

Self-consistent one-electron states of substitutional and interstitial $5d$ transition-atom impurities in silicon

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The electronic structure of the $5d$ transition-metal impurities Hg, Au, Pt, Ir, Os, Re, and W in silicon has been studied theoretically within the framework of a nonrelativistic self-consistent one-particle model. The energy spectra of the substitutional and tetrahedral-site interstitial neutral atoms have been obtained by using the Watson-sphere-terminated multiple-scattering $X\alpha$ molecular cluster method. The role played by the metal $5d$ states in the formation of impurity levels within the crystal band gap and resonances in the valence band has been established. The observed chemical trends of the impurity level positions for the $5d$ elements are analyzed and compared with those inferred from previous cluster and Green's-function calculations for the $3d$ transition-metal series. The results of our one-electron theory provide a good description of the observed physical properties of the widely studied Au and Pt impurities in silicon. A good correlation between our calculations and the sparse data which are available for Hg, Ir, Os, Re, and W has been established.

I. INTRODUCTION

Transition-metal (TM) impurities in semiconductors have deserved a great deal of attention for many years due to their fundamental importance both from a technological and a theoretical point of view.¹⁻¹¹ They are commonly associated with deep levels within the crystal band gap and appear as contaminants, or are judiciously introduced in the lattice for useful purposes. Despite the wealth of experimental data available for these impurities in semiconductors, only recently has significant progress been made on the theoretical knowledge of their physical properties.¹²⁻⁵⁵ The recent enhancement of our understanding of these systems is a consequence of the merits of the various theoretical methods that have been developed in the last ten years for the study of deep levels associated with point defects and impurities in semiconductors. The theoretical formulation as well as the analysis of applications of these methods have been the object of recent review articles.⁵⁶⁻⁶² In this work one of these methods, based on the molecular cluster approximation, is used to carry out self-consistent one-electron state calculations for substitutional and tetrahedral-site (T) interstitial $5d$ TM impurities in silicon.

The different solutions of the deep-level problem in semiconductors can be separated in two general groups. One group contains the methods based on the high degree of localization of the perturbation induced by the defects or impurities in the lattice. A representative number of host atoms surrounding the defect is selected, and the solutions of the energy-eigenvalue problem for this molecular cluster are found through some quantum-chemistry technique. This approach has been extensively used to perform electronic state calculations for TM impurities in semiconductors.¹²⁻³⁹ The other group contains the methods derived from band-structure calculations. Starting with the perfect-crystal electronic structure and an

impurity potential, the electron eigenstates are found, in most applications, by adopting the Green's-function (GF) formalism.⁵⁶ Only recently have these band-structure-based methods been successfully applied to TM impurities in semiconductors.⁴⁰⁻⁵³

The first rigorous applications of the molecular cluster model to study TM impurities in semiconductors were made by using a hydrogen-terminated 17-atom cluster, within the framework of the $X\alpha$ multiple-scattering (MS) method.⁶³ The one-electron energy spectra of substitutional $3d$ atoms in silicon were reported by Cartling *et al.*¹² (Fe), Cartling¹³ (Fe,Zn), and Hemstreet¹⁴ (Cr, Co, Ni, Cu, Zn). Shortly thereafter the same model was applied to carry out electronic state calculations for $3d$ impurities replacing Ga in GaAs by Hemstreet and Dimmock¹⁵ (Cr) and Hemstreet¹⁶ (Cr to Cu). Substitutional $3d$ impurities replacing an In atom in InP was studied by Hemstreet¹⁷ using this technique (Cr to Ni). The model has been extended to interstitial $3d$ impurities in silicon by using a 26-Si-atom cluster by DeLeo *et al.*¹⁹⁻²² (V to Ni). By eliminating the hydrogen saturators and terminating the 17-atom cluster by a Watson sphere, the MS cluster model was applied to carry out one-electron energy state calculations for substitutional impurities replacing Ga in GaAs by Fazio *et al.*^{23,24} and Fazio and Leite²⁵ (Fe, Co, Ni, Cu) and by Dal Pino, Jr. *et al.*²⁶ (Mn). Despite the relatively small size of the cluster utilized,⁶⁴ one important feature of these calculations was the establishment of the correct correspondence between the metal $3d$ -shell states and the impurity levels in the crystal band gap. The need for going beyond the local-density one-electron approximation in order to obtain the correct impurity ionization energies was recognized, and successful attempts were made to incorporate the many-electron effects in the calculations.^{17,20-22} Spin and space correlations were taken into account by either carrying out the calculations to the spin-polarized limit or by computing

the multiplet terms according to the pioneering work of Hemstreet and Dimmock.¹⁵ From the calculations performed by Dal Pino, Jr. *et al.*,²⁶ it was possible, for the first time, to confirm the mechanism proposed by Haldane and Anderson⁵ to explain the occurrence of multiple charge states of TM impurities in semiconductors.

Other applications of the molecular cluster model for the study of TM impurities in semiconductors have been performed recently. Majewski,³³ by adopting a 17-atom Watson-sphere-terminated cluster model and by generalizing the MS method to potentials consisting of a muffin-tin potential plus a spherically symmetric potential, performed one-electron state calculations for $3d$ impurities replacing Zn in ZnSe (Ti) and ZnS ($_{21}\text{Sc}$ to $_{28}\text{Ni}$). Substitutional Cu was also studied in ZnS by Liegener³⁹ within the framework of a 17-atom cluster and the complete neglect of differential overlap (CNDO) approximation. Gemma³⁴ adopted a 59-atom cluster and a self-consistent numerical basis-set (LCAO method within the local-density-functional formalism to study $3d$ impurities replacing Zn in ZnO and ZnS ($_{24}\text{Cr}$ to $_{29}\text{Cu}$) and replacing Ga in GaP (Cr, Ni, Co). Recently, the Watson-sphere-terminated MS method was applied by Khowash *et al.* to study the electronic states of substitutional TM impurities in InP ($_{24}\text{Cr}$ to $_{29}\text{Cu}$).²⁸ A suitable renormalization of the original Coulson-Kearsley⁶⁵ defect-molecule approach was proposed by Picoli *et al.*³⁸ to describe substitutional TM impurities in semiconductors. In the applications of this model reported for the Cu impurity in Si and GaAs, the multiplet effects were taken into consideration. Another model calculation has been conducted by Mdaa *et al.* for interstitial Mn and Co in silicon.³¹ The first attempt to perform rigorous self-consistent calculations for a complex defect involving TM impurities in semiconductors has been reported recently by Leite *et al.*²⁷ for a nearest-neighbor substitutional pair of iron atoms in silicon. A bond-centered 26-atom cluster was used in these calculations, according to the Watson-sphere-terminated cluster model. The complex pair Au-Fe in silicon was also studied by using this model and a tetrahedral-site-centered 26-atom cluster by Assali *et al.*³²

The electronic structure of neutral substitutional $3d$ impurities ($_{22}\text{Ti}$ to $_{90}\text{Zn}$) and an infinite silicon crystal has been calculated by Zunger and Lindefelt⁴¹ for the first time by using nonlocal first-principles pseudopotentials and the recently proposed quasiband crystal-field (QBCF) Green's-function formalism.⁴⁰ The method has been applied to interstitial $3d$ impurities ($_{22}\text{Ti}$ to $_{30}\text{Zn}$) in silicon by Lindefelt and Zunger⁴² and to substitutional impurities ($_{22}\text{Ti}$ to $_{30}\text{Zn}$) replacing the Ga atom in GaP by Singh and Zunger.⁴³ Many-electron effects were incorporated in the theory by Fazzio *et al.*⁵⁴ and taken into account in GaAs and GaP in order to improve the theoretical description of the excitation and ionization spectra of the $3d$ impurities in these compound semiconductors.^{43,54} Significant progress has been achieved recently by Katayama-Yoshida and Zunger^{46,47} on the understanding of the magnetic properties of $3d$ impurities in silicon and GaAs. Spin-polarized calculations for interstitial impurities⁴⁷ ($_{21}\text{Sc}$ to $_{27}\text{Co}$) in different charge states in silicon and for substitutional vanadium in GaAs have been carried out using a

first-principles GF approach within a single-site impurity-centered dynamic basis set and the local-density formalism (LSD).⁴⁵ Detailed calculations for interstitial iron⁴⁶ show the need to include the electron self-interaction correction on the LSD formalism⁴⁴ in order to obtain the correct symmetry of the impurity ground state. Other applications of band-structure—GF—based methods to study $3d$ impurities in semiconductors have been reported.^{49–52} The empirical tight-binding formalism applied to silicon was used to perform calculations for interstitial Zn by Sankey and Dow⁴⁹ and for substitutional and interstitial Cr, Mn, and Fe by Pecheur and Toussaint;⁵⁰ a spin-polarized version of this formalism has been used to describe the electron structure of the substitutional impurities ($_{21}\text{Sc}$ to $_{29}\text{Cu}$) in CdS, CdSe, and CdTe by Vogl and Baranowski;⁵¹ recently, Beeler *et al.*,⁵² using a linear-muffin-tin-orbital (LMTO) representation of the crystal band structure, conducted electronic state calculations for substitutional and interstitial $3d$ impurities ($_{22}\text{Ti}$ to $_{29}\text{Cu}$) in silicon.

