

First-Principles Calculation of the Temperature-Dependent Transition Energies in Spin Defects

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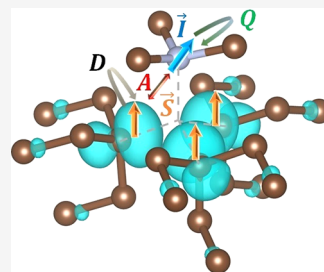


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ABSTRACT: Spin qubits associated with color centers are promising platforms for various quantum technologies. However, to be deployed in robust quantum devices, the variations of their intrinsic properties with the external conditions, in particular temperature and strain, should be known with high precision. Unfortunately, a predictive theory on the temperature dependence of the resonance frequency of electron and nuclear spin defects in solids remains lacking. In this work, we develop a first-principles method for the temperature dependence of the zero-field splitting, hyperfine interaction, and nuclear quadrupole interaction of color centers. As a testbed, we compare our ab initio calculations with experiments for the nitrogen-vacancy (NV^-) center in diamond, finding good agreements. We identify the major origin of the temperature dependence as a second-order effect of dynamic phonon vibrations, instead of the thermal-expansion strain. The method can be applied to different color centers and provides a theoretical tool for designing high-precision quantum sensors.



Color centers, the fluorescent lattice defects in insulators, have been intensively studied as solid-state qubits for quantum computing,^{1,2} quantum communication,^{3,4} and quantum sensing.^{5,6} The temperature (and strain) dependence of the spin defect properties is a critical factor in their performance: their spatiotemporal fluctuations in the crystal host would result in degraded coherence times, while the sensitivity of the defects to their small variations can be exploited in quantum sensing.⁵ A predictive theoretical model accompanied by a robust computational protocol would be invaluable in both mitigating deleterious effects and selecting the best host/defect combinations for quantum sensing. Here, we developed a first-principles method for predicting the temperature dependence of optical, electronic, and nuclear spin-transition frequencies. We benchmark our calculations using the properties of the nitrogen-vacancy (NV^-) center in diamond. Our first-principles calculations achieve excellent agreement with the temperature dependence of the NV^- zero phonon line (ZPL), zero-field splitting (ZFS), hyperfine interaction, and nuclear quadrupole interaction. Crucially, we find that the dominant part of the temperature dependence is from a second-order dynamical phonon effect. Our method paves the way for computation-assisted design of novel quantum sensors using color centers in solids.

We select the NV^- center as our testbed, since it has been accurately characterized in experiments for its applications to quantum sensing of magnetic fields,^{7–9} electric fields,¹⁰ temperature,^{11,12} pressure,^{13,14} and rotation.^{15,16} While the temperature dependence of the NV^- electronic spin resonance frequency¹⁷ has been exploited to probe the local temperature with ultrahigh spatial resolution in nanothermometry devices,^{18–25} it is also detrimental to some quantum devices, since its fluctuations can lead to decoherence.²⁶

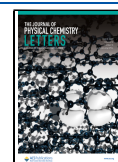
Despite extensive experimental study on the temperature dependence of both electronic and nuclear spin frequencies,^{27–32} a predictive theoretical method is still lacking. The temperature dependence has been previously attributed to the thermal-expansion strain, but the calculated temperature shifts are far smaller in absolute magnitude than the experimental values^{27,31–33} (approximately by an order of magnitude). This discrepancy indicates that other effects dominate the temperature dependence. Various explanations have been proposed for such a discrepancy. Doherty et al. proposed that the dynamical phonon effect might play an important role in the temperature dependence of the ZFS.¹⁷ However, in the absence of a method to evaluate the dynamical phonon effect from first-principles, its contribution to the temperature dependence could not be unambiguously determined. To overcome these challenges, here we develop a theoretical model of the defect transition energy ν dependence on the temperature-induced atomic displacement up to the second order. We combine a full calculation of the phonon spectrum including density functional perturbation theory (DFPT)³⁴ with density functional theory (DFT) calculation of the spin-transition energies with the supercell method.³⁵

