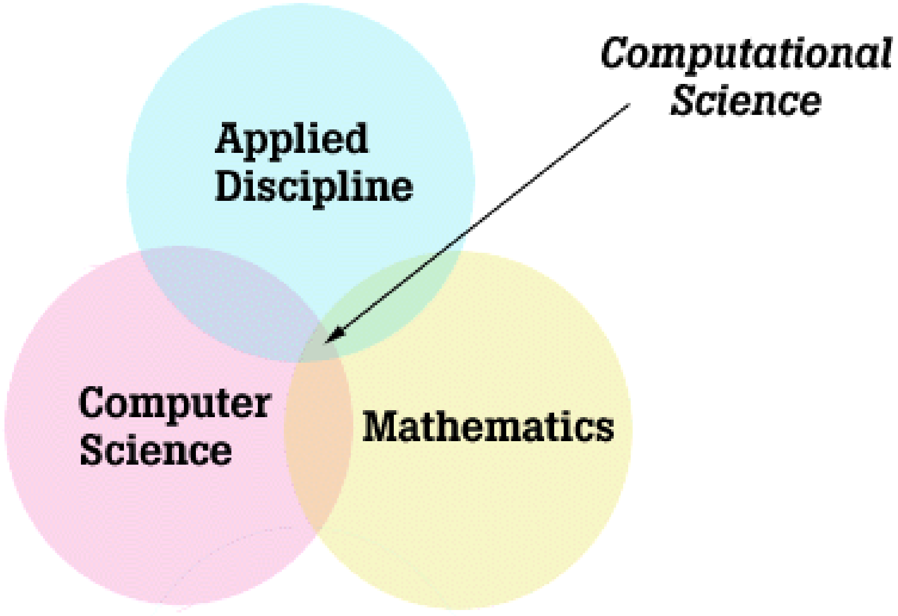
- Allows us to build models that help in making predictions of what might happen in the lab, so that we are perhaps better prepared to make good observations or to understand better what we are seeing.

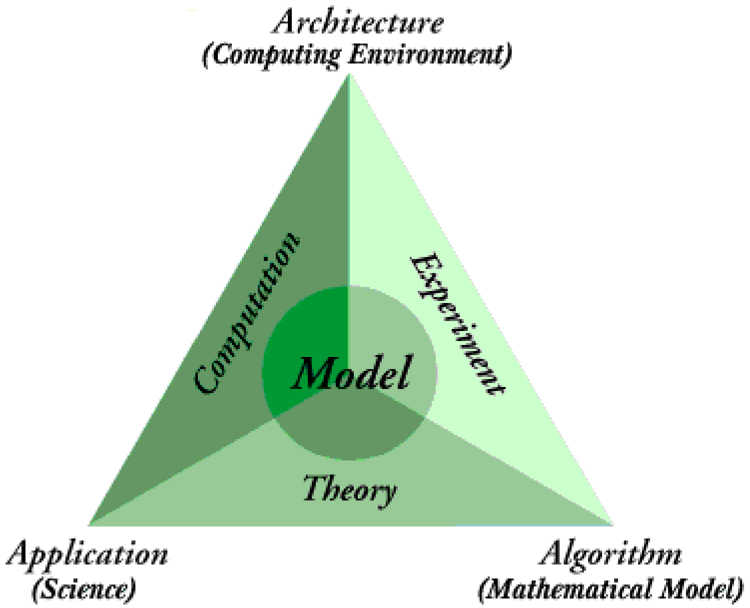
- Use computational techniques to perform experiments that might be too expensive or too dangerous to do in the lab.

- It cannot replace the lab, but it has certainly become an intricate part of the overall search for scientific knowledge.

- It is a fourth method of doing research, an addition to observational, experimental, and theoretical methods.

- Theory, Modeling, Computation & Simulation go hand in hand.





Computational Science

- A branch of science (chemistry, physics, materials science) that generates data, which complements experimental data on the structures, properties and functions/reactions of substances.

- Computational science is particularly useful for determining molecular and materials properties which are inaccessible experimentally and for interpreting experimental data

:Scientific Objective:

- To understand Nature

- Understanding systems & phenomena

- Equilibrium aspects
  “Why are things the way they are”

- Dynamical aspects
  “From being to becoming”

- Structure: Appearance: How does it look ?
- Function : What does it do ?
- Properties: What are its qualities ?
- Dynamics: How does it go from one structure to another ?

Theory & Modeling

Systems

Phenomena

- Molecules
- Materials

- Chemical Reactions
- Physical Processes
- Biological Phenomena

Different Nuclei bonded together by Electron Glue

- Transition from one Spatial Configuration of Atoms to another

Modeling: Complexity:

- Large Number of Variables: Many-Body Problem
- Hierarchy of Length Scales & Multiple Time Scales

Nano-Scale Materials: Design of Novel Molecules & Materials with desired Tunable Properties

Microscopic Length Scale: Electronic Structure Calculation
Mesoscopic Length Scale: Atomistic Modeling & Simulation

"I think the next century will be the century of complexity"—
Stephen Hawking (Jan 20, 2000 San Jose Mercury News)

Theory & Modeling: Scientific Objective:

- To understand Nature
- Understanding systems & phenomena
- Equilibrium aspects
  "Why are things the way they are"
- Dynamical aspects
  "From being to becoming"

- View through windows of different length & time scales
- Macroscopic, Mesoscopic & Microscopic
- Slow, Fast, Ultrafast

View through Windows of Different Length Scales

Macroscopic Scale

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Mesoscopic Scale

Microscopic Scale

- **Hierarchical** nature of scales inherent in all materials
  For understanding a property on a given length and time scales,
  it is crucial to understand / simulate
  the properties / mechanisms at all
  shorter length and time scales

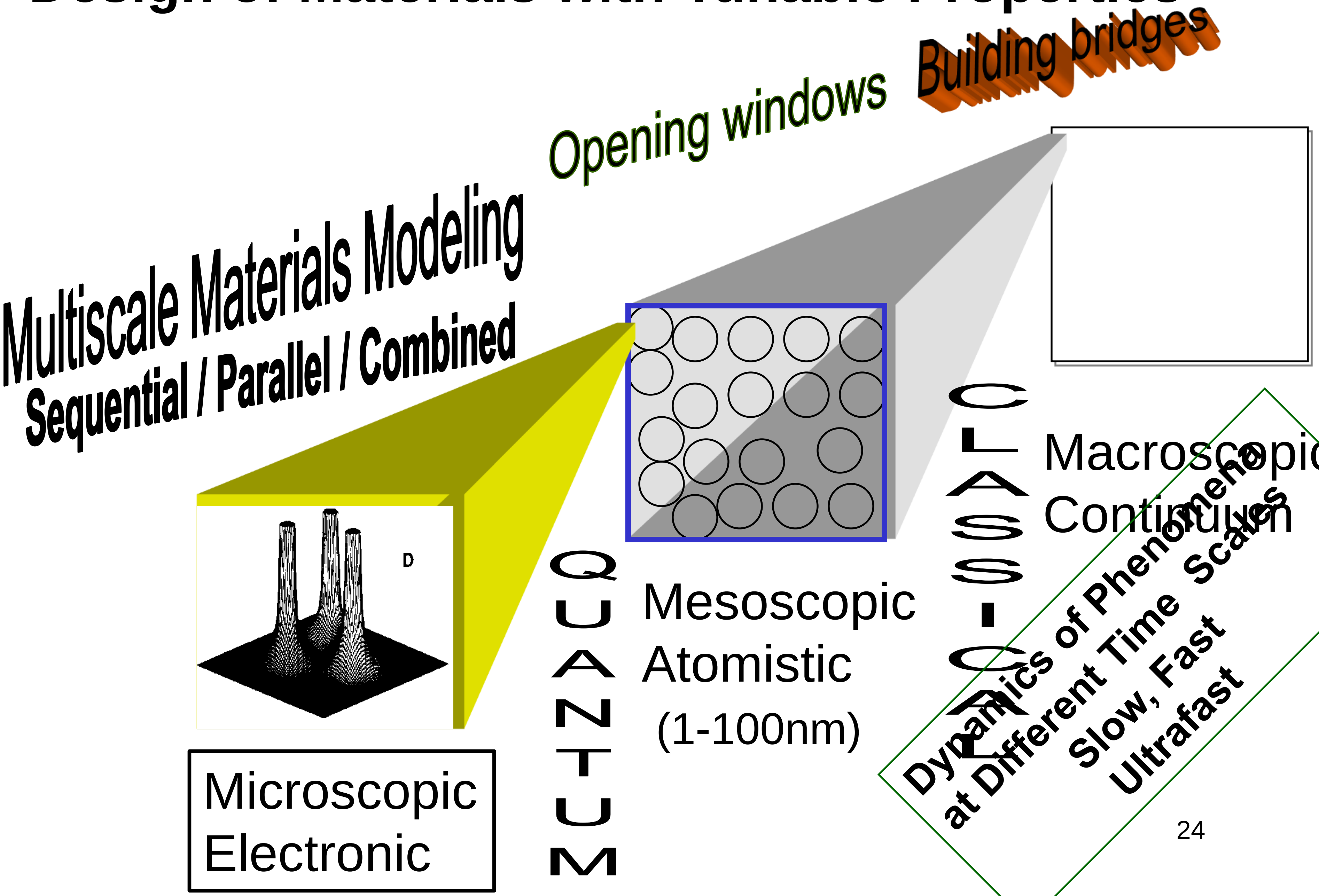
- **Multiscale ?**

- **One can look at the Density**

- **Density** is a unique variable at all length scales and helps in developing unified approaches.
- Density Concept is also an Example of Simplicity in Complexity

