Solid State Communications, Vol. 34, pp. 933—936. Pergamon Press Ltd. 1980. Printedin Great Britain.

A SELF-INTERACTION CORRECTED APPROACH TO MANY-ELECTRON SYSTEMS: BEYOND THE LOCAL SPIN DENSITY APPROXIMATION

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(Received 22 January 1980 by A.A. Maradu din)

A self-consistent self-interaction correction to the local spin density approximation is shown to remove many of the anomaliesin the pre-dicted exchange, correlation and total energies of atoms, stability of negative ions and band gaps ofinsulators. It also suggests a new inter-pretation ofthe calculated cohesive energies oftransition metals.

DESPITE the striking success of the local density (LD) more detailed account of our work wifi be presented
[1] and spin-density (LSD) [2] functional approaches elsewhere [12].
to many-electron systems, some significant discrepancies Spin-density functional theory [1, 2] expresses
remain. These include the facts that: (i) While the LSD the ground-state energy of a many-electron system,
total energy of a metal surface istoo low when com- coupled to an external potential Vext(r) and charac-
pared with the exact value [3],the LSD energy for terizedby electron density p(r) = p~(r)+ p~(r)and
atoms is too high [4]. Furthermore, the lowest-order spin-polarization ~(r) = (Pt — p~)/p,as:
correction to the LSD exchange-correlation energy — 1 + 1 1 1
predicted by many-body theory, i.e., the density- E — T[p, ~j Eext[pj + ~Eq~[pj + E~~[p,~‘j, (1)
gradient correction [5], is positive, and so can only where Tis the non-interacting kinetic energy,~ =

worsen the calculated energies of atoms. (ii) For atoms f d

3rp(r)V~t(r)is the interaction of p with Vext, Eee
[4] the magnitude of the exchange energy in LSD is isthe interaction of p with the time-averaged Coulomb

consistently underestimated by 10—15% while the mag- potential V~([p]; r) = f d3r’ p(r)/Ir — r’I, and ~ is
nitude of the correlation energy is overestimated by the sum of exchange and correlation energies. The self-
100—200%. (iii) The experimentally stable negative ions consistent one-electron equation found variationally
(e.g. W, O, F) are predicted to be unstable [6]. (iv) from equation (1)is
Self-consistent LD band stmcture calculations under- 2 ~
estimate the one-electron energy gap of insulators by as ~ ~ + V (r)} ~/i
1~a(r)= e%(/~(r), (2)
much as 40% (see [7—11]), and more generally the LSD where the potential (with spin index a) is implicitly a
one-electron eigenvalues are not close to physical re- functional of p and ~:
rnoval energies from bound states. The conventional 1,

remedies have been delta-SCF or Slater transition-state V (r) = V~t(r)+ Vee([p]; r) + V~~([p,~]; r), (3)
type calculations, which are very tedious, especially for and the density is determined via p(r) = ~, i.~0(r)
solids where they break the translational periodicity. from the spin—orbital densities p~0(r)= N~I~t’~0(r)I

2.

In this letter we show that these problems are inter- (Naq is an occupation number, 0 or 1). The exchange-
related and that a simple, physically transparent correlation potential V~°~isthe functional derivative of
correction to LSD — the subtraction ofspurious self- ~ withrespect top~(r).
interaction — accounts for and corrects the qualitative The imperfectly-known exchange-correlation func-
as well as most of the quantitative discrepancies. This tional ~ is usually replacedby the local (LSD)

self-interaction correction is a “non-homogeneity approximation [1, 2]: E~D= f d3rp(r)the

934 SELF-INTERACTION CORRECTED APPROACH TO MANY-ELECTRON SYSTEMS Vol. 34, No. 12 Table 1. (— 1) x total energy in eVfor atoms scheme was

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Table 2. (— 1) x exchange and (— 1) x correlation o.

