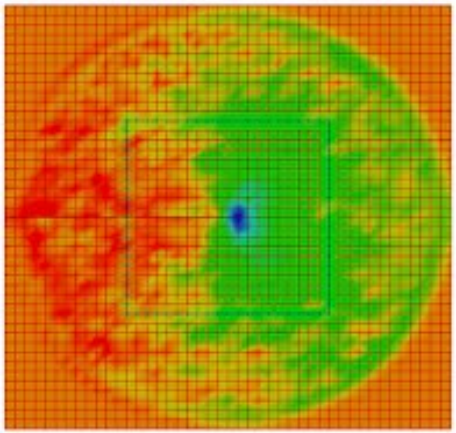
SAND2013-8828P

October 2013-January 2014

ESP900: Atomistic/Molecular Simulation:

Lecture 2: Computational Quantum Mechanics



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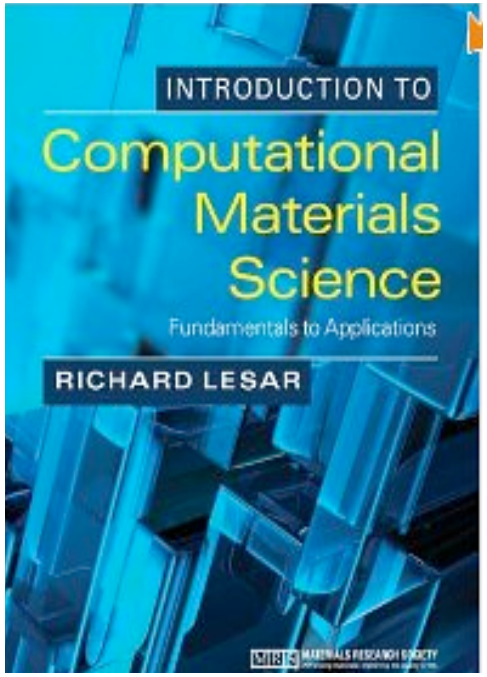
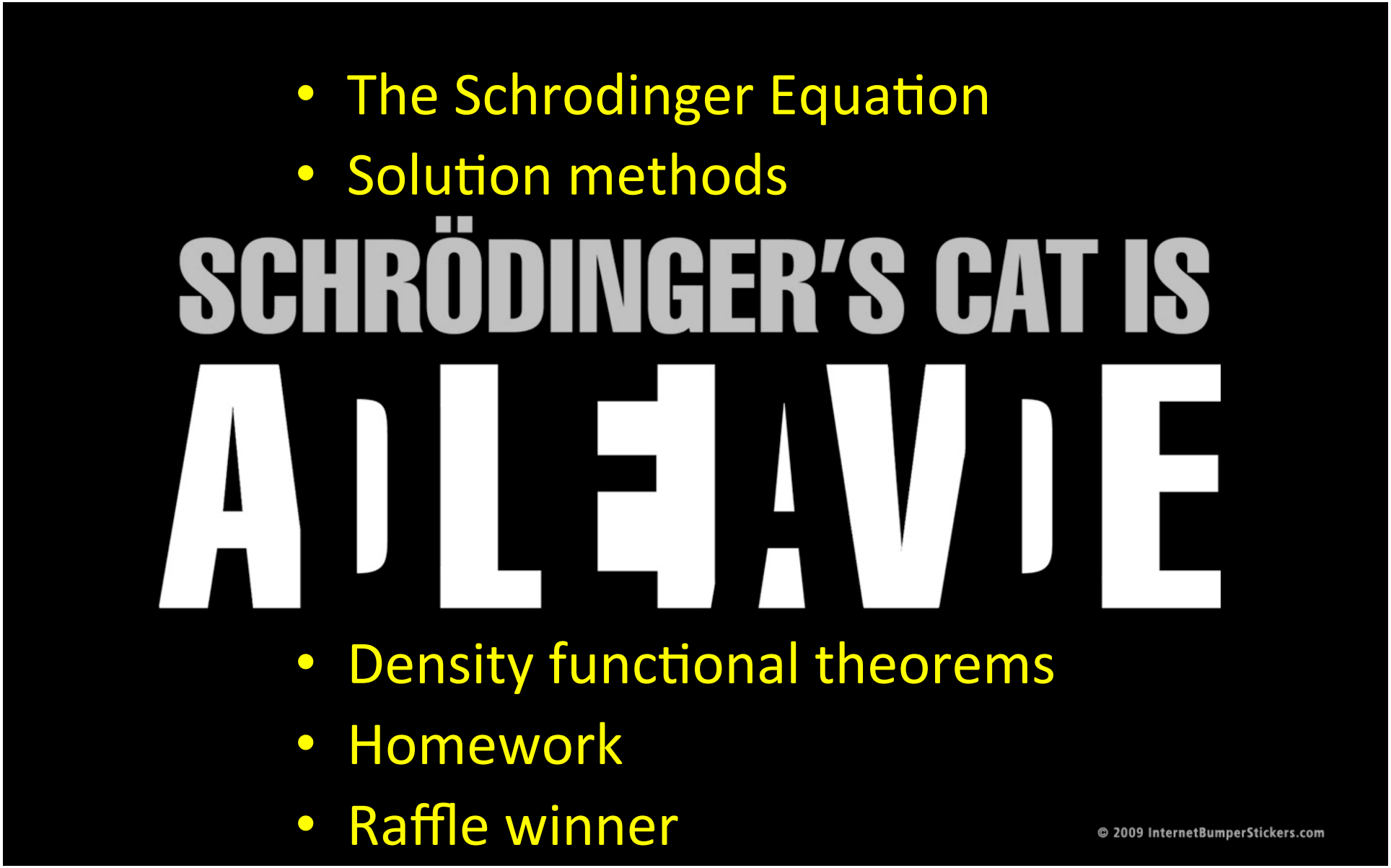


Questions?

