Calculation of Berry curvature using non-orthogonal atomic orbitals

Gan Jin\textsuperscript{1,2}, Daye Zheng\textsuperscript{1,2} and Lixin He\textsuperscript{1,2,}\textsuperscript{*}

\textsuperscript{1} Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, Anhui, 230026, People’s Republic of China
\textsuperscript{2} Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, 230026, People’s Republic of China

E-mail: helx@ustc.edu.cn

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Abstract

We present a derivation of the full formula to calculate the Berry curvature on non-orthogonal numerical atomic orbital (NAO) bases. Because usually, the number of NAOs is larger than that of the Wannier bases, we use an orbital contraction method to reduce the basis sizes, which can greatly improve the calculation efficiency without significantly reducing the calculation accuracy. We benchmark the formula by calculating the Berry curvature of ferroelectric BaTiO\textsubscript{3} and bcc Fe, as well as the anomalous Hall conductivity for Fe. The results are in excellent agreement with the finite-difference and previous results in the literature. We find that there are correction terms to the Kubo formula of the Berry curvature. For the full NAO base, the differences between the two methods are negligibly small, but for the reduced bases sets, the correction terms become larger, which may not be neglected in some cases. The formula developed in this work can readily be applied to the non-orthogonal generalized Wannier functions.

Keywords: Berry curvatures, anomalous Hall effect, non-orthogonal atomic orbitals

\textsuperscript{*} Author to whom any correspondence should be addressed.

1. Introduction

Berry curvature is of fundamental importance for understanding some basic properties of solid materials and is essential for the description of the dynamics of Bloch electrons \cite{1,2}. It acts as a magnetic field in momentum space, which leads to some anomalous transport effects, including the first order \cite{1,3–8}, and second order \cite{9–13} anomalous Hall effects (AHE). It may introduce shift current in polar materials \cite{14–17}. Berry curvature also plays a crucial role in the classification of topological materials \cite{18–20}.

The first-principles calculations of the Berry curvature and the AHC have been reviewed in reference \cite{21}. Especially, the Berry curvature and AHC have been calculated via the Kubo formula \cite{5,6}. However, this method requires to calculate band structures at very dense \textit{k} points, and sum over a large number of unoccupied states to converge the results. Therefore the computational cost is very high, even for simple materials. Vanderbilt and co-works developed a very efficient interpolation scheme \cite{22} to calculate Berry curvature and AHC \cite{23,24} based on maximally localized Wannier functions (MLWFs) \cite{25,26}, which has been demonstrated to calculate the AHC to very high accuracy with only a tiny fraction of time of the original Kubo formula. However, it is not always easy to construct high-quality MLWFs, for complex systems. More seriously, in some cases, the MLWFs may not respect the point group symmetries of the crystal. Breaking of the symmetry may lead to qualitatively incorrect results. Special attention has to be paid to construct the symmetry adapted MLWFs \cite{26–28}.

Recently, Lee \textit{et al} derived the Kubo formula of optical matrices as well as Berry curvature using non-orthogonal numerical atomic orbitals (NAOs) \cite{29}. Wang \textit{et al} also derived the formula of Berry connection and its higher order deriva-
tives based on NAOs [17]. The NAOs are strictly localized and more importantly, have spherical symmetries, and therefore, no extra effort is needed to construct the symmetry-adapted MLWFs. This is of great advantage for the applications in complex systems. In this work, we derive the full formula to calculate the Berry curvature bases on NAOs [30].

The derivation of Berry curvature for non-orthogonal bases is transparent for people who are not familiar with the orthogonal NAO bases similar to that of the orthogonal Wannier bases. In this work, we derive the full formula to calculate the Berry curvature bases on NAOs [30]. We show in section 3. In section 4, we introduce a technique to reduce the number of NAOs to accelerate Berry curvature calculations.

2. Berry curvature in non-orthogonal atomic bases

2.1. Derivation of Berry curvature formula

The derivation of Berry curvature formula expressed in a non-orthogonal NAO basis is similar to that of the orthogonal Wannier bases, but there are also some considerable differences. The derivation is transparent for people who are not familiar with the Wannier functions. We start from the definition of the Berry curvature [2],

\[ \Omega_{\alpha}(k) = \nabla \times A_{\alpha}(k), \]

where,

\[ A_{\alpha} = i \langle u_{nk} | \nabla_{k} | u_{mk} \rangle \]

is the Berry connection, and \( u_{nk} \) are the cell-periodic Bloch functions, whose expression on a NAO basis is given by equation (A.5) in the appendix.

