Beyond-DFT Electronic Structure: Spin-Orbit Coupling and Surface Defect Calculations

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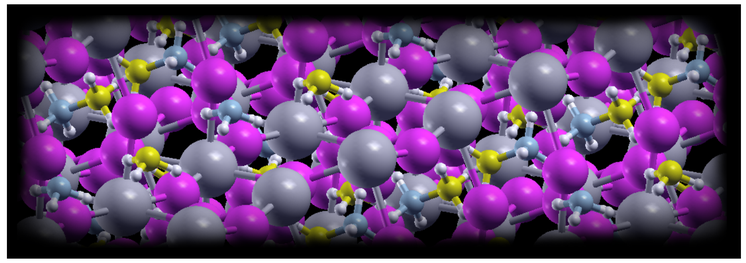
Introduction

Materials development is a critical component for advancements in applications such as solar energy production and next-generation computation hardware. Computational simulations allow new materials to be studied before fabrication, and also elucidate the physics behind new materials discoveries.

Density functional theory (DFT) is widely used, but fails in important situations. A new software developed by some of us, WEST [1], allows large systems to be simulated at a more accurate level of theory.

Here we present extensions and applications of WEST to new challenges in electronic structure theory:

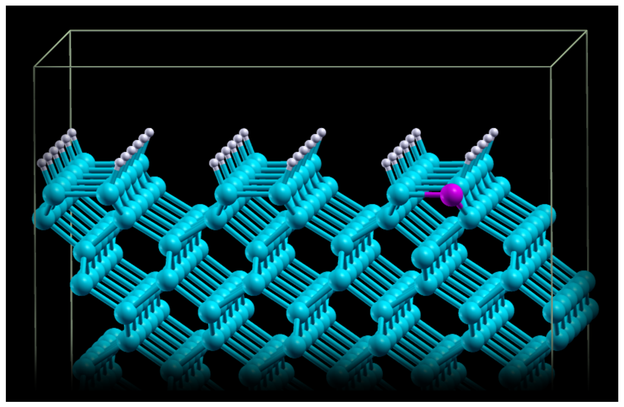
Spin-orbit coupling (SOC) interactions are included, so that heavy atoms can be treated accurately [2]. This also increases the computational difficulty, however.



Perovskites, such as $CH_3NH_3PbI_3$ here, are strongly influenced by SOC.

Defects on surfaces are studied for the purpose of investigating the utility of a dangling bond on a silicon surface for quantum information [3].

Dangling bonds (DBs) form when one hydrogen atom is missing from a hydrogen-passivated Si surface. These localized electronic states can be created and manipulated with an STM.



A perspective view of a Si(100) surface. The atom containing the DB is highlighted.

References and Acknowledgements

[1] M. Govoni and G. Galli, "Large Scale GW Calculations." JCTC **11** 2680 (2015). WEST is available at http://west-code.org/

[2] P. Scherpelz, M. Govoni, I. Hamada, and G. Galli, "Implementation and Validation of Spin-Orbit Coupling in Large Scale GW Calculations." In preparation.

[3] P. Scherpelz and G. Galli, "Electronic Structure of Dangling Bonds in H-passivated Si(100)." In preparation.

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The GW Approximation and Its Extension to Spin-Orbit Coupling

WEST uses many-body perturbation theory (MBPT) to correct results from DFT. Specifically, it uses the GW approximation to the Dyson equation:

$$\Sigma^\sigma = \overset{W_{\mathrm{RPA}}}{\overset{\frown}{\underset{\longrightarrow}{}}}\ G^\sigma_{\mathrm{KS}}$$

Here the new energy, E^{QP}, depends on a self-consistent solution to a self-energy-based correction to the Kohn-Sham (DFT) energy ϵ^{KS}:

$$E^{\mathrm{QP}}_{n\mathbf{k}\sigma} = \epsilon^{\mathrm{KS}}_{n\mathbf{k}\sigma} + \langle\psi_{n\mathbf{k}\sigma}|\hat{\Sigma}^\sigma(E^{\mathrm{QP}}_{n\mathbf{k}\sigma})|\psi_{n\mathbf{k}\sigma}\rangle - \langle\psi_{n\mathbf{k}\sigma}|\hat{V}^\sigma_{\mathrm{xc}}|\psi_{n\mathbf{k}\sigma}\rangle\,.$$

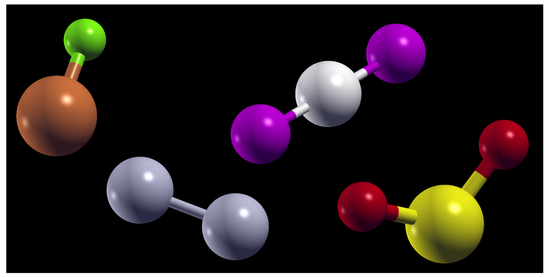
Spin-orbit interactions require each electron to have both an up-spin and down-spin component to their wavefunctions. Pseudopotentials, representing core electrons in each ion, are modified to include spin-orbit interactions.

$$\psi_i \to \begin{pmatrix}\psi_i^\uparrow\\ \psi_i^\downarrow\end{pmatrix}, \qquad V_{\mathrm{pseudo}} \to V^{\sigma,\sigma'}_{\mathrm{pseudo}}.$$

Validation of Spin-Orbit Interactions in GW Calculations

Spin-orbit interactions between electrons are typically not significant in light elements, but become substantial in heavy elements such as mercury, lead, and tellurium.

