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BASICS OF GROUNDSTATE
DENSITY FUNCTIONAL THEORY

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Electronic Structure Problem
For Atoms, Molecules, and Solids

What Atoms, Molecules, and Solids Can Exist, and With What Properties?

What Are the Groundstate Energies $E$ and Electron Densities $n(r)$?

What Are the Bond Lengths and Angles?

What Are the Nuclear Vibrations?

How Much Energy Is Needed to Ionize the System, or to Break Bonds?
WAVEFUNCTION APPROACH

HAMILTONIAN FOR N ELECTRONS (i=1...N) IN THE PRESENCE OF EXTERNAL POTENTIAL \( u(x) \):
\[
\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i} u(x_i)
\]
\[
\hat{T} = \frac{\hbar^2}{2m} \sum_{i} \nabla_i^2
\]
\[
\hat{V}_{ee} = \frac{1}{2} \sum_{i<j} \frac{\epsilon}{r_{ij}}
\]

OFTEN \( u(x) = \frac{\varepsilon}{\beta} \frac{-2}{|x-R|} \)

= ELECTRON-NUCLEUS ATTRACTION,

AND E INCLUDES ALSO
\[
\frac{1}{2} \sum_{i<j} \frac{Z_i Z_j}{\beta |x_i-x_j|^2}
\]

= NUCLEUS-NUCLEUS REPULSION.
Schrödinger Equation for Stationary States

\[ \hat{H} \psi = E \psi \]

\[ \psi = \psi \left( f_1, f_2, \ldots, f_n \right) \]

\( \psi \) is normalized: \( \langle \psi | \psi \rangle = 1 \), and antisymmetric:

\[ \psi \left( \ldots, f_i, f_j, \ldots \right) = -\psi \left( \ldots, f_j, f_i, \ldots \right) \]

\( E \rightarrow \Delta E \)

\[ n(f) = N \prod_{i} \int_{-\infty}^{\infty} \prod_{j \neq i} \int_{-\infty}^{\infty} \left| \psi \left( f_i, f_2, \ldots, f_n \right) \right|^2 \]
\[ h[\psi] = \langle \psi | H | \psi \rangle \]

is a functional: a rule that assigns a number \( h \) to every function \( \psi \).

**Wavefunction Variational Principle:**

The extrema of \( h[\psi] \) are the stationary states, and the absolute minimum is the ground state.

Wavefunctions are never used for large electron number \( N \)!
WHY NOT MANY-ELECTRON WAVE FUNCTIONS?

IMAGINE A GRID OF M POINTS IN POSITION SPACE FOR EACH ELECTRON. WE MUST THEN COMPUTE Y STORE M^N VALUES OF \( \psi \). (KOHM)

LET M = 10^2 (NOT REALLY ENOUGH).

FOR N=2, M^N = 10^4 IS OK.

FOR N=10, M^N = 10^{20} IS NOT OK.

AVOIDING GRIDS, ONE CAN STUDY AT MOST (AND AT GREAT EXPENSE) 10 TO 100 ELECTRONS.

THE DENSITY N(\( \psi \)) HOWEVER WOULD REQUIRE COMPUTING & STORING ONLY M VALUES.
HOHENBERG-KOHN THEOREM 1964:  
CENTRAL THEOREM OF DFT

(i) THERE EXISTS A FUNCTIONAL $F[n]$  
of the electron density, such that  
the GS energy and density for  
$n$ electrons in the presence of  
external potential $v(\vec{r})$ is  

$$E_{gs} = \min_n \left\{ F[n] + \int d^3 \nu(\vec{r}) n(\vec{r}) \right\}.$$  

The minimum is taken over all  
positive $\nu(\vec{r})$ such that $\int d^3 \nu(\vec{r}) = n$.  

$F[n]$ is universal (independent of $v$).  

The problem is to find (approximate  
the functional $F[n]$).
(2) The external potential $\phi(\mathbf{r})$ and hence the Hamiltonian $\hat{H}$ are determined to within an additive constant by $\psi/\hbar$.

