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Letter

Decoherence in Molecular Electron Spin Qubits: Insights from Quantum Many-Body Simulations

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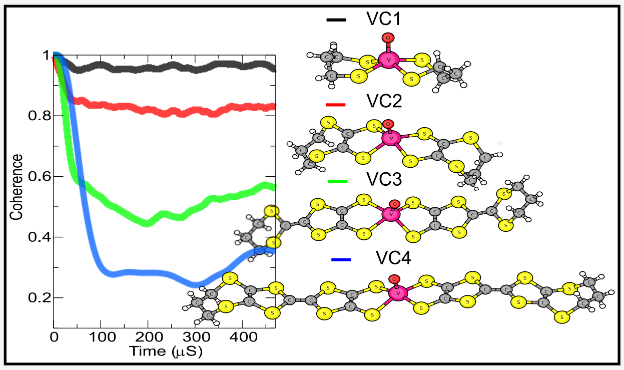
ABSTRACT: Quantum states are described by wave functions whose phases cannot be directly measured but which play a vital role in quantum effects such as interference and entanglement. The loss of the relative phase information, termed decoherence, arises from the interactions between a quantum system and its environment. Decoherence is perhaps the biggest obstacle on the path to reliable quantum computing. Here we show that decoherence occurs even in an isolated molecule, although not all phase information is lost, via a theoretical study of a central electron spin qubit interacting with nearby nuclear spins in prototypical magnetic molecules. The residual coherence, which is molecule-dependent, provides a microscopic rationalization for the nuclear spin diffusion barrier proposed to explain experiments. The contribution of nearby molecules to the decoherence has a nontrivial dependence on separation, peaking at intermediate distances. Molecules that are far away affect only the long-time behavior. Because the residual coherence is simple to calculate and correlates well with the coherence time, it can be used as a descriptor for coherence in magnetic molecules. This work will help establish design principles for enhancing coherence in molecular spin qubits and serve to motivate further theoretical work.



Electron and nuclear spins provide a natural realization of qubits and have been identified as potential building blocks for quantum technologies.[1,2] Dynamical considerations are such that electron spins hold a clear advantage in terms of operational speed[3] but suffer in terms of decoherence because of stronger interactions with their environment. Electron spins can be accessed through magnetic materials. Magnetic molecules are uniquely attractive because synthetic methodologies allow optimization of their quantum properties by tuning both the immediate coordination environment of the electronic qubit, i.e., the underlying spin-Hamiltonian, and the peripheral molecular structures that mediate interactions with the environment.[4,5]

Spin dynamics can be characterized in terms of longitudinal and transverse relaxation times: T_1 and T_2, respectively.[6] For molecular qubits at low temperatures, T_2 typically limits the number of quantum operations that can be performed before phase coherence is lost, because T_1 is usually much longer than T_2.[7] A successful strategy to extend T_2 involves modifying the environment through dilution of the magnetic molecules in diamagnetic solvents.[4] Examples of molecules with very long T_2 times that were realized in this way include $[Cu(mnt)_2]^{2-}$ (ref 8) and $[V(C_8S_8)]^{2-}$ (ref 9). In these dilute cases at low temperatures, experimental studies agree that the main source of electron spin decoherence involves relatively weak couplings to nuclear spins.[10]

Earlier work on factors influencing the spin relaxation time measured by EPR in organic radicals and transition-metal ions has been reviewed by Eaton and Eaton.[11] Recently, the relationship between molecular structure and T_2 has been illuminated,[7] and it was later expanded upon[12] by Freedman et al. Further experimental work along these lines is emerging.[13] In the work done by Freedman and co-workers, a series of four vanadyl complexes, $(Ph_4P)_2[VO(C_3H_6S_2)_2]$, $(Ph_4P)_2[VO(C_5H_6S_4)_2]$, $(Ph_4P)_2[VO(C_7H_6S_6)_2]$, and $(Ph_4P)_2[VO(C_9H_6S_8)_2]$ (see Figure 1), with increasing distance between the magnetic vanadium ion and the spin-active hydrogen nuclei, were synthesized and T_2 was measured in dilute frozen solutions by monitoring the decay of the Hahn echo. The study found that smaller complexes with stronger electron−nuclear interactions actually had longer T_2 times. This counterintuitive result was rationalized on the basis of a nuclear spin diffusion barrier.[7]

