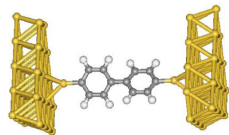
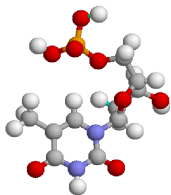


AB-INITIO COMPUTATIONAL METHODS
FOR
ELECTRONIC STRUCTURE DETERMINATION

OR

Why Stuff Sticks Together

Part 2



HOMER REID

2/16/2006

Review: The Story So Far

- Goal of quantum chemistry: Given $V(\mathbf{r}) = \sum \frac{Z_i}{|\mathbf{r}-\mathbf{r}_i|}$, predict E and $n(\mathbf{r})$.



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while the **wavefunction** ψ must satisfy **constraints**:

$$\begin{aligned} \int |\psi|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_n &= 1 && \text{(normalization)} \\ \text{and} &&& \\ |\psi|^2(\dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots) &= |\psi|^2(\dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots) && \text{(all electrons are identical)} \end{aligned}$$

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- The energy functional is an integral over all space:

$$E[\psi] = \int \psi^* \times \left\{ \begin{array}{ll} \beta \nabla_{\mathbf{r}_1}^2 \psi & + \cdots + \beta \nabla_{\mathbf{r}_n}^2 \psi & \text{(kinetic)} \\ + V(\mathbf{r}_1) \psi & + \cdots + V(\mathbf{r}_n) \psi & \text{(potential)} \\ + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi & + \cdots + \frac{e^2}{|\mathbf{r}_{n-1} - \mathbf{r}_n|} \psi & \text{(interaction)} \end{array} \right. d\mathbf{r}_1 \cdots d\mathbf{r}_n$$

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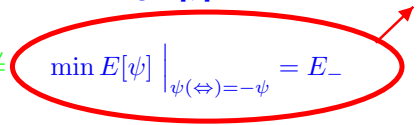
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Hartree: Construct many-particle ψ from product of single-particle orbitals:

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Minimize with respect to ϕ_i to get **Schrödinger equation for particle i** :

$$\frac{\partial E[\psi]}{\partial \phi_i^*(\mathbf{r})} = 0 \quad \Rightarrow \quad \left[\beta \nabla^2 + V(\mathbf{r}) + \sum_{j \neq i} U_j(\mathbf{r}) \right] \phi_i(\mathbf{r}) = E \phi_i(\mathbf{r})$$

$$\text{where } U_j(\mathbf{r}) = \int \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \text{electrostatic potential of } j\text{th electron}$$

Interpretation: i th electron moves in potential field of **backbone + electrons $j \neq i$** .

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Hartree fails for $n > 2$ because $\psi(\mathbf{r}_i, \mathbf{r}_j) \neq -\psi(\mathbf{r}_j, \mathbf{r}_i)$.

Minimizing $E[\psi]$: Hartree-Fock Method

The absolute simplest possible approach *that preserves the antisymmetry of ψ* .

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These trial wavefunctions are called **orthomers**, and the process of constructing them is called **orthomerization**.

Orthomerization: Where do I fit in?

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ort **HOMER** ization

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These trial wavefunctions are actually called **Slater determinants**, and the process of constructing them is actually called **antisymmetrization**.

Slater Determinants

Antisymmetrized combinations of products of single-particle orbitals.

Hartree-Fock: Find optimal orbitals $\{\phi_i\}$ whose **antisymmetrized** product minimizes $E[\psi]$.

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- ... so much that Hartree-Fock yields accurate binding energies for single atoms
- ... but not enough for more complicated bonding problems.

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Again solve self-consistently, now at **much higher cost**.

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Disastrous scaling notwithstanding, HF and CI *dominated* quantum chemistry well into the 90s.

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- Alive and well in 21st century because $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$.

Where We Are

0. Invitation

1. Formal Statement Of Problem

2. Strategies Of Attack

- Hartree
- Hartree-Fock
- Configuration Interaction
- Quantum Monte Carlo
- Density Functional Theory

3. Actual DFT Calculations

4. MOR for DFT?

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Interpret $\psi(\mathbf{r} \in \mathbb{R}^{3n})$ as a **concentration** and tune E parameter to obtain steady state.

