

Applicability of the local-density theory to interstitial transition-metal impurities in silicon

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It is shown that the local-density formalism does not describe correctly the symmetry of the many-electron ground state of unrelaxed interstitial transition-atom impurities in silicon, but that a self-interaction correction to it produces the observed ground-state symmetries.

Transition-atom (TA) impurities in silicon have provoked considerable interest both because of their profound influence on the performance of silicon devices and because of the wealth of unique physical phenomena they exhibit (e.g. Refs. 1 and 2, and references therein). Experimental evidence suggested that, under normal conditions, all $3d$ TA impurities appear in silicon as tetrahedral interstitials.¹ Such impurities show two localized defect levels in the fundamental band gap: an e level above a t_2 level with a crystal field (CF) splitting Δ_{CF} between them. The optical, electrical, and spin properties of the system are determined by the lowest-energy many-electron multiplet states that derive from the various possible one-electron $t_2^2 e^m$ configurations. Application of the Sugano-Tanabe diagrams³ for $n + m = 4, 5, 6,$ and 7 (Si:Ti, Si:V, Si:Cr, and Si:Mn, respectively) shows that a bistable ground state is possible: If the crystal-field splitting is smaller than a critical value $\Delta_{CF} < \Delta_c$ and the localization of the gap level wave functions q_i exceeds a critical value $q_i > q_c$, then the ground state corresponds to a high-spin (Hund's rule) configuration. If, on the other hand, $\Delta_{CF} > \Delta_c$ and $q_i < q_c$, the low-spin configuration is the ground state. Electron paramagnetic resonance (EPR) data available¹ for Si:Cr, Si:Mn, and Si:Fe reveal high-spin 5T_2 , 4T_1 , and 3A_2 ground-state configurations, respectively. One of the major theoretical challenges in this field therefore is to establish the proper formulation of the effective one-body interactions leading to a physically correct description of Δ_{CF} and q_i and hence the correct ground-state properties. Experience from atomic physics indicates⁴⁻⁶ that, whereas the widely used local-density formulation of interelectronic interactions correctly predicts for the $3d$ atoms the chemical trends in the single-particle energies with the atomic number, it also shows a number of glaring discrepancies with experiment, among which I mention the underestimation by 2-5 eV of the $s-d$ and $p-d$ level separations,⁴ the erroneous trends in the interconfigurational energies,⁴ the systematic errors in the multiplet energies,⁵ and the underestimation by 1-4 eV of the variation of the $3d$ binding energies with orbital localization.⁴ It was shown previously that these errors are reduced dramatically⁴⁻⁶ if one goes beyond the local-density model by introducing the self-interaction correction⁴ (SIC). Because of the great resemblance of the highly localized ($q_i \approx 50\%$) and nearly pure d (98%) gap states of Si:TA to the atomic d orbitals,^{7,8} one might suspect that the shortcomings of the uncorrected local-density formalism for transition atoms will bear on the Si:TA system as well. Nevertheless, the local-density approach has been implemented for Si:TA in two different computational schemes: first,⁷ by the $Si_{10}H_{12}$ finite cluster

model with spherical atomic potentials and hydrogen terminators [the multiple-scattering $X\alpha$ (MS- $X\alpha$) cluster model], and, more recently,⁸ by the infinite crystal Green's-function scheme [the quasiband crystal-field (QBCF) method] in which spherical approximations to the potential are unnecessary and nonlocal first-principles pseudopotentials are used. Both applications neglect lattice relaxation. The application of the MS- $X\alpha$ cluster model leads to very small crystal-field splittings (e.g., 0.02 and 0.15 eV for Si:Fe and Si:Mn, respectively) and to a strong localization of the charge in the impurity sphere. This model hence produced the observed high-spin ground states for Si:Mn (it failed to produce the high-spin ground state of Si:Cr by only 0.15 eV). This leads to the optimistic outlook that despite the failure of the local-density formalism in the free TA, it is appropriate for describing the electronic structure of the TA as interstitial impurities in Si. Disappointingly, however, the subsequent development and application⁸ of the more general QBCF scheme to the same system had revealed considerably larger crystal-field splittings (e.g., 0.58 and 0.55 eV for Si:Fe and Si:Mn, respectively) and a lower charge content of the impurity site,⁸ leading to low-spin ground-state configurations for Si:Mn and Si:Cr, in contrast with experiment.¹ Since the QBCF method avoids finite-cluster or muffin-tin approximations necessary in the MS- $X\alpha$ model, and since it uses highly converged basis-set expansions and accurate pseudopotentials,⁹ the results on TA impurities lead to the rather pessimistic conclusion that, as in the free TA case, the local-density model is deficient in describing the ground state of the highly localized interstitial TA impurities. In view of the divergence of the conclusions of the two models, I undertook a comparative study aimed at understanding the physically relevant differences between the two one-electron models. I find that the neglect of the potential anisotropy around the defect⁷ in the MS- $X\alpha$ reduces dramatically the covalency of the system and hence the crystal-field splitting, leading spuriously to high-spin ground-state configurations. If, however, the full anisotropy is retained,⁸ then, like the situation in the isolated TA, a self-interaction correction is required to produce the correct ground state.

