Joint ICTP-TWAS Caribbean School on Electronic Structure Fundamentals and Methodologies (an Ab-initio Perspective)
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Introduction to DFT and Quantum Espresso

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(slides courtesy of Shobhana Narasimhan)

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International Centre
for Theoretical Physics

UNESCO

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International Atomic Energy Agency

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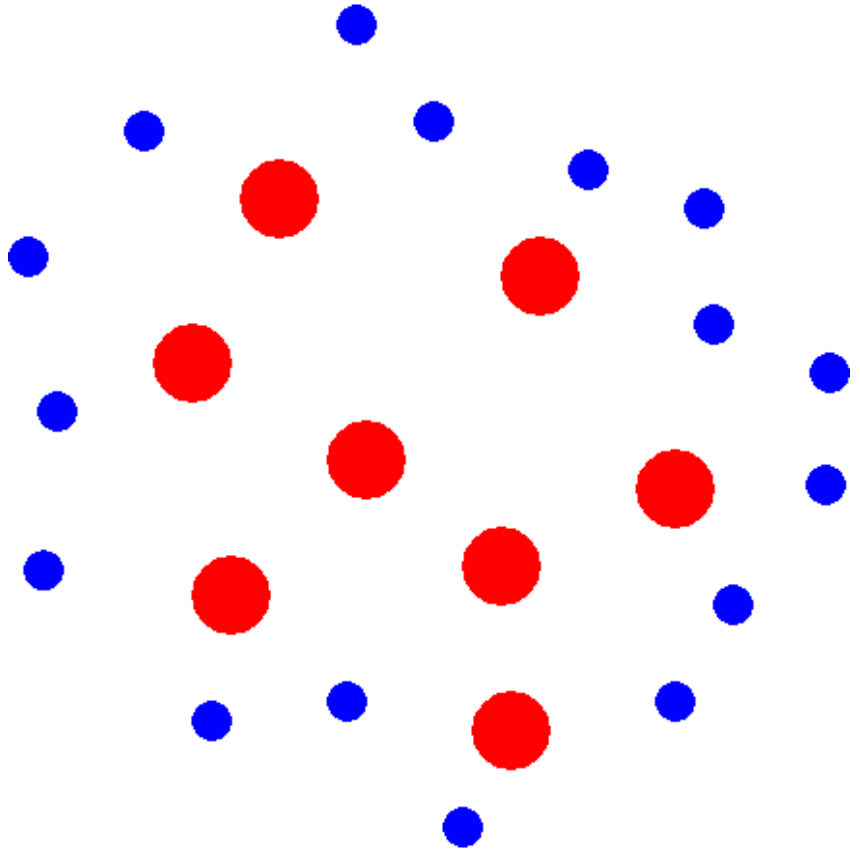
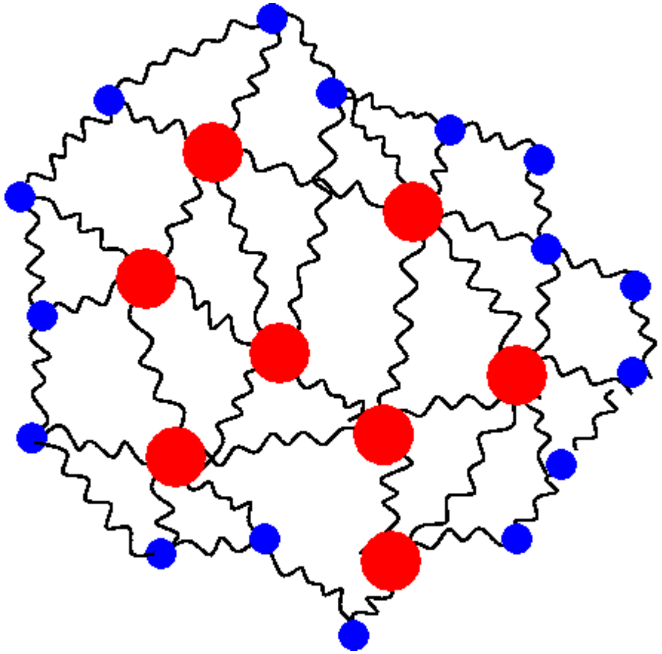
Computational Atomistic Materials Science:



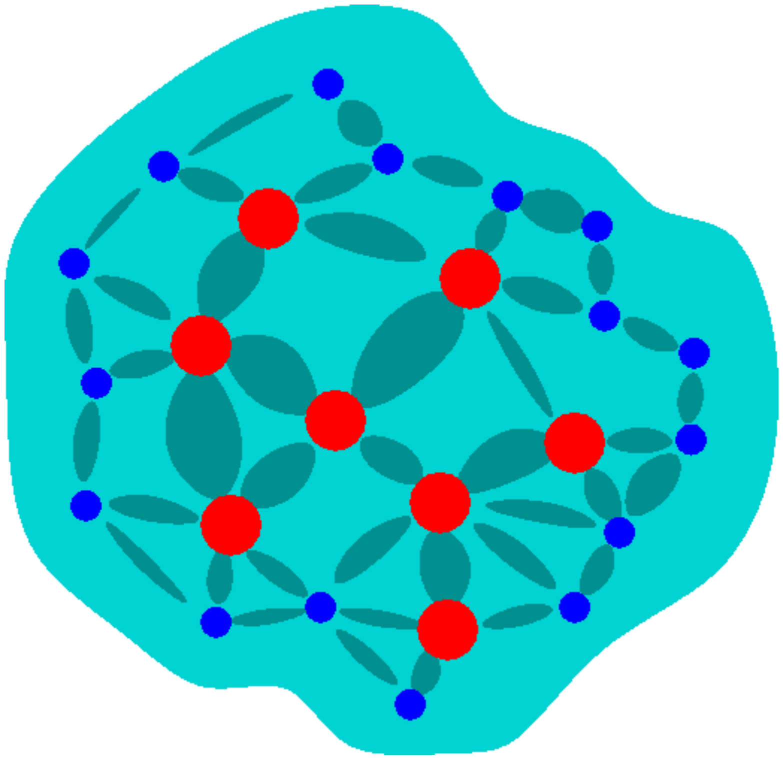
Treat nuclei as classical particles
(Borm-Oppenheimer approx.)

Computational Atomistic Nanoscience: Two approaches

Classical Models

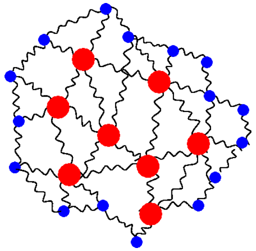


Quantum models



Computational Atomistic Nanoscience: Two approaches

Classical Models

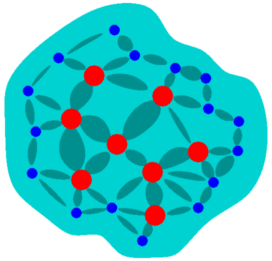


Can treat very large systems

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 nuclei $\{Z_i, \boldsymbol{R}_i\}$ + N electrons $\{\boldsymbol{r}_j\}$

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

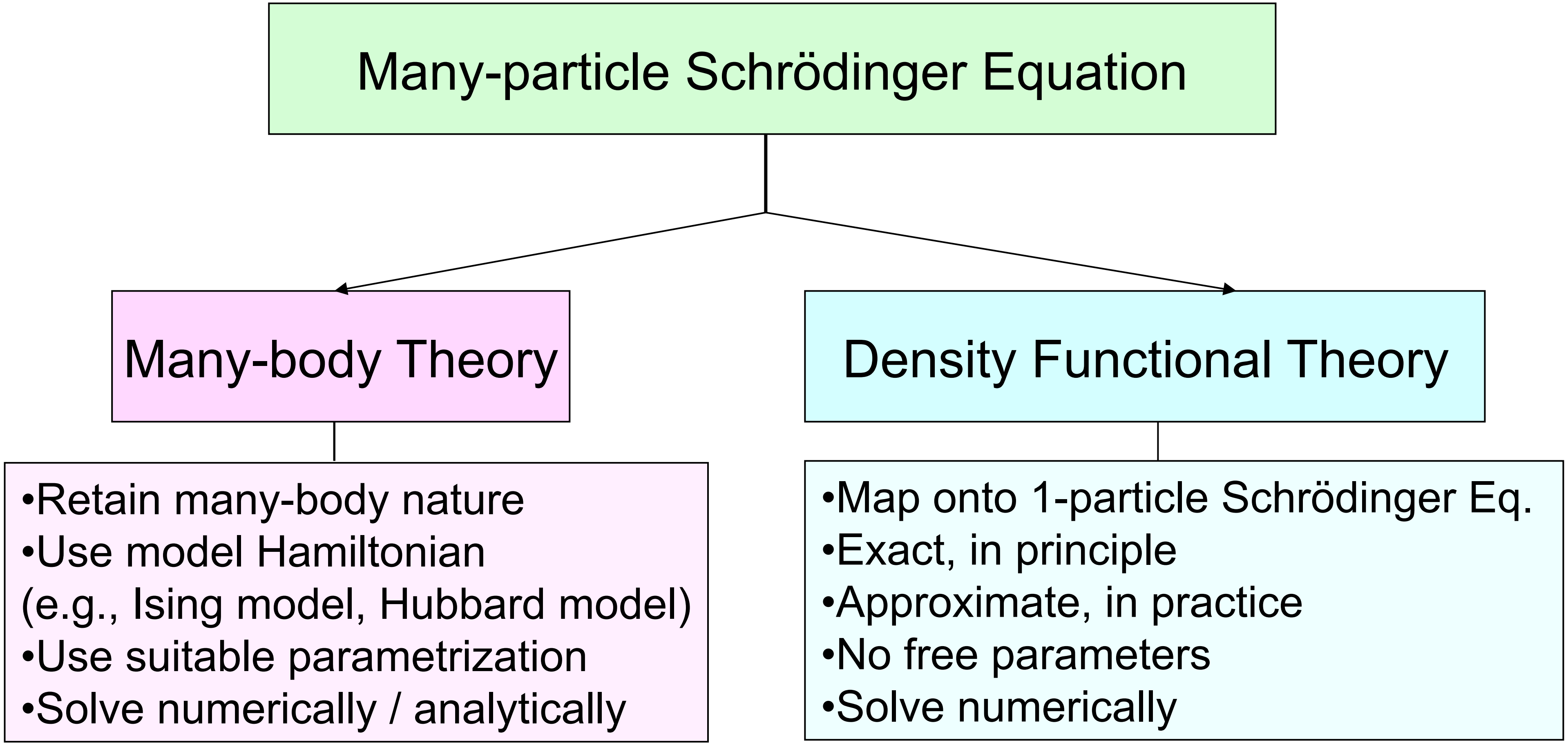
  $$H\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) = E\,\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N)$$

