



An efficient method for hybrid density functional calculation with spin–orbit coupling

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ABSTRACT

In first-principles calculations, hybrid functional is often used to improve accuracy from local exchange correlation functionals. A drawback is that evaluating the hybrid functional needs significantly more computing effort. When spin–orbit coupling (SOC) is taken into account, the non-collinear spin structure increases computing effort by at least eight times. As a result, hybrid functional calculations with SOC are intractable in most cases. In this paper, we present an approximate solution to this problem by developing an efficient method based on a mixed linear combination of atomic orbital (LCAO) scheme. We demonstrate the power of this method using several examples and we show that the results compare very well with those of direct hybrid functional calculations with SOC, yet the method only requires a computing effort similar to that without SOC. The presented technique provides a good balance between computing efficiency and accuracy, and it can be extended to magnetic materials.

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1. Introduction

Density functional theory (DFT) is a powerful method for predicting properties of materials such as crystal structures, electronic bands, phonon dispersions and other physical quantities. Practically, using appropriate exchange correlation (XC) functional is very important for accuracy, especially for predicting band gaps of materials. It is well known that the local density approximation (LDA) and general gradient approximation (GGA) XC functionals tend to severely underestimate band gaps [1]. Consequently, hybrid functionals (HF) such as PBE0[2–5], HSE03 and HSE06[6–9] were proposed and they often predict very good band gap values comparable to experiments. A drawback of HF is that it needs very significant computing resources, generally several orders of magnitude more compared to that of LDA or GGA.

In recent years, materials with strong spin–orbit coupling (SOC) have attracted great attention, including topological insulators [10,11] Bi₂Se₃ [12], silicene [13,14], germanene [13,14], stanene [13–15], BiH [16,17], ZrTe₅ [18], Bi₄Br₄ [19], ZrSiO [20], photoelectric materials PbI₂ [21] and BiOCl [22], two-dimensional group-VI_B transition metal dichalcogenides MoS₂, MoSe₂, WS₂, and WSe₂ [23], III_A–V_A direct band-gap semiconductors with heavy elements GaSb and InSb [24], etc. DFT calculations including SOC involve non-collinear spin which requires at least eight times more computing time as compared to that without SOC, due

to the $O(N^3)$ scaling for solving the Kohn–Sham DFT equations (KS-DFT). Since many of these SOC materials are semiconductors, HF calculations are desired to more accurately predict their band gaps and electronic structures. Unfortunately, HF+SOC calculations are numerically intractable thus rarely used – unless the unit cell is extremely small, due to the huge computational demand. It is the purpose of this paper to report a practical solution to this problem.

In particular, we propose an efficient approximate technique for HF+SOC calculations based on a mixed linear combination of atomic orbital (LCAO) scheme. The mixed LCAO Hamiltonian is constructed by two parts: an SOC-free part whose parameters are obtained from HF calculations without SOC, and an SOC part whose parameters are obtained from GGA+SOC calculations (DFT at the GGA level with SOC). Applying this approach to several non-magnetic materials, the results are demonstrated to be very close to those of direct HF+SOC calculation and much more accurate than the GGA+SOC calculation. Importantly, the required computing time of the mixed LCAO technique is comparable to that of HF calculation without SOC.

In the rest of the work, the DFT calculations are performed using the projector augmented wave method implemented in VASP [25]. The Perdew–Burke–Ernzerhof (PBE) parametrization of GGA functional [26,27] and Heyd–Scuseria–Ernzerh hybrid functional (HSE06) [6–9] are used in the DFT calculations, and the VASP2WANNIER90 interface [28–30] is used to obtain the LCAO parameters from the DFT results. Since numerical calculations are for the purpose of demonstrating the mixed LCAO technique, structure optimization is omitted.

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2. The method

WANNIER90 [28,29] is used to construct LCAO or Wannier-bases Hamiltonian from DFT calculations, and the resulting LCAO Hamiltonian can reproduce the original energy dispersion very well. We start by constructing an LCAO Hamiltonian to treat HF+SOC using DFT calculations.

