

Density functional theory II

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The Schrodinger Equation for a particle

Schrödinger Equation for a particle

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = \varepsilon\psi(x)$$

In 3 dimensions

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

In general

$$H\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

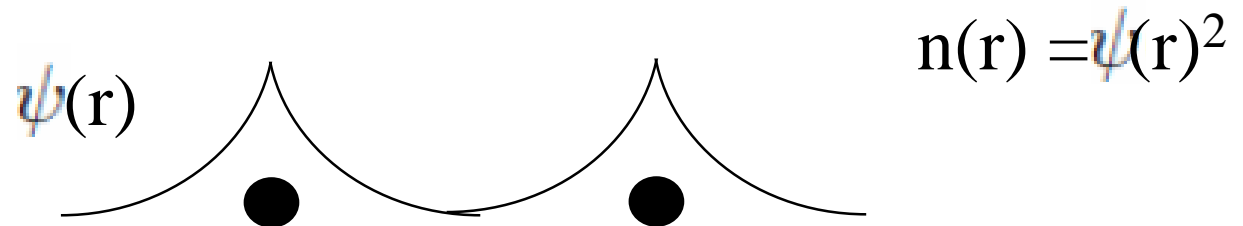
What about more than one particle?

The Schrodinger Equation for one electron

Example of H_2

First consider H_2^+ with one electron

Lowest energy -- ground state



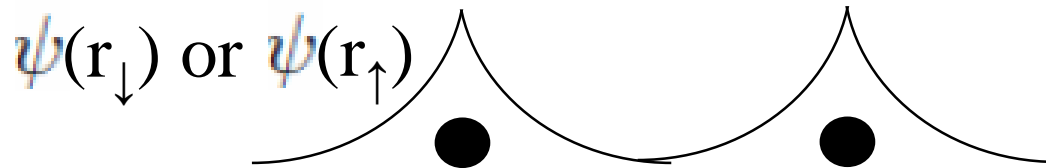
The Schrodinger Equation for two electrons

For H₂ with an up and a down spin electron:

If there were no interactions the wave function
would be a product -- uncorrelated

$$\psi(r_{\downarrow}, r_{\uparrow}) = \psi(r_{\downarrow})\psi(r_{\uparrow})$$

$$n(r) = 2\psi(r)^2$$



The Schrodinger Equation for two electrons

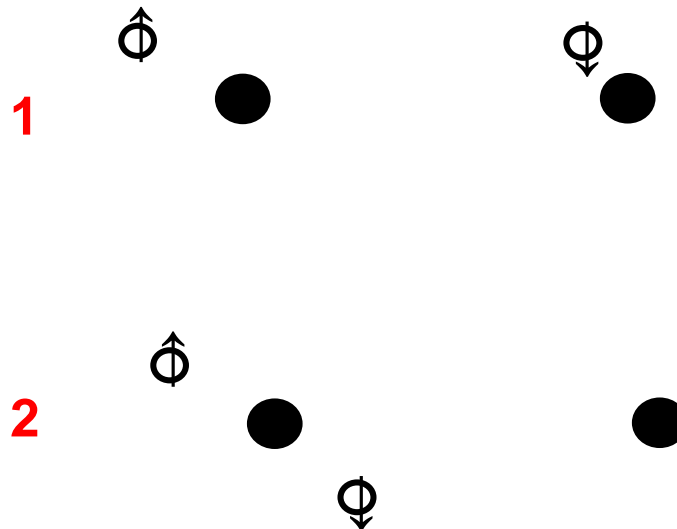
For H₂ with an up and a down spin electron:

If we include interactions, the electrons are
correlated

$$\psi(r_{\downarrow}, r_{\uparrow}) \neq \psi(r_{\downarrow})\psi(r_{\uparrow})$$

One function in 6 dimensions

Two snapshots



The Schrodinger Equation for two electrons

For H₂ with an up and a down spin electron:

If we include interactions, the electrons are correlated

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One function in 6 dimensions

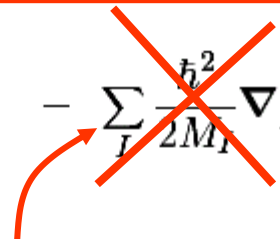
Solved essentially exactly in 1929

In a solid with 10²³ electrons ???