Although considerable progress has been achieved hitherto on the understanding of the physical properties of $3d$ TM elements in semiconductors, the theoretical study of $4d$, $4f$, and $5d$ TM impurities is still at its beginning. Very few attempts have been made to perform rigorous electronic structure calculations for these impurities in semiconductors. Results are reported by Lowther⁴⁸ for substitutional Pt and Au impurities in silicon obtained according to a band-structure-based tight-binding approximation. This theory has also been used by Sankey and Dow⁴⁹ to study Cd and Hg interstitial impurities in silicon. Recently, Fazzio *et al.*⁵³ conducted comparative QBCF-GF calculations for the substitutional group-IB (Cu, Ag, Au) and interstitial Au impurities in silicon. Semirelativistic pseudopotentials (not including spin-orbit interactions) were used in these calculations. A comparative study of nonrelativistic and relativistic $5d$ atoms as substitutional impurities ($_{80}\text{Hg}$ to $_{74}\text{W}$) in silicon was performed by Alves and Larsson³⁵ using a hydrogen-terminated 17-atom cluster model within the framework of the semiempirical extended Hückel theory. Finally, the rare-earth substitutional Er and Yb impurities, replacing the In atom in InP, were studied by Hemstreet¹⁸ using a semirelativistic version of the MS cluster method applied to a hydrogen-terminated 17-atom cluster.

In the present investigation the one-electron energy spectra of the $5d$ TM impurities ($_{80}\text{Hg}$ to $_{74}\text{W}$) in silicon are obtained by using the MS theory within the framework of the Watson-sphere-terminated cluster model. The calculations reported here were performed for the neutral substitutional and interstitial impurities by adopting site-centered clusters of 17 and 27 atoms, respectively. The aim of our work is to establish the role played by the metal $5d$ states in the formation of gap levels and resonances. By performing a comparative study we intend to determine the overall trends in the impurity-induced levels along the $5d$ series. Comparisons with previous calculations for the $3d$ TM series in silicon are performed and attempts are made to infer whether the $5d$ impurity behaves predominantly as d -like or hostlike. Our theoretical model is based on a first-principles local-density one-

electron theory where relaxation effects, lattice distortions, many-electron effects (spin-polarization and/or multiplet corrections), self-interaction corrections, and relativistic effects are neglected. Thus we are not in a position to correctly describe the experimental excitation and ionization spectra of the impurities. However, the single-electron energy eigenstates analyzed here provide the information needed to recognize the role played by the mentioned corrections, as well as being the starting point for taking these corrections into account. Preliminary reports of our calculations for the isoelectronic Hg^+ , Au^0 , and Pt^- impurities in silicon have been published elsewhere.^{29,30}

In Sec. II a brief description of the Watson-sphere-terminated molecular cluster model as used in this work is given and the results of our calculations are presented and analyzed. In Sec. III a comparative analysis between theory and experiment is performed and our final remarks are included in Sec. IV.

II. RESULTS

A. Theoretical model

The results presented for the substitutional impurities were obtained through the study of a 17-Si-atom cluster centered at the regular lattice site where the impurity was placed. The model has been currently applied to investigate deep-level impurities in IV elemental^{27,29,30} and III-V compound semiconductors.²³⁻²⁶ The cluster comprises a central atom (impurity), a first shell (4 Si), and a second shell (12 Si) in tetrahedral symmetry (T_d). The interstitial impurities were studied by adopting a 26-Si-atom cluster centered at the tetrahedral interstitial site (T) where the impurity was placed. The model has been recently applied to investigate isolated interstitial impurities⁶⁶ as well as complex defects in silicon.^{36,37} As a T -centered cluster it comprises a central atom (impurity), a first shell (4 Si), a second shell (6 Si), a third shell (4 Si), and a fourth shell (12 Si) in T_d symmetry. The characteristics of the Watson-sphere-terminated clusters used in the calculations are described in Ref. 27. Details about the muffin-tin geometrical parameters, the exchange factor α , as well as the angular-momentum quantum number l used in the wave-function expansions are provided in our previous works,^{29,30} and therefore no further information will be given here. All the calculations were carried out to the self-consistent-field limit by including all the electrons.

B. Substitutional impurities

We present in Fig. 1 the self-consistent energy spectra of the clusters 16 Si + TM simulating the electronic structure of the substitutional neutral atoms from $_{80}\text{Hg}$ to $_{74}\text{W}$. The band edges are defined from the "perfect" 17-Si-atom cluster calculations and are indicated by the dashed lines. The uppermost occupied level of the 17-Si-atom cluster, $3t_2$, corresponds to the top of the valence band and is placed at the zero of energy. In order to simplify the analysis of the obtained results, the electronic structure of a 16 Si + V cluster, simulating a missing host atom (vacancy), is also included in Fig. 1.

We start by first analyzing the trends displayed by the impurity-induced levels which originate from the $5d$ TM atomic orbitals and appear as resonances within the valence band or hyperdeep levels below it. The $5d$ atomic states are split by the crystal field into a twofold $e(d)$ degenerate state and a threefold $t_2(d)$ degenerate state. For the Hg and Au impurities these states are highly concentrated, showing an atomiclike behavior. As we proceed to lighter impurities the $5d$ states interact with the host states and move up into the valence band. Due to the hybridization with the e and t_2 valence states, the $e(d)$ and $t_2(d)$ resonances become progressively more delocalized when we move to lower values of the impurity atomic number (Z). This behavior can be observed by analyzing the results depicted in Fig. 2(a). The percentage of charge inside the metal sphere (radius 2.22 a.u.), normalized to one electron, is shown for some selected levels of the cluster energy spectra. The labels for the levels are the same indicated in Fig. 1. According to Fig. 2(a) the charge in the substitutional impurity sphere for the $e(d)$ resonance ranges from 95% for Hg to 20% for W. The corresponding percentage of charge for the $t_2(d)$ states ranges from 93% for Hg to 41% for W. Whereas at the high- Z limit the $e(d)$ and $t_2(d)$ states are atomiclike, at the low- Z limit these states have contributions from the s and p host silicon atomic orbitals.

Our calculations yield the conclusion that the overall trend shown by the $e(d)$ and $t_2(d)$ resonant states for the $5d$ TM elements in silicon is quite similar to that inferred from other calculations for the $3d$ TM impurities in

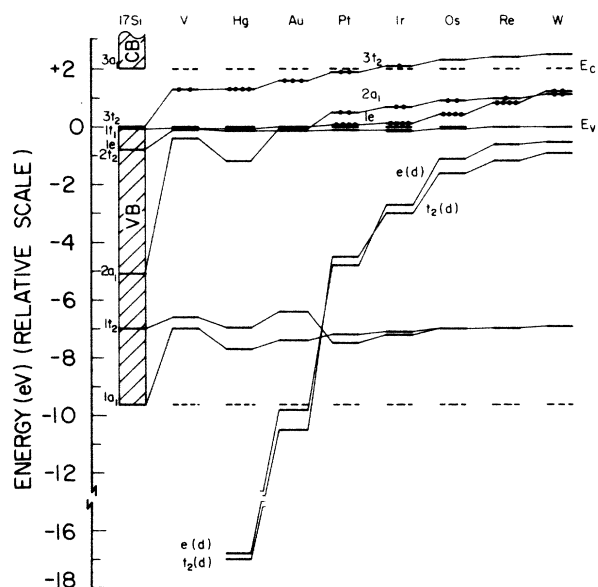


FIG. 1. One-electron self-consistent energy spectra of the 17-Si-atom; 16 Si + V , and 16 Si + TM clusters simulating the electronic structure of the silicon crystal, the single vacancy, and the substitutional TM (Hg, Au, Pt, Ir, Os, Re, and W) impurities in silicon, respectively. The zero of energy is placed at the top of the valence band ($3t_2$) and the solid circles indicate the occupancies below the top of the valence band are fully occupied. The dashed lines indicate the crystal band edges.

