Session Index

Session K46: Excited State II: Method development-quantum embedding and X-ray Spectroscopy

Focus

Sponsoring Units: DCOMP DMP
Chair: Sahar Sharifzadeh, Boston University
Room: *McCormick Place W-470A*

Tuesday, March 15, 2022 3:00PM - 3:36PM	K46.00001: Absorption Spectra of Solids from Periodic Equation-of-Motion Coupled-Cluster Theory Invited Speaker: Xiao Wang
Tuesday, March 15, 2022 3:36PM - 3:48PM	K46.00002: Ground- and Excited-State energies of copper oxide molecules and anions from first principles via the Spin-Flip Bethe-Salpeter Equation approach Bradford A Barker, David A Strubbe
Tuesday, March 15, 2022 3:48PM - 4:00PM	K46.00003: Efficient Treatment of Molecular Excitations in the Liquid phase using stochastic many-body theory Guorong Weng, Vojtech Vlcek
Tuesday, March 15, 2022 4:00PM - 4:12PM	K46.00004: An Exact Double Counting Scheme for Quantum Defect Embedding Theory Nan Sheng, Christian W Vorwerk, Marco Govoni, Giulia Galli
Tuesday, March 15, 2022 4:12PM - 4:24PM	K46.00005: Benchmarking the Quantum Chemical Methods to Examine Ground and Excited States Electronic Structure of Diatomic Molecules Deepak K Rai, B. R. K. Nanda
Tuesday, March 15, 2022 4:24PM - 4:36PM	K46.00006: Model analysis of multiplet excitation of RE ions using QSGW Katsuhiro Suzuki, Hirofumi Sakakibara, Takao Kotani, Kazunori Sato
Tuesday, March 15, 2022 4:36PM - 4:48PM	K46.00007: Transition from Lorentz to Fano Spectral Line Shapes in Non-Relativistic Quantum Electrodynamics Davis M Welakuh, Prineha Narang
Tuesday, March 15, 2022 4:48PM - 5:00PM	K46.00008: Real-space Green's function approach for the Langreth cumulant John Rehr, Joshua J Kas
Tuesday, March 15, 2022 5:00PM - 5:12PM	K46.00009: Resonant inelastic x-ray scattering beyond the quasiparticle approximation Keith Gilmore, Joshua J Kas
Tuesday, March 15, 2022 5:12PM - 5:24PM	K46.00010: All-electron BSE@GW method for K-edge Core Electron Excitation Energy Yi Yao, Dorothea Golze, Patrick Rinke, Volker Blum, Yosuke Kanai
Tuesday, March 15, 2022 5:24PM - 5:36PM	K46.00011: Combined Cumulant and Ligand Field Multiplet Theory approach to X-ray spectra Joshua J Kas, John Rehr, Thomas P Devereaux
Tuesday, March 15, 2022 5:36PM - 5:48PM	K46.00012: Finite-temperature self-energy correction to XANES Tun Sheng Tan, Joshua J Kas, John Rehr
Tuesday, March 15, 2022 5:48PM - 6:00PM	K46.00013: Predicting Core Electron Binding Energies in 1st Row Transition Metal Elements Using the Δ-Self-Consistent-Field Approach Juhan Matthias Kahk, Johannes C Lischner

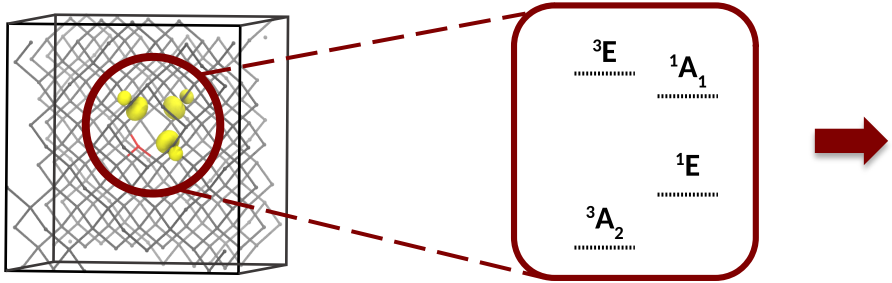
Exact double counting for quantum defect embedding theory

