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CENTER FOR MOLECULAR ENGINEERING
ARGONNE NATIONAL LABORATORY

GREEN'S FUNCTION FORMULATION OF QUANTUM DEFECT EMBEDDING THEORY

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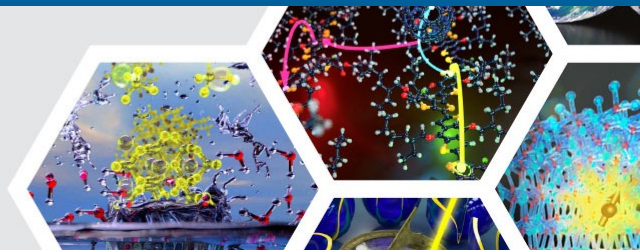
[3]Argonne National Laboratory



APS March Meeting 2023, Las Vegas
Session A60: Quantum Embedding: Materials and Methods for Materials
03/06/2023

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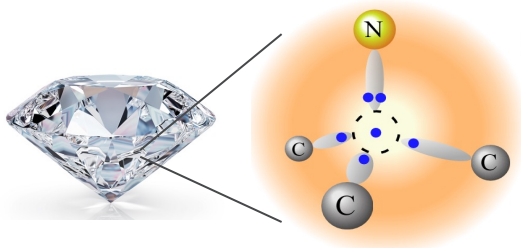
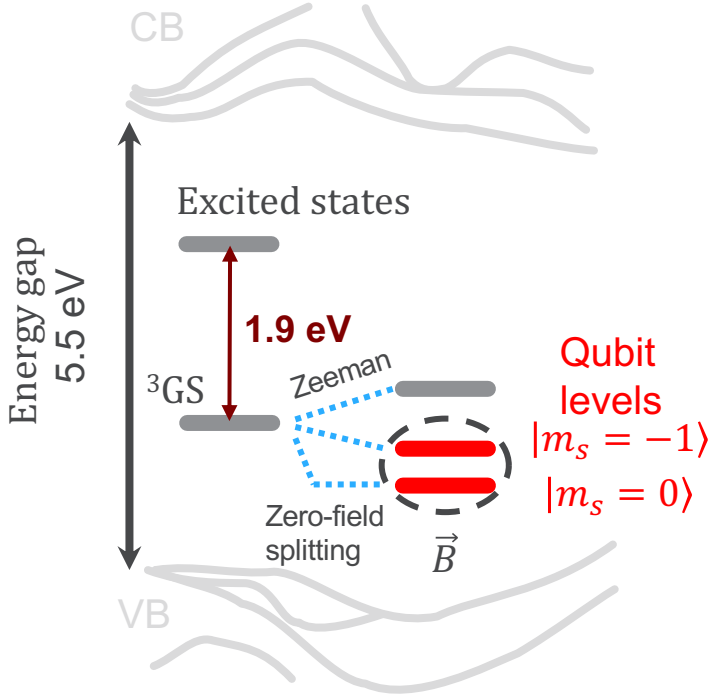
SPIN DEFECTS AS MOLECULAR SYSTEMS

- **Optically active spin defects in semiconductors** are interesting platforms for the development of solid-state quantum technologies
  - **two-level system**
  - **optical read-out**
  - **wide temperature range** operation
  - compatible with **semiconductor technology**



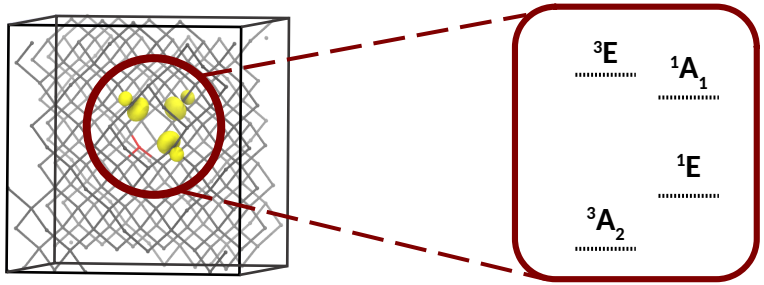
NV- in diamond



NEUTRAL EXCITATIONS IN EMBEDDED SYSTEMS

Spin defect

Many-body spectrum



DFT

Correlated excitations: relevant for quantum information science, yet challenging for mean-field theories

