First-principles Studies of Strongly-Correlated States in Spin Defects in Diamond

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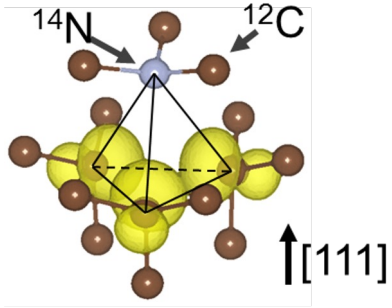
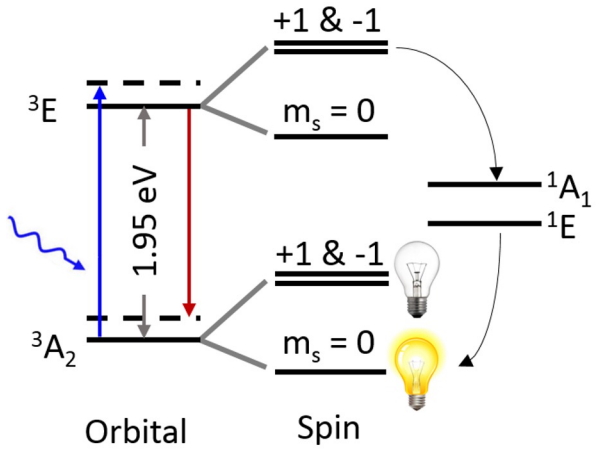
Outline

- Strongly-correlated states in spin defects
- Quantum embedding theory
- Quantum embedding theory applied to spin defects

Strongly-correlated states in spin defects used as qubits





Strongly-correlated states: important for the initialization and read-out of spins, yet challenging for mean-field theories such as Kohn-Sham Density Functional Theory (DFT)

Example: 2 electrons in 2 degenerate orbitals

Spin singlet state:
S = 0

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

Spin triplet states:
S = 1

$$\uparrow\uparrow$$

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right)$$

$$\downarrow\downarrow$$

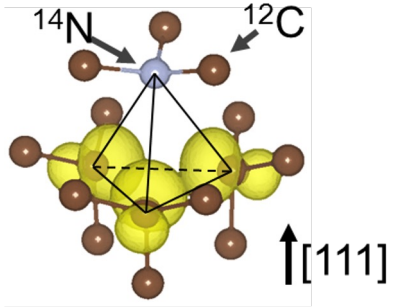
Most existing methods to describe strongly correlated states are computationally **very expensive** (limited to tens of electrons):

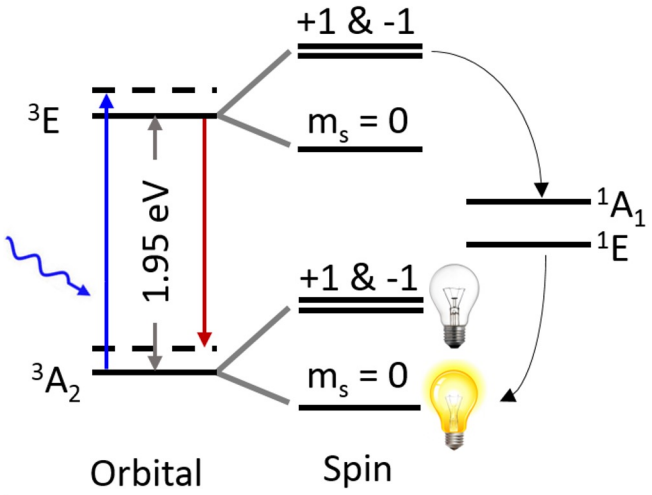
- Dynamical mean-field theory
- Quantum Monte-Carlo
- Multi-reference quantum chemistry methods

Ivady, V., Abrikosov, I. A. & Gali, A. npj Comput. Mater. 4 (2018)

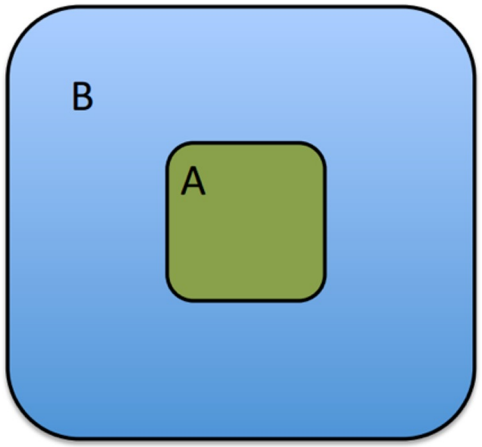
From dielectric screening to quantum embedding

