Correlating geminal $^2J_{\text{Si–O–Si}}$ couplings to structure in framework silicates†

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The dependence of a $^{29}$Si geminal $J$ coupling across the inter-tetrahedral linkage on local structure was examined using first-principles DFT calculations. The two main influences on $^2J_{\text{Si–O–Si}}$ were found to be a primary dependence on the linkage Si–O–Si angle and a secondary dependence on mean Si–O–Si linkage of the two coupled $^{29}$Si nuclei. An analytical expression describing these dependencies was proposed and used to develop an approach for relating the correlated pair of $^2J_{\text{Si–O–Si}}$ coupling and mean $^{29}$Si isotropic chemical shift to the linkage Si–O–Si angle and the mean Si–O–Si angle of the two coupled $^{29}$Si nuclei. An example of this analysis is given using $^{29}$Si NMR results from the siliceous zeolite Sigma-2.

1 Introduction

The isotropic chemical shift of $^{29}$Si NMR has long been a valuable probe of structure in silicate materials. 1–4 In changing coordination from SiO$_4$ to SiO$_5$ to SiO$_6$ the chemical shift range of $^{29}$Si in silicates varies from approximately $-100$ to $-150$ to $-200$ ppm, respectively. 5 In the case of tetrahedral coordination, the chemical shift varies over a range of $-120$ to $-70$ ppm as the second coordinate sphere changes from fully connected Q$^4$ to fully disconnected Q$^6$, respectively. 6 For Q$^4$ sites it is well established that variations in the range of $-105$ ppm to $-120$ ppm in the isotropic chemical shift of $^{29}$Si are correlated to the mean of the Q$^4$'s four inter-tetrahedral angles. 7–9

The anisotropy of the $^{29}$Si chemical shift is also strongly correlated to changes in the first-coordination sphere. As first noted by Grimmer and coworkers, 10,11 as the Si–O bond length decreases there is an increase in the s-character of the bonding orbital at Si and corresponding increase in shielding along the direction of the shorter bond. This strong dependence of the $^{29}$Si chemical shift anisotropy has been exploited not only for distinguishing and quantifying Q$^n$ sites, 12–16 but recently has been found to be an effective probe of the modifier cation coordination to the non-bridging oxygen of Q$^4$ sites 17 and useful in the NMR examination of Q$^3$ sites. 18

In contrast to the $^{29}$Si chemical shift, accurate measurements of geminal $^2J_{\text{Si–O–Si}}$ Couplings across the inter-tetrahedral linkage in silicates have yielded no clear relationships between coupling constant and local structure. While $^2J_{\text{Si–O–Si}}$ couplings in solution have been measured, 19–21 motional averaging makes it difficult to use these measurements to establish empirical relationships. The number of $^2J_{\text{Si–O–Si}}$ measurements in solids have been limited, particularly at $^{29}$Si natural abundance levels, 4.67%, and thus far few efforts 24–26 have been made in trying to establish quantitative relationships between $^2J_{\text{Si–O–Si}}$ and structure. Compounding this issue is that commercial computational chemistry packages have only recently reached the level where accurate $J$-couplings can be calculated through using expensive density function theory (DFT) methods. 27 Nevertheless, geometric dependences have been reproduced using modest DFT calculations. The most recent attempts in determining such relationships, using ab initio DFT methods, were in 2009 by Cadars et al. 28 and Florian et al. 29 Although both groups acknowledged a dependence of $^2J_{\text{Si–O–Si}}$ coupling on Si–O–Si bond angle, Florian et al. suggested a one-to-one mapping, whereas Cadars et al. found that the dependence of the $^2J_{\text{Si–O–Si}}$ coupling is not limited to the Si–O–Si bond angle but is also influenced significantly by local geometry around the Si–O–Si linkage. Cadars et al. concluded that such dependencies led to a relatively “large scatter” of $^2J_{\text{Si–O–Si}}$ coupling, with respect to Si–O–Si bond angle, and did not attempt to deduce any empirical relationship between the $^2J_{\text{Si–O–Si}}$ coupling and the local structure. To get a sense of that scatter, we plot the $^2J_{\text{Si–O–Si}}$ couplings—calculated here—as a function of Si–O–Si bond angle in Fig. S5 of the ESI.

Here we re-examine the variation in $^2J_{\text{Si–O–Si}}$ using Q$^4$–Q$^4$ clusters that are centered on the Si–O–Si linkage extending out to four coordination spheres away from the bridging oxygen between the two coupled silicon. With greater computational resources than were available to Cadars et al. 8 years ago...
We were able to increase the level of theory and obtain excellent agreement with known experimental $J_{\text{Si-O-Si}}$ couplings. Through systematic structural variations of the cluster, we investigated the influence of (1) the Si–O–Si linkage angle, (2) the Si–O bond distance, (3) the inter-tetrahedral dihedral angle, and (4) the outer Si–O–Si linkage angles of the two coupled $^{29}$Si nuclei. Most significantly, we show here that after the central Si–O–Si linkage angle it is the outer Si–O–Si linkage angles of the Q$^4$–Q$^4$ couple that play the next most significant role in determining $J_{\text{Si-O-Si}}$. A smaller dependence on the dihedral angle is observed while a negligible dependence on Si–O distance over relevant length scales is observed. In this study we assume the SiO$_4$ tetrahedron does not deviate from local tetrahedral symmetry and take the intra-tetrahedral O–Si–O angle as constant. While this is a reasonable approximation in a fully connected Q$^4$ network, it is likely that this assumption will break down as the silicate network becomes depolymerized. Further work will be required to understand the dependence of $J$ coupling on local structure in networks having significant distortions around SiO$_4$ tetrahedra.

As the isotropic chemical shift has a well-known dependence on the mean Si–O–Si angle, we also show here that a correlation plot of mean $^{29}$Si isotropic chemical shift versus $J_{\text{Si-O-Si}}$ coupling can be mapped into a two-dimensional structural correlation of linkage Si–O–Si angle to mean Si–O–Si angle of the two coupled $^{29}$Si nuclei.

