

# Computation of the Stark effect in P impurity states in silicon

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We compute within the effective-mass theory and without adjustable parameters the Stark effect for shallow P donors in Si with anisotropic band structure. Valley-orbit coupling is taken into account in a nonperturbative way and scattering effects of the impurity core are included to properly describe low-lying impurity states. The ground-state energy slightly decreases with increasing electric field up to a critical value  $E_{cr} \sim 25$  keV/cm, at which the donor can be ionized by tunneling due to a field-induced mixing of the “1s-like” singlet ground state with a “2p<sub>0</sub>-like” excited state in zero field. The resulting ground-state wave function at high field extends significantly outside the potential barrier surrounding the impurity. Calculations of the hyperfine splitting and of the A-shell superhyperfine coupling constants as a function of the electric field complete the work.

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## I. INTRODUCTION

In 1998 Kane proposed a scheme of a quantum computer<sup>1</sup> in which the nuclear spins of <sup>31</sup>P substitutional impurities in silicon are used as quantum bits. Within this scheme, the single-qubit manipulation depends on the capability of tuning with an electric field the hyperfine splitting of the impurity ground state which results from the interaction between the nuclear spin of the P atom and the electron spin of the hydrogenlike impurity, proportional to the square modulus of the electron wave function at the P nucleus. The interaction between the nuclear spins (qubit-qubit interaction) at different impurity sites is mediated by the electron orbital of the impurity which—for shallow donors like Si:P—has a radius of a few nanometers. Kane’s proposal<sup>1,2</sup> has revived intense interest in shallow impurities in semiconductors, and several computational studies of the properties of such systems have been published recently.<sup>3–10</sup>

Shallow impurity states can conveniently be studied with the envelope function approximation. To calculate in a realistic way the dependence of the hyperfine splitting on the electric field, it is mandatory to take into account the following features: (i) band structure effects of the host material, i.e., the band anisotropy of silicon near the conduction band minima (CBM), (ii) the valley-orbit (VO) interaction,<sup>11</sup> i.e., the coupling by the impurity potential of electronic states belonging to different degenerate CBMs (valleys) of Si; (iii) the central-cell corrections, i.e., the difference (expected to be significant only in the central cell<sup>12</sup> containing the impurity) between the actual potential of the impurity and the screened Coulomb potential that is used to approximate its long-range part.

Several authors<sup>3–6</sup> attempted to compute P-impurity states in bulk Si or Si nanocrystals within the envelope function approximation. Most of them neglected the valley-orbit interaction; a few take it into account in an approximate<sup>10</sup> or a phenomenological way.<sup>9</sup> So far, a reliable approach including both valley-orbit effects and central-cell corrections to compute electronic properties of shallow impurities in external

electric fields is missing. In our approach we take into account the band anisotropy within the effective-mass approximation, and we are able to compute exactly, within the numerical accuracy due to the use of a finite basis set, the valley-orbit interaction of a realistically screened Coulomb potential, of the core potential, and of the electric field. By means of the envelope function of the conduction band and of a Gaussian basis set, we compute the energy levels of the shallow P impurity in silicon and the hyperfine splitting of the ground state as well as their dependence on a uniform electric field applied along the [001] direction. We will show that to reproduce correctly the Si:P ground state one has to include the central-cell corrections contribution due to impurity core electrons, a quantity that, to the best of our knowledge, nobody has taken into account before in this type of calculation. We found that the ground-state energy decreases on increasing the magnitude of the field, and that at high electric field (20–30 keV/cm) the spectrum narrowing of the 1s manifold, predicted in Ref. 9, is quite small, while the main effect is the mixing of *s,p*-like states that, at a critical value of the field  $E_{cr}$ , has as a consequence the vanishing of the hyperfine splitting. Further, we predict the dependence of the superhyperfine (SHF) splitting of the A shell as a function of electric field.

