Optimal basis set for electronic structure calculations in periodic systems

Sandro Scandolo\textsuperscript{a,b} and Jorge Kohanoff\textsuperscript{b,c}

\textsuperscript{a) International School for Advanced Studies (SISSA) and INFM, Via Beirut 4, I-34014 Trieste, Italy}
\textsuperscript{b) International Centre for Theoretical Physics (ICTP), I-34014 Trieste, Italy}
\textsuperscript{c) Atomistic Simulation Group, The Queen’s University, Belfast BT7 1NN, Northern Ireland}

An efficient method for calculating the electronic structure of systems that need a very fine sampling of the Brillouin zone is presented. The method is based on the variational optimization of a single (i.e. common to all points in the Brillouin zone) basis set for the expansion of the electronic orbitals. Considerations from \textit{k}-p-approximation theory help to understand the efficiency of the method. The accuracy and the convergence properties of the method as a function of the optimal basis set size are analyzed for a test calculation on a 16-atom Na supercell.

\section{I. INTRODUCTION}

First-principles methods have become a widespread tool for studying the microscopic aspects of a wide class of condensed systems, including their crystalline phases. No empirical modelling of the interatomic interactions is required in first-principles simulations, since the electronic ground state is evaluated at each atomic configuration. In a large set of systems, mostly in metals, but also in some molecular crystals like hydrogen\textsuperscript{1}, a very fine sampling of the Brillouin Zone (BZ) is required to provide a sufficiently accurate description of the electronic ground state. Since the computational load for refining BZ sums grows linearly with the number of sampling points (k-points), special k-point grids that minimize sampling errors, as well as interpolation techniques (the so called tetrahedron method\textsuperscript{2}) have been introduced in the past\textsuperscript{3,4}.

However, little attention has been paid to the fact that Bloch states at nearby k-points are not totally uncorrelated. In fact, once the Bloch states at a given k-point are known, those at a nearby k-point can be easily estimated by perturbation theory, within the so-called \textit{k} \cdot \textit{p} approximation\textsuperscript{5}. This extremely helpful piece of information has been little exploited so far in standard first-principles approaches, where for each k-point a full solution of the Kohn-Sham equations is instead calculated independently, e.g. through diagonalization of the Kohn-Sham hamiltonian on a finite basis set (typically plane waves in the case of crystalline systems). An approximate technique based on the exact solution of the Kohn-Sham hamiltonian at a few k-points has been proposed\textsuperscript{6}, but the analysis of the errors associated with such method, as well as their correction, has proved rather difficult\textsuperscript{6,7}.

In this work we propose a simple and efficient method for solving the Kohn-Sham equations for a very large number of k-points in the BZ, with an effort that in most cases is comparable to that of solving the problem for just a few k-points. The method is based on a rigorous formulation of the ideas sketched above, and relies on the construction of a single, optimal basis set for the expansion of the Bloch orbitals, which is common to all k-points. The application of this method to the study of the compressed phases of molecular hydrogen has been recently reported\textsuperscript{8}. In Section II we formulate the method. In Section III we analyze the reliability of the method on a test case (16 Na atoms in the bcc lattice), and in Section IV we analyze the computational cost. Section V contains the conclusions.

\section{II. THE METHOD}

In first-principles simulations the electronic ground state is calculated within the Kohn-Sham, self-consistent one-electron formalism of density functional theory\textsuperscript{9}. Translational invariance is introduced by averaging the external, Hartree, and exchange-correlation contributions to the energy, and depend on the BZ averaged electronic density\textsuperscript{10}. Atomic units are used throughout this work.

Variational equations for the periodic part of the Kohn-Sham orbitals \(u^i_k(r)\) are readily obtained from expression (2):

\[ \left(-\frac{\nabla^2}{2} - ik \cdot \nabla + \frac{k^2}{2} + V[\rho(r)]\right)u^i_k(r) = \epsilon^i_k u^i_k(r) , \]  

(4)
where $V[\rho]$ is the Kohn-Sham potential, containing external, Hartree and exchange-correlation contributions. Normally, equations (4) are solved independently for each k-point, a new density is constructed via (6), and the cycle is iterated to self-consistency. Equations (4) are often solved by expanding the orbitals corresponding to the various k-points in a basis set of plane waves, which remains unchanged when the atomic configuration is changed. The choice of a plane-wave basis set offers some practical advantages, including the convenience of calculating a number of quantities (matrix elements, form factors, etc) a single time throughout the calculation. However, working with a plane-wave basis set becomes particularly demanding from the computational point of view when a large supercell and/or a large number of k-points has to be considered, a situation which is often encountered when dealing with metals. Moreover, a plane-wave basis set cannot straightforwardly exploit the similarity of Bloch states at closely k-points.

