

COMP LAB

G. Mallia

Timetable  
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types

Quantum-  
mechanical  
simulation

First step

How to write  
a report

# INTRODUCTION to the Computational Laboratory

**Giuseppe Mallia**

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Imperial College London - Chemistry Department  
Thomas Young Centre:  
the London Centre for Theory and Simulation of Materials

18 January 2010 – 22 February 2010

# Outline

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**1** TIMETABLE and DEADLINE

**2** AIMS and SYSTEMS

**3** HOW

**4** SIMULATION TYPES

**5** QUANTUM-MECHANICAL SIMULATION

**6** FIRST STEP

**7** HOW TO WRITE A REPORT

# Outline II: QUANTUM-MECHANICAL SIMULATION

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- 1 Schroedinger equation
- 2 Hamiltonian operator
- 3 Hamiltonian operator for a system of nuclei and electrons
- 4 Schroedinger equation: solutions
- 5 Born-Oppenheimer approximation
- 6 Hartree-Fock method
- 7 Wavefunction
- 8 From Hartree product to Slater determinant
- 9 Variational principle
- 10 Self Consistent field

# TIMETABLE and DEADLINE → GROUP A

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- The Electronic Structure of Molecules, Polymers, Surfaces and Solids

	Mon	Tue	Thur	Fri
2:00-5:00	22/02/10	23/02/10	25/02/10	26/02/10

## DEADLINE:

when? **13:00am on Wed the 3rd of March**

where? ROOM 442 to Ms Lisa Benbow

- Statistical Mechanics: The Thermal Expansion of MgO

	Mon	Tue	Thur	Fri
2:00-5:00	08/03/10	09/03/10	11/03/10	12/03/10

## DEADLINE:

when? **13:00pm on Wed the 17th of March**

where? ROOM 442 to Ms Lisa Benbow

# TIMETABLE and DEADLINE → GROUP B

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- The Electronic Structure of Molecules, Polymers, Surfaces and Solids

	Mon	Tue	Thur	Fri
2:00-5:00	18/01/10	19/01/10	21/01/10	22/01/10

## DEADLINE:

when? **13:00am on Wed the 27th of January**

where? ROOM 442 to Ms Lisa Benbow

- Statistical Mechanics: The Thermal Expansion of MgO

	Mon	Tue	Thur	Fri
2:00-5:00	01/02/10	02/02/10	04/02/10	05/02/10

## DEADLINE:

when? **13:00pm on Wed the 10th of February**

where? ROOM 442 to Ms Lisa Benbow

# AIM: The Electronic Structure of Molecules, Polymers, Surfaces and Solids

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- to show that a solid can be considered as an infinite molecule
- to understand how the **energy level diagram** of a molecule (a finite system) becomes a **band structure** for a periodic system, like a polymer/chain, a slab/layer and a crystal.
- to connect the band structure of a system with its density of state (DOS)
- to analyse the band structure of a generic periodic system under investigation and to predict its electronic properties, depending on the band structure.

## 1 FINITE SYSTEMS:

- the H atom → THE STARTING POINT
- the H<sub>2</sub> molecule
- the hypothetical **linear and cyclic** H<sub>*n*</sub> clusters, with  $n = 3, 4, \dots, 100$

## 2 INFINITE SYSTEMS:

- Polymer/Chain: the 1D periodic system
- Slab/Layer: the 2D periodic system
- Crystal: the 3D periodic system

# HOW?

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## COMPUTATIONAL EXPERIMENT / SIMULATION

- program
- input

Environment:  
the choice of the Operating System → **linux**

Interface:  
**DLV** = package for the visualisation of materials  
structures and properties.

# SIMULATION TYPES

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- CLASSICAL SIMULATION  
**Newton law**
- QUANTUM-MECHANICAL SIMULATION  
**Schroedinger equation**

Systems under investigation

Properties

Accuracy

Computational time

Resources

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# QUANTUM-MECHANICAL SIMULATION

# SCHROEDINGER EQUATION

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## Nonrelativistic time-dependent

$$H|\Phi\rangle = i\hbar \frac{\partial |\Phi\rangle}{\partial t}$$

evolution of a system with time

## Nonrelativistic time-independent

$$H|\Phi\rangle = E|\Phi\rangle$$

$H$  is the Hamiltonian operator for a system of nuclei and electrons

# HAMILTONIAN OPERATOR

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$$\hat{H} = \hat{K} + \hat{V}$$

where

$\hat{K}$  is the kinetic energy operator

$\hat{V}$  is the potential energy operator

If  $\hat{V} = 0$ , free particle.