## II. SHALLOW IMPURITIES IN UNIFORM ELECTRIC FIELD

In the limit of small concentration, the Hamiltonian of a substitutional impurity in an uniform electric field  $\mathcal{E}$  reads (electron charge  $-|e|$ )

$$H = H_0 + V_{imp} - |e|\mathcal{E} \cdot \mathbf{r}, \quad (1)$$

where  $V_{imp}$  is the donor impurity potential which includes all the effects due to the presence of the guest atoms in the crystal, and  $H_0$  is the periodic Hamiltonian of the host crystal whose Bloch eigenfunctions  $e^{ik \cdot \mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$  can be calculated, e.g., by density-functional plane-wave pseudopotential tech-

niques, as is done in the present work. For shallow states, where the extra electron is weakly bound to the impurity ion, it is convenient to solve the eigenvalue problem of Hamiltonian (1) using the envelope function approximation<sup>12</sup>

$$\Psi(\mathbf{r}) \simeq \sum_{i \in \text{CBM}} e^{i\mathbf{k}_i \cdot \mathbf{r}} u_{c,\mathbf{k}_i}(\mathbf{r}) F_i(\mathbf{r}), \quad (2)$$

where the summation index  $i$  labels all the equivalent CBMs and  $\mathbf{k}_i$  are the corresponding wave vectors (hereafter, we shall omit for simplicity the conduction band index). Within this approximation one assumes that only conduction band wave functions  $u_{\mathbf{k}}$  with energy close to the CBM contribute to the expansion of the impurity wave function (for which one can safely put  $u_{\mathbf{k}} \simeq u_{\mathbf{k}_i}$ ) and neglects, in reciprocal space, the overlap between envelope functions  $F_i$  of different minima, since they are the Fourier transforms of highly delocalized shallow wave functions in real space. With these assumptions, one can also approximate the conduction band near the CBM by a quadratic form (effective-mass approximation). By taking the expectation value of the Hamiltonian  $\langle \Psi | H - E | \Psi \rangle = 0$ , one obtains a Shindo-Nara-like equation<sup>13</sup>

$$\sum_{i,j} \int d\mathbf{r} F_i^*(\mathbf{r}) \{ (\mathbf{p} \cdot \mathbf{M}_i^{-1} \cdot \mathbf{p} - E) \delta_{i,j} + e^{-i(\mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{r}} u_{\mathbf{k}_i}^*(\mathbf{r}) [V_{\text{imp}}(\mathbf{r}) - |e|\mathcal{E} \cdot \mathbf{r}] u_{\mathbf{k}_j}(\mathbf{r}) \} F_j(\mathbf{r}) = 0, \quad (3)$$

where  $\mathbf{M}_i^{-1}$  is the inverse mass tensor of the CBM,  $\mathbf{p}$  is the momentum operator, and the energy  $E$  is computed relative to the CBM.

The functions  $u_{\mathbf{k}_i}$  have the periodicity of the host crystal; we expand their product in Eq. (3) in Fourier series,

$$u_{\mathbf{k}_i}^*(\mathbf{r}) u_{\mathbf{k}_j}(\mathbf{r}) = \sum_{\mathbf{G}} C_{i,j}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (4)$$

where  $\mathbf{G}$  denotes the reciprocal lattice vectors and, as usual,<sup>14</sup> we consider only the  $\mathbf{G} = \mathbf{0}$  terms.

For  $i \neq j$ , the second term in curly bracket in Eq. (3) gives the intervalley coupling due to the impurity potential (and to the external electrostatic potential if it is present). It is convenient to decompose the impurity potential into two terms:

$$V_{\text{imp}}(\mathbf{r}) = -\epsilon^{-1} \frac{e^2}{r} + \Delta V_{\text{cell}}(\mathbf{r}); \quad (5)$$

where the first term is the Coulomb potential of the hydrogenlike impurity screened by the dielectric constant of the host crystal  $\epsilon$ ,<sup>15</sup> while the second term  $\Delta V_{\text{cell}}(\mathbf{r})$  represents the difference between the potential of the impurity (when the Coulomb tail is subtracted) and the potential of the bulk Si atom.

In the computation of  $\Delta V_{\text{cell}}$ , we have neglected the difference between the valence densities of Si:P and Si, as well as the relaxation of the host atoms surrounding the impurity, and we have approximated the central-cell correction

$$\Delta V_{\text{cell}}(\mathbf{r}) \simeq \Delta V_{\text{cc}}(\mathbf{r}) \equiv V_{\text{P}}^{\text{core}}(\mathbf{r}) - V_{\text{Si}}^{\text{core}}(\mathbf{r}) \quad (6)$$

by the difference between the (short-range) potential of (filled-shell) core electrons of Si and P atoms. The core correction potential  $\Delta V_{\text{cc}}$  has spherical symmetry, and practically vanishes outside the impurity core.