Given an electron–nuclear spin system, such as the NV^- center, we aim at calculating the temperature-induced shift of a transition frequency ν between any two levels that can be

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probed experimentally (e.g., by Rabi experiments.) The shift in ν arises from the temperature-induced atomic displacement, as the thermal excitation of electrons is negligible due to the large energy gap in a broad temperature range. For a general transition, the atomic displacement effect is described by the energy surfaces of the two levels as a function of atomic coordinates, as shown in Figure 1(a). Expressing the atomic

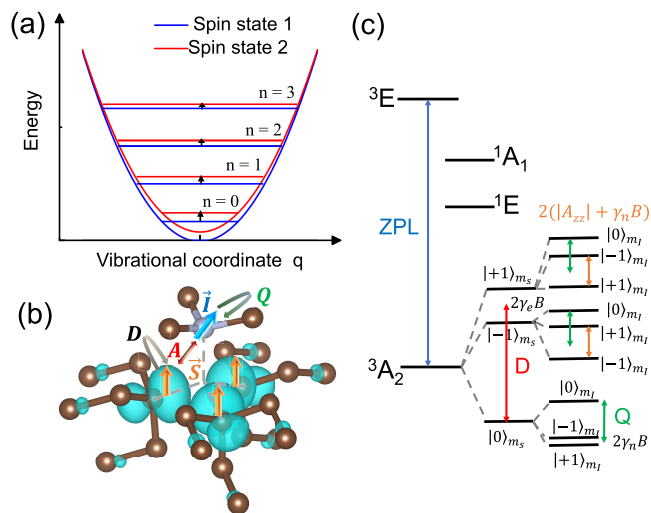


Figure 1. (a) Illustration of the second-order phonon effect to spin resonance. (b) Electron and nuclear spin interaction in an NV[−] center. The blue isosurface of electron spin density is from the DFT, and the brown and silver spheres represent carbon and nitrogen atoms, respectively. (c) The energy levels of NV[−] centers.

configuration by the normal coordinates of phonon modes $\{q_i\}$, the transition frequency is then a function of $\{q_i\}$: $\nu(\{q_i\}) \equiv [E_2(\{q_i\}) - E_1(\{q_i\})]/h$ (E_1 and E_2 are the energy level 1 and energy level 2, respectively). At finite temperature, $\{q_i\}$ has both thermal and quantum fluctuations. As all electron and nuclear spin-transition frequencies (zero-field splitting D , hyperfine interaction A , and nuclear quadrupole interaction Q) are at least 3 orders of magnitude smaller than the typical phonon frequency,³⁶ the measured ν is a statistical average over the phonon mode distribution:

$$\langle \nu \rangle = \nu_0 + \sum_i \left[\left. \frac{\partial \nu}{\partial q_i} \right|_0 \langle q_i \rangle + \frac{1}{2} \left. \frac{\partial^2 \nu}{\partial q_i^2} \right|_0 \langle q_i^2 \rangle \right] + O(q^3) \quad (1)$$

The first-order term represents the change of atomic equilibrium positions, corresponding to thermal expansion. Here we emphasize that the first-order term is typically smaller than the second-order term, as $\langle q_i \rangle$ originates from the weak phonon anharmonicity. Then, what appears to be a “first-order term” in eq 1 is actually the product of first-order and third-order terms, as a purely harmonic system will have zero thermal expansion with $\langle q_i \rangle = 0$. We evaluate the first-order term through the quasiharmonic approximation³⁷ as a static lattice expansion effect. The temperature-dependent lattice parameter $a(T)$ of nitrogen-rich diamond is obtained from the previous experiments,³⁸ and $\nu(a)$ is calculated for different a at the equilibrium atomic configuration. The thermal-expansion contribution to the spectral drift is then:

$$\left. \frac{\partial \nu}{\partial T} \right|_{\text{quasiharmonic}} = \left. \frac{\partial \nu}{\partial a} \right|_{a=a(T)} a(T) \alpha(T) \quad (2)$$

where $\alpha(T)$ is the linear thermal-expansion coefficient at temperature T .