# KINETIC ENERGY OPERATOR

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- One particle in 1D

$$\hat{K} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

- One particle in 3D

$$\hat{K} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{\hbar^2}{2m} \frac{d^2}{dy^2} - \frac{\hbar^2}{2m} \frac{d^2}{dz^2} = -\frac{\hbar^2}{2m} \nabla^2$$

- N particles in 3D

$$\hat{K} = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2$$

# HAMILTONIAN OPERATOR FOR A SYSTEM OF NUCLEI AND ELECTRONS

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the operator for the kinetic energy of the electrons

the operator for the kinetic energy of the nuclei

the operator for the repulsion energy between electrons

the operator for the repulsion energy between nuclei

Number of electrons

Number of nuclei

$$H = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M'_A} \nabla_A^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e}{4\pi\epsilon_0 r_{iA}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Distance between the  $i$ th and  $j$ th electron

the operator for the attraction energy between electrons and nuclei

Distance between the  $i$ th electron and  $A$ th nucleus

Distance between the  $A$ th and  $B$ th nucleus

# HAMILTONIAN OPERATOR FOR A SYSTEM OF NUCLEI AND ELECTRONS IN ATOMIC UNITS

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The diagram illustrates the Hamiltonian operator  $H$  for a system of nuclei and electrons in atomic units. The equation is:

$$H = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}$$

Annotations and their corresponding terms in the equation:

- the operator for the kinetic energy of the electrons:** Points to the first term,  $-\sum_{i=1}^N \frac{1}{2} \nabla_i^2$ . The number of electrons  $N$  is circled in red.
- Number of electrons:** Points to the circled  $N$ .
- Number of nuclei:** Points to the circled  $M$ .
- the operator for the kinetic energy of the nuclei:** Points to the second term,  $-\sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2$ .
- the operator for the repulsion energy between electrons:** Points to the third term,  $+\sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}}$ . The distance  $r_{ij}$  is circled in blue.
- the operator for the repulsion energy between nuclei:** Points to the fifth term,  $+\sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}$ . The distance  $r_{AB}$  is circled in blue.
- Distance between the  $i$ th and  $j$ th electron:** Points to the circled  $r_{ij}$ .
- Distance between the  $i$ th electron and  $A$ th nucleus:** Points to the circled  $r_{iA}$ .
- the operator for the attraction energy between electrons and nuclei:** Points to the fourth term,  $-\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}$ .
- Distance between the  $A$ th and  $B$ th nucleus:** Points to the circled  $r_{AB}$ .

# SCHROEDINGER EQUATION: SOLUTIONS

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- Hydrogen atom and hydrogenic atoms  
(H, He<sup>+</sup>, Li<sup>2+</sup>, ..., U<sup>91+</sup>)  
EXACT SOLUTION wavefunction  
coordinates of a single electron
- He, Hydrogen molecule, H<sub>2</sub><sup>+</sup>  
APPROXIMATED SOLUTION wavefunction  
coordinates of all electrons manybody system

# BORN-OPPENHEIMER APPROXIMATION

Nuclei, being so much heavier than electrons, move relatively slowly and may be treated as stationary while the electrons move in their field.

$$H_{elec} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}}$$

$$H_{elec} \Phi_{elec} = E_{elec} \Phi_{elec}$$

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\}; \{\mathbf{r}_A\})$$

explicit dependence on the electron coordinates:  $\mathbf{r}_i$   
parametric dependence on the nuclear coordinates:  $\mathbf{r}_A$

$$E_{tot} = E_{elec} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}$$

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# HARTREE-FOCK METHOD

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The essence of HF approximation is to replace the complicated many electron problem by a one electron problem.

Fock operator

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{HF}(i)$$

$v^{HF}(i)$  the average potential experienced by the  $i$ th electron due to the presence of the other electrons

$$f(i)\psi_{i,\alpha}(\mathbf{r}_1) = \epsilon_i\psi_{i,\alpha}(\mathbf{r}_1)$$

where  $\psi_{i,\alpha}(\mathbf{r}_1)$  is a molecular/cristalline orbital  
 $\epsilon_i$  is the molecular/cristalline orbital energy

# WAVEFUNCTION

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$$\Phi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N)$$

$N$  is the number of electrons

To completely describe an electron is necessary to specify its spin.

