Scheme of angstrom-resolution magnetic resonance imaging of single molecules via dynamical decoupling enhanced quantum sensing

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Nuclear magnetic resonance (NMR) with single molecule sensitivity and magnetic resonance imaging (MRI) with angstrom resolution are the highest challenges in magnetic microscopy [1]. Recent development in dynamical decoupling (DD) enhanced diamond quantum sensing [2,3] has enabled NMR of single nuclear spins [4-8] and nanoscale NMR [9,10], via the effect that the sensor decoherence induced by the noise from target nuclear spins is greatly enhanced when the DD period matches the noise frequency [2]. The current DD-based quantum sensing, however, cannot resolve different nuclear spins that have the same noise frequency or identify correlations in nuclear spin clusters [11], which are critical information for angstrom-resolution MRI. Here we demonstrate a scheme of angstrom-resolution MRI by DD-based quantum sensing, which is capable of counting and individually localising single nuclear spins of the same frequency weakly coupled to a sensor and characterizing correlations in nuclear spin clusters by quantized numbers. We find that for DD resonant with the noise frequency of a species of nuclear spins, the sensor coherence presents a sharp dip, whose depth oscillates as a function of the DD pulse number. The oscillation features unambiguously determine the number of nuclear spins coupled to the sensor, the individual coupling strengths, and the correlations, in a quantized manner.
Therefore a nitrogen-vacancy centre spin sensor near a diamond surface can be employed to determine, with angstrom-resolution, the positions and conformation of single molecules (e.g., trimethylolpropane and protein) that are isotope-labelled. This work offers an approach to angstrom-resolution magnetic resonance imaging, which may be useful for quantum computing [12] and conformation analysis of single macromolecules (such as proteins).

Introduction.

Detection of single nuclear spins has broad applications, such as molecular structure analysis in chemistry and biology [1] and spin-based quantum computing [12]. However, the weak signals from single nuclear spins cannot be detected by conventional nuclear magnetic resonance (NMR) [11]. Recently the nitrogen-vacancy (NV) center in diamond, for its long coherence time at room temperature [13-15], has been used to detect single nuclear spins via dynamical decoupling (DD) enhanced quantum sensing [4-8]. When the frequency of a DD sequence on the quantum sensor (the electron spin of an NV center) matches the transition frequency of a target nuclear spin or a spin cluster (resonant DD), the noise from the target is resonantly enhanced and hence the sensor coherence presents a sharp dip. This is the principle of the DD-enhanced quantum sensing [2].

The application of DD-enhanced quantum sensing to magnetic resonance imaging (MRI) of single molecules, however, is restricted by two critical issues. First, it cannot distinguish target nuclear spins that have the same noise frequency. Thus the target spins of the same species, when weakly coupled to the sensor, would precess with the same
Larmor frequency under an external magnetic field and cannot be individually resolved (Fig. 1a,b). Second, the DD-based quantum sensing cannot distinguish the correlated transitions in a nuclear spin cluster from independent multiple transitions that are of the same frequencies as in the correlated cluster, and therefore does not reach the same level of sophistication as the multi-dimensional NMR [11].

Here, we propose a scheme of angstrom-resolution MRI of single molecules. We discover that different numbers of single nuclear spins of the same species and transitions in single nuclear spin clusters, even if they have the same frequencies, have qualitative, quantized differences in effects on the coherence dips of a quantum sensor (such as an NV center spin in diamond) as a function of the DD pulse number. The sensor coherence dip, for DD resonant with a transition of a target spin or spin cluster, oscillates with the number of DD pulses. The features of such oscillations determine the number of nuclear spins, the individual coupling strengths, and the types of correlations, in a quantized manner: (1) The number of coherence zeros within a certain evolution time equals the number of nuclear spins of the same species coupled to the sensor with strength above a certain threshold; (2) The positions of the zeros determine the individual strengths of the coupling between the nuclear spins and the sensor; (3) The maximum depth of the sensor coherence dip, being a quantized number, determines the types of correlations in a nuclear spin cluster. Therefore, we can determine the number and positions of nuclear spins of the same species weakly coupled to a quantum sensor, such as an NV center near a diamond surface, and therefore identify, with angstrom-resolution, the positions and conformations of single molecules (such as proteins) that are isotope labeled.
Resolving multiple spins of the same frequency.

