Density Functional Theory for beginners

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❶ Hartree-Fock approximation

❷ Introduction to Density Functional Theory

❸ Approximations to exchange and correlations

Slater determinants

antisymmetrized n-electron wave function:

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_n) \equiv |\alpha_1 \alpha_2 \ldots \alpha_n\rangle = \frac{1}{\sqrt{n!}} \begin{pmatrix} \phi_{\alpha_1}(\mathbf{r}_1) & \phi_{\alpha_1}(\mathbf{r}_2) & \ldots & \phi_{\alpha_1}(\mathbf{r}_n) \\ \phi_{\alpha_2}(\mathbf{r}_1) & \phi_{\alpha_2}(\mathbf{r}_2) & \ldots & \phi_{\alpha_2}(\mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{\alpha_n}(\mathbf{r}_1) & \phi_{\alpha_n}(\mathbf{r}_2) & \ldots & \phi_{\alpha_n}(\mathbf{r}_n) \end{pmatrix}$$

$\phi_\alpha(\mathbf{r})$: orthonormalized solutions of the single electron Hamiltonian

$$\hat{h} = -\nabla^2 + V_{ext}(r); \quad \langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha\beta}$$

$V_{ext}(r)$: external (nuclear) potential; $\alpha \equiv nlms$: quantum numbers

$$\phi_\alpha(\mathbf{r}) = R_{nl}(r) Y_{lm}(\hat{\mathbf{r}}) \chi_s$$

- $R_{nl}(r)$: radial solution
- $Y_{lm}(\hat{\mathbf{r}})$: spherical harmonics
- χ_s: spin functions
- atomic units: $\hbar = 1$, $e^2 = 2$, $m = 1/2$

matrix elements

$$|\alpha\beta\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}\phi_\alpha(\mathbf{r}_1) & \phi_\alpha(\mathbf{r}_2)\\ \phi_\beta(\mathbf{r}_1) & \phi_\beta(\mathbf{r}_2)\end{pmatrix} = (\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) - \phi_\alpha(\mathbf{r}_2)\phi_\beta(\mathbf{r}_1))/\sqrt{2}$$

one-electron Hamiltonian:

$$\langle\alpha\beta|\hat{h}|\alpha\beta\rangle = \sum_i \langle\phi_{\alpha_i}|\hat{h}|\phi_{\alpha_i}\rangle$$

two-electron Coulomb interaction:

$$\left\langle \alpha\beta \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \alpha\beta \right\rangle = \overbrace{\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\alpha^*(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_\beta^*(\mathbf{r}_2)\phi_\beta(\mathbf{r}_2)}^{U_{\alpha\beta}}$$

$$- \overbrace{\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\alpha^*(\mathbf{r}_1)\phi_\beta(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\phi_\beta^*(\mathbf{r}_2)\phi_\alpha(\mathbf{r}_2)}^{J_{\alpha\beta}}$$

$$= \sum_{\alpha\beta}{}' (U_{\alpha\beta} - J_{\alpha\beta}\delta_{s_\alpha s_\beta})$$

Coulomb $U_{\alpha\beta}$ and $J_{\alpha\beta}$ exchange terms; $\sum' \equiv \alpha \neq \beta$

Hartree-Fock energy (HF)

Electron energy calculated using a Slater determinant $|\alpha_1 \dots \alpha_n\rangle$:

$$
\begin{aligned}
E_{HF} \equiv & \langle \alpha_1 \dots \alpha_n | \hat{H} | \alpha_1 \dots \alpha_n \rangle \\
= & \sum_{\alpha} \langle \phi_{\alpha_i} | \hat{h} | \phi_{\alpha_i} \rangle \\
& + \frac{1}{2} \overbrace{\sum_{\alpha\beta}{}' \int d\mathbf{r}_2 \phi_\beta^*(\mathbf{r}_2) \phi_\beta(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_\alpha^*(\mathbf{r}_1) \phi_\alpha(\mathbf{r}_1)}^{\text{Coulomb}} \\
& - \frac{1}{2} \overbrace{\sum_{\alpha\beta}{}' \delta_{s_\alpha s_\beta} \int d\mathbf{r}_2 \phi_\beta^*(\mathbf{r}_2) \phi_\alpha(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_\alpha^*(\mathbf{r}_1) \phi_\beta(\mathbf{r}_1)}^{\text{exchange}}
\end{aligned}
$$

sums over n occupied orbitals

Variation of E_{HF} w.r.t. ϕ_α gives a set of Hartree-Fock equations

Hartree-Fock equations

$$h\phi_\alpha(\mathbf{r}_1) + \overbrace{\left[\sum_\beta{}' \int d\mathbf{r}_2 \phi^*_\beta(\mathbf{r}_2)\phi_\beta(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\phi_\alpha(\mathbf{r}_1)}^{V_\mathsf{H}(\mathbf{r}_1)\phi_\alpha(\mathbf{r}_1)}$$

$$-\overbrace{\sum_\beta{}' \delta_{s_\alpha s_\beta}\left[\int d\mathbf{r}_2 \phi^*_\beta(\mathbf{r}_2)\phi_\alpha(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\phi_\beta(\mathbf{r}_1)}^{\text{nonlocal }(\hat{V}_x\phi_\alpha)(\mathbf{r}_1)} = \varepsilon_\alpha\phi_\alpha(\mathbf{r}_1)$$

