Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for First-principles Studies of Strongly Correlated States in Defect Spin Qubits in Diamond

He Ma,[†] Nan Sheng,[†] Marco Govoni,[*,‡,¶] and Giulia Galli[*,‡,†,¶]

†*Department of Chemistry, University of Chicago, Chicago, IL 60637, USA.*

‡*Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, USA.*

¶*Materials Science Division and Center for Molecular Engineering, Argonne National Laboratory, Lemont, IL 60439, USA.*

E-mail: mgovoni@anl.gov; gagalli@uchicago.edu

1 Convergence tests of active space

A minimum model of 9 defect orbitals and 16 electrons can be constructed for group-IV vacancy centers, as depicted in Fig. 2 of the main text. The 9 defect orbitals for SiV are visualized in Fig. S1; the corresponding orbitals for GeV, SnV, and PbV are similar in shape.

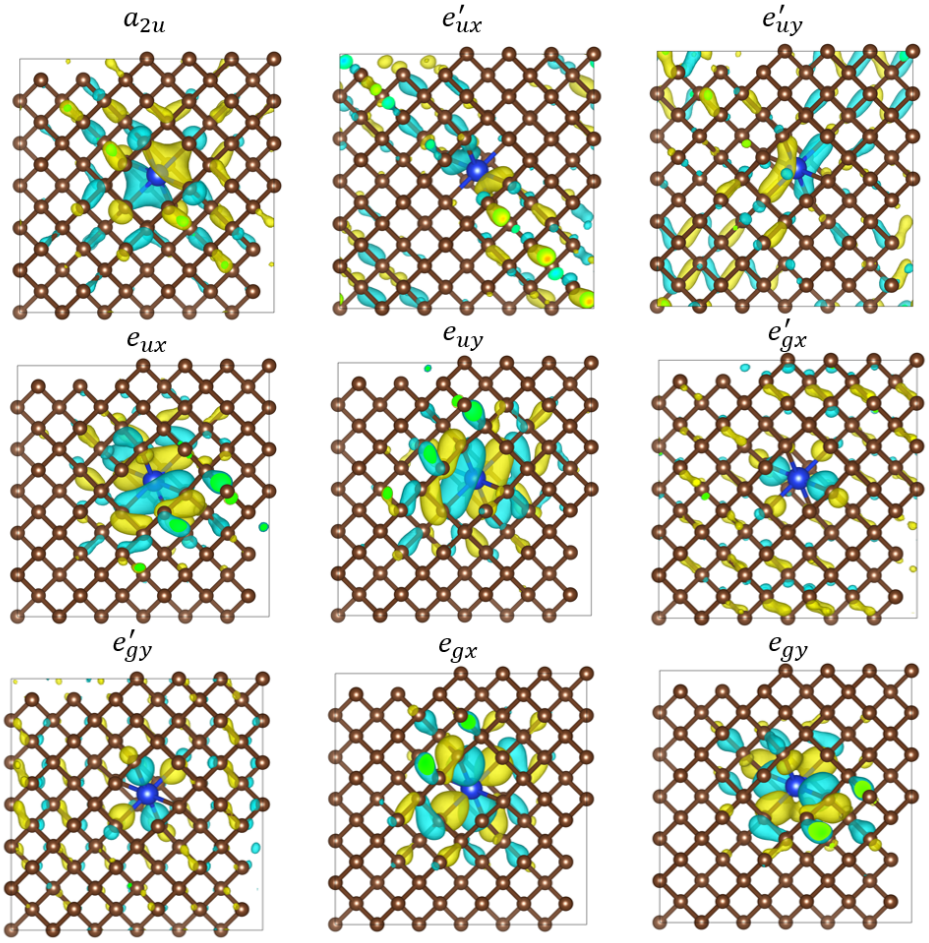

Figure S1: Shape of orbitals in the minimum model of SiV. a_{2u}, e_u and e_g are defect orbitals localized around the Si atom, e'_u and e'_g are resonance orbitals.

Active spaces that are larger than the minimum model are obtained by including in the active space valence and conduction orbitals. In the following figures, active spaces are denoted by a tuple of electron number and orbital number, and the minimum model is marked with dashed lines. Following each figure a precise definition of active spaces with band indices is given. All results shown in this section are obtained with the dielectric

dependent hybrid (DDH) functional. In all cases, FCI eigenvalues are found to be insensitive to the choice of active spaces.