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

where  $x = \alpha$  or  $\beta$

# FROM HARTREE PRODUCT TO SLATER DETERMINANT

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## HARTREE PRODUCT

$$\psi_{i,\alpha}(\mathbf{r}_1)\psi_{i,\beta}(\mathbf{r}_2)\psi_{j,\alpha}(\mathbf{r}_3)\psi_{j,\beta}(\mathbf{r}_4)\dots\psi_{k,\alpha}(\mathbf{r}_{N-1})\psi_{k,\beta}(\mathbf{r}_N)$$

### Pauli principle:

No more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spin must be paired.

## SLATER DETERMINANT

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i,\alpha}(\mathbf{r}_1) & \psi_{i,\beta}(\mathbf{r}_1) & \dots & \psi_{k,\beta}(\mathbf{r}_1) \\ \psi_{i,\alpha}(\mathbf{r}_2) & \psi_{i,\beta}(\mathbf{r}_2) & \dots & \psi_{k,\beta}(\mathbf{r}_2) \\ \dots & \dots & \dots & \dots \\ \psi_{i,\alpha}(\mathbf{r}_N) & \psi_{i,\beta}(\mathbf{r}_N) & \dots & \psi_{k,\beta}(\mathbf{r}_N) \end{vmatrix}$$

# VARIATIONAL PRINCIPLE

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According to the variation principle for the ground state  $|\Phi_0\rangle$ , the energy of an approximate wave function  $|\tilde{\Phi}\rangle$  is always higher.

$$H|\Phi_0\rangle = E_0|\Phi_0\rangle$$

$$E_0 = \frac{\int \Phi_0^* H \Phi_0 d\tau}{\int \Phi_0^* \Phi_0 d\tau}$$

$$E_{\tilde{\Phi}} = \frac{\int \tilde{\Phi}^* H \tilde{\Phi} d\tau}{\int \tilde{\Phi}^* \tilde{\Phi} d\tau}$$

$$E_{\tilde{\Phi}} \geq E_0$$

Thus one measure of the quality of a wave function is its energy:

The lower the energy, the better the wave function.

# SELF CONSISTENT FIELD

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The HF potential  $v^{HF}(i)$  depends on the other electrons.

The HF equation,  $f(i)\psi_{i,\alpha}(\mathbf{r}_1) = \epsilon_i\psi_{i,\alpha}(\mathbf{r}_1)$  is NONLINEAR and must be solve iteratively.

The procedure for solving the HF equation is called self-consistent-field (SCF) method

- 1 to make an initial guess of the spin orbitals ( $\psi(\mathbf{r})\alpha$  or  $\psi(\mathbf{r})\beta$ : the wave function of an electron describing both its spatial distribution and its spin );
- 2 to calculate the average potential  $v^{HF}(i)$ ;
- 3 to solve the HF equation for a new set of spin orbitals
- 4 to repeat until there are no change in the potential;

# RESULTS: FINITE SYSTEMS

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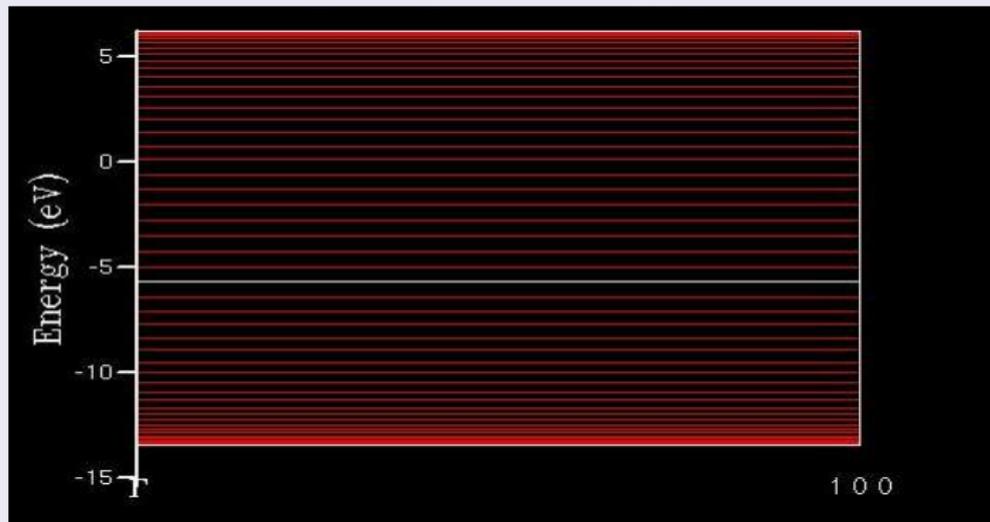
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## Energy level diagram for $H_{100}$