  – 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 $v(\mathbf{r})$

- Usually:

$$\begin{tikzcd}
v(\mathbf{r}) \arrow[r, "\text{Solve many-particle}", "\text{Schrödinger Eq.}"'] & \Psi_{\text{many-particle}} \arrow[r, dashed] \arrow[dr] & \text{all properties of system} \\
 & & n(\mathbf{r}) = \Psi^*\Psi
\end{tikzcd}$$

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

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

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:

  - $E_\upsilon[n] \equiv F\,[n] + \int \upsilon(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}$ has its minimum value when

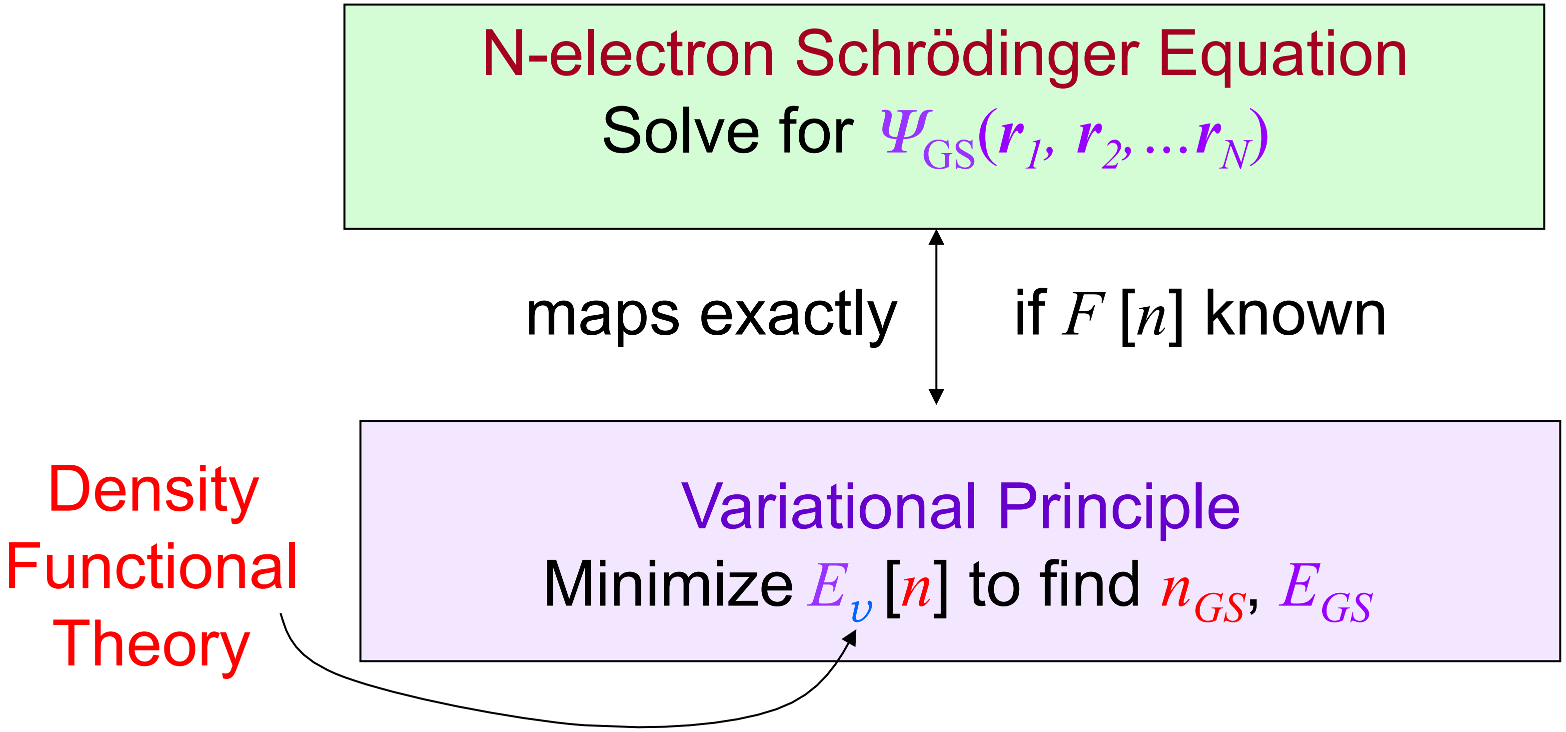
    $n(\mathbf{r}) = n_{GS}(\mathbf{r})$ → density of system in ground state
  - $E_\upsilon[n = \mathrm{n}_{\mathrm{GS}}] = E^{tot}{}_{GS}$ → total energy in ground state

- 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 → $n_{GS}(\mathbf{r}),\ E^{tot}{}_{GS}$ ☺

What have we achieved? - I



N-electron Schrödinger Equation

Solve for $\Psi_{\mathrm{GS}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N)$

maps exactly

if $F\,[n]$ known

Variational Principle

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

Density Functional Theory

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

What would we want now?

