

**Donor electron wave functions for phosphorus in silicon: Beyond effective-mass theory**

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We calculate the electronic wave function for a phosphorus donor in silicon by numerical diagonalization of the donor Hamiltonian in the basis of the pure crystal Bloch functions. The Hamiltonian is calculated at discrete points localized around the conduction band minima in the reciprocal lattice space. Such a technique goes beyond the approximations inherent in the effective-mass theory, and can be modified to include the effects of altered donor impurity potentials and externally applied electrostatic potentials, as well as the effects of lattice strain. Modification of the donor impurity potential allows the experimentally known low-lying energy spectrum to be reproduced with good agreement, as well as the calculation of the donor wave function, which can then be used to calculate parameters important to quantum computing applications.

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**I. INTRODUCTION**

The electronic states of phosphorus donors in silicon are of increasing interest in the field of quantum computing due to the fundamental role they play in several promising proposals for a scalable quantum information processor. The precise nature of the qubits differ between proposals, and include nuclear spin,<sup>1</sup> electron spin,<sup>2</sup> or the low-lying electronic states of an ionized two-donor system.<sup>3</sup> Common to all these proposals, however, is the way in which quantum information processing is implemented, through external coherent control of the electron wave function of the phosphorus donor. The rigors of implementing large-scale quantum algorithms on such a device are such that these wave functions must be controlled to a remarkable precision—for example, standard estimates require an error of no more than one part in 10 000 per fundamental quantum operation. To meet these stringent requirements it is vital to have a detailed understanding of the electronic wave function of the phosphorus donor. Although the study of these states is quite mature, this level of understanding is currently lacking.

Experimentally, the spectrum of these donor electron states is quite well known,<sup>4–6</sup> and much sophisticated theory has been developed to try and understand these results. The standard description of these donor states, the effective-mass theory of Kohn and Luttinger,<sup>7–9</sup> has been very successful in predicting the qualitative nature of these states; however, precise numerical agreement with experiment has been elusive. The theory is based around the expansion of the wave function in the Bloch states of the pure silicon crystal. The coefficients of this expansion form an envelope function, and it is the reduction of the equation determining this envelope function to a set of six, nonisotropic, hydrogenlike equations that forms the core of the effective-mass approach. Modifications to this model can then be made to include effects such as the valley-orbit coupling that is responsible for the lifting of the sixfold ground-state degeneracy observed experimentally. Generally, however, these additions to the theory are handled in a somewhat *ad hoc* manner, and are often inconsistent with the approximations made in deriving the theory in the first place.

In this paper we address these issues by applying a numerical approach where some of the simplifications inherent in the effective-mass theory are avoided, and the exact Hamiltonian describing the donor electron is solved, using a truncated basis. This approach allows the inclusion of non-Coulombic donor potentials, which can provide the valley-orbit coupling necessary to lift the ground-state degeneracy, in a manner that is consistent with the theory.

The paper is organized as follows. We begin with a review of the standard effective-mass theory in Sec. II, paying particular attention to the approximations inherent in the treatment. In Sec. III we outline our numerical approach to the problem, focusing on the construction of the donor Hamiltonian matrix, and the choice of Bloch-basis states. Section IV contains results for a corrected impurity potential, which provides the necessary valley-orbit coupling to reproduce the known ground-state energy, and approximate the energy of the low-lying excited states. In Sec. V the wave function obtained from these calculations is used to calculate the strength of the exchange coupling between neighboring donors, as a function of the donor separation. These results are compared with results obtained using Kohn-Luttinger-type effective-mass wave functions for a Coulombic impurity potential.<sup>10–12</sup> The effect of the non-Coulombic impurity potential is to increase the localization of the donor wave function, which leads to a reduced exchange coupling when compared to estimates based on a Coulombic impurity potential. In Sec. VI we calculate the electronic wave function for donors in uniaxially stressed silicon, and use the resulting wave function to calculate the exchange coupling between neighboring donors. We qualitatively reproduce the results of Koiller *et al.*<sup>12</sup> which show that this strain can be used to eliminate the exchange oscillations for donors in the same [001] plane, and that the strength of the interaction is generally increased when compared to the unstrained case. Section VII illustrates how this numerical method also has the freedom of including externally applied electric potentials, such as those generated by the control gates used to manipulate the state of the donor electron with the goal of implementing quantum information processing, in a straight-forward fashion. We solve for the case of a uniform applied electric field, and calculate the shift in the electron-nuclear contact hyper-

fine coupling strength, as both a function of the strength of the applied field, and the distance of the donor from a silicon oxide barrier. We compare these results with those obtained using a tight-binding approach<sup>13</sup> in which the donor wave function is solved by expanding in a basis of states localized in real space, and extending over several hundreds of thousands of silicon atoms. We finish with some concluding remarks and a brief discussion of some potential applications for this approach.

## II. EFFECTIVE-MASS THEORY

The theory of shallow donor electron states in silicon was developed by Kohn and Luttinger in the mid 1950s,<sup>7,9,14</sup> in what has become known as effective-mass theory. In this section we will briefly review this theory; a more detailed discussion can be found in Ref. 15.

