

Introduction to DFT and Quantum Espresso

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(slides courtesy of Shobhana Narasimhan)

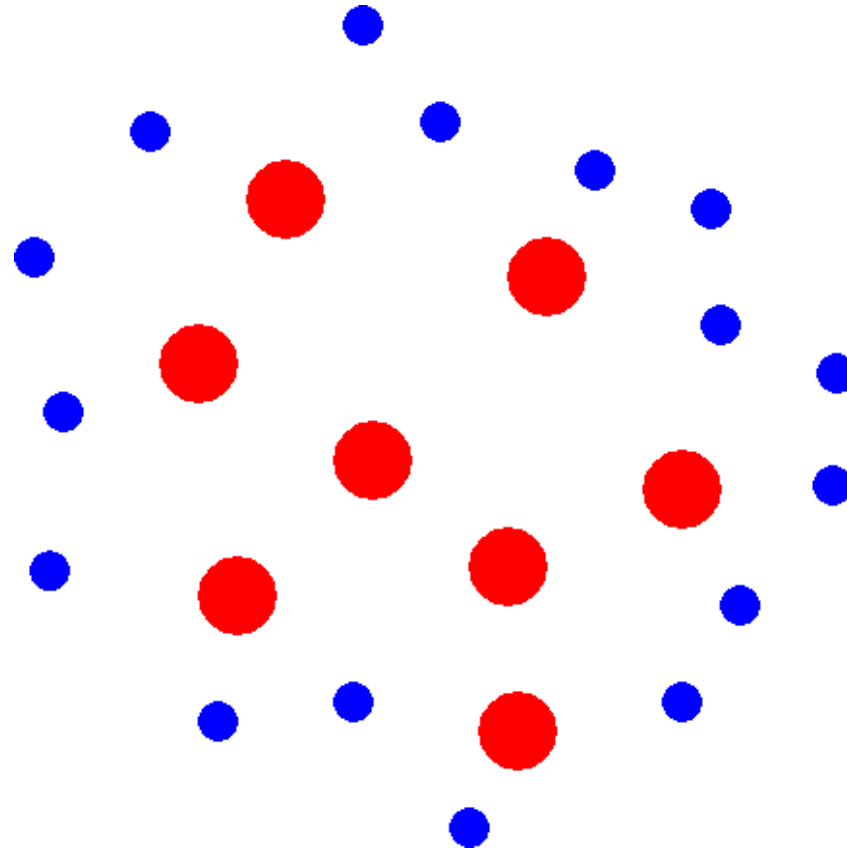


The Abdus Salam
**International Centre
for Theoretical Physics**



Monday, September 3rd, 2012

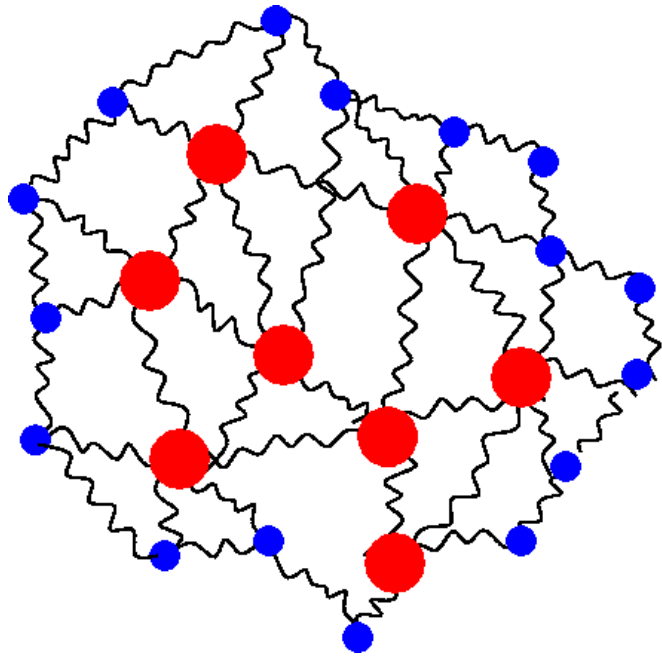
Computational Atomistic Materials Science:



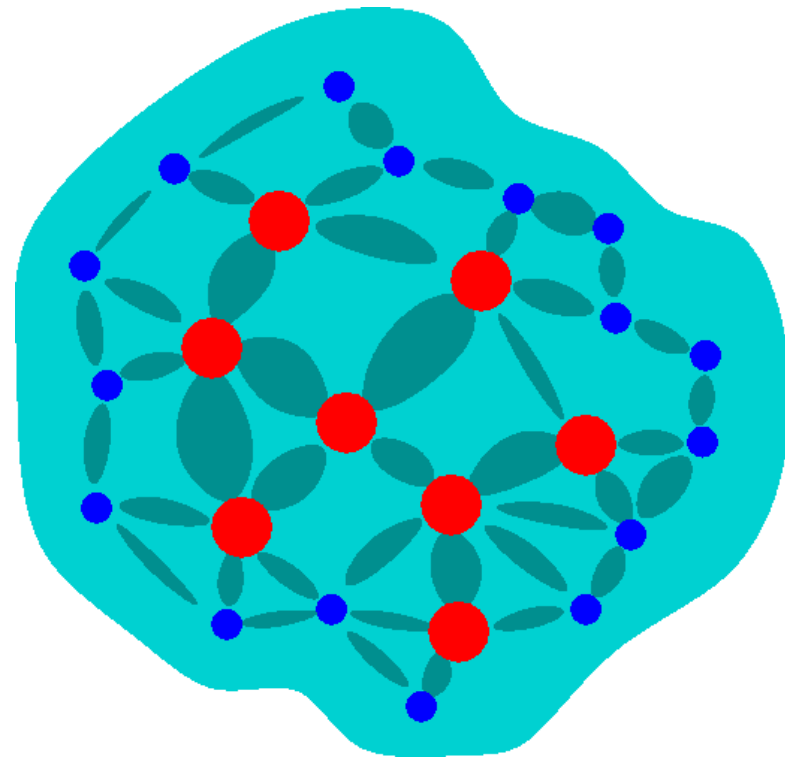
Treat nuclei as classical particles
(Born-Oppenheimer approx.)

