Experiment and Modelling in Structural NMR

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INSTN – CEA Saclay, France

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Introduction to
Materials Studio

[04001]

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Introduction to Materials Studio

Materials Studio

The screenshot shows the Materials Studio interface with several key components highlighted by blue arrows and text labels:

- Files & Folders:** Points to the Project tree on the left, showing a hierarchy of files like '3D Atomistic Document VAMP GeomOpt' and 'Indigo_1 VAMP GeomOpt'.
- Properties:** Points to the Properties panel at the bottom left, which displays a table of properties for the selected bond.
- Tools:** Points to the top toolbar containing various simulation and visualization tools.
- Figures & Tables:** Points to the central workspace, which displays a 'Vamp Optimization Convergence' plot and a 3D ball-and-stick molecular model.
- Jobs running:** Points to the bottom status bar, which shows the progress of the 'VAMP' job.

Property	Value
BondOrder	
BondType	
ChemicalType	
IsVisible	Yes
Length	
MidPoint	
Name	
SpecialPositionO	1
Style	Bell and Stick
SymmetryCentr...	xyz
SymmetryCentr...	Identity
SymmetryDerivat...	xyz
SymmetryDerivat...	Identity
...	...

Different Builders

Build Polymers

Homopolymer

Polymerize | Advanced | Branches

Library:

Repeat unit:

Tacticity: Chiral inversion:

Chain length: Number of chains:

Build a Homopolymer

Build Block Copolymer

Block Copolymer

Polymerize | Advanced | Branches

Block definition

Repeat Unit	Block Size	Invert	Flip
ethylene	5	0.0	0.0
isobutene	5	0.0	0.0

Number of superunits: Number of chains:

Build Random Copolymer

Dendrimer

Build Crystals

Tools for building nanostructures with the Materials Visualizer

Nanocluster Builders

- Wide range of shapes
- Element substitution function (linear, quadratic or exponential) along symmetry directions.
- Vacancy function.
- Optional capping of broken bonds

Display Style

- Various styles
- Scale factor
display length (Å) = scale * vector magnitude
- Use with Vectors dialog to select specific vectors

Vibrational Analysis

Vibrational Analysis

Analysis | Options

Calculate modes:

Frequency (1/cm)	Intensity (km/mol)
-673.85	0.00
-310.59	0.00
799.62	0.00
857.25	0.00
1078.97	0.00
1170.28	0.00
1247.53	0.00
1263.78	0.00
1450.74	0.00
1460.81	0.00
1465.00	0.00

Output

Animation Grid Spectrum

From: hessian.xsd

Help

Part II: Introduction to Materials Modeling

Why modeling?

- structures, processes and properties are numerically simulated based fully or in part on fundamental laws of physics
- besides modeling stable molecules, some methods may be used to model also short-lived species (unstable intermediates and transition states)
- important in supporting or replacing experimental studies

Motivation for modeling and simulation

- More efficient use of R&D resources
Better understanding of how and why a product or a process is working
- Faster delivery of products to market
“Trial and error” experiment is time-consuming
- Solutions to critical research problems (Shelf-life, Stability, Compatibility...)
Solutions often come from adapting or controlling molecular level behaviour

What is materials simulation?

Multi-Scale modeling

Issues that simulation can address...

Modeling and simulation methods in MS

- Quantum Mechanics
- Atomistic Modeling
- Mesoscale Modeling
- Crystal Modeling
- Correlation Methods - QSAR

Quantum Mechanics

- The Schrödinger equation

$$\mathbf{H} \Psi = E \Psi$$

- Methods differ in how $\mathbf{H}$ and Ψ are described

$\mathbf{H}$... kinetic energy + potential energy + Exc

Ψ ... described with electronic wave -functions
(numerical, STO, GTO) or plane waves

Quantum Mechanics: DFT

Density Functional Theory (DFT)- All ground-state properties of a system are function of the charge density

