SpinVibe: Simulating spin-phonon coupling for molecular qubits

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Summary

Molecular qubits have emerged as versatile candidates for quantum information technologies. Their appeal lies in the chemical tunability, the possibility of large-scale synthetic control and their integration with solid-state and solution-phase architectures.(Bayliss et al., 2022; Wojnar et al., 2024) In contrast to solid-state defects or superconducting qubits, molecular qubits can be engineered at the atomic level, allowing researchers to systematically tailor their electronic, magnetic, and vibrational properties.(Laorenza & Freedman, 2022) However, the practical implementation of molecular qubits is limited by decoherence and relaxation processes, which shorten the time window over which quantum information can be stored and manipulated.

Relaxation dynamics fundamentally determine the practical utility of molecular qubits. The spin–spin relaxation time T_2 establishes the maximum duration for quantum information storage and directly limits the achievable sensitivity in sensing applications. Simultaneously, the spin–lattice relaxation time T_1 governs vibrationally mediated decoherence processes and determines how long the molecular spin can maintain its initialized state before it returns to thermal equilibrium after excitation. Critically, short T_1 values impose additional constraints on T_2, creating interdependent relationships that must be carefully managed through molecular design.(Mullin et al., 2024; Warner et al., 2013) T_1 is limited by the coupling of electronic spins with lattice vibrations, commonly known as phonons.(Laorenza et al., 2021) This spin–phonon coupling governs energy exchange between the spin system and the vibrational bath, providing the dominant relaxation pathway in many molecular crystals.

Depending on the phonon spectrum and the local molecular environment, different mechanisms such as the (i) direct processes, (ii) Raman processes, and (iii) Orbach relaxation can contribute to T_1.(Abragam & Bleaney, 2012) Recent experimental and theoretical efforts have highlighted how molecular structure, ligand field symmetry, and host lattice dynamics dictate the magnitude and anisotropy of spin–phonon coupling.(Bayliss et al., 2022; Laorenza & Freedman, 2022; Lunghi & Sanvito, 2020)

SpinVibe is a Python package for simulating spin-phonon coupling and calculating T_1 of molecular qubits in a crystal lattice from first-principles calculations. This is achieved by connecting periodic lattice dynamics and molecular electronic structure calculations. In addition, SpinVibe enables the parametric analysis of T_1 under different factors, including temperature, crystal/molecule orientation and applied magnetic fields. The code is written in Python3 and is MPI-parallelized over phonon modes and q-points using mpi4py.
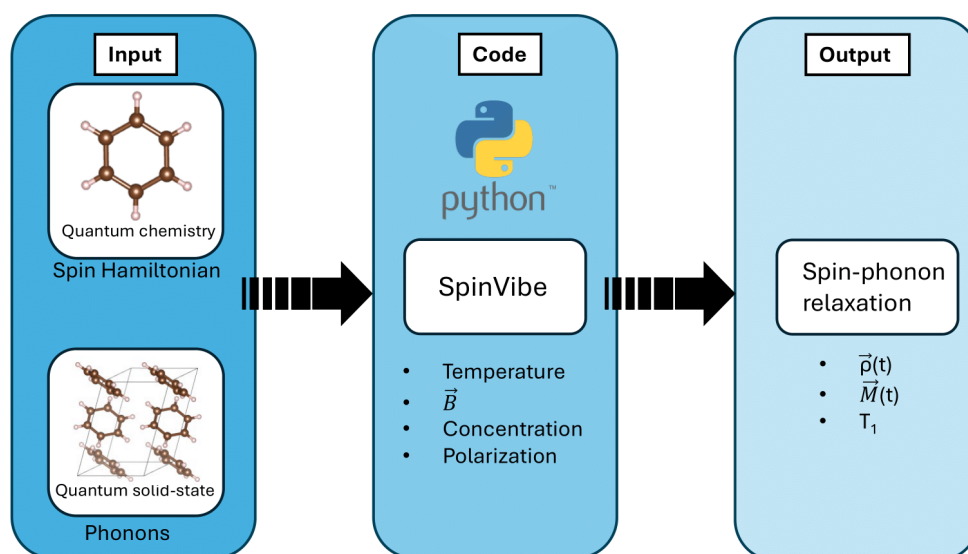
Figure 1: .