sums over occupied orbitals

- $V_\mathsf{H}(\mathbf{r}) = \int \frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\left[\sum_\beta \phi^*_\beta(\mathbf{r}')\phi_\beta(\mathbf{r}')\right] = \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}$; $\rho(\mathbf{r})$ is charge density
- exchange term $(\hat{V}_x\phi_\alpha)(\mathbf{r}) \equiv \int V_x(\mathbf{r},\mathbf{r}')\phi_\alpha(\mathbf{r}')d\mathbf{r}'$ is nonlocal
- Coulomb and exchange terms with $\alpha = \beta$ cancel exactly
  no "self-interaction" of an electron with itself
- the equations to be solved self-consistently
- only lowest n states are occupied; others are exciting states
- Koopmans' theorem: ε_n is the ionization energy;
  $\varepsilon_\alpha - \varepsilon_\beta$ are excitation energies

missing are correlations

configuration interaction

Hartree-Fock equations $\Longleftrightarrow$ single Slater determinant

- each electron moves *independently* in the Coulomb potential corresponding to *average* positions of all electrons
- Hartree-Fock is a mean field theory

configuration interaction (CI):

to take multiple Slater determinants which include also excited orbitals

- "exact", controllable solution
- allows to calculate, e.g., atomic multiples

\- basis size N grows exponentially with the number of electrons n and orbitals m ($N = m!/n!/(m-n)!$).
For f shell (m=14):
$N(1)$=14, $N(2)$=91, $N(3)$=364, $N(4)$=16.016, $N(5)$=800.800;
$N(6)$=43.243.200, $N(7)$=2.421.619.200

\- applicable only to small molecules

correlation energy:

energy difference between the exact (CI) and Hartree-Fock energies

from Hartree-Fock to density functional

weighted average of exchange density:

$$(\hat{V}_x\phi_\alpha)(\mathbf{r}_1) \approx \frac{\sum_{\beta\gamma}\int d\mathbf{r}'\phi^*_\beta(\mathbf{r})\phi^*_\gamma(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\gamma(\mathbf{r})\phi_\beta(\mathbf{r}')}{\sum_\beta \phi^*_\beta(\mathbf{r})\phi_\beta(\mathbf{r})}\phi_\alpha(\mathbf{r}) = \tilde{V}_x(\mathbf{r})\phi_\alpha(\mathbf{r})$$

J. C. Slater, PR **81**, 385 (1951)

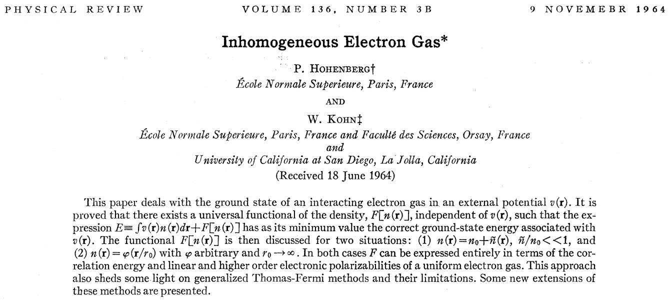
- $\tilde{V}_x(\mathbf{r})$ has a form of potential energy!
- less accurate but much easier to implement
- the Bloch theorem can be used

for uniform electron gas

$$V_x(\mathbf{r}) = 3\left(\frac{3}{\pi}\rho(\mathbf{r})\right)^{1/3} = \frac{3}{2}V_x^{\mathsf{KS}}(\mathbf{r}); \quad V_{x\alpha}(\mathbf{r}) = 3\alpha\left(\frac{3}{\pi}\rho(\mathbf{r})\right)^{1/3}$$

- an electron at $\mathbf{r}$ is surrounded by an exchange hole which contains exactly one electron with the same spin (no correlation hole yet)
- $\alpha \geq 2/3$: an adjustable parameter which mimics correlations gave name to Xα-Scattered Wave (SW) method

Density Functional Theory (DFT)



PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

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AND
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and
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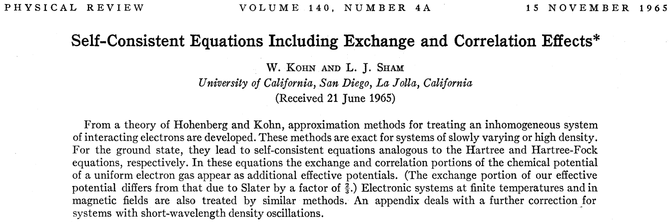
(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0\to\infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.



PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

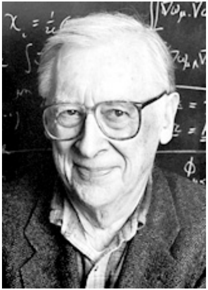
W. Kohn and L. J. Sham
University of California, San Diego, La Jolla, California

(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

The Nobel Prize in Chemistry 1998

Walter Kohn
Prize share: 1/2



John A. Pople
Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

spin-density matrix

The independent variable in the SDFT is the space-diagonal density matrix:

$$n(\mathbf{r}\sigma, \mathbf{r}\sigma') = \begin{pmatrix} n_{\uparrow\uparrow}(\mathbf{r}) & n_{\uparrow\downarrow}(\mathbf{r}) \\ n_{\downarrow\uparrow}(\mathbf{r}) & n_{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

It is given by the product of wave functions $\Psi_i(\mathbf{r})$ of occupied states:

$$n_{\sigma\sigma'}(\mathbf{r}) = \sum_k \theta(\varepsilon_F - \varepsilon_k) \langle \chi_\sigma | \Psi_k(\mathbf{r}) \rangle \langle \Psi_k(\mathbf{r}) | \chi_{\sigma'} \rangle$$

The off-diagonal elements can often be neglected:

$$n_{\uparrow\downarrow}(\mathbf{r}) = n_{\downarrow\uparrow}(\mathbf{r}) = 0; \quad n_{\uparrow\uparrow}(\mathbf{r}) \equiv n_\uparrow(\mathbf{r}); \quad n_{\downarrow\downarrow}(\mathbf{r}) \equiv n_\downarrow(\mathbf{r})$$

collinear spin-density are expressed in terms of electron and spin densities

$$n(\mathbf{r}) \equiv n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}); \qquad m(\mathbf{r}) \equiv n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$$

A.R. Mackintosh and O.K. Andersen in *"Electrons at the Fermi Surface"*, 1980

DFT

Two basic theorems:

- the ground state wave function is a unique functional of the charge density
- there exists a ground state energy functional which is stationary with respect to variations in the charge density

We can determine the ground state energy of a real system if we manage to construct an appropriate functional and to minimize it with respect to the charge and spin density

The total energy of the real system:

$$\mathcal{E}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} = \mathcal{T}_0\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} + \mathcal{U}_H\{n(\mathbf{r})\} + \mathcal{E}_{xc}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} \\ + \int v_{ext}(\mathbf{r})n(\mathbf{r}\sigma,\mathbf{r}\sigma')d\mathbf{r}$$

trial densities are generated by auxiliary fictitious non-interacting system

$$\sum_{\sigma'}\left[-\nabla^2 + v(\mathbf{r}\sigma,\mathbf{r}\sigma')\right]\psi_k(\mathbf{r}\sigma') = \varepsilon_k\psi_k(\mathbf{r}\sigma), \quad \sigma = \uparrow\downarrow$$

$$n(\mathbf{r}\sigma,\mathbf{r}\sigma') = \sum_k \theta(\varepsilon_F - \varepsilon_k)\psi_k(\mathbf{r}\sigma)\psi_k^*(\mathbf{r}\sigma')$$

DFT

Kinetic energy of the non-interacting system:

$$\mathcal{T}_0\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} = \sum_k \theta(\varepsilon_F - \varepsilon_k) \int \sum_\sigma \psi_k^*(\mathbf{r}\sigma)(-\nabla^2)\psi_k(\mathbf{r}\sigma)d\mathbf{r}$$

Coulomb (Hartree) energy:

$$\mathcal{U}_H\{n(\mathbf{r})\} = \frac{1}{2}\int n(\mathbf{r})\left(\int \frac{2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}')d\mathbf{r}'\right)d\mathbf{r} \equiv \frac{1}{2}\int n(\mathbf{r})v_H(\mathbf{r})d\mathbf{r}$$

Exchange-correlation energy functional:

$$\begin{aligned}\mathcal{E}_{xc}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} &= \mathcal{T}\{n(\mathbf{r}\sigma,\mathbf{r}'\sigma')\} - \mathcal{T}_0\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} \\ &+ \mathcal{U}\{n^{(2)}(\mathbf{r}\sigma,\mathbf{r}'\sigma')\} - \mathcal{U}_H\{n(\mathbf{r})\}\end{aligned}$$

accounts for the difference between kinetic and Coulomb energies of the real and non-interacting systems
External potential:

$$v_{ext}(\mathbf{r}\sigma,\mathbf{r}\sigma')$$

includes potential created by nuclei, spin-orbit coupling,. . .

DFT

Let us require that $\mathcal{E}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\}$ and

$$\mathcal{E}_0\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} = \mathcal{T}_0\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} + \sum_{\sigma\sigma'}\int v(\mathbf{r}\sigma,\mathbf{r}\sigma')n(\mathbf{r}\sigma,\mathbf{r}\sigma')d\mathbf{r}$$

are minimized by the same $n(\mathbf{r}\sigma,\mathbf{r}\sigma')$ under condition of constant number of electrons

$$\sum_{\sigma}\int n(\mathbf{r}\sigma,\mathbf{r}\sigma')d\mathbf{r} = N$$

This defines the effective one-electron potential

$$v(\mathbf{r}\sigma,\mathbf{r}\sigma') = v_H(\mathbf{r}) + v_{xc}(\mathbf{r}\sigma,\mathbf{r}\sigma') + v_{ext}(\mathbf{r}\sigma,\mathbf{r}\sigma')$$

with the (still unknown) exchange-correlation potential

$$v_{xc}(\mathbf{r}\sigma,\mathbf{r}\sigma') \equiv \frac{\delta\mathcal{E}_{xc}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\}}{\delta n(\mathbf{r}\sigma,\mathbf{r}\sigma')}$$

Local Spin Density Approximation (LSDA)

