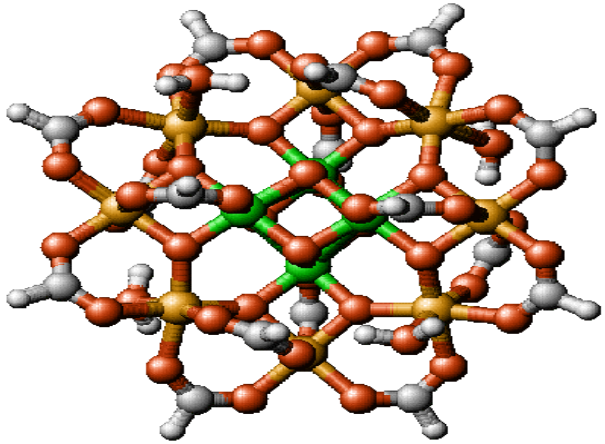
Computational Materials Science



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CY03D003

Outline

- Introduction
- Fundamentals
- How to start
- Application examples
- Softwares
- Sophisticated methods
- Summary
- References

Introduction

- Uses computers to model, understand, predict materials properties.
- Yields unique insights into experimental data
- Used to guide experimenters toward new materials with unique and important properties.
- Automated theoretical chemistry
- Schrodinger equation

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0$$

Fundamentals

- Energy
- Electrostatics
- Atomic units
- Thermodynamics
- Quantum mechanics
- Statistical mechanics

Ab initio methods

- Hatree-Fock approximation
  - Central field approximation
  - Many electron SE split into many one electron wavefunction – orbital, energy – orbital energy
- Moller – Plesseet Perturbation theory
  - Correlation can be added as perturbation from HF wave function
- Quantum monte carlo method
  - Explicitly correlated wave function (function of e^- - e^- distance)
- Natural orbitals
  - Eigen functions of the first-order reduced density matrix

Semi empirical Methods

- Core electrons not included, minimal basis set used
- Two electron integrals approximated/omitted.
- Parameterized - curve fitting.
- Faster than ab initio
- Results can be erratic
- Molecules similar to parameterization database molecule – better results

Methods

- Huckel
- CNDO
- MINDO
- MNDO
- INDO
- ZINDO etc.

Structure – Property Relationships

- Qualitative or quantitative empirically defined relationships between molecular structure & observed properties.
- Curve-fitting – linear combination of molecular properties that best predicts the property for a set of known compounds.
- Interpolation
- QSPR (Quantitative Structure Property Relationship)-B.P, M.P etc.
- QSAR (Quantitative Structure Activity Relationship)-drug activity etc.

$$\text{Property} = c_0 + c_1 d_1 + c_2 d_2 + \ldots\ldots\ldots\ldots$$

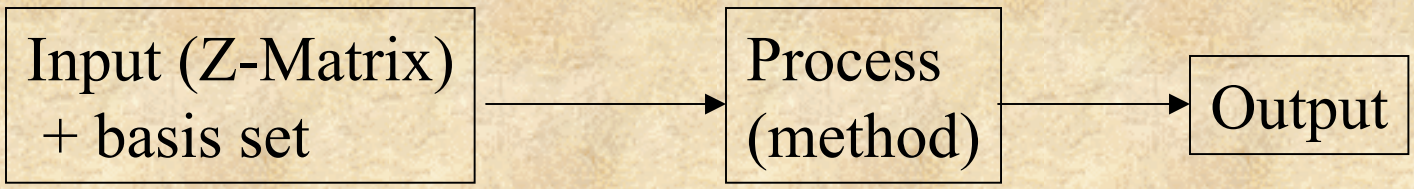
Where c_i=fitted parameters, d_i=descriptors

Descriptors: Constitutional(eg. M.W), Topological(eg.Weiner index), Electrostatic(eg.Partial charges), Geometrical(eg. Moments of inertia), Quantum Chemical(eg. Net atomic charges), Statistical mechanical(eg. Vibrational frequencies)

How to go about it?

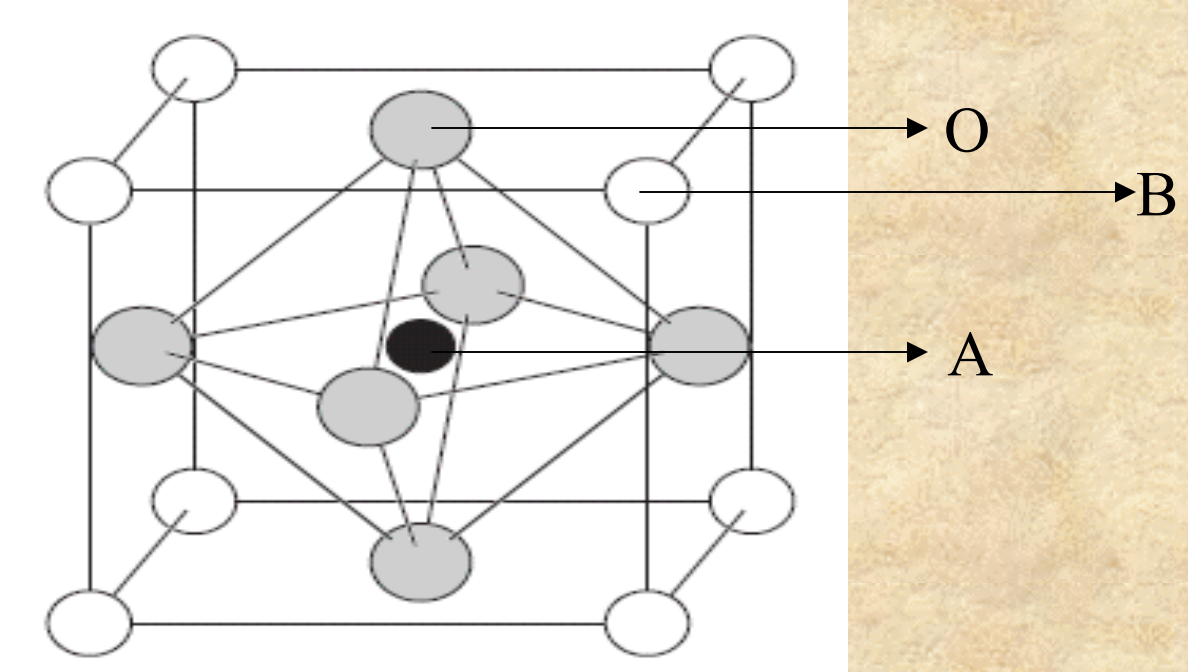
- Clear idea of what is needed, accuracy
- Prediction of accuracy of answer
- Time needed for the process
- Approximations made, which are significant
- Software choice

