Free induction decays in nuclear spin- $\frac{1}{2}$ lattices with a small number of interacting neighbors: The cases of silicon and fluorapatite

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Nuclear spin-1/2 lattices where each spin has a small effective number of interacting neighbors represent a particular challenge for first-principles calculations of free induction decays (FIDs) observed by nuclear magnetic resonance. The challenge originates from the fact that these lattices are far from the limit where classical spin simulations perform well. Here we use the recently developed method of hybrid quantum-classical simulations to compute nuclear FIDs for ²⁹Si-enriched silicon and fluorapatite. In these solids, the small effective number of interacting neighbors is either due to the partition of the lattice into pairs of strongly coupled spins (silicon), or due to the partition into strongly coupled chains (fluorapatite). We find a very good overall agreement between the hybrid simulation results and the experiments. In addition, we introduce an extension of the hybrid method, which we call the method of coupled quantum clusters. It is tested on ²⁹Si-enriched silicon and found to exhibit excellent performance.

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I. INTRODUCTION

Nuclear free induction decay (FID) measured by nuclear magnetic resonance (NMR) is a quantity proportional to an infinite temperature time auto-correlation function of the nuclear total spin polarization [1,2]. The Fourier transform of the FID gives the shape of NMR absorption peak [1–3]. The measurements of FIDs can be used to extract microscopic information about solids such as the distances between nuclear spins or electronic spin susceptibility. Beyond NMR, the simulations of high-temperature spin dynamics belong to the broader field of dynamic thermalization.

First-principles calculation of NMR FID in solids is a long-standing problem, which is almost as old as the field of NMR itself [1,3,4]. Quite a number of methods for the firstprinciples calculations were proposed in the past [1,2,5-18], however, none of them are widely applied today. This situation is, in part, due to the nonperturbative character of the FID problem: There is no clear separation of timescales, hence, there is no apparent small parameter for an approximate expansion. As a result, the above-cited methods were, typically, based on uncontrolled approximations. Another reason for the absence of a widespread adoption of a single method is that the FID approximation schemes were rarely tested beyond the case of the NMR benchmark material calcium fluoride (CaF_2) [19]. As a consequence, the predictive performance of these schemes for a broader class of systems remained unclear.

Recently, we proposed [20] a hybrid quantum-classical method based on simulating a large quantum spin lattice by a small cluster of quantum spins coupled to an environment of interacting classical spins via a correlation-preserving scheme. The unique feature of the method is that it affords an effective estimate of the uncertainty of its predictions by comparing the results of simulations for different sizes of the quantum cluster. This means that the reliability of the hybrid predictions can be assessed without comparing with an experiment or with a numerically exact quantum result. In Ref. [20], we extensively tested the hybrid method on various model one- and two-dimensional lattices of spins-1/2 with nearest-neighbor interactions, as well as on the experimentally measured FIDs in CaF₂ [19]. In almost all the cases, the observed performance was excellent, and when it was not, the above-mentioned uncertainty estimate indicated a discrepancy prior to the comparison with the reference data.

For spin lattices where each spin strongly interacts with a sufficiently large number of neighbors $n_{\rm eff}$, purely classical simulations were found to describe the FIDs quite accurately [18]. An example here is CaF₂. In this case, the hybrid method generates results that exhibit only small deviations from the classical predictions. Hybrid calculations are still useful for large- $n_{\rm eff}$ lattices, because the deviation between the classical and the hybrid results quantifies the predictive uncertainty of both methods [20]. However, the true value of the hybrid method is in the simulations of three-dimensional spin-1/2 lattices with small $n_{\rm eff}$. In such a setting, classical simulations are not expected to be quantitatively accurate, while direct purely quantum simulations are not feasible.

Two examples of small- $n_{\rm eff}$ spin-1/2 systems are ²⁹Sienriched silicon, where, for certain orientations of external magnetic field, the lattice breaks into strongly interacting spin

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pairs, and fluorapatite $Ca_{10}(PO_4)_6F_2$, where ¹⁹F nuclei are positioned in parallel chains with weak interchain coupling. In the present paper, we test the hybrid method by comparing its predictions with the measured FIDs in ²⁹Si-enriched silicon and fluorapatite. In addition, we introduce an extension of the hybrid method, which we call the method of coupled quantum clusters. The latter method is tested on ²⁹Si-enriched silicon.

II. GENERAL FORMULATION

Let us consider a material with one type of magnetic nuclei and no disorder.

The FID experiment in solids measures the relaxation of the total spin magnetization transverse to a strong static magnetic field \mathbf{B}_0 . In the Larmor rotating reference frame, the relaxation is described by the effective truncated Hamiltonian of the general form

$$\mathcal{H} = \sum_{\alpha, i < j} J_{i,j}^{\alpha} S_i^{\alpha} S_j^{\alpha}, \quad \alpha \in \{x, y, z\},$$
(1)

where S_i^{α} is the operator of spin projection on axis α for the *i*th lattice site and the *z* axis is chosen along the direction of **B**₀. The coupling constants $J_{i,j}^{\alpha}$ correspond to the magnetic dipolar interaction between nuclear spins averaged over the fast Larmor precession. They have the form

$$J_{i,j}^{z} = -2J_{i,j}^{x} = -2J_{i,j}^{y} = \frac{\gamma^{2}\hbar^{2}(1-3\cos^{2}\theta_{ij})}{|\mathbf{r}_{ij}|^{3}}.$$
 (2)

Here, \mathbf{r}_{ij} is the vector connecting lattice sites *i* and *j*, θ_{ij} is the angle between \mathbf{r}_{ij} and \mathbf{B}_0 , γ is the gyromagnetic ratio of nuclear spins.