Exchange-correlation functional is approximated by

$$\mathcal{E}_{xc}\{n(\mathbf{r}\sigma,\mathbf{r}\sigma')\} \approx \int \sum_{\sigma} \varepsilon_{xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))n_{\sigma}(\mathbf{r})d\mathbf{r} = \int \varepsilon_{xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

$\varepsilon_{xc}(n_{\downarrow},n_{\uparrow})$ the exchange-correlation energy of homogeneous electron gas with density $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$ and spin density $m(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$

Exchange-correlation potential is diagonal in spin:

$$v_{xc\,\sigma} = \frac{\delta \int \varepsilon_{xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))n(\mathbf{r})d\mathbf{r}}{\delta n_{\sigma}} = \frac{\partial \varepsilon_{xc}(n_{\uparrow},n_{\downarrow})n}{\partial n_{\sigma}}$$

$$v_{xc\uparrow\downarrow} = \frac{\delta \int \varepsilon_{xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r}))n(\mathbf{r})d\mathbf{r}}{\delta n_{\uparrow\downarrow}} = 0$$

$$n_{\uparrow} \neq n_{\downarrow} \quad \Rightarrow \quad v_{xc\uparrow} \neq v_{xc\downarrow}$$

LSDA

new variables: average electron radius r_s and spin-polarization ζ

$$\frac{4\pi}{3} r_s^3 = 1/n; \quad \zeta = m/n \equiv (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$$

ε_{xc} is sum of exchange and correlations energies:

$$\varepsilon_{xc}(n_\downarrow, n_\uparrow) = \varepsilon_x(n_\downarrow, n_\uparrow) + \varepsilon_c(n_\downarrow, n_\uparrow)$$

$\varepsilon(\zeta)$ is interpolated between fully polarized F and nonpolarized P limits

$$\varepsilon_{x/c} = \varepsilon_{x/c}^P + (\varepsilon_{x/c}^F - \varepsilon_{x/c}^P) f(\zeta)$$

$$\varepsilon_x^P = -\frac{\varepsilon_x^0}{r_s}; \quad \varepsilon_F^P = 2^{1/3}\varepsilon_x^P; \qquad \varepsilon_c^{F/P} = -c^{F/P} F\left(\frac{r^{F/P}}{r_s}\right)$$

RPA results for homogeneous electron gas

U. von Barth and L. Hedin (1972)

or more accurate parameterizations of quantum Monte-Carlo results
+ correct $r_s \to 0$ and $r_s \to \infty$ limits

J.P. Perdew and Y. Wang (1992), D.M. Ceperely and B.J. Alder (1980)

exchange and corelation holes in LSDA

interaction with an exchange-correlation hole:

$$E_{xc}(n_\downarrow, n_\uparrow) = \int d\mathbf{r}\, n(\mathbf{r}) \int d\mathbf{u}\, n_{xc}(\mathbf{r}, \mathbf{r}+\mathbf{u})/u$$

O. Gunnarsson and B. Lundqvist (1976)

LSDA hole density is that of uniform electron gas:

$$n_{xc}^{LSDA}(\mathbf{r}, \mathbf{r}+\mathbf{u}) = n_{xc}^{\mathsf{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}); u)$$

the LSDA hole satisfies sum rules

$$\int d\mathbf{u}\, n_x(\mathbf{r}, \mathbf{r}+\mathbf{u}) = -1$$

$$\int d\mathbf{u}\, n_c(\mathbf{r}, \mathbf{r}+\mathbf{u}) = 0$$

$$n_x(\mathbf{r}, \mathbf{r}+\mathbf{u}) \leq 0$$

Generalizd Gradient Approximation (GGA)

- LSDA underestimates exchange energies of atoms and molecules
- underestimates by $\sim 1\%$ equilibrium lattice constants, i.e., overbinds atoms in solids
- underestimates gaps in insulators and semiconductors

"obvious" extention to LSDA:

$$\mathcal{E}_{xc}\left[n_\uparrow, n_\downarrow\right] \approx \int f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) d\mathbf{r}$$

- straightforward gradient expansion does not converged
- incorrect long-range behaviour of an exchange-correlation hole

$$\Downarrow$$

expansion in generalized gradients s and t with real space cut-off

$$s = |\nabla n|/2k_F n, \qquad k_F = (3\pi^2 n)^{1/3}$$

$$t = |\nabla n|/2k_s \phi(\zeta) n, \quad k_s = (4k_F/\pi)^{1/2}$$

Fermi wavelength $2\pi/k_F$ and Thomas-Fermi screening length $1/k_s$

- improved atomization and total energies (PW91, PBE)

J. Perdew. . . PRB (1992), J. Perdew, K. Burke, M. Ernzerhof PRL (1996)

- improved lattice parameters, chemical bonds (PBEsol)

J. Perdew. . . PRL (2008)

GGA vs LSDA: equilibrium lattice constants

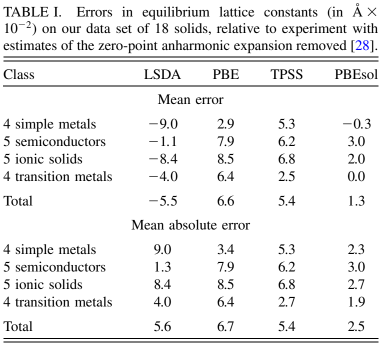


TABLE I. Errors in equilibrium lattice constants (in Å $\times 10^{-2}$) on our data set of 18 solids, relative to experiment with estimates of the zero-point anharmonic expansion removed [28].