- Theory
- Applications
- Programming?
  - E.g. Python
- Scope?
- Logistics?

Lecture 2: Outline

- The Schrodinger Equation
- Solution methods



- Density functional theorems
- Homework
- Raffle winner

Dirac-von Neumann axioms

(something like Newton's postulates for a quantum system)

- The *observables* of a quantum system are self-adjoint operators A on a complex, countably infinite Hilbert space.
- A *state* ϕ of the quantum system is a unit vector of the Hilbert space.
- The *expectation value* of an observable A for a system in a state ϕ is given by the inner product $(\phi, A\phi)$ in the Hilbert space.

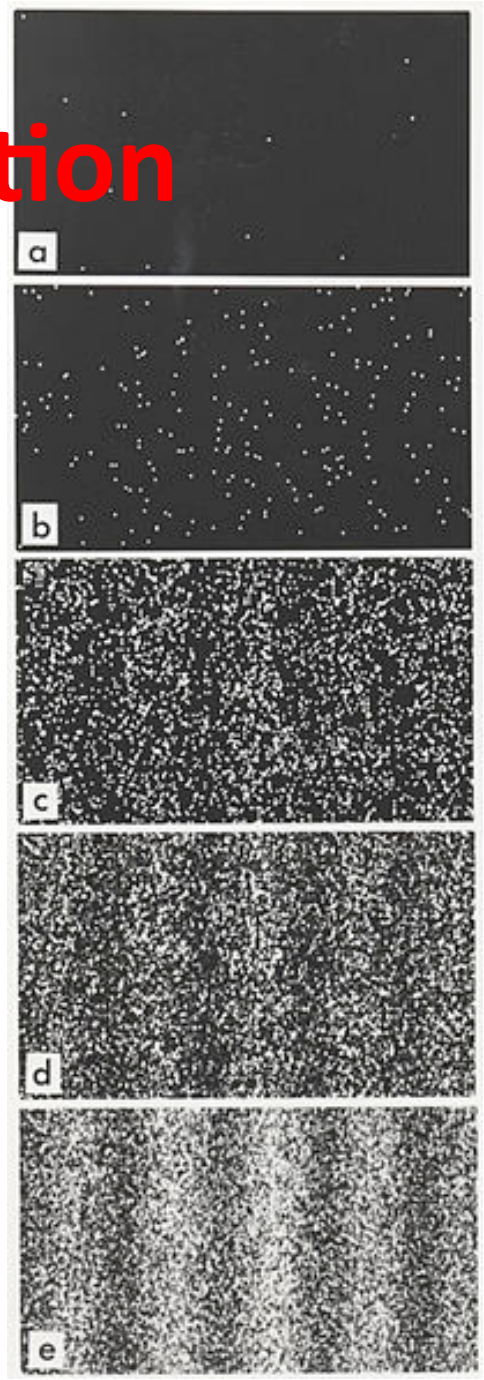
The Schrodinger Equation

$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle$$

- This is essentially a statement of **conservation of energy** in a quantum context
- The Hamiltonian, H, is an *operator* that when acting on the wave function ψ gives the energy, an observable
- Inside the Hamiltonian is an kinetic energy *operator* that uses the momentum *operator*

$$p = -i\hbar\nabla$$

which is straight from Hamiltonian mechanics, i.e. the derivative of the Hamiltonian wrt position



The double slit experiment: An illustration of the wave-particle duality

The Schrodinger Equation

connection to classical mechanics

$$\text{Kinetic Energy} + \text{Potential Energy} = E$$

Classical

Conservation of Energy

$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2 = E$$

Harmonic oscillator example.

Newton's Laws

$$F = ma = -kx$$

Quantum

Conservation of Energy

Schrodinger Equation

$$\frac{p^2}{2m} + \frac{1}{2}kx^2$$

The energy becomes the Hamiltonian operator

$$H\Psi = E\Psi$$

Wavefunction

Energy "eigenvalue" for the system.

In making the transition to a wave equation, physical variables take the form of "operators".