The Fundamental Hamiltonian

Interacting electrons in an “external potential”

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


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

- Only one small term: The kinetic energy of the nuclei
- If we omit this term, the nuclei are a fixed external potential acting on the electrons
- The final term is essential for charge neutrality – but is a classical term that is added to the electronic part

Many-Body Electron Problem

The many-electron wavefunction is a function in $3N$ dimensional space

**electron
kinetic energy**

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (2)$$

The total energy is the expectation value

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V}_{int} \rangle + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}). \quad (3)$$

**electron-electron
interactions**

The ground state wavefunction Ψ_0 is the state with lowest energy *that obeys the symmetries of the particles and conservation laws.*

**potential
due to nuclei,
other sources
“external” to
electrons**

$$E_0 = \min \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (4)$$

The problem for many interacting particles

What do those simple looking equations mean?

$$E = \min \frac{\langle \Psi | H | \Phi \rangle}{\langle \Psi | \Phi \rangle}$$

where

$$\langle \Psi | \Phi \rangle = \int d^3 r_1 d^3 r_2 \dots d^3 r_N |\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)|^2$$

$$\langle \Psi | H | \Phi \rangle = \int d^3 r_1 d^3 r_2 \dots d^3 r_N \Psi^* (\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N) H \Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$$

Soluble for 2 particles in a potential - already in 1929!

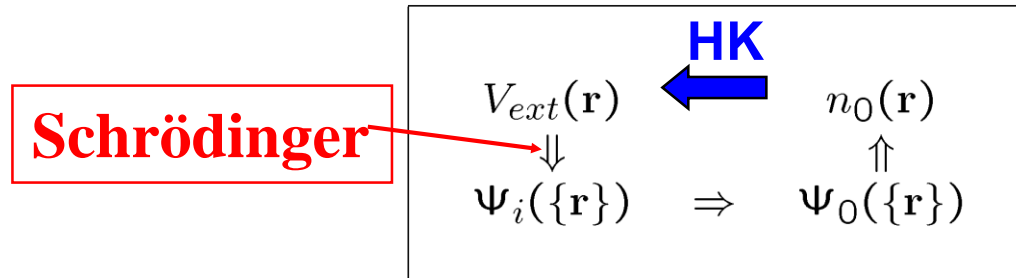
Hard for 3 particles!

Today numerically very accurate for ~ 10 particles

11 particles is much, much harder

Density Functional Theory (DFT) - I

- Hohenberg-Kohn (1964)



- All **properties** of the **many-body** system are determined by the ground state density $n_0(\mathbf{r})$
- Each **property** is a **functional** of the ground state density $n_0(\mathbf{r})$ which is written as **$F[n_0]$**
- A **functional $F[n_0]$** maps a function to a result: **$n_0(\mathbf{r}) \rightarrow F$**
- In 1965 Mermin extended the idea to equilibrium thermodynamic quantities in terms of the density as a function of temperature

Proof by Hohenberg and Kohn

Suppose that there were two different external potentials $V_{\text{ext}}^{(1)}(\mathbf{r})$ and $V_{\text{ext}}^{(2)}(\mathbf{r})$ which differ by more than a constant and which lead to the same ground state density $n(\mathbf{r})$. The two external potentials lead to two different hamiltonians, $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$, which have different ground state wavefunctions, $\Psi^{(1)}$ and $\Psi^{(2)}$, which are hypothesized to have the same ground state density $n_0(\mathbf{r})$.