We first demonstrate how to identify a number of independent nuclear spins that are of the same transition frequency and weakly coupled to a quantum sensor. The quantum sensor is taken as a spin-1/2 ($S=1/2$) and $M$ distant target nuclear spins are of the same species ($I=1/2$). The total spin Hamiltonian is in the pure-dephasing form

$$H = S_z \sum_{k=1}^{M} A_k I_k^z + \omega_0 \sum_{k=1}^{M} I_k^x,$$

where $A_k$ is the coupling strength between the sensor and the $k$-th target spin, $\omega_0$ is the Larmor frequency of the target spins. In quantum sensing, the coupling to the targets is weak, i.e., $|A_k| \ll \omega_0$ such that the target spins have the same noise frequency. The eigenstates of the sensor are denoted as $|\pm\rangle$ (with +/- being spin-up/down along the magnetic field direction). To suppress the background environmental noise and selectively enhance the noise from the target spins [4], we apply DD [2, 3] to the sensor (consisting of a sequence of $\pi$-flips at times $\{t_1, t_2, \ldots, t_N\}$ for the evolution from 0 to $t$).

In the classical noise picture, the sensor accumulates random phases due to the magnetic noise produced by the environment and the target spins [16]. For the environment with a large number of particles, the magnetic noise can be approximated as a Gaussian stochastic process, which can be characterized by the two-point correlation function. For our model, the noise correlation function [17, 18] is defined as

$$C(t) = \langle \beta(t) \beta(0) \rangle = \langle e^{iH_0} \beta(0) e^{-iH_0} \beta(0) \rangle,$$

where $\beta = \sum_{k=1}^{M} A_k I_k^x$ is the noise operator, and $H_0 = \omega_0 \sum_{k=1}^{M} I_k^x$ is the free Hamiltonian for the target spins. We assume the temperature is much higher than the target spin frequencies. The correlation function is
\[ C(t) = \sum_{k=1}^{M} |A_k|^2 \cos(\omega_k t) / 4 \] and the noise power spectrum

\[ S(\omega) = \frac{\pi}{4} \sum_{k=1}^{M} |A_k|^2 \left[ \delta(\omega + \omega_k) + \delta(\omega - \omega_k) \right], \]

with the same frequencies as the transitions of the target spins. Then the sensor coherence under DD control is [19]

\[ L(t) = \exp \left[ -\frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\omega) \frac{F^2(\omega, t)}{\omega^2} \right], \quad (1) \]

where \( F(\omega, t) = \sum_{p=0}^{N} (-1)^p (e^{i\omega t_p} - e^{i\omega t}) \) is the DD filter function. In this paper we consider \( N \)-pulse Carr-Purcell-Meiboom-Gill (CPMG-N) control [20, 21] with \( t_p = (2p - 1)\tau \) (where \( 2\tau \) is the interval between pulses and \( p = 1, 2, \ldots, N \)). For the CPMG-N control, the sensor coherence present dips when then pulse interval matches the noise frequency, i.e., \( 2\tau_{\text{dip}} = \pi(2q - 1) / \omega_0 \) with \( q = 1, 2, \ldots \) denoting the dip order, as shown in Fig. 1b. In the following we always consider the first-order coherence dip \( (q = 1) \). At these dips (resonance points), \( F(\omega_0, t) = 2N \), so the sensor coherence dip depth is

\[ L_{\text{dip}}(N) = \exp \left( -\sum_{k=1}^{M} |A_k|^2 \frac{N^2}{2\omega_0^2} \right), \quad (2) \]