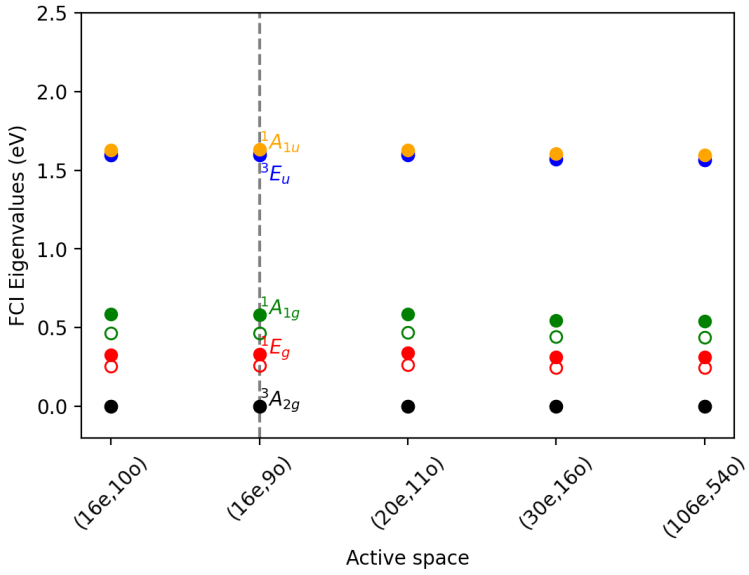

Figure S2: Convergence of vertical excitation energies of SiV in diamond as a function of active space size.

(16e,9o): minimal model including band indices 412, 415-416, 425-428, 430-431

(16e,10o): minimal model + index 450

(20e,11o): minimal model + indices 413-414

(30e,16o): minimal model + indices 378-382, 413-414

(106e,54o): indices 378-431

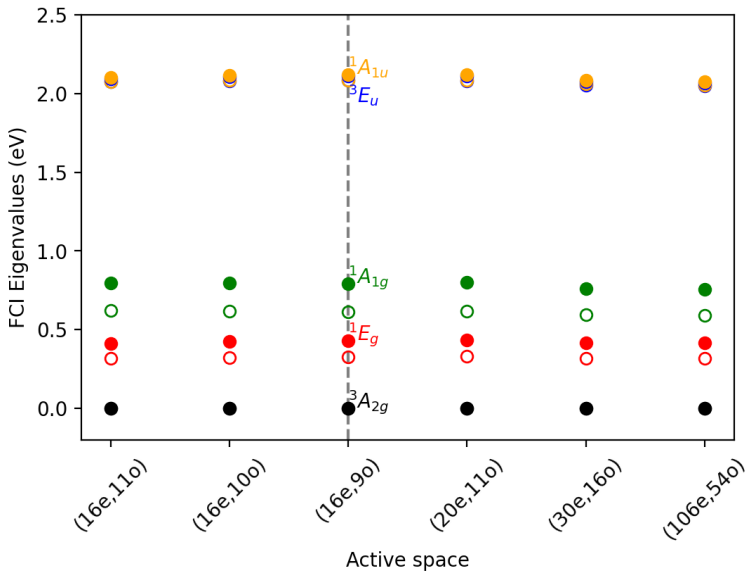

Figure S3: Convergence of vertical excitation energies of GeV in diamond as a function of active space size.

(16e,9o): minimal model including band indices 417, 420-421, 430-433, 435-436

(16e,11o): minimal model + indices 443, 455

(16e,10o): minimal model + index 443

(20e,11o): minimal model + indices 418-419

(30e,16o): minimal model + indices 383-387, 418-419

(106e,54o): indices 383-436

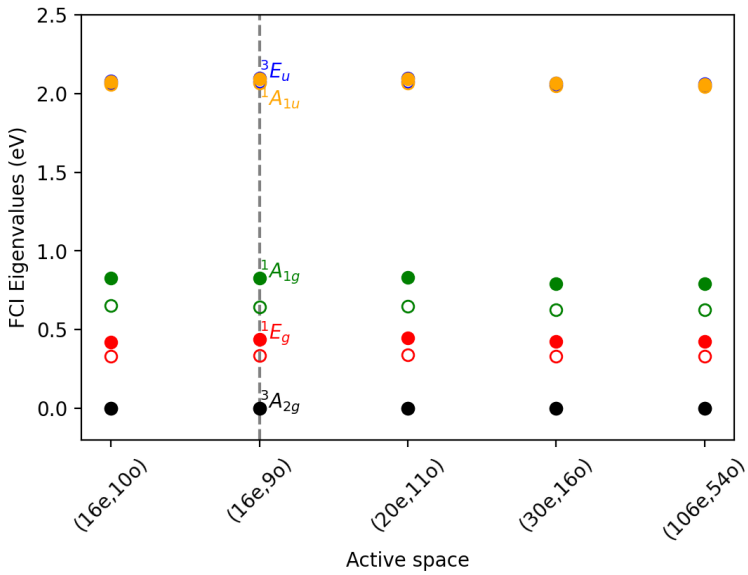

Figure S4: Convergence of vertical excitation energies of SnV in diamond as a function of active space size.