Number of molecular orbitals = Number of atomic orbitals



# RESULTS: INFINITE SYSTEMS (PERIODIC)

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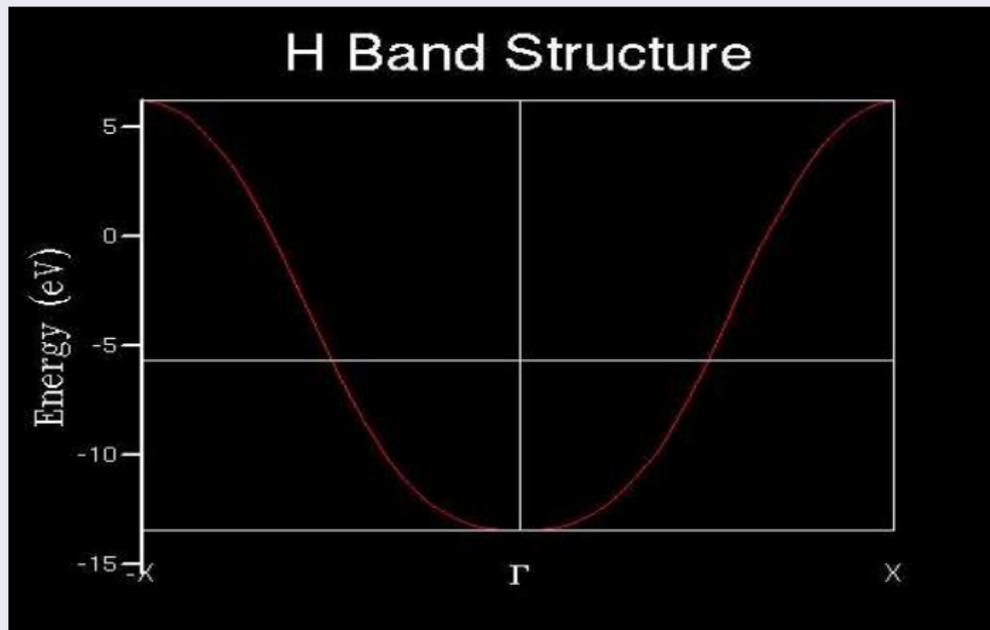
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## Band structure

Number of bands = Number of atomic orbitals



# BLOCK FUNCTION

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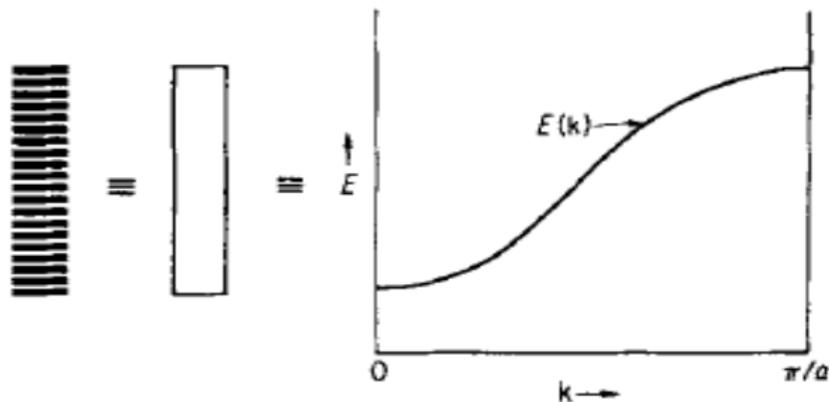
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## Block function

$$\begin{array}{cccc}
 & \text{---} a \text{---} & & \\
 n=0 & 1 & 2 & 3 \\
 \bullet & \bullet & \bullet & \bullet \\
 x_0 & x_1 & x_2 & x_3
 \end{array}$$

$$\psi_k = \sum_n e^{ikna} \chi_n$$

$$k=0 \quad \psi_0 = \sum_n e^{i0} \chi_n = \sum_n \chi_n = x_0 + x_1 + x_2 + x_3 + \dots$$

$$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n = x_0 - x_1 + x_2 - x_3 + \dots$$