Since $\Psi^{(2)}$ is not the ground state of $\hat{H}^{(1)}$, it follows that

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle. \quad (6.7)$$

The strict inequality follows if the ground state is non-degenerate, which we will assume here following the arguments of Hohenberg and Kohn.³ The last term in (6.7) can be written

$$\langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = \langle \Psi^{(2)} | \hat{H}^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | \hat{H}^{(1)} - \hat{H}^{(2)} | \Psi^{(2)} \rangle \quad (6.8)$$

$$= E^{(2)} + \int d^3r \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n_0(\mathbf{r}), \quad (6.9)$$

so that

$$E^{(1)} < E^{(2)} + \int d^3r \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n_0(\mathbf{r}). \quad (6.10)$$

On the other hand if we consider $E^{(2)}$ in exactly the same way, we find the same equation with superscripts (1) and (2) interchanged,

$$E^{(2)} < E^{(1)} + \int d^3r \left[V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r}) \right] n_0(\mathbf{r}). \quad (6.11)$$

QED!

A Nobel prize for that?

Density Functional Theory (DFT) - II

The Kohn-Sham Auxiliary System

- Kohn-Sham (1965) – Replace original many-body problem with an independent electron problem – that can be solved!
- The ground state density is required to be the same as the exact density

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

- Only the ground state density and energy are required to be the same as in the original many-body system

- But how do you decide on what are the independent particle functions?

The Kohn-Sham Auxiliary System

- From Hohenberg-Kohn the ground state energy is a functional of the density $E_0[n]$, minimum at $n = n_0$
- **From Kohn-Sham**

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + \underline{E_{xc}[n]}.$$

Equations for independent particles - **soluble**

Exchange-Correlation Functional – Exact theory but **unknown** functional!

- **The new approach to the many-body problem**
– find **useful, approximate** functionals for $E_{xc}[n]$

The Kohn-Sham Equations

- Assuming a form for $E_{xc}[n]$
- Minimizing energy (with constraints) → **Kohn-Sham Eqs.**

$$n_0(\mathbf{r}) = \sum_{\sigma} \sum_{i=1} |\psi_i^{\sigma}(\mathbf{r})|^2,$$

$$E_{KS} = \frac{1}{2} \sum_{\sigma} \sum_{i=1} |\nabla \psi_i^{\sigma}|^2 + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n].$$

$$\frac{\delta E_{KS}}{\delta \psi_i^{\sigma*}(\mathbf{r})} = 0, \quad (1)$$

Kohn Sham Equations!

Constraint – required
Exclusion principle for
independent particles →

$$\langle \psi_i^{\sigma} | \psi_j^{\sigma'} \rangle = \delta_{i,j} \delta_{\sigma,\sigma'}. \quad (2)$$

$$\left(-\frac{1}{2} \nabla^2 + V_{KS}^{\sigma}(\mathbf{r}), -\epsilon_i^{\sigma} \right) \psi_i^{\sigma}(\mathbf{r}) = 0 \quad (3)$$

$$\begin{aligned} V_{KS}^{\sigma}(\mathbf{r}) &= V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\mathbf{r}, \sigma)} \\ &= V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + \underline{V_{xc}^{\sigma}(\mathbf{r})} \end{aligned} \quad (4)$$

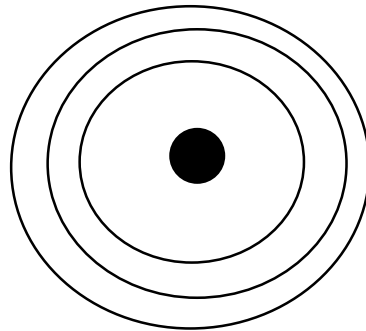
This is what got a Nobel prize!

The Kohn-Sham construction
plus

**The wisdom that it could lead to very useful
approximations for one of the most difficult
problems in physics and chemistry**

Functional $E_{xc}[n]$ in Kohn-Sham Eqs.