2 Method

All ab initio calculations were carried out using Gaussian 09$^{28}$ at the Ohio supercomputing center, running HP SL390G7 two-socket servers with Intel Xeon x5650 (Westmere-EP, 6 core, 2.67 GHz) processors and 48 GB memory. The natural atomic orbital and natural bond orbital analysis was performed using Gaussian NBO version 3.1.$^{30}$ The $J_{\text{Si-O-Si}}$ couplings were calculated using DFT with B3LYP functional on a small O centered SiH$_3$ terminated cluster, (H$_3$SiO)$_3$–Si–O–Si–(OSiH$_3$)$_3$, shown in Fig. 1. A perfect tetrahedron angle $\angle$O–Si–O = 109.5° was imposed about Si atoms in all calculations.

A locally dense basis set was implemented on this cluster, as suggested by Cadars et al.$^{26}$ for accurate $J_{\text{Si-O-Si}}$ coupling calculations. This follows an implementation of cc-PV5Z basis set on the two central Si (labeled Si$^{(i)}$ and Si$^{(j)}$ in Fig. 1), 6-31+G basis set on all H, and 6-31+G* basis set on all O and remaining Si. Single point NMR calculations were run with tight self consistent field (SCF) convergence criteria. The integration grid size was increased to a pruned (99, 590), ‘ultrafine’ grid, although no differences in $J_{\text{Si-O-Si}}$ couplings were observed from the pruned (75, 302) ‘fine’ integration grid. All further calculations were, therefore, subjected to a ‘fine’ integration grid. With this setup each calculation took approximately four and a half hours split over 12 cpu cores.

Systematic structural variations of the cluster were performed to investigate the $J_{\text{Si-O-Si}}$ coupling dependence on and correlations between the central Si–O–Si bond angle, $\Omega_0$, and (a) Si–O bond distances, $d_{\text{Si-O}}$, (b) O–Si–Si–O inter-tetrahedral dihedral bond angle, $\phi$ (index O$_{\text{1–2}}$–Si($^{(i)}$)–Si($^{(j)}$)–O$_{\text{4}}$ in Fig. 1) and (c) outer Si–O–Si bond angles, $\Omega_1$ to $\Omega_6$, with the geometry constrained out to the third coordination sphere of the central linkage oxygen, a geometry optimization of the outermost Si–H bond distances and the remaining dihedral angles was performed once using restricted Hartree–Fock, RHF/6-311G(d) basis set. We found, as did Cadars et al.$^{26}$ that variations in these fourth coordination sphere geometries had negligible effect on the predicted $J$-coupling. We confirmed this finding with several $J_{\text{Si-O-Si}}$ coupling calculations starting with RHF/6-311G(d) optimized initial geometries and the results are tabulated in Table S3 of the ESI.$^\dagger$ A complete list of all geometrical constraints imposed in this study is tabulated in Tables S1–S5 of the ESI.$^\dagger$

Si–O bond distance, $d_{\text{Si-O}}$

The $J_{\text{Si-O-Si}}$ coupling dependence on and correlation between $\Omega_0$ and $d_{\text{Si-O}}$ was explored by performing a series of $J_{\text{Si-O-Si}}$ coupling calculations on the optimized structure by varying $\Omega_0$ from 120° to 180° on a uniform grid for three Si–O bond distances, $d_{\text{Si-O}}$ = 1.58 Å, 1.60 Å and 1.62 Å, respectively, Fig. 2C.

O–Si–Si–O dihedral angle, $\phi$

A similar series of calculations were performed on the optimized geometry to investigate the $J_{\text{Si-O-Si}}$ coupling dependence on and correlation between $\Omega_0$ and $\phi$. This was accomplished by independently varying $\phi$ and $\Omega_0$ from −60° to +60° and 120° to 180°, respectively, Fig. 2B. All Si–O bond distances were set to 1.6 Å.

Outer Si–O–Si–Si bond angle, $\Omega_{k=0}$

A complete systematic exploration of the $J_{\text{Si-O-Si}}$ dependence on the six outer Si–O–Si bond angles would have exceeded our computational capabilities. In light of the well established$^4$ linear dependence of the isotropic $^{29}$Si chemical shift on the mean Si–O–Si bond angle for a Q$^4$ tetrahedra we attempted to reduce the dimensionality of the problem by using the mean Si–O–Si bond angle for each Q$^4$ tetrahedra, (Si$^{(i)}$ and Si$^{(j)}$) involved in the $J_{\text{Si-O-Si}}$ coupling, that is,

$$J_j = \frac{1}{4} \sum_{k=0.1.2.3} \Omega_k, \quad \text{and} \quad J_j = \frac{1}{4} \sum_{k=0.4.5.6} \Omega_k$$

Fig. 1. (H$_3$SiO)$_3$–Si–O–Si–(OSiH$_3$)$_3$ symmetric cluster used in calculating the $^2J_{\text{Si-O-Si}}$ coupling across Si$^{(i)}$–O–Si$^{(j)}$. Si–O–Si bond angles ($\Omega_1$ to $\Omega_6$). With the geometry constrained out to the third coordination sphere of the central linkage oxygen, a geometry optimization of the outermost Si–H bond distances and the remaining dihedral angles was performed once using restricted Hartree–Fock, RHF/6-311G(d) basis set. We found, as did Cadars et al.$^{26}$ that variations in these fourth coordination sphere geometries had negligible effect on the predicted $J$-coupling. We confirmed this finding with several $J_{\text{Si-O-Si}}$ coupling calculation starting with RHF/6-311G(d) optimized initial geometries and the results are tabulated in Table S3 of the ESI.$^\dagger$ A complete list of all geometrical constraints imposed in this study is tabulated in Tables S1–S5 of the ESI.$^\dagger$
to calculate a double mean

$$\bar{(\Omega)} = \frac{\langle \Omega \rangle I + \langle \Omega \rangle F}{2} = \frac{1}{8} \left( 2\Omega_0 + \sum_{k=1}^{6} \Omega_k \right). \quad (2)$$

Through systematic variation of $\Omega_0$ (the central linkage angle) and $\bar{(\Omega)}$ we show (vide infra) that a combined measurement of isotropic $^{29}\text{Si}$ chemical shift and $^{2}J_{\text{Si-O-Si}}$ can be exploited to determine the local structure around the $Q^1$-$Q^{\perp}$ linkage.