The electronic band structure of Si displays six CBMs located along the [001] and equivalent directions at a distance  $k_0 \simeq 0.85 \frac{2\pi}{a_L}$  ( $a_L$  denotes the lattice parameter of Si) from the Brillouin zone center. We use the experimental values for the high-frequency dielectric constant [ $\epsilon(\mathbf{k}=0)=11.4$ ] and the effective masses ( $m_T=0.191m_e$ ,  $m_L=0.916m_e$ ) of bulk Si. All other quantities used to solve Eq. (3) are obtained by first principles.<sup>15,16</sup>

### III. NUMERICAL TECHNIQUE

We expand the envelope functions  $F_i(\mathbf{r})$  on a Gaussian basis set:

$$e^{-\alpha r^2} r^l Y_{l,m}, \quad (7)$$

where the spherical harmonics  $Y_{l,m}$  describe the angular dependence of the impurity envelope function. The core correction term is computationally inexpensive because it involves a radial integral in the core region.<sup>17</sup> All the other matrix elements are analytically computed (i.e., we write them by elementary or special functions) with a considerable reduction of computational effort.<sup>18,19</sup> We include spherical harmonics up to  $f$  states ( $l=3$ ). The Gaussian parameters are chosen according to the formula  $\alpha = \alpha_0 \delta_\alpha^n$  where  $n = -9, -8, \dots, 8, 9$ ,  $\alpha_0 = 0.005$  a.u., and  $\delta_\alpha = 1.85$ . In total we use about  $\sim 1800$  basis functions, which ensures an accurate convergence of the results for both zero and nonzero fields, for states that are localized at the impurity.<sup>20</sup>

### IV. THEORETICAL RESULTS FOR Si:P

First, we validate our results by comparing them with experimental data for vanishing electric field. If VO interaction is neglected, the ground state of a substitutional impurity in Si is sixfold degenerate. The VO interaction partially removes this degeneracy, mixing these six  $1s$  states to obtain, according to the symmetry of the system, a singlet ( $A_1$ ), a doublet ( $E$ ), and a triplet ( $T_2$ ) state. Our computed splitting of the ground state reproduces well the experimental data at zero field. The lowest-energy states, corresponding to the  $1s$  manifold, are (experimental data from Ref. 12 are in parentheses)  $A_1 = -41.7$  ( $-45.5$ ) meV,  $E = -30.1$  ( $-32.6$ ) meV,  $T_2 = -32.3$  ( $-33.8$ ) meV. Our results are obtained without any adjustable parameters.

We stress the importance of including the core correction term, which gives the correct scattering of the shallow wave function with the impurity core. In fact, neglecting the  $\Delta V_{\text{cc}}$  contribution and considering only the intervalley coupling due to the screened Coulomb potential, we found that the  $A_1$  ground state has an energy that is considerably lower (less than  $\sim -120$  meV) than the core-corrected one, while we find very similar results (with differences within  $\sim 2$  meV) for  $E$  and  $T_2$  states. The importance of including  $\Delta V_{\text{cc}}$  in the