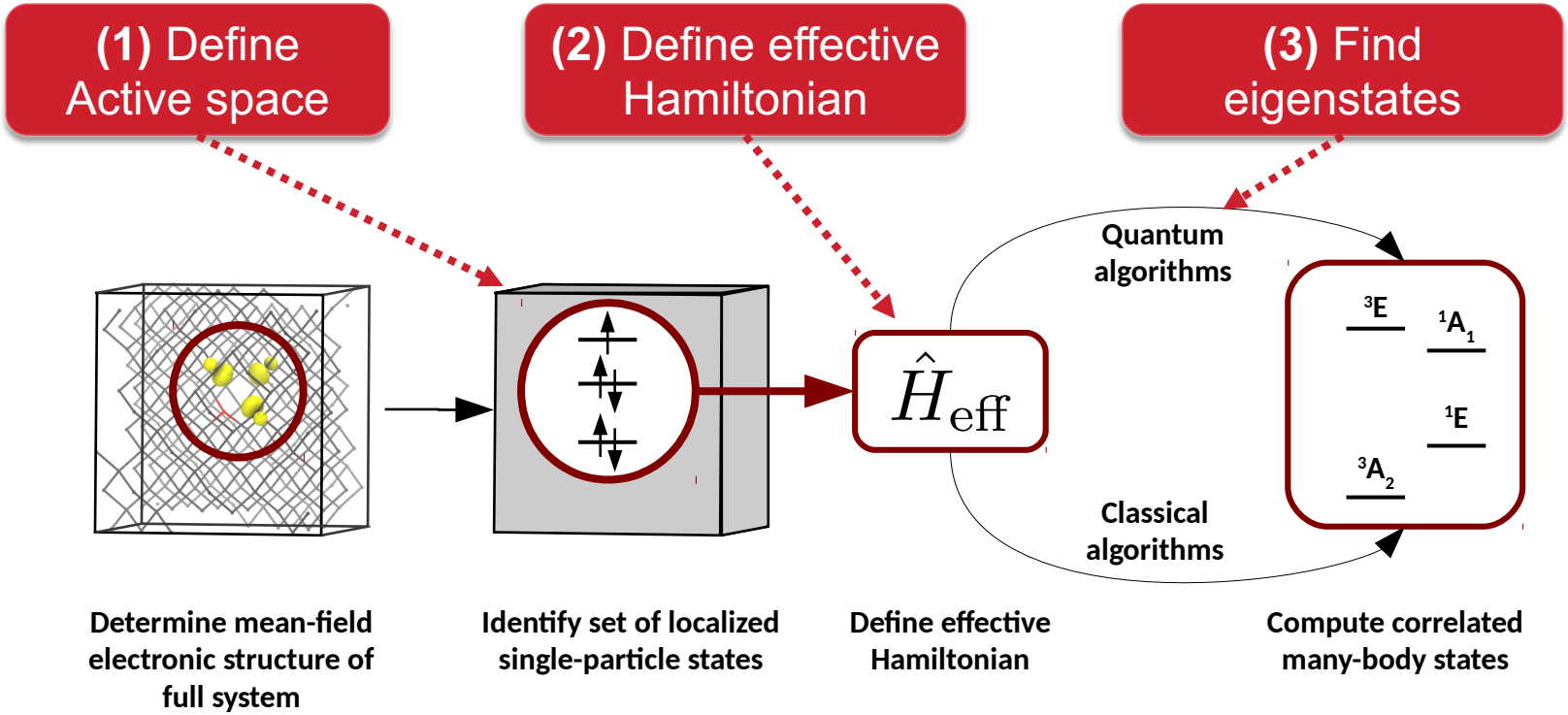
$$|X\rangle = \underbrace{\sum_{vc} A^X_{vc}|vc\rangle}_{\text{single}} + \underbrace{\sum_{vv'cc'} A^X_{vv'cc'}|vv'cc'\rangle}_{\text{double}} + \cdots \quad \text{n-ple}$$

FCI

How can FCI be embedded in DFT?