Contributors to this decoherence process include molecular vibrations, dipole−dipole interactions between electron spins,

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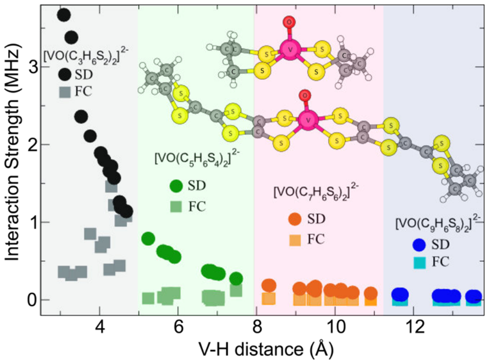


Figure 1. Electron−proton hyperfine coupling as a function of V−^{1}H separation for the four vanadyl complexes, including the isotropic Fermi-contact (FC) interaction from B3LYP calculations and the anisotropic through-space spin-dipolar (SD) contribution. The molecular structures of $[VO(C_3H_6S_2)_2]^{2-}$ and $[VO(C_7H_6S_6)_2]^{2-}$ are shown above the data: V, pink; O, red; S, yellow; C, gray; H, white.

and hyperfine coupling between electron and nuclear spins. In this work, we focus on hyperfine coupling. One of the first proposed spin decoherence mechanisms is nuclear spin diffusion mediated by energy-conserving spin flip-flop processes via hyperfine coupling.[14] However, this process is suppressed for nuclear spins that are close to electron spins, because their effective Zeeman energies are significantly detuned from their neighbors in comparison to less proximate spin pairs. This region within which nuclei have limited contribution to decoherence is described by the diffusion barrier.[15] Experiments in different settings have reported the sizes for barriers ranging from 3 to 17 Å.[16−22] Because of the connection between decoherence and structure,[7] a first-principles theory for spin decoherence in molecular qubits that can be connected to molecular structure is clearly a desirable research objective. Such a theory, with the promise of gaining insights and making predictions about spin decoherence, would also provide practical benefits to the experimental community.

For all four vanadyl complexes studied in this work, each molecule contains 12 distal hydrogen atoms, believed to be the main source of electron spin decoherence at low temperatures. We calculated hyperfine coupling tensors between electron spin and nuclear spins of both ^{51}V and ^{1}H using density functional theory.[23] Comparison of calculations and experimental measurements of coupling to ^{51}V can be found in the Supporting Information; reasonable agreement is achieved. Therefore, we lean on calculations for hyperfine coupling of ^{1}H, and the results are summarized in Figure 1. Paramagnetic spin−orbit (PSO) terms are smaller than 0.05 MHz in all cases and are neglected in this work. Spin-dipolar (SD) interactions decay as $1/d^3$, where d is the distance between the central vanadium ion and any given hydrogen atom. Meanwhile, the Fermi-contact (FC) term is insignificant for all but the smallest complex. This is to be expected because the electron spin density is mostly confined to the vanadium d orbitals. Therefore, as the V−^{1}H distance increases, the direct electron−proton contact rapidly diminishes. Consequently, the spin−dipole interaction dominates the results, as seen in Figure 1, and this can be computed on the basis of the atomic coordinates.

Decoherence can be understood in terms of the dynamics of a closed quantum system that includes the central spin (the qubit) and a finite number of environmental, or bath, spins.[24,25] Correlations between the central spin and the bath spins result in leakage of quantum information to the environment.[26] We have adopted a bottom-up approach to study this decoherence, induced by electron−nuclear hyperfine coupling in molecular qubits. Starting from a single molecule, we extend the approach to include the effects of more distant molecules with active nuclear spins surrounding the central vanadyl complex. Because the dipolar interaction is a tensorial property, the spin will evolve uniquely for different molecular orientations, i.e., the decoherence process is intrinsically anisotropic. Therefore, in order to reproduce the results of experiments performed on ensembles of randomly oriented molecules in frozen solutions, we employed an algorithm[27] to sample a uniform distribution of molecular orientations. Also, initial nuclear wave functions were generated by uniformly distributed random coefficients. Results reported here are averaged over both random orientations and initial wave functions.

