EXC of DFT



Exchange-Correlation functionals



FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

Kieron Burke, "Perspective on density functional theory" JCP 136 (2012) 150901



Jacob's ladder of Density Functional Theory

Chemical Accuracy



Hartree World

FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.



Rev. Mod. Phys. 61, 689 (1989)

The density functional formalism, its applications and prospects

R.O. Jones

Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, Federal Republic of Germany

O. Gunnarsson

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

A scheme that reduces the calculations of ground-state properties of systems of interacting particles exactly to the solution of single-particle Hartree-type equations has obvious advantages. It is not surprising, then, that the density functional formalism, which provides a way of doing this, has received much attention in the past two decades. The quality of the energy surfaces calculated using a simple local-density approximation for exchange and correlation exceeds by far the original expectations. In this work, the authors survey the formalism and some of its applications (in particular to atoms and small molecules) and discuss the reasons for the successes and failures of the local-density approximation and some of its modifications.



HK:
$$n(\mathbf{r}) \longrightarrow F[n] = \min_{\Psi \to n} \langle \Psi | T_e + W_{ee} | \Psi \rangle$$

It is useful to introduce a ficticious system of non-interacting electrons

KS:
$$n(\mathbf{r}) \longrightarrow T_s[n] = \min_{\Psi \to n} \langle \Psi | T_e | \Psi \rangle$$

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]$$
 This defines E_{xc}

The energy becomes

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



Self-consistent equations [Kohn-Sham, 1965]

$$V_{eff}(\mathbf{r}, \mathbf{R}) = V_{ext}(\mathbf{r}, \mathbf{R}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathbf{r}, \mathbf{R})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = 2\sum_{i} |\phi_i(\mathbf{r})|^2$$



It is as simple as a Mean-field approach but it is exact !

 $E_{xc}[n]$ is not known exactly \rightarrow approximations



n(r) is a smooth and simple function of r, so...



FIG. 1. Spherically averaged density n(r) in ground state of carbon atom as a function of distance r from nucleus.



... F[n] is a very non trivial functional of n(r) !



FIG. 1. Spherically averaged density n(r) in ground state of carbon atom as a function of distance r from nucleus.



Simple approximations to Exc are possible

$$E[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$



FIG. 4. Relative magnitudes of contributions to total valence energy of Mn atom (in eV).





Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

Analogous to the Thomas-Fermi approximation for the Kinetic Energy term but applied to the much smaller Exchange-Correlation term



Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)



$$\begin{aligned} & \textbf{Total Energy expression in DFT} \\ E(R) = \min_{\rho} \left[T_s[\rho] + \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho] + \int V_0(r)\rho(r) dr \right] \\ & + W_{II}(R) \\ \rho(r) = 2 \sum_{k,i} |\phi_{k,i}(r)|^2 \Longrightarrow T_s[\rho] = 2 \sum_{k,i} \langle \phi_{k,i}| - \frac{\hbar^2}{2m} \nabla^2 |\phi_{k,i}\rangle \\ E_{xc}^{LDA}[\rho] = \int \rho(r) \ \varepsilon_{xc}^{hom}(\rho(r)) dr \\ & \implies V_{xc}^{LDA}(r) = \frac{d(\rho \varepsilon_{xc}^{hom}(\rho))}{d\rho} \Big|_{\rho=n(r)} \end{aligned}$$

Magnetism needs to be explicitly accounted



FIG. 6. Density of metallic Fe and Cu as a function of the radius r. The density n is expressed in terms of the parameter r_s , where $n = (4\pi r_s^3/3)^{-1}$.



Local Spin Density Approximation (LSDA)

- Electrons have spin $+/- \frac{1}{2}$ bohr magneton
- Spin is treated as a scalar quantity (this is approximate)
- Two spin states often referred to $% ({\mathbb T}^{n})$ as "up" \uparrow and "down" \downarrow
- up-up xc interaction is different from up-down E_{xc} depends on both n_{\uparrow} and n_{\downarrow}
- Two auxiliary sets of eqs for the two spin components

$$V_{\uparrow}^{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{xc}[n_{\uparrow}, n_{\downarrow}]}{\partial n_{\uparrow}(\mathbf{r})}$$
$$V_{\downarrow}^{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{xc}[n_{\uparrow}, n_{\downarrow}]}{\partial n_{\downarrow}(\mathbf{r})}$$

In magnetic systems $n_{\uparrow}(\mathbf{r}) \neq n_{\downarrow}(\mathbf{r})$



Kohn-Sham, Phys Rev 140, A1133 (1965)

In atoms and molecules one can distinguish three regions: (1) A region near the atomic nucleus, where the electronic density is high and therefore, in view of case (b) above, we expect our procedure to be satisfactory. (2) The main "body" of the charge distribution where the electronic density $n(\mathbf{r})$ is relatively slowly varying, so that our approximation (2.3) for ϵ_{xc} is expected to be satisfactory as discussed in case (a) above. (3) The "surface" of atoms and the overlap regions in molecules. Here our approximation (2.3) has no validity and therefore we expect this region to be the main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course, this "surface" region becomes of less importance. (The surface is more satisfactorily handled in the nonlocal method described under *B* below.)

For metals, alloys, and small-gap insulators we have, of course, no surface problem and we expect our approximation (2.3) to give a good representation of exchange and correlation effects. In large-gap insulators, however, the actual correlation energy will be con- a) n(r) smooth siderably reduced compared to that of a homogeneous electron gas of the same density.