Despite this effort to reduce the dimensionality of this problem from seven to two, there still exist infinite combinations of $\Omega_{k\neq 0}$ that lead to the same $\bar{(\Omega)}$ in eqn (2), with the exception of the singular—and highly unlikely—occurrence of $\langle \Omega \rangle = 180^\circ$. To ensure a systematic variation of the local structure, we choose to constrain all $\Omega_{k\neq 0} = \Omega_{\text{out}}$. A series of $^{2}J_{\text{Si-O-Si}}$ calculations were performed by independently vary $\Omega_{\text{out}}$ and $\Omega_0$ from $120^\circ$ to $180^\circ$ on a uniform grid. The calculated $^{2}J_{\text{Si-O-Si}}$ as a function of $\bar{(\Omega)}$ and $\Omega_0$ is presented in Fig. 2A. All Si–O bond distances were set to 1.6 Å. Of course, the constraint $\Omega_{k\neq 0} = \Omega_{\text{out}}$, implemented only to ensure a systematic local structural variation, is unrealistic even for most crystalline silicates and highly siliceous zeolites, as well as in silica glass and other silica rich disordered materials. To break free from this constraint numerous $^{2}J_{\text{Si-O-Si}}$ coupling calculations were performed at arbitrary outer Si–O–Si bond angles $\Omega_{k\neq 0}$ and $\phi$, with values listed in Tables S3 and S4 of the ESI.† These calculations are used to further verify agreement with our proposed $^{2}J_{\text{Si-O-Si}}$ coupling model.

All additional numerical analysis codes were written in python using NumPy libraries. The least square analysis was performed using python’s LMFIT module. The graphics were produced using python’s matplotlib library.33

### 3 Theory

The J coupling contribution to the nuclear spin Hamiltonian can be written

$$\hat{H}_J = \mu_N \hat{\mathbf{N}} \cdot \hat{\mathbf{N}} = \hbar^2 \gamma_N N \hat{\mathbf{N}} \cdot \hat{\mathbf{N}}, \quad (3)$$

The convention is to combine the gyromagnetic ratio constants and the reduced $\mathbf{K}$ tensor such that

$$\hat{H}_J = \hbar 2\pi \hat{\mathbf{N}} \cdot \mathbf{J} \hat{\mathbf{N}}, \quad (4)$$

with

$$\mathbf{J} = \frac{\hbar \gamma_N N}{2\pi} \mathbf{K}. \quad (5)$$

This gives a $\mathbf{J}$ tensor with dimensions of inverse time.

As we explored the calculated variations in $^{2}J_{\text{Si-O-Si}}$ with changing cluster structure, we searched for the possible empirical relationships that might characterize the observed correlation of $^{2}J_{\text{Si-O-Si}}$ to structure. In our calculations we found that the majority of the $J$-coupling arises from the Fermi contact (FC) contribution, and the remaining contributions from spin–dipolar (SD), paramagnetic spin–orbit (PSO), and diamagnetic spin–orbit (DSO), as illustrated in Fig. S2 of the ESI.† for account less than 10% of the net $J$-coupling. With this in mind, we looked for guidance in the older literature of $J$ coupling theory and focused on the simple and highly approximate MO theory approach outlined by Pople and Santry, which considers only the isotropic Fermi contact contribution and yields the expression

$$\mathbf{K}^{(\text{FC})} = \frac{4}{9} \mu_0 \mu_B \gamma_N(0) s_N(0) \pi_{\text{N,N}}, \quad (6)$$

where $\mu_0$ is the magnetic constant, $\mu_B$ is the Bohr magneton, $s_0(0)$ and $s_N(0)$ are the values of the valence s-orbitals of atoms N and N at the nuclei, and $\pi_{\text{N,N}}$ is the mutual atom–atom polarizability of Coulson and Longuet-Higgins, given by

$$\pi_{\text{N,N}} = -4 \sum_i \sum_{\text{occ}} \sum_j c_{\mu,j} c_{\mu,i} f_{\nu,j} / e_j - e_i \quad (7)$$

Here the summation is over occupied ($\mu$) and unoccupied ($\nu$) molecular orbitals, $|\psi_\mu\rangle$, with energy $e_\mu$ and given by

$$|\psi_\mu\rangle = \sum_{\mu} c_{\mu,i} |\phi_\mu\rangle, \quad (8)$$

which are expressed in terms of the valence hybrid type orbitals (HTOs), $|\phi_\mu\rangle$, which are given by

$$|\phi_\mu\rangle = a_\mu |s\rangle + (1 - a_\mu^{1/2}) |p\rangle, \quad (9)$$
where $|s\rangle$ and $|p\rangle$ are the atomic-type orbitals and $a_i^s$ is the s-character of the HTO. In the summation of eqn (7) the $\mu$ and $\nu$ index the HTOs on N and N', respectively.

