Efficient First—Principles Modeling of Photoionization Cross Sections: A Case Study of the NV Center

Jorūnas Dobilas[1], Lukas Razinkovas[1]

[1]Department of Fundamental Research, Center for Physical Sciences and Technology, Vilnius

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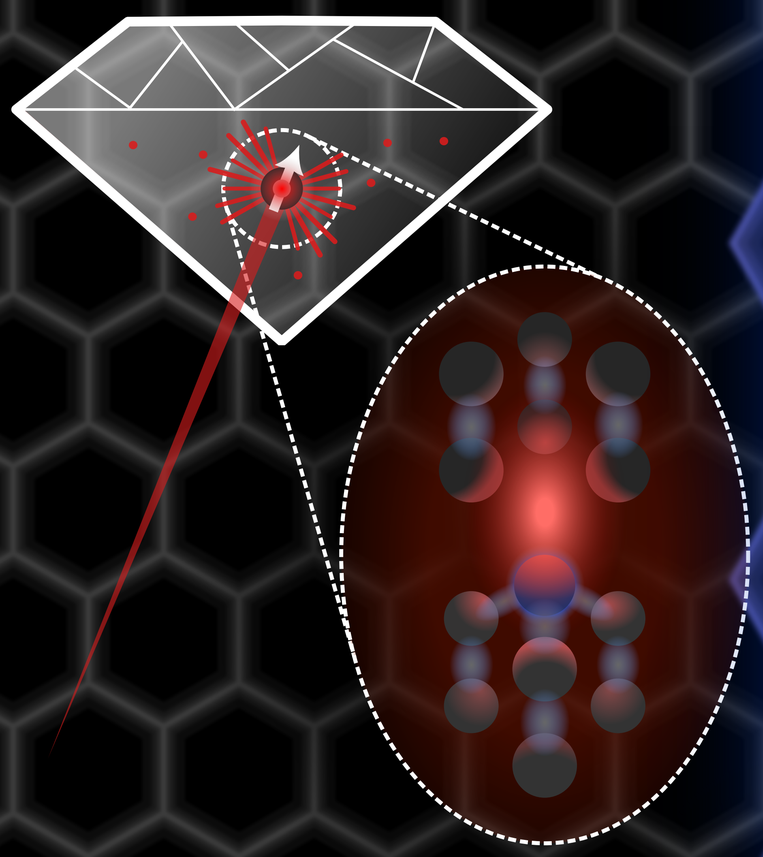
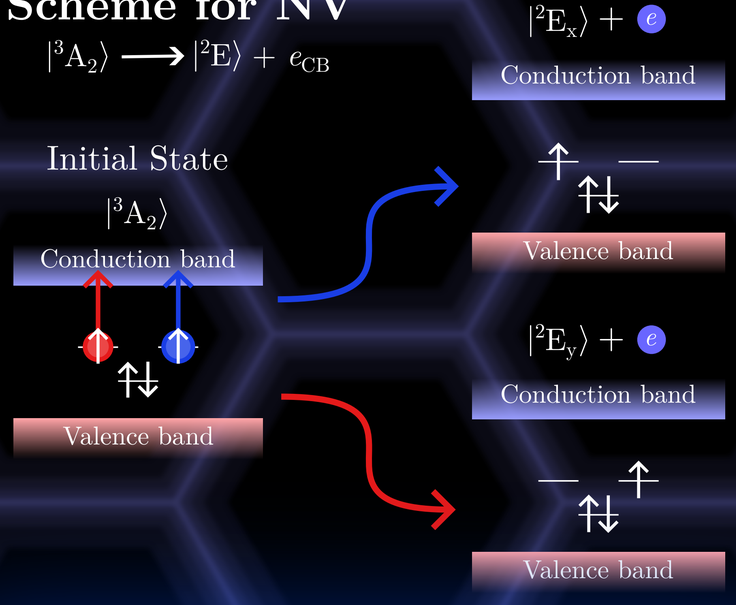
Why Charge-State Dynamics Matter

Color centers in wide-bandgap semiconductors are among the leading platforms for quantum technologies, with applications in sensing, communication, and information processing. The nitrogen-vacancy (NV) center in diamond is a prominent example[1]. These defects can exist in multiple charge states; however, typically only one state has the desired optical and spin properties required for operation. Upon optical excitation, color centers may undergo photoionization, which involves the emission or capture of an electron and a change in charge state[2]. While such processes can be detrimental, leading to loss of the operational charge state, they can also be harnessed for controlled charge manipulation and spin readout.