Flow chart of a process



Designing a magnetoelectric multiferroic material

- Ferro - broken symmetry, related character
- Perovskites ABO_3



- Choosing a trial material
  - B cation - magnetic(Fe^{3+})
  - A cation - stereochemically active ns^2 A ion(Ge^{2+}, Pb^{+2}, Sn^{2+}, Tl^{+}, Bi^{3+} etc.)

Calculation of properties of $BiMnO_3$ using DFT

- Flat bands – high density of states
- Broad series of bands: -2 & -7eV due to O 2p orbitals
- Mn 3d bands splitted – lower enery t_{2g}, higher energy e_g
- Fermi level lies near top of Mn 3d t_{2g} bands
- Ground state – insulator (requirement for ferroelectricity)
- Bi 6p-O 2p σ interactions larger than Bi 6s-O 2p interactions

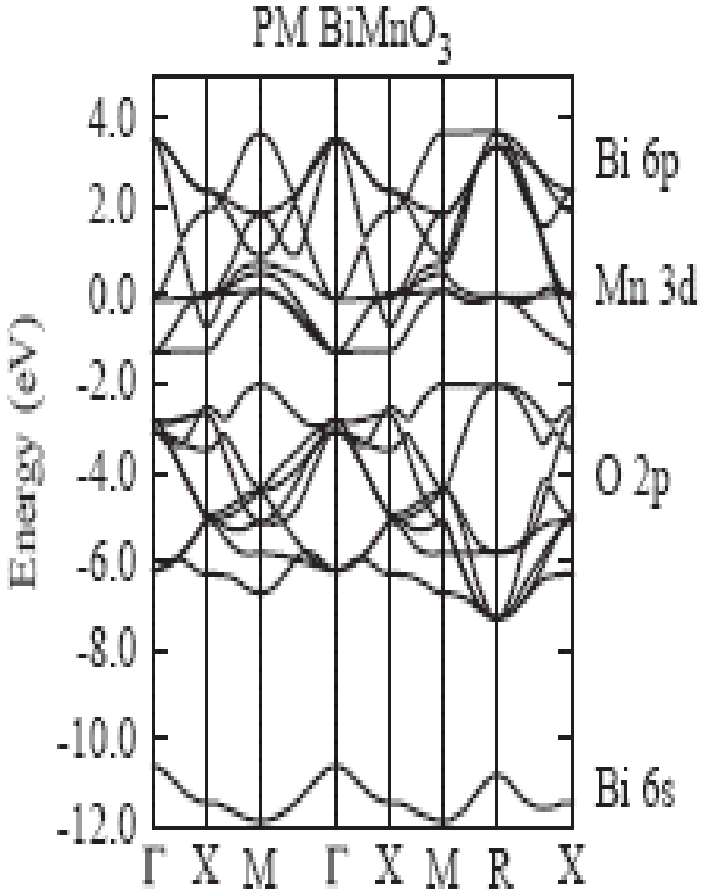


Fig. 3. Calculated band structure for cubic paramagnetic $BiMnO_3$ along the high symmetry axes of the Brillouin zone.

N. A. Spaldin et al., J. Solid State Chem. , **176** (2003) 615.

Stereochemical activity of Bi lone pair

- First principle electronic properties calculation (DFT)
- Lone pair drives the off center distortion – novel multiferroic property
- Mn at the center, large cations at the corners
- Deep blue – non localilzed white – localized
- ELFs similar in Mn-O plane – Mn-O interactions ruled out for different magetic orderings
- Different ground state structures