Computational Atomistic Nanoscience: Two approaches

Classical Models

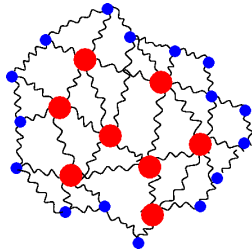


Quantum models



Computational Atomistic Nanoscience: Two approaches

Classical Models

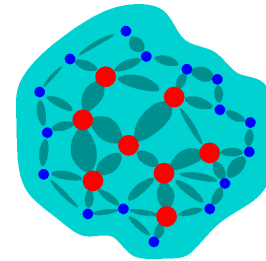


Can treat very large systems

Problems with “chemistry”

Treat easily 10^4 - 10^5 atoms

Quantum models



Can treat relatively small systems

Chemical bonding well described

Treat ≈ 100 atoms

What is DFT?

- A very successful approach to calculating the (ground state) properties of many-electron systems from first principles
- Features:
 - *Ab initio* (only I/P = Z, A)
 - Quantum Mechanical
 - Numerical
 - Approximate (could be exact, in principle?)



Nice things about DFT

- *Ab initio*, no empirical information
- Predictive power
- Very accurate for most materials (errors typically < few %)
- Can calculate lots of properties of scientific / technological interest
- Nobel Prize to Walter Kohn, 1998.





Not-so-nice things about DFT

- Computationally intensive.
- Therefore (currently) limited to small length / time scales.
- For computational reasons, introduce further approximations, might not always work....
- Not very successful in strongly-correlated systems (e.g., high- T_c superconductors).
- Problems with van der Waals interactions, etc.

Outline of talk



- How to set up the problem
 - Hohenberg-Kohn theorem
 - Kohn-Sham equations
- How to solve the problem
 - Numerical techniques and approximations
- What one gets out of calculations

I. How to set up the problem



The Basic Problem

- Many-electron system:

$$N_n \text{ nuclei } \{Z_i, \mathbf{R}_i\} + N \text{ electrons } \{r_j\}$$

- Interact via Coulomb interaction
- Examples: atoms, molecules, condensed matter systems.
- Want to solve Many-electron Schrödinger Equation:

$$H\Psi(r_1, r_2, \dots, r_N) = E \Psi(r_1, r_2, \dots, r_N)$$

- Solutions must also be properly antisymmetrized
(to satisfy Pauli Exclusion Principle)
- Don't know how to solve!!

How to deal with many-particle Schrödinger Eq.??



Many-particle Schrödinger Equation

Many-body Theory

- Retain many-body nature
- Use model Hamiltonian (e.g., Ising model, Hubbard model)
- Use suitable parametrization
- Solve numerically / analytically

Density Functional Theory

- Map onto 1-particle Schrödinger Eq.
- Exact, in principle
- Approximate, in practice
- No free parameters
- Solve numerically

Hohenberg-Kohn Theorem - I

- [Phys. Rev. 136 B 864 (1964)]

- Density as basic variable:

- Collection of particles in external potential $v(r)$

- Usually:

$v(r)$ $\xrightarrow[\text{Schrödinger Eq.}]{\text{Solve many-particle}}$ $\Psi_{\text{many-particle}}$

all properties
of system

$$n(r) = \Psi^* \Psi$$

- Hohenberg & Kohn showed (simple 3-line proof!)

$n(r)$ $\xrightarrow[\text{exists}]{\text{1-1 mapping}}$ $v(r)$ \dashrightarrow all properties of system

Variational Formulations

- When solving various complicated problems, it might be possible to formulate the problem in terms of the **calculus of variations** (e.g., Fermat's principle in optics, Rayleigh-Ritz variational principle in Quantum Mechanics).
- Typically, one guesses a solution of a given form (**ansatz**), with some free parameters that have to be determined.
- The value of the parameters is determined by **minimizing** some quantity.
- There are **sophisticated numerical techniques** available for minimization problems.
- Solution may be **exact / approximate** (depending on ansatz).

Hohenberg-Kohn Theorem - II

- Variational Principle:

There exists a universal functional $F[n]$, such that:

- $E_v[n] \equiv F[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$ has its minimum value when
 $n(\mathbf{r}) = n_{GS}(\mathbf{r}) \rightarrow$ density of system in ground state
- $E_v[n = n_{GS}] = E_{GS}^{tot} \rightarrow$ total energy in ground state

- Note: only proof of existence of $F[n]$; we don't know form. 😞

- IF $F[n]$ were known...

