Accurate and efficient simulation of donors in silicon

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For sixty years researchers have studied the electronic structure of donors in silicon using the effective mass approximation. Despite a recent surge of theoretical activity, inconsistent predictions and discrepancies with experiment call into question the extent to which effective mass theory can quantitatively describe donor physics. Earlier this year, Salfi et al. made the first direct measurements of a donor wave function and found extremely good theoretical agreement with atomistic tight-binding simulation. That work motivates the comparison with tight-binding as an essential test of any candidate theory. Here, we apply a multi-valley effective mass theory to the problem of inter-donor tunnel coupling, a critical figure of merit for multi-qubit gates in donor-based quantum computing, and find close agreement with tight-binding. An orders-of-magnitude speedup over atomistic methods, combined with quantitative accuracy, allows us to show conclusively that the tunnel coupling is rapidly oscillatory everywhere. Nonetheless, we identify experimentally accessible regions where donors placed with scanning tunneling microscopy technology achieve large tunnel couplings with > 90% yield.

Building on the pioneering work of Kohn and Luttinger, and later motivated by the promise of using donors in silicon for quantum information processing researchers to this day continue to develop and improve effective mass theories (EMTs). These theories are appealing both because they provide excellent physical intuition and also because they require minimal computational resources to implement. In most cases, parameters to the theory are chosen so that the donor binding energies match experimental values, and attempts are made to justify the approximations used in deriving an effective mass Hamiltonian. Despite this, differences in the particular approximations adopted have led to dramatic discrepancies (e.g., orders of magnitude differences in exchange oscillations between Refs. 17 and 13), and one is often left wondering which, if any, of multiple, seemingly well-justified theories to believe. It is this muddy picture, where small changes to the theories lead to large differences in outcomes, that has cast doubt upon whether EMT is well suited to making quantitative predictions.

Effective mass treatments have seldom compared their wavefunctions to tight-binding results, perhaps with the excuse that the results lacked strong experimental support. But the picture is different now: Earlier this year, Salfi et al. performed the first direct measurement of a donor wave function and found excellent theoretical agreement with atomistic tight-binding simulation. This places the burden of matching these simulations upon any theory claiming to accurately describe a donor. The primary contention of this work is that EMT can be trusted to make accurate predictions when applied properly. By avoiding unjustified approximations, we present an effective mass framework that, in addition to matching experimental energies, agrees quantitatively with experimentally validated atomistic tight-binding theory.

The central tenet of effective mass theory for a low-energy conduction electron in silicon is that its wave function $\psi(r)$ has support only within the immediate vicinity of the six equivalent valley minima, sketched in Fig. 1:

$$\psi(r) = \sum_{j=1}^{6} F_j(r)\phi_j(r). \quad (1)$$

Here, the sum runs over the six valley minima $k^*_j$, located 0.84 nm along the cartesian axes ($a = 0.543$ nm is the cubic unit cell length of Si), and $\phi_j(r) = u_{k^*_j}(r)e^{i(k^*_j\cdot r)}$ is the Bloch function belonging to the minimum of the $j$th valley. The prefactors $F_j(r)$ are called envelope functions, and are slowly varying on the length scale of the lattice. The multi-valley EMT formalism we use here was first derived by Shindo and Nara (see Supplemental Information).

A common approximation performed in EMT treatments involves substantially simplifying the Bloch functions. However, we find that such approximations lead to uncontrolled error, significantly disrupting the reliability of EMT (see Supplemental Information). Because the design of solid-state quantum information processors requires accurate predictions of quantities that depend on the oscillatory form of the wave functions and not just their envelopes, we include the full Bloch function in all the calculations presented here.