- Approximation for $F[n]$
- Ansatz for form of $n(\boldsymbol{r})$
- Good prescription for minimizing $E_v[n]$ wrt variations in $n(\boldsymbol{r})$

  OR an alternative to this.

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

- Recall:

$$E_{\upsilon}[n] \equiv F[n] + \int \upsilon(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}$$

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

- For a non-interacting system,

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

- 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:

$$E_{\upsilon}[n] \equiv F[n] + \int \upsilon(\mathbf{r})\, n(\mathbf{r})\, d\mathbf{r}$$

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

- For a non-interacting system,

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

Hartree potential

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'$$

- For an interacting system,

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

Hartree [Coulomb]

Exchange-Correlation

Kohn-Sham Equations

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

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

Kohn-Sham Equations

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

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

Kohn-Sham Equations

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

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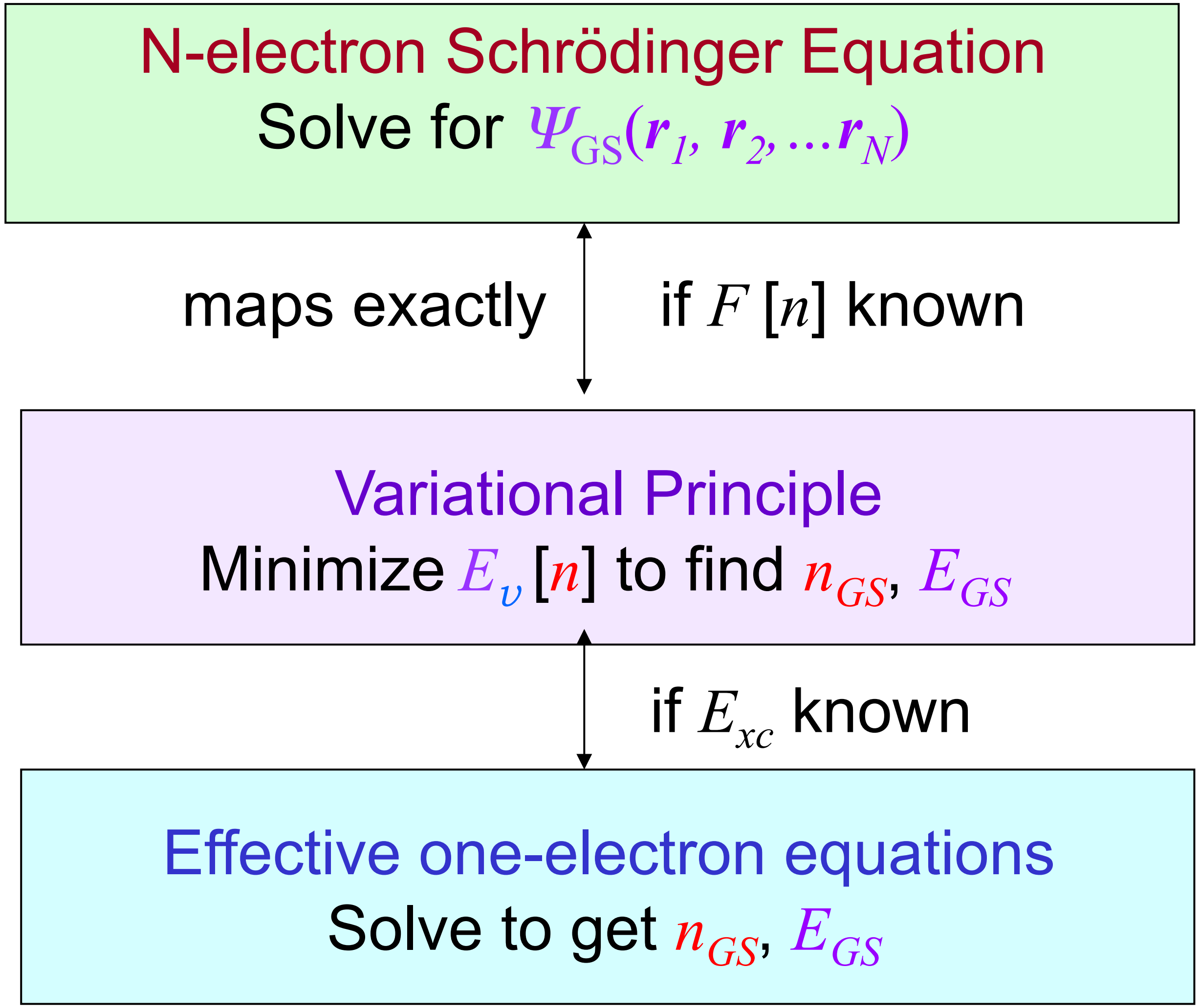
Solving Schrödinger Eq.	$[-\frac{1}{2}\nabla^2 + \upsilon(\mathbf{r})]\, \psi_i(\mathbf{r}) = \varepsilon_i\, \psi_i(\mathbf{r})$	$[-\frac{1}{2}\nabla^2 + \upsilon_{eff}(\mathbf{r})]\, \psi_i(\mathbf{r}) = \varepsilon_i\, \psi_i(\mathbf{r})$