The aim is to find the low-energy solutions of the Schrödinger equation for the donor electron wave function,

$$[H_0 + U(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1)$$

where  $H_0$  is the Hamiltonian for the pure silicon crystal and  $U(\mathbf{r})$  is the impurity potential due to the presence of the phosphorus ion. To this end it is natural to expand solutions in terms of the eigenstates of the pure crystal Hamiltonian, the Bloch functions for silicon,  $\phi_{\mathbf{k}}(\mathbf{r})$ ,

$$\psi(\mathbf{r}) = \int F(\mathbf{k})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{k}. \quad (2)$$

Substituting this into Eq. (1), multiplying from the left by  $\phi_{\mathbf{k}'}^*(\mathbf{r})$ , and integrating over all space leads to

$$EF(\mathbf{k}') = E_{\mathbf{k}'}F(\mathbf{k}') + \int \phi_{\mathbf{k}'}^*(\mathbf{r})U(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})F(\mathbf{k})d\mathbf{k}d\mathbf{r}, \quad (3)$$

where we have used the eigenstructure of the pure crystal,  $H_0\phi_{\mathbf{k}'}(\mathbf{r}) = E_{\mathbf{k}'}\phi_{\mathbf{k}'}(\mathbf{r})$ . The Bloch states can be expanded in terms of functions that share the periodicity of the crystal lattice  $\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$ , with  $u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$ . The  $\mathbf{G}$  are reciprocal lattice vectors of the silicon crystal, and have the property  $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ , where  $\mathbf{R}$  is an integer multiple of the fundamental translation vectors of the crystal. The coefficients  $A_{\mathbf{k},\mathbf{G}}$  are obtained using a pseudopotential method which has been parametrized to reproduce the band structure of the pure silicon crystal.<sup>16</sup> Expanding the Bloch functions in Eq. (3) yields

$$\begin{aligned} EF(\mathbf{k}') &= E_{\mathbf{k}'}F(\mathbf{k}') + \int \sum_{\mathbf{G},\mathbf{G}'} A_{\mathbf{k}',\mathbf{G}'}^* A_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} U(\mathbf{r}) \\ &\quad \times F(\mathbf{k})d\mathbf{k}d\mathbf{r} \\ &= E_{\mathbf{k}'}F(\mathbf{k}') + \int \sum_{\mathbf{G},\mathbf{G}'} A_{\mathbf{k}',\mathbf{G}'}^* A_{\mathbf{k},\mathbf{G}} \\ &\quad \times \tilde{U}(\mathbf{k}-\mathbf{k}'+\mathbf{G}-\mathbf{G}')F(\mathbf{k})d\mathbf{k}, \end{aligned} \quad (4)$$

where  $\tilde{U}(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{r}}U(\mathbf{r})d\mathbf{r}$  is the Fourier transform of the impurity potential. It is at this point that the three main approxi-

mations which lead to the effective-mass equation (EME) are made.

The first is to expand  $E_{\mathbf{k}'}$  to second order in  $\mathbf{k}' - \mathbf{k}_{\mu}^{(0)}$ , around the six, degenerate, conduction-band minima located at the points

$$\{\mathbf{k}_{\mu}^{(0)}\}_{\mu=1..6} = \frac{2\pi}{d} \{(0,0,\pm 0.85), (0,\pm 0.85,0), (\pm 0.85,0,0)\}, \quad (5)$$

where  $d=5.43 \text{ \AA}$  is the lattice constant of silicon. This expansion allows the Bloch energies to be written in the form of an effective kinetic energy  $E_{\mathbf{k}'} \approx \sum_{\mu} [k_{\parallel}'^2/(2m_{\parallel}^*) + \mathbf{k}_{\perp}'^2/(2m_{\perp}^*)]$ , with nonisotropic effective masses  $m_{\perp}^* \neq m_{\parallel}^*$ . In this expression  $k_{\parallel}'$  is the component of  $\mathbf{k}' - \mathbf{k}_{\mu}^{(0)}$  that is parallel to the displacement from the origin of the  $\mu$ th conduction band minimum in reciprocal space, and  $\mathbf{k}_{\perp}'$  denotes the components perpendicular to this direction. The  $m_{\perp}^*, m_{\parallel}^*$  are the effective electron masses, which are nonisotropic, reflecting the nonisotropic nature of the conduction-band minima. This approximation holds as long as the donor electron wave function is sufficiently localized around the conduction-band minima, which is a condition that seems to be well satisfied for phosphorus donors in silicon, and yields from Eq. (4)

$$\begin{aligned} EF(\mathbf{k}') &= \sum_{\mu} [k_{\parallel}'^2/(2m_{\parallel}^*) + \mathbf{k}_{\perp}'^2/(2m_{\perp}^*)]F(\mathbf{k}') \\ &\quad + \int \sum_{\mathbf{G},\mathbf{G}'} A_{\mathbf{k}',\mathbf{G}'}^* A_{\mathbf{k},\mathbf{G}} \tilde{U}(\mathbf{k}-\mathbf{k}'+\mathbf{G}-\mathbf{G}')F(\mathbf{k})d\mathbf{k}. \end{aligned} \quad (6)$$