The attractive binding potential $U(r)$ due to a donor in silicon is well approximated at long distances as a bulk-screened Coulomb potential (see Supplemental Information). However, close to the impurity the dielectric screening effect of silicon is lessened, and the potential is enhanced. The deviation of the potential $U(r)$ from bulk-screened Coulomb form at short distances is called a central cell correction. In order to reproduce experimentally observed donor energy levels, we tune the central cell correction using a nested variational optimization. It is worth noting that central cell corrections tuned with the crude approximations of the Bloch func-
FIG. 1. Multi-valley effective mass calculations for a single phosphorous donor in silicon. a, Sketch of the band structure of silicon and the resulting donor physics. The conduction band valleys are initially six-fold degenerate; valley orbit coupling causes level splitting due to the sharp confinement of an impurity potential. The resulting energy levels for phosphorous are shown. b, Our converged donor potential, including the central cell correction, which exhibits tetrahedral symmetry. The constant energy surfaces shown are −0.5 (white), −1.0 (yellow), and −4.0 eV (red), respectively. c-d, Multi-valley effective mass ground state for a single phosphorous donor in silicon. c shows a side view, while d shows a top-down view of the x−y plane. The silicon lattice is superposed toward the center of the plots for scale; the white curtain indicates when the envelope |F|² is one percent of its maximum value. e-f, Atomistic tight-binding simulations corresponding to c-d, performed in NEMO-3D. The envelope curtain is copied from c-d for comparison. g-h, Cuts along the parallel and perpendicular directions of the envelope function in one conduction band valley. The dashed lines are the effective mass theory from the present work; the shaded bands are ±4σ statistical uncertainty limits, determined by the uncertainty quantification techniques described in Methods. The lower bold curves show the corresponding Kohn-Luttinger envelope functions, for comparison. i-k, Cuts along the x−axis of the entire effective mass electron density for effective mass (red curves) and NEMO-3D (dotted black curve in i). i shows the A₁ ground state, j shows one of the three degenerate T₂ first excited states, and k shows one of the two degenerate E first excited states.

The calculations outlined above do not maintain experimental agreement when the full, correct Bloch functions are used. Likewise, for a central cell correction tuned to the full Bloch functions, using the approximate forms results in markedly different energies (see Supplemental Information). To date, all EMT studies of electron donor energy levels that employ a central cell correction have assumed a spherically-symmetric or contact (δ-function) correction. However, to accurately reproduce experimentally observed donor binding energies, we find it necessary to allow for a tetrahedrally-symmetric central cell correction, as anticipated in Refs. 19 and 20 and shown in Fig. [1].

Figs. [1]–d illustrate the charge density of the ground (A₁) state of a phosphorous donor in silicon given by our calculations. For comparison, we solved the same problem using the atomistic tight-binding code NEMO-3D, as shown in Figs. [1]–f (see Methods); we find striking agreement between the two very different methods. In Figs. [1]–h, we show the variation of the envelope func-
FIG. 2. Tunnel couplings computed for two phosphorous donors in silicon. a–d, Comparison of tunnel couplings computed within multi-valley effective mass theory (points with error bars) and NEMO-3D atomistic tight-binding (connected points with no error bars). Here, the tunnel coupling is defined as the energy difference between the first excited state and ground state of the one-electron, two-donor problem. Panel a shows tunnel coupling along the [100] direction, panel b along [110], and panel c along [111]. Panel d depicts typical random instances, not along any particular direction. In all cases, the atomistic and effective mass theory exhibits very similar trends and magnitude of oscillations. Along [111], there appears to be a phase discrepancy, likely due to differing placements of the conduction band minima (see the main text for details). The error bars on the effective mass predictions are ±4σ statistical uncertainty limits, determined by the uncertainty quantification techniques described in Methods. e, Exhaustive tunnel coupling enumeration for two phosphorous donors. Here, we placed one donor at the origin and the second at every possible point within a 30 nm cube surrounding it (∼1.3 million instances). The spherical shells show cuts (with nearest-neighbor interpolation) of the tunnel coupling at fixed donor separation distances. The tunnel coupling is highly oscillatory, and there is no large region of stability in the tunnel coupling. The full results of the enumeration are tabulated in a supplementary data file.
weak-coupling regimes occurs, in which the first excited state changes character. Shown as a kink in the curves of Fig. 2a, this transition occurs at about 6 nm separation along [100].