An exhaustive search of the literature reveals few MO theory studies considering the geminal $J_{\text{Si–O–Si}}$ coupling between tetrahedrally coordinated atoms. The most relevant and detailed discussion we could find on this topic is a chapter in 1988 by Klessinger and Barfield,\textsuperscript{42} examining the dependence of geminal $^{13}\text{C},^{13}\text{C}$ coupling constants. In this case they derive the mutual atom–atom polarizability as

$$\pi_{C_i,C_j} = \frac{a_i^2 a_j^2}{16\beta^4} \left[ -4\beta_{2,2}^2 - (\beta_{1,3} - \beta_{2,2})^2 + \left( \sum_x \beta_{2,2}^x + \sum_x \beta_{2,2}^{-x} \right)^2 \right]$$

(10)

where $a_i^2$ and $a_j^2$ are the s-character of the HTOs at carbon $C_i$ and $C_j$ along C–C bond directed towards $C_2$, in a $C_1$–$C_2$–$C_3$ linkage. The integral $\beta_{\mu,\nu}$ is the matrix element of the Hamiltonian operator in the HTO basis set $|\phi_{\mu}\rangle$,

$$\beta_{\mu,\nu} = \langle \phi_{\mu} | H | \phi_{\nu} \rangle.$$ (11)

The definition of these integrals are given in Klessinger and Barfield.\textsuperscript{42} If all integrals in eqn (10) except $\beta_{2,2}^2$ are ignored, the mutual atom–atom polarizability term can be approximated\textsuperscript{42} to

$$\pi_{C_i,C_j} \propto a_i^2 a_j^2 a_{2,2}^4,$$ (12)

where $a_i^2$ is the s-character of the valence HTO at $C_i$. The $^2J_{C_i,C_j}$ can then be approximated to

$$^2J_{C_i,C_j} \propto a_i^2 a_j^2 a_{2,2}^2.$$ (13)

While eqn (13) predicts a simple linear correlation of $^2J_{C_i,C_j}$ to the s-character product, we expect this highly approximated correlation to deviate from linearity due to the neglect of the vicinal integrals.\textsuperscript{42} Nevertheless, this approximate model provides a useful starting point for developing an empirical expression for geminal $J$ coupling across two coupled $^{29}\text{Si}$. On the basis of eqn (13), we propose that $^2J_{\text{Si–O–Si}}$ is approximately given by

$$^2J_{\text{Si–O–Si}} \propto \alpha_{\text{Si}}^2 \alpha_{\text{O}}^2 \alpha_{\text{O}}^2 = \left( \alpha_{\text{Si}}^2 \alpha_{\text{O}}^2 \right) \left( \alpha_{\text{Si}}^2 \alpha_{\text{O}}^2 \right),$$ (14)

where $(\alpha_{\text{Si}}^2 \alpha_{\text{O}}^2)$ and $(\alpha_{\text{Si}}^2 \alpha_{\text{O}}^2)$ are the products of the s-character of the valence HTOs associated with the $\text{Si}^{[0]}$–$\text{O}$ and $\text{Si}^{[0]}$–$\text{O}$ bonds across $\text{Si}^{[0]}$–$\text{O}$–$\text{Si}^{[0]}$ linkage, respectively, as illustrated in Fig. 3.

**Fig. 3** Simple illustration of valence HTOs associated with the $\text{Si}^{[0]}$–$\text{O}$ and $\text{Si}^{[0]}$–$\text{O}$ bonds across $\text{Si}^{[0]}$–$\text{O}$–$\text{Si}^{[0]}$ linkage.

### 4 Results and discussion

#### 4.1 Dependence on local structure

In this subsection, we discuss and examine the contributions to the net $^2J_{\text{Si–O–Si}}$ coupling arising from the variations in the local structure on the basis of the underlying s-characters $a_{\text{Si}}^2$, $a_{\text{O}}^2$, and $a_{\text{Si}}^2$ at the bridging oxygen and adjacent silicons respectively. These values were determined from the quantum chemistry DFT cluster calculation using Gaussian NBO version 3.1. For clarity, we only present a subset of results from Fig. 2 per structural parameters considered.

Shown in Fig. 4A is the expected dependence of $^2J_{\text{Si–O–Si}}$ coupling on $\Omega_o \in [120°,180°]$, for a subset of results from Fig. 2A where the outer Si–O–Si angles are held constant at $\Omega_{\text{Si–O}} = 180°$ and the distances held constant at $d_{\text{Si–O}} = 1.6$ Å. This dependence of $^2J_{\text{Si–O–Si}}$ coupling on the Si–O–Si linkage angle, $\Omega_o$, has been previously discussed by both Cadars et al.\textsuperscript{26} and Florian et al.\textsuperscript{25} In Fig. 4B we see the more intriguing result that the $^2J_{\text{Si–O–Si}}$ coupling has a markedly linear correlation to the product $a_{\text{Si}}^2 a_{\text{Si}}^2 a_{\text{O}}^2$, as predicted by eqn (14). As noted earlier, the slight deviation from linearity observed is not unexpected and is likely attributed to the neglected terms in the mutual atom–atom polarizability term.

In Fig. 4C and D we see that the variation in $^2J_{\text{Si–O–Si}}$ primarily arises from variation in $a_{\text{O}}^2$—the s-character product of the two valence HTOs at the bridging oxygen—while there is a minor yet non-negligible variation coming from $a_{\text{Si}}^2 a_{\text{Si}}^2 a_{\text{Si}}^2$—the s-character product of the two silicon valence HTOs in the Si–O–Si linkage. The change in $a_{\text{O}}^2$ is the result of the change in the hybridization of the valence orbitals at the bridging oxygen from sp$^2$ (33.33% s-character) at $\Omega_o = 120°$ to sp$^3$ (50% s-character) at $\Omega_o = 180°$.
A popular approximation for the s-character at the bridging oxygen\(^{3,42}\) is given by

\[
\alpha_i^2 \approx f_0(\Omega) = \cos \Omega \cos \Omega - 1.
\] (15)

Here we use the symbol \(f_0(\Omega)\) to distinguish the approximated s-character at the bridging oxygen from the symbol \(\alpha_i^2\) for the s-character calculated using quantum chemistry DFT calculations.

