1. Report of the First Referee

The authors compare nuclear spin characterization using ESEEM and DD sequences. Overall the work seems timely and appropriate for publication in PRB.

However, I think some sections and figures would benefit from further revisions. Below is a list of comments and inquiries:

1) In some places the authors refer to second order hyperfine coupling, I assume this is in regard to the Zeeman splitting of the central spin but this could be clarified in the text.

2) I am not sure whether this is intentional but the equations miss punctuation and equation references the brackets.

3) Some equations are hard to read because they overlap with the text of the next column.

4) Related to 1) additional details to derive the Hamiltonian in Eq. (1) would be helpful, for instance when does this equation hold, I believe $\Delta \gg$ hyperfine elements is assumed to neglect coupling to Sx and Sy and then the nuclear spins are rotated such that there occur no terms with Iy? Is there a difference in the derivation for S=1 and S=1/2? Maybe an appendix applying the secular approximation and the appropriate rotation to the frame leading to this form would be helpful for future readers.

5) Fig. 2 misses the labels for the subfigures the same applies to Fig. 3 where I think that additionally the heading of the top left panel should read "Electron Spin 1".

6) In Eq. (2) it would help to provide the state that is used for the calculation as well as an intuition why it is sufficient to include the exponential decay term after solving the dynamics (and when this is valid).

7) The last paragraph of App. B is very hard to read and would benefit from some work on the language.

8) Could the authors comment on whether they have an intuition whether adapted approaches would be feasible for systems with an additional central spin like the (15N)V center or defects with even larger spin like vanadium defects in silicon carbide?

9) Could the authors provide a short comment comparing to entanglement based approaches for nuclear spin control, e.g., https://www.nature.com/articles/ncomms14660?

Concluding, if the above points are addressed, I deem the article suited for publication within PRB.

Reply to the First Referee

We appreciate the comments made by the referee. We clarify each point as follows:

1. Second order hyperfine couplings means terms like $(\frac{A_{zz}}{\omega_L})^2$ and $(\frac{A_{zx}}{\omega_L})^2$. This is stated in the sentence: ((... the second-order term $\frac{A_{zx}^2}{\omega_L^2}$ can be neglected ...))

To clarify this point, we add the following explanation to the text:
((... Each nuclear spin is identified with two hyperfine parameters A_{zz} and A_{zx}, which shows coupling to the central electron spin. Hence, characterizing this 23-nuclear spins requires identifying 56 hyperfine coupling parameters. ...))

((... which is the inner product of precession axes of a nuclear spin condition on the electron spin sublevel. This expression indicates the advantage of using DD sequence for sublevels where either s_0 or s_1 is zero, only first order parallel hyperfine coupling $\frac{A_{zz}}{\omega_L}$ play a role. On the other hand, in spin-1/2 systems ($s_0 = -\frac{1}{2}$ and $s_1 = \frac{1}{2}$), the first order hyperfine coupling vanishes and only second order parallel hyperfine coupling $(\frac{A_{zz}}{\omega_L})^2$ and second order perpendicular hyperfine coupling $(\frac{A_{zx}}{\omega_L})^2$ remain present. This indicates weak sensitivity of DD sequence on different nuclear spins...))

Also the following text is added to the caption of Fig 2:
((... It indicates the covariance between two parameters. The main diagonal appears as each parameter is correlated with itself. The side-diagonals indicate the two hyperfine parameters that belong to the same nuclei. ...))

No unit for Fig. 2c,d and Fig 3c,d are needed since these figures visualize the Fisher Information matrix elements.

2.

3. We thank the referee for noting this point. We fixed this issue in Eq. 4 and Eq. 7

4. The Hamiltonian in Eq. 1 is very well-understood in this community [ref here]. The Hamiltonian conventionally is written in the rotating frame of applied microwave and consist of Electron and nuclear spin Zeeman energy and dipole interaction between them. As it is mentioned in the text, the secular approximation is considered so terms like S_x, S_y do not appear. Traditionally, the nuclear spins' frame are rotated such that I_y term do not appear. This Hamiltonian applied to any two-level system, e.g., this could be any two spin sublevels in Silicon Carbide (S=3/2)

5. We thank the referee for pointing out labels for subfigures (pdf is corrected but latex does not show). We fixed this issue. In Fig. 3, we are discussing 5pESEEM sequence mostly for Electron spin 1/2 system. We did not include FFT of 5pESEEM sequence for spin 1 system because it works just as good as DD

sequence, and does not bring any additional information. However, the Fisher information obtained for spin 1 system in Fig. 3c is good metrics to compare with the result of electron spin 1/2 system in Fig 3d.

6. The initial state for the Ramsey sequence can be any of the two sublevels of spin system. Indeed, the gray exponential decay is not sufficient to describe spin relaxations as mentioned in the text, but it shows the time scale of the decay. We thank the referee for this point and we decided to remove this exponential decay to avoid confusion.

