Electronic structure interpolation via atomic orbitals

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Abstract

We present an efficient scheme for accurate electronic structure interpolation based on systematically improvable optimized atomic orbitals. The atomic orbitals are generated by minimizing the spillage value between the atomic basis calculations and the converged plane wave basis calculations on some coarse \( k \)-point grid. They are then used to calculate the band structure of the full Brillouin zone using the linear combination of atomic orbitals algorithms. We find that usually 16–25 orbitals per atom can give an accuracy of about 10 meV compared to the full \( ab \) initio calculations, and the accuracy can be systematically improved by using more atomic orbitals. The scheme is easy to implement and robust, and works equally well for metallic systems and systems with complicated band structures. Furthermore, the atomic orbitals have much better transferability than Shirley’s basis and Wannier functions, which is very useful for perturbation calculations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Very often one needs to calculate physical properties that require highly dense \( k \) points to get accurate results. For example, Yao et al [1] used \( 2 \times 10^6 \) \( k \) points in order to get a converged value of the intrinsic anomalous Hall conductivity. Direct calculations of the properties via the first-principles method are too expensive in these cases. An efficient electronic structure interpolation method is therefore a powerful tool to reduce the computational cost while retaining the accuracy at the \( ab \) initio level.

Maximally localized Wannier functions (MLWFs) [2] have been demonstrated as a powerful tool for interpolating electronic structures accurately [3, 4]. They have been used to calculate the anomalous Hall conductivity [4], low-field Hall conductivity, and magnetic circular dichroism spectrum [3], etc, with great success. In this approach, the band connectivity, band crossings and avoided crossings are treated correctly. The evaluation of the velocity matrix can also be performed analytically. Because of their local character, the MLWFs serve as a kind of exactly tight-binding basis of minimal size. The recently proposed quasiatomic orbitals [6, 7] can also be used for band structure interpolation, and have very similar features to those of the MLWF basis.

The electronic structures can also be interpolated by the Bloch states. Shirley proposed an interpolation scheme in 1996 [8]. The optimal basis set is extracted from the full \( ab \) initio calculations on a coarse \( k \)-point grid. It has been shown that by using about 35 basis functions per atom, the optimal basis can reproduce the band structures of Si and LiF within an accuracy of 10 meV. Recently, Shirley’s scheme has been extended to more general \( k \)-point sampling [9]. Shirley’s method can be used well for both insulators and metals. However, Shirley’s scheme does not obey the symmetries of the crystal [5].

Atomic orbitals have been popular recently for self-consistent \( ab \) initio calculations. Relatively compact basis size can give quite satisfactory results compared to plane wave calculations [10–13]. However, to get extremely high accuracy band structures (errors \( \sim 2-3 \) meV), the small, rigid atomic basis sets are obviously not adequate. Recently the authors (CGH) developed a method to generate systematically
improvable fully optimized atomic orbitals for \textit{ab initio} calculations [14]. The CGH scheme can generate orbitals with arbitrary angular momentum and multi-zeta functions in a unified procedure. The CGH orbitals offer highly accurate and transferable atomic basis sets, which have been tested for a wide variety of systems, including semiconductors, oxides, metals, clusters, etc.

We show in this paper that the CGH method can be revised to give an efficient scheme for electronic structure interpolations. This scheme keeps the advantages of both MLWFs and Shirley’s method and gets rid some of their disadvantages. The atomic orbitals are highly localized (more localized than MLWFs), and therefore can take advantage of the locality. The atomic orbitals are very neat, and only the one-dimensional radial functions are stored. The atomic basis sets always obey the symmetries of the crystal. We show that the scheme works well for both metals and insulators. The highly localized orbitals can always be generated for metallic systems. Additionally, the transferability of local orbitals for interpolation purposes is explored. Once the atomic orbitals are generated, the electronic properties can be calculated efficiently by the well established linear combination of atomic orbitals (LCAO) algorithms, with the accuracy of \textit{ab initio} plane wave calculations.

The rest of the paper is organized as follows. In section 2, we introduce briefly the method we use to perform the band structure interpolation via atomic orbitals. In sections 3.1 and 3.2, we show, via a few examples, how the present interpolation scheme works for both metallic and insulating systems, and systems with complicated band structures. In section 3.3, we discuss the transferability of our interpolation bases. We demonstrate, via an example, the excellent accuracy of calculating the optical spectrum using the current interpolation scheme in section 3.4, and discuss the efficiency of the method in section 3.5. We conclude in section 4.