with the total evolution time \( t_{\text{dip}} = N\pi / \omega_0 \) for resonant DD. In previous studies, the above formula has been used to extract the coupling strength between the sensor and target spins [4,8]. However, the result in formula (2) is independent of the target spin number \( M \), as long as the noise strength \( \sum_{k=1}^{M} |A_k|^2 \) is kept constant. This means that from Gaussian noise approximation one cannot distinguish whether the sensor coherence dips
result from single or multiple target spins. To resolve multiple target spins of the same species weakly coupled to a sensor, the quantum decoherence model is needed.

In the quantum decoherence model, the decoherence is caused by the sensor-target entanglement [22-24]. Under DD control, the sensor-target system can evolve with entanglement and disentanglement, leading to oscillation between decoherence and coherence recovery with increasing DD pulse number [2, 4]. The entanglement is due to the target spin evolution conditioned on the sensor states $|\pm\rangle$, namely,

$$U_{(\pm)}^N(t) = e^{-i(\tilde{H}_z \pm \tilde{c}) N \beta / 2} \cdots e^{-i(\tilde{H}_z \pm \tilde{c}) N \beta / 2} e^{-i(\tilde{H}_z \pm \tilde{c}) t_0}.$$  

Using the Magnus expansion [25], we obtain an approximate expression for the sensor coherence (see Supplementary Information)

$$L(t) = \frac{1}{2M} \text{Tr} \left[ \left( \hat{U}_{(-)}^N \right)^\dagger \hat{U}_{(\pm)}^N \right] \approx \prod_{k=1}^M \cos \left( \frac{A_k}{2 \alpha_0} F(\omega_k, t) \right).$$  

(3)

for $M$ target spin-1/2's of the same frequency ($\omega_k$). In particular, when the period of the CPMG DD matches the noise frequency ($2\tau_{\text{dip}} = \pi / \omega_k$), the sensor coherence dip depth is

$$L_{\text{dip}}(N) \approx \prod_{k=1}^M \cos \left( \frac{NA_k}{\omega_k} \right).$$  

(4)

To check the validity of the above formula, we compare it to the exact quantum results in Fig. 1c and find excellent agreement in the weak coupling regime ($\sum_{k=1}^M |A_k|^2 \ll \omega_k$). In the case of one target spin ($M = 1$) the sensor coherence dip oscillates periodically between 1 and −1 with increasing the CPMG pulse number $N$. The oscillation period
\( N_k = 2\pi \omega_0 / A_k \) is inversely proportional to the coupling strength \( A_k \). For multiple target spins with the same noise frequency (but with different coupling strengths \( A_k \) to the sensor), the sensor coherence dip, being the product of \( M \) different periodic oscillations with periods \( N_k = 2\pi \omega_0 / A_k \), oscillates non-periodically with \( N \). For a large number of target spins (\( M \gg 1 \)), the interference between oscillations of different periods \( N_k = 2\pi \omega_0 / A_k \) leads to a damped decay with \( N \), and the coherence dip depth is well described by the Gaussian noise approximation in Eq. (2) (see Supplementary Information).

The coupling strength \( A_k \) of each target spin can be individually determined. The dip reaches zero whenever the pulse number is \( N_k^{(0)} = \pi \omega_0 / (2A_k) \) for a target spin. Therefore the number of zeros of the sensor coherence dip \( N < N_{\text{max}} \) determines the number of target spins coupled to the sensor with strength above a threshold \( A_k > \pi \omega_0 / (2N_{\text{max}}) \); the position of the zeros \( N_k^{(0)} = \pi \omega_0 / (2A_k) \) determines quantitatively the individual coupling strengths. The zeros of the sensor coherence dip \( L_{\text{dip}}(N) \) are indeed clearly seen in Fig. 1d. Thus by identifying the zeros of the sensor coherence dip as a function of DD pulse number, we can resolve, in a quantized manner, multiple target spins that have the same noise frequency and are weakly coupled to the sensor with different coupling strengths.