- **How to find a [approximate] functional $E_{xc}[n]$**
- **Requires information on the many-body system of interacting electrons**
- **Key point – around each electron, there is a reduced probability for finding other electrons**
 - **The “exchange correlation hole”**



The energy depends only on the spherical average

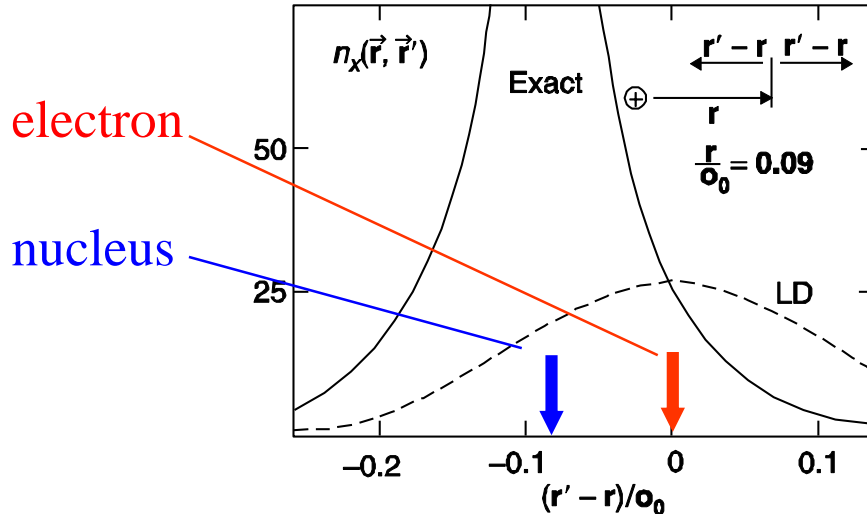
Approximate Functionals $E_{xc}[n]$

- **How to find a [approximate] functional $E_{xc}[n]$**
- **Requires information on the many-body system of interacting electrons**
- **Local Density Approximation - LDA**
 - Proposed by Kohn and Sham in the original paper
 - Assume the functional is the same as a model problem – the homogeneous electron gas
 - E_{xc} has been calculated as a function of density using quantum Monte Carlo methods (Ceperley & Alder)
- **Gradient approximations - GGA**
 - Various theoretical improvements for electron density that is varies in space

Approximate Functionals $E_{xc}[n]$

- Exchange and correlation \rightarrow around each electron, other electrons tend to be excluded – “x-c hole”
- E_{xc} is the interaction of the electron with the “hole” – which involves only a **spherical average**