The effective number of interacting neighbors, which controls the applicability of the classical simulations, is defined as [18]

$$n_{\rm eff} \equiv \frac{\left[\sum_{i} \left(J_{i,j}^{x\,2} + J_{i,j}^{y\,2} + J_{i,j}^{z\,2}\right)\right]^{2}}{\sum_{i} \left(J_{i,j}^{x\,2} + J_{i,j}^{y\,2} + J_{i,j}^{z\,2}\right)^{2}}.$$
(3)

The signal measured in an FID experiment is proportional to the equilibrium infinite-temperature time auto-correlation function $C_x(t)$ of the total spin polarization $M_x(t)$ along a transverse direction,

$$C_x(t) = \langle M_x(t)M_x(0)\rangle, \qquad (4)$$

where

$$M_x = \sum_i S_i^x.$$
 (5)

In the case of purely quantum dynamics, the notation $\langle ... \rangle$ in Eq. (4) is defined as

$$\langle M_x(t)M_x(0)\rangle = \frac{1}{D} \operatorname{Tr} \left[M_x(t)M_x(0)\right],\tag{6}$$

where *D* is the dimensionality of the Hilbert space of the entire lattice.

III. HYBRID METHOD

The idea of the hybrid method is to approximate the dynamics of the fully quantum lattice by that of the hybrid

one consisting of a cluster of quantum spins surrounded by an environment of classical spins [20,21]. We denote the set of all sites of the hybrid lattice as \mathcal{L} . Among them, we choose the subset of lattice sites $\mathcal{Q} \in \mathcal{L}$ for the spins of the quantum cluster, the latter being described by a wave function $|\psi\rangle$. The spins on the rest of the lattice sites $\mathcal{C} = \mathcal{L}/\mathcal{Q}$ are treated classically, i.e., they are described as a set of three-dimensional vectors $\{\mathbf{s}_m\}$. The entire hybrid lattice has periodic boundary conditions.

The evolution of the quantum and the classical parts of the system are determined by the quantum and the classical Hamiltonians $\mathcal{H}_{\mathcal{Q}}$ and $H_{\mathcal{C}}$, respectively,

$$\mathcal{H}_{\mathcal{Q}} = \sum_{i < j, \alpha}^{i, j \in \mathcal{Q}} J_{i, j}^{\alpha} S_{i}^{\alpha} S_{i}^{\alpha} - \sum_{i \in \mathcal{Q}} \mathbf{h}_{i}^{\mathcal{C}\mathcal{Q}} \cdot \mathbf{S}_{i},$$
(7)

$$H_{\mathcal{C}} = \sum_{m < n, \alpha}^{m, n \in \mathcal{C}} J_{m, n}^{\alpha} s_{m}^{\alpha} s_{n}^{\alpha} - \sum_{m \in \mathcal{C}} \mathbf{h}_{m}^{\mathcal{QC}} \cdot \mathbf{s}_{m},$$
(8)

where S_i^{α} are the operators of spin projections as in Eqs. (1), $\mathbf{s}_m \equiv (s_m^x, s_m^y, s_m^z)$ are vectors of length $\sqrt{S(S+1)}$ representing the classical spins. In this paper, S = 1/2, hence $\sqrt{S(S+1)} = \sqrt{3}/2$. Also, $\mathbf{h}_i^{\mathcal{CQ}}$ and $\mathbf{h}_m^{\mathcal{QC}}$ are the effective magnetic fields coupling the quantum cluster and the classical environment to each other:

$$\mathbf{h}_{i}^{\mathcal{CQ}} = -\sum_{n \in \mathcal{C}} \begin{pmatrix} J_{i,n}^{x} s_{n}^{x} \\ J_{i,n}^{y} s_{n}^{y} \\ J_{i,n}^{z} s_{n}^{z} \end{pmatrix},$$
(9)

$$\mathbf{h}_{m}^{\mathcal{QC}} = -\sqrt{D_{\mathcal{Q}} + 1} \sum_{j \in \mathcal{Q}} \begin{pmatrix} J_{m,j}^{x} \langle \psi | S_{j}^{x} | \psi \rangle \\ J_{m,j}^{y} \langle \psi | S_{j}^{z} | \psi \rangle \\ J_{m,j}^{z} \langle \psi | S_{j}^{z} | \psi \rangle \end{pmatrix}, \qquad (10)$$

where $D_Q = 2^{N_Q}$ is the dimensionality of the Hilbert space of the quantum cluster consisting of N_Q spins. The equilibrium noise of quantum expectation values $\langle \psi | S_i^{\alpha} | \psi \rangle$ is smaller than its classical counterpart s_m^{α} by the factor $1/\sqrt{D_Q + 1}$ (for the explanation, see Refs. [20,21]). The above suppression is compensated by the factor $\sqrt{D_Q + 1}$ in Eq. (10). This factor corrects the amplitude mismatch between \mathbf{h}_m^{QC} and \mathbf{h}_m^{QC} that would happen in its absence.