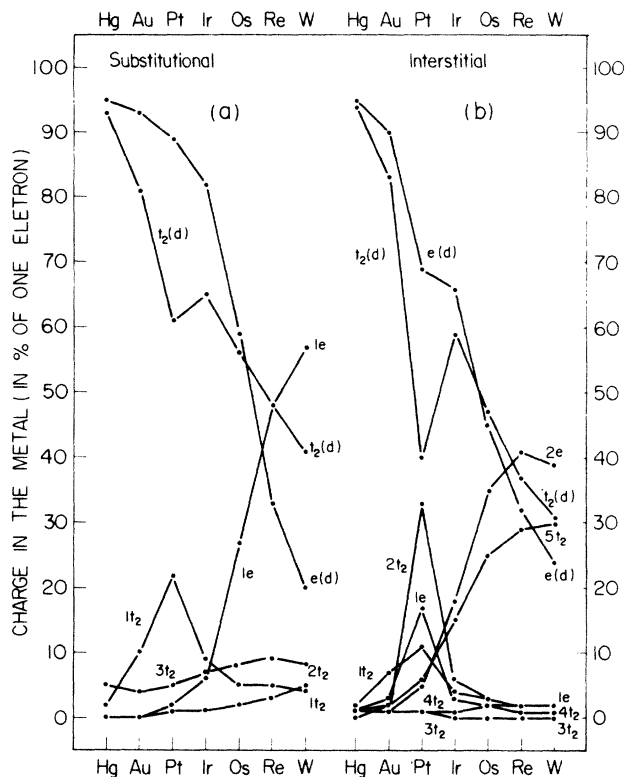


FIG. 2. Percentage of charge normalized to one electron inside the central impurity sphere (radius 2.22 a.u.) for some levels selected from the spectra shown in Figs. 1 and 3. (a) refers to the spectra shown in Fig. 1 for the substitutional impurities; (b) refers to the spectra shown in Fig. 3 for the interstitial impurities. The same label is used to identify each level indicated in Fig. 2(a) [(b)] with the corresponding one in Fig. 1 (3).

Si,^{14,41} GaAs,^{16,25} and GaP.⁴³ By comparing the $e(d)$ and $t_2(d)$ energy-level positions found by us for the 5d TM impurities with those derived from a hydrogen-terminated MS cluster calculation for the 3d TM series in silicon,¹⁴ the following differences and similarities are found. These levels are deeper for Hg and Au than those obtained for their counterparts Zn and Cu at groups IIB and IB in the Periodic Table, respectively. From $_{78}\text{Pt}$ to $_{74}\text{W}$ the level positions are remarkably similar to those found for their counterparts at the same column in the Periodic Table, say, from $_{28}\text{Ni}$ to $_{24}\text{Cr}$. It is also interesting to observe that the crystal-field splitting [$e(d)$ - $t_2(d)$] is of the same order (less than 0.5 eV) along the two series. In both series it is found that the $e(d)$ and $t_2(d)$ levels are pinned inside the valence band, in the vicinity of the band edge, at the lower-Z limit. The origin of the pinning of these levels, which has been discussed previously,^{41,43} is the attraction by the valence-band e and t_2 states and the repulsion by the conduction-band e and t_2 states. At the lower-Z limit the interaction between the $e(d)$ and $t_2(d)$ states with the host states is strong enough to cause the pinning of the $e(d)$ and $t_2(d)$ levels. Since at the high-Z limit these levels correspond to highly localized atomic-like states interacting weakly with the lattice, the pinning mechanism is not operative. Another striking similarity

observed between the results obtained for the two series is the $e(d)$ and $t_2(d)$ level crossing that occurs successively when we proceed from $_{80}\text{Hg}$ to $_{71}\text{Ir}$ in the 5d series or from $_{30}\text{Zn}$ to $_{27}\text{Co}$ in the 3d series.

Gold is the only element from the 5d series that has been the object of studies by the *ab initio* GF method. According to recent QBCF-GF calculations performed by Fazio *et al.*,⁵³ the replacement of a silicon atom by Au gives rise to 5d-derived highly localized $e(d)$ and $t_2(d)$ resonances⁶⁸ near the middle of the valence band, at about 5 eV above the 5d-derived levels obtained from our calculations. Although semirelativistic pseudopotentials (not including spin-orbit interactions) were used in the GF calculations, we do not expect this improvement to be enough to explain this discrepancy. Recently, Alves and Larsson³⁵ have shown that the relativistic effects, when fully included in an extended Hückel theory applied to the 5d TM impurities in silicon, force the localized 5d-derived states to move up in energy by about 3 eV. Another possible source of discrepancies between the two calculations is the different approximations adopted for the exchange-correlation effects. The use of an exchange parameter $\alpha=1$ in the GF calculation,³⁸ which overestimates the exchange-correlation effects mainly in the regions of high electronic density, may directly affect the highly localized core states. Another interesting point related to the comparison between our calculations and the GF results has to do with the pinning of the $e(d)$ level inside the valence band at the lower-Z limit. From the GF calculations it is concluded that for the 3d TM impurities in Si (Ref. 41) and GaP (Ref. 43) the $e(d)$ is not pinned inside the valence band but penetrates the band gap. According to both the previous MS cluster calculations for the 3d series in Si (Ref. 14) and the present work, the interactions between the $e(d)$ resonances and the bulk states are strong enough to prevent them from penetrating into the band gap at the lower-Z limit.

We now analyze the calculated impurity-induced $3t_2$, $2a_1$, and $1e$ energy levels which, according to Fig. 1, appear within or in the vicinity of the fundamental band gap. In order to better characterize these levels, we display in Table I the charge distribution associated with them for the different regions of the cluster. Figure 2(a) also shows the charge inside the impurity spheres for the $3t_2$ and $1e$ states.

The first interesting feature that can be inferred from the results shown in Fig. 1 is that the relevant electrical, optical, and magnetic properties of the substitutional Hg and Au impurities are dictated by the presence of the threefold-degenerate $3t_2$ level in the crystal band gap. The $e(d)$ and $t_2(d)$ states interact weakly with the continuum valence-band states and remain fully occupied; therefore they play a minor role in determining the major physical properties of the impurities. According to the results shown in Table I, the $3t_2$ states are mostly dangling-bond-like on the nearest and next-nearest silicon neighbors. They are closely related to the $3t_2$ gap level obtained for the undistorted silicon vacancy. Similar results were obtained for the 3d-analogous Zn and Cu as substitutional impurities in Si,^{13,14,41} GaAs,^{16,25} and GaP,⁴³ according to cluster and GF calculations. A

TABLE I. Charge distribution normalized to one electron associated with the $2a_1$, $1e$, and $3t_2$ levels for the 1-Si-atom "perfect" cluster, the Si vacancy, and the substitutional impurities $_{80}\text{Hg}$ to $_{74}\text{W}$. The levels are labeled according to Fig. 1.