Nan Sheng[1], Christian Vorwerk[2], Marco Govoni[2,3] and Giulia Galli[1,2,3]

[1]Department of Chemistry, University of Chicago
[2]Pritzker School of Molecular Engineering, University of Chicago
[3]Materials Science Division, Argonne National Laboratory

Strongly-correlated states in spin defects as qubits

Spin defects Many-body spectrum



Strongly-correlated states: relevant for quantum information science, yet challenging for mean-field theories, e.g. DFT

Quantum defect embedding theory (QDET) is a natural framework for this!

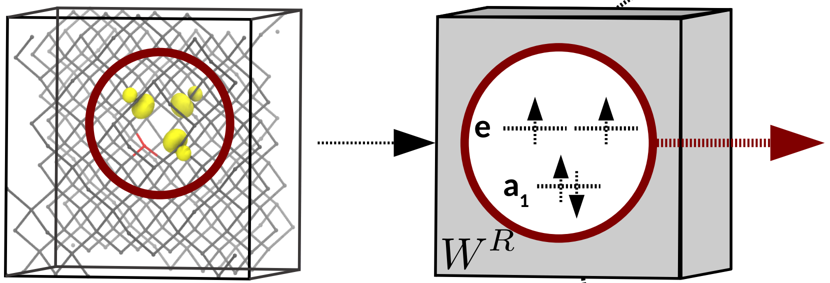
Ivady, Abrikosov & Gali, *npj CM 4,* 1, 1-13 (2018)
Ma, Govoni & Galli, *npj CM 6,* 1, 1-8 (2020)
Ma, **Sheng**, Govoni & Galli, *JCTC 17*(4), 2116-2125 (2021)
Sheng, Vorwerk, Govoni & Galli, *arXiv:2105.04736* (2021)

Quantum defect embedding theory (QDET)

A: active space
R: rest of the system

Partially screened Coulomb potential from constrained random-phase approximation (cRPA)

$v^{\text{eff}} = W^R$



$\hat{H}^{\text{eff}} = t_{ij}^{\text{eff}} \hat{a}_i^\dagger \hat{a}_j + v_{ijkl}^{\text{eff}} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k$

$t^{\text{eff}} = H^{\text{KS}} - t^{\text{dc}}$?

Determine mean-field electronic structure of full system

Identify set of localized single-particle orbitals

Ma, Govoni & Galli, *npj CM 6,* 1, 1-8 (2020)
Ma, **Sheng**, Govoni & Galli, *JCTC 17*(4), 2116-2125 (2021)
Sheng, Vorwerk, Govoni & Galli, *arXiv:2105.04736* (2021)
Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)

Exact double counting (within G_0W_0) for QDET

A: active space
R: rest of the system

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

Hartree-Fock double counting (HFDC)

$$t^{\text{dc}}_{ij} \approx \sum_{kl}^{A} \left[W_0^R\right]_{ikjl} \rho^A_{kl} - \sum_{kl}^{A} \left[W_0^R\right]_{ijkl} \rho^A_{kl}$$

Hartree "Exchange"

- Inconsistent with underlying DFT
- Uncontrollable errors

Exact double counting (EDC)

$$t^{\text{dc}}_{ij} = \left[V_{\text{xc}}\right]_{ij} + \sum_{kl}^{A} \left[W_0^R\right]_{ikjl} \rho^A_{kl} - \left[\mathrm{i}G_0^R W_0\right]_{ij}$$

