Supplementary Information for Spin-spin interactions in defects in solids from mixed all-electron and pseudopotential first-principles calculations

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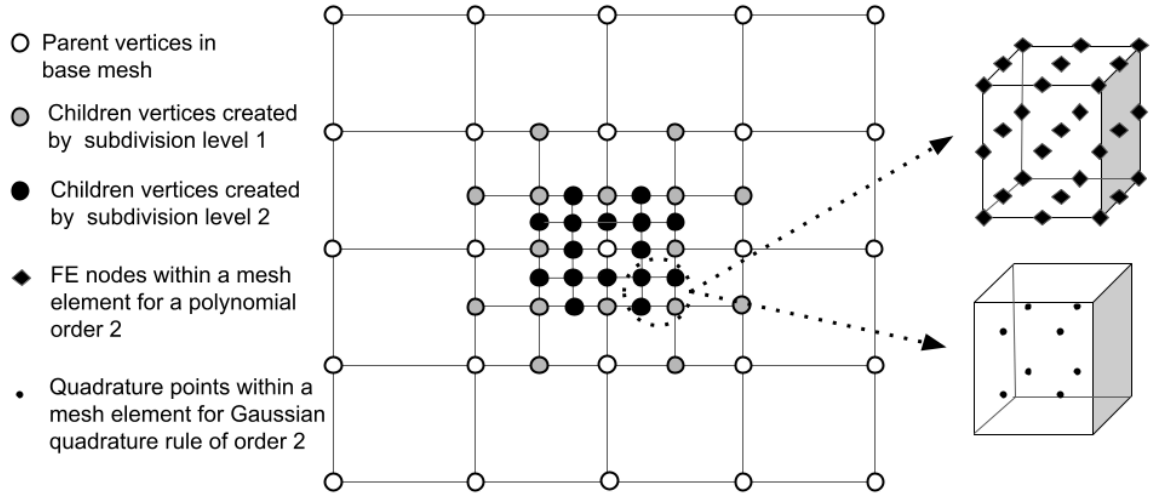
SUPPLEMENTARY NOTES

Finite element (FE) basis [1] is used to discretize the Kohn-Sham (KS) equation and the Poisson equation implemented in the open source code DFT-FE [2, 3]. Finite elements provide a complete basis set, thus enabling systematic convergence of any physical quantity of interest that is derived from the KS wave functions. Further, the localized nature of the FE basis functions makes it attractive for large-scale simulations particularly for systems with defects, owing to the efficient parallel scalability possible using the FE basis. In addition, the feasibility of representing the fields using adaptive spatial resolution aids efficient and systematically convergent all-electron calculations. In particular, the adaptive basis resolution can be realized by using a refined finite element mesh near the nuclei, while coarse-graining away from the atomic core regions. This capability of adaptive basis resolution is also central to realizing efficient mixed all-electron pseudopotential calculations, which is one of the key aspects of this work.

Before discussing the convergence aspects of spin Hamiltonian (SH) parameters with respect to the FE basis, we provide a brief discussion on the finite element basis and discretization. The finite element basis is a continuous piecewise polynomial basis which is realized via a finite element discretization. In a finite element discretization, the simulation domain is partitioned into subdomains that are referred to as *elements* (or finite elements). The finite element discretization can be spatially uniform, or spatially adaptive. A spatially adaptive discretization can be realized by starting with a uniform finite element mesh and subdividing selected finite elements. In each finite element, the fields of interest (such as Kohn-Sham wavefunctions) are represented via a polynomial basis such that the field is continuous across the element boundaries. The polynomial basis in each finite element is constructed via a Lagrange polynomial interpolated through special points in the finite element referred to as *nodes* (or finite element nodes). In the hexahedral finite elements employed in this work, an element with $(p+1)^3$ nodes provides a FE basis that is complete to polynomial order p. We note that, owing to the partition of unity property of the FE basis, the coefficients of expansion of a field in the FE basis are also the values of the field at the finite element nodes. The solution of a partial differential equation in the FE basis involves the evaluation of integrals over the finite elements. These integrals are computed using numerical quadratures, where the function value is evaluated at the quadrature points. The quadrature points are chosen such that the numerical integration error is higher order compared to the FE basis discretization error. The schematic in Supplementary Figure 1 shows the FE discretization with spatial adaptivity, as well as the FE nodes and quadrature points in a finite element. We refer to [1**?**] for a comprehensive discussion of the finite element method, and refer to [2, 3] for the use of adaptive higher-order finite element basis in the solution of the Kohn-Sham equations.