System	Orbital (occupancy)	Central sphere	First shell	Second shell	Interatomic region
17 Si	$3t_2$ (6)	0.04	0.24	0.47	0.25
	$2a_1$ (2)	0.23	0.50	0.08	0.19
	$1e$ (4)	0.00	0.25	0.49	0.25
V	$3t_2$ (2)	0.03	0.28	0.46	0.22
	$2a_1$ (2)	0.26	0.32	0.17	0.25
	$1e$ (4)	0.00	0.24	0.50	0.25
Hg	$3t_2$ (4)	0.05	0.36	0.35	0.23
	$2a_1$ (2)	0.22	0.39	0.11	0.28
	$1e$ (4)	0.00	0.29	0.46	0.25
Au	$3t_2$ (3)	0.04	0.27	0.46	0.22
	$2a_1$ (2)	0.13	0.41	0.17	0.28
	$1e$ (4)	0.00	0.27	0.47	0.24
Pt	$3t_2$ (2)	0.05	0.18	0.55	0.21
	$2a_1$ (2)	0.08	0.40	0.24	0.28
	$1e$ (4)	0.02	0.25	0.48	0.24
Ir	$3t_2$ (1)	0.07	0.12	0.60	0.20
	$2a_1$ (2)	0.06	0.39	0.28	0.27
	$1e$ (4)	0.06	0.22	0.49	0.23
Os	$3t_2$ (0)	0.08	0.08	0.63	0.19
	$2a_1$ (2)	0.05	0.36	0.32	0.26
	$1e$ (4)	0.27	0.12	0.42	0.19
Re	$3t_2$ (0)	0.09	0.08	0.63	0.19
	$2a_1$ (1)	0.04	0.35	0.35	0.26
	$1e$ (4)	0.48	0.01	0.31	0.16
W	$3t_2$ (0)	0.08	0.08	0.63	0.20
	$2a_1$ (2)	0.03	0.33	0.37	0.25
	$1e$ (2)	0.57	0.01	0.25	0.16

threefold-degenerate level within the gap was also found for Au in silicon according to the recent GF calculations reported by Fazzio *et al.*⁵³ It is interesting to point out that the $3t_2$ gap level for both Au and the vacancy corresponds to almost the same charge distribution. According to the entries shown in Table I, the $3t_2$ state is more concentrated for Hg than for the vacancy.

The dangling-bond-like character of the $3t_2$ state as well as its partial electronic occupancy suggests that the Hg and Au impurities are expected to display the lattice distortions characteristic of a silicon vacancy. Therefore the different charge states of the impurities may be related to such distortions and the Haldane-Anderson mechanism is not operative here.⁵ It is also clear that the original Ludwig-Woodbury^{2,3} (LW) model is not appropriate for describing the Hg and Au impurities in silicon.

As we proceed to lighter impurities, the orbitals of the TM interact with the host states and push the $3t_2$ level up towards the band edge for Pt and to the continuum of the

conduction band for the remaining elements. For the Ir impurity the $3t_2$ level lies just above the bottom of the conduction band and is occupied by one electron. Thus, according to our calculations, Ir as a stable substitutional impurity in silicon is expected to be found in a positive charge state. The comparison with previous cluster¹⁴ and GF⁴¹ calculations for the $3d$ TM atoms in silicon shows that the $3t_2$ gap level on both series displays almost the same trend. It is within the band gap from $_{80}\text{Hz}$ ($_{30}\text{Zn}$) to $_{78}\text{Pt}$ ($_{28}\text{Ni}$), very close to the bottom of the conduction band for $_{77}\text{Ir}$ ($_{27}\text{Co}$), and in the continuum of the conduction band from $_{76}\text{Os}$ ($_{26}\text{Fe}$) to $_{74}\text{W}$ ($_{24}\text{Cr}$). This behavior is different from that inferred for the $3d$ TM as substitutional impurities in GaAs (Refs. 16 and 25) and GaP (Ref. 43). According to the cluster and GF calculations the $3t_2$ level is always found within the band gap of these compounds from $_{30}\text{Zn}$ to $_{24}\text{Cr}$. According to Fig. 1 the Pt impurity is an active Jahn-Teller (JT) center due to the partial occupancy of the $3t_2$ gap level. Figure 2(a) em-

phasizes the dangling-bond-like character of the $3t_2$ impurity level. Less than 10% of charge is found inside the metal sphere for this state. We observe that the $3t_2$ states are resonances in the conduction band for $_{77}\text{Ir}$, $_{76}\text{Os}$, $_{75}\text{Re}$, and $_{74}\text{W}$.

As the $t_2(d)$ and $e(d)$ resonances move up in the valence band, the $1e$ level penetrates into the band gap for the Pt impurity. This energy level increases monotonically as we proceed to lighter impurities. Similar behavior was inferred from previous calculations for the e level introduced by the $3d$ TM impurities in the band gap of Si,¹⁴ GaAs,^{16,25} and GaP.⁴³ Both cluster and GF calculations indicate that the e and t_2 impurity levels do not coexist within the band gap for any $3d$ TM impurity in silicon. Here we observe that Pt does not follow this rule and both $1e$ and $3t_2$ are found within the band gap. The entries in Table I show how the $1e$ impurity level changes its character as the $t_2(d)$ and $e(d)$ resonances move up in the valence band. By comparing the results obtained for the 17 Si and 16 Si + V clusters, we observe that the $1e$ state is a bulk state which is slightly perturbed by the removal of a Si atom from the lattice. For Hg, Au, and Pt impurities the $e(d)$ and $t_2(d)$ levels are far apart from the $1e$ level; thus the predominant interaction between the $e(d)$ states and the $1e$ state is rather weak. As a consequence the $1e$ level remains almost unchanged for Hg and Au and is slightly displaced and introduced in the band gap for Pt. As we proceed to lower values of the impurity atomic number the interactions between the d resonances and the bulk $1e$ state become stronger and the $1e$ level moves up in the band gap. Its charge inside the impurity sphere increases from 6% for Ir to 57% for W. The composition of the $1e$ state as a function of the impurity atomic number ranges from a pure Si s and p hybridization for heavy impurities to a strong TM $5d$ atomic-orbital contribution for lighter elements. Figure 2(a) emphasizes the $5d$ contribution to the $1e$ impurity state.

The most striking difference between the present calculations and those performed for the $3d$ TM atoms in silicon is concerned with the behavior of the $2a_1$ level shown in Fig. 1. Previous works report for Zn and a_1 resonance at about $E_v - 3$ eV and $E_v - 2$ eV according to the cluster¹⁴ and GF⁴¹ calculations, respectively. Proceeding to lower values of Z , this resonant level moves towards the band edges but never gets into the band gap. Similar results were obtained for GaP according to GF calculations.⁴³ However, for the $5d$ TM impurities analyzed here the $2a_1$ level appears in the band gap for Pt and for the remaining lighter elements. We consider this behavior one of the most interesting features of the $5d$ TM substitutional impurities in silicon. It clearly indicates a complex structure of impurity levels for the elements from $_{78}\text{Pt}$ to $_{74}\text{W}$. Indeed, it also shows that the LW model is not applicable in describing these substitutional impurities in silicon.

C. Interstitial impurities

Figure 3 summarizes the single-particle energy levels, obtained from the 26 Si + TM cluster calculations, simulating the electronic structure of the $5d$ TM interstitial

neutral impurities in silicon. The crystal band edges are determined from the energy spectrum of the "perfect" 26-Si-atom cluster and are indicated by the dashed lines. The uppermost occupied level of the 26-Si-atom cluster defines the top of the valence band and is placed at the zero of energy.

According to Fig. 3, the Hg and Au interstitial impurities give rise to compact, filled, $5d$ -derived $e(d)$ and $t_2(d)$ hyperdeep levels in silicon. They correspond to highly localized states with more than 80% of charge inside the impurity sphere. As we proceed to lower values of Z along the series, the $e(d)$ and $t_2(d)$ levels rise, appearing near the middle of the valence band for Pt and at the upper part of the valence band for the remaining elements. This raising in energy is followed by a correspondent delocalization of the $e(d)$ and $t_2(d)$ states. Figure 2(b) shows that the charge inside the impurity sphere for the $e(d)$ and $t_2(d)$ states is a monotonically decreasing function of decreasing Z , with the $t_2(d)$ states of Ir being the only exception. The crystal-field splitting [$e(d)-t_2(d)$] is less than 1 eV for Au and less than 0.5 eV for the remaining elements along the series. It is also found that the $e(d)$ and $t_2(d)$ levels are pinned inside the valence band, in the vicinity of the band edge, at the