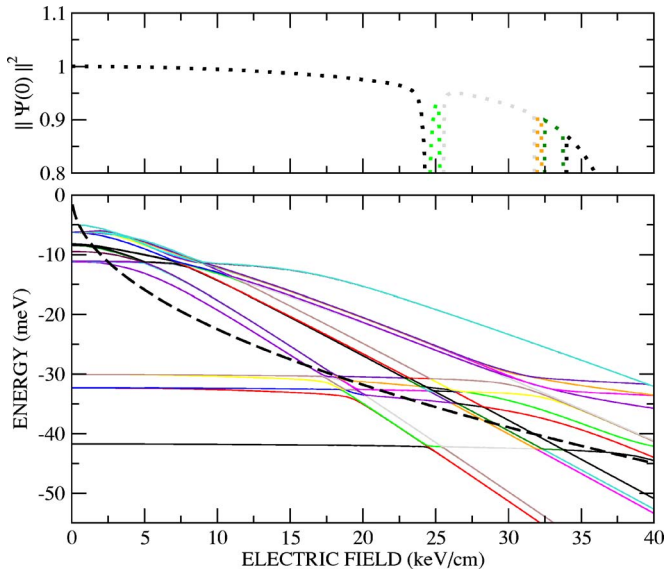


FIG. 1. (Color online) Bottom panel: the lowest-energy levels of Si:P (solid lines); the black dashed line denotes the minimum of the barrier energy. Top panel: the square modulus of the corresponding wave functions computed at the impurity site and normalized to the zero-field value. Each  $\|\Psi(0)\|^2$  is denoted with the same gray scale (color) of the corresponding energy level (the black dotted line denotes the ground state).

study of VO effects has not been noticed in the past since intervalley coupling has frequently been neglected or included in an approximate or in a phenomenological way (i.e., by using experimental parameters). Considering the studies<sup>11,21</sup> where VO effects due to the screened Coulomb potential were included in the Hamiltonian and the ground energy was obtained with a variational wave function,<sup>12</sup> our data suggest that the agreement between theory and experiment must be considered as fortuitous, and that the neglect of the repulsive  $\Delta V_{cell}$  potential term is likely compensated by the use of a variational trial function with a few adjustable parameters only.

In the bottom panel of Fig. 1 we display the calculated impurity-level energy [continuous (colored) lines] as a function of a uniform electric field applied along the [001] direction; the dashed line denotes the ionization threshold, i.e., the minimum of the energy barrier that separates bound states localized inside the barrier near the impurity from states localized outside the barrier, in a region of space where they are superposed on the free-wave solutions of Eq. (1), and corresponding to ionized states. Looking at Fig. 1 we notice that the  $2s$  and  $2p$  manifolds (at  $\mathcal{E}=0$  these states have an energy  $-6$  to  $-11$  meV) are ionized at fields of a few keV/cm. The excited states that at zero field have energy  $\sim -11$  meV correspond to the  $2p_0$  manifold (they form a doublet, a singlet, and a triplet which are separated in energy by  $\sim 0.1$  meV). In particular, the states that originate from the  $2p_0$  doublet have the lowest energy among the states of this manifold also at nonvanishing field and, by increasing the field, at  $\mathcal{E} \sim 3$  keV/cm their energy equals the ionization threshold and they become ionized; however, at  $\mathcal{E} \gtrsim 16$  keV/cm their energy is again lower than the ioniza-