For the use of spin defects to realize qubits, electronic states should be localized in well defined regions of space and separated in energy from the levels of the host solid





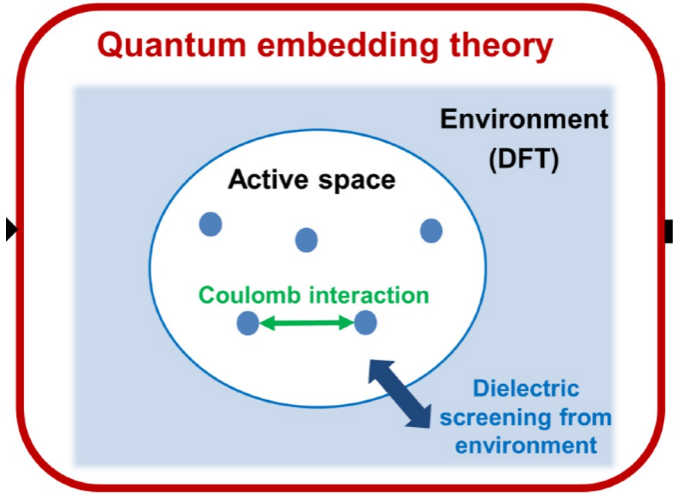
Multi-level description



A – higher level theory
B – lower level theory

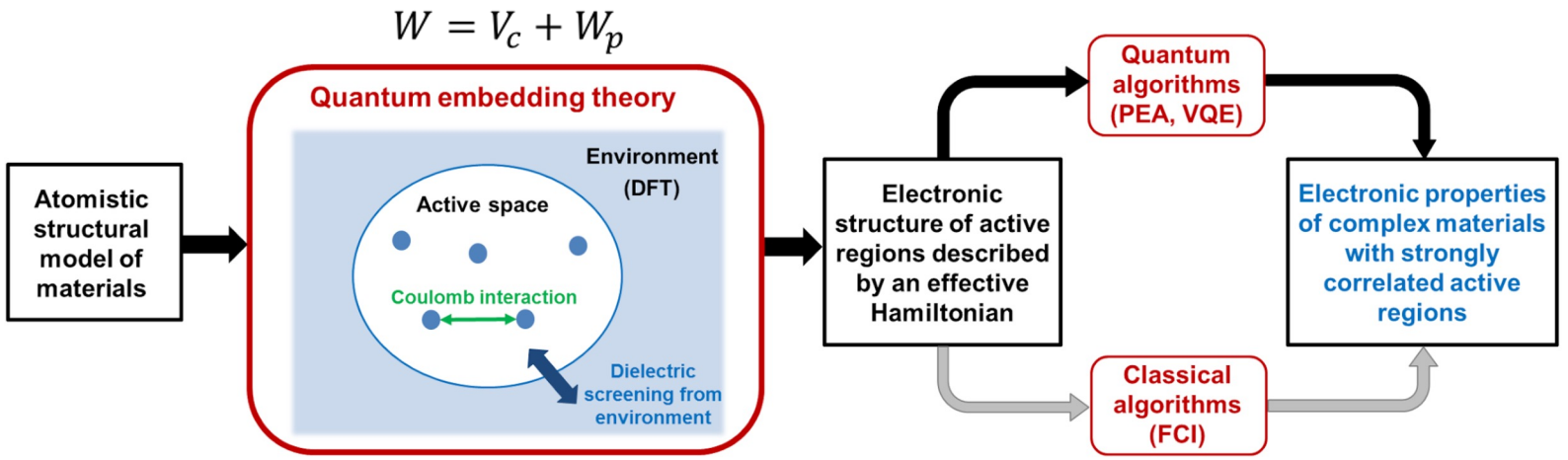
Dielectric screening

$$W = V_c + W_p$$



Ma, H., Govoni, M. & Galli, G. npj Comput Mater 6, 85 (2020)
Ma, H., **Sheng, N.**, Govoni, M. & Galli, G. J. Chem. Theory Comput., accepted (2021)

Quantum embedding theory



Features of the embedding theory:

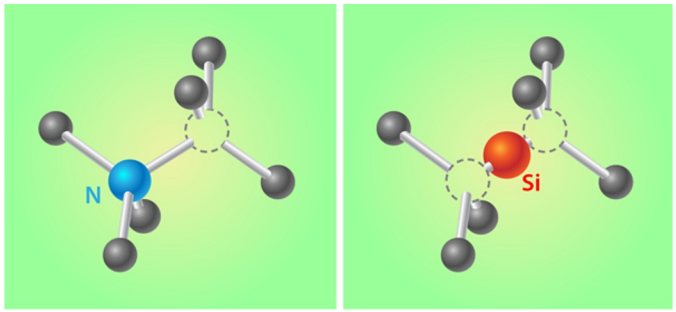
- Based on many body perturbation theory (the GW method)
- No explicit summation over empty electronic states scalable to large systems
- Dielectric screening is computed including exchange-correlation effects, thus going beyond the random phase approximation (RPA)
- The use of hybrid functions, for example, dielectric-dependent hybrid functional (DDH), is straightforward and yields improved results over GGA (PBE)

Ma, H., Govoni, M. & Galli, G. npj Comput Mater 6, 85 (2020)

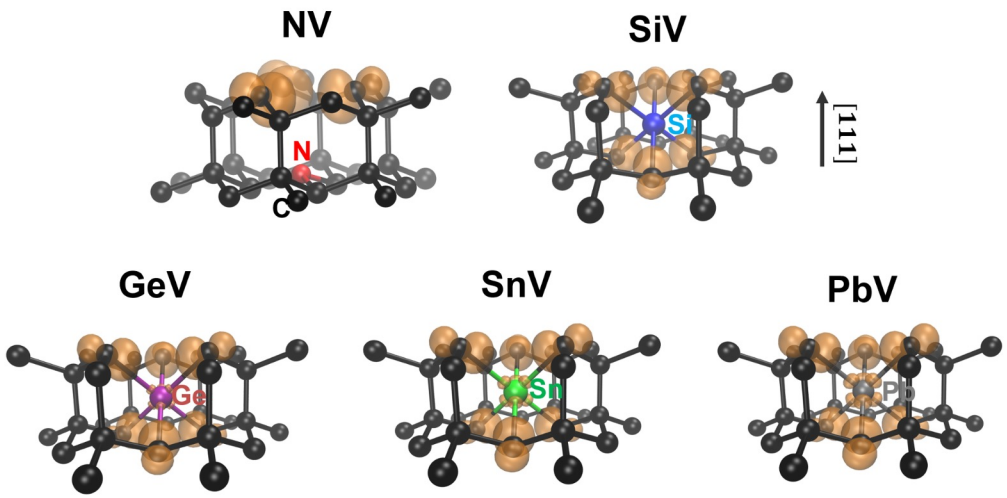
Ma, H., **Sheng, N.**, Govoni, M. & Galli, G. J. Chem. Theory Comput., accepted (2021)

Quantum embedding theory applied to spin-defects

We applied the quantum embedding theory to study NV^- in diamond & group-IV^0 defects in diamond. We choose active spaces to include defect levels and band edge states



Spin polarization density $\Delta\rho = \rho_\alpha - \rho_\beta$



Computational setup:

- Dielectric dependent hybrid functional
- 50 Ry Ecut; ONCV PP
- 3*3*3 supercell for diamond; Γ-point sampling
- Finite-field calculation of exchange-correlation kernel