Having verified EMT predictions for tunnel coupling, we next leverage the computational efficiency of our EMT to perform an exhaustive enumeration of tunnel couplings within a specified volume. In Fig. 2c, we position one donor at the origin and sweep the second through all valid locations located in an enclosing 30 nm cube, resulting in ~1.3 million donor placements. To visualize these data, we plot the tunnel coupling on concentric shells of varying radii using nearest-neighbor interpolation. For quantum computing applications, since donor placement has experimental uncertainty (placement straggle), it is desirable for tunnel coupling to be stable under small perturbations of position. Unfortunately, we see here that the tunnel couplings are highly oscillatory. Using this exhaustive analysis, we conclude that there does not exist a sizable region of adjacent donor placements that exhibits stability with respect to straggle.

Since two-qubit gates rely on large couplings between donors, the preceding calculations cast severe doubt on their experimental viability. Having ruled out deterministically stable tunnel couplings, we turn now to statistical analysis. We accept a donor placement configuration if the tunnel coupling satisfies $t > 0.1$ meV, which is roughly an order of magnitude larger than typical dilution refrigerator electron temperatures. We performed 20000-shot Monte-Carlo, sampling from a 3D isotropic Gaussian distribution with varying widths: panel a corresponds to 1 nm, panel b to 5 nm, and panel c to 10 nm straggle. Panel a depicts an experimentally realistic straggle for STM-based donor placement, while panels b and c depict the results of increasing donor straggle. The white curtain shown in each plot indicates the contour of constant probability as labeled. These results show that STM placement can ensure large tunnel coupling with high yield, while ion implantation technology can only ever achieve low yield, rendering ion implantation ineffective for deterministic use.

To study the effects of different placement technologies on achieving high tunnel couplings, in Fig. 3 we show the probability of achieving $t > 0.1$ meV for three different donor straggles: 1 nm in panel a, 5 nm in panel b, and 10 nm in panel c. In each case, the straggle distribution is taken to be an isotropic Gaussian distribution. We determine the probabilities shown by dividing our 30 nm placement cube into a $201 \times 201 \times 201$ grid of target donor locations and perform 20000 Monte Carlo samples of the tunnel coupling at each point. For STM-compatible placement we find large regions where acceptably large tunnel coupling occurs with high probability, while deterministic ion implantation is not favorable.

We have demonstrated that properly parameterized effective mass theory obtains results that agree quantitatively with both experimental energy spectroscopy and atomistic tight-binding theory that has been recently validated against direct measurement. After benchmarking against tight-binding, we leveraged the computational efficiency of EMT to exhaustively enumerate about 1.3 million donor placements, a task not presently feasible with atomistic methods. Despite showing that there do not exist any regions of stable tunnel coupling, we nonetheless demonstrate that there do exist regions where experimentally realistic donor placement uncertainty results in large tunnel couplings with high yield. Our work shows that effective mass theory can not only be used for qualitative exploration of donor physics, but also for quantitatively reliable, physically transparent, and high-throughput statistical surveys that are not feasible using more computationally intensive techniques.
Methods

Bloch function calculation: We calculated the Bloch function at the conduction band minimum of pure bulk silicon using Kohn-Sham density functional theory. While we tested a variety of pseudization schemes and exchange-correlation functionals, we found little variation among methods. The results presented were calculated using a Bloch function obtained with the VASP software package\cite{28} within the projector augmented wave formalism\cite{27} and the Heyd-Scuseria-Ernzerhof (HSE) approximation to the exchange-correlation functional\cite{29}

NEMO-3D atomistic tight-binding calculation: We performed the tight-binding calculations using the Nanoelectronic Modeling Tool (NEMO-3D)\cite{28}. For the work presented here we utilized a set of 10 localized orbital bases $sp^3d^5s^*$ on a 3D zincblende relaxed silicon atomistic lattice\cite{30}. The phosphorus donor is modeled by a Coulomb potential screened by the dielectric constant of Si and with a cutoff potential $U_0$ at the donor site\cite{31}

Uncertainty quantification procedure: The nested variational optimization we use to determine the central cell correction and wavefunctions takes as input only the experimentally measured energy levels. To quantify the degree to which fitting to the energies constrains the wavefunction, we performed an uncertainty quantification analysis for the wavefunctions induced by the experimental error bars for the energies. For more details, see Supplemental Information.