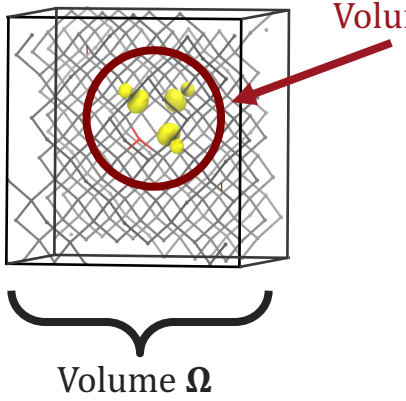
Bockstedte, Schütz, Garratt, Ivady, Gali, npj Comput Mater *3*, 31 (2018)
Ma, Govoni, Galli, npj Comput Mater 6, 85 (2020)
Ma, Sheng, Govoni & Galli, JCTC 17, 2116 (2021)
Sheng, Vorwerk, Govoni, Galli, JCTC 18, 3512 (2022)

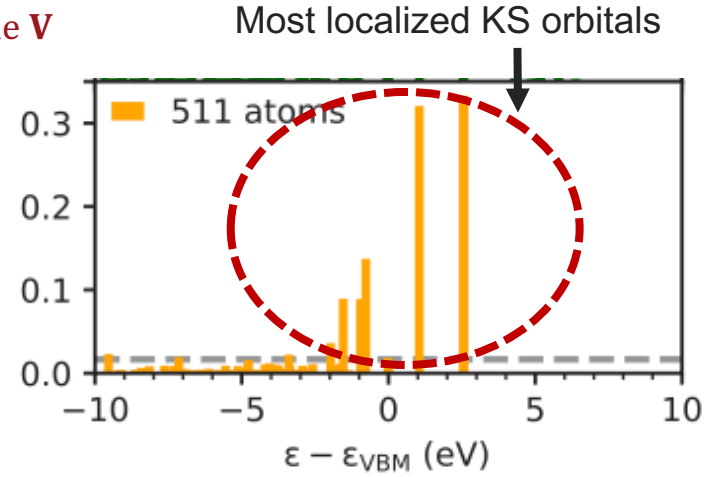
QUANTUM DEFECT EMBEDDING THEORY (QDET)

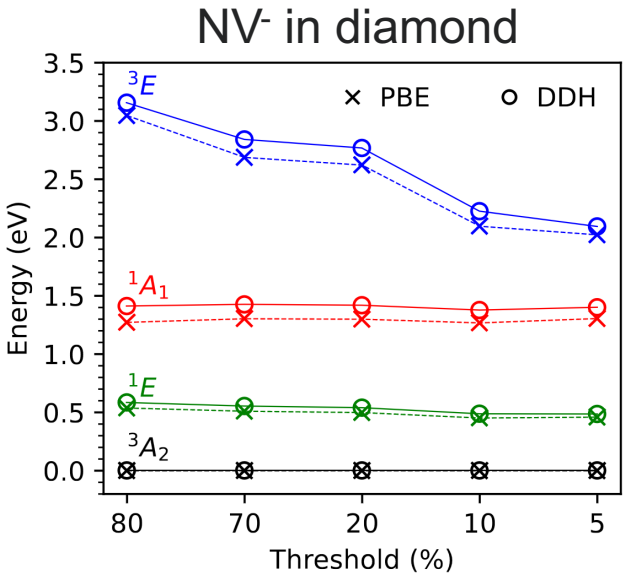


Sheng, Vorwerk, Govoni, Galli, J. Chem. Theory Comput. 18, 3512 (2022)

DEFINE ACTIVE SPACE







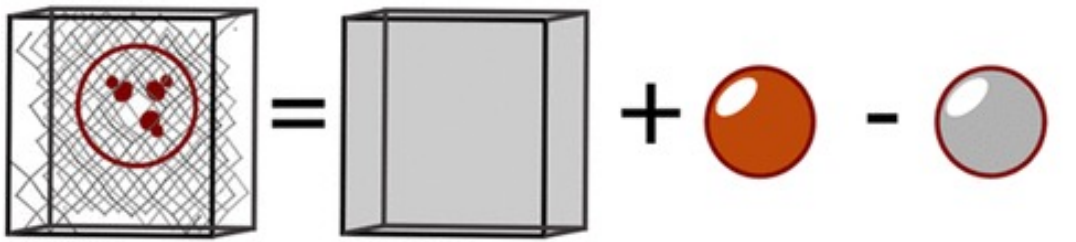
Active space = $\{ \psi_n^{KS} \mid f_n = \int_{V \in \Omega} |\psi_n^{KS}(\boldsymbol{r})|^2 d\boldsymbol{r} > \text{Threshold} \}$