**Characterization of spin correlations.**

Now we show that the correlations in a single spin cluster weakly coupled to a sensor can also be characterized, in a quantized manner, by observing the sensor
coherence dip as a function of DD pulse number. Let us first consider how to distinguish two specific types of target spin clusters, namely, type-II and type-V (Fig. 2a), being uncorrelated and correlated, respectively. Type-II transitions are produced by two independent target spin-1/2's $\mathbf{I}_A$ and $\mathbf{I}_B$; type-V transitions are produced by a correlated cluster (such as a spin-1 $\mathbf{J}$ formed by two interacting spin-1/2's). The Hamiltonians for the sensor coupling with these two types of target spins are

$$H_{\text{II}} = \lambda_{\text{II}} z I_A + I_B + \omega_A I_A^z + \omega_B I_B^z,$$

$$H_{\text{V}} = \lambda_V z J + \frac{\omega_A + \omega_B}{2} J_2^z + \frac{\omega_A - \omega_B}{2} J_z,$$

where the transitions frequencies $\omega_{A/B}$ are set the same for type-II and type-V transitions and the couplings to the sensor $\lambda_V = \sqrt{3} \lambda_{\text{II}} / 2$. The parameters are chosen such that the two types of target spins are identical in terms of the noise power spectrum they produce to the sensor. The conventional noise spectroscopy cannot distinguish the correlated transitions from the uncorrelated ones.

However, the different types of correlations in the target spins would induce different behaviors of sensor-target entanglement and disentanglement under DD control. In particular, the sensor coherence dip as a function of CPMG pulse number $N$ presents different features for different types of correlations (Fig. 2b). Again, by the Magnus expansion [25], we get

$$L^N(t) \approx \cos \left( \frac{\lambda_{\text{II}}}{2\omega_A} F(\omega_A,t) \right) \cos \left( \frac{\lambda_{\text{II}}}{2\omega_B} F(\omega_B,t) \right).$$

(7)
Without loss of generality, we assume \( \omega_b \neq \omega_A \). Then in the case of DD resonant with transition A, i.e., \( 2\tau_{\text{dip}} = \pi/\omega_A \), the DD filter functions \( F(\omega_A, t_{\text{dip}}) = 2N \) and \( F(\omega_A, t_{\text{dip}}) \ll F(\omega_A, t_{\text{dip}}) \) for large \( N \), so the sensor coherence dips for the two types of target spins are

\[
L_{\text{dip}}^\Pi (N) \approx \cos(\lambda_N N / \omega_A),
\]

\[
L_{\text{dip}}^\nu (N) \approx \frac{1}{3} \left[ 1 + 2 \cos \left( \sqrt{2}\lambda_N N / \omega_A \right) \right].
\]

The sensor coherence dips oscillate with different amplitudes for the two different types of target spin correlations: For type-II correlations (independent target spins), the minimum sensor coherence dip is \(-1\), but for type-V transitions (correlated target spins), the minimum sensor coherence dip is \(-1/3\).

As a more general case, now we show that the DD quantum sensing can distinguish the transitions of independent spin-1/2’s and those in a higher spin (ladder-type in Fig. 2a), even if the two types of target systems have the same noise power spectrum. We assume the coupling between a sensor and a target spin with spin \( J \) has the Hamiltonian

\[
H = \lambda J_x J_x + \sum_{m=-J}^{J} \varepsilon_m |m\rangle \langle m| \quad \text{(where basis states are assumed to satisfy \( J_z |m\rangle = m |m\rangle \)).}
\]