... then have converted many-electron pbm. to one of
minimizing a functional $\rightarrow n_{GS}(\mathbf{r}), E_{GS}^{tot}$ 😊

What have we achieved? - I

N-electron Schrödinger Equation

Solve for $\Psi_{GS}(r_1, r_2, \dots, r_N)$

maps exactly

if $F[n]$ known

Variational Principle

Minimize $E_v[n]$ to find n_{GS}, E_{GS}

Density
Functional
Theory

$$\int \delta n(\mathbf{r}) \left\{ \frac{\delta E_v[n(\mathbf{r})]}{\delta n(\mathbf{r})} \right\} d\mathbf{r} = 0$$

What would we want now?

- Approximation for $F[n]$
- Ansatz for form of $n(\mathbf{r})$
- Good prescription for minimizing $E_v[n]$ wrt variations in $n(\mathbf{r})$
OR an alternative to this.

$F[n]$: non-interacting & interacting systems

- Recall:

$$E_v[n] \equiv F[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

- For a **non-interacting** system,

$$F[n] = T_0[n]$$

External potential
(e.g., due to nuclei)

- For an **interacting** system,

$$F[n] \equiv T_0[n] + \frac{1}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n]$$

Hartree [Coulomb]

Exchange-Correlation

$F[n]$: non-interacting & interacting systems

- Recall:

$$E_v[n] \equiv F[n] + \int v(r) n(r) dr$$

- For a **non-interacting** system,

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- For an **interacting** system,

$$F[n] \equiv T_0[n] + \frac{1}{2} \iint \frac{n(r) n(r')}{|r - r'|} dr dr' + E_{xc}[n]$$

Hartree [Coulomb]

Exchange-Correlation

External potential
(e.g., due to nuclei)

Hartree potential

$$V_H(r) = \int \frac{n(r')}{|r - r'|} dr'$$

Kohn-Sham Equations

- [Phys. Rev. 140 A 1133 (1965)]

	Non-interacting system	
Using H-K theorem	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$	

Kohn-Sham Equations

- [Phys. Rev. 140 A 1133 (1965)]

	Non-interacting system	
Using H-K theorem	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$	
Solving Schrödinger Eq.	$\left[-\frac{1}{2} \nabla^2 + v(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$	

Kohn-Sham Equations

- [Phys. Rev. 140 A 1133 (1965)]

	Non-interacting system	Interacting system
Using H-K theorem	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + V_H(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$
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Kohn-Sham Equations

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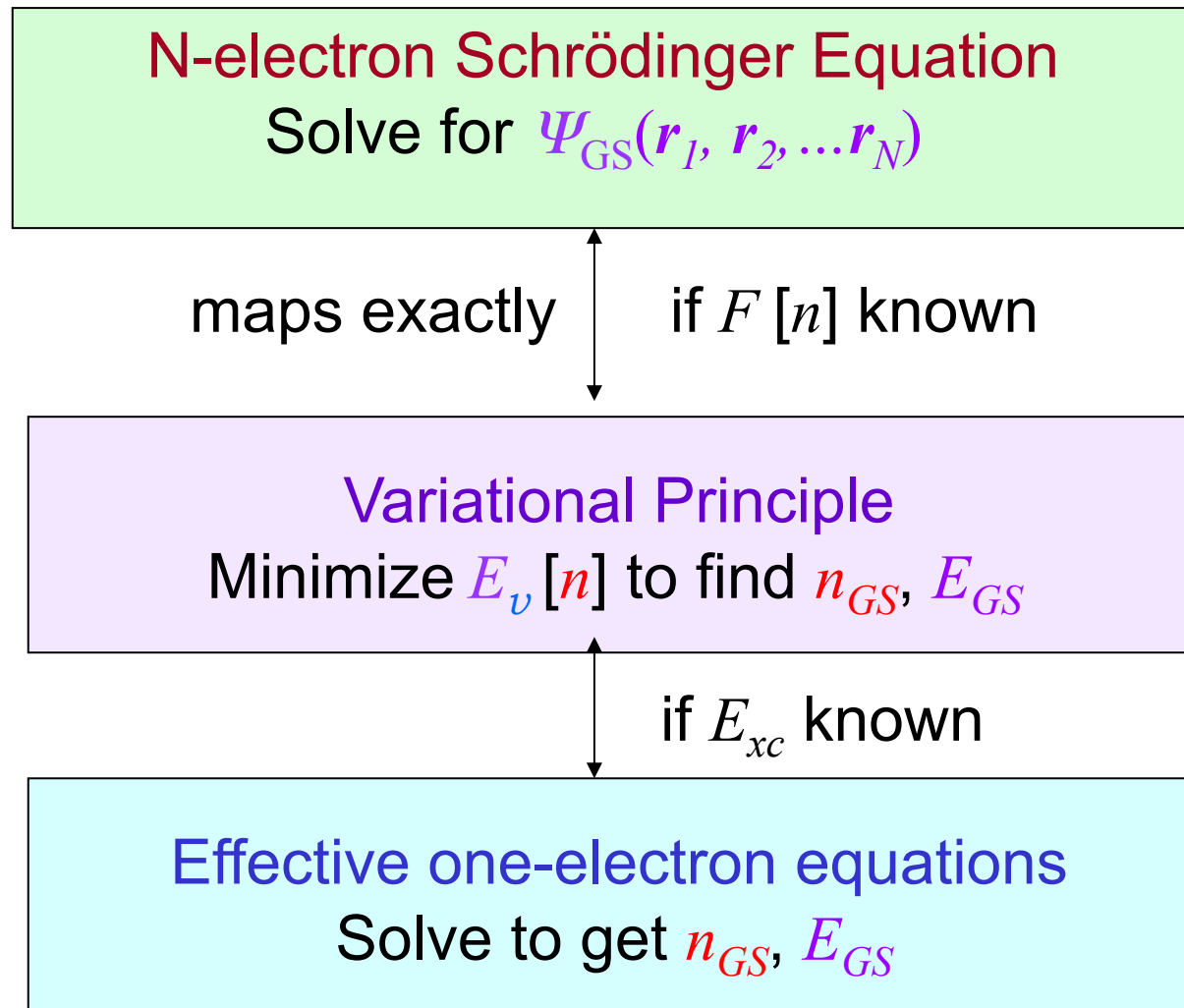
	Non-interacting system	Interacting system
Using H-K theorem	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + V_H(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$
Solving Schrödinger Eq.	$[-\frac{1}{2}\nabla^2 + v(\mathbf{r})] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$	$[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$