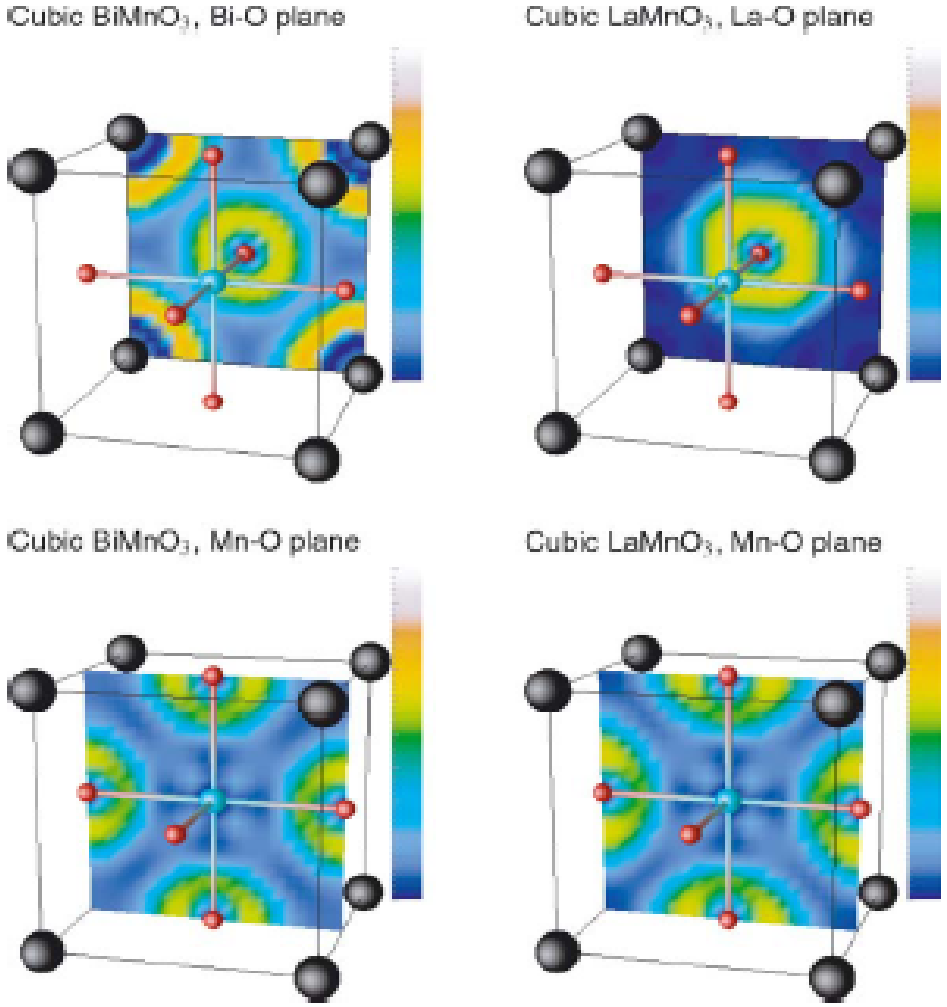


Fig. 4. Valence ELFs in the A–O and Mn–O planes of the cubic structures of $BiMnO_3$ and $LaMnO_3$. The perovskite *A* atom (Bi or La) is in the corner of the cell and the *B* atom (Mn) is at the center, six-coordinate with O. See Ref. [70].