Hohenberg - Kohn equation

$$E_{total} = T[\rho] + U[\rho] + E_{xc}[\rho]$$

Kohn - Sham equation

$$\left\{ -\frac{\hbar}{2m} \nabla^2 + V(\{\mathbf{r}_i\}) \right\} \Psi(\{\mathbf{r}_i\}) = E \Psi(\{\mathbf{r}_i\})$$

Quantum Mechanics

- Strong points
 - Chemical reactions and transition state
 - Electronic, optical and magnetic properties
- Limitations
 - Simulation time grows as N^3 where N is the number of electrons. There is a computational limit of ~ 250 atoms or a few picoseconds

DMol3, CASTEP

What can be calculated?

DMOL³ (numerical functions)

- Molecules in the gas phase/periodic systems
- Reaction Modeling, (gas phase, solution, on surfaces)
- Thermodynamics
- Optical Spectra (IR spectra)
- TD-DFT (UV-vis and optical properties)
- Molecular Dynamics (Diffusion)
- LST/QST
- Solvent effects
- workfunctions
- Dispersion correction

CASTEP (plane waves)

- Periodic systems
- Structural Properties
- Electronic and Magnetic Properties
- Diffusion
- Bulk and Elastic Properties
- LST/QST
- STM (scanning tunneling microscopy) analysis
- Workfunctions
- EELS/ELNES spectra
- Raman/Intensities
- Dispersion Correction

Extra Tool: CASTEP solid state NMR

Semiempirical methods

- They solve an approximate form of the Schrödinger equation

$$FC = SCE \rightarrow FC = CE$$

- Only valence electrons are considered
- These methods use parameters derived from experimental data to simplify the computation

VAMP

Semiempirical methods

- Strong points
 - They are relatively inexpensive and provide reasonable qualitative descriptions of molecular systems, can be used on a PC
- Limitations
 - Can only be used for elements and interactions for which it has been parameterised
 - PM6 covers 70 elements

What can be calculated?

- Fast structure Optimization
- Fast transition state localization
- Structural properties
- Optical spectra (UV-vis)
- ^{13}C Chemical shift
- Electrostatics
- Solvent effects

QM/MM

For Example: Reactive centre on a zeolite

Usual approach: selecting a cluster comprising enough framework to mimic the active site plus a bit of the bulk

Problem: there is vacuum all around and the electrostatic interactions are severely neglected

With QMERA, we can do the following:

QM region:
electronic structure
changes

MM region:
embedding of QM region
environment effects

QMERA

Molecular Mechanics (MM)

- A molecule is described as a series of charged points (atoms) linked by springs (bonds).

- A mathematical description of this system is known as a **forcefield**
- The **forcefield** is used to calculate the relative potential energy of the molecule (relative to other conformations of the same molecule).

MM - Representation of a forcefield

Potential Energy

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{crossterm}} + E_{\text{non-bond}}$$

Valence Interactions

$$E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{UB}}$$

Non-bond Interactions

$$E_{\text{non-bond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{hbond}}$$

MM - Representation of a forcefield

MM - Molecular Dynamics (MD)

- Molecular Dynamics (MD) solves the Newton's equations of motion for each atom

$$\mathbf{f}_i = m_i \mathbf{a}_i$$

$$\mathbf{f}_i = m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2}$$

Classical equations of motion are **deterministic!!!**

This allows us to study the **evolution of systems as a function of time, temperature and pressure** which are related by statistical mechanics

Molecular Mechanics

- Strong points
 - We can deal with bigger systems
 - We can simulate dynamic processes (e.g. diffusion, phase transition)
- Limitations
 - Forcefields are valid for a 'limited' type of material
 - There is no bond breaking or forming involved (i.e. no chemisorption)
 - Size of system $\sim 10^4$ atoms or a few nanoseconds (1 s possible)

Discover, GULP, Forcite plus

What can be calculated?

