Element-sensitive measurement of the hole–nuclear spin interaction in quantum dots

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It has been proposed that valence-band holes can form robust spin qubits5–8 owing to their weaker hyperfine coupling compared with electrons5,6. However, it was demonstrated recently9–13 that the hole hyperfine interaction is not negligible, although a consistent picture of the mechanism controlling its magnitude is still lacking. Here we address this problem by measuring the hole hyperfine constant independently for each chemical element in InGaAs/GaAs, InP/GaInP and GaAs/AlGaAs quantum dots. Contrary to existing models10,11 we find that the hole hyperfine constant has opposite signs for cations and anions and ranges from −15% to +15% relative to that for electrons. We attribute such changes to the competing positive contributions of p-symmetry atomic orbitals and the negative contributions of d-orbitals. These findings yield information on the orbital composition of the valence band12 and enable a fundamentally new approach for verification of computed Bloch wavefunctions in semiconductor nanostructures13. Furthermore, we show that the contribution of cationic d-orbitals leads to a new mechanism of hole spin decoherence.

Owing to the s-type character of the Bloch wavefunction, the hyperfine interaction of the conduction band electrons is isotropic (the Fermi contact interaction) and is described by a single hyperfine constant $A$, positive ($A > 0$) for most III–V semiconductors and proportional to the electron density at the nucleus. In contrast, for valence-band holes the contact interaction vanishes owing to the symmetry properties of the wavefunction, and the non-local dipole–dipole interaction dominates10,11,13–15. As a result, the sign, magnitude and anisotropy of the hyperfine interaction depend on the actual form of the valence-band Bloch wavefunction, which is usually not available with sufficient precision. Thus, predicting the properties of the hole hyperfine coupling using first-principle calculations remains a difficult task.

In this work we perform direct measurements of the hyperfine constants that describe the hole hyperfine interaction with nuclear spins polarized along the growth axis of the structure (that is, the diagonal elements of the hole hyperfine Hamiltonian). This is achieved by simultaneous and independent detection of the electron and hole Overhauser shifts using high-resolution photoluminescence spectroscopy of neutral quantum dots. In contrast to previous work1, we now also apply excitation with a radiofrequency oscillating magnetic field, which allows isotope-selective probing of the valence-band hole hyperfine interaction16. Using this technique we find that in all studied materials, cations (gallium, indium) have a negative hole hyperfine constant, whereas it is positive for anions (phosphorus, arsenic), a result attributed to the previously disregarded contribution of the cationic $d$-shells into the valence-band Bloch wavefunctions.

Using the experimentally measured diagonal components of the hyperfine Hamiltonian (hole hyperfine constants) we calculate its non-diagonal part. We show that the admixture of the $d$-shells has a major effect on the symmetry of the hyperfine Hamiltonian in quantum dots: unlike pure heavy holes constructed only of $p$-symmetry shells for which the hyperfine interaction has an Ising form14, the $d$-shell contribution results in non-zero non-diagonal elements of the hyperfine Hamiltonian. We predict this to be a major source of heavy-hole spin decoherence.

Our experiments rely on detection of photoluminescence of both bright and dark neutral excitons15–18 formed by electrons $\uparrow$ (\downarrow) with spin $\pm 1/2$ and heavy holes $\uparrow$ $\uparrow$ (\downarrow) with momentum $\pm 3/2$ parallel (antiparallel) to the growth axis $Oz$ (Fig. 1a). As the quantum dots contain of the order of $10^8$ nuclei, non-zero average nuclear spin polarization of the $k$th isotope ($I_k^z$) along the $Oz$ axis can be treated as an additional magnetic field acting on the electron and hole spins. The coupling strength of the electron to the nuclear spins of isotope $k$ is described by the hyperfine constant $A^k$. The additional energy of the exciton state with electron spin $\uparrow$ $\uparrow$ is equal to $+(1/2)\Delta E_k^z$ $-(1/2)\Delta E_k^z$, where the electron hyperfine shift induced by the $k$th isotope is defined as

