Exchange-Correlation–Induced Negative Effective U

H. Katayama-Yoshida[a] and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

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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 interstitial Cr impurity in Si through a self-consistent local-spin-density Green's-function calculation.

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A localized center A can exist in a medium in a series of charge (q) states $A^q(N)$ if it has localized levels α that can accommodate different electronic occupations N. Electron or hole exchange between level α and the itinerant states of the medium can then produce a sequence of first, second, etc., ionization transitions with energies $\Delta E((q-1)/q) = E^{(N+1)} - E^{(N)}$, or $\Delta E(q/(q+1)) = E^{(N)} - E^{(N-1)}$, etc., where $E^{(N)}$ is the total energy of the system with N electrons in level α. For the vast majority of observed centers,[1] Coulomb interactions make it energetically more costly to ionize $A^{q+1}(N-1)$ than to ionize $A^q(N)$, i.e., the effective Mott-Hubbard energy of orbital α,

$$U^{(\alpha\alpha)}(A^q) \equiv \Delta E((q-1)/q) - \Delta E(q/(q+1)) = E^{(N-1)} + E^{(N+1)} - 2E^{(N)},$$

is positive. However, this convexity of $E^{(N)}$ (i.e., $U > 0$) is not mandated by any physical principle.[2] Indeed, Anderson[3] envisioned a particular situation where $U < 0$. He noted that in addition to the ever-positive effective Coulomb repulsion

$$U_{\text{ver}}^{(\alpha\alpha)}(A^q) = U_{\text{ver}} = E_{\text{ver}}^{(N+1)} + E_{\text{ver}}^{(N-1)} - 2E_{\text{ver}}^{(N)}$$

attendant upon *vertical* (ver) ionizations of a bond in a static lattice, a relaxation (R) of the bond can alter its total energy by $\delta E_R^{(N)}$; hence U changes by the amount

$$\Delta U_R = \delta E_R^{(N+1)} + \delta E_R^{(N-1)} - 2\delta E_R^{(N)}.$$

He modeled[3] ΔU_R as $-(V^2/2K)N_{\text{eff}}$, where K is the harmonic force constant, V is the electron-ion coupling constant, and $N_{\text{eff}} = n_{N+1}^2 + n_{N-1}^2 - 2n_N^2$ is the effective number of electrons participating in this coupling. For the case $n_{N-1} = 0$, $n_N = 1$, and $n_{N+1} = 2$ treated by Anderson,[3] one has $N_{\text{eff}} = 2 > 0$, leading to the possibility of $U = U_{\text{ver}} + \Delta U_R < 0$ if the negative relaxation correction $\Delta U_R = -V^2/K$ outweighs the positive repulsion U_{ver}. This has since been shown to be the case for the Si vacancy,[1,4] interstitial boron in Si,[5] defect pairs on chalcogen glasses,[6] and In ions in solution.[1,7] While ionization energies are positive in all cases, if $U(A^q) < 0$ the second ionization energy is *smaller* than the first one, and hence $2A^q(N)$ disproportionates into $A^{q-1}(N+1) + A^{q+1}(N-1)$ and $A^q(N)$ is never the ground state of the system. This leads to a variety of unusual electronic, magnetic, and transport properties.[3-7]

In this Letter we describe an *intrinsic electronic mechanism* that can lead to $U < 0$ without lattice relaxation. This[8] "electronic negative effective U" pertains to the situation where an intrinsic electronic effect can stabilize the end-point species $A^{q+1}(N-1)$ and $A^{q-1}(N+1)$ more than $A^q(N)$. For example, if the gain in many-electron correlation (MC) energy

$$\Delta U_{\text{MC}} = \delta E_{\text{MC}}^{(N-1)} + \delta E_{\text{MC}}^{(N+1)} - 2\delta E_{\text{MC}}^{(N)}$$

outweighs the usual static Coulomb energy U_{ver}, one can have $U_{\text{ver}} + \Delta U_{\text{MC}} < 0$ even in vertical (Franck-Condon) optical transitions where $\Delta U_R = 0$. Detailed first-principles self-consistent Green's-function calculations within the local-spin-density approach illustrate this mechanism for an interstitial Cr impurity in Si.