$$p \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad x \rightarrow x$$

$$H \rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

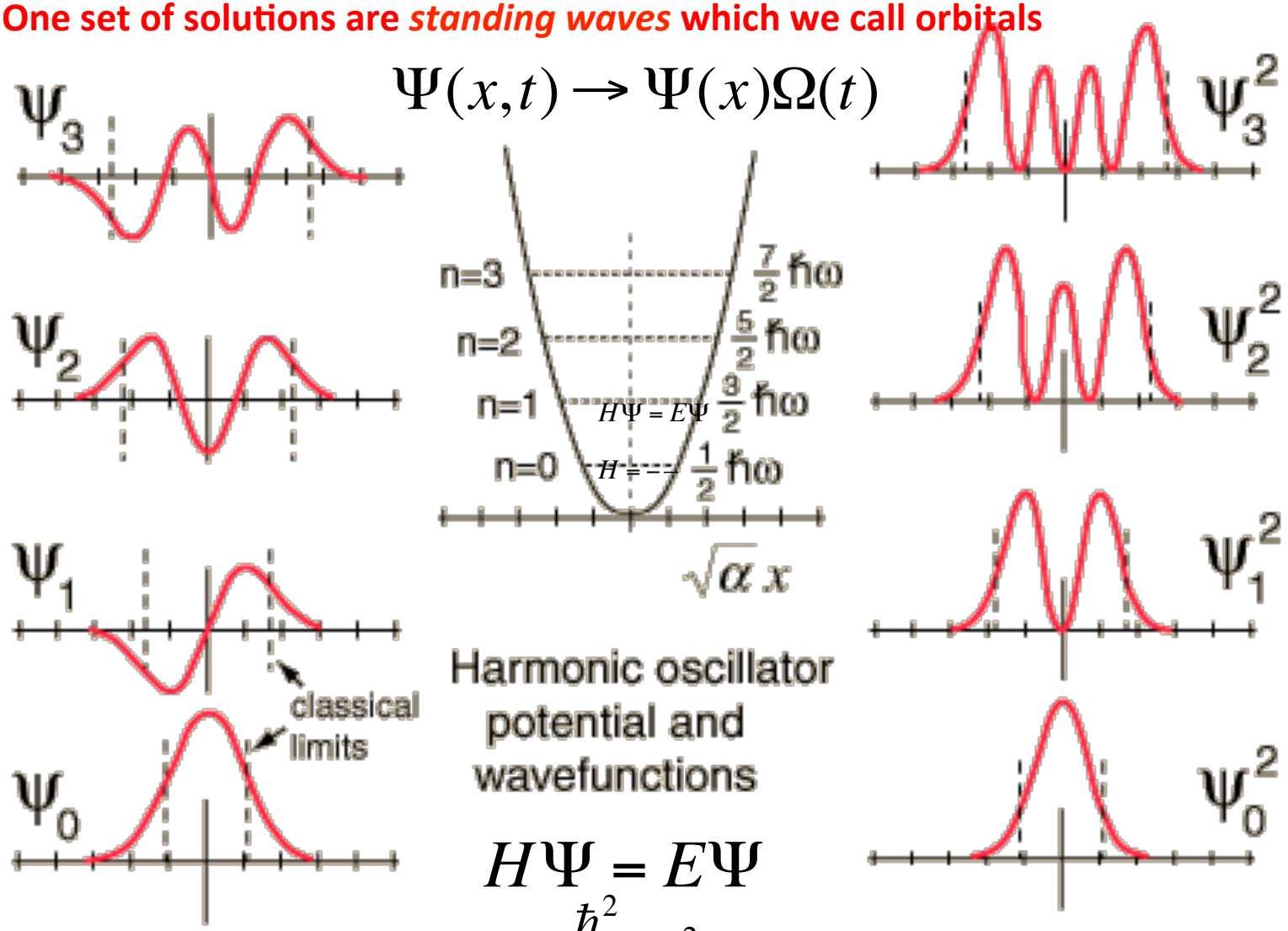
The form of the Hamiltonian operator for a quantum harmonic oscillator.

From hyperphysics

1D oscillator in a harmonic/quadratic well

One set of solutions are *standing waves* which we call orbitals

$$\Psi(x,t) \rightarrow \Psi(x)\Omega(t)$$



Wave functions

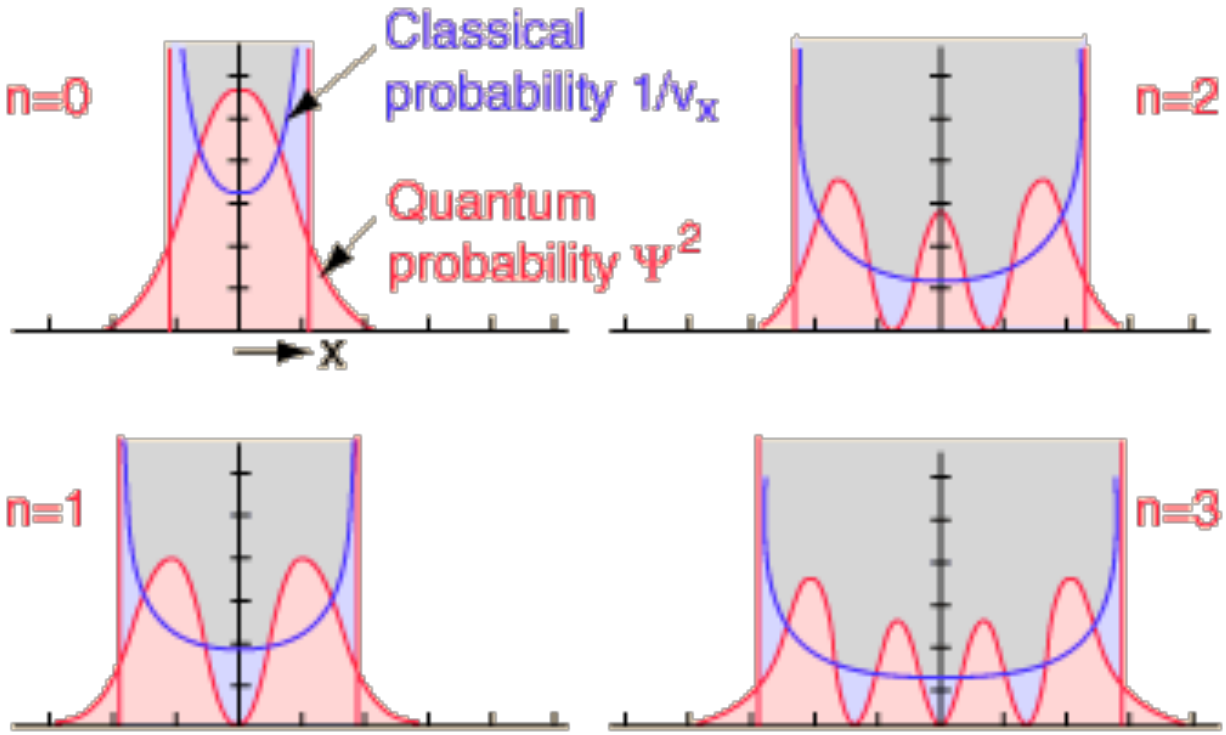
$$H\Psi = E\Psi$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(x)$$

