

## HYPERFINE INTERACTION OF THE IRON IMPURITY NUCLEI AT THE TETRAHEDRAL INTERSTITIAL SITE IN SILICON

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Most electronic structure calculations on transition metal impurities in semiconductor<sup>1-6</sup> were performed within the local density formalism<sup>7</sup>, implemented either in an extended-crystal Green's function approach<sup>1-2</sup>, or within finite cluster models<sup>3-6</sup>. Involving a local (statistical) approximation to exchange and correlation, the local density approximation, much like its predecessor, the Thomas-Fermi model involves an unphysical interaction of each spin-orbital with itself<sup>8</sup> (self-interaction). Whereas this interaction has a vanishing effect on extended delocalized states, it may have a significant effect on localized states. Such is the case for isolated transition atoms, where a self-interaction corrected model shows<sup>8</sup> that relative to LSD (i) the 3d orbitals move to substantially more negative energies (increasing thereby the s-d separation), (ii) the 3d orbitals become more localized, whereas the non-d (valence) orbitals become more expanded, (iii) the exchange splitting between spin-up and spin-down 3d orbitals increases, (iv) the contact spin density at the nucleus is reduced, (v) the total exchange energy becomes more negative, whereas the total correlation energy becomes less negative, and (vi) the total ground state density becomes more localized. Whereas self-interaction corrections (SIC) were applied recently with great success to atoms,<sup>8</sup> molecules<sup>9</sup> and solids<sup>8,10</sup>, showing substantial improvements relative to the uncorrected formalism, until recently<sup>11</sup> they were not considered for impurities. Of particular interest here are the interstitial 3d impurities that are likely to maintain their localized atomic-like characteristics more than the substitutional impurities, (the former have only weak bonds with the chemically saturated host ligand atoms). Following the recent demonstration<sup>11</sup> of the significance of the SIC to such systems (treated perturbatively), we have undertaken here a self-consistent SIC study of Si:Fe.<sup>12</sup>

We use the impurity Green's function formalism discussed by us previously<sup>1,2</sup>, with the following modifications needed for the present applications: (i) since nuclear contact spin densities, (which are dominated by core polarization effects) are needed, we cannot use a coreless (pseudopotential) model for the impurity site, as appropriate in previous applications<sup>1,2</sup>. Instead, we use an all-electron representation where both the core and the valence orbitals are treated as spin-polarizeable states on the same footing. (ii) The great sensitivity of core polarization to basis set effects suggests to us that a nonlinearly varied basis would be far more effective than a linearly varied set<sup>1,2</sup>. We hence optimize the impurity-centered 1s, 2s, 3s, 3p, 3d, 4s, 4p, 4d, and 4f spin-polarized basis orbitals at each self-consistency iteration  $i$  by integrating numerically the atomic-like Schrödinger equation of Fe within a impurity subspace, subject to a fixed potential of the host crystal in its interstitial volume, plus an iteration-dependent potential perturbation  $\Delta V^{(i)}(\vec{r})$ , determined from the Green's function problem. As this dynamic basis set is updated iteratively, responding to charges

in the self-consistent potential, we economize on the basis size using only the 1s-through-4f orbitals. Twenty host crystal bands are used at each  $\vec{k}$  point. (iii) We have experimented with the Williams, Feibelman and Lang<sup>13</sup> adspace augmentation instead of the equivalent quasi band method<sup>1</sup> for generating a variationally sufficient Green's function. We use the Ceperley-Alder exchange correlation as given by Perdew and Zunger<sup>8</sup>, adjust the host band structure to fit the experimentally observed interband transitions, and assume an unrelaxed lattice geometry.

Figure 1 (left) gives the change in local density of states obtained for Si:Fe<sup>0</sup> in the LSD formalism, and Fig. 1 (right) gives the corresponding results obtained in the LSD-SIC calculation. The major effects of SIC are seen to be: (i) a shift of all occupied pure d levels (i.e. e-representation) to more negative energies (e.g.  $e_+^b$  by 0.42 eV, and  $e_+^a$  by 0.33 eV), as they are relieved from the (repulsive) self-interaction, (ii) a corresponding upward shift of the occupied orbitals that contain substantial non-d character (e.g. the  $t_+^b$ ,  $t_-^b$  and  $t_-^a$  move up by 0.09 eV, 0.4 eV and 0.08 eV, respectively). This is a result of a feed-back effect (non-d orbitals are now screened better by the 3d orbitals that became more localized). (iii) an upward shift of the unoccupied orbitals relative to the occupied orbitals (e.g.  $e_-^a$  moves up by 0.42 eV, penetrating the conduction band). The main consequences of these SIC-induced shifts are a strong enhancement of  $\Delta_X/\Delta_{CF}$  (from 0.33 to 0.88), an increase in the local

