Introduction to Density Functional Theory

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What is Density Functional Theory?

- DFT is an exact many-body theory for the ground state properties of an electronic system.
  - Atoms, molecules, surfaces, nanosystems, crystals
- Although DFT is formally exact, the exact functional is unknown.
- The exact functional probably does not have a closed form, and would be extremely non-local.
- Nevertheless, very good approximations are known which work well for many systems.
- In practice, DFT is good for structural stability, vibrational properties, elasticity, and equations of state.
- There are known problems with DFT, and accuracy is limited--there is no way to increase convergence or some parameter to obtain a more exact result. In other words there are uncontrolled approximations in all known functionals.
- Some systems are treated quite poorly by standard DFT.
Outline

• Motivation: an example—Quartz and Stishovite, DFT versus QMC
• What is DFT used for in QMC studies?
• The steps for Diffusion Monte Carlo.
• Density Functional Theory
  – What is a functional?
  – Hohenburg Kohn Theorems
  – Kohn–Sham method
  – Local Density Approximation (LDA)
  – Total energy calculations
  – Typical Errors
  – What is known about exchange and correlation functionals?
  – The exchange correlation hole and coupling constant integration
  – LDA and GGA (more)
  – Band theory
  – Self-consistency
  – A new GGA (WC) and the potential for more accurate density functionals
Quartz and Stishovite

Stishovite (rutile) structure

Dense
octahedrally coordinated Silicon

Quartz structure

Open structure
tetrahedrally coordinated Silicon
CaCl$_2$ transition in SiO$_2$

Prediction: $A_{1g}$ Raman mode in stishovite decreases until phase transition to CaCl$_2$ structure, then increases. Does NOT go to zero at transition.

Prediction: $C_{11}-C_{12}$ decreases until phase transition to CaCl$_2$ structure, then increases. Does go to zero at transition -> superplasticity

Predicted transition (Cohen, 1991) was found by Raman (Kingma et al., Nature 1995).

LDA works for stishovite/CaCl$_2$. 
Silica

Simple close shelled electronic structure, yet problems with DFT

Generalized Gradient Theory for Silica Phase Transitions

D. R. Hamann
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974
(Received 16 October 1995)

difference in GGA and LDA valence density

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE*</th>
<th>WC**</th>
<th>Exp.</th>
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<td>-0.05</td>
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<td>0.2</td>
<td>0.5</td>
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<td>6.2</td>
<td>2.6</td>
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<td>$V_{qz}$</td>
<td>244</td>
<td>266</td>
<td>261</td>
<td>254</td>
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<td>$K_{qz}$</td>
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<td>$V_{st}$</td>
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<tr>
<td>$K_{st}$</td>
<td>303</td>
<td>257</td>
<td>330</td>
<td>313</td>
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</table>

DFT (WC) energies for quartz and stishovite


A diffuse cut-off for the exchange fits low and slowly varying densities. $F^x$ agrees well with advanced DFTs with simple GGA functional.

- We tested the following 18 solids: Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Ru, Rh, Pd, Ag.
- The new GGA is much better than other approximations.

Mean errors (%) of calculated equilibrium lattice constants $a_0$ and bulk moduli $B_0$ at 0K.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>WC</th>
<th>TPS</th>
<th>PKZB</th>
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<tbody>
<tr>
<td>$a_0$</td>
<td>1.74</td>
<td>1.30</td>
<td>0.29</td>
<td>0.83</td>
<td>1.65</td>
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<tr>
<td>$B_0$</td>
<td>12.9</td>
<td>9.9</td>
<td>3.6</td>
<td>7.6</td>
<td>8.0</td>
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</table>

TPSS and PKZB results: Staroverov, et al. PRB 69, 075102
QMC results CASINO
(at DFT WC minimum)

<table>
<thead>
<tr>
<th></th>
<th>Quartz (H)</th>
<th>Stishovite (H)</th>
<th>(\Delta E) (eV/fu)</th>
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<tr>
<td>Exp.</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>LDA</td>
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</tr>
<tr>
<td>PBE</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>WC</td>
<td>-35.7466</td>
<td>-35.7397</td>
<td>0.2</td>
</tr>
<tr>
<td>DMC MPC stish 3x3x3</td>
<td>-35.8071</td>
<td>-35.7912</td>
<td>0.43</td>
</tr>
<tr>
<td>qz 2x2x2</td>
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No finite size corrections
Comparison of QMC and DFT (WC xc)

Shifts in energy and pressure from DFT (WC) to QMC (QMC-DFT)

<table>
<thead>
<tr>
<th></th>
<th>Stishovite</th>
<th>Quartz</th>
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<tr>
<td>$E_0$</td>
<td>-0.77</td>
<td>-1.76</td>
</tr>
<tr>
<td>eV/SiO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>-4.6</td>
<td>-8.0</td>
</tr>
<tr>
<td>GPa</td>
<td></td>
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Quartz to stishovite transition

<table>
<thead>
<tr>
<th></th>
<th>qz</th>
<th>st</th>
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<tbody>
<tr>
<td>$V_0$ (au)</td>
<td>247</td>
<td>156</td>
</tr>
<tr>
<td>$V_0$ (exp)</td>
<td>254</td>
<td>157</td>
</tr>
<tr>
<td>$K_0$ (GPa)</td>
<td>39</td>
<td>309</td>
</tr>
<tr>
<td>$K_0$ (exp)</td>
<td>38</td>
<td>313</td>
</tr>
</tbody>
</table>
What is DFT used for in QMC?

- DFT is used to relax ground state structures, since QMC relaxation is not yet tractable for crystals.
- DFT is used to compute phonons to obtain quasiharmonic estimates of zero point and thermal contributions to the free energy.
- DFT is used to generate trial wavefunctions for QMC.
- Sometimes DFT is used to estimate finite size corrections to QMC.
Procedure

Develop and Test Pseudopotentials
Self-consistent DFT computation

Generate orbitals for trial functions for k-point set and find blip representation

Perform variation optimization of Jastrow parameters

DMC Statistics Generation

DMC equilibration

VMC to generate Initial configurations or get VMC energy
Functionals + Functional Derivatives

Functionals are mappings from function spaces to the real (or complex) numbers. A general representation for a functional $F$ is

$$F[g] = F_0 + \int dx \; F_1(x) g(x) +$$

$$+ \int dx_1 \int dx_2 \; F_2(x_1, x_2) g(x_1) g(x_2)$$

$$+ \int dx_1 \int dx_2 \int dx_3 \; F_3(x_1, x_2, x_3) g(x_1) g(x_2) g(x_3) + \cdots$$

(1)

where the kernels $F_i$ may themselves be either ordinary functions or generalized functions containing, for example, the delta function and its derivatives.