In the following we will show that relaxing the requirement of a “simple” but inmutable basis set in favor of a variational search for the “best” basis set at each atomic configuration may improve substantially the efficiency of BZ summations. To this aim, let us expand the Kohn–Sham orbitals on a generic basis set $\phi_i$ ($i = 1, ..., N$) of size $N$

$$u_i^k(r) = \sum_{j=1}^{N} a_{ij}(k) \phi_j(r) \ .$$

In the case of standard calculations $\phi_i$ would be a plane wave $- \phi_i(r) \sim \exp(ig \cdot r)$, being $g$ a reciprocal lattice vector and solving the Kohn-Sham equations would amount to minimize the energy functional (2) with respect to the expansion coefficients $a_{ij}$, without modifying the basis set. In the present approach we minimize the energy functional (2) with respect to both the expansion coefficients $\{a_{ij}\}$ and the basis set functions $\{\phi_i\}$. In other words, we look simultaneously for the ground state orbitals and for basis set that better describes them. For the sake of clarity, we note that this would be a redundant request for calculations with a single k-point, where a single set of Kohn-Sham equations have to be solved. The request of an optimal basis set becomes non redundant when the basis set is used to describe Kohn-Sham equations at many k-points.

 Explicit minimization of (2) with respect to simultaneously, $a_{ij}$ and $\phi_i$ leads to the following system of equations. For the expansion coefficients we have the usual eigenvalue equations:

$$\sum_{j=1}^{N} \left( \lambda^0_{ij} + \frac{k^2}{2} \delta_{ij} + k \cdot p_{ij} \right) a_{jl}(k) = \epsilon^l_{ij} a_{il}(k) \ ,$$

with

$$\lambda^0_{ij} = \left\langle \phi_i \left| \left(- \frac{\nabla^2}{2} + V_{KS}[\rho] \right) \phi_j \right. \right\rangle$$

and

$$p_{ij} = -i \left\langle \phi_i | \nabla | \phi_j \right\rangle \ .$$

For the basis-set functions we have

$$\frac{\delta E[\phi, a]}{\delta \phi_i^*(r)} = \sum_{j=1}^{N} B_{ij}(0) \left[ -\frac{\nabla^2}{2} + v_{KS}[\rho] \right] \phi_j^*(r) +$$

$$+ \sum_{j=1}^{N} \left\{ \sum_{l=1}^{N} \Lambda_{il} \phi_l(r) \right\} \phi_j^*(r) +$$

$$+ \frac{\delta E_{NL} \phi_i b_j(k)}{\delta \phi_i^*(r)} = \sum_{l=1}^{N} \Lambda_{il} \phi_l(r) \ ,$$

where

$$B_{ij}^{(0)} = \sum_k \omega_k b_{ij}(k)$$

$$B_{ij}^{(1)} = \sum_k \omega_k b_{ij}(k)$$

$$B_{ij}^{(2)} = \frac{1}{2} \sum_k \omega_k k^2 b_{ij}(k)$$

and

$$b_{ij}(k) = \sum_{i=1}^{N} f_i(k) a_{ij}(k)a_{il}(k) \ .$$

The $\Lambda$ coefficients in (6) are Lagrange multipliers introduced to enforce the orthonormalization of the basis functions. The electron density in (2) is constructed from the Kohn-Sham orbitals (4) using (11), as

$$\rho(r) = \sum_{j=1}^{N} \sum_{l=1}^{N} \phi_j^*(r) \beta_{jl} \phi_l(r) \ ,$$

where

$$\beta_{jl} = \sum_k \omega_k b_{jl}(k) \ .$$

More detailed expressions for the above equations as well as for atomic forces and stress are given in the Appendix, for the case of pseudopotential plane wave (PPW) calculations.