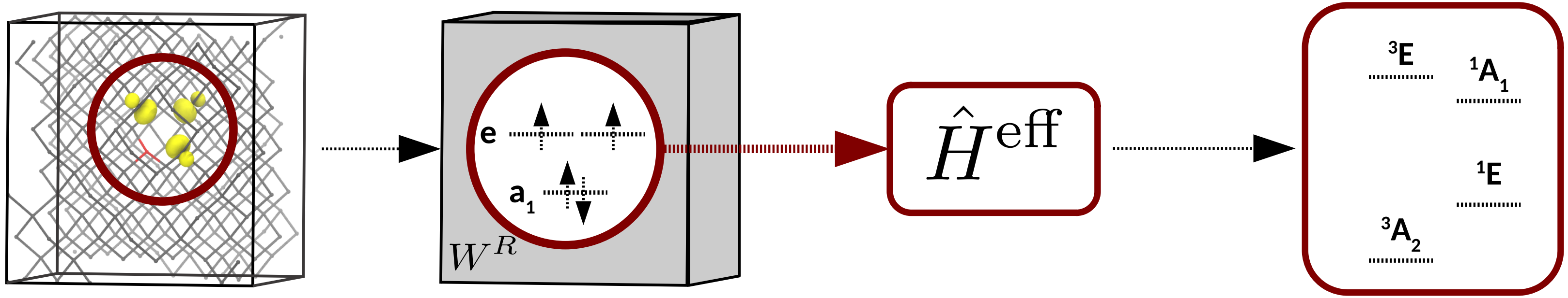
DFT Hartree Exchange + Correlation

- Fully consistent with DFT+G_0W_0
- No error introduced

Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)
Hirayama, Miyake & Imada, *PRB 87*, 195144 (2013)

QDET with *exact* double counting in practice

DFT calculation | Active space selection | Effective Hamiltonian | FCI calculation



QUANTUM ESPRESSO

Localization function

$$L_V(\psi_n^{\text{KS}}) = \int_{V\subseteq\Omega} |\psi_n^{\text{KS}}(\mathbf{x})|^2 \mathrm{d}\mathbf{x}$$

⟨WEST!⟩

pyscf

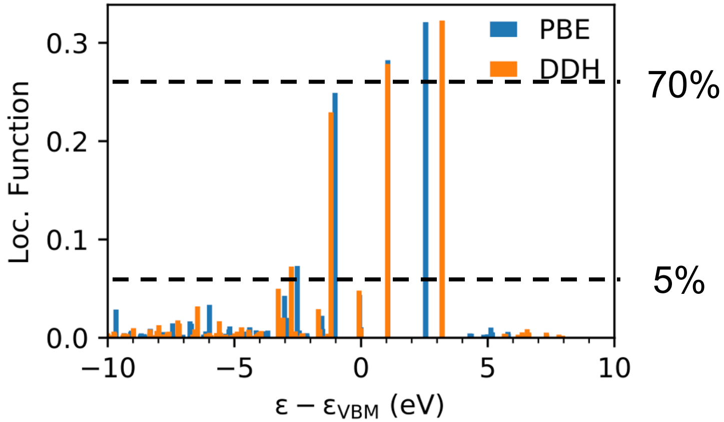
QDET is scalable to large systems with hundreds of atoms!

Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)

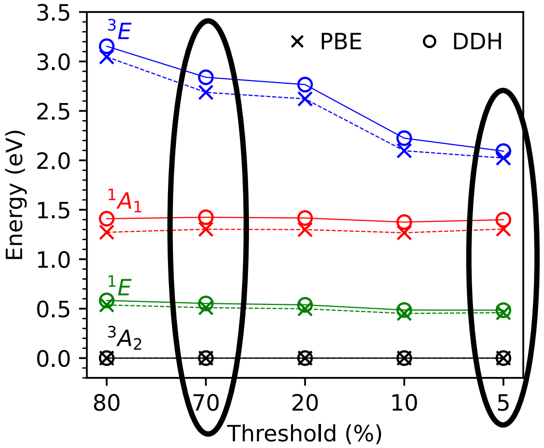
NV^- in diamond

Localization function

$$L_V(\psi_n^{\mathrm{KS}}) = \int_{V \subseteq \Omega} |\psi_n^{\mathrm{KS}}(\mathbf{x})|^2 \mathrm{d}\mathbf{x}$$