Figure 1 displays the t_2 and e gap energy levels for neutral interstitial Si:TA as calculated by the MS- $X\alpha$ cluster model⁷ [Fig. 1(a)], and by the QBCF Green's-function model⁸ [Fig. 1(b)], in identical high-spin configurations. The one-electron occupation numbers are indicated in parentheses; the finite-width valence-band resonances are represented by their centers of gravity. Computational details are given in Refs. 7 and 8. Compared with the QBCF results the MS- $X\alpha$ cluster model reveals an upward shift of the energy lev-

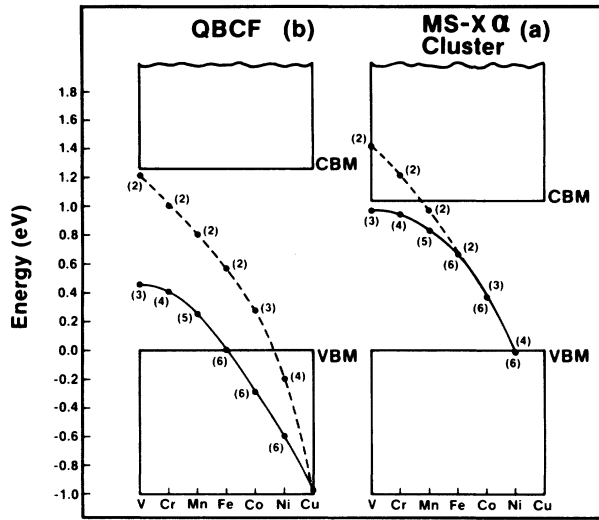


FIG. 1. One-electron gap energy levels of interstitial Si:TA, as obtained in the MS- $X\alpha$ cluster model (a), and in the QBCF Green's-function model (b). VBM and CBM denote the valence-band maximum and conduction-band minimum, respectively. ---, e levels; —, t_2 levels. Occupation numbers are shown in parentheses.

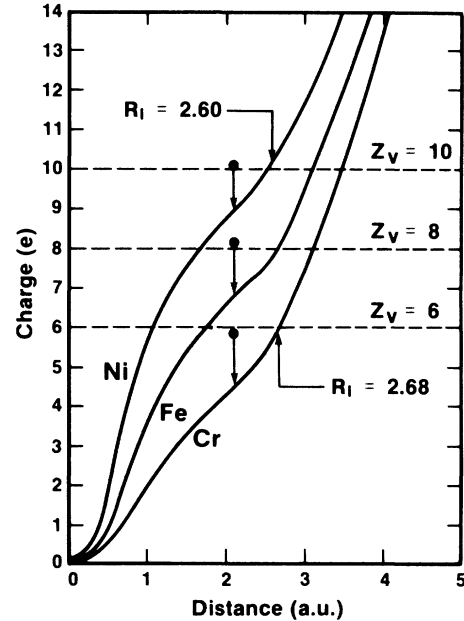


FIG. 2. Total valence electron density $Q_D(R)$ enclosed in a sphere of radius R around the impurity. Solid lines: QBCF results; solid circle: the MS- $X\alpha$ value for $R = R_{MT} = 2.22$ a.u. Z_v is the impurity valence and R_I is the impurity covalent radius, i.e., $Q_D(R_I) = Z_v$.

els (with the partially occupied e levels for Si:Cr and Si:V overlapping the empty conduction band) and a dramatic reduction in the crystal-field splitting (with Fe, Co, and Ni having nearly zero splitting). Figure 2 displays the total electronic charge $Q_D(R) = \int_0^R \rho_D(\vec{r}) d\vec{r}$ enclosed in a sphere of radius R around the impurity, where $\rho_D(\vec{r})$ is the self-consistent electronic charge density. The solid lines, corresponding to the QBCF results, show that $Q_D(R)$ equals the number Z_v of the TA valence electrons at radii R_I (2.68, 2.65, and 2.60 a.u. for Cr, Fe, and Ni, respectively) that are very close to the experimental Bragg-Slater covalent radii of the bonded TA.⁸ The solid circles denote the values of $Q_D(R_{MT})$ calculated by the MS- $X\alpha$ method for a sphere of radius $R_{MT} = 2.22$ a.u. The MS- $X\alpha$ result shows that the impurity attains electronic charge neutrality $Q_D = Z_v$ at a radius $R \approx R_{MT}$ that is considerably ($\sim 17\%$) shorter than the covalent radius R_I of a bonded TA. As a result, the impurity sphere contains at $R = R_{MT}$ about one extra valence electron relative to the QBCF results (a difference denoted in Fig. 2 by the vertical arrows). It is this reduced covalency in the MS- $X\alpha$ model (the directional covalent bond charge is forced into the spherical regions of the potential) that results in a weakening of the bonds and a