Physical principle.—The vertical energy $U_{\text{ver}} = U_{\text{ver}}^{(\alpha\alpha)}(A_q)$ is the change in the total spin-restricted energy $E_{\text{ver}}^{(N)}$ of the combined system upon removal of an electron from orbital α on center $A^q(N)$ [thereby converting the center to $A^{q+1}(N-1)$] and placement of the electron on the *same* orbital of a distant center $A^q(N)$ [converting it to $A^{q-1}(N+1)$], without deforming the lattice (i.e., a Franck-Condon transition). However, the mean-field energy $E^{(N)}$ can be further lowered by the many-electron correction[9] term $\delta E_{\text{MC}}^{(N)} = E^{(N)}(\alpha_\uparrow^{N\uparrow}\alpha_\downarrow^{N\downarrow}) - E^{(N)}(\alpha^N)$ if the electron does not go into the same space orbital α but instead polarizes the orbital, resulting in $N^\uparrow$ spin-up electrons in orbital $\alpha^\uparrow$ and $N_\downarrow$ spin-down electrons in orbital $\alpha^\downarrow$. In *isolated* systems (e.g., free atoms) $U_{\text{ver}} >> |\Delta U_{\text{MC}}|$, as can be verified from the values of the corresponding atomic integrals.[10] The key point, however, is that when a free atom is placed into a polarizable host system, its Coulomb and exchange-correlation interactions respond in fundamentally different ways to screening: The former, responding to long-wavelength (monopole) screening, is reduced far more than the latter (multipole screening).[11] This has been demonstrated experimentally in a recent elegant set of measurements[12] for Mn impurities in noble metals, showing that, relative to free ions, the Coulomb repulsion is reduced in the solid 20 times more than exchange interactions. What is special about deep impurities in *semiconductors* is that they often show[13,14] both localized gap levels and hybridized $3d$ valence-band resonances. Under these conditions, Haldane and Anderson[15] have shown that the effective charge $Q^*(q)$ on the impurity can depend very weakly on the formal charge q, resulting in a strong reduction in the vertical repulsion energy $U_{\text{ver}} \propto (\partial Q^*/\partial q)^2 U_0$, relative to the free-atom value U_0. The reason for this weak dependence is that the loss of charge attendant upon the ionization of the gap orbital α is nearly compensated by an increased localization of the valence-band resonance wave functions in the immediate vicinity of the impurity.[13] We show here by a detailed self-consistent calculation how this screening mechanism can reduce U_{ver} dramatically *without affecting appreciably the exchange interactions* ΔU_{MC}, leading therefore to the possibility of $U_{\text{ver}} + \Delta U_{\text{MC}} < 0$.