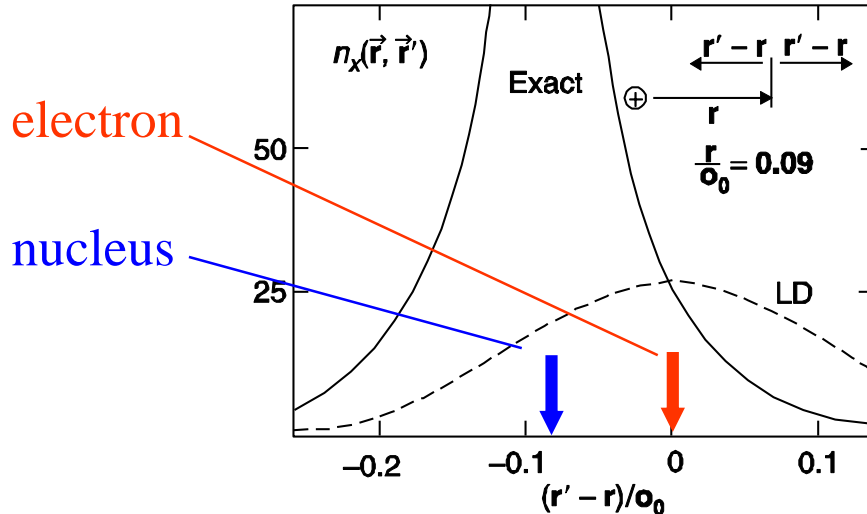
Exchange hole in Ne atom



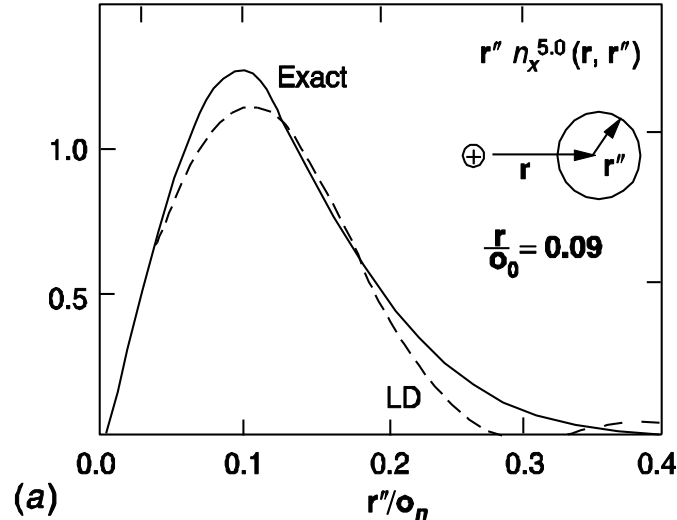
Approximate Functionals $E_{xc}[n]$

- Exchange and correlation \rightarrow around each electron, other electrons tend to be excluded – “x-c hole”
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Exchange hole in Ne atom



Spherical average



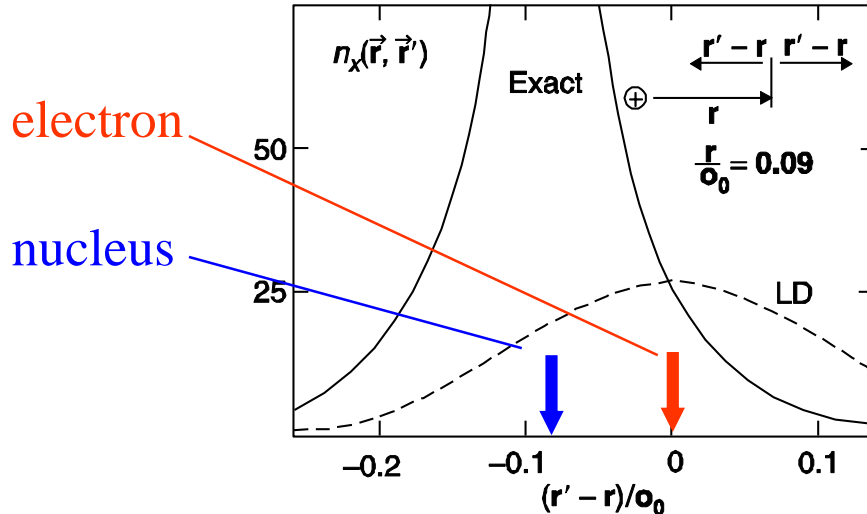
Supports the local density approximation!

(Gunnarsson, et. al.)