Real Space depiction

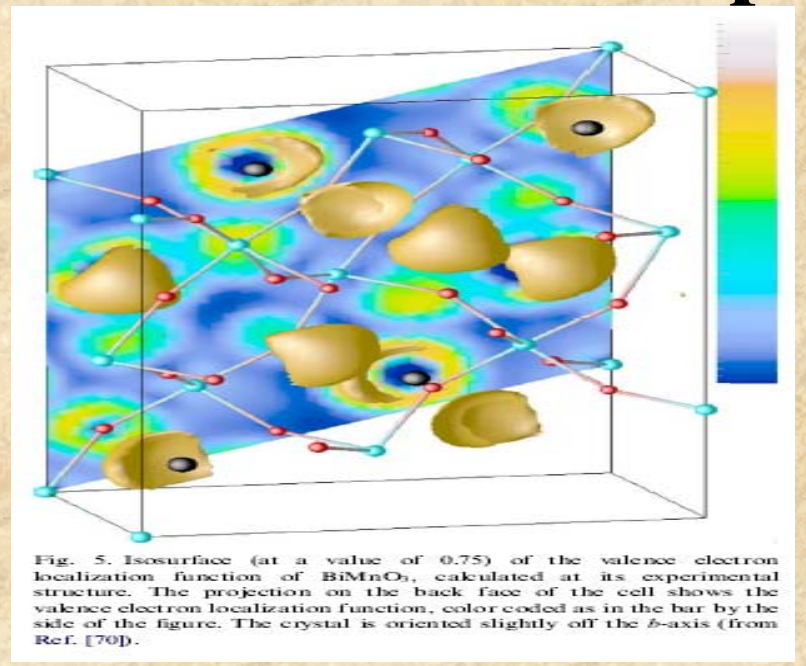
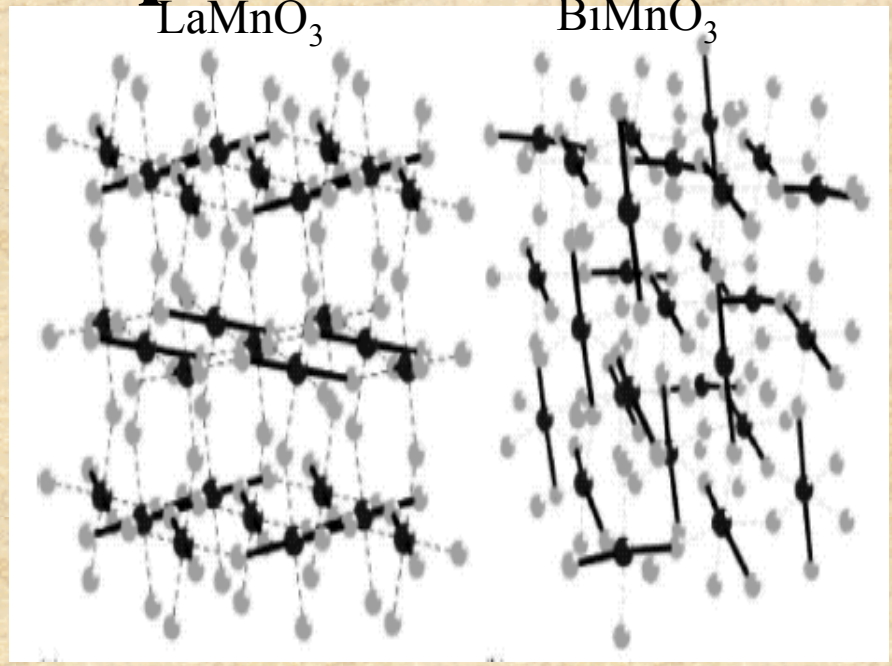
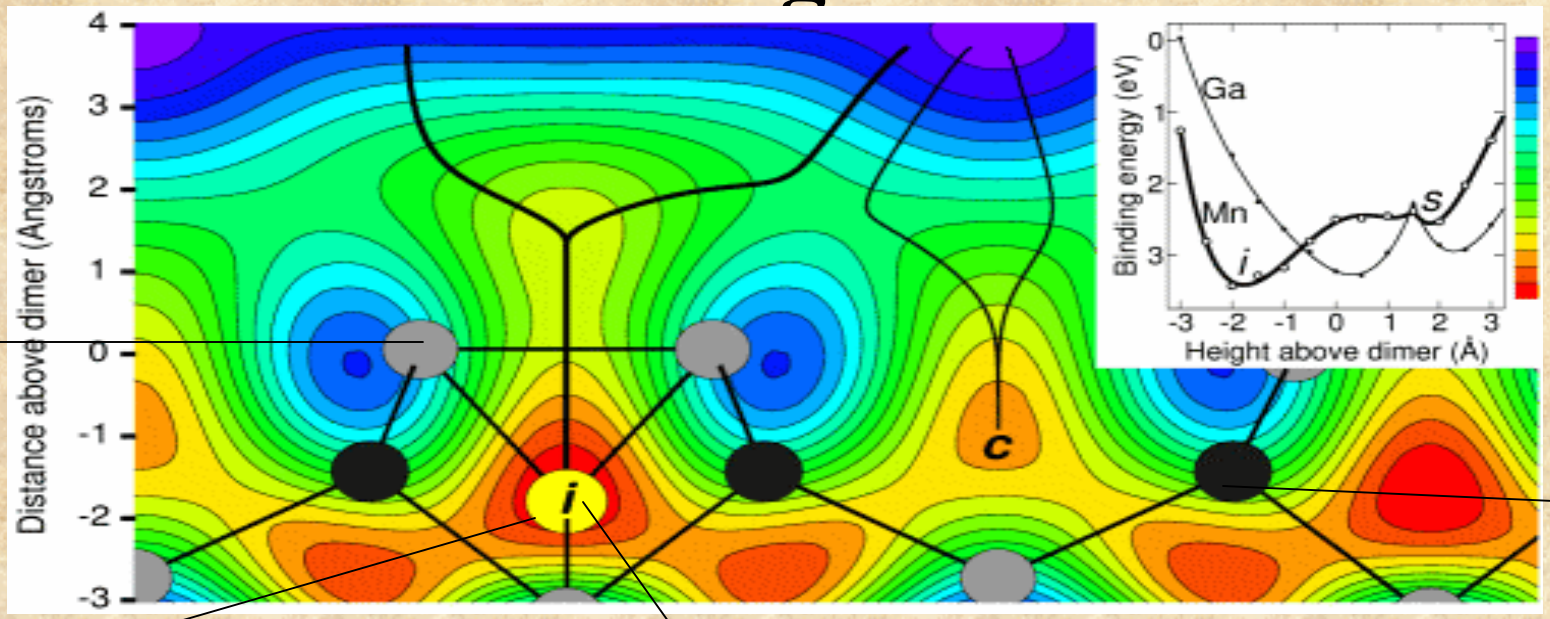


Fig. 5. Isosurface (at a value of 0.75) of the valence electron localization function of $BiMnO_3$, calculated at its experimental structure. The projection on the back face of the cell shows the valence electron localization function, color coded as in the bar by the side of the figure. The crystal is oriented slightly off the *b*-axis (from Ref. [70]).



- Yellow lobe-like regions – lone-pair (Bi) geometry in distorted monoclinic structure
- Spherical lone pair ⟶ lobe like lone pair – structural distortion
- Large distortion by Bi lone pair – over-rides tendency of short bonds to align in a plane
- Orbital ordering – 3D, structure is ferromagnetic
- Stereochemically active lone pair – symmetry lowering structural distortion.

Self compensation in Mn doped ferromagnetic SC



As

Ga

Mn

Potential energy surface for Mn adsorption on GaAs(001)

Minimum energy adsorption site

- MnGaAs
- Electrical activity of Mn impurity determined by formation energy as a function of its charge state.
- Calculations predict ferromagnetism
- Ferro magnetism absent for no compensation, complete compensation

Nanoscale plasticity

- Intricate interplay between dislocations and grain boundaries
- Small grains put severe limitations on the dislocation behavior
- Atomistic simulations
- Smaller the size – harder the material
- Too small – softening
- Confining grain structure – change dislocation behavior.
- Grain boundary engineering