Materials Modeling

Design of Materials with Tunable Properties



Building bridges

Opening windows

Multiscale Materials Modeling

Sequential / Parallel / Combined

Microscopic
Electronic

QUANTUM

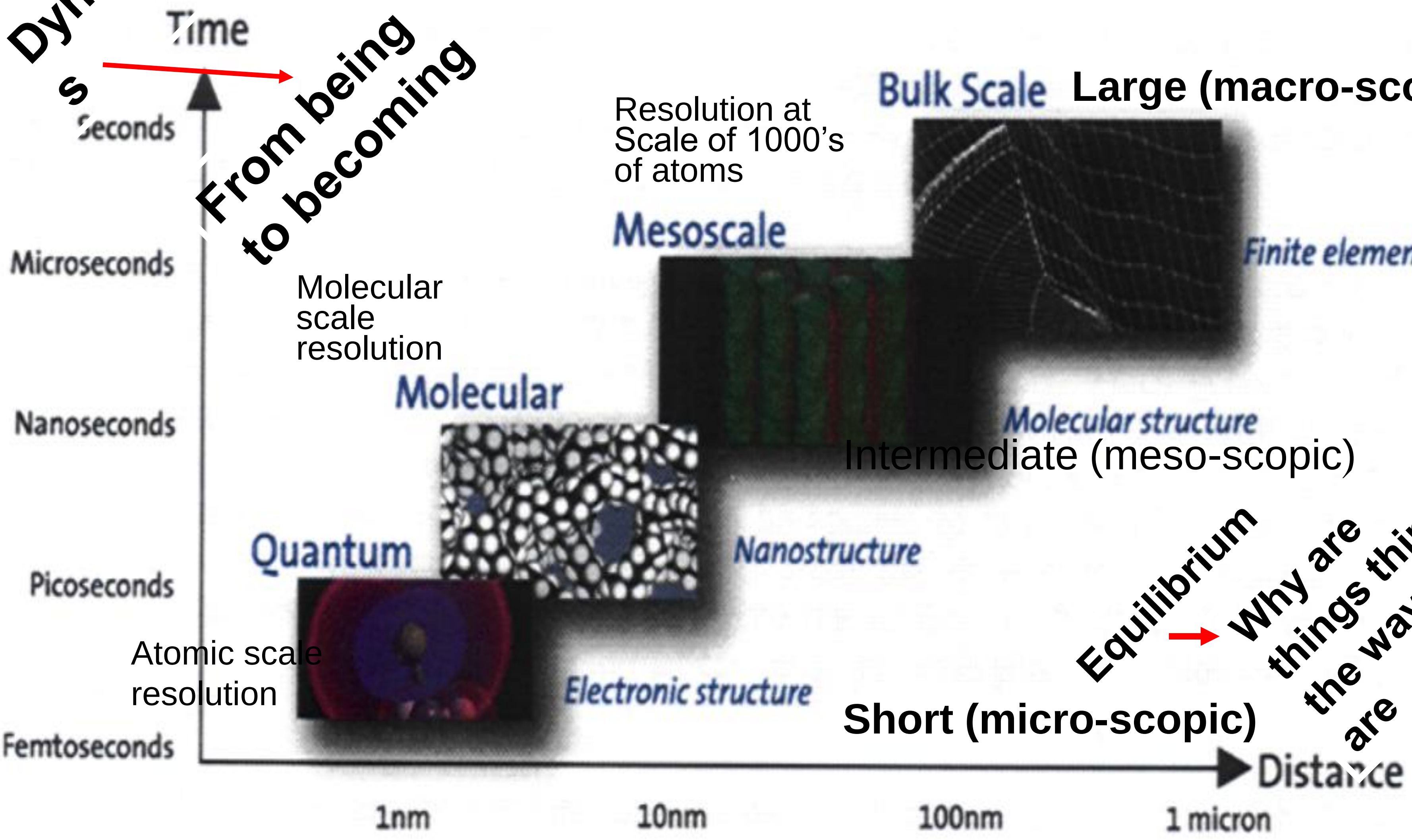
Mesoscopic
Atomistic
(1-100nm)

CLASSICAL

Macroscopic
Continuum

Dynamics of Phenomena
at Different Time Scales
Slow, Fast
Ultrafast

Scales in Modeling Materials & Phenomena



Dynamics → **From being to becoming**

Large (macro-scopic)

Resolution at Scale of 1000's of atoms

Molecular scale resolution

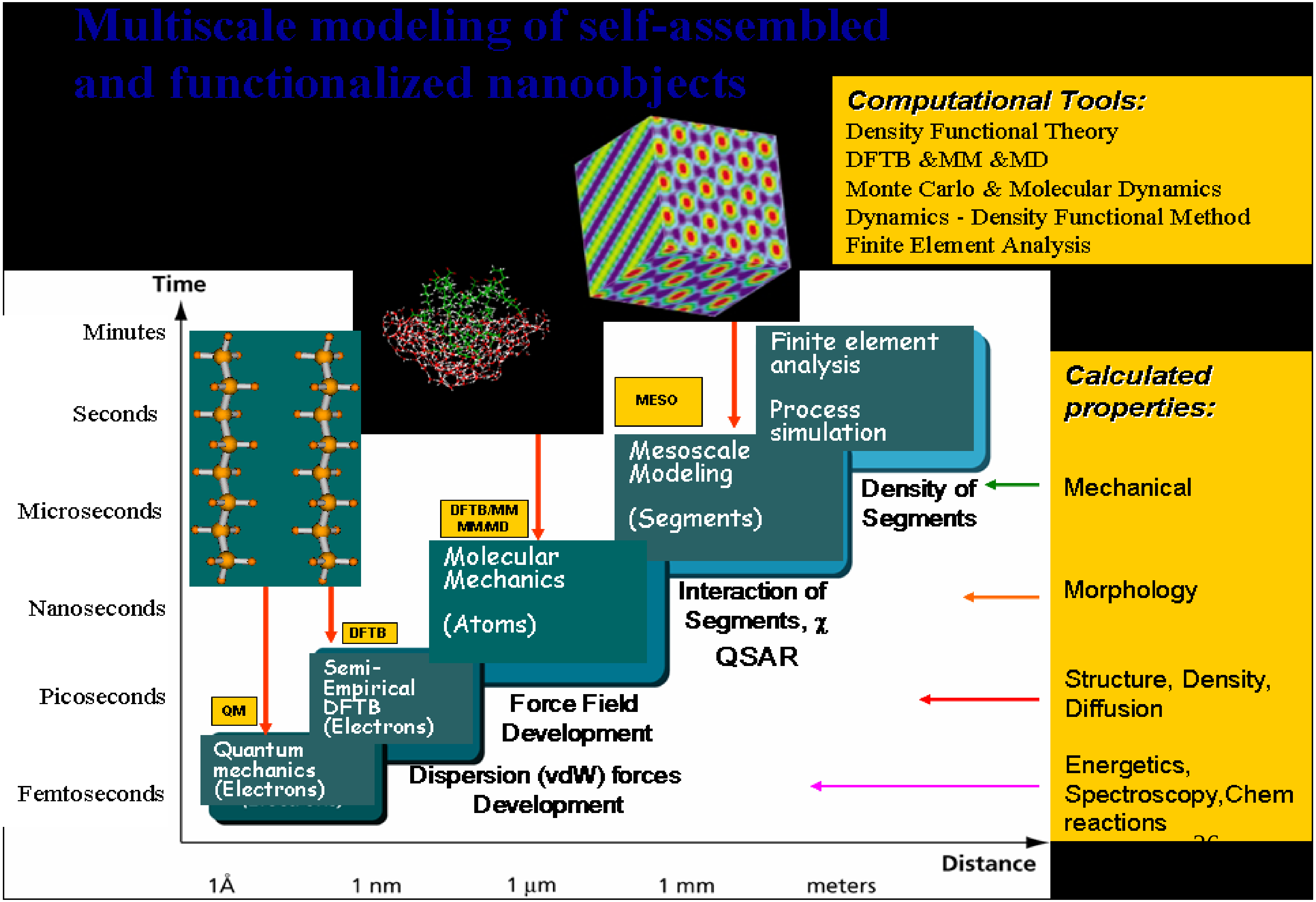
Intermediate (meso-scopic)

Atomic scale resolution

Short (micro-scopic)

Equilibrium → **Why are things the way they are**

Different Scales of Applications



Multiscale modeling of self-assembled and functionalized nanoobjects

Computational Tools:

Density Functional Theory
DFTB &MM &MD
Monte Carlo & Molecular Dynamics
Dynamics - Density Functional Method
Finite Element Analysis

Calculated properties:

Mechanical

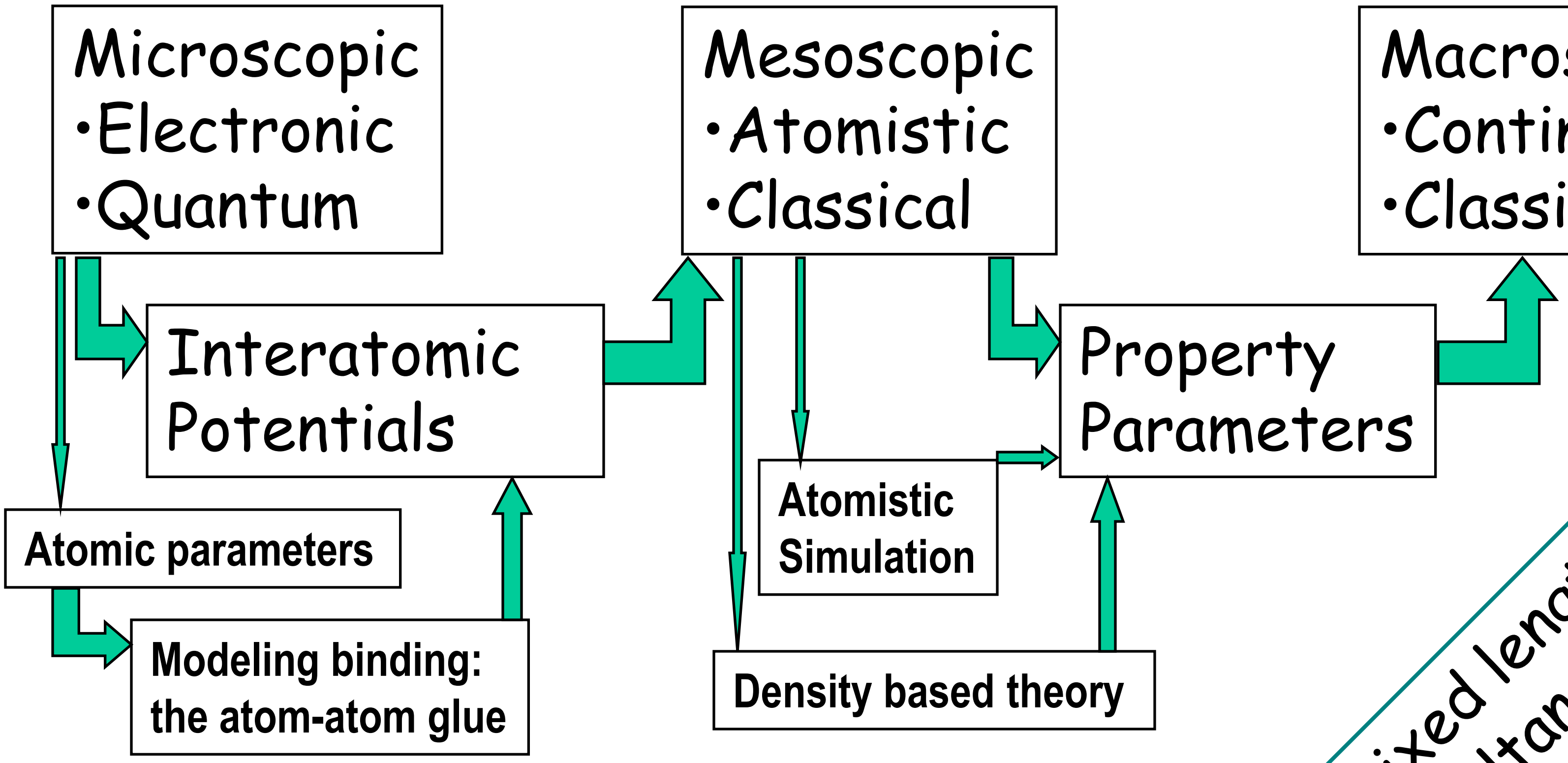
Morphology

Structure, Density, Diffusion

Energetics, Spectroscopy, Chem reactions

BUILDING BRIDGES & OPENING WINDOWS

Multi-Scale Materials Modeling



Microscopic
- Electronic
- Quantum

Mesoscopic
- Atomistic
- Classical

Macroscopic
- Continuum
- Classical

Interatomic Potentials

Property Parameters

Atomic parameters

Modeling binding: the atom-atom glue

Atomistic Simulation

Density based theory

Mixed length scales simultaneously treated

Sequential approach: Divide & Conquer

Combined approach : Bridging the Length Scales

: Car-Parrinello & Analogous approaches

SEQUENTIAL APPROACH

Electronic Length Scale:

- Interelectronic potential is known
- Pseudopotentials used for simplification of ion-electron potential

Atomistic Length Scale

- Interatomic potential unkown (obtainable from Electronic Length Scale)
    - Ab initio calculation at various atomic positions
        - Problem: Too many data: Parametrization
    - Modeling the atom-atom glue
        - Hard Sphere, Lennard Jones
        - Point charge / dipole model, (Polarizable charge/dipole)
        - Embedded atom model
        - Reactive force field
        - Electronegativity equalization method

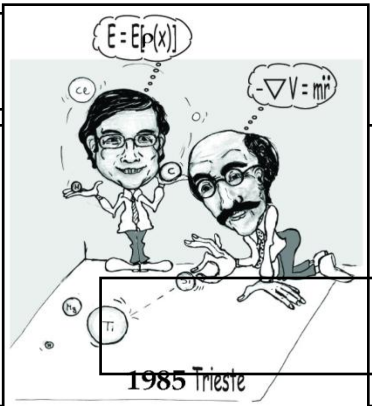
To next length scale …………

COMBINED APPROACH

Electronic & atomistic length scales

- Interatomic potential in situ
- Car Parrinello approach
- Others ???