Converged excitation energies with a 5% threshold → (12o,22e) active space

Sheng, Vorwerk, Govoni, Galli, J. Chem. Theory Comput. 18, 3512 (2022)

DEFINE EFFECTIVE HAMILTONIAN

Describe excitations within the active space at the FCI level of theory (high), starting from a description of the whole system at the level of DFT (low)



DFT | low | high | double counting

Necessary to remove any **double counting** terms arising from the separation of the whole system into active space + environment

$$H^{\text{eff}} = \sum_{ij}^{\text{A}} t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^{\text{A}} v_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k$$

one-body | two-body

EFFECTIVE TWO-BODY TERM

$$H^{\text{eff}} = \sum_{ij}^{A} t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^{A} v_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k$$

one-body two-body

The particles of the active space are subject to an effective interaction, screened by the other particles

v^{eff} effective Coulomb

bare Coulomb

$W^{-1} = v^{-1} - P$ Separate the polarizability

$$P = \underbrace{-iG^R G^R - iG^A G^R - iG^R G^A}_{P^R} \underbrace{-iG^A G^A}_{P^A}$$

$$W^{-1} = \boxed{v^{-1} - P^R} - P^A$$

$$\left[v^{eff}\right]^{-1}$$

v^{eff} includes excitations that involve states that are NOT part of the active space

Aryasetiawan, Imada, Georges, Kotliar, Biermann, Lichtenstein, Phys. Rev. B 70, 195104 (2004)

EFFECTIVE ONE-BODY TERM

$$H^{\text{eff}} = \sum_{ij}^{\text{A}} t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^{\text{A}} v_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k$$

one-body two-body

$$G^{-1} = g^{-1} - \Sigma \qquad [\omega - t^{eff}]^{-1}$$

$$G^{-1} = g^{-1} - \Sigma^{\text{low}} + \Sigma^{dc} - \Sigma^{high}$$

Separate the self-energy

Interactions that are **doubly counted (dc)**:

- Hartree: already described by DFT
- Exchange & correlation: to be removed from DFT

$$\Sigma^{dc} = \Sigma_H^{high} + \left(\Sigma_{XC}^{low}\right)_A$$

$$\Sigma_H^{high} = v^{eff} \rho^A$$

$$\left(\Sigma_{XC}^{low}\right)_A = ?$$

While ρ and G are easily separable, $v_{xc}[\rho]$ is NOT

EFFECTIVE ONE-BODY TERM

$$H^{\text{eff}} = \sum_{ij}^{\text{A}} t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^{\text{A}} v_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k$$

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$$\Sigma_H^{high} = v^{eff} \rho^A$$

$$\left(\Sigma_{XC}^{low}\right)_A = iG^A W$$

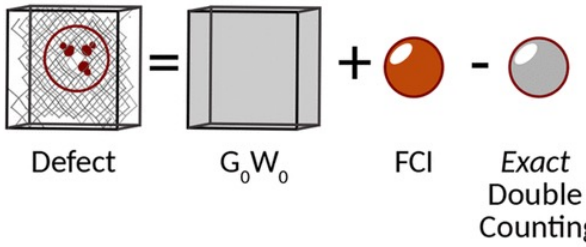
DFT+GW as “low” level of theory allows us to define a robust dc scheme

Biermann, Aryasetiawan, Georges, Phys. Rev. Lett. 90, 086402 (2003)

GREEN'S FUNCTION EMBEDDING FORMALISM

- An **effective Hamiltonian** allows us to treat correlation using **two levels of theory**

$$H^{\text{eff}} = \sum_{ij}^{\text{A}} t_{ij}^{\text{eff}} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl}^{\text{A}} v_{ijkl}^{\text{eff}} a_i^\dagger a_j^\dagger a_l a_k$$