Kohn-Sham Equations

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

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

What have we achieved? - II



N-electron Schrödinger Equation

Solve for $\Psi_{GS}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N)$

maps exactly

if $F\,[n]$ known

Variational Principle

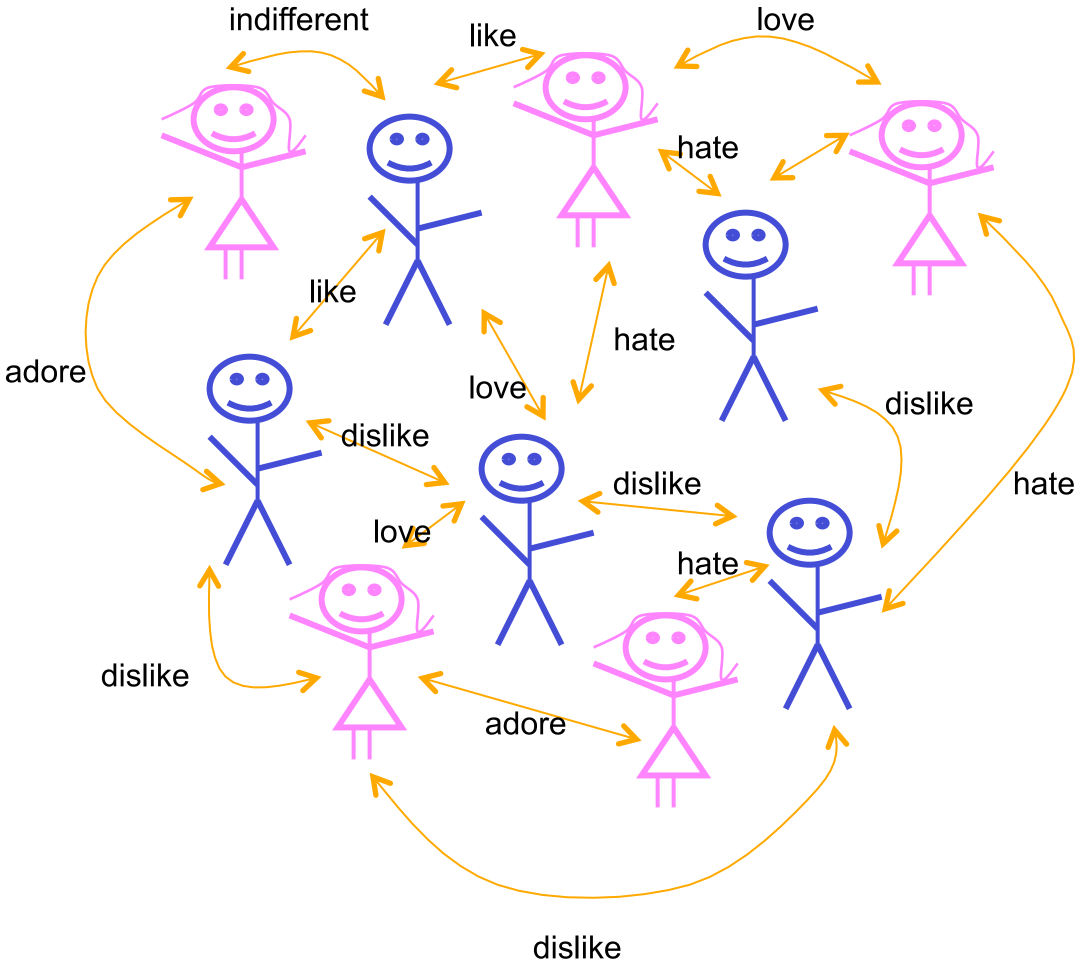
Minimize $E_v\,[n]$ to find n_{GS}, E_{GS}