Class	LSDA	PBE	TPSS	PBEsol
	Mean error			
4 simple metals	-9.0	2.9	5.3	-0.3
5 semiconductors	-1.1	7.9	6.2	3.0
5 ionic solids	-8.4	8.5	6.8	2.0
4 transition metals	-4.0	6.4	2.5	0.0
Total	-5.5	6.6	5.4	1.3
	Mean absolute error			
4 simple metals	9.0	3.4	5.3	2.3
5 semiconductors	1.3	7.9	6.2	3.0
5 ionic solids	8.4	8.5	6.8	2.7
4 transition metals	4.0	6.4	2.7	1.9
Total	5.6	6.7	5.4	2.5

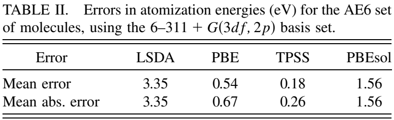


TABLE II. Errors in atomization energies (eV) for the AE6 set of molecules, using the 6–311 + $G(3df, 2p)$ basis set.

Error	LSDA	PBE	TPSS	PBEsol
Mean error	3.35	0.54	0.18	1.56
Mean abs. error	3.35	0.67	0.26	1.56

J. Perdew. . . PRL **100**, 136406 (2008)

meta-GGA TPSS adds to the functional the kinetic energy density

$$\tau_\sigma(\mathbf{r}) = \sum_{\alpha}^{\text{occ}} |\nabla \psi_\alpha(\mathbf{r})|^2$$

GGA vs LSDA: equilibrium lattice constants

Solid	LSDA	PBE	TPSS	PBEsol	Expt-ZPAE
Li	3.383	3.453	3.475	3.453	3.451
Na	4.049	4.199	4.233	4.159	4.210
K	5.093	5.296	5.362	5.232	5.212
Al	4.008	4.060	4.035	4.038	4.020
C	3.537	3.579	3.579	3.562	3.556
Si	5.410	5.479	5.466	5.442	5.423
SiC	4.355	4.404	4.394	4.381	4.349
Ge	5.634	5.776	5.744	5.693	5.646
GaAs	5.626	5.772	5.745	5.687	5.643
NaCl	5.471	5.696	5.696	5.611	5.580
NaF	4.505	4.700	4.706	4.633	4.594
LiCl	4.968	5.146	5.113	5.072	5.090
LiF	3.904	4.063	4.026	4.002	3.987
MgO	4.178	4.270	4.247	4.229	4.197
Cu	3.530	3.635	3.593	3.578	3.596
Rh	3.791	3.871	3.846	3.819	3.793
Pd	3.851	3.950	3.917	3.888	3.877
Ag	3.997	4.129	4.076	4.045	4.064

J. Perdew... PRL **100**, 136406 (2008)

GGA vs LSDA

improved

- atomization and total energies
- equilibrium lattice constants
- optimized crystal structures
- phonons

no improvement

- for gaps in semiconductors and insulators
- for ionization energies, electron affinities

similar band structures for the same crystal structure

hybrid functionals (PBE0, B3LYP . . .)

"adiabatic connection"

$$E_{xc} = \int_0^1 E_{xc,\lambda} d\lambda$$

- λ is the strength of Coulomb interaction $\lambda/|\mathbf{r}_1 - \mathbf{r}_2|$
- $\lambda = 0$ noninteracting Kohn-Sham reference system
  single Slater determinant ⇒ only exchange without correlations
- $\lambda = 1$ fully interacting system

in hybrid functionals $E_{xc,0}$ is replaced by exact exchange E_x^{HF}

$$E_{xc}^{\text{hybr}} = cE_X^{HF} + (1-c)E_{xc}^{GGA}$$

c is an adjustable parameter

A.D. Becke (1993), J.P. Perdew, M. Ernzerhof, and K. Burke (1996)

- even more accurate atomization and total energies for molecules
- \- difficult to implement for solids because of E_X^{HF}

sEX (screened EXchange) may reduce computations efforts

modified BJ potential

TABLE I. Theoretical and experimental fundamental band gaps (in eV). The structure is indicated in parenthesis. For comparison, results from the literature which were obtained by other methods are also shown (HSE03, HSE06, G_0W_0, and GW). The experimental values were taken from Refs. [4,7,10,14,18,23–26].