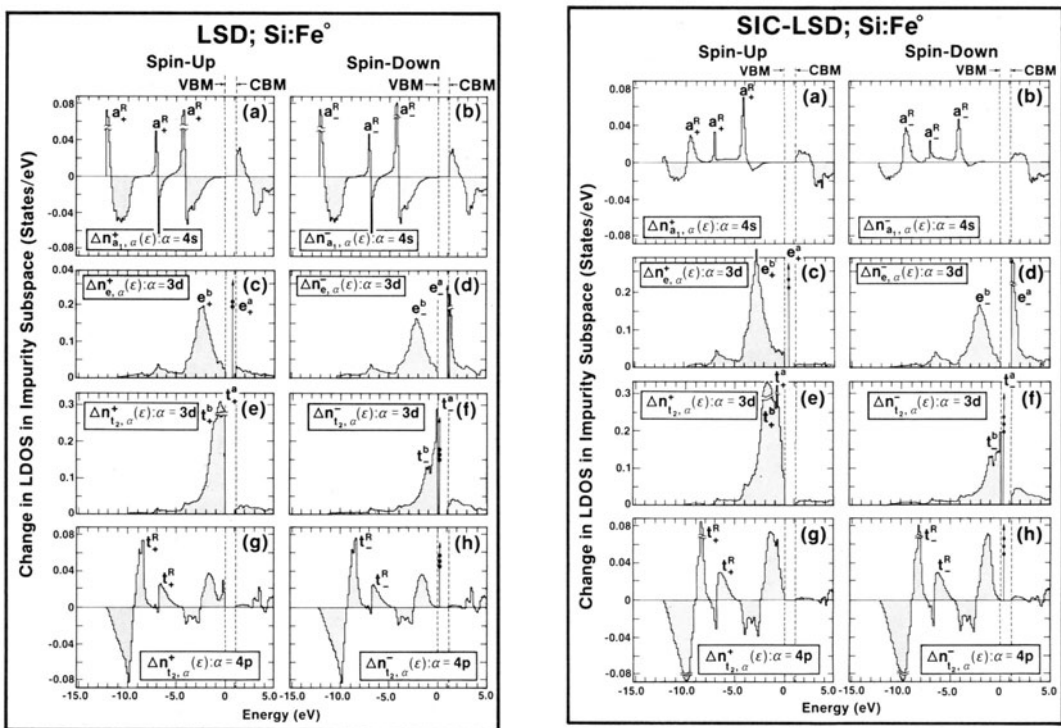


Fig.1 : Change in local density of states  $\Delta n_{T_0}^{\sigma}(\epsilon)$  in Si:Fe<sup>0</sup> for representation  $T=a_1, e$  and  $t_2$ , spin  $\sigma=+$  or  $-$ , projected on the local orbitals  $\alpha$  (4s for  $a_1$ , 3d for  $e$ , and 3d, 4p for  $t_2$ ). Left:LSD. Right:LSD-SIC.

**Table I:** Comparison of different orbital contributions (in KG) to the contact hyperfine field in Si:Fe<sup>0</sup>.

Orbital	LSD	LSD-SIC	exptl. (Ref. 14)
1s	-19.61	-24.50	
2s	-202.23	-278.52	
3s	136.81	179.70	
4s	5.21	8.18	(absolute value)
Total	-79.82	-115.14	152.4 - 147.6

**Table II:** Effective occupation numbers of Fe in Si:Fe<sup>0</sup>.

Orbital	LSD	LSD-SIC
Core	18.0	18.0
4s	-0.1128	0.0605
4p	0.0773	-0.1312
3d	7.9069	8.1791
4d	-0.4253	-0.3820
4f	-0.0013	-0.0028
Total	25.4448	25.7236
Net charge	0.5552	0.2764

magnetic moment (from  $1.14 \mu_B$  to  $1.42 \mu_B$ ), a corresponding reduction of the contact hyperfine field (from -79.82 KG to -115.14 KG) and an overall attraction of more electronic charge to the impurity site [0.31 more d electrons and 0.03 less non-d electron, changing the net ionic impurity charge from +0.555e (LSD) to +0.276e (LSD-SIC)]. Table I shows the SIC effect on the various orbitals contributing to  $H_{hf}$ . Table II compares the population analysis of the various local orbitals of the effective impurity atom.