Kohn-Sham Equations

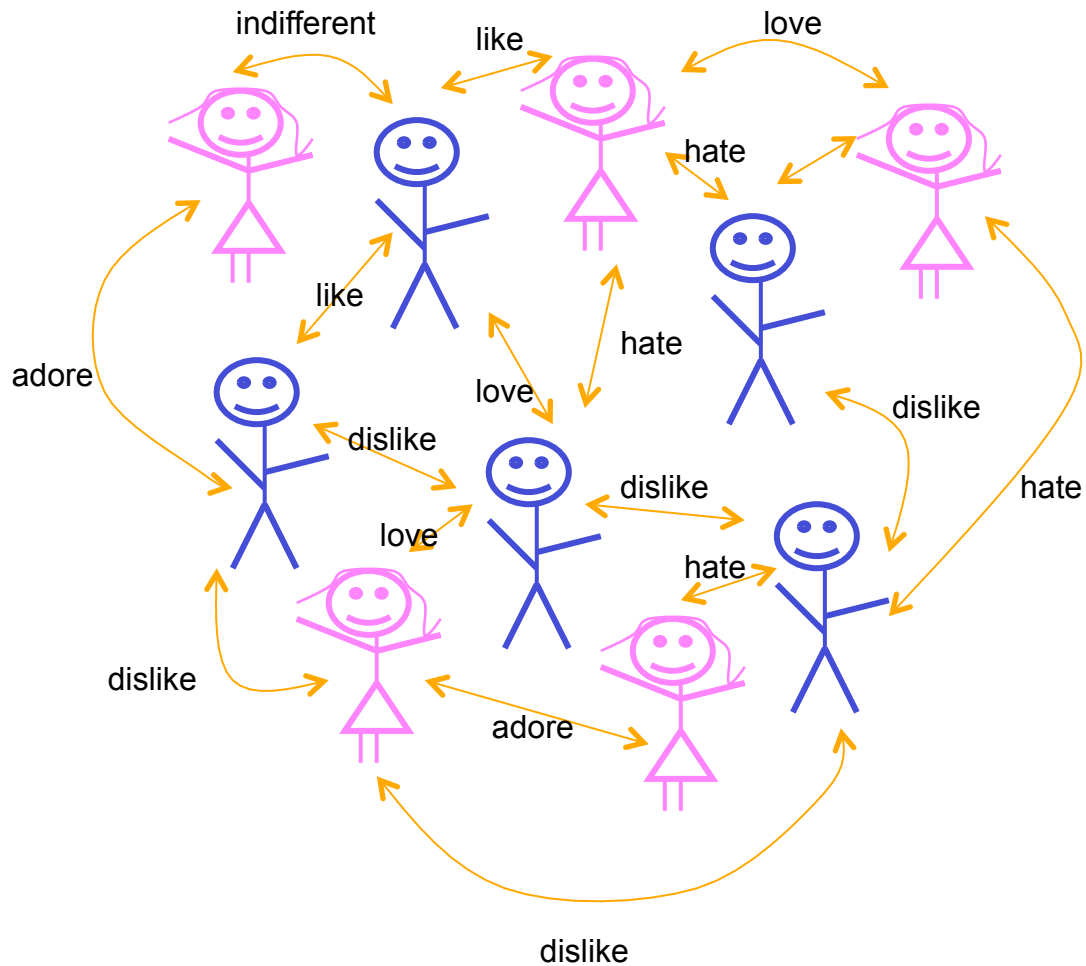
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	Non-interacting system	Interacting system
Using H-K theorem	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$	$\int \delta n(\mathbf{r}) \left\{ \frac{\delta T_0}{\delta n} + V_H(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n} + v(\mathbf{r}) \right\} d\mathbf{r} = 0$
Solving Schrödinger Eq.	$[-\frac{1}{2}\nabla^2 + v(\mathbf{r})] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$	<p>Kohn-Sham equations</p> $[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$ <p>(1-electron eqns. for interacting system!)</p>