if E_{xc} known

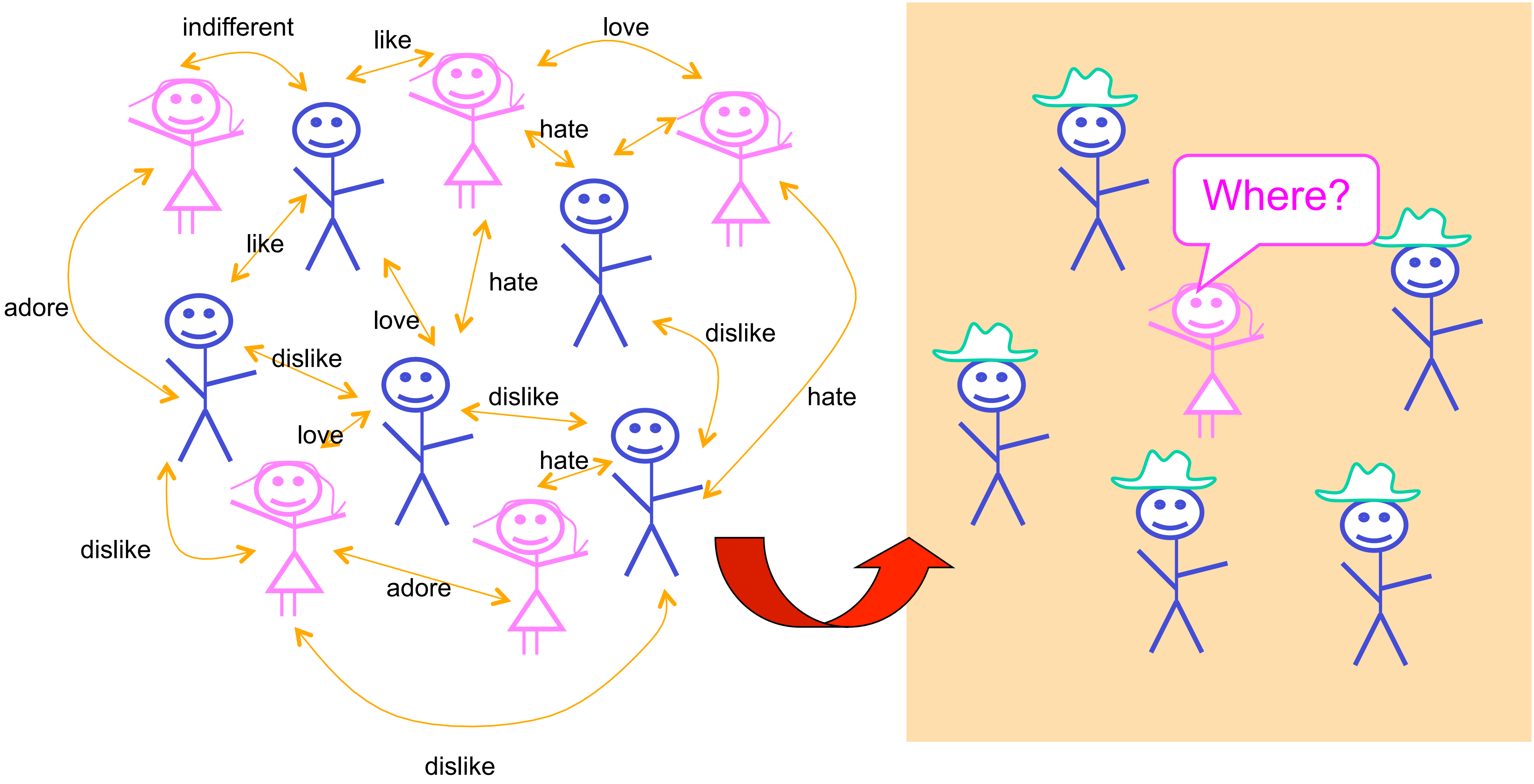
Effective one-electron equations

Solve to get n_{GS}, E_{GS}

What have we achieved? - III



What have we achieved? - III



II. How to Solve the Problem

Determining K-S Hamiltonian

Want to solve:

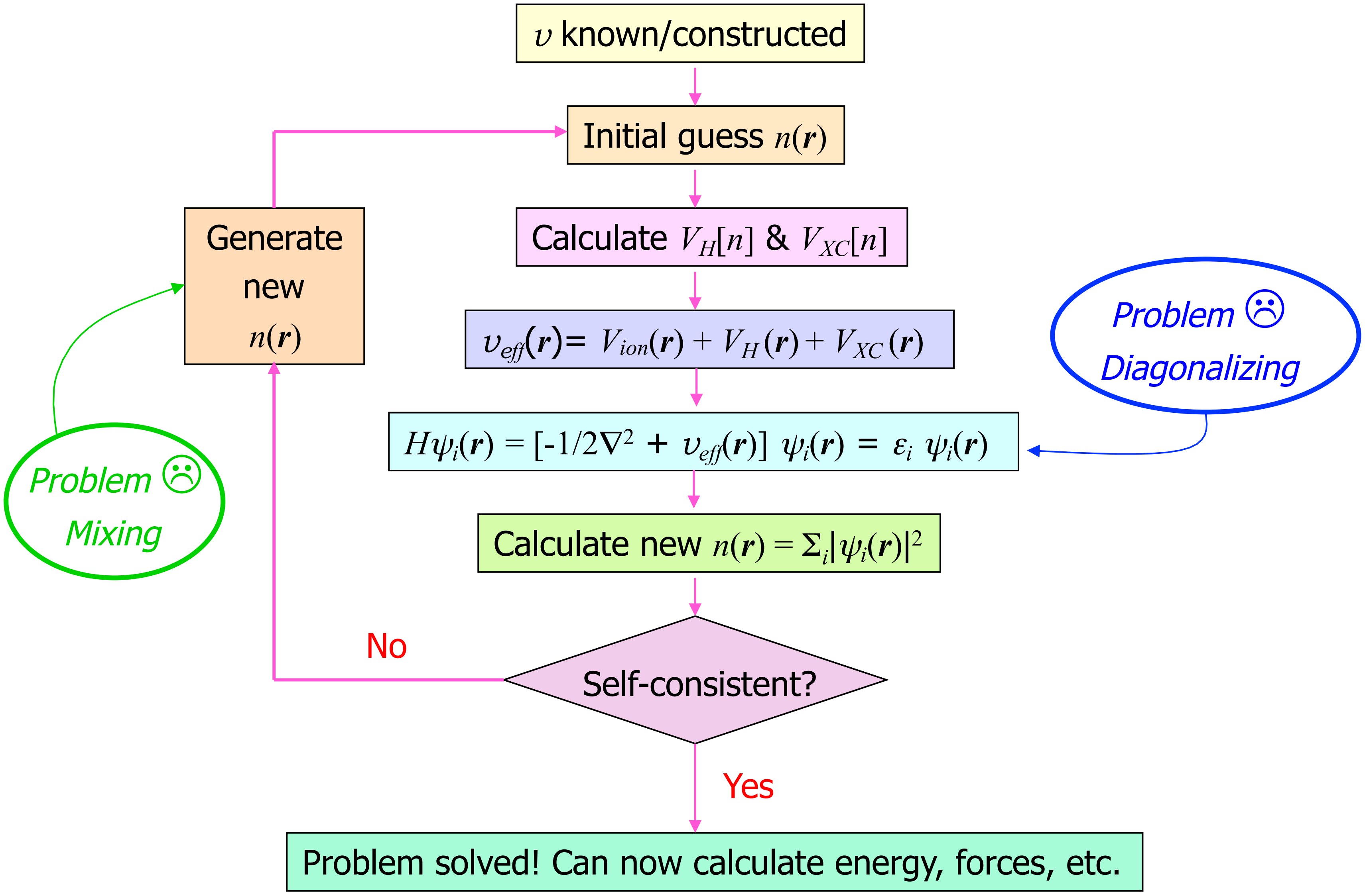
$$[-\tfrac{1}{2}\nabla^2 + \upsilon_{eff}(\mathbf{r})]\,\psi_i(\mathbf{r}) = \varepsilon_i\,\psi_i(\mathbf{r})$$