(16e,9o): minimal model including band indices 419-421, 430-433, 435-436

(16e,10o): minimal model + index 458

(20e,11o): minimal model + indices 417-418

(30e,16o): minimal model + indices 383-387, 417-418

(106e,54o): indices 383-436

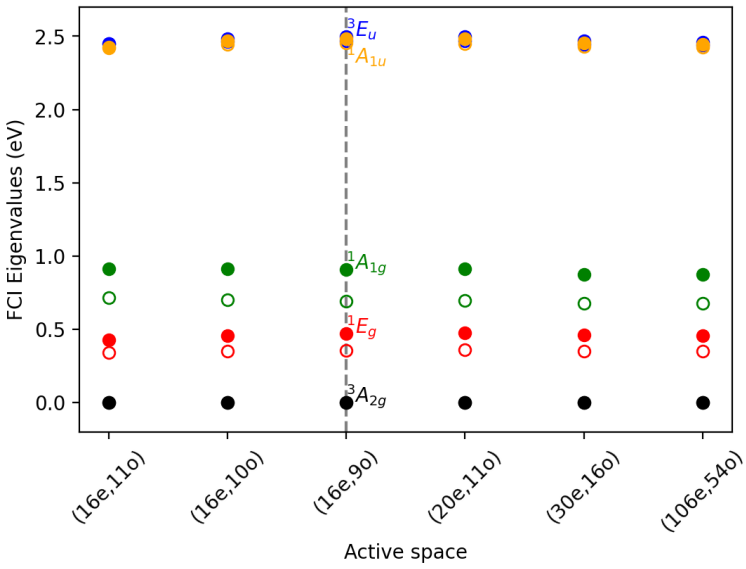

Figure S5: Convergence of vertical excitation energies of PbV in diamond as a function of active space size.

(16e,9o): minimal model including band indices 419-420, 422, 430-433, 435-436

(16e,11o): minimal model + indices 443, 455

(16e,10o): minimal model + index 443

(20e,11o): minimal model + indices 417-418

(30e,16o): minimal model + indices 383-387, 418-419

(106e,54o): indices 383-436

2 Results using HSE functional

Table S1: Vertical excitation energies (eV) of the negatively charged nitrogen vacancy (NV) in diamond (64-atom supercell), obtained using different DFT starting points.

	PBE		HSE		DDH	
	RPA	Beyond-RPA	RPA	Beyond-RPA	RPA	Beyond-RPA
Excitation						
${}^3E \leftrightarrow {}^3A_2$	1.512	1.655	1.941	2.162	2.057	2.281
${}^1A_1 \leftrightarrow {}^3A_2$	1.222	1.590	1.371	1.933	1.367	1.941
${}^1E \leftrightarrow {}^3A_2$	0.452	0.552	0.520	0.677	0.530	0.695
${}^1A_1 \leftrightarrow {}^1E$	0.770	1.038	0.850	1.256	0.837	1.247

3 Projected density of states

The following figures show the projected density of states (PDOS) of SiV, GeV, SnV and PbV obtained with spin-unrestricted DFT calculations using the PBE functional. The e_g defect orbitals in the band gap of diamond are dominated by C character.