- Property calculations
 - Pair correlation function - **probing specific interactions**
 - Length, angle, dihedral distributions - effects on **molecular geometry**
 - Concentration profiles - **interfacial properties**
 - Orientational correlation - **liquid crystalline phases**
- Dynamic calculations
 - MSD, velocity autocorrelation, space-time correlation - **transport**
 - Dipole autocorrelation - vibrational behaviour - **spectroscopy**
 - Shear-stress time correlation - **fluid viscosity**
 - Elastic constants - **mechanical properties**
 - Multicomponent systems
 - Interaction energy - **compatibility**

Mesoscale modeling

- Smallest unit is a group of atoms called 'bead'

Longer time
and length
scales!!!!

- Laws of classical physics

DPD (Dissipative Particle dynamics):
Newton's equations of motion

$$\mathbf{f}_i = \sum_{j \neq i} \left(\mathbf{F}_{ij}^{Cons} + \mathbf{F}_{ij}^{Disip} + \mathbf{F}_{ij}^{Random} \right)$$

MesoDYN: Stochastic Diffusion equations

$$\frac{d\rho_A(\mathbf{r})}{dt} = Mv \nabla \rho_A \rho_B \nabla [\mu_A - \mu_B] + \eta$$

Mesoscale modeling

- Strong points
 - In Meso methods atoms are not specifically treated : reach much larger length and time scales
- Limitations
 - Specific interactions are harder to model, defining the average forces that best represent a specific system can be difficult
 - Minimum of two components

MesoDYN, DPD

What can be calculated?

- Segregation
- Interfacial tension
- Stress tensor
- Bulk viscosity
- Shear viscosity
- Temperature dependence of miscibility
- Critical Micelle Concentration (CMC)
- Pressure
- Bead correlations
- Diffusivities

Mesocite

- combines two bead based methods
 - Coarse-grained molecular dynamics (CGMD)
 - Hard body interactions, charged beads
 - Includes steric effects, detailed description of interactions required
 - Dissipative particle dynamics (DPD)
 - Soft potentials, fewer parameters, longer time and length scales, long chain polymers
- Study properties at longer time and length scales than atomistic simulations (mesophase formation, diffusion in bilayers, nanotube orientation etc.)

Crystal structure determination from powder diffraction data

- Crystal structure important for patenting
- Crystal structure important as prerequisite for the understanding of most solid state properties
- Single crystals large enough for diffraction experiments are frequently difficult or impossible to obtain

Reflex, Reflex Plus, Reflex QPA, X-Cell

Routes to determine crystal structures

Direct space methods

Other crystallography tools

Morphology: prediction of the morphology of the crystal starting from the atomic structure of a crystal (crystal shape, surface stability, aids the development of tailor-made additives)

Polymorph predictor: prediction of potential polymorphs directly from the molecular structure.

Failry rigid, (non-)ionic molecules (C,N,O,H)

Possible packing arrangements are generated in all reasonable space groups, searching for minimum lattice energy

What can be calculated?

- Powder diffraction pattern of a crystal (Reflex Powder Diffraction)
- Crystal structure
 - From powder data (Powder Solve)
 - From a list of theoretical trial structures (Polymorph)
- Morphology prediction (Morphology)
 - Consider possible effects (qualitatively) of tailor-made additives and solvents by identifying important interactions at key growth faces.
 - Predict the morphological effects of modifying the growth rates of particular faces
 - Relate predicted morphology to experiment, enabling indexing of experimental data

Correlative methods

- Addresses two questions:
 - What features of a molecule affect its activity?
 - What can be modified to enhance its properties?
- Quantitative in that a mathematical model is used to account for the observed activity.

Happiness = f(money + love + car + holiday..)

QSAR ➡ property = f(no. of carbon atoms + surface area +....)