Systematic convergence using FE basis can be achieved via: (i) reducing the finite element size, referred to as h-refinement; or (ii) increasing the polynomial order in each finite element, referred to as p-refinement. h-refinement provides spatial adaptivity, where higher resolution can be realized in regions of interest—such as the atomic cores

where the wavefunctions are highly oscillatory. On the other hand, p-refinement improves the basis approximation in the complete simulation domain. We demonstrate the convergence of the Fermi contact and spin dipolar contributions to the **A**-tensor of the nitrogen atom in an NV-diamond system for a mixed all-electron pseudopotential calculation (referred to as FE-mixed in the main article) in $2 \times 2 \times 2$ diamond supercell. Supplementary Table 1.(a) shows the convergence with respect to FE polynomial order (p-refinement) for an adaptive FE mesh that is generated using a target minimum mesh size of 0.1 a.u.. Supplementary Table 1.(b) shows the convergence trend for increasingly refined finite element meshes (h-refinement) for a fixed FE polynomial order of 4. We note that both h- and p-refinements yield the same converged values of the hyperfine spin Hamiltonian parameters.



Supplementary Figure 1: Schematic of the cross-section of a finite element mesh with spatial adaptivity. There are two levels of adaptive subdivision shown in this schematic. The FE nodes for p=2 and $2 \times 2 \times 2$ Gaussian quadrature points in an individual element are also depicted.

Supplementary Table 1: Systematic convergence of **A**-tensor with respect to FE basis discretization for nitrogen atom of NV center in $2 \times 2 \times 2$ diamond supercell.

Supplementary Table 1.a: Convergence with respect to FE polynomial order (p-refinement) for an adaptive FE mesh generated using a target minimum mesh size of 0.1 a.u.

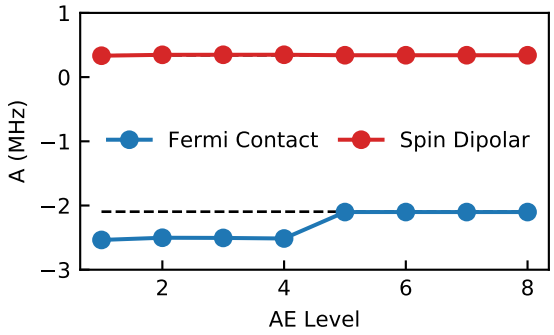
FE polynomial	Fermi Contact (MHz)	Spin Dipolar (MHz)
2	-2.76	-0.458
3	-2.46	-0.051
4	-2.36	-0.049
5	-2.34	-0.049

Supplementary Table 1.b: Convergence with respect to mesh refinement (h-refinement) for a fixed FE polynomial of 4

Target minimum mesh size (a.u.)	Fermi Contact (MHz)	Spin Dipolar (MHz)
1.0	-1.82	-0.196
0.5	-2.12	-0.180
0.2	-2.49	-0.036
0.1	-2.36	-0.049
0.05	-2.34	-0.049

SUPPLEMENTARY DISCUSSION

We present the convergence and validation of the mixed AE-PP approach. Supplementary Figure 2 shows the convergence of the Fermi contact and spin dipolar terms of nitrogen atom of NV diamond as the extent of the region with all-electron treatment is increased. Further, as shown in Supplementary Table 2, the converged values of the hyperfine SH parameters obtained using the mixed AE-PP approach agrees well with the values obtained using pure all-electron calculations (FE-AE).