The noise spectrum caused by the target spin is

\[
S(\omega) = \frac{2\pi}{2J+1} \sum_{m=-J}^{J} \lambda_m^2 \left[ \delta(\omega+\omega_m) + \delta(\omega-\omega_m) \right] \quad \text{where the transition \( |m\rangle \leftrightarrow |m+1\rangle \)}
\]

causes the noise with frequency \( \omega_m = |\varepsilon_{m+1} - \varepsilon_m| \) with the amplitude

\[
L'(t) \approx \frac{1}{3} \left[ 1 + 2 \cos \left( \frac{F^2(\omega_A, t)}{2\omega_A^2} + \frac{F^2(\omega_B, t)}{2\omega_B^2} \right) \right].
\]
\[ \lambda_m = \lambda \sqrt{(J-m)(J+m+1)} / 2. \]

Then in the case of DD resonant with a transition \((2\tau_{\text{dip}} = \pi/\omega_m)\), the sensor coherence dip as a function of the DD pulse number \(N\) is (see Supplementary Information)

\[ L_{\text{dip}}^{(m)}(N) = \frac{2J-1}{2J+1} + \frac{2}{2J+1} \cos \left( \frac{2\lambda_m N}{\omega_m} \right). \tag{11} \]

Here we assume the general case that different transitions have different frequencies such that if \(F(\omega_m, \tau_{\text{dip}}) = 2N\) then \(F(\omega_n, \tau_{\text{dip}}) \approx 0\) for \(n \neq m\). Thus a spin-\(J\), or a ladder-type system with \(2J+1\) levels, is characterized by a quantized depth of the sensor coherence dip, that is

\[ \min \left( L_{\text{dip}}^{(m)} \right) = \frac{2J-3}{2J+1}, \tag{12} \]

which occurs at the characteristic DD pulse number \(N_m = \pi \omega_m / (2\lambda_m)\). Such quantized features of sensor coherence dip caused by correlated transitions of target spins are clearly seen in Fig. 2c.

The above results for type-II, type-V and ladder-type correlations can be easily extended to the most general case where a bonded nuclear spin cluster weakly coupled to a spin-1/2 sensor. If this nuclear spin cluster has \(d\) eigenstates, then for DD resonant with a specific transition the sensor coherence dip has a quantized minimum of sensor coherence dip, \(\min \left( L_{\text{dip}}^{(m)} \right) = (d-4)/d\) (see Supplementary Information). Thus we have a quantum sensing approach to characterizing, in a quantized manner, the correlation size of nuclear spins - through the quantized, universal values of minimum sensor coherence dips as functions of the DD pulse number.
MRI of spin-labeled single molecules.

We now demonstrate that the coherence dip features of a quantum sensor under DD control can be employed for angstrom-resolution MRI of single molecules that are spin-labeled. We take a shallow NV center in diamond near the surface as the sensor and consider MRI of single trimethylphosphite (TMP) molecules with $^{31}\text{P}$ nuclear spins as labels and conformation analysis of a single Villa (2F4K) protein molecule [26] labeled by $^{15}\text{N}$ nuclear spins in PHE amino acids. We assume that the diamond is $^{13}\text{C}$-depleted [4] (with $^{13}\text{C}$ abundance 0.01%) such that the effect of the background $^{13}\text{C}$ nuclear spins on the sensing is negligible (see Supplementary Information).

The Hamiltonian for an NV electron spin weakly coupled to multiple nuclear spins is

$$H = S_z \sum_{k=1}^{M} A_k \cdot \hat{I}_k + \gamma_n \sum_{k=1}^{M} B \cdot \hat{I}_k,$$

where the NV spin-$1/2 \ S_z$ has eigenstates \(\{|0\rangle, |\pm 1\rangle\}\), \(A_k\) is the hyperfine interaction, \(B\) is the external magnetic field, and \(\gamma_n\) is the gyromagnetic ratio of target spins. Similar to Eq. (4), the NV electron spin coherence dip as a function of CPMG pulse number is (see Supplementary Information)

$$L_{\text{dip}}(N) \approx \prod_{k}^{M} \cos\left(2A_k^{\perp} N/\omega_b\right),$$

where \(A_k^{\perp}\) is the component of the hyperfine field perpendicular to the magnetic field, and \(\omega_b = \gamma_n |B|\) is the Larmor frequency of target nuclear spins.