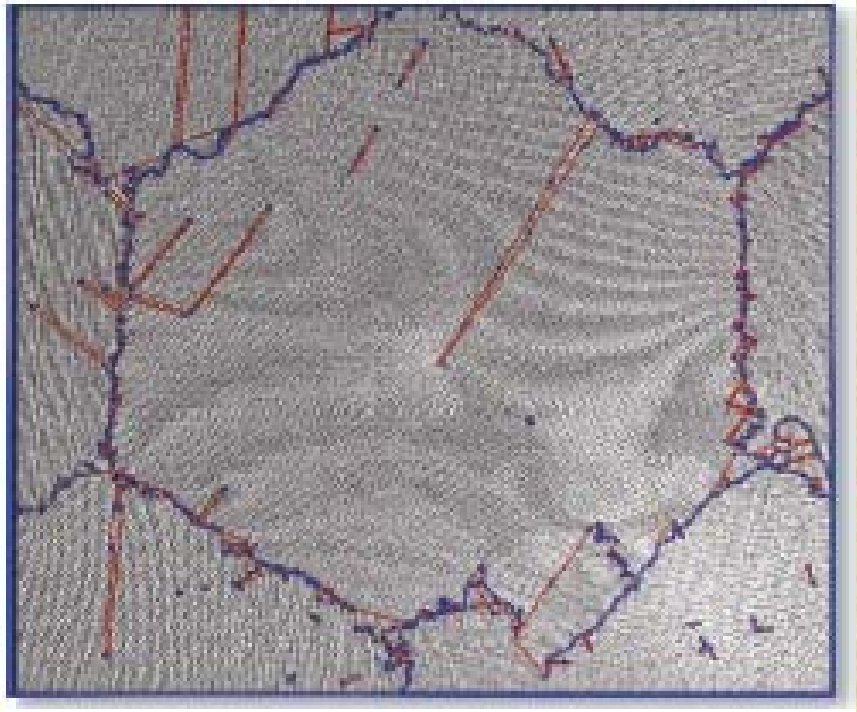


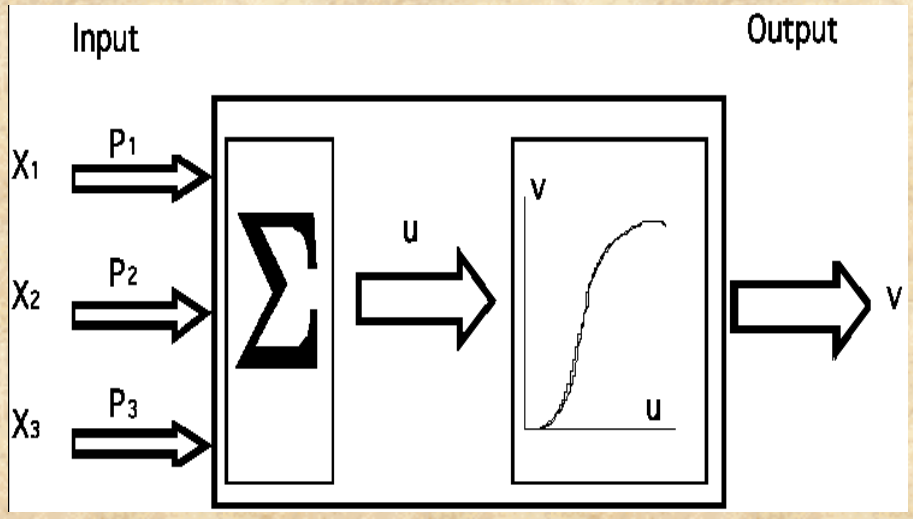
Figure 1 Snapshot from a molecular-dynamics simulation by Yamakov *et al.*[1] showing the behaviour of nanocrystalline aluminium during deformation. The crystal grain at the centre is 70 nm in diameter and is defined by clear grain boundaries (blue atoms). Partial dislocations, created at the grain boundaries, leave behind planar defects such as twin boundaries (red atoms) when they move.

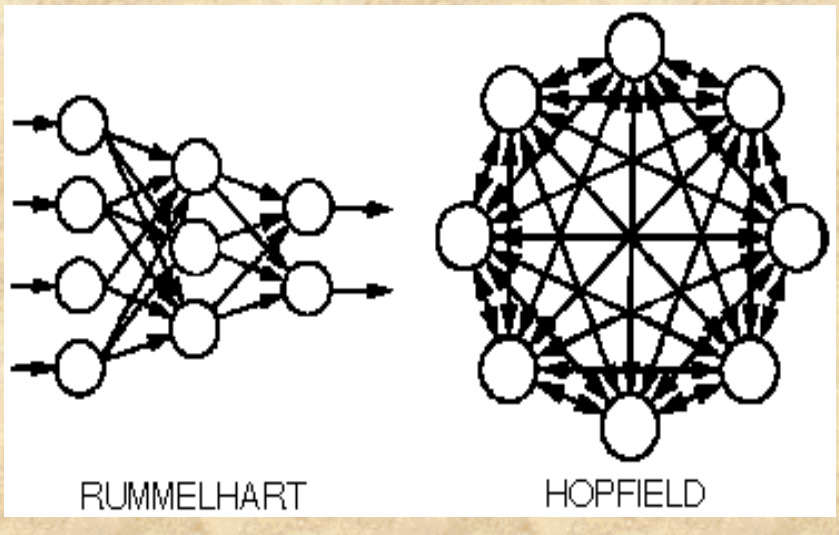
Softwares

- GAMESS (ab initio)
- Gaussian
- ADF
- MOLPRO
- AMPAC (semi empirical)
- MOPAC
- Crystal
- Alchemy(Integrated packages)
- Chem3D
- HyperChem
- SPARTAN
- UniChem