The second approximation is to ignore terms in potential for which  $\mathbf{G} \neq \mathbf{G}'$ , the assumption being that  $|\tilde{U}(\mathbf{k}-\mathbf{k}'+\mathbf{G}-\mathbf{G}')| \ll |\tilde{U}(\mathbf{k}-\mathbf{k}')|$ , over the range in which  $F(\mathbf{k})$  is significant. This is well satisfied for a Coulombic impurity potential  $\tilde{U}(\mathbf{k}) \sim 1/\mathbf{k}^2$  in silicon, where the magnitude of the reciprocal lattice vectors is  $|\mathbf{G}| = n2\pi/d$ . It is, however, well known that this approximation is not consistent with the lifting of the sixfold ground-state degeneracy observed experimentally. Such a spectrum can only be produced by a potential that introduces significant valley-orbit coupling, that is, coupling between Bloch functions located at different conduction-band minima, which are separated in reciprocal space by  $\Delta\mathbf{k} \approx 1.2 \times 2\pi/d$  and  $1.7 \times 2\pi/d$ , for valleys on orthogonal and parallel axes, respectively. Thus any potential that is sufficiently broad in reciprocal space to produce the required valley-orbit coupling to correctly predict the low-energy donor spectrum, will not satisfy this approximation in the effective-mass formalism. None the less, this approximation is inherent in the effective-mass approach and allows Eq. (6) to be reduced to

$$\begin{aligned} EF(\mathbf{k}') &= \sum_{\mu} [k_{\parallel}'^2/(2m_{\parallel}^*) + \mathbf{k}_{\perp}'^2/(2m_{\perp}^*)]F(\mathbf{k}') \\ &\quad + \int \sum_{\mathbf{G}} A_{\mathbf{k}',\mathbf{G}}^* A_{\mathbf{k},\mathbf{G}} \tilde{U}(\mathbf{k}-\mathbf{k}')F(\mathbf{k})d\mathbf{k}. \end{aligned} \quad (7)$$

Finally, in deriving the EME, it is assumed that the Bloch coefficients are independent of  $\mathbf{k}$ ,  $A_{\mathbf{k}',\mathbf{G}} \approx A_{\mathbf{k},\mathbf{G}}$ , in the vicinity of the conduction-band minima, over which the magnitude of the envelope function is significant. This is true in the immediate vicinity of the conduction-band minima, but breaks down in the vicinity of the Brillouin zone boundary. This approximation, along with the identity  $\sum_{\mathbf{G}} |A_{\mathbf{k},\mathbf{G}}|^2 = 1$ , finally yields from Eq. (7) the multivalley effective-mass equation (MV EME):

$$E \sum_{\mu} F_{\mu}(\mathbf{k}') = \hbar^2 [k_{\parallel}'^2 / (2m_{\parallel}^*) + \mathbf{k}_{\perp}'^2 / (2m_{\perp}^*)] \sum_{\mu} F_{\mu}(\mathbf{k}') + \int \tilde{U}(\mathbf{k} - \mathbf{k}') \sum_{\mu} F_{\mu}(\mathbf{k}) d\mathbf{k}. \quad (8)$$

Here we have written the envelope function  $F(\mathbf{k}) = \sum_{\mu} F_{\mu}(\mathbf{k})$ , which is consistent with the final approximation above, where it is assumed that the envelope functions are strongly localized around each of the conduction-band minima.

In the absence of so-called valley-orbit coupling, that is, for potentials for which the second approximation is well satisfied, Eq. (8) decouples into six independent single-valley effective-mass equations (SV EMEs):

$$E F_{\mu}(\mathbf{k}') = \hbar^2 [k_{\parallel}'^2 / (2m_{\parallel}^*) + \mathbf{k}_{\perp}'^2 / (2m_{\perp}^*)] F_{\mu}(\mathbf{k}') + \int \tilde{U}(\mathbf{k} - \mathbf{k}') F_{\mu}(\mathbf{k}) d\mathbf{k}. \quad (9)$$

For a Coulombic impurity potential, this is isomorphic to a nonisotropic, hydrogenic, Schrödinger equation in momentum space. Such an equation cannot, in general, be solved analytically; however, for the case of phosphorus donors Kohn and Luttinger<sup>8</sup> proposed approximate solutions of the form

$$F_{\pm z}(\mathbf{r}) = \frac{\exp[-\sqrt{(x^2 + y^2)/a_{\perp}^2 + z^2/a_{\parallel}^2}]}{\sqrt{6\pi a_{\perp}^2 a_{\parallel}}}, \quad (10)$$

where  $F_{\mu}(\mathbf{r}) = \int e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} F_{\mu}(\mathbf{k}) d\mathbf{r}$ . The nonisotropic effective Bohr radii  $a_{\perp}$  and  $a_{\parallel}$ , are variational parameters, determined by minimizing the energy of the state.

The ground-state donor electron wave function, found in this way, is sixfold degenerate, and is given by linearly independent combinations of the functions

$$\psi(\mathbf{r})_{\mu} = F_{\mu}(\mathbf{r}) \phi_{\mathbf{k}^{(0)}}(\mathbf{r}). \quad (11)$$

