Diagonalization without Diagonalization: A Direct Optimization Approach for Solid-State Density Functional Theory

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We present a novel approach to address the challenges of variable occupation numbers in direct optimization of solid-state density functional theory (DFT).[1] By parameterizing both the eigenfunctions and the occupation matrix, our method minimizes the free energy with respect to these parameters. As the stationary conditions require the occupation matrix and the Kohn-Sham Hamiltonian to be simultaneously diagonalizable, this leads to the concept of "self-diagonalization," where, by assuming a diagonal occupation matrix without loss of generality, the Hamiltonian matrix naturally becomes diagonal at stationary points. Our method incorporates physical constraints on both the eigenfunctions and the occupations into the parameterization, transforming the constrained optimization into an fully differentiable unconstrained problem, which is solvable via gradient descent.

This builds on our previous work in which the traditional self-consistent field (SCF) approach (i.e. solving the Kohn-Sham equation to self-consistency) is converted to a direct-gradient-descent minimization of the total energy with respect to one-electron orbitals and an occupation function, subject to orthogonality constraints.[2-3]

At the heart of our method is a novel reparameterization of the orthogonality constraint by QR decomposition.[2] Our programs are written using Google's JAX deep-learning framework and are designed to be end-to-end differentiable to provide additional tools that are essential for discovery and design of advanced materials. Ultimately any available input variable can be targeted by the direct-gradient-descent optimization function, enabling; alchemical analysis by making nuclear charge a variable; on-the-fly adjustment of density functional parameters; and incorporation of neural networks to train a wide range of solutions.

Experiments are carried out to demonstrate the efficacy of our approach on representative systems, an example of optimization from randomly initialized occupations to the expected Fermi Dirac distribution is presented in Figure 1. Finally, we discuss some of the cutting-edge applications we are actively working towards.

References

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[2] Tianbo Li, Min Lin, Zheyuan Hua, Kunhao Zhenga, Giovanni Vignalec , Kenji Kawaguchib, A. H. Castro Netoc, Kostya S. Novoselovc, Shuicheng Yan, ICLR, (2023).
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Figures

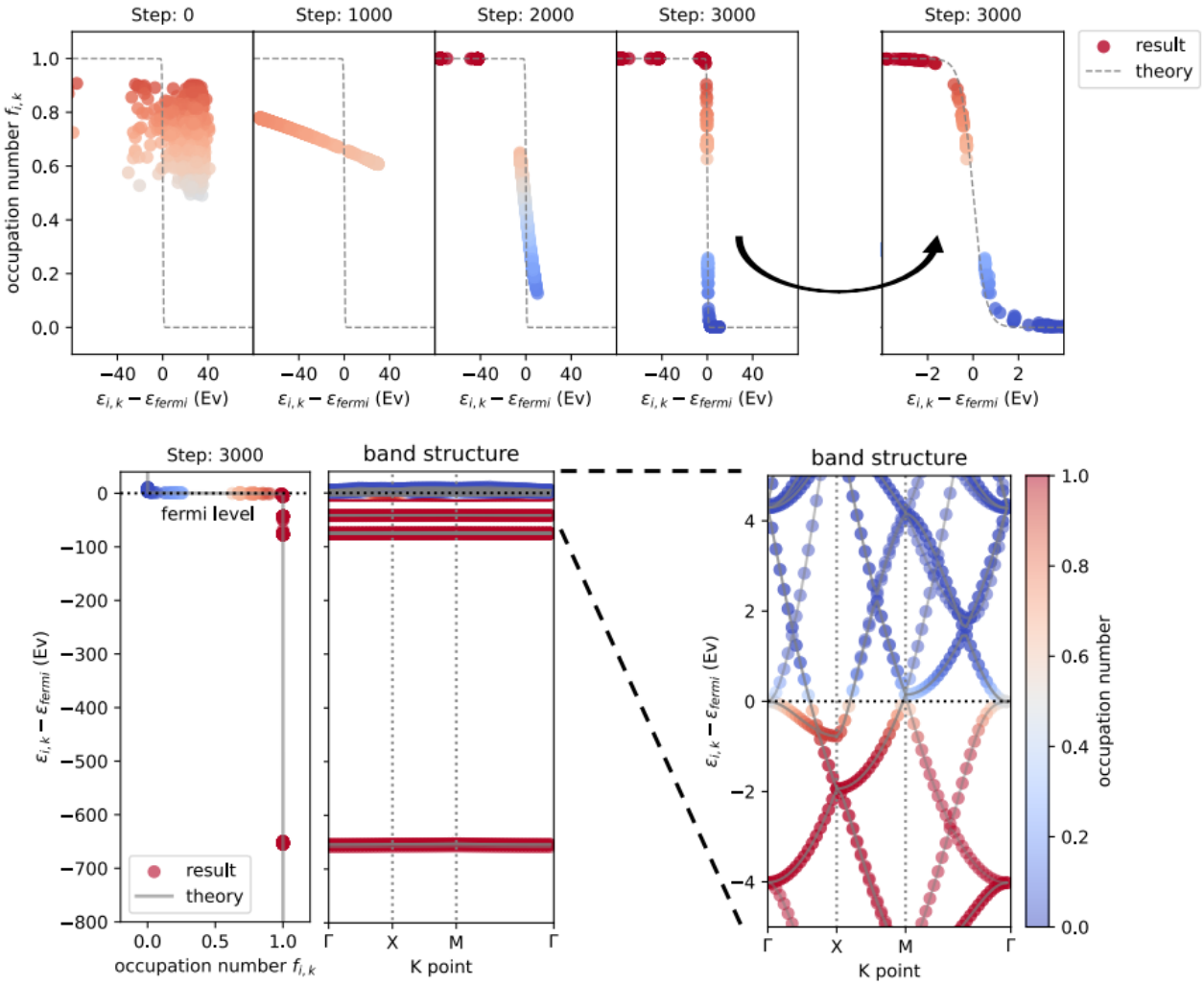

Figure 1: A visualization of the change of occupation numbers during the optimization for a FCC aluminum crystal. Top: Occupation numbers as a function of Hamiltonian diagonal matrix elements relative to the Fermi level (εi(k) − εfermi). Each point represents a diagonal element-occupation number pair for a potentially occupied orbital. The color indicates the value of the occupation number, with red representing 1 and blue representing 0. A theoretical Fermi-Dirac distribution is shown as a dotted line. The occupation number distributions are displayed at steps 0, 1000, 2000, and 3000. The rightmost figure focuses on the eigen-values near the Fermi level within a narrow energy range (x-axis) at step 3000. Bottom: An illustration of the band structure of a metal (aluminum based on an FCC conventional unit-cell) and its relation to the occupation numbers.