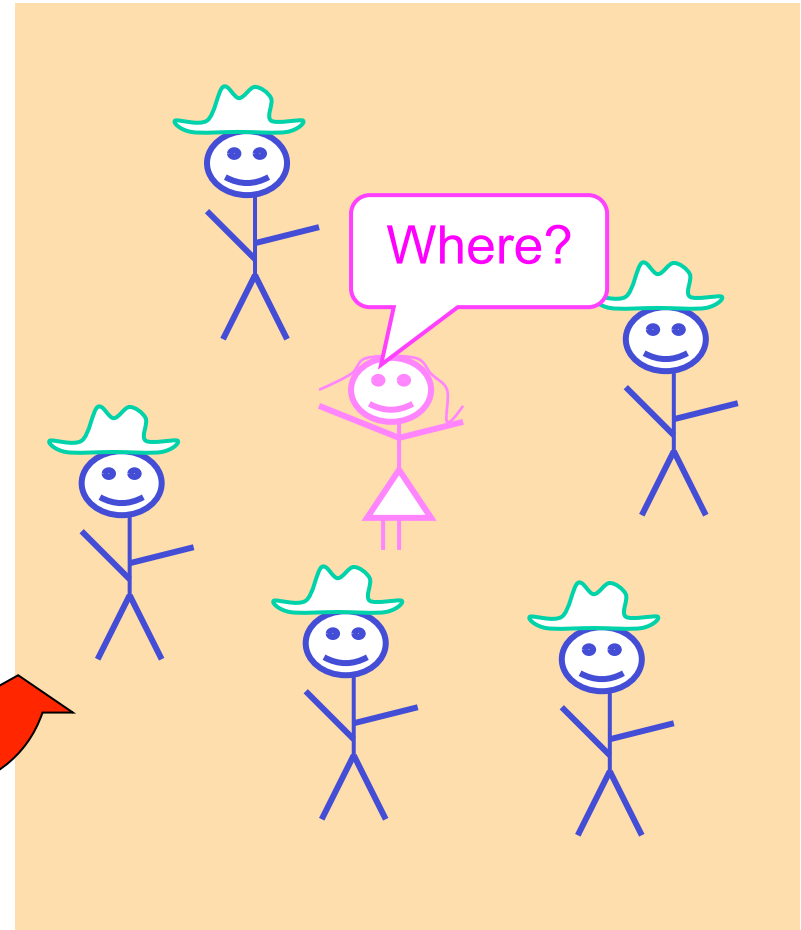
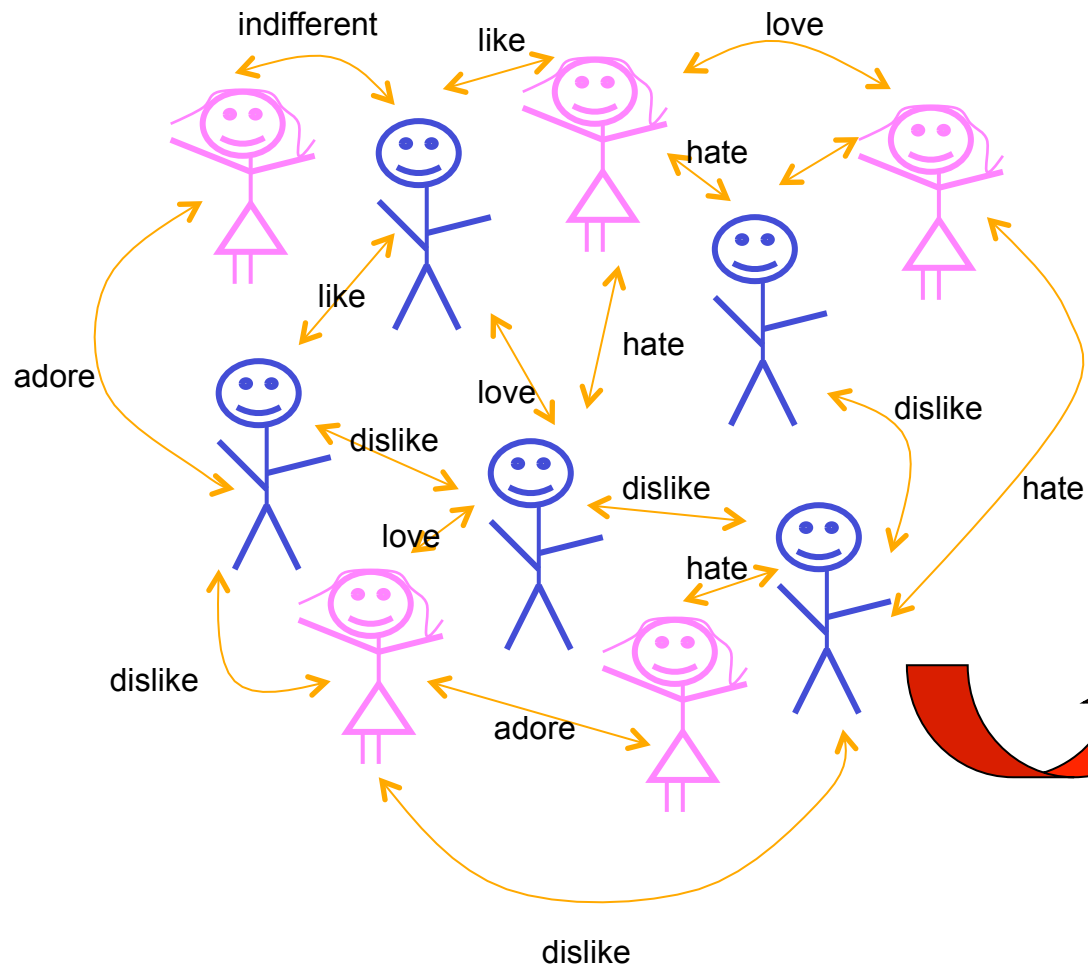
What have we achieved? - II



