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Self-interaction correction to density-functional approximations for many-electron systems
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transition atoms.

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In addition, the LSD ordering
of s and d levels in the d" 's' configuration of the
3d elements Sc to Mn is reversed relative to HF.
Much of the criticism of the LSD approximation has been directed toward its incomplete descrip-tion of many-body

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and the exchange-correlation potential is

v„',([nk, n,];r) = ——,Z„,[nk, kk,]

. (20)

The significance of the eigenvalue q, can be seen by an argument of Slater' and Janaksv: Differenti-ation of Eq. (15) with respect to the occupation
number f~~ (wkth all ok'bitals fkxed) ykelds

cA 4*,(r) [

-'v'+ v',kk(r)]y, (r)

(21}

Since E has been minimized with respect to nor-malization-preserving variations of the orbitals, it follows that in any infinitesimal, normalization-preserving variation of the occupation numbers and orbitals,

i.e.,

the electron and its hole together constitute
a neutral object.
Spin-density-functional calculations would yield exact results if the exact E„,[n&, n&] were known and used. In practice one often makes the local-spin-density (LSD) approximation"

E (2V)

is the density at r' of the hole around an electron at r. +, is the ground state of a fictitious system in which the electron-electron interaction is

A/If'-r'I and the spin densities are those of the real system (A.= 1). The A integration appears be-cause of the definitions of T[n&, n&] (e (7})and II[n] +&„,[nk, n&] (e (V„)); the integrand of Eq. (25) at the limit X=O is the exchange hole. From the def-inition (25), one gets

d'~'p(r, r)=-1, (26)

(2) Now minimize E with respect to the f „sub- =¹ ject to the particle-conserving constraint Q,f,

This is equivalent to the unconstrained" min-

imization of 8- pN, where p, is the chemical po-
tential [=—electronegativity]":

5(g ik~)=g(&.. P}5/.. O. (23)

E, d,,t +, kk(r)P(r r')

(24)

where

p(r, r') = dik(+,

I

[n(r) —n(r)]

x [n(r) —n(r)]/&(&) —~(r —r }I+„&
(25)

From Eq. (23) we immediately find an "aufbau

principle"'": orbitals with &,& p have f,= 1,

and those with q)ik have f =0. Fk'actiokkal oc-cupation is found only for q, = p,. If it turns out that all occupation numbers are O or 1, then the
ground-state spin densities of the real system are
also ground-state spin densities of a fictitious sys-tern of noninteracting electrons moving in the po-tential v',s(r), as was assumed in the original
Kohn-Sham' derivation of Eq. (17). This assump-
tion may not be universally true, and in the pres-ent formulation it is unnecessary. If this assump-tion is true, and if in addition the interacting ground state is adiabatically connected

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of E„,to noninteger numbers of electrons,

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d'y'p~&(r r'}= — Q f n

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Since the screening effect from the

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E. Long-range behavior of the potential and

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0$

I

0.1-

p.p

-0.1
-0.2
-0.3

-0.6.
-0.7
-0.8-

RM RT

ergy as a functional of orbitals and occupation numbers, the SIC energy will be a functional of the density if the orbitals and occupation numbers are. The needed functional relationship is gener-ated by the following rule: Given any pair of trial spin densities n~(r) of

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Eq. (17) using these model potentials to find the orbitals tt„,(r), which are now functionals of the spin density. For small systems such as atoms and ions, the Kohn-Sham orbital densities n„(r) can be substituted directly into the SIC energy ex-
pression. (2) This expression can then be mini-
mized by varying the spin densities; in practice,
however, one varies the model potentials v',«(r).
If the model potentials have sufficient variational flexibility, they will approach a self-consistent
solution. 'This method of potential variation was
suggested as a practical scheme for LSD calcula-tions by Rose and Shore.

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[The minimization dis-
cussed here is constrained to the "Kohn-Sham"
space of orbitals belonging to orbital-independent
potentials, so the resulting self-interaction-cor-
rected total energy will be greater than the value found by the method of Sec. II 8, Eq. (37), which does not impose this constraint.]
'The scheme just defined is a Kohn-Sham for-
malism which is self-interaction free in the sense

that it satisfies Eq. (29). Unfortunately, the self-
interaction error reappears in the form of a size-
consistency problem: The theory will be useful for an isolated atom, but not for a lattice of atoms in the limit of infinite lattice constant, since in the latter case the Kohn-Sham orbitals will be atomic-