Sheng, Vorwerk, Govoni, Galli, J. Chem. Theory Comput. 18, 3512 (2022)

one-body

$$t^{eff} = H^{KS} - t^{dc}$$

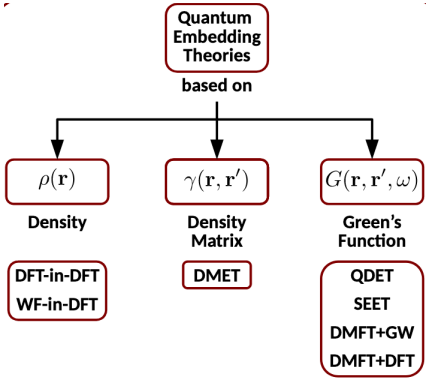
two-body

$$v^{eff} = [1 - P^R v]^{-1} v$$

double-counting

$$t_{ij}^{dc} = [V_{xc}]_{ij} + \sum_{kl}^{A} [v^{eff}]_{ikjl} \rho_{kl}^{A} - [iG^R W]_{ij}$$

DFT | Hartree | Exchange & correlation



Sheng, Vorwerk, Govoni, Huang, Galli, Nature Comput. Sci. 2, 424 (2022)

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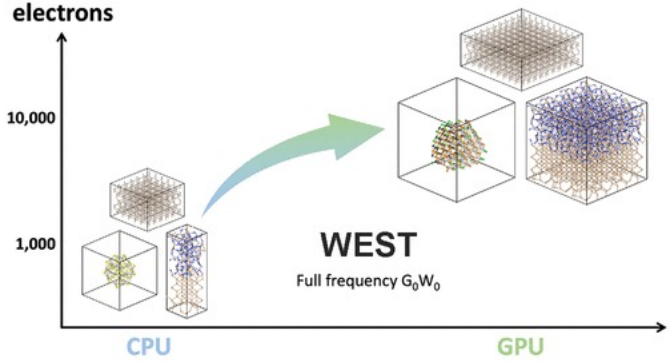

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$$t_{ij}^{dc} = [V_{xc}]_{ij} + \sum_{kl}^{A} [v^{eff}]_{ikjl} \rho_{kl}^{A} - [iG^R W]_{ij}$$

DFT | Hartree | Exchange & correlation

⟨ WEST! ⟩

Efficient calculation of matrix elements for large systems on GPUs

Yu, Govoni, J. Chem. Theory Comput. 18, 4690 (2022)

NV CENTER IN DIAMOND

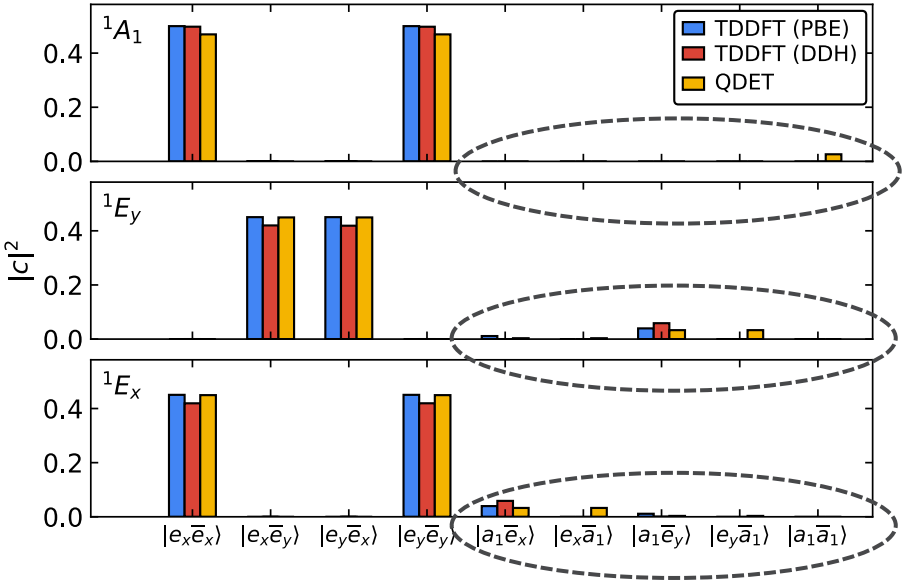
- Results obtained using the exact double counting (**DFT+G_0W_0**) correction are closer to the experimental values than those computed using a Hartree−Fock double counting (**HF dc @ DFT**) correction

reference/electronic states	^1E	$^1A_1$	^3E
Exp[56]			2.18
Exp ZPL[56−58,69,70]	0.34−0.43	1.51−1.60	1.945
QDET (DFT+G_0W_0)	0.463	1.270	2.152
QDET (HF dc @ DFT)	0.375	1.150	1.324