What have we achieved? - III



What have we achieved? - III



II. How to Solve the Problem



Determining K-S Hamiltonian

Want to solve:

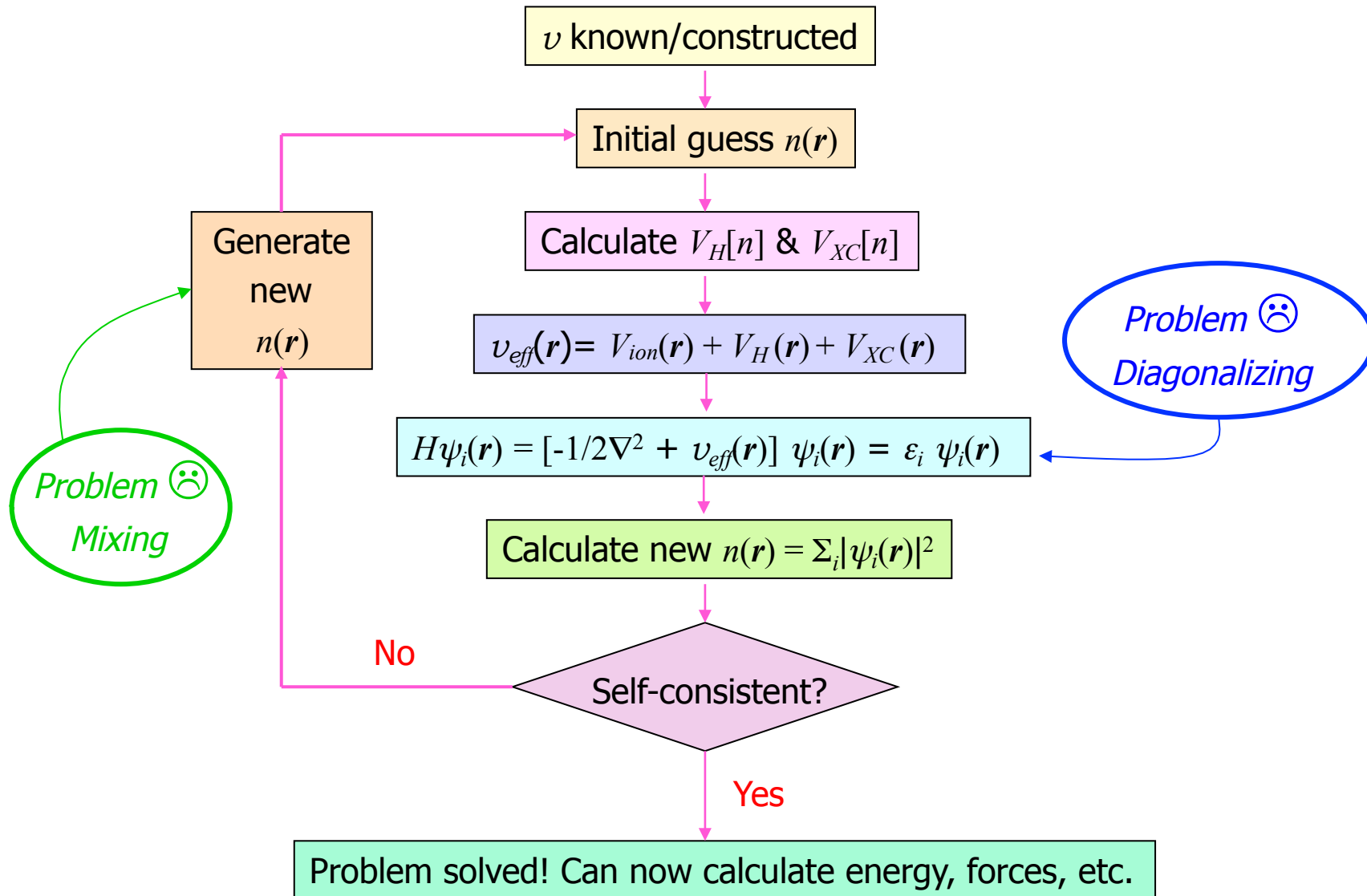
$$[-\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r})] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where

$$v_{eff}(\mathbf{r}) = V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})] + v(\mathbf{r})$$

- Problem 1: $V_H, V_{xc} \leftarrow n \leftarrow$ solution of problem!
- Problem 2: Form of $V_{xc}[n]$ not known....

Self-Consistent loop



Initial Choice of $n(\mathbf{r})$

Various possible choices, e.g.,:

- Converged $n(\mathbf{r})$ from a closely related calculation (e.g., one where ionic positions slightly different).
- Superpositions of atomic densities.
- Approximate $n(\mathbf{r})$, e.g., from solving problem in a smaller/different basis.
- Random numbers.