To next length scale……



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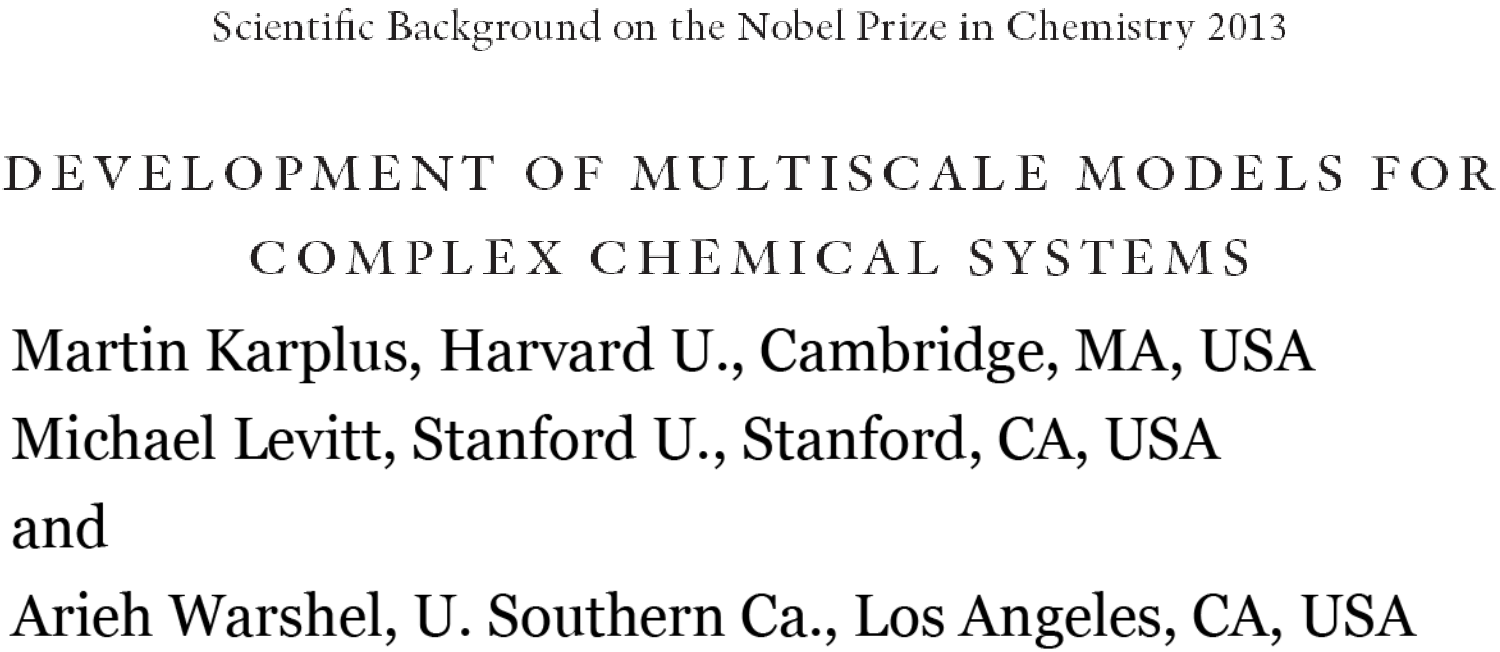

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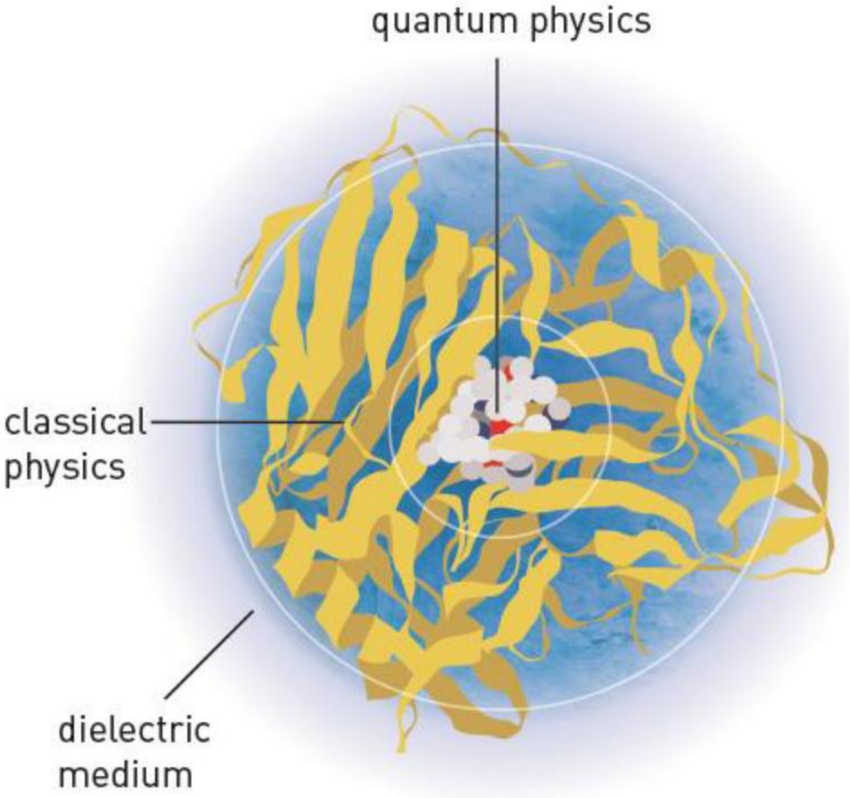
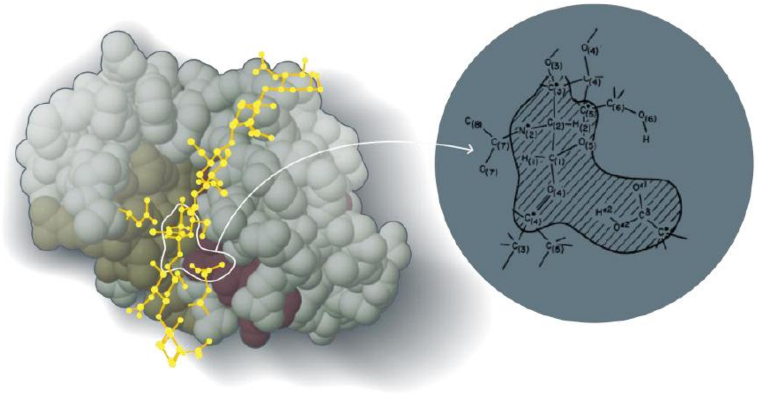
Quantum Mechanics / Molecular Mechanics (QM/MM)

Bridging the electronic and atomistic length scales





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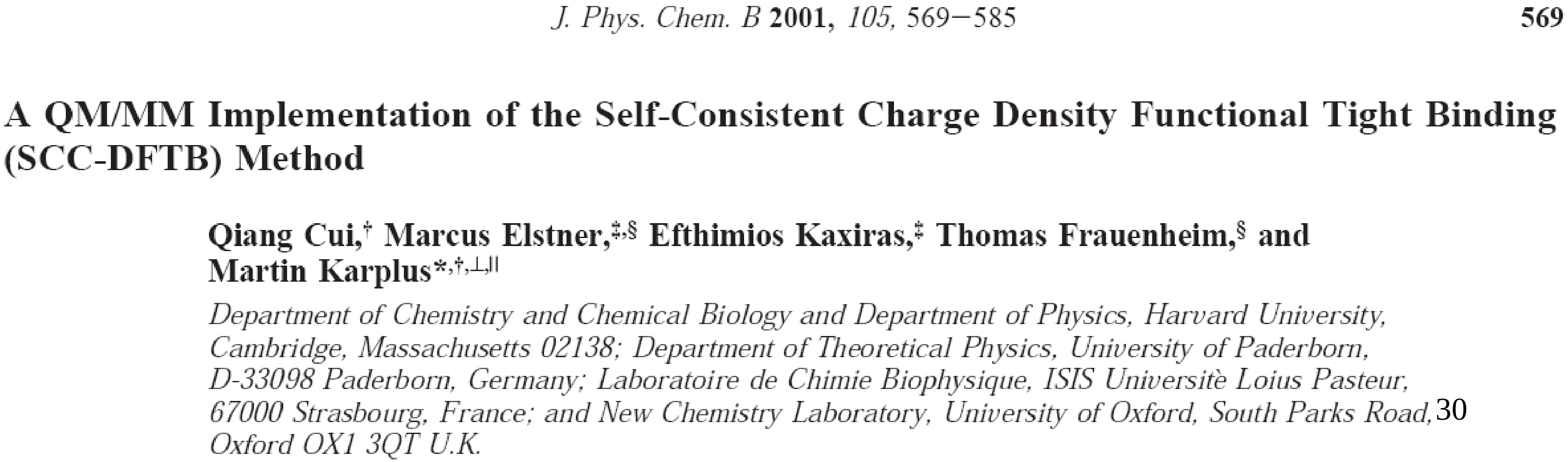

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Conventional approaches

Microscopic

ATOMS, MOLECULES, CLUSTERS, SOLIDS

- Quantum mechanical approach

LIQUIDS & SOLIDS

Mesoscopic

- Statistical Mechanical approach
- Computer Simulation
  - Atomistic Description:
    - Classical (interaction assumed)
    - Ab-initio (on the fly quantum calculation)

Macroscopic

- Continuum Approach:
  - Hydrodynamics
  - Continuum mechanics

Form of MAT TER that MAT TERS

- *Traditional Bulk Solids : 3-D*
  - New class of materials of nanometer dimensions
    - ⇒ Nanomaterials: *"Small is beautiful"*
      - Confinement: 2-D : Interfaces: Thin Films
        1-D : Quantum Wires
        0-D : Quantum Dots
  - Cluster-assembled materials: Quantum Dot Solids
    - Clusters (artificial atoms) as building blocks

- *Traditional Bulk Liquids : 3-D*
    - Confinement: Liquids at interfaces: 2-D
  - Soft Matter: Liquids, polymers, colloids, biological fluids
  - Granular Matter: Sands etc: Liquid like flow patterns
- *Molecules: Chemistry & biology*

Molecules & Materials through Theorist’s Window:
Atoms (Nuclei) bonded together by Electron Glue