We implemented SOC in WEST, and used a set of molecules containing heavy elements to perform validation. The vertical ionization potential (listed below in eV) was computed for 49 diatomic and triatomic molecules. The inclusion of spin-orbit coupling was shown to significantly improve the accuracy compared to experimental values.



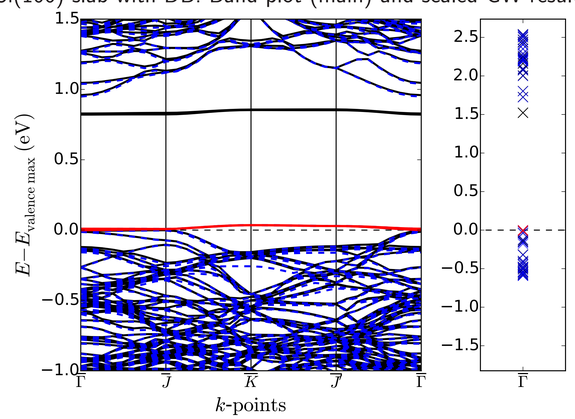
Molecules among those used for validation:
From left to right, CuF, Sb_2, CdI_2, SeO_2.

Molecule	PBE SR	PBE FR	PBE0 SR	PBE0 FR	Experiment
AgI	10.00	9.69	9.58	9.25	10.51
CaI_2	9.77	9.51	10.18	9.84	9.39
...	...	...	...	...	...
Y_2	4.28	4.36	4.58	4.94	4.96
ZnI_2	10.37	10.01	10.67	10.31	9.73
ME	0.02	-0.15	0.30	0.14	
MAE	0.58	0.47	0.54	0.41	
MARE	6.15%	4.80%	5.85%	4.33%	

The band gap of the perovskite $CH_3NH_3PbI_3$, shown to the left, was also computed with SOC as 1.50 eV, in good agreement with experiment (1.60 eV). Future use of the SOC code will include simulations of nanoparticles and bulk systems for photovoltaics.

Defects on Si(100) Surfaces for Quantum Information

12-layer Si(100) slab with DB: Band plot (main) and scaled GW results (right)

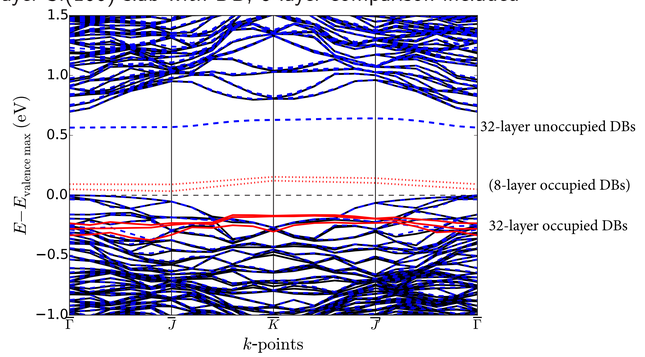


DFT and GW calculations were performed with silicon slabs of varying geometries to determine the location of DB states, and to what degree they are isolated from the bulk electronic states nearby. The position of these localized dangling bonds is quite sensitive to simulation details. In order to explore this more thoroughly, WEST was used to calculate the GW corrections to DFT band structure (above). Such corrections were ultimately small apart from an overall scaling.

Instead, it was found that the sample size (layer thickness) was critical in determining DB position (below).

A visualization of the wavefunction of the DB electronic state.

32-layer Si(100) slab with DB; 8-layer comparison included



Conclusion and Computing Resources

- Spin-orbit coupling in GW has been implemented and validated.
- Dangling bonds on silicon surfaces have only one isolated state, unoccupied in an undoped system. The other state hybridizes with the bulk.
- Both the level of theory, and the system size, have strong effects on computational results.

RCC's Midway cluster, with the Cluster Partnership Program, was used extensively for SOC validation and DFT simulations of silicon surfaces (500,000+ core-hours used). GW calculations for silicon surfaces and perovskites were done on the Mira supercomputer in the Argonne Leadership Computing Facility at Argonne National Laboratory.

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