Now let $g = g_0 + \Delta g$. To linear order in $\Delta g$ we have

$$F[g] = F[g_0] + \int dx \; F_1(x) \Delta g(x) +$$

$$+ 2 \int dx_1 \int dx \; F_2(x_1, x) \; g_0(x_1) \Delta g(x)$$

$$+ 3 \int dx_1 \int dx_2 \int dx \; F_3(x_1, x_2, x) \; g_0(x_1) g_0(x_2) \Delta g(x) + \cdots$$

(2)
(To obtain (2) I have assumed the kernels $F_i$ are symmetric functions of their arguments; This clearly does not restrict the generality of (1).

We can rewrite (2) as

$$F[g_0 + \Delta g] = F[g_0] + \int dx \frac{SF[g_0]}{\delta g(x)} \Delta g(x) \quad (3)$$

where

$$\frac{SF[g_0]}{\delta g(x)} = F_1(x) + 2 \int dx_1 g_0(x_1) F_2(x_1, x)$$

$$+ 3 \int dx_1 \int dx_2 g_0(x_1) g_0(x_2) F_3(x_1, x_2, x) \quad (4)$$

$$+ \cdots$$

Alternatively, when (as is often the case) we do not have an explicit representation such as (1) for $F$, equation (3) serves to define the functional derivative $\frac{SF}{\delta g(x)}$.

The higher functional derivatives are defined by
analogy to (2):

\[ F[g_0 + \Delta g] = F[g_0] + \int dx \frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} \Delta g(x) \delta g(x') + \frac{1}{2} \Delta g \frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} \Delta g(x) \Delta g(x') + O(\Delta g)^3 \]  

(5)

From (1) we find an explicit representation for 
\[ \frac{\delta^2 F}{\delta g(x) \delta g(x')} : \]

\[ \frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} = 2 F_2(x, x') + 6 \int dx_1 g_0(x_1) F_3(x_1, x, x') + \ldots \]

(6)

Example: The Coulomb energy of a charge distribution \( \rho(r) \) is given by a functional \( U[\rho] \), with

\[ U_0 = 0, \quad U_1 = 0, \quad U_2(r, r') = \frac{e^2}{2} \frac{1}{|r - r'|}, \quad U_{n>2} = 0 \]

\[ \frac{\delta^2 U[\rho_0]}{\delta \rho(r)} = e^2 \int d^3r_1 \frac{n_0(r_1)}{|r - r'|} \quad \frac{\delta^2 U[\rho_0]}{\delta \rho(r) \delta \rho(r')} = \frac{e^2}{|r - r'|} \]
Examples of Functional Derivatives

\[ I[f] = \int w(x) f(x) \, dx \]

\[ \frac{\delta I}{\delta f} = w(x) \]

\[ J[g] = \int (g(x))^\alpha \, dx \]

\[ \frac{\delta J}{\delta g} = \alpha (g(x))^{\alpha - 1} \]

\[ E = \int g \left( \frac{\partial c}{\partial x} \right) \mid_{\partial \Omega} \, d\Omega \]

\[ S E = \int \left[ \frac{\delta g}{\delta f} \int g \left( \frac{\partial c}{\partial x} \right) \mid_{\partial \Omega} \, d\Omega + \frac{\delta^2 g}{\delta f^2} \int g \left( \frac{\partial c}{\partial x} \right) \mid_{\partial \Omega} \, d\Omega \right] \, dx \]

\[ S E = \int \left[ \frac{\delta g}{\delta f} \int \left( \frac{\partial c}{\partial x} \right) \mid_{\partial \Omega} \, d\Omega - \frac{\delta^2 g}{\delta f^2} \int \left( \frac{\partial c}{\partial x} \right) \mid_{\partial \Omega} \, d\Omega \right] \, dx \]
Density Functional Theory

\[ \Psi \leftrightarrow V \leftrightarrow \rho \]

- exact many-body wave function
- external potential (nuclei)
- ground state charge density

All properties of the system are functionals of the charge density, i.e., there is a one-to-one correspondence between \( \rho \) and \( V \).
Density Functional Theory

Hohenberg - Kohn Theorem

Exact:
\[ H = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i \neq j}^{N} v(r_{ij}) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{\varepsilon |r_i - r_j|} \]

\[ KE \quad V \quad U \]

\[ H \Psi = E \Psi \quad \rho(r) = \langle \Psi^* \Psi \rangle \]

\( \Psi \) exact many body wave function
Hohenberg-Kohn Theorem

1. Can two different \( \nu \)'s give the same charge density \( \rho(r) \)?

\[
\nu(r) - \nu'(r) \neq \text{constant}
\]

Assume: \( \rho'(r) = \rho(r) \)

\( \nu' \neq \nu \) since they solve different Schrödinger equations

\[
\begin{align*}
E' &= \langle \Phi' | H' | \Phi' \rangle \\
&= \langle \Phi' | H + V' - 10 | \Phi' \rangle \\
&= \langle \Phi' | H | \Phi' \rangle + \langle \Phi' | V' - 10 | \Phi' \rangle \\
&= E + \left( \int d^3r [\nu'(r) - \nu(r)] \rho(r) \right)
\end{align*}
\]

So

\[
E' < E + \int d^3r [\nu'(r) - \nu(r)] \rho(r) \]

\[\text{Note: } E = \langle \Psi | H | \Psi \rangle \\
E < E' + \int d^3r [\nu'(r) - \nu(r)] \rho(r) \]

\[E < E' + \int d^3r [\nu'(r) - \nu(r)] \rho(r) \]

Add 1 and 2:

\[E + E' < E + E' \]

Contradiction!

So \( \nu = \nu' \) if \( \rho = \rho' \)
Hohenberg-Kohn Theorem #2: Minmax principle

The calculated ground state energy is a minimum for the ground state density \( \rho(r) \):

Define \( F[\rho] = \langle \Phi | (-\nabla^2 + V + U) \Phi \rangle \)

where

\[ T: \quad \text{Kinetic energy} = \frac{\hbar^2}{2m} \sum_i \frac{\mathbf{p}_i^2}{2} \]

\[ U: \quad \text{Hartree energy} = \frac{1}{2} \sum_{i,j} \frac{\mathbf{e}_i^2}{|\mathbf{r}_i - \mathbf{r}_j|} \]

since \( \Phi = \Phi[\rho] \), \( F = F[\rho] \)

\[ E_{\text{\Phi}}[\rho] = \int d^3r \cdot V(r) \rho(r) + F[\rho] \]

\( E_{\text{\Phi}}[\rho] \) is the ground state energy for external potential \( V \) in the correct density \( \rho(r) \).