Reduction of U_{ver} *in a semiconductor.*—We illustrate this reduction in Fig. 1 for the three charge states of an unrelaxed interstitial Cr impurity in Si, $\text{Cr}^{3+}(d^3)$, $\text{Cr}^{2+}(d^4)$, and $\text{Cr}^{1+}(d^5)$, by performing three separate self-consistent all-electron local-spin-density Green's-function calculations[14] (including the Ceperley-Alder exchange-correlation and the self-interaction correction). We find for Si:Cr^{3+} [Figs. 1(a) and 1(d)] that in its ground state it has unoccupied $e^{\uparrow}$ and $t^{\downarrow}$ levels in the gap and a triply occupied impurity-induced $t^{\uparrow}$ orbital in resonance with the valence band (VB). To illustrate the self-regulating response mechanism,[13,15] we decompose[13,14] the impurity local electronic charge Q^* and the local magnetic moment μ in the (orthogonal) impurity subspace into the contributions Q_g and μ_g from the gap (g) orbital α and the contributions $\Delta Q_{\text{VB}} = Q^e_{\text{VB}} + Q^t_{\text{VB}} + Q^a_{\text{VB}}$ and $\Delta\mu_{\text{VB}} = \mu^e_{\text{VB}} + \mu^t_{\text{VB}} + \mu^a_{\text{VB}}$ from the impurity-induced changes in the valence-band resonances (including the contributions from e, t_2, and a_1 representations; cf. Fig. 1, which gives only the dominant e and t_2 contributions). For Si:Cr^{3+} with empty gap levels, we have $Q_g^{N-1} = \mu_g^{N-1} = 0$. All of the impurity charge ($\Delta Q_{\text{VB}}^{N-1} = 5.33e$) and magnetism ($\Delta\mu_{\text{VB}}^{N-1} = 1.15\mu_{\text{B}}$) is, hence, contributed by the impurity-induced $3d$ valence-band resonances. As we raise the Fermi energy E_{F}, the orbital $\alpha = e^{\uparrow}$ can capture one [Fig. 1(b)] or two [Fig. 1(c)] electrons, changing the formal charge state q from Cr^{3+} to Cr^{2+} or Cr^{+}, respectively. (Occupation of $t^{\downarrow}$ is found to raise the energy more, forming an excited state.) Occupation of the gap level contributes to the charge Q^* on the impurity site the amounts $Q_g^{N-1} = 0$, $Q_g^{N} = 0.41e$, and $Q_g^{N+1} = 0.76e$. However, the impurity-induced valence-band resonances respond to occupation of these "outer" gap levels in the *opposite direction,* minimizing the effect of this perturbation by reducing their contributions to the impurity site from $\Delta Q_{\text{VB}}^{N-1} = 5.33e$ to $\Delta Q_{\text{VB}}^{N} = 4.95e$ and $\Delta Q_{\text{VB}}^{N+1} = 4.72e$. As a result of this feedback self-regulating response,[13] the *total* electronic charge $Q^* = Q_g + \Delta Q_{\text{VB}}$ on the impurity changes extremely slowly with the formal charge q, i.e., $\partial Q^*/\partial q \cong -0.12$ for Cr^{1+} and Cr^{2+}, and -0.03 for Cr^{2+} and Cr^{3+} (linear dielectric screening yields $\partial Q^*/\partial q = -1/\epsilon_0 \cong -0.1$), leading to a strong renormalization[13] $U_{\text{ver}} \propto (\partial Q^*/\partial q)^2 U_0$ of the bare U_0. (In insulators,[14], the distance from the im-

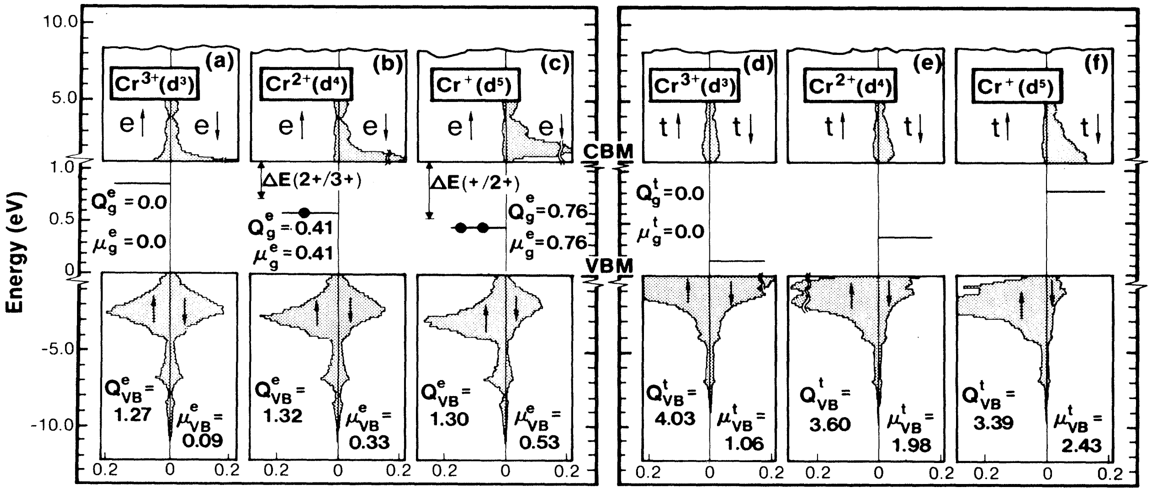

FIG. 1. Local density of states of interstitial Cr in Si for (a)–(c) the e and (d)–(f) the t_2 representations. VBM and CBM denote valence-band maximum and conduction-band minimum, respectively. The insets give local charges (Q) and magnetic moment (μ).