Ionization Scheme for NV^-

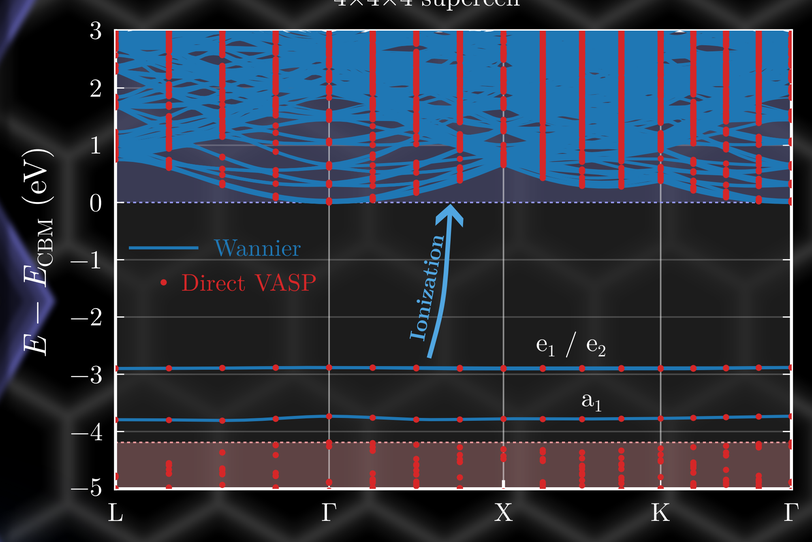
$|^3A_2\rangle \longrightarrow |^2E\rangle + e_{CB}$



Wannier Framework Validation

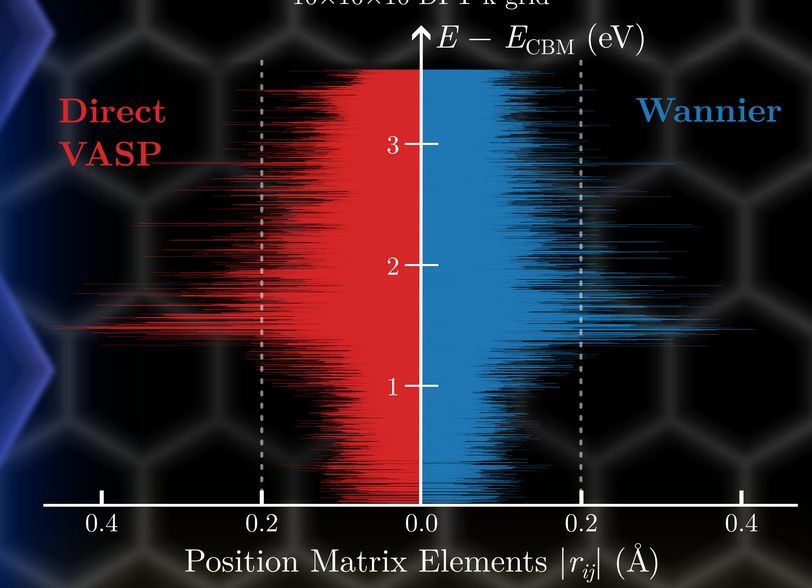
Band-structure

4×4×4 supercell

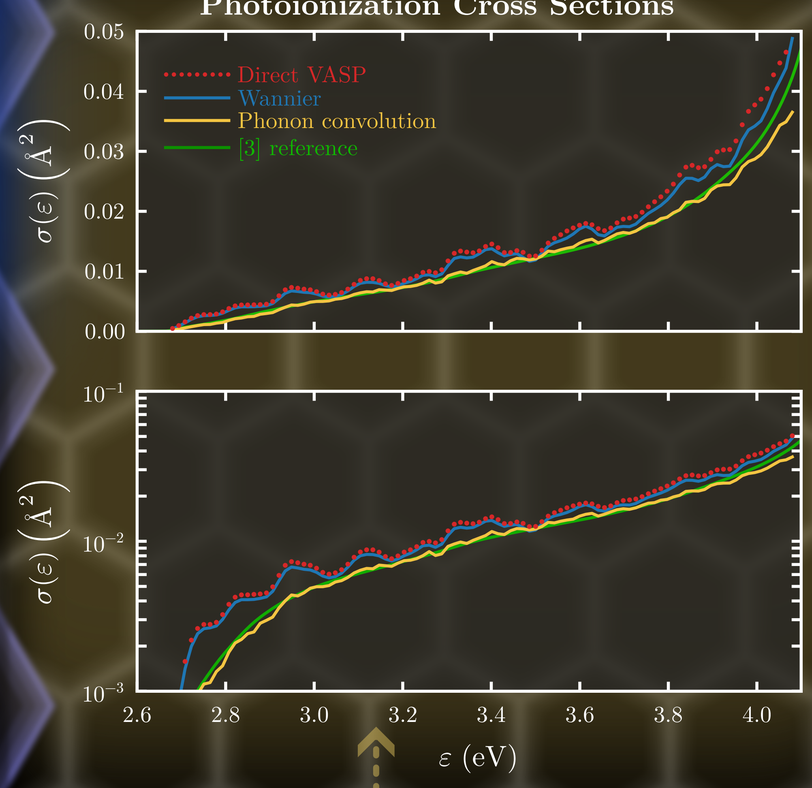


Matrix-element comparison

10×10×10 DFT k-grid



Photoionization Cross Sections



Wannier Interpolation Framework

Localized Wannier orbitals provide a compact real-space representation of the electronic structure. Hamiltonian and optical-transition matrix elements obtained from a coarse DFT calculation can be efficiently interpolated to arbitrarily dense k-point grids. Gauge-covariant velocity matrix elements can then be used to calculate accurate optical transition rates[4].