Gunnarsson-Lundqvist, Phys Rev B 13, 4274 (1974)

In the first application to atoms, Tong and Sham⁷⁶ found that, while the calculated exchange energies for various atoms are about 10% too small in magnitude, the correlation energies are too large by a factor of about two, the errors partially balancing each other. The relative accuracy for both quantities improves for large atoms. The error in the exchange energy is surprisingly small, considering the nonlocal nature of the exchange forces and the strong inhomogeneity of the system. As has been pointed out by Tong, 77 the major source of error in the correlation energy is that the discreteness and the nonzero spacing of the low-lying levels of a finite system, in principle, would not be well described by expressions derived from an infinite electron liquid. A reason for the increased relative accuracy for larger atoms is the decrease of the exchange-correlation hole compared with the inhomogeneity length, as an electron shell is getting filled. All these results and arguments suggest the LSD approximation to be less satisfactory for a *detailed* description of tightly bound core electrons, while it is likely to give useful results for valence electrons. In this section we will give results supporting that view.



A good Ground State theory

LDA/LSDA describes well a variety of materials and materials properties (amenable to an el. GS description)

- energetics, phase stability, defects thermodynamics
- equilibrium geometries of complex systems
- response functions to external perturbations static dielectric constants piezoelectric constants elastic constants
- within the adiabatic approximation lattice dymamics is a ground state property vibrational properties defect diffusion thermodynamic properties





P Ballone, C Umrigar, P Delaly, PRB 45, 6293 (1992)

And the second state of th

Local Spin Density Approximation (LSDA)



FIG. 2. Electron-spin density $\rho_s(r)$ times r^2 as a function of distance from the center of the jellium sphere. Solid line, VMC computation; dashed line, LSDA computation.

P Ballone, C Umrigar, P Delaly, PRB 45, 6293 (1992)



First Ionization Energies

FIG. 8. First ionization energy of atoms in the local-density (LD), local spin-density (LSD), and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. For reasons of clarity, the zero of energy is shifted by 5, 10, and 15 eV for the second row, the third row, and the transition-element row, respectively. The LD results for the first and second rows are increased by an additional 2 eV.

Rev. Mod. Phys., Vol. 61, No. 3, July 1989

Jones & Gunnarsson









Structure of bulk Be

	a_0 (a.u.)	$(c/a)_0$	B_0 (Mbar)	ν_P
Theory	4.25	1.572	1.25	0.04
Expt.	4.33	1.568	1.1	0.02-0.05

Bulk Phonon Dispersion



M Lazzeri & SdG, Surf Sci 402-404,715 (1998)
Exp: Stedman et al., J. Phys. F 6, 157 (1976)



Bulk Thermal Expansion



• American Institute of Physics Handbook, (McGraw-Hill, NY 1972)



Be (0001) Surface



[300K] H.L.Davis *et al.* PRL 68, 2632 (1992)
[LDA] R.Stumpf and P.J.Feibelmann, PRB 51, 13748 (1995)
[LDA] <u>Present calculation</u>

M.Lazzeri (SISSA PhD 1999)



Anomalously Large Thermal Expansion !

K.Pohl, J.-H.Cho, K.Terakura, M.Scheffler, and E.W.Plummer, to appear in PRL 23/3/1998



At low temperature theory and experiment are in excellent agreement α_{Surf} is 6 times larger than α_{Bulk} ! J.B.Hannon, E.J.Mele and E.W.Plummer, PRB 53, 2090 (1996)



- Intense EELS features (Rayleigh wave)
- Weak EELS features
- --- Truncated bulk model





W(110) Surface









E. Hulpke and J. Lüdecke, Surf. Sci. 287-288, 837 (1993).

Surface Phonons : EELS data



The deep anomaly present in the HAS spectra is not detected by EELS






White to Grey Tin Phase Transition



P. Pavone, SB, SdG, PhysRevB 57,10421 (1998)





VOLUME 45, NUMBER 12

PHYSICAL REVIEW LETTERS

22 September 1980

Microscopic Theory of the Phase Transformation and Lattice Dynamics of Si

M. T. Yin and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720 (Received 14 July 1980)

PHYSICAL REVIEW B

VOLUME 26, NUMBER 10

15 NOVEMBER 1982

Theory of static structural properties, crystal stability, and phase transformations: Application to Si and Ge

M. T. Yin* and Marvin L. Cohen

Department of Physics, University of California, Berkeley, California 94720 and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720 (Received 29 March 1982)



$$H(P) = \min_{V} [E(V) + PV]$$

$$P = -\frac{\partial E}{\partial V}, \qquad \frac{\partial H}{\partial P} = V(P)$$

$$H_A(P^*) = H_B(P^*)$$

$$E_A(V_A^*) + P^* V_A^* = E_B(V_B^*) + P^* V_B^*$$

$$P^* = -\frac{E_A(V_A^*) - E_B(V_B^*)}{V_A^* - V_B^*} = -\frac{\partial E_A}{\partial V_A^*} = -\frac{E_B}{\partial V_B^*}$$





FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β -tin phase (c/a=0.552).

PHYSICAL REVIEW B

VOLUME 51, NUMBER 13

1 APRIL 1995-I

High-pressure low-symmetry phases of cesium halides

Marco Buongiorno Nardelli

Laboratorio TASC dell'Istituto Nazionale di Fisica della Materia and BULL-Unix Competence Center, AREA di Ricerca di Trieste, Padriciano 99, I-34012 Trieste, Italy

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati (SISSA) Via Beirut 2/4, I-34014 Trieste, Italy

Paolo Giannozzi Scuola Normale Superiore (SNS) Piazza dei Cavalieri 7, I-56126 Pisa, Italy (Received 5 August 1994)



FIG. 1. Sketch of the CsI cell with the atomic displacements corresponding to an M_5^- acoustic phonon. The magnitude of cesium displacements with respect to iodine displacements is exaggerated for clarity. The solid lines indicate the cell of the distorted (orthorhombic) structure, while the cell of the undistorted (cubic) structure is indicated by a dashed line. The shaded area correspond to the (110) plane.