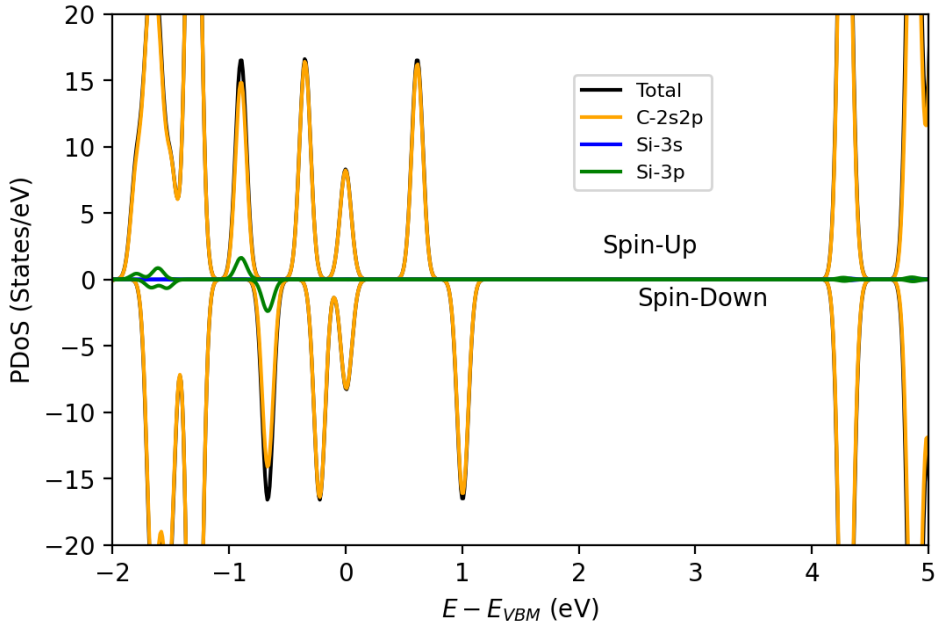

Figure S6: Projected density of states of SiV in diamond.

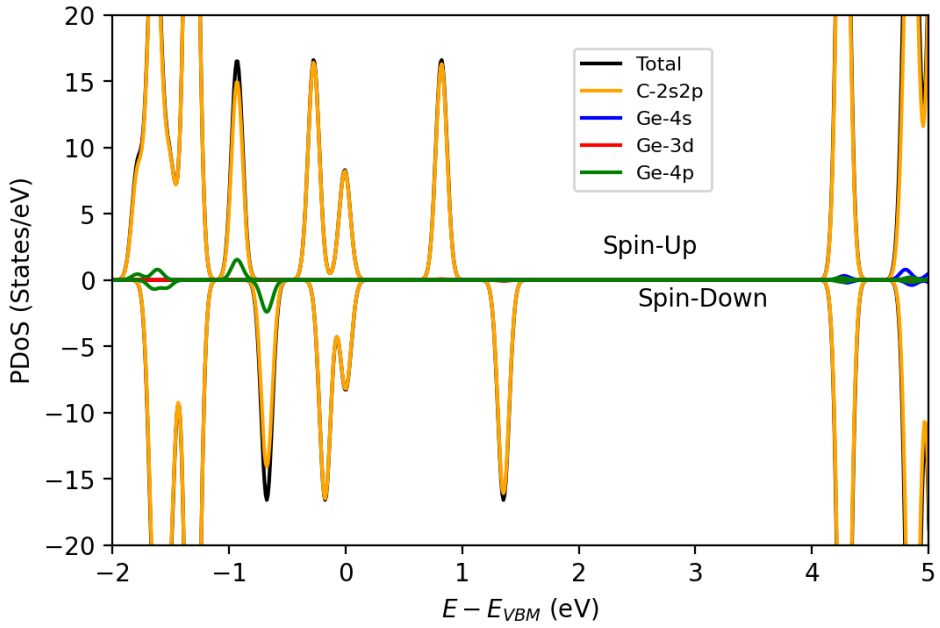

Figure S7: Projected density of states of GeV in diamond.