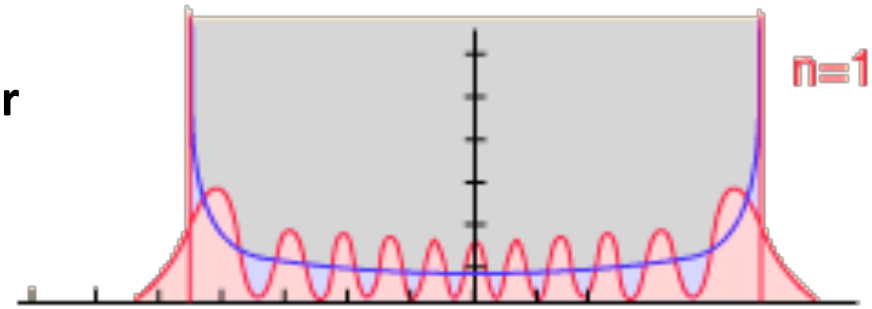
Probabilities

Quantum to Classical

the correspondence principle



As the number of states grows the quantum behavior approaches the classical



Also note that the quantum system doesn't stay in the classical box

The Schrodinger Equation

the *real* Hamiltonian

$$\hat{H} = \frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i,j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

electronic part

$$- \frac{\hbar^2}{2M}\sum_I \nabla_I^2 + \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- The Hamiltonian is composed of **Coulomb interactions**, electron-electron, electron-nucleus, nucleus-nucleus, and **kinetic energy**, *recall the momentum is related to* $\nabla\Psi$
- Locations of the electrons: r_i
- Locations of the nuclei: R_I
- Valence of the nuclei: Z_I

Methods of Approximation/Solution

Recall the *Born-Oppenheimer* approximation: the electrons move and relax much faster than the nuclei, so we are only simulating the electronic structure and in most cases only the valence electrons

- Tight-binding
- Hartree-Fock
- Variational formulation
- Density Functional theory

Tight binding

Tight-binding assumes the superposition of isolated atom wave functions located at each atomic site, i.e. assuming minimal overlap of the wave functions, is a good approximation to the true wave function

$$\psi(\boldsymbol{r}) = \sum_{m,\boldsymbol{R_n}} b_m(\boldsymbol{R_n})\ \varphi_m(\boldsymbol{r} - \boldsymbol{R_n})$$

And uses this ansatz to form Hamiltonian that can be used to calculate electronic band structure (allowed energies)

One artifact is that the energy of the electron is approximately the ionization energy of an electron in an isolated atom

Hartree-Fock

molecular orbitals

The ansatz (trial wave function) as a **product** of single-particle/isolated functions

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2).$$

The problem this guess does not satisfy the **Pauli exclusion principle** (identical electrons can not occupy the same state) that requires antisymetry

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

The Slater **determinant** is the fix for this problem

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv \begin{vmatrix} \chi_1 & \chi_2 & \cdots & \chi_N \end{vmatrix},$$

Unfortunately**, electron correlation i.e. repulsion is neglected for the electrons of opposite spin** (exchange is accounted for)

Variational formulation and Basis functions

- The idea of basis functions comes naturally from the *variational* statement (like the Galerkin method of finite elements) of the Schrodinger problem

$$\langle \Psi \mid H \mid \Psi \rangle = E \langle \Psi \mid \Psi \rangle$$

- A basis set for (approximate) solution of this linear problem is a linear combination of *atomic orbitals* or *Gaussian*-type orbitals,
- Other bases are useful, e.g. for a periodic lattice, *plane waves* are the typical basis

Hohenberg-Kohn theorem

the germ of DFT

Theorem: the energy of a system of electrons in the presence of an external field, due to the nuclei, is given ***exactly*** as a functional of the electron density

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

It allows us to solve for the electron density (a scalar field) instead of 3N wave functions.

The energy is of the form:

$$E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

interaction with nuclei and any other field

The functional (a map from a function to a scalar) F[n] is independent of the external field, but ***unknown.***

Kohn-Sham ansatz

a prescription for practical calculations

The energy is decomposed into terms with known form, e.g. Coulomb interactions, and one (correction) term in particular of unknown form: the ***exchange-correlation*** energy due to electron-electron interactions.

$$E[n] = T_s[n] + \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}d\mathbf{r}' + E_{xc}[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

With this one can solve a system of **fictitious non-interacting** electrons in an effective field (whose density is equal to the true ground state density of the *real interacting* electrons).