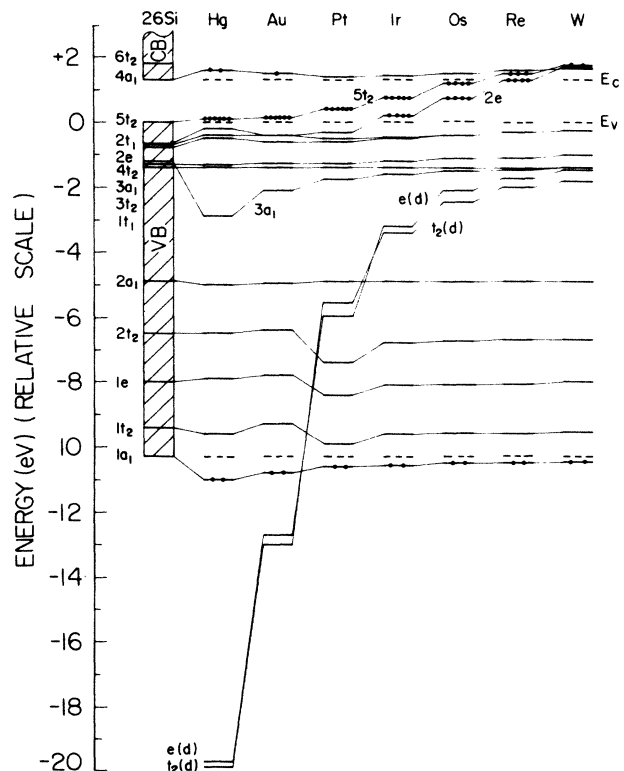


FIG. 3. One-electron self-consistent energy spectra of the 26-Si-atom and 26 Si + Tm clusters simulating the electronic structure of the silicon crystal and the interstitial TM (Hg, Au, Pt, Ir, Os, Re, and W) impurities in silicon, respectively. The zero of energy is placed at the top of the valence band ($5t_2$) and the solid circles indicate the occupancies of the gap levels. All levels below the top of the valence band are fully occupied. The dashed lines indicate the crystal band edges.

lower- Z limit. The comparison between these results and those derived from previous hydrogen-terminated MS cluster calculations¹⁹ for the $3d$ TM interstitial impurities in silicon yields the conclusion that they are quite similar. The $e(d)$ and $t_2(d)$ level positions within the valence band obtained for the elements from $_{78}\text{Pt}$ to $_{74}\text{W}$ are more or less the same as reported for their $3d$ counterparts at the same column in the Periodic Table, say, from $_{28}\text{Ni}$ to $_{24}\text{Cr}$. Interstitial gold has been the object of investigations by QBCF-GF calculations⁵³ which also indicate that the $e(d)$ and $t_2(d)$ states are compact and highly localized. However, Fazzio *et al.* report the $e(d)$ and $t_2(d)$ states as resonances within the valence band.

The strong localization of the $e(d)$ and $t_2(d)$ states found for Hg and Au indicates a weak interaction between these impurities and the silicon lattice. Although a small perturbation of the top of the valence band $5t_2$ is detectable in the calculations, we are not in a position to decide if this level is an active impurity level in the gap. Other interesting features of the Hg and Au interstitial impurities are related to the $1a_1$ and $4a_1$ impurity levels. The $1a_1$ bonding state appears as a hyperdeep level close to the bottom of the valence band. The $4a_1$ antibonding state remains as a resonance close to the bottom of the conduction band and is occupied by two electrons and one electron for Hg and Au, respectively. The position and occupancy of the $4a_1$ level found in the calculations allow us to conclude that the impurities only exist in the charge states Hg^{2+} and Au^+ . It is interesting to observe that recent LMTO calculations⁵² lead to the conclusion that interstitial Cu, belonging to group IB, as does Au, also only exists in the single-positive charge state. On the other hand, no shallow donor activities are found for Hg and Au interstitial impurities in silicon. This is in disagreement with previous tight-binding calculations⁴⁹ for Hg, which predict that the impurity is a shallow double donor, as well as with previous GF calculations,⁵³ which ascribe a single shallow donor activity for gold.

As we proceed now to Pt, the $5d$ -derived $t_2(d)$ and $e(d)$ states, interacting strongly with the lattice, push the $5t_2$ impurity state into the gap. The results indicate that Pt shows quite different properties when compared with the elements at the end of the series, $_{80}\text{Hg}$ and $_{79}\text{Au}$. In a neutral charge state Pt is an active deep donor center and is expected to show no EPR signal. The $1a_1$ hyperdeep level as well as the $4a_1$ resonance are only slightly modified.

Most of the analysis performed above for Hg, Au, and Pt impurities were already made in our previous works.^{29,30} We summarize the main conclusions here in order to relate them to the properties of the remaining $5d$ impurities. The comparison between the results along the series becomes clearer if we analyze the charge distribution associated with the main impurity states. Table II displays the charge distribution normalized to one electron associated with the $5t_2$, $2e$, and $1a_1$ impurity states for the 26-Si-atom "perfect" cluster and the interstitial impurities $_{80}\text{Hg}$ to $_{74}\text{W}$. The different shells of the clusters are described in Sec. IIA. Figure 2(b) also provides information about the charge distribution inside the impurity sphere for the $5t_2$ and $2e$ impurity states, as well as

for some other states in the valence band.

Figure 3 shows that as we proceed to lower values of Z along the series the $e(d)$ and $t_2(d)$ states force the $5t_2$ and $2e$ levels up, introducing both into the gap for Ir and Os. These levels lie close to the bottom of the conduction band for Re and in the continuum of the conduction band for W. According to Fig. 2(b) and Table II, the raising of these levels is followed by a localization of the impurity states within the central region of the cluster. The trend in the impurity $5d$ hybridization with the s and p silicon states can be followed by comparing the charge inside the impurity central sphere, which ranges from 1% in Hg to 30% in W for the $5t_2$ state. For the $2e$ impurity state these values are 1% and 39%, respectively.

Relevant conclusions can be reached based on the results obtained for the $5t_2$ and $2e$ impurity levels. It is verified that the original LW model^{2,3} is not applicable to any interstitial impurity studied here. When both the $5t_2$ and $2e$ levels occur in the gap, they appear in a reversed LW order, say, the $2e$ below the $5t_2$ level. Thus, there is a striking difference between our results for Ir, Os, and Re and those derived from cluster^{19–22} and GF⁴² calculations for the corresponding $3d$ elements. These techniques predict a LW ordering for the e and t_2 gap levels of Co, Fe, and Mn interstitial impurities in silicon. The calculations indicate that neutral Ir and Os are stable deep donor and acceptor centers, which may show EPR signal. On the other hand, Os, Re, and W lead to impurity levels close to the bottom of the conduction band, occupied by various electrons. This opens the possibility for many ionized states of the impurities that would favor the formation of complexes with other lattice defects or impurities.

Finally, we address ourselves to the hyperdeep $1a_1$ level. Fazzio *et al.*⁵³ stresses that this level is an important "fingerprint" of the interstitial gold impurity. Here we verify that this level is, in fact, a common characteristic of all interstitial $5d$ impurities in silicon. The entries in Table II show that this level originates from a perturbation of the bottom of the valence band by the TM impurity.

Before concluding this section one more comment should be made. The $5d$ TM impurities in silicon show entirely different properties, depending on whether they are at the substitutional or interstitial lattice sites. In the particular case of Pt, Fig. 2 shows that the interaction of the d atomic states with the host lattice is stronger for the impurity at the interstitial site than at the substitutional site. This seems to indicate that Pt is more stable as an interstitial impurity than as a substitutional impurity.

III. DISCUSSION

As we pointed out in the Introduction, our calculations lead to impurity energy levels within the crystal band gap which are not directly comparable with the experimental excitation and ionization spectra associated with the impurities. However, there are general correlations between the present one-electron theory and experiment that are of considerable interest.

We recall that gold is one of the most studied impuri-

ties in silicon from an experimental point of view because of its importance as a lifetime-control impurity and as a convenient material for ohmic contacts with this semiconductor.^{4,6,7,69} Moreover, platinum has been the object of experimental work for many years⁷⁰⁻⁷³ and is also considered a practical contender for lifetime control in silicon. Due to the relevant importance of these two $5d$ impurities in silicon, we start by first discussing the correlation between our calculations and the main experimental results related to them.