More generally, one may generalize the above definition of Berry connection and Berry curvature to a multi-bands case,

\[ A_{nm,\alpha}(k) = i \langle u_{nk} | \partial_{\alpha} u_{mk} \rangle, \]

and

\[ \Omega_{nm,\alpha,\beta}(k) = \partial_{\alpha} A_{nm,\beta}(k) - \partial_{\beta} A_{nm,\alpha}(k) \]

\[ = i(\partial_{\alpha} u_{nk} | \partial_{\beta} u_{mk}) - i(\partial_{\beta} u_{nk} | \partial_{\alpha} u_{mk}), \]

where \( \partial_{\alpha} = \partial / \partial k_{\alpha} \).

Substituting the cell-periodic wave functions equation (A.5) into equation (4), we have,

\[ i(\partial_{\alpha} u_{nk} | \partial_{\beta} u_{mk}) \]

\[ = i \sum_{\nu,\mu} C_{n\nu} C_{m\mu} \sum_{R} e^{ikR} \langle 0\nu | - r_{\alpha}(R_{\beta} - r_{\beta}) | R_{\mu} \rangle \]

\[ + i \sum_{\nu,\mu} (\partial_{\alpha} C_{n\nu}) S_{\nu\mu} (\partial_{\beta} C_{m\mu}) \]

\[ + \sum_{\nu,\mu} (\partial_{\alpha} C_{n\nu}) C_{m\mu} \sum_{R} e^{ikR} \langle 0\nu | r_{\beta} - R_{\beta} | R_{\mu} \rangle \]

\[ - \sum_{\nu,\mu} C_{n\nu} (\partial_{\beta} C_{m\mu}) \sum_{R} e^{ikR} \langle 0\nu | r_{\alpha} | R_{\mu} \rangle \]

To simplify the above equation, we introduce a dipole matrix \( A_{R}^{R} \), as follows,

\[ A_{\nu\mu,\alpha}(k) = \sum_{R} e^{ikR} \langle 0\nu | r_{\alpha} | R_{\mu} \rangle, \]

where the superscript ‘\( R \)’ in \( A_{R}^{R} \) refers to the dipole matrix is summed over the lattice \( R \). This quantity is similar to the \( A_{W}^{W} \) in reference [22]. While it is somehow cumbersome to calculate the dipole matrix in the Wannier bases, \( A_{\nu\mu,\alpha}(k) \) can be easily calculated by two-center integrals on the NAO bases by taking the advantages of the spherical symmetry of the NAOs [32, 33].

One part of the contribution to the Berry curvature comes from the dipole matrix,

\[ \tilde{A}_{nm,\alpha} = C_{n}^{\dagger} A_{R}^{R} C_{m}, \]

which is due to the lack of inversion symmetry of the crystal.

The other contribution to the Berry curvature comes from the change of the Bloch wave function coefficient \( C(\mathbf{k}) \) with \( \mathbf{k} \). Following reference [22], we may also introduce a \( \mathbf{D} \) matrix in the non-orthogonal NAO bases, as follows,

\[ D_{nm,\alpha} = C_{n}^{\dagger} S(\partial_{\alpha} C_{m}). \]

There are useful relations between \( \tilde{A} \) and \( \tilde{A}^{\dagger} \), \( \mathbf{D} \) and \( \mathbf{D}^{\dagger} \), and the proof is given in the appendix.

\[ \tilde{A}_{nm,\alpha} - (\tilde{A})^{\dagger}_{nm,\alpha} = -i \tilde{S}_{nm,\alpha} \]

\[ D_{nm,\alpha} + (D)^{\dagger}_{nm,\alpha} = -\tilde{S}_{nm,\alpha} \]

where

\[ \tilde{S}_{nm,\alpha} = C_{n}^{\dagger} (\partial_{\alpha} S) C_{m}. \]

For the orthogonal Wannier bases, where \( \tilde{S}_{nm,\alpha} = 0 \), we have \( \tilde{A}_{nm,\alpha} = (\tilde{A})^{\dagger}_{nm,\alpha} \), and \( D_{nm,\alpha} = -(D)^{\dagger}_{nm,\alpha} \), i.e., \( \tilde{A} \) is Hermitian, and \( \mathbf{D} \) is anti-Hermitian in the orthogonal Wannier bases. It is easy to show that Berry connection \( \mathbf{A}_{nm} = i \mathbf{D}_{nm} + \tilde{\mathbf{A}}_{nm} \).