Applying the SIC method to the ionized impurity (using Slater's transition state construct) we find that upon removing charge from the  $t_{-}^a$  gap level, the  $e_{+}^a$  level moves down, exposing  $t_{-}^a$  as the highest occupied level of the ion. The net spin is  $S = 3/2$  (i.e. Hund's rule high-spin), in accordance with experiment<sup>12</sup>. The reason for this  $t_{-}^a$  vs  $e_{+}^a$  level reversal is that upon ionizing  $t_{-}^a$  the valence band resonances are relieved from their Coulomb repulsion with the ionized orbital and consequently move to more negative energies. Becoming more localized, their exchange splitting increases, pushing to higher energies the antibonding  $t_{-}^a$  orbital that becomes now the highest occupied state. The donor energy is calculated as the energy difference between the ionized  $t_{-}^a$  orbital and the valence band maximum. It is  $E_v + 0.32$  eV which compares well with the experimental value<sup>15</sup> of  $E_v + 0.385 \pm 0.01$  eV.

Self-interaction corrections in solids have few similarities and differences relative to the similar corrections in free atoms and ions<sup>8</sup>. First, the magnitude of the energy lowering of the 3d orbitals is reduced substantially in the solid (0.2-0.4 eV, relative to 8.44 and 7.88 eV for  $3d_{+}$  and  $3d_{-}$  orbitals in the  $d^6s^2$  free-atom). This results both from the delocalization of the impurity orbitals in the solid and from the development of orthogonality nodes that cut down substantially on SIC. Second, since in a bonded situation there are both bonding and antibonding states through hybridization, the direction of energy shifts due to SIC can differ from that obtained in the pure  $\ell$ -states of the atom. In particular, whereas both in atoms and in solids the non-d orbitals expand and d orbitals contract upon introducing SIC, in a bonded environment, p-d hybrids (e.g. the  $t_2$  states) can move in an opposite-direction to that of the pure d states (e.g. e states). Third, the displacement of orbitals in the solid due to SIC can change their energy separation from host crystal state of the same symmetry, enhancing or reducing thereby impurity-host hybridization.

Note that whereas the LSD formalism emphasizes the difference between spin-up and spin-down orbitals, the LSD-SIC method correctly emphasizes the difference between occupied and unoccupied orbitals. Hence, whereas the  $e_+^a - e_-^a$  exchange splitting between the occupied  $e_+^a$  and unoccupied  $e_-^a$  gap levels of  $\text{Si:Fe}^0$  is only 0.25 eV in LSD, it is three times larger in LSD-SIC, predominantly due to an upwards shift in  $e_-^a$ . This upward shift of  $e_-^a$  has an important physical consequence. Whereas in the cluster calculation of DeLeo et. al.<sup>5</sup> it was predicted that a stable acceptor state  $\text{Fe}^0/\text{Fe}^-$  exists in the gap, (in contrast with experiment<sup>15</sup>), the combination of the larger crystal-field splitting and upward shift of  $e_-^a$  obtained here makes such an acceptor unstable, as the extra electron would occupy  $e_-^a$  which is now inside the conduction band. This effect has been recognized previously by Brandow<sup>16</sup> in the context of the band structure of the Mott insulators NiO and CoO.

We summarize by noting that SIC is necessary for obtaining the correct high-spin ground state of  $\text{Si:Fe}^+$ , (as concluded from the perturbative argument<sup>11</sup>), that it changes the hyperfine field by 30%, bringing it closer to experiment, reduces substantially the ionicity of the system and increases the local magnetic moment by 20%. We suspect that a similar treatment may be necessary to describe other systems supporting localized 3d states, e.g. Mott insulators, chemisorption of transition atoms and Heme proteins.

This work was supported in part by the Office of Energy Research, Materials Sciences Division, U.S. Department of Energy, Grant No. DE-AC02-77-CH00178.

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