purity necessary to attain complete screening of the bare charge q is large; hence within the impurity central cell $\partial Q^*/\partial q \simeq -1$, leading to $U_{\rm ver} \simeq U_0$.) In contrast to the strong attenuation in the impurity local charge Q^*, no compensating cancellation occurs in the local magnetic moment μ: For Si:Cr both the VB and the gap level contribute *in the same direction* to μ, increasing it from $\mu^{N-1} = 1.15\mu_{\rm B}$ to $\mu^N = 2.71\mu_{\rm B}$ and $\mu^{N+1} = 3.72\mu_{\rm B}$. This indicates a far weaker screening of the exchange interactions.

Coulomb versus exchange-correlation screening. — Figure 2 shows the change in spin density $\Delta S(r) = S_{{\rm Cr}^{2+}}(r) - S_{{\rm Cr}^{3+}}(r)$ and in the electronic charge density $\Delta\rho(r) = \rho_{{\rm Cr}^{2+}}(r) - \rho_{{\rm Cr}^{3+}}(r)$ upon ionization of a $\rm Cr^{2+}$ impurity in Si to form $\rm Cr^{3+}$. Since the ionization takes place from the band-gap orbital $e\uparrow$ (having one and zero electrons, respectively, in $\rm Cr^{2+}$ and $\rm Cr^{3+}$), the changes in spin and charge densities can be written respectively as $\Delta S(r) = |\psi_e|^2 + \Delta S_h(r)$ and $\Delta\rho(r) = |\psi_e|^2 + \Delta\rho_h(r)$, where $|\psi_e|^2$ is the orbital density of the gap level in $\rm Cr^{2+}$, and $\Delta S_h(r)$ and $\Delta\rho_h(r)$ are (by definition) the changes in the spin and charge densities of all states below the valence-band maximum. Integrated over all space, the total change (over the macroscopic crystal) is $\int_0^\infty \Delta\rho(\mathbf{r})\, d^3r = \int_0^\infty \Delta S(\mathbf{r})\, d^3r = 1$. Figure 2 shows a strong screening of the *charge density* change and a far weaker screening of the *spin density* change: $\Delta\rho_h(r)$ equals approximately $-|\psi_e|^2$ in most of the bond region, and hence cancels most of it. Consequently, $\Delta\rho(r)$ encloses only a small net charge in the impurity subspace (of the order of $\lesssim 1/\epsilon_0$), with the remaining charge being delocalized through the crystal. In contrast, most of $\Delta S(r)$ is confined to the bond region, as in a free ion,[14] enclosing almost a full spin in this region. The resulting dominance of exchange over Coulomb interactions is evident in Fig. 1 from the fact that the orbital energy of the electron-rich orbital ($e\uparrow$ in $\rm Cr^+$) is *lower* than that of the electron-poor orbital ($e\uparrow$ in $\rm Cr^{2+}$). This leads to a negative $U^{(ee)}$ for the impurity e orbital.

