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Exchange-Correlation —Induced Negative Effective U

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In addition to Anderson's mechanism for a "negative effective U" induced in localized systems
by lattice distortions, we propose an independent microscopic mechanism —stabilization of
electron-rich configurations through exchange interactions. This is illustrated for an unrelaxed in-
terstitial Cr impurity in Si through a self-consistent local-spin-density Green s-function calculation.

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A localized center 3 can exist in a medium in a
series of charge (q) states A«(N) if it has localized
levels a that can accommodate different electronic oc-

cupations N. Electron or hole exchange between level n and the itinerant states of the medium can then pro-duce a sequence of first, second, etc.,

ionization tran-

sitions with energies bE((q —1)/q) =E +' —E or bE(q/(q+1)) =E —E ~ ', etc., where E(
is the total energy of the system with N electrons in
level n. For the vast majority of observed centers, '
Coulomb interactions make it energetically more cost-

ly to ionize A«+'(N —1) than to ionize A«(N), i.e., the effective Mott-Hubbard energy of orbital u,

U((A«) =bE((q —1)/q) —bE(q/(q+1))
E~&-»+ E~&+» 2E~»

is positive. However, this convexity of E(~) (i.e.,
U) 0) is not mandated by any physical principle. 2

Indeed, Anderson3 envisioned a particular situation

where U (0. He noted that in addition to the ever-

positive effective Coulomb repulsion

U (aa) (g «) U E (%+1) + E

(N —1) 2E ()v)

attendant upon vertical (ver) ionizations of a bond in a
static lattice, a relaxation (8) of the bond can alter its total energy by 5E~~ ', hence U changes by the amount ~E (w+» + ~E (w —» 2~E (w)

He modeled be as —(V/2K)N„„, where K is the
harmonic force constant, V is the electron-ion cou-
pling constant, and N, ff n&+ & +n& ~ —2n& is the effective number of electrons participating in this cou-
pling. For the case nz ~

= 0, nz = 1, and nz+ & = 2
treated by Anderson, one has N,ff= 2 & 0, leading to

the possibility of U= U „+AU& (0 if the negative

relaxation correction b U~ = —V /K outweighs the
positive repulsion U„„. This has since been shown to
be the case for the Si vacancy,

'

interstitial boron in

Si, defect pairs on chalcogen glasses, and In ions in solution.

'

%hile ionization energies are positive in

all cases, if U(A «) (0 the second ionization energy is

smaller than the first one, and hence 2A«(N) dispro-

portionates into A« '(N+1) +A«+'(N —1) and A«(N) is never the ground state of the system. This leads to a variety of unusual electronic, magnetic, and transport properties.
In this Letter we describe an intrinsic electronic mechanism that can lead to U & 0 without lattice relax-

ation. This "electronic negative effective U" that5 pertains

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surements' for Mn impurities in noble metals, show-
ing that, relative to free ions, the Coulomb repulsion
is reduced in the solid 20 times more than exchange
interactions.

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ncce band at

) =E +0.74 eV, as(2+/ 3+)=s(4) E(3

/s.s(1+/2++ =Et'& E(4 =—
1+)=E —E(5) E +

d)tk l

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ts —S„+0.9 eV, tndicating a
tion energy

+ Cr (d) the resu
electron volts, as

E =E)+2p„,

' —E(') +0.74+ &, E(4)

0.3—

0.2

0.1

(2)
"'=Et"+1.29,

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of the d -d -d sequence. In contrast, the reaction
2Cr'+ (d) ~ Cr +

(d) +Cr (d) is unfavorable since
its energy
U

"

(Cr'+) = 0.74 + 2.28 —2 x 1.29 = +0.44 eV

is positive. Hence, Cr'+(d~) is stable. This is so be-cause the correlation energy 5 UM('c1