Artificial Neural Networks

- Simulation of the brain
- Novel structure of the information processing system
- ANNs, like people, learn by example
- Configured for a specific application, such as pattern recognition or data classification





Schematic representation of a neuron

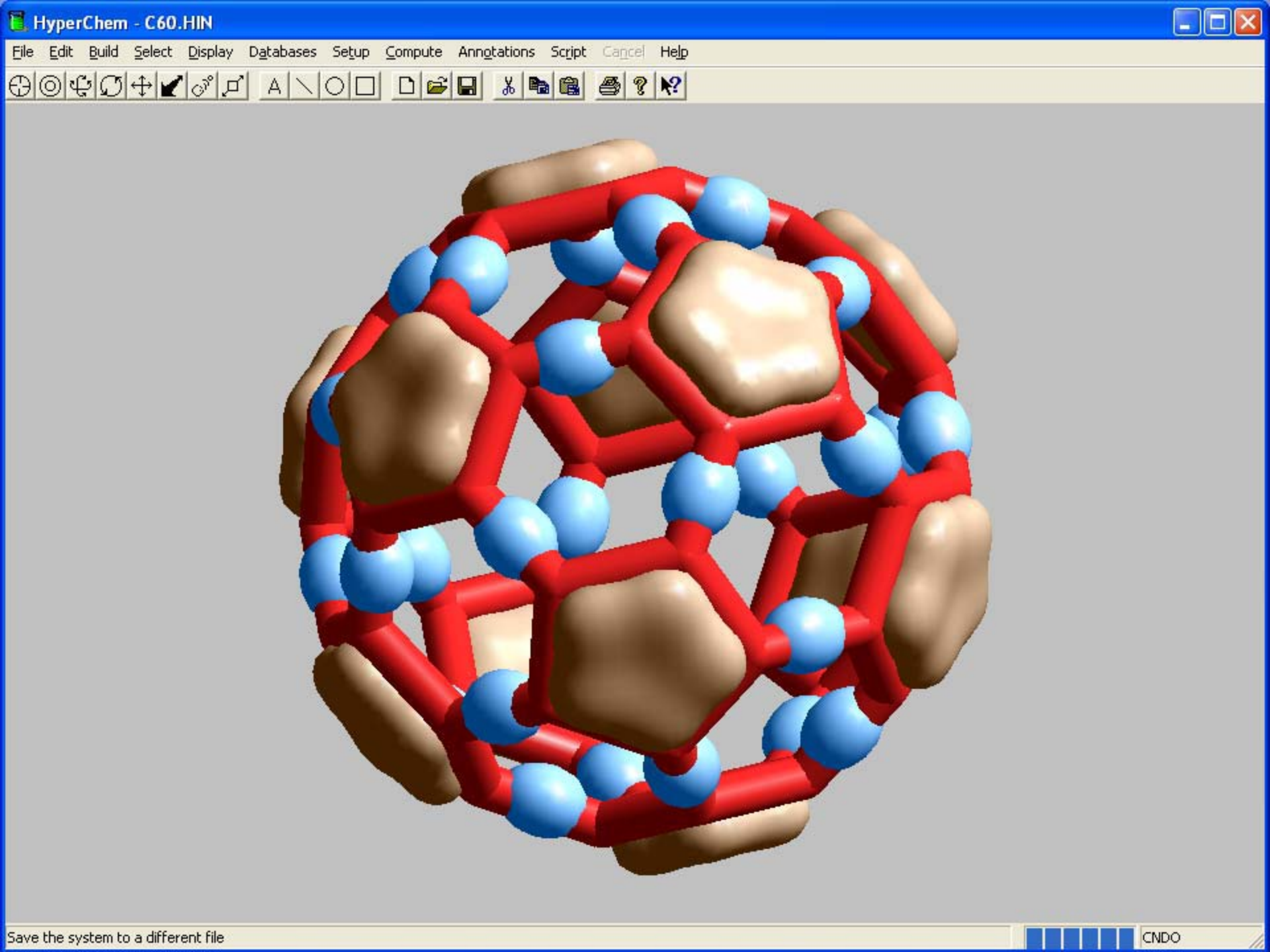
Summary

- To analyze critical materials processes
- Simulations – control over initial and boundary conditions
- Access to complete information on electronic structure and molecular levels
- Unravel microscopic mechanisms underlying a particular phenomenon

References

- Computational Chemistry by David Young.
- Jorgen B. Bilde-Sorensen & Jakob Schiotz, *Science*, 300 (2003) 1244.
- K. W. Jacobsen et al., *Nature Materials*, 1 (2002) 15.
- N. A. Spaldin and W. E. Pickett, *J. Solid State Chem.*, 176 (2003) 615.
- S. C. Erwin & A. G. Petukhov, *Cond.-mat*, (2002).
- S. Yip, *Nature Materials*, **2** (2003) 3.