QSAR, Synthia (Polymers)

Correlative methods

- Strong points
 - Allows to cover time and size range over the “standard” molecular modeling (ageing, odour, brilliance...)
- Limitations
 - The correlations are limited to a very specific range of components
 - Success of the correlations depend on the quality of the data

QSAR-Quantitative Structure Activity Relationship

	A	B	C	D	E	F	G	H	I
	Structures	Structure Name	Corrosion inhibition	Rotatable bonds (Fast Descriptors)	Hydrogen bond donor (Fast Descriptors)	Hydrogen bond acceptor (Fast Descriptors)	Chiral centers (Fast Descriptors)	AlogP (Fast Descriptors)	AlogP98 (Fast Descriptors)
1		Corrosion -1	6.20000000	0	1	1	0	1.28970000	1.34550000
2		Corrosion -2	4.30000000	0	3	1	0	1.00960000	1.14060000
3		Corrosion -3	7.50000000	1	3	2	0	1.13260000	0.64470000
4		Corrosion -4	6.30000000	2	3	2	0	1.31390000	0.69290000
5		Corrosion -5	2.75000000	3	3	2	0	1.58560000	1.21410000
6		Corrosion -6	4.00000000	4	3	2	0	1.96190000	1.67030000
7		Corrosion -7	2.00000000	5	3	2	0	2.35820000	2.12650000
8		Corrosion -8	4.50000000	6	3	2	0	2.75450000	2.58270000
9		Corrosion -9	4.50000000	7	3	2	0	3.15080000	3.03690000
10		Corrosion -10	9.60000000	10	3	2	0	4.33970100	4.40749900
11		Corrosion -11	11	11	3	2	0	4.73600200	4.86369900
12		Corrosion -12	6.60000000	3	2	2	0	1.72220000	1.32470000
13		Corrosion -13	7.60000000	3	1	2	0	2.08360000	1.86060000
14		Corrosion -14	6.70000000	4	2	2	0	1.97390000	1.64590000

Other Modules in MS

- Adsorption Locator
- Amorphous Cell
- Blends
- Conformers
- Scripting
- Sorption

Adsorption Locator

Determines energetically favourable positions of a adsorbate in periodic and aperiodic structures

Amorphous Cell

Construction of complex amorphous systems

Construction

Packing

Confined Layer

Blends

A tool to estimate the **miscibility behaviour of binary mixtures**
(solvent-solvent, polymer-solvent, and polymer-polymer mixtures)

the thermodynamics of mixing is directly predicted from the chemical structures of the two components (molecular structures and a forcefield as input)

- Phase diagrams (critical points, binodal and spinodal curves)
- Interaction parameter, χ
- Mixing energy
- Free energy of mixing isotherms
- Energy distribution functions
- Binding configurations sorted by energy

Conformers

The module provides methods for searching the conformational space of non-periodic molecular systems in order to derive a reasonable sampling of the low energy conformations

The set of rotatable torsion angles of the molecular system is explored systematic and stochastic (random) searches

A set of conformers is obtained and a range of descriptors enabling to perform a detailed analysis of the structures

Simple!

Not so simple ...

Scripting in MS

- What is it?

- Server side scripting
- Will be an evolving project, will be looking for feedback for improvements for the next release

- Chemistry model and Forcite, DMol, CCDC, DFTB, Crystallography, CASTEP, Amorphous Cell, Mesocite, VAMP

- Will be extended to include other modules in future releases
- Access is to a lot of Materials Visualizer functionality - chemistry model and associated objects

- Perl is the scripting language

- Write and test script on client before submitting to server
- Fully documented API and example scripts and tutorial

Scripting Editor

Sorption

- Put molecules (sorbates) into a three-dimensional periodic structure with pores (sorbent)
- Typical examples of sorbents include zeolites, aluminophosphates, clays, nanotubes, polymer membranes, silica gels, activated carbons, and metal-organic frameworks.
- The information that can be obtained: adsorption isotherms, binding sites, binding energies, global minimum sorbate locations, density and energy fields, energy distributions, sorption selectivities, solubilities, isosteric heats, and Henry constants.