$$\Delta E_k^z = \rho^k A^k \langle I_k^z \rangle$$

(1)

with $\rho$ describing the relative concentration of the $k$th isotope. For the heavy-hole states the hyperfine interaction is described using a constant $C^k$ expressed in terms of the normalized heavy-hole hyperfine constant $\gamma^k$ as $C^k = \gamma^k A^k$. The variation of the energy of the exciton with hole spin $\uparrow$ (\downarrow) is $+(1/2)\Delta E_k^z$ $-(1/2)\Delta E_k^z$, where the hole hyperfine shift is

$$\Delta E_k^z = \rho^k \gamma^k A^k \langle I_k^z \rangle$$

(2)

By taking the same values of $\rho$ in equations (1) and (2) we assume for simplicity a uniform distribution of the average nuclear spin polarization and concentration of chemical elements within the volume of the quantum dot. According to equations (1) and (2), hole and electron hyperfine shifts depend linearly on each other ($\Delta E_k^e = \gamma^k \Delta E_k^h$). In the experiment, hyperfine shifts are measured

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from photoluminescence spectra of the quantum dot (see Fig. 1a) and the slope of the resulting dependence of \( \Delta E_h^b \) on \( \Delta E_h^e \) is used to determine \( \gamma^h \) (see further details in Methods).

We start by presenting results for strain-free GaAs/AlGaAs quantum dots. The dependence of \( \Delta E_h^k \) on \( \Delta E_h^b \) for \( k = As \) (squares) and \( k = Ga \) (circles) is shown in Fig. 2a for GaAs quantum dot A1. It can be seen that the dependences for both Ga and As are linear as predicted by equations (1) and (2). Fitting gives the following values for the hole hyperfine constants \( \gamma^{Ga} = -7.0 \pm 4.0\% \) and \( \gamma^{As} = +15.0 \pm 4.5\% \). Similar measurements were performed on three other GaAs quantum dots. The resulting values are given in Table 1. As the variation between different dots is within experimental error, we take average values for all dots yielding \( \gamma^{Ga} = -7.5 \pm 3.0\% \) and \( \gamma^{As} = +16.0 \pm 3.5\% \). We thus conclude that different chemical elements have opposite signs of the hole hyperfine constants: they are positive for arsenic and negative for gallium. This is an unexpected result in comparison with previous theoretical studies and experiments insensitive to individual chemical elements where negative values of \( \gamma \) have been found in InP and InGaAs quantum dots.

We have also performed isotope-sensitive measurements of the hole nuclear interaction in InGaAs/GaAs quantum dots. The dependence of \( \Delta E_h^b \) on \( \Delta E_h^e \) for InGaAs quantum dot B1 is shown in Fig. 2b for \( ^{71}Ga \) (circles), \( ^{75}As \) (squares) and for the total hyperfine shifts of \( ^{69}Ga \) and \( ^{115}In \) (triangles). The values of \( \gamma^h \) obtained from the fitting (see details in Methods) are summarized in Table 1. Similar to GaAs, we find that arsenic has a positive hole hyperfine constant whereas for gallium induction it is negative.

Applying the isotope selection techniques to InP/GaInP quantum dots studied previously, we find \( \gamma^{In} = -12.5 \pm 3.0\% \), consistent with our previous results obtained without isotope selection. Similar to GaAs and InGaAs quantum dots, we find a large positive constant for anions (phosphorus) \( \gamma^P = +18.0 \pm 8.0\% \).

The values of \( \gamma \) presented in Table 1 describe the hyperfine interaction of the valence-band states that are in general mixed states of heavy and light holes. However, as we show in detail in Supplementary Section S5, such mixing cannot account for the opposite signs of \( \gamma \) observed for the cations and anions, but might be the reason for the dot-to-dot variation of \( \gamma \) observed in InP quantum dots (see Table 1). Such variation may also arise from the dot-to-dot-dependent spatial separation of electron and hole wavefunctions.