Solid	LDA	MBJLDA	HSE	G_0W_0	GW	Expt.
Ne (A1)	11.42	22.72		19.59^{e}	22.1^{g}	21.70
Ar (A1)	8.16	13.91	10.34^{a}	13.28^{e}	14.9^{g}	14.20
Kr (A1)	6.76	10.83				11.6
Xe (A1)	5.78	8.52				9.8
C (A4)	4.11	4.93	5.49^{b}	5.50^{e}	6.18^{g}	5.48
Si (A4)	0.47	1.17	1.28^{b}	1.12^{e}	1.41^{g}	1.17
Ge (A4)	0.00	0.85	0.83^{b}	0.66^{f}	0.95^{g}	0.74
LiF (B1)	8.94	12.94		13.27^{e}	15.9^{g}	14.20
LiCl (B1)	6.06	8.64				9.4
MgO (B1)	4.70	7.17	6.67^{b}	7.25^{e}	9.16^{g}	7.83
ScN (B1)	−0.14	0.90		0.95^{f}	1.4^{h}	∼0.9
MnO (B1)	0.76	2.95	2.8^{c}		3.5^{i}	3.9 ± 0.4
FeO (B1)	−0.35	1.82	2.2^{c}			2.4
NiO (B1)	0.42	4.16	4.2^{c}	1.1^{f}	4.8^{i}	4.0, 4.3
SiC (B3)	1.35	2.28	2.40^{b}	2.27^{e}	2.88^{g}	2.40
BN (B3)	4.39	5.85	5.99^{b}	6.10^{e}	7.14^{g}	∼6.25
GaN (B3)	1.63	2.81	3.14^{b}	2.80^{e}	3.82^{g}	3.20
GaAs (B3)	0.30	1.64	1.12^{b}	1.30^{e}	1.85^{g}	1.52
AlP (B3)	1.46	2.32	2.51^{b}	2.44^{e}	2.90^{g}	2.45
ZnS (B3)	1.84	3.66	3.49^{b}	3.29^{e}	4.15^{g}	3.91
CdS (B3)	0.86	2.66	2.25^{b}	2.06^{e}	2.87^{g}	2.42
AlN (B4)	4.17	5.55	5.81^{b}	5.83^{f}		6.28
ZnO (B4)	0.75	2.68	2.49^{d}	2.51^{f}	3.8^{g}	3.44

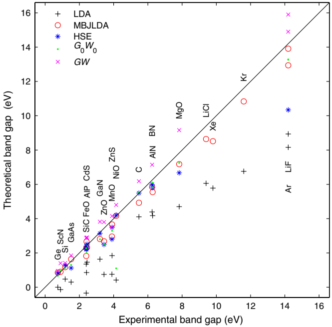


FIG. 1 (color online). Theoretical versus experimental band gaps. The values are given in Table I (Ne is omitted).

F. Tran and P. Blaha, RPL **102**, 226401 (2009)

- band gaps are much closer to experimental values than LSDA(GGA)
- computationally inexpensive

modified BJ potential

$$v_{x,\sigma}^{\mathsf{mBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\mathsf{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2\tau_\sigma(\mathbf{r})}{n_\sigma(\mathbf{r})}}$$

- optimized exchange potential $v_{x,\sigma}^{\mathsf{BJ}}$: local potential with orbitals minimizing the energy of the corresponding Slater determinant
  A.D. Becke and E.R. Johnson J. Chem. Phys. **124**, 221101 (2006)
- $v_{x,\sigma}^{\mathsf{BR}}(\mathbf{r})$: an approximation to the Slater weighted exchange
  A.D. Becke and M.R. Roussel, PRA **39**, 3761 (1989)
- $\tau_\sigma(\mathbf{r}) = \sum_\alpha |\nabla\psi_\alpha(\mathbf{r})|^2$: the kinetic energy density
- $c = \alpha + \beta\left(\frac{1}{V}\int\frac{|\nabla n_\sigma(\mathbf{r}')|}{n_\sigma(\mathbf{r}')}d\mathbf{r}'\right)^{1/2}$ with adjustable parameters α and β
- is not variational, i.e., no E_x such that $v_{x,\sigma}^{\mathsf{mBJ}} = \delta E_x/\delta n_\sigma$
- should not be used for total energy calculations

self-interaction

electron density

$$n(\mathbf{r}) = \sum_{\beta} \phi_{\beta}^{*}(\mathbf{r})\phi_{\beta}(\mathbf{r}) = n_{\alpha}(\mathbf{r}) + \sum_{\beta\neq\alpha} n_{\beta}(\mathbf{r})$$

LSDA(GGA) α contribution to Hartree (Coulomb) and exchange energies:

$$E_{H,\alpha} = \int \frac{n_{\alpha}(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$

$$E_{xc,\alpha} = \int f_{xc}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}), \nabla n_{\uparrow}, \nabla n_{\downarrow}) n_{\alpha}(\mathbf{r}) d\mathbf{r}$$

- in HF Coulomb $U_{\alpha\alpha}$ and exchange $J_{\alpha\alpha}$ terms cancel each other
- no cancellation in LSDA; α electron interacts with its own density n_{α}

self-interaction

- negligible for delocalized electrons in metals
- strong for localized electrons (atoms, core electrons,. . .)

Self-Interaction Correction (SIC)

$$E_{xc}^{SIC}[n] = E_{xc}^{LSDA}[n] - \sum_{\alpha} \left[\int d\mathbf{r} d\mathbf{r}' \frac{n_\alpha(\mathbf{r}) n_\alpha(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r}\, n_\alpha(\mathbf{r}) \varepsilon_{xc}(n_\alpha(\mathbf{r}), 0) \right]$$

J. P. Perdew and A. Zunger (1981), A. Svane and O. Gunnarsson (1990)

- removes unphysical self-interaction for occupied electron states
- reduces errors in the total exchange and correlation energies of atoms
- improves agreement between orbital energies and ionization energies
- improves gaps in insulators
- broken symmetry solution lifts degeneracy of a partially filled shell

- nonlocal orbital dependent potential
- orbitals are non orthogonal
- not invariant under the unitary transformation of occupied orbitals
  exactly zero for a Bloch state
  but finite for localized Wannier orbitals