Convergence as a function of localization threshold

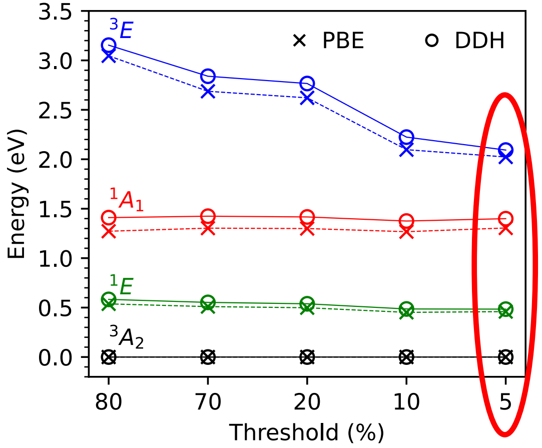


- Localization (L_V) as a function of energy is weakly dependent on starting point (PBE or DDH)
- The active space is formed by KS orbitals with L_V higher than a chosen threshold
- We find converged excitation energies with a 5% threshold → (26,14) active space

Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)

NV$^-$ in diamond

Convergence as a function of localization threshold



Vertical Excitation Energies (eV)

	HFDC @PBE[1]	HFDC @DDH[1]	EDC @PBE[2]	EDC @DDH[2]	Exp Ref[3]
^1E	0.396	0.476	0.459	0.484	
$^1A_1$	1.211	1.376	1.305	1.399	
^3E	1.395	1.921	2.023	2.093	2.18

HFDC: **H**artree-**F**ock based **D**ouble **C**ounting corrections

EDC: **E**xact **D**ouble **C**ounting corrections

- Use of EDC yields results showing a negligible dependence on starting point (PBE or DDH)
- Use of EDC yields results in closer agreement with experiments

[1] Ma, **Sheng**, Govoni & Galli, *PCCP 22*, 25522-25527 (2020)
[2] **Sheng**, Vorwerk, Govoni & Galli, *in preparation* (2022)
[3] Davies & Hamer, *Proc. R. Soc. London, Ser. A, 348*, 285–298 (1976)

SiV^0 in diamond

Vertical Excitation Energies (eV)

	HFDC @PBE[1]	HFDC @DDH[1]	EDC @PBE[2]	EDC @DDH[2]	Theo Ref[4]	Exp Ref[3]
^1E_g	0.232	0.261	0.324	0.309	0.54	
$^1A_{1g}$	0.404	0.466	0.645	0.612	1.10	
^3E_u	1.247	1.590	2.011	1.899	2.16	1.31 (ZPL)

HFDC: **H**artree-**F**ock based **D**ouble **C**ounting corrections

EDC: **E**xact **D**ouble **C**ounting corrections

- Use of EDC with 5% threshold [→ active space (78,40)] yields results showing a negligible dependence on starting point (PBE or DDH) & consistent with other embedding theories[4]
- The difference between theoretical and experimental results (zero phonon line, ZPL) may be due to dynamical Jahn-Teller effects, neglected in theoretical studies

[1] Ma, **Sheng**, Govoni & Galli, *PCCP 22*, 25522-25527 (2020)
[2] **Sheng**, Vorwerk, Govoni & Galli, *in preparation* (2022)
[4] Mitra, Pham, Pandharkar, Hermes & Gagliardi, *JPCL 12,* 11688–11694 (2021)
[3] Green et al., *PRB 99,* 161112 (2019)