Software Screens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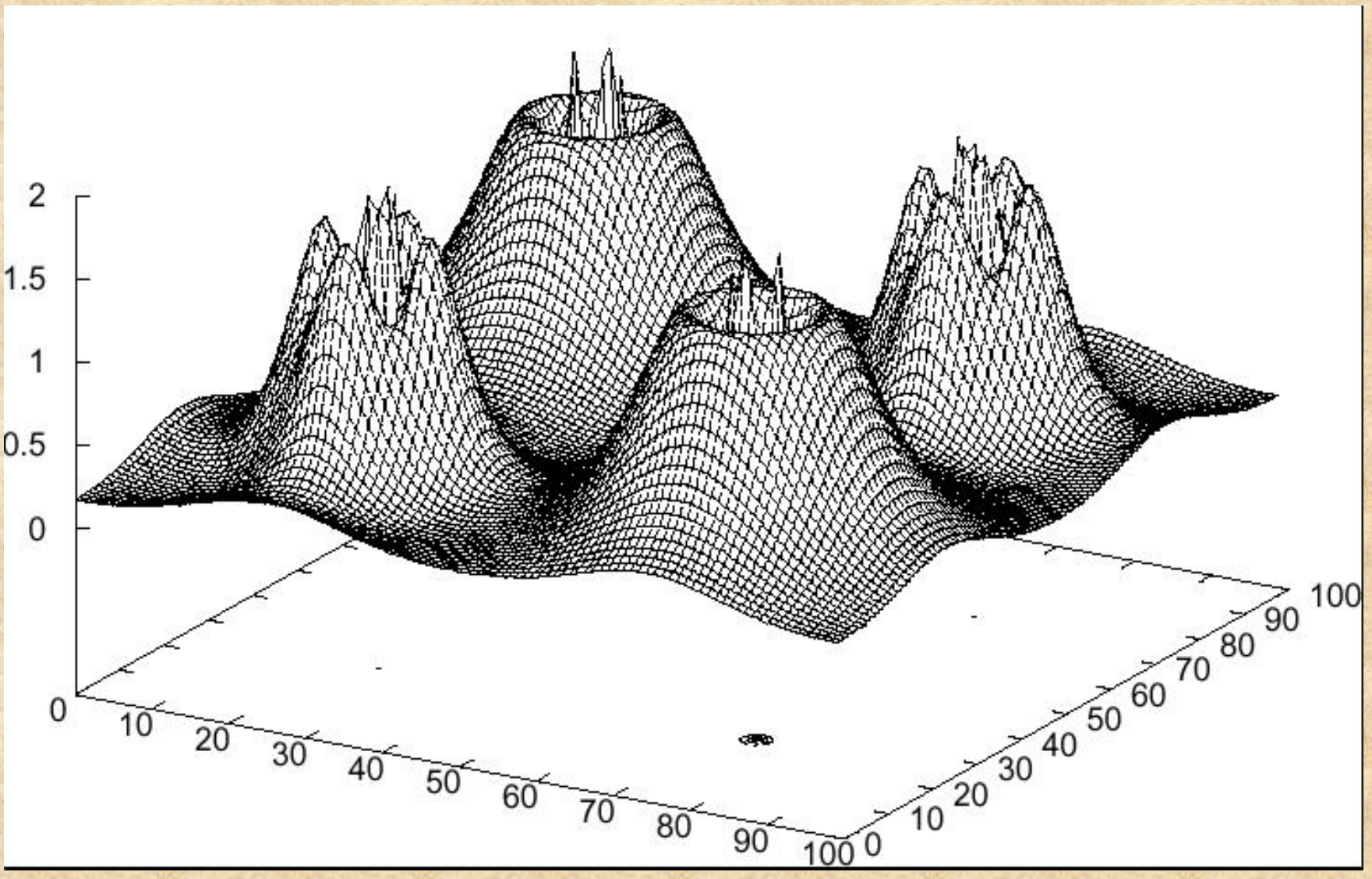
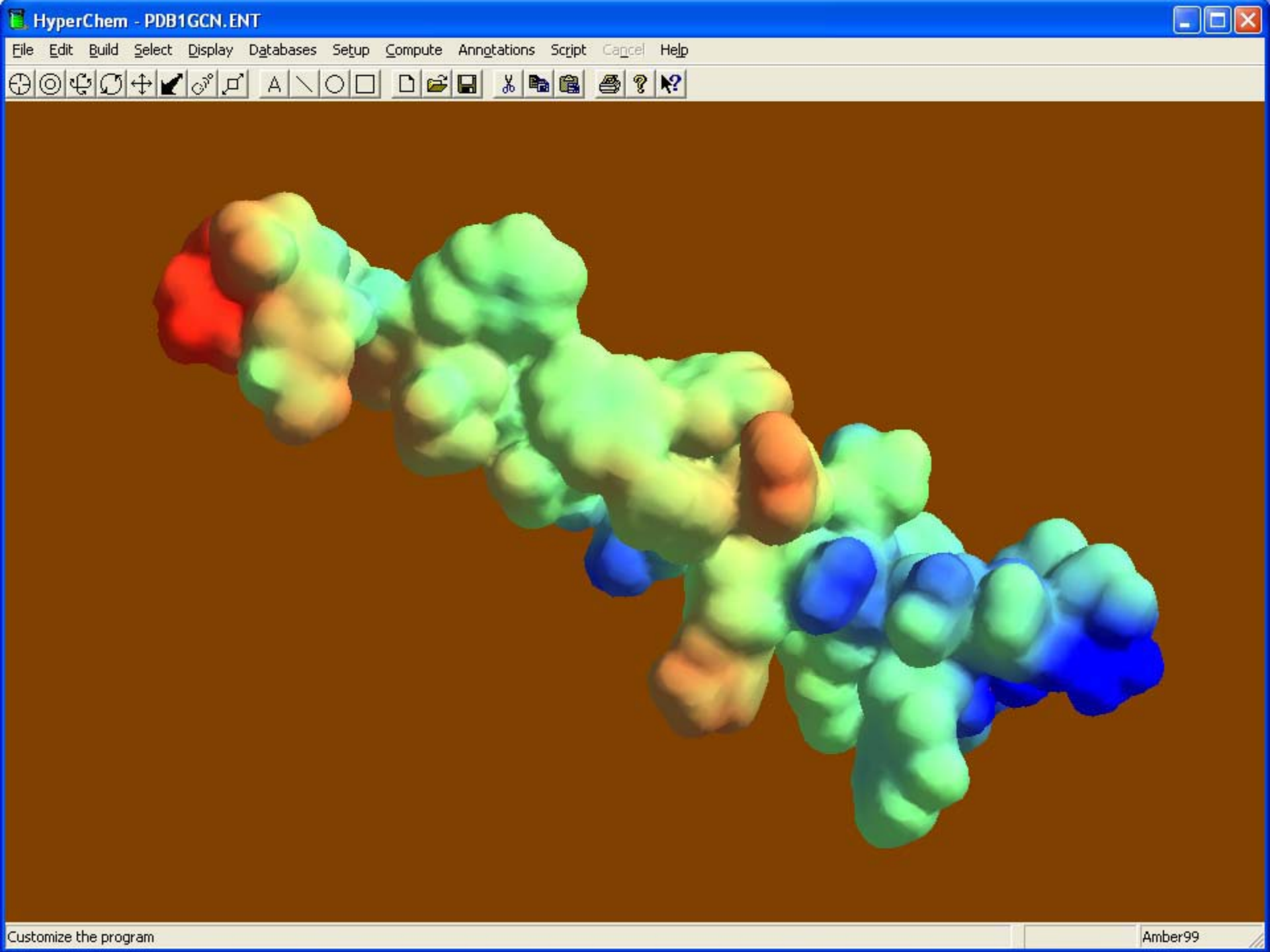
Electron density mapping