Form of MAT TER that MAT TERS

Hard Matter

Nanoscale Materials

Soft matter

Nanoscale Materials: Surface area larger:
Surfaces play important role

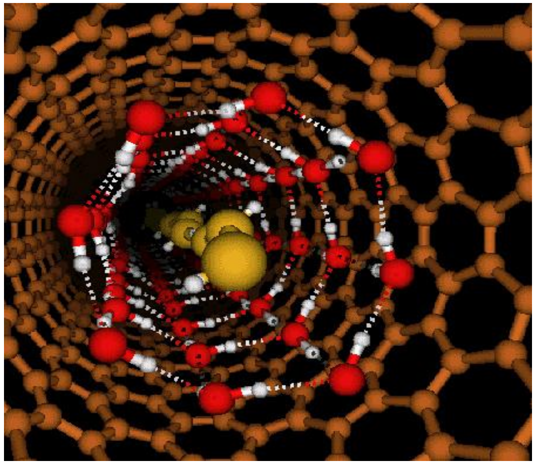
Shape of the Surface: Planar, spherical, Cylindrical
Curvature plays an important Role

Size of the Nanoscale Materials: also determines the curvature
Effect of Confinement

Surfaces & Interfaces:
Curvature & Confinement Effects

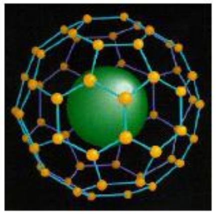
Nanoscale Materials: Bottom up approach:
Nucleation, Growth, self-Assembly

Confinement Effect



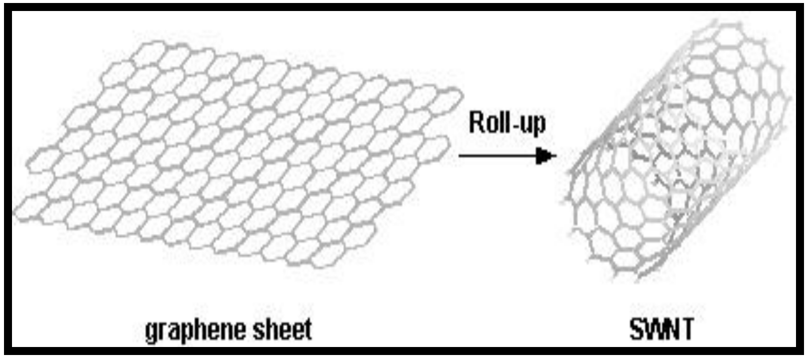
Water molecules confined in a Carbon Nanotube

No Confinement please



I am confined in C_{60}. Take me out please

Curvature Effect

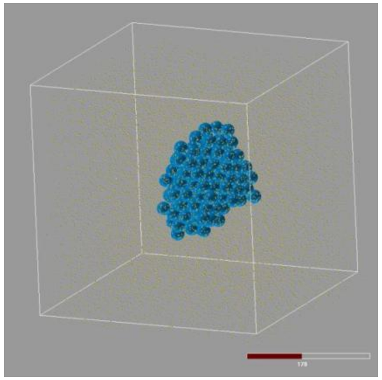


I like plain talk:
No twist &
Curvature please

Creation of Novel Materials:
Nucleation & Self Assembly

Nucleation

Self Assembly
Formation



Molecular Group
Organization

Directed
Self assembly

What governs the structure & dynamics

- Field driven (Directed)
- Fluctuation driven) (spontaneous)

Role of Correlation Effects

- Short Range Correlation
- Long Range Correlation

Theoretical & Computational Chemistry:
A broad view of the research problems

- Development of new Theoretical & Computational Tools
- Systems: Molecules, Clusters, Nanomaterials, Bulk Solids, Bulk Liquids, Soft Condensed Matter (Polymers, Colloids, Bio-fluids) at Interfaces, Organised Assemblies, Molecular Devices
- Investigations: Structure & Dynamics
- Phenomena: Solvation, Electron & Proton Transfer, Diffusion, Polymer Folding & Network, Gel
- Multiscale Materials Modeling
- Energy related Research
- Diffusion in solids, High temperature properties of nuclear fuels, Diffusion in glassy systems
- Biomolecules

It is not enough to measure and get a result; understanding the result is important and for this one requires a suitable theoretical framework

Quantum Systems: Microscopic length scale

- Electronic structure theory
- Hartree Fock theory
- Density Functional theory
- MC-SCF
- Coupled cluster theory

Solution of Schroedinger equation

Classical Systems: Mesoscopic length scale

- Statistical Mechanical approach
- Density Functional theory
- Computer simulation

Solution of Newton’s equations

Ab initio calculations

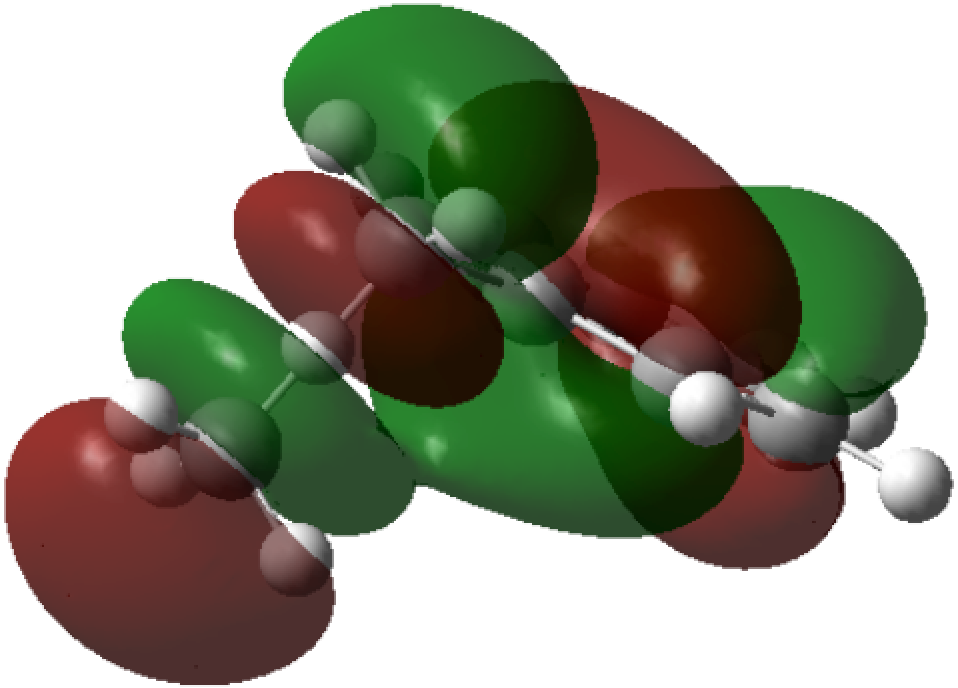
- **The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that that the exact application of these laws lead to equations much too complicated to be solvable.**

– P.A.M. Dirac (1930)

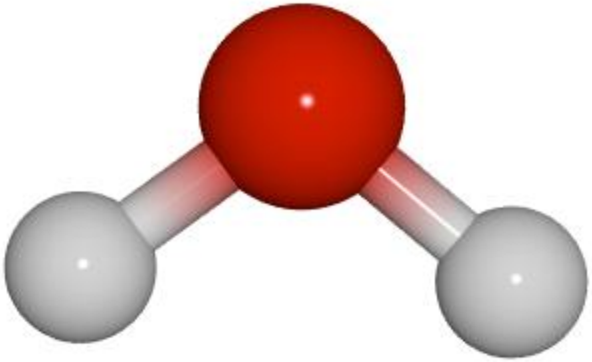
- **The challenge in computational chemistry is to simplify the calculation enough to be solvable, but still accurate enough to predict the desired physical quantity.**

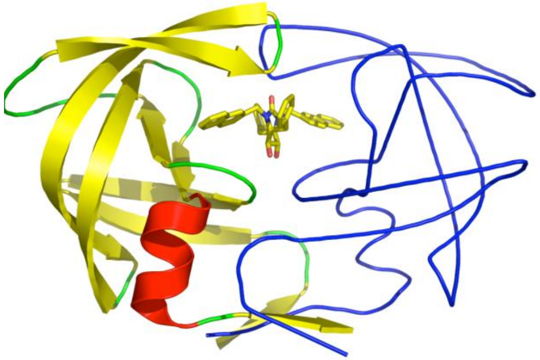
After we have an electronic wavefunction

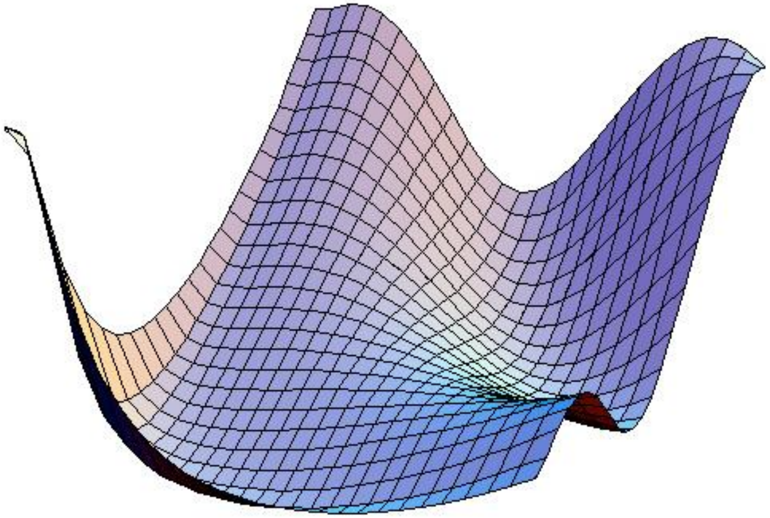
- After we have solved for a wavefunction for our system, we can extract and display many properties.
- To the right is a plot of a molecular orbital. These can be used to better understand the nature of chemical bonding in various systems.



Input: Z, N, R
Geometry optimization: • After optimizing a geometry, we can predict experimental structures.