Conclusions

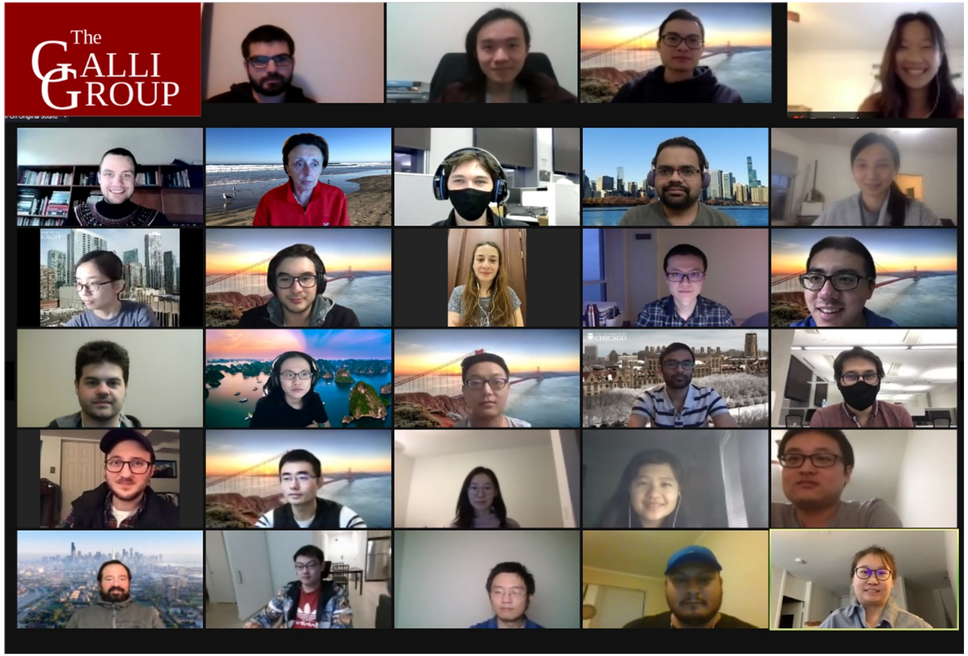
- We derived and implemented an *exact* double counting correction to the Quantum Defect Embedding theory (QDET), which is diagrammatically exact within G_0W_0, making QDET a robust scheme for the calculations of strongly correlated states of defects
- We showed that a DFT+$G_0 W_0$ calculation is required as starting point for QDET to obtain accurate results
- We applied QDET to spin defects in diamond and SiC

Future work

- Application of QDET to other spin defects
- Exploration of schemes beyond the G_0W_0 approximation

Acknowledgement

Galli Group



MICCoM

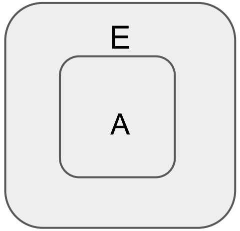
Computing resources

THE UNIVERSITY OF CHICAGO | Research Computing Center

NERSC

Exact double counting for QDET

Hamiltonian description of the active region



$$\hat{H}^{\text{eff}}\left[t^{\text{eff}}, v^{\text{eff}}\right]$$

$$v^{\text{eff}} = \left[v^{-1} - \left(P_0 - P_0^{\text{dc}}\right)\right]^{-1}(\omega = 0)$$
$$P_0 = -iG_0G_0$$
$$P_0^{\text{dc}} = -iG_0^{\mathcal{A}}G_0^{\mathcal{A}}$$

Hartree-Fock double counting (HFDC)

$$t_{ij}^{\text{eff}} = H_{ij}^{\text{KS}} - \left(v_{ikjl}^{\text{eff}} - v_{ijkl}^{\text{eff}}\right)\rho_{kl}$$

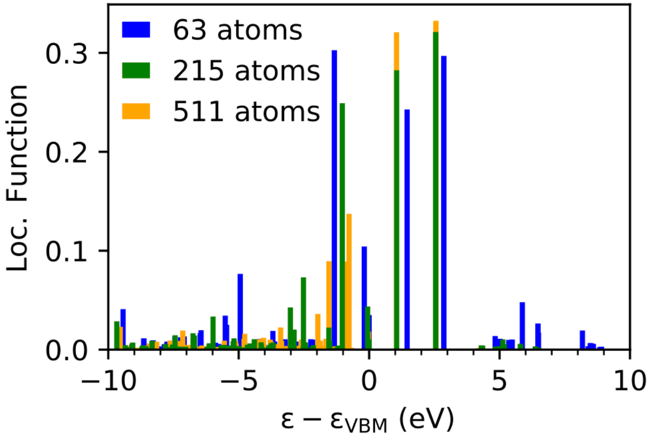
Exact double counting (EDC)

$$t^{\text{eff}} = g^{-1} - \left(\Sigma - \Sigma^{\text{dc}}\right)$$
$$\Sigma_{ij} = v_{ikjl}\rho_{kl} + \frac{1}{2}\left[iG_0W_0(\epsilon_i^{\text{KS}}) + iG_0W_0(\epsilon_j^{\text{KS}})\right]$$
$$\Sigma_{ij}^{\text{dc}} = v_{ikjl}^{\text{eff}}\rho_{kl} + \frac{1}{2}\left[iG_0^{\mathcal{A}}W_0(\epsilon_i^{\text{KS}}) + iG_0^{\mathcal{A}}W_0(\epsilon_j^{\text{KS}})\right]$$