A. Au

According to the results presented in Sec. II, the $5d$ levels of substitutional gold in silicon behave atomically, the electrons interacting very weakly with the lattice. On the other hand, gold introduces a threefold degenerate $3t_2$ level in the band gap, occupied by three electrons, which is not d -like, but rather mostly dangling-bond-like on the 4 and 12 silicon neighbors. These findings play a basic role in explaining most of the physical properties of gold in silicon.

Although there has been much discussion in recent years concerning the amphoteric behavior of gold in silicon,^{69,74} it seems well established on experimental

grounds⁷⁵⁻⁷⁷ that the gold donor ($E_v + 0.35$ eV) and acceptor ($E_c - 0.55$ eV) are levels belonging to the same center. According to our point of view, the amphoteric activity of gold is related to an isolated substitutional impurity. The almost identical energy spectra (Fig. 1) and charge distribution (Table I) for neutral gold and the vacancy show that this impurity behaves basically as a "perturbed" silicon vacancy with a filled, atom-derived d shell localized far below the top of the valence band. The fact that the $3t_2$ gap state is mostly dangling-bond-like indicates that the impurity displays the lattice distortions characteristic of a silicon vacancy.²² We propose that the amphoteric activity of gold is directly related to the multiple charge states $\text{Au}^+(3t_2^2)$, $\text{Au}^0(3t_2^3)$, and $\text{Au}^-(3t_2^4)$, which are then associated with lattice distortions characteristic of V^0 , V^- , and V^{2-} charge states of a vacancy, respectively. Of course, the demonstration of the present proposal would require total-energy calculations which are not performed here. However, there is some experimental evidence that indicates a distorted stable configuration for an isolated gold impurity in silicon. Experiments were carried out⁷⁸ to investigate the orientational dependence of the internal friction in single crystals of gold-doped silicon in order to determine the symmetry of the impurity center. It was found that the center had

TABLE II. Charge distribution normalized to one electron associated with the $5t_2$, $2e$, and $1a_1$ levels for the 26-Si-atom "perfect" cluster and the T -site interstitial impurities $_{80}\text{Hg}$ to $_{74}\text{W}$.

System	Orbital (occupancy)	Central sphere	First shell	Second shell	Third shell	Fourth shell	Interatomic region
26 Si	$5t_2$ (6)		0.34	0.13	0.24	0.06	0.23
	$2e$ (4)		0.15	0.31	0.00	0.31	0.23
	$1a_1$ (2)		0.39	0.39	0.00	0.01	0.21
Hg	$5t_2$ (6)	0.01	0.30	0.19	0.12	0.16	0.21
	$2e$ (4)	0.01	0.18	0.34	0.00	0.25	0.22
	$1a_1$ (2)	0.05	0.41	0.32	0.00	0.00	0.21
Au	$5t_2$ (6)	0.02	0.33	0.16	0.19	0.08	0.22
	$2e$ (4)	0.01	0.17	0.31	0.00	0.28	0.22
	$1a_1$ (2)	0.03	0.41	0.34	0.00	0.01	0.21
Pt	$5t_2$ (6)	0.06	0.30	0.15	0.24	0.03	0.21
	$2e$ (4)	0.05	0.15	0.27	0.00	0.31	0.21
	$1a_1$ (2)	0.02	0.41	0.35	0.00	0.01	0.21
Ir	$5t_2$ (5)	0.15	0.21	0.16	0.26	0.00	0.20
	$2e$ (4)	0.18	0.13	0.19	0.00	0.32	0.18
	$1a_1$ (2)	0.02	0.41	0.36	0.00	0.01	0.20
Os	$5t_2$ (4)	0.25	0.12	0.17	0.26	0.00	0.19
	$2e$ (4)	0.35	0.08	0.10	0.00	0.32	0.15
	$1a_1$ (2)	0.01	0.42	0.36	0.00	0.01	0.20
Re	$5t_2$ (3)	0.29	0.07	0.16	0.27	0.02	0.18
	$2e$ (4)	0.41	0.04	0.05	0.00	0.34	0.15
	$1a_1$ (2)	0.01	0.42	0.36	0.00	0.01	0.20
W	$5t_2$ (2)	0.30	0.04	0.16	0.27	0.03	0.19
	$2e$ (4)	0.39	0.01	0.04	0.00	0.40	0.16
	$1a_1$ (2)	0.01	0.42	0.36	0.00	0.01	0.20

orthorhombic symmetry with $\langle 110 \rangle$ orientation. This is a typical configuration of the negative-charge state of a silicon vacancy,²² V^- , which is related to Au^0 in our model. This symmetry is compatible with a displacement of the impurity from the silicon along one of the six equivalent $\langle 100 \rangle$ directions. If such a displacement is present it can be explained in terms of a covalent effect which binds the gold atom to two out of four silicon neighbors. The small fraction of d character found for the $3t_2$ impurity state, as shown in Table I and Fig. 2(a), is expected to play a role in this binding mechanism. This information could be complemented by electron paramagnetic resonance (EPR), but gold has not been observed by this technique. Although Höhne⁷⁹ reported an EPR signal which he ascribed to interstitial gold in silicon, Kleinhenz *et al.*⁸⁰ have shown that the spectrum was actually due to a substitutional gold–interstitial-iron pair complex. According to our model, the substitutional neutral gold impurity is expected to be a paramagnetic center with spin $S = \frac{1}{2}$, as is the V^- defect.

Intimately related to the determination of impurity energy levels and electron emission or capture cross sections as functions of temperature, there is the problem of knowing the value of the degeneracy factor g which appears in the equation of detailed balance.⁴ This parameter for an acceptor level, g_A , is defined as the ratio of the degeneracy of the ground level of the neutral impurity to that of the negatively charged impurity. For a donor level the degeneracy factor, g_D , is the ratio of the degeneracy of the ground state of the positively charged impurity to that of the neutral impurity. Determination of the degeneracy factor then requires the determination of the degeneracy of the individual charge states of the center. As far as the gold impurity is concerned, there are no reliable experimental data on g . For instance, values ranging from 1 to 40 have been suggested for the gold-related acceptor level.⁷ Several attempts have been made to derive degeneracy factors of gold in silicon based on some assumed bonding model of the gold atom in the silicon lattice.^{81–83}

One current model adopted to calculate g for gold starts with the impurity at a substitutional lattice site.⁸³ If such a configuration is assumed, then three more electrons are required to make up a complete sp^3 -bonding arrangement between the neutral impurity and the four silicon nearest neighbors. Therefore the center has two, three, or four holes associated with it, depending on whether it is a negatively charged, neutral, or positively charged state, respectively. One can then think of the holes as being in the bonding orbitals between the gold impurity and the host silicon atoms, or located in the $5d$ shell of gold as determined by the LW model. Ralph⁸³ has analyzed on very general grounds the degeneracy factor of the gold acceptor level in silicon in both cases mentioned above. He found that if there are no accidental degeneracies, g_A must lie in the range $\frac{2}{3}$ –4 in the case of the holes being in the bonding orbitals and be equal to 4 in the case of the holes being in the $5d$ shell of gold. However, our calculations do not provide any support to the model described above. Firstly, the gold atom does not remake the broken sp^3 bonds left by removing a silicon atom and creating a vacancy; secondly, the $5d$ shell is

compact and fully occupied.

According to our model for the substitutional gold impurity in silicon, the natural starting point for the derivation of the degeneracy factors of the gold donor and acceptor levels is consideration of the ground states of the vacancy charge states V^0 , V^- , and V^{2-} . It is well established from molecular orbital calculations⁸⁴ including configuration interactions that the ground state of V^0 is 1E . Thus, a spin $S=0$ and a degeneracy equal to 2 are expected for the Au^+ ground state. V^- has been examined by Lannoo,⁸⁵ who found a nondegenerate 4A_2 multiplet as the ground state if lattice distortions are neglected. However, it is pointed out that in order to match the experiments the distortions pull down the 2T_1 multiplet, which becomes the ground state. This finding gives the value 6 for the degeneracy of the Au^0 ground state. Therefore, the donor degeneracy factor of gold in silicon is estimated as $g_D = \frac{1}{3}$. In order to obtain g_A we need to know the ground state of V^{2-} in silicon, which has not been determined. However, V^{2-} has been examined by Yamaguchi⁸⁶ for diamond, and a 3T_1 multiplet was found for the ground state. If this result is assumed to be valid for silicon, the value 9 is ascribed to the degeneracy of the Au^- ground state. With this assumption we estimate the value $g_A = \frac{2}{3}$ for the acceptor degeneracy factor of gold. Of course, we have to bear in mind that these values are speculative in the sense that the ground states of V^- and V^{2-} deserve more investigations in order to be accurately determined.