2. Methods

All the calculations performed in this paper are based on the density functional theory (DFT) within the local (spin) density approximation (L(S)DA). Although our method is demonstrated for the norm-conserving [15] pseudopotentials, in principle, it should also work well for the ultrasoft or PAW (projector augmented wave) pseudopotentials. Monkhorst-Pack \(k\) points [16] are used in the following calculation.

2.1. Generating local orbitals

The details of how to construct systematically optimized atomic basis for \textit{ab initio} calculations have been given in [14]. Here we give a brief review of our earlier approach to generating local orbitals. Each atomic orbital is written as a radial function times a spherical harmonic function, i.e.,

\[
\phi_{\mu}(r) = f_{\mu,l}(r)Y_{lm}(\hat{r}).
\]

The radial function is taken as a linear combination of spherical Bessel functions within a certain range \(r_c\), i.e.,

\[
f_{\mu,l}(r) = \begin{cases} 
\sum_q c_{\mu q} j_q(qr), & r < r_c, \\
0, & r \geq r_c,
\end{cases}
\]

where \(\mu = \{\alpha, i, \zeta, l, m\}\), and \(\alpha, i, \zeta, l, m\) are the element type, the index of the atom of each element type, the multiplicity of the radial functions, the angular momentum and the magnetic quantum number, respectively. \(j_q(qr_c)\) is the spherical Bessel function, where \(q\) satisfies \(j_q(qr_c) = 0\). The coefficients \(c_{\mu q}\) are chosen to minimize the ‘spillage’ [17, 18]

\[
S = \frac{1}{N_k N_k^*} \sum_{\mu} \sum_{l} \sum_k \langle \Psi_\mu(k) | 1 - \hat{P}(k) | \Psi_\mu(k) \rangle
\]

between the Hilbert space spanned by the atomic orbitals and the plane wave calculations, for selected reference states. In equation (2), \(\Psi_\mu(k)\) is the eigenstate of plane wave calculations, and \(N_k\) and \(N_k^*\) are the number of states of interest and the number of \(k\)-points in the Brillouin zone. \(\hat{P}(k)\) is a projector spanned by the atomic orbitals, i.e.,

\[
\hat{P}(k) = \sum_{\mu, l} | \phi_{\mu}(k) \rangle S^{-1}_{\mu l}(k) \langle \phi_{\mu}(k)|,
\]

with

\[
\langle r | \phi_{\mu}(k) \rangle = \sum_{R} \phi_{\mu}(r - \mu R) e^{i(k,\mu R)},
\]

where \(\mu\) is the atom center of the \(\mu\)th orbital and \(R\) is the lattice vector. \(S_{\mu l}(k) = \langle \phi_{\mu}(k) | \phi_{\mu}(k) \rangle\) is the overlap matrix element. The minimization of the spillage is performed by using a simulated annealing method. Because the orbitals generated from this step usually have unphysical oscillations, an additional step is added to smooth out the orbitals by minimizing the kinetic energy of each orbital [14]. Unlike the quasiatom orbitals [6, 7], our atomic orbitals strictly preserve the spherical symmetry.

We have performed extensive tests of this scheme for a wide variety of systems, including semiconductors, oxides, metals, clusters, etc. The results show that the obtained atomic bases are very satisfactory for both accuracy and transferability [14]. However, to perform high accuracy electronic structure interpolation, we need to modify the scheme for the task.

In [14], where the aim is to carry out self-consistent \textit{ab initio} calculations in complex chemical environments, to get maximal transferability of the basis sets, a set of dimers with different bond lengths is selected as the reference system. The valence states are chosen as the reference states. However, in order to interpolate the electronic structures with extremely high accuracy for a particular system, the system itself is used as the reference system. In many cases, the states of interest lie only in a given energy window (i.e., valence bands as well as conduction bands); therefore, we can choose these states (instead of all the valence bands) as the reference states.