FIG. 2. Phonon dispersion relations along some symmetry directions of the Brillouin zone in CsI at equilibriumi volume. Experimental data indicated by open and black circles are from Ref. 30; an infrared measurement for $\omega_{LO}(\Gamma)$ is indicated by an open square (Ref. 31).





FIG. 3. Phonon dispersion relations along the Σ (110) for CsI at equilibrium volume and just above and below the softening pressure of the M_5^- acoustic mode. "Negative" frequencies actually mean "imaginary" (i.e., negative squared frequencies).











FIG. 4. Frequencies of the M_5^- acoustic phonon as functions of the molar volume for CsI, CsBr, and CsCl. Arrows indicate the softening volume. P^* is the softening pressure.



c/a

FIG. 6. c/a parameter as a function of pressure for CsI and CsBr. P_{tet} indicates the transition pressure to the tetragonal phase.











Preliminary Reference Earth Model



Siesmic data allow to map sound velocity profiles inside Earth Upper Mantle, Lower Mantle, Outer Core (lq), Inner Core



Phonon Dispersion Curves of MgO at Zero Pressure





BB Karki, RM Wentzcovitch, SdG, SB, Science 286, 1705 (1999)







First Row Dimers

	Req (a.u.)		BE	(eV)	freq(cm-1)		
	exp	LSD	exp	LSD	exp	LSD	
H ₂	1.40	1.45	4.75	4.81	4400	4277	
Li ₂	5.05	5.12	1.06	1.01	351	347	
Be ₂	4.71	4.63	0.11	0.50	294	362	
B ₂	3.04	3.03	3.08	3.93	1051	1082	
C ₂	2.35	2.36	6.31	7.19	1857	1869	
N ₂	2.07	2.08	9.91	11.34	2358	2387	
O ₂	2.28	2.31	5.23	7.54	1580	1563	
F ₂	2.68	2.62	1.66	3.32	892	1075	



Summary (LDA)

Lattice constants: 1-3% too small

Cohesive Energies: 5-20% too strongly bound

Bulk Modulus: 5-20% (largest errors for late TM)

Bandgaps: too small













The Gradient Expansion Approximation (GEA)

From L(S)DA

$$E_{\rm XC}^{\rm LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \, \epsilon_{\rm XC}^{\rm unif}(n_{\uparrow}, n_{\downarrow})$$

to GEA

$$E_{XC}^{GEA}[n_{\uparrow}, n_{\downarrow}] = E_{XC}^{LSD} + \int d^3r \frac{|\nabla n|^2}{n^{4/3}} f(n_{\uparrow}, n_{\downarrow})$$

Contrary to big hopes results were worse than LDA !



$$E_{\rm xc}^{\rm LSD}[n_{\uparrow},n_{\downarrow}] = \int d^3r \ n(\mathbf{r}) \epsilon_{\rm xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r})), \qquad (1)$$

where $\epsilon_{\rm xc}(n_{\uparrow}, n_{\downarrow})$ is the known⁵ exchange-correlation energy per particle of an electron gas with uniform spin densities n_{\uparrow} , n_{\downarrow} , and $n = n_{\uparrow} + n_{\downarrow}$. Equation (1) is clearly valid when the spin densities vary slowly over space, but this condition is *violated* by real atoms, molecules, and solids. Indeed, the next systematic correction in the slowly varying limit, the second-order gradient expansion approximation⁶⁻¹¹ (GEA),

$$E_{\rm xc}^{\rm GEA}[n_{\uparrow},n_{\downarrow}] = E_{\rm xc}^{\rm LSD}[n_{\uparrow},n_{\downarrow}] + \sum_{\sigma,\sigma'} \int d^{3}r \ C_{\rm xc}^{\sigma\sigma'}(n_{\uparrow},n_{\downarrow})$$
$$\times \nabla n_{\sigma'} \cdot \nabla n_{\sigma'} / n_{\sigma}^{2/3} n_{\sigma'}^{2/3}, \qquad (2)$$

is less accurate than LSD.^{6,12,13}



Formal expression for $E_{xc}[n]$ via coupling-constant integration

$$H^{(\lambda)} = T_e + \lambda W_{ee} + V_{ext}^{(\lambda)}$$

$$F_{\lambda}[n] = \min_{\Psi \longrightarrow n} \langle \Psi | T_e + \lambda W_{ee} | \Psi \rangle$$

1-1

non-interacting electrons

$$\lambda = 0$$
 $F_0[n] = T_s[n],$ $V_{ext}^{(0)} = V_{KS}$

interacting electrons

$$\lambda = 1$$
 $F_1[n] = F[n],$ $V_{ext}^{(1)} = V_{ext}$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$



$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{dF_\lambda}{d\lambda}$$

thanks to Hellmann-Feynman theorem $F[n]=T_s[n]+\int_0^1 d\lambda \langle \Psi_\lambda|W_{ee}|\Psi_\lambda\rangle$

$$F[n] = T_s[n] + \int_0^1 d\lambda \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}, \mathbf{r}', \lambda)$$

 $g(\mathbf{r}, \mathbf{r}', \lambda)$ pair correlation function for interaction λW_{ee}



if
$$|\mathbf{r} - \mathbf{r}'| \longrightarrow \infty$$
 then $g(\mathbf{r}, \mathbf{r}', \lambda) \longrightarrow 1$
 $(g(\mathbf{r}, \mathbf{r}', \lambda) - 1) \longrightarrow 0$

$$F[n] = T_s[n] + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \int_0^1 d\lambda [g(\mathbf{r}, \mathbf{r}', \lambda) - 1]$$