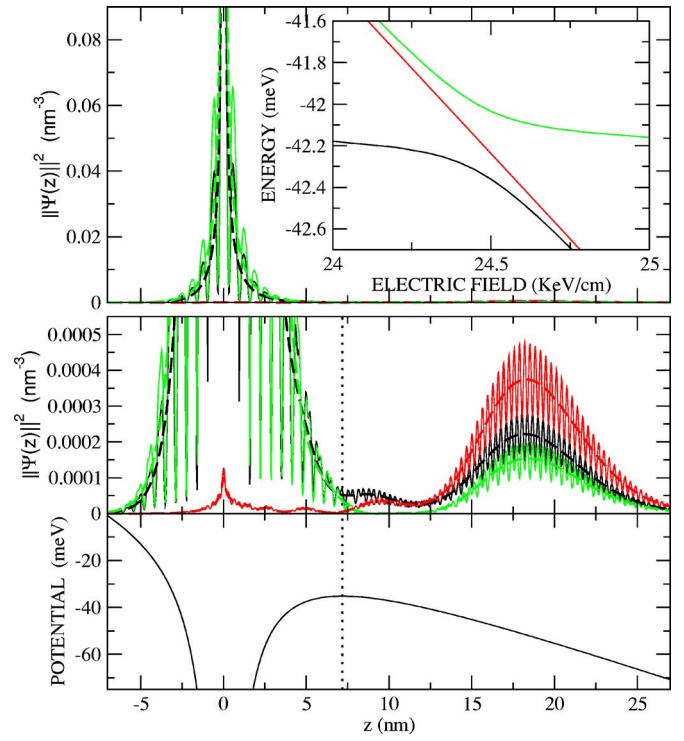


FIG. 2. (Color online) Square modulus of the impurity wave function (solid lines) and of the corresponding envelope function ( $\sum_i \|F_i(z)\|^2$ , dashed lines) for the three lowest-energy states (in black, red, and green) of Si:P (top and middle panel with different vertical scales) and the sum of electric field and screened Coulomb potential (bottom panel) as a function of the Cartesian coordinate  $z$ . The rapid oscillatory behaviors are fingerprints of interferences between states from different conduction band valleys.  $\mathcal{E}=(0,0,24.5)$  keV/cm. The vertical dotted line corresponds to (the saddle point at) the minimum of the energy barrier surrounding the impurity. Inset: the same as bottom panel of Fig. 1 on a magnified scale.

tion threshold. This astonishing behavior will be explained later. Now we focus on the critical field  $\mathcal{E}_{cr} \approx 24.5$  keV/cm,<sup>22</sup> when the energy of these two  $2p_0$ -like states becomes comparable (see inset of Fig. 2) to the energy of the singlet ( $A_1$ )  $1s$ -like state corresponding to the ground state of the system. This is the case relevant for quantum computing (similar crossings also occur between the  $2p_0$  states and the  $E$  and  $T_2$  states of the  $1s$  manifold). At this field the  $A_1$  ( $1s$ ) state and one of the  $2p_0$  states anticross each other and at fields larger than  $\mathcal{E}_{cr}$  the ground state of the system becomes  $p$ -like. As a consequence, the square modulus of the ground-state wave function at the impurity site (displayed in the top panel of Fig. 1) decreases dramatically at  $\mathcal{E}_{cr}$  and, with it, the hyperfine interaction between nuclear and electron spins. Notice that, since  $1s$  and  $2p_0$  states have the same magnetic quantum number  $m=0$  their energy levels display anticrossing behavior<sup>23</sup> at  $\mathcal{E}_{cr}$ . To understand the physical mechanisms involved we have plotted in Fig. 2 the wave functions of these states along the  $z$  axis (top and middle panel), and the energy barrier (bottom panel) separating the states localized near the impurity (at the origin) from the free-electron region (in the right part of the figure). At  $\mathcal{E}_{cr}$  the first excited states



(in red) is a “pure”  $2p_0$ -like state and it is mainly localized outside the barrier at the “hill” at  $z \sim 18$  nm. It corresponds to an ionized state even if its energy is lower than the ionization threshold: the electron in this state can cross over the energy barrier at  $\mathcal{E} \sim 3$  keV/cm, when its energy is higher than the ionization threshold and, by increasing the field, the energy is lowered below the threshold but the state remains localized outside the barrier. For fields slightly smaller than  $\mathcal{E}_{cr}$ , the second excited state is localized outside the barrier since it is a  $2p_0$ -like state, while the  $A_1$  ( $1s$ ) ground state is localized within the impurity barrier. At  $\mathcal{E}_{cr}$  the latter two states mix as shown in Fig. 2; analysis of their wave function shows that the electron in the ground state is mainly localized at the impurity, but it has also a non-negligible probability to be outside the barrier (the hill in black on the right of the middle panel of Fig. 2). At fields larger than  $\mathcal{E}_{cr}$  the ground state is  $2p_0$ -like and is outside the barrier, in the region corresponding to ionized states. Physically, since the ground state always has an energy lower than the ionization threshold, it is localized within the barrier up to  $\mathcal{E}_{cr}$ , but at the critical field it becomes ionized since by a tunnel effect it mixes with the  $2p_0$ -like state outside the barrier.

Our results show that the energy range of the  $1s$  manifold narrows for increasing electric field, as predicted by Friesen,<sup>9</sup> the ground state slightly decreases with increasing field up to  $\mathcal{E}_{cr}$ ; however, the narrowing of the energy range of the  $1s$  manifold is quite small before the  $1s$  state mixes with upper ( $p$ -like) states (this latter effect was not considered in Friesen’s work).