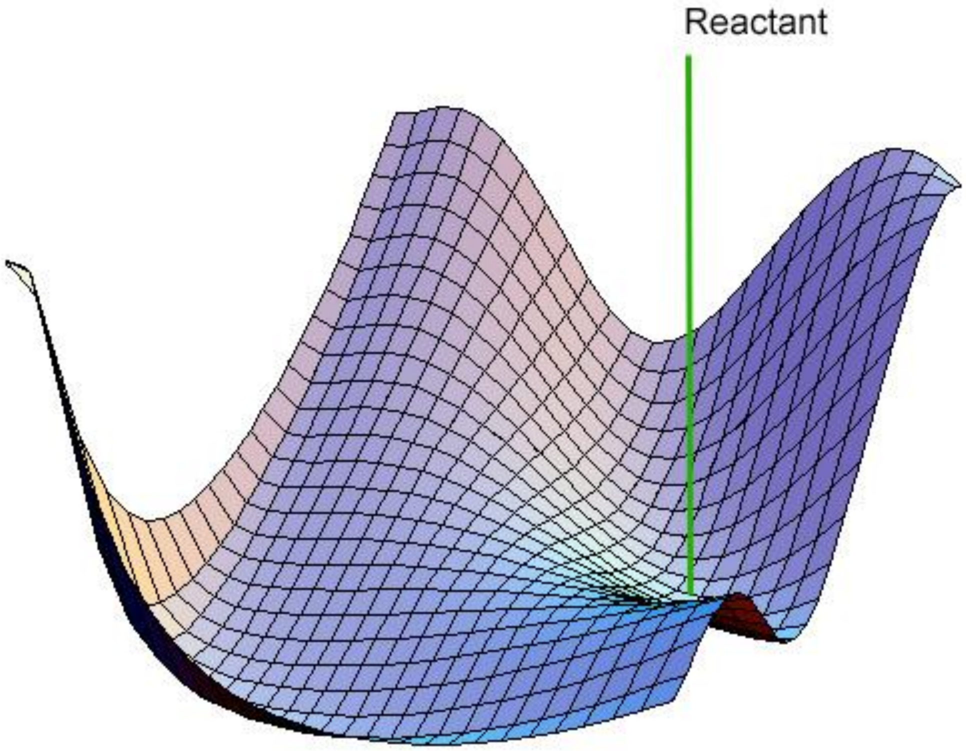


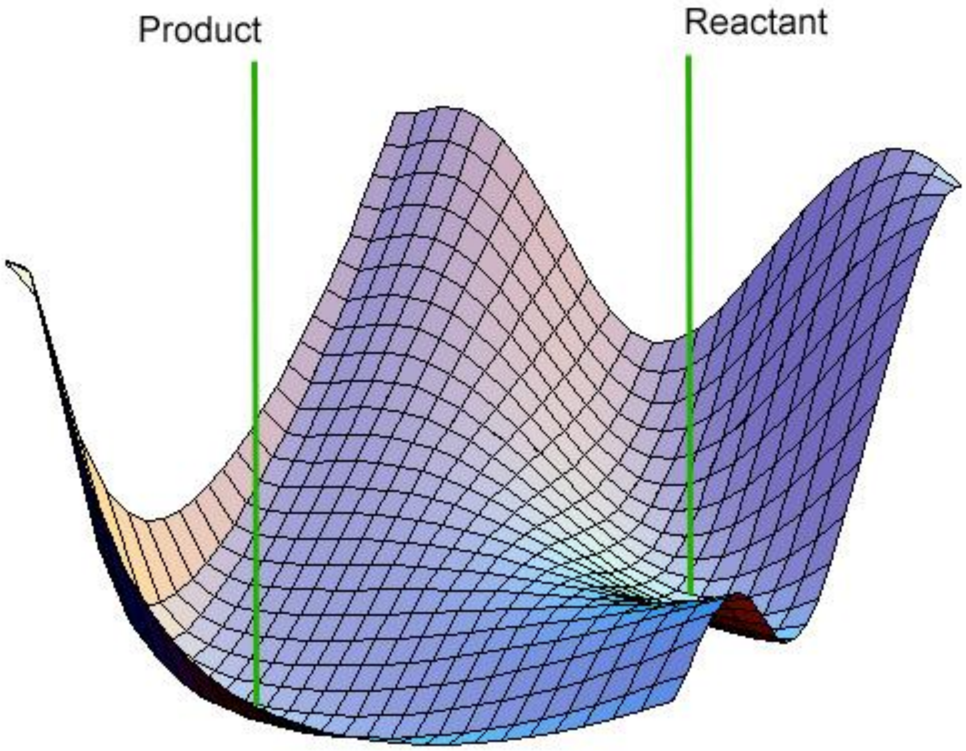


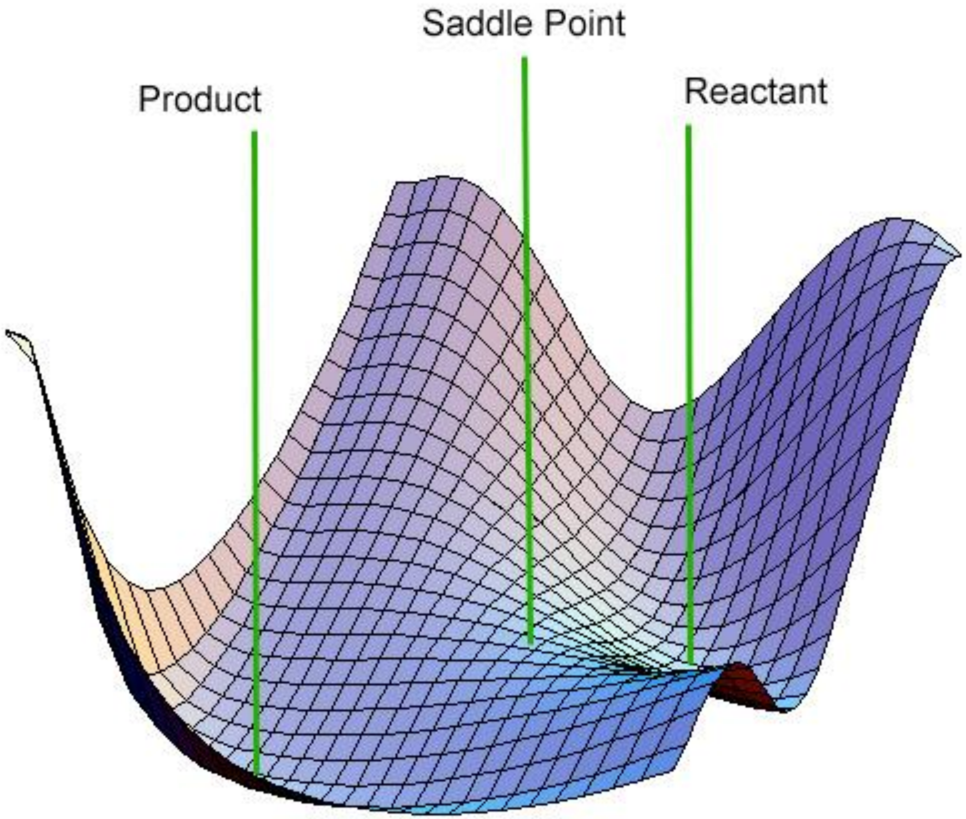


This is a picture of the potential energy as function of two coordinates

The potential surface is a Born-Oppenheimer potentials surface, where the potential energy
is a function of geometry.
Motion of the nuclei is assumed to be
independent of the motion of the electrons

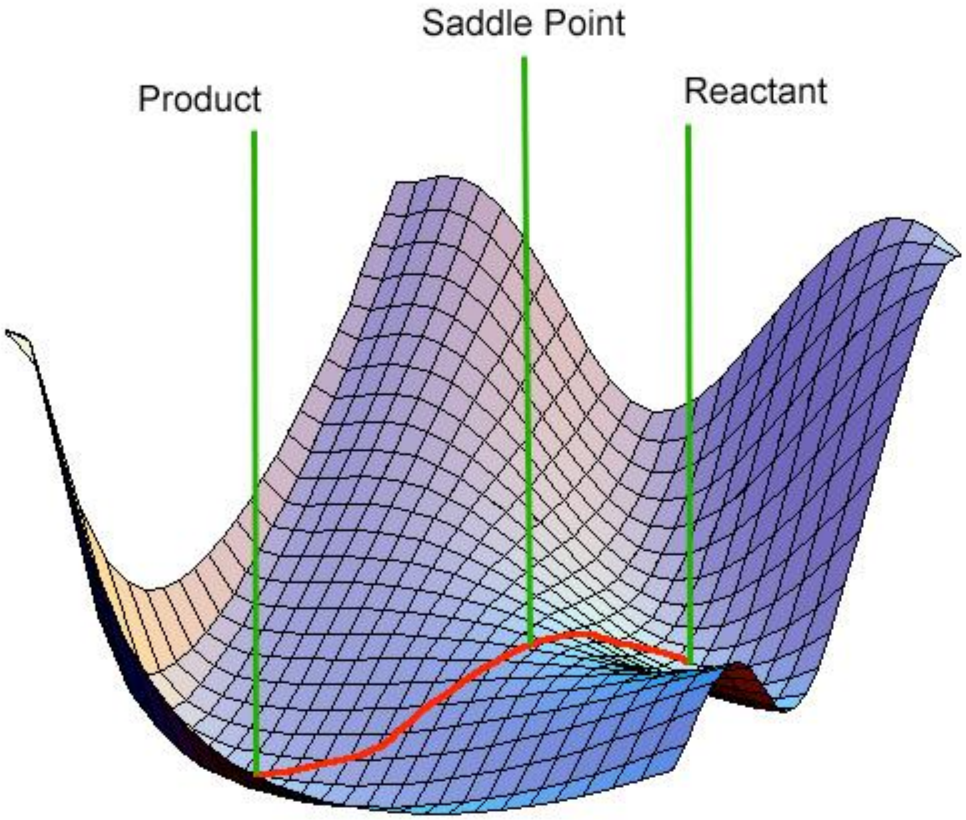

Reactant


Product
Reactant



These are all Stationary points

Transition state theory can be used to calculate reaction rates



- What is needed is to solve the Schrodinger equation to obtain the electronic energy levels and orbitals
- Solution possible for only simple problems
- Numerical solution needed in most cases
- Hartree-Fock Theory
- Density Functional Theory
- Coupled Cluster Theory
- MCSCF theory

Direct Numerical Solution using Modern Computer and Software

$$H\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)=E\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)$$

$$E=<\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)|H|\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)>$$

- Solve the differential equation
- Use variational method

Many-electron (N) wave function

$\psi(r_1, r_2, \ldots\ldots, r_N)$: 3N-variables

Theoretical/Computational Chemistry

- Mathematical description of Chemical systems
- Use of Computers to Help Solving Chemical Problems
- Quantitative estimates of important parameters such as molecular geometry, heats of formation, heats of reaction, entropies, heat capacities, reaction rate constants, transport properties like viscosity and thermal conductivity
- Valuable insight into the properties of new materials and the efficient design of new products at the macro level.

The Language of Computational Quantum Chemistry

***ab initio* Molecular Orbital Theory** - describes the electronic structure (e.g., electrons, nuclei) of molecules using rigorous quantum mechanical principles. A solution of the Schroedinger equation for electronic motion in the fixed nuclei approximation using orbitals.

Basis sets - a complete set of known functions which represent the atomic orbitals.

Car-Parrinello - an approach to finding the energy and structure simultaneously by performing molecular dynamics simulations while optimizing the energy. Usually used in a density functional theory approach.

Density Functional Theory (DFT) - a theoretical model by which the energy of an N-electron system can be described as a functional of the density.

Electron Correlation - defines the treatment of electron-electron interactions. These interactions are missing in the simpler Hartree-Fock approximation.

Hartree-Fock - a theoretical model which solves the Schroedinger equation, self-consistently, using an antisymmetrized, linear combination of atomic orbitals and a single arrangement of electrons within those orbitals.

Heavy Atom - any atom other than hydrogen. The number of non-hydrogen atoms is used loosely to characterize the difficulty of a quantum calculation.

Perturbation Theory - a size-consistent, systematic procedure for finding the correlation energy neglected by Hartree-Fock methods based on a perturbation expansion of the energy. Other approaches to finding the correlation energy include coupled cluster methods and configuration interaction.

Scaling - describes the rate of increase in computational cost with problem size proportional to N^m where N is the number of basis functions and m is an exponent which is method-dependent.

Atomistic/Molecular Scale Terminology

Molecular Dynamics Methods - atomistic molecular simulation methods in which Newton's classical equations of motion are solved numerically for a system of atoms or molecules

Monte Carlo Methods atomistic molecular simulation methods in which the equilibrium configurations of systems of atoms or molecules are sampled statistically

Non-equilibrium Molecular Dynamics - molecular dynamics method in which systems that are not at equilibrium are simulated

Gibbs Ensemble Method- Method in which the conditions of phase equilibrium are directly simulated

Gibbs-Duhem Method - method of determining phase equilibrium by integrating the Gibbs-Duhem equation

Intermolecular Potentials - force fields existing between atoms, molecules, or sites within molecules.