In this work, the dynamics of nuclear spins are simulated by solving the time-dependent Schrödinger equation, and their effects on electron spin decoherence are accounted for via the cluster-correlation expansion scheme,[25] which divides decoherence into contributions from clusters of nuclear spins. The lowest-order pair-correlation approximation,[24] in which each cluster consists of two nuclear spins, is already able to capture the nuclear spin flip-flop process. Inclusion of larger clusters will lead to more accurate results by including correlations of more bath spins. The time dependence of electron spin coherence, which is quantified by the magnitudes of the off-diagonal elements of the reduced density matrix, is determined after forward and backward time evolution,[25] in a manner that is consistent with Hahn echo measurements of T_2.[7] Results of simulations using the pair-correlation approximation[24] are shown in Figure 2.

For the smaller complexes, $[VO(C_3H_6S_2)_2]^{2-}$ and $[VO(C_5H_6S_2)_2]^{2-}$, simulations for a single molecular orientation reveal oscillating behavior, with very different oscillation amplitudes and periods for different orientations. Upon

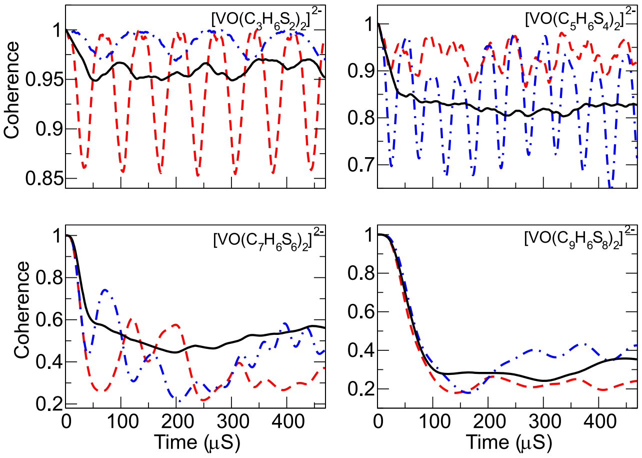
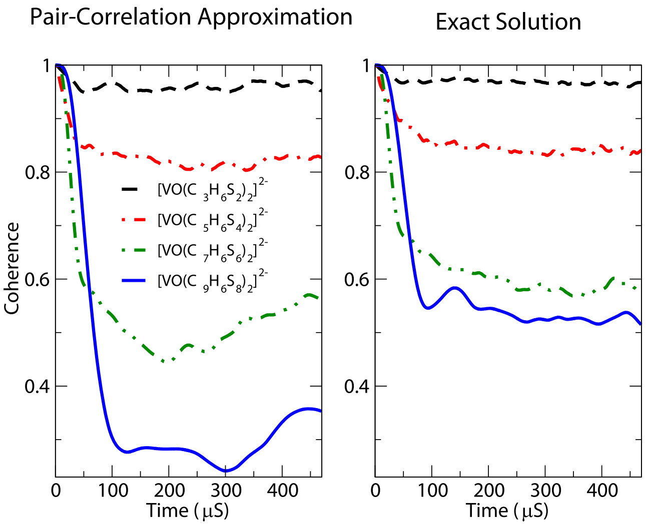


Figure 2. Decay of Hahn echo for a single molecule calculated using the pair-correlation approximation, averaging over 20 random initial wave functions and 100 random orientations. The external magnetic field is set to 1.0 T. Red and blue dashed lines are results for one random molecular orientation. The black line is a result of averaging over 100 random orientations.

averaging over 100 uniformly distributed orientations, we find that, after an initial decay, the coherence plateaus at a nonzero "residual coherence" value. This can be understood as arising from dephasing of oscillations corresponding to different molecular orientations after the initial sharp decay, which essentially represents the ensemble average coherence over multiple periods of oscillations. For the larger complexes, $[VO(C_7H_6S_6)_2]^{2-}$ and $[VO(C_9H_6S_8)_2]^{2-}$, a clear decay is seen for just a single molecular orientation, and the residual coherence decreases with increasing intramolecular distance between the electron and nuclear spin. The reduced coherence and the more complex oscillations for the individual orientations indicate enhanced participation of protons in the decoherence process as their separation from the central spin increases.