With the s-character of each sp\(^3\) valence HTO on a tetrahedral silicon expected to be 25\%, the calculated value of \(\alpha_i^2, d_{\text{Si-O}}\) is also as expected at \(\sim (25\%)^2 = 6.25\%\). The slight increase in \(\alpha_{\text{Si,O}}^2, d_{\text{Si-O}}\) from 6.1\% to 6.7\% in Fig. 4D with decreasing \(\Omega_0\) may seem surprising from a simple hybrid orbital picture—as all intra-tetrahedral angles and Si–O distances are held constant at \(\perp\text{O-Si-O} = 109.5^\circ\) and \(d_{\text{Si-O}} = 1.6\,\AA\), respectively, in these calculations. In fact, for this subset of results, even the outer Si–O–Si angles are held fixed at \(180^\circ\), so it is only the variation of the linkage angle \(\Omega_0\) that is responsible for this slight change in \(\alpha_{\text{Si,O}}^2, d_{\text{Si-O}}\). We will examine the origin of this variation shortly when the influence of the outer Si–O–Si angles on \(\alpha_{\text{Si,O}}^2\) are considered.

In Fig. 5A is the variation of \(\alpha_{\text{Si,O}}^2\) with the two central linkage Si–O bond distances, \(d_{\text{Si-O}} \in [1.58\,\AA, 1.62\,\AA]\), for a subset of results from Fig. 2C where the central linkage angle was fixed at \(\Omega_0 = 180^\circ\) and the outer Si–O–Si angles and outer distances are held constant at \(\perp\text{O-Si-O} = 146^\circ\) and \(d_{\text{Si-O}} = 1.6\,\AA\), respectively. The \(\alpha_{\text{Si,O}}^2\) coupling remains relatively constant around 21.5 Hz over this range of central linkage Si–O bond distances, with a slight decrease from \(\sim 22\) to \(\sim 21\) Hz with increasing bond length. This relative independence of \(\alpha_{\text{Si,O}}^2\) on the central linkage Si–O bond distances is consistent with previous observations by Florian et al.\(^{23}\).

In Fig. 6A we find again that the \(J_{\text{Si-O-Si}}\) coupling has a linear correlation to the product \(a_{\text{Si-O}}, d_{\text{Si-O}}\), and in Fig. 5C we see no observable dependence of \(J_{\text{Si-O-Si}}\) coupling on the s-character product \(\alpha_{\text{Si,O}}^2\) at the bridging oxygen. This is because, for this subset of calculations, the hybridization at the bridging oxygen was locked to sp through the constraint \(\Omega_0 = 180^\circ\). Since the s-character at the bridging oxygen predominantly depends on the Si–O–Si bond angle, as noted in eqn (15), the change in Si–O bond distance, \(d_{\text{Si-O}}\), shows no observable change in its s-character. In Fig. 5D we find that the minor variation in \(J_{\text{Si-O-Si}}\) coupling is dominated by the change in \(a_{\text{Si}}, a_{\text{Si}}^2\). While a decrease in the \(\alpha_{\text{Si}}\) with increasing Si–O bond distance has been previously reported by Grimmer and coworkers\(^{10,11}\) it was in the context of correlated changes in the intra-tetrahedral angle \(\perp\text{O-Si-O}\). With the intra-tetrahedral angles in this calculation fixed at \(\perp\text{O-Si-O} = 109.5^\circ\), it seems that changes in Si–O length alone lead to minor variations in \(a_{\text{Si}}^2\)—although these result in relatively insignificant variations in \(J_{\text{Si-O-Si}}\).
In Fig. 7A is the variation of $J_{\text{Si-O-Si}}$ with $\Omega_i$, as calculated by eqn (2), for a subset of results from Fig. 2A subjected to the constraint $\Omega_0 = 180^\circ$, $\Omega_{\text{out}} = \Omega_{\text{out}}$ and $d = 1.6$ Å where $\Omega_{\text{out}}$ varied from 120$^\circ$ to 180$^\circ$. The variation in Fig. 7A is about 25% of that shown in Fig. 4A and is found to be the second most dominant dependence of $J_{\text{Si-O-Si}}$ coupling. As $\Omega_0$ is fixed, it is the change in the outer Si–O–Si bond angles, $\Omega_{\text{out}}$, that leads to this variation in $J_{\text{Si-O-Si}}$. In Fig. 7B we again find the markedly linear correlation of $J_{\text{Si-O-Si}}$ coupling with $a_{\text{Si}}^2 a_{\text{O}}^2$ as predicted by eqn (14). As might be expected, no observable dependence of $J_{\text{Si-O-Si}}$ coupling on $a_{\text{O}}^2$ is observed in Fig. 7C since the hybridization at the bridging oxygen was fixed to sp with the constraint $\Omega_0 = 180^\circ$. Clearly, the origin of the $J_{\text{Si-O-Si}}$ dependence on the outer angles, $\Omega_{\text{out}}$ comes from the variation in $a_{\text{Si}}^2 a_{\text{O}}^2$ as seen in Fig. 7D. Why would the $a_{\text{Si}}^2$ or $a_{\text{O}}^2$ increase as the outer angles, $\Omega_{\text{out}}$ increase? This is the same question alluded to earlier with respect to Fig. 4D. The logic is as follows. We expect the sum of the $s$-characters for the four HTO around each silicon to be constant. So, as the $s$-character of one HTO deviates from 25%, the $s$-characters of the other HTO compensate to maintain the constant sum. Hence, we expect the $s$-character of the HTO that is part of the central linkage to increase as the average $s$-character of the other three HTOs decreases. Close examination of the variation in $a_{\text{Si}}^2$, as the function of the Si–O–Si tetrahedral angle, $\Omega_0$, and average Si–O–Si bond angle, $\langle \Omega \rangle$, also shown in Fig. S3 of the ESI, reveals an approximate proportionality given by

$$a_{\text{Si}}^2 \propto \cos \Omega_0 - \cos \langle \Omega \rangle.$$  

(16)

In regard to Fig. 4D, since the outer Si–O–Si bond angles are held constant, $\Omega_{\phi=0} = 180^\circ$, the individual $s$-characters at Si(i) and Si(j) and, therefore, the product, $a_{\text{Si}}^2 a_{\text{O}}^2$, decreases as $\Omega_0$ increases.