Supplementary Figure 2: DFT prediction of Fermi contact and spin-dipolar term of the $\boldsymbol{A}$-tensor for the nitrogen atom of NV center in $3 \times 3 \times 3$ diamond supercell, using a finite-element (FE) basis with a mixed all-electron pseudopotential scheme. FE DFT results converge rapidly with increasing number of all-electron (AE) atoms, denoted by AE level. Eigenvalues with the largest absolute magnitude are shown for spin-dipolar term.

Supplementary Table 2: Fermi contact and spin dipolar components of the **A**-tensor for the nitrogen atom of NV center in $3 \times 3 \times 3$ diamond supercell, computed using both the mixed calculation as well as pure all-electron calculation (FE-AE). Eigenvalues with the largest absolute magnitude are shown for spin-dipolar term.

A (MHz)	AE Level 4	AE Level 5	FE-AE
Fermi Contact	-2.513	-2.101	-2.096
Spin Dipolar	0.232	0.227	0.227

SUPPLEMENTARY DATA

Supplementary Tables 3 and 4 provide the SH parameters for the various cell-sizes and Brillouin zone (BZ) samplings computed using mixed AE-PP approach with FE basis (FE-mixed), pure all-electron calculations using FE basis (FE-AE), and the plane-wave basis (PW).

Supplementary Table 3: Computed SH parameters of negatively-charged nitrogen-vacancy (NV) center in diamond for various cell-sizes. (a) Fermi-contact and (b) spin-dipolar component of $\boldsymbol{A}$-tensor corresponding to the nitrogen atom and dangling bond carbon (DB-C) atom in NV diamond (eigenvalues with the largest absolute magnitude are shown); (c) the zero-field splitting $\boldsymbol{D}$-tensor, where the quantity reported is $\frac{3}{2}|D_3|$ with D_3 being the eigenvalue with largest absolute magnitude. Calculations are performed with finite element (FE) and plane-wave (PW) basis. In the case of FE calculations, we used the proposed mixed all-electron and pseudopotential scheme (FE-mixed), and for select cases we also performed pure all-electron (AE) calculations.

Supplementary Table 3.a: Fermi Contact (in MHz)

Atom	System size	Number of atoms	BZ sampling	PW	FE-mixed	FE-AE
N	$2\times2\times2$	63	Γ	-2.605	-2.360	-2.344
			$2\times2\times2$	-1.967	-1.692	-
			$3\times3\times3$	-1.930	-1.733	-
	$3\times3\times3$	215	Γ	-2.180	-2.125	-2.095
			$2\times2\times2$	-1.993	-1.939	-
	$4\times4\times4$	511	Γ	-2.021	-1.986	-1.949
DB-C	$2\times2\times2$	63	Γ	100.114	100.077	99.658
			$2\times2\times2$	103.651	105.494	-
			$3\times3\times3$	103.932	104.774	-
	$3\times3\times3$	215	Γ	116.891	122.813	121.809
			$2\times2\times2$	117.293	123.360	-
	$4\times4\times4$	511	Γ	119.809	124.927	125.228

Supplementary Table 3.b: Spin Dipolar (in MHz)

Atom	System size	Number of atoms	BZ sampling	PW	FE-mixed	FE-AE
N	$2\times2\times2$	63	Γ	-0.052	-0.049	-0.054
			$2\times2\times2$	0.416	0.349	-
			$3\times3\times3$	0.346	0.353	-
	$3\times3\times3$	215	Γ	0.233	0.219	0.227
			$2\times2\times2$	0.273	0.255	-
	$4\times4\times4$	511	Γ	0.270	0.262	0.261
DB-C	$2\times2\times2$	63	Γ	58.451	54.674	54.657
			$2\times2\times2$	57.898	54.366	-
			$3\times3\times3$	57.914	54.332	-
	$3\times3\times3$	215	Γ	57.628	54.254	54.235
			$2\times2\times2$	57.394	54.054	-
	$4\times4\times4$	511	Γ	57.360	54.450	54.496