According to the Hamiltonians (7) and (8), the equations of motion for the hybrid lattice take the form

$$|\dot{\psi}(t)\rangle = -\frac{i}{\hbar}\mathcal{H}_{\mathcal{Q}}|\psi(t)\rangle, \qquad (11)$$

$$\dot{\mathbf{s}}_m = \mathbf{s}_m \times \left(\mathbf{h}_m^{\mathcal{CC}} + \mathbf{h}_m^{\mathcal{QC}} \right), \tag{12}$$

where

$$\mathbf{h}_{m}^{\mathcal{CC}} = -\sum_{n \neq m}^{n \in \mathcal{C}} \begin{pmatrix} J_{m,n}^{x} s_{n}^{x} \\ J_{m,n}^{y} s_{n}^{y} \\ J_{m,n}^{z} s_{n}^{z} \end{pmatrix}.$$
 (13)

The hybrid version of the total spin polarization is defined as

$$\mathcal{M}_{x}(t) = \sqrt{D_{\mathcal{Q}} + 1} \langle \psi(t) | \sum_{i \in \mathcal{Q}} S_{i}^{x} | \psi(t) \rangle + \sum_{m \in \mathcal{C}} s_{m}^{x}(t).$$
(14)

Our actual implementation of the hybrid method involves the following technical detail. Due to the translational invariance of the original quantum system, the quantum correlation function (4) can be re-expressed as [20,21]

$$C_x(t) = \frac{N_{\mathcal{L}}}{N_{\mathcal{Q}'}} \langle M_x(t) M'_x \rangle, \qquad (15)$$

where $Q' \in \mathcal{L}$ is an arbitrary subset of lattice sites, $N_{\mathcal{L}}$ is the total number of spins in the lattice, $N_{Q'}$ is the number of spins in the subset Q', and

$$M'_x = \sum_{i \in \mathcal{Q}'} S^x_i.$$
(16)

Once we transition to the hybrid dynamics, the presence of the quantum-classical border breaks the translational invariance of the lattice, thereby making different choices of Q' inequivalent. To minimize the influence of the quantumclassical border, we take Q' in the fully quantum definition (15) to consist of one or several central spins within the quantum cluster Q.

Finally, the exact quantum correlation function (15) is replaced by the one for the infinite-temperature equilibrium noise generated by the hybrid dynamics,

$$C_x(t) = \frac{N_{\mathcal{L}}}{N_{\mathcal{Q}'}} [\mathcal{M}_x(t)\mathcal{M}'_x(0)]_{i.c.}, \qquad (17)$$

where $[\cdots]_{i.c.}$ denotes the averaging over initial conditions [22], $\mathcal{M}_x(t)$ is given by Eq. (14) and

$$\mathcal{M}'_{x}(t) = \sqrt{D_{\mathcal{Q}} + 1} \cdot \langle \psi(t) | \sum_{m \in \mathcal{Q}'} S^{x}_{m} | \psi(t) \rangle.$$
(18)

The infinite-temperature ensemble of initial conditions is generated through a fully random choice of $|\psi(0)\rangle$ in the Hilbert space of the quantum cluster and fully random orientations of classical spins $\mathbf{s}_m^{\alpha}(0)$. The time evolutions of $|\psi(t)\rangle$ and $\mathbf{s}_m^{\alpha}(t)$ are computed using the fourth-order Runge-Kutta routines for direct time integration as in Refs. [18,20,21,23]. The numbers and the durations of the computational runs behind the plots presented below are given in the Supplemental Material [24].

IV. METHOD OF COUPLED QUANTUM CLUSTERS

Classical spins in the hybrid method can be thought of as each representing the quantum-mechanical expectation values for a quantum cluster consisting of one spin 1/2 [20]. From such a perspective, the hybrid method partitions the original quantum lattice into a larger central quantum cluster Q and one-spin clusters represented by classical spins.

In this section, we formulate a generalization of the hybrid method, which we call the method of coupled quantum clusters. It is based on partitioning the original quantum lattice into quantum clusters of arbitrary sizes and then coupling these clusters using the quantum-mechanical expectation values of the relevant observables. This method is to be tested in Sec. V on the FID in ²⁹Si-enriched silicon, where the lattice can be naturally divided into pairs of spins 1/2. (In fluorapatite, magnetic nuclei form a more complex lattice, which cannot be naturally partitioned into small clusters.)

Let us partition the quantum lattice defined by the Hamiltonian (1) into smaller clusters. A cluster labeled by index μ contains a set of sites Q_{μ} . It is represented by wave function $|\psi_{\mu}\rangle$ belonging to the Hilbert space of dimension $D_{Q_{\mu}}$. The Hamiltonian for cluster Q_{μ} is defined as

$$\mathcal{H}_{\mathcal{Q}_{\mu}} = \sum_{i < j, \alpha}^{i, j \in \mathcal{Q}_{\mu}} J_{i, j}^{\alpha} S_{i}^{\alpha} S_{i}^{\alpha} - \sum_{i \in \mathcal{Q}_{\mu}} \mathbf{h}_{i}^{\mathcal{Q}_{\mu}} \cdot \mathbf{S}_{i}, \qquad (19)$$

where

$$\mathbf{h}_{i}^{\mathcal{Q}_{\mu}} = -\sum_{\nu}^{\nu \neq \mu} \sqrt{D_{\mathcal{Q}_{\nu}} + 1} \sum_{j \in \mathcal{Q}_{\nu}} \begin{pmatrix} J_{m,j}^{x} \langle \Psi_{\nu} | S_{j}^{x} | \Psi_{\nu} \rangle \\ J_{m,j}^{y} \langle \Psi_{\nu} | S_{j}^{z} | \Psi_{\nu} \rangle \\ J_{m,j}^{z} \langle \Psi_{\nu} | S_{j}^{z} | \Psi_{\nu} \rangle \end{pmatrix}.$$
(20)

The dynamics of each wave function $|\psi_{\mu}\rangle$ is governed by the Schrödinger equation $|\dot{\psi}_{\mu}(t)\rangle = -\frac{i}{\hbar}\mathcal{H}_{Q_{\mu}}|\psi(t)\rangle$. This leads to a system of coupled differential equations for all clusters, which is to be solved by the method of direct numerical time integration.