The problem of simultaneously solving Kohn-Sham equations for $N_k$ k-points independently, as done in standard electronic structure calculations, is here replaced by the problem of solving a single set of Kohn-Sham-like equations, eqs. (7), supplemented with $N_k$ diagonalizations of the $N \times N$ matrix in (6). As we will show in the next Section, the number of basis functions $N$ required for the optimal basis set $\{\phi_i\}$ can be chosen to be much smaller than that in the basis set used to describe each single $\phi_i$, e. g. the number of plane wave components in PPW calculations. This implies that, if $N_k$ is large, the
computational effort required by this procedure is much smaller than the effort required to solve the standard set of Kohn-Sham equations at all k-points. The main limitation of the method resides, then, in the size $N$ of the optimal basis set. If $N$ turns out to be comparable to the original number of basis functions, there is no point on pursuing this strategy.

While in standard calculations the number of Kohn-Sham equations is roughly (exactly for insulators) half the number of electrons, in our approach $N$ has to be sufficiently large to guarantee the proper description of the Kohn-Sham orbitals $\{\phi_i\}$ at all k-points. A full analysis of the convergence of the method as a function of $N$ will be presented later, for a specific case. There are however reasons to expect that $N$ need not be too large. In fact, a reasonable approximation to the exact optimal basis set is given by the Kohn-Sham orbitals at one selected k-point, say at zone center ($\Gamma$). We call this basis set: $\{\phi^\Gamma_i\}$. Since the optimal basis set is defined as the best basis set in a variational fashion, $\{\phi^\Gamma_i\}$ will necessarily provide a worse description of the Kohn-Sham orbitals (except, of course, at $\Gamma$) than $\{\phi_i\}$. The convergence properties of $\{\phi_i\}$ will thus be better than those of $\{\phi^\Gamma_i\}$. If the BZ of the system of interest is sufficiently small (which is equivalent to ask that the unit cell of the calculation is large), then $k \cdot p$ perturbation theory suggests that Kohn-Sham orbitals at any k-point other than $\Gamma$ may be expressed in terms of a few number of energetically close $\Gamma$-point orbitals $\{\phi^\Gamma_i\}$. In other words, only a few excited $\Gamma$-point orbitals are required for a reasonable description of the orbitals at all other k-points. This property has been already noted and used in the context of first-principles electronic structure calculations Ref. 1, 2. Our approach differs from that of Robertson and Payne in the fact that their basis set is given by the Kohn-Sham orbitals at $\Gamma$ (or at a small set of k-points), while our method includes a variational search for the best basis set. A comparison of the convergence properties of the two approaches is given in the next Section.

We also observe that our method has only one variational parameter, namely the size $N$ of the basis set. This implies that systematic improvements of the accuracy can be achieved by simply increasing $N$.

Finally, we notice that eqs. 1), like ordinary Kohn-Sham equations, have to be solved self-consistently, since the Kohn-Sham potential $v_{KS}$ depends on the density, and thus on wavefunctions. However, unlike ordinary Kohn-Sham equations, eqs. 1) depend also on the expansion coefficients $a_{ij}$. The ordinary self-consistent iterative procedure has, consequently, been modified in the following way:

1. an initial guess of the density is provided, e.g. as a sum of atomic densities; the $a_{ij}$ coefficients are initially set to $\delta_{ij}$,
2. eqs. 1) are solved,
3. the orbitals (which are no longer Kohn-Sham orbitals) are used to construct $\lambda^0_{ij}$ and $p_{ij}$,
4. eq. 2) is solved for each k-point, via direct diagonalization,
5. a new density is constructed,
6. back to 2.

Notice that this procedure does not involve a major implementation effort, but only a few modifications to the usual self-consistency methods.

III. CONVERGENCE OF THE OPTIMAL BASIS SET

In order to analyse the convergence properties of the method we have chosen the case of Na metal, which is properly described with a soft, local pseudopotential Ref. 8. The Ceperley-Alder local density functional was adopted for the exchange-correlation term Ref. 9. Sixteen Na atoms in the bcc structure have been placed in a simple cubic supercell ($2 \times 2 \times 2$ bcc conventional cells), and the full Brillouin zone of the supercell has been sampled with 108 k-points. A plane wave energy cutoff of 15 Ry was chosen, amounting to 1596 plane waves in the expansion of the optimal basis set. The convergence of the method has been analysed by performing calculations with $N = 19$, $32$, $51$, $81$, and $1596$. Since our aim is at checking the convergence properties of the method, and not the overall accuracy as determined by the other approximations (LDA, k-point grid, etc.), we will consider as converged the values obtained with $N = 1596$ and $N_k = 108$. As a comparison, we have also determined the convergence properties of a calculation where the basis set, instead of being “optimal”, is chosen to be the set of Kohn-Sham orbitals resulting from a self-consistent calculation using the $\Gamma$ point only. This corresponds to the approach of Ref. 8.