As mentioned earlier, this sixfold degeneracy of the ground state is at odds with experimental observation that the ground state is a singlet with binding energy 45.5 meV, lying 11.85 meV below a triplet state which is, in turn, 1.42 meV below a doublet state. This lifting of the ground-state degeneracy can be predicted from group-theoretical considerations, due to the breaking of the crystal symmetry. The splitting can only be produced by a potential that is strong enough to couple the different valleys. Group-theoretical arguments give the low-lying energy states as

$$\psi(\mathbf{r})^i = \sum_{\mu} \alpha_{\mu}^i F_{\mu}(\mathbf{r}) \phi_{\mathbf{k}^{(0)}}(\mathbf{r}), \quad (12)$$

where the coefficients are given by

$$\left. \begin{aligned} \alpha^1 &= \frac{1}{\sqrt{6}}(1, 1, 1, 1, 1, 1), A_1, \\ \alpha^2 &= \frac{1}{\sqrt{12}}(-1, -1, -1, -1, 2, 2) \\ \alpha^3 &= \frac{1}{2}(1, 1, -1, -1, 0, 0) \end{aligned} \right\}, \quad E, \\ \left. \begin{aligned} \alpha^4 &= \frac{1}{\sqrt{2}}(1, -1, 0, 0, 0, 0) \\ \alpha^5 &= \frac{1}{\sqrt{2}}(0, 0, 1, -1, 0, 0) \\ \alpha^6 &= \frac{1}{\sqrt{2}}(0, 0, 0, 0, 1, -1) \end{aligned} \right\}, \quad T_1. \quad (13)$$

Here the labels on the right denote the irreducible representation of the  $T_d$  symmetry group to which the states belong; states in the same representation are degenerate. This wave function is the cornerstone of the effective-mass formalism, and it is axiomatic within the theory that the ground-state wave function is of this form; however, the effect of the valley-orbit coupling has been handled in a rather *ad hoc* manner. While the effective-mass formalism can be used to give a reasonable prediction of the low-lying energy spectrum, with the inclusion of a phenomenological valley-orbit term in the potential, the inclusion of such a term is inconsistent with the approximations inherent in the effective-mass procedure.

### III. BEYOND THE EFFECTIVE-MASS FORMALISM

To correctly predict the low-lying energy spectrum of a phosphorus donor electron in silicon, it is necessary to treat the intervalley or valley-orbit coupling, produced by the impurity potential. In the previous section we have argued that the treatment of such a potential is beyond the scope of some of the approximations that go into deriving the EME. Therefore, instead of looking for solutions of the EME, we take the approach of directly solving the exact Schrödinger equation for the donor electron, Eq. (4). This is done by discretizing the integral equation to reduce the problem to that of finding the eigensolution of the Hamiltonian matrix in a truncated basis of Bloch states. Our method proceeds as follows. The discretized version of the Schrödinger equation, Eq. (4), can be written as a matrix equation

$$E f_{\mathbf{k}'} = E_{\mathbf{k}'} f_{\mathbf{k}'} + \sum_{\mathbf{k}, \mathbf{G}, \mathbf{G}'} \sqrt{\omega_{\mathbf{k}} \omega_{\mathbf{k}'}} A_{\mathbf{k}', \mathbf{G}'}^* A_{\mathbf{k}, \mathbf{G}} \times \tilde{U}(\mathbf{k} - \mathbf{k}' + \mathbf{G} - \mathbf{G}') f_{\mathbf{k}}, \quad (14)$$

where  $\omega_{\mathbf{k}} \propto \Delta \mathbf{k}$  is an integration constant, and  $f_{\mathbf{k}} = F(\mathbf{k}) \sqrt{\omega_{\mathbf{k}}}$ .

TABLE I. Ground-state binding energies (meV) obtained for single- and multivalley methods using isotropic and nonisotropic point sampling as described in the text. Compare these with 28.9 meV for the multivalley EME and 28.8 meV for the single-valley EME.

	$N$						
	5	7	9	11	13	15	17
MV nonisotropic	19.6	25.0	29.3	30.3			
MV isotropic	19.3	20.6	25.4	28.6			
SV nonisotropic	19.6	24.9	29.1	30.1	30.3	30.4	30.4
SV isotropic	19.3	20.6	25.3	28.4	29.5	29.8	29.9

Of course, in the limit that we sample  $\mathbf{k}$  at an infinitely dense set of points along the entire conduction band, this equation is completely equivalent to Eq. (4). Computational limitations restrict us to a much more limited set of sample points, which need to be chosen carefully to optimize the accuracy of the solution.

We initially solve the problem for the Coulombic impurity potential, before proceeding to include corrections. The use of a Coulombic potential  $U(\mathbf{q})=2/(\kappa\pi^2\mathbf{q}^2)$  presents a difficulty, namely, the presence of a singularity at  $\mathbf{q}=0$ . This singularity is, of course, integrable; however, it does present problems for the discretized equation. The singularity can be treated by the use of an appropriate regularizing function<sup>17</sup>

$$S(\mathbf{q}, \mathbf{q}') = \frac{(1/\alpha^2 + \mathbf{q}^2)^2}{(1/\alpha^2 + \mathbf{q}'^2)^2}. \quad (15)$$

This function has the key properties that  $S(\mathbf{q}, \mathbf{q})=1$ , and it is analytically integrable,

$$\int S(\mathbf{q}, \mathbf{q}')/(\mathbf{q} - \mathbf{q}')^2 d\mathbf{q}' = \pi^2(1/\alpha + \alpha q^2). \quad (16)$$