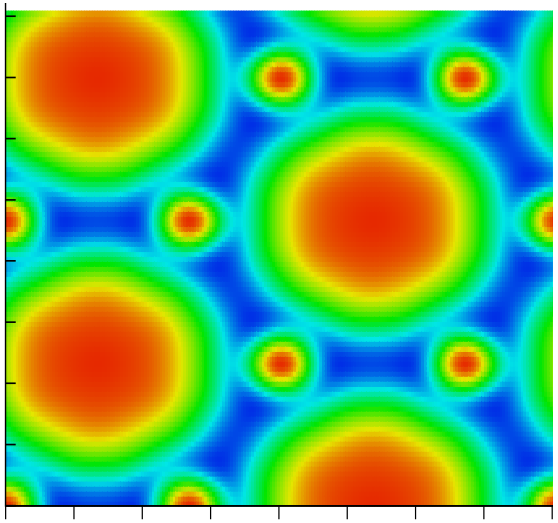
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Here, the potential V is defined as the derivative of E with respect to n

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$$

And the 2nd term is just the solution to the classical Poisson/electrostatics equation

DFT self-consistent algorithm



Guess density $n(\mathbf{r})$

Construct effective potential

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n] + V_{\text{xc}}[n]$$

Solve KS equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

Calculate new density and Compare

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Self-consistent ?

no

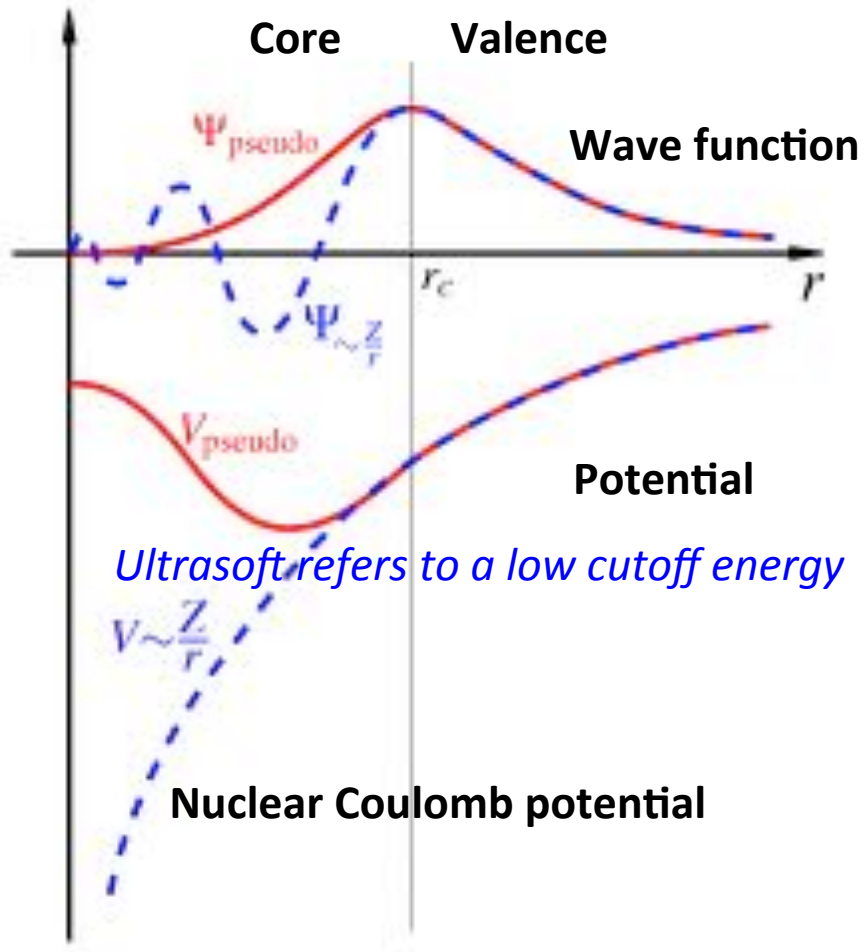
yes

Obtain output: Total energy, Force, Eigenvalues, …

- Converges to the minimum of the **given basis set** i.e. completeness is an issue
- Note the system **energy is not simply the sum of the energie**s associated with the basis

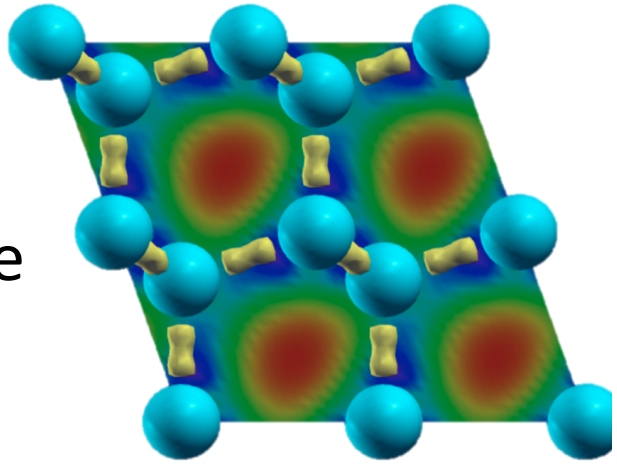
Pseudo potentials

- The core electrons are lumped into an effective ionic potential.
- Only valence electron wavefunctions are computed explicitly
- The oscillations in the actual wave function are due to the requirement that ψ be orthogonal to the wave functions of the core electrons.