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Innards of QMC: **Really** cool stuff that I can't go into here.

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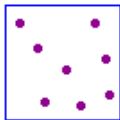
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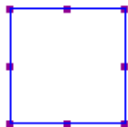


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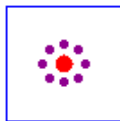
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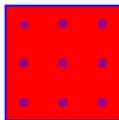


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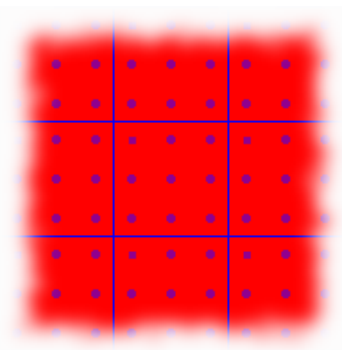


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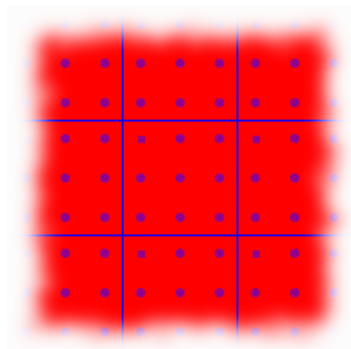


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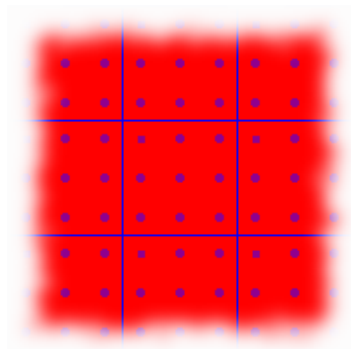
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Question: For a given density n , what is the **energy** $E[n]$ of the homogeneous electron gas?

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Step 1: Compute energy density $\mathcal{E}[n]$ of electron gas ignoring antisymmetry.

- Hartree picture: $\psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1) \cdots \phi_n(\mathbf{r}_n)$, $\psi(\mathbf{r}_i, \mathbf{r}_j) \neq -\psi(\mathbf{r}_j, \mathbf{r}_i)$

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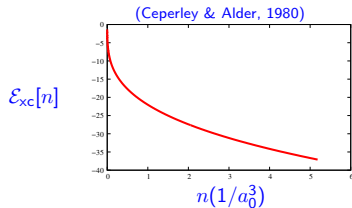
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Note that \mathcal{E}_{xc} is **negative**. As we saw before, QM-Lite **overestimates** the electron-electron repulsion energy, so putting in correlation effects **reduces** the energy.

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Solve with ansatz $\psi(\mathbf{r}_1, \cdots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1) \cdots \phi_n(\mathbf{r}_n)$, not asymmetrized.

$$\frac{\partial E_{\text{DFT}}[\psi]}{\partial \phi_i^*(\mathbf{r})} = 0 \quad \implies \quad \left[\beta \nabla^2 + V(\mathbf{r}) + \underbrace{\sum_{i \neq j} U_j(\mathbf{r}) + V_{xc}(n(\mathbf{r}))}_{V_H(\mathbf{r})} \right] \phi_i(\mathbf{r}) = E_i \phi_i(\mathbf{r})$$

$$V_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \text{electrostatic potential of total electron density}$$

$$V_{xc}(n(\mathbf{r})) = \text{exchange-correlation potential of electron gas (from QMC).}$$

Summary: The Story So Far

Original problem: Find $\psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$ to minimize

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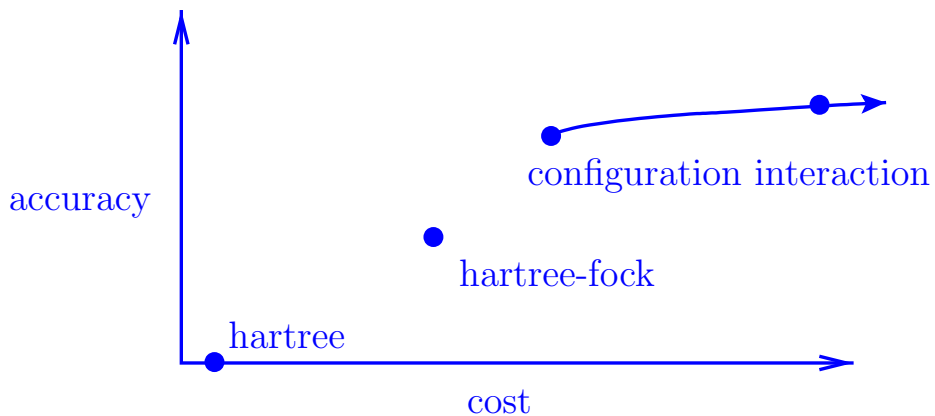
with no antisymmetry requirement.