Although gold is usually assumed to replace a silicon atom in the lattice,⁸⁰ the interstitial configurations play an important role in the diffusion mechanisms of this impurity. A high interstitial diffusion rate is observed for gold in silicon.⁸⁷ If we take into account the fact that gold at an interstitial site is weakly bonded to the host lattice and that the $5d$ -derived states are highly localized, we understand why gold is a fast diffusor in silicon. Still, according to our calculations the diffusive flux is carried by the positively ionized impurity.

It is worth mentioning that Fazzio *et al.*, by using the QBCF-GF theory,⁵³ were able to ascribe the amphoteric behavior of gold in silicon to a substitutional impurity in three charge states. By using Slater transition-state arguments the authors determined the energy difference U between the final states of the acceptor ($-/0$) and donor ($0/+$) transitions. By assuming no lattice distortion effects, it was shown that U is in very good agreement with the experimental value for the Mott-Hubbard potential for the center. Of course, this result does not demonstrate that the Jahn-Teller lattice distortions are small or absent for the three charge states of gold in silicon. The importance of these effects could be indicated by examining the calculated acceptor and donor transitions with respect to the crystal band edges. These energies were not reported by Fazzio *et al.* By taking into account the delocalized character of the $3t_2$ gap level, which indicated small exchange level splittings, Fazzio *et al.* ascribed a spin $S = \frac{1}{2}$ to the on-center substitutional Au^0 impurity. Although the QBCF-GF method and ours give the same spin for the center, rather different arguments are used in the two calculations. In our case the lattice distortions are expected

to play an important role, as in the case of the V^- center.⁸⁵

B. Pt

EPR signals were first observed for platinum in n -type silicon by Woodbury and Ludwig.⁷⁰ Two paramagnetic species were detected, both with spin $S = \frac{1}{2}$. The center responsible for the dominant spectrum, Pt(I), displayed orthorhombic (C_{2v}) symmetry and was interpreted as arising from an isolated single substitutional Pt^- ion, which is distorted off center in a $\langle 100 \rangle$ direction. The results also showed that Pt acts as an acceptor in this center. The Pt(II) center, which displayed axial symmetry along the $[111]$ direction, showed some correlation with the oxygen content in the samples. Thus, Pt(II) may represent Pt associated with oxygen.

Different microscopic models were proposed for the Pt(I) center, consistent with the experimentally determined principal axes:⁷⁰ (i) one model assumes that the impurity completes the tetrahedral bonding with its four nearest neighbors, and ascribes a d^8 diamagnetic configuration for the center with a bound hole in a $J = \frac{3}{2}$ state localized about the impurity. The remaining electronic degeneracy is lifted by a JT distortion in a $\langle 100 \rangle$ direction; (ii) another model assumes that the impurity forms bonds with two of its four silicon nearest neighbors, as does oxygen in the silicon A center, which has the same principal axes. The other two silicon nearest neighbors bond to each other. There are then two possibilities. Either the impurity has the d^8 diamagnetic configuration, while, as in the silicon A center, the unpaired electron occupies the antibonding orbital of the two paired silicon atoms, or the impurity has the d^9 paramagnetic configuration, the antibonding orbital of the two paired silicon atoms being empty. It has been argued⁷⁰ that in view of the difference existing between the spectra of the Pt(I) center and the silicon A center the latter alternative is favored.

Let us now correlate the EPR results for the Pt(I) center with our calculations for the substitutional platinum impurity. According to Fig. 1, an open-shell configuration $3t_2^3$ is obtained for the Pt^- center. Table I and Fig. 2 show that although a significant bonding between platinum and silicon neighbors occurs, the $3t_2$ gap level for the impurity is mostly dangling-bond-like. Therefore, the electronic properties of the center are expected to be similar to those of the V^- defect, which has a spin $S = \frac{1}{2}$ and also displays a large $\langle 100 \rangle$ static dihedral JT distortion resulting from the partially filled $3t_2$ gap level. We conclude that our microscopic model for the center yields a description in perfect agreement with the EPR results. On the other hand, our calculations do not provide support for the speculative models described above since substitutional platinum in a negative charge state can be thought of as a closed d^{10} ion in a negatively charged lattice vacancy V^- .

Recently, Henning⁷¹ and Henning and Egelmeers⁷² reported strain-modulated EPR measurements on Pt in silicon. A superhyperfine structure observed in the spectra was explained as arising from the interaction between a near-substitutional Pt^- with a second nearby interstitial

neutral Pt atom. However, Milligan *et al.*⁷³ have observed that the structure noted by Henning and Egelmeers, seen as shoulders on each of the main lines of the spectrum, is insensitive to the ^{195}Pt abundance in the sample and, therefore, does not arise from a hyperfine interaction with a second nearby Pt atom. Based on this observation as well as on preliminary static stress measurements Milligan *et al.* concluded that the original model of an isolated substitutional Pt^- ion, as given by Woodbury and Ludwig,⁷⁰ is correct. Although there is evidence that the pairs $Pt_s^--Pt_i^0$, in fact, are not related to these experiments, we cannot exclude the possibility of their formation in silicon. According to the results shown in Fig. 3, the neutral interstitial platinum impurity has a $5t_2^6$ gap-level configuration. Thus, the ground state of the center is an 1A_1 singlet state which should not present any EPR signal. On the other hand, we pointed out that interstitial platinum seems to be more stable in silicon than substitutional platinum. These facts, of course, suggest that the occurrence of the pair should not be discarded. We may infer that this center is a low-spin complex ($S = \frac{1}{2}$).

It seems to be established that platinum can compensate both n - and p -type silicon and can give rise to at least a donor level at about 0.35 eV above the valence-band edge in p -type material and to an acceptor level at about 0.25 eV below the conduction-band edge in n -type material.^{88,89} Very recently, the measurements of the photoionization cross section of this acceptor level (0.23 eV) by Santos Mayo *et al.*⁹⁰ provided a clear experimental evidence of lattice distortions associated with this level in silicon, in agreement with EPR experiments taken on the Pt(I) center.⁷⁰ We can then ascribe this acceptor activity to a transition ($-/0$) occurring for a substitutional Pt in the configurations $Pt_s^0(3t_2^2)$ and $Pt_s^-(3t_2^3)$. These configurations can be associated with the V^0 and V^- centers and total-energy calculations including lattice distortions are required to obtain the acceptor energy.

Recently, Armelles *et al.*⁹¹ carried out photoluminescence (PL) studies of platinum in silicon. A no-phonon PL line at 805 meV was observed, which suggests that the transition is associated with the $E_v + 0.32$ eV donor level of platinum ($E_c - 0.83$ eV). The final state of the transition shows no splitting under an uniaxial stress or a magnetic field. Since no orientational degeneracy is detected, the authors concluded that the symmetry of the center is tetrahedral, T_d . Assuming then that the observed PL line corresponds to the ($+/0$) or (Pt^+/Pt^0) transition, we correlate this experiment with our calculations. It is clear that the final state of the transition cannot be the substitutional platinum ground state. According to our results, the partial occupancy of the $3t_2$ gap level for Pt_s^0 indicates that the center undergoes JT distortions, as does the V^0 center. On the other hand, we already pointed out that the interstitial neutral platinum ground state is an 1A_1 single state. Thus, this center is stable in a T_d configuration and is probably the final state for the $E_v + 0.32$ eV donor activity observed for platinum in silicon. This finding raises the important conclusion that the currently accepted donor activity at $E_v + 0.32$ eV and acceptor activity at $E_c - 0.25$ eV of platinum in silicon are not associated with the same center. Contrary to gold impurity in sil-

icon, platinum does not seem to be an amphoteric center.