From the measurements without radiofrequency pulses (similar to earlier isotope-non-selective experiments of refs 8,9), we find that in GaAs quantum dots the total hole hyperfine shift (induced by all isotopes) is positive and amounts to \( \gamma \approx +5\% \) relative to the total electron hyperfine shift. For the studied InGaAs quantum dots where indium and gallium concentrations are estimated to be \( \rho^{In} \approx 20\% \) and \( \rho^{Ga} \approx 80\% \) (see ref. 16), we find negative \( \gamma \approx -4\% \), whereas for more indium-rich InGaAs dots emitting at \( E_{PL} \approx 1.30\,eV \) the value of \( \gamma \approx -9\% \) has been reported. This suggests that for quantum dots with a particular indium concentration \( \rho^{In} \approx 10\% \) one can expect close to zero \( \gamma \approx 0\% \) total hole hyperfine shift induced by nuclear spin polarization along the \( Oz \) direction. Hole spin qubits in such structures will be insensitive to static nuclear fields that are induced by the optical control pulses and cause angle errors in spin rotations. Such spin qubits will benefit from a simplified implementation of the coherent control protocols.

We now turn to analysis of the experimental results presented in Table 1. First-principle calculation of the valence-band hyperfine coupling requires integration of the hyperfine Hamiltonian using explicit expressions for the Bloch wavefunctions. However, it has been shown that reasonable estimates can be obtained using a simplified approach. Bloch wavefunctions can be approximated by linear combinations of hydrogenic wavefunctions (further details may be found in Methods). Previous calculations based on this approach considered valence-band states constructed from atomic \( p \)-orbitals (with orbital momentum \( l = 1 \)), which yields positive hole hyperfine constant \( \gamma^h > 0 \) for all chemical elements, in contradiction with our experimental findings.

This disagreement can be overcome by taking into account the contribution of shells with higher orbital momenta \( l \), resulting in more accurate approximation of the hole wavefunction; in particular we consider the contribution of the \( d \)-shell states...
(l = 2). Both p- and d-orbitals are schematically depicted in Fig. 3a. We assume that the heavy-hole states can be taken as linear combinations of p-shells with weight \( \alpha_p \) and d-shells with weight \( \alpha_d \) \((|\alpha_p|^2 + |\alpha_d|^2 = 1)\). Calculation of the relative hole hyperfine constant yields:

\[
y^k = \frac{12}{5} |\alpha_p|^2 M_p - \frac{18}{7} |\alpha_d|^2 M_d
\]

\[
M_l = \frac{1}{|S(0)|^2} \int_0^\infty \frac{R_l^2(r)}{r} \, dr
\]

where positive integrals \( M_l \) \((l = p, d)\) depend on the hydrogenic radial wavefunctions \( R_l(r) \) corresponding to the shell with orbital momentum \( l \) and normalized by the density \((4\pi)^{-1}|S(0)|^2\) of the conduction band electron wavefunction at the nuclear site (see further information in Methods and Supplementary Section S4).

It follows from equation (3) that unlike the p-shell, the d-shell gives rise to a negative contribution to \( y^k \); importantly, the sign of the hyperfine interaction is totally determined by the angular symmetry of the wavefunction, whereas the radial part \( R_l(r) \) affects only the magnitude of the contribution. We note that any hybridization of the valence-band states with s-orbitals due to quantum-dot symmetry reduction would lead to a positive contribution to \( y^k \) and thus cannot account for the negative hyperfine constants\(^{11}\). To obtain numerical estimates we consider GaAs material and approximate \( S(r) \), \( R_p(r) \), \( R_d(r) \) with radial hydrogenic wavefunctions corresponding to 4s-, 4p-, and 3d-shells, respectively, taken with effective orbital radii\(^{11,21}\). The resulting calculated dependence of \( y^k \) on d-shell admixture \( |\alpha_d|^2 \) is shown in Fig. 3b for \( k = Ga \) and \( k = As \) nuclei. On comparing this with the experimental results of Table 1 (shown by the horizontal bands in Fig. 3b), we conclude that the symmetry of the wavefunction at the anions (arsenic) is close to pure p-type, whereas for the cation gallium a significant contribution of the d-shell (~20%) is required to account for the negative hole hyperfine constant measured experimentally.