Part III: Case Studies

Visualising Reactivity

- Electrostatic potential (ESP)
 - Positive regions (red) correspond to electron-deficient areas - subject to nucleophilic attack
 - Negative regions (blue) correspond to electron-rich areas - subject to electrophilic attack

Towards Improved Zinc Corrosion Inhibitors

- Understanding the Role of Silanes on ZnO

Outline:

The aim is to produce coatings which prevent corrosion of zinc as zinc oxide forms as a thin film under atmospheric conditions.

The behaviour of three silane molecules [1] on ZnO oxide surfaces has been studied.

Amorphous Cell was used to create solvent-silane cells which are placed on the oxide substrate.

▲ Fig. 1 The amorphous cell containing the ZnO substrate, the solvent molecule (blue) and the silane (green).

Towards Improved Zinc Corrosion Inhibitors - Understanding the Role of Silanes on ZnO II

▲ Fig. 3(a) The A configuration of the silane. Solvent is blue.

Two configurations:

A - only the silane head group binds to the surface

B - both the head and tail are in contact with the surface

Both effects are only seen in the presence of solvent, without the solvent, the B is the most dominant for all of the silanes.

▲ Fig. 3(b) The B configuration of the silane molecule. Solvent is blue.

E_{ads} correspond to the degree of polarity; amino > thiol > octyl

Reaction pathway. Transition State (TS)

- Transition State
 - Stationary point on PES
 - Energy gradient vanishes
 - Hessian matrix has one imaginary frequency

Ring-opening polymerization reaction

Two possible sites for the ring-opening of caprolactone

- the acyclic carbon
- an alkylic site

① Calculation of the potential surface for a full set of intermediates

② Calculation of Transition State (LST/QST)

Analysis showed that the ring-opening at the acyclic site has a much lower energy → more favorable. Agreement with NMR results

Microphase formation - DPD

- Researchers at Unilever studied the mesophase formation of linear (A_mB_n) diblock melts (applications: food, detergents, personal care)

Morphology of copolymer blends with varying ratios of head-to-tail group size

- Explaining microphase mechanisms enables researchers to design materials processes more easily, saving time and reducing processing problems

Part V:

Problem Solving Approach in Molecular Modeling

...or what a modeler does ...

Which method?

- All methods for everything?

REMEMBER

If larger time and space domains are accessed ,
specificity and accuracy are lost

- It is **essential** to **choose the right method** for getting the best results. Results have to be **analyzed**. This is the work of a modeler, too.

How to choose?

- **DFT - Electronic properties or chemical phenomena**
 - Break/form bonds
 - Electronic properties
 - Accuracy is my main concern, time is secondary
 - The system is small (about 100 atoms)
- **Semiempiric - Electronic properties or chemical phenomena**
 Still interested in breaking/forming bonds and electronic properties but...
 - Interested only in a first guess
 - Time is more important than accuracy
 - Need to deal with a big quantity of atoms

How to choose?

- **Atomistic - Physical phenomena**
 - Not interested in electrons
 - Huge quantity of molecules/atoms
 - Targeting systems of 100 Å maximum
 - Processes involving $< 1 \times 10^{-9}$ s
- **Mesoscale - Soft materials**
 - Not interested in electrons
 - Not interested in conformations
 - My systems are not crystalline/semi-crystalline
 - I have at least 2 different components
 - I'm targeting systems size $<$ micrometer and time $<$ microsecond

Rule of thumb - part 1

- How much time do you have?
- How accurately do you need your results to be? (or what approximations are acceptable and what aren't)
- How many atoms do you have in your system?
- What computational resources do you have access to?
- What Materials do you want to study?

Rule of thumb - part 2

- Small organic molecules - All techniques applicable
- Polymers - Usually too big to use QM techniques. Generally use Molecular Mechanics, Mesoscale and QSAR tools to study them. Recently, have been able to use QM methods to study small oligomers
- Inorganic materials - Quantum Mechanics and Molecular Mechanics. Limited applications of QSAR
- Pure metals - Quantum Mechanics. Some limited studies using Molecular Mechanics, GULP

Rule of thumb - part 3

When using forcefields...