The highly approximate $J$-coupling model in eqn (14) predicts a linear correlation of $J_{\text{Si-O-Si}}$ coupling with respect to the $s$-character product, $a_{\text{Si}}^2 a_{\text{O}}^2$. From the ab initio calculations, shown in Fig. 8, however, we find that the $J_{\text{Si-O-Si}}$ coupling is better described by a quadratic in the $s$-character product, $a_{\text{Si}}^2 a_{\text{O}}^2$, with $R^2 = 0.99164$. As mentioned earlier, this slight curvature is not unexpected, since the model in eqn (14) neglects all the vicinal integrals from the mutual atom–atom polarizability term. Further discussion on the effect of vicinal integrals can be found in the chapter by Klessinger and Barfield.42

Fig. 8 shows the $J_{\text{Si-O-Si}}$ couplings in two different colors, gray and black. The gray dots correspond to couplings evaluated by systematic variation of the local structure, also shown in Fig. 2, and are provided in the Tables S1 and S2 of the ESI.† The black dots correspond to couplings evaluated at arbitrary $\Omega_0$ and $\phi$ and are listed in Tables S3 and S4 of the ESI.† Most notably a consistent trend in $J_{\text{Si-O-Si}}$ is observed with respect to the $s$-character product, $a_{\text{Si}}^2 a_{\text{O}}^2$, for both systematic and arbitrary structural variation.

On the basis of the results and discussion presented here we can now construct an expression relating $J_{\text{Si-O-Si}}$ to local structure. The most straightforward approach would be a substitution of eqn (15) and (16) into eqn (14). We found, however, that such an approach leads to an excessive number of coefficients for calibrating the relationship. Instead we found that the same relationship can be expressed with fewer coefficients using

$$J \left( \Omega_0, \langle \Omega \rangle, \phi \right) \approx -\langle \Omega \rangle \cos \Omega_0 \left( m_1 f_1^2(\Omega_0) - m_2 \cos 3\phi \right) + J_0.$$  

(17)
For this expression the coefficients \( m_1 = 0.778 \pm 0.004 \) Hz per \( ^\circ \), \( m_2 = 0.0058 \pm 0.0005 \) Hz per \( ^\circ \) and \( J_0 = -8.3 \pm 0.1 \) Hz were determined by least square minimization of the objective function

\[
\arg \min_{J_0} \left| J(ab \text{ initio}) - J(\Omega, \phi, \Omega) \right|^2_{2, \ell}.
\]

Note there is a strong cross correlation coefficient \( \rho \approx -0.918 \) between \( m_1 \) and \( J_0 \) in this determination. A comparison of \( ab \text{ initio} \) \( ^2J_{\text{Si-O-Si}} \) couplings with respect to the \( ^2J_{\text{Si-O-Si}} \) coupling model in eqn (17) is presented in Fig. 9A. Again, the points in gray and black correspond to systematic and arbitrary variation of the local structure, respectively. Excellent agreement between the \( ^2J_{\text{Si-O-Si}} \) coupling model and \( ^2J_{\text{Si-O-Si}} \) coupling from \( ab \text{ initio} \) calculation is observed with \( R^2 = 0.99518 \). Note that in this approach the slight dependence on Si–O bond distance, \( d_{\text{Si-O}} \), has been neglected.

Given that \( m_2 \ll m_1 \), we find that the \( ^2J_{\text{Si-O-Si}} \) coupling model of eqn (17) can be simplified by dropping the \( m_2 \cos 3\phi \) term to obtain

\[
J(\Omega_0, \phi) \approx -m_1 \cos \Omega_0 \left( \frac{\cos \Omega_0}{\cos \Omega_0 - 1} \right)^2 + J_0. \tag{19}
\]

A comparison of \( ab \text{ initio} \) \( ^2J_{\text{Si-O-Si}} \) couplings with respect to the \( ^2J_{\text{Si-O-Si}} \) coupling model in eqn (19) is presented in Fig. 9B. Neglecting the \( \phi \) dependence leads to slightly greater scatter which is more noticeable at the higher couplings and a small drop of linear correlation coefficient to \( R^2 = 0.99016 \). Given this agreement all further analysis will use the \( ^2J_{\text{Si-O-Si}} \) coupling model of eqn (19).

### 4.2 Mapping to local structure

Even with our approximate model for \( ^2J_{\text{Si-O-Si}} \) in eqn (19) being only a function of \( \Omega_0 \) and \( \Omega_0 \), there is no unique mapping of a single \( ^2J_{\text{Si-O-Si}} \) coupling back to local structure. Fortunately, the \( ^{29}\text{Si} \) isotropic chemical shift of a Q4 site has a well established correlation \( ^{29}\text{Si} \) to the mean inter-tetrahedral angle, \( \langle \Omega \rangle \), of a given Q4, of which, the linear correlation

\[
\delta_{CS} = a_0(\Omega) + b_0,
\]

is the simplest, while still giving a reasonably accurate correlation in the relevant range of \( \langle \Omega \rangle \in [140^\circ, 160^\circ] \) as detailed further in the ESI.† The data for a number of crystalline silicas and siliceous framework silicates taken from the literature \(^9,44,45\) is shown in Fig. 10, along with a fit to eqn (20) with coefficients \( a_0 \) and \( b_0 \) provided in Table 1.