The singularity is removed by addition and subtraction of this regularizing function into the summand. If we ignore the possibility that  $\mathbf{k} - \mathbf{k}' + \mathbf{G} - \mathbf{G}' = 0$ ,  $\mathbf{G} \neq \mathbf{G}'$ , which is a weaker form of approximation 2 in the effective-mass formalism above, this gives

$$\begin{aligned} Ef_{\mathbf{k}'} = E_{\mathbf{k}'}f_{\mathbf{k}'} - \frac{1}{\kappa\pi^2} \sum_{\mathbf{k}} \left( \sum_{\mathbf{G} \neq \mathbf{G}'} \frac{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}A_{\mathbf{k}',\mathbf{G}'}^*A_{\mathbf{k},\mathbf{G}}}{(\mathbf{k} - \mathbf{k}' + \mathbf{G} - \mathbf{G}')^2} f_{\mathbf{k}} \right. \\ \left. - \frac{A_{\mathbf{k}',\mathbf{G}'}^*A_{\mathbf{k},\mathbf{G}}[f_{\mathbf{k}}\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}} - f_{\mathbf{k}'}\omega_{\mathbf{k}}S(\mathbf{k}', \mathbf{k})]}{(\mathbf{k} - \mathbf{k}')^2} \right) \\ \left. - \frac{f_{\mathbf{k}'}(1/\alpha + \alpha k'^2)}{\kappa} \right). \end{aligned} \quad (17)$$

The parameter  $\alpha$ , in the regularizing function, can be adjusted to optimize the efficiency of the method. In the case of an isotropic hydrogenic Schrödinger equation, setting  $\alpha = \kappa/m^*$ , where  $\kappa = \epsilon/\epsilon_0$  and  $m^*$  is the (isotropic) effective mass, is optimal. In our case, we use  $m^* = m_{\perp} = 0.191$ .

The set of points chosen, in the case of the bare Coulombic potential, is guided by the optimized Kohn-Luttinger solution to the SV EME, which we expect to be a good ap-

proximation for the exact solution using this potential. Accordingly, we choose points located around the six conduction-band minima. Due to the known anisotropy of the EME solution, we find that best results are obtained when the spacing of points in the longitudinal direction around each minimum are 1.7 times greater than those in the transverse directions. The points are chosen in such a way that  $\Delta k_{\parallel} = 0.29 \times 2\pi/[d(N-1)]$ ,  $\Delta k_{\perp} = \Delta k_{\parallel}/1.7$ , with the total number of points  $N_t = 6 \times N^3$ . Points chosen in this way ensure that a point is taken at each of the conduction-band minima, and that a point is taken close to the edge of the Brillouin zone. In practice, memory limitations restrict  $N \leq 11$ . In Table I we present ground-state binding energies obtained using both the nonisotropic and the isotropic ( $\Delta k_{\perp} = \Delta k_{\parallel}$ ) sampling. The nonisotropic sampling produces the best results in this situation, and for  $N=11$  the results seem to have converged, and are in good agreement with those obtained from effective-mass theory.

#### IV. CORRECTED IMPURITY POTENTIALS

Pantelides<sup>18</sup> introduced a non-Coulombic correction to the impurity potential based on the nonstatic properties of the dielectric function:

$$\frac{1}{\epsilon(\mathbf{q})} = \frac{Aq^2}{q^2 + \alpha^2} + \frac{(1-A)q^2}{q^2 + \beta^2} + \frac{1}{\epsilon(0)} \frac{\gamma^2}{q^2 + \gamma^2}, \quad (18)$$

where  $\epsilon(0) = 11.9\epsilon_0$  is the static dielectric constant for silicon. The parameters, in atomic units, are  $A=1.175$ ,  $\alpha=0.7572$ ,  $\beta=0.3123$ , and  $\gamma=2.044$ . If considered as a correction to a Coulombic potential with static dielectric constant, the corrected potential can be written

$$U_{\text{cor}}(\mathbf{q}) = \frac{1}{\pi^2\kappa} \left( \frac{\kappa A q^2}{q^2 + \alpha^2} + \frac{\kappa(1-A)q^2}{q^2 + \beta^2} - \frac{q^2}{q^2 + \gamma^2} \right). \quad (19)$$

In our work we take the liberty of varying the strength of this correction, using a parameter  $\eta$ , which we vary to obtain a ground-state binding energy in agreement with experiment. The corrected potential has a broader Fourier spectrum and introduces coupling between different valleys, breaking the ground-state degeneracy that the Coulomb potential fails to significantly lift. It is also found that the solutions of the Schrödinger equation for the corrected potential are more diffuse in the reciprocal space, that is, they extend over



TABLE II. Comparison between energies calculated using  $N=11$  and experimentally observed values. Energies are quoted in meV.

	1S(A)	1S(T)	1S(E)
Theory ( $\eta=5.8$ )	45.5	29.1	27.1
Experiment <sup>a</sup>	45.5	33.6	32.2

<sup>a</sup>Experimental data from Ref. 6 corrected using  $3p_{\pm}$  state from Ref. 20.

greater values of  $\mathbf{k}$ , and are more isotropic. This encourages us to use the isotropic sampling procedure to ensure that points are taken over a sufficient range to cover the wave-function solution. A correction strength of  $\eta=5.8$  is found to give a ground-state binding energy in agreement with that observed experimentally, with the excited-state energies also in relatively good agreement, as seen in Table II, with the correct multiplicities predicted.