like Bloch functions and the correction per atom
will be zero. As mentioned in Sec. II 8, there will
in this latter case be a correction to the total en-ergy proportional to the volume of the system to the & power, which looks at first like a contribu-tion to the surface energy, but is not; it is simply
a shadow of the size-consistency problem. This
example, and another discussed in Appendix B, show how subtle the self-interaction problem can be: Satisfaction of Eq. (29) is a necessary condi-tion for solving it but not a sufficient one.
The reason for the size-consistency problem is that the self-interaction correction depends on the
choice of orbital representation. For example,
the core electrons in a solid could be represented' either by localized Wannier orbitals which carry
self-interaction, or by delocalized Bloch orbitals
which do not. Stated differently, the self-inter-
action 6~, depends on the number of atoms which share the orbital P«, as illustrated by the SIC band-structure calculation for solid Ar presented in Sec. IIH.
Thus, the key to resolution of the size-consis-tency problem lies in unitary transformation of the fully occupied orbitals. Such a transformation leaves invariant a Slater determinant and any one-electron property that can be evaluated from a Slater determinant, such as the spin density [Eq. (13)], the kinetic energy [Eg. (14)], or the ex-change energy [Eq. (7)]. As a result, the Hartree-

Fock and Kohn-Sham total energies are invariant under such a transformation. Since the orbital

densities n, (r) change under the transformation, the SIC total energies are not invariant.
To get a size-consistent self-interaction-cor-rected Kohn-Sham theory, insert between steps
(1) and (2) above another step: (1') Perform a unitary transformation of the Kohn-Sham fully occupied (molecular or Bloch) orbitals to a second set of (more localized) orbitals which will gener-ate the orbital densities to be used in step (2). The right unitary transformation might be the one which minimizes the SIC energy expression. Since the spin densities and the kinetic energy re-main invariant, so does each piece of the energy
(15) excePt the self-interaction correction, so this choice amounts to finding the equivalent orbi-tals that carry

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we have matched smoothly to the correct high-
density limit. As shown in Appendix C, other
parametrized correlation energies commonly used
in density-functional calculations are in error at
the high densities which are important in atoms.
For atoms and

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of transition-element impurities in solids.

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Table V compares the exchange energies of
atoms calculated in these three approximations.
LSD underestimates the magnitude of the exchange
energy by 10-15%, while SIC-LSD gives values in better agreement with HF. (Note that SIC-LSD for exchange only and HF are the same approximation in the case of atomic H and He.)
It was once hoped that LSD exchange energies would be improved by including the first correc-tions from the density-gradient expansion (e.g., the X&P method, Ref. 61). For exchange alone (as opposed to exchange and correlation), the
a priori gradient correction is negative and so improves the LSD exchange energy, but the im-provement is slight for all but the lightest atoms; the coefficient of the gradient term must be arti-ficially magnified by a factor of 5 to get agree-ment with Hartree-Fock energies.

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It might be
interesting to reexamine the convergence

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TABLE VII. Calculated correlation energies of

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losoex than for the neutral atom, and the difference
is

a rough estimate of the true binding energy. 6)
This kind of misbehavior cannot occur in

a self-
interaction-free theory like HF or SIC-LSD: Be-cause of the inequality (57), the eigenvalue of the extra electron will always be negative

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the LSD eigenvalues only capture about 60/p of the
ionization potential.
Qualitatively similar conclusions apply when the
ionization process leaves the atom in an excite
state. Table X displays a detailed comparison between ground-state orbital eigenvalues and re-laxed energy differences due to hole creation in Ar. First consider the relaxed energy differences &E~ „& in comparison with measured removal ener-gies": The SIC-I SD values show the best overall agreement with experiment, while the HF values are somewhat in error for the outer orbitals (due to neglect of correlation) and the LSD values are slightly in error for the inner orbitals (due to self-interaction). Note in particular the serious error of the HF approximation for the Ss hole in Ar, where &E" ~«~ is 4 eV greater than the ex-
perimental removal energy. Bagus '

has attribu-
ted this error to an anomalous inc~ease in the
magnitude of the

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TABLE XI. Self-interaction corrections 4&zc to the
LSD band-structure error 4E~ in the band gaps of rare-
gas solids and the core ionization in solid LiF. Energies
in eV.

Solid

Ne
Ar
Kr
Xe

LiF (Li ls)
LiF (F2@)

21.4

~

14 2
11.6

~

9.3'
64.4'
37 6"

11.2
8.3
6.8

47.2'
301'

9.9
- 5.9 5.8
4.9
4.2
- 17.2 18.0
- 7.5 7.9

-4.9

~Reference 27.
~References 28 and 31.
cReference 29.
dReference 30.
'Reference 31.