The \( ^2J_{\text{Si-O-Si}} \) coupling across \( ^{29}\text{Si}^{0}-\text{O}^{29}\text{Si}^{(j)} \) linkage involves two \( ^{29}\text{Si} \) isotropic chemical shifts, \( \delta_{CS,j} \) and \( \delta_{CS,p} \) associated with \( ^{29}\text{Si}^{0} \) and \( ^{29}\text{Si}^{(j)} \) respectively. Using the linear correlation

![Fig. 9](image)

(A) Plot comparing prediction of \( ^2J_{\text{Si-O-Si}} \) Coupling model, eqn (17), and \( ^2J_{\text{Si-O-Si}} \) coupling from \( ab \text{ initio} \) calculations. Gray and black dots correspond to \( ^2J_{\text{Si-O-Si}} \) couplings evaluated by systematic and arbitrary structural variations, respectively. The calculated Pearson correlation coefficient is \( R^2 = 0.99518 \). (B) Plot comparing prediction of \( ^2J_{\text{Si-O-Si}} \) coupling model, eqn (19) and \( ^2J_{\text{Si-O-Si}} \) coupling from \( ab \text{ initio} \) calculations. The calculated Pearson correlation coefficient is \( R^2 = 0.99016 \).

![Fig. 10](image)

Linear correlation between average Si–O–Si bond angle, \( \langle \Omega \rangle \), about the Si tetrahedron and \( ^{29}\text{Si} \) isotropic chemical shift, \( \delta_{CS} \). Twelve \( ^{29}\text{Si} \) isotropic chemical shift sites in Tridymite were taken from Kitchin et al.\(^6\) and average Si–O–Si bond angles from Baur.\(^{45}\) The remaining were obtained from Engelhardt and Radeglia\(^9\) and references within.
The X-ray determined Si–O–Si bond angle, \( \Omega_0 \), is the Si–O–Si bond angle inferred from single crystal X-ray analysis, and \( \Omega_0 \) is the Si–O–Si bond angle calculated using eqn (23) with \( m_1 = 0.778 \) Hz per \( ^\circ \) held constant. With this approach we obtain best agreement with \( J_0 = -7.5 \pm 0.6 \) Hz.

A plot of measured \(^J\)J_{\text{Si-O-Si}} coupling vs. \( \overline{\delta_{\text{C2}}} \) from Sigma-2 is presented in Fig. 11B. Overlaid on top is a grid map of calibrated (\( \overline{\Omega} \)) and \( \Omega_0 \). In Fig. 11C, the calculated (\( \overline{\Omega} \)) and \( \Omega_0 \) (filled circles) along with X-ray determined (\( \overline{\Omega} \)) and \( \Omega_0 \) (open circles) are presented. Overlaid on top is the grid map of \( J \) coupling and \( \overline{\delta_{\text{C2}}} \). Agreement to within \( \sim 3^\circ \) between \( \Omega_0 \) from the X-ray and NMR measurements is observed for pairs 4-1, 2-3 and 1-3, while there is a mismatch of \( \sim 7^\circ \) for the 4-2 pair. With only the limited data from Sigma-2, it is clear that additional experimental efforts in refinement of the calibration of eqn (23) would be helpful. Such efforts are, in fact, currently in progress in our laboratory on highly silicious zeolites using the recently developed PIETA method\(^{26} \) for rapid and sensitive 2D J/NMR spectroscopy.

Overall, the results presented here are extremely promising and open the door to new opportunities to more fully exploit \(^J\)J_{\text{Si-O-Si}} couplings as quantitative probes of structure in silicates. With only a \( \sim 1 \) Hz change from the ab initio derived value of \( J_0 = -8.3 \pm 0.1 \) Hz, to the Sigma-2 calibrated value of \( J_0 = -7.5 \pm 0.6 \) Hz, the proposed correlated models of \(^{29}\)Si chemical shift and \(^J\)J_{\text{Si-O-Si}} coupling provide an acceptable model for the quantitative interpretation of the \(^J\)J_{\text{Si-O-Si}} Coupling. It will be interesting to see if a similar analysis can be applied with other geminal \( J \) couplings across a bridging oxygen, such as a \(^{31}\)P–O–\(^{31}\)P or \(^{27}\)Al–O–\(^{29}\)Si linkage.

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### Table 1: Final coefficients for eqn (22) after calibration with the results of Fig. 10 and eqn (23) after calibration with Sigma-2

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_j )</td>
<td>-0.6148 ppm per ( ^\circ )</td>
<td>( b_j )</td>
<td>-19.297 ppm</td>
</tr>
<tr>
<td>( a_j )</td>
<td>107.88</td>
<td>( b_j )</td>
<td>223.49</td>
</tr>
<tr>
<td>( c_j )</td>
<td>0.00002487 ( ^\circ )</td>
<td>( d_j )</td>
<td>53.01</td>
</tr>
<tr>
<td>( m_1 )</td>
<td>0.778 Hz per ( ^\circ )</td>
<td>( J_0 )</td>
<td>-7.5 Hz</td>
</tr>
</tbody>
</table>

---

**Fig. 11** (A) Schematic of highly silicious zeolite Sigma-2 adapted from Cadars et al.\(^{26} \) (B) A correlation plot of \( \overline{\delta_{\text{C2}}} \) and \( J \) coupling for Sigma-2 with superimposed calibrated (\( \overline{\Omega} \)) and \( \Omega_0 \) grid. (C) Comparison of single crystal X-ray vs. NMR determined (\( \overline{\Omega} \)) and \( \Omega_0 \) for the four different \(^{29}\)Si pairs in Sigma-2. Superimposed is the \( \overline{\delta_{\text{C2}}} \) and \( J \) coupling grid. A good agreement between the two results is observed for pair 4-1, 2-3 and 1-3.
Table 2: Observed $^2J_{\text{Si-O-Si}}$ couplings (column 3) and $^{29}$Si average isotropic chemical shift, $\Delta
u_\text{C}$, (column 2) for the $^{29}$Si pairs (column 1) in highly siliceous zeolite Sigma-2. Listed along column 4 and 5, is $\Theta_0$ and $[\Omega]$ obtained from the crystal structure determined by single crystal X-ray analysis. Listed in column 6 and 7, is the $\Omega_0$ and $[\Omega]$ calculated using eqn (22) and (23).