Car-Parrinello Methods - molecular dynamics methods in which the intermolecular potential is approximately calculated quantum mechanically at each time step.

Current Applications of Computational Chemistry

- Atmospheric Chemistry
- Drug Design
- Catalyst/Biocatalyst Design
- Materials Design
- Physical Properties for Process Simulation
- Polymer Structures/Properties
- Adhesives/Coatings Design
- Lubricant Properties/Chemistry
- Surfactant Chemistry

Bridging Techniques and Terms

Seamless Data Interfaces - permit interactions between calculations performed at different size scales (e.g., between quantum and atomistic scales).

Coarse-Graining Techniques - theory-based techniques which allow knowledge gained from calculations or experiments at a small scale to be usefully applied at a larger scale.

Quantum Mechanics and Chemistry

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

Paul Dirac (1930)

“...in the Schrodinger equation we very nearly have the mathematical foundation for the solution of the whole problem of atomic and molecular structure”

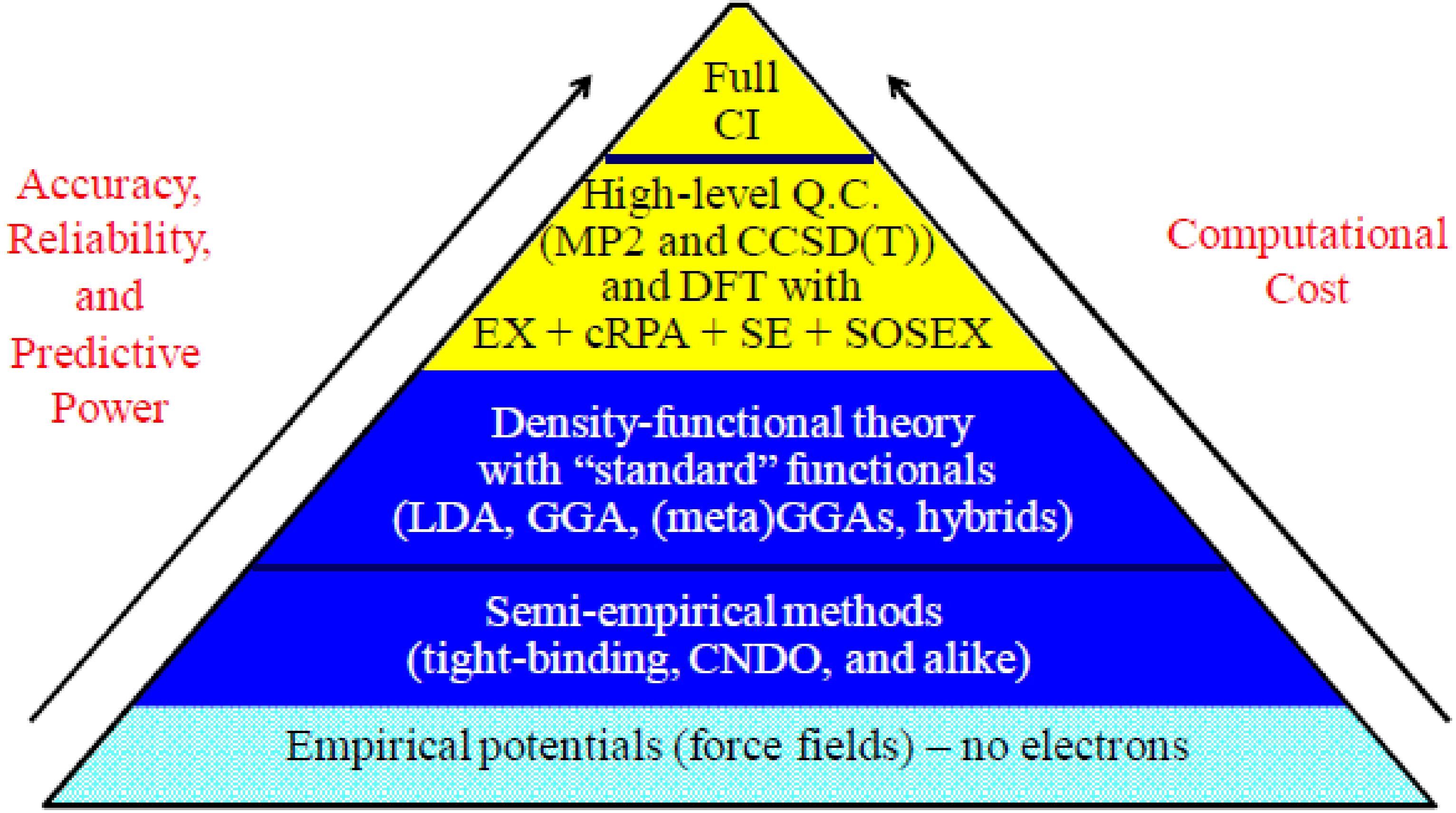
but…

“… the problem of the many bodies contained in the atom and the molecule cannot be completely solved without a great further development in mathematical technique.”

G. N. Lewis, J. Chem. Phys. 1, 17 (1933).

State-of-The-Art of (Electronic) Structure Theory

$$H\,\Psi = E\,\Psi$$



Full CI

High-level Q.C.
(MP2 and CCSD(T))
and DFT with
EX + cRPA + SE + SOSEX

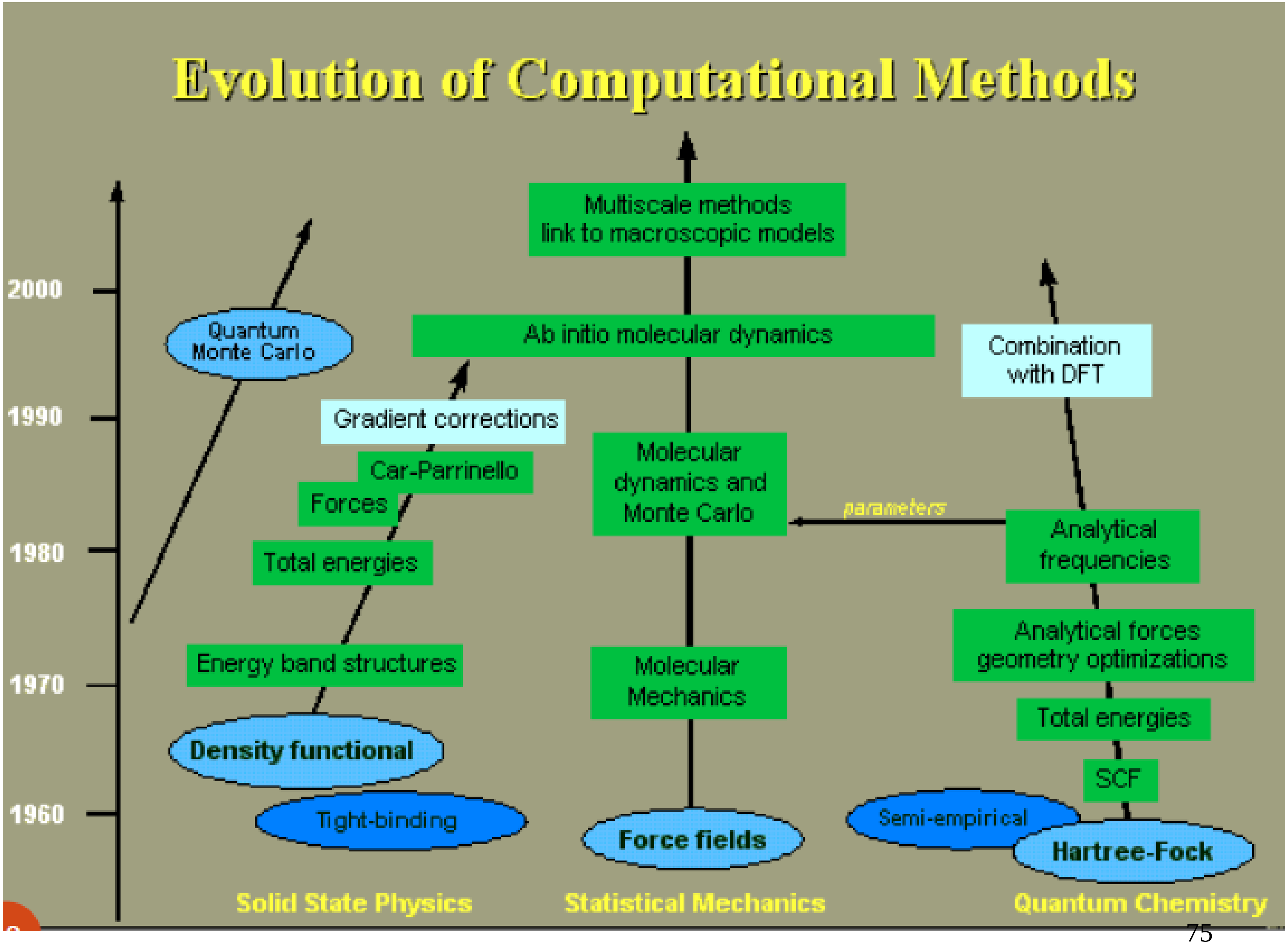
Density-functional theory
with “standard” functionals
(LDA, GGA, (meta)GGAs, hybrids)

Semi-empirical methods
(tight-binding, CNDO, and alike)

Empirical potentials (force fields) – no electrons

Accuracy,
Reliability,
and
Predictive
Power

Computational
Cost



Evolution of Computational Methods

2000

1990

1980

1970

1960

Solid State Physics

Quantum Monte Carlo

Gradient corrections

Car-Parrinello

Forces

Total energies

Energy band structures

Density functional

Tight-binding

Statistical Mechanics

Multiscale methods link to macroscopic models

Ab initio molecular dynamics

Molecular dynamics and Monte Carlo

Molecular Mechanics

Force fields

Quantum Chemistry

Combination with DFT

parameters

Analytical frequencies

Analytical forces geometry optimizations

Total energies

SCF

Semi-empirical

Hartree-Fock

Direct Numerical Solution using Modern Computer and Software

$$H\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)=E\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)$$

$$E=<\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)|H|\psi(\mathbf{r}_1,\mathbf{r}_2.....\mathbf{r}_N)>$$

- Solve the differential equation
- Use variational method

Many-electron (N) wave function

$\psi(r_1, r_2, \ldots\ldots, r_N)$: 3N-variables

- For an atom of N electrons, the solution is a function of 3N variables, and even if it were possible to evaluate such a solution to any degree of numerical accuracy required, no satisfactory way of representing the results, either in tabular or graphical form, is known.
- It has been said that the tabulation of one variable requires a page, of two variables a volume, and of three variables a library; but the full specification of a single wave function of neutral Fe is a function of seventy eight variables.
- It would be rather crude to restrict to ten the number of values of each variable at which to tabulate this function, but even so full tabulation of it would require 10^{78} entries, and even if this number could be reduced somewhat from considerations of symmetry, there would still not be enough atoms in the whole solar systems to provide the material for printing such a table.