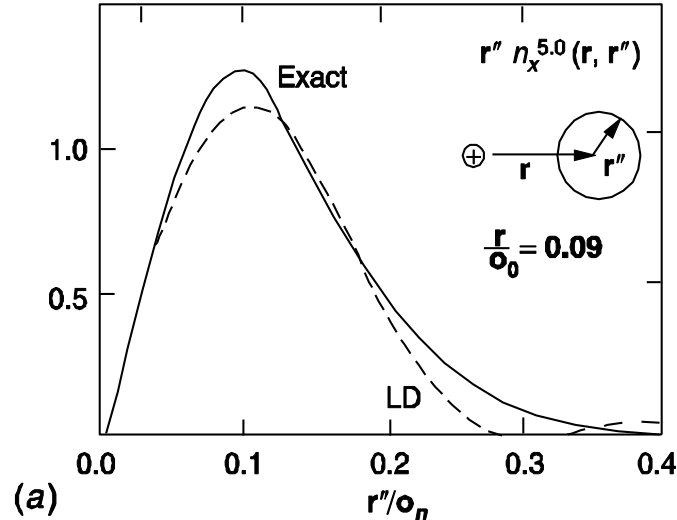
Approximate Functionals $E_{xc}[n]$

- This also shows what is NOT given by DFT
 - The local approximation is good for the energy in the ground state
 - It does NOT describe actual correlation

Exchange hole in Ne atom



Spherical average

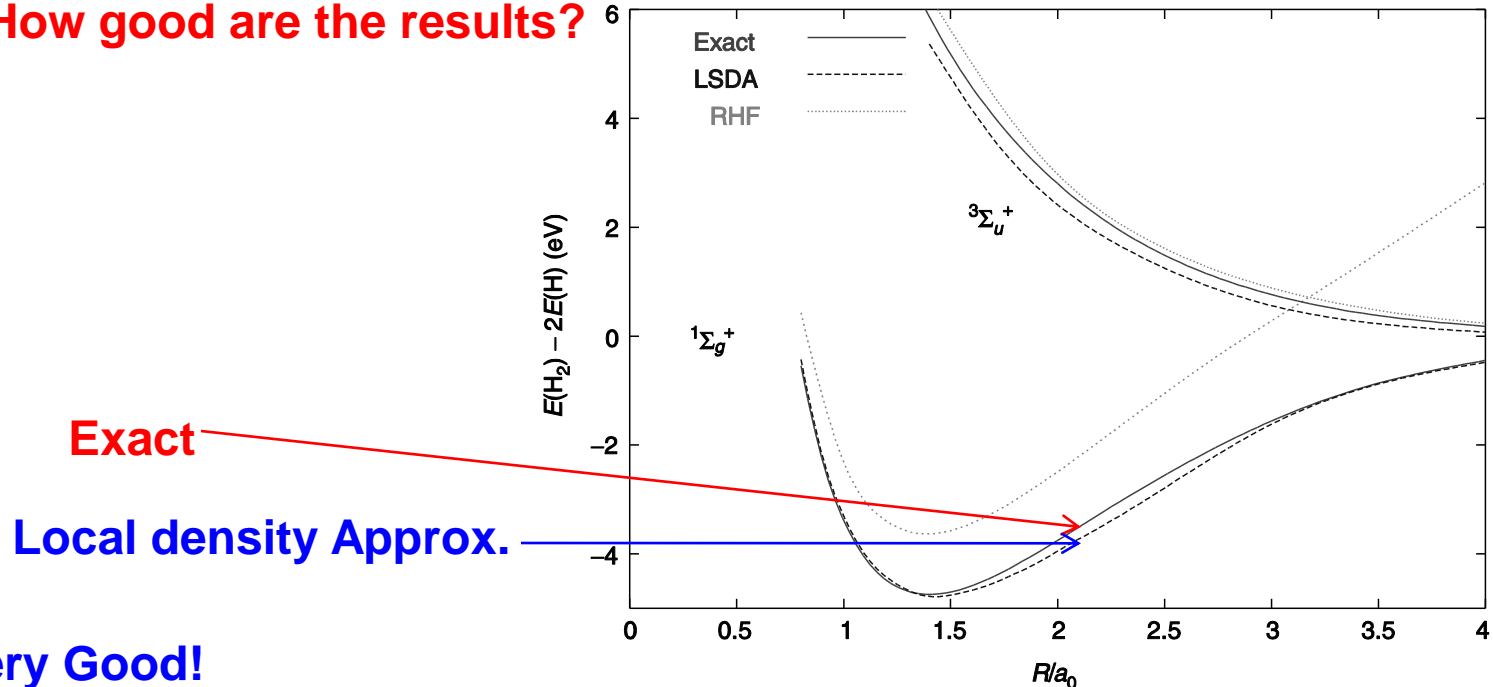


Supports the local density approximation!