We know that:

\[ E_{\text{\Phi}}[\rho] = \langle \Phi | (-\nabla^2 + V + U) \Phi \rangle \]

\[ E_{\text{\Phi}}[\rho] = 0 \quad \text{Grand state energy} \]

\[ \langle \Phi | V \rangle = \langle \Phi | \rho \rangle \]

\[ E_{\Phi}[\rho] \xrightarrow{\Delta \rho} E_{\Phi}[\rho'] \]

So:

\[ \Delta E_{\Phi} \geq 0 \]

\[ E_{\Phi}[\rho'] \geq E_{\Phi}[\rho] \]
Hohenberg-Kohn Second Proof
(Levy Constrained Search)

\[ E = \min_{\rho} \langle \Psi | H | \Psi \rangle \]

First consider:

\[ \min_{\Psi} \langle \Psi | H | \Psi \rangle = \min_{\Psi} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d^3 r \, v(r) \rho(r) \]

Because \( v(r) \) implies \( \Psi \) and thus \( \rho \)!

Define:

\[ F[\rho] = \min_{\Psi} \langle \Psi | T + V_{ee} | \Psi \rangle = \langle \Psi^{\text{min}} | T + V_{ee} | \Psi^{\text{min}} \rangle \]

Now minimize overall \( N \) electron densities \( \rho(r) \)

\[ E = \min_{\rho} E_{\Psi} [\rho] = \min_{\rho} \left\{ \int F[\rho] + \int d^3 r \, v(r) \rho(r) \right\} \]

Use Lagrange multiplier to fix \( N \):

\[ 5 \int F[\rho] + \int d^3 r \, v(r) \rho(r) - \mu \left( \int d^3 r \, \rho(r) \right)^2 = 0 \]

\[ \frac{5}{\rho^2} \Rightarrow \frac{5F[\rho]}{\rho} + 5v(r) = \mu \]

So \( v(r) \propto \rho(r) \)

\( \rho(r) \) - \( N \)-representable for \( \Psi \) and \( \rho(r) \)

\( \frac{\delta F}{\delta \rho} \) - \( V \)-representable for \( \Psi \) and \( \rho(r) \)
Kohn–Sham: Self-consistent equations for obtaining the ground state properties

Define: \( T_s [\rho] = \) kinetic energy of a non-interacting system with density \( \rho(r) \)

\[
E[\rho] = \int v(r) \rho(r) \, d^3r + T_s [\rho] + \frac{1}{2} \int \int \frac{(\rho(r) \rho(r')) \, d^3r \, d^3r'}{|r-r'|}
\]

Define: \( \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} = \rho_{xc}(r) \)

Now \( \frac{\delta E}{\delta \rho(r)} = 0 \) for \( N_{xc} = \int \rho(r) \, d^3r \)

Use a Lagrange multiplier:

\[
\frac{\delta}{\delta \rho(r)} \left( E[\rho] - \mu N_{xc} \right) = 0
\]

Define Hartree potential \( \nu_h \equiv \int d^3r' \frac{\rho(r')}{|r-r'|} \)

Then:

\[
\frac{\delta T_s}{\delta \rho(r)} + v(r) + \nu_h(r) + \rho_{xc}(r) = \mu
\]

If \( \frac{\delta T_s}{\delta \rho} \) and \( \rho_{xc} \) were known exactly and were simple functions of \( \rho \), \( \rho(r) \) could be found to satisfy this equation.
Kohn-Sham (contd)

Non-interacting system:
We do know how to solve:

\[
\frac{\text{ST} \mathcal{E} + N_0(r)}{\text{Sp}(r)} = \mu
\]

for a non-interacting system:

\[
\left[-\nabla^2 + V_0(r)\right] \psi_i = \epsilon_i \psi_i
\]

\[
\rho(r) = \sum_{c=1}^{S} \psi_{c}^{*}(r) \psi_{c}(r)
\]

since this is the correct ground state density \(\rho(r)\),
it must satisfy (1).

Interacting system:
We want to solve:

\[
\frac{\text{ST} + V(r) + N_0^n(r) + N_{xc}(r)}{\text{Sp}(r)} = \mu
\]

for \(\rho(r)\), but we do not know \(\frac{\text{ST} + V}{\text{Sp}(r)}\).

But if \(V_0 = V + N_0^n + N_{xc} = \text{neff}\), we could solve the non-interacting problem:

\[
\frac{\text{ST}}{\text{Sp}(r)} + \text{neff} = \mu
\]
Local Density Approximation

\[ \text{Exc} \{ \rho \} = \int d^3 r \, \rho(r) \text{Exc}(\rho(r)) \]

Local Excursion

Exchange correlation functional:
\[ N_{\text{exc}} = \frac{S_{\text{Exc}}}{S_{\rho}} \]

Local Exchange Correlation Functional

Total energy for noninteracting electron gas

Consider \( S_{\text{Exc}} \{ \rho \} \)

\[ \text{Exc} \{ \rho + \delta \rho \} - \text{Exc} \{ \rho \} = \int d^3 r \, \delta \rho \frac{S_{\text{Exc}}}{S_{\rho}} \]

\[ = \int d^3 r \left[ (\rho + \delta \rho) \text{Exc}(\rho + \delta \rho) - \rho \text{Exc}(\rho) \right] \]

\[ = \int d^3 r \left[ \rho \text{Exc}(\rho) + \delta \rho \text{Exc}(\rho) \right] + \delta \rho \text{Exc}(\rho) \left[ \cdots \right] - \rho \text{Exc}(\rho) \]

\[ = \int d^3 r \left[ \delta \rho \text{Exc}(\rho) + \delta \rho \text{Exc}(\rho) \right] + O(\delta \rho^2) \]

So we see:
\[ \frac{N_{\text{exc}}^{\text{LDA}}}{\rho} = \frac{\delta}{\delta \rho} \left( \rho \text{Exc}(\rho) \right) \]

\[ E_x^{\text{LDA}} \{ \rho \} = A_x \int d^3 r \, \rho(r)^{4/3} \]

\[ E_x(r) = A \rho^{4/3} \]

\[ S_{\text{Exc}} = N_{\text{exc}} = A_x \frac{4}{3} \rho^{2/3} \]

\[ \frac{S_{\text{Exc}}}{S_{\rho}} = \text{Exc} \]

\[ \frac{S_{\text{Exc}}}{S_{\rho}} = \text{Exc} \]

\[ \text{Exc} = E - T_S - V^0 \]
Total Energy Calculations

$$\mathcal{E}[\rho] = \int v(r) \rho(r) \, d^3r + \mathcal{T}_s \mathcal{E}[\rho] + \frac{1}{2} \iint \rho(r) \rho(r') \frac{\rho(r')}{|r-r'|} \, d^3r \, d^3r'$$

$$+ \text{Exc}[\rho]$$

Now

$$\mathcal{T}_s \mathcal{E}[\rho] + \int d^3r \rho(r) \left\{ \Delta^2 \rho(r) + \int d^3r' \frac{\rho(r')}{|r-r'|} + \nu \xi \langle \rho \rangle \right\}$$

$$= \mathcal{E}_e$$

Two equivalent expressions for the ground state energy for non-interacting (independent) electrons.