![Graph](image-url)
FIG. 1. Convergence of the total energy of solid \( \text{bcc Na} \) using a 16-atom supercell, as a function of the number of the basis set size \( N \). Dashed lines correspond to the approach of Ref. 8, 9, and solid lines to the present method. The horizontal line is the converged value.

In Figs. 1 to 3 we show the convergence of the different physical properties as a function of \( N \), namely the total energy, stress, and electronic density of states. The total energy (Fig. 1) shows an extremely good convergence even for the smallest value of \( N \). The accuracy is better than 0.5% for \( N = 19 \), and better than 0.1% for \( N = 32 \) states. The same behavior is observed in the force constant calculated for a distortion along an optical phonon: the force is already converged to better than 0.1% using 32 states in the expansion. Thus, the errors introduced in energies and forces due to truncation of the expansion are much smaller than, e.g., the typical accuracy of the usual density functionals used, namely the LDA or the GGA. Stresses also show good convergence properties, as reported in Fig. 2. Variations of stress (\( \Delta \sigma \)) with respect to \( N \) should in this case be compared with the value of the bulk modulus of Na (\( B = 64 \text{ kbar} \)). In fact, an error \( \Delta \sigma \) in the stress yields an error in the equilibrium lattice spacing that can be estimated as \( \Delta a/a \sim \Delta \sigma/3B \). Thus, even with \( N = 19 \) the equilibrium lattice spacing is converged within less than 1%.

The electronic density of states (EDOS) is also sufficiently accurate for the relevant portion of the spectrum, namely the one below the Fermi energy (\( E_F \)), using \( N = 32 \). In contrast, \( N = 19 \) appears to give an inaccurate EDOS, particularly in the vicinity of \( E_F \), as expected in a \( k \cdot p \) picture. In fact, as discussed in Section II, a small basis set is more likely to affect the accuracy in the description of states with higher energy, i.e. closer to \( E_F \), due to the insufficient number of high energy states in the optimal basis set.

We now compare the results obtained with our method against those obtained with the method of Ref. 8, 9. Our energies are always lower, for a given basis set size \( N \), than energies calculated using the method of Ref. 8, 9. This is not unexpected, since the optimal basis set is variationally the best basis set. Moreover, we find that the method of Ref. 8, 9 provides results with an accuracy similar to ours only when the size of the basis set is 30-50% larger than ours. The most striking difference, however, is in the convergence of the stress tensor. While our method converges very smoothly to the exact value, the method of Ref. 8, 9 shows an erratic behavior, that clearly prevents every attempt to determine the exact value on the basis of size scaling. We believe that such a marked difference in the convergence properties has to be traced to the variational nature of our approach. Therefore, our method not only improves on that of Ref. 8, 9 in the rate of convergence (which, in the case of energy, results in a 30-50% saving in computational time, as shown in the
IV. ESTIMATE OF THE COMPUTATIONAL LOAD

The computational effort in a standard plane wave calculation scales as \(N_k N_{\text{bands}} N_{\text{pw}}^2\), where \(N_{\text{bands}}\) is the number of occupied bands (equal or slightly larger than half the number of electrons) and \(N_{\text{pw}}\) is the size of the plane wave basis set. This estimate is based on the assumption that standard diagonalization methods are used, such as iterative diagonalization, where the effort of determining the first \(N_{\text{bands}}\) eigenvalues of a \(N_{\text{pw}} \times N_{\text{pw}}\) matrix scales like \(N_{\text{bands}} N_{\text{pw}}^2\). Since every k-point requires a separate diagonalization, the total effort scales as \(N_k N_{\text{bands}} N_{\text{pw}}^2\).

In the present approach, if we assume that the effort of diagonalizing \(N_k\) times the \(N \times N\) matrix is negligible with respect to the effort required to solve eqs. (8), then the load scales as \(N N_{\text{pw}}^2\). Thus, a gain of a factor \(N_k N_{\text{bands}} / N\) is expected with our method. Since in typical applications \(N \sim 2 \div 4 N_{\text{bands}}\), and \(N_k \sim 10^2\), a computational gain of more than one order of magnitude is obtained. The neglected term increases becoming important as the size of the system (\(N\)) increases, scaling as \(N_k N_{\text{bands}} N^3\). Therefore, it becomes dominant for sufficiently large \(N\), thus discouraging the use of the present methodology in the case of large unit cells and BZs sampled in a few k-points.