The "clustered" version of the total spin polarization is defined as

$$\mathcal{M}_{x}(t) = \sum_{\mu} \sqrt{D_{\mathcal{Q}_{\mu}} + 1} \langle \psi_{\mu}(t) | \sum_{i \in \mathcal{Q}_{\mu}} S_{i}^{x} | \psi_{\mu}(t) \rangle.$$
(21)

As in the hybrid method, one can choose within each cluster Q_{μ} a subset of sites Q'_{μ} maximally separated from cluster's boundary and define

$$\mathcal{M}'_{x}(t) = \sum_{\mu} \sqrt{D_{\mathcal{Q}_{\mu}} + 1} \langle \psi_{\mu}(t) | \sum_{i \in \mathcal{Q}'_{\mu}} S^{x}_{i} | \psi_{\mu}(t) \rangle.$$
(22)

Finally, the expression for the correlation function of interest is still given by Eq. (17), but now the definitions (21) and (22) should be substituted there.

The computational advantage of the method of coupled quantum clusters in comparison with the hybrid method is that each simulation run produces more statistically independent contributions to $\mathcal{M}'_x(t)$, because it tracks simultaneously many quantum clusters. The disadvantage, obviously, is that the time evolution of many quantum clusters is more computationally expensive to calculate than that of classical spins. Here, however, interesting compromises can be explored with not-too-large quantum clusters.

The method of coupled quantum clusters as defined in this section is qualitatively different from the correlated cluster expansions reviewed in Ref. [25] both in terms of the character of the simulations and in terms of the agenda. Our method aims at describing strongly correlated dynamics of a dense spin system, while the correlated cluster expansion targets the decoherence of a central spin in an environment of a dilute spin bath. At the same time, as far as the coupling scheme between different quantum clusters is concerned, the present method has certain parallels with the cluster truncated Wigner approximation proposed in Ref. [26].

V. FID FOR ²⁹Si-ENRICHED CRYSTALLINE SILICON

A. Preliminary remarks

Crystalline silicon has a diamond-type crystal structure same as regular diamonds made of carbon atoms. Both silicon



FIG. 1. Diamond-type crystal structure of crystalline silicon. The red arrows represent the primitive vectors of the lattice.

and carbon have stable isotops with nuclear spins 1/2: ²⁹Si and ¹³C, respectively. The natural abundance of these isotopes is quite low: 4.7% for ²⁹Si and 1.1% for ¹³C. However, crystals enriched to almost 100% content of these particular isotopes have been grown artificially.

The FIDs of 99% ¹³C-enriched diamond were measured in the past by Lefmann *et al.* [27] and Schaumburg *et al.* [28], while the FIDs of 96.9% ²⁹Si-enriched silicon were measured by Verhulst *et al.* [29]. The FID shapes obtained in both cases are supposed to coincide once the time axes are properly rescaled, and, indeed, the two experimentally measured FIDs reasonably agree with each other provided experimental uncertainties are taken into account (see the Supplemental Material [24]). These uncertainties are, however, noticeable, as manifested, in particular, by the asymmetry of the measured absorption curves (the Fourier transforms of the FIDs) and by the discrepancy between the experimental and the theoretical values of second moments $M_2 \equiv -C''_x(0)/C_x(0)$, the latter being computed for the truncated magnetic dipolar interaction.

In the present paper, we chose to compare the hybrid method predictions with the ²⁹Si FIDs measured by Verhulst *et al.* [29]. The gyromagnetic ratio for ²⁹Si is $\gamma = -5319$ rad s⁻¹ Oe⁻¹. Our theoretical calculations are to be done for 100% ²⁹Si-enriched samples.

On the theoretical side, the Fourier transforms of the FIDs for the diamond lattice were calculated by Schaumburg *et al.* [28], who used the exact calculation of a five-spin problem supplemented by a Gaussian broadening of the resulting lineshapes; by Jensen [13], with the help of a continued fraction representation of the Laplace transform of the FID; and by Lundin and Zobov [30], who relied on the scheme introduced in the 1996 work of Lundin [14], which, in turn, was based on the hypothesis of the asymptotic similarity of correlation functions of various orders.

B. Lattice structure of silicon

The diamond-type crystal structure of silicon is presented in Fig. 1. It is a face-centered cubic lattice with a two-site basis. The center of the unit cell is an inversion center of the lattice. As a consequence, two lattice sites of the unit cell are equivalent. In terms of the orthonormal vectors $(\hat{a}, \hat{b}, \hat{c})$ shown in Fig. 1, the primitive vectors of the lattice are expressed as

$$\mathbf{l}_{1} = \frac{a_{0}}{2}(\hat{a} + \hat{b}), \quad \mathbf{l}_{2} = \frac{a_{0}}{2}(\hat{b} + \hat{c}), \quad \mathbf{l}_{3} = \frac{a_{0}}{2}(\hat{a} + \hat{c}), \quad (23)$$

and two vectors of the basis are

$$\mathbf{v}_0 = \mathbf{0}, \quad \mathbf{v}_1 = \frac{a_0}{4}(\hat{a} + \hat{b} + \hat{c}),$$
 (24)

where a_0 is the period of the fcc lattice (see also Ref. [31]). For silicon diamond, $a_0 = 5.431$ Å.

According to definition (3), the effective numbers of interacting neighbors n_{eff} for the external magnetic field **B**₀ oriented along the [001], [011], and [111] crystal directions are, respectively, 27.4, 5.9, and 2.4. As explained in the introduction, we are primarily interested in small n_{eff} , which are supposed to yield more rigorous tests of the hybrid method. Hence, we primarily focus on the setting where **B**₀ is parallel to the [111] direction. In this case, n_{eff} is small, because each spin has one very strongly coupled neighbor along the [111] direction $[\cos \theta_{ij} = \pm 1 \text{ in Eq. (2)}]$. The displacement vectors pointing at the three other nearest neighbors, while having the same length, are oriented with respect to [111] at angles corresponding to $\cos \theta_{ij} = \pm 1/3$, which makes the absolute value of the coupling constants (2) by a factor of three smaller than the largest one.