In Kane’s quantum computer the electric field is used not only to tune the hyperfine interaction, but also to allow, via the exchange interaction, the shallow wave function of a P impurity to interact with a neighboring P nucleus. For this reason, it is important to know how the ground-state wave function is modified by an electric field not only at the impurity site but also at other nuclear sites. To deal with a directly measurable quantity we consider the Fermi contact SHF constant obtained in electron-nuclear double resonance (ENDOR) measurements.<sup>24</sup> The SHF constants are proportional to the square modulus of the (impurity) ground-state wave function evaluated at the nucleus of atoms surrounding the impurity.<sup>25</sup> At zero field, due to symmetry, all atoms belonging to a given shell of neighbors, have the same SHF constant.

To study the dependence of the SHF splitting on the electric field strength we consider here only the  $A$  shell corresponding to the largest SHF constant at zero field (and it has atoms placed according to the field direction). This shell consists of the six Si atoms at  $(\pm a_L, 0, 0)$ ,  $(0, \pm a_L, 0)$ , and  $(0, 0, \pm a_L)$ . At zero field, for symmetry reasons, all these atoms have the same value of SHF constant, but the electric field lifts this degeneracy.

TABLE I. SHF interaction of  $A$  shell (in MHz) for Si:P at different values of (001)-directed electric field (in keV/cm).

|                   | Field |       |       |       |       |
|-------------------|-------|-------|-------|-------|-------|
|                   | 0     | 5     | 10    | 15    | 20    |
| (0,0,4)           | 5.238 | 5.253 | 5.251 | 5.230 | 5.180 |
| (0,0, $\bar{4}$ ) | 5.238 | 5.206 | 5.158 | 5.090 | 4.995 |
| (4,0,0)           | 5.238 | 5.232 | 5.213 | 5.179 | 5.122 |

Our result for the SHF interaction<sup>26</sup> of the  $A$  shell at zero field is  $a=5.238$  MHz to be compared with the experimental value  $a=5.962$  MHz;<sup>24</sup> other theoretical results taken from the literature are  $a=2.963$  MHz obtained by first-principles calculations,<sup>7</sup>  $a=5.848$  MHz obtained with a multiband approach,<sup>27</sup> and  $a=8.414$  MHz obtained in a traditional envelope function calculation.<sup>27</sup>

In Table I we display the SHF interaction calculated for all nonequivalent positions of the  $A$  shell and for different values of a [001] electric field. They show both linear and quadratic dependence of the SHF coupling on the electric field and, more remarkably, they suggest the possibility of measuring these effects also at small fields (at  $\mathcal{E}=5$  keV/cm the difference between SHF couplings of nonequivalent atoms in the  $A$  shell is  $\sim 1.0\%$ ).<sup>28</sup> We see in Table I that, while in general the shell atoms with negative or null  $z$  have a reduction of the wave density, as expected (the field is pointing to positive  $z$ ), the atom at (004) has a SHF coupling that increases for small electric field and decreases for  $\mathcal{E} \gtrsim 10$  keV/cm since the electron is taken away from the impurity in the direction of the field.<sup>29</sup>

## V. CONCLUSIONS

In summary, we have developed a robust and efficient method based on a Gaussian basis set for the computation of shallow impurity states in semiconductors without adjustable parameters. The method takes into account valley-orbit coupling in a nonperturbative way and the interaction with the impurity core. Application of the method to the Stark effect for shallow P impurities in silicon shows that the energy of the  $1s$ -like ground state decreases with increasing electric field up to a value at which it anticrosses a  $2p_0$ -like excited state: the ground state becomes  $p$ -like, the hyperfine coupling drops, and the wave function extends significantly in the region of space corresponding to free (ionized) states.<sup>30</sup> Our technique allows us to give reliable predictions of the hyperfine and SHF coupling as a function of electric field.

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- <sup>17</sup>The core term can also be computed analytically by fitting the core density with an appropriate function.
- <sup>18</sup>A. Debernardi (unpublished).
- <sup>19</sup>All computations have been performed on a PC with a Pentium IV 2.80 GHz processor.
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- <sup>28</sup>The accuracy of ENDOR data (measured at zero field) in Ref. 24 is about 0.1%.
- <sup>29</sup>Similar SHF effects were also found for the other shells (Ref. 18).
- <sup>30</sup>This prediction seems to be confirmed by recent experiments, M. Fanciulli *et al.* (unpublished).