- D R Hartree

Towards a Simple Approach: Reduced Space

Single-particle density

$$\rho(\mathbf{r}) = N\int d\mathbf{r}_2 \int d\mathbf{r}_3 .... \int d\mathbf{r}_N \ \boxed{\psi^*(\mathbf{r}_1,\mathbf{r}_2......\mathbf{r}_N)\psi(\mathbf{r}_1,\mathbf{r}_2......\mathbf{r}_N)}$$

Two-particle density

$$\rho_2(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)\int d\mathbf{r}_3 \int d\mathbf{r}_4 .... \int d\mathbf{r}_N \psi^*(\mathbf{r}_1,\mathbf{r}_2......\mathbf{r}_N)\psi(\mathbf{r}_1,\mathbf{r}_2......\mathbf{r}_N)$$

Single-particle (reduced) density matrix

$$\gamma(\mathbf{r};\mathbf{r}') = N\int d\mathbf{r}_2 \int d\mathbf{r}_3 .... \int d\mathbf{r}_N \boxed{\psi^*(\mathbf{r},\mathbf{r}_2......\mathbf{r}_N)\psi(\mathbf{r}',\mathbf{r}_2......\mathbf{r}_N)}$$

$$E = E_{kin} + V_{ne} + V_{ee}$$

$$= < \psi \left| -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^{\;2} \right| \psi > + < \psi \left| \sum_{i=1}^{N} \sum_{\alpha=1}^{n} \frac{Z_\alpha}{\left| \mathbf{r}_i - \mathbf{R}_\alpha \right|} \right| \psi > + < \psi \left| \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} \right| \psi >$$

$$= -\frac{1}{2} \int d\mathbf{r} \; \left| \nabla^2 \gamma(\mathbf{r};\mathbf{r}') \right|_{r=r'} + \int d\mathbf{r} \; v(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 . u(\mathbf{r}_1, \mathbf{r}_2) \rho_2(\mathbf{r}_1, \mathbf{r}_2)$$

The total energy is thus written in terms of the first order reduced density matrix γ(r;r'), single particle density ρ(r) and the two particle density $\rho_2(r_1,r_2)$.

Can the energy be minimized variationally using the quantities ρ(r), γ(r;r'), and $\rho_2(r_1,r_2)$?

Interrelations: ρ(r) = γ(r;r), $\rho(r_1)=(N-1)\int d\mathbf{r}\ \rho_2(r_1,r_2)$.

- Problems: N-representability:
- Conditions for derivability from an antisymmetric wave function are unknown for γ(r;r'), and $\rho_2(r_1,r_2)$, but they are known for ρ(r).

$$E = E_{kin} + V_{ne} + V_{ee}$$

$$= <\psi\left|-\frac{1}{2}\sum_{i=1}^{N}\ \nabla_i{}^2\right|\psi> + <\psi\left|\sum_{i=1}^{N}\ \sum_{\alpha=1}^{n}\frac{Z_\alpha}{\left|\mathbf{r}_i - \mathbf{R}_\alpha\right|}\right|\psi> + <\psi\left|\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}\right|\psi>$$

$$= -\frac{1}{2}\int d\mathbf{r}\ \left|\nabla^2\gamma(\mathbf{r};\mathbf{r}')\right|_{r=r'} + \int d\mathbf{r}\ v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2 . u(\mathbf{r}_1,\mathbf{r}_2)\rho_2(\mathbf{r}_1,\mathbf{r}_2)$$

The total energy is thus written in terms of the first order reduced density matrix γ(r;r'), single particle density ρ(r) and the two particle density $\rho_2(r_1,r_2)$.
Can the energy be expressed in terms of the density ρ(r) alone ?
Proof by Hohenberg and Kohn: Theorem (1964)

Advantages of using single particle density variable ρ(r) :

- Function in 3-D space
- Simpler to tabulate or plot
- Conceptual simplicity & Computational economy
- Experimental observable-direct comparison possible

N-representibility
v-representibility

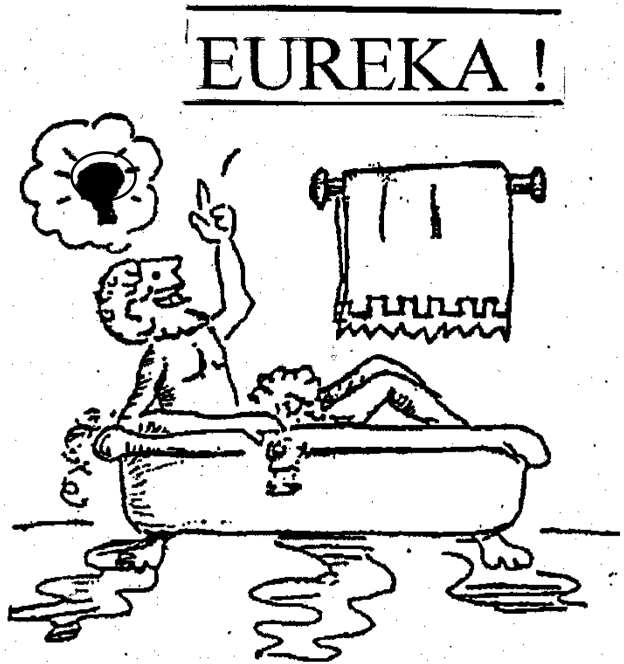
Distribution of Particles in Space and Time:

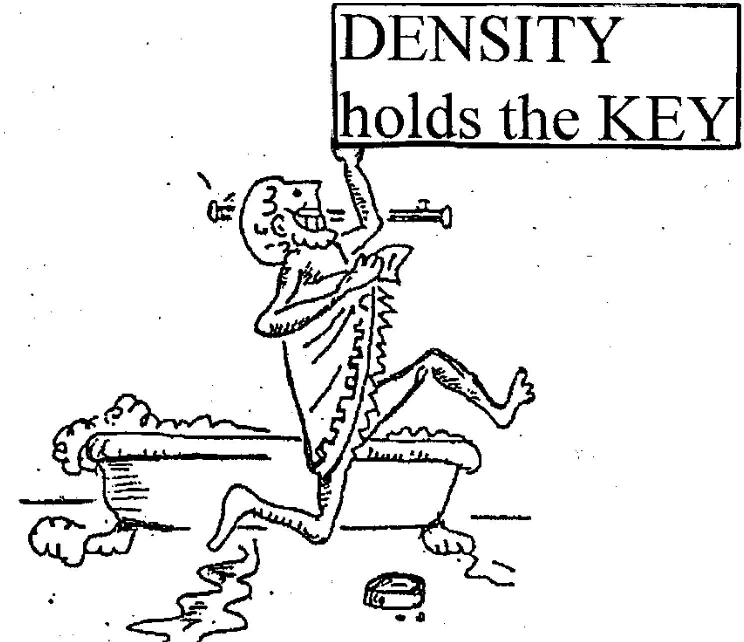
The Concept of Density

Covers all length scales

Provides a unified nature of Methodology

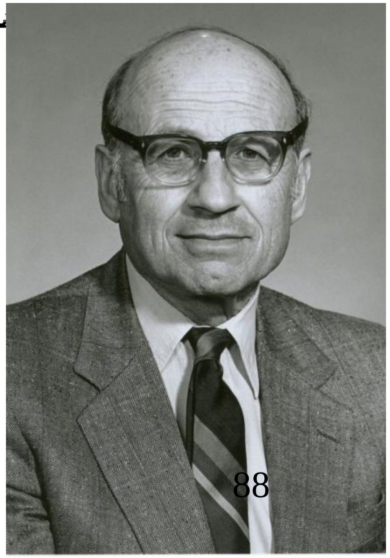
ARCHIMEDES
GREECE (287 BC – 212 BC)

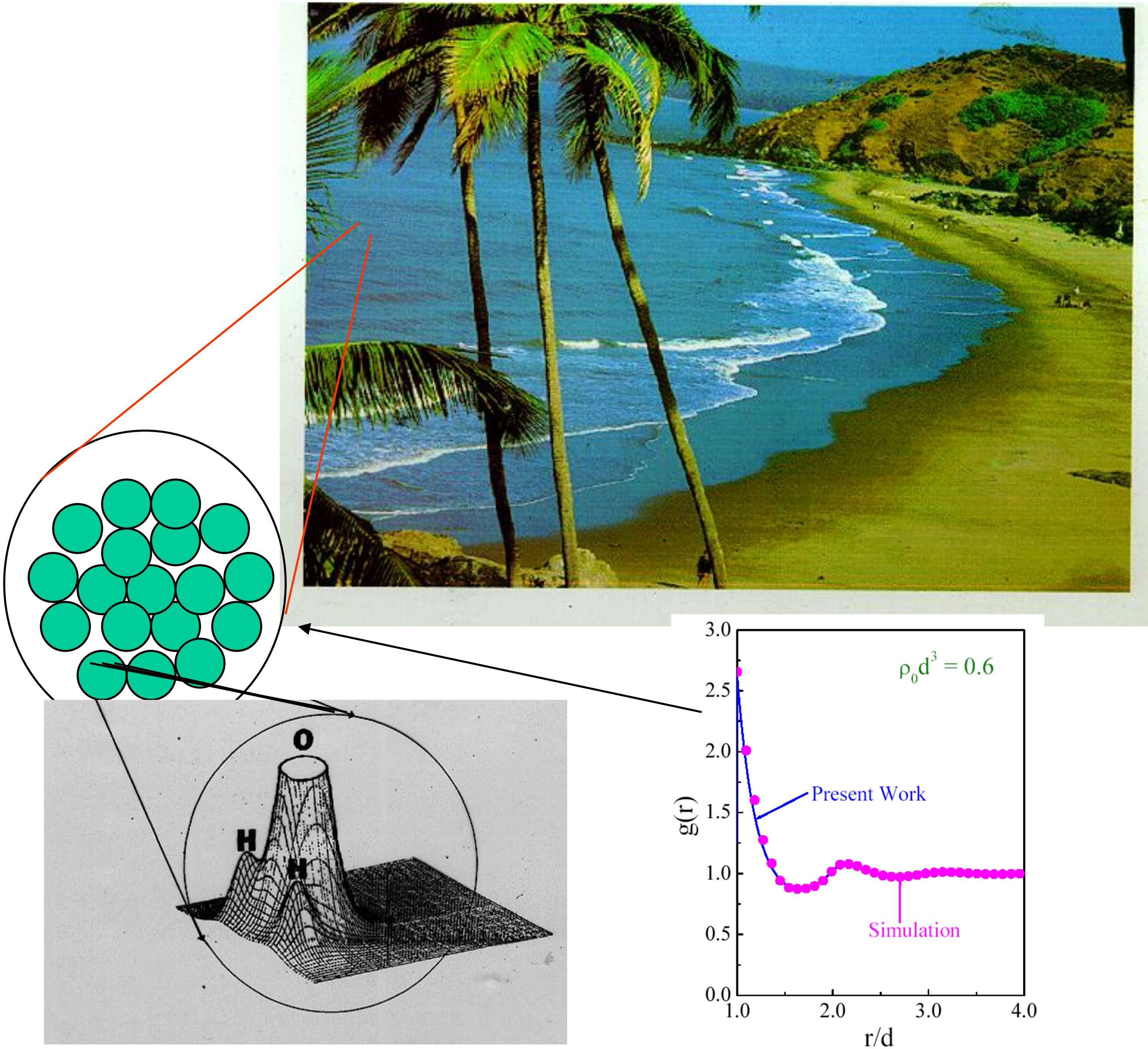




2000 YEARS LATER

WALTER KOHN (USA, 1964)
DENSITY DETERMINES EVERYTHING
Nobel Prize (1998)




O
H
H
3.0
2.5
2.0
1.5
1.0
0.5
0.0
g(r)
$\rho_0 d^3 = 0.6$
Present Work
Simulation
1.0
2.0
3.0
4.0
r/d

Length scale	*Unit*	*Basic variable*
Short	electron	electron density
Intermediate	atom	atom number density
Large	volume element	property density

:Problem:

How to calculate the density distribution for particles subjected to an external field/potential

Density: $\rho(r_1) = N \int..\int dr_2 ..dr_N \, P(r_1, r_2, ..., r_N)$

DENSITY FUNCTIONAL THEORY (DFT)

A wide variety of systems can be studied through quantum DFT or classical DFT or both.