So:

$$\mathcal{E}[\rho] = \mathcal{E}_e - \frac{1}{2} \iint \rho(r) \rho(r') \frac{\rho(r')}{|r-r'|} \, d^3r \, d^3r' + \text{Exc}[\rho]$$

$$- \int \rho(r) \nu \xi \rho(r) \, d^3r$$

Note: near nuclei, there is a very large kinetic energy density and a very negative potential energy density. Extreme accuracy is required. Say $10^{-9}$ or smaller.
Typical errors

<table>
<thead>
<tr>
<th>Atoms, molecules &amp; solids</th>
<th>LSD</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex</td>
<td>5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Ec</td>
<td>100% (negative)</td>
<td>5%</td>
</tr>
<tr>
<td>bond length</td>
<td>190 (short)</td>
<td>190 (too short)</td>
</tr>
<tr>
<td>structure</td>
<td>close packed</td>
<td>more correct</td>
</tr>
<tr>
<td>energy barrier</td>
<td>100% (too low)</td>
<td>30% (too low)</td>
</tr>
</tbody>
</table>

Atomization energy for 20 molecules

- Unrestricted Hartree Fock: 3.1 eV underbinding
- LSD: 1.3 eV overbinding
- GGA: 0.3 eV (mostly over)

"Chemical accuracy" 0.05 eV
Exchange and Correlation Energies (general case)

\[ \text{Ex}^\text{e}[p] = \text{Ex}^\text{e}[\Phi] + \text{Ec}^\text{e}[p] \]

**Exact**

\[ \text{Ex}^\text{e}[\Phi] = \langle \Phi_0^{\text{min}} | V_{ee} | \Phi_0^{\text{min}} \rangle - U \Phi_0^{\text{e}[p]} \]

- Single Slater determinant of ground state orbitals (like Hartree-Fock)

Note that:
\[ \langle \Phi_0^{\text{min}} | T + V_{ee} | \Phi_0^{\text{min}} \rangle = T_0 \text{c}[\Phi] + U \text{c}[\Phi] + \text{Ex}^\text{e}[\Phi] \]

**Correlation**

\[ \text{Ec}^\text{e}[p] = F^\text{e}[p] - \{ T_0 \text{c}[\Phi] + U \text{c}[\Phi] + \text{Ex}^\text{e}[\Phi] \} \]

\[ = \langle \Phi_0^{\text{min}} | T + V_{ee} | \Phi_0^{\text{min}} \rangle - \langle \Phi_0^{\text{min}} | T + V_{ee} | \Phi_0^{\text{min}} \rangle \]

\[ \text{Ec}^\text{e}[p] \leq 0 \]

- Positive KE part, negative FG part
Scaling Properties

Consider first the Hartree energy:

\[ U_E = \frac{1}{2} \int \int \frac{P(r)P(r')}{|r-r'|} \, \, dr \, dr' \]

scale \( r, r' \) by \( \gamma \):

\[ U_{E \gamma} = \frac{1}{2} \int \int \frac{\gamma^3 P(\gamma r)P(\gamma r')}{|r-r'|} \, \, d\gamma^3 r \, d\gamma^3 r' \]

\[ = \gamma \frac{1}{2} \int \int \frac{P(r)P(r')}{|r-r'|} \, \, dr \, dr' = \gamma U_E \]

Similarly:

\[ E_x E_{\gamma} = \gamma E_x E_{\gamma} \]

Kinetic energy:

\[ \psi_\gamma(r_1, r_2, ..., r_n) = \gamma^{3n/2} \psi(\gamma r_1, \gamma r_2, ..., \gamma r_n) \]

\[ \rho_\gamma(r) = \gamma^3 \rho(\gamma r) \]

\[ \langle \psi_\gamma | \nabla^2 | \psi_\gamma \rangle = \gamma^2 \langle \psi | \nabla^2 | \psi \rangle \]

\[ \langle \psi | \nabla^2 | \psi \rangle = \frac{3}{2} \]

so:

\[ T_S [\rho_\gamma] = \gamma^2 T_S [\rho] \]
Consider any functional $G\rho_f$ and a local density approximation:

$$G\rho_f = \int d^3r \frac{\rho_f(\rho_f - \rho)}{\rho_f}$$

If $G\rho_f = \lambda \rho_f G\rho_f$ then

$$\frac{1}{\rho_f} \int d^3r \frac{\rho_f(\rho_f - \rho)}{\rho_f} = \frac{1}{\rho_f} \int d^3r \frac{\rho_f(\rho_f - \rho)}{\rho_f}$$

or:

$$\rho_f(\rho_f - \rho) = \rho_f^2 \rho$$

$$G(\rho) \propto \rho^{1+p/3}$$

For $G_f, \rho = 1$ so

$$G_f(\rho_f) \propto \rho_f^{4/3}$$

For $G_f, \rho = 2$ so

$$G_f(\rho_f) \propto \rho_f^{5/3}$$
Exchange and Correlation Hole

Joint probability function

\[ n(r, \sigma; r', \sigma') = n(r, \sigma)n(r', \sigma') + \Delta n(r, \sigma; r', \sigma') \]

Exact Exchange hole

\[ \Delta n_x = \Delta n_{HF}(r, \sigma; r', \sigma') \]

\[ = -\delta_{\sigma\sigma'} \left| \sum_{C} \psi_\sigma^*(C)(r)\psi_{\sigma'}^*(C)(r') \right|^2 \]

\[ = -\delta_{\sigma\sigma'} \left| \rho_0(r, r') \right|^2 \]