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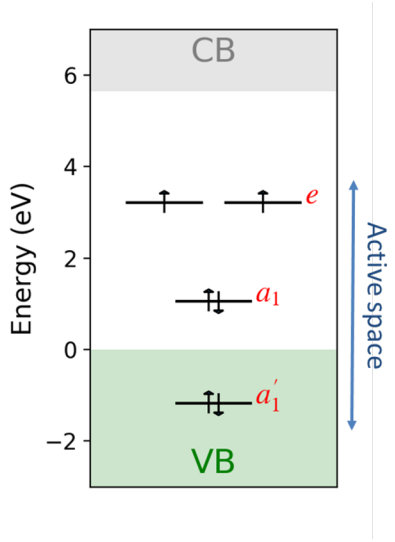
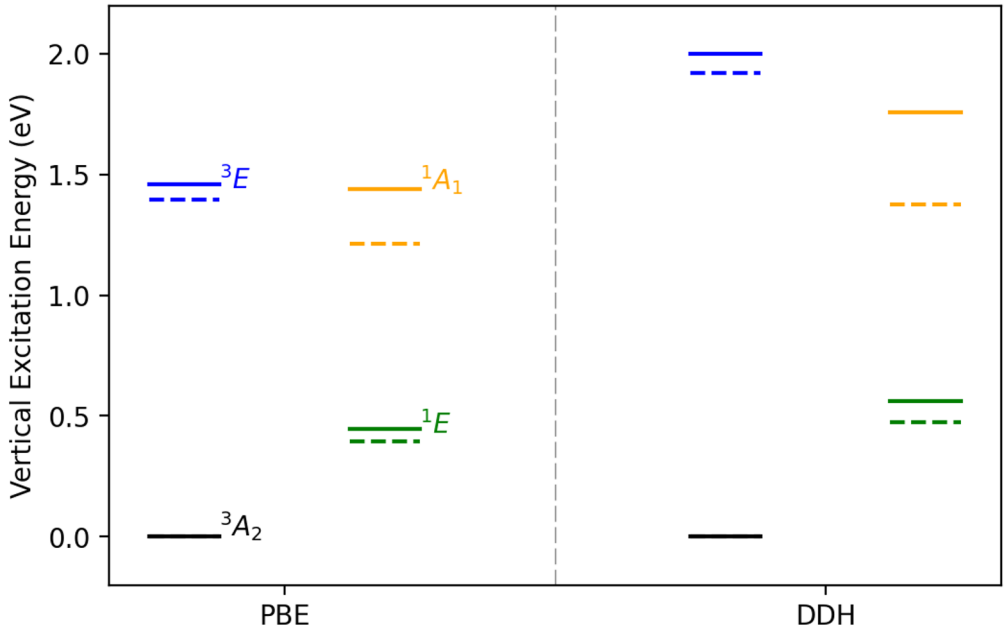
Ma, H., **Sheng, N.**, Govoni, M., & Galli, G. Phys. Chem. Chem. Phys. (2020)

Electronic structure of NV^- in diamond

Single-electron levels (DFT)



Many-electron states (embedding theory)



Vertical excitation energies (eV)

Excitation	RPA	Beyond-RPA	Exp.
	1.921	2.001	2.180*
	0.900	1.198	1.190**

*1.945 eV ZPL + 0.235 eV Stokes energy; **ZPL

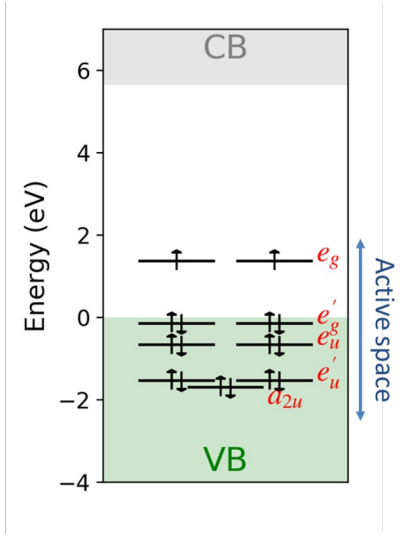
Davies, G. & Hamer, M. F. Proc. R. Soc. A 348, 285{298 (1976).
Rogers, L. J., Armstrong, S., Sellars, M. J. & Manson, N. B. New J. Phys. 10, 103024 (2008).

- Ordering and symmetry of low-lying states are correctly reproduced
- We obtained better agreement with experiments by computing dielectric screening beyond the RPA

Ma, H., **Sheng, N.**, Govoni, M., & Galli, G. Phys. Chem. Chem. Phys. (2020)