Sheng, Vorwerk, Govoni, Galli, J. Chem. Theory Comput. 18, 3512 (2022)

NV CENTER IN DIAMOND

Contribution of Slater determinants to the many body wavefunction



single excitations

double excitations

TDDFT

$$|X\rangle = \sum_{vc} A^X_{vc}|vc\rangle + \sum_{vv'cc'} A^X_{vv'cc'}|vv'cc'\rangle + \cdots$$

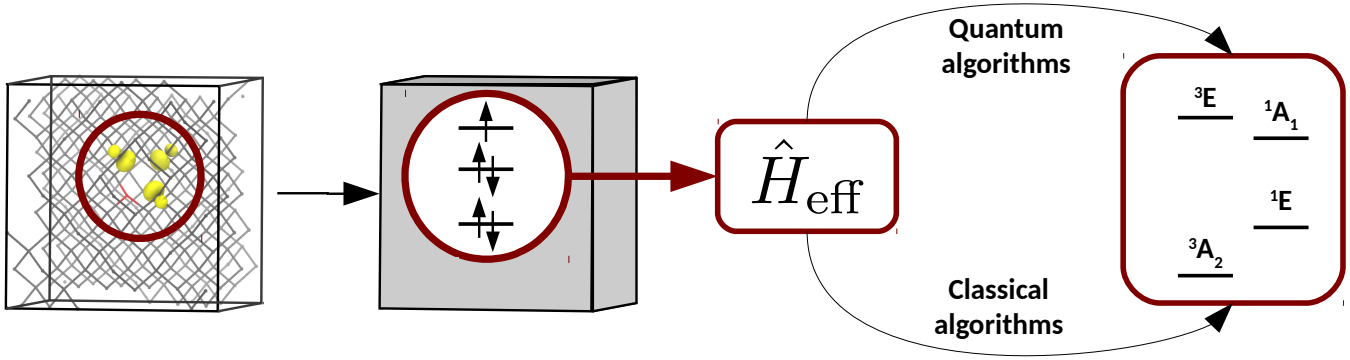
single double n-ple

FCI

Ongoing work: comparison between BSE, TDDFT@hybrid, QDET

Jin, Govoni, Galli, npj Comput. Mater. 8, 238 (2022)