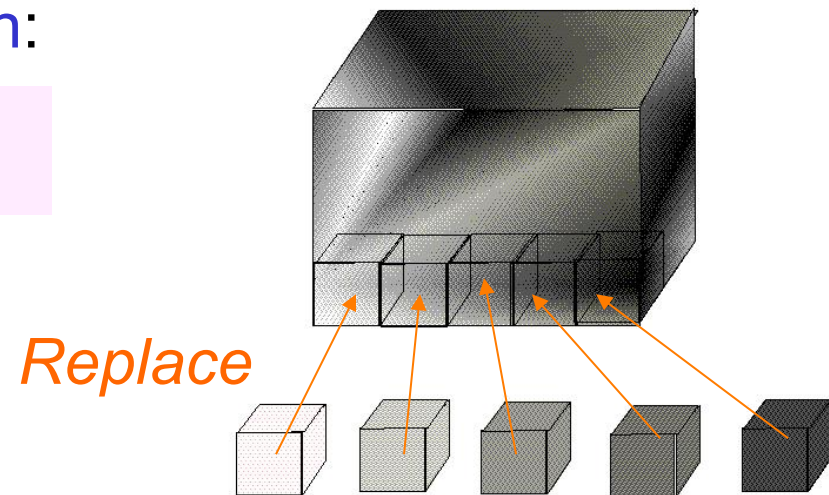


Exchange-Correlation Potential

- $V_{xc} \equiv \delta E_{xc} / \delta n$ contains all the many-body information.
- Known [numerically, from Quantum Monte Carlo ; various analytical approximations] for **homogeneous electron gas**.
- **Local Density Approximation:**

$$E_{xc}[n] = \int n(\mathbf{r}) V_{xc}^{\text{HOM}}[n(\mathbf{r})] d\mathbf{r}$$

Surprisingly successful!



- **Generalized Gradient Approximation(s):** Include $\nabla n(\mathbf{r})$

Choice of Basis

- Can choose to expand wavefunctions in a **basis** set:

$$\psi_i(\mathbf{r}) = \sum_{\alpha} c_{i\alpha} \mathbf{f}_{\alpha}(\mathbf{r})$$

- Eigenvalue equation then becomes:

$$\sum_{\beta} H_{\alpha\beta} c_{i\beta} = \epsilon_i c_{i\alpha}$$

- Have to diagonalize a matrix of size $N_b \times N_b$
- Various possible **choices of basis**:
 - Plane waves
 - Localized sets (atomic orbitals, Gaussians, etc.)
 - Choose so that calculation is fast, accurate, convenient.

Pseudopotentials

- **Frozen core**: remove core-electron degrees of freedom.
- Valence electrons see a **weaker potential** than the full Coulomb potential.
- **Further tailor this potential** so that wavefunctions behave 'properly' in region of interest, yet computationally cheap.

(Numerical) Advantages when solving Kohn-Sham eqns.:

- Have to solve for **fewer eigenvalues**.
- When solving using a basis (especially plane waves), **basis size drastically reduced** (smaller matrices to diagonalize).
- No Coulomb singularity (cusp in wavefunction) at origin.

Disadvantages:

- Can lose accuracy, especially due to **transferability** issues.

Pseudopotentials: An analogy!

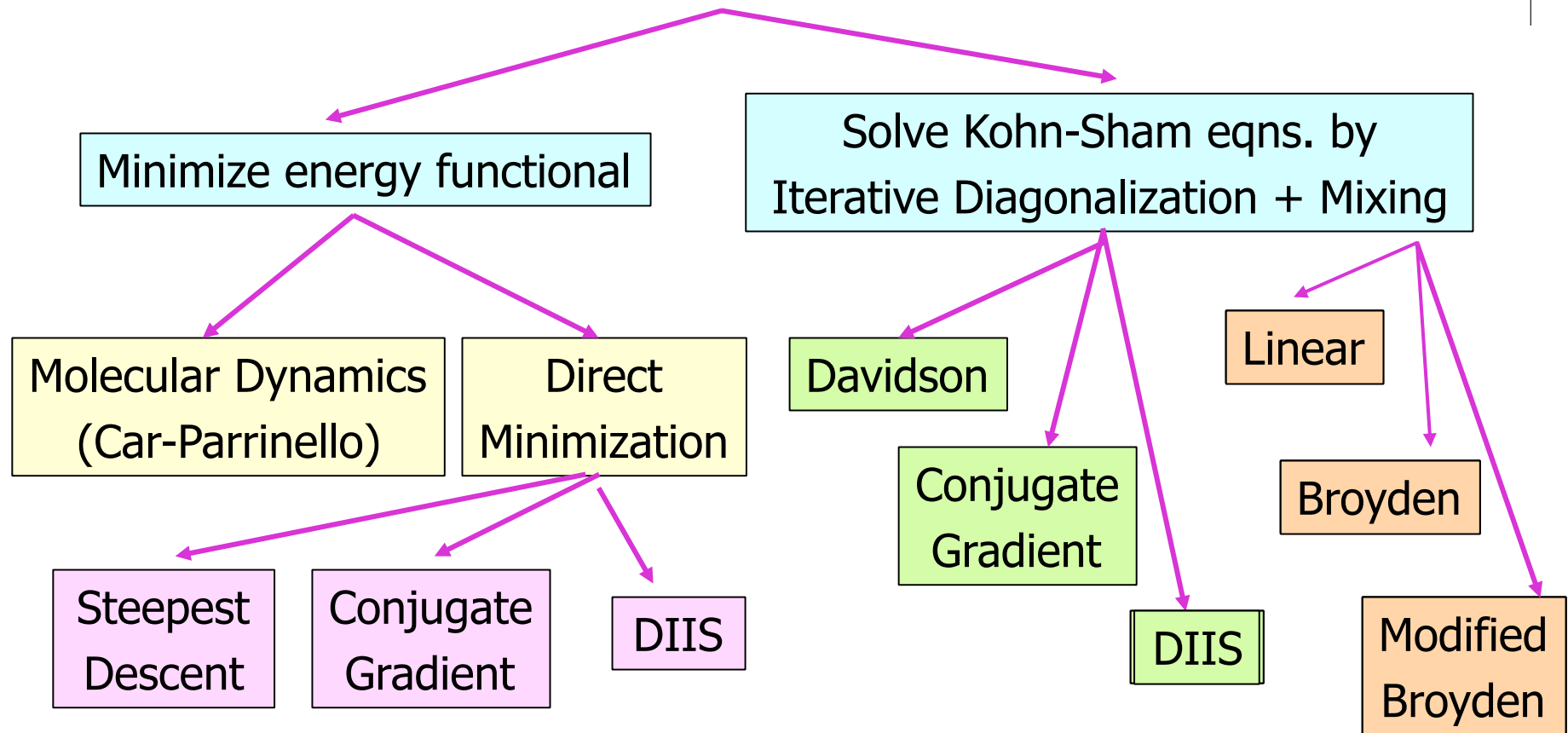
- “Dummy cops” used by many law-enforcement agencies!
- Stick a mannequin in uniform by the highway ... if it looks like a cop, it works like a cop!
- Don't care about internal structure as long as it works right!
- But cheaper!!
- Obviously it can't reproduce all the functions of a real cop, but **should be convincing enough** to produce desired results....