The non-zero contribution of the d-symmetry orbitals has a further unexpected effect on the hole hyperfine interaction: we find (see Supplementary Section S5) that the hyperfine interaction induces spin flips between the heavy-hole states \( |\uparrow\rangle \) and \( |\downarrow\rangle \). This is in contrast to the case of pure heavy holes constructed only of p-symmetry states for which the hyperfine interaction has an Ising form\(^{12}\): in that case the symmetry of the system is artificially raised to spherical, resulting in hyperfine interaction conserving angular momenta. The inclusion of the d-shells reduces the symmetry of the system down to that of the real crystal (described by the \( T_d \) point group). Under these conditions the hyperfine interaction does not conserve angular momentum and has non-zero non-diagonal elements coupling heavy holes with the opposite spins.

It was demonstrated previously that heavy–light hole mixing can result in a non-Ising form of the hyperfine interaction\(^{10,11}\). However, our estimates show that for gallium in GaAs the contribution of the d-shells to the non-diagonal matrix elements of the hyperfine Hamiltonian dominates over the effect of the heavy–light hole mixing even if the valence-band states have a light-hole contribution as large as ~30% (see Supplementary Section S5). A similar effect is expected for the other materials studied, because for all of them significant contribution of the cation d-shells is observed (resulting in \( y^k < 0 \)). Thus, the d-orbital contribution will be a source of heavy-hole spin dephasing even in the absence of mixing with light holes and should be taken into account when analysing experimentally measured hole spin coherence times.

The hyperfine interaction is particularly strong in the small volume around the atomic core\(^{13}\). To estimate this volume we limit the integration in equation (3) to a sphere of a radius \( r_0 \), which makes \( M_l \) (and hence \( y^k \)) a function of \( r_0 \). The

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**Table 1 | Experimentally measured photoluminescence energies \( E_{PL} \) and hole hyperfine constants \( y^k \) for different chemical elements \( k \) in several GaAs and InGaAs quantum dots.**

| Material/quantum dot | \( y^{Ga} \) (%) | \( y^{In} \) (%) | \( y^{As} \) (%) | \( y^{P} \) (%) | \( E_{PL} \) (eV) |
|----------------------|----------------|----------------|----------------|----------------|----------------|
| **GaAs/AlGaAs**      |                |                |                |                |                |
| QD A1                | -7.0 ±4.0      | —              | +15.0 ±4.5     | —              | 1.713          |
| QD A2                | -8.5 ±3.5      | —              | +17.0 ±5.0     | —              | 1.713          |
| QD A3                | -5.5 ±4.5      | —              | +15.0 ±4.0     | —              | 1.702          |
| QD A4                | -7.5 ±4.5      | —              | +18.5 ±5.5     | —              | 1.707          |
| **InGaAs/GaAs**      |                |                |                |                |                |
| QD B1                | -6.5 ±5.5      | -16.0 ±4.0     | +10.5 ±2.0     | —              | 1.358          |
| QD B2                | -3.0 ±6.5      | -15.5 ±5.0     | +10.0 ±3.0     | —              | 1.358          |
| QD B3                | -5.5 ±5.0      | -16.0 ±4.0     | +8.0 ±2.0      | —              | 1.357          |
| QD B4                | -4.5 ±7.0      | -13.0 ±4.5     | +8.5 ±3.0      | —              | 1.357          |
| **InP/GaInP**        |                |                |                |                |                |
| QD C1                | —              | -15.5 ±1.5     | —              | +17.5 ±11.0    | 1.834          |
| QD C2                | —              | -15.0 ±1.5     | —              | +18.5 ±12.5    | 1.851          |
| QD C3                | —              | -9.0 ±1.5      | —              | +19.0 ±12.0    | 1.844          |
| QD C4                | —              | -10.5 ±1.5     | —              | +17.5 ±11.0    | 1.834          |
| **Average**          |                |                |                |                |                |
| GaAs/AlGaAs          | -7.5 ±3.0      | —              | +16.0 ±3.5     | —              | 1.834          |
| InGaAs/GaAs          | -5.0 ±4.5      | -15.0 ±3.5     | +9.0 ±2.0      | —              | 1.834          |
| InP/GaInP            | —              | -12.5 ±3.0     | —              | +18.0 ±8.0     | —              |