Exchange-correlation hole

$$n_{xc}(\mathbf{r};\mathbf{r}'-\mathbf{r}) = n(\mathbf{r}') \int_0^1 d\lambda [g(\mathbf{r},\mathbf{r}',\lambda) - 1]$$

$$E_{xc}[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}(\mathbf{r},\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$





$$n_{xc}^{sph.avg.}(\mathbf{r};R) = \frac{1}{4\pi} \int d\Omega \ n_{xc}(\mathbf{r};\mathbf{R}), \qquad \mathbf{R} = \mathbf{r}' - \mathbf{r}$$

Sum-rule: $4\pi \int R^2 n_{xc}^{sph.avg.}(\mathbf{r},R) dR = -1$

$$E_{xc}[n] = \frac{e^2}{2} \int d\mathbf{r} n(\mathbf{r}) \ 4\pi \int R^2 \frac{n_{xc}^{sph.avg.}(\mathbf{r},R)}{R} dR$$



$g(\mathbf{r},\mathbf{r}',\lambda)$ of the homogeneous electron gas

the hole is localized around the probing electron

G.Ortiz & P.Ballone

PRB 50, 1391 (1994)





Local Density Approximation

$$E_{xc}[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}$$

replace the real xc hole with a model hole that satisfies the sum-rule.

$$n_{xc}(\mathbf{r},\mathbf{r}'-\mathbf{r}) \longrightarrow n_{xc}^{hom}(\mathbf{r},|\mathbf{r}'-\mathbf{r}|)$$

$$E_{xc}^{LDA}[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n_{xc}^{hom}(\mathbf{r}, |\mathbf{r}' - \mathbf{r}|)}{|\mathbf{r}' - \mathbf{r}|}$$





FIG. 7. Exact (solid line) and approximate (dashed line) exchange hole $n_x(\mathbf{r},\mathbf{r'-r})$ [Eq. (3.10)] for a spin-up electron in a nitrogen atom for r = 0.13 and 0.63 a.u. The top figure shows the hole along a line through the nucleus and the electron. The arrow indicates the nuclear position and $\mathbf{r-r'=0}$ gives the electron position. The exact hole has a large weight at the nucleus, while the approximate hole is centered at the electron. The lower figure shows the spherical average of the hole around the electron. The area under the curve is proportional to the exchange energy. The figure also shows the value of $\langle 1/\mathbf{R} \rangle_r$ defined in Eq. (3.13).



The Gradient Expansion Approximation (GEA)

From L(S)DA

$$E_{\rm XC}^{\rm LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \, \epsilon_{\rm XC}^{\rm unif}(n_{\uparrow}, n_{\downarrow})$$

to GEA

$$E_{XC}^{GEA}[n_{\uparrow}, n_{\downarrow}] = E_{XC}^{LSD} + \int d^3r \frac{|\nabla n|^2}{n^{4/3}} f(n_{\uparrow}, n_{\downarrow})$$

GEA xc-hole did not satisfy the sum rule ! => no error cancellation to be expected



$$E_{\rm xc}^{\rm LSD}[n_{\uparrow},n_{\downarrow}] = \int d^3r \ n(\mathbf{r}) \epsilon_{\rm xc}(n_{\uparrow}(\mathbf{r}),n_{\downarrow}(\mathbf{r})), \qquad (1)$$

where $\epsilon_{\rm xc}(n_{\uparrow}, n_{\downarrow})$ is the known⁵ exchange-correlation energy per particle of an electron gas with uniform spin densities n_{\uparrow} , n_{\downarrow} , and $n = n_{\uparrow} + n_{\downarrow}$. Equation (1) is clearly valid when the spin densities vary slowly over space, but this condition is *violated* by real atoms, molecules, and solids. Indeed, the next systematic correction in the slowly varying limit, the second-order gradient expansion approximation⁶⁻¹¹ (GEA),

$$E_{\rm xc}^{\rm GEA}[n_{\uparrow},n_{\downarrow}] = E_{\rm xc}^{\rm LSD}[n_{\uparrow},n_{\downarrow}] + \sum_{\sigma,\sigma'} \int d^{3}r \ C_{\rm xc}^{\sigma\sigma'}(n_{\uparrow},n_{\downarrow}) \\ \times \nabla n_{\sigma'} \cdot \nabla n_{\sigma'} / n_{\sigma}^{2/3} n_{\sigma'}^{2/3}, \qquad (2)$$

is less accurate than LSD.^{6,12,13}



FIG. 1. Spherically averaged exchange hole density n_X for s=1 in LSD (circles), GEA (crosses), and GGA (solid line).

Generalized Gradient Approximations modify/truncate the GEA xc-hole so that the sum-rule is satisfied !



From L(S)DA

$$E_{\rm XC}^{\rm LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \, \epsilon_{\rm XC}^{\rm unif}(n_{\uparrow}, n_{\downarrow})$$

to GGA

$$E_{\rm XC}^{\rm GGA}[n_{\uparrow},n_{\downarrow}] = \int d^3r f(n_{\uparrow},n_{\downarrow},\nabla n_{\uparrow},\nabla n_{\downarrow})$$

Such that the xc-hole sum-rule is satisfied !