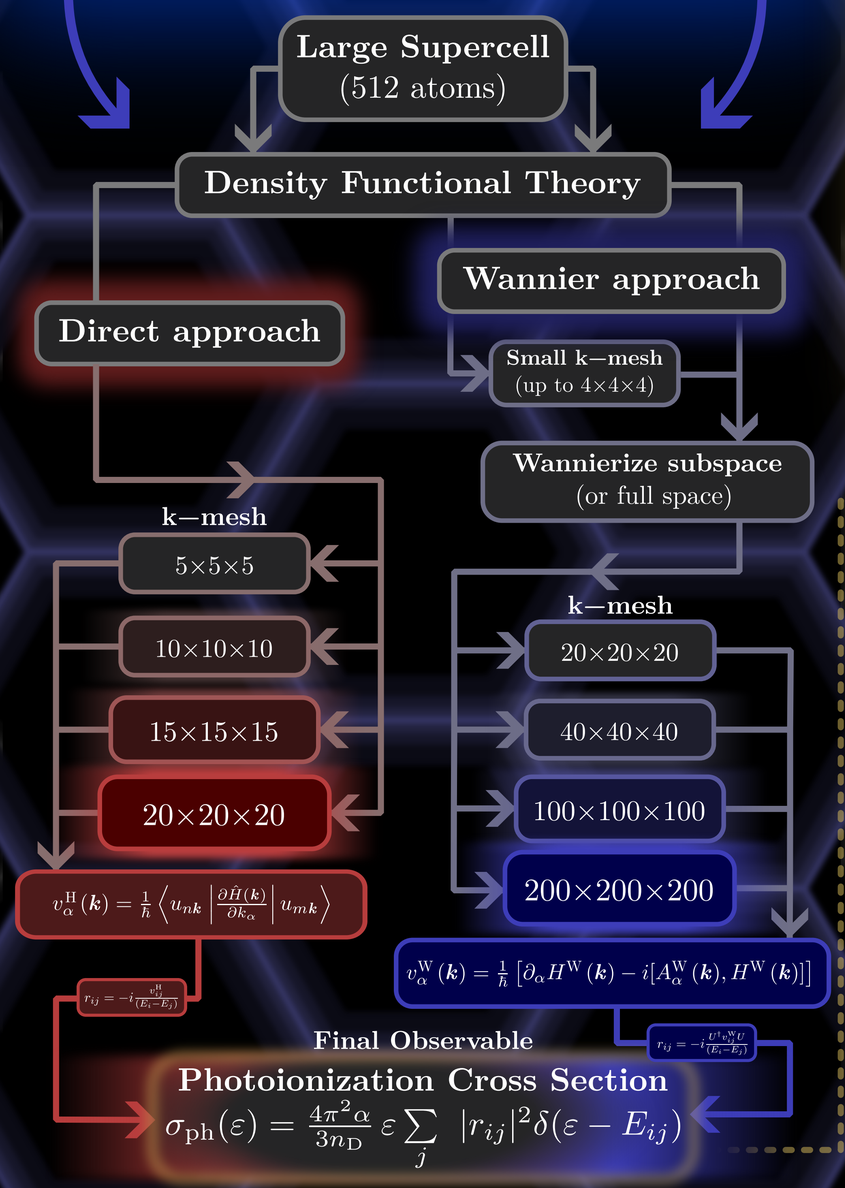
The resulting tight-binding model can be reused for dense Brillouin-zone sampling, convergence studies, and calculations employing computationally demanding exchange-correlation functionals, where direct evaluation on large k-point grids would be prohibitively expensive. This reduces computational cost by orders of magnitude while preserving the underlying ab initio description.

Direct First-Principles Modeling is Expensive

Accurate first-principles modeling of photoionization processes requires transition matrix elements between localized defect states and extended bulk continuum states. Capturing these processes reliably demands dense Brillouin-zone sampling together with large supercells to minimize finite-size effects.

In conventional density functional theory (DFT) calculations, optical transition matrix elements must therefore be evaluated on very dense k-point meshes, making such calculations computationally demanding for defect systems involving hundreds or thousands of electronic bands. Previous first-principles studies of NV-center photoionization relied on direct plane-wave calculations of optical matrix elements and dense Brillouin-zone integration[3].

In this work, we address this challenge using a Wannier-based interpolation framework, enabling efficient evaluation of optical matrix elements and transition rates across dense k-space grids at substantially reduced computational cost.



Summary

- Wannier interpolation reproduces direct VASP band structures, position matrix elements, and photoionization cross sections.
- Dense Brillouin-zone sampling becomes computationally inexpensive while preserving ab initio accuracy.
- The framework enables efficient calculations for large defect supercells and computationally demanding exchange-correlation functionals.

References

[1] M. W. Doherty et al. Physics Reports 528.1 (2013): 1-45.
[2] N. Aslam et al. New Journal of Physics 15.1 (2013): 013064.
[3] L. Razinkovas et al. Physical Review B 104.23 (2021): 235301.
[4] X. Wang et al. Physical Review B 74.19 (2006): 195118