By using the fact that platinum ($5d^96s^1$) is isoelectronic to nickel ($3d^94s^1$) and that the interstitial Ni^0 ground state is $^1A_1(e^4t_2^6)$,^{19–22} Armelles *et al.*⁹¹ also reached the conclusion that the final state of the 805-meV PL transition is the Pt_i^0 ground state. However, we point out that this analogy cannot be carried out further because, although the two centers have an 1A_1 ground state, they have quite different electronic structures. According to previous calculations^{19–22} interstitial Ni^0 introduces two levels in the band gap, e and t_2 , with the e level lying just above the t_2 level. On the other hand, our calculations show that Pt_i^0 introduces a single level, of t_2 symmetry, in the band gap, occupied by six electrons. This result indicates that the initial state for the 805-meV PL transition should be obtained from the $5t_2^5$ gap-state configuration of Pt_i^+ instead of assuming the $t_2^6e^3$ or $t_2^5e^4$ configurations, as suggested by analogy with nickel.

Recently, Armelles and collaborators reported optical-absorption spectra associated with the acceptor level of Au and Pt in silicon.⁹² A striking similarity is found between the two spectra and a symmetry lower than T_d is suggested for both centers. These findings comprise strong evidence confirming the conclusions that arise from our calculations. We are ascribing the acceptor activity of Au and Pt centers to a transition involving a hole in the $3t_2$ gap state of the substitutional impurity. As we pointed out, both impurities at substitutional sites give rise to quite similar dangling-bond-like $3t_2$ gap states, with the $3t_2$ level of Pt lying above the $3t_2$ level of Au. The similar nature of the final states of the transitions explains the similarity between the two spectra. The same argument can be used to suggest that the substitutional mercury impurity should display an absorption spectrum similar to those associated with Au and Pt, with a photon absorption threshold displaced to lower energy. On the other hand, the fact that a symmetry lower than T_d was observed from both spectra confirms our proposal that the acceptor state of gold, like that of Pt, corresponds to a stable distorted configuration of the substitutional impurity.

Pearton and Haller⁹³ have studied the neutralization of deep-level centers associated with platinum in silicon, after exposure to a low-temperature hydrogen plasma, using transient function-capacitance spectroscopy. In n -type silicon, a platinum-related level at $E_c - 0.28$ eV was neutralized, but a level at $E_v + 0.33$ eV was unaffected by hydrogen-plasma exposure. Our calculations provide a clear explanation for the fact that only the acceptor activity of platinum is neutralized by hydrogen. It is well known that hydrogen migrates interstitially in silicon and reacts with lattice defects and impurities.⁶⁷ The platinum acceptor state is an empty vacancylike state which can easily bond to hydrogen, probably at interstitial sites. The high efficiency of hydrogen in passivating dangling-bond-like states in several kinds of semiconductor materials is well documented.⁶⁷ On the other hand, the donor state originates from a closed-shell gap-state configuration of platinum at interstitial sites. Thus, we can expect that the impurity in this configuration would be less amenable to neutralization than at the substitutional site. It is in-

teresting to point out that both the donor and acceptor levels of gold in silicon are neutralized by hydrogen.⁹⁴ We recall that for gold both the $(0/+)$ and $(-/0)$ transitions are related to dangling-bond-like states of the substitutional impurity.

C. Hg, Ir, Os, Re, and W

The remaining elements of the $5d$ series have deserved much less attention than gold and platinum as impurities in silicon. Among them, mercury and iridium are elements that have been considered for practical applications. Silicon doped with Hg and Ir have been used to fabricate negative-resistance diodes.⁹⁵

The results of the investigation of the photoconductivity spectra and the electrical properties showed that Hg in silicon introduces donor and acceptor levels within the band gap.^{96–99} The number and the precise locations of those levels are not well established. Two acceptor levels at $E_c - 0.31$ eV and $E_c - 0.36$ eV and two donor levels at $E_v + 0.25$ eV and $E_v + 0.33$ eV have been observed.⁹⁶ Ionization energies for only one acceptor level at $E_c - 0.33$ eV and only one donor level at $E_v + 0.36$ eV have also been reported.⁹⁸ A level with ionization energy $E_v + 0.51$ eV, thought to be an acceptor, has been recently observed.⁹⁷ Ion-implanted data⁹⁹ showed levels at $E_c - 0.39$ eV and $E_v + 0.35$ eV. Our results indicate, as in the case of gold, that the reported donor and acceptor actions of mercury in silicon are related to the same center, the substitutional impurity. The lattice distortions, which are expected to occur for the center, may allow for various charge-state configurations. At least a first donor activity is highly likely to be related to the transition $(0/+)$ or $[\text{Hg}^0(3t_2^4)/\text{Hg}^+(3t_2^3)]$. This donor action is expected to be analogous to the (V^{2-}/V^-) transition. It may be possible that a second donor action is allowed and it would be related to the transition $(+/2+)$ or $[\text{Hg}^+(3t_2^3)/\text{Hg}^+(3t_2^2)]$, which should be analogous to the (V^-/V^0) transition. We may infer that the first and second acceptor levels correspond to the transitions $(-/0)$ and $(2-/-)$ involving the substitutional mercury at the final-state configurations $3t_2^5$ and $3t_2^6$, respectively. In particular, the Hg^+ substitutional impurity, analogous to the V^- center, should be paramagnetic ($S = \frac{1}{2}$) and is expected to display a JT $\langle 100 \rangle$ tetragonal distortion. On the other hand, the interstitial mercury should be stable in the Hg^{2+} charge state and no EPR signal should be observed ($S = 0$). The results shown in Fig. 3 seem to indicate that interstitial mercury does not clearly introduce deep levels in the band gap of silicon.

Ir, Os, Re, and W as impurities in silicon give rise to many levels in the crystal band gap, most associated with complexes formed with the usual dopants boron and phosphorus.⁷ It has been suggested that these impurities as isolated atoms introduce levels near the middle of the crystal band gap.⁷ The results of our calculations depicted in Fig. 1 show that these impurities at substitutional sites give rise to two one-electron levels in the band-gap, of a_1 and e symmetries. For all impurities the a_1 level is always close to the central region of the gap. For Re and W the energy difference between the a_1 and e states is

very small. Therefore, the calculations confirm the hypothesis that isolated Ir, Os, Re, and W lead to deep levels near the central region of the gap.

As far as the levels associated with complexes are concerned, one should first observe that Ir, Os, and Re are elements which have a strong tendency to form coordination compounds and may exhibit many valence states, the higher ones being most stable. According to the results shown in Fig. 3, interstitial Os, Re, and W introduce impurity levels close to the continuum of the conduction band occupied by various electrons. Therefore, we observe that the lighter $5d$ elements at interstitial sites have the possibility of exhibiting highly ionized states. As a consequence, they are candidates to form complexes with other impurities. The assumption that the observed complex-related levels are associated with the impurity ions at the interstitial sites is highly likely.

IV. FINAL REMARKS

We have studied the chemical trends of the resonances and impurity gap levels induced by the substitutional and T -site interstitial $5d$ TM atoms in silicon. The one-electron energy spectra have been determined for Hg, Au, Pt, Ir, Os, Re, and W neutral impurities. The calculations yield the conclusion that the overall trends displayed by the $5d$ -derived resonances and by the impurity gap levels are quite similar to those inferred from previous calculations for the $3d$ TM impurities in silicon. However, there are two striking differences between the present calculations and those carried out previously for the $3d$ TM atoms in silicon: Firstly, our results show the presence of a nondegenerate a_1 level within the band gap for substitutional Pt and the remaining lighter elements. According

to previous calculations for the $3d$ substitutional TM atoms in silicon, this level remains a resonance in the upper part of the valence band; secondly, our calculations for the interstitial Ir, Os, and Re impurities show that the t_2 impurity level in the gap lies above the e level. Previous cluster and Green's-function calculations for their $3d$ interstitial counterparts Co, Fe, and Mn indicate that the t_2 level is placed below the e level, therefore, in a reversed order.

Despite the fact that the present calculations are based on a nonrelativistic one-electron model, the theory appears to be successful in reproducing the main physical properties of the widely studied Au and Pt impurities in silicon. The comparison between our calculations and the data which are available for the remaining elements analyzed here has been hindered by the fact that these impurities are much less studied than Au and Pt. However, the correlation between our calculations and the available data for these elements seems to be fairly consistent.

We remark that in the present investigation we establish some guidelines that we expect to be useful to those investigators who are performing studies of the $5d$ TM impurities in silicon.

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