We can simplify equation (5) by inserting the identity matrix,

\[ I = \sum_{n} C_{n} C_{n}^{\dagger} S = \sum_{n} S C_{n} C_{n}^{\dagger}. \]

For example, for the second term on the right side of equation (5), we have,
After some derivation, we obtain the formula of the Berry curvature in the non-orthogonal NAO bases,

\[
\Omega_{\alpha\nu\beta} = \Omega_{\alpha\nu\beta} + i \left( D_{\alpha} D_{\beta} - D_{\beta} D_{\alpha} \right)_{nm} + \left( \bar{D}_{\alpha} \bar{A}_{\nu} + \bar{A}_{\alpha} D_{\nu} \right)_{nm} - \left( \bar{D}_{\beta} \bar{A}_{\nu} + \bar{A}_{\beta} D_{\nu} \right)_{nm},
\]

(14)

where

\[
\Omega_{\alpha\nu\beta} = i \sum_{\nu\beta} C_{\mu\nu} C_{\mu\beta} \sum_{\mathbf{R}} e^{i \mathbf{R} \cdot \mathbf{r}} \left\{ \delta_{\nu\beta} f_{\mu} \bar{S}_{\mu\alpha} \delta_{\alpha\beta} \right\}.
\]

(15)

We note that equation (14) is very similar to equation (27) in reference [22], but also with notable differences. Because A is not Hermitian, and D is not anti-Hermitian for the non-orthogonal NAO bases, we cannot write the equation in the form of commutators as equation (27) in reference [22].

2.2. Calculation of D matrix

From the linear response theory given in appendix A, one obtains [17] (for \( m \neq n \)),

\[
D_{\alpha\nu\beta} = \frac{H_{\alpha\nu\beta} - E_{\nu k} \bar{S}_{\nu\alpha}}{E_{\nu k} - E_{\alpha k}},
\]

(16)

where

\[
H_{\alpha\nu\beta} = C_{\alpha}^*(\partial_{\nu} H) C_{\beta}.
\]

(17)

There is some freedom to choose D_{\alpha\nu\beta}. However, since D_{\alpha\nu\beta} = C_{\alpha}^*(k)S(k)\delta_{\alpha\nu}C_{\beta}(k), it must satisfy the following constrain,

\[
\bar{D}_{\alpha\nu} + D_{\alpha\nu} = -C_{\alpha}^*(k)\delta_{\alpha\nu}C_{\beta}(k).
\]

(18)

For the orthogonal bases, one can just take D_{\alpha\nu\beta} = 0 [22]. However, this choice is generally not feasible for the non-orthogonal base. Instead, we can use the parallel transport gauge, A_{\alpha\nu\beta} = i (\bar{u}_{\alpha\beta} \partial_{\alpha} u_{\nu\beta}) = 0, i.e., D_{\alpha\nu\beta} = iA_{\alpha\nu\beta}. Using the relation, A_{\alpha\nu\beta} = iD_{\alpha\nu\beta} + \bar{A}_{\alpha\nu\beta}, and the relations in equations (9) and (10) for m = n, we can easily prove that the parallel transport gauge, automatically satisfies the constrain of equation (18). Note that the parallel transport gauge defined here for the cell-periodic functions is different from the ‘parallel transport gauge’ in reference [22] for the state vectors \( \langle \phi_{\alpha} \rangle \) in the ‘tight-binding space’ of the MLWFs. As shown in the next section, D_{\alpha\nu\beta} would not appear in the Berry curvature calculations, and therefore the choice of particular gauge would not change the Berry curvature, but it may affect the Berry connection.

2.3. Total Berry curvature

The total Berry curvature is calculated as follows,

\[
\Omega_{\alpha\nu\beta}(k) = \sum_{n} f_{n}(k) \Omega_{nm\alpha\nu\beta}(k),
\]

(19)

where, \( f_{n} \) is the Fermi occupation function. To avoid the numerical instability caused by the canceling contributions of large values of \( D_{\alpha\nu\beta} \) (see equation (16)), originated from the small energy splitting between a pair of occupied bands \( n \) and \( m \), we would like to operate the summation between the occupied and unoccupied states, similar to the MLWF interpolation method [22]. However, this is a little bit more tricky for the non-orthogonal bases.

We first rewrite equation (14) by replacing \( D_{\alpha} \) and \( D_{\beta} \) with \( D_{\alpha} \) and \( D_{\beta} \) using equation (10),

\[
\Omega_{\alpha\nu\beta}(k) = \sum_{n} f_{n}(k) \Omega_{nm\alpha\nu\beta}(k) + \sum_{n,m} (f_{n} - f_{m}) \left[ D_{nm\alpha\nu\beta} \right] + \left[ D_{\alpha\nu\beta} \bar{A}_{\alpha\nu\beta} \right] - i \left[ D_{\alpha\nu\beta} \bar{A}_{\nu\alpha} \right] - \left[ \bar{S}_{\alpha\nu\beta} \bar{A}_{\alpha\nu\beta} \bar{S}_{\alpha\nu\beta} \right],
\]

(20)

where the first four terms closely resemble those of equation (27) in reference [22]. One can proof the Berry curvature defined above is gauge invariant (see appendix A.3). In this form, the contribution from D matrices are exactly canceled for a pair of occupied states \( n, m \). The last term is due to the non-orthogonality of the NAO bases. We can therefore calculate the total Berry curvature \( \Omega_{\alpha\nu\beta} \) as [22],

\[
\Omega_{\alpha\nu\beta}(k) = \sum_{n} f_{n}(k) \Omega_{nm\alpha\nu\beta}(k) + \sum_{n,m} (f_{n} - f_{m}) \left[ D_{nm\alpha\nu\beta} \right] + \left[ D_{\alpha\nu\beta} \bar{A}_{\alpha\nu\beta} \right] - \left[ \bar{S}_{\alpha\nu\beta} \bar{A}_{\alpha\nu\beta} \bar{S}_{\alpha\nu\beta} \right],
\]

(21)

We immediately see that for the orthogonal bases, the last line in the above equation vanishes, and the total Berry curvature reduces to equation (32) in reference [22].

2.4. Comparison with the naive Kubo formula

The Berry curvatures are often calculated via the naive Kubo formula [21, 29],

\[
\Omega_{\alpha\nu\beta}(k) = -2 \text{Im} \sum_{n} \sum_{m} \sum_{\text{occ}} \frac{v_{\text{occ}} v_{\text{occ}}}{(E_{\text{occ}} - E_{\text{occ}})^2},
\]

(22)

where \( v_{\text{occ}} \) is the velocity matrix. According to reference [34, 35], we have

\[
\frac{v_{\text{occ}}}{(E_{\text{occ}} - E_{\text{occ}})} = (\partial_{\nu} E_{\text{occ}}) \delta_{\mu n} - i(E_{\text{occ}} - E_{\text{occ}}) A_{\mu\nu\alpha},
\]

(23)

where the Berry connection \( A_{\mu\nu\alpha} = iD_{\mu\nu\alpha} + \bar{A}_{\mu\nu\alpha} \). One easily obtain the velocity operator matrix for \( m \neq n \),

\[
\frac{v_{\text{occ}}}{(E_{\text{occ}} - E_{\text{occ}})} = H_{\mu\nu\alpha} - E_{\text{occ}} \delta_{\mu n} + i(E_{\text{occ}} - E_{\text{occ}}) A_{\mu\nu\alpha},
\]

(24)

which is identical to that derived in reference [29] via a different approach.
By comparing equations (21) and (22), one finds that the full Berry curvature actually includes some correction terms to the naive Kubo formula, i.e., $\Omega_{\alpha\beta} = \Omega^{\text{kubo}}_{\alpha\beta} + \Delta \Omega_{\alpha\beta}$, and,

$$
\Delta \Omega_{\alpha\beta} = \sum_n \bar{\Omega}_{nn,\alpha\beta} - i \sum_n \sum_m \bar{A}_{nm,\alpha} (\bar{A}^\dagger)_{mn,\beta} \left[ \bar{A}_{nm,\alpha} (\bar{A}^\dagger)_{mn,\beta} \right],
$$

where $\bar{\Omega}$ is defined in equation (15). These additional terms are also presented in the MLWF bases [22]. These correction terms come from the incompleteness of the tight-binding bases to the original Hilbert space [36, 37]. Even though the contributions of $\Delta \Omega_{\alpha\beta}$ are often very small, and sometimes negligible, it is still useful to have a strict formula to compare with. This will be further addressed in the following sections.

### 3. Results and discussion

We take BaTiO$_3$ and ferromagnetic Fe as examples to benchmark the calculation of the Berry curvature using NAOs. These choices represent two typical systems where Berry curvature is nonzero that either break the inversion symmetry (BaTiO$_3$) or time-reversal symmetry (Fe). While the SOC is not needed for BaTiO$_3$ to get nonzero Berry curvature, it is essential for Fe to have nonzero Berry curvature, which is well explained in reference [2].

#### 3.1. Computational details

We first perform self-consistent density functional theory calculation implemented in the atomic-orbital based ab-initio computation at UStc (ABACUS) code [30, 32]. The generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) [38] form is adopted. We adopt optimized norm-conserving Vanderbilt [39] multi-projector, SG15 pseudopotentials [40, 41].

For the BaTiO$_3$, the 5s$^2$5p$^6$5d$^1$6s$^1$ electrons for Ba, the 2s$^2$3p$^4$4s$^2$3d$^2$ electrons for Ti, and the 2s$^2$2p$^4$ electrons for O are treated as valence electrons. The cutoff energy for the wave function is set to 60 Ry. A $4 \times 4 \times 4$ $k$-mesh is used in the self-consistent calculations. The NAO bases for Ba, Ti, O are 4s2p2d, 4s2p2d1f, 2s2p1d, respectively.

For bcc Fe, the 3s$^2$3p$^6$4s$^2$3d$^6$ electrons are included self-consistently. Spin–orbit interactions are tuned on. The cutoff energy for the wave function is set to 120 Ry. A $4 \times 4 \times 4$ $k$-mesh is used in the self-consistent calculations. The NAOs of Fe is 4s2p2d1f.

After the self-consistent calculations, the tight-binding Hamiltonian $H$($R$) and overlap matrices $S$($R$) in the NAO bases, which are generated during the self-consistent calculations, are readily outputted and are used for the Berry curvature calculations.

#### 3.2. Berry curvature of BaTiO$_3$

As the first example, we calculate the Berry curvature of rhombohedral BaTiO$_3$ with space group $R3m$ (No. 160, Rhombohedral axes). The lattice constant $a = 4.081$ Å, and $\alpha = 89.66^\circ$.

The Berry curvatures calculated by equation (21) are shown in the black dashed lines. We compared the results to those calculated by the finite-difference (FD) method via equation (26).
Figure 2. (Upper panels) The Berry curvatures, (a) $\Omega_x$, (b) $\Omega_y$ and (c) $\Omega_z$ of BaTiO$_3$ along the high symmetry $k$ points. (Lower panels) The corrections to the Kubo formula, (d) $\Delta\Omega_x$, (b) $\Delta\Omega_y$ and (c) $\Delta\Omega_z$ along the high symmetry $k$ points. The red solid lines are calculated by FD, and the black dotted lines are results of the original bases, whereas the green dashed lines are the results of the reduced bases. (A.18), which are shown in the solid red lines. As we see, the Berry curvatures calculated by the equation (21) are in excellent agreement with the FD method.

Figures 2(d)–(f) show the differences $\Delta\Omega_{\alpha\beta}$ between this work and Kubo formula of BaTiO$_3$ along the $a$, $b$ and $c$-axes respectively, in black solid lines. As seen from the figure, $\Delta\Omega_{\alpha\beta}$ is extremely small, which are less than 1% of the total Berry curvature. These results suggest that the NAO bases used in the calculations are rather complete for this problem.

3.3. AHC of Fe

In this section, we calculate the Berry curvature and the AHC for bcc Fe. The lattice constant of bcc Fe is taken as $a = 2.870\,\text{Å}$. The band structure of Fe is shown in figure 1(b) in red solid lines around Fermi level $E_F = 0$.

The Berry curvature of bcc Fe along the $c$-axis is given in figure 3(a). The black dotted line is the Berry curvature calculated via equation (21), which is in excellent agreement with the Berry curvature calculated via FD method, shown in the red solid line. For most $k$ points, the Berry curvature is very small except at a few $k$ points, which have huge Berry curvature, due to the spin–orbit–split avoided crossings near the Fermi level [6, 22].

We then calculate the dc AHC [23, 24],

$$
\sigma_{xy} = -\frac{e^2}{\hbar} \sum_n \int_{BZ} \frac{dk}{(2\pi)^3} f_n(k) \Omega_n(z)(k). \tag{27}
$$

To calculate the AHC of bcc Fe, a 300 × 300 × 300 $k$-mesh is used and if the Berry curvature of a certain $k$ point is greater than 100 Å$^2$, the Berry curvature is recalculated at a refined 7 × 7 × 7 submesh around the $k$ point, following the scheme of reference [6, 22]. The calculated AHC for Fe is 738 (Ω cm)$^{-1}$. This result is in good agreement with 751 (Ω cm)$^{-1}$, obtained from full-potential all-electron calculations by Yao et al [6], which is also close to 756 (Ω cm)$^{-1}$ obtained from normal conserving pseudopotential calculations via Wannier interpolation techniques [22]. The Fe pseudopotential in reference [22] is specially optimized to reproduce the all-electron result of AHC, and the difference between this work and reference [22] might come from the different pseudopotentials used in the calculations.
The reduced NAOs atom positions or other high-symmetry points [27]. In contrast, the sets of the MLWFs is that their centers are not necessarily on the original bases, whereas the green dashed lines are results of the reduced bases.

![Figure 3](image)

**Figure 3.** (a) Berry curvature $\Omega_z$ of bcc Fe along the high symmetry $k$ points. (b) The corrections $\Delta\Omega_z$ to the Kubo formula. The solid red line is calculated by FD, and the black dotted lines are results of the original bases, whereas the green dashed lines are the results of the reduced bases.

4. Berry curvatures calculated with reduced basis sets

In the previous section, we showed that the Berry curvatures calculated by equation (21) are in excellent agreement with FD results. However, the NAO basis sets have too many orbitals compared to the Wannier bases, and therefore computationally more expensive. We would like to reduce the basis size to accelerate the calculations, but maintain the accuracy. The idea is to use reduced basis sets, to reproduce the band structures in a smaller energy window. This is done via a revised band interpolation technique [42] via NAOs.

To reduce the number of NAOs, we reconstruct a new set of NAOs as the linear combination of original on-site orbitals, i.e.,

$$|\tilde{\phi}_{I,\nu}\rangle = \sum_{\mu} U_{I,\nu \mu} |\phi_{I,\mu}\rangle,$$  \hspace{1cm} (28)

where $|\phi_{I,\mu}\rangle$ is the $\mu$th orbit of the $I$th atom. One of the problems of the MLWFs is that their centers are not necessarily on atom positions or other high-symmetry points [27]. In contrast, the reduced NAOs $|\tilde{\phi}_{I,\nu}\rangle$ are linear combinations of on-site NAOs, so they are still atom centered and strictly localized. The number $N_I$ of the reduced NAO bases $|\tilde{\phi}_{I,\nu}\rangle$, is less than the number $N_I$ of $|\phi_{I,\mu}\rangle$, $U_I$ is a real orthogonal matrix to keep the reduced NAOs real.

We obtained the reduced NAOs by minimizing the *spillage* between the wave functions calculated by original NAOs and the reduced basis set at a coarse $k$-mesh in a chosen energy window. Details of this process are given in appendix B.

4.1. BaTiO$_3$

Figure 1(a) compares the band structure of BaTiO$_3$ calculated by the original bases (solid red lines) and the reduced bases (black dashed lines). The reduced bases set is optimized by fitting the wave functions in the energy window of $-6$ to $4.8$ eV (The energy window is represented by a solid green line) which covers the lowest three bands above the Fermi level. A uniform grid of $8 \times 8 \times 8$ $k$-mesh is used to generate the reduced basis set. The reduced base has 38 orbitals compared to the 86 orbitals in the original bases. As we see from figure 1(a), the band structures calculated by the reduced bases are in excellent agreement with the original band structures within the energy window. The lower energy bands above the energy window also agree very well. For the bands far above the energy window, the agreement becomes worse as expected.

The Berry curvatures of BaTiO$_3$ calculated by the reduced bases are shown in green dashed lines in figures 2(a)–(c), compared to those calculated by the original bases. The overall agreement is rather good, with only small differences at some $k$-point.

We now check the $\Delta \Omega$ for the reduced bases, depicted in figures 2(d) and (e), which are shown in green dashed lines. We see that for the reduced basis, $\Delta \Omega$ is significantly larger than that of the full basis calculations, which suggests that if a reduced basis is used, the corrections to the Kubo formula may not be ignored in some cases. One may expect that if an even smaller non-orthogonal Wannier bases are used, the correction may have an even larger contribution, which cannot be ignored.

4.2. Bcc Fe

The reduced basis set of the figure 1(b) is optimized in the energy window of $-9 \sim 5$ eV, on a uniform grid of $8 \times 8 \times 8$ $k$-points. We obtain 28 orbitals (include spin) from the original 54 orbitals. The energy bands obtained by the reduced basis set are almost identical to the original bands. In fact, the agreement is still very well even outside the energy window, below 14 eV.

The Berry curvature $\Omega_z$ calculated by the reduced bases are also shown in figure 3(a) in the green dashed line compared to the original result. There are only very small differences between the results obtained by the original and reduced bases. The correction to the naive Kubo formula $\Delta \Omega_z$ for the reduced bases are shown in the green dashed line in figure 3(b). The correction is much larger than that for the original bases, shown in the black dotted line. However, the correction is still negligibly small compared to the total Berry curvature, because the dominant contribution to the contribution comes from the $D$–$D$ terms [22].

The AHC of bcc Fe calculated by the reduced basis set is $734 \,(\Omega \text{ cm})^{-1}$, which is in good agreement with that calculated by the full basis set $738 \,(\Omega \text{ cm})^{-1}$.
5. Summary

We derive the formula to calculate the Berry curvature using non-orthogonal NAOs. We find that there are some additional correction terms besides the usual Kubo formula. We calculate the Berry curvature of Rhombohedral BaTiO3 and bcc Fe, as well as the AHC for Fe. The results are in excellent agreement with the FD method. We develop a method that can significantly reduce the number of orbitals in the NAO bases but can still maintain the accuracy of the calculations. We also compare the Berry curvature and AHC calculated via our formula and the Kubo formula. We find for the original basis, the differences between the two methods are negligibly small, but for the reduced bases sets, the correction terms become larger. The methods developed in this work can be applied to non-orthogonal generalized Wannier functions.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Appendix A. Electronic structure by LCAO

In the NAO basis, the Hamiltonian matrix is calculated as,

$$H_{\mu\nu}(k) = \sum_{R} e^{ik\cdot R} \langle 0\nu|H|0\mu \rangle,$$

where $|0\nu \rangle$ is a short notation of the $\nu$th NAO in the $R$th unit cell, i.e., $\psi_\nu(r - \mathbf{R} - \tau_\nu)$, and $\tau_\nu$ is the center of the orbital. The Hamiltonian $H$ is self-consistently determined by the Kohn–Sham equations. In general, the NAOs are not orthogonal to each other, and their overlap matrix is

$$S_{\nu\mu}(k) = \sum_{R} e^{-ik\cdot R} \langle 0\nu|0\mu \rangle.$$

Therefore, in the NAO bases, the corresponding Kohn–Sham equation (under the converged charge density) is

$$H(k)C_{\mu}(k) = E_{\mu}(k)C_{\mu}(k).$$

The Bloch wave function is,

$$|\Psi_{\mu}(k)\rangle = \frac{1}{\sqrt{N}} \sum_{\nu} C_{\nu\mu}(k) \sum_{R} e^{ik\cdot R} |0\mu \rangle,$$

and the corresponding cell-periodic part is

$$|n_{\mu}(k)\rangle = \frac{1}{\sqrt{N}} \sum_{\nu} C_{\nu\mu}(k) \sum_{R} e^{ik\cdot R} |0\mu \rangle.$$

A.1. Linear response theory in non-orthogonal NAO bases

According to the perturbation theory, we derive the first-order term of equation (A.3) with respect to the parameter $k$ in the non-degenerate case,

$$[E_n - H] \partial_{\alpha}C_n = [\partial_{\alpha}H - E_n \partial_{\alpha}S - (\partial_{\alpha}E_n) S]C_n.$$

We use $\{C_m\}$ to expand $\partial_{\alpha}C_n$, i.e.,

$$\partial_{\alpha}C_n = \sum_m \left[C_m^\dagger S(\partial_{\alpha}C_m)\right] C_m.$$

Multiply $C_m^\dagger$ to the left of equation (A.6), we have

$$(E_n - E_m)C_m^\dagger S(\partial_{\alpha}C_n) = C_m^\dagger \left[\partial_{\alpha}H - E_n \partial_{\alpha}S\right] C_n.$$

We obtain for $m \neq n$,

$$C_m^\dagger S(\partial_{\alpha}C_n) \neq 0.$$

and can be determined by choice of a particular gauge as discussed in section 2.2.

A.2. Relations between $\bar{A}$ and $\tilde{A}^\dagger$, $D$ and $D^\dagger$

There are two useful relations between $\bar{A}$ with $\tilde{A}^\dagger$ and $D$ with $D^\dagger$ that appear in equations (9) and (10), respectively.

To prove equation (9), we note that, the conjugated form of equation (6),

$$(A^R)_{\mu\nu,\alpha} = \sum_{R} e^{-ik\cdot R} \langle 0\mu|\rho_{\alpha}\rangle_{0\nu}$$

$$= \sum_{R} e^{-ik\cdot R} \langle 0\mu|\rho_{\alpha} + R_{\alpha} - R_{\nu}\rangle_{0\nu}$$

$$= A^R_{\mu\nu,\alpha} + i(\partial_{\mu}S)_{\mu\nu}.$$

We can readily get the relation,

$$\bar{A}_{nm,\alpha} - (\tilde{A}^\dagger)_{nm,\alpha} = -i\tilde{S}_{nm,\alpha}.$$

Due to the orthonormal condition,

$$C_m^\dagger S(k)C_m (k = \delta_{mn},$$

at each $k$ point, we have $\partial_{\alpha} \left[C_m^\dagger S(k)C_m(k)\right] = 0$, i.e.,

$$\left(\partial_{\alpha}C_m^\dagger\right) S C_m + C_m^\dagger (\partial_{\alpha}S) C_m + C_m^\dagger (\partial_{\alpha}C_m) = 0.$$
which gives the relation equation (10),

\[
D_{nm,\alpha} + (D^\dagger)_{nm,\alpha} = -\tilde{S}_{nm,\alpha}.
\]  

(A.15)

A.3. Proof of gauge invariance of Berry curvature

We prove that the Berry curvature \(\Omega_{\mu}\) is defined in equation (20) is gauge invariant. When \(C_\mu\) is changed to \(C_\mu^\prime = e^{i\phi_\mu}C_\mu\), the corresponding \(D, S, A^\dagger\) matrix will change to,

\[
\tilde{D}_{nm,\alpha} = e^{i\phi_\mu - \phi_\mu^\prime}(D_{nm,\alpha} + iC_{nm,\alpha}^\prime \delta_{nm}),
\]

\[
\tilde{S}_{nm,\alpha} = e^{i\phi_\mu - \phi_\mu^\prime}S_{nm,\alpha},
\]

\[
(A^\dagger)_{nm,\alpha} = e^{i\phi_\mu - \phi_\mu^\prime}(A^\dagger)_{nm,\alpha}.
\]  

(A.16)

The fourth term in equation (20) becomes

\[
[D_{\alpha}, D_{\beta}]_{nm} = \sum_m (D_{nm,\alpha}D_{mn,\beta} - D_{nm,\beta}D_{mn,\alpha})
= \sum_m (D_{nm,\alpha} + iC_{nm,\alpha}^\prime \delta_{nm}) (D_{mn,\beta} + iC_{mn,\beta}^\prime \delta_{mn})
- \sum_m (D_{mn,\beta} + iC_{mn,\beta}^\prime \delta_{mn}) (D_{nm,\alpha} + iC_{nm,\alpha}^\prime \delta_{nm})
= \sum_m D_{nm,\alpha}D_{mn,\beta} - D_{nm,\beta}D_{mn,\alpha}
= [D_{\alpha}, D_{\beta}]_{nm},
\]

(A.17)

i.e., it is invariant under the gauge change. Similarly, we can prove that all other terms of equation (20) are also gauge invariant, and therefore the Berry curvature is gauge invariant.

A.4. Calculating the Berry curvature by finite difference

The Berry curvature can be calculated via the FD method, using the relationship between Berry phase and Berry curvature [2],

\[
\Delta \phi = \oint A(k)dk = \int_\Omega(k) \cdot dS.
\]  

(B.1)

We choose a small square loop around a \(k\) point in the Brillouin Zone and calculate the discretized Berry phase [43] of the loop. The Berry curvature at the given \(k\) point can be obtained as \(\Omega(k) \cdot \hat{n} = \Delta \phi / \Delta S\), where \(\hat{n}\) is the normal direction of the square loop and \(\Delta S\) is its area. In principles the Berry phase is correct only modulo 2\(\pi\). [2] But here, we have no ambiguity of chosen the correct branches, as \(\Delta \phi\) is significantly smaller than the quanta when \(\Delta S\) is very small.

Appendix B. Optimize the reduced bases

The reduced bases orbitals \(\{\hat{\phi}_{\mu}\}\) are obtained by minimizing the spillage between the reduced bases and the Bloch wave functions in the selected energy window and \(k\) mesh. The spillage [42] is defined as,

\[
S = \frac{1}{N_{\mu}N_k} \sum_{\mu} \sum_k \langle \hat{\phi}_{\mu}\rangle (1 - \hat{P}(k))|\hat{\psi}_{nk}\rangle,
\]

(B.1)

where \(n\) is the energy bands within the energy window. \(\hat{P}(k)\) is a projector spanned by the reduced NAOs,

\[
\hat{P}(k) = \sum_{\mu,\nu} \langle \hat{\phi}_{\mu}\rangle \tilde{S}_{\mu\nu}(k)|\hat{\phi}_{\nu}\rangle,
\]

(B.2)

where, \(\tilde{S}_{\mu\nu}(k)\) is the overlap matrix of the reduced NAOs. The reduced NAOs are the linear combination of the on-site original NAOs. Using equation (28), we have,

\[
\tilde{S}_{\mu\nu}(k) = \sum_{\alpha,\beta} U_{\mu\alpha}^* S_{\nu\beta}(k) U_{\beta\nu} = (U^\dagger S(k) U)^{\mu\nu},
\]  

(B.3)

where \(S(k)\) is the overlap matrix of the original NAOs. The spillage can be written as,

\[
S = \frac{1}{N_{\mu}N_k} \sum_{\mu} \sum_k [1 - C^\dagger_{\mu\nu} S(k) C_{\nu\mu}]
\]

(B.4)

where \(X\) is an invertible matrix, we get the derivative of Spillage to the \(U\) matrix,

\[
\frac{\partial S}{\partial U} = \frac{1}{N_{\mu}N_k} \sum_{\mu} \sum_k \left[ - (U^\dagger S(k) U)^{-1} U^\dagger S(k) C^\dagger_{\mu\nu} S^T (U^\dagger S(k) U)^{-1}
+ S(k) U^\dagger S(k) C^\dagger_{\mu\nu} S^T (U^\dagger S(k) U)^{-1}
+ (U^\dagger S(k) U)^{-1} U^\dagger S(k) C^\dagger_{\nu\mu} S^T (U^\dagger S(k) U)^{-1}
- S(k) U^\dagger S(k) U^\dagger S(k)^T \right].
\]

(B.6)

Once we have the gradients, we optimize the spillage via the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method implemented in the numpy [44] and scipy package [45]. To determine the initial reduced NAOs, we evaluate the coefficients of each orbital in the full bases of the wave functions using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method. To determine the initial reduced NAOs, we evaluate the energy windows and \(k\)-mesh. We keep the NAOs, whose coefficients are larger than some threshold as the initial reduced NAOs, which give the corresponding initial \(U\) matrices. We then minimize the spillage to obtain the optimized NAOs. When optimize the \(U\) matrix using equation (B.6), the wave functions \(C_{\nu}\), overlap matrix \(S\), and initial \(U\) matrix all have the point group symmetry, and therefore in principle, the reduced NAOs should still preserve the symmetry. However, there might be small symmetry breaking, due to numerical noise. The reduced NAOs can be symmetrized using the algorithms of reference [27] if necessary.

ORCID iDs

Lixin He 🐤 https://orcid.org/0000-0003-2050-134X

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