In the above setting, the full quantum lattice can be naturally partitioned into pairs of strongly coupled spins 1/2. The two spins within such a pair are displaced with respect to each other along the [111] direction. Each of them is the strongestcoupled neighbor of the other one, which, in turn, implies that the interaction between different pairs is significantly smaller than the interaction within a pair. Given such a hierarchy, it is natural to expect that the method of coupled quantum clusters introduced in Sec. IV would be particularly efficient, provided the strongly coupled spin pairs are chosen as quantum clusters Q_{μ} into which the full lattice is partitioned.

C. Simulations vs experiment for silicon

The results of our simulations for \mathbf{B}_0 along the [111] direction both by the hybrid method and by the method of coupled quantum clusters are presented and compared with the experiment of Verhulst *et al.* [29] in Fig. 2. Frame (a) displays the absorption line shape f(v), which is given by the Fourier transform of the FID:

$$f(\nu) = \frac{2}{C_x(0)} \int_0^{+\infty} dt \ C_x(t) \cos 2\pi \nu t.$$
 (25)

Frame (b) displays the FID.

To estimate the accuracy of the hybrid simulations, we compare the hybrid results for two different quantum clusters shown in Fig. 3. The very small difference between the two results is a measure of the predictive uncertainty of the hybrid method. Detailed information about the simulations can be found in the Supplemental Material [24].

The simulations by the method of coupled quantum clusters were performed by partitioning the full quantum



FIG. 2. (a) Absorption line shape and (b) FID in ²⁹Si-enriched silicon for \mathbf{B}_0 along the [111] crystal direction: comparison of the results of simulations with the experiment of Verhulst *et al.* [29]. The simulations were done by the hybrid method and by the method of correlated quantum clusters. The schemes of quantum clusters 1 and 2 used in the hybrid simulations are displayed in Fig. 3. The coupled quantum cluster simulations were based on partitioning the full quantum lattice into pairs of strongly coupled spins 1/2 as described in the text. The experimental absorption line shape is extracted directly from Ref. [29], while the experimental FID is obtained by the Fourier transform of the absorption line shape. The shaded area around the experimental lines is a measure of nonsystematic experimental error obtained as explained in Ref. [24].

lattice into clusters Q_{μ} consisting of pairs of strongly coupled spins 1/2 as described at the end of Sec. V B. We also chose $Q'_{\mu} = Q_{\mu}$. The plots for the coupled quantum clusters in Fig. 2 nearly coincide with the hybrid plots. At the same time, the convergence of the statistical averaging for coupled quantum clusters method is significantly faster than that for the hybrid method.

As one can see in Fig. 2, the agreement between both kinds of simulations and the experiment is very good, and, moreover, the small residual discrepancy might be due to experimental uncertainties or due to microscopic details not included into the model Hamiltonian. The former can be quantified through the ratio 1.33 of the experimental and the first-principles theoretical values of the second FID moments [24]. The latter can be associated with crystal defects, paramagnetic impurities, or less than 100% abundance of ²⁹Si. As further illustrated in Fig. 6 of Appendix A, the theoretical predictions of Jensen and of Lundin and Zobov appear to exhibit somewhat larger deviations from the experiment.

It is worth remarking that the absorption line shape in Fig. 2(a) inherits its two-peak structure from the Pake doublet [32] associated with an isolated pair of spins 1/2. The Pake doublet is sometimes viewed as an essentially quantum phenomenon originating from the discreteness of quantum energy levels. Yet, even in this case, simulations of two classical spins were shown [33] to qualitatively reproduce the two-peak character of the absorption line shape. This is an example of a rather subtle relation between classical and quantum dynamics: On the one hand, classical spin systems can be useful for practical calculations [8,18,34,35] and also exhibit significant qualitative similarities with quantum ones as far as the long-time relaxation is concerned [36-41]; on the other hand, classical spin lattices are chaotic [42,43], while quantum lattices are not [44] in the sense of the absence of the Lyapunov regime, even though they can imitate the Lyapunov regime over a limited time range [45]. In Fig. 2, to highlight the difference between quantum and classical FIDs for small $n_{\rm eff}$, we also include the results of purely classical simulations of the kind done in Ref. [18].

Finally, we also performed hybrid and classical simulations for \mathbf{B}_0 parallel to the [011] and [001] crystal directions. The results are presented in Appendix A.



FIG. 3. Schemes of the quantum clusters Q for the hybrid simulations of ²⁹Si-enriched silicon for **B**₀ || [111] presented in Fig. 2: (a) and (b) show cluster 1 and cluster 2, respectively. In (a), two sites belonging to the subset Q' are marked with +. In (b), all sites belonging to Q also belong to Q'.



FIG. 4. Scheme of a unit cell of fluorapatite. Only fluorine (blue) and phosphorous (red) atoms are shown.

VI. ¹⁹F FID FOR FLUORAPATITE

A. Preliminary discussion

Fluorapatite Ca₁₀(PO₄)₆F₂ is a material often used to study spin dynamics of low-dimensional lattices [46–52]: Fluorine nuclei in fluorapatite are arranged in parallel chains. For the orientation of external magnetic field parallel to the chains, the interactions between them are much smaller than the interaction within the chain. As a result, $n_{\text{eff}} \approx 2$, which means the fluorapatite lattice with coupling constants (2) can be viewed as a collection of weakly coupled spin chains. In this section, we focus on ¹⁹F FID in the above setting. We compute this FID and compare the result with the measurements of Engelsberg *et al.* [53].