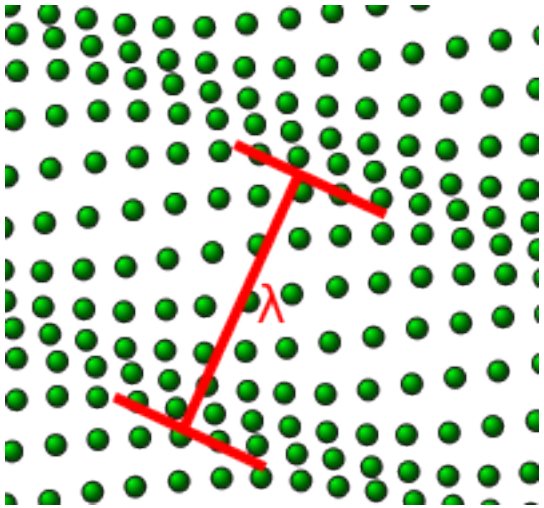


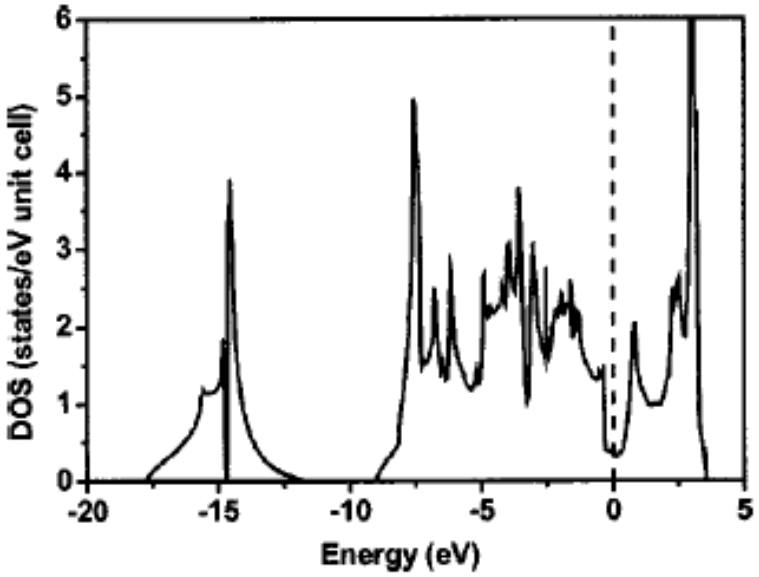
We'll talk about LDA and GGA forms of the exchange-correlation energy & PAW next week

What can DFT calculate ?



- Ground state energy
- Forces on atoms/ equilibrium structure
- Charge density/electronic structure
- Band structure and density of states
- Vibrational properties





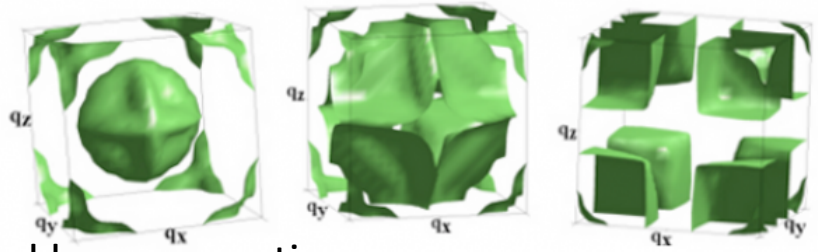
- Bond lengths are accurate within 1-2%.
- Vibrational frequencies are within 5-10%.

QUANTUMESPRESSO

http://www.quantum-espresso.org/tutorials/

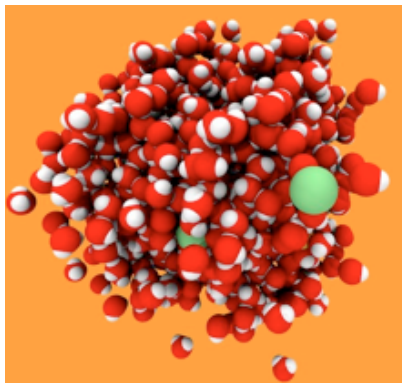
http://www.fisica.uniud.it/~giannozz/QE-Tutorial/

Quantum ESPRESSO is an integrated suite of **open-source** computer codes for electronic-structure calculations and materials modeling at the nanoscale.



It is uses (like VASP)

- density-functional theory,
- plane wave basis,
- pseudopotentials



Maintained by a consortium:

- *Scuola Internazionale Superiore di Studi Avanzati,*
- *Abdus Salam International Centre for Theoretical Physics (Trieste),*
- *CINECA National Supercomputing Center (Bologna),*
- *Ecole Polytechnique Fédérale de Lausanne,*
- *University of North Texas (Dallas)*

QUANTUMESPRESSO build

For a mac laptop:
./configure --disable-parallel FC=g95

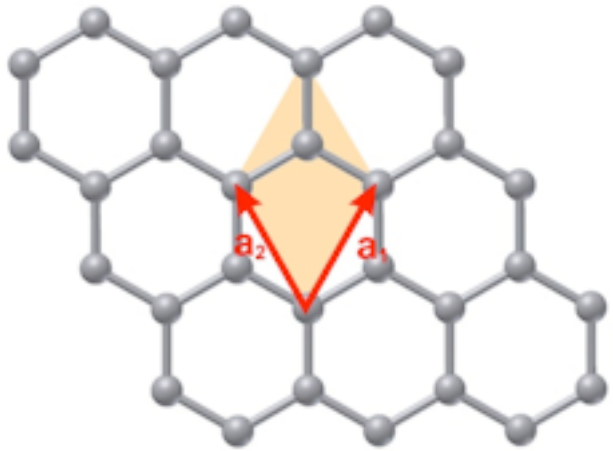
- http://www.quantum-espresso.org/download/
- Click through *download page* on left
- Download espresso-5.0.tar.gz
- Tar –xvzf espresso-5.0.tar.gz
- Cd espresso-5.0
- ./configure
- Make all