Proof by Levy constrained search $\psi$:

$$E_{ee} = \min_{\psi} \langle \psi | \hat{H} + \hat{V}_{ee} + \phi(\mathbf{r}) \psi \rangle$$

$$= \min_{\psi} \min_{n} \sum_{\Psi_n} \langle \psi | \hat{H} + \hat{V}_{ee} \psi \rangle + S\delta_{\psi, \Psi_n}$$

$$= \min_{n} \sum_{\Psi_n} \langle \psi | \hat{H} + \hat{V}_{ee} \psi \rangle + S\delta_{\psi, \Psi_n}$$

$$F[n] = \min_{\psi} \langle \psi | \hat{H} + \hat{V}_{ee} \psi \rangle$$

$$= \langle \psi_n | \hat{H} + \hat{V}_{ee} \psi_n \rangle$$

$\Psi_n$ is the wave function yielding density $\psi_n$ that minimizes $\langle \hat{H} + \hat{V}_{ee} \rangle$. 
Euler Equation for \( n(x) \):

\[
\delta \int \left[ F[n] + Sd^2 n \right] dx - \mu Sd^2 n = 0
\]

\[
\delta \int F[n] + \mu (\delta n) - \mu = 0 \quad \text{for} \quad \text{GS} \quad n(x)
\]

\[\delta n(x) = \mu - \frac{\delta F}{\delta n(x)}\]

Functional derivative \( \frac{\delta F}{\delta n(x)} \):

\[
\delta F = Sd^2 \left( \frac{\delta F}{\delta n(x)} \right) \delta n(x)
\]

Example:

\[E_x^{\text{Lam}}[n] = -C Sd^2 n^{4/3}(x)\]

\[\delta E_x^{\text{Lam}}[n] = -C Sd^2 \frac{4}{3} n^{1/3}(x) \delta n(x)\]

\[\frac{\delta E_x^{\text{Lam}}}{\delta n(x)} = -\frac{4}{3} C n^{1/3}(x)\]
THE CONSTRAINED SEARCH IS FOR UNDERSTANDING, NOT FOR CALCULATING!

THE EXACT $F[n]$ REQUIRES A CONSTRAINED SEARCH OVER N-ELECTRON WAVEFUNCTIONS, WHICH IS IMPractical.

APPROXIMATIONS FOR $F[n]$ THAT ARE EXPLICIT FUNCTIONALS OF $\rho(\mathbf{r})$ ARE TOO CRUDE TO BE VERY USEFUL.

Kohn-Sham Non-Interacting System:

A fictional non-interacting ground state \( \Phi^* \) (usually a single Slater determinant) with the same density \( \rho^* \) and chemical potential as the physical interacting ground state \( \Phi_n \).

\[
H_s = \hat{T} + \sum_i V_s (\hat{\mathbf{P}}_i)
\]

\( s = \text{single particle} \)

\[
\hat{H}_s \Phi^*_n = E^*_s \Phi^*_n
\]

\( \Phi^*_n = \text{the non-interacting wave function yielding density } \rho^* \text{ and minimizing } \langle \hat{H} \rangle. \)
NON-INTERACTING KINETIC ENERGY

\[ T_s [n] = \langle \Phi_n | \frac{\hbar^2}{2m} \Phi_n \rangle \]

\[ E[n] = \langle \Phi_n | \hat{\mathbf{v}} + \hat{\mathbf{v}}_e | \Phi_n \rangle \]

\[ = \langle \Phi_n | \hat{\mathbf{v}} + \hat{\mathbf{v}}_e | \Phi_n \rangle + E_c [n] \]

CORRELATION ENERGY

\[ E_c [n] = \langle \Phi_n | \hat{\mathbf{v}}_e | \Phi_n \rangle - \langle \Phi_n | \hat{\mathbf{v}} | \Phi_n \rangle \leq 0 \]

\[ \langle \Phi_n | \hat{\mathbf{v}}_e | \Phi_n \rangle = U[n] + E_x [n] \]

HARTREE ELECTROSTATIC ENERGY

\[ U[n] = \frac{1}{2} \sum_{\pi \sigma} \sum_{\pi' \sigma'} \langle \pi \sigma | n \pi' \sigma' \rangle \langle n \pi' \sigma' | \pi \sigma \rangle \]

EXCHANGE ENERGY \[ E_x [n] \]

\[ F[n] = T_s [n] + U[n] + E_x [n] \]