In terms of contributions to nuclear magnetism, fluorapatite contains stable nuclear isotopes ¹⁹F and ³¹P, which have spins 1/2 and natural abundances 100%. We include both of them in the simulations. Their gyromagnetic ratios are $\gamma_F = 25166.2 \text{ rad s}^{-1} \text{ Oe}^{-1}$ and $\gamma_P = 10829.1 \text{ rad s}^{-1} \text{ Oe}^{-1}$ respectively. At the same time, magnetically active isotopes of calcium and oxygen have natural abundances less then 1%; hence, we neglect them.

B. Lattice structure of fluorapatite

Fluorapatite has hexagonal crystal structure with the space group $P6_3/m$ [54]. The lattice parameters are a = b =9.462 Å and c = 6.849 Å. We denote the respective primitive vectors as **a**, **b**, and **c**. The angle between **a** and **b** is 120°, and the *c* axis is orthogonal to the hexagonal *ab* plane. The basis cell of the sublattice of magnetically active nuclei contains two F nuclei at positions

$$[0.0, 0.0, 0.25], [0.0, 0.0, 0.75]$$
(26)

and six P nuclei at positions

$$[x, y, 0.25], [1 - y, x - y, 0.25], [y - x, 1 - x, 0.25], [1 - x, 1 - y, 0.75], [y, y - x.0.75], [x - y, x, 0.75], (27)$$

where x = 0.369 and y = 0.3985. The coordinates are given in the basis of vectors **a**, **b**, and **c**. An illustration of the unit cell of fluorapatite is presented in Fig. 4. The positions of the ¹⁹F nuclei inside the basis cell are equivalent, since they are transformed into each other by the discrete symmetry transformations of the lattice. The positions of the ³¹P nuclei inside the basis cell are equivalent as well.

The above-mentioned strongly coupled chains of ¹⁹F nuclei extend along the [001] direction. The interchain distance between nuclei is approximately 2.8 times smaller then the intrachain one. In the case where the external magnetic field B_0 is parallel to the [001] direction, the largest value of intrachain coupling is at least 21 times smaller then the nearest-neighbor coupling within a chain.

In comparison with CaF_2 and silicon, the simulations of ¹⁹F FID in fluorapatite are complicated by the presence of "unlike" ³¹P nuclei and by lattice disorder. Below we introduce technical modifications required to accommodate these two aspects.

C. Unlike spins

Two nuclear spins with different gyromagnetic ratios are referred to in NMR literature as "unlike spins" [2]. The truncated Hamiltonian averaged over fast precession of ¹⁹F and ³¹P nuclear spins, takes the form similar to Eqs. (1) and (2):

$$\mathcal{H} = \sum_{i < j, \alpha} J_{i,j}^{\alpha} S_i^{\alpha} S_j^{\alpha} + \sum_{k < l, \alpha} \tilde{J}_{k,l}^{\alpha} I_i^{\alpha} I_j^{\alpha} + \sum_{i,k,\alpha} \tilde{J}_{i,k}^{\alpha} S_i^{\alpha} I_k^{\alpha}.$$
 (28)

Here, S_i^{α} and I_k^{α} are the spin operators of ¹⁹F and ³¹P nuclei, respectively. The coupling constants $J_{i,i}^{\alpha}$, $\tilde{J}_{k,l}^{\alpha}$ and $\tilde{J}_{i,k}^{\alpha}$ are

$$J_{i,j}^{x} = J_{i,j}^{y} = -\frac{1}{2}J_{i,j}^{z} = \frac{\gamma_{F}^{2}(1 - 3\cos^{2}\theta_{ij})}{r_{ij}^{3}},$$
 (29)

$$\tilde{\tilde{J}}_{k,l}^{x} = \tilde{\tilde{J}}_{k,l}^{y} = -\frac{1}{2}\tilde{\tilde{J}}_{i,j}^{z} = \frac{\gamma_{P}^{2}(1 - 3\cos^{2}\theta_{kl})}{r_{kl}^{3}},$$
(30)

$$\tilde{J}_{i,j}^x = \tilde{J}_{i,j}^y = 0, \qquad (31)$$

$$\tilde{J}_{i,j}^{z} = \frac{\gamma_F \gamma_P (1 - 3\cos^2\theta_{ik})}{r_{ik}^3}.$$
 (32)

As in the homonuclear case, the ¹⁹F FID is proportional to $C_x(t)$ defined by Eq. (4), but the dynamics is now determined by the Hamiltonian (28).

D. Lattice disorder

The main type of defects in fluorapatite is the substitutions of F⁻ ions by other X⁻ ions. Usually, F⁻ ions are substituted by Cl⁻ ions or by hydroxyl groups (OH)⁻ [54]. The presence of defects disrupts the fluorine chains and, in principle, leads to an adjustment of the positions of the neighboring atoms. In addition, both the stable isotopes of chlorine and protons of the (OH)⁻ group are magnetically active. While the gyromagnetic ratio of chlorin nuclei is relatively small and hence the respected site can be treated as nonmagnetic vacancy, the strongly magnetic proton spins would generate the inhomogeneous broadening of the *z* components of the local magnetic fields sensed by the neighboring ¹⁹F and ³¹P nuclei. In principle, an accurate calculation of the ¹⁹F FID should account for all such effects. However, to the best of our knowledge, there is no detailed data about the concentrations of different types of defects in the sample used in the experiment [53]. Therefore, we choose to follow the approach of Ref. [55], namely, we assume that the fluorine atoms in fluorapatite are randomly replaced by nonmagnetic substitutions with probability ρ . The concentration of non-magnetic substitutions is then determined by matching the experimentally measured second moment of the FID.