eV) and transition-metal oxides like Coo (predic-ted erroneously by LSD to be metallic'). While for years such anomalies were often disguised by computational devices which "fixed" the gaps, it has
become clearer in the last few years" "'~'""'""
that they reflect a fundamental limitation of the LSD band-structure model. In what follows we

will present evidence (see also Refs. 31, 75, and 76 for our earlier corrections to LSD band gaps due to SIC) that these discrepancies arise largely (but not entirely) from self-interaction errors, and that the SIC scheme can form the basis for

a new and improved band theory.
It is not difficult to see why self-interaction cor-rections should significantly alter the results of band theory for atomic crystals like solid Ar (Ref. 77): Although an electron should see an Ar'-like potential in the valence band and an Ar'- like potential in the conduction band, LSD actually forces an Ar'-like potential for both bands. The difference between the two corresponding orbital energies has both a kinetic component W (inclu-ded in band theory) and an intra-atomic self-direct component II (neglected in LSD but not in SIC). For localized electronic states one expects U 8 W. We show in Table XI, along with the LSD band-
structure error &E (=E",' —E;*"')for rare-gas
solids, the difference ~»c between the LSD and SIC-LSD eigenvalues of the outermost atomic or-bital forming the valence-band maximum (e.g., 2p, 3p, 4p for Ne, Ar, and Kr, respectively). The

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for the modified Wigner-Seitz boundary conditions
at the sphere boundary), while the more diffuse
wave-function components outside the sphere can
be treated in the standard LSD form. The wave
functions are normalized over the entire unit cell.
This

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error for the K 4s orbital is much smaller than the cohesive energy.
The 3d transition metals are a notable exception
to this rule. Figure 9 shows a comparison of LSD
(Ref. 12) and measured" cohesive energies across the 3d series. Note that LSD gives accurate co-hesive energies at both ends of the series, but overestimates them by as much as 70/q near the middle.
As we cross the transition sex'ies from Ca to

CU, the 3d band is progressively fiBed, and the orbitals contract in response to the increasing nuclear charge. As a result the LSD self-inter-action 6„, of each orbital grows progressively,
as shown in Fig. 10. The 3d orbitals are xathex' localized and each carries a self-interaction

(0.2 to 1.2 8V per electron) that is large on the scale of the cohesive energy, but they are not inert core orbitals until we reach Cu; in fact, they hybridize strongly with the 4s orbitals. As we
move to the post-transition elements, the 3d or-
bitals carry even mox'e self-interaction but they are largely chemically inert when the solid is formed from atoms; this leads to an effective
cancellation of SIC core terms in the cohesive

eQergy x'ende11Qg LSD a good appl oxlmatlon. It seems likely, then, that the s-d valence shell, car-x'les a gl eater LSD self-1ntex'act1on ex'1 ox' 1Q the transition atom than it does in the solid, leading
to the LSD ovex'estimation of the cohesive energy.
Let us define the error of the LSD cohesive ener-

valence

N&5',.

"'d valence,

wllere onl)I VRlellce orbltais contribute Il ~ 8

P"I"(core) = 5„",'m(core)]. The solid-state self-
interaction 5& need not be evaluated in the present estimate, but is in principle to be calculated from sultabi)I localized (Wannler-tiIpe) fllIlc'tlolls fol'
the valence bands. Vfe take the 6 values from Fig.
9, gLffrom Janak et al.

"

and 5„'",'

(valence) from
Fig. 10, and calculate Q&&& P,."'~(valence) from Eq. (V9). From this we get the ratio between the valence self-interaction in the solid and in the

0.00

-0.6

Following the argument of the preceding para-graph, we equate 6 to the difference between the LSD self-interaction per atom in the gas and in the

-$.0-

- 1.2

I
LU

C

-20-

a O
gp CP
hJ

CO ~~

Cl

Du
td

40—

0'=
t~~ l)) l l I l) l l i

Li No K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Go

FIG. 9. Percent error in the LSD cohesive energies for some alkali metals and the sd metals. The LSD

and experimental values were taken from Refs. 12.and 88, respectively.

Ca Sc Ti V Cr Mn Fe Co Ni Cu

FIG. 10. LSD self-interaction error of the atomic orbitals in the 3d transition series. The self-interaction

~o~~g~ggo@ -g„& is plotted here for the majority-spin orbitals. This correction is small (and in some cRses positive) for the 4g orbitals, but large and negative for the 3d orbitals.

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atom. We find that the valence self-interaction

in the solid is negligible for the free-electron
metals Li and Na [e.g. ZP' 68"'~ (valence) equals
0.00 and 0.01 eV for Li and Na, whereas the co-
hesive energies are 1.6 and 1.1 eV, respectively],
and it varies from -8% of the atomic valence self-interaction at the beginning of the 3d series

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4—

CQ

L,
CO

4J

C9 z
I:
O
X
4l

~ Fe
~ Co

Ni—

dn o n-I I

d s
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dn-I 2

FIG. 12. Spin splitting in atomic Fe, Co, and Ni as a function of atomic configuration. The difference bet-ween the energy eigenvalues of minority- and majority-spin occupied 3d orbitals. is plotted' here. (The LSD values for Fe and Co in the d"s configuration are un-certain due to convergence difficulties.) The observed (Ref. 32) spin splittings in the solid, indicated by horizontal arrows, are shown for comparison.