Supplementary Table 3.c: **D**-tensor (in MHz)

System size	Number of atoms	PW-GIPAW	PW-ONCV	FE-mixed	FE-AE
$2\times2\times2$	63	3011.47	3011.13	2928.31	2939.47
$3\times3\times3$	215	3046.91	3042.61	2992.58	-
$4\times4\times4$	511	3057.04	3051.45	2901.28	-

Supplementary Table 4: Computed SH parameters of divacancy (VV) in SiC for various cell-sizes. (a) Fermi-contact and (b) spin-dipolar component of $\boldsymbol{A}$-tensor corresponding to the dangling bond carbon (DB-C) and dangling bond silicon (DB-Si) atom in VV-SiC (eigenvalues with the largest absolute magnitude are shown); (c) the zero-field splitting $\boldsymbol{D}$-tensor, where the quantity reported is $\frac{3}{2}|D_3|$ with D_3 being the eigenvalue with largest absolute magnitude. Calculations are performed with finite element (FE) and plane-wave (PW) basis. In the case of FE calculations, we used the proposed mixed all-electron and pseudopotential scheme (FE-mixed), and for select cases we also performed pure all-electron (AE) calculations.

Supplementary Table 4.a: Fermi Contact (in MHz)

Atom	System size	Number of atoms	BZ Sampling	PW	FE-mixed	FE-AE
DB-C	$4\times4\times1$	126	Γ	47.612	40.046	40.100
			$2\times2\times2$	50.994	43.999	-
			$3\times3\times2$	-	43.794	-
	$6\times6\times1$	286	Γ	53.822	44.305	-
			$2\times2\times2$	54.568	45.261	-
	$6\times6\times2$	574	Γ	55.608	48.831	-
	$8\times8\times2$	1022	Γ	-	50.272	-
DB-Si	$4\times4\times1$	126	Γ	0.518	0.402	0.315
			$2\times2\times2$	0.419	0.093	-
			$3\times3\times2$	-	0.081	-
	$6\times6\times1$	286	Γ	0.248	0.271	-
			$2\times2\times2$	0.320	0.118	-
	$6\times6\times2$	574	Γ	0.082	0.122	-
	$8\times8\times2$	1022	Γ	-	0.111	-

Supplementary Table 4.b: Spin Dipolar (in MHz)

Atom	System size	Number of atoms	BZ Sampling	PW	FE-mixed	FE-AE
DB-C	$4\times4\times1$	126	Γ	47.540	44.937	44.928
			$2\times2\times2$	46.728	44.455	-
			$3\times3\times2$	-	44.189	-
	$6\times6\times1$	286	Γ	46.452	43.449	-
			$2\times2\times2$	46.373	43.506	-
	$6\times6\times2$	574	Γ	46.449	43.793	-
	$8\times8\times2$	1022	Γ	46.345	43.144	-
DB-Si	$4\times4\times1$	126	Γ	0.710	0.708	0.717
			$2\times2\times2$	0.574	0.571	-
			$3\times3\times2$	-	0.569	-
	$6\times6\times1$	286	Γ	0.839	0.759	-
			$2\times2\times2$	0.592	0.538	-
	$6\times6\times2$	574	Γ	0.567	0.550	-
	$8\times8\times2$	1022	Γ	0.573	0.574	-

Supplementary Table 4.c: **D**-tensor (in MHz)

System size	Number of atoms	PW	ONCV	FE-mixed
$4\times4\times1$	126	1766.900	1775.320	1941.214
$6\times6\times1$	286	1503.270	1510.340	1669.392
$6\times6\times2$	574	1608.980	1615.900	1580.365

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