In the self-consistent LCAO calculations, which are usually applied to deal with extremely large systems, it is important to keep the basis size compact. Often used bases are DZP (double zeta orbitals plus a polar orbital), etc. The small basis set is not sufficient for high accuracy electronic structure interpolations. One must use much higher angular momentum and more zeta orbitals. In these cases, the CGH orbitals have obvious advantages, because they can generate the fully...
optimized orbitals with arbitrary angular momentum and any number of radial functions for a given angular momentum.

It has been shown in [14] that increasing the orbital radius cutoff \( r_c \) can reduce the spillage value, and therefore improve the quality of the orbitals. However, a larger \( r_c \) also means more computational costs. In the self-consistent calculations, one has to balance the computational costs and the accuracy, and choose a modest \( r_c \). Yet, for band structure interpolations, the systems under study are usually considerably smaller, and a larger \( r_c \) can be used.

Once we obtain the atomic orbitals, the electronic structures can be calculated efficiently by using the well established LCAO methods. To calculate the band structure, we first calculate the Hamiltonian \( \hat{H} \) matrix in real space in the small atomic basis,

\[
H_{\mu \nu}(\mathbf{R}_n) = \langle \phi_{\mu n} | \hat{H} | \phi_{\nu m} \rangle,
\]

where \( \phi_{\mu n} = \phi_{\mu}(\mathbf{r} - \mathbf{r}_n - \mathbf{R}_n) \). The matrix element \( H_{\mu \nu}(\mathbf{R}_n) \) decays very fast with lattice vector \( \mathbf{R}_n \), since the atomic orbitals are strictly localized. Therefore only a small number of them need to be computed and stored once for all. The matrix is then transferred to the \( \mathbf{k} \) space,

\[
H_{\mu \nu}(\mathbf{k}) = \sum_{\mathbf{R}_n} e^{i \mathbf{k} \cdot \mathbf{R}_n} H_{\mu \nu}(\mathbf{R}_n),
\]

and diagonalized. Further details on how to construct the Hamiltonian matrix \( H_{\mu \nu}(\mathbf{R}_n) \) can be found in a review paper on the LCAO method [12]. One can also easily calculate the matrix element of a quantum mechanical operator between two Bloch states \( \langle \Psi_{\mathbf{k}_{\mu}} | \hat{O} | \Psi_{\mathbf{k}_{\nu}} \rangle \) in the atomic basis, where

\[
\Psi_{\mathbf{k}_{\mu}}(\mathbf{r}) = \sum_{\mathbf{R}_n} c_{\mu \mathbf{k}}(\mathbf{R}_n) \phi_{\mu}(\mathbf{r} - \mathbf{r}_\mu - \mathbf{R}_n) e^{i \mathbf{k} \cdot \mathbf{R}_n}.
\]

It is easy to show that

\[
O_{\mathbf{j}_{\mu \nu}}(\mathbf{k}, \mathbf{q}) = \sum_{\mathbf{R}_n \mathbf{R}_m} e^{-i \mathbf{k} \cdot \mathbf{R}_n + i \mathbf{q} \cdot \mathbf{R}_m} c^*_{\mathbf{j}_{\mu \nu}}(\mathbf{k}) c_{\mathbf{j}_{\mu \nu}}(\mathbf{q}) \langle \phi_{\mu n} | \hat{O} | \phi_{\nu m} \rangle.
\]

Because the matrix elements \( \langle \phi_{\mu n} | \hat{O} | \phi_{\nu m} \rangle \) can also be calculated once for all, the method is very efficient.

3. Results and discussion

In this section, we show via a few examples how the present band structure interpolation scheme works, including some simple materials with complicated band structures. We start the tests with simple solid structures like Na, Si and Al. Na and Al are metallic while Si is a semiconductor. A more complex material, an iron based superconductor BaFe\(_2\)As\(_2\), is then tested. We further show that the atomic bases have much better transferability than the Bloch bases and Wannier bases for the purpose of band structure interpolation. We then discuss the transferability of our interpolation bases. We demonstrate, via an example, the excellent accuracy of calculating the optical spectrum using the current interpolation scheme and discuss the efficiency of the method.