The above estimate is based on the assumption that solving eqs. (8) is as time consuming as solving the standard Kohn-Sham equations, except for the fact that the requested number of states is larger. Our experience on Na (this work) and molecular hydrogen shows that the computational overload of solving eqs. (8) basically scales linearly with the number of states; the extra effort required for solving a single state is negligible when compared to that of solving one of the usual Kohn-Sham states. Nevertheless, we are currently not in a position to generalize this conclusion to a generic system.

V. SUMMARY AND CONCLUSIONS

We have presented and analysed the convergence properties of a method for performing electronic structure calculations and first-principles molecular dynamics simulations for systems that need a very fine sampling of the electronic Brillouin zone. The method is based on the construction of a basis set which optimally describes the Kohn-Sham orbitals at all k-points. The rapid convergence of the method on the size \(N\) of the basis set is connected with the properties of the \(k \cdot p\) approximation and has been fully analysed in the case of a sixteen Na atoms supercell. We have shown that \(N\) can be kept reasonably small, of the order of a few times the number of occupied bands (2 to 4 times, depending on the accuracy desired), resulting in a gain in computational load of about one order of magnitude, with respect to standard methods.

Even if our analysis was mainly done in connection with PPW calculations, the same philosophy can be adopted in other electronic structure schemes like the LAPW method, provided that the number of orbitals required in the optimal basis set remains significantly smaller than the number of basis functions in the original basis set.

In conclusion, this technique constitutes a useful tool for studying the electronic, structural and dynamical properties of metals and more generally for any system whose proper description requires a fine sampling of the BZ, like, for example, molecular hydrogen.

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VII. APPENDIX

In this appendix we give some useful expressions for the total energy, atomic forces and stress, in the case of pseudopotential plane wave calculations.

The different contributions to the total energy \(\mathcal{E}\) can be divided into the class of terms that only depend on the density (the hartree, the exchange-correlation, and the local part of the pseudopotential), and the class of terms that explicitly depend on the wavefunctions (the kinetic and the nonlocal pseudopotential contributions). While the former can be calculated in the usual way once the density is known (see below for an efficient way to evaluate density), the latter can be expressed more conveniently as follows. For the kinetic energy we have

\[
T = \sum_k \sum_{i=1}^N \sum_{j=1}^N b_{ij} \sum_{t=1}^{N_{\text{bands}}} \left\{ t_{ij}^0 \phi_i + k \cdot \mathbf{p}_{ij} + \frac{k^2}{2} \delta_{ij} \right\} = \\
= \sum_{i=1}^N \left\{ B_{ii}^{(0)} \phi_i + B_{ii}^{(2)} \right\} + \\
+ \sum_{i=1}^N \sum_{j \neq i}^N \left\{ B_{ij}^{(0)} \phi_i + B_{ij}^{(1)} \phi_j \right\} ,
\]

with

\[
t_{ij}^0 \phi_i = \langle \phi_i | - \nabla^2 | \phi_j \rangle ,
\]

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and for the non-local contribution we have

\[ E_{NL} = \sum_{s=1}^{\sigma} \sum_{m=-l}^{l} \alpha_{lm}^s \sum_{ij} \sum_{k} \omega_k b_{ij}(k) \times \]
\[ \times \sum_{I=1}^{N_s} F_{Iilm}^*(k) F_{Ijlm}(k) \], \quad (16) \]

where, in a plane waves basis set, \( F_{Iilm}(k) \) assumes the following form:

\[ F_{Ijlm}(k) = \sum_{s} w_{ilm}^s(g + k) \exp(ig \cdot R_I) \phi_s(g) \], \quad (17) \]

being \{g\} the reciprocal lattice vectors and \( R_I \) the coordinates of atom \( I \) belonging to species \( s \). The coefficient \( w_{ilm}^s \) is the projection of the \( g \)-th plane wave component expanded around the \( k \)-vector \( k \), onto the \( lm \)-th subspace according to the Kleinman-Bylander prescription:

\[ w_{ilm}^s(g + k) = \langle \delta \phi_l^s \phi_m^s | Y_{lm} | g + k \rangle \], \quad (18) \]

with \( \delta \phi_l^s \) the \( l \)-th angular momentum pseudopotential component for species \( s \), \( \phi_m^s \) the corresponding pseudocystal orbital, and \( Y_{lm} \) the spherical harmonic functions. Equation (14) also contains a normalization factor, which is given by the expression \( \alpha_{lm}^s = \langle \delta \phi_l^s \phi_m^s | \phi_m^s \rangle^{-1} \). \( N_s \) is the number of atoms of species \( s \), and \( \sigma \) is the number of species described through angular-dependent pseudopotentials.

