Wannier Interpolation with Nonorthogonal Localized Orbitals: Application to \textit{ab initio} Calculation of Nonlinear Optical Responses

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Wannier interpolation is an efficient and useful method widely used in modern first-principles materials calculations, which typically demands orthogonal and localized Wannier basis functions. The optimization of Wannier functions, however, is a challenging task due to the conflicting requirements of orthogonality and localization. In this work, we extend the Wannier interpolation scheme to accommodate the usage of nonorthogonal localized orbitals. The generalized method can be easily applied as a post processing procedure for various \textit{ab initio} calculation codes using localized orbitals. We test the performance of this method by calculating nonlinear optical responses of materials, like the shift current conductivity of monolayer WS\textsubscript{2}, and achieve good agreement with previous calculations. In no need of optimizing Wannier functions, our method enables automated high throughput calculations of response functions and other materials properties.

I. INTRODUCTION

Wannier functions encode all the information of a band structure. Moreover, due to their highly localized nature, Wannier functions can be constructed with Bloch functions at just a few reciprocal \( k \)-points.\textsuperscript{12} After obtaining Wannier functions, information of Bloch functions at arbitrary \( k \)-points can be obtained by Fourier transformation. This procedure is called Wannier interpolation.\textsuperscript{3} Wannier interpolation captures the physics of Bloch electrons and is an efficient way to compute various physical observables of solids within the independent particle approximation. Previous researches have proven its success on anomalous Hall effect\textsuperscript{4}, optical conductivity\textsuperscript{5}, orbital magnetization\textsuperscript{6} and nonlinear optical effects including shift current\textsuperscript{7,8} and second harmonic generation.\textsuperscript{2}

Current dominating algorithm of obtaining Wannier functions is maximally localized Wannier function (MLWF) theory, which mixes bands in a way that maximizes the localization of Wannier function.\textsuperscript{3} This method is universal and serves as a post processing tool for various \textit{ab initio} calculation packages,\textsuperscript{3} regardless of their implementation schemes of density functional theory (DFT). However, since MLWF algorithm is essentially an optimization process, to avoid local minimum, trial Wannier functions and other parameters have to be carefully tested. This inevitable human intervention hampers its usage in high throughput material discovery. One way to avoid this caveat is to use real space localized orbital (RSLO) based density functional theory scheme, which is already implemented in many \textit{ab initio} calculation packages. However, most packages use nonorthogonal localized orbitals (NoLO) as basis functions to span the Hilbert space. This practice is rationalized by two practical reasons: (i) NoLOs can be made more localized than orthogonal orbitals; (ii) It’s generally easier to construct NoLOs, especially when a huge amount of them is needed. On the other hand, current Wannier interpolation method has been developed with the assumption of orthogonality and cannot be directly applied to NoLOs. Therefore, a generalized Wannier interpolation method for NoLOs is highly favorable.

In this work, we develop a generalized Wannier interpolation scheme for NoLOs. This method allows calculation of derivatives of arbitrary orders of band energies and Bloch wave functions. Therefore, it is suitable for calculation of various linear and nonlinear response functions. As an example, we calculate dielectric constant and shift current conductivity of monolayer WS\textsubscript{2}, as a proof of calculations of linear response and nonlinear response functions. The results are consistent with previous works. Finally, we discuss the performance and symmetry properties of this method.

II. METHOD

Berry connection\textsuperscript{10} \( A_{nm} = \langle u_{nk} \nabla_k u_{m k} \rangle \) and its derivative \( \nabla_k A \) lie at the heart of response functions. However, due to the random phase generated by diagonalization, direct derivative calculation by finite difference is not possible. Wannier interpolation scheme solves this problem by fixing the phase by a definite gauge choice. Here we extend this method to nonorthogonal localized orbitals.