May need:

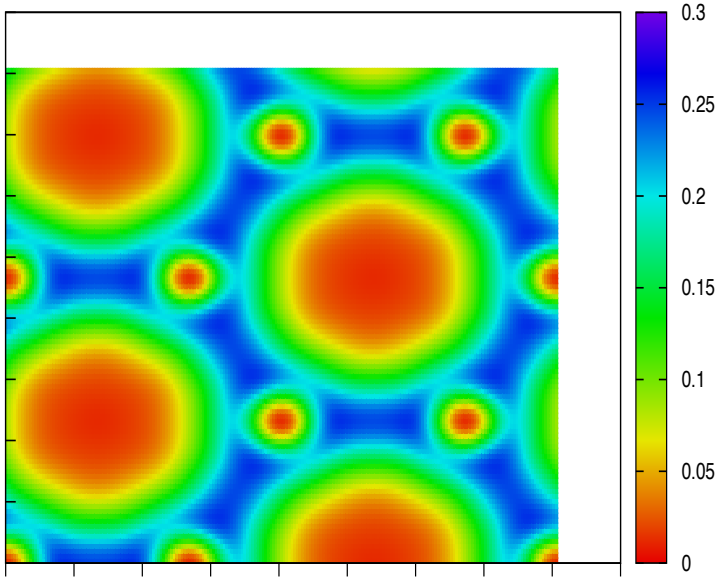
- **Mpi (e.g. openmpi)**
- **Fortran and c compiliers (e.g. gcc with g++ & gfortran)**

“Homework”

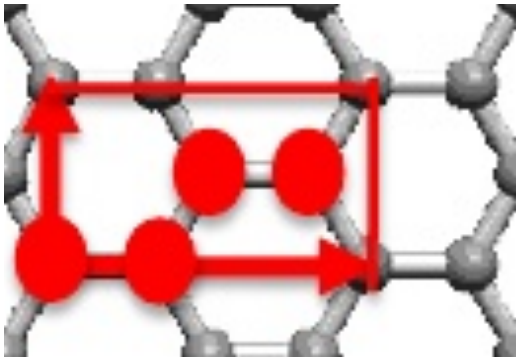
- Calculate the ground state (zero temperature, equilibrium) electron density of graphene using quantum espresso
- Graphene is a sheet of carbon arranged in hexagons that tile a plane
- The C-C distance is about 1.42 Angstroms
- What is the unit cell i.e. the smallest repeating unit? *Trick question* there is more than one depending if you allow the cell to be non-orthogonal



INPUT




```
&control
  calculation='scf'
  restart_mode='from_scratch',
  prefix='graphene'
  pseudo_dir = './',
  outdir='./tmp/'
&system
  ibrav= 8   orthorhombic
  a = 4.2750
  b = 2.4682
  c =10.0000
  nat= 4
  ntyp= 1
  ecutwfc =18.0
&electrons
  conv_thr =  1.0d-8
  mixing_beta = 0.7
```

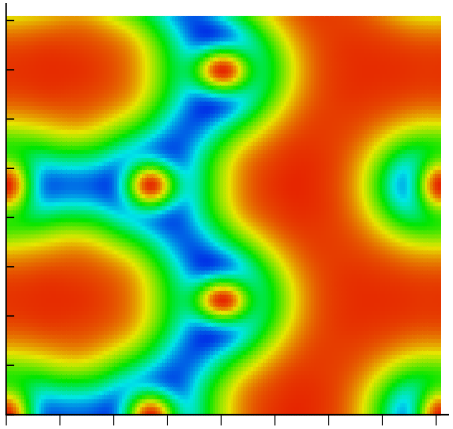


```
ATOMIC_SPECIES
 C  12.0107  C.pz-rrkjus.UPF

ATOMIC_POSITIONS angstrom
C 0.0000 0.0000 0.0
C 1.4250 0.0000 0.0
C 2.1375 1.2341 0.0
C 3.5625 1.2341 0.0

K_POINTS automatic
16 16 1 0 0 0
```