... not a unique recipe

A lot of work went in proposing and comparing new functionals

A few functionals are widely used today

PW91, PBE, revPBE, RPBE ... BLYP (Perdew,Burke) (Becke)



Property	ELDA Rel. [4]	ELM Ref. [34]	E ^{PW91} Ref. [36]	Ex B88 Ref. [37]	ECMV Ref. [36]	Ec WL	EC140
$\rho_{\mathbf{x}}(\mathbf{r},\mathbf{r}') \leq 0$ $= \int \rho_{\mathbf{x}}(\tilde{\mathbf{r}},\mathbf{r}') d\mathbf{r}' = -1$		-		-	-	-	-
$\int \rho_{\rm c}(\mathbf{r},\mathbf{r}') d\mathbf{r}' = 0$				-		4- <u>1</u> 4 .	-
$E_{x}[\rho] < 0$ $E_{c}[\rho] \leq 0$ $E_{x}[\rho], E_{xc}[\rho] \geq -c \int \rho^{4/3} dr^{-\alpha}$						-	
$\begin{array}{c} \overline{c} E_{\mathbf{x}}\left[\rho_{\lambda}\right] = \lambda E_{\mathbf{x}}\left[\rho\right] b \\ \overline{c} E_{\mathbf{c}}\left[\rho_{\lambda}\right] < \lambda E_{\mathbf{c}}\left[\rho\right], \ \lambda < 1 c \end{array}$							
$\lim_{\lambda \to \infty} E_{c}[\rho_{\lambda}] > -\infty$ $\lim_{\lambda \to 0} \frac{1}{\lambda} E_{c}[\rho_{\lambda}] > -\infty$				-	-		
$\lim_{\lambda \to \infty} E_{\mathbf{x}} \left[\rho_{\lambda}^{\mathbf{x}} \right] > -\infty$ $\lim_{\lambda \to 0} E_{\mathbf{x}} \left[\rho_{\lambda}^{\mathbf{x}} \right] > -\infty$ $\lim_{\lambda \to 0} E_{\mathbf{x}} \left[\rho_{\lambda}^{\mathbf{x}} \right] > -\infty$						-	-
$\lim_{\lambda \to \infty} \frac{1}{\lambda} E_{x} \left[\rho_{\lambda}^{xy} \right] > -\infty$ $\lim_{\lambda \to \infty} \lambda E_{c} \left[\rho_{\lambda}^{xy} \right] > -\infty$						-	-
$\lim_{\lambda \to 0} \frac{1}{\lambda} E_{c} \left[\rho_{\lambda}^{x} \right] = 0$ $\lim_{\lambda \to \infty} E_{c} \left[\rho_{\lambda\lambda}^{xy} \right] = 0$							
$\lim_{\lambda \to 0} \lim_{\overline{\lambda^2}} E_{\mathbf{c}} \left[\hat{\rho}_{\lambda\lambda} \right] > -\infty$ $\lim_{\tau \to 0} \epsilon_{\mathbf{x}}(r) \to -\frac{1}{2r}, r \to \infty$				- YN 9	-	-	-
$\frac{v_{\rm x}(r) \to -\frac{1}{r}, \ r \to \infty}{v_{\rm x}(r), v_{\rm c}(r) \to \text{finite value}, \ r \to 0}$						-	-
²² LDA limit for constant $\rho(\mathbf{r})$							

- Note that $E_{c}[\rho_{\lambda}] < \lambda E_{c}[\rho], \ \lambda < 1$ is equivalent to $E_{c}[\rho_{\lambda}] > \lambda E_{c}[\rho], \ \lambda > 1$.
- J But it diverges to +∞
- " ")" for exponential $\rho(\mathbf{r})$, but "N" in general, e.g. $\epsilon_x^{BS3}(r) \rightarrow -1/r$ for a gaussian.


Accurate and simple analytic representation of the electron-gas correlation energy

John P. Perdew and Yue Wang*

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118 (Received 31 January 1992)

PW91

We propose a simple analytic representation of the correlation energy ε_c for a uniform electron gas, as a function of density parameter r_s and relative spin polarization ζ . Within the random-phase approximation (RPA), this representation allows for the $r_s^{-3/4}$ behavior as $r_s \to \infty$. Close agreement with numerical RPA values for $\varepsilon_c(r_s, 0)$, $\varepsilon_c(r_s, 1)$, and the spin stiffness $\alpha_c(r_s) = \partial^2 \varepsilon_c(r_s, \zeta = 0)/\delta \zeta^2$, and recovery of the correct $r_s \ln r_s$ term for $r_s \to 0$, indicate the appropriateness of the chosen analytic form. Beyond RPA, different parameters for the same analytic form are found by fitting to the Green's-function Monte Carlo data of Ceperley and Alder [Phys. Rev. Lett. 45, 566 (1980)], taking into account data uncertainties that have been ignored in earlier fits by Vosko, Wilk, and Nusair (VWN) [Can. J. Phys. 58, 1200 (1980)] or by Perdew and Zunger (PZ) [Phys. Rev. B 23, 5048 (1981)]. While we confirm the practical accuracy of the VWN and PZ representations, we eliminate some minor problems with these forms. We study the ζ -dependent coefficients in the high- and low-density expansions, and the r_s -dependent spin susceptibility. We also present a conjecture for the exact low-density limit. The correlation potential $\mu_c^{\sigma}(r_s, \zeta)$ is evaluated for use in self-consistent density-functional calculations.