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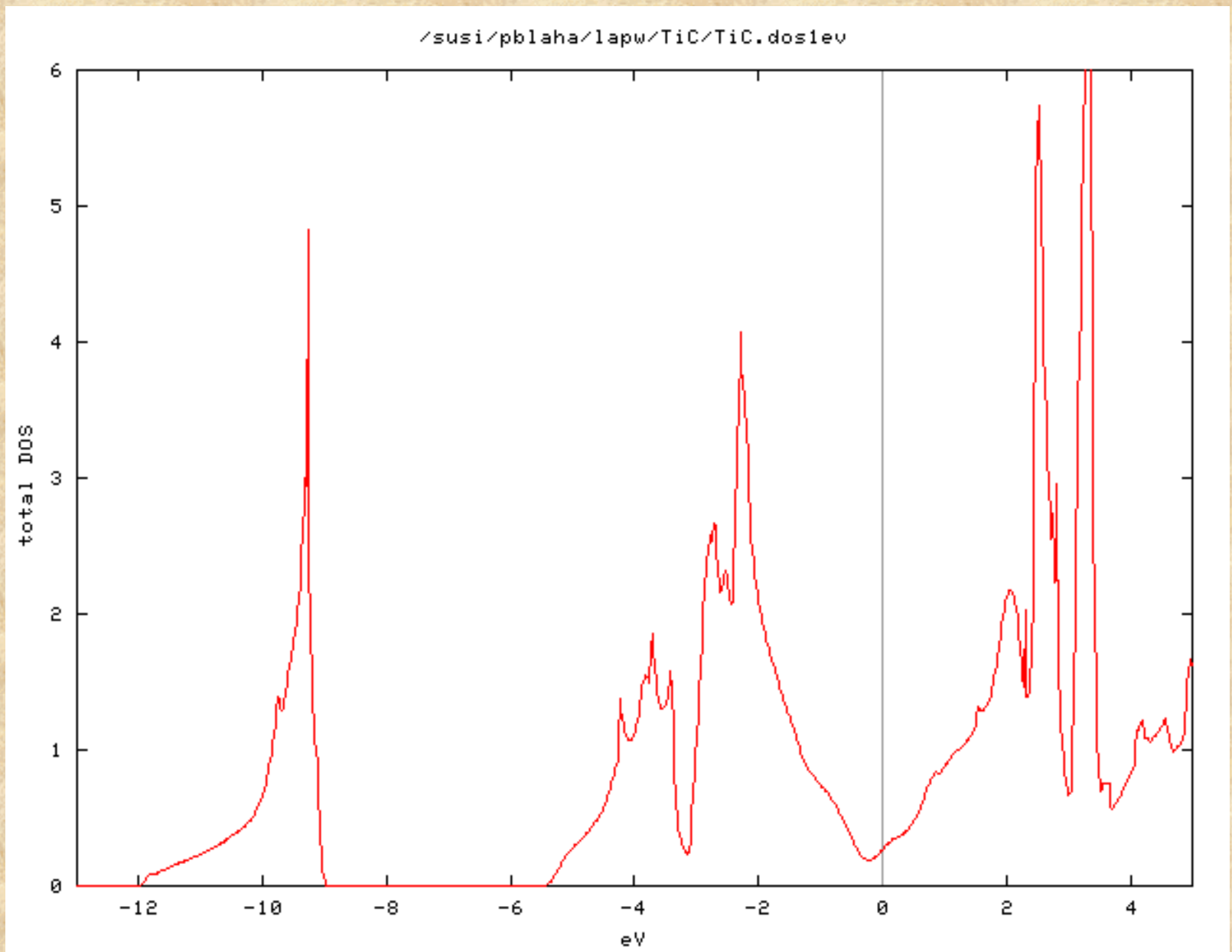
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