The dominant second-order term represents the atomic vibration around the equilibrium positions caused by phonon excitations at finite temperature. The second-order term is evaluated by the dependence of the spin-transition energy ν on the phonon occupation number $n_i = 0, 1, 2, \dots$ (i is the vibrational mode index), which affects $\langle q_i^2 \rangle$ in eq 1. By evaluating $\langle q_i^2 \rangle$ for a quantum harmonic oscillator (harmonic phonon theory) at thermal equilibrium,

$$\langle q_i^2 \rangle = \frac{\hbar}{M_i \omega_i} \left(\langle n_i \rangle + \frac{1}{2} \right) = \frac{\hbar}{M_i \omega_i} \left(\frac{1}{e^{\hbar \omega_i / kT} - 1} + \frac{1}{2} \right), \quad (3)$$

where M_i is the mode-specific effective mass (conjugate to the q_i definition) in real-space harmonic lattice dynamics expansion. Here we already included the “first-order” thermal-expansion term in eqs 1 and 2 by taking ν_0 not at the zero-temperature lattice constant a_0 but at finite-temperature lattice parameter $\nu_0 = \nu_0(a(T))$. We notice that the dynamical phonon effect contributes a finite zero-point vibration term to the spin-transition frequency even at zero temperature.

We can gain additional physical intuition of this result by considering the Franck–Condon discussions³⁹ and graphically analyzing the expected frequency shift, as shown in Figure 1(a). We consider two spin energy levels within vibrational energy levels ($n_i = 0, 1, 2, \dots$) associated with orthogonal vibrational wave functions of the ions. Suppose the upper energy surface (red, associated with the higher spin energy) has a slightly softer phonon frequency, which is true on average for the NV[−] center. Therefore, the spin-transition energy ν decreases as the phonon number $n_i^{\text{red}} = n_i^{\text{blue}} = n$ increases. Although the typical radio frequency and microwave (MHz to GHz) spin control cannot induce direct transitions between different phonon levels n_i ($\sim$ THz), these vibration energy levels still affect the average spin-transition frequencies by inducing relatively small shifts in total energy $(n_i + \frac{1}{2}) \hbar \Delta \omega_i$, where $\Delta \omega_i = \omega_i^{\text{red}} - \omega_i^{\text{blue}}$ is the difference in modal frequency between the upper energy surface (red) and the lower energy surface (blue).

More specifically, the mean value of the spin-transition frequency can be calculated as

$$\begin{aligned} \langle \nu \rangle &= \sum_{\{n_i\}} \frac{e^{-\sum_i \hbar \omega_i (n_i + \frac{1}{2}) / kT}}{Z} \left[\nu_0(a(T)) + \sum_i \frac{\Delta \omega_i}{2\pi} \left(n_i + \frac{1}{2} \right) \right] \\ &= \nu_0(a(T)) + \sum_i \frac{\Delta \omega_i}{2\pi} \left(\frac{1}{e^{\hbar \omega_i / kT} - 1} + \frac{1}{2} \right) \end{aligned} \quad (4)$$

As $\Delta \omega_i \ll \omega_i \equiv (\omega_i^{\text{red}} + \omega_i^{\text{blue}})/2$, the expression can be evaluated by the second-order derivative of the spin-transition energy (vertical distance between red and blue) to the normal-mode coordinates $\Delta \omega_i = \frac{\hbar}{2M_i \omega_i} \frac{\partial^2 (2\nu)}{\partial q_i^2}$, where $2\pi \hbar \nu = E^{\text{red}} - E^{\text{blue}}$ is the difference in red and blue potential energy surfaces,

and we have used the fundamental relation of harmonic oscillators for each phonon mode:

$$M_i \omega_i^2 = \frac{\partial^2 E}{\partial q_i^2} \rightarrow 2M_i \omega_i \Delta \omega_i = \frac{\partial^2 (E^{\text{red}} - E^{\text{blue}})}{\partial q_i^2} \quad (5)$$

Thus, this independent derivation from (4) gives

$$\langle \nu \rangle = \nu_0(a(T)) + \sum_i \frac{1}{4\pi M_i \omega_i} \frac{\partial^2 (2\pi \hbar \nu)}{\partial q_i^2} \left(\frac{1}{e^{\hbar \omega_i / kT} - 1} + \frac{1}{2} \right) \quad (6)$$

which is identical to eq 3.