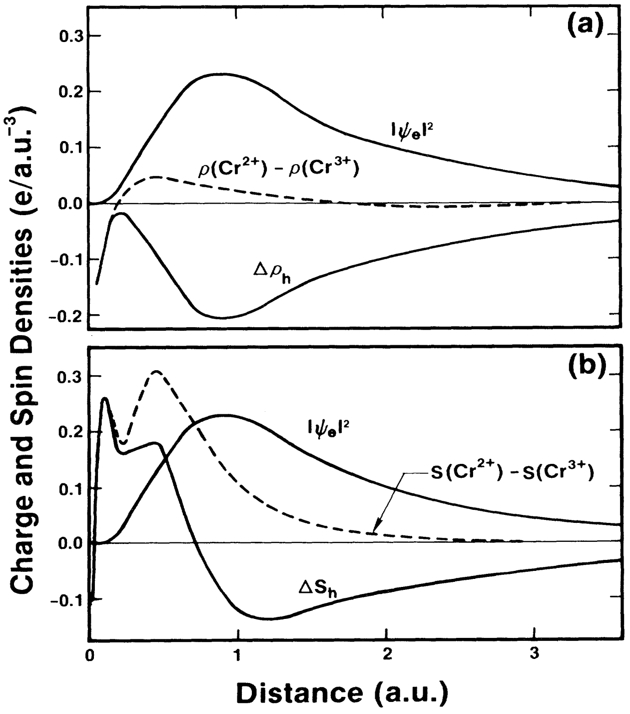

FIG. 2. Changes in (a) charge density and (b) spin density associated with the $\mathrm{Cr}^{2+}(e^{\uparrow 1}) \rightarrow \mathrm{Cr}^{3+}(e^{\uparrow 0})$ ionization.

Inverted excitation energies.—We calculated the Franck-Condon donor transition energies $\Delta E(q/(q+1))$ for electron emission from the gap level to the conduction band using Slater's transition-state construct[16] (cf. Fig. 1). We find, relative to the valence band at E_v (our calculated band gap is 1.1 eV),

$$\begin{aligned} \Delta E(2+/3+) &= E^{(4)} - E^{(3)} = E_v + 0.74 \text{ eV}, \\ \Delta E(1+/2+) &= E^{(5)} - E^{(4)} = E_v + 0.55 \text{ eV}, \qquad (1) \\ \Delta E(0/1+) &= E^{(6)} - E^{(5)} = E_v + 0.99 \text{ eV}, \end{aligned}$$

i.e., an inverted order, where ionization of d^4 to vacuum (or to the conduction band) takes *less* energy than ionization of d^5. The observed (relaxed) value[17,18] of $\Delta E(0/+)$ is $\sim E_v + 0.9$ eV, indicating a small relaxation energy of -0.1 eV. Relative to the energy of $\mathrm{Cr}^{3+}(d^3)$ the results of Eq. (1) can be expressed, in electronvolts, as

$$\begin{aligned} \tilde{E}^{(3)} &= E^{(3)} + 2\mu, \\ \tilde{E}^{(4)} &= E^{(3)} + 0.74 + \mu, \\ \tilde{E}^{(5)} &= E^{(3)} + 1.29, \qquad (2) \\ \tilde{E}^{(6)} &= E^{(3)} + 2.28 - \mu, \end{aligned}$$

where $\tilde{E}^{(N)}$ denotes the energy of the N-electron system plus the ionized electrons at the Fermi energy μ. Hence, for $0 \leqslant \mu \leqslant 0.645$ eV we have d^3 as the ground state, whereas for $0.645 < \mu < 0.99$ eV the ground state is d^5. Note that the energy of $\mathrm{Cr}^{2+}(d^4)$ is *higher* than the average of $\mathrm{Cr}^{3+}(d^3)$ and $\mathrm{Cr}^{+}(d^5)$. Consequently, $U^{(ee)}(\mathrm{Cr}^{2+}) = 1.29 - 2\times 0.74 = -0.19$ eV is negative (independent on μ); unrelaxed $\mathrm{Cr}^{2+}(d^4)$ is never the ground state, disproportionating into the stable $\mathrm{Cr}^{3+}(d^3) + \mathrm{Cr}^{1+}(d^5)$ pair. This is so because the positive (but reduced) Coulomb term $U_{\rm ver}^{(ee)}(\mathrm{Cr}^{2+}) = 0.12$ eV (~ 15 eV in the free ion) is outweighed by the large negative correlation term

$$\begin{aligned} \Delta U_{\rm MC}^{(ee)}(\mathrm{Cr}^{2+}) &= U^{(ee)}(\mathrm{Cr}^{2+}) - U_{\rm ver}^{(ee)}(\mathrm{Cr}^{2+}) \\ &= -0.31 \text{ eV} \end{aligned}$$

of the d^3-d^4-d^5 sequence. In contrast, the reaction $2\mathrm{Cr}^{1+}(d^5) \rightarrow \mathrm{Cr}^{2+}(d^4) + \mathrm{Cr}^0(d^6)$ is *unfavorable* since its energy