3.1. Simple solids

We take bcc sodium as the first example. We use the energy cutoff \( E_c = 50 \) Ryd. An \( 8 \times 8 \times 8 \) \( \mathbf{k} \)-point mesh is used for the reference states to generate the local orbitals. We choose the lowest six bands to interpolate. In order to quantify the quality of the interpolation, we calculate the root-mean-square errors (RMSE) which are defined as

\[
\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\epsilon_{i}^{\text{PW}} - \epsilon_{i}^{\text{LCAO}})^2},
\]

where \( N \) is the number of \( \mathbf{k} \) points where the comparison has been taken between \( \epsilon^{\text{PW}} \), the eigenvalue calculated from the plane wave basis, and \( \epsilon^{\text{LCAO}} \), the eigenvalue calculated from atomic orbitals. We use a much denser \( 24 \times 24 \times 24 \) \( \mathbf{k} \) points to calculate the RMSE. The RMSEs of the six interpolated bands of Na are shown in figure 1(a). Three levels of atomic orbitals are generated and compared. At each level, we use one group of s, p, d, and f orbitals (1s1p1d1f). The radius cutoff \( r_c \) is chosen as 12 \( \text{au} \). We find that the quality of the basis set is much better if all the orbitals of the same level are generated simultaneously than if they are generated separately. As shown in figure 1(a), the RMSEs of the 1s1p1d1f, 2s2p2f2f, and 3s3p3d3f local basis sets are less than 8 meV, 3 meV, and 2 meV, respectively. Figure 2 illustrates how the angular momenta and radial cutoff affect the interpolation accuracy. The black lines indicate the spillage values while the red lines indicate the averaged RMSEs of the six bands. The radius cutoff changes from 6 to 15 \( \text{au} \). The largest angular momentum of the orbitals is set from \( l = 2 \) (d orbitals) to \( l = 4 \) (g orbitals). We use five radial orbitals (zeta functions) for each angular momentum, which ensures that the accuracy improved by multi-zeta orbitals is converged. We find a consistent change between the spillage values and the RMSE, confirming that the spillage is a good criterion for the interpolation quality. The RMSEs reduce considerably as \( r_c \) increases from 6 to 9 \( \text{au} \), while only a small improvement is found when \( r_c \) is larger than 9 \( \text{au} \). The d orbitals are not sufficient for the high accuracy interpolation, because the corresponding RMSEs are around 50–100 meV even if a very large \( r_c \) is used. Adding in f orbitals improves greatly upon the d orbitals. For example, for \( r_c = 10 \) \( \text{au} \), adding f orbitals to the interpolation basis reduces the RMSE to 0.86 meV. The g orbitals improve further upon the f orbitals, but not as much as the f orbitals on the d orbitals. Since the spillage can be as small as \( 10^{-4} \), one can get highly accurate physical properties related to the wavefunctions, as will be demonstrated in section 3.4.

The interpolation results for Si diamond structure and fcc Al are shown in figures 1(b) and (c), respectively. For both materials, we find that g orbitals must be included to get highly accurate interpolation results. For Si, the lowest eight bands are interpolated. The 1s1p1d1f1g orbitals can interpolate the band structure with the RMSEs being about 10 meV for all the bands. If the basis set is doubled, the RMSEs for all eight bands are smaller than 2 meV, showing extremely good accuracy. When it further increases to the level of three orbitals, the RMSEs can be reduced to within 1 meV. For Al, if the first
1s1p1d1f1g orbitals are used, the RMSEs can be reduced to 10 meV. When we double the basis to 2s2p2d2f2g, the RMSEs of all the bands fall within 3 meV. The RMSEs can be further reduced to less than 1 meV, when 3s3p3d3f3g orbitals are used, also showing remarkable accuracy.

We also test GaAs, fcc Cu and CuZn alloys, and the results are all similar to those above. We find that the 1s1p1d1f1g basis is adequate to reduce the RMSEs of GaAs and fcc Cu to within 10 meV. We generate 3s3p3d3f (the orbital number is 48 per atom) orbitals from 60 bands around the Fermi level of CuZn alloys and find that the RMSEs are around 2 meV, which are quite similar to the results in [9]. The authors of that study used 42 bases per atom and obtained 2 meV for the RMSE [9].

The above examples show that the method applies equally well for insulators and metals.
Figure 4. The RMSEs of the interpolated bands for (3, 3) CNTs with (a) normal, (b) 10% stretching, and (c) 10% compression structures. (d)–(f) show corresponding interpolated band structures (blue lines) using the 4s4p4d4f basis compared to the plane wave results (red dots).