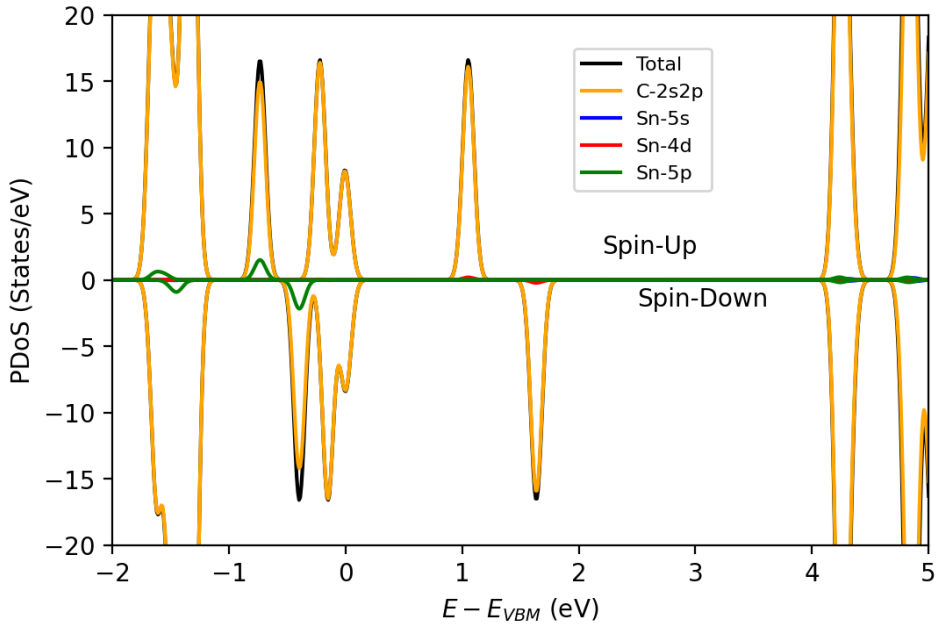

Figure S8: Projected density of states of SnV in diamond.

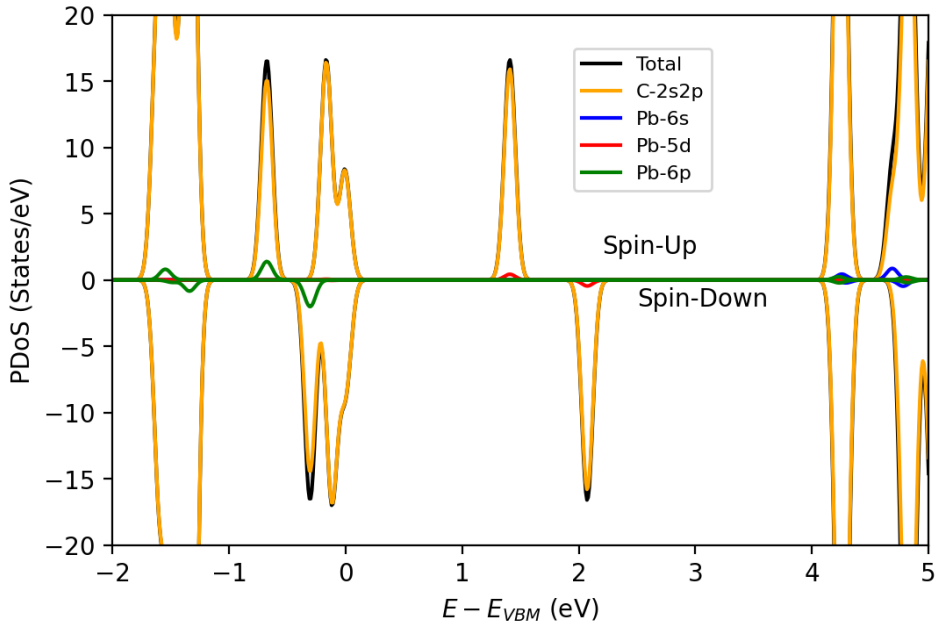

Figure S9: Projected density of states of PbV in diamond.

4 Fully relativistic calculations of PbV

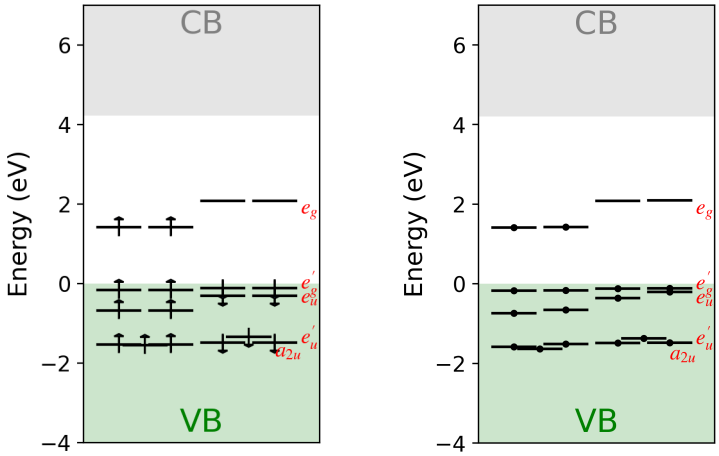

Figure S10: Kohn-Sham eigenvalues for important defect levels of PbV obtained by (unrestricted) collinear-spin DFT calculation (left) and fully relativistic noncollinear-spin DFT calculations (right). The split of degenerate e_g orbitals in the band gap induced by spin-orbit coupling is less than 0.02 eV.