For a given system, the required computing effort is most demanding for HF+SOC, followed by HF without SOC and next followed by GGA+SOC. Clearly and as explained in the Introduction, if HF+SOC were computationally affordable in general, the work of this paper would not be necessary. That is not the case. In the following we utilize HF without SOC and GGA+SOC to construct a mixed LCAO Hamiltonian H^{MIX} which we show to be a very good approximation to $H^{\text{HF+SOC}}$. In particular, H^{MIX} has two terms, H_0^{HF} which is obtained from HF without SOC, and $H_{\text{so}}^{\text{GGA}}$ which is obtained from GGA+SOC,

$$H^{\text{MIX}} = H_0^{\text{HF}} + H_{\text{so}}^{\text{GGA}}. \quad (1)$$

Clearly, constructing H^{MIX} only consumes a time that is comparable to HF without SOC, thus much more efficient than that of a full HF+SOC calculation. The fact that H^{MIX} compare very well with direct HF+SOC calculations (see below), suggests that the mixed LCAO scheme provides a viable approximation for the complicated HF+SOC analysis.

On the technical side, while H_0^{HF} can be constructed directly from DFT calculation of HF without SOC, $H_{\text{so}}^{\text{GGA}}$ is obtained from DFT of GGA+SOC involving a procedure for separating out the SOC contributions. The latter procedure and an associated technical detail are discussed in the following two subsections.

2.1. Separating out the SOC contribution

The Hamiltonian H of SOC systems can be divided into a non-SOC term H_0 plus the SOC term H_{so} :

$$H = H_0 + H_{\text{so}}. \quad (2)$$

In LCAO representation, H_0 involves on-site energy and hopping integral between different atomic orbitals, and H_{so} comes from SOC effects.

In the spin-up and spin-down bases $|\uparrow\rangle$ and $|\downarrow\rangle$, the non-SOC term H_0 can be written as a diagonal 2×2 matrix:

$$H_0 = \begin{pmatrix} H_0^\uparrow & 0 \\ 0 & H_0^\downarrow \end{pmatrix}. \quad (3)$$

For simplicity, we consider non-magnetic systems in the rest of this work, but extension to magnetic system can be readily made without fundamental difficulty. For non-magnetic materials, $H_0^\uparrow = H_0^\downarrow$.

For the SOC term H_{so} , its original operator form is:

$$H_{\text{so}} = \frac{\hbar}{4m_0^2c^2} (\nabla V \times \mathbf{p}) \cdot \mathbf{s} \equiv \xi \mathcal{L} \cdot \mathbf{s}, \quad (4)$$

where \hbar is the reduced Planck constant, m_0 is the bare mass of electron, c is the velocity of light, $V(\mathbf{r})$ is the potential energy, \mathbf{p} the momentum, and \mathbf{s} the vector of Pauli matrices representing the spin degrees of freedom. For clarity we define a constant $\xi \equiv \hbar/(4m_0^2c^2)$ and a vector operator $\mathcal{L} \equiv \nabla V \times \mathbf{p}$. H_{so} can then be rewritten in the following matrix form:

$$H_{\text{so}} = \xi (\mathcal{L}_x s_x + \mathcal{L}_y s_y + \mathcal{L}_z s_z) \\ = \xi \begin{pmatrix} \mathcal{L}_z & \mathcal{L}_x - i\mathcal{L}_y \\ \mathcal{L}_x + i\mathcal{L}_y & -\mathcal{L}_z \end{pmatrix} \equiv \begin{pmatrix} H_{\text{so}}^{\uparrow\uparrow} & H_{\text{so}}^{\uparrow\downarrow} \\ H_{\text{so}}^{\downarrow\uparrow} & H_{\text{so}}^{\downarrow\downarrow} \end{pmatrix}, \quad (5)$$

in which $H_{\text{so}}^{\downarrow\downarrow} = -H_{\text{so}}^{\uparrow\uparrow}$ and $H_{\text{so}}^{\downarrow\uparrow} = H_{\text{so}}^{\uparrow\downarrow}$.

According to Eq. (2) to Eq. (5), the total Hamiltonian for a non-magnetic system with SOC is:

$$H \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} H_0^\uparrow & 0 \\ 0 & H_0^\downarrow \end{pmatrix} + \begin{pmatrix} H_{\text{so}}^{\uparrow\uparrow} & H_{\text{so}}^{\uparrow\downarrow} \\ H_{\text{so}}^{\downarrow\uparrow} & -H_{\text{so}}^{\uparrow\uparrow} \end{pmatrix}. \quad (6)$$

Then, from Eq. (6), we can separate the total Hamiltonian H to obtain H_0 and H_{so} as the following:

$$H_0 = \begin{pmatrix} (H_{11} + H_{22})/2 & 0 \\ 0 & (H_{11} + H_{22})/2 \end{pmatrix}, \quad (7)$$

$$H_{\text{so}} = \begin{pmatrix} (H_{11} - H_{22})/2 & H_{12} \\ H_{21} & -(H_{11} - H_{22})/2 \end{pmatrix}. \quad (8)$$

Hence, after obtaining the LCAO Hamiltonian $H^{\text{GGA+SOC}}$ from the corresponding DFT calculation, its SOC part $H_{\text{so}}^{\text{GGA}}$ can be separated out using Eq. (8).

2.2. Mixing the Hamiltonian

With the obtained non-SOC part H_0^{HF} and SOC part $H_{\text{so}}^{\text{GGA}}$, the mixed LCAO Hamiltonian H^{MIX} that approximates HF+SOC is determined by Eq. (1). Hereinafter we use the HSE functional for HF, and PBE functional for GGA. Then Eq. (1) becomes

$$H^{\text{MIX}} = H_0^{\text{HSE}} + H_{\text{so}}^{\text{PBE}}. \quad (9)$$

The “mixing” procedure appears to be a simple addition. However it should be noted that only when H_0^{HSE} and $H_{\text{so}}^{\text{PBE}}$ are constructed under the same bases can they be added directly. We achieve this by constructing H_0^{HSE} and $H_{\text{so}}^{\text{PBE}}$ in the same bases $|\tilde{\varphi}_{mk}\rangle$, and details are presented in Appendix A. This way, we finally constructed the mixed Hamiltonian H^{MIX} to treat HSE+SOC.

3. Results, analysis and discussion

Having constructed H^{MIX} to efficiently treat HSE+SOC, in this section we demonstrate its accuracy using several material systems. Predicting band gap is important, which is one of the reasons to use HSE in the first place [6–9]. We calculated band gaps for eight semiconductor materials having heavy elements thus large SOC, including two-dimensional (2D) mono-layers of PbI_2 , WSe_2 , BiH , Bi_4I_4 and Bi_4Br_4 ; 3D crystals BiOCl , GaSb , and InSb [24]. The SOC effect is important for these materials, especially for their band gaps.

For the eight materials, we performed (very time-consuming) direct HSE+SOC calculations and using the results, we constructed an LCAO Hamiltonian $H^{\text{HSE+SOC}}$; this would not be possible without the full direct HSE+SOC calculation. Then, we constructed H^{MIX} following the procedure in the last section which does not require full HSE+SOC calculation. The three sets of results are compared: direct numerical data from full HSE+SOC calculations and from $H^{\text{HSE+SOC}}$, as well as from H^{MIX} .

First, band structures of the eight compounds calculated by our method via H^{MIX} of Eq. (9) is plotted in Fig. 1, together with those from the direct HSE+SOC calculation and its fitting $H^{\text{HSE+SOC}}$. The full HSE+SOC data are presented in black circles and the bands from $H^{\text{HSE+SOC}}$ are in thick red lines; these are used as benchmarks to compare to our results by H^{MIX} which are presented in thin blue lines. We can see that the bands calculated by our method via H^{MIX} of Eq. (9) (thin blue lines) are qualitatively consistent to the benchmark results for all cases. In particular, band dispersions by H^{MIX} and the benchmark $H^{\text{HSE+SOC}}$ agree well for PbI_2 , WSe_2 , GaSb , and InSb ; and the agreement is somewhat reduced for BiOCl , BiH , Bi_4I_4 , and Bi_4Br_4 . In the latter cases, although the heavy element Bi gives rise to some quantitative difference, there is no qualitative discrepancy for the full range of the Brillouin zone.

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