where

$$\upsilon_{eff}(\mathbf{r}) = V_H[\mathrm{n}(\mathbf{r})] + V_{xc}[n(\mathbf{r})] + \upsilon(\mathbf{r})$$

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

Self-Consistent loop



υ known/constructed

Initial guess $n(\mathbf{r})$

Calculate $V_H[n]$ & $V_{XC}[n]$

$\upsilon_{eff}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$

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

Calculate new $n(\mathbf{r}) = \Sigma_i|\psi_i(\mathbf{r})|^2$

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

Problem solved! Can now calculate energy, forces, etc.

Problem ☹ *Diagonalizing*

Problem ☹ *Mixing*

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

Various possible choices, e.g.,:

- Converged $n(\mathbf{r})$ from a closely related calculation

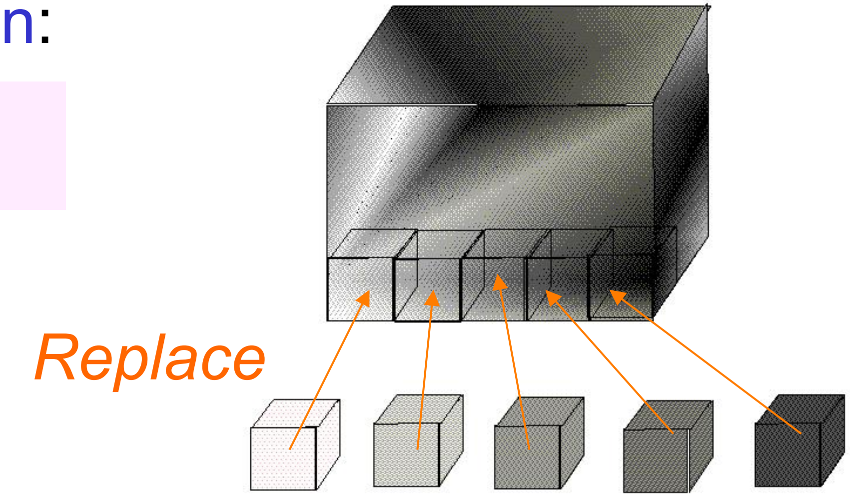
  (e.g., one where ionic positions slightly different).
- Superpositions of atomic densities.
- Approximate $n(\mathbf{r})$, e.g., from solving problem in a smaller/different basis.
- Random numbers.

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:

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

Surprisingly successful!



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

Choice of Basis

- Can choose to expand wavefunctions in a basis set:

$$\psi_i(\boldsymbol{r}) = \Sigma_\alpha\ c_{i\alpha}\ \mathrm{f}_\alpha(\boldsymbol{r})$$

- Eigenvalue equation then becomes:

$$\Sigma_\beta\ \ H_{\alpha\beta}\ c_{i\beta} = \ \varepsilon_i\ c_{i\alpha}$$

- Have to diagonalize a matrix of size N_b x 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.