With a single TMP molecule on the diamond surface (Fig. 3a), the oscillations of NV coherence dip with the CPMG pulse number have different periods depending on the magnetic field direction (Fig. 3b), which determines \(A_k^{\perp}\), the component of the hyperfine field orthogonal to the magnetic field. By measuring the periods of the sensor coherence dip oscillations for three different magnetic field directions, the hyperfine
interaction can be fully reconstructed and therefore the position of the target $^{31}$P nuclear spin in the TMP can be precisely determined (Fig. 3c). For a TMP molecule placed about 4 nm away from the NV center and a magnetic field $B \sim 20$ Gauss, 

$$A_k^+/(2\pi) \sim 300 \text{ Hz} \text{ and } \omega_h/(2\pi) \sim 34.5 \text{ kHz.}$$

The minimum number of DD pulses needed to observe half a period of the coherence dip oscillation is

$$\min(N) = \pi \omega_h / (2A_k^+) \approx 180$$

and the minimum evolution time

$$\min(t_{\text{dip}}) = \pi^2 / (2A_k^+) \approx 2.6 \text{ ms}$$

(which is independent of the external magnetic field).

The measurement time is still well below the longitudinal relaxation time ($T_1 \approx 7.7$ ms) of an NV electron spin at room temperature [27]. If the temperature is lowered with longer $T_1$ time, nuclear spins with weaker couplings to the sensor can be detected.

With three TMP molecules on the diamond surface (Fig. 3d), the NV coherence dip shows non-periodic oscillations with increasing the CPMG pulse number (Fig. 3e), with zeros corresponding to couplings $A_k^+$ of different $^{31}$P nuclear spins to the NV center. By choosing three different magnetic field directions (Fig. 3f), we can individually determine the couplings and hence the positions of the $^{31}$P nuclear spins, realizing angstrom-resolution MRI of the TMP molecules (Table I).

The DD-based MRI can be applied to analyze conformational analysis of bio-molecules. In a 2F4K protein molecule that has 35 residues, for example, we can label the four PHE amino acids with $^{15}$N and perform MRI of the $^{15}$N nuclear spins and hence the conformation analysis of the protein molecule. In Fig. 3g-i, we show that the positions of the four $^{15}$N nuclear spin labels can be precisely determined by using the oscillation features of the NV center spin coherence dip under resonant DD control (Table I).
In conclusion, we have discovered that the sensor coherence, under resonant DD control, presents oscillation as a function of DD pulse number, with quantized, universal features due to weak coupling to nuclear spins. Such coherence dip oscillation features can be used to resolve couplings to multiple nuclear spins of the same species and characterize the correlations in single nuclear spin clusters. Thereby we put forward a scheme of angstrom-resolution MRI of single molecules and conformation analysis of single bio-molecules.

References


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**Author Contributions** R.B.L. conceived the idea and designed the project, W.L.M. formulated the theory and performed the numerical calculations, W.L.M. and R.B.L. wrote the paper.