The zero-phonon line (ZPL), unlike the spin-transition energies D , A , and Q , will have much larger transition energy/frequency than the vibrational frequency. For ZPL, there is also no vibrational transition (direct mixing with first-order $\hbar \omega_i$), as this is the “zero-phonon” vibronic transition. But the second-order phonon-frequency softening argument due to $n^{\text{blue}} = n \rightarrow n^{\text{red}} = n$ in Figure 1(a) still holds, and therefore, the eq 6 derivation is still valid as well as eq 3. The absolute transition rate can be computed through total vibronic wave function overlap (joint electronic-vibrational wave function overlap between the red and blue)³⁹.

Thus, the temperature-dependent frequency due to the dynamic-harmonic-phonon effect is given by eq 3, which is the form we will adopt for the numerical computations in this paper. At first, a full phonon calculation is implemented through the phonopy package⁴⁰ combined with DFPT implemented in Vienna ab initio simulation package (VASP)^{41,42} to derive the frequency ω_i and effective mass M_i of the full phonon spectrum. The second-order derivatives are then calculated by the finite-differential method:

$$\frac{\partial^2 \nu}{\partial q_i^2} = \frac{1}{\delta q_i^2} [\nu(\delta q_i) + \nu(-\delta q_i) - 2\nu(0)] + O(\delta q_i^2) \quad (7)$$

where $\nu(q_i)$ is calculated by exerting a small displacement of δq_i relative to the relaxed atomic configuration in the DFT calculations (see Supporting Information (SI) for details⁴³).

We simulate the NV[−] center in diamond by a $4 \times 4 \times 4$ rhombohedral supercell with the single defect at the center. First, we calculate the zero-temperature electronic structures of the NV[−] center for the fully relaxed atomic configuration (Figure 1b). The electronic structure calculation employs the DFT and projector-augmented-wave (PAW) method implemented by VASP. The ground state 3A_2 contains electron spin $S = 1$ and ${}^{14}\text{N}$ nuclear spin $I = 1$, leading to the fine and hyperfine structure shown in Figure 1(c). The spin state splittings originate from three types of interaction: the electron–electron magnetic dipolar interaction D , the hyperfine interaction A , and the nuclear quadrupole interaction Q .⁴⁴

$$\hat{H} = \vec{S} \cdot \vec{D} \cdot \vec{S} + \vec{S} \cdot \vec{A} \cdot \vec{I} + \vec{I} \cdot \vec{Q} \cdot \vec{I} \quad (8)$$

D , A , and Q are calculated by the first-order perturbation theory to the DFT ground state^{33,45–48} (see SI⁴³ for details). Selecting the C_3 axis of the NV[−] center as the z -direction and taking into account that $H_D \gg H_A$, H_Q , the effective Hamiltonian, reduces to³⁶

$$\hat{H} = DS_z^2 + QI_z^2 + A_{zz}S_zI_z \quad (9)$$

where $D = \frac{3}{2}D_{zz}$ and $Q = \frac{3}{2}Q_{zz}$ (magnetic field coupling terms are not included). The temperature variations of D , Q , and A_{zz}

are then calculated by relating them to transitions ν between two selected spin states (illustrated in Figure 1c). Similarly, the ZPL's temperature dependence is calculated by eq 4 using the Δ SCF method^{45,49,50} (see SI⁴³ for details).

Applying our method to electronic transition, we calculate the temperature dependence of the ZPL and ZFS (Figure 2).