- Forcefield parameters are derived empirically. Typically the parameters are adjusted iteratively to match experimental data
- Not all materials have been parameterized...
 - Polymers - Most forcefields do well. COMPASS is the preferred approach (also good for molecular crystals)
 - Small organic molecules - As above
 - Inorganic materials - Limited availability, some parameters in COMPASS, some in cvff_aug. Forcefields from the open literature.
 - Pure metals - special forcefields

But ...

What if you want to study the evolution of a system during hours or a phenomena that has a size of 1 cm?

- Try to study the problem from another angle
 - What about studying the “initial” and the “final” systems (before and after a reaction)?
 - What about studying the interface?
- If reducing the time/size scale does not give you the information
 - QSAR
 - If you have a lot of data but little chemical or physical knowledge of the system
 - Useful to generate correlations in systems or to find out which factors control a certain property

Steps required for molecular modeling

- Molecular Modeling (in most cases) involves four main steps

How to proceed ?

Important

- Sometimes not only one technique will give all the answers
 - Different techniques will tackle different angles of the problem
- You need scientific background on the domain of study
 - Right choice of model/simulation tool
 - Correct analysis of the results
 - You want to keep the referees happy
- Minimum computer requirements are ok but...
 - Memory - the more RAM your computer has, the better
 - CPU speed - the faster, the better

More Information

Our Websites:

www.accelrys.com
www.accelrys.org

NMR CASTEP

NMR CASTEP predicts key magnetic resonance properties of molecules and solid state materials from first principles. Based on density functional theory (DFT), NMR CASTEP enables users to compute NMR chemical shifts and electric field gradient tensors, with unprecedented accuracy. The method can be applied to compute the NMR shifts of molecules, solids, interfaces, and surfaces for a wide range of materials classes including organic molecules, ceramics, and semiconductors. First principle calculations allow researchers to investigate the nature and origin of the magnetic resonance properties of a system without the need for any empirical parameters. NMR CASTEP is thus well suited to research problems in solid state physics, materials science, and chemistry where using computer simulations to perform virtual experiments can lead to tremendous benefits over using experimental NMR techniques alone.

NMR

- NMR chemical shielding tensor shows how each atom responds to external magnetic field $\mathbf{B}_{\text{ext}}$
 - $\mathbf{B}_{\text{in}} = -\sigma \mathbf{B}_{\text{ext}}$
 - Isotropic shielding is trace of $\sigma \rightarrow \sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$
 - Chemical shift is computed relative to a standard $\rightarrow$

$$\delta = \sigma_{\text{iso}}^{\text{ref}} - \sigma_{\text{iso}}^{\text{obs}}$$

- NMR chemical shifts
 - Sensitive to local electronic environment of nucleus - serves as probe
 - Provide fingerprints for identification of unknowns
 - Give information about molecular or crystal structure

NMR CASTEP

Computes NMR chemical shielding and electric field gradient

Isotropic chemical shift, $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$

Anisotropy $\Delta = \sigma_{zz} - \sigma_{iso}$

Asymmetry $\eta = (\sigma_{xx} - \sigma_{yy})/\Delta$

Quadrupole coupling constant $C_q = eQV_{zz}/h$

Electric Field Gradient (EFG) asymmetry $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$

IMPORTANT: Separate module in addition to CASTEP

NMR CASTEP: Practical aspects

- NMR yields absolute chemical shielding values but experimentalists generally report shifts relative to a standard
- Convert from absolute to relative numbers
 - NOT recommended to do a computation on a known standard (TMS) and subtract
 - Differences in environment introduce errors (e.g., liquid vs. solid)
 - Compare calculated to one known experimental result to determine a correction factor empirically
 - Example: *J. Phys. Chem. A* 108, 6032 (2004) determination of glutamic acid polymorphs