TREATED EXACTLY

SOME APPROX. FOR \[ E_x + E_c \]
EULER EQUATIONS
\[
\frac{\delta T_2}{\delta n(\vec{r})} + \nabla \cdot \vec{v}_2(\vec{r}) = \mu \\
\frac{\delta T_2}{\delta n(\vec{r})} + \frac{\delta u}{\delta n(\vec{r})} + \frac{\delta E_{xc}}{\delta n(\vec{r})} + \nabla (\vec{v}) = \mu \\
\text{SOLUTION}
\]
\[
\vec{v}_2(\vec{r}) = \vec{v}_1(\vec{r}) + \frac{\partial^2 n(\vec{r})}{\partial \vec{r}^2} + \vec{v}_x(\vec{r}_n, \vec{r})
\]
\[
\vec{v}_x(\vec{r}_n, \vec{r}) = \frac{\delta E_{xc}}{\delta n(\vec{r})}
\]

SELF-CONSISTENT Kohn-Sham SCHEME
\[
\begin{align*}
\left[ -\frac{1}{2} \nabla^2 + V(\vec{r}) + \sum_{n' \neq n} \frac{n(\vec{r})}{\mid \vec{r} - \vec{r}_{n'} \mid} + V_x(\vec{r}, \vec{r}_n) \right] \psi_{n} = \epsilon_{n} \psi_{n} \\
n(\vec{r}) = \frac{\psi_{n}^* \psi_{n}}{2} \\
\mathcal{Z}(\vec{r}) = \frac{\psi_{n}^* \sum_{n' \neq n} \frac{n(\vec{r})}{\mid \vec{r} - \vec{r}_{n'} \mid} \psi_{n'}}{\psi_{n}^* \psi_{n}} \\
\text{THE Kohn-Sham ORBITALS } \psi_n(\vec{r}) \text{ ARE IMPLICIT FUNCTIONALS OF } n(\vec{r}).
\end{align*}
\]
COUPLING CONSTANT INTEGRAL FOR EXC

LANGRETH + PERDEW 1975

\[ \hat{H}_2 = \hat{T} + 2 \hat{V}_{ee} + \frac{2}{\xi} \hat{v}_a(\hat{r}_1) \]

ADJUST \( \hat{v}_a(\hat{r}_1) \) TO HOLD THE GS DENSITY FIXED AT ITS \( \lambda = 1 \) VALUE.

\( \lambda = 1 \): REAL INTERACTING SYSTEM

\[ \hat{v}_a(\hat{r}) = v(\hat{r}) \]

\( \lambda = 0 \): KOHN-SHAM NON-INTERACTING SYSTEM

\( \psi_n^2 = \) THAT WAVEFUNCTION YIELDING DEGREE \( \eta(\hat{r}) \) THAT MINIMIZES \( \langle \hat{T} + 2 \hat{V}_{ee} \rangle \)

\[ \psi_n^2 = \psi_n \], \( \psi_n^0 = \Phi_n \)
$$E_{xc} \text{[eV]} = \left\langle \frac{\alpha^2}{2} + \alpha \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle$$

$$= \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle$$

$$= \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle - \left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle$$

By HELLMAANN-FEYNMAN

$$\left\langle \frac{\alpha^2}{2} \left\langle \frac{\alpha^2}{2} \right\rangle \right\rangle = \frac{1}{2} \int d^3 \mathbf{r}_2 \frac{\rho_2(\mathbf{r}_2)}{\rho_2(\mathbf{r}_2)}$$

WHERE

$$\rho_2(\mathbf{r}_2) = N(N-1) \prod_{\alpha} \frac{\delta}{\delta v_{\alpha}} \delta v_{\alpha}...d^3 \mathbf{v}_{\alpha}$$

$$= \text{TWO-PARTICLE DENSITY MATRIX}$$
\[ \rho_z(\vec{r}, \vec{r}') = \text{Joint probability density} \]
\[ = n(\vec{r}) \left[ n(\vec{r}') + \eta_{xc}(\vec{r}, \vec{r}') \right] \]
\[ S_{\vec{r}} S_{\vec{r}'} \rho_z(\vec{r}, \vec{r}') = N/N' \]
\[ S_{\vec{r}} S_{\vec{r}'} n(\vec{r}) n(\vec{r}') = N(N) \]
so \[ S_{\vec{r}'} \eta_{xc}(\vec{r}, \vec{r}') = -1 \] sum rule
\[ \eta_{xc}(\vec{r}, \vec{r}') = \text{Density at } \vec{r}' \text{ of the } \]
\[ xc \text{ hole around an electron at } \vec{r}. \]
\[ \text{Around an electron at } \vec{r}, \text{ one electron is missing from the } \]
\[ \text{space } \vec{r}' \neq \vec{r}. \]
\[ E_{xc} = \int S_{\vec{r}} d\vec{r} \frac{1}{2} S_{\vec{r}} S_{\vec{r}'} n(\vec{r}) n(\vec{r}') \eta_{xc}(\vec{r}, \vec{r}') \]
\[ \text{per cell} \]
\( E_x \) can be expressed as a puck integral of occupied orbitals:

\[
\eta_x (F_x \Phi_{11}) = \eta_{xc}^{\alpha=0} (F_x \Phi_{11})
\]

\[
= - \frac{1}{\pi \hbar^2} \int \rho_x \Phi_{11} \Phi_{11}^2
\]

where

\[
\rho_x (F_x \Phi_{11}) = \frac{\Delta F_x}{\Delta \Phi_{11}} \Phi_{11}^2 (\Phi_1 \Phi_{11})
\]

= Kohn-Sham one-particle density matrix

Exact constraints: We know many exact constraints on the hole (such as the sum rule) or on the \( xc \) energy.
EX: UNIFORM DENSITY SCALING OF \( E_x [n] \)
LEVY + PEDDEL

FOR ANY POSITIVE SCALE PARAMETER \( a \),
DEFINE A SCALED DENSITY

\[
\eta_a (n) = n^3 \eta (n/a^3)
\]

\[
\frac{\eta_a (n)}{\eta (n)} \xrightarrow{a \to 1} \frac{n^3}{n} = n^2,
\]

\[
\frac{\eta_a (n)}{\eta (n)} \xrightarrow{a \to \infty} a^{-3/2} \frac{n^3}{n}
\]

\[
E_x [\eta_a] = a E_x [n]
\]

HIGH-DENSITY LIMIT: \( a \to 0^+ \)

\[
E_c [\eta_a] \to \text{CONSTANT (NOKS DETERMINISM)}
\]

\( E_x \) DOMINATES \( E_c \)
Many other exact constraints on \( \pi_{xc}^2(R,T,T') \) or \( E_{xc}[n] \) have been derived. These constraints have been used to construct approximations to \( E_{xc}[n] \), without (or with) fitting to data.

Fully nonempirical:

Local density approximation

PBE generalized gradient approximation

TPSS meta-generalized gradient approximation

PBE/skr: Monday afternoon

DFT Symposium
We can construct the exact $e_{x}(n)$ from Kohn-Sham orbitals (as in OEP), but bonds are described better when we make the same local or semi-local approximation for $e_{x}$ and for $e_{c}$. That is because $n_{xc}^{2}(\mathbf{r},\mathbf{r}')$ is typically deeper, more short-ranged in $|\mathbf{r}'-\mathbf{r}|$, and thus more semi-local than is $n_{x}(\mathbf{r},\mathbf{r}')$. 
SIMPLEST DENSITY FUNCTIONAL:
LOCAL DENSITY APPROXIMATION

\[ \varepsilon_{xc}^{\text{LDA}}[n] = \sum_{n,m} n \rho(n) \varepsilon_{xc}^{\text{LDA}}(n,m) \]

\[ \varepsilon_{xc}^{\text{LDA}}(n) = x_0 \text{ ENERGY PER ELECTRON} \]
FOR AN ELECTRON GAS OF UNIFORM DENSITY \( n \).

EXACT FOR A UNIFORM DENSITY.
CORRECTIONS FOR A SLOWLY-VARYING DENSITY \( \sim |d\rho|/\rho \).

\[ \varepsilon_{xc}^{\text{LDA}}(n,\nabla \rho) = \eta_{xc}^{\text{LDA}}(n,\rho; |\nabla \rho|) \]
SATISFIES SUM RULE AND SEVERAL OTHER EXACT CONSTRAINTS,
INCLUDING SCALING FOR \( x_0 \).
Jacob's Ladder of Density Functional Approximations

\[ E_{xc} = S(l^q + f(n, \rho_v, \pi, \ldots)) \]

\[ \pi \psi \psi \frac{\hbar^2}{2m} \frac{1}{10} \chi_1 \frac{1}{2} = \text{Positve} \]

\[ \chi \psi \psi \text{Density} \]

Heaven of Chemical Accuracy

- GGA
- HSE06A
- M06-6H
- GGA
- LDA

Hartree World

- Accurate
- Generalized RPA
- Hyper-DCA
- Meta-GGA
- GGA
- LDA