Procedure: Find the ϕ_i as the lowest-lying eigenvectors of a differential operator:

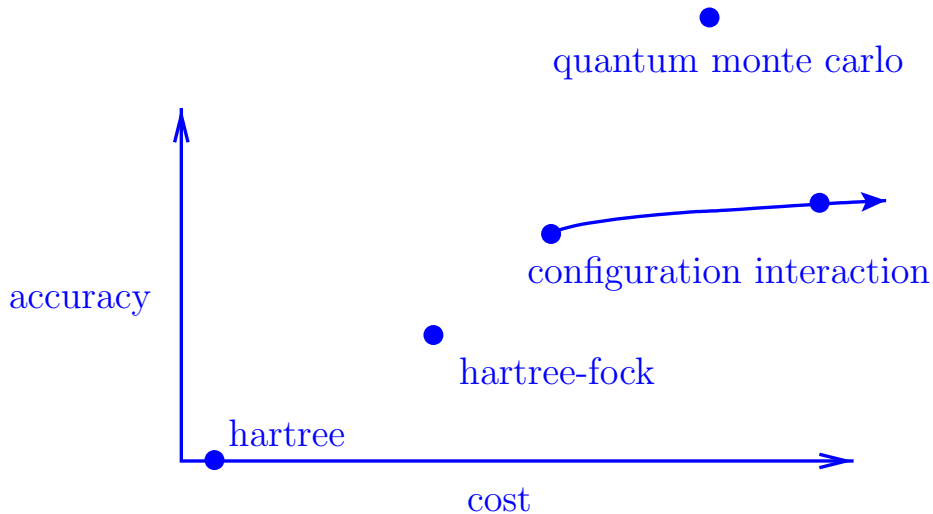
$$H\phi_i = [\beta\nabla^2 + V(\mathbf{r}) + U_H(\mathbf{r}) + U_{\text{xc}}(\mathbf{r})] \phi_i = E_i\phi_i.$$

U_H and U_{xc} depend on $n(\mathbf{r}) \implies$ solve self-consistently.

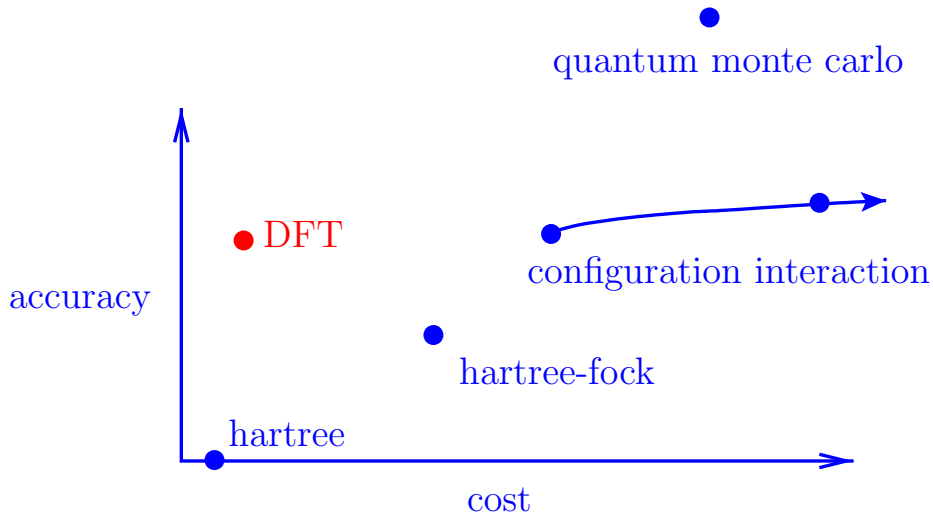
Accuracy Vs. Cost (Highly Schematic)



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Where We Are

0. Invitation

1. Formal Statement Of Problem

2. Strategies Of Attack

- Hartree
- Hartree-Fock
- Configuration Interaction
- Quantum Monte Carlo
- Density Functional Theory

3. Actual DFT Calculations

4. MOR for DFT?

DFT Calculation Procedure

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4. Relax $n(\mathbf{r})$ toward $n'(\mathbf{r})$; **Goto Step 1**

and iterate until converged.