We point out here that similar corrections have been made within the effective-mass approximation (for examples see Refs. 18 and 19), with equally good agreement obtained for the low-lying energy states. However, as discussed previously, such an approach is not consistent with the approximations inherent in the effective-mass approach. The numerical approach outlined in this paper, however, allows the calculation of the donor wave function for an impurity potential of any form. In Fig. 1 we show the probability density of the donor electron, obtained from numerical solution of the donor Hamiltonian, for both the Coulomb potential and the corrected,  $\eta=5.8$ , potential. The first plot here, for the uncorrected potential, is similar to that obtained using the Kohn-Luttinger effective-mass wave function, as plotted in Fig. 2(d), of Ref. 22. In the second plot we have included a core-corrected potential, which has the effect of localizing the donor more tightly around the impurity, as we would expect from the increased binding energy.

## V. EXCHANGE

The increased localization of the electron wave function around the donor nucleus, which is caused by the added correction to the donor potential necessary to lift the ground-state degeneracy, will have consequences on the construction of a spin-based phosphorus donor quantum computer (QC). The exchange energy between neighboring donor electrons, which mediates the interqubit interactions in most Si:P QC proposals, depends on the overlap of the two electronic wave functions. It is, therefore, necessary to calculate the exchange coupling between these donors, using wave functions calculated in such a way that the impurity core correction has been included. This has not, to the knowledge of the authors, been done until now, and cannot be easily done in the effective-mass formalism where the effect of the valley-orbit coupling on the donor wave functions is not treated consistently.

To this end, we calculate the exchange coupling between neighboring donor electrons, using the Heitler-London approach, as a function of the donor separation in the  $[110]$  direction (Fig. 2), using the wave functions calculated in the

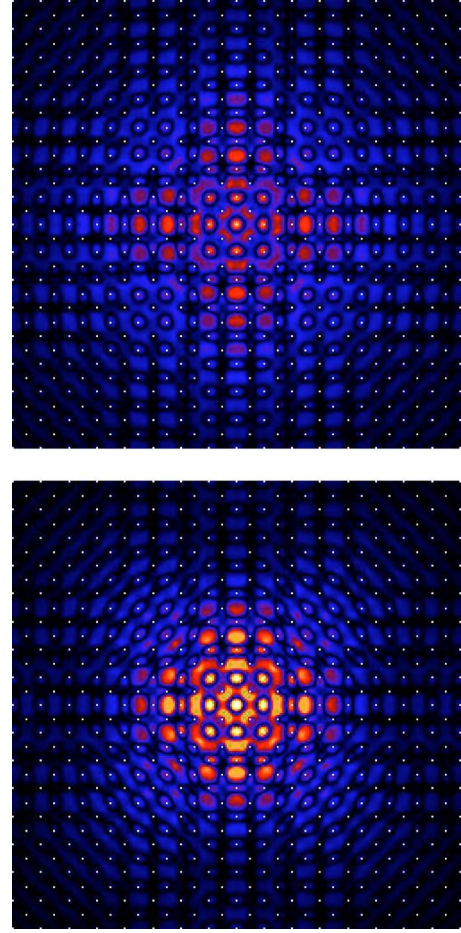


FIG. 1. (Color online) Probability density of the phosphorus donor electron in the  $[001]$  plane for the case  $N=11$ , with  $\eta=0$  and  $5.8$ . The white dots mark atomic sites of the silicon lattice.

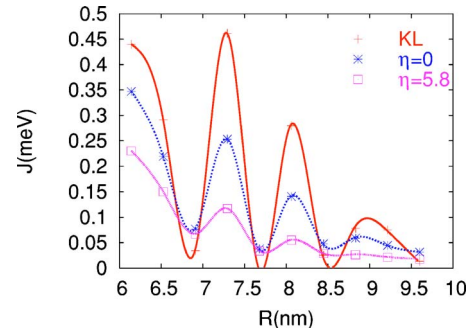


FIG. 2. (Color online) The strength of the exchange coupling between neighboring donors located in the same  $[001]$  plane as a function of their separation along the crystallographic  $[110]$  axis. The plot compares results calculated using the Kohn-Luttinger effective-mass wave function, as well as wave functions obtained using the numerical technique described in this paper, both with and without a corrected impurity potential. Note that the points refer to substitutional sites in the silicon matrix; the lines between these points are a guide to the eye only as the wave functions used are only valid for substitutional donors.

manner described previously. We find, as expected, that the corrected potential reduces the strength of this coupling, due to the increased localization of the electron states. We compare our results to those obtained using solutions of the SV EME, and find that the strength of the exchange coupling is, in general, reduced. It is also pertinent to note that although still present, the oscillatory behavior of the exchange coupling with donor separation is somewhat reduced in amplitude when calculated using states obtained by solution of the exact Hamiltonian. This is expected, and comes from the fact that the wave function is not as strongly localized around the conduction-band minima as was the case for the effective-mass solution, thus reducing the strength of the interference.

We note here that in calculating the exchange coupling between donors we are limited, in this study, to separations of the order of 10 nm. This limit is due to aliasing in the real-space wave function, which is used in the Heitler-London calculation of the exchange coupling. This limit is set by the number of points in reciprocal space that are used to calculate the wave function. Here we have managed to include up to 7986 points, which seems to be enough to obtain convergence for the low-lying energy states; however, the range over which the real-space wave function can be accurately reconstructed with this number of points is limited by aliasing to approximately 150 Å from the position of the donor nucleus. Since the exchange coupling is dependent on the overlap of the neighboring donor electron wave functions, this limits the donor separations for which we can reliably calculate the strength of the exchange coupling. To increase this range it is necessary to include more Bloch states in the Hamiltonian.