reduction in the level splitting.¹⁰ The multiplet structure was calculated for both models with use of the Hemstreet-Dimmock method,¹¹ utilizing the crystal-field splitting (Fig. 1) and the charge localization parameters as input. The results are shown in the first two columns of Table I.

To understand how the chemical bonding affects the level splitting, I consider in Fig. 3 the quantities that determine Δ_{CF} . Figure 3(a) shows the spherical ($l=0$) and the anisotropic ($l \neq 0$) portions of the self-consistent crystal potential around the interstitial site. Figures 3(b) and 3(c) depict the d part of the e and t_2 gap level wave functions (ψ_e and ψ_{t_2} , respectively) for Si:Fe. Clearly, the regions where ψ_e and ψ_{t_2} overlap most with the anisotropic ($l=3, 4$) part of the potential provide the significant contribution to Δ_{CF} . The shaded areas in Fig. 3 denote the amplitudes enclosed in a sphere of radius $R \leq R_{MT}$, where the MS- $X\alpha$ model assumes a zero contribution to the anisotropic crystal-field splitting. Figure 3 hence suggests that the physical basis for the small Δ_{CF} values obtained in the MS- $X\alpha$ model is that, whereas the potential anisotropy extends to large distances [Fig. 3(a)], its volume sampled by the localized gap wave

TABLE I. Ground-state multiplets for interstitial TA in silicon.

Impurity	QBCF	MS- $X\alpha$	Spherical QBCF	Expt. (Ref. 3)	SIC QBCF
Fe	3A_2	3A_2	3A_2	3A_2	3A_2
Mn	2E	4T_1	4T_1	4T_1	4T_1
Cr	1A_1	1A_1	1A_1	5T_2	5T_2
V	2T_2	2T_2	2T_2	...	2T_2

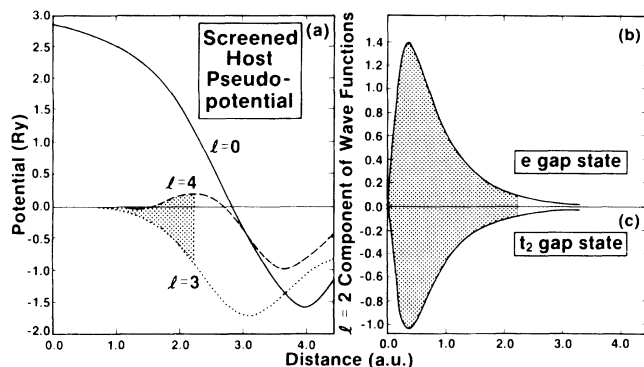


FIG. 3. (a) Angular momentum decomposition of the crystal potential around the interstitial site. (b) and (c) depict, respectively, the d component of the e and t_2 gap-state wave functions. The shaded areas indicate the anisotropic contributions to the crystal-field splitting neglected by the MS- $X\alpha$ model.

functions [Figs. 3(b) and 3(c)] is confined to only $R \leq 3$ a.u., where the MS- $X\alpha$ model neglects most of $V_{l \neq 0}(r)$.

These considerations can be quantified by performing a QBCF calculation and zeroing the potential anisotropy in the impurity sphere $R \leq R_{MT}$, hence simulating the muffin-tin approximation. This spherical QBCF model shows for Si:Fe that the e level moves down by 0.24 eV and the t_2 level moves up by 0.18 eV, yielding a new crystal-field splitting of 0.16 eV, almost four times smaller than the value obtained with the full potential. Hence, over 70% of Δ_{CF} comes from within the impurity sphere¹² (shaded area in Fig. 3). (Recall that in the classical crystal-field approximation, Δ_{CF} arises solely from the potential anisotropy.) This explains most of the discrepancy between the MS- $X\alpha$ and the QBCF values of Δ_{CF} . Using the values obtained from such spherical QBCF calculations, we obtain via the Hemstreet-Dimmock method¹¹ the ground-state multiplets shown in the third column of Table I. These are in perfect agreement with the MS- $X\alpha$ results (second column).