Figure 1: Schematic representation of the SpinVibe framework. The spin Hamiltonian, derived from quantum chemistry calculations, and the phonon modes, obtained from quantum solid-state simulations, are merged within SpinVibe to compute spin–phonon relaxation dynamics and T1 under various enironmental factors.

Statement of need

Computational approaches based on density functional theory (DFT) have proven to be valuable for analyzing phonon modes and lattice dynamics in molecular systems.(Baroni et al., 2001) Complementarily, multiconfigurational electronic structure methods, such as CASSCF combined with NEVPT2, provide an accurate description of the spin states and their energy splittings, which are essential for modeling qubit performance.(Baldinelli et al., 2025; Janicka et al., 2022) Integrating these two perspectives into a unified framework for simulating spin–phonon coupling enables a microscopic understanding of the relaxation mechanisms in molecular qubits. Such an approach represents a powerful tool for the rational design of next-generation molecular qubits, with the potential to accelerate the discovery of systems that exhibit long-lived spin states.

To this end, we developed `SpinVibe`, a Python package that is designed to be user-friendly, providing streamlined workflows that are readily adapted to any *ab initio* code. Since it only requires the storage of minimal data from first-principles calculations as `NumPy` arrays in HDF5 files, it is not restricted to specific codes. Any ab-initio package can be used to generate the input data, provided that the relevant quantities are extracted and saved in this format.

First principles spin-phonon coupling

Our code implements the theoretical framework developed by Lunghi and Sanvito(Lunghi, 2022, 2023; Lunghi & Sanvito, 2020), where in the weak-coupling regime the interaction between the spin Hamiltonian and the phonons is expanded as a Taylor series truncated at the quadratic term:

$$\hat{H}_{sph} = \sum_{\alpha q} \left(\frac{\partial \hat{H}_s}{\partial Q_{\alpha q}} \right) \hat{Q}_{\alpha q}(t) + \sum_{\alpha q} \sum_{\beta q'} \left(\frac{\partial^2 \hat{H}_s}{\partial Q_{\alpha q} \partial Q_{\beta q'}} \right) \hat{Q}_{\alpha q}(t) \hat{Q}_{\beta q'}(t) \,. \qquad (1)$$

62 % In Equation 1, the first order term represents the interaction of the spin with a single phonon
63 $ Q_{ q}$. The second order term describes the interaction of the spin with two phonons $
64 Q_{ q}$ and $Q_{\beta q'}$.

65 To describe the time evolution of the system, we employ the secular Redfield equation under
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67 the secular Redfield equation under the the Born-Markov approximation %

$$\frac{\partial \rho_{ab}^s(t)}{\partial t} = \sum_{cd} e^{i(\omega_{ac} + \omega_{db})t} R_{ab,cd} \rho_{cd}^s(t) \,, \qquad (2)$$

68 % where $R_{ab,cd}$ denotes the Redfield superoperator. The single-phonon contribution to the
69 Redfield tensor, under the secular approximation, is

$$R_{ab,cd}^{\text{1-ph}} = -\frac{\pi}{2\hbar^2} \sum_{\alpha} \left\{ \sum_j \delta_{bd} V_{aj}^{\alpha} V_{jc}^{\alpha} G^{\text{1-ph}}(\omega_{jc}, \omega_{\alpha}) - V_{ac}^{\alpha} V_{db}^{\alpha} G^{\text{1-ph}}(\omega_{ac}, \omega_{\alpha}) \qquad (3)$$

$$-V_{ac}^{\alpha} V_{db}^{\alpha} G^{\text{1-ph}}(\omega_{bd}, \omega_{\alpha}) + \sum_j \delta_{ca} V_{dj}^{\alpha} V_{jb}^{\alpha} G^{\text{1-ph}}(\omega_{jd}, \omega_{\alpha}) \right\} \,, \qquad (4)$$