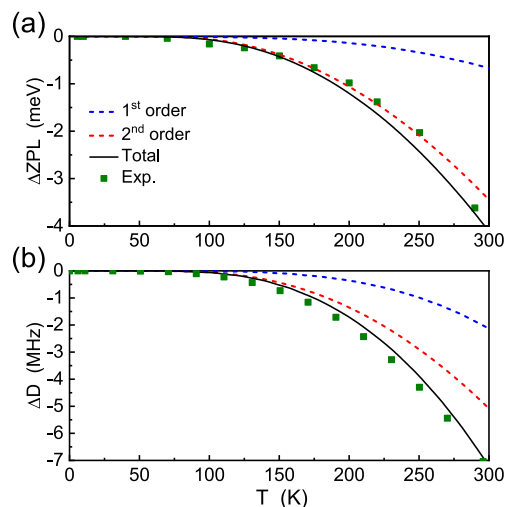


Figure 2. (a) The ZPL and (b) ZFS from simulation and experiment. The blue and red dashed lines represent the first-order (thermal expansion) and second-order (dynamical phonon) effects, respectively. The black line is the total shift from simulation, and the green dots are experimental data points from refs 17 and 31. The well-known first-order effect in (b) is obtained from ref 17.

The “first-order” thermal-expansion effect is, as found in previous computational work,^{27,33} far smaller than the experimental results for the measured temperature drifts. This is not surprising, since the quasiharmonic “first-order” effect is physically a “cubic-order” Grüneisen parameter $\times$ “first-order” effect. Including the second-order dynamical phonon effects corrects the discrepancy. The overall simulation results (summation of the first- and second-order) for both quantities are now consistent with prior experimental results. The calculated temperature derivative $\frac{dD}{dT}$ at room temperature is -75.99 kHz/K, consistent with the widely used experimental value of -74.27 kHz/K.²⁷ Different from ref 17, where the dynamical phonon effect is fitted by experiment, we evaluate the effect in a parameter-free manner from first-principles calculations. Our result indicates that the main mechanism of the temperature dependence of the ZPL and ZFS is the dynamical phonon effect, with a much smaller contribution from the thermal-expansion strain, at least near room temperature. The temperature shift of the ZFS in NV[−] centers provides promising prospects for nanothermometry, where the magnitude of $\frac{dD}{dT}$ is crucial for its temperature sensitivity.⁶ Our method provides a predictive tool to search for different color centers for optimal temperature sensitivity.

We notice that the method we used to calculate the ZFS (developed in ref 33) does not take an exact estimation to the contribution of the electron wave functions in the atomic core regions. The method also involves errors from the spin contamination issue.⁵² Despite this, as the core contribution is estimated to be less than 5%³³ and the predicted response of the ZFS to external perturbations is reasonably consistent with