3.2. BaFe$_2$As$_2$

The recent discovery of superconductivity in doped iron arsenide has attracted great attention [19]. Here we show that our electronic structure interpolation scheme also works well for materials like BaFe$_2$As$_2$ which have complicated band structures. We interpolate the 14th–24th bands, which span a 6 eV energy window around the Fermi level. Figure 3(a) depicts the RMSE for each band using different numbers of numerical orbitals. When using the 1s1p1d1f1g orbital (25 bases per atom), the RMSEs of all the bands are under 6 meV except for the last one, which is 15.7 meV. Once the second radial functions are used, the RMSEs of all bands are reduced to below 1.3 meV except the last one which is 2.48 meV. When the third radial functions are used, all the RMSEs are under 0.6 meV except the last one which is 1.23 meV.

Figure 3(b) depicts the band structures of BaFe$_2$As$_2$ along the $\Gamma$–Z–X–$\Gamma$ line. The band structures calculated by plane waves are shown by blue dotted lines, whereas the band structures calculated by 3s3p3d3f3g numerical orbitals are plotted as black solid lines. The interpolated bands and the full ab initio calculations are essentially indistinguishable.

3.3. Transferability of the basis sets

Sometimes one needs to calculate the physical properties under certain perturbations, such as strain, defects, electric field, etc. In these cases, a transferable basis set is highly desirable. Shirley’s Bloch interpolation does not have any transferability, i.e., even with a small change of the system (e.g. a deformation of the unit cell), the Bloch basis needs to be regenerated. It has been shown that Wanner functions do not have satisfactory transferability either [20, 21], because they have too many details. Here we demonstrate that the CGH orbitals have very good transferability for interpolation purposes.

We take a (3, 3) carbon nanotube (CNT) as an example, which is a metallic armchair nanotube. The system contains
bands. We calculate \( \langle \cdot \rangle \) using the following formula:
\[
\varepsilon_2(\omega) = \frac{2e^2 \pi}{\Omega \varepsilon_0} \sum_{k,c,v} |\Psi_{k,c}(\hat{e} \cdot \hat{r})|\langle \Psi_{k,v} \rangle|^2 \delta(E_c(k) - E_v(k) - \hbar \omega),
\]
where \( \hat{e} \) is the vector defining the polarization of the incident electric field. \( |\Psi_{k,c}\rangle \) are the wavefunctions of the conduction bands, whereas \( |\Psi_{k,v}\rangle \) are the wavefunctions of the valence bands. We calculate \( \langle \Psi_{k,c}|\hat{e} \cdot \hat{r}|\Psi_{k,v}\rangle \approx \frac{1}{N_{\text{atoms}}} \sum_{\text{atoms}} \langle \Psi_{k,c}|\hat{e} \cdot \hat{p}|\Psi_{k,v}\rangle \) in the reciprocal space, where \( \omega_k \) is the phonon frequency. Here, we neglect the commutator term correction due to the non-local pseudopotential, which is small for Si [22]. The operator \( \hat{p} = -i\hbar \nabla \) can be evaluated in the general scheme according to equation (8), where the dipole matrix element \( \langle \phi_{\text{atom}}| -i\hbar \nabla |\phi_{\text{atom}}\rangle \) can be easily calculated using the two-center integration formula [12]. The spectra are calculated on a \( 13 \times 13 \times 13k \)-point mesh, using four valence bands and four conduction bands. As illustrated in figure 5, the spectra calculated from the plane wave basis and from the 1s1p1d1f1g basis are in excellent agreement. However, if DZP orbitals are used, there are large discrepancies between the spectra calculated from the plane wave basis and the local basis. Because our interpolation scheme is based on the wavefunction overlaps between the plane wave basis and the atomic bases rather than the energies, it is not surprising that our method can obtain highly accurate expectation values of the operators.