We label localized orbitals as \(| R_n \rangle\), where \( n \) is label of the orbital inside the unit cell labeled by lattice vector \( R \). \( n \) runs from 1 to \( N \), where \( N \) is number of localized
orbitals in one unit cell. Bloch summations of these localized orbitals constitute a complete basis of Hamiltonian at a \( k \) point,

\[
|\psi_{nk}^{(W)}\rangle \equiv \sum_{R} e^{i\mathbf{k} \cdot \mathbf{R}} |\mathbf{R} n\rangle, \tag{1}
\]

whose cell periodic part is

\[
|\psi_{nk}^{(W)}\rangle \equiv e^{-i\mathbf{k} \cdot \hat{\mathbf{r}}} |\psi_{nk}^{(W)}\rangle = \sum_{R} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{r})} |\mathbf{R} n\rangle. \tag{2}
\]

Under this basis, Hamiltonian matrix is

\[
H_{nm}(k) \equiv \langle \psi_{nk}^{(W)} | \hat{H} | \psi_{mk}^{(W)} \rangle = \sum_{R} e^{i\mathbf{k} \cdot \mathbf{R}} \langle 0n | \hat{H} | 0m \rangle, \tag{3}
\]

Unlike common Wannier interpolation scheme, \( |\psi_{nk}^{(W)}\rangle \) are not necessarily normalized and orthogonal to each other. An overlapping matrix is needed to capture this property,

\[
S_{nm}(k) \equiv \langle \psi_{nk}^{(W)} | \psi_{mk}^{(W)} \rangle = \sum_{R} e^{i\mathbf{k} \cdot \mathbf{R}} \langle 0n | \mathbf{R} | 0m \rangle. \tag{4}
\]

Eigenstates of Hamiltonian \( \hat{H} \) are linear combinations of \( |\psi_{nk}^{(W)}\rangle \),

\[
|\psi_{nk}^{(H)}\rangle = \sum_{m} V_{mn}(k) |\psi_{mk}^{(W)}\rangle, \tag{5}
\]

\[
\hat{H} |\psi_{nk}^{(H)}\rangle = E_{nk} |\psi_{nk}^{(H)}\rangle, \tag{6}
\]

where \( V \) and \( E \) can be obtained by solving a generalized eigenvalue problem,

\[
H(k)x_{nk} = E_{nk} S(k)x_{nk}, \tag{7}
\]

which is just Schrödinger equation expressed in the nonorthogonal basis \( |\psi_{nk}^{(W)}\rangle \). \( x_{nk} \) is a column vector and has \( N \) independent solutions constituting the columns of matrix \( V \). Notice that \( V \) is not a unitary matrix now. Assuming the localized orbitals are linearly independent, \( S \) is Hermitian and positive definite. One way to connect with MLWF-based Wannier interpolation is to do orthogonalization by \( S^{-1/2} \), but derivatives of \( S^{-1/2} \) will be needed to calculate derivatives of the transformed Hamiltonian. In principle derivatives of \( S^{-1/2} \) can be calculated by finite difference, but for numerical stability considerations we do not choose this approach. Instead, we try to calculate derivatives of eigenvectors for generalized eigenvalue problem directly. This type of generalized eigenvalue problem is well behaved and the eigenvector can be normalized as

\[
\langle x_{n}^{\dagger} S x_{m} \rangle = \delta_{nm}. \tag{8}
\]

\( V \) can be used to express Berry connection in the basis of \( |\psi_{nk}^{(W)}\rangle \),

\[
A^{\alpha} = i V^{\dagger} \partial_{\alpha} V + V^{\dagger} A^{\alpha(W)} V, \tag{9}
\]

where

\[
A_{nm}^{\alpha(W)} = i \langle u_{n}^{(W)} | \partial_{\alpha} u_{m}^{(W)} \rangle = \sum_{R} e^{i\mathbf{k} \cdot \mathbf{R}} \langle 0n | \partial_{\alpha} \psi_{m}^{(R)} - \psi_{m}^{(0)} \partial_{\alpha} | 0n \rangle. \tag{10}
\]