VOLUME 77, NUMBER 18

PHYSICAL REVIEW LETTERS

28 October 1996

Generalized Gradient Approximation Made Simple

John P. Perdew, Kieron Burke,* Matthias Ernzerhof

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118 (Received 21 May 1996)

PBE

Generalized gradient approximations (GGA's) for the exchange-correlation energy improve upon the local spin density (LSD) description of atoms, molecules, and solids. We present a simple derivation of a simple GGA, in which all parameters (other than those in LSD) are fundamental constants. Only general features of the detailed construction underlying the Perdew-Wang 1991 (PW91) GGA are invoked. Improvements over PW91 include an accurate description of the linear response of the uniform electron gas, correct behavior under uniform scaling, and a smoother potential. [S0031-9007(96)01479-2]



$$\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}}$$

$$s = \frac{|\nabla n|}{n^{4/3}}$$







TABLE I. Atomization energies of molecules, in kcal/mol (1 eV = 23.06 kcal/mol). $E_{\rm XC}$ has been evaluated on self-consistent densities at experimental geometries [33]. Nonspherical densities and Kohn-Sham potentials have been used for open-shell atoms [34]. The calculations are performed with a modified version of the CADPAC program [35]. The experimental values for ΔE (with zero point vibration removed) are taken from Ref. [36]. PBE is the simplified GGA proposed here. UHF is unrestricted Hartree-Fock, for comparison.

System	$\Delta E^{ m UHF}$	ΔE^{LSD}	$\Delta E^{\rm PW91}$	$\Delta E^{\rm PBE}$	ΔE^{expt}
H ₂	84	113	105	105	109
LiH	33	60	53	52	58
CH_4	328	462	421	420	419
NH ₃	201	337	303	302	297
OH	68	124	110	110	107
H ₂ O	155	267	235	234	232
HF	97	162	143	142	141
Li ₂	3	23	20	19	24
LiF	89	153	137	136	139
Be_2	-7	13	10	10	3
C_2H_2	294	460	415	415	405
C_2H_4	428	633	573	571	563
HCN	199	361	326	326	312
CO	174	299	269	269	259
N 2	115	267	242	243	229
NO	53	199	171	172	153
O 2	33	175	143	144	121
F ₂	-37	78	54	53	39
P_2	36	142	120	120	117
Cl ₂	17	81	64	63	58
Mean abs. error	71.2	31.4	8.0	7.9	



PW91 / PBE / RevPBE /RPBE

 $E_{\rm XC}^{\rm GGA}[n_{\uparrow},n_{\rm I}]$

different enhancement factors in the inhomogeneous limit $\ s \to \infty$

It affects chemisorption energies, etc..



 $F_{\rm XC}(r_s,\zeta,s).$

a)







Energies of Atoms

energy in Ry	Li	Be	В	С	N	0	F	Ne
GGA: PW91	214.928	229.296	249.24	275.561	2108.926	2149.997	2199.433	2257.893
LDA	214.668	228.892	248.686	274.849	2108.045	2148.939	2198.189	2256.455
Expt.	214.958	229.334	249.308	275.688	2109.174	2150.126	2199.45	2257.856
energy in Ry	Na	Mg	AI	Si	Р	S	CI	Ar
GGA: PW91	2324.514	2400.12	2484.686	2578.669	2682.386	2796.152	2920.278	21055.077
LDA	2322.867	2398.265	2482.618	2576.384	2679.88	2793.419	2917.313	21051.876
Expt.	2324.49	2400.086	2484.672	2578.696	2682.764	2796.2	2920.298	21055.098
energy in Ry	K	Ca	Ga	Ge	As	Se	Br	Kr
GGA: PW91	21199.825	21355.144	23850.018	24154.2	24471.917	24803.334	25148.619	25507.943
LDA	21196.383	21351.466	23843.66	24147.583	24465.038	24796.191	25141.209	25500.263

LDA underestimates stability of atom, GGA is closer



Small Molecules

Binding Energy

	exp (ev)	LDA	GGA	HF
H2	-4.753	-4.913	-4.540	-3.64
LiH	-2.509	-2.648	-2.322	
02	-5.230	-7.595	-6.237	-1.28
H20	-10.078	-11.567	-10.165	
F2	-1.66	-3.32		1.37

Binding energy is too high in LDA; GGA is closer but sometimes binds too weakly. Pure Hartree-Fock w/o correlation is terrible



Lattice Parameters in Solids

	exp	LDA	Δ	GGA	Δ
Si	5.427	5.4	-0.50%	5.49	1.16%
Ge	5.65	5.62	-0.53%	5.74	1.59%
GaAs	5.65	5.62	-0.53%	5.73	1.42%
AI	4.03	3.98	-1.31%	4.09	1.57%
Cu	3.60	3.52	-2.35%	3.62	0.44%
Ag	4.07	4.00	-1.69%	4.17	2.47%
Та	3.30	3.26	-1.12%	3.32	0.80%
W	3.16	3.14	-0.67%	3.18	0.67%
Pt	3.91	3.90	-0.41%	3.97	1.49%
Au	4.06	4.05	-0.13%	4.16	2.48%

LDA tends to "overbind", GGA "underbinds" GGA error more variable



Bulk Modulus in Solids (in GPA)

	exp	LDA	Δ	GGA	Δ
Si	99	96	-3.03%	83	-16.16%
Ge	77	78	1.30%	61	-20.78%
GaAs	76	74	-2.63%	65	-14.47%
AI	77	84	9.09%	73	-5.19%
Cu	138	192	39.13%	151	9.42%
Ag	102	139	36.27%	85	-16.67%
Та	193	224	16.06%	197	2.07%
W	310	337	8.71%	307	-0.97%
Pt	283	307	8.48%	246	-13.07%
Au	172	198	15.12%	142	-17.44%

LDA tends to be too stiff. GGA too soft



Oxides

	exp	LDA	Δ	GGA	Δ
MgO	4.21	4.17	-0.95%		
TiO2 (a)	4.59	4.548	-0.92%	4.623	0.72%
TiO2 (c)	2.958	2.944	-0.47%	2.987	0.98%
AI2O2	5.128	5.091	-0.72%	5.185	1.11%
BaTiO3	4	3.94	-1.50%		
PbTiO3	3.9	3.833	-1.72%	3.891	-0.23%
SnO2	4.737	4.637	-2.11%		
β -MnO2 (a)	4.404	4.346	-1.32%	4.444	0.91%
b-MnO2 (c)	2.876	2.81	-2.29%	2.891	0.52%



Summary (LDA & GGA)

Lattice constants: 1-3% too small Cohesive Energies: 5-20% too strongly bound Bulk Modulus: 5-20% (largest errors for late TM) Bandgaps: too small

GGA gives better cohesive energies. Effect on lattice parameters is more random. GGA important for magnetic systems.