CLASSICAL/QUANTUM PROTOCOL FOR COMPUTATIONAL SPECTROSCOPY



Determine mean-field electronic structure of full system

Identify set of localized single-particle states

Define effective Hamiltonian

Compute correlated many-body states

exascale

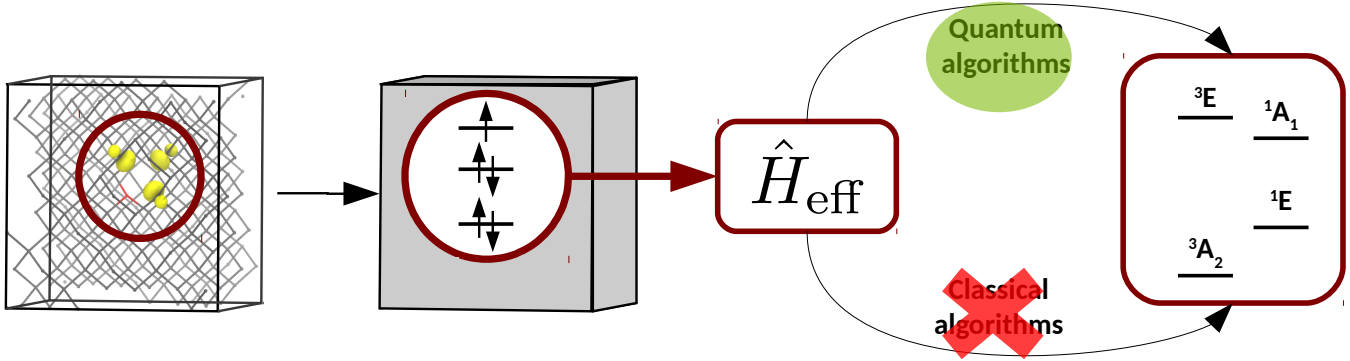
pre-exascale

CPU/GPU

QUANTUMESPRESSO ⟨WEST!⟩ pyscf

http://quantum-espresso.org
http://west-code.org
https://pyscf.org/

CLASSICAL/QUANTUM PROTOCOL FOR COMPUTATIONAL SPECTROSCOPY



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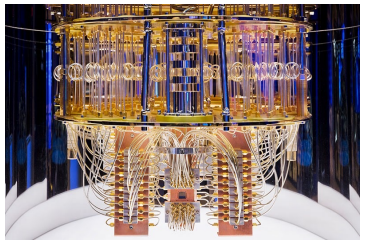


QPU

QDET ON QUANTUM COMPUTERS

QDET

Define H^{eff} in second quantization

Map to Qubit Hamiltonian

Parametrize wfc

Variational Quantum Eigensolver

Quantum Subspace Expansion

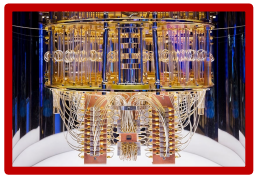
Error mitigation

QEE

Shee, Tsai, Hong, Cheng, Goan, Phys. Rev. Res. 4, 023154 (2022)

QCC

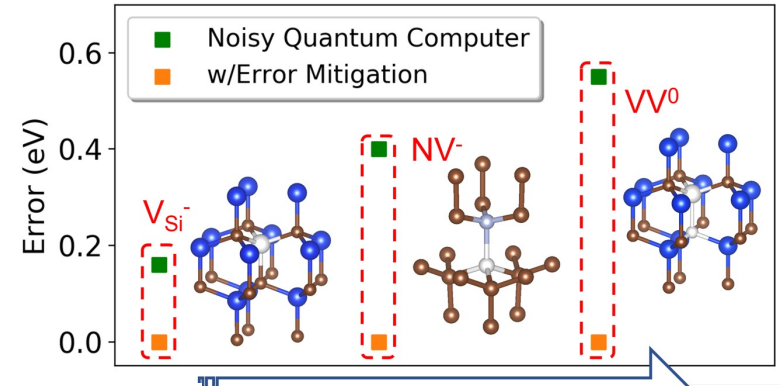
Ryabinkin, Yen, Genin, Izmaylov. JCTC 14, 6317 (2018)



	Jordan-Wigner	Quantum Efficient Encoding
# Slater det	2^N	$O(N^h)$
# qubits	N	$O(\log(N))$
# Pauli terms	$O(N^4)$	$O(N^{2h})$

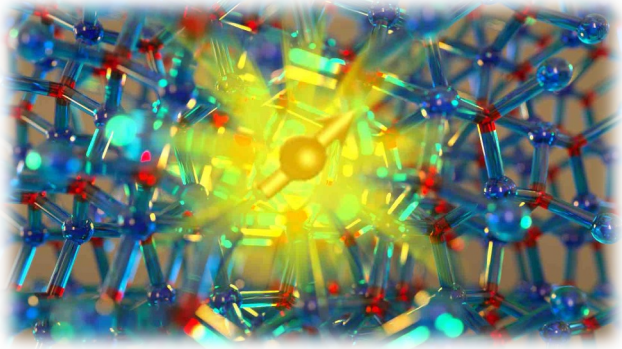
Size of active space: N

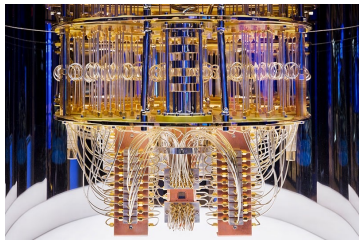
Number of "holes": $h = N - m_\uparrow - m_\downarrow$



Huang, Sheng, Govoni, Galli, JCTC accepted, arXiv:2212.01912 (2023)

CONCLUSIONS





- Presented quantum embedded simulations of **FCI in DFT**, applied to spin-defects in semiconductors

- **DFT+GW** is required as starting point for QDET to define a robust double counting removal scheme and obtain accurate results