**Author Information** The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to R.B.L. (rbliu@phy.cuhk.edu.hk)
Figure 1 | Individual resolution of multiple nuclear spins of the same species weakly coupled to a quantum sensor. a, Schematic illustration of detecting multiple distant target spin of the same species by a sensor spin. The target spins precess with the same Larmor frequency and are not distinguished in their noise spectra. b, Sensor coherence caused by different numbers of target nuclear spins as a function of time under the 10-pulse CPMG DD control (CPMG-10). The sharp dips correspond to the DD timing resonant with the noise frequency of the nuclear spins (resonant DD), with $q$ denoting the coherence dip order. The parameters are such that the nuclear spin precession frequency $\omega_0=0.1$ MHz and $\sum_{k=1}^{M}|A_k|^2=5$ kHz (with the coupling coefficients $A_k$ randomly chosen within the constraint). c, Sensor coherence dip as a function of the CPMG DD pulse number $N$ for various numbers of target spins ($M=1, 2, 4 & 10$).
Symbols are the exact results from quantum decoherence model while solid lines are the analytical results from Eq. (4). d, Logarithm plot of the absolute value of the sensor coherence dip caused by 3 target spins ($M=3$) as a function of the CPMG pulse number. The coherence dip zeros determine the number of target spins $M$ and the individual coupling strengths $|A_k| = \pi \omega_k / (2N_k^{(0)})$, where $N_k^{(0)}$ is the pulse number at which the sensor coherence dip is zero.
Figure 2 | Quantized features of sensor coherence dips due to different types of correlations of nuclear spins. a, Schematic illustration of different types of correlations of nuclear spins. Type-II transitions represent two independent target spin-1/2’s, type-V transitions represent a single target spin-1, and ladder-type transitions represent a single target spin-J or a strongly-bonded spin cluster with dimension 2J+1. b, Sensor coherence dip as a function of the CPMG pulse number for type-II and type-V transitions (with the same noise spectrum). Symbols are the exact results from the quantum decoherence model while solid lines are the results from the analytical formula in Eq. (7) and (8). The parameters are $\omega_A = 0.11$ MHz, $\omega_B = 0.09$ MHz, $\lambda_{II} = 5$ kHz, and $\lambda_v = \sqrt{3}\lambda_{II}/2$. c, Sensor coherence dip as a function of the CPMG pulse number, for ladder-type transitions with different number of levels (2J+1). The DD timing is
fixed to be resonant with one noise frequency. Symbols are the exact results from quantum decoherence model while solid lines are the results from the analytical formula in Eq. (11). The transition frequency resonant with DD is $\omega_n = 0.1$ MHz and the coupling to sensor is $\lambda_n = 2.5$ kHz.
Figure 3 | Angstrom-resolution imaging of nuclear spin labels in single molecules. a, Schematic illustration of detecting the $^{31}$P nuclear spin in a TMP molecule by a shallow NV center (3 nm from the surface) in a $^{13}$C-depleted diamond. The NV axis along the [111] crystal direction is set as the $z$ axis, and the magnetic field has the polar angle $\theta$ and azimuth angle $\phi$ (relative to the crystal axis $[\bar{T}\bar{T}2]$). b, Contour plot of sensor coherence dip as a function of the CPMG pulse number and the azimuth angle $\phi$ for a 20 Gauss magnetic field with $\theta=20^\circ$. c, Sensor coherence dip as a function of the CPMG pulse number for three different magnetic field directions (for three values of $\phi$ with fixed $\theta=20^\circ$). d, Schematic illustration of MRI of three TMP molecules near the
diamond surface using $^{31}$P labelling. e, Similar to b but here the contour represents the logarithm of the absolute value of coherence dip. f, Similar to b but here for three TMP molecules. g, Schematic of conformation analysis of a 2F4K protein molecule via MRI of four $^{15}$N nuclear spin labels in the PHE amino acids (with residue sequence number 6, 10, 17 and 35). h, i similar to e, f, respectively, but for the four $^{15}$N nuclear spins in proteins.
Table I | Positions of nuclear spin labels in TMP molecules and in a 2F4K protein molecule obtained by the DD-based MRI, in comparison with their real positions

<table>
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<th>Nuclear spin labels</th>
<th>Real positions $(x, y, z)$ (Å)</th>
<th>DD-based MRI positions $(x, y, z)$ (Å)</th>
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<tr>
<td>TMP-1$^{31}$P</td>
<td>(20.41, 7.07, 40.41)</td>
<td>(20.42, 7.00, 40.40)</td>
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<tr>
<td>TMP-3$^{31}$P</td>
<td>(16.33, 0.00, 46.19)</td>
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