Summary of Geometry Prediction

LDA under-predicts bond lengths (always ?)

GGA error is less systematic though over-prediction is common.

errors are in many cases < 1%, for transition metal oxides < 5%



E	Elemental Crystal Structures: GGA pseudopotential																
	method experimentally found to be fcc																
H -0.12	E E													cc			
Li 0.13 0.11 0.11	Bt 2.19 0.04 0.50	-	_	E (k	bcc J/mol	• E _{fco} e)	2					B 34.77	C -19.71 -6.00	N -21.12	0 10.24	F -4.53	
Na 0.12 0.05 0.05	Mg 1.37 0.50 0.50	ŧ				VASP SGTI Saunde	-PAW E data rs et al.				*	Al 9.21 10.08 10.08	Si -1.89 -4.00 -4.00	P -16.04 7.95	S -17.65	Cl -4.46	
K 0.04 -0.05 -0.05	Ca 1.64 1.41 0.93	Sc 5.80 -3.02	Ti 4.79 0.48	V -23.95 -7.50 -15.30	Cr -36.76 -6.13 -9.19	Mn 7.41 0.78 1.80	Fe -8.45 -7.97	Co 8.36 1.71 4.20	Ni 9.23 7.99 7.49	Cu 2.84 4.02 4.02	Zn 5.94 -0.08 6.03	Ga 1.48 0.70 0.70	Ge 0.70 -1.90 -1.90	As -10.71	Se -14.67	Br -2.85	
Rb 0.08 -0.20 -0.20	Sr 0.43 1.33 0.75	Y 10.02 1.19	Zr 3.61 -0.29	Nb -31.20 -13.50 -22.00	Mo -38.74 -15.20 -28.00	Tc 19.04 8.00 8.00	Ru 48.93 9.00 14.00	Rh 32.39 19.00 19.00	Pd 3.74 10.50 10.50	Ag 2.27 3.40 3.40	Cd 4.90	In 1.02 0.64 0.65	Sn 0.99 -1.11 0.25	Sb -8.96	Te -11.19	I -1.26	
Cs 0.10 -0.50 -0.50	Ba -1.62 -1.80 -1.80		Hf 10.14 2.38 -4.14	Ta -23.75 -16.00 -26.50	W -45.03 -19.30 -33.00	Re 24.87 6.00 18.20	Os 70.92 14.50 30.50	Ir 59.39 32.00 32.00	Pt 7.85 15.00 15.00	Au 1.90 4.25 4.25	Hg -1.02	Tl -1.40 -0.09 0.07	Pb 4.06 2.40 2.40	Bi -4.53 1.40	Po	At	
		La 12.22	Ce 22.40	Pr 11.55	Nd 11.99	Pm 12.55	Sm 12.88	Eu -1.61	Gd 13.11	Tb 12.97	Dy 12.73	Ho 12.36	Er 11.86	Tm	Yb	Lu 9.91	
Fr	Ra	Ac 12.56	Th 13.95	Pa 17.09	U -10.36	Np -23.17	Pu 11.73	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

data taken from:

Y. Wang,*a S. Curtarolo, ^{et al.} Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability, Computer Coupling of Phase Diagrams and Tomore Neuropean States and States an

El	Elemental Crystal Structures: GGA pseudopotential															
	method experimentally found to be hep														be hcp	
H -0.01				E	hcn.	- E _{fc}	c				expe	erime	ntally	four	nd to	be fcc
Li 0.19 -0.05 -0.05	Be -7.91 -6.35	5		(1	cJ/mol	le)	- -					B -78.73	C -6.18 -3.00	N -34.15	0 1.00	F -14.64
Na 0.06 -0.05 -0.05	Mg -1.22 -2.60 -2.60	ŧ				VASP SGTT Saunde	-PAW E data es et al.				*	Al 2.85 5.48 5.48	Si -3.26 -1.80 -1.80	P -3.77	S -43.63	Cl -16.81
K 0.26 0.00	Ca 0.31 0.50 0.50	Sc -4.48 -5.00	Ti -5.51 -6.00 -6.00	V 0.53 -3.50 4.80	Cr 0.91 -2.85 -1.82	Mn -3.01 -1.00 -1.00	Fe -7.76 -2.24	Co -1.95 -0.43 -0.43	Ni 2.22 2.89 1.50	Cu 0.52 0.60 0.60	Zn -0.79 -2.97	Ga 0.69 0.70 0.70	Ge -0.28 -1.00 -1.00	As -4.83	Se -35.43	Br 3.00
Rb -0.01 0.00	Sr 0.38 0.25 0.25	¥ -2.13 -6.00	Zr -3.69 -7.60 -7.60	Nb -3.08 -3.50 -5.00	Mo 1.14 -3.65 -5.00	Tc -6.53 -10.00 -10.00	Ru -10.79 -12.50 -12.50	Rh 3.26 3.00 3.00	Pd 2.50 2.00 2.00	Ag 0.29 0.30 0.30	Cd -1.00 -0.89	In 0.35 0.37 0.65	Sn -0.50 -1.61 -0.25	Sb -3.94	Te 23.40	I 0.99
Cs -0.06 0.00	Ba -0.40 0.20 0.20		Hf -6.82 -10.00 -10.00	Ta 3.06 -4.00 -6.50	W -1.79 -4.55 -6.00	Re -6.26 -11.00 -11.00	Os -13.26 -13.00 -13.00	Ir 6.55 4.00 4.00	Pt 5.02 2.50 2.50	Au 0.08 0.24 0.55	Hg -1.51 -2.07	Tl -1.80 -0.31 -0.31	Pb 1.80 0.30 0.30	Bi -4.03	Po	At
		La 2.63	Ce 8.50	Pr 2.07	Nd 1.94	Pm 1.77	Sm 1.53	Eu 0.24	Gd 0.77	Tb 0.24	Dy -0.41	Ho -1.18	Er -1.97	Tm	Yb	Lu -3.85
Fr	Ra	Ac 0.93	Th 4.00	Pa 0.49	U -15.79	Np -14.01	Pu 0.69	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