LSDA(GGA) total energy

not just a sum of eigenenergies: $\mathcal{E} = \mathcal{T}_0\{n_\uparrow, n_\downarrow\} + \mathcal{U}_C\{n\} + \mathcal{E}_{xc}\{n_\uparrow, n_\downarrow\}$

Kinetic energy

$$\begin{aligned} \mathcal{T}_0 &= \sum_{k\sigma} f(\varepsilon_{k\sigma}) \int \sum_{\sigma} \psi^*_{k\sigma}(\mathbf{r})(-\nabla^2)\psi_{k\sigma}(\mathbf{r}) d\mathbf{r} \\ &= \sum_{k\sigma} f(\varepsilon_{k\sigma})\varepsilon_{k\sigma} - \sum_{\sigma} \int v_\sigma(\mathbf{r}) n_\sigma(\mathbf{r}) d\mathbf{r} \end{aligned}$$

$f(\varepsilon_{k\sigma}) = \theta(\varepsilon_F - \varepsilon_{k\sigma})$: Fermi function

$v_\sigma(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r})$: effective Kohn-Sham potential

$$(-\nabla^2 + v_\sigma)\psi_{k\sigma} = \varepsilon_{k\sigma}\psi_{k\sigma}, \quad n_\sigma(\mathbf{r}) = \sum_k f(\varepsilon_{k\sigma})\psi^*_{k\sigma}(\mathbf{r})\psi_{k\sigma}(\mathbf{r})$$

Coulomb energy:

$$\mathcal{U}_C = \frac{1}{2}\iint \frac{2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r})n(\mathbf{r}') d\mathbf{r} d\mathbf{r}' - \int \sum_i \frac{Z_i}{|\mathbf{r}-\mathbf{R}_i|} n(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\sum_{i\neq j} \frac{2Z_iZ_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Exchange-correlation energy:

$$\mathcal{E}_{xc}\{n(\mathbf{r}\sigma, \mathbf{r}\sigma')\} = \int \varepsilon_{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

exchange energy as a function of spin density

The exchange energy of homogeneous electron gas

$$\varepsilon_x(n_\downarrow, n_\uparrow) = -6\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \frac{n_\uparrow^{\frac{4}{3}} + n_\downarrow^{\frac{4}{3}}}{n_\uparrow + n_\downarrow} = -3\left(\frac{3}{8\pi}n\right)^{\frac{1}{3}} \left[(1+\zeta)^{\frac{4}{3}} + (1-\zeta)^{\frac{4}{3}}\right]$$

and the exchange potential ($\sigma = \uparrow \equiv -1$, $\sigma = \downarrow \equiv +1$)

$$v_{x\,\sigma} = \frac{\partial}{\partial n_\sigma}\varepsilon_x(n_\downarrow, n_\uparrow)(n_\uparrow + n_\downarrow) = -8\left(\frac{3}{4\pi}n_\sigma\right)^{\frac{1}{3}} = -8\left(\frac{3}{8\pi}n\right)^{\frac{1}{3}}(1-\sigma\zeta)^{\frac{1}{3}}$$

The larger $n_\uparrow$ ($n/2 < n_\uparrow \leq n$) the deeper the potential $\Rightarrow$ Hund's rule is satisfied

Expansion in ζ around non-spin-polarized densities:

$$\varepsilon_x(n, \zeta) \approx -3\left(\frac{3}{\pi}n\right)^{\frac{1}{3}}\left(1 + 2\zeta^2/9\right) \quad \text{quadratic}$$

$$b_x(\zeta) = v_{x\uparrow}(\zeta) - v_{x\downarrow}(\zeta) \approx -\frac{8}{3}\left(\frac{3}{\pi}n\right)^{\frac{1}{3}}\zeta \quad \text{linear}$$

Stoner criterion

Q Why not all metals are ferromagnets?

A gain in the exchange-correlation energy due to spin-polarization $M = \int m(\mathbf{r})d\mathbf{r}$ is (over)compensated by loss in the kinetic energy

Stoner criterion for ferromagnetism: $N(E_F) \cdot I > 1$
for $3d$ $(l = 2)$ transition metals:

$$I \sim \frac{1}{M} \int b_{xc}(n(\mathbf{r}))\phi_2^2(\mathbf{r})d\mathbf{r}$$

O. Gunnarsson, J. Phys. F **6** 587 (1976)

Susceptibility:

$$\chi = \frac{\chi_0}{1 - IN(E_F)}$$

The magnetic instability is driven by I instead of U as in the Hubbard model

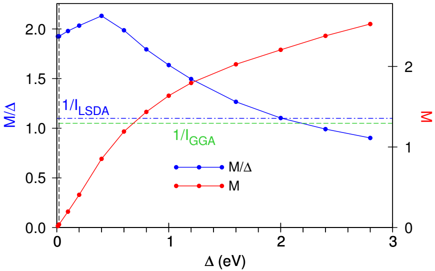
Let us consider

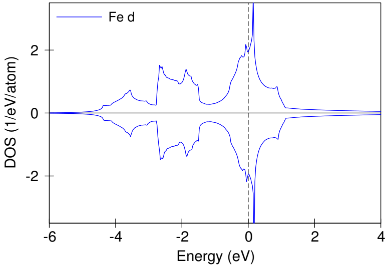
$$\tilde{\chi}_0(\Delta) = \frac{M}{\Delta}$$