3.4. Optical spectra

In this section, we demonstrate that high quality optical spectra can be obtained via the present band structure interpolation scheme. We calculate the imaginary part of dielectric functions using the following formula:
\[
\varepsilon_2(\omega) = \frac{2e^2 \pi}{\Omega \varepsilon_0} \sum_{k,c,v} \langle \Psi_{k,c}|\hat{e} \cdot \hat{r}|\Psi_{k,v}\rangle^2 \delta(E_c(k) - E_v(k) - \hbar \omega),
\]
where \( \hat{e} \) is the vector defining the polarization of the incident electric field. \( |\Psi_{k,c}\rangle \) are the wavefunctions of the conduction bands, whereas \( |\Psi_{k,v}\rangle \) are the wavefunctions of the valence bands. We calculate \( \langle \Psi_{k,c}|\hat{e} \cdot \hat{r}|\Psi_{k,v}\rangle \approx \frac{1}{N_{\text{atoms}}} \sum_{\text{atoms}} \langle \Psi_{k,c}|\hat{e} \cdot \hat{p}|\Psi_{k,v}\rangle \) in the reciprocal space, where \( \omega_k \) is the phonon frequency. Here, we neglect the commutator term correction due to the non-local pseudopotential, which is small for Si [22]. The operator \( \hat{p} = -i\hbar \nabla \) can be evaluated in the general scheme according to equation (8), where the dipole matrix element \( \langle \phi_{\text{atom}}| -i\hbar \nabla |\phi_{\text{atom}}\rangle \) can be easily calculated using the two-center integration formula [12]. The spectra are calculated on a \( 13 \times 13 \times 13k \)-point mesh, using four valence bands and four conduction bands. As illustrated in figure 5, the spectra calculated from the plane wave basis and from the 1s1p1d1f1g basis are in excellent agreement. However, if DZP orbitals are used, there are large discrepancies between the spectra calculated from the plane wave basis and the local basis. Because our interpolation scheme is based on the wavefunction overlaps between the plane wave basis and the atomic bases rather than the energies, it is not surprising that our method can obtain highly accurate expectation values of the operators.

3.5. Efficiency of the method

We now briefly address the efficiency of the current interpolation scheme. We compare the computational time to calculate the band structures of 1000k points by using the plane wave basis and the atomic bases. The fixed time cost to set up the atomic basis is neglected in the comparison, because it is a small fraction of the total time when the number of k-points to be interpolated is large, e.g. thousands of k-points. For BaFe\(_2\)As\(_2\), we calculate 25 bands, and find that the calculations using the atomic bases are 884, 212, and 81 times faster than using the plane wave basis, if the 1s1p1d1f1g, 2s2p2d2f2g, and 3s3p3d3f3g orbitals are used, respectively. In the test of a (3,3) CNT, the atomic bases are about 828, 178, and 65 times faster than the plane wave basis if 1s1p1d1f, 2s2p2d2f2g, and 3s3p3d3f3g orbitals are used, respectively. Usually, the 1s1p1d1f1g basis is sufficient for most purposes, and therefore the acceleration rate of the interpolation is remarkable. Note that the exact acceleration rates depend strongly on the test conditions, including the computer’s hardware and software environment. However, in our tests, we find that the computational time using atomic bases is dominated by the matrix diagonalization, and because our method uses a similar number of orbitals to Shirley’s method to achieve similar accuracy, the efficiency of the two methods is expected to be close. The Wannier function method could be faster, because the method uses smaller basis size.

4. Conclusion

We have presented an efficient scheme for accurate electronic structure interpolations based on the systematically improvable optimized atomic orbitals. The current scheme has several advantages over the existing interpolation schemes. We find usually 16–25 orbitals per atom can give an accuracy of about 10 meV compared to the full \textit{ab initio} calculations, similar to
that of the revised Shirley’s scheme. However, unlike Shirley’s method, in which a large number of three-dimensional wavefunctions have to be stored in the calculations, the present scheme only needs to store the one-dimensional radial functions. The atomic orbitals are highly localized, and therefore the scheme has as many good features as the interpolation schemes based on maximally localized Wannier functions. Even though the number of atomic orbitals is larger than that of Wannier functions, generally the atomic orbitals are more localized than Wannier functions, and therefore have much fewer neighboring atoms. The efficiency of our method is similar to that of Shirley’s scheme, but slower than the Wannier method. The scheme is easy to implement and robust, working equally well for metallic systems and systems with complicated band structures. Furthermore, the atomic orbitals have much better transferability than Shirley’s basis and Wannier functions, which is very useful for perturbation calculations.

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