70 % where $V^{\alpha} = \left(\frac{\partial \hat{H}_s}{\partial Q_{\alpha}} \right)$ and %

$$G^{\text{1-ph}}(\omega_{ij}, \omega_{\alpha q}) = \frac{1}{\pi} \left[\frac{\Delta_{\alpha q}}{\Delta_{\alpha q}^2 + (\omega_{ij} - \omega_{\alpha q})^2} \bar{n}_{\alpha q} + \frac{\Delta_{\alpha q}}{\Delta_{\alpha q}^2 + (\omega_{ij} + \omega_{\alpha q})^2} (\bar{n}_{\alpha q} + 1) \right] \qquad (5)$$

71 % is the phonon correlation function in the presence of anharmonic terms that leads to a decay
72 in the phonon lifetime with a rate $\Delta_{\alpha q}$. %%

73 %% The two-phonon contribution is given by %

$$R_{ab,cd}^{\text{2-ph}} = -\frac{\pi}{4\hbar^2} \sum_{\alpha \geq \beta} \left\{ \sum_j \delta_{bd} V_{aj}^{\alpha\beta} V_{jc}^{\alpha\,\beta} G^{\text{2-ph}}(\omega_{jc}, \omega_{\alpha}, \omega_{\beta}) \right.$$

$$-V_{ac}^{\alpha\beta} V_{db}^{\alpha\,\beta} G^{\text{2-ph}}(\omega_{ac}, \omega_{\alpha}, \omega_{\beta})$$

$$-V_{ac}^{\alpha\beta} V_{db}^{\alpha\,\beta} G^{\text{2-ph}}(\omega_{bd}, \omega_{\alpha}, \omega_{\beta})$$

$$\left. +\sum_j \delta_{ca} V_{dj}^{\alpha\beta} V_{jb}^{\alpha\,\beta} G^{\text{2-ph}}(\omega_{jd}, \omega_{\alpha}, \omega_{\beta}) \right\} \qquad (6)$$

74 % where $V^{\alpha\beta} = \left(\frac{\partial^2 \hat{H}_s}{\partial Q_{\alpha} \partial Q_{\beta}} \right)$ and

$$G^{2-\mathsf{ph}}(\omega_{ij}, \omega_{\alpha q}, \omega_{\beta q'}) = \frac{1}{\pi}\Bigg[\frac{\Delta_{\alpha q \beta q'}}{\Delta_{\alpha q \beta q'}^2 + (\omega_{ij} - \omega_{\alpha q} - \omega_{\beta q'})^2}\bar{n}_{\alpha q}\bar{n}_{\beta q'}$$

$$+ \frac{\Delta_{\alpha q \beta q'}}{\Delta_{\alpha q \beta q'}^2 + (\omega_{ij} + \omega_{\alpha q} + \omega_{\beta q'})^2}(\bar{n}_{\alpha q} + 1)(\bar{n}_{\beta q'} + 1)$$

$$+ \frac{\Delta_{\alpha q \beta q'}}{\Delta_{\alpha q \beta q'}^2 + (\omega_{ij} - \omega_{\alpha q} + \omega_{\beta q'})^2}\bar{n}_{\alpha q}(\bar{n}_{\beta q'} + 1)$$

$$+ \frac{\Delta_{\alpha q \beta q'}}{\Delta_{\alpha q \beta q'}^2 + (\omega_{ij} + \omega_{\alpha q} - \omega_{\beta q'})^2}(\bar{n}_{\alpha q} + 1)\bar{n}_{\beta q'}\Bigg] \qquad (7)$$

Once the time-evolution is performed, we can study the time-evolution of the magnetization of the system

$$\vec{M}(t) = \mathsf{Tr}(\vec{S}\hat{\rho}(t)) \qquad (8)$$

from which the T_1 can be extracted by fitting the decay to

$$M_z(t) = [M_z(t=0) - M_z^{\mathsf{eq}}]e^{-t/T_1} + M_z^{\mathsf{eq}}. \qquad (9)$$

Acknowledgments

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