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Author Contributions JKG, NTJ, EN, JEM, and RPM developed the effective mass theory. JKG and NTJ implemented and performed the effective mass calculations, and analyzed the simulated data. ADB performed the density functional theory calculations. IM performed the NEMO-3D calculations. IM and EN analyzed the NEMO-3D simulated data. All authors discussed the results and prepared the manuscript.

Additional Information Supplementary information accompanies this paper. The authors declare that they have no competing financial interests. Correspondence and requests for materials should be addressed to John King Gamble (jkgambl@sandia.gov).

I. SUPPLEMENTAL INFORMATION

A. Variational solution of Shindo-Nara EMT

The central equation of the Shindo-Nara multi-valley effective mass theory is\cite{11}

$$EF_l(r) = \left(\mathbf{T}_l + U(r)\right)F_l(r) + \sum_{j \in \pm\{x,y,z\}} V_{lj}^{V\text{O}}(r)F_j(r),$$

which is an effective Schrödinger-like equation for the envelope functions. Here, $\mathbf{T}_l$ is the kinetic energy operator of the $l$th valley, where for example $\mathbf{T}_{\pm z} = -\hbar^2/(2m)\left(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \gamma \partial^2/\partial z^2\right)$ with $\gamma = m_{xx}/m_{zz}$ the ratio of effective masses, $U(r)$ is the external (non-crystal) potential energy, and $V^{V\text{O}}(r)$ is the valley-orbit coupling $V_{lj}^{V\text{O}}(r) = \phi_l^*(r)\phi_j(r)U(r)$. We solve this equation variationally, by expanding each $F_j$ over a finite orbital basis set of size $N$,

$$F_j(r) = \sum_{\nu=1}^{N} A_{(j,\nu)}F_{(j,\nu)}(r),$$

where the coefficients $A_{(j,\nu)}$ are unknowns to be determined. For each phosphorus atom and valley, we construct a basis from nine atom-centered Cartesian Gaussian functions. For an atom at the origin and the $+z$ valley, for example, we have

$$F_{(+z,\nu)}(r) = \mathcal{N}x^{n_x}y^{n_y}z^{n_z}e^{-\alpha_z(r^2+y^2)}e^{-\alpha_\perp z^2},$$

where the normalization factor $\mathcal{N}$ is chosen such that $\int_{\text{all space}} d^3r |F_{(j,\nu)}|^2 = 1$. By symmetry, the orbital basis for one valley is equivalent up to a coordinate permutation to that of other valleys.

Within this basis, we express Eq. \ref{eq:2} as the generalized eigenvalue problem

$$\sum_{j,\nu} \mathbf{H}_{(l,\mu),(j,\nu)} A_{(j,\nu)} = E \sum_{j,\nu} \mathbf{S}_{(l,\mu),(j,\nu)} A_{(j,\nu)},$$

where the Hamiltonian matrix elements are

$$\mathbf{H}_{(l,\mu),(j,\nu)} = \int d^3r F_{(l,\mu)}^*(r)F_{(j,\nu)}(r)\left[\mathbf{T}_l + U(r)\right] \delta_{l,j} + V_{lj}^{V\text{O}}(r)$$
FIG. 4. The total Bloch function density, with the silicon lattice superimposed on the plots for scale. Panel a shows well-converged Bloch functions, including high-frequency terms due to their periodic parts. Panel b truncates to form factors, where each pair \( u_{k_0}^*(r)u_{k_1}(r) \) is set equal to its constant-frequency component. Panel c simplifies the situation further, using trivial \( (u_{k_0}(r) = 1) \) Bloch functions. Using the central cell parameters given in Table I, the energies of the states found using these approximations of the Bloch function are shown in the lower right of each panel. As shown in panels b and c, these represent drastic approximations, so it is not surprising that they lead to errors.

and the overlap matrix, block-diagonal with respect to the valleys, is given by

\[
S_{(l,\mu),(j,\nu)} = \int d^3r F_{(l,\mu)}(r)F_{(j,\nu)}(r)\delta_{l,j}. \quad (7)
\]