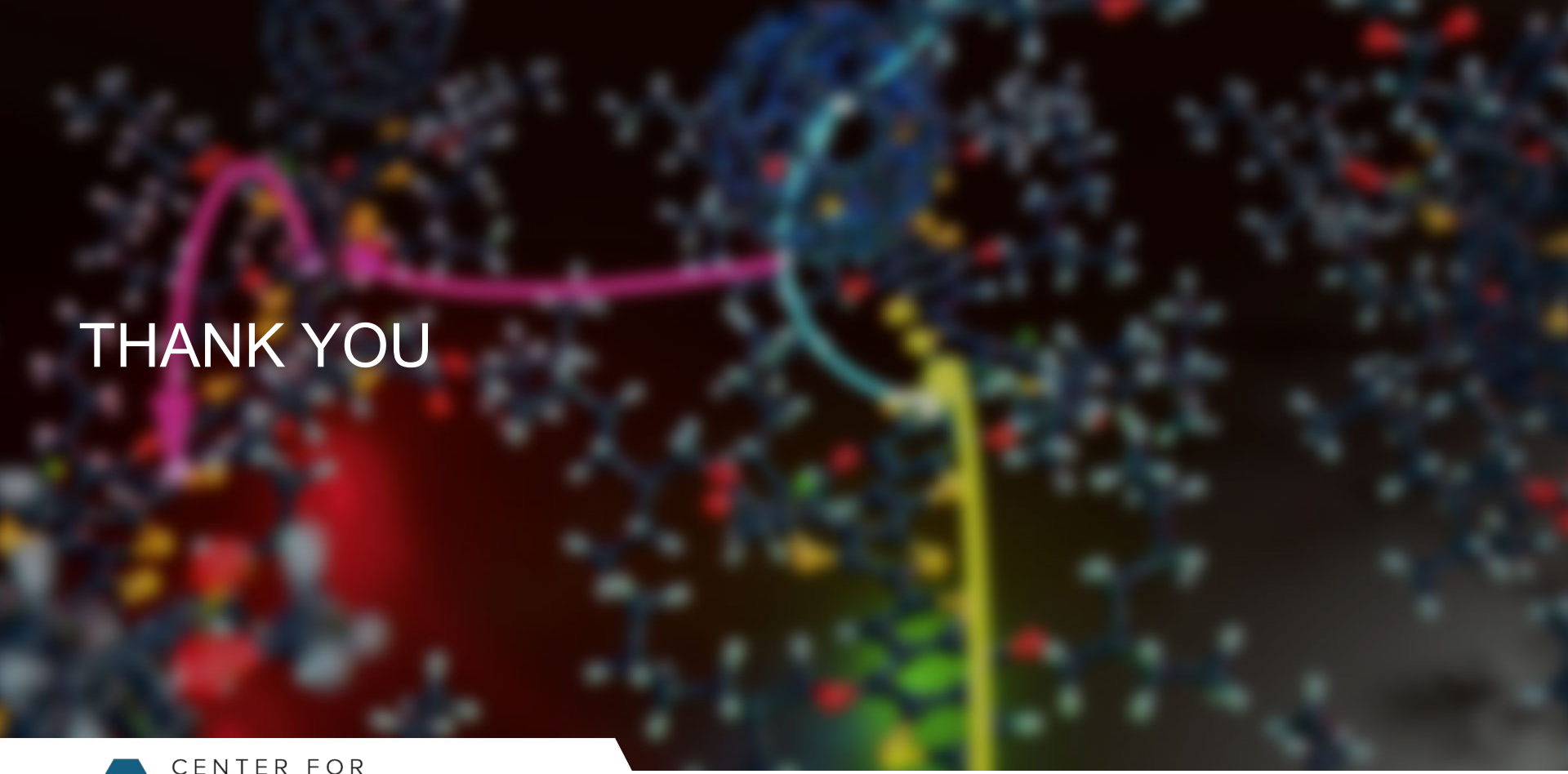
- Within QDET, **pre-exascale computing** is used to obtain the parameters of the effective Hamiltonian that describes the active space, **quantum computing** can be used to solve FCI

ACKNOWLEDGMENTS

- Computational facilities used:
  - ALCF-Theta, NERSC-Perlmutter
  - OLCF-Summit
  - IBM Quantum Experience
- Allocations:
  - INCITE, ALCC, NERSC-NESAP
  - IBM Quantum Hub, NERSC-QIS

http://miccom-center.org

Thank you!



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