It is interesting to remark that, since now the factors \( w_{ilm}^s \) depend explicitly on the \( k \)-vector, there is no longer possible to perform the BZ summation on the coefficients \( b_{ij}(k) \) once and for all, as it is done for the kinetic and local potential terms. Now this sum has to be carried out for each PW component \( g \), and this is likely to result in a costly computational scheme. So far we have not studied this issue in detail, because this method has only been applied to hydropon and sodium, where a local pseudopotential description is feasible, but we hope that alternatives can be found so that the non-local part does not become the bottleneck of the calculation.

The calculation of the density is a subtle issue, because expression (12) involves a double sum of matrix products over all states, occupied and empty. Even if it has been suggested [8] that this operation is computationally convenient, we have found it more efficient to first transform the orbitals at \( \Gamma \) by multiplying them with the rotation matrices \( a_{ij}(k) \), and then carry out a single summation over the occupied states.

The last term in (15) is easier to compute in reciprocal space, where it assumes the following expression:

\[ \frac{\partial E_{NL}[\phi, b]}{\partial \phi_l^s(g)} = -\sum_{s=1}^{\sigma} \sum_{lm} \alpha_{lm}^s \sum_{ij} \sum_{k} \omega_k b_{ij}(k) \times \]
\[ \times w_{ilm}^s(g + k) \sum_{I=1}^{N_s} \exp(ig \cdot R_I) \cdot F_{Ijlm}(k) \]. \quad (19) \]

The forces on the nuclei are trivially unchanged from the original ones, as long as local pseudopotentials are used. This is because the electronic kinetic term does not depend explicitly on the nuclear positions. In the case of angular-dependent pseudopotentials the contribution from the last term in (15) to the force on atom \( I \) belonging to species \( s \), is modified from the standard result in the following way:

\[ \frac{\partial E_{NL}}{\partial R_I} = 2 \sum_{lm} \alpha_{lm}^s \sum_{ij} \sum_{k} \omega_k \times \]
\[ \times \text{Re} \left( b_{ij}(k) \frac{\partial F_{Ijlm}^*(k)}{\partial R_I} F_{Ijlm}(k) \right) \]. \quad (20) \]

The calculation of the stress matrix is also modified with respect to standard calculations only for the kinetic (kin) and nonlocal pseudopotential (NL) contributions. The resulting expression for the kinetic contribution is:

\[ \sigma^\text{kin}_{\alpha\beta} = \sum_{ij} B_{ij}^{(0)} t_{ij\alpha\beta} + \sum_{ij} \left( B_{ij\alpha}^{(1)} \partial E_{jlm}(k) + B_{ij\beta}^{(2)} \right) + \]
\[ + \sum_i B_{ij\alpha\beta}^{(2)} \], \quad (21) \]

with

\[ t_{ij\alpha\beta} = \langle \phi_i | \frac{\partial^2}{\partial x_\alpha \partial x_\beta} | \phi_j \rangle \] \quad (22) \]

and

\[ B_{ij\alpha}^{(1)} = \sum_k \omega_k k_{ji} \]
\[ B_{ij\beta}^{(2)} = \sum_k \omega_k k_{ji} b_{ij}(k) \]. \quad (23) \]

The nonlocal contribution is instead:

\[ \sigma^\text{NL}_{\alpha\beta} = -2 \sum_{s=1}^{\sigma} \sum_{lm} \alpha_{lm}^s \sum_{ij} \sum_{k} \omega_k b_{ij}(k) \times \]
\[ \times \sum_{I=1}^{N_s} \text{Re} \left( \frac{\partial F_{Ijlm}^*(k)}{\partial h_{\alpha\beta}} F_{Ijlm}(k) \right) \]. \quad (24) \]

where \( b_{ij} \) is the matrix of the three primitive Bravais vectors, and the partial derivative in (24) is given in Ref. [8].

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