Using this matrix formalism, for a fixed \( U(r) \), we perform a nonlinear optimization to minimize the ground state energy with respect to the nonlinear basis parameters (the \( \alpha \) and \( \alpha' \) parameters above). For each step in the nonlinear optimization we solve the linear matrix problem. Hence, for any basis ansatz we determine the optimal linear combination of basis functions that minimizes the ground state energy. The linear combinations of basis functions detailed in Table I that form the lowest six energy eigenstates are tabulated in a supplementary data file.

| Index | \( (n_x, n_y, n_z) \) | \( \alpha_J \) (nm\(^{-2}\)) | \( \alpha_J' \) (nm\(^{-2}\)) |
|-------|------------------------|---------------------|---------------------|
| 1     | (0, 0, 0)              | 3.48877             | 0.93542             |
| 2     | (0, 0, 0)              | 0.84055             | 3.06020             |
| 3     | (0, 0, 0)              | 0.30326             | 1.23742             |
| 4     | (0, 0, 0)              | 0.03096             | 0.12142             |
| 5     | (0, 0, 0)              | 0.01209             | 0.06195             |
| 6     | (0, 0, 0)              | 0.00732             | 0.03747             |
| 7     | (2, 0, 0)              | 0.20364             | 0.70775             |
| 8     | (0, 2, 0)              | 0.20364             | 0.70775             |
| 9     | (0, 0, 2)              | 0.20364             | 0.70775             |

and the form factor

\[
\phi_j(r) = u_{k_0}(r)e^{i\mathbf{k}_j\cdot r} = e^{i\mathbf{k}_j\cdot r}\sum_G A^j_G e^{i\mathbf{G}\cdot r}, \quad (8)
\]

where \( \mathbf{G} \) is a reciprocal lattice vector. We compute the set of Fourier coefficients \( \{A^j_G\} \) that determine \( u_{k_0}(r) \) using density functional theory (Sec. I D), and we list our coefficients in a supplemental data file.

Using this matrix formalism, for a fixed \( U(r) \), we perform a nonlinear optimization to minimize the ground state energy with respect to the nonlinear basis parameters (the \( \alpha \) and \( \alpha' \) parameters above). For each step in the nonlinear optimization we solve the linear matrix problem. Hence, for any basis ansatz we determine the optimal linear combination of basis functions that minimizes the ground state energy. The linear combinations of basis functions detailed in Table I that form the lowest six energy eigenstates are tabulated in a supplementary data file.

### B. Inadequacy of Bloch function approximations

One of the most common approximations employed in effective mass theory is to simplify the form of the valley-orbit coupling by using only an approximation for the Bloch function product \( \phi^*_i(r)\phi_j(r) \). Here, each of the

| TABLE II. Parameters for central cell correction \( U_{cc}(r) \) |
|----------------|------------------------|---------------------|---------------------|
| \( A_0 \)     | -1.2837 meV             | \( A_1 \)           | -2642.0 meV         |
| \( a \)       | 0.12857 nm              | \( b \)             | 0.21163 nm          |
| \( c \)       | 0.09467 nm              | \( \mathbf{G} \)    | \( e^{i\mathbf{k}_j\cdot r} \) |

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The most drastic way to approximate the Bloch function product is to set \( \phi_j(r) \approx e^{i\mathbf{k}_j\cdot r} \), amounting to trivial Bloch functions. Another approximation is to write the product as \( \phi^*_i(r)\phi_j(r) \approx C_{ij}e^{i(k_i'-k_j')\cdot r} \), where the factors \( C_{ij} \) are called form factors. In Fig. 4a, we plot the full Bloch function density \( \sum_j |\phi_j(r)|^2 \). In Figs. 4b-c we plot the same quantity with the form factor and trivial approximations, respectively. As can be seen from these plots, the Bloch functions under either approximation are not qualitatively similar to the full Bloch function. In addition, using the approximate forms results in markedly different energies, as noted in Figs. 4b-c.