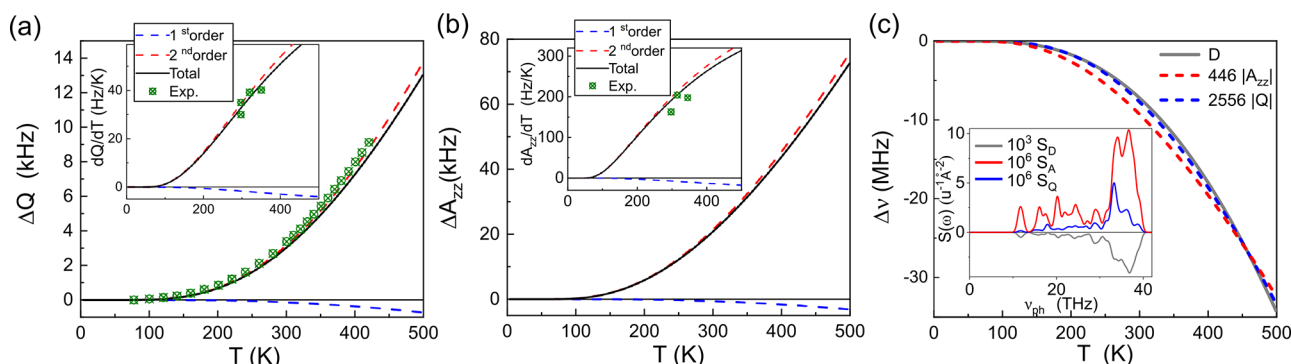


Figure 3. (a) Nuclear quadrupole interaction Q and (b) hyperfine interaction A_{zz} from simulation. The blue, red, and black curves represent the calculated temperature-induced change from the thermal-expansion effect, the second-order vibration effect, and their summation, respectively. The insets are the derivative of Q and A_{zz} results, where the green dots are experimental data obtained from refs 17, 28, 29, and 51. (c) Overlap behavior of $D(T)$, $Q(T)$, and $A_{zz}(T)$ from simulation. The inset shows the spectral density S_D , S_Q , and S_A as defined in eq 10, where Gaussian broadening is applied to the $\delta(\omega - \omega_i)$ for each phonon mode with a width of 2 THz.

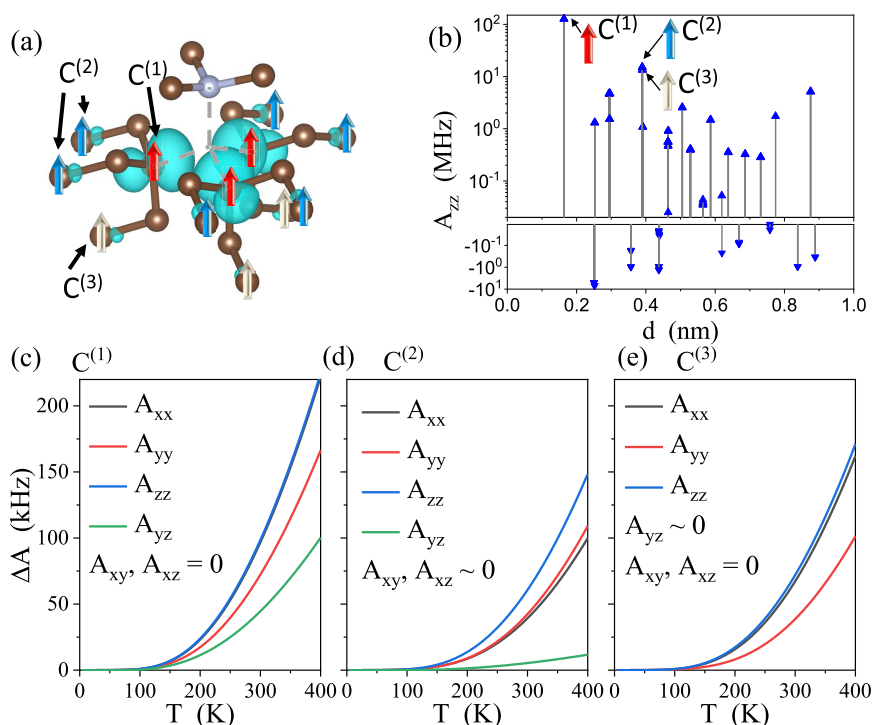


Figure 4. Hyperfine interaction A_{zz} with ¹³C nuclear spin from simulation. (a) Illustration of the three groups of identical nuclear spins with the strongest hyperfine interaction. (b) A_{zz} for different ¹³C nuclear spins around the NV⁻ center plotted against the distance d between the ¹³C site and the NV⁻ center. (c) Temperature shifts of different components of the hyperfine tensor A for ¹³C atoms at different sites. The z -axis orients from the vacancy site to the ¹⁴N site, the x -axis is along the vector between the two C(2) atoms pointed by black arrows (toward the upper one), and $\hat{y} = \hat{z} \times \hat{x}$. In the label, $A_{ij} = 0$ means the exact zero by symmetry and $A_{ij} \approx 0$ means numerically almost zero.

experiments in both previous work and our work, we expect the method can approximately output the temperature dependence of the ZFS.