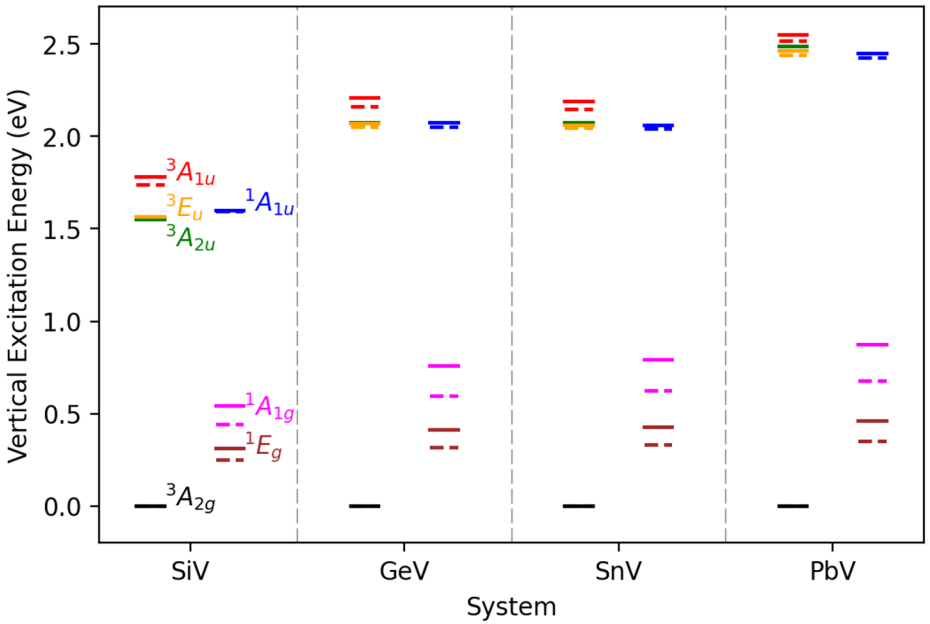
Electronic structure of group-IV^0 defects in diamond

Single-electron levels (DFT)



Many-electron states (embedding theory)

DDH



Vertical excitation energies of SiV^0 (eV):

Excitation	Beyond-RPA	Exp
	1.594	1.568*
	0.011	0.007**

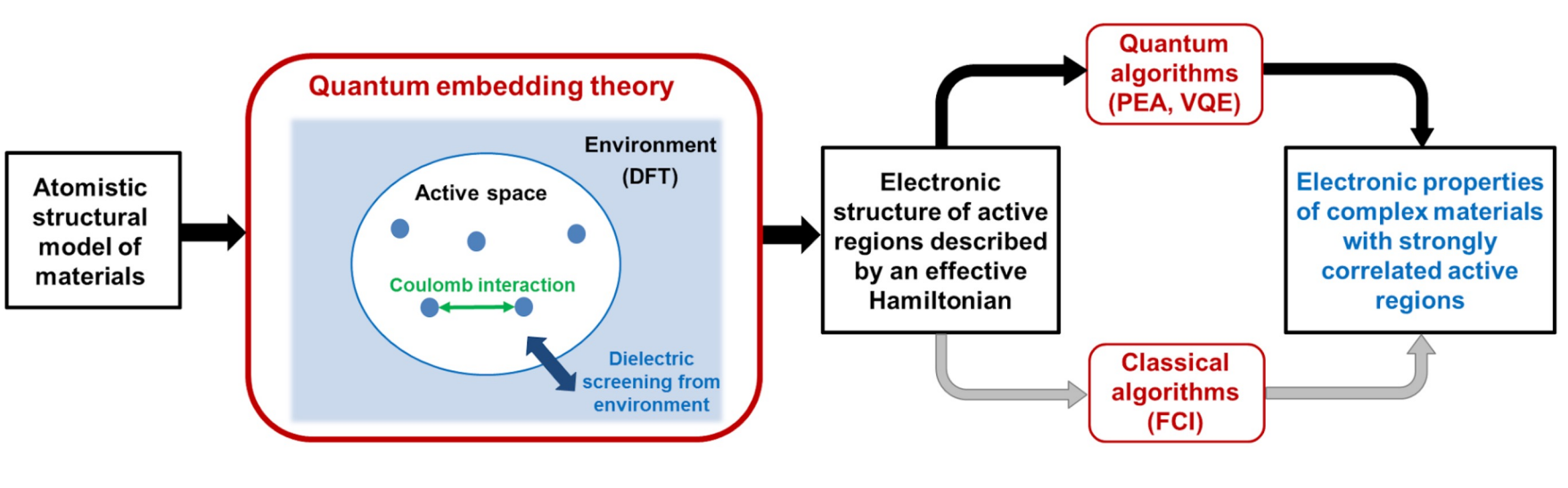
*1.31 eV ZPL + 0.258 eV Stokes energy
Thiering, G. & Gali, A. npj Comput. Mater. 5, 18 (2019).