I proceed beyond the local-density formalism by including self-interaction corrections.⁴ This corresponds to the removal of the spurious self-Coulomb and self-exchange-correlation interactions which are present in the local-density formalism. Whereas the states of the host crystal are also subject to a SIC (if rotated into a local Wannier-like representation⁴), in the present work this is not needed since only energy differences between the gap levels (crystal-field splittings) are of interest. Since the impurity wave functions are calculated in the QBCF method in an

impurity-centered local orbital expansion,⁸ the SIC can be readily calculated perturbatively by using the same technique used in atomic calculations.⁴ The essence of the SIC is that it lowers the orbital energies proportionately with the degree of localization of the corresponding wave functions. Hence the energy of the upper (more localized) e state is lowered further than that of the lower (less localized) t_2 state, resulting in a smaller Δ_{CF} . Using the gap wave functions calculated⁸ in a sphere of radius 7.5 a.u., I find that the SIC reduces the crystal-field splittings of Fe, Mn, Cr, and V impurities by 0.50, 0.38, 0.36, and 0.30 eV, respectively. (In the same approximations, with use of the local orbital expansion of the host states within a sphere of radius 7.5 a.u., the top of the valence band is lowered by 0.05 eV.) This leads to the ground-state multiplets shown in the fifth column of Table I, which are in close agreement with the available experimental data. I conclude that the near cancellation between the neglect of potential anisotropy and self-interaction effects leads to the "correct" ground state, but that a full-potential local-density model alone is insufficient to describe the correct many-electron ground state of unrelaxed interstitial impurities. Notice that the reduction in Δ_{CF} due to SIC effects may even reverse the order of the e and t_2 levels in the MS- $X\alpha$ model¹³ (where Δ_{CF} is smaller than the SIC) while the order is preserved in the QBCF model (where Δ_{CF} is larger than the SIC). Notice further that the magnitude of the SIC in the solid is reduced by a factor of 5–10 relative to the corresponding effect in free atoms,⁴ yet this effect is significant on the scale of the band gap and leads to the predicted stability of the high-spin (Hund's rule) configurations for all impurities but V. (The neutral V interstitial has not been observed in EPR.) I conclude that, whereas the chemical trends in the one-particle properties of Si:TA impurities can be described in the local-density formulation,^{7,8} the correct description of the symmetry of the many-electron ground state of unrelaxed interstitial impurities requires extension of this model to include the SIC. The effect of multiplet corrections on substitutional impurities is complicated by significant lattice-relaxation effects and is under study.

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⁹Basis-set convergence tests were reported in Ref. 8 and show a precision of ~ 0.05 eV. The precision in the pseudopotentials is similar or better and was demonstrated previously [A. Zunger and M. L. Cohen, *Phys. Rev. B* **18**, 5449 (1979); **20**, 4082 (1979)]. Note that the MS- $X\alpha$ and QBCF models produce similar results for the Si vacancy [cf. B. G. Cartling, *J. Phys. C* **8**, 3171, 3183 (1975), and Ref. 8].

¹⁰The reduced covalency attendant upon the spherical approximation to directional bonds leads in muffin-tin band-structure calculations to a significant reduction of the lowest band gap [e.g., by 1.6 eV in diamond, cf. G. S. Painter, D. E. Ellis, and A. R. Lubinsky, *Phys. Rev. B* **4**, 3610 (1971)], and a reduction to zero gap in silicon [cf. D. A. Papaconstantopoulos and B. M. Klein, *Solid*

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¹²In principle, the spherical potential can also lead to a crystal-field

splitting if ψ_e and ψ_{t_2} differ radially. The present calculation shows, however, that most (70% in Fe, 82% in Mn) of the difference between the Δ_{CF} values in MS- $X\alpha$ and QBCF is accounted for by the neglect of the anisotropy in the former model.

¹³However, application of the SIC to the wave functions of the MS- $X\alpha$ cluster model is expected to exaggerate the effect since the cluster states are artificially too localized both because of reduced covalency and because the discrete representation suppresses the formation of broad resonances.

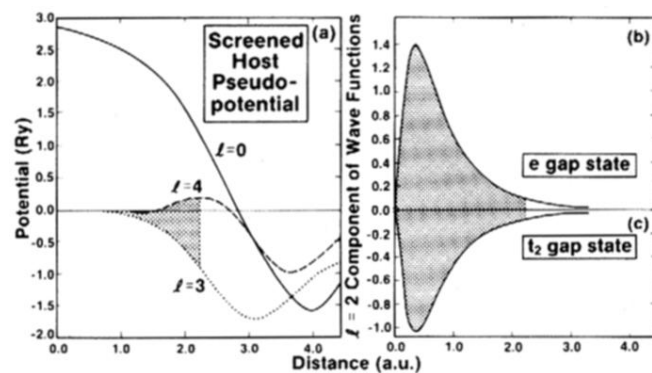


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