Numerical Techniques

- Lots of **further tricks** to **speed up** calculations....
- Replace exact diagonalization by **iterative diagonalization / minimization**.
- Map onto fictitious molecular dynamics (**Car-Parrinello**).
- **Mixing** techniques when updating in iterative SCF loop.
- **Fast Fourier transforms** to go back and forth between real and reciprocal space.

Fast, new(ish) methods for iterative solution



(and lots of 'etc.'s scattered plentifully about!)

III. What can we calculate?

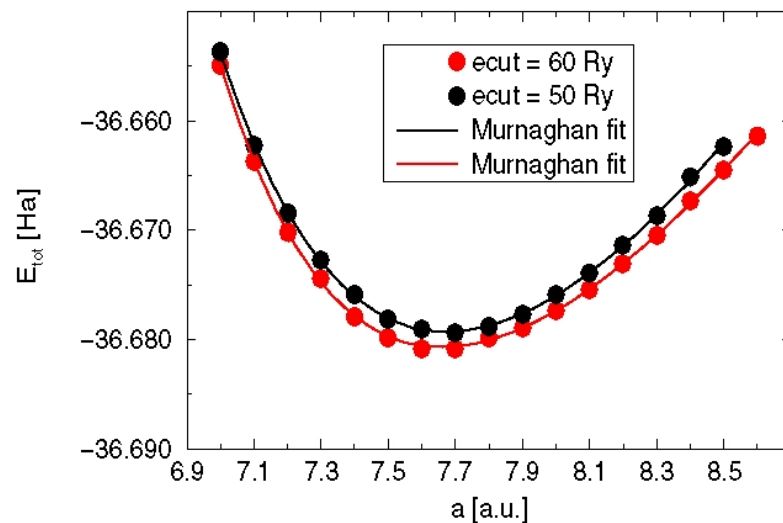
What we can calculate

- Total energy in the ground state
- Density in the ground state
- Forces on nuclei
- Eigenvalues (*not rigorously exact*)
- Vibrational frequencies (e.g., by Density Functional Perturbation Theory)
- Magnetic properties (e.g., using Local Spin Density Approximation)
- Ferroelectric properties (e.g., using Berry's phase formulation)
- Excited state properties (using Time Dependent Density Functional Theory)
- etc., etc.!

Total Energy

- Very useful quantity!
- Can use to get structures, heats of formation, adsorption energies, diffusion barriers, activation energies, elastic moduli, vibrational frequencies, ...

Ag bulk – E_{tot} vs. a



From this curve, can get

- lattice constant
- bulk modulus
- pressure derivative of bulk modulus

Forces

- Born-Oppenheimer approximation: separate electronic and nuclear degrees of freedom.
- Obtain forces on nuclei using Hellmann-Feynman theorem.
- Particularly easy to obtain with plane wave basis.
- Can use to obtain equilibrium structures (minima), transition states (saddle points), vibrational frequencies.
- Can use in molecular dynamics (e.g., to get properties at finite temperatures).

Why we love DFT- I



Can reproduce experimental results .

- Can do ~ 100 atoms on PC, can do few 1000 atoms on bigger computers.
- Typically, accuracy is less than few %.
- Recall, no empirical input!
- Only failures: strongly correlated systems, systems where van der Waals interactions are important...
- Work in progress!

Why we love DFT- II



- Can use to understand complicated observations of diversity
 - Why do bizarre structures form on surfaces of some metals?
 - Why are some materials reactive and others not?
 - Why do some materials/objects melt at low temperatures, and others not?
 - Why do some materials show thermal expansion, and others thermal contraction?
 - etc.

Why we love DFT- IV

- Can study conditions that are impossible / expensive to measure experimentally
- e.g., planetary interiors...



Is the earth's core liquid?



Is Jupiter's core metallic?

Conclusions



Density Functional Theory is a very successful approach to calculating the properties of many-electron systems from first principles.

Conclusions



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Bibliography



Richard Martin: "Electronic Structure, Basic Theory & Practical Methods", Cambridge, 2004
...and references therein.