A direct comparison of the four complexes under study can be seen in Figure 3. As noted above, it is clear that the decoherence is incomplete for a single molecule with just 12 protons, and that the level of residual coherence decreases as the intramolecular distance between electron and nuclear spins increases. This suggests a quantum information "leakage bottleneck", dictated by the finite number of protons and their freedom to participate in the decoherence process. In essence, protons in close proximity to the central spin have a limited capacity to decohere the central spin. This rationalizes the observed trend of T_2 seen in experiments,[7] with larger residual coherence tracking longer T_2 values.


Pair-Correlation Approximation

Exact Solution

Figure 3. Single-molecule Hahn echo decay calculated for the four complexes by averaging over 20 random initial wave functions and 100 random orientations, based on the pair-correlation approximation (left panel) and exact solution (right panel).

To study multispin correlation effects on decoherence in these vanadyl complexes, we need to go beyond pair-correlation approximation. The quantum dynamics of all 12 ^{1}H nuclear spins in one molecule can be solved exactly via matrix diagonalization. In the cluster-correlation expansion scheme,[25] the exact solution for one molecule corresponds to one cluster with 12 spins. Such exact solutions can be found in the right panel of Figure 3. Important qualitative features of the decoherence observed from the pair-correlation approximation calculations are reproduced in the exact solutions: "residual coherence" corresponds to the plateau reached after initial decay, and the level of residual coherence decreases as the intramolecular distance between electron and nuclear spins increases. Therefore, we will use the pair-correlation approximation to gain additional insights for larger systems. However, the residual coherence from the exact solutions is somewhat larger, especially for larger molecules, suggesting that correlations involving multiple spins must be considered in order to achieve quantitative agreement.

Because single-molecule residual coherence can be calculated from the molecular electronic structure alone using the procedure described here, and magnetic dilution can isolate molecular qubits in solutions, we propose residual coherence to be used as a theoretical proxy for T_2 in this setting. Identifying such descriptors for surface chemical reactions and in the search for new catalysts has been a driving force for recent developments in the field of theoretical surface chemistry and catalysis.[28] It is enticing to propose that residual coherence can play a similar role for molecular spin qubits. Moreover, residual coherence provides a microscopic picture for the nuclear spin diffusion barrier. After adopting a diffusion barrier of 6.6 Å to 4.0 Å, as reported in experiments,[7] we can connect residual coherence to the diffusion barrier, and the value of residual coherence turns out to be 0.9 in this case. Residual coherence can be viewed as a calculable measure of

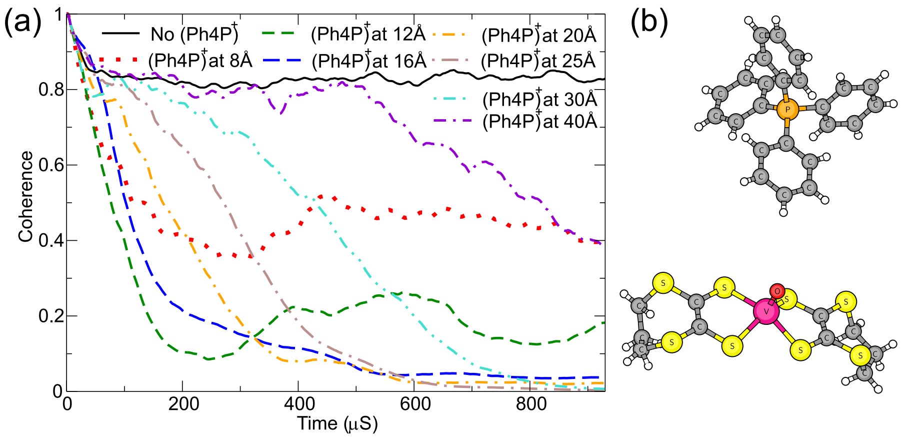


Figure 4. (a) Electron Hahn echo decay for $[VO(C_5H_6S_4)_2]^{2-}$ with one Ph_4P^+ counterion after averaging over 100 molecular orientations and 20 initial wave functions at various distances. (b) Molecular model for $[VO(C_5H_6S_4)_2]^{2-}$ and Ph_4P^+ at a separation of 10 Å: V, pink; O, red; S, yellow; C, gray; H, white; P, orange.