7. We thank the referee for pointing out this issue. We added more explanation to the last paragraph in the Appendix B.

((...The blind spot term depends on both τ_1 and τ_2. It means if one resonant frequency is blinded, the other resonant frequency and all the multiple quantum resonances also vanishes. This can be used as a manifestation that which two peaks in the frequency spectrum are originating from the same nuclei. In other words, choosing τ such that a particular resonant frequency in the spectrum is blinded, the other resonant frequency of the same nuclear spin will also be blinded and both of them disappear from the frequency spectrum together. Moreover, this is very helpful especially in the presence of strongly coupled nuclear spin that suppress other nuclei. By sweeping τ_1 and τ_2, one can go through different bright and blind spots of each nuclear spin, and observe correlations between different peaks....))

8. This equations are valid as long as the condition stated before Eq. 1 are valid. Most importantly secular approximation is crucial, and also the nuclear spin should be spin 1/2 like Carbons. The Spin of electron spin is not play an important role since they can be well separated and pulses resonant with only an effective two level system can be considered.

9. In this work, we address nuclear spins only with microwave driving of the electron spin (did we mention this in the text?). Applying another radio frequency (RF) driving adds another experimental challenge to the problem. In this case, RF spectroscopy to find and drive individual nuclear spins is required, which can add the required time to image nuclear spins.

2. Report of the Second Referee

The authors propose a blueprint for efficient nuclear spin characterization with color centers. The authors claim that they propose a more straightforward approach for determining the hyperfine interactions among each nuclear and the

electron spin. The manuscript is written clearly by comparing dynamical decoupling (DD) and Electron Spin Echo Envelop Modulation (ESEEM), the numerical results are valid and may could be of use in other future experiments. I think the results obtained by the authors are of interest for Phys. Rev. B readers, so I support the publication in its present form.

As some minor remarks which the authors may take into account to beatify their study further, I would like to mention:

1) There are no a, b, c and d in Fig. 2, Fig. 3 and Fig.5. There is lack of definitions and units of "Hyperfine Parameters" in abscissa in Fig. 2 and Fig. 3. This sentence is confusing: "The first 23 hyperfine parameters are Azz and the second 23 parameters are Azx of the nuclear spin register." What are the specific meanings of hyperfine parameters along horizontal axis and vertical axis in Figs2?

2) Are there any reasons for the exponential decay part in gray for almost all the equations? It is a little bit strange, and the exponential decay part looks not in same size as well.

3) Styles of references [9], [14], [19] and [21] are not uniform with other references.

Reply to the Second Referee

We appreciate the comments made by the referee. We clarify each point as follows:

1. We thank the referee for pointing out labels for subfigures (pdf is corrected but latex does not show). We fixed this issue. Fig. 5 does not require subfigure labelling. We provided more explanation regarding the hyperfine coupling parameters in the text: ((... the summation is over τ, the pulse timing used in the sequence, and A is the array including all hyperfine coupling parameters. For the considered nuclear spin register, A includes 56 hyperfine coupling parameters, the first 23 parameters are A_{zz} of different nuclear spins and the second 23 parameters are A_{zx} respectively, resulting in the Fisher information as a 56 by 56 Matrix. ...))

2. Indeed, the gray exponential decay is not sufficient to describe spin relaxations as mentioned in the text, but it shows the time scale of the decay. We thank the referee for this point and we decided to remove this exponential decay to avoid confusion.

3.

3. Report of the Third Referee

Zahedian et al. present a theoretical study on a the appropriateness of various methods of nuclear spin spectroscopy using electron spins in solid state materials as probes. They compare dynamical decoupling based techniques and consider how using a spin-1/2 system as a probe differs to the more common case of a spin-1 (such as the NV center in diamond). As the authors note, spin-1/2 electron spin systems are emerging in materials such as diamond and silicon and so expanding

the existing nuclear spectroscopy machinery to this case will be of interest to the community.

The paper and its main result that correlation-style dynamical decoupling sequences are most appropriate for performing nuclear spin spectroscopy with spin-1/2 electron spin systems should be of interest to the community, and so in principle I think it is appropriate to publish in PRB. In parts I found the arguments a little unclear and so I would recommend some minor revisions before publication. Some specific points:

1) It is not clear to me why the correlation sequence performs much worse for the spin-1 probe (comparing Fig 2(c) and 3(c)) and there is not much discussion of this point in the text. This result also seems to conflict with Fig 5. It also does not seem like the spin-1 probe should be worse than spin-1/2 in this case. Also, what are the parameters used to generate the plots Fig 3c,d - is it simulating the 72 pulse DDESEEM?

2) It would be interesting to know, roughly, how the results of e.g. Fig 5 scale with properties such as probe T1 and T2. Does this strongly impact the optimal sequence choice? Some spin-1/2 systems may have short T1 times as they are able to cross relax with other g=2 spins present in the crystal (or on the diamond surface, for instance).

3) One goal of mapping e.g. a nuclear spin cluster is to also use the central electron spin to selectively manipulate individual nuclear spins to use as ancillae or implement quantum information protocols. Is it straightforward that the spectral resolution offered by the correlation style measurements also allow this sort of control? At minimum the extra time overhead from using the longer sequence would need to be considered in practice. Could the authors comment on the outlook here?

4) Minor comment on figures: some labels are missing and fig 4 appears a bit blurry.

Reply to the Third Referee

We appreciate the comments made by the referee. We clarify each point as follows:

1.

2.

3.

4.