** Green, B. L. et al. Phys. Rev. B 99, 161112 (2019).

- We confirmed the existence of the $^3A_{2u}/^3E_u$ manifold proposed by experimental studies
- Our results on singlet states provide a possible explanation for the experimental difficulty to perform optical spin polarization of SiV^0
- Possible intersystem crossing in SnV^0 and PbV^0
- Spin-orbit coupling effects are negligible on defect states

Ma, H., **Sheng, N.**, Govoni, M., & Galli, G. Phys. Chem. Chem. Phys. (2020)

Conclusions



- We used a quantum embedding theory (QET) to investigate and predict strongly-correlated electronic states, e.g. singlet states for spin defects in diamond. These states cannot be described with DFT. Our results may help the experimental design of qubits.
- The QET used here is scalable to large systems.
- Going beyond the RPA in the calculation of dielectric screening of the environment provides results more accurate than those at the RPA level.

Ma, H., Govoni, M. & Galli, G. npj Comput Mater 6, 85 (2020)
Ma, H., **Sheng, N.**, Govoni, M., & Galli, G. Phys. Chem. Chem. Phys. (2020)
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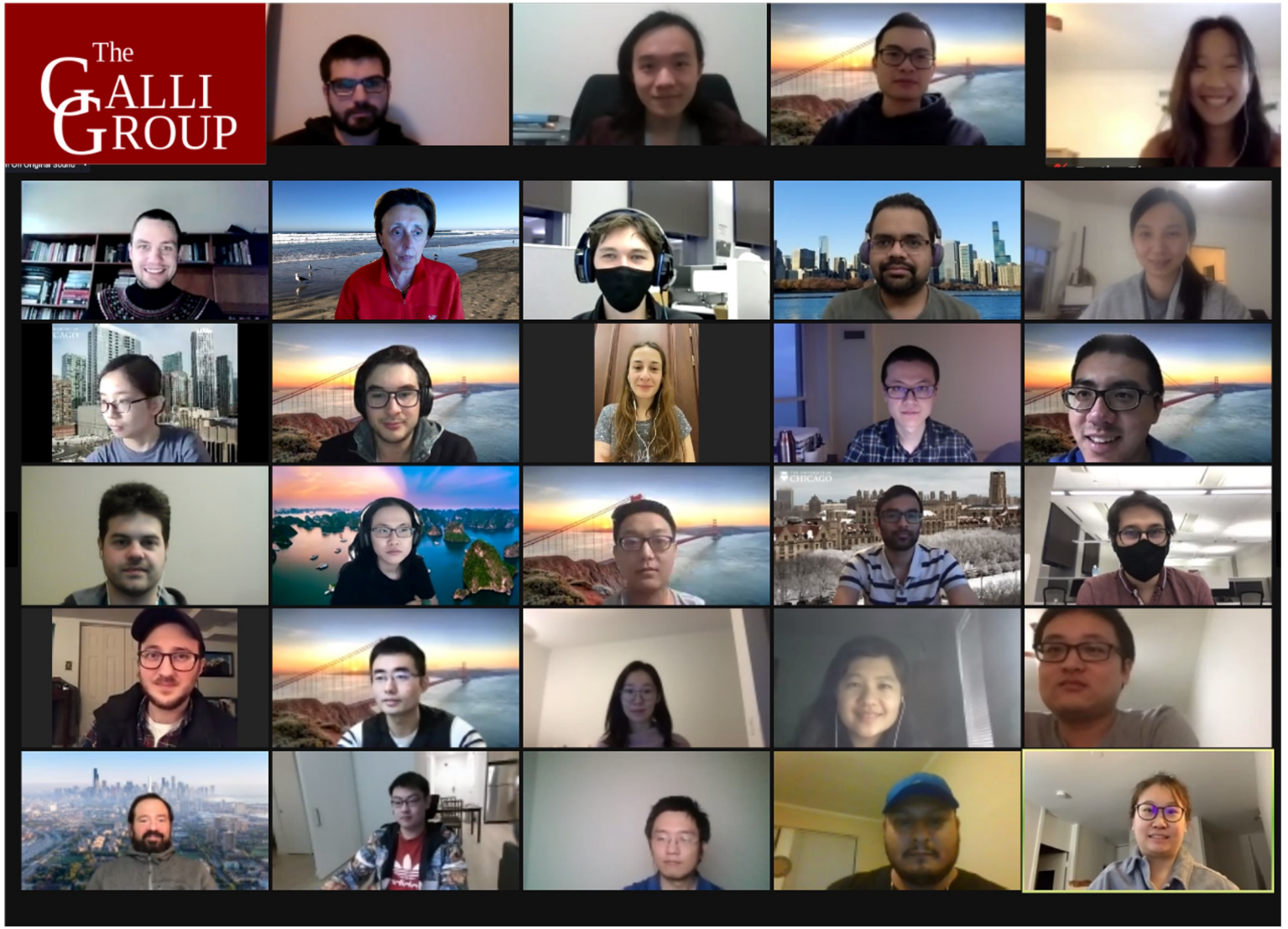
Acknowledgement