(0)- and majority (0)-spin 3d electrons. Figure 12 shows this quantity as a function of atomic con-figuration in LSD and SIC-LSD; the measured
solid-state spin splittings are also shown for
comparison.
Note that self- interaction correction increases
the spin splitting, although the increase for Ni
is only marginal. The reason is very simple: The majority spins see a more attractive exchange-
correlation potential than the minority spins do,
and so have more localized orbitals. The self-
interaction correction lowers the eigenvalues of
all occupied d orbitals, but the eigenvalues of the more localized majority-spin orbitals get lowered more, leading to an increase in the spin splitting.
[This argument, due to L. Kleinman and K. Mednick
(private communication}, is based on treating the
self- interaction correction to the one- electron po-
tential as a first-order perturbation on the LSD
eigenvalue, a treatment which gives numerical
results in rather good agreement with our self-
consistent ones. However, the success of this
approach should not be interpreted to mean that the self-interaction correction has no effect on the orbitals of transition-metal atoms; in fact, at self-consistency it contracts the 3d

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exchange. However, they rejected any attempt to treat self-exchange exactly because, unlike the total exchange energy, it

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n =0 (the Wigner

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upon removal of the electron from this orbital. This inequality is often close to an equality, and amounts to an "extended Koopmans's theorem", less precise but possibly more powerful then the original.
When applied to LSD, the self-interaction cor-rection properly satisfies the sum rule of Eq.
(26) for systems without fractional occupation numbers, and improves the shape of the exchange-correlation hole. We have applied this SIC-LSD scheme in atomic calculations, with results that are far more accurate than those of LSD for a modest increase of computational effort. (In com-parison with HF, SIC-LSD is both simpler gnd more accurate.) Calculations of this type were recently shown'" to generate accurate a priori pseudopotentials to describe

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bitals, being solutions of Eq. (17), are of course orthogonal.
These

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where &,' ~" is the correlation energy in the ran-dom- phase approximation and

&~ = 0.023

TABLE XIII. Correlation energy per electron of the unpolarized and polarized uniform electron gas. CA: parametrized Ceperley-Alder, HPA: numerical random-phase approximation. r~ in eV.

is the second- order exchange constant (indepen-dent of spin potarization). Using Misawa's'" RPA scaling relation

Unpolarized
CA HI A

Polarized
CA It PA

4. P, RPA(r) —~

e

Ui RPA(r /24/3)

me find

(C10)

e,(r„f)= e (r)+f(t)[~ (r,) —e,'(r,)],
)I.'(r, &) = u.'()r+f(K) [I1.'(r,) —)1.'(r,)]

(C12)

(C13)

+ [a P(r,) —«,U(r,)][sgn(o) —1]—,

Z =0.01555, a =-0.0269.

We used Elis. (C3) and (C4) for r,)1, and Elis.
(C5) and (C6) for r, &1. The coefficients C, and D,. were chosen to match &,'and p,,

' at r, =l, and
'till'lied oil't 'to tie 1'atilel' smaU. [Tills ls all llltel'- polation procedure and not a precise determina-tion of the 0(r) terms in the high-density expan-sion.]
For intermediate spin polarizations 0 & g & 1, me used a standard interpolation formula, first proposed by von Barth and Hedin, a

in which the

correlation energy has

a

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0.05 —0.8

a

K

0.02

CL ~

uJ

O

0.0I—
ir
O

hl
K
O
O

0

Moruzzi et al.

o.e &

—0.2

Gunnarsson-

Lundqvist

I

4

DENSITY PARAMETER I'

s

FIG. 14. Same as Fig. 13, but for the polarized
electron gas.

careful fit to their numbers. For the densities

they considered (v, =l, 2, 5, 10, 20, 50, 100), our parametrization never deviates from their results by more than 0.0001 a.u. In Table XIII we compare the parametrized Ceperley-Alder correlation ener-
gies with numerical RPA correlation energies. "'
The difference between the Ceperley-Alder values and Ceperley values we used in our calculations can be gleaned from Figs. 13 and 14; although the difference is very small, the Ceperley-Alder

values should be preferred in future work. Vosko, Wilk, and Nusair"' have independently parame-trized the Ceperley-Alder results in a different way, but for the r, values shown in Table XIII their numbers never deviate from ours by more than 1.3/p relatively or by more than 0.0013 a.u. absolutely.
One way to assess the accuracy of the correla-
tion energy is to plot &,' —&,"

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