Error estimates give 90% confidence values; Average values for each chemical element in each material are given at the bottom of the table.
parameters obtained in this work provide a means for probing the hole Bloch wavefunction: they allow direct analysis of the wavefunction orbital composition in the close vicinity of the nuclei, where theoretical modelling is the most difficult. Furthermore, our experimental method is unique in being isotope-selective, thus allowing independent study of cation and anion wavefunctions. The techniques developed in this work for quantum dots have the potential to be extended to other semiconductor systems, for example, bound excitons in III–V and group-IV bulk semiconductors where dark excitons are observed26 and hyperfine shifts can be induced and detected27.

A rigorous modelling of the hyperfine parameters28 has not been carried out so far for the valence-bands states of III–V semiconductor nanostructures. Progress in this direction will provide a better understanding of the mechanisms controlling the sign and magnitude of the valence-band hyperfine coupling. In particular, the potential effect of large inhomogeneous elastic strain (present in self-assembled quantum dots) on the microscopic Bloch wave function needs to be examined. This may be a possible route to engineering of holes with reduced hyperfine coupling.

Methods

Samples and experimental techniques. Our experiments were performed on undoped GaAs/AlGaAs (ref. 28), InP/GaInP (ref. 9) and InGaAs/GaAs (ref. 16) quantum-dot samples without electric gates (further details can be found in Supplementary Section S1). The photoluminescence spectra of quantum dots placed at $T = 4.2 \, \text{K}$, in an external magnetic field $B$, normal to the sample surface, were measured using a double spectrometer and a CCD (charge-coupled device) camera.

Detection of the hyperfine shifts, required to measure hole hyperfine constants is achieved using pump–probe techniques2 (see timing diagram in Fig. 1b). Nuclear spin polarization is prepared with a long ($\sim 6 \, \text{s}$) high-power optical pump pulse. Following this, a radiofrequency oscillating magnetic field is switched on to achieve isotope-selective depolarization of nuclear spins (radiofrequency pulse duration varies between 0.15 and 35 s depending on the material). Finally, the sample is excited with a low-power short ($\sim 0.3 \, \text{s}$) probe laser pulse, during which the photoluminescence spectrum (see Fig. 1a) of both bright and dark excitons is measured. In all experiments the durations of the radiofrequency and probe pulses are much smaller than the natural decay time of the nuclear polarization. See further details of experimental techniques in Supplementary Sections S2 and S3.

Techniques for isotope-selective measurement of the hole hyperfine constant.

The concept of the valence-band hyperfine constant measurement is based on detecting hole hyperfine shift $\Delta E^h_k$ (equation (1)) by varying the nuclear spin polarization $I^1$. Non-zero $I^1$ is induced by optical nuclear spin pumping: circularly polarized light of the pump laser generates spin-polarized electrons that transfer their polarization to nuclei10–12,17,18 through the hyperfine interaction. The magnitude of $I^1$ is controlled by changing the degree of circular polarization12. According to equations (1) and (2), hole and electron hyperfine shifts depend linearly on each other ($\Delta E^h = \gamma^h \Delta E^e_k$) with a slope equal to the normalized hole hyperfine constant $\gamma^h$. The electron (hole) hyperfine shift of a chosen (kth) isotope is deduced from a differential measurement: the spectral splitting between excitons with opposite electron (hole) spins (Fig. 1a) is measured with a radiofrequency pulse that depolarizes only the kth isotope and without any radiofrequency pulse. The difference between these two splittings is equal to $\Delta E^e_k$ (equation (1)). As an example, Fig. 2 shows measurements where electron hyperfine shift $\Delta E^e_k$ is found as the difference of the energy splitting $(E_{\uparrow} - E_{\downarrow})$ of the $\uparrow$ and $\downarrow$ excitons measured without radiofrequency excitation and the splitting $(E_{\uparrow} - E_{\downarrow})$ of the same excitons but measured after erasure of the nuclear polarization corresponding to the kth isotope by the radiofrequency pulse. In the same way, the hole hyperfine shift is measured as $\Delta E^h = (E_{\uparrow} - E_{\downarrow}) - (E_{\uparrow} - E_{\downarrow})$.