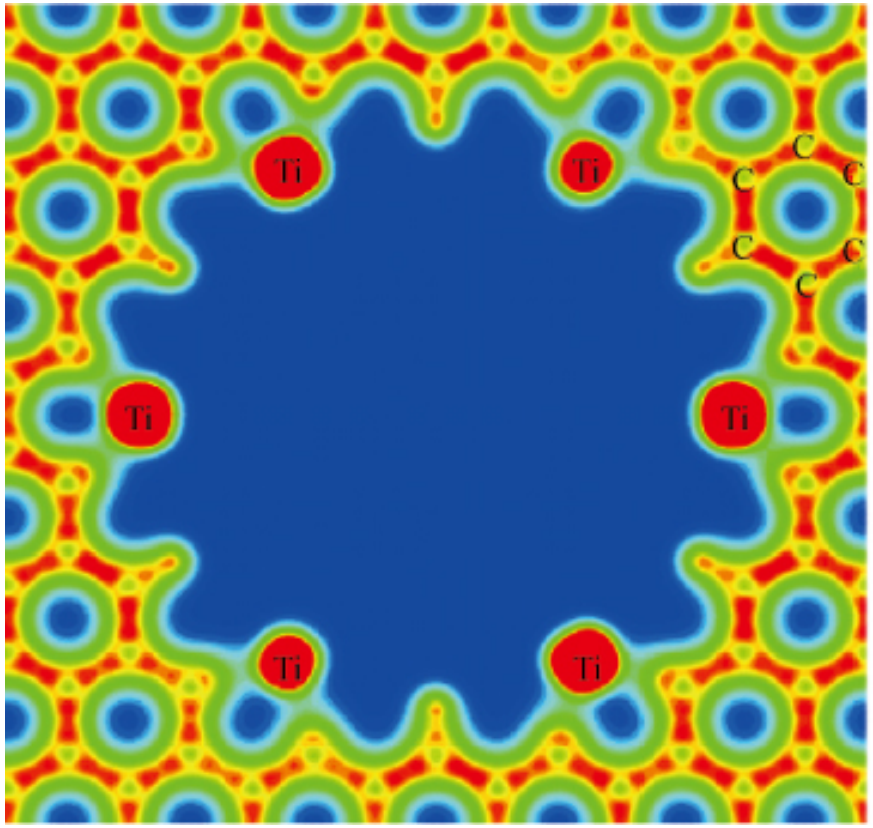
BONUS

- Determine the out-of-plane spacing sufficient to isolate the graphene from its periodic images (*hint* change ***c*** and observe the charge density)

- Create a defect in the structure (e.g. remove one nucleus) and recompute the electron density



- Relax the structure using ground-state energy minimization (*relax* or *vc-relax*)



Lecture 3

Week 2 : Computational Quantum Mechanics

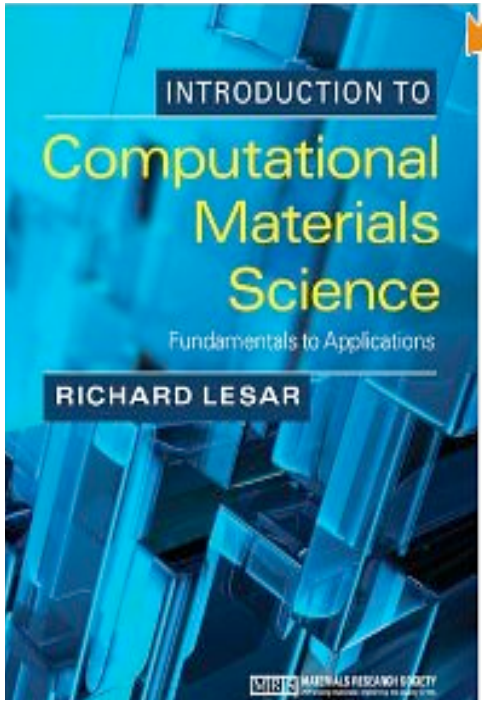
- Methods and approaches
- Schrödinger Equation – theoretical aspects and implementation details
- Electronic structure calculations – basis sets and properties
- *Homework*: Electronic structure around a defect

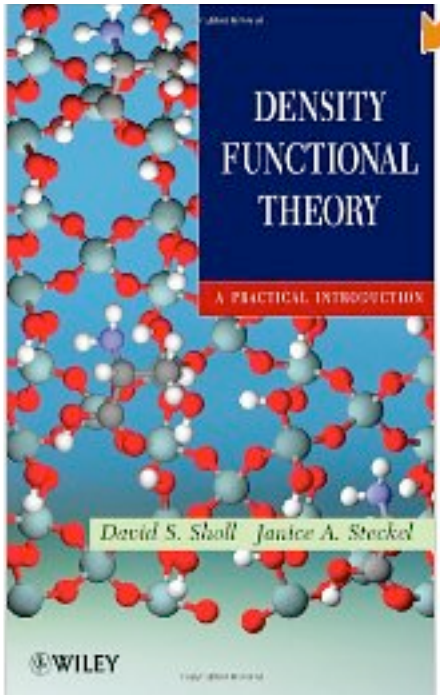
Week 3 : **Application of Density Functional Theory**

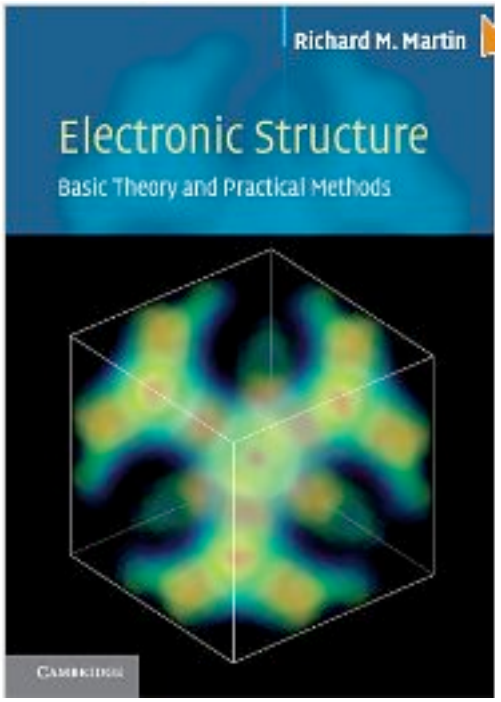
- Solution of Kohn-Sham equations and exchange-correlation functionals
- Brief survey of more advanced methods (coupled-cluster, perturbation theory, configuration interaction)
- *Homework*: Calculation of separation energy between a metal substrate & graphene

Reading Suggestions for Lec. 3

- Chapter 4 of LeSar
- http://en.wikipedia.org/wiki/Density_functional_theory
- Chapter 3 of Schol
- Chapter 10, 6 of Martin







Raffle

- Phil Dreike
- Anton Sumali
- Jeff Kay
- Tom Laub

- The winner is…..