Cancels self-interaction in Hartree term:

\[ E_H = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} \]

\[ E = \left[ \langle V_{\text{ex}} n > - E_H \right] = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3r d^3r' \Delta n_{x_{HF}}(r, \sigma; r', \sigma') \left| \frac{\Delta n_x}{\sigma, \sigma'} \right| \]

\[ \int d^3r \Delta n_x(r, \sigma; r', \sigma') = -1 \]
Exchange Correlation Hole

\[ \Delta n_{xc} (r_j \sigma_j; r_j' \sigma_j') = n_x + n_c \]

\[ \int d^3 r' \ n_c = 0 \]

Coupling Constant Integration

Vary electron charge from 0 to e

Then

\[ E_{xc} [\psi] = \int d \lambda \ < \psi_\lambda | \frac{dV_{\text{int}}}{d\lambda} | \psi_\lambda > \]

\[ = -\bar{E}_H \]

\[ = \frac{1}{2} \int d^3 r \int d^3 r' \ n(r) \bar{n}_{xc}(r') \]

Where

\[ \bar{n}_{xc} (r_j r_j') = \int d \lambda n_{xc}^\lambda (r_j r_j') \]

\[ \int d^3 r' \ n_c = 0 \]
Summary of D1=T

HK1
\[ \Phi \leftrightarrow V \leftrightarrow \rho \]

HK2
\[ \text{SEE} [\rho] = 0 \]

KS
\[ H \psi = \varepsilon \psi \quad \rho = \frac{\text{SEE}}{\delta} \psi^* \psi \]
\[ H = -\frac{1}{2} \nabla^2 + V_{\text{eff}} \]
\[ V_{\text{eff}} = V_{\text{ext}} + U + V_{\text{exc}} \]
\[ V_{\text{ext}}: \text{external potential (nuclear)} \]
\[ U: \text{Hartree potential} \quad U(r) = \int d^3r' \frac{\rho(r')}{|r-r'|} \]
\[ V_{\text{exc}} = \frac{\text{SEE}}{\delta \rho} \]

Solve self-consistently

Total Energy:
\[ E = E_{\text{tot}} + \int d^3r \rho(r) \varepsilon(r) + \frac{1}{2} \int d^3r d^3r' \frac{\rho(r) \rho(r')}{|r-r'|} + E_{\text{exc}} \]
\[ E_{\text{tot}} = \sum \varepsilon_{\text{exc}} <\psi_\Phi^*/-\frac{1}{2} \nabla^2 \psi_\Phi> \]

Or:
\[ E = \sum \varepsilon_{\text{exc}} - U(\rho) - \int d^3r \rho(r) V_{\text{exc}}(r) + E_{\text{exc}} \]
Summary of LDA

\[ E_{xc} = \int d^3r \, \rho(r) \, e_{xc}(\rho) \]

\[ \nu_{xc} = \frac{\delta E_{xc}}{\delta \rho} = \frac{d}{dp} \left( \rho \left( \frac{\partial}{\partial \rho} e_{xc}(\rho) \right) \right) \]

See this from definition:

\[ F_{E g o + A g} = F_{E g o} + \int dx \, \frac{\delta F_{E g o}}{\delta g} \left( \frac{\partial}{\partial \rho} \right) \]

\[ E_{xc} \rho + \delta \rho \]

\[ = \int e_{xc}(\rho + \delta \rho) (\rho + \delta \rho) \, d^3r \]

\[ = \int \rho \, d^3r \left( e_{xc}(\rho) + e_{xc}(\rho) \delta \rho + \cdots \right) + \int \delta \rho \, e_{xc}(\rho + \delta \rho) \, d^3r \]

\[ = E_{xc} \rho + \delta \rho \left( e_{xc} + e_{xc}(\rho) \right) \]

\[ = E_{xc} \rho + \int d^3r \, \delta \rho \left( e_{xc} + e_{xc}(\rho) \right) \]

\[ \frac{\delta E_{xc}}{\delta \rho} = \frac{d}{dp} \left( \rho \, e_{xc} \right) \]
Explicit LDA Functionals

Free Electron Gas

Exchange:

\[ \text{exc}(H) = -\frac{3}{4\pi} \left( 3\pi^2 \rho(n) \right)^{\frac{1}{3}} \]

\[ \frac{\delta E_x}{\delta \rho} = -\frac{1}{\pi} k_F \]

Correlation:

\[ \rho = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi^2 r_s^3} \]

high density: \( r_s \to 0 \)

\[ e_c = c_0 \ln r_s - c_1 + c_2 \ln r_s - c_3 r_s + \ldots \]

low density: \( r_s \to \infty \)

Wigner crystal

\[ e_c \to -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \ldots \]

Perdew + Wang, PRB 45, 13244 (1992) fit

Monte Carlo Results of Ceperley + Alder, PRL 45, 566 (1980):

\[ e_c(\rho(r)) = -2c_0 (1 + c_1 r_s) \ln \left[ 1 + 2c_0 (\frac{r_s}{r_s^{3/2}} + \frac{r_s^{3/2}}{2} + \frac{3}{2} r_s^{3/2}) \right] \]
Local Spin Density Approximation

\[
\text{Fractional Spin Density: } S(r) = \frac{\rho_n(r) - \rho_s(r)}{(\rho_n + \rho_s)}
\]

\[
e^x(\rho_n, \rho_s) = e^x(\rho) \left[ \frac{(1 + S)^{4/3} + (1 - S)^{4/3}}{2} \right]
\]

RPA:
\[
e^c(\rho_n, \rho_s) = e^c(\rho) + \alpha c(\rho) s^2 + O(s^4)
\]

\(\alpha c\) “spin stiffness”
FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times $r_s^2$ in rydbergs vs $r_s$ in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$. 
Free Electron Gas II

Thomas-Fermi Kinetic Energy

Solution: \( V_2 = \frac{1}{\sqrt{V}} e^{k_r r} \)

In a large box of volume \( V \), and lengths \( L_x, L_y, L_z \)

Solutions must have nodes at boundaries \( L_x, L_y, L_z \):

\( k_x = \frac{2\pi n_x}{L_x} \) are the allowed values of \( k_x \) for integers \( n_x \)

Allowed wave numbers, 1 per \( k_x k_y k_z = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V} \)

Density of states \( \frac{V}{(2\pi)^3} \)

KE of each state is \( \frac{1}{2} \frac{1}{2m} k^2 \)

\( N = \rho V = \frac{4}{3} \pi k_f^3 \cdot 2 \cdot \frac{V}{(2\pi)^3} \)

\( k_f = (3\pi^2 \rho)^{1/3} \)