$$U^{(et)}(\mathrm{Cr}^{1+}) = 0.74 + 2.28 - 2\times 1.29 = +0.44 \text{ eV}$$

is positive. Hence, $\mathrm{Cr}^{1+}(d^5)$ is stable. This is so because the correlation energy $\Delta U_{\mathrm{MC}}^{(et)}(\mathrm{Cr}^{1+}) = 0.30$ eV of the d^4-d^5-d^6 sequence is positive (d^6 has two *paired* spins which do not contribute to the spin correlation energy), while the Coulomb energy $U_{\mathrm{ver}}^{(et)}(\mathrm{Cr}^{1+}) = 0.14$ eV is normal.

Equilibrium behavior.—To what extent can lattice relaxation destabilize the system? Application of Anderson's mechanism[3] suggests that Jahn-Teller (JT) distortions (the main mechanism leading to $U_{\mathrm{ver}} + \Delta U_{R,\mathrm{JT}} < 0$ in the silicon vacancy[4]), to the extent that they exist,[18] will *raise* $U_{\mathrm{ver}} + \Delta U_{\mathrm{MC}}$ by a *positive* $\Delta U_{R,\mathrm{JT}}$. This is so since for Si:Cr we have the configurations $(d^3, t^3e^0, {}^4A_2)$, $(d^4, t^3e^1, {}^5E)$, and $(d^5, t^3e^2, {}^6A_1)$ and only the nonspherical ${}^5E$ term can undergo JT distortion; hence $n_{N-1} = n_{N+1} = 0$, $n_N = 1$, and thus $N_{\mathrm{eff}} = -2$, or $\Delta U_{R,\mathrm{JT}} > 0$. This leads to the interesting possibility that while for unrelaxed transitions $U < 0$, a distorted (equilibrium) lattice may have $U > 0$ if $\Delta U_{R,\mathrm{JT}} > U_{\mathrm{ver}} + \Delta U_{\mathrm{MC}}$. Furthermore, relaxation corrections to the higher ionization energies[19] may be sufficiently negative to place such ionization transitions [e.g., $\Delta E\,(3+/2+)$] inside the valence band, so that at *equilibrium* this transition would escape detection (as a result of overlap with band-to-band transitions). This may well be the experimental situation[17] in Si:Cr (where only thermal equilibrium data are available): Despite the fact that the first donor $\Delta E(0/+)$ of Cr is the highest in the gap of all $3d$ impurities in Si,[19] no double or triple donors have been found in the gap[18] (although double donors have been observed[18] for the neighboring elements V and Mn).

In conclusion, we suggest that localized centers which are capable of sustaining local magnetic moments can show a negative-U behavior when the exchange (or, in general, many-electron) interactions outweigh the strongly reduced Coulomb repulsions. This electronic (i.e., nonstructural) mechanism holds the potential of explaining the phenomenon of "missing oxidation states" in chemistry[7]; e.g., while both $\mathrm{Mn}^{2+}(d^5)$ and $\mathrm{Mn}^{4+}(d^3)$ are observed in MgO:Mn and CaO:Mn, the $\mathrm{Mn}^{3+}(d^4)$ center is missing[19] (also[8] in GaAs:Mn); also, while both $\mathrm{In}^{1+}(s^2)$ and $\mathrm{In}^{3+}(s^0)$ occur in solution, $\mathrm{In}^{2+}(s^1)$ is unstable.[1,7]

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[a] Permanent address: Department of Physics, Tohoku University, Sendai 980, Japan.

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[9] In general, δE_{MC}^N includes both *orbital* correlation effects (separating multiplets of the same total spin by configuration-interaction effects) as well as *spin* correlation effects (i.e., spin polarization, treated here). In Ref. 8 we deduced both from experiment. Our numerical calculations here are limited to spin correlation which is the dominant effect: The multiplets ${}^4A_2$, ${}^5E$, and ${}^6A_1$ for Cr^{3+}, Cr^{2+}, and Cr^{1+}, respectively, have essentially no configuration interaction.

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