DFT Calculations: Practical Aspects

- Work inside a box (“supercell”) of dimensions $\sim 10 - 20 \text{ \AA}$.
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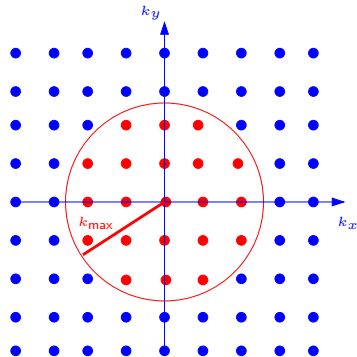
Plane-Wave Supercell DFT Calculations

Expand $\phi_i(\mathbf{r})$ in plane waves:

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_p C_p e^{i\mathbf{k}_p \cdot \mathbf{r}},$$

where $\{\mathbf{k}_p\} =$ all \mathbf{k} with $|\mathbf{k}| \leq k_{\max}$

Wavevector cutoff k_{\max} imposes spatial granularity length $\Delta L \rightarrow$ get real-space grid $\{\mathbf{r}_i\}$



$$\{C_p\} \xLeftrightarrow{\text{FFT}} \{\phi(\mathbf{r}_i)\}$$

Follow usual procedure to obtain discrete eigenvalue equation for vector C_p :

$$\begin{aligned} \hat{H}\phi &= E\phi \\ \Rightarrow \sum H_{pq} C_q &= EC_p \\ \text{or } \mathbf{H} \cdot \mathbf{C} &= E\mathbf{C} \end{aligned}$$

$$H_{pq} = \int_{\text{supercell}} e^{-i\mathbf{k}_q \cdot \mathbf{r}} \hat{H} e^{i\mathbf{k}_p \cdot \mathbf{r}} dV$$

Typically have $\sim 10^5$ plane waves \Rightarrow need indirect MVP

Plane Wave DFT: Indirect Matrix-Vector Product

- **Problem:** Given ϕ , compute $\hat{H}\phi$.
- **Input:** $\{C_p\}$, where $\phi = \sum C_p e^{i\mathbf{k}_p \cdot \mathbf{r}}$
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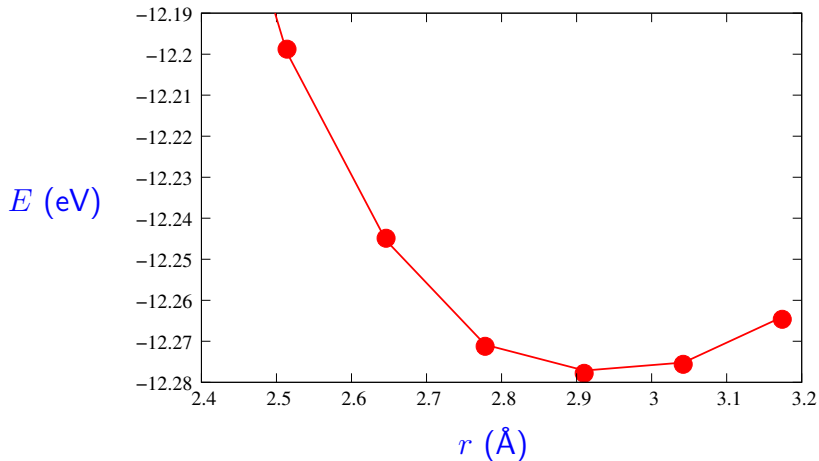
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- **MVP operation:** $\{C'_p\} = \{C'_p{}^T + C'_p{}^P\}$.

Example Calculation: Bond Length of Li₂ Dimer



Next Time: MOR for DFT + applications to device modeling.