Modern DFT: Practical Implementation

Quantum DFT

One-particle Schrodinger eqn.

$\{-(1/2)\nabla^2 + v(r)\}\,\psi_i = \varepsilon_i\psi_i$

Non-interacting particles

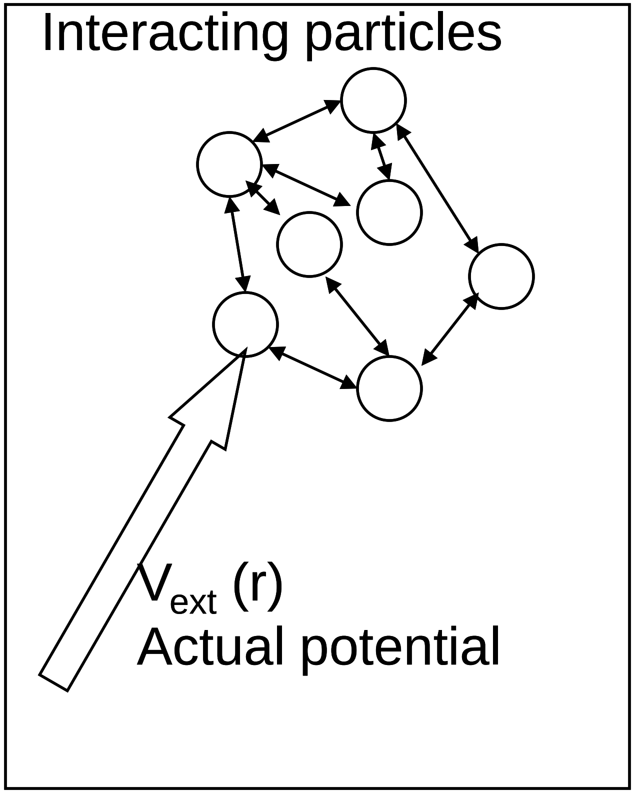
Classical DFT

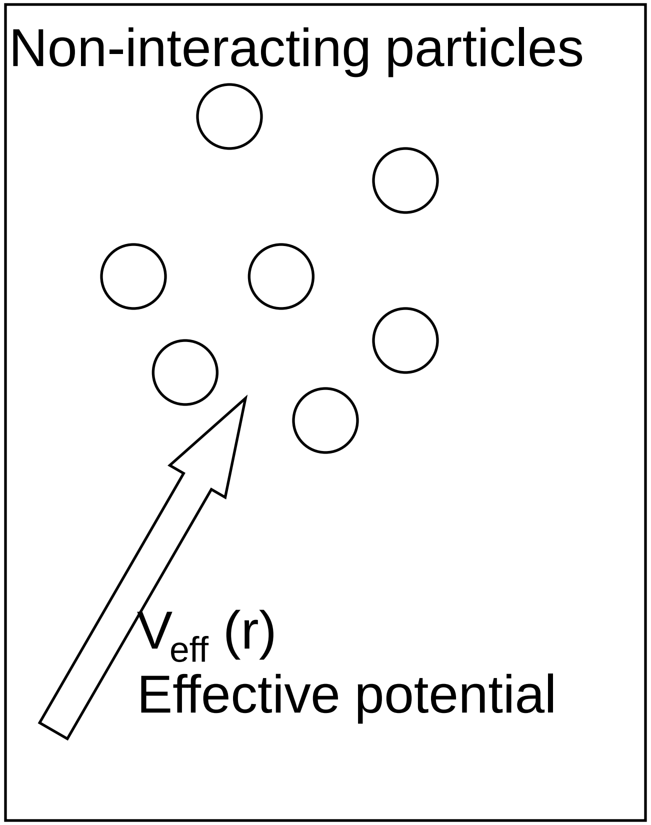
Boltzmann distribution

$\rho_\alpha(r)=\rho_\alpha^0\exp(-v_\alpha(r)/kT)$

Real interacting system

Concept of noninteracting particles moving in an effective potential





Modern DFT: Practical Implementation

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Boltzmann distribution

$\rho_\alpha(r)=\rho_\alpha^0\exp(-v_\alpha(r)/kT)$

Real interacting system

Concept of noninteracting particles moving in an effective potential

Kohn-Sham equation: Effective one-particle Schrodinger eqn.

$\{-(1/2)\nabla^2 + v_{eff}(r)\}\ \psi_i = \varepsilon_i\psi_i$

$\rho(r)=\Sigma\, n_i|\psi_i|^2$

Energy $E = \int dr\, v(r)\rho(r) + T_s[\rho(r)] + E_{COUL}[\rho] + E_{xc}[\rho]$

$v_{eff}(r;\rho)= v(r) + (\delta E_{COUL}[\rho]/\delta\rho) + (\delta E_{xc}[\rho]/\delta\rho)$

Kinetic energy functional (exact)

Exchange correlation energy functional (need approximation)

Density equation: Effective Boltzmann like distribution

$\rho_\alpha(r)=\rho_\alpha^0\exp(-v_{eff,\alpha}(r)/kT)$

Free Energy $F = \int dr\, v(r)\rho(r) + F_{id}[\rho(r)] + F_{ex}[\rho(r)]$

$v_{eff}(r;\rho)= v(r) + kT\, C^{(1)}(r;\rho)$

where $kT\, C^{(1)}(r;\rho) = (\delta F_{ex}[\rho]/\delta\rho)$

Ideal gas free energy functional: Classical entropy terms (exact)

Excess free energy functional (need approximation)

QUANTUM MECHANICS of MOLECULES, CLUSTERS, SOLIDS
An Electron Density Description

$\{-(1/2)\nabla^2 + v_{eff}(r)\}\ \psi_i = \varepsilon_i \psi_I\ ;\ \rho(r) = \Sigma\, n_i |\psi_i|^2$

$v_{eff}(r;\rho) = v(r) + (\delta E_{COUL}[\rho]/\delta\rho) + (\delta E_{xc}[\rho]/\delta\rho)$

Interparticle correlations

Statistical mechanics of LIQUIDS:
A Mesoscopic Density Description

$\rho_\alpha(r) = \rho_\alpha^0 \exp(-v_{eff,\alpha}(r)/kT)$

$v_{eff}(r;\rho) = v(r) + kT\, C^{(1)}(r;\rho);\ \ kTC^{(1)}(r;\rho) = (\delta F_{ex}[\rho]/\delta\rho)$

Interparticle correlations

Functions & Functionals

Function: $y = f(x)$: Mapping of one number to another

Functional: $G[f(r)] = \int dr\, g(f(r))$: Mapping of one function to a number: Many to one

Functional derivative:

For the functional $F[\rho(r)] = \int dr\, f(\rho(r))$, if one can write $\delta F[\rho(r)] = \int dr\, \delta\rho(r)\, h(\rho(r))$, then the functional derivative is given by $\delta F[\rho(r)]/ \delta\rho(r) = h(\rho(r))$

For simple cases, $h = (df/d\rho)$

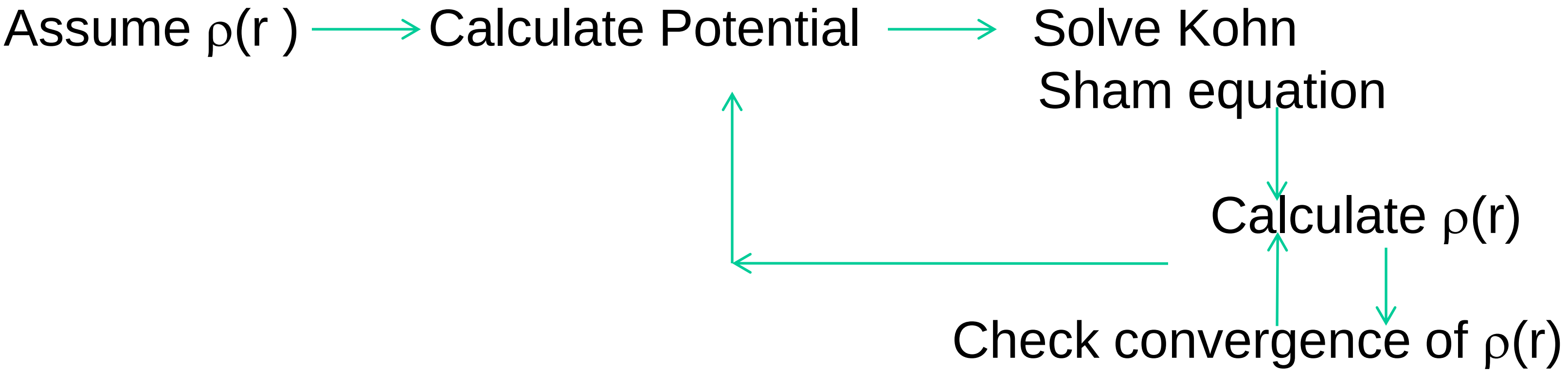
Practical Density Functional Theory

Kohn-Sham Density Functional Theory

$$\left[-\tfrac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + V_{coul}(\mathbf{r}) + \frac{\delta E_{xc}[\rho]}{\delta\rho(r)}\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$

with density calculated as $\rho(\mathbf{r}) = \sum_{i=1}^{N}\psi_i^{*}(r)\psi_i(r)$

Iterative Solution



Assume ρ(r) → Calculate Potential → Solve Kohn Sham equation

Calculate ρ(r)

Check convergence of ρ(r)

Comparison of DFT with HF and Other Methods

KS DFT

$$\left[-\tfrac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + V_{coul}(\mathbf{r}) + \frac{\delta E_{xc}[\rho]}{\delta\rho(r)}\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$

$$V_{coul} = \int d\mathbf{r}_2\,\rho(\mathbf{r}_2)/r_{12}$$

$$E[\rho] = \sum_i \varepsilon_i - E_{coul} + E_{xc} - \int d\mathbf{r}\,\rho(\mathbf{r})\frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$$

with density calculated as $\rho(\mathbf{r}) = \sum_{i=1}^{N}\psi_i^*(r)\psi_i(r)$

Hartree-Fock: Correlation not included

$$\left[-\tfrac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + V_{coul} + V_X\left[\{\psi_k\}\right]\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$

with nonlocal exchange potential

Hartree-Fock-Slater: Correlation not included

$$\left[-\tfrac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + V_{coul} + V_X\left[\rho\right]\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$

with local exchange potential

Xα method: α~0.6-0.8

Practical Calculations

- Choice of a software for Electronic Structure Calculation
  - GAUSSIAN, GAMESS, Band Structure codes
- Choice of Exchange-Correlation
  - B3LYP, GGA etc
- Choice of a System
  - Molecule and Materials of interest
- What does it give
  - Molecular Geometries & Crystal structure of solids
  - Energies, Orbitals, Properties, Band structure, etc
  - Hessians, Force constants, Vibrational frequencies (Vibrational Spectra, phonons)
- Choice of a software for TDDFT Calculation
  - GAUSSIAN, GAMESS, OCTOPUS, etc
- What does it give
  - Transition probabilities (Electronic Spectra)
  - Excited states

- Computer Simulation
- Monte Carlo
- Molecular Dynamics
- ab-initio Molecular Dynamics