## VI. LATTICE STRAIN

It has been pointed out that the oscillatory nature of the spatial dependence of the exchange coupling between donors can be partially suppressed by the application of strain to the silicon substrate.<sup>12,21</sup> Koiller *et al.*<sup>12</sup> have calculated the exchange splitting for donors located in the same [001] plane, parallel to the direction of a tensile strain produced by overgrowth of the silicon substrate on a relaxed  $\text{Si}_x\text{Ge}_{1-x}$  substrate. This uniaxial strain breaks the tetrahedral symmetry of the silicon crystal, and thus lowers the conduction-band energy minima in the direction perpendicular to the overgrowth, relative to those that are parallel. This ensures that the ground-state wave function has contributions from the two perpendicular minima alone, eliminating the oscillatory dependence of the exchange coupling for displacements within the plane.

These effects can be incorporated into our calculation by recalculating the silicon band structure in the presence of strain, which we achieve by altering the silicon lattice spacings in the different directions appropriately. The donor electron wave function is then expanded in the basis of these strained Bloch functions, and used to calculate the exchange coupling in the Heitler-London approximation. To illustrate this we have reproduced some of the results of Koiller<sup>12,22</sup> and calculated the exchange coupling as a function of separation along the [110] axis parallel to the plane of the tensile

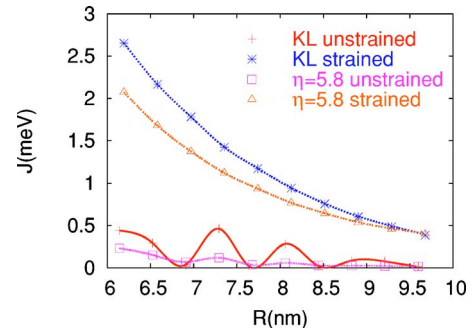


FIG. 3. (Color online) The strength of the exchange coupling between neighboring donors located in the same [001] plane as a function of their separation along the crystallographic [110] axis. The plot compares results for strained and unstrained silicon, calculated using both the effective-mass theory and the wave functions obtained as described in this paper. The tensile strain is obtained by overgrowth on a relaxed [001]  $\text{Si}_{0.8}\text{Ge}_{0.2}$  surface. Note that the points refer to substitutional sites in the silicon matrix; the lines between these points are a guide to the eye only and do not have any physical meaning, as the wave-functions are only valid for substitutional donors

strain. The results are shown in Fig. 3 where it can be seen that the exchange coupling strength decays monotonically with the separation distance, as opposed to the unstrained case in which oscillatory behavior is observed. Of course the dependence will still be oscillatory for displacements out of the plane,<sup>12,22</sup> as we can see in Fig. 4, which shows the exchange coupling for small deviations perpendicular to the expected [110] separation of the two donors. In these calculations, the exchange coupling was calculated using wave functions obtained from the numerical diagonalization technique, with a core correction, while in Refs. 12 and 22 wave functions obtained from effective-mass theory were used. The reduction in the strength of the exchange coupling caused by the inclusion of a core-corrected potential, discussed in the previous section, is clearly evident in Fig. 3;

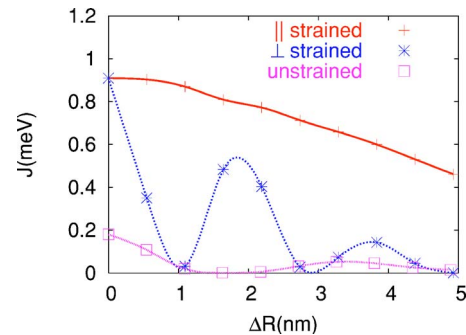


FIG. 4. (Color online) The strength of the exchange coupling between donors that are displaced by an amount  $\Delta\mathbf{R}$  from a separation  $\mathbf{R}$  of 18 lattice spacings, 9.8 nm, along a [100] axis. Results are shown for the case of an unstrained silicon substrate, and the case in which the silicon substrate is grown on the [001] surface of a  $\text{Si}_{0.8}\text{Ge}_{0.2}$  substrate, applying a tensile strain in this plane. Only displacements perpendicular to  $\mathbf{R}$  are considered; in the strained case these can be either within ( $\parallel$ ) or perpendicular ( $\perp$ ) the plane of the tensile strain.

however, it is clear that the qualitative dependence of the coupling on the donor separation is unchanged.

## VII. APPLIED ELECTROSTATIC POTENTIALS

An important problem in the construction of a phosphorus-in-silicon quantum computer is to calculate the response of the donor electron wave function to electrostatic potentials created by voltage biases applied to control gates. It is through the application of such biases that coherent control of the electron wave function is to be achieved and quantum information processing implemented. In both nuclear-spin<sup>1</sup> and some electron-spin<sup>23</sup> proposals, one of the key issues is the control of the electron-nuclear contact hyperfine coupling strength with externally applied voltage biases. The dependence of the hyperfine coupling strength on the applied bias has been studied, using simplified hydrogenic-type donor wave functions in the presence of realistic control-gate biases,<sup>24,25</sup> as well as for more sophisticated tight-binding wave functions in the presence of simple uniform electric fields.<sup>13</sup>

We illustrate the flexibility of this technique of direct numerical diagonalization of the system Hamiltonian in the basis of Bloch states by using it to reproduce the results of Martins *et al.*<sup>13</sup> This is easily achieved by simply including the potential term due to the uniform electric field in the Hamiltonian to be diagonalized. As was the case in the tight-binding approach, a slight complication arising from the choice of boundary conditions has an accidental realistic physical interpretation. In our case we assume that the electric field is being applied in the positive  $z$  direction. To make the calculation tractable we must assume that the field is finite in extent, this is obviously physically reasonable, and we vary extent of the field. This leads to a discontinuity in the potential at the edge of this region. At the  $-z$  edge this discontinuity qualitatively reflects the barrier potential an electron would experience due to the presence of a silicon oxide barrier, as would be present in a metal-oxide-silicon device.