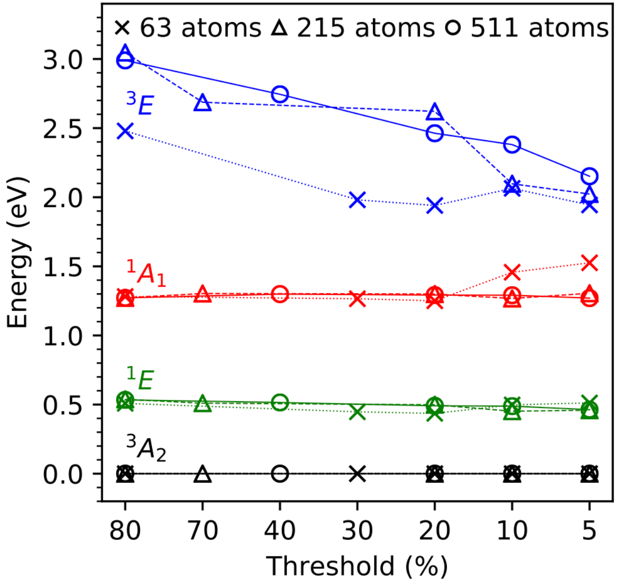
Ma, **Sheng**, Govoni & Galli, *JCTC 17*(4), 2116-2125 (2021)
Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)

Supercell convergence (NV^- in diamond)

Localization function



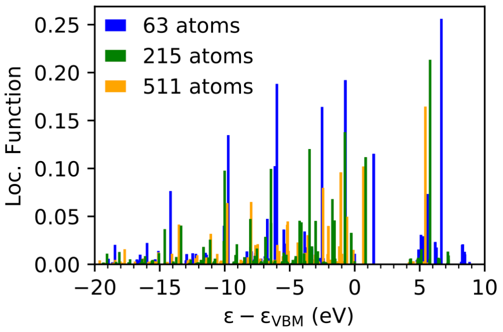
Convergence



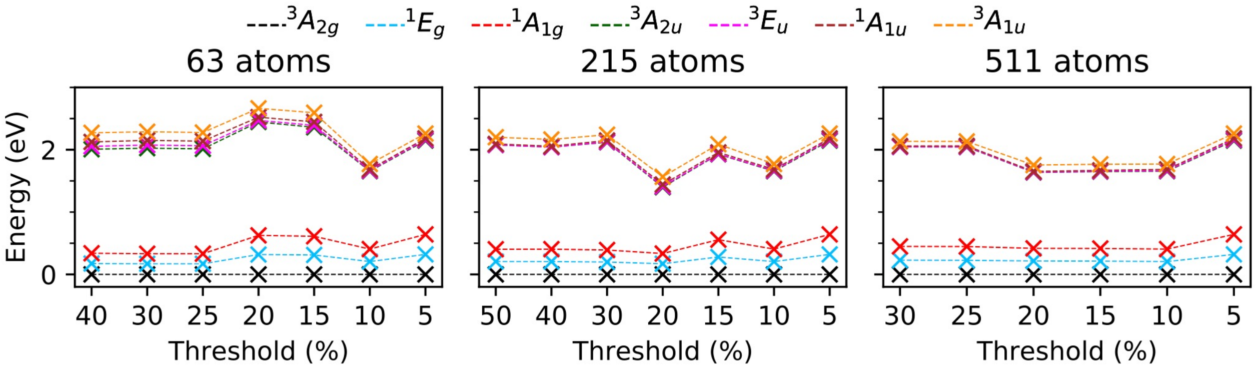
Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)

Supercell convergence (SiV^0 in diamond)

Localization function



Convergence



Sheng, Vorwerk, Govoni & Galli, *in preparation* (2022)