We then calculate the temperature dependence of the nuclear spin interaction. The temperature dependence of ¹⁴N-related nuclear spin transition is shown in Figures 3(a,b). Both A_{zz} and Q are negative quantities, and their absolute values decrease with increasing temperature, yielding positive dQ/dT and dA_{zz}/dT . The thermal-expansion contribution to the temperature shifts has an opposite slope with respect to the experiments. The dynamical phonon effect is more than 1 order of magnitude larger than the thermal-expansion effects, so it corrects both the trend and the magnitude, obtaining $\frac{dQ}{dT}$

and $\frac{dA_{zz}}{dT}$ in good agreement with the previous experiments.^{17,28,29,51}

A_{zz} is much more sensitive to T than Q . The sensitivity of A_{zz} mainly comes from the Fermi contact term, which is highly sensitive to the atomic displacement in the dynamical phonon effects according to our calculations. In comparison, the electric field gradient (EFG) is relatively insensitive to atomic displacement, so Q has a smaller temperature shift. Therefore, we expect that the higher sensitivity of A_{zz} than Q is also a general behavior in many other color centers. It has been recently proposed that with $\frac{dA_{zz}}{dQ} > 1$, the coherence time of nuclear spin qubits can be robustly protected by at least 1

order of magnitude through noise decoupling techniques.⁵¹ The generality of the higher sensitivity of A_{zz} indicates a broad applicability of such a method to various solid state spin defects. The relative shift of the hyperfine transition, $\frac{dA_{zz}}{dT} \frac{1}{A_{zz}}$ approaches $8.9 \times 10^{-5} \text{ K}^{-1}$ at room temperature. While the absolute value of the ZFS shift is much larger, the relative frequency change $\frac{dD}{dT} \frac{1}{D} \approx 2.58 \times 10^{-5} \text{ K}^{-1}$ is smaller than for the hyperfine interaction. Thus, to operate a quantum sensor based on the nuclear spin, it is imperative to recalibrate the temperature effects.²⁶ The perpendicular hyperfine interaction A_{xx} is also important for nuclear spin dynamics,³⁶ whose temperature dependence is shown in SI section V.

Previous experimental results had observed a strong, but so far unexplained, correlation between $D(T)$ and $Q(T)$.²⁹ Our first-principles results not only confirm such a correlation over a broad temperature range from 100 to 500 K (Figure 3c) but also provide approaches to revealing the underlying mechanism of such a correlation. As the dynamical phonon effects are dominant for all these interactions, we investigate the overlap behavior by defining the spectral density of the second-order derivative of ν as

$$S^i(\omega) = \sum_j \frac{1}{M_j} \frac{\partial^2 \nu^j}{\partial q_j^2} \delta(\omega - \omega_j^i) \quad (10)$$

as shown in the inset of Figure 3(c). The large intensities of S^D , S^Q , and S^A at around 32–38 THz are attributed to the high phonon density of states (DOS)⁵³ and large second-order derivatives in eq 10 at that frequency range. The ratio between two temperature-induced frequency shifts (second-order) is then a weighted average between their spectral density:

$$\frac{\Delta \nu^1}{\Delta \nu^2} = \frac{\int S^1(\omega) f_{BE}(T, \omega) / \omega d\omega}{\int S^2(\omega) f_{BE}(T, \omega) / \omega d\omega} \quad (11)$$

where f_{BE} is the Bose-Einstein distribution. As the spectral densities S_Q and S_D have a similar shape, the ratio $\Delta Q/\Delta D$ is relatively insensitive to temperature. In comparison, S_A shows a more striking difference, undermining A_{zz} 's overlap with Q and D . Thus, although $A_{zz}(T)$ also shows an approximate correlation with Q and D , it has a relatively larger deviation with a larger slope in the low-temperature region and a smaller slope in the high-temperature region as shown in Figure 3(c). We note that the spectral correlation between different interactions can be quite accurate and paves the way to designing robust coherence protection protocols by refocusing one-interaction variations using other correlated interactions over a broad range of temperatures.⁵¹

Beyond accurately reproducing experimental results, we can predict the hyperfine temperature shift of ^{13}C nuclear spins around the NV^- center, which have been actively investigated as qubits^{30,54–57} (Figure 4a). A_{zz} for ^{13}C atoms at different lattice sites around the NV^- centers is shown in Figure 4b as a function of their distance to the NV^- center, where we identify three groups of equivalent ^{13}C lattice sites with the strongest interaction. The ^{13}C atom at the first-shell lattice sites ($\text{C}^{(1)}$) of the NV^- center shows a strong hyperfine splitting of 129 MHz, well consistent with the experimental value of 127 MHz.³⁰