\( \hat{r} \) is position operator, \( \partial_{\alpha} = \partial_{\alpha} x \) and \( \alpha \) is Cartesian indices. The behavior of \( \langle 0n | \partial^{\alpha} | 0m \rangle \) is unexpectedly different from that of orthogonal Wannier functions,

\[
\langle 0m | \partial^{\alpha} \hat{r} | 0n \rangle = (\langle \hat{r} | \partial^{\alpha} | 0m \rangle)^{*} = (\langle 0n | \partial^{\alpha} \hat{r} | 0m \rangle)^{*} - R^{\alpha} \langle 0m | \hat{r} | 0n \rangle. \tag{11}
\]

However, calculation of \( V^{\dagger} S \partial_{\alpha} V \) still suffers from arbitrary phases from diagonalization. Fortunately, since the three matrices \( \langle 0n | \hat{H} | 0m \rangle \), \( \langle 0n | \mathbf{R} | 0m \rangle \) and \( \langle 0n | \partial^{\alpha} \hat{r} | 0m \rangle \) are known from \textit{ab initio} calculations, arbitrary derivatives of \( H \), \( S \) and \( A^{(W)} \) are known, which makes it possible to calculate \( V^{\dagger} S \partial_{\alpha} V \).

As an example, we calculate \( \partial_{\alpha} \psi_{m}^{(R)} = \langle 0| \partial_{\alpha} \psi_{m}^{(R)} | 0 \rangle \) at \( \Gamma \) point. Differentiating Eq. (7),

\[
(\partial_{\alpha} H) x_{n} + H \partial_{\alpha} x_{n} = (\partial_{\alpha} E_{n} S_{\alpha n} x_{n} + E_{n} \partial_{\alpha} S_{\alpha n} x_{n}). \tag{12}
\]

Hit Eq. (12) with \( x_{n}^{\dagger} \) on the left, we have

\[
\partial_{\alpha} E_{n} = x_{n}^{\dagger} H \partial_{\alpha} x_{n} - E_{n} x_{n}^{\dagger} (\partial_{\alpha} S) x_{n}. \tag{13}
\]

Hit Eq. (12) with \( x_{m}^{\dagger} (m \neq n) \) on the left, we have

\[
x_{m}^{\dagger} S \partial_{\alpha} x_{n} = x_{m}^{\dagger} (\partial_{\alpha} H) x_{n} - E_{n} x_{m}^{\dagger} (\partial_{\alpha} S) x_{n}. \tag{14}
\]

However, due to the intrinsic phase ambiguity of \( x_{n} \), it is necessary to introduce an extra gauge fixing condition to obtain \( x_{n}^{\dagger} S \partial_{\alpha} x_{n} \),

\[
x_{n}^{\dagger} S_{\alpha n} \psi_{0} x_{nk} \in \mathbb{R}, \tag{15}
\]

which is smooth across \( \Gamma \) point since \( x_{n}^{\dagger} S_{\alpha n} \psi_{0} x_{nk} = 1 \in \mathbb{R} \). Differentiate both Eq. (8) and Eq. (15), we have

\[
x_{n}^{\dagger} S \partial_{\alpha} x_{n} = -\frac{1}{2} x_{n}^{\dagger} (\partial_{\alpha} S) x_{n}. \tag{16}
\]

We have assumed in the above equations that \( n \) is not degenerate. Degenerate eigenvalues can be treated in principle[22] but are not important in our calculations.

Every ingredient needed for linear response are obtained to this point. However, we still need \( \nabla_{\mathbf{k}} A \) for nonlinear responses. Differentiating Eq. (9) again, we have

\[
\partial_{\beta} A^{\alpha} = i (\partial_{\beta} V^{\dagger}) S (\partial_{\alpha} V) + i V^{\dagger} (\partial_{\beta} S) (\partial_{\alpha} V) + i V^{\dagger} S \partial_{\beta} \psi_{m}^{(R)} + (\partial_{\beta} V^{\dagger}) A^{\alpha(W)} V + V^{\dagger} (\partial_{\beta} A^{\alpha(W)}) V + V^{\dagger} A^{\alpha(W)} (\partial_{\beta} V). \tag{17}
\]
Calculation of $V^\dagger S \partial_3 \partial_6 V$ follows exactly the same logic of calculating $V^\dagger S \partial_6 V$. However, it is not difficult to imagine how complex the final expression would become. Therefore, we introduce in the appendix an iteration procedure to calculate derivatives of $x_n$ of arbitrary orders for nondegenerate $E_n$.