Let us consider some particular realization of disorder in the system. It can be specified by introducing a set of independent random binary variables $\{p_i\}$, which take value 0 with probability ρ and value 1 with probability $(1 - \rho)$. Here *i* is the index of the fluorine lattice site and ρ is the concentration of defects. The values $p_i = 1$ or $p_i = 0$ correspond to the spin being either present or absent on site *i*, respectively. As a result, in the full truncated dipolar-dipolar Hamiltonian given by Eq. (28), spin operators S_i^{α} are substituted by $p_i S_i^{\alpha}$.

The definition of the autocorrelation function measured in experiment [Eqs. (4) and (6)] is now changed to

$$C_x(t) \equiv \left\langle \frac{1}{D^{\{p\}}} \operatorname{Tr} \left[e^{i\mathcal{H}t} M_x^{\{p\}} e^{-i\mathcal{H}t} M_x^{\{p\}} \right] \right\rangle_{\{p\}}, \qquad (33)$$

where $\{p\}$ denotes a particular realization of disorder, $\langle \cdots \rangle_{\{p\}}$ is the disorder average, and

$$M_x^{\{p\}} = \sum_i p_i S_i^x.$$
 (34)

According to the hybrid scheme, the correlation function (33) is then reexpressed as a counterpart of Eq. (17),

$$C_{x}(t) = \frac{N_{\mathcal{L}}}{N_{\mathcal{Q}'}} \Big[\mathcal{M}_{x}^{\{p\}}(t) \mathcal{M}_{x}^{\prime\{p\}}(0) \Big]_{i.c.,\{p\}},$$
(35)

where

$$\mathcal{M}_{x}^{\{p\}}(t) = \sqrt{D_{\mathcal{Q}}^{\{p\}} + 1} \langle \psi(t) | \sum_{i \in \mathcal{Q}} p_{i} S_{i}^{x} | \psi(t) \rangle + \sum_{m \in \mathcal{C}} p_{m} s_{m}^{x}(t),$$
(36)

and

$$\mathcal{M}_{x}^{\{p\}}(t) = \sqrt{D_{\mathcal{Q}}^{\{p\}} + 1} \langle \psi(t) | \sum_{i \in \mathcal{Q}'} p_i S_i^x | \psi(t) \rangle.$$
(37)

E. Simulations vs experiment for fluorapatite

The comparison of the results of hybrid simulations with the experimental data of Ref. [53] is presented in Fig. 5. We used the concentration of fluorine vacancies $\rho = 0.077$ obtained by fitting of the experimental second moment of the FID with the theoretical value computed from first principles (see the Supplemental Material [24]). The size of the simulated hybrid lattice was $9 \times 9 \times 7$ basis cells. The central quantum cluster Q was chosen as a single chain of fluorine spins extending along the *c* axis: it covered seven basis cells and, therefore, included 14 fluorine spins. The rest of the spins were simulated classically. Since the quantum cluster Q in this case was closed periodically, all its spins were equivalent with respect to the classical environment. Hence, each of the 14 lattice sites belonging to Q also belonged to the subset Q' appearing in the definition (35) of the hybrid



FIG. 5. ¹⁹F FID in fluorapatite. Comparison of the results of the hybrid simulations including fluorine spins, phosphorous spins, and lattice disorder with the experimental data of Engelsberg *et al.* [53].

correlation function. We also performed hybrid simulations for a smaller system of $9 \times 9 \times 6$ basis cells with the central quantum cluster of 12 fluorine spins. The difference between the computed FIDs for the two hybrid lattices is smaller than the thickness of the plot lines in Fig. 5. This implies that the above result amounts to a quantitatively reliable prediction of the FID of the fully quantum dynamics for the given interaction Hamiltonian and the chosen model of the lattice disorder. In Appendix B, we also present the results of hybrid FID calculations without the lattice disorder for an isolated fluorine chain and for a three-dimensional lattice with and without phosphorus nuclear spins.

Overall, the agreement between the numerical and the experimental results shown in Fig. 5 is good. However, there is still a discrepancy, which, while being small in absolute terms, is larger than the predictive uncertainty estimate for the hybrid simulations. Therefore, this discrepancy is due to either the experimental uncertainty or the approximate character of our lattice disorder model, which we had to resort to in the absence of more detailed information about the material.

Finally, we note that, in principle, it is possible to also apply the method of coupled clusters (Sec. IV) to fluorapatite. One can, for example, divide the ¹⁹F sublattice into parallel chains along the \hat{c} direction. However, one also needs to take into account ³¹P spins. If ³¹P spins are included in quantum clusters, then the Hilbert space of each cluster would become impractically large. A feasible alternative is to treat ³¹P spins as classical, but then we do not expect the results to be much different from the hybrid calculation presented earlier. Using coupled quantum clusters for fluorapatite would be further complicated by the need to incorporate random lattice vacancies, which, in turn, would make different clusters nonequivalent. In view of the above considerations, we did not attempt to apply the method of coupled quantum clusters to fluorapatite.

VII. CONCLUSIONS

Overall, we observe good quantitative agreement of the hybrid simulations of FIDs in ²⁹Si-enriched silicon and in



FIG. 6. (a) Absorption line shape and (b) FID in ²⁹Si diamond for \mathbf{B}_0 along [111] crystal direction: Comparison of the theoretical predictions of Jensen [13] and of Lundin and Zobov [30] with the experiment of Verhulst *et al.* [29]. The experimental lines are the same as in Fig. 2.

fluorapatite with experiments. Both settings are characterized by a low effective number of interacting neighbors $n_{\rm eff}$ of each nuclear spin and, hence, are crucial for testing the predictive performance of the hybrid method as far as the essentially quantum aspects of the FID behavior are concerned. However, the conclusive assessment of the predictive power of the hybrid method is hindered by the experimental uncertainties and/or by the insufficient knowledge about lattice disorder, including vacancies, substitutions, and paramagnetic impurities. More accurate NMR experiments on better characterized samples with small $n_{\rm eff}$ need to be performed to conduct more stringent tests of the hybrid method. We also introduced the coupled quantum clusters method, which was shown to exhibit excellent performance when applied to the FID in ²⁹Si-enriched silicon with the orientation of the external magnetic field imposing the natural partition of the full lattice into pairs of strongly coupled spins. Given these promising results, the performance of the latter method for a broader class of systems merits further systematic investigation.