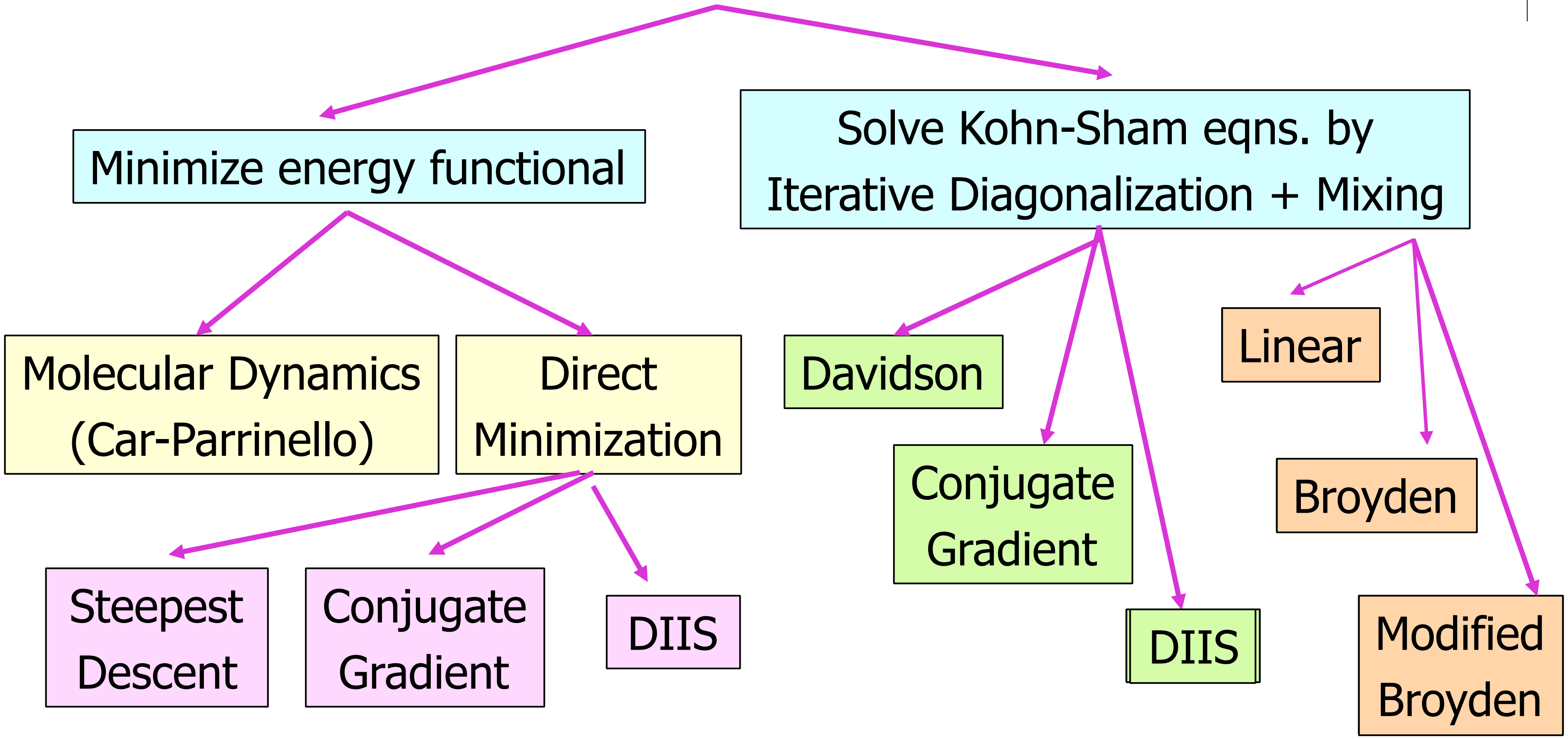
Pseudopotentials: An analogy!

- "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



Minimize energy functional

Solve Kohn-Sham eqns. by Iterative Diagonalization + Mixing

Molecular Dynamics (Car-Parrinello)

Direct Minimization

Steepest Descent

Conjugate Gradient

DIIS

Davidson

Conjugate Gradient

DIIS

Linear

Broyden

Modified Broyden

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

III. What can we calculate?

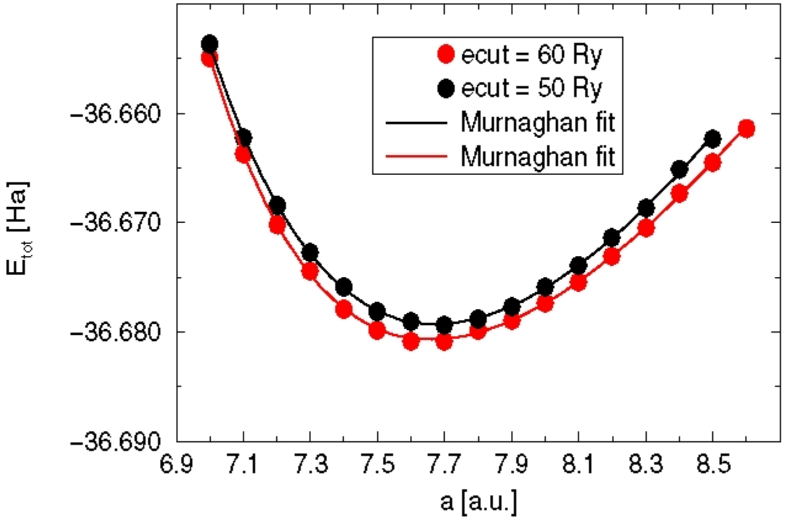
What we can calculate

- Total energy in the ground state
- Density in the ground state
- Forces on nuclei
- Eigenvalues *(not rigourously 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.

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Bibliography

Richard Martin: “Electronic Structure, Basic Theory & Practical Methods”, Cambridge, 2004

…and references therein.