<table>
<thead>
<tr>
<th>$^{29}$Si pair</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
</table>
|               | $\Delta
u_\text{C}$/ppm | $J$/Hz | $\Theta_0$/C | $\Omega_0$/C | $\Delta
nu_0$/ppm | $J_0$/Hz |
| 1-3           | -118.0      | 23.5      | 172.8        | 158.2        | 176.0        | 160.5      |
| 2-3           | -116.8      | 16.5      | 153.5        | 155.6        | 152.0        | 158.6      |
| 4-2           | -111.25     | 10.0      | 148.7        | 148.9        | 141.5        | 149.5      |
| 4-1           | -112.4      | 6.3       | 137.2        | 151.6        | 134.0        | 151.4      |

5 Summary

While both scalar $J$-couplings and homonuclear dipolar coupling are used qualitatively to establish connectivities between Si sites, it has been primarily homonuclear $^{29}$Si-$^{29}$Si dipolar couplings through measurements of double quantum buildup curves that have provided some of the most useful quantitative details in the structure refinement of many siliceous zeolites and NMR crystallographic structural studies of meso- and microporous silicate materials. Here we have examined whether $^2J_{\text{Si-O-Si}}$ the geminal coupling across a Si–O–Si linkage, can be turned into a more quantitative probe of the local structure in silicate networks.

Using high level density function theory (DFT) methods, we have found that the two main influences on the $^2J_{\text{Si-O-Si}}$ couplings are a primary dependence on the linkage Si–O–Si angle and a secondary dependence on mean Si–O–Si linkage of the two coupled $^{29}$Si nuclei. We show that the simple and highly approximate MO theory approach outlined by Pope and Santry can provide key insights when developing approximate models for geminal $J$-couplings based on results from high level density function theory (DFT) methods. Exploiting a well established correlation between $^{29}$Si isotropic chemical shift and the mean Si–O–Si angle of a $Q^2$ site, we have developed an approach where a correlation plot of $^2J_{\text{Si-O-Si}}$ to mean $^{29}$Si isotropic chemical shift can be mapped into a 2D correlation of linkage Si–O–Si bond angle, $\Theta_0$, to mean Si–O–Si bond angle of the two coupled $^{29}$Si. Using available experimental $^2J_{\text{Si-O-Si}}$ couplings from Sigma-2, we found that only a minor adjustment of one ab initio derived coefficient in our $^2J_{\text{Si-O-Si}}$ model was needed to bring our model in line with experimental results.

Conflicts of interest

There are no conflicts to declare.

Appendix

A Inversion of $^2J_{\text{Si-O-Si}}$ to $\Theta_0$

For inversion of eqn (19) with respect to $\Theta_0$, a close form solution can be obtained by first recasting eqn (19) into the form of a cubic equation

$$\lambda^3 + x\lambda^2 - \frac{x^2}{2} \lambda + x = 0,$$

where $\lambda = \cos \Theta_0$, and

$$x = \frac{J - J_0}{m_1 [\Omega]}.$$  (26)

The roots of eqn (25) are

$$\lambda_1(x) = -\frac{1}{3}x + [S(x) + T(x)],$$  (27a)

$$\lambda_2(x) = -\frac{1}{3}x - \frac{1}{2}[S(x) + T(x)] + \frac{i}{2}\sqrt{3}[S(x) - T(x)],$$  (27b)

$$\lambda_3(x) = -\frac{1}{3}x - \frac{1}{2}[S(x) + T(x)] - \frac{i}{2}\sqrt{3}[S(x) - T(x)],$$  (27c)

where we have defined

$$T(x) = \sqrt[4]{R(x) - \sqrt{D(x)}},$$  (28a)

$$S(x) = \sqrt[4]{R(x) + \sqrt{D(x)}},$$  (28b)

$$R(x) = -\frac{1}{54}x(2x^2 + 18x + 27),$$  (28c)

$$D(x) = \frac{1}{108} x^2(4x + 27).$$  (28d)

The number of real and complex roots can be determined from the sign of the discriminant, $D(x)$ in eqn (29):

- If $D(x) > 0$, one root is real and two are complex conjugate.
- If $D(x) = 0$, all roots are real with at least two equal.
- If $D(x) < 0$, all roots are real and unequal.

For the given problem, the discriminant $D(x)$, eqn (28d), is positive if $x > -6.75$. For given $J_0 < 0$ Hz and $m_1 > 0$ Hz$^{-1}$, $x$ is always positive and so is the discriminant. Therefore, there exists only one real root of eqn (25) given by eqn (27a). Thus, the inversion of eqn (19) with respect to $\Theta_0$ is

$$\Theta_0(x) = \frac{180 \cos^{-1}[\lambda(x)]}{\pi}.$$  (29)

To further simplify this result, $\Theta_0(x)$ was approximated to a function $g(x)$ that closely resembles $\Theta_0(x)$ within the relevant range of 120° to 180°. For $\Theta_0(x) \in [120°,180°]$, $\lambda_1(x)$ maps to a range $\lambda_1(x) \in [-0.5, -1.0]$ which further maps to a range $x \in [1/18,1/4]$. Within the relevant range $x \in [1/18,1/4]$, $\Theta_0(x)$ can be approximated as

$$g(x) = a_x + b_x x + c_x \exp[d_x x],$$  (30)

where the coefficients are listed in Table 1. The function $g(x)$ provides a good approximation of $\Theta_0(x)$ with $|g(x) - \Theta_0(x)| < 0.5°$ within the range $\Theta_0(x) \in [120°, 176°]$. Deviations from 176° and onwards to a maximum of 3.7° at $\Theta_0(x) = 180°$ is significant although it can be neglected because of its low probability. A comparison of $\Theta_0(x)$ and $g(x)$ as a function of $x$ is provided in the ESL.

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References