### C. Form of the central cell correction

Far from the donor, the donor’s binding potential takes the form of a bulk-screened Coulomb potential, \( U_c(r) = -e^2/(4\pi\epsilon_S r) \), where \( \epsilon_S = 11.7\epsilon_0 \) is silicon’s
dielectric constant, $\epsilon_0$ is the permittivity of free space, and $e$ is the electron’s charge. Near the donor, the local potential deviates from this simple $1/r$ behavior, as a result of reduced dielectric screening from the silicon lattice and complex reorganization of the local electronic structure.\cite{24,25} To describe this effect, we include a central cell correction $U_{cc}(r)$, such that the full donor impurity potential takes the form $U(r) = U_{cc}(r) + U_{cc}(r)$. Due to the tetrahedral symmetry of the covalent bonding between the donor and the neighboring silicon atoms in the lattice, we allow for the central cell correction $U_{cc}(r)$ to be tetrahedrally symmetric, to be contrasted with the more restrictive spherical symmetry assumed in previous studies.\cite{26,27,28} We find that this tetrahedral symmetry is necessary in order to obtain the correct donor binding energies when the full Bloch function is considered.

We allow the central cell correction to be a function of five parameters,

$$U_{cc}(r) = A_0 e^{-r^2/(2a^2)} + A_1 \sum_{i=1}^{4} e^{-|\mathbf{r} - \mathbf{t}_i|^2/(2c^2)},$$

where $\mathbf{t}_i \in \{(1,1,1), (-1,1,-1), (1,-1,-1), (-1,-1,1)\}$. This potential takes the form of a Gaussian centered at the origin plus four identical Gaussians centered at points along the bond directions. In our convention for the lattice coordinates, we take the position of the sites of the primitive unit cell to be $(0,0,0)$ and $(a/4)(1,1,1)$, where $a = 0.543$ nm. The tetrahedral directions $\mathbf{t}_i$ are taken to be oriented along the bonds, for the donor assumed to be located at the coordinate $(0,0,0)$. If the donor is located at a site equivalent to the coordinate $(a/4)(1,1,1)$, the tetrahedral directions must be inverted, $\mathbf{t}_i \rightarrow -\mathbf{t}_i$, to preserve agreement with the bond directions. Following the nested optimization process described earlier, we list the parameters for the tetrahedrally-symmetric central cell correction of Eq. (9) in Table II. Note in particular that the strength of the tetrahedral lobes, $A_1$, is large compared to the central spherical term $A_0$. This underscores the importance of allowing our central cell to have tetrahedral symmetry.

We remark now on an inconsistency inherent to using $\delta$-function contact potentials to fit the energy levels, as in Refs \cite{22} and \cite{33}. In three dimensions, it is well known that attractive potentials of the form $U(r) = -\alpha \delta^{(3)}(r)$ exhibit infinitely many bound states, with a ground state of infinite negative energy. While this approach captures the essential physics necessary for first-order perturbation theory, it is inconsistent with any sufficiently rich variational optimization for the orbital basis.

\section{Calculation of the Bloch function}

The Bloch function at the conduction band minimum of pure bulk silicon was calculated using Kohn-Sham density functional theory within a variety of different approximations. A plane wave basis was applied in all cases, and both the Vienna Ab-initio Simulation Package (VASP)\cite{24,33} and Quantum Espresso\cite{25} packages were utilized to check for consistency among results. In VASP, the Projector Augmented Wave (PAW) formalism was used to treat the electron-ion interaction, whereas a variety of norm-conserving pseudopotentials (NCP) were used in Quantum Espresso. While the plane wave coefficients are strictly $L_2$-normalized in NCP calculations, they are not in PAW. Rather than explicitly including the effect of the PAW projectors on the normalization, coefficients were rescaled to achieve strict normalization. In a typical case, the uncorrected norm is within 3\% of unity due to the delocalized nature of the conduction band minimum orbital. In both methods, calculations were done using different parameterizations of the local density approximation (LDA) and generalized gradient approximation (GGA) exchange-correlation functionals, as well as the hybrid Heyd-Scuseria-Ernzerhof (HSE) functional\cite{29}.