# BLOCH'S THEOREM IN 1D

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1D periodic  
potential

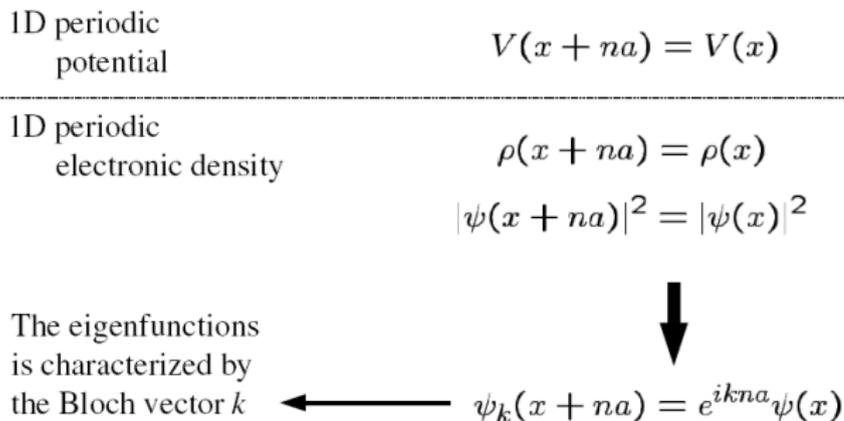
$$V(x + na) = V(x)$$

1D periodic  
electronic density

$$\rho(x + na) = \rho(x)$$

$$|\psi(x + na)|^2 = |\psi(x)|^2$$

The eigenfunctions  
is characterized by  
the Bloch vector  $k$


$$\psi_k(x + na) = e^{ikna}\psi(x)$$

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

FIRST BRILLOUIN ZONE

# FIRST STEP

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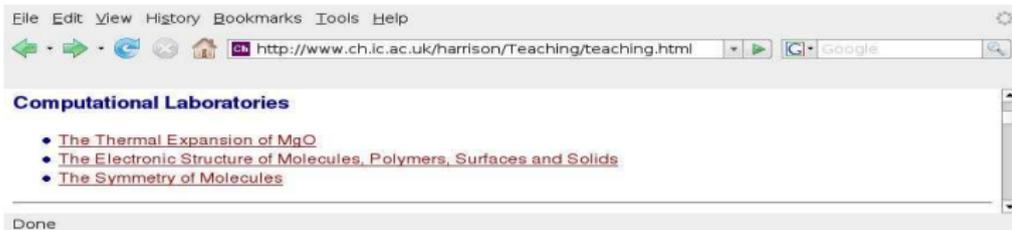
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- 1 Restart the PCs that are running Windows;
- 2 Once you have a black screen with the following line:  
> **boot:**  
Type linux  
> **boot: linux**  
Press Enter
- 3 Use your login and passwd as in Window
- 4 Open firefox: the web browser
- 5 <http://www.ch.ic.ac.uk/harrison/Teaching/teaching.html>



# HOW TO WRITE A REPORT I

by Giulia C. De Fusco

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## Introduction

- the system
- the methodology (theory in use)
- the aims of the exercise
- the tools in use (programs)

## Body of the text

- write it like a scientific paper (well-articulated sentences, NOT a list of two-word answers)
- analyse *critically* obtained data and given answers
- round numerical answers to a specific number of decimal places (i.e. 4)
- add literature/web citations whenever a comparison with experimental data is required
- check spelling

# HOW TO WRITE A REPORT II

by Giulia C. De Fusco

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## Pictures

- max 20
- reasonably sized (NOT one-page sized pictures, but still readable)
- described in caption or in the text

## Graphs

- add labels and units
- add a *critical* comment whenever required (NOT a merely descriptive comment)

## Conclusions

- give a general description of your calculations and your main findings

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THANK YOU!!!