data taken from:

Y. Wang,*a S. Curtarolo, at al. Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability, Computer Coupling of Phase Diagram and Thermochemistry (Calphad) Vol. 28, Issue 1, March 2004, Pages 79-90.

Summary: Comparing Energy of Structures

For most elements, both LDA and GGA predict the correct structure for a material (as far as we know)

Notable exceptions: Fe in LDA; materials with substantial electron correlation effects (e.g. Pu)



The high-throughput highway to computational materials design S Curtarolo, GLW Hart, M Buongiorno Nardelli, N Mingo, S Sanvito & O Levy *No mixing* increasing mixing: *Nature Materials* **12**, 191 (2013)



Figure 1 | High-throughput analysis of binary intermetallics²⁴**.** Top left triangle: ordering tendency of the mixtures, as defined in the main text, for elements ordered by Pettifor's chemical scale⁵⁴. Grey circles indicate no ordering, whereas darker blue circles indicate increasing capability to form stable compounds. Bottom right triangle: comparison of HT versus experimental results²⁴. Green and grey circles denote agreement between calculation and experimental data on the existence (green) or absence (grey) of compounds. Purple (red) triangles indicate disagreement of HT predictions of compound absence (existence) versus experimental existence (absence). Yellow triangles indicate that data is unavailable for comparison.



Marco is a scientist, composer and flutist at the University of North Texas SISSA PhD 1993

Reaction Energies

Reaction	Exp (eV)	LDA (eV)	Δ
Li (bcc) + AI (fcc) -> LiAI (compound)	-0.2457	-0.2234	9.08%
0.5 Cu(fcc) + 0.5 Au(fcc) -> CuAu	-0.053	-0.0193	63.58%
Li(bcc) + CoO2 -> LiCoO2	-4.25	-3.75	11.76%



MOLECLII AR Miller experiment in atomistic computer simulations <u>AM Saitta</u>, F Saija, *PNAS* **111**, 13768 (2014)





$M \cap I \in C \cup I \cap A = R$

Miller experiment in atomistic computer simulations <u>AM Saitta</u>, F Saija, *PNAS* **111**, 13768 (2014)

Formamide reaction network in gas phase and solution via a unified theoretical approach: Toward a reconciliation of different prebiotic scenarios.

F Pietrucci, <u>AM Saitta</u>, *PNAS* **112**, 15030 (2015)

Synthesis of RNA Nucleotides in Plausible Prebiotic Conditions from ab Initio Computer Simulations A Perez-Villa, <u>AM Saitta</u>, *et al.*, JPCLett **9**, 4981 (2018)



SISSA PhD 1997







From GGA

$$E_{\rm XC}^{\rm GGA}[n_{\uparrow},n_{\downarrow}] = \int d^3r f(n_{\uparrow},n_{\downarrow},\nabla n_{\uparrow},\nabla n_{\downarrow})$$

to Meta-GGA $E_{\rm xc}[n_{\uparrow}, n_{\downarrow}] = \int d^3r \, n \, \epsilon_{\rm xc}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}),$

where $n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r})$ is the total density, and

$$\tau_{\sigma}(\mathbf{r}) = \sum_{i}^{\text{occup}} \frac{1}{2} |\nabla \psi_{i\sigma}(\mathbf{r})|^2$$

Formulation is significantly more complicated and it is not widely used.

Still

Electron Localization Function

$$C(\vec{r}) = \frac{1}{2} \sum_{i} n_{i} |\nabla \varphi_{i}|^{2} - \frac{1}{8} \frac{|\nabla \rho|^{2}}{\rho}$$

$$\rho = \sum_{i} n_{i} |\varphi_{i}|^{2} \qquad C_{h}(\vec{r}) \sim \rho^{5/3}$$

$$\mathrm{ELF} = \left\{ 1 + \left[\frac{C(\vec{r})}{C_{\mathrm{h}}(\rho(\vec{r}))} \right]^2 \right\}^{-1}$$

ELF can distinguish metallic (ELF= ~ 0.5) from covalent (ELF= ~ 1.0) regions of the electron density

Meta-GGA has the potential to treat in a different way correlation in electronically different materials.

Problems with LDA / GGA functionals

- Chemical accuracy (1 kcal/mol) is far.
 - trends are often accurate for strong bonds (covalent, ionic, metallic)
 - weak bonds/small overlaps are problematic
- Self interaction cancellation is only approximately verified in LDA and GGA.
 - molecular dissociation limit, TMO & RE and other atom-in-solid system.
- Van der Waals interactions are not taken into account
 - occasional agreement with exp. from compensation of errors



LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

META-GGA: PKZB, TPSS,

... to be continued

SIC, DFT+U, hybrids

Van der Waals functionals







THE END