For each pseudization scheme and functional, the following procedure for calculating the Bloch function was used. An initial highly-converged self-consistent calculation is done to generate the Kohn-Sham potential which reproduces the ground state electronic density and energy of pure bulk silicon within a specific exchange-correlation approximation. Our criterion for self-consistency is that the change in the total energy between cycles is less than 1 meV/atom. A second non-self-consistent calculation is done with the fixed Kohn-Sham Hamiltonian at 1000 equally-spaced k-points between the $\Gamma$ and X points, i.e., along $\Delta$. The resultant Kohn-Sham orbital energies of the lowest conduction band are then assessed to determine the location of the conduction band minimum. The plane wave coefficients of this particular orbital are then extracted as the Bloch function.

The coefficients generated using different codes and functionals show a high degree of consistency. Applying a uniform phase shift to make the $(0,0,0)$ coefficient of each Bloch function real, the $L_2$ distance between any given pair of Bloch functions is $\approx 0.025$ or less. A similar degree of consistency is observed relative to results published elsewhere.\cite{32} While the different exchange-correlation approximations utilized give a reasonably accurate description of the equilibrium lattice constant of silicon as well as the ordering and character of its near-gap bands, they vary dramatically in precise value of the band gap.\cite{30} This deficiency seems to be irrelevant to the Bloch function of interest. Due to this consistency, there is no specific choice that seems to give a best Bloch function and we choose to use the results of the PAW/HSE calculation, which are tabulated in a supplementary data file.

It is worth commenting on the use of Kohn-Sham orbitals in this capacity. Strictly speaking the direct physical significance of these orbitals is limited, as they are solely intended to serve an auxiliary role in representing the interacting electronic density which is the real
quantity of interest in DFT. Here, we are simply using Kohn-Sham DFT as a convenient tool to generate an effective mean-field Hamiltonian, the eigenfunctions of which have qualitative atomically-resolved features that are needed by our effective mass theory. The high degree of consistency of relevant quantities between calculations gives us confidence that this approach is reasonable.

The contact hyperfine interaction between the spins of the electron and donor nucleus, nonzero for the $A_1$ ground state and zero for all other five states in the $1s$ manifold, is proportional to the charge density of the full electron wavefunction at the donor nucleus, $|\psi(0)|^2$. We find that our calculated value of $|\psi_{A_1}(0)|^2 = 1.0 \text{ nm}^{-3}$ is consistent with a Bloch function bunching factor $^{33}$ at the donor of about 440 in order to give the measured contact hyperfine interaction strength of 117.5 MHz.$^{17,18}$ The precise value of this bunching factor is not physically meaningful; for this calculation we include only the plane wave part of the full PAW wave function. This approximation does not affect the long-wavelength physics studied here, but does impact the precise form of the wave function close to the nucleus.$^{25}$ In particular, we note that the dominant contribution of the central cell correction lies well outside the augmentation sphere around the donor, so we expect the central cell parameterization to not be significantly sensitive to the wave function form near the nucleus. To obtain quantitative accuracy for the hyperfine interaction, it is necessary to either perform all-electron DFT$^{35}$ or include the full PAW wave function.$^{39}$

E. Details of the uncertainty quantification procedure

Taking a conservative estimate of the experimental error bars synthesized from the literature, we assume that the energy levels $(A_1, T_2, E)$ take the form of a multivariate normal distribution with mean $\mu = (-45.59, -33.89, -32.58) \text{ meV}$ and covariances $E \left[ (E_i - \mu_i)^2 \right] = \Delta^2$ and $E \left[ ((E_i - \mu_i) - (E_j - \mu_j))^2 \right]_{i \neq j} = \delta^2$, with $\delta = 0.05 \text{ meV}$ and $\Delta = 0.2 \text{ meV}$. Here, $\Delta$ and $\delta$ quantify the uncertainty in the absolute value of the energy levels and energy differences, respectively. Given this distribution for the energy levels, we randomly perturb all central cell correction parameters by 1% and evaluate the energy spectrum and eigenstates. This variation of the central cell correction parameters is chosen to adequately sample over the support of the energy level distribution. We then associate the probability density of the energy levels with the envelope function and use this weighted ensemble of envelope functions to determine qualitative error bars for the wavefunctions.

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