The actual techniques for isotope-selective depolarization of nuclear spins depend on quantum-dot material. For example, in the case of GaAs/AlGaAs quantum dots, we take into account that both 69Ga and 71Ga isotopes have nearly equal chemical properties resulting in equal values of the relative hole hyperfine interaction constants $\gamma^h_{69Ga} = \gamma^h_{71Ga} = \gamma^h_{Ga}$. Thus, measurement of $\gamma^h_{Ga}$ can be accomplished by erasing both 69Ga and 71Ga polarization (which improves the measurement accuracy). In contrast, InGaAs/GaAs quantum dots, 113In and 115In Ga NMRI spectra overlap owing to strain-induced quadrupole effects15,16, and $\gamma_{115In}$ is extracted by calculating the hyperfine shifts of 115In from the measured hyperfine shifts of 113In. Further details of the isotope-selective experimental techniques can be found in Supplementary Section S3.
Theoretical model. First-principle calculation of the valence-band hyperfine coupling requires integration of the hyperfine Hamiltonian using explicit expressions for the Bloch wavefunctions. Each nucleus is coupled to a hole that spreads over many unit cells. However, it has been shown that the main effect arises from the short-range part of the dipole–dipole interaction\cite{Chekhovich2009} that spreads over many unit cells. This allows a simplified approach to be used: the Bloch functions of the valence-band maximum (corresponding to heavy-hole states) can be taken in the form \((-\sqrt{3}/2)(X_r + Y_r)\) and \((\sqrt{3}/2)(X_r - Y_r)\), where \(X_r\) and \(Y_r\) are orbitals that transform according to the \(T_2\) representation of the \(T_d\) group relevant to bulk zinc-blende crystals (such as GaAs). Here, \(X(r)\) and \(Y(r)\) orbitals are decomposed into a real radial part \(R(r)\) and angular parts \(X(\theta, \phi), \ Y(\theta, \phi)\). As a first approximation, the angular parts of the orbitals can be taken in the form \(X, \alpha x/r, \ Y, \alpha y/r\) (corresponding to p-type states with orbital momentum \(l = 1\), and \(R, \alpha z/r\) can be approximated by the hydrogenic radial functions\cite{VanDeWalle1997, VanDeWalle1998}.

To explain the opposite signs of the hole hyperfine constants observed experimentally we also need to take into account the contribution of the \(d\)-shell states \((l = 2\). To calculate the hyperfine constants (equation (31)) we assume that the heavy-hole orbitals can be taken as normalized linear combinations of the form \(X(r) = a_x X_x(\theta, \phi) R_x(r) + a_y X_y(\theta, \phi) R_y(r) + a_z X_z(\theta, \phi) R_z(r) + a_p (\theta, \phi) R_p(r)\), where \(a\) are weighting coefficients \(|a_x|^2 + |a_y|^2 = 1\) and all orbitals \(X_i\) corresponding to orbital momentum \(l = 1\) transform according to the same \(F_2\) representation (\(d\)-shell states have the form \(X_0, \alpha x/r, \ Y_0, \alpha y/r\)). Further details of the theoretical model can be found in Supplementary Sections S4 and S5.

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Author contributions

A.B.K., M.H., P.S. and A.L. developed and grew the samples. E.A.C. and A.I.T. conceived the experiments. E.A.C. developed the techniques and carried out the experiments. E.A.C., M.M.G. and A.I.T. analysed the data. E.A.C., M.M.G., A.I.T. and M.S.S. wrote the manuscript with input from all authors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to E.A.C. or A.I.T.

Competing financial interests

The authors declare no competing financial interests.