The temperature dependence $\Delta A(T)$ of the three groups of ^{13}C lattice sites is shown in Figure 4(c–e). As specifying a given ^{13}C nuclear spin reduces the C_{3v} symmetry, there are more independent components of the hyperfine matrix: $\text{C}^{(1)}$

and $\text{C}^{(3)}$'s C_{1h} symmetry gives four independent components (with two constraints $A_{xy} = A_{xz} = 0$), and $\text{C}^{(2)}$'s C_1 symmetry allows all six components of $A(T)$ to be independent variables. The diagonal components of A are positively related to T for all three groups of lattice sites, exhibiting sensitive temperature dependence with temperature shifts ranging from 39.3 to 98.5 kHz at 300 K. Previously, experimental work on the temperature dependence of the ^{13}C hyperfine interaction did not provide definite results due to the high noise, while a computational study did not consider the second-order dynamical phonon effect.³⁰ Our results provide a theoretical prediction for $A(T)$ of ^{13}C atoms near NV^- centers, which could be measured by the nuclear spin transition.⁵¹

In the discussion above, we focus on the temperature shift under thermal equilibrium, but the dynamical phonon effect on spin-transition frequency can be extended to kinetic processes such as nonequilibrium phonon transport. In general, the temperature shift at a single NV^- center measures a linear combination $\hat{O}(r) = \sum_i \frac{\hbar}{2M_i \omega_i} \frac{\partial^2 \nu}{\partial q_i^2} \hat{n}_i(\vec{r})$ of the particle number

operators $\hat{n}_i$ of ambient phonons, where the electron or nuclear spin of an NV^- ensemble can probe phonon distribution in the sample. While most materials characterization methods probe the atomic equilibrium position, the second-order temperature shift of spin defects provides a potential route to probe out-of-equilibrium local atomic vibrations.

Our work provides a general scheme to study the temperature dependence of transition frequencies of color centers. An integrated python program that interfaces with VASP and phonopy is made publicly accessible, which can carry out the numerical workflow automatically. Besides the NV^- center, various other color centers such as SiV , SnV , PbV , GeV , and MgV in diamond are also widely studied due to their potential in quantum sensing and communication.^{5,58–60} Besides diamond, point defects in silicon,^{61–63} silicon carbide,^{64–66} Y_2SiO_5 ,⁶⁷ CaWO_4 and YVO_4 ^{68,69} also attract broad interests. The temperature dependence data of transition frequency remains lacking for many of these systems. Applying our method to these spin defects can establish a database for temperature-dependent transition frequency of electronic excitation as well as electron and nuclear spin transitions, which provides critical information for searching and designing high-performance quantum devices such as highly sensitive sensors and long-lived memories. Thus this result paves the way to perform a systematic study on the energy levels of point defects targeted for different quantum applications.

Finally, we raise caution that our current codes calculate the ZFS by evaluating the electron spin–spin dipolar interaction term. In some other color center systems (for example, SiV^- center in diamond), the spin–orbit coupling is also an important source of the ZFS.⁴⁶ Especially, the spin–orbit coupling is significant in systems with heavy elements like Y_2SiO_5 . In order to calculate the temperature-dependent ZFS of these systems, one can incorporate the spin–orbit coupling calculations into our scheme, which is left to future work.

■ ASSOCIATED CONTENT

Data Availability Statement

The codes are available at <https://github.com/htang113/First-principles-Calculation-of-the-Temperature-dependent-Transition-Energies-in-Spin-Defects>.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00314>.

Additional computational details and supplementary results, including the DFT settings, methods for transition energy calculations, convergence test, and analysis/results of nonsecular terms in the spin Hamiltonian (PDF)

Transparent Peer Review report available (PDF)

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Notes

The authors declare no competing financial interest.

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