The contact hyperfine coupling strength between the donor electron and nucleus is proportional to the probability of the electron being found at the position of the nucleus; thus to calculate the change in the coupling constant as a function of applied field, it is necessary to calculate the electron wave function for various field strengths. This has been done using the corrected Coulomb potential,  $\eta=5.8$ , for donors located at various distances from the silicon oxide barrier. We show our results, normalized with respect to the zero-field case, in Fig. 5. The fact that the pseudopotential approach used to calculate the Bloch structure of the silicon lattice is insufficiently sophisticated to give a good description of the electron wave functions in the vicinity of the silicon ion cores means that the absolute values calculated for the hyperfine interaction are not in agreement with experimental observation, and only relative shifts of this quantity can be calculated with any confidence.

The results are in good agreement with those obtained by Martins *et al.* in a tight-binding study, and indicate that donors close to the silicon-oxide barrier require a greater field

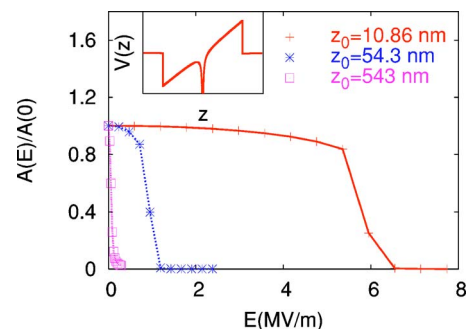


FIG. 5. (Color online) A plot of the field dependence of the electron-nuclear contact hyperfine coefficient ( $A$ ), in units of the zero-field coupling ( $A_0$ ), for donors located at different distances from an oxide barrier ( $Z_0$ ); the lines between points are a guide to the eye. Donors closer to the barrier require a stronger field to significantly deform the wave function.

strength to achieve a certain shift in the hyperfine coupling than do those that are further away. This is simply due to the intuitive fact that the potential well created by the applied field at the oxide boundary is relatively shallower for donors close to the barrier than it is for those further from the barrier.

The change in the hyperfine coupling as a function of field becomes very sudden, as the distance between the donor and oxide barrier,  $z$ , is increased. Indeed, for the values of  $z$  considered here, the transition can be characterized by a critical field strength  $E_c$ , at which the hyperfine coupling drops to zero. Martins *et al.*<sup>13</sup> fitted a rough scaling form,  $E_c \sim k/z$ , for the critical field strength as a function of  $z$ , where  $k \sim 6 \times 10^{-2} \text{ V m}^{-1}$ . Our results are in good qualitative agreement with this scaling law, even for values of  $z$  beyond those obtained by Martins *et al.* In this calculation, we are not limited to small values of  $z$ , as we were for small donor separations in the calculation of the exchange coupling. The hyperfine coupling strength is only dependent on the value of the wave function at the nucleus, and not on its value at large distances where aliasing effects can have an effect; as a result we are able to calculate the hyperfine coupling strength for arbitrarily large values of  $z$ . In contrast, tight-binding methods are limited by the number of lattice sites which can be included; this currently restricts  $z$  to tens of nanometers.

## VIII. CONCLUSIONS AND OUTLOOK

We present a method for calculating the electronic states of phosphorus donors in silicon by numerical diagonalization of the exact donor Hamiltonian, in a truncated basis of Bloch states. This technique avoids the approximations inherent in the effective-mass formalism and allows the calculation of eigenstates for a variety of potentials, including corrected impurity potentials, as well as applied electrostatic potentials. We use a correction impurity potential to calculate the low-lying energy spectrum of the phosphorus donor electron and obtain good agreement with experiment. We then use the wave functions obtained in this manner to calculate the exchange coupling strength between neighboring donor electrons, and find that the valley-orbit coupling reduces the



strength of this interaction due to the increased localization of the states. The effects of lattice strain are incorporated in the calculation and the exchange coupling between donors in a strained substrate is calculated. The ability of the technique to include the effects of externally applied electrostatic potentials is illustrated by calculating the electron-nuclear hyperfine coupling constant as a function of applied uniform field.

Ultimately the usefulness of this method is determined by the number of points in reciprocal space that can be included in the Hamiltonian matrix. We have managed to include up to 7986 points. While this seems to be enough to obtain convergence for the energy, the range over which the real-space wave function can be reproduced with this number of points is limited, by aliasing, to a distance of approximately 150 Å from the position of the donor nucleus. To calculate exchange couplings for donors separated by distances of

more than this will require the inclusion of more points in the Hamiltonian.

Finally we wish to emphasize that the results obtained using this technique vary only quantitatively from what is predicted using effective-mass theory. These quantitative differences are, however, important for quantum information applications, where the demands on precision are high.

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