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APPENDIX A: ADDITIONAL CALCULATIONS AND DISCUSSION OF FIDs IN ²⁹Si-ENRICHED SILICON

To facilitate the comparison between the performance of the hybrid method for the calculation of ²⁹Si FID with \mathbf{B}_0 ||[111] as presented in Fig. 2 with the performance of alternative theoretical methods, we include in Fig. 6 the same kind of theory-vs-experiment plots for the (properly rescaled) theoretical predictions of Jensen [13] and of Lundin and Zobov [30].

We also computed ²⁹Si FIDs for the external magnetic field \mathbf{B}_0 parallel to [011], [001]. The values of $n_{\rm eff}$ in these two cases are 5.9 and 27.4, respectively. According to the investigations of Elsayed and Fine [18], the classical simulations are expected to perform well when $n_{\rm eff} > 4$. Thus, following the argumentation of Ref.[20], we estimate the uncertainty of the hybrid simulations by comparing their results with the results of purely classical simulations. The schemes of the quantum clusters used in the hybrid simulations are shown in Fig. 7. For the details of the simulations, see the Supplemental Material [24].

The results of our simulations are presented in Figs. 8 and 9 for external magnetic field \mathbf{B}_0 along [011] and [001] crystal directions respectively. The figures have identical structure. The upper row [frames (a) and (b)] presents the comparison of the



FIG. 7. Schemes of the quantum clusters for the hybrid simulations of ²⁹Si-enriched silicon presented in Figs. 8 and 9: (a) for $\mathbf{B}_0 \parallel [011]$; (b) for $\mathbf{B}_0 \parallel [001]$. Sites belonging to the subset Q' are marked with +: two in (a) and one in (b).



FIG. 8. (a, a') Absorption line shapes and (b, b') FIDs in ²⁹Si-enriched silicon for $\mathbf{B}_0 \parallel [011]$. (a, b): Comparison of the results of hybrid simulations with the experiment of Verhulst *et al.* [29] (a', b'): Comparison of the theoretical predictions of Jensen [13] and of Lundin and Zobov [30] with the same experimental data. The scheme of the quantum cluster used in the hybrid simulations is displayed in Fig. 7(a).

results of our simulations with experimental data of Verhulst *et al.* [29]. The lower row [frames (a') and (b')] presents the

comparison of the theoretical predictions of Jensen [13] and of Lundin and Zobov [30] with the same experimental data.



FIG. 9. (a, a') Absorption lineshapes and (b, b') FIDs in ²⁹Si-enriched silicon for $\mathbf{B}_0 \parallel [001]$. (a, b): comparison of the results of hybrid simulations with the experiment of Verhulst *et al.* [29] (a', b'): comparison of the theoretical predictions of Jensen [13] and of Lundin and Zobov [30] with the same experimental data. The scheme of the quantum cluster used in the hybrid simulations is displayed in Fig. 7(b).



FIG. 10. ¹⁹F FID in fluorapatite. Comparison of hybrid simulations with the experiment of Engelsberg *et al.* [53] for different levels of modeling defined in the text: black dotted line—single fluorine chain, green dotted line—three-dimensional lattice of fluorine nuclei only; magenta dashed line—three dimensional lattice of fluorine and phosphorous nuclei. None of the hybrid simulations presented in this figure included lattice disorder.

In the case of $\mathbf{B}_0||[001]$, we are reasonably confident that the large discrepancy between the hybrid predictions and the experiments is due to the experimental uncertainties, which is evidenced by the fact that the ratio of the experimental and the theoretical second moments in this case is 2.73. In the case of $\mathbf{B}_0||[011]$, the second moment ratio is 1.4, i.e. closer to 1, and hence the agreement between the hybrid calculations and the experiment is more satisfactory.

In the Supplemental Material, we also included the plots of the rescaled experimental results of Lefmann *et al.* [27]

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for 13 C-enriched diamond together with the data presented in Figs. 2, 6, 8, and 9.

APPENDIX B: ADDITIONAL CALCULATIONS AND DISCUSSION OF FID IN FLUORAPATITE

In Fig. 10, we present the results of the hybrid simulations for different levels of modeling ¹⁹F FID in fluorapatite. We consider a series of models, which gradually become more realistic:

(1) isolated fluorine chain without disorder;

(2) three-dimensional fluorine lattice without disorder and without phosphorus nuclear spins;

(3) three-dimensional lattice with phosphorus nuclei, but without disorder;

(4) three-dimensional lattice with phosphorus nuclei and disorder.

Model (iv) corresponds to the simulations described in Section VI and presented in Fig. 5.

The parameters of the simulated hybrid lattices are the following. For model (i) the hybrid lattice was a chain of length 201 with periodic boundary conditions; the size of the quantum cluster Q was 12 and the subset Q' included two central spins of cluster Q. For model (ii), the fluorine sublattice of the size $7 \times 7 \times 13$ spins was used, and both Q and Q' were chosen in the form of a periodic 13-spin fluorine chain. The parameters for model (iii) were the same as for the model (iv) used in Section V: the lattice size was $9 \times 9 \times 7$ basis cells, while Q and Q' were chosen as a 14-spin fluorine chain.

We, finally, note that the results of the simulations for models (i) and (ii) nearly coincide with each other, thereby corroborating the quasi-one-dimensional character of the fluorine sublattice.

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