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

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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

Vol. 34, No. 12 SELF-INTERACTION CORRECFED APPROACH TO MANY-ELECTRON SYSTEMS 935

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

0.3824 TmT 38 t1FrgyU 96 3vondifc253lep-

936 SELF-INTERACTION CORRECTED APPROACH TO MANY-ELECTRON SYSTEMS Vol. 34, No.12

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

is