Average KE: \( \langle \frac{1}{2} k^2 \rangle = \int_0^{k_f} \frac{1}{2m} \frac{4\pi k^2 \, dk}{2m} = \frac{3}{5} \frac{k_f^2}{2m} \)

KE at \( k_f \) = \( \frac{3}{5} \frac{k_f^2}{2m} (3\pi^2 \rho)^{2/3} \rightarrow \frac{3}{10} (3\pi^2 \rho)^{2/3} \) in Hartrees
Self-consistent LDA (GGA)

1. Initial guess for potential or density

2. Solve \( H \psi_i = E_i \psi_i \)
   for \( H = -\frac{1}{2} \nabla^2 + V_{\text{eff}} \)
   \( V_{\text{eff}} = V(e-n) + V_H + V_{xc} \)

3. Compute \( \rho = \sum_i \psi_i^* \psi_i \)

4. Compute potential:
   a) \( V(e-n) = \sum_i \int d^3r \rho(r) \frac{Z_i}{|r-R_i|} \)
   b) \( V_H = \int d^3r' \frac{\rho(r')}{|r'-r|} \)
   c) \( V_{xc} \)

5. Check for self-consistency

6. Mix input and output density

7. Compute potential

8. Compute total \( E \) and output results.
What are the eigenvalues in DFT?

They are not excitation energies.

One can show (Perdew & Zunger, 1981) that

$$\varepsilon_\alpha = \frac{\partial E}{\partial f_\alpha}$$

where $f_\alpha$ is the occupation of state $\alpha$.

Band gap problem:

Gaps are too small, and sometimes zero for insulators.

Band gap is the difference in ground state energy for the $N$-electron and $N+1$ electron system, so it seems the exact DFT should give this energy difference correctly (though not necessarily for the eigenvalues).

(Nevertheless, there is an argument based on defects that the eigenvalues should also give the correct gap.)
Excitation Energies in DFT

Band gap: $E_g = (E(N+1) - E(N)) - (E(N) - E(N-1))$

$E_g = E^N_{\text{conduction}} - E^N_{\text{valence}} + \Delta V_{xc}$

$E_g = E_{N+1} - E_N$

$\neq E_{N+1} - E_N$

$\Delta V_{xc} = E_{N+1} - E_{N+1}$

Much more can be said...

Another point: Excitation energies can all be obtained by applying a time-varying potential and looking for resonances.
Perdew Burke * Ernzerhof (PBE) GGA
Generalized Gradient Approximation

1) non-empirical
2) universality
3) simplicity
4) accuracy

A) Keep everything that LDA does right. Scaling, xc hole = -1, bounds, rs limits
B) reduce to LDA for \( \rho \rho > 0 \)

\[
E_{\text{GGA}}[\rho_0, \rho_2] = \int d^3 r \rho \text{ ex} \ \text{Exc}(r_5, \xi, s)
\]

\[
s = \left( \frac{4}{3} \pi \rho \right)^{\frac{1}{3}} \text{ avg dist between electrons}
\]

\[
\xi = \frac{\rho_1 - \rho_2}{\rho}
\]

\[
s = \frac{1}{2} \rho_1 = \frac{1}{2} \rho_2 = \frac{3}{2} \left( \frac{4}{9 \pi} \right)^{\frac{1}{3}} |\rho_1 - \rho_2|^{\frac{1}{3}}
\]
FIG. 1. Electron number density $n(r)$ of the hydrogen atom as a function of the radius. Shown are the exact density (solid line), and the self-consistent densities in LSDA (dashed line) and GGA PW91 (dot-dashed line).
TABLE 1. Values (in Rydbergs) for total energy $E_{\text{tot}}$, kinetic energy $T$, potential energy $V$, Hartree energy $E_H$, exchange energy $E_x$, correlation energy $E_c$, and exchange-correlation energy $E_{xc}$. A self-consistent electron density is used for the GGA PW91 functional and the LSDA.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{tot}}$</th>
<th>$T$</th>
<th>$V$</th>
<th>$E_H$</th>
<th>$E_x$</th>
<th>$E_c$</th>
<th>$E_{xc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact</td>
<td>$-1$</td>
<td>$1$</td>
<td>$-2$</td>
<td>$0.625$</td>
<td>$-0.625$</td>
<td>$0$</td>
<td>$-0.625$</td>
</tr>
<tr>
<td>LSDA</td>
<td>$-0.958$</td>
<td>$0.933$</td>
<td>$-1.891$</td>
<td>$0.597$</td>
<td>$-0.513$</td>
<td>$-0.044$</td>
<td>$-0.557$</td>
</tr>
<tr>
<td>PW91</td>
<td>$-1.003$</td>
<td>$0.993$</td>
<td>$-1.991$</td>
<td>$0.615$</td>
<td>$-0.606$</td>
<td>$-0.013$</td>
<td>$-0.619$</td>
</tr>
</tbody>
</table>

FIG. 2. Exchange-correlation potential $u_{xc}(r)$ in Rydbergs for the hydrogen atom as a function of the radius. Shown are the exact $u_{xc}$ (solid line), and the self-consistent $u_{xc}$ in LSDA (dashed line) and GGA PW91 (dot-dashed line).
FIG. 2. Spherical average of the neon exchange hole times $R$ for (a) $r=0.09$ a.u. and (b) $r=0.39$ a.u. The full, dashed, and dotted curves are the exact, SIC-LSD and LSD results, respectively. In part (a), the SIC-LSD curve is almost indistinguishable from the exact one.
FIG. 1. Exchange hole about an electron located at distance $r$ from the nucleus in the neon atom. The full curves are exact, while the dashed and dotted curves represent the SIC-LSD and LSD approximations.
Periodic Solids

Nuclei are at \( \mathbf{r}_i = \frac{2}{3} \sum_{\alpha} \mathbf{a}_\alpha n_i + \mathbf{b}_i \)

\( \mathbf{a}_\alpha \) lattice vectors

\( \mathbf{b}_i \) basis vectors

14 Bravais lattices

630 space groups

Lattice: \( \mathbf{R}_{i,j,k} = i \mathbf{a}_1 + j \mathbf{a}_2 + k \mathbf{a}_3 \)

Reiprocal lattice: \( \mathbf{G}_{h,k,l} = h \mathbf{g}_1 + k \mathbf{g}_2 + l \mathbf{g}_3 \)

\( \mathbf{G} \cdot \mathbf{R} = 2\pi n, \) \( n \) integer

\( a_i \cdot g_j = 2\pi S_{ij} \)

\( g_j = 2\pi E_{j,\alpha \beta \gamma} \frac{a_\alpha \times a_\beta}{V} \)

\( V = a_1 \cdot (a_2 \times a_3) \)

\( E_{j,\alpha \beta \gamma} = 1 \) even \(-1 \) odd

First Brillouin zone:

All points closer to \( \mathbf{K} = 0 \) than to any other point \( \mathbf{G} \).