M is magnetic moment induced by external spin splitting

$\tilde{\chi}_0(\Delta)$ for Fe

$$\chi_0(\Delta \to 0) = N(E_F) > 1/I$$



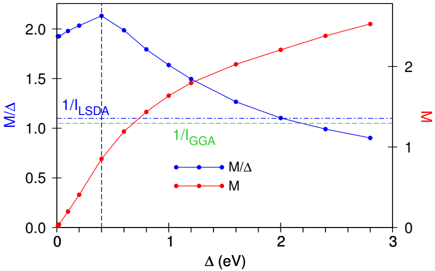


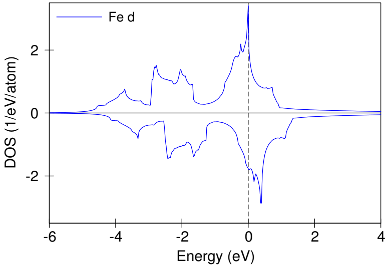
$$\frac{M(\Delta)}{\Delta} = \frac{1}{I}$$

$M(\Delta)$ is approximately equal to the self-consistent moment of 2.26 μ_{B}

$\tilde{\chi}_0(\Delta)$ for Fe

$$\chi_0(\Delta \to 0) = N(E_F) > 1/I$$





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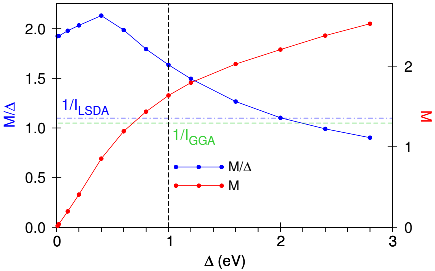

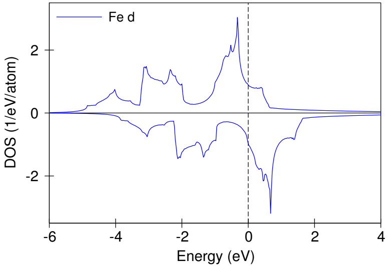

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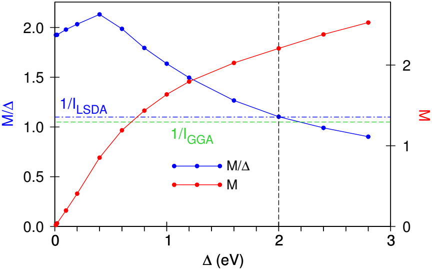
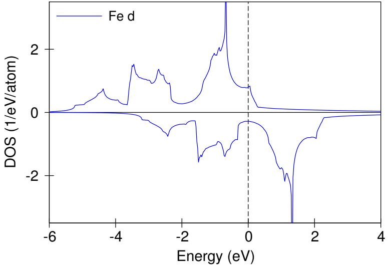


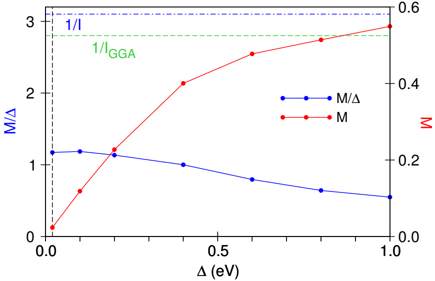


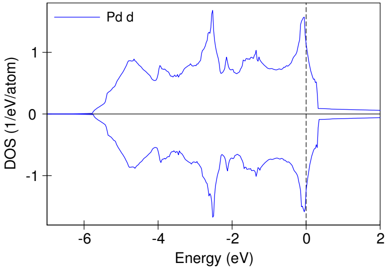
$$\frac{M(\Delta)}{\Delta} = \frac{1}{I}$$

$M(\Delta)$ is approximately equal to the self-consistent moment of 2.26 μ_{B}

$\tilde{\chi}_0(\Delta)$ for Pd

- High DOS peak almost at E_F
- but I is low due to larger extent of Pd $4d$ states



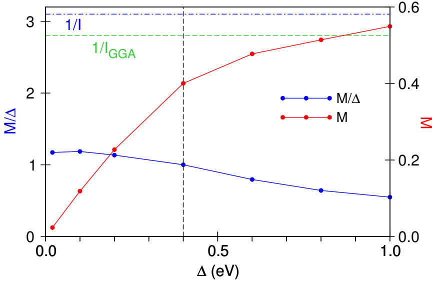


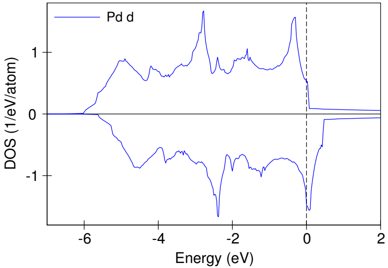
$$\chi_0(\Delta) = \frac{M}{\Delta} < \frac{1}{I}$$

Stoner criterion is not fulfilled

$\tilde{\chi}_0(\Delta)$ for Pd

- High DOS peak almost at E_F
- but I is low due to larger extent of Pd $4d$ states





$$\chi_0(\Delta) = \frac{M}{\Delta} < \frac{1}{I}$$

Stoner criterion is not fulfilled