(Gunnarsson, et. al.)

Example of H₂ Molecule

- It seems ridiculous to approximate the correlation of the two electrons by the LDA derived from the homogeneous gas
- How good are the results?



Very Good!

Supports a local approximation – exact is the homogeneous limit and amazingly good for the H₂ molecule!

What do the Ne atom and the H₂ molecule have in common?

Closed shell systems with large gaps to all excitations

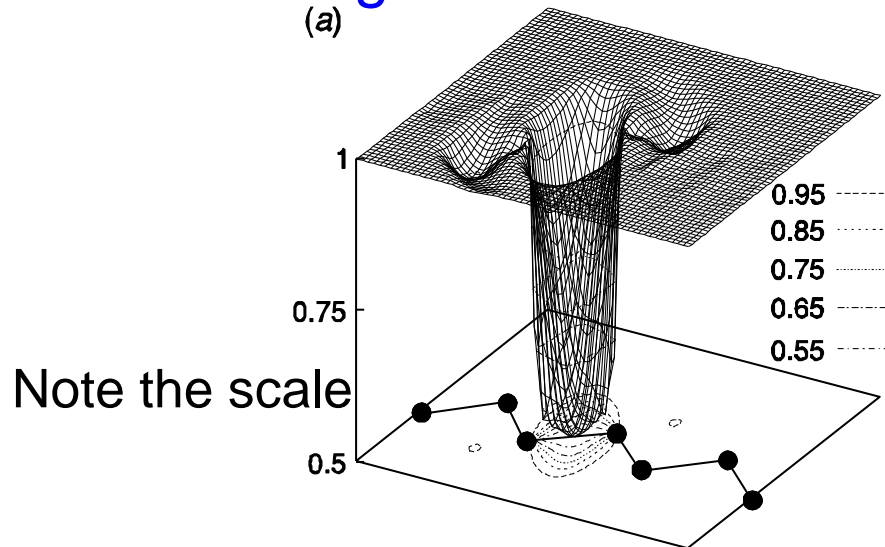
In general NOT so good for open shells that are “more correlated”

Exchange-correlation (x-c) hole in silicon

- Calculated by Monte Carlo methods

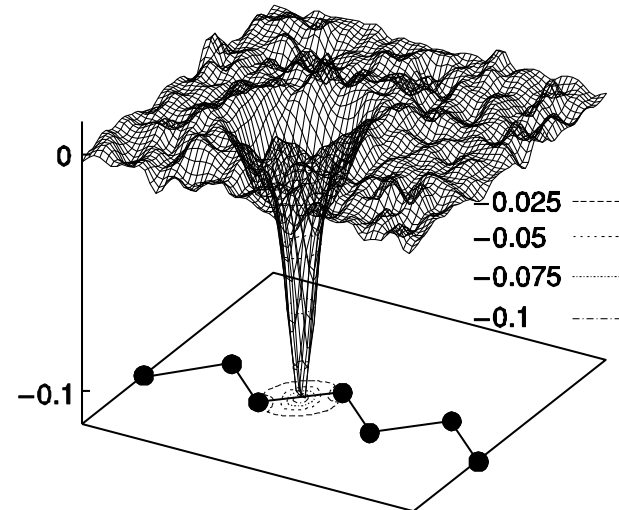
Exchange

(a)



Correlation

(b)



Hole is reasonably well localized near the electron
Supports a local approximation

Hood, et. al.

Conclusions

The essential aspects of density functional theory

- Kohn Sham Auxiliary system with independent particles
 - Kohn-Sham Equation
- Key is to have a [good approximate] functional $E_{xc}[n]$
 - Example – Local Density Approximation
- More advanced Functionals
 - See talk by Nicola Seriani later