Van der Waals boundary conditions (periodic):

allowed \( \mathbf{K} = 2\pi \left( \frac{n_1}{L_1}, \frac{n_2}{L_2}, \frac{n_3}{L_3} \right) \)

\( \mathbf{G} \) reciprocal lattice vector

\( \mathbf{K} \) reciprocal lattice vector

\( \mathbf{R} \) reciprocal lattice vector
Band Theory

Consider the Fourier transform of the potential

$$V(r) = \sum_G \frac{e^{i \vec{G} \cdot \vec{r}}}{G} V_G$$

This is a periodic potential with periodicity given by

$$\vec{G} = h\vec{a}_1 + k\vec{a}_2 + l\vec{a}_3$$

constant

$$|\vec{G}| = 0 \rightarrow$$ 1 period per cell

$$\frac{|\vec{G}|}{2} \rightarrow$$ 2 periods per cell etc.

The orbitals (wave functions) do not have to have the periodicity of the cell.

$$\psi(r) = \sum_{\vec{K}} \frac{e^{i \vec{K} \cdot \vec{r}}}{\sqrt{K}} C_{\vec{K}}$$

Now $$\vec{K} = \vec{K} + \vec{G}$$

$$\vec{K}$$ is not a reciprocal lattice vector.

Consider

$$(-\frac{1}{2} \nabla^2 + V) \psi = \varepsilon \psi$$

$$-\frac{1}{2} \nabla^2 \psi = \frac{1}{2} \sum_{\vec{K}} K^2 e^{i \vec{K} \cdot \vec{r}} C_{\vec{K}}$$

$$V \psi = (\sum_G \frac{e^{i \vec{G} \cdot \vec{r}}}{G} V_G) \left( \sum_{\vec{K}} \frac{e^{i \vec{K} \cdot \vec{r}}}{\sqrt{K}} C_{\vec{K}} \right)$$
Band Theory (contd)

\[ V\psi = \left( \sum e^{iG \cdot r} V_0 \right) \left( \sum e^{ik \cdot r} C_k \right) \]

\[ = \sum V_0 C_k e^{i(k+G) \cdot r} = \sum V_0 C_{k+G} e^{ik' \cdot r} \]

So Schrodinger's eq. becomes:

\[ \sum e^{ik' \cdot r} \left( \frac{1}{2} k'^2 - \varepsilon \right) C_k + \sum V_0 C_{k-G} e^{i(k-G) \cdot r} = 0 \]

Now since plane waves are orthogonal, each term must be zero (can also prove by multiplying by \( C_k \) and integrating).

Let \( \vec{K} = \vec{k} + \vec{G} \) and we set:

\[ \left( \frac{1}{2} |\vec{k}+\vec{G}|^2 - \varepsilon \right) C_{\vec{k}+\vec{G}} + \sum V_0 C_{\vec{k}+\vec{G}-\vec{G}'} = 0 \]

\[ \vec{G}' \rightarrow \vec{G}' - \vec{G} \]

\[ \left( \frac{1}{2} |\vec{k}+\vec{G}|^2 - \varepsilon \right) C_{\vec{k}+\vec{G}} + \sum V_0 C_{\vec{k}+\vec{G}-\vec{G}'} = 0 \]

Note \( \vec{G} \) vectors are independent. Solve secular equation for each \( \vec{G} \), set \( \varepsilon i \vec{K}, C_{\vec{k}+\vec{G}} \)

Bloch's theorem: \( \psi(r) = \sum C_k e^{i(k+G) \cdot r} \)
Band Theory cont'd

Bloch's Theorem:

\[ \psi_k(r) = \sum_{G} C_G e^{i(G \cdot r)} \]

\[ \psi_k(r) = e^{i \frac{2\pi}{a} \cdot \frac{r}{a}} \sum_{G} C_G e^{-iG \cdot r} \]

This is a periodic function of \( r \)

\[ \psi_k(r) = e^{i \frac{2\pi}{a} \cdot \frac{r}{a}} u(r) \]

Summary: assumption of band theory periodic external potential.

To solve: could form \( H_{G_1} \) and diagonalize, but need too many \( G \)'s (1 million for 41) for full potential.
Self-consistent crystalline computations

Initial \( p \)

Compute \( V = \frac{V_h}{V_m} \) (Poisson's eq.)

Use

Solve KS equations for each \( \kappa \)-point

Determine \( E_F \)

Compute point \( \sum_{k} \left( \frac{\epsilon_{ik}}{k} \frac{\psi_{ik}}{\psi_{ik}} + (E - E_F) \right) \)

Compute \( E \)

\( \text{No} \) Converged ?
States are labeled by $k$ in the first Brillouin zone ($BZ$) and
$$
\Psi = \sum_{\mathbf{k}} \psi_i^{\mathbf{k}} \psi_i^* + (\varepsilon_i - \varepsilon_F) F(\varepsilon_i - \varepsilon_F) \text{ Fermi function}
$$

How to accurately integrate over $BZ$?

$$
\int_{BZ} dk^2 \rightarrow \sum_k
$$

Two main methods used: Tetrahedron method
- Assume linear between mesh points,
- Special $k$-points
  - Integrates Fourier series exactly up to some $G_{\text{max}}$
Special Points: Monkhorst-Pack (1976, 1977)
- Generate uniform grid, displaced by $0.5 a$ increment
- Use space group operations to rotate all points into the irreducible part of $BZ$ ($IBZ$)
- Determine weights

3 points rather than 16
Density functional theory (DFT)

- All of the ground state properties of an electronic system are determined by the charge and spin densities.
- DFT is an exact many-body theory, but the exact functional is unknown. However, exact sum-rules are known.

Solve the Kohn-Sham equations:

\[
\begin{bmatrix}
-\nabla^2 + V(\mathbf{r}) + \varepsilon_i \\
\end{bmatrix}\psi_i = 0
\]

\[V(\mathbf{r}) = V_{\text{electrostatic}} + V_{\text{xc}}\]

\[E = E_{\text{kinetic}}^{\text{non-interacting}} + E_{\text{electrostatic}} + E_{\text{xc}}\]

Why it works (usually) quite well:

- Known exactly
- Interactions for valence (bonding) electrons are most important
- Known for uniform electron gas and other model systems
Calculation of physical properties from first-principles

Exact theory is known

\[ H \psi = E \psi \]

Schrödinger’s equation

\[ H = V(E - N) + V(E - E) + KE \]

Local Density Approximation of DFT

Complicated many-body interactions in material of interest (atom, molecule, crystal…) at each point...