energiesineVfo::toms Correlation

Atom:i ~:ir~:~

6.0

Table 3. SI corrections Asic to the LSDband-structure -3.0

7ornOa~,~nin the band gaps ofrare-gas solids and the core

Solid ~ E~D £~Eg ~~sic ~
I I I I I

Ne 21.4~ 11.2~ — 10.2 9.9 1 2 ~ Distance Ia.u) 8 9 10
Ar 14.2(a) 8.3~ — 5.9 5.8

Kr 11.6(a) 68(d) — 4.9 Fig. 1. The LSDand SIC atomic potentials forNi
Xe 9,3(a) — — 4.2 3da4s

2. Shaded areas indicate the spin splitting.
UF(U ls) 64.4~ 47.2(e) — 17.2 18.0
T~VIL’~\ .,-

7~(b) .,~1(e) — 75 7fl
LA1~j~.~) .~I.U dV.i “ one-electron potential. But in our SIC approach, since
an electron is “forbidden” to interactwith itself, e00
(a)Ref [7]; ~Ref. [8, 11]; ~Ref. [9]; ~Ref. can depend on N~,only indirectly (hence less strongly),
[10]; (e)Ref. [111. through the reflection backonto orbital ac of its self-

consistent effect on the other orbitals. Thus, to the
E~and correlationE~energies with LSD and exact extent that physical relaxation effects are small, the
values [17, 18]. The long-known [4] 10—15% discrep- SIC eigenvalue gives the change in total energy func-
ancy ofE~’

2from the exact value islargely corrected. tional due to removal of an electron.
Similarly, the large (100—200%) errors in~ which The energy elgenvalues ofthe SICapproachdo in
haveb5mt-oTj 1 0 0 1 111 372 Tm (5o11 372 Tm (b5mt-oTj 1 0 0 1 111F11 372 Tm s7 (the) Tj 1 0 0 1 429 408 Tm~4e8-j 1 0 0 1 429 40

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We next consider the implications of SIC for cal- the SI corrected total energy of equation (4). The result
culations ofthe cohesive energy EB ofmetals within of this first minimization is the energy corresponding
LSD [21]. These assume that ER is the difference to Pt and p~a further minimization overp~and p~
between the calculated atomic and solid LSD total ener- gives the ground-state energy.
gies, and agree closely with experiment except in the 3d
transition series (e.g.ER is overestimated by 70, 45, 45
and 25% for Mn, Fe, Co and Ni respectively [21]). It Acknowledgements — One of us (J.P.) acknowledges
discussions with S.H. Vosko, L. Kleinman, D. Koelling,
seems reasonable to assume that the core SI corrections D.C. Langreth and M. Levy, and NSF support.

are similar in the atom and the solid, and nearly cancel
inEB. This still leaves the SI corrections — 6~for the
valence orbitals, which we find are sizeable for atomic REFERENCES
3d electrons (— 0.1 to — I eV/electron)on the scale of ~ W. Kohn & L.J. Sham, Phys. Rev. 140, Al 133
ER (1—6 eV/atom). One is then tempted to analyze the (1965).
discrepancies between the LSD and observed ER as the 2. 0. Gunnarsson & B.I. Lundqvist, Phys. Rev. B13,
result ofincomplete cancellation between the SI cor- 4274 (1976).
rections ofthe atomic 3d orbitals and the lesser SI 3. D.C. Langreth & J.P. Perdew,Phys. Rev. B 15,

2884 (1977). corrections of the more diffuseWannier-like orbitals in 4. B.Y. Tong& L.J. Sham,Phys. Rev. 144,1(1966).

the solid. Using the LSD and observed EB and our 5. D.J.W. Geldart &M. Rasolt,Phys. Rev. B13, 1477
values for atoms, we find that the valence SI in the solid (1976).
ranges from 10% at the beginning to as much as 80% of 6. K. Schwarz, Chem. Phys. Lett. 57, 605 (1978).
the atomic value at the end of the 3d series. The same ~ U. Rössler, Rare Gas Solids (Edited by M.L. Klein
& J.A. Venables), p. 505, Academic Press, New analysis yields negligible valence SI for the alkali metals York (1976).
(l0~—l0~eV), in accord with their free-electron 8. K. Hamrin, G. Johansson, U. Gelius,