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how much certain nuclear spins contribute to decoherence. Because it is a continuous variable, residual coherence contains more information than the diffusion barrier as a single cutoff.

The effects of environmental decoherence were further studied by considering hyperfine coupling to nuclear spins outside of the molecule on which the electron spin resides. In the experiments, the vanadyl complexes were diluted in the deuterated solvents d_7-dimethylformamide/d_8-toluene,[7] in which d_7 and d_8 signify 7 and 8 protons have been replaced by deuterons in each molecule. Thus, only the vanadyl complexes and the counterion, Ph_4P^+, contain protons which are the most destructive nuclei for electron spin coherence. Because the negatively charged vanadyl and positively charged Ph_4P^+ counterion experience an attractive Coulomb interaction, dilution may not be able to separate them effectively. Consequently, Ph_4P^+ provides an additional source of environmental protons that can couple to the electronic spin, and we performed further simulations to elucidate their effect.

The simplest model has one vanadyl complex and one Ph_4P^+ counterion. We then studied the coherence as a function of the distance between Ph_4P^+ and the vanadyl. Results for $[VO(C_5H_6S_4)_2]^{2-}$ are shown in Figure 4 and are representative of what was found for all four complexes. In panel a, we see that the counterion facilitates decoherence tremendously, with a single Ph_4P^+ at 8 Å away reducing the residual coherence from 0.8 to 0.4. As we move the Ph_4P^+ ion from 8 to 12 Å from the vanadyl complex, the residual coherence decreases even more. This indicates that the effectiveness of environmental molecules for decoherence has a nonlinear dependence on their distance to central spin. Within a short distance, being closer actually compromises the environmental molecules' ability to decohere. Recently, Zadrozny and co-workers demonstrated that counterions can impact T_2 in more ways than just the number of ^1H nuclear spins,[29] suggesting that ^1H position plays a role in experimental observations.

As we move Ph_4P^+ farther away, decoherence shows the behavior of a two-step process. This becomes apparent when Ph_4P^+ is farther than 30 Å away. After the initial decay, a recurrence is seen, and the second and much slower decoherence process commences. Initial decay is similar to the behavior of a single molecule, because an inflection point can be found at the value of the residual coherence without environmental molecules. Therefore, we can conclude that the initial decay is due to nuclear spins within $[VO(C_5H_6S_4)_2]^{2-}$: when Ph_4P^+ is farther than 30 Å, it makes no contribution to the short-time decoherence.

Observations from the simulations provide perspective regarding more effective dilution schemes to extend T_2. Because counterions are an important source of decoherence, it may be possible to tune or even optimize the T_2, if their proximity to the molecular qubit can be modulated by the choice of solvent. Realization of such tunability will require knowledge of the frozen solution structure. Simple options, such as using deuterated or aprotic polar solvents, can obviously still impact T_2.

To summarize, electronic structure calculations and quantum many-body simulations offer valuable insights into electron spin decoherence in vanadyl molecular qubits. Electron spins in all four complexes are localized on the V^{4+} ion. Hyperfine interaction tensors were calculated as analytic derivatives using density functional theory. Electron spin decoherence from the dominant spin−dipole interaction mechanism was studied via quantum many-body simulations based on the cluster-correlation expansion. For a single vanadyl molecule, decoherence is always incomplete; it reaches a plateau of residual coherence whose magnitude scales inversely with the distance between the electron spin and the distal ^1H nuclei. Further effects of the environment on the decoherence were studied by including an additional molecular counterion in the simulations containing nuclear spin. The residual coherence shows a pronounced dependence on the intermolecular distances. Molecules far away generally do not contribute to short-time decoherence. Agreement between the calculated residual coherence and the trend observed experimentally suggests that the residual coherence is an appropriate descriptor for T_2 in molecular spin qubits. This is convenient, as it is a simple function of molecular electronic structure and is amenable to straightforward computational characterization. Thus, it may be that a predictive model of spin decoherence is now at hand, which clearly has profound potential for the study of molecular qubits.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00193.

> Theoretical methods used to calculate hyperfine coupling and do quantum many-body simulations (PDF)

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Notes

The authors declare no competing financial interest.

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