...are like those of homogeneous electron gas with same density as the density at that point.

Becomes more accurate with increasing \( P \)
Calculation of physical properties from first-principles

Exact theory is known

\[ H \psi = E \psi \]

Schrödinger’s equation

\[ H = V(E - N) + V(E - E) + KE \]

Generalized Gradient Approximation (GGA)

Complicated many-body interactions in material of interest (atom, molecule, crystal...) at each point...

are like those of homogeneous electron gas with same density as the density at that point, and imposed gradients at that point.
LDA or GGA do not work for everything

- LDA and (PBE) GGA provide accurate predictions of many properties at expt. volume.
- However, LDA underestimates while (PBE) GGA overestimates lattice constant by 1-2%.
- Certain properties, such as ferroelectricity, are very sensitive to volume.
- For ground state structures of ferroelectrics with strains, GGAs are particularly bad:

  Equilibrium volume and strain of tetragonal PbTiO₃

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>revPBE</th>
<th>RPBE</th>
<th>WDA*</th>
<th>Expt.</th>
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<tr>
<td>$V_0(\text{Å}^3)$</td>
<td>60.37</td>
<td>70.58</td>
<td>74.01</td>
<td>75.47</td>
<td>68.48</td>
<td>63.08</td>
</tr>
<tr>
<td>c/a</td>
<td>1.046</td>
<td>1.239</td>
<td>1.286</td>
<td>1.301</td>
<td>1.19</td>
<td>1.075</td>
</tr>
</tbody>
</table>
Exchange-Correlation Energy

- Density functional theory (DFT): electron density \( n(\vec{r}) \) is the basic variable.

- Kohn-sham Equation:

\[
\left[ -\frac{1}{2} \nabla^2 + \nu_{\text{ext}}(\vec{r}) + \nu_{\text{H}}(\vec{r}) + \nu_{\text{xc}}(\vec{r}) \right] \psi_i = \lambda_i \psi_i
\]

where \( \nu_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[n(\vec{r})]}{\delta n(\vec{r})} \), \( \nu_{\text{H}}(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \)

- LDA and GGA:

\[
E^{\text{LDA}}_{\text{xc}}[n] = \int n(\vec{r}) \varepsilon_{\text{xc}}^{\text{hom}}(n) d\vec{r}
\]

\[
E^{\text{GGA}}_{\text{xc}}[n] = \int f[n(\vec{r}), \nabla n(\vec{r})] d\vec{r}
\]

\[
= \int F_x \cdot n(\vec{r}) \varepsilon_{\text{x}}^{\text{hom}}(n) d\vec{r} + E_{\text{c}}^{\text{GGA}}
\]
PBE GGA

- Perdew-Burke-Ernzerhof (PBE) formalism is the most widely used GGA. *(PRL 77, 3865)*
- Correlation correction was derived from the low and high variation limits, plus linear scaling.
- Exchange enhancement factor was derived from a sharp cutoff of the exchange hole in real space.

\[
F_{x}^{\text{PBE}} = 1 + \kappa - \kappa / (1 + \mu s^2)
\]

where \( s \) : reduced gradients, \( \kappa = 0.804 \)

- Here \( \mu \) is set to 0.21951 to cancel the correlation correction for \( s \to 0 \).
Construction of a new GGA

- The xc hole in solids can have a **diffuse** tail, not in atoms or small molecules.
- A diffuse cutoff of the exchange hole leads to a smaller $\mu$ than the PW91.
  (Perdew et al., PRB 54, 16533)
- For slowly varying density systems, (Svendsen and von Barth, PRB 54, 17402)

\[
F_x = 1 + \frac{10}{81} p + \frac{146}{2025} q^2 - \frac{73}{405} pq + O(\nabla^6)
\]

where $p = s^2, q :$ reduced Laplacian.

- A new based on above observations:

\[
F_{x}^{WC} = 1 + \kappa - \kappa/(1 + x/\kappa)
\]

and \(x = \frac{10}{81} s^2 + (\mu - \frac{10}{81})s^2 \cdot \exp(-s^2) + \ln(1 + cs^4)\)

- and \(E_{c}^{wc} = E_{c}^{PBE}\)

[1] Perdew, Burke, and Wang, PRB 54, 16533
[2] Tao et al., PRL 91, 146401
Simple solids

- We tested the following 18 solids: Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Ru, Rh, Pd, Ag.
- The new GGA is much better than other approximations.

Mean errors (%) of calculated equilibrium lattice constants $a_0$ and bulk moduli $B_0$ at 0K.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>WC</th>
<th>TPSS</th>
<th>PKZB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>1.74</td>
<td>1.30</td>
<td>0.29</td>
<td>0.83</td>
<td>1.65</td>
</tr>
<tr>
<td>$B_0$</td>
<td>12.9</td>
<td>9.9</td>
<td>3.6</td>
<td>7.6</td>
<td>8.0</td>
</tr>
</tbody>
</table>

TPSS and PKZB results: Staroverov, et al. PRB 69, 075102
More accurate $E_{xc}$ for Ferroelectrics

- The new GGA is very accurate for the ground state structure of ferroelectrics.
- $V_x^{WC}$ differs from $V_x^{PBE}$ significantly only in core regions.
- In bonding regions, the difference $V_x^{WC}$ and $V_x^{PBE}$ is much smaller.

$P4mm$ PbTiO$_3$

$R3m$ BaTiO$_3$

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>WC</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0(\text{Å}^3)$</td>
<td>60.37</td>
<td>70.54</td>
<td>63.47</td>
<td>63.09</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.046</td>
<td>1.239</td>
<td>1.078</td>
<td>1.071</td>
</tr>
<tr>
<td>$u_z$(Pb)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>$u_z$(Ti)</td>
<td>0.5235</td>
<td>0.5532</td>
<td>0.5324</td>
<td>0.538</td>
</tr>
<tr>
<td>$u_z$(O$_{1,2}$)</td>
<td>0.5886</td>
<td>0.6615</td>
<td>0.6106</td>
<td>0.612</td>
</tr>
<tr>
<td>$u_z$(O$_3$)</td>
<td>0.0823</td>
<td>0.1884</td>
<td>0.1083</td>
<td>0.112</td>
</tr>
</tbody>
</table>

$u_z$ are given in terms of the lattice constants