Galli Group



Grants:

QISpin

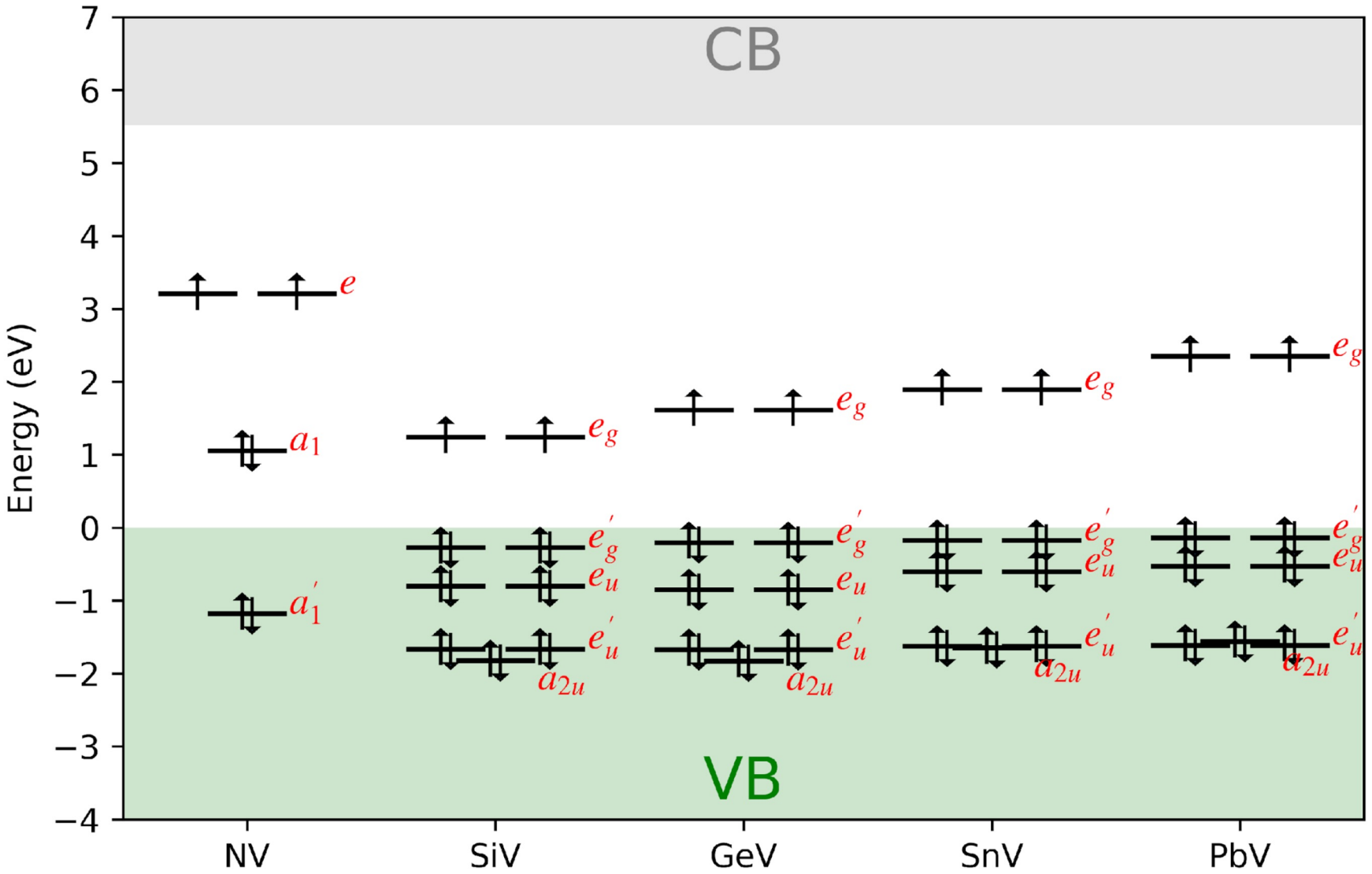
MICCoM

Computing resources:

THE UNIVERSITY OF CHICAGO | Research Computing Center

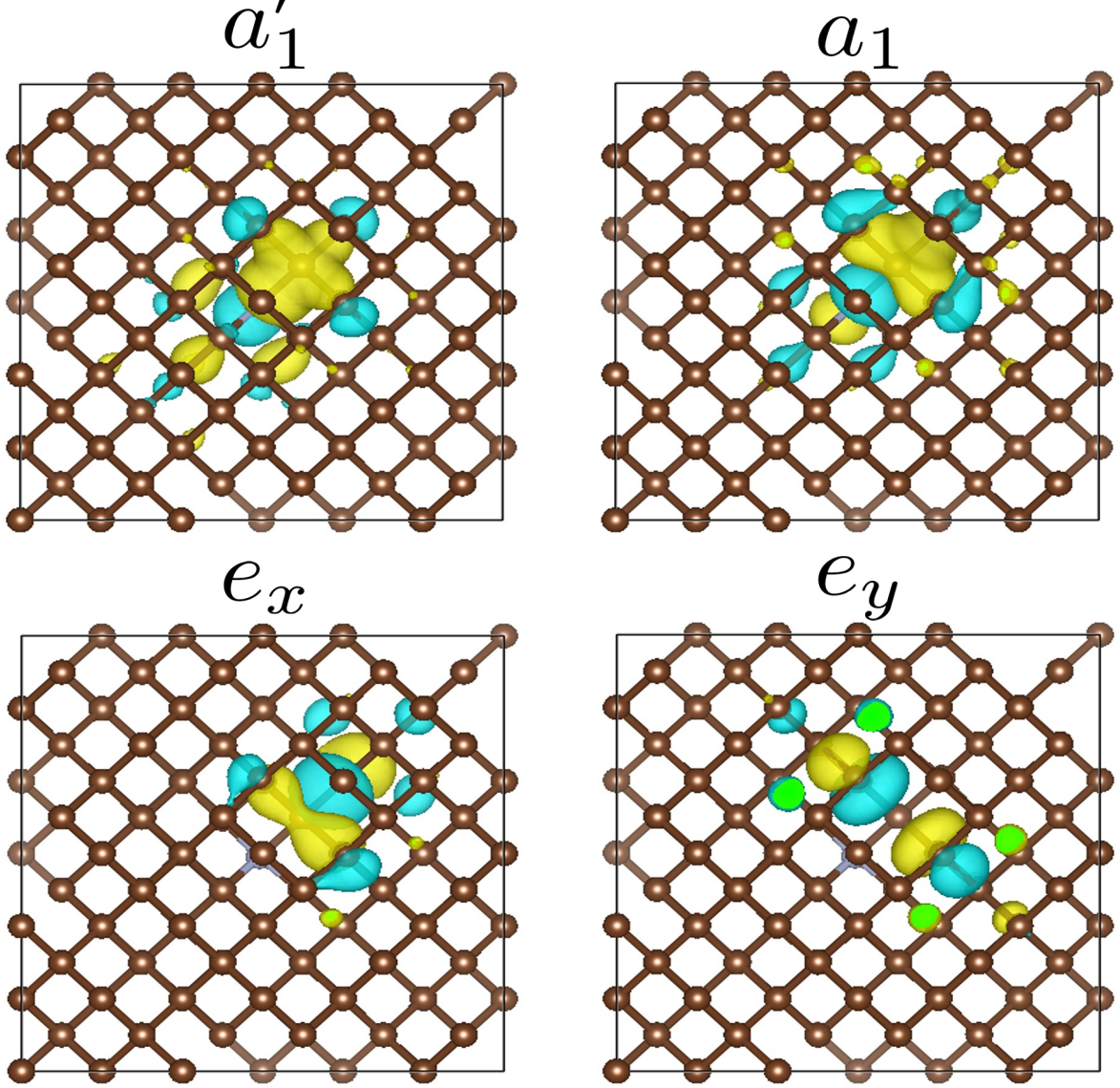
NERSC

DFT defect orbitals



DFT defect orbitals

Minimum model of NV^-



Minimum model of SiV^0