Now that every ingredient of linear and nonlinear response functions are known, we test the method by calculating shift current conductivity of monolayer WS$_2$ and compare the results with previous calculations.

III. SHIFT CURRENT OF MONOLAYER WS$_2$

A. Background and Computation Details

Shift current\cite{13,14} is a second order bulk photovoltaic effect arising from the difference of real space positions of Bloch electrons between valence band and conduction band,

$$J^\alpha = \sigma^{\alpha\beta\gamma}(\omega)E^\beta(\omega)E^\gamma(-\omega),$$

where shift current conductivity $\sigma^{\alpha\beta\gamma}$ is given by\cite{13,14}

$$\sigma^{\alpha\beta\gamma}(\omega) = \frac{2g_s\pi e^3}{\hbar^2} \int \frac{d^3k}{(2\pi)^3} \sum_{n,m} f_{nm}r_{nm}^{\alpha\beta\gamma,\delta}(\omega_{nm} - \omega),$$

where $g_s$ is the spin degeneracy, $\hbar\omega_{nm} = E_n - E_m$ represents photon energy, $f_{nm} = f(E_n) - f(E_m)$ and $f$ is Fermi-Dirac distribution. The integrand $r_{nm}^{\alpha\beta\gamma,\delta}$ is composed of transition rate from band $n$ to band $m$ and shift vector between the two bands. Transition rate and shift vector contain Berry connections and derivatives of Berry connections, which can be calculated using the method described in Sec.\ref{background}. Then an numerical integration would produce the result of $\sigma^{\alpha\beta\gamma}$. Since a $\delta$ function is present in the expression of $\sigma^{\alpha\beta\gamma}$, a very fine $k$ mesh is needed to achieve convergence.

Since monolayer WS$_2$ has the point group $D_{6h}$, there's only one independent shift current conductivity component $\sigma^{yy\gamma}$\cite{14}. Following the convention of Ref.\cite{7} we choose a two dimensional (2D) definition of current. $ab\text{ initio}$ calculations are performed with a full potential FHI-AIMS package\cite{15} with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals\cite{16} describing electron-electron interactions. Slab model is used to characterize monolayer WS$_2$ with a vacuum layer thicker than 15 Å. A $k$ grid $12 \times 12 \times 1$ is used to sample the Brillouin Zone in self consistent calculations and a much finer $k$ grid $400 \times 400 \times 1$ is used to perform the numerical integration in the expression of shift current conductivity. Species default type ‘tight’ is chosen as RSLOs to span the Hilbert space.\cite{15} Spin orbital interaction is not included and $\delta$ function is simulated using the following numerical approximation

$$\delta(x) = \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + x^2},$$

where the broadening factor $\epsilon$ is chosen to be 0.04eV.

B. Results

The shift current conductivity of monolayer WS$_2$ is presented in Fig.\ref{fig1}(a), compared with shift current conductivity calculated using methods and software packages introduced in Ref.\cite{7} with the same parameters. Despite using different software packages and DFT schemes, the two shift current conductivity curves are almost the same. Optical absorptions, represented by imaginary part of dielectric constant calculated by both MLWF- and NoLO-based Wannier interpolation, are plotted in Fig.\ref{fig1}(b). Both dielectric constant and shift current conductivity have two peaks at 2.75eV and 3.05eV respectively. However, although for dielectric constant, peak at 3.05eV is higher than that at 2.75eV, shift current conductivity at 2.75eV is larger. This discrepancy should be attributed to the difference of shift vector. The contribution of these two peaks can be decomposed to bands and is shown in Fig.\ref{fig1}(c). Size of red and blue dots represent contributions to the 2.75eV peak and 3.05eV absorption peak respectively. It is obvious that both peaks are contributed by the highest valence band and lowest four band around $\Gamma$ point and $K$ point.

C. Discussion of the Method

MLWFs are known to break symmetry slightly, which is revealed by small avoid crossings in the interpolated band structure where they should have been direct crossings. This behavior results in a small but nonvanishing value for symmetry forbidden components of shift current conductivity even for well convergent MLWFs. This problem does not arise for NoLO-based Wannier interpolation since symmetry is enforced in $ab\text{ initio}$ calculations by only sampling irreducible Brillouin Zone in the calculation. Fig.\ref{fig2}(a) shows a forbidden component of shift conductivity of WS$_2$ ($\sigma^{xxx}$) calculated by current method and MLWF-based Wannier interpolation. It can be observed that while MLWF-based Wannier interpolation gives a value around $1\mu$A·Å/V$^2$ for this component, results of nonorthogonal localized orbitals based Wannier interpolation vanish identically (no more than $10^{-4}\mu$A·Å/V$^2$). Therefore, NoLO-based Wannier interpolation preserves symmetry properties quite well.

Compared to MLWF-based Wannier interpolation, NoLO-based Wannier interpolation is computationally heavier, since $ab\text{ initio}$ packages, especially full potential packages, need to use quite a lot of NoLOs to span the Hilbert space, while MLWFs are usually constructed for bands near Fermi surface only. Therefore, it is necessary to test the scaling behavior of this method with respect to number of NoLOs. This scaling behavior is presented in Fig.\ref{fig2}(b). It is observed that computation time roughly scales as $O(N^2)$, where $N$ is number of NoLOs. This is
FIG. 1. (Color online) Shift current conductivity of monolayer WS$_2$. (a) $\sigma_{yyy}$ of monolayer WS$_2$ as a function of photon energy calculated with MLWF- and NoLO-based Wannier interpolation. (b) Imaginary part of dielectric constant of monolayer WS$_2$ as a function of photon energy calculated with MLWF- and NoLO-based Wannier interpolation. Contributions to first peak and second peak are decomposed to bands, shown by size of red and blue dots in (c). We have adopted 2D versions of current and polarization, thus extra Ås are introduced in units of $\sigma$ and $\epsilon$. (c) Band structure of WS$_2$ near Fermi surface.

FIG. 2. Test of NoLO-based Wannier interpolation. (a) Calculation of symmetry forbidden components of shift current conductivity of monolayer WS$_2$. (b) Time complexity of NoLO-based Wannier interpolation with respect to number of NoLOs ($N$). Black dots are actual data. The slope is roughly 2.

A closer analysis of the performance reveals that the computation is dominated by Fourier transformations in calculating $H$, $S$, $A^{(W)}$ and their derivatives. Therefore, for common bulk materials, we can safely assume the time complexity is $O(N^2)$.

IV. CONCLUSION

RSLO-based *ab initio* packages have the potential of achieving $O(N)$ computational resource scaling with respect to number of atoms. In addition, vacuum is treated quite trivially in these packages, making them competitive tools in research for low dimensional materials. Here we demonstrate these packages can be more powerful by extending Wannier interpolation to NoLOs.

Although computationally heavier compared to MLWF-based Wannier interpolation, NoLO-based Wannier interpolation scheme avoids human intervention and can be used in high throughput material discovery. The correctness of this scheme is proved by calculating shift current conductivity of monolayer WS$_2$. This NoLO-based Wannier interpolation scheme is quite general and can be used to calculate different kinds of linear response and nonlinear responses.

Note added: During the preparation of this manuscript, we noticed a related work Ref. 20 